UNIVERSITY OF SOUTHAMPTON

FACULTY OF NATURAL AND ENVIRONMENTAL SCIENCES

SCHOOL OF CHEMISTRY

Synthesis of Polyaromatic Molecules for Applications in Organic Electronics

by

Ayham Al-Muhammad

Thesis for the degree of Doctor of Philosophy

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ABSTRACT

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The synthesis of a number of novel polyaromatic compounds are reported, starting with novel polyheterocyclic systems containing sulphur and oxygen, otherwise known as thienoacenes and furanoacenes. These were generally produced *via* a four-step synthetic strategy utilising palladium-catalysed cross-coupling reactions such as Sonogashira and Suzuki cross-couplings to build the precursors, which were then subjected to a base-catalysed cycloisomerisation to give the final angular systems of several fused aromatic rings. Eight thienoacenes and seven furanoacenes, all consisting of between five and eight fused rings, were synthesised, as well as a mixed system featuring a thiophene and furan ring at either end of the molecule. Use of a five-ring thienoacene as a building block allowed for extension of the aromatic framework, and a stable fifteen-ring thienoacene was synthesised in a total of nine steps.

The same synthetic method was applied in producing a series of polycyclic aromatic hydrocarbons (PAHs) with phenyl and naphthyl substituents replacing thiophene and furan. Within this chapter, significant work was carried out in investigating the final cyclisation mechanism. Six highly crystalline PAHs are reported, consisting of five to eight fused benzene rings, and the addition of extra steps enabled longer polyaromatics of nine, eleven and twelve rings to be created.

The final challenge was the design and synthesis of a series of polyaromatic compounds for use as molecular wires. Similar approaches were used to build systems

containing terminal pyridine and nitrile substituents which can act as anchoring groups to secure the molecule to a metal surface. Nine compounds containing five to eight fused aromatic rings with a suitable anchoring group were brought through, and the development of strategies for significantly lengthening these wires gave five systems of either nine or twelve rings.

Optical and electrochemical characterisation of the compounds was carried out at the University of Caen Lower Normandy, France, in collaboration with Prof. Bernhard Witulski. The results of these measurements generally gave good correlation with computationally calculated values.

DECLARATION OF AUTHORSHIP

I, Ayham Al-Muhammad,

declare that this thesis and the work presented in it are my own and has been generated by me as the result of my own original research.

Synthesis of Polyaromatic Molecules for Applications in Organic Electronics

I confirm that:

1. This work was done wholly or mainly while in candidature for a research degree at this University;
2. Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;
3. Where I have consulted the published work of others, this is always clearly attributed;
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6. Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

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Date:

ACKNOWLEDGEMENTS

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I am very grateful to those who have helped me with the often tricky characterisation of many of my final compounds, notably NMR and mass spectrometry: Dr. Neil Wells, for constantly taking the time to carry out elevated temperature and overnight NMR's, Julie Herniman for running all the MS samples that did not work on the open access systems, and Dr. Mark Light for all the crystal structures.

Finally, none of this would have been possible without the support and love of my family in Sheffield, to whom I am eternally thankful.

LIST OF ABBREVIATIONS

APCI	atmospheric pressure chemical ionisation
APPI	atmospheric pressure photoionisation
aq.	aqueous
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCE	1,2-dichloroethane
DCM	dichloromethane
DIPA	diisopropylamine
DMA	*N, N*-dimethylacetamide
DME	1,2-dimethoxyethane
DMF	*N, N*-dimethylformamide
dppf	1,1-bis(diphenylphosphino)ferrocene
eq.	equivalents
EI	electron ionisation
ESI	electrospray ionisation
EtOAc	ethyl acetate
GC	gas chromatography
h	hours
HOMO	highest occupied molecular orbital
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrometry
IR	infrared
-br	broad
-m	medium
-s	strong

-w	weak
LRMS	low resolution mass spectrometry
LUMO	lowest unoccupied molecular orbital
n-BuLi	*n*-butyllithium
NMP	*N*-Methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
-s	singlet
-d	doublet
-t	triplet
-q	quartet
-quin.	quintet
-sxt	sextet
-m	multiplet
-br	broad
odcb	*o*-dichlorobenzene
OFET	organic field-effect transistor
OLED	organic light-emitting diode
OPVC	organic photovoltaic cell
PAH	polycyclic aromatic hydrocarbon
PCC	pyridinium chlorochromate
ppm	parts per million
RCM	ring-closing metathesis
TBAB	tetra-*n*-butylammonium bromide
TBAF	tetra-*n*-butylammonium fluoride
TCE	1,1,2,2-tetrachloroethane
TEA	triethylamine

TFA	trifluoroacetic acid
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin layer chromatography
Tol	toluene
UV	ultraviolet

Contents

1 Introduction

1.1 Background

The area of organic electronics deals with the use of organic materials – polymers, plastics and small molecules – in electronic devices. Organic semiconductors have been used commercially in electronic devices such as organic light-emitting diodes (OLEDs) for displays, organic field-effect transistors (OFETs) and organic pholtovoltaic cells (OPVCs) and there have been many reports of the use of functionalised acenes and heteroacenes for use in organic electronics.[1] These materials can be fabricated at room temperature over a large area and on thin, flexible substrates, and have the advantage of being low cost, light-weight and generally easier to process than traditional inorganic semiconductors. Figure 1 shows a monolayer OLED structure which consists of a layer of organic material embedded between two electrodes.

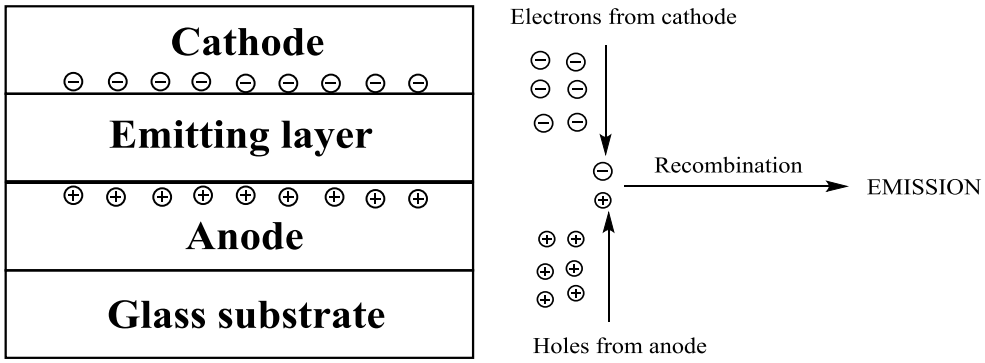


Figure 1: typical monolayer OLED structure and working principle.

When a voltage is applied across the OLED, the electron-donating metal cathode (such as calcium, magnesium or aluminium) is negative with respect to the anode, which is typically composed of indium tin oxide (ITO), a transparent and electrically conductive material. Electrons are injected from the cathode into the LUMO of the organic material, and positively charged holes are injected into the HOMO from the anode. Electrons and holes move in opposite directions through the organic emitting layer, and their recombination leads to photon emission. Nowadays, multilayer OLEDs are more commonly fabricated due to the fact that good electron and hole transporting properties in organic semiconductors is rare, and hole transport normally dominates. Addition of separate electron and hole transporting organic layers, containing acceptor and donor materials respectively, can improve device efficiency.

While OLED devices convert electrical energy to light energy *via* recombination of electrons and holes, OPVCs or organic solar cells can be viewed as doing the opposite, converting sunlight to electricity by pulling apart excitons, generated from photon absorption, to give separate holes and electrons. Monolayer OPVCs can be fabricated similarly to the OLED depiction in figure 1, but bulk heterojunction devices are more common. These contain a dispersed mixture of organic donor and acceptor materials, which separate holes and electrons respectively, and transport these charge carriers in opposite directions to the electrodes. Electron- and hole-transporting layers (ETLs and HTLs respectively) can be added to improve this charge carrier transport (figure 2).

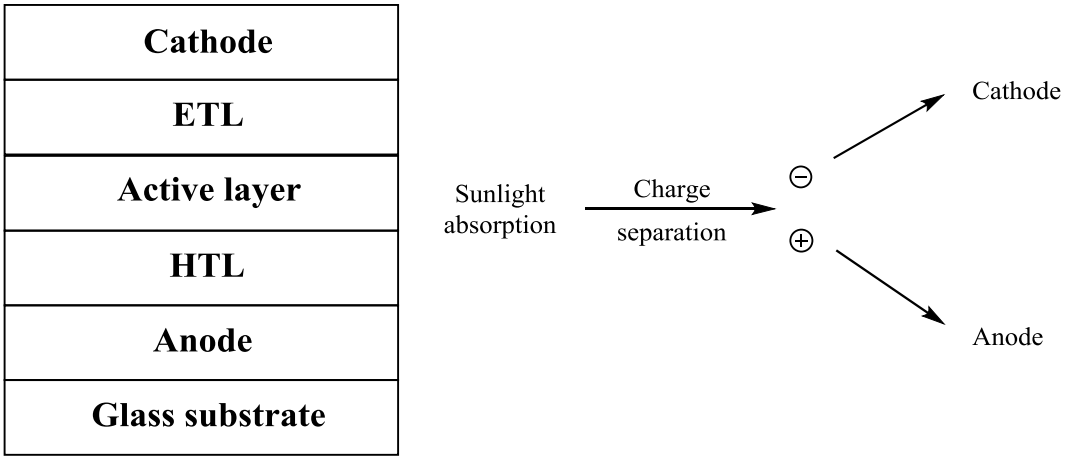


Figure 2: OPVC structure and working principle.

OFETs, meanwhile, are devices which can use one electrical signal to control another and in which the mobility of charge carriers (electrons and holes) through a semiconductor can be measured. Most commonly, the efficacy of novel organic semiconductors will be tested by fabricating an OFET based on the new materials. Different positions of the various components of an OFET can yield different geometries, such as the bottom-gate/top-contact device (figure 3).

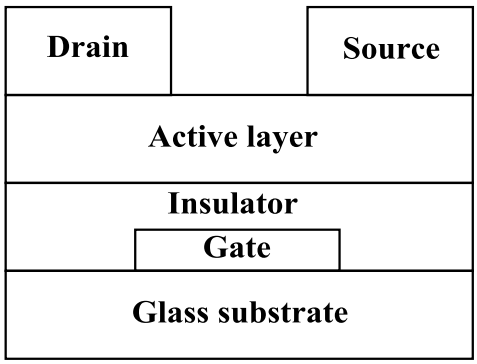


Figure 3: bottom-gate/top-contact OFET.

Organic semiconducting materials are generally based on conjugated π-electron systems. Some of the earliest examples of these were conducting polymers, such as polyacetylene, polyphenylenevinylene and polythiophene (figure 4).

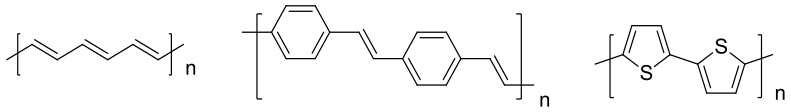


Figure 4: conducting polymers.

These polymers can display good conductivity when doped – the Nobel prize-winning work of Shirakawa, Heeger and MacDiarmid in the 1970's demonstrated that the oxidation of polyacetylene with substances such as bromine, iodine and arsenic pentafluoride resulted in a huge increase in electrical conductivity.[2] However, one limitation of these conducting polymers is that they can suffer from poor charge mobility due to rotation about single bonds. In addition, polymers may contain defects which are difficult to detect, and can display poor solubility.

Moving on from polymers, small molecules are now very widely synthesised and used as potential semiconductors.[1] These compounds, examples of which are shown in figure 5, consist of fused aromatic rings to give a rigid polyaromatic system, and provide an attractive alternative to conducting polymers. The crystallinity of these compounds enhances intermolecular interactions, thereby enhancing intermolecular charge transport.

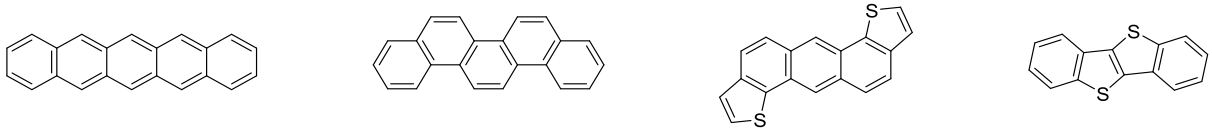


Figure 5: examples of small molecule organic semiconductors.

Electronic performance of organic semiconductors depends largely upon their HOMO-LUMO band gap, which is directly connected with the position of HOMO and LUMO levels in individual molecules. The energy differences between the HOMO of the semiconductor and the anode, and between the LUMO and cathode, are also key to device performance. In general, organic systems with narrow band gaps are the target for synthetic chemists, and one way to reduce this band gap is to extend π-conjugation, although this can lead to instability such as in the higher acenes.

Semiconducting properties of organic small molecules also depend upon their solid-state molecular interactions. X-ray crystallography reveals the arrangement of molecules in the solid state, and two common packing motifs are generally adopted by crystalline organic

semiconductors; edge-to-face, or 'herringbone' packing where C-H to π interactions dominate, or the more favourable face-to-face arrangement where π-stacking can yield strong electron coupling (figure 6).

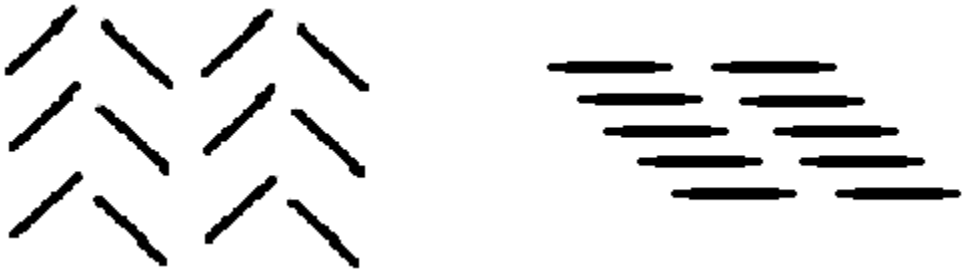


Figure 6: herringbone (left) and π-stacking (right) arrangements.

Depending on the proximity of molecules, the herringbone arrangement can exist with or without favourable face-to-face, π-π interactions. The alternative 'lamellar' motif can show 1D or 2D π-stacking, with the latter arrangement considered as the best for effective charge transport in semiconductors.[3] Intermolecular interactions heavily influence the reorganisation energy of a semiconductor, which is defined as the energy loss when a charge carrier (a hole or electron) passes through a conjugated molecule.

HOMO/LUMO energy levels and band gaps can be determined by electrochemical and optical methods, and crystal structures reveal the intermolecular interactions present in an organic compound. These features all contribute to the charge carrier mobility, μ, of an organic semiconductor. It is this mobility which reveals how effective a semiconductor will be for its application, and is defined as the drift velocity of the charge carrier per unit of electric field, expressed in units $cm^2\ V^{-1}\ s^{-1}$. Construction of OFETs is used to calculate this property for organic semiconductors, and mobilities of 0.5 $cm^2\ V^{-1}\ s^{-1}$ are desired in order for organic semiconductors to be competitive with traditional amorphous silicon. OFET fabrication will usually measure hole mobility, as the very large majority of polyaromatic compounds show p-type conductivity where holes are the dominant charge carriers. Semiconductors in which electrons are the major charge carriers are described as being n-type, and contain strongly electron-withdrawing groups or atoms, such as fluorine.[4]

To summarise the various points mentioned, an ideal organic semiconductor displaying high charge carrier mobility will have good stability due to a low-lying HOMO level, favourable intermolecular interactions and a small reorganisation energy.

1.2 Polycyclic aromatic hydrocarbons (PAHs)

Organic compounds based on a system of fused benzene rings are known as polycyclic aromatic hydrocarbons (PAHs). Graphene and carbon nanotubes (figure 7) are two well-known examples of PAHs, containing among the largest π-conjugated systems which give them exceptional properties.

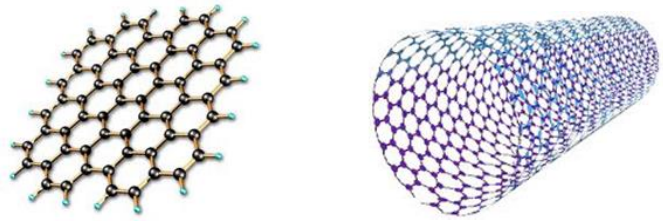


Figure 7: graphene and carbon nanotubes.

Focusing on small molecules, linear acenes (figure 8) represent a class of PAHs which have attracted a lot of interest as organic semiconductors.

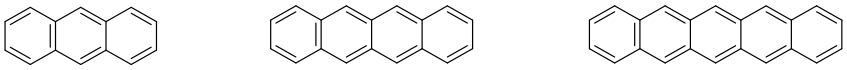


Figure 8: linear acenes.

Pentacene is one of the most widely-studied organic semiconductors and can be considered as the benchmark material in this area.[5] The strong electronic performance of pentacene arises from its high molecular order in the solid state and narrow band gap of 1.8 eV in thin films, and mobilities of over 5 $cm^2 V^{-1} s^{-1}$ have been reported in pentacene-based OFETs.[6] However, this compound suffers from instability under atmospheric conditions and poor solubility. Furthermore, pentacene crystallises in a herringbone motif, allowing for potential to improve π-stacking in the solid state. In producing substituted pentacene derivatives, several attempts have been made to improve these drawbacks while maintaining good device performance.

Although other functionalised pentacenes had been reported before it, 2,3,9,10-tetramethylpentacene (figure 9) was the first to be used in transistor applications.[7]

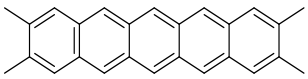


Figure 9: 2,3,9,10-tetramethylpentacene.

While this substitution pattern did not significantly change the crystal packing of the pentacene unit, it did give a decrease in oxidation potential from unsubstituted pentacene and mobilities of up to 0.31 $cm^2\ V^{-1}\ s^{-1}$.

Substitution at the peri positions is more common and was reported as far back as 1942 with the synthesis of 6,13-diphenylpentacene.[8] Nuckolls and co-workers reported a variety of aryl-substituted pentacenes (figure 10) and the effect of their substitution patterns on crystal packing and electrical properties.[9]

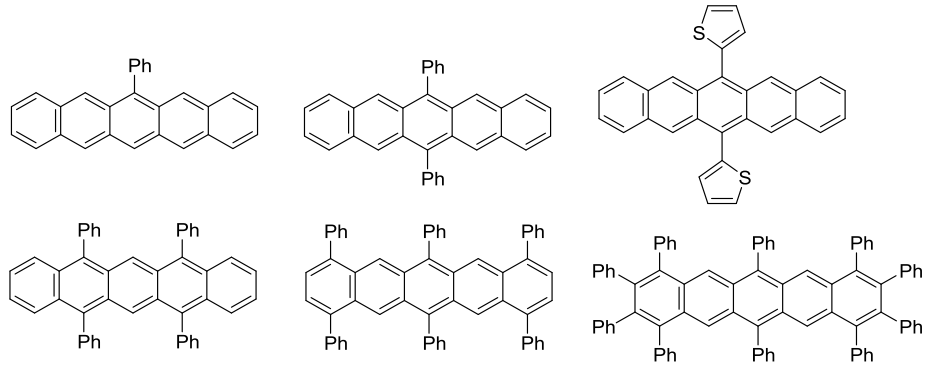
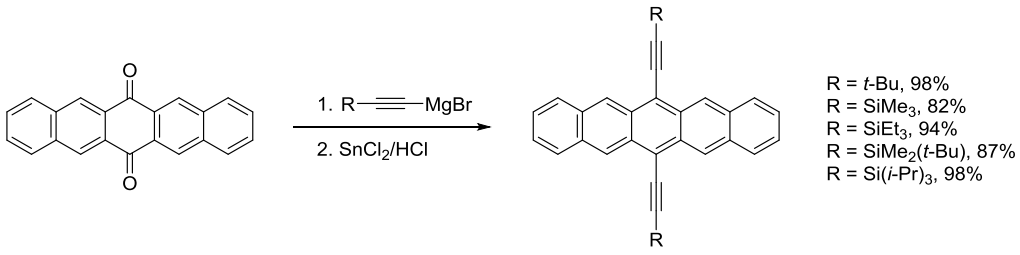


Figure 10: aryl-substituted pentacenes.

The thiophenyl derivative was found to have the best π-stacking of all the series, and as a result showed the best thin-film hole mobility, 0.1 $cm^2\ V^{-1}\ s^{-1}$. However, the crystal structures of all these molecules showed prominent edge-to-face interactions. Among the most successful strategies that have been used to enhance the more desired π-π face interactions in pentacene is the incorporation of trialkylsilylethynyl groups at the peri 6- and 13-positions of the acene.[10] The triple bonds act as a rigid 'spacer' separating the substituents from the acene and therefore selectively disrupting edge-to-face interactions but not the π-stacking. These functionalised compounds were synthesised using similar methods reported to those reported in the very first functionalised pentacene synthesis in 1942,[8] by Grignard reaction of pentacenediquinone followed by reduction (scheme 1).



Scheme 1: syntheses of 6,13-dialkynyl substituted pentacenes.

These compounds were synthesised in high yields compared to similar derivatives using alkyl and aryl Grignard reagents,[11] and as predicted, crystallised predominantly in the π-stacking order to avoid steric interactions of the bulky substituents. The alkynyl substituents also gave them good solubility and oxidative stability compared to pentacene. The so-called TIPS-pentacene (R = *i*-Pr) is now one of the most popular functionalised pentacenes used in thin-film transistors.[12]

Another interesting functionalisation strategy was the fluorination of pentacene reported by Suzuki and co-workers.[13] Perfluoropentacene (figure 11) was prepared in five steps from tetraflurophthalic anhydride and hydroquinone, with the final zinc-catalysed defluorination giving a 65% yield.

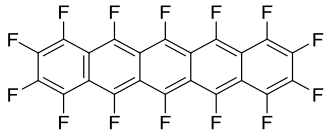


Figure 11: perfluoropentacene.

By introducing several small, electronegative fluorine atoms, the HOMO level relative to pentacene was reduced, thus enhancing electron injection and inferring n-type semiconductivity without dramatically altering the size of the molecule. Thin-film transistors based on perfluoropentacene were later reported to give mobilities of up to 0.22 $cm^2 V^{-1} s^{-1}$.[14] Several other functionalised acenes have been reported, often combining the substitution patterns shown in figures 9-11. These all maintain the 6,13-dialkyne substitution pattern and examples are shown in figure 12 – additional functionalisation by partial fluorination to decrease interplanar spacing,[15] alkylation to lower oxidation potentials,[16] and by incorporation of ether groups to utilise the strong π-electron-donating properties of oxygen.[17]

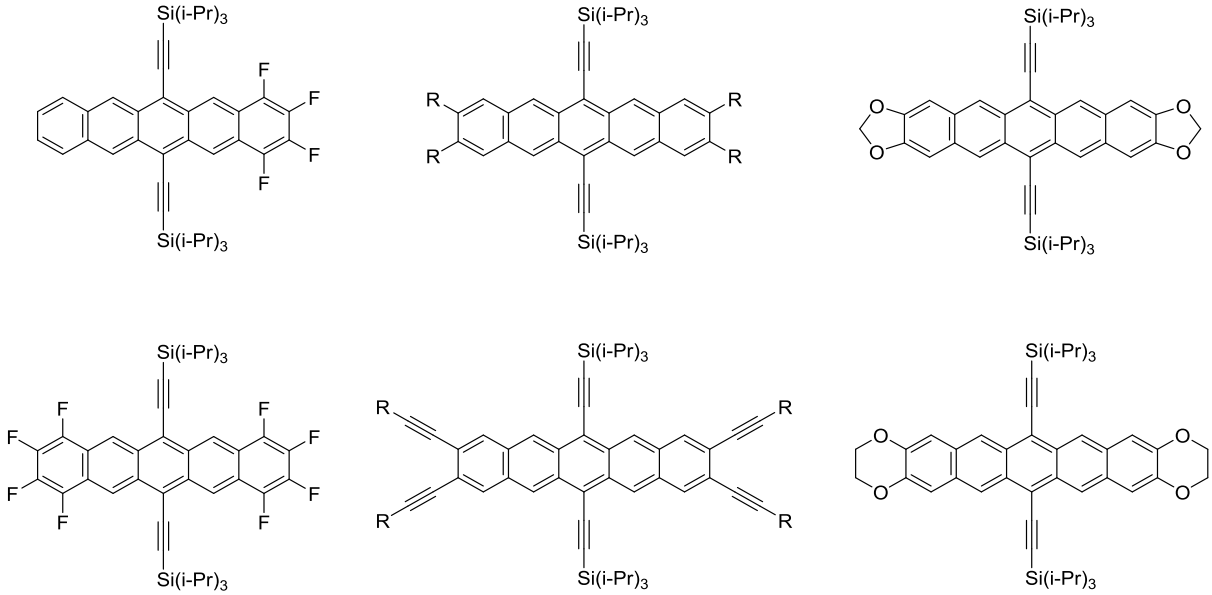


Figure 12: functionalised pentacenes.

The need for functionalisation of pentacene is largely due to its instability under ambient conditions. This is a problem for linear acenes in general, as particularly after tetracene they become very unstable. Isolations of the longest reported acene, heptacene, are considered controversial,[18] although stable, functionalised hexacenes[19] and heptacenes[20] are known. The synthesis of more stable non-linear acenes is another alternative to linear acenes, and in the last ten years picene has emerged as a prominent and air-stable semiconductor.[21] Picene is an isomer of pentacene, belonging to the phenacene class of PAHs (figure 13).

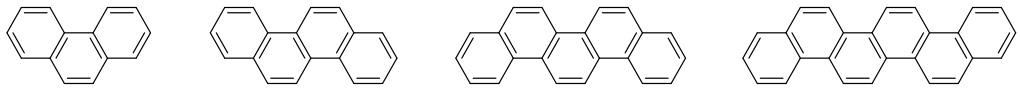


Figure 13: [3]-[6]phenacenes.

These compounds are invariably more stable than their linear analogues,[22] which is in agreement with calculations[23] showing that phenacenes, as well as other classes of non-linear, or angular, PAHs show a much more controlled decrease in HOMO-LUMO band gap with increasing length (figure 14).

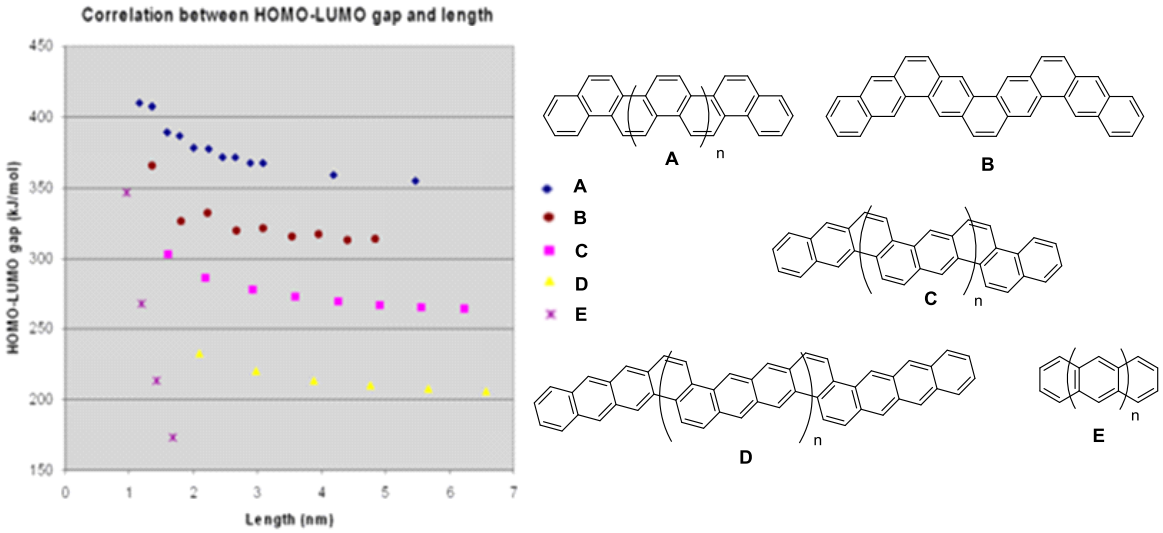


Figure 14: correlation between HOMO-LUMO gap and length of PAHs.

The patterns seen in the graph in figure 14 can be explained by Clar's aromatic sextets.[24] As linear acenes (class **E**, figure 14) are extended, they sequentially lose aromatic character as each newly added ring is a non-sextet. Contrarily, each ring in a phenacene (class **A**, figure 14) can be described as containing three double bonds and therefore six π-electrons, concurring with Hückel's 4*n*+2 rule of aromaticity. In going from class **B-D** in figure 14, while keeping length constant, the degree of linearity increases and so HOMO-LUMO band gap decreases. The graph in figure 14 shows that non-linear PAHs can, in theory, be extended to infinite length without significantly losing stability in the same way as acenes.

The HOMO levels and band gaps of PAHs can be used to quantitatively illustrate differences in stability. Picene has a lower HOMO level of -5.5 eV[21] compared to -5.0 eV in isomeric pentacene,[25] and almost twice as high a band gap of 3.3 eV compared to 1.8 eV. The HOMO level only decreases to -5.7 eV in extending the phenacene series from picene to [7]phenacene,[26] and the band gap decreases by the same amount to 3.1 eV. In fact, it has been reported that the difference in onset energy of UV absorption between phenanthrene and picene was too small to be detected,[27] and so the decrease in phenacene stability is really very minimal even after the addition of four rings.

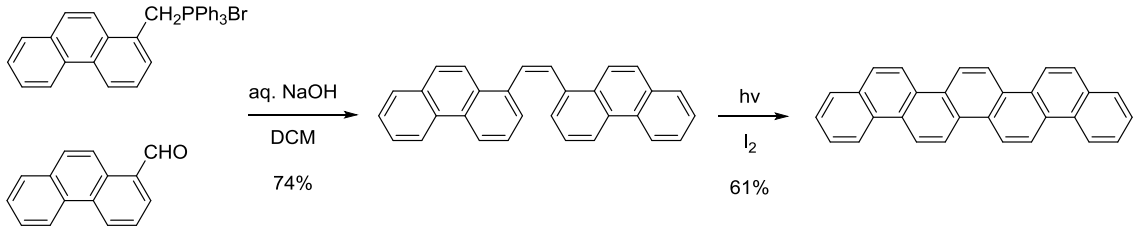
The first transistor-based application of phenacenes was based on picene and reported in 2008,[21] giving a mobility of 1.1 $cm^2\ V^{-1}\ s^{-1}$ in air-assisted thin-film FETs. This performance has further improved since then, with mobilities of up to 3.2 $cm^2\ V^{-1}\ s^{-1}$ reported in 2009[28] and up to 21 $cm^2\ V^{-1}\ s^{-1}$ in a publication describing alkyl-substituted picene-based FETs.[29] Promising device performance has also been reported in [6]phenacenes[30] and [7]phenacenes.[31]

1.3 PAH synthesis

This section of the introduction will focus on the synthesis of angular PAHs, for which there have been many different strategies employed.

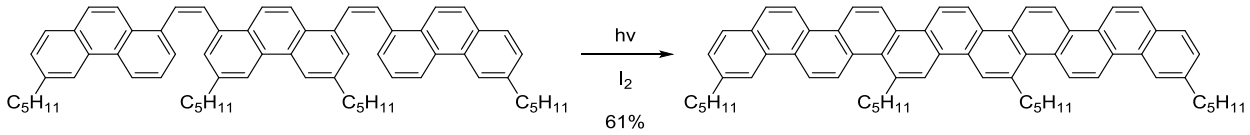
Photocyclisations

Photocyclisations have often been used to synthesise PAHs, particularly phenacenes, largely through the work of Mallory.[32-34] The first synthesis of [7]phenacene was reported in four steps using phenanthrene building blocks (also synthesised *via* photocyclisations) and Wittig chemistry to build the stilbene precursor (scheme 2).[34]



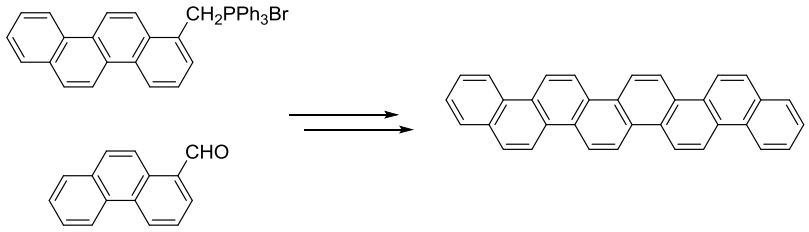
Scheme 2: synthesis of [7]phenacene.

Mallory also reported an [11]phenacene using this chemistry (scheme 3).[33]



Scheme 3: synthesis of an [11]phenacene.

By using this Wittig chemistry to combine a chrysene and an anthracene unit, the first synthesis of [8]phenacene was recently reported (scheme 4).[35]



Scheme 4: synthesis of [8]phenacene.

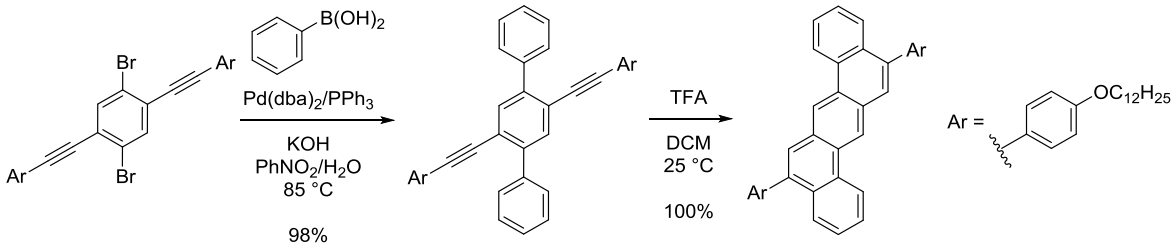
This phenacene was synthesised in 28% yield after photoirradiation of the precursor with iodine, and was found to be a promising molecule for transistor applications as five [8]phenacene thin-

film FETs gave an average mobility of 8 cm^2 V^{-1} s^{-1}, with a maximum of 16.4 cm^2 V^{-1} s^{-1} achieved.

These oxidative photocyclisations have also been used for the synthesis of helicenes,[36-38] picene,[39] and other five-ring PAHs.[40] Okamoto et al. also reported the preparation of several [3]-[7]phenacenes using a continuous flow reactor,[41] mostly giving yields over 70% and with the capability to scale up and bring through several grams per day. The scalability of these photolysis reactions is traditionally a drawback as dilute concentrations of 10^{-3} M are required, and continuous flow chemistry can be used to overcome this.

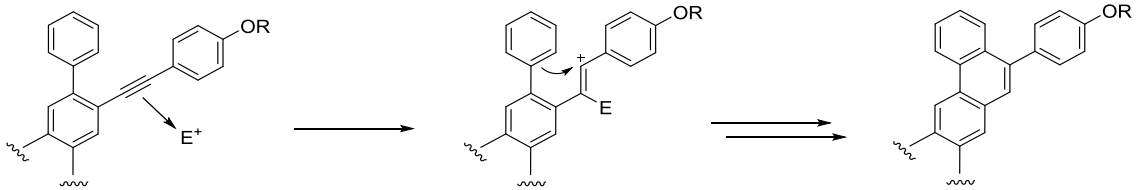
The Swager reaction

Swager first reported the electrophilic-induced synthesis of PAHs in 1994, using $I(py)_2BF_4$ as a source of electrophilic iodine, or alternatively trifluoroacetic acid. An example is shown in scheme 5, giving a dibenz[*a*,*h*]anthracene structure.[42]



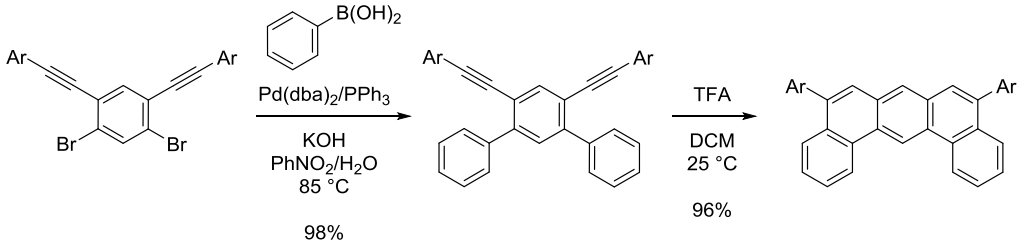
Scheme 5: PAH synthesis *via* electrophilic-induced cyclisation.

The terphenyl precursor was synthesised in two palladium-catalysed steps, Sonogashira and Suzuki cross-couplings, from 1,4-dibromo-2,5-diiodobenzene. A limitation of the final cyclisation step in this methodology is that an electron donating group is required on the acetylene substituent in order to favour exclusive formation of six-membered rings, and *p*-alkoxyphenyl groups have most commonly been used. This ensures that electrophilic attack leaves a positive charge on the acetylenic carbon further away from the central benzene ring, as this carbocation is resonance stabilised by the *p*-alkoxyphenyl group. The subsequent electrophilic attack on this carbocation from the outer terphenyl rings furnishes the new six-membered ring (scheme 6).



Scheme 6: electrophilic-induced cyclisations.

Extension of the Swager reaction to synthesise different PAH architectures was reported in 1997.[43] By using regioisomeric precursors to those shown in scheme 6, where aromatic substituents were situated meta to one another, an alternative dibenzanthracene structure was produced *via* the same synthetic steps (scheme 7).

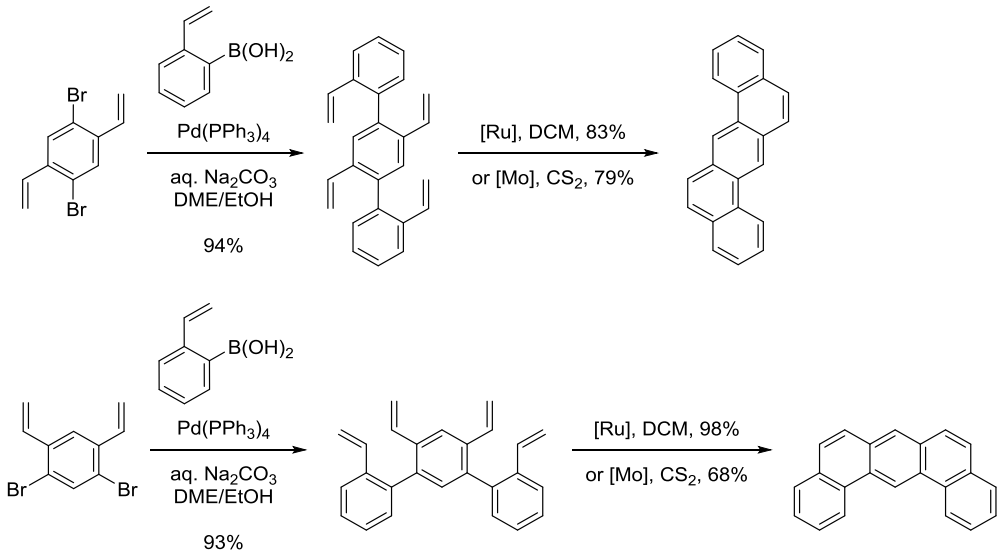


Scheme 7: regioselectivity of electrophilic-induced cyclisations.

Again, *p*-alkoxydodecyl was used as the electron donating group, and both of the final two steps proceeded in near-quantitative yield. Cyclisation of a precursor containing ortho-aromatic substituents to give a pentahelicene was more troublesome and lower-yielding, giving 20% yield after optimisation and use of a mixture of iodine and silver triflate. The Swager reaction has also been used in the synthesis of polyaromatic heterocycles.[44]

Ring-closing metathesis

RCM was first reported as a novel approach to phenanthrenes using a second-generation Grubbs catalyst.[45] Under mild conditions, phenanthrene and derivatives were all synthesised in quantitative yields after reaction in DCM at 40 °C for 2 h. This chemistry was applied to the synthesis of dibenzanthracene structures (scheme 8) with second- and third-generation Grubbs catalysts and molybdenum-based Schrock catalysts all effective.[46]

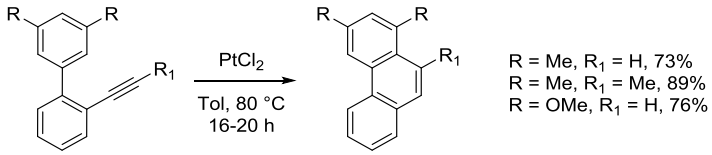


Scheme 8: syntheses of dibenzanthracenes *via* RCM.

Reactions were carried out at 25-35 °C, and gave the PAH targets in generally high yields. RCM has also been employed for the synthesis of helicenes.[47]

Metal-catalysed cycloisomerisations

Many researchers have used metal-catalysed cyclisations as a route to PAHs. Perhaps the most common metal salt to be used is platinum chloride, capitalising on the high affinity of Pt^{II} for π-systems. The pioneering work of Murai et al. demonstrated the effectiveness of platinum chloride as a catalyst for cyclorearrangements of 1,6- and 1,7-enynes, synthesising a variety of 1-vinylcycloalkenes in yields of over 60%.[48] Fürstner reported the flexible synthesis of phenanthrenes by platinum-catalysed cycloisomerisations of biphenyl compounds containing an *ortho*-alkyne substituent (scheme 9).[49] Like the Swager reaction, good preference for the 6-endo-dig over the possible 5-exo-dig was demonstrated, this time without the need for strongly electron donating substituents.

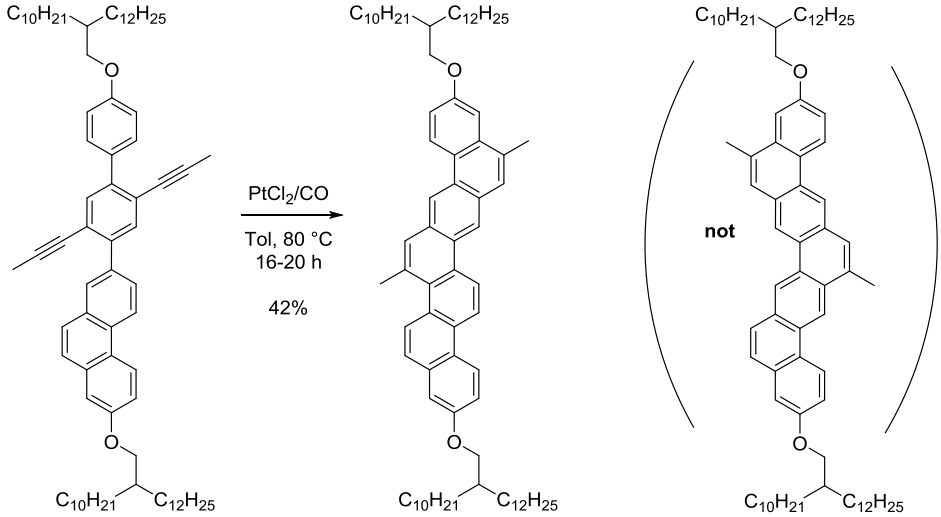


Scheme 9: $PtCl_2$-catalysed synthesis of phenanthrenes.

Fürstner has reported the synthesis of four- and five-ring PAHs as well as heterocyclic systems, with other metal salts, such as AuCl, $AuCl_3$, $GaCl_3$ and $InCl_3$, proving effective in various

cases.[50] Syntheses of several other PAHs using platinum chloride have also been reported, including helicenes[51, 52] and picenes.[53]

Platinum chloride was used in the cyclisation of four precursors to give PAHs of seven, nine, eleven and thirteen rings *via* double cycloisomerisations.[54] These reactions showed an interesting regioselectivity where attack of a naphthalene unit, where two conceivable cyclisations were possible, occurred on the more hindered carbon atom (scheme 10).



Scheme 10: $PtCl_2$-catalysed synthesis of a seven-ring PAH.

The regioselectivity of this cycloisomerisation gave an anthracene unit in all five compounds. In going from seven to thirteen rings, more methyl groups were introduced to aid solubility of the precursors. Figure 15 shows examples of these extended PAHs.

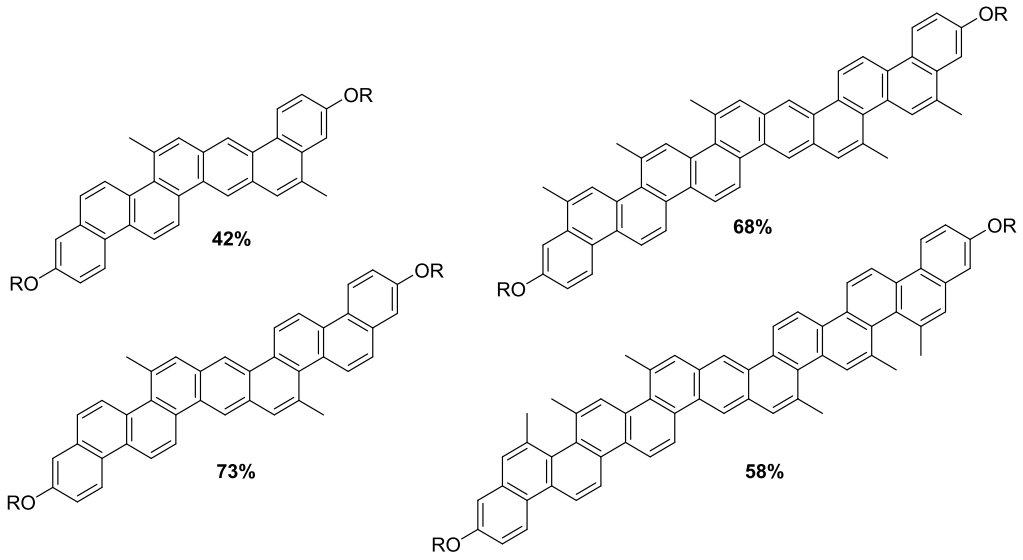
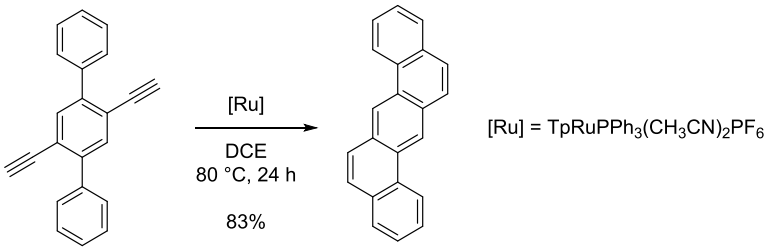


Figure 15: extended PAHs synthesised by $PtCl_2$-catalysed cycloisomerisations.

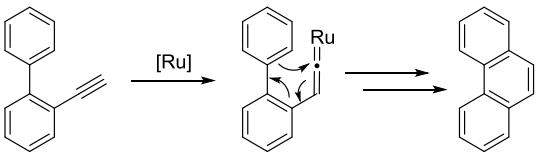
This publication nicely demonstrated the theory supported by the graph shown in **1.2** (figure 14) that angular PAHs can be considerably extended without significantly losing stability. All of the compounds shown in figure 15 were obtained as air-stable products, and photophysical studies showed that the HOMO-LUMO band gap decreased from 3.07 eV to 2.80 eV in going from five to thirteen rings. The HOMO level in going from five to eleven rings increased from -5.57 and -5.36 eV – this was not determined for the thirteen-ring PAH due to its extremely low solubility for cyclic voltammetry.

Ruthenium is another metal commonly employed in the synthesis of PAHs. Liu and co-workers synthesised a variety of compounds by ruthenium-catalysed cyclisation of terminal alkynes onto a benzene ring, including coronene derivatives and unsubstituted dibenz[*a*,*h*]anthracene (scheme 11).[55]



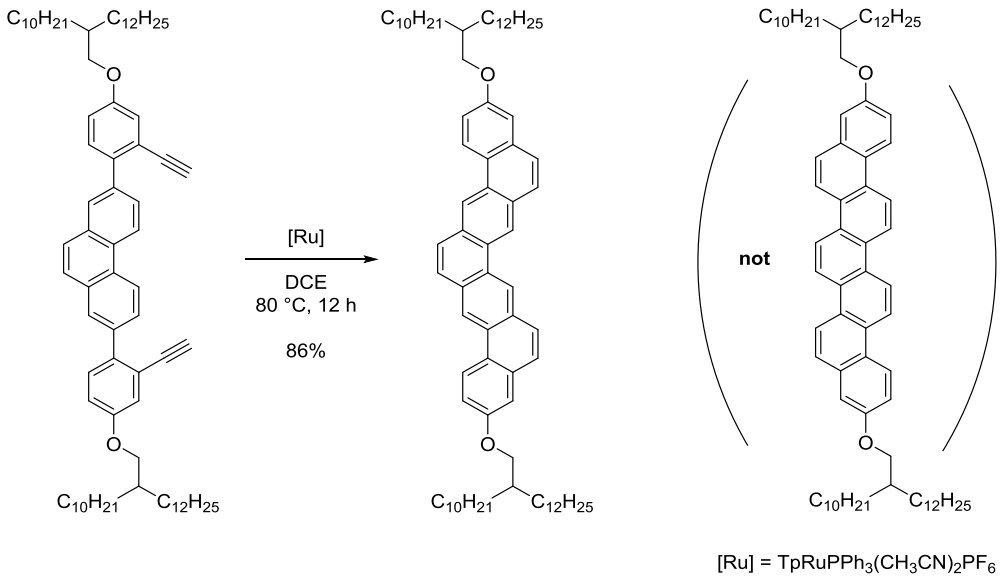
Scheme 11: ruthenium-catalysed synthesis of dibenz[*a*,*h*]anthracene.

This reaction proceeds through a ruthenium-vinylidene intermediate (scheme 12), explaining the strong preference for 6-endo-dig cyclisation.



Scheme 12: mechanism of ruthenium-catalysed cyclisation *via* a ruthenium-vinylidene intermediate.

Ruthenium-catalysed cyclisations were used for the synthesis of extended PAHs by Chen et al. in the same publication reporting the compounds shown in scheme 10.[54] The group observed that the ruthenium catalyst demonstrated the opposite regioselectivity to $PtCl_2$, with attack of a naphthalene unit this time occurring on the less hindered aromatic carbon atom (scheme 13).



Scheme 13: ruthenium-catalysed synthesis of a seven-ring PAH.

The likely explanation for this observation was that complexation of the bulky ruthenium catalyst to give the ruthenium-vinylidene intermediate meant the less sterically hindered site of the central phenanthrene moiety was favoured. Five-, seven- and nine-ring PAHs were synthesised by this method (figure 16), containing one, two or three anthracene units respectively based on the regioselectivity of the cyclisation.

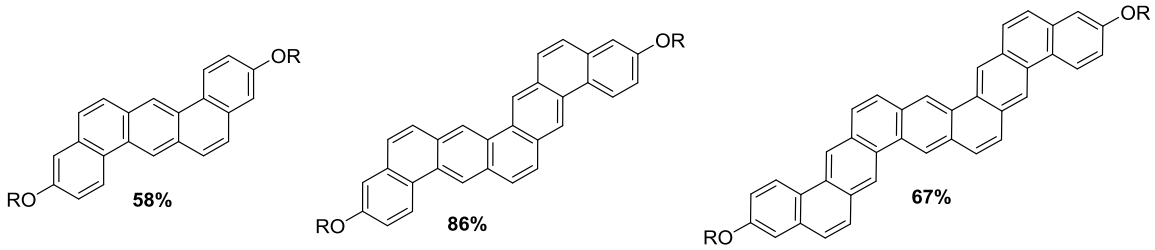
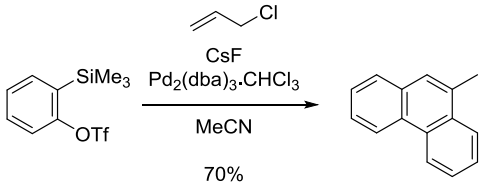


Figure 16: extended PAHs synthesised by ruthenium-catalysed cycloisomerisations.

Again, the effect of PAH extension on stability was not very significant, with the band gap decreasing from 3.07 eV to 2.84 eV in going from five to nine rings. A major drawback of this ruthenium-catalysed chemistry is its limitation to terminal alkynes, which means potentially solubilising alkyl groups cannot be incorporated into the PAH in the same way they are in $PtCl_2$-catalysed cyclisations.

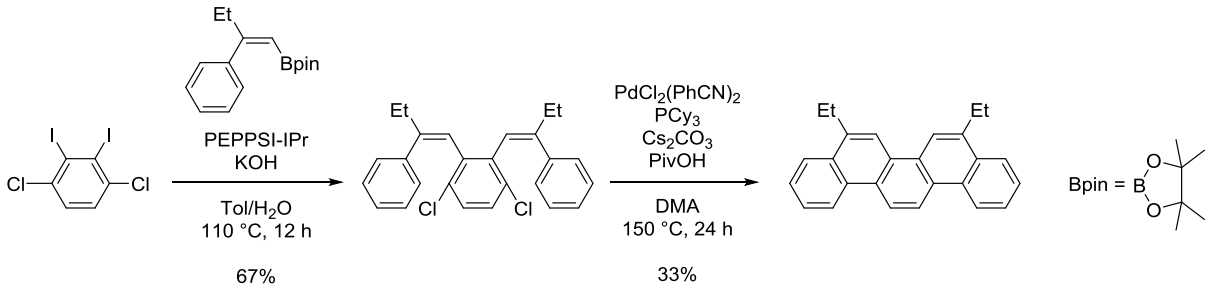
Palladium has also been successfully utilised as a catalyst for PAH synthesis. Palladium-catalysed cross-couplings such as Sonogashira[56] and Suzuki[57] reactions are now widely used in organic chemistry and the synthetic procedure for any PAH will almost always include at least one such reaction. Various publications in the 1990s reported the palladium-

catalysed annulation of aryl iodides and diphenylacetylene to give substituted phenanthrenes.[58-60] Yoshikawa et al. also reported benzyne carbopalladations as a route to phenanthrenes, using 2-(trimethylsilyl)phenyl triflate as a benzyne precursor for reaction with allylic chlorides (scheme 14).[61]



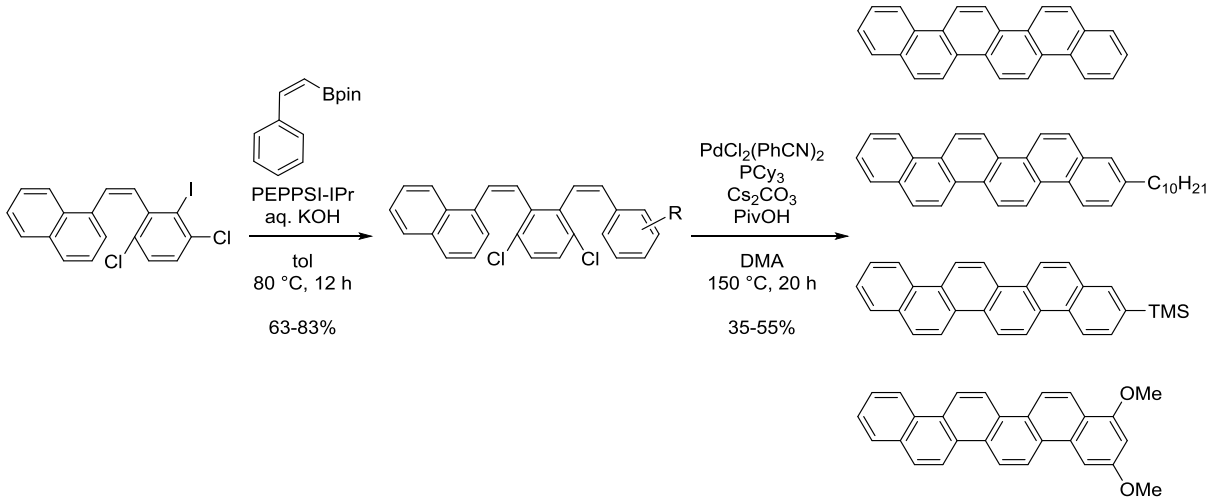
Scheme 14: phenanthrene synthesis *via* benzyne carbopalladations.

Palladium-catalysed cyclisations have been reported in the preparation of tetracenes and pentacenes,[62] polyaromatic heterocycles,[63] and phenacenes.[64-66] Nishihara and co-workers synthesised a variety of substituted picenes in just two steps from 1,4-dichloro-2,3-diiodobenzene, such as 5,8-diethylpicene (scheme 15).[64]



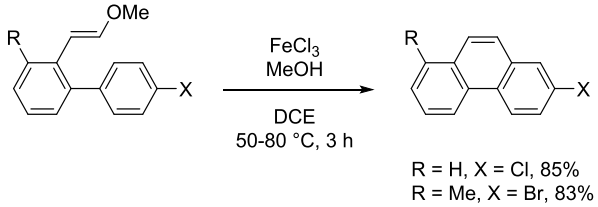
Scheme 15: palladium-catalysed synthesis of a substituted picene.

Picenes with a substituent on the outer rings were also synthesised in moderate yields, and similar chemistry has been used to make fluorinated chrysenes and picenes.[66] The Nishihara group later reported substituted [6]phenacenes (scheme 16) preparation of which required the addition of an extra Suzuki cross-coupling due to the asymmetry of the precursor.[65]



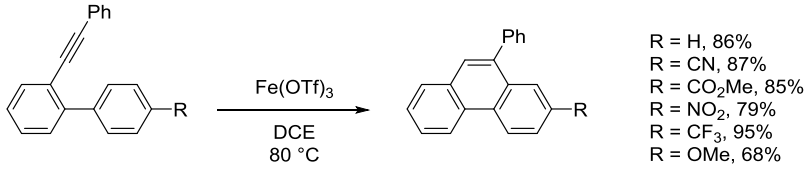
Scheme 16: palladium-catalysed synthesis of fulminenes.

Copper,[67, 68] indium,[69] gold[70] and nickel[71] are among other metals which have been used in the preparation of various PAHs. More recently, Takai and co-workers have developed the synthesis of phenanthrenes, chrysene and fulminenes using bismuth chemistry.[72, 73] Their work also found that the synthesis of phenanthrenes containing electron-withdrawing halide substituents was a lot higher yielding when iron(III) chloride was used in place of bismuth(III) triflate (scheme 17).



Scheme 17: iron-catalysed synthesis of halide-substituted phenanthrenes.

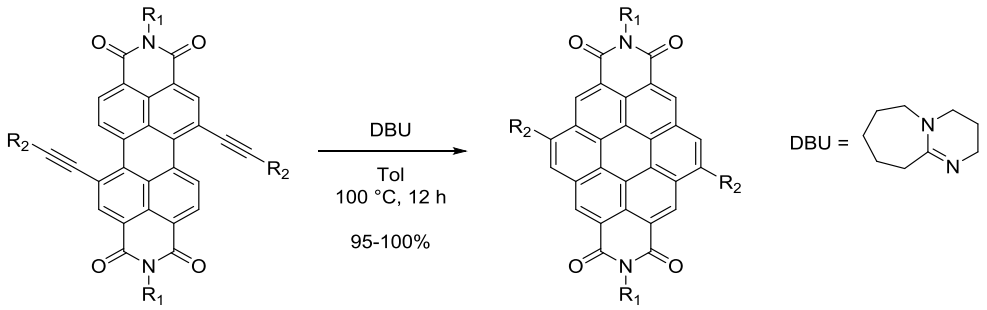
Using similar precursors, and milder conditions of 25 °C, alkyl- and phenyl-substituted precursors were synthesised using $Bi(OTf)_3$ as a catalyst, in yields over 90%.[72] From a green chemistry point of view, the use of more environmentally benign and inexpensive iron in place of heavier metals is an attractive prospect for PAH synthesis and organic chemistry in general. Iron (III) triflate has also been reported as a catalyst in the cyclisations of *ortho*-alkynyl biaryls, mostly featuring electron withdrawing groups (scheme 18).[74]



Scheme 18: iron-catalysed synthesis of phenanthrenes.

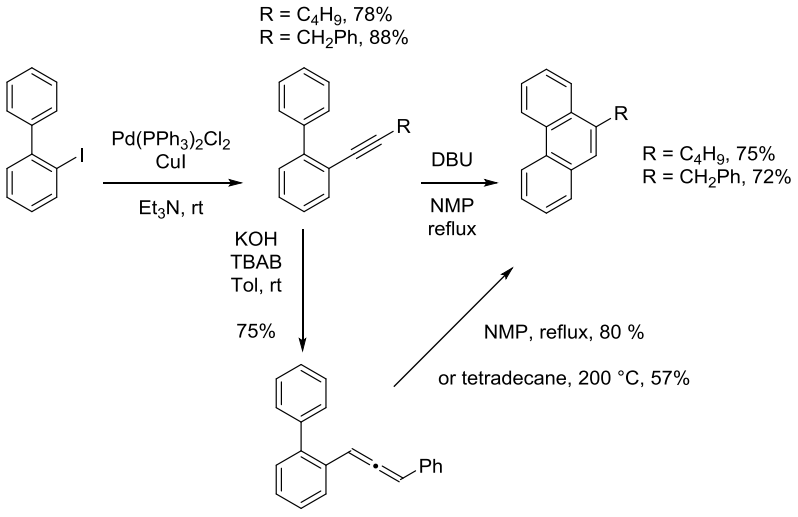
Base-catalysed cyclisations

Unlike the Swager or platinum-catalysed reactions which use electrophiles, *ortho*-alkynyl biaryls can be cyclised to form a new aromatic ring using an organic, basic catalyst. This was first reported by Müllen, who used DBU in the synthesis of coronene diimides from isomeric dialkyne-substituted perylene diimides (scheme 19).[75]



Scheme 19: DBU-catalysed synthesis of coronene diimides.

This base-catalysed perylene to coronene transformation has been reported by other groups,[76, 77] typically using DBU in refluxing toluene. The cyclisation was rediscovered by Burton, who was the first to propose an allene intermediate which is formed by isomerisation from an alkyne after propargylic deprotonation by the organic base. This was first speculated in a publication reporting the synthesis of 3-fluoro-1-substituted naphthalenes,[78] and confirmed in the synthesis of phenanthrenes in 2006 (scheme 20).[79]



Scheme 20: synthesis of phenanthrenes by base-catalysed cyclisation of 2-alkynylbiphenyls and uncatalysed cyclisation of a model allene compound.

One interesting observation in the synthesis of polysubstituted naphthalenes by Burton was that cyclisation onto a 4-nitro-substituted aromatic ring required a lower temperature of 170 °C

compared to 200 °C for other systems. This is consistent with the coronene diimide formation carried out at 100 °C, and it appears that electron-withdrawing groups lower the activation energy of this isomerisation reaction. DBU-catalysed cycloisomerisations have been more commonly seen in heterocyclic synthesis.[80-84]

1.4 Incorporation of heteroatoms into PAHs

1.4.1 Thienoacenes

In trying to overcome the problems associated with unsubstituted pentacene, functionalised pentacene derivatives and non-linear PAHs have been discussed as more stable classes of organic semiconductor. Another strategy aimed at improving the stability of acenes is the replacement of benzene rings with aromatic heterocycles. Incorporation of sulphur atoms into an acene framework is known to lower the HOMO level and create a wider band gap, offering superior ambient stability to pentacene and protecting against photochemical degradation. Through combining features of pentacene and polythiophene, two prominent semiconductors, stable thienoacene compounds with high charge carrier mobilities have been synthetic targets for several years.

Thienoacenes can generally be divided into four groups – [*n*]thienoacenes, benzene-thiophene alternating molecules (BTAs), diacene-fused thienothiophenes (DAcTTs) and acenedithiophenes (AcDTs).[85] Examples of each classification are shown in figure 17, where it is worth noting that only the aromatic frameworks, with no substituent patterns, are shown.

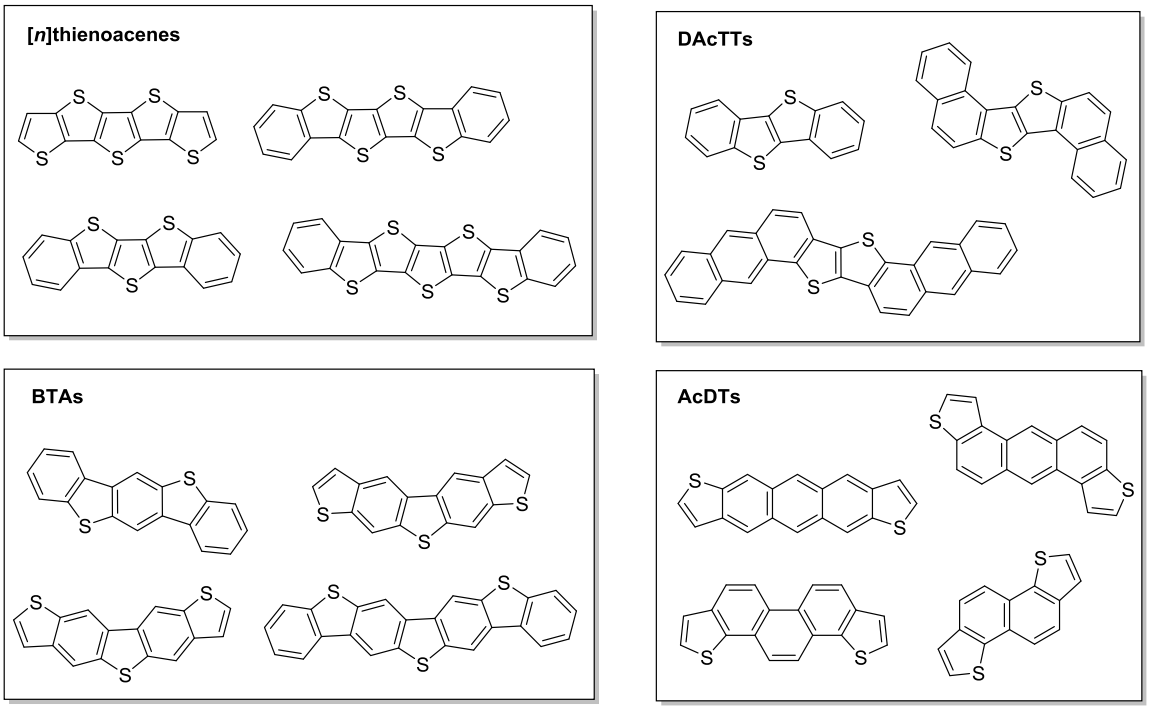


Figure 17: classes of thienoacenes.

These compounds generally have a HOMO level lower than -5.0 eV and much wider band gaps than pentacene (table 1).

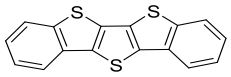
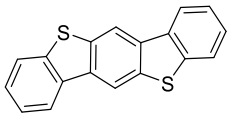
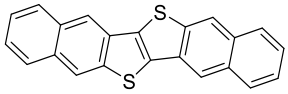
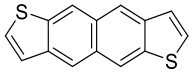
Compound	Thienoacene class	HOMO / eV	Optical band gap / eV	Reference
	[*n*]thienoacene	-5.6	3.46	(86)
	BTA	-5.40	3.30	(87)
	DAcTT	-5.44	3.0	(88)
	AcDT	-5.3	3.0	(89)

Table 1: thienoacenes, their HOMO energy levels and optical band gaps.

As well as having lower-lying HOMOs, there have been several reports of good device performance using thienoacenes. Mobilities of over 1.0 cm^2 V^{-1} s^{-1} have been reported for examples of [*n*]thienoacenes, BTAs and AcDTs (table 2).

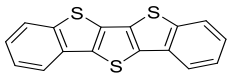
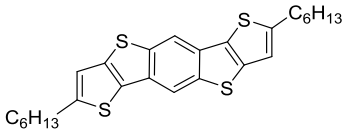
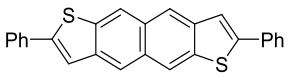
Compound	μ / cm^2 V^{-1} s^{-1}	Reference
	1.8	(90)
	1.7	(91)
	1.5	(89)

Table 2: different exemples of thienoacenes and their mobilities.

DAcTTs represent the most successful class of thienoacenes in device performance – notably [1]benzothieno[3,2-*b*]benzothiophene (BTBT) as well as dinaphtho[2,3-*b*:2′,3′-*f*]thieno[3,2-*b*]thiophene (DNTT) and dianthra[2,3-*b*:2′,3′-*f*]thieno[3,2-*b*]thiophene (DATT), figure 18.

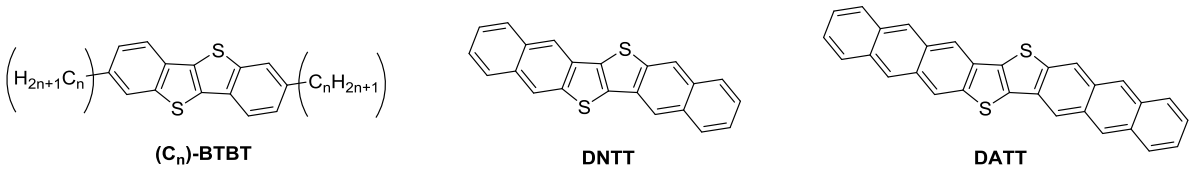


Figure 18: DAcTTs.

Unsubstituted and decyl-substituted DNTT-based devices have shown mobilities of 8.3 and 12 $cm^2\ V^{-1}\ s^{-1}$ respectively,[92,93] while OFETs based on the stable DATT achieved a mobility of 3.0 $cm^2\ V^{-1}\ s^{-1}$.[94] Ebata et al. synthesised 2,7-dialkyl BTBT derivatives (C_n-BTBTs, n = 5-14),[95] and solution-processed OFET devices typically gave mobilities approaching, or higher than, 1.0 $cm^2\ V^{-1}\ s^{-1}$. C_8-BTBT has been studied by several groups,[96-99] and inkjet printing of thin films using single crystals of this compound yielded transistors with an average charge carrier mobility of 16 (and a maximum of 31) $cm^2\ V^{-1}\ s^{-1}$.[98] Devices based on the mono-alkylated C_{13}-BTBT also gave a very high mobility of 17 $cm^2\ V^{-1}\ s^{-1}$, the highest at the time for organic thin-film transistors.[100]

As with PAHs, several different synthetic strategies are reported for thienoacenes, including acid-, base- and metal-catalysed reactions and photocyclisations. The rest of the discussion will mostly focus on synthesis of AcDTs, as the compounds synthesised in this project fall into this category.

Acenedithiophenes

AcDTs can be split into linear and angular molecules, and syntheses of both are discussed. Examples of AcDTs include benzodithiophene (BDT), naphthodithiophene (NDT) and anthradithiophene (ADT), figure 19, the linear analogues of which are isoelectronic with anthracene, tetracene and pentacene respectively.

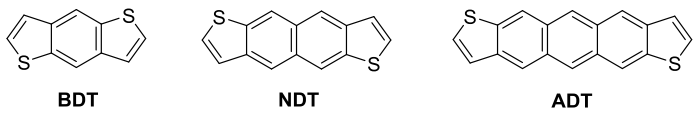
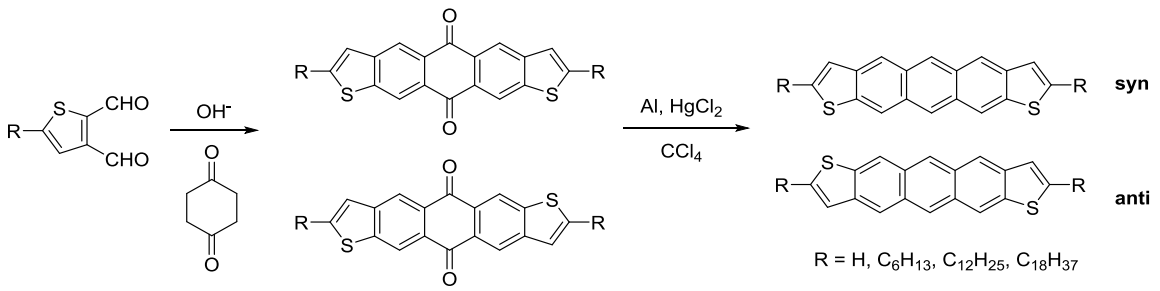


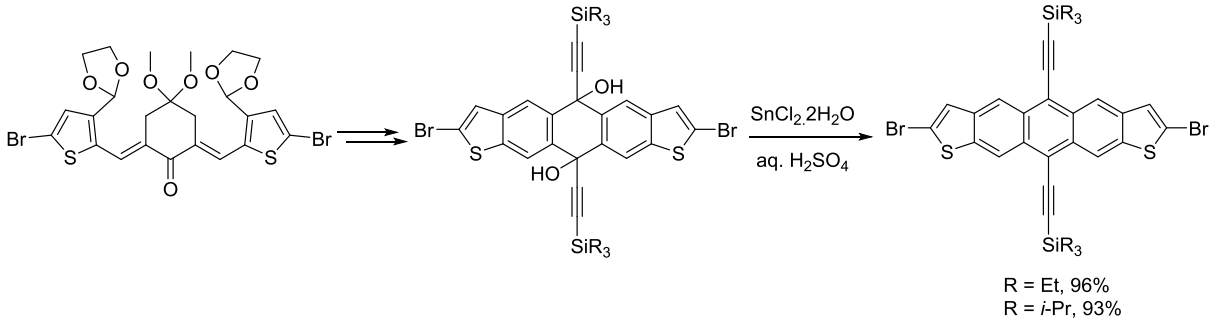
Figure 19: linear AcDTs.

The first synthesis of linear ADTs was reported by Laquindanum et al. in 1998,[101] using the traditional preparation of pentacene *via* quinone reduction. This methodology, involving cyclisation to give a dione which was reduced to the polyaromatic system, afforded an inevitable mixture of syn and anti isomers (scheme 21).



Scheme 21: synthesis of syn- and anti-ADTs.

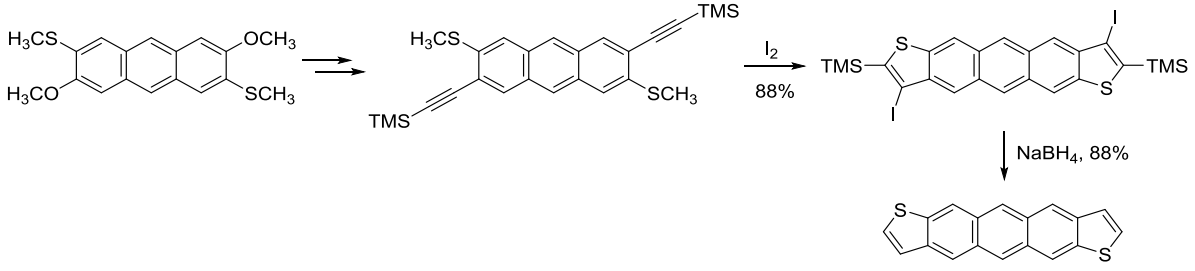
Aldol condensation between the thiophene-2,3-dicarbaldehyde and 1,4-cyclohexadione is regiorandom, leading to the inseparable mixture of isomers. Regioselectivity can be achieved by mono-protection of both components of this first aldol, such as in the synthesis of syn-ADTs (scheme 22).[102]



Scheme 22: synthesis of syn-ADTs.

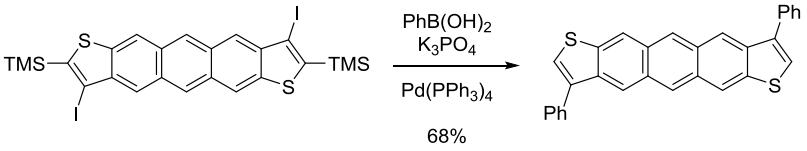
The first aldol reaction was followed by a one-pot global deprotection and aldol condensation with $In(OTf)_3$, then alkynylation and reduction using tin chloride and aqueous sulphuric acid to give the syn-ADTs in near-quantitative yields. Incorporation of trialkylsilylethynyl groups at the 5- and 11-positions is a common substitution pattern of anthradithiophenes, as it is in functionalised pentacenes.

Takimiya and co-workers reported the synthesis of anti-ADT in six steps from 2,6-dimethoxyanthracene, the first step of which was a double lithiation followed by reaction with dimethyldisulphide to give the starting material shown in scheme 23.[103]



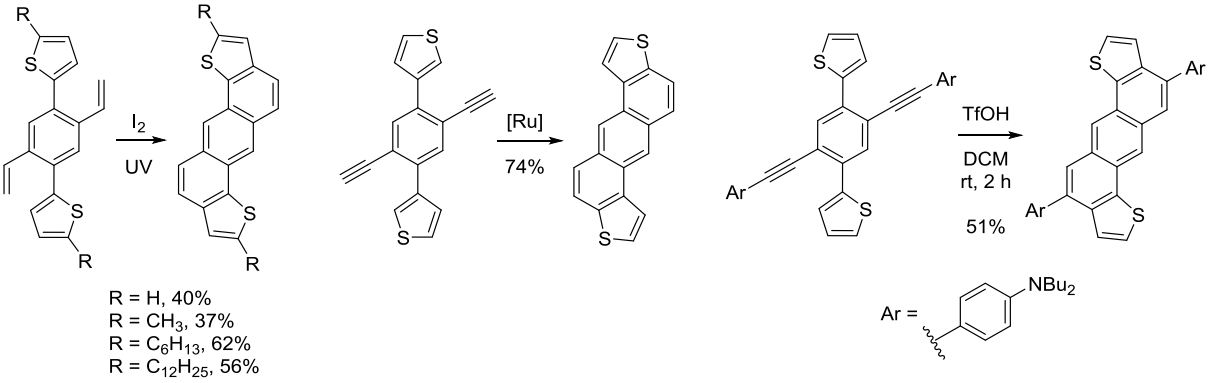
Scheme 23: synthesis of anti-ADT.

Demethylation to the diol using BBr_3 was followed by triflation and Sonogashira reactions, and treatment with iodine in DCM at room temperature gave the cyclised product in high yield. Reductive desilylation and deiodination, using sodium borohydride, to give anti-ADT was also high-yielding. An added advantage to this method, due to the iodine substituent, was the possibility of functionalising at the β-thiophene position, unlike most examples where functionalisation at the α-carbon can be achieved by using substituted thiophene starting materials, substituted acetylenes or by exploiting the acidity at this position. The synthesis of diphenyl-substituted anti-ADT *via* a double Suzuki cross-coupling was also reported (scheme 24).



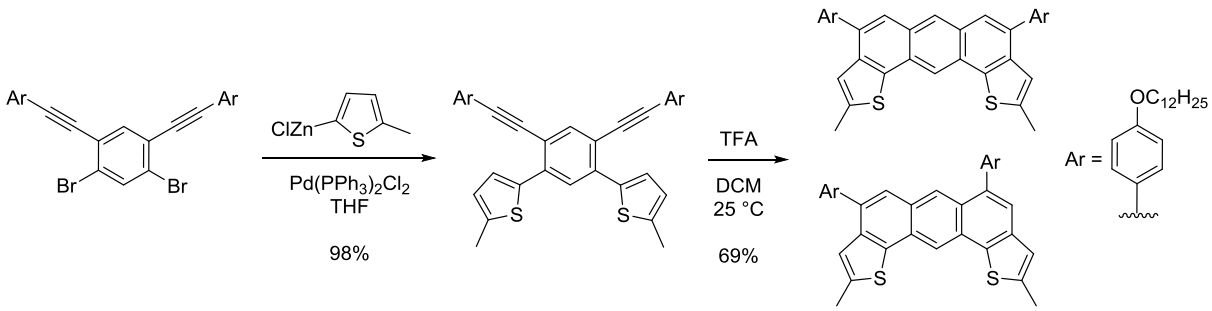
Scheme 24: synthesis of 3,9-diphenyl-ADT.

Angular ADTs have been prepared using photocyclisations,[104, 105] ruthenium-catalysed cyclisations[55] and the Swager reaction (scheme 25).[43, 44]



Scheme 25: syntheses of angular ADTs.

These structures are isoelectronic with dibenz[*a*,*h*]anthracene, where the terminal aromatic substituents can be described as being on 'opposite sides' of the central anthracene unit. By changing the starting material to position dialkynyl and dibromide at different positions on a benzene ring, Swager synthesised a different and rarely seen architecture of angular ADTs, although an inseparable mixture of isomers was produced (scheme 26).[43]



Scheme 26: syntheses of angular ADTs.

More extended and novel nine-ring thienoacene systems were synthesised (figure 20) by changing the substituent to a dibenzothiophene.

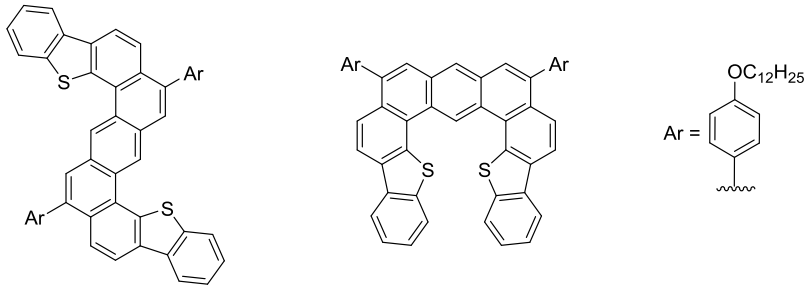
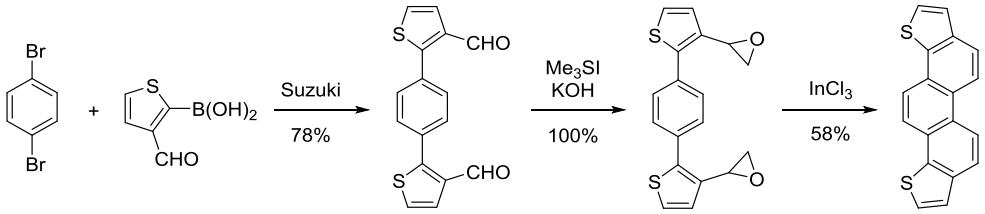


Figure 20: nine-ring angular AcDTs.

A newer development in the synthesis of AcDTs was the preparation of phenanthro[1,2-*b*:8,7-*b*']dithiophene (PDT), first reported in 2014. This is isoelectronic with picene and was synthesised in three steps from 1,4-dibromobenzene (scheme 27).[106]



Scheme 27: first synthesis of PDT.

After screening of several Lewis acids for the final Friedel-Crafts-like cycloaromatisation, $InCl_3$ was used. The selectivity towards giving PDT over an angular ADT was speculated to be due to an electronic effect, with the relatively electron-rich aromatic site favoured once one 'end' of the molecule had already reacted (figure 21).

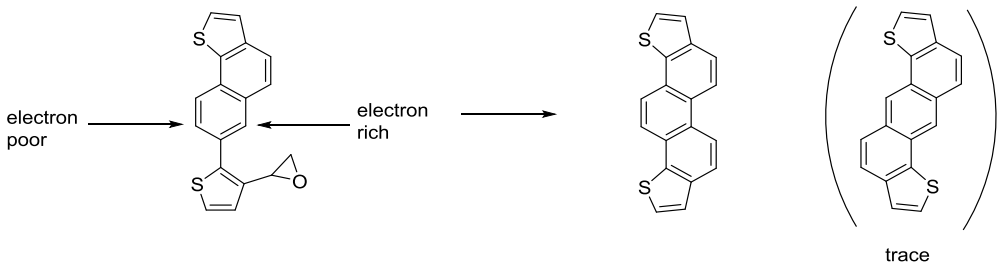
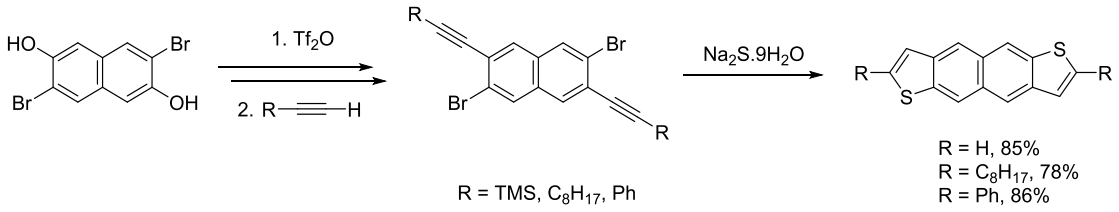


Figure 21: regioselectivity of PDT synthesis.

NDTs have become more prominent recently, with the synthesis and properties of linear and angular versions. Takimiya has reported a four-step approach which can give four different NDT structures, all of which follow the same chemical sequence.[89, 107] The structures are determined by the position of two hydroxyl substituents on a naphthalene diol starting material and by the subsequent selective double halogenation. This step is followed by triflation of the hydroxyl groups, chemoselective Sonogashira coupling at the triflate sites and a ring closure using sodium sulphide. An example of this strategy for the synthesis of anti-NDT and derivatives, which begins with naphthalene-2,6-diol, is shown in scheme 28.



Scheme 28: synthesis of anti-NDTs.

Octyl- and phenyl-derivatives were incorporated onto all of the NDT series by using the respective substituted acetylenes. Trimethylsilylacetylene was used for the synthesis of unsubstituted systems, with desilylation achieved in the final step. Figure 22 shows the other NDT structures and their respective dihalonaphthalenediols.

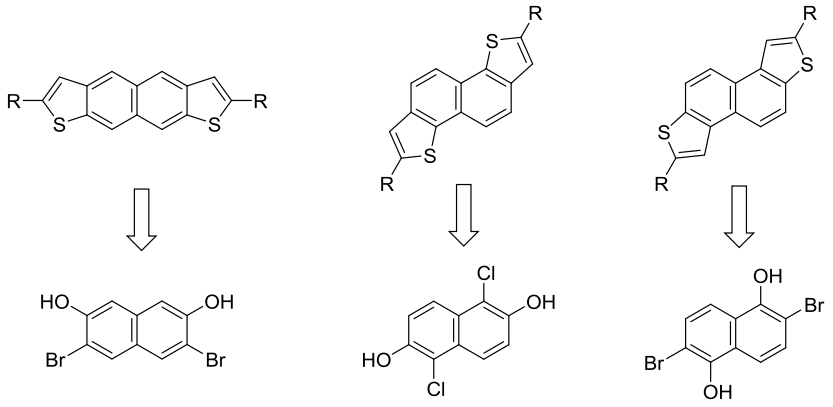
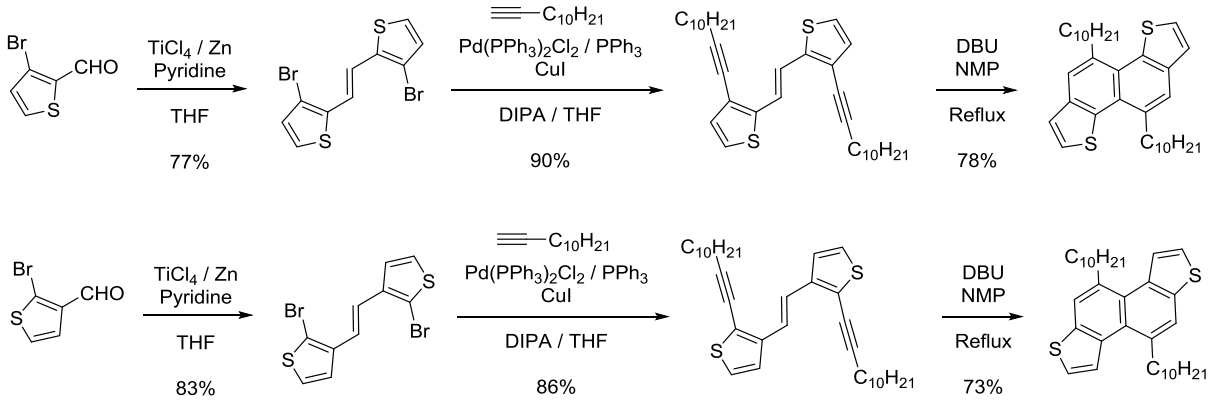


Figure 22: linear and angular NDTs and their precursors.

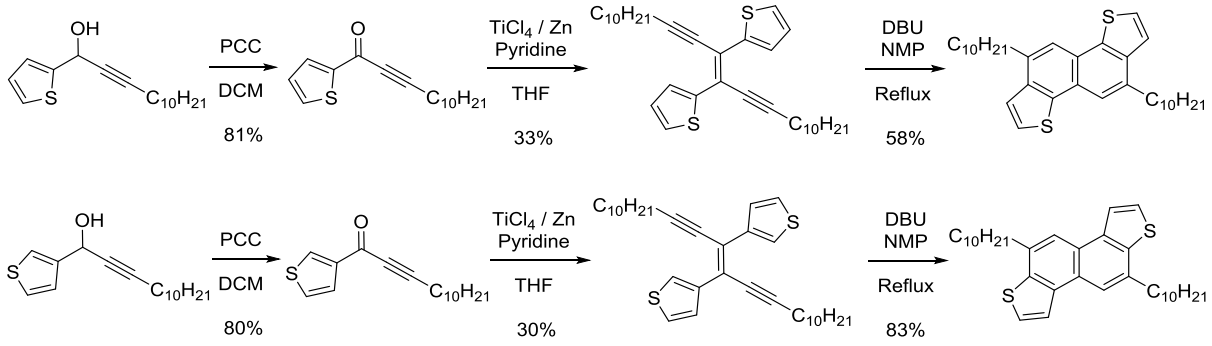
Comparison of all four unsubstituted structures showed that the angular NDTs had wider band gaps and lower-lying HOMO levels than the linear molecules, and this is expected from Clar's aromatic π-sextet rule. These NDTs generally showed good device performance, giving OFETs with mobilities typically greater than 0.1 $cm^2\ V^{-1}\ s^{-1}$. The diphenyl-substituted anti-ADT (scheme 24) yielded the best devices giving mobilities of up to 1.5 $cm^2\ V^{-1}\ s^{-1}$.[89]

Synthesis of angular NDTs by base-catalysed cyclisation has also been reported.[81] 4,9-dialkylated angular NDTs were synthesised from two isomeric starting materials, which underwent McMurry coupling and a double Sonogashira cross-coupling followed by isomerisation catalysed by DBU (scheme 29).



Scheme 29: synthesis of 4,9-dialkylated angular NDTs.

McMurry couplings and base-catalysed cyclisations were also the key steps in synthesis of the isomeric 5,10-dialkylated angular NDTs, which began with oxidation of thiophenyl propargyl alcohols using pyridinium chlorochromate (scheme 30).



Scheme 30: synthesis of 5,10-dialkylated angular NDTs.

Taking advantage of the acidic α-thiophenyl carbon atom, these NDTs were further functionalised by double lithiation and addition of trimethyltin chloride, giving stannylated monomers which could be used for synthesis of larger molecules and polymers.

Higher linear acenedithiophenes have also been reported, using the traditional route of aldol chemistry followed by alkynylation of acenequinones to give inseparable mixtures of anti and syn compounds (figure 23).[108]

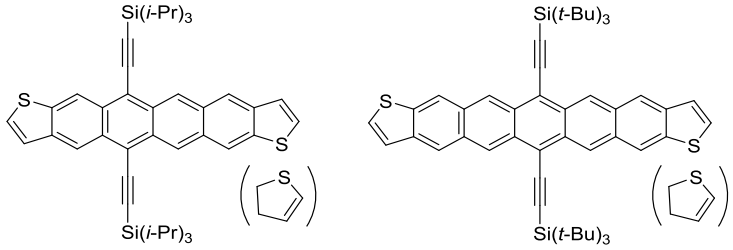
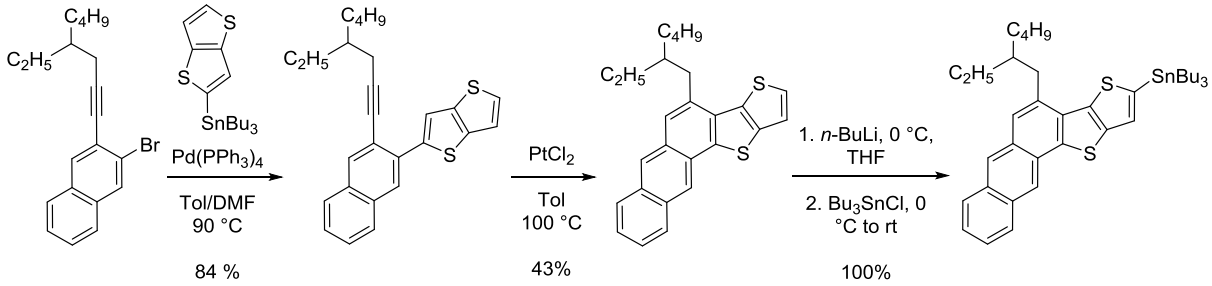


Figure 23: linear tetradithiophene and pentadithiophene derivatives.

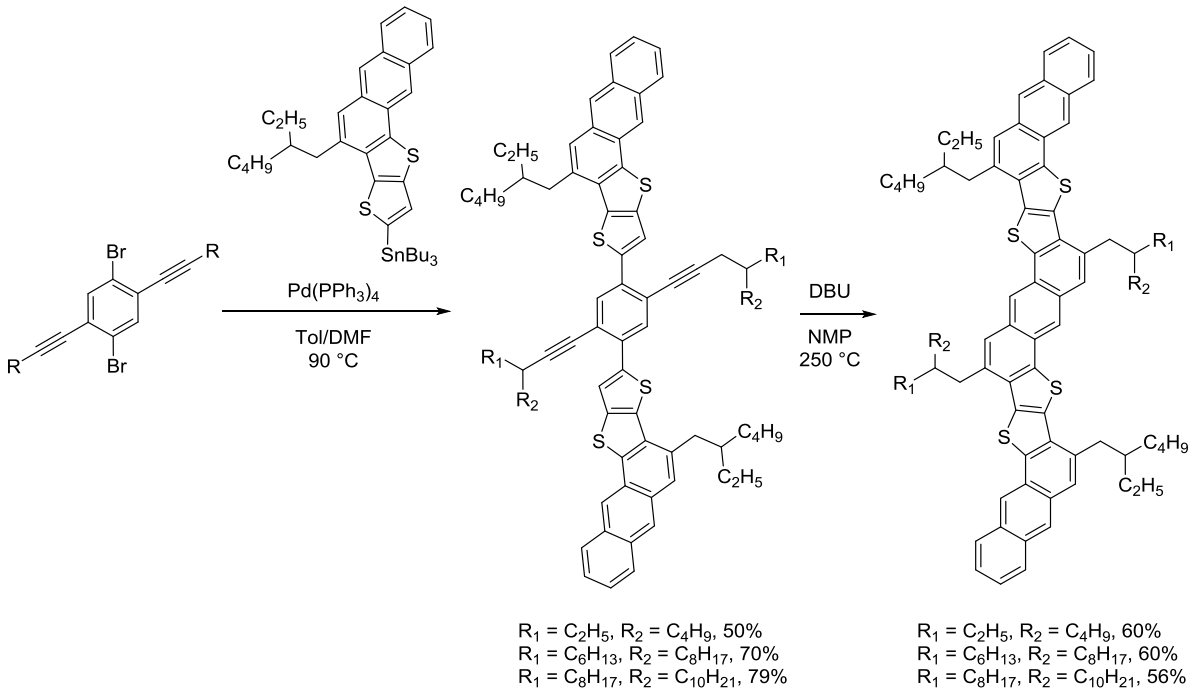
These compounds were isolated, showing good solubility and stability, with minimal decomposition on silica gel, and also showed strong π-stacking in the solid state. In the pentadithiophene example, use of *tert*-butyl chains protected the seven-ring system against dimerisation observed when TIPS (triisopropylsilyl) was used.

A key idea in this project was the synthesis of extended polyaromatic compounds going beyond what had previously been seen in the literature. While several reports exist of four- to nine-ring systems, extension of thienoacenes beyond this was not seen until a recent publication by Shao et al. reported a compound of thirteen fused rings.[84] Synthesis and functionalisation of a five-ring thienoacene was required for this, with the starting material shown in scheme 31 synthesised from triflation of 3-bromonaphthalen-2-ol and selective Sonogashira coupling.



Scheme 31: synthesis of a functionalised five-ring thienoacene.

Attachment of thieno[3,2-*b*]thiophene to the naphthalene core *via* Stille cross-coupling and a platinum-catalysed cyclisation gave the five-ring system, and deprotonation followed by transmetallation using tributyltin chloride gave an organotin reagent which was used in another Stille cross-coupling with a benzene core. Cyclisation of the resulting precursor with DBU in NMP under microwave conditions gave the final extended thienoacene (scheme 32).



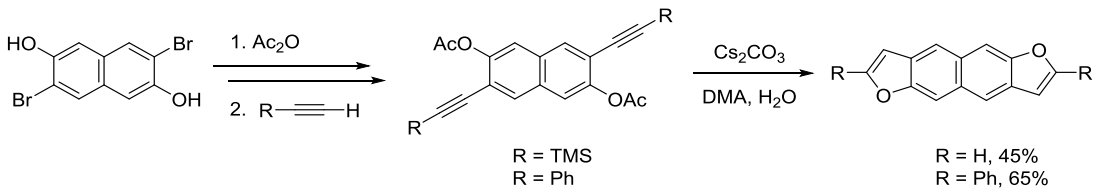
Scheme 32: synthesis of thirteen-ring thienoacenes.

The extended thienoacene system with octyl and decyl chains, synthesised in 56% yield, was the compound most extensively studied due to being the most soluble. In air-saturated toluene, this compound showed good photochemical stability consistent with its low-lying HOMO level of -5.25 eV and optical band gap of 2.70 eV.

1.4.2 Furanoacenes

Furyl-fused polyaromatic systems are less explored in organic electronics than thienoacenes. The lower aromaticity and higher electronegativity of furan compared to thiophene should yield distinct molecular and electronic properties of furanoacenes, and give stable compounds with lower-lying HOMO levels. In the past decade there have been an increasing number of reports of such systems.

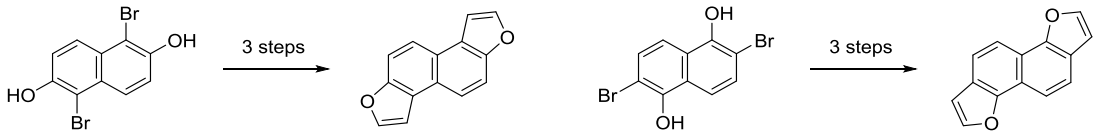
Furyl-fused materials have often been synthesised using very similar methods described in **1.4.1** to give analogous thiophenyl-fused compounds, with which their electronic properties and device performance can be compared. For example, like NDTs, unsubstituted and diphenyl-substituted linear naphthodifurans (NDFs) were synthesised in four steps from 2,6-dihydroxynaphthalene.[109] This differed from NDT synthesis in that the hydroxyl groups were protected rather than triflated, so that subsequent Sonogashira cross-coupling could occur at the bromide sites and leave the oxygen atoms required for furan synthesis intact. A base-catalysed cyclisation using caesium carbonate gave the four-ring systems (scheme 33).



Scheme 33: synthesis of linear NDFs.

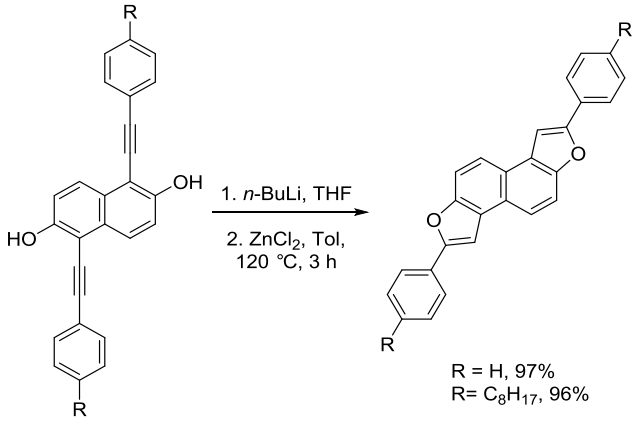
Unsubstituted linear NDF had a slightly lower HOMO level of -5.5 eV compared to -5.3 eV for the analogous unsubstituted NDT, and a wider band gap of 3.4 eV compared to 3.0 eV. The diphenyl NDF derivative yielded OFETs which gave a good mobility of 0.6 cm^2 V^{-1} s^{-1}, although this was not as high as the analogous diphenyl NDT derivative. This NDF did however give better performance in OPV devices.

Angular NDFs were synthesised by using an identical chemical sequence to the one shown in scheme 33.[110] For the two compounds shown in scheme 34, TBAF was used for the final step in place of caesium carbonate.



Scheme 34: synthesis of angular NDFs.

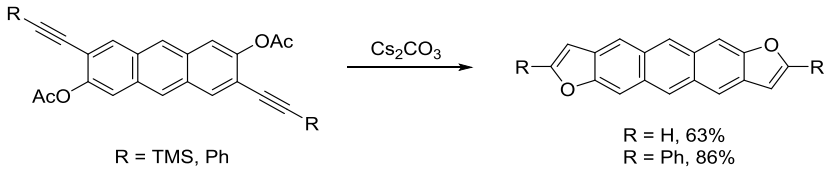
Diphenyl-substituted angular NDFs (DPNDFs) have also been synthesised, using similar chemistry to build the precursors followed by zinc-mediated cyclisations.[111] Lithiation and transmetallation of the hydroxyl substituents was followed by intramolecular attack of the resulting zinc phenolate on the alkyne substituents to give the angular systems (scheme 35).



Scheme 35: synthesis of aryl-substituted angular NDFs.

Use of both compounds in devices was promising, with the unsubstituted DPNDF giving a hole mobility of 1.3 $cm^2\ V^{-1}\ s^{-1}$, 1.6 times higher than the analogous and isolectronic NDT.[89] Devices using the octyl-substituted DPNDF showed mobilities of up to 3.6 $cm^2\ V^{-1}\ s^{-1}$.

Anthradifurans (ADFs) are also now well-known, and similar methods have been used to synthesise linear and angular versions of these, such as Cs_2CO_3-catalysed cyclisations to give isomerically pure anti compounds (scheme 36).[103]



Scheme 36: synthesis of linear anti-ADFs.

By using anthracene instead of naphthalene starting materials, the same strategy shown in scheme 33 was used to give the target compounds. Comparison of unsubstituted anti-ADF with analogous ADT showed a slightly lower HOMO level (-5.1 eV and -5.0 eV respectively) and slightly wider band gap (-2.6 eV and -2.4 eV respectively). Like the naphthalene-derived systems, sulphur incorporation appeared to be advantageous over oxygen for OFET performance. The best mobility obtained for diphenyl-substituted anti-ADT was 1.3 $cm^2\ V^{-1}\ s^{-1}$, slightly over double that of the diphenyl ADF derivative.

Diphenyl-substituted linear ADF, as well as angular isomers (figure 24) were synthesised using the zinc-catalysed method shown in scheme 35.[112]

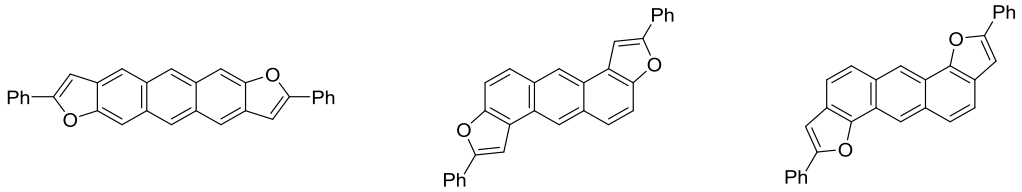


Figure 24: linear and angular ADFs synthesised *via* zinc-mediated cyclisations.

As has been shown several times now in the synthesis of thienoacenes and furyl-based acenes, linear and angular isomers containing four or five fused rings can be synthesised by very similar chemical sequences using regioisomeric starting materials.

Higher acenedifurans have also recently been synthesised. Watanabe et al. have reported TIPS-difuranoacenes of five to seven rings (figure 25) and compared their electronic properties and stabilities.[113]

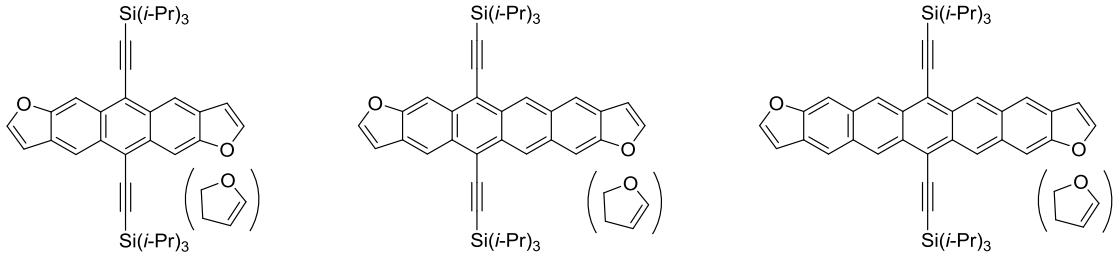
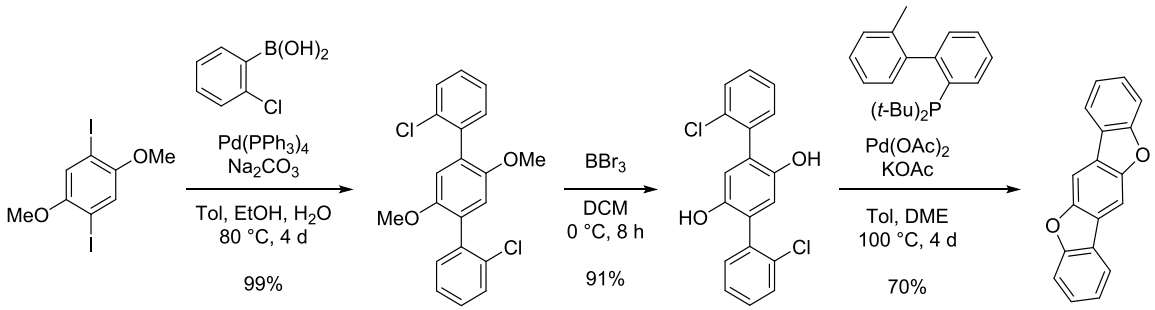


Figure 25: TIPS-difuranoacenes.

As with acenes and thienoacenes, the incorporation of bulky triisopropylsilyl groups can protect the more extended polyaromatics against self-dimerisation. The decrease in optical band gap upon each addition of a new ring is not surprising, as the proportion of non-aromatic Clar π-sextets increases, and the trend is similar to that of linear TIPS-acenes and TIPS-thienoacenes. Band gaps of 2.52, 2.08 and 1.75 eV were reported TIPS-ADF, TIPS-NDF and TIPS-PDF respectively, although even the latter showed good stability in the solid state under ambient conditions. In solution however, TIPS-TDF and TIPS-PDF were quite reactive under light.

Like thienoacenes, there have been reports of furanoacenes in which furans are incorporated as the inner rings in a fused system. For example, dibenzo[*d*,*d*']benzo[1,2-*b*:4,5-*b*']difuran (DBBDF) was synthesised *via* an intramolecular palladium-catalysed arylation also used for the synthesis of carbazoles.[114] This synthesis was carried out in four steps from 1,4-diiodo-2,5-dimethoxybenzene (scheme 37), which itself was synthesised by reaction of commercially available 1,4-dimethoxybenzene with ICl. A double Suzuki cross-coupling with (2-chlorophenyl)boronic acid, demethylation using BBr_3 and the final cyclisation, catalysed by $Pd(OAc)_2$ in the presence of base, furnished the furan-fused compound in 48% overall yield over five steps.



Scheme 37: synthesis of DBBDF.

By addition of an extra Suzuki cross-coupling to give a terphenyl precursor with two different aromatic substituents, alkyl- and nitrile-substituted DBBDFs were synthesised (figure 26).[115] The functionalisation of DBBDF was also reported by selectively lithiating and then iodinating at the 6- and 12-positions,[115] giving a precursor useful for polymer synthesis.

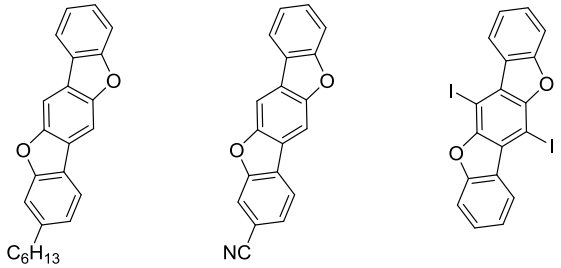
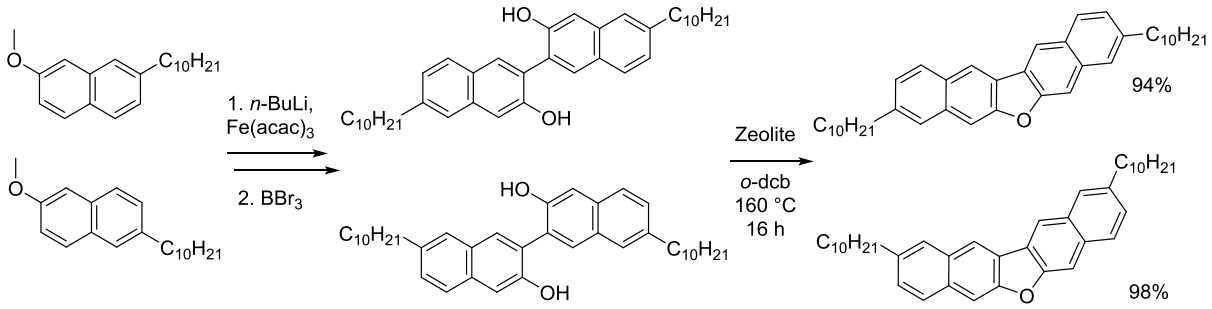


Figure 26: DBBDF derivatives.

V-shaped dinaphthofurans have been reported, containing furan as the central ring.[116] These systems were prepared in three steps from alkylmethoxynaphthalenes. Homo-coupling of the starting materials was followed by demethylation using BBr_3, and a zeolite-catalysed dehydration gave the V-shaped targets in high yields (scheme 38).



Scheme 38: synthesis of V-shaped dinaphthofurans.

Crystalline films of both isomers shown in scheme 38 gave hole mobilities of over 1 $cm^2\ V^{-1}\ s^{-1}$. V-shaped dinaphthothiophenes have also been reported as promising semiconductors, with mobilities of up to 9.5 $cm^2\ V^{-1}\ s^{-1}$ achieved.[117]

1.5 Aims of the project

The objective of this research was the synthesis of extended aromatic and heteroaromatic molecules for potential applications in organic electronics. Ideal molecules for this application should show good ambient and operational stability as well as high performance in devices such as OFETs, notably showing high charge carrier mobility. With this in mind, the design concept was to use staggered rather than linear acene structures as calculations indicated that these would keep the HOMO-LUMO band gap relatively large, resulting in stability even at very long lengths. Extension of staggered polyaromatics was postulated to increase mobility as it would increase the number of π-π close contacts and overlaps between molecules, but also reduce the number of charge carrier hops between molecules as intramolecular charge transport would be more prevalent.

An efficient bidirectional synthetic sequence was to be devised which could incorporate a variety of aromatic and heteroaromatic components into the target framework. Both polyaromatic hydrocarbons (1D graphenes) and sulphur-, oxygen- and nitrogen-containing compounds were targets.

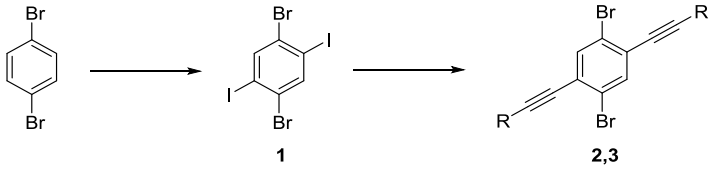
This bidirectional synthesis could be used to make compounds with potential in the field of molecular electronics. Highly conducting molecular wires could be produced by incorporating pyridine and nitrile functionalities able to act as stable contacting groups to secure the polyaromatic molecule between two metal electrodes. This would also demonstrate the compatibility of the proposed synthetic route with electron-deficient aromatic rings as well as relatively electron-rich rings like thiophene and furan.

The photophysical properties of the polyaromatic compounds were to be investigated in collaboration with Prof. Bernhard Witulski at the University of Caen Lower Normandy, France, and correlations with calculated properties (e.g. HOMO and LUMO levels) established allowing reliable in silico design of future targets.

2 Results and Discussion

2.1 Polyaromatic heterocycles

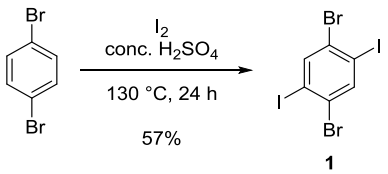
2.1.1 Optimisation and scale-up of early steps



Scheme 39: first two steps of polyaromatic heterocyclic synthesis.

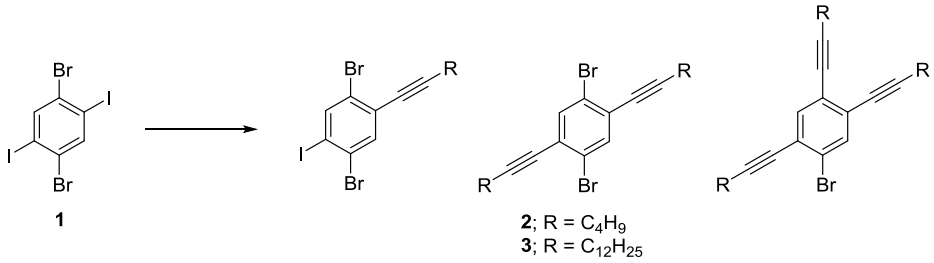
Scheme 39 shows the first two steps of the synthetic strategy employed for the first series of polyaromatic heterocycles reported. Scaled-up syntheses of **2** and **3** were crucial for the success of the project as the next step was, most often, a double Suzuki cross-coupling where a wide range of aromatic substituents could be introduced. As a result, a large number of polyaromatic compounds could be synthesised in two reactions once gram quantities of **2** and **3** were available.

The first step of the synthetic strategy was the di-iodination of *p*-dibromobenzene to give 1,4-dibromo-2,5-diiodobenzene **1**. This reaction is widely seen in the literature, with several good yields reported (65-84%).[118-120] However, it proved fairly problematic as selectivity was not ideal, with mono-iodinated and tris-iodinated compounds formed as side-products with the latter particularly difficult to remove by recrystallisation. Another problem observed was the sublimation of iodine and starting material from the reaction mixture, and this was regularly washed back into the reaction mixture to avoid losses. Several experiments were carried out on a 10-50 g scale in an effort to optimise the reaction as well as bring material through. In doing this and improving recrystallisation methods in DCM and toluene, yields of 50-60% were consistently achieved, and this was considered acceptable for an early reaction on a relatively large scale.



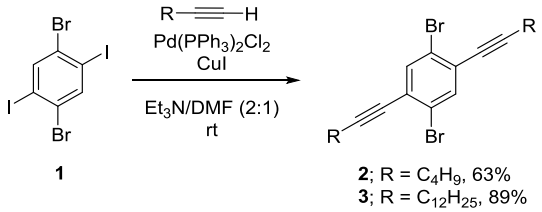
Scheme 40: synthesis of 1,4-dibromo-2,5-diiodobenzene 1.

The second step was a double Sonogashira cross-coupling[56] to introduce alkynyl groups of variable length in place of the iodide substituents.[84, 121, 122] Alkyl chains were considered important in the synthetic methodology, to offer greater solubility for the final polyaromatic compounds, and this reaction also required optimisation due to similar selectivity problems, with mono-alkyne and tris-alkyne compounds regularly observed as by-products (scheme 41).



Scheme 41: possible products of Sonogashira cross-coupling of 1,4-dibromo-2,5-diiodobenzene 1.

The best results for these cross-couplings were achieved by giving the reactions a longer time at lower temperature, which ensured formation of the tris-alkyne product, monitored by reverse-phase HPLC, was minimal. Room temperature Sonogashira reactions are well known in the literature,[123-125] and compounds **2** and **3** were synthesised in yields of 63% and 89% respectively (scheme 42).

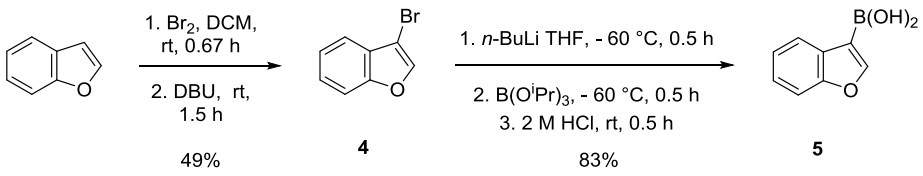


Scheme 42: syntheses of 2 and 3 *via* double Sonogashira cross-couplings.

Both of these yields are for reactions carried out on > 18 g scale, and large batches of both compounds were available for the next step.

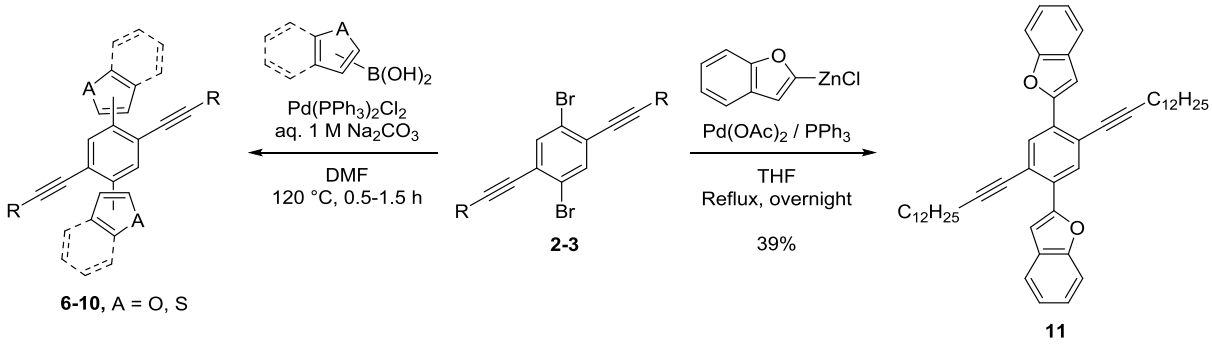
2.1.2 Synthesis of polyaromatic heterocycles

With the first two steps (schemes 40 and 42) optimised and scaled-up, two further reactions could give a variety of polyaromatic systems. The first of these was a double Suzuki cross-coupling[57] to give isomeric precursors to the final compounds (scheme 44). All boronic acids used were commercially purchased, except for benzofuran-3-ylboronic acid **5** which was synthesised in two steps from benzofuran (scheme 43).



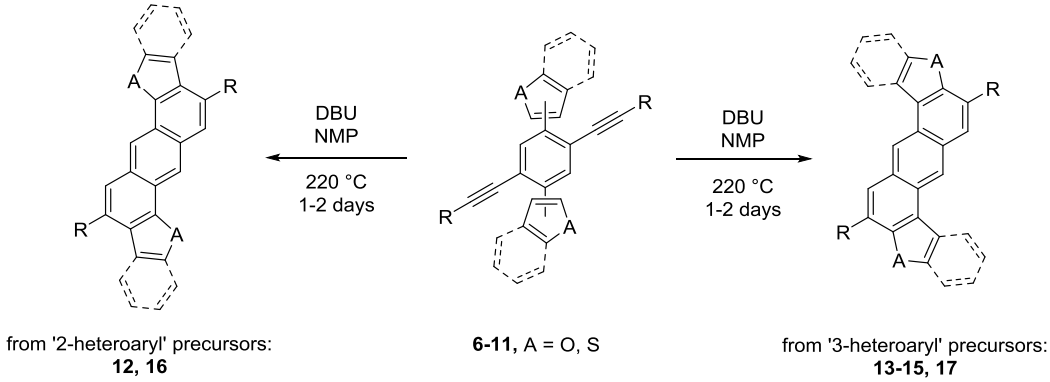
Scheme 43: synthesis of benzofuran-3-ylboronic acid 5.

One target, with '2-benzofuran' substituents, was synthesised by a double Negishi cross-coupling,[126] as the purchased boronic acid gave very poor NMR yields. Deprotonation of benzofuran using *n*-BuLi at 0 °C, followed by *in situ* formation of the organozinc reagent and palladium-catalysed cross-coupling, gave the target compound **11** (scheme 44).



Scheme 44: palladium-catalysed cross-couplings to give 6-11. Yields are given in table 3.

Reactions of **6-11** with DBU in NMP at 220 °C, typically overnight, furnished the polyheterocyclic compounds **12-17**. Scheme 45 shows how position of the heteroatom (referred to as being '2' or '3' depending on the boronic acid used) determined the structure of the final systems.



Scheme 45: base-catalysed cyclisations of 6-11 to give 12-17.

The yields of all palladium-catalysed precursor syntheses and base-catalysed cyclisations (schemes 44 and 45) are given in table 3.

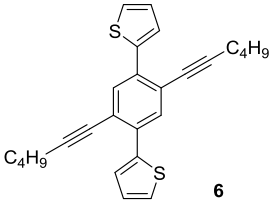
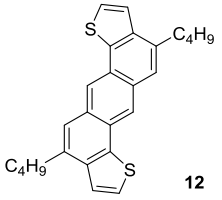
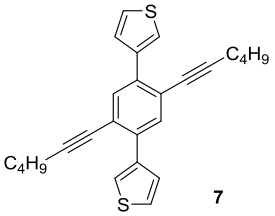
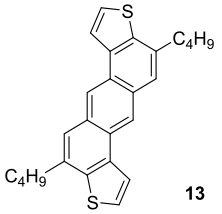
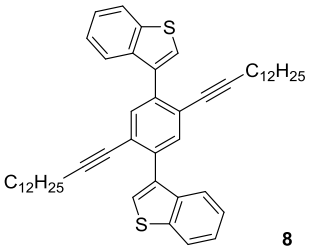
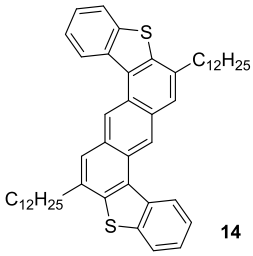
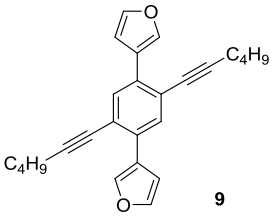
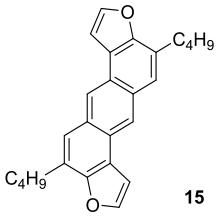
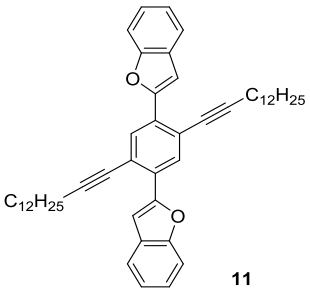
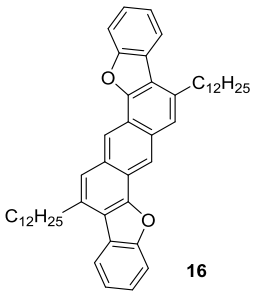
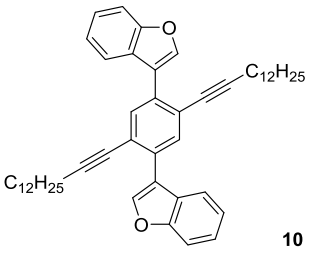
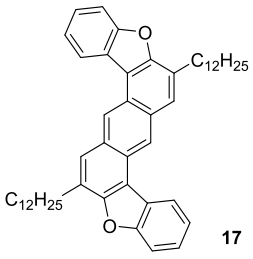
Entry	Precursor	% yield	Final compound	% yield
1	 **6**	94	 **12**	19
2	 **7**	81	 **13**	68
3	 **8**	72	 **14**	33
4	 **9**	69	 **15**	67
5	 **11**	39	 **16**	54
6	 **10**	42	 **17**	67

Table 3: syntheses and yields of 6-17.

All synthesised compounds were recrystallised for optical/electrochemical studies with Prof. Bernhard Witulski at the University of Caen Lower Normandy, France. X-Ray crystal structures were obtained for **12-15** (figure 27).

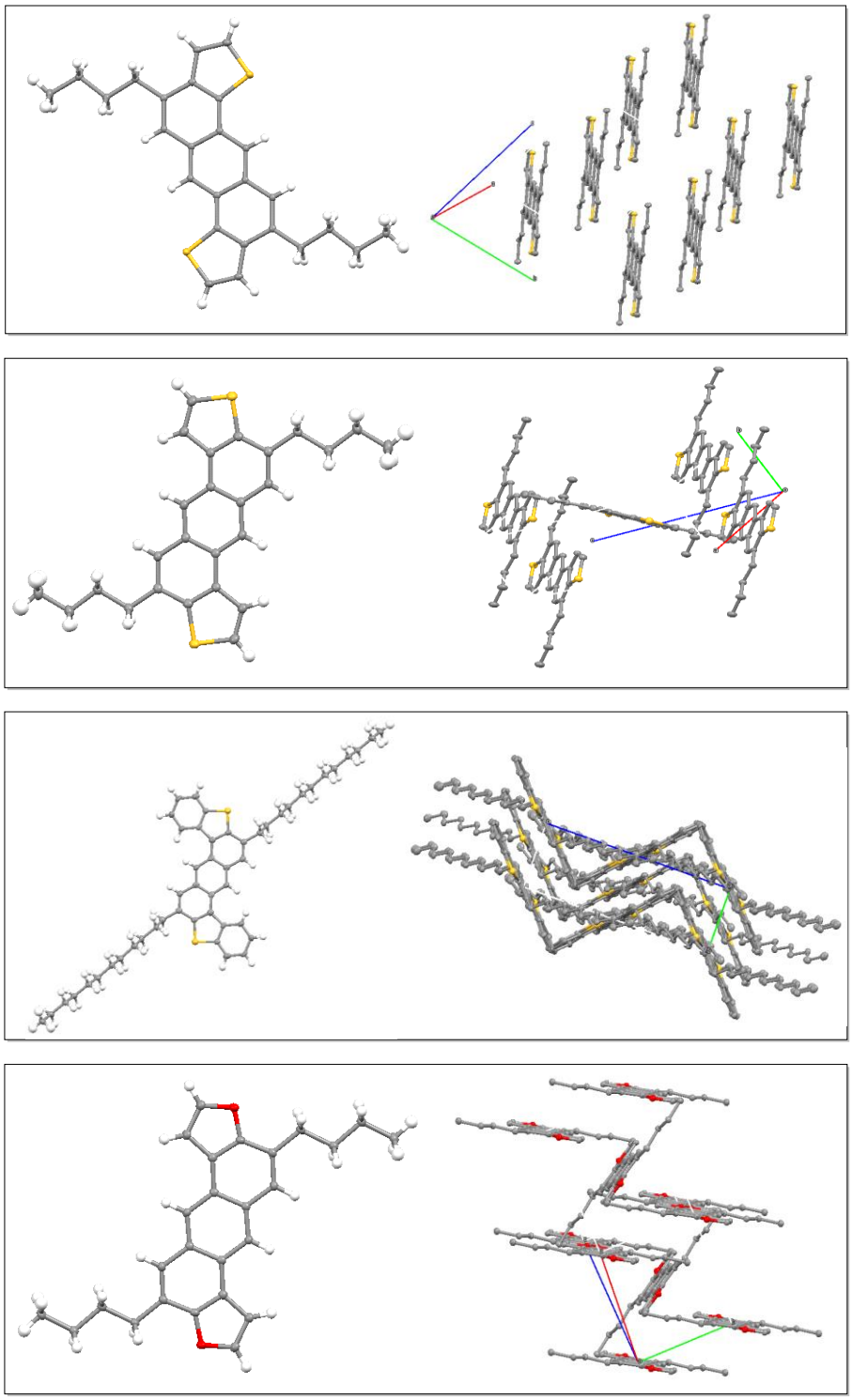
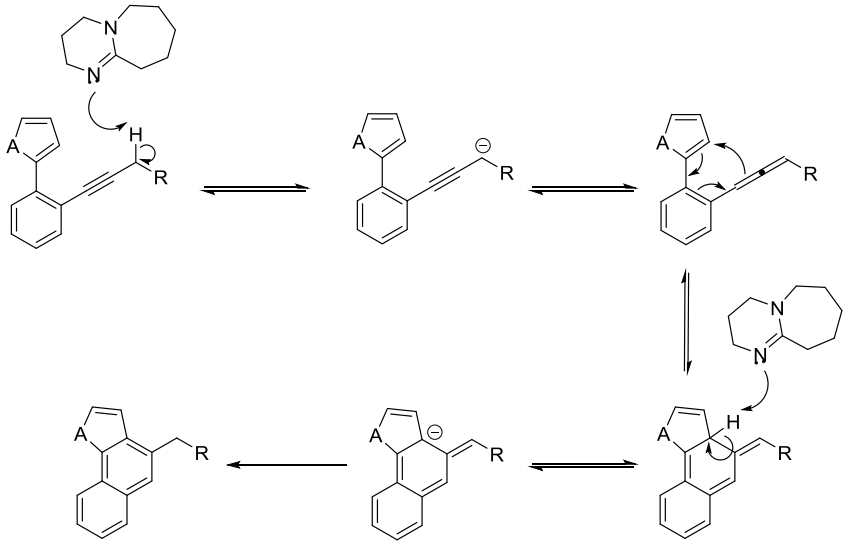


Figure 27: crystal structures, from top to bottom, of 12-15, and packing. Yellow = S, red = O.

All four compounds show C-H…π shortest contacts of 2.7-2.9 Å. No π-π close contacts shorter than the sum of the Van der Waals radii were observed in any of the systems, and the shortest intermolecular contact between two sp2 carbon atoms was 3.4-3.6 Å in each case. It was interesting to observe that in all three compounds **13-15**, derived from '3-heteroaryl' precursors, the closest chalcogen-chalcogen contact was over 5 Å, while an S-S contact of 3.9 Å was found for **12**. These interactions are thought to contribute significantly to the mobility of heteroacenes.[85] **12** showed stacked layers of molecules, while **13-15** crystallised predominantly in a herringbone manner. In **14**, the packing consists of layers of aromatic moieties separated by aliphatic layers, which may be due to the effect of using a long alkyl side chain.

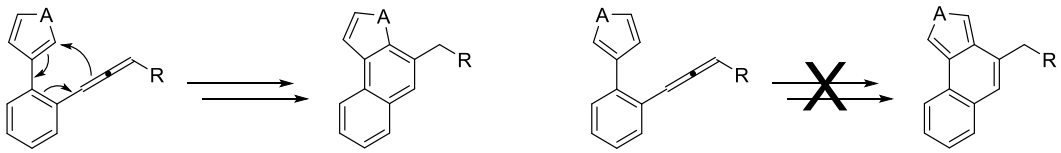
2.1.3 Mechanism of base-catalysed cyclisation

The final cyclisation step to give the polyaromatic compounds follows a well-known procedure where DBU is used as a catalytic base.[75, 79] The mechanism for these cyclisations (scheme 46) begins with abstraction of a propargylic proton, followed by formation of an allene intermediate which undergoes a 6π electrocyclisation. Another deprotonation and rearomatisation then occurs to give the final fused aromatic system.



Scheme 46: mechanism of the base-catalysed cyclisation, using DBU.

This mechanism explains why reaction of the '3-heteroaryl' precursors (to give **13-15** and **17**) positioned the heteroatom adjacent to the newly formed aromatic ring, as the 6π cyclisation could not take place otherwise, and gave one product in each case (scheme 47).

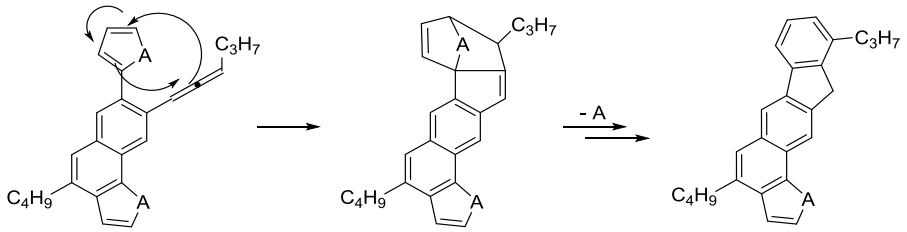


Scheme 47: regioselectivity of '3-heteroaryl' cyclisations.

Burton was the first to notice this reaction could take place using 'unactivated' systems, unlike the coronene diimides used by Müllen several years earlier,[75] and the first to propose an allene intermediate. This reaction was further studied in the next chapter **2.2**, including use of different bases and temperatures, and determination of the rate-limiting step.

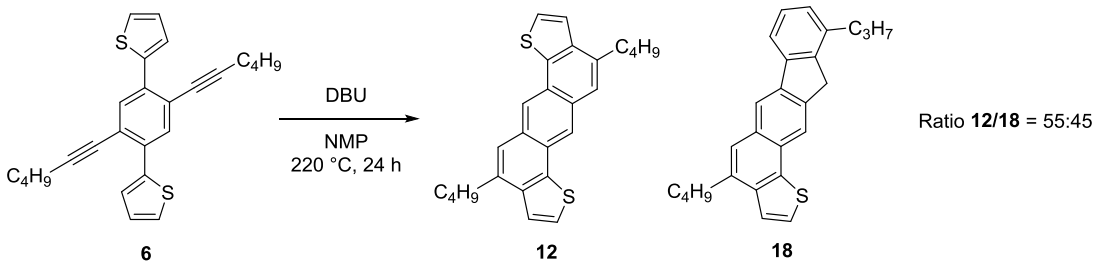
2.1.4 Diels-Alder side reactions

Close inspection of table 3 reveals two things; **12** was synthesised in low yield, and the analogous furyl system has not been reported. Unsubstituted and alkyl-substituted compounds of the same structure as **12** have been synthesised *via* photocyclisations,[105] and aryl-substituted versions *via* the Swager reaction,[43] but these reactions do not feature an allene intermediate and gave higher yields. The low yield of the synthesis of **12**, and the absence of its furyl analogue, can be explained by the observation of a side-product arising from a Diels-Alder reaction that the allene intermediate can undergo with the '2-thiophenyl' and '2-furyl' substituents, in competition with the desired electrocyclisation (scheme 48).



Scheme 48: side-product formation, beginning with a Diels-Alder reaction of the allene intermediate.

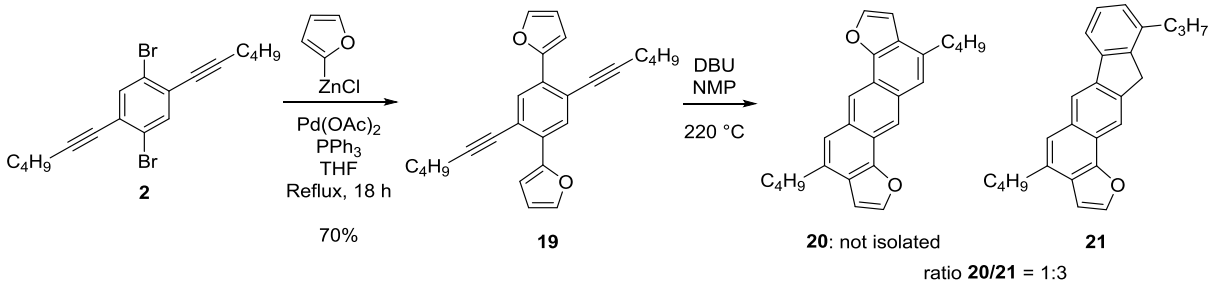
The second part of the mechanism, involving the loss of one heteroatom, was less clear. However, crude NMR of the reaction of **6** under the DBU/NMP conditions showed a singlet at ~4.0 ppm, characteristic of fluorenyl protons. The side-product **18** was produced as a mixture with the target cyclised compound, **12**, in almost a 1:1 ratio, estimated by NMR integration (scheme 49).



Scheme 49: base-catalysed reaction of 6 to give two products, 12 and 18.

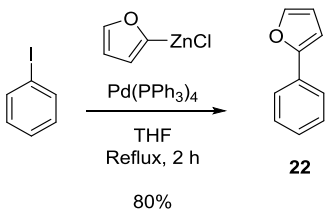
Attempts to separate the two products by column chromatography and also radial chromatography were unsuccessful and eventually two successive recrystallisations gave **12** in good purity, but consequently a poor yield. Single crystals suitable for X-ray were grown using the slow diffusion method (DCM/hexane), and the crystal structure is shown in figure 27.

Having synthesised **12**, cyclisation of the furyl-substituted compound **19** was attempted under the same conditions. **19** was synthesised *via* a double Negishi cross-coupling but not cyclised successfully. Crude NMR, using the characteristic fluorenyl proton of side-product **21**, revealed the Diels-Alder to be the dominant pericylic reaction in this case (scheme 50).

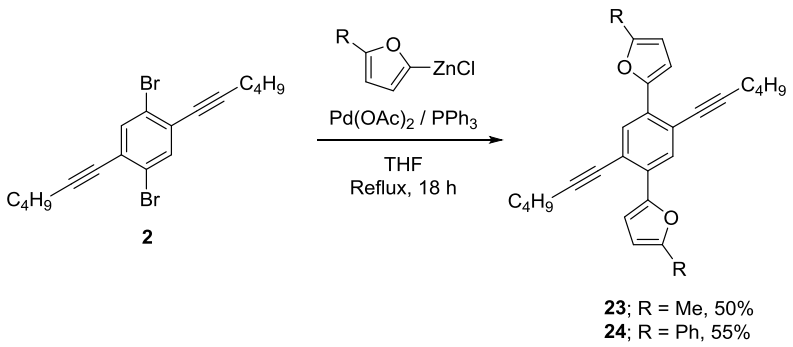


Scheme 50: synthesis of 19 and attempted cyclisation.

Purification of this reaction was not attempted. Instead, one idea was to see if a substituent on the α-carbon of the furyl moiety could sterically hinder the Diels-Alder reaction and in turn favour the electrocyclisation. Negishi cross-couplings were used to synthesise methyl- and phenyl-substituted versions of **19** (scheme 52), with the latter requiring synthesis of 2-phenylfuran **22**[127] (scheme 51).

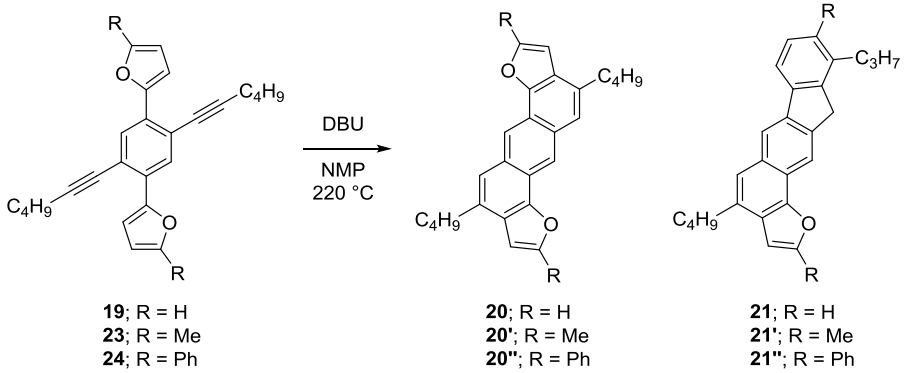


Scheme 51: synthesis of 2-phenylfuran 22.



Scheme 52: syntheses of 23 and 24 *via* Negishi cross-couplings.

However, no significant difference in the reaction of **23** and **24** to the original precursor **19** was observed (scheme 53), and the Diels-Alder reaction continued to dominate (table 4).



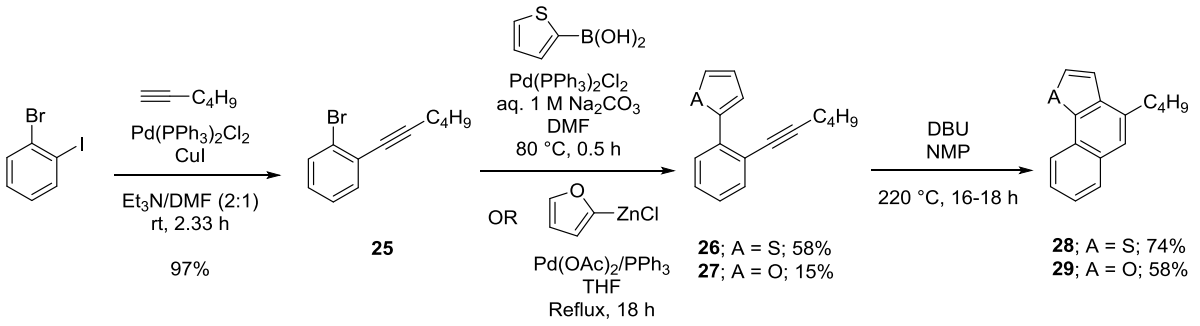
Scheme 53: base-catalysed reactions of 19, 23 and 24.

Entry	Starting material	R	Ratio of 20/21 by NMR
1	**19**	H	25:75
2	**23**	Me	27:73
3	**24**	Ph	34:66

Table 4: table showing conversions of the base-catalysed reactions shown in scheme 53.

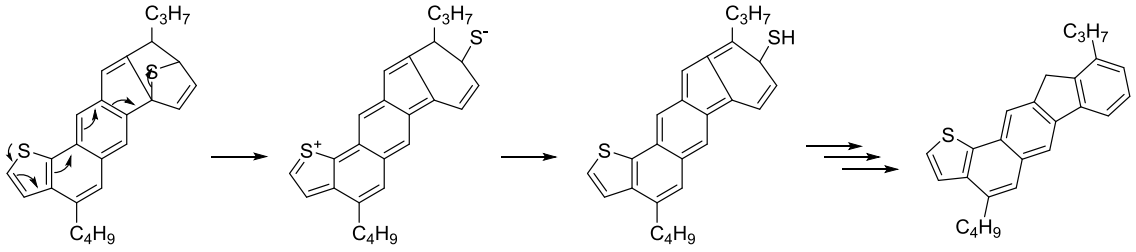
Two interesting observations were helpful in trying to elucidate a mechanism for this side-product formation. First, in all the attempted cyclisation reactions using **6**, **19**, **23** and **24**, crude NMR did not appear to indicate a 'double Diels-Alder' side-product in which both heteroatoms had been abstracted and two fluorene units were formed. Secondly, when using a system with just one heteroaryl and alkynyl substituent, rather than two, cyclisation proceeded much more

cleanly. Burton reported the synthesis of 4-butylnaphtho[1,2-*b*]thiophene **28**,[128] and this was repeated, along with synthesis of the analogous furyl system **29** (scheme 54).



Scheme 54: syntheses of 28 and 29 in three steps.

Both **26** and **27** cyclised cleanly, with the Diels-Alder side-product only present as a < 5% impurity in both cases. These observations suggested that the mechanism of side-product formation, after the Diels-Alder step, was dependent upon the other 'end' of the molecule already being cyclised and pushing electron density towards the other thiophene or furan ring. One hypothesis is that the Diels-Alder step is reversible, and the ring-opening shown as the first step in scheme 55 is what leads to loss of a heteroatom and formation of side-products **18** and **21**.



Scheme 55: suggested mechanism for side-product formation after the Diels-Alder step.

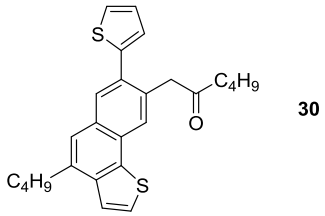
Another speculated theory was that DBU was acting as a nucleophile and abstracting the heteroatom to form an *N*-oxide or sulphide. To try and support this mechanism, two parallel reactions were prepared identically in which **6** was subjected to the standard cyclisation conditions, but in one of the reaction tubes, one equivalent of nucleophilic triphenylphosphine was also present (table 5).

Entry	Ratio of 12/18 by NMR
1 (no PPh_3)	27:73
2 (1 eq. PPh_3)	32:68

Table 5: comparison of base-catalysed reactions of 6 with and without triphenlyphosphine.

The difference in the outcomes of the two reactions was not significantly different, and the mechanism remained unclear, although the results shown in table 5 laid further evidence to the originally suggested mechanism (scheme 55).

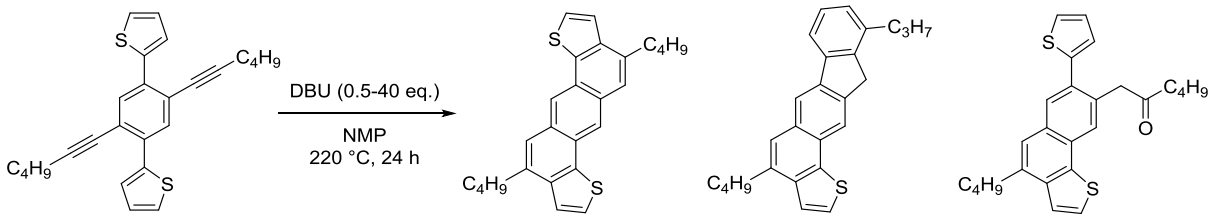
With this mechanistic work not carried further, attention was turned towards isolating a pure sample of side-products **18** and/or **21**. In one reaction using two equivalents of DBU with respect to **6**, a minor ketone side-product **30** was isolated (figure 28).



30

Figure 28: ketone side-product 30 formed during base-catalysed reaction of 6.

The structure was confirmed by NMR, HRMS and IR spectroscopy, with a strong absorption at 1708 cm^{-1} observed in the latter. The presence of a characteristic C=O peak in the ^{13}C-NMR spectrum at 208.6 ppm laid further evidence to formation of this ketone. This was most likely formed as a product of hydration, and a series of experiments were carried out with different amounts of DBU to observe the effect on formation of both side-products **18** and **30** in relation to **12** (scheme 56). The results are shown in table 6.



6 **12** **18** **30**

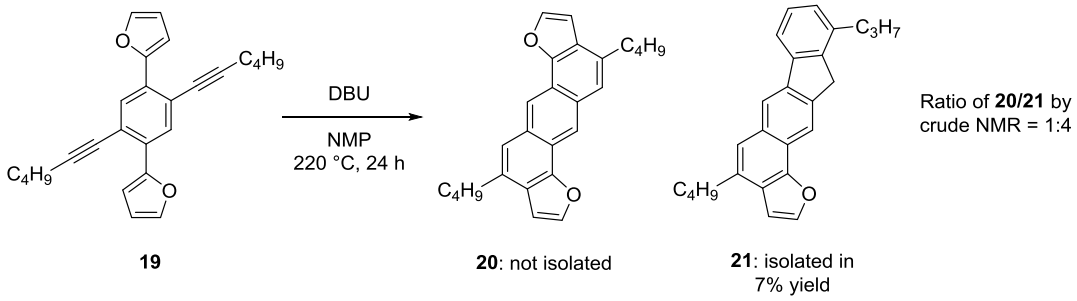
Scheme 56: base-catalysed reaction of 6 using variable amounts of DBU.

No. of equivalents base	Ratio of 12/18/30 by NMR
0.5	56:39:5
1	51:39:10
2	49:39:12
4	44:31:25
6	39:28:33
8	32:21:47
10	34:20:46
40 (neat)	28:12:60

Table 6: results of the reactions shown in scheme 56.

More ketone was formed as the concentration of base increased, and it was likely that water was coming from the DBU, which was not purified before use. Addition of a drop of water into two otherwise identical reactions, of **12** with one equivalent of DBU, gave an increase in ketone formation – the ratio of **12**/**18**/**30** calculated by crude NMR was 42:22:36 respectively with water, compared to 48:37:15 without.

One final effort to isolate one of the side-products was carried out by repeating the base-catalysed reaction of **19** and purifying by column chromatography. Surprisingly, although not completely separated, the two main products were much more separable than in the thiophene example, and the target side-product **21** was isolated albeit in a very low yield (scheme 57).

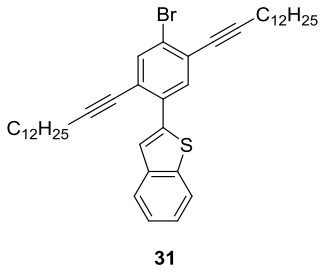


Scheme 57: base-catalysed reaction of 19.

Mass recovery after organic extraction and column chromatography were both low, despite crude NMR indicating a fairly pure mixture of the two compounds. **21** was isolated, with **20** as a 5% impurity, but the purity was high enough to assign the NMR spectrum, which was consistent with the structure, and HRMS also confirmed the correct product. **21** was characterised except for UV-vis spectroscopy, due to the likely impurity.

2.1.5 Synthesis of 'mixed' polyaromatic systems

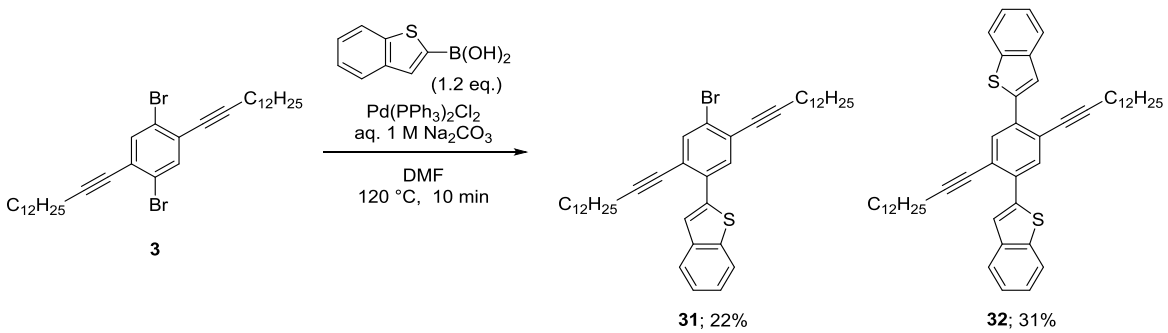
Within the heterocycles project, the next targets were unsymmetrical, 'mixed' systems where two different substituents could provide different electronic contributions to the central anthracene unit. These were more synthetically challenging targets, requiring two extra steps and the unsymmetrical precursor **31** (figure 29).



31

Figure 29: 31, required for the synthesis of unsymmetrical polyaromatic systems.

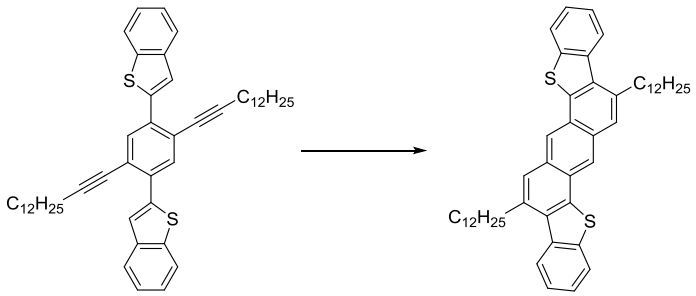
Initially, the most obvious route to **31** was a 'statistical' approach using 1.0 equivalent of boronic acid which might be expected to give a 50% yield of **31**, 25% of the 'bis' compound **32** (scheme 58) and 25% recovered starting material, if the reactivity of the two bromides was independent of the other. However, in practice, this method was not as high-yielding as expected, most likely due to the well-known tendency of such boronic acids to protodeboronate under the conditions of Suzuki cross-coupling,[129] leaving the actual stoichiometry of the reagent unknown. The highest isolated yield of **31** was achieved using 1.2 equivalents of boronic acid (scheme 58).



31; 22% **32**; 31%

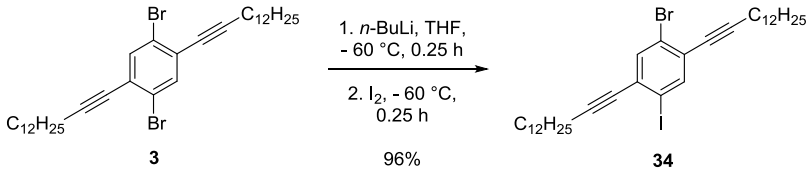
Scheme 58: synthesis of 31 and 32.

This reaction also gave **32**, which had previously been synthesised and cyclised to give gram quantities of **33** (scheme 59).[130]



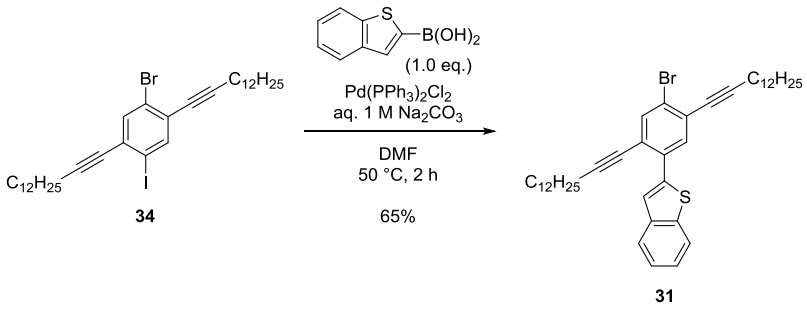
Scheme 59: synthesis of 33.

As **33**, and therefore **32**, were not needed, a more efficient alternative to the synthesis of **31** was used. Precedent in the literature exists for selective lithiation of only one of two *para*-dibromide substituents on a benzene ring.[54, 131] Lithiation of **3** using 1.1 equivalents of BuLi and subsequent iodination gave **34** in near-quantitative yield (scheme 60).



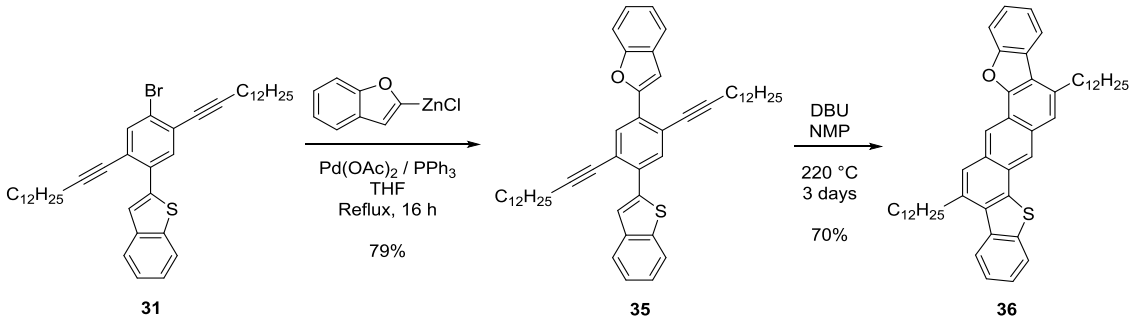
Scheme 60: synthesis of 34.

Due to the higher reactivity of the iodide substituent compared to the bromide, synthesis of **34** allowed for a selective mono-Suzuki coupling, using milder conditions to give **31** (scheme 61).



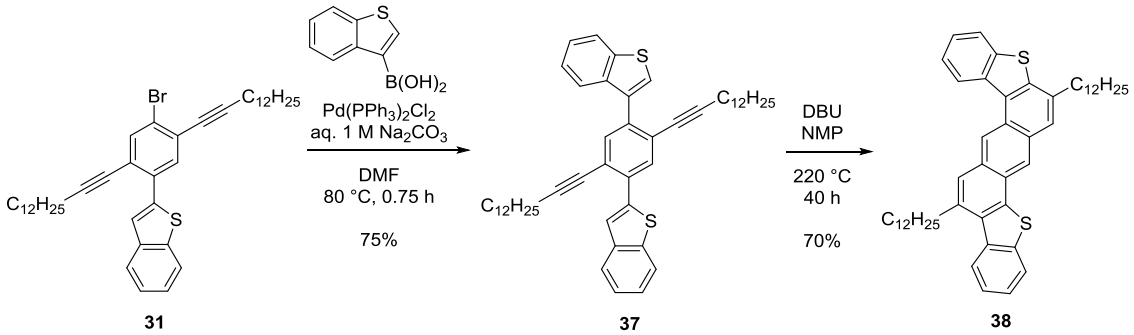
Scheme 61: synthesis of 31.

From this compound, two steps were required to give the unsymmetrical targets, starting with a mixed benzothiophene-benzofuran polyaromatic system **36** (scheme 62).



Scheme 62: synthesis of 36.

The regioisomeric benzothiophene substituent was coupled onto **31** to give **37**, which was cyclised to give **38** and a new architecture not previously seen (scheme 63).

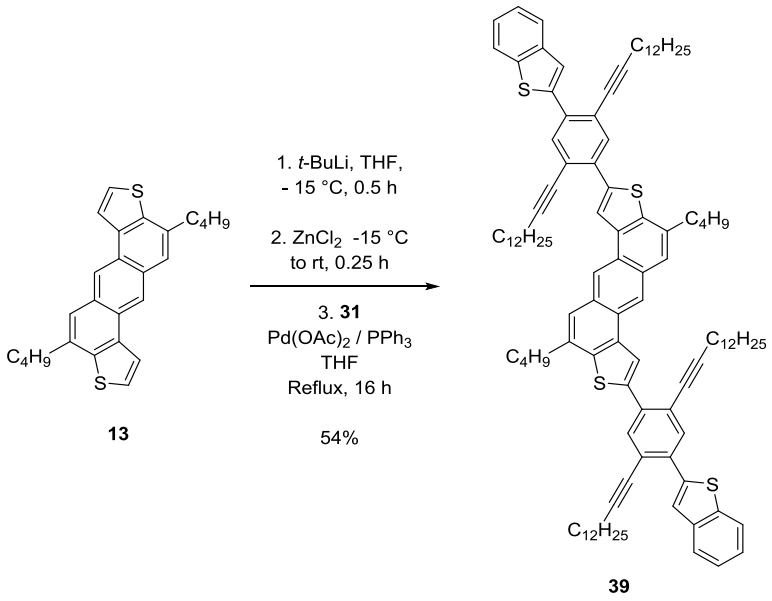


Scheme 63: synthesis of 38.

2.1.6 Synthesis of a fifteen-ring thienoacene

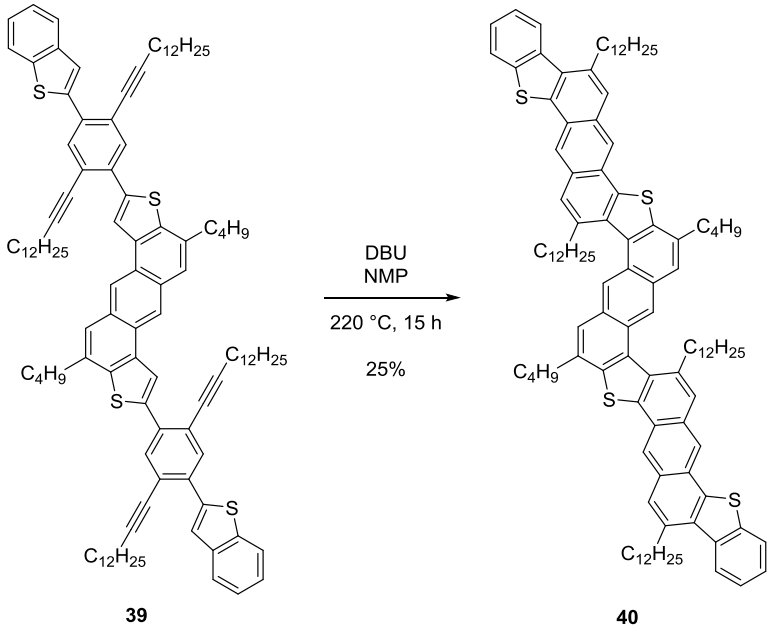
31 was also required for synthesis of an extended polyaromatic compound. This was the first attempt at a system made by four cyclisations in one molecule rather than two, to give fifteen fused aromatic rings. Synthesis of such a system could substantiate the theory shown in the introduction **1.2** (figure 14), that these angular systems could be significantly extended and remain stable and isolable. Electronic performance in a compound like this could be enhanced due to more overlaps between the longer molecules, and less of a reliance on strong intermolecular interactions for good charge carrier mobility.

The synthetic strategy for this idea used a previously synthesised thienoacene, **13**, as a building block, exploiting its acidity at the α-position. Double deprotonation and transmetallation using zinc chloride were carried out *in situ*, and coupling of the organozinc reagent to **31** in a double Negishi cross-coupling gave **39** (scheme 64).



Scheme 64: synthesis of 39.

Low solubility of the polyaromatic starting material in THF at low temperatures was a problem for this reaction and initial efforts at -30 °C gave yields of under 40%. However, carrying out the deprotonation and transmetallation at -15 °C gave an improved yield of 54% and a suitable amount of material to carry out the final step. The extended thienoacene **40** was synthesised from **39** in 25% yield after column chromatography (scheme 65).



Scheme 65: synthesis of 40.

NMR carried out at elevated temperatures showed peaks consistent with **40** in good purity, and this was confirmed by LRMS. During photophysical studies, **40** showed no signs of

decomposition after three days in DCM, and this stability was consistent with its band gap of 2.63 eV, determined from UV-vis spectroscopy. Figure 30 shows the UV-vis spectrum of **40** with the complementary fluorescence emission spectrum.

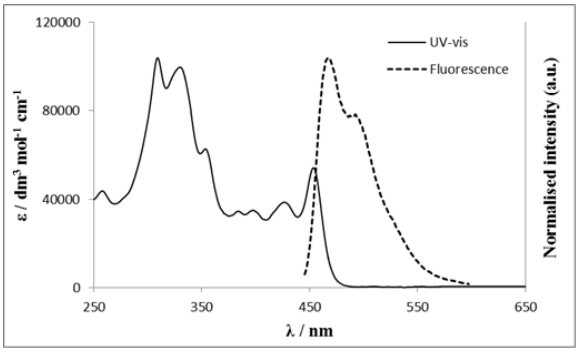


Figure 30: absorption and emission spectra of 40.

Determination of the HOMO energy level of **40** was attempted by cyclic voltammetry, but the compound was too poorly soluble for this. Photophysical characterisation and determination of HOMO-LUMO band gaps of all polyaromatic heterocycles is described later in chapter **2.1.8**, and spectra are shown in the experimental section **3.2.1**.

2.1.7 Synthesis of polyaromatic heterocycles from a naphthalene core

The polyaromatic heterocycles project was extended by use of a naphthyl core to provide a new architecture of polyaromatic systems. Employing the same synthetic steps as before, use of this central naphthalene core gave a chrysene unit (figure 31) as opposed to anthracene.

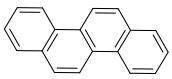
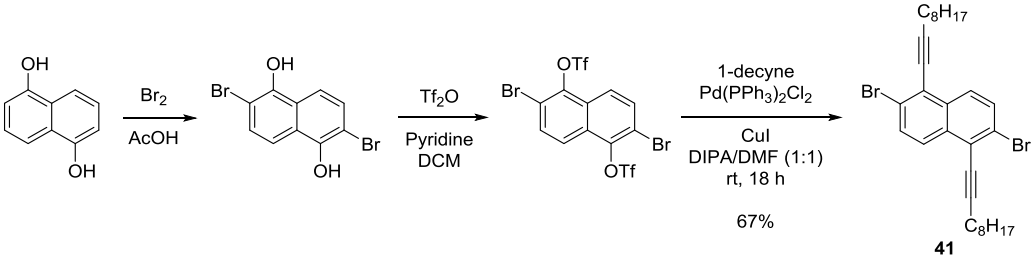


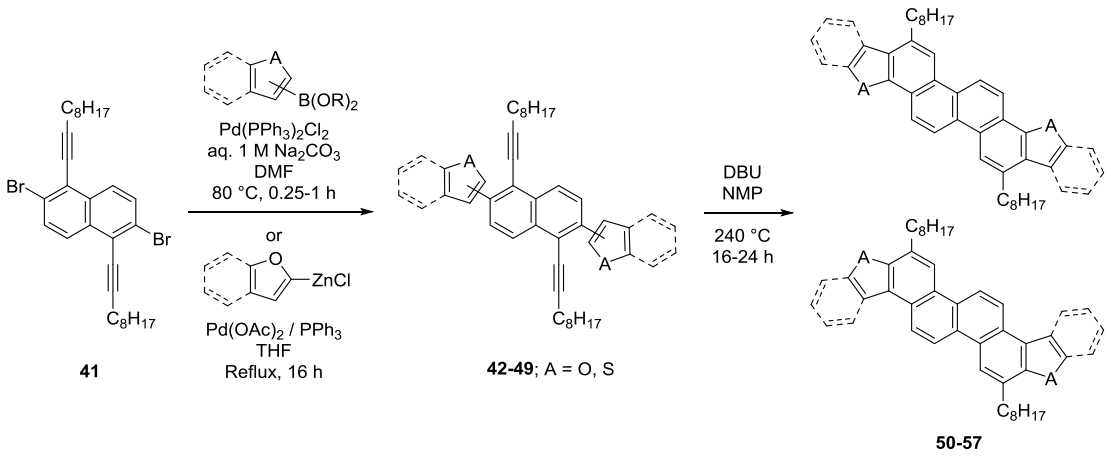
Figure 31: chrysene.

Again, synthesis of a large batch of 'pre-Suzuki' precursor *via* a double-Sonogashira cross-coupling was vital and this was carried out from the bis-triflated compound shown in scheme 66,[89] which was synthesised in two steps by several undergraduate research project students according to literature procedures (bromination,[132] triflation[89]) and was readily available.

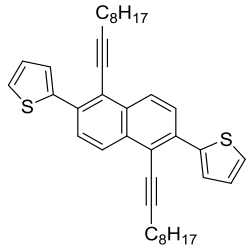
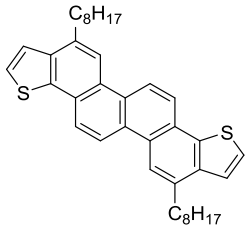
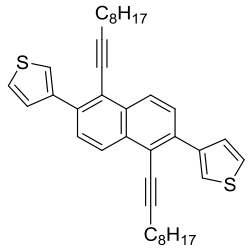
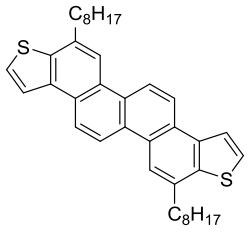
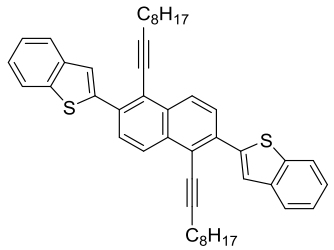
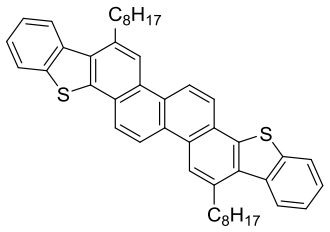


Scheme 66: three-step route to 41.

Heteroaryl substituents were bis-coupled onto **41** to give eight polyaromatic precursors (scheme 67). Suzuki reactions were used except for the '2-furyl' and '2-benzofuryl' systems **46** and **48** respectively (table 7), where Negishi cross-couplings were employed. All eight compounds were successfully cyclised (scheme 67, table 7).



Scheme 67: palladium-catalysed cross-couplings give the polyaromatic precursors 42-49, and cyclisations to give 50-57.

Precursor	% yield	Final compound	% yield
 **42**	70	 **50**	84
 **43**	72	 **51**	85
 **44**	85	 **52**	69

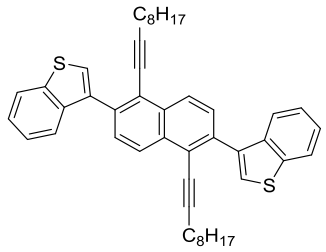
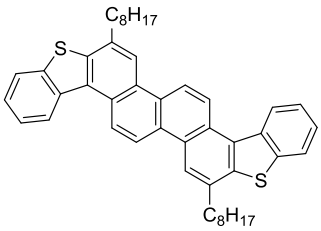
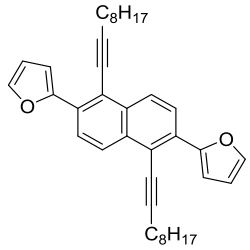
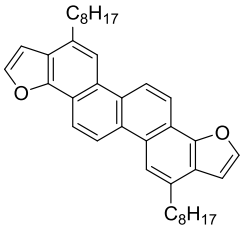
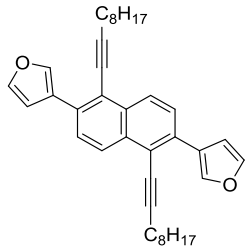
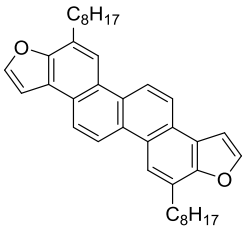
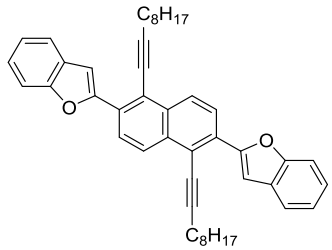
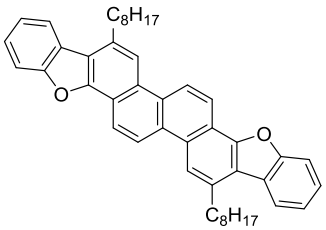
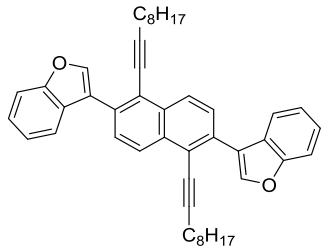
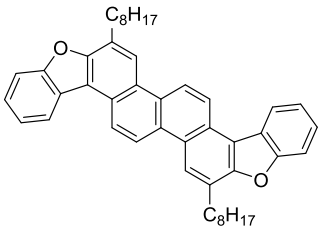
Precursor	% yield	Final compound	% yield
 **45**	63	 **53**	93
 **46**	59	 **54**	35
 **47**	72	 **55**	80
 **48**	56	 **56**	70
 **49**	24	 **57**	60

Table 7: syntheses of 41-56 (scheme 67) and yields.

Unlike the previous series **12-17** (**2.1.2**, scheme 45, table 3) all yields given are before recrystallisation, as NMR was required for a purity check and in all cases showed good purity of the compounds. Furthermore, in most cases, not all the material obtained from the reaction

was recrystallised for optical and electrochemical studies in France, as these were generally carried out on a larger scale. Crystal structures were obtained for **50** and **54**-**56** (figure 32).

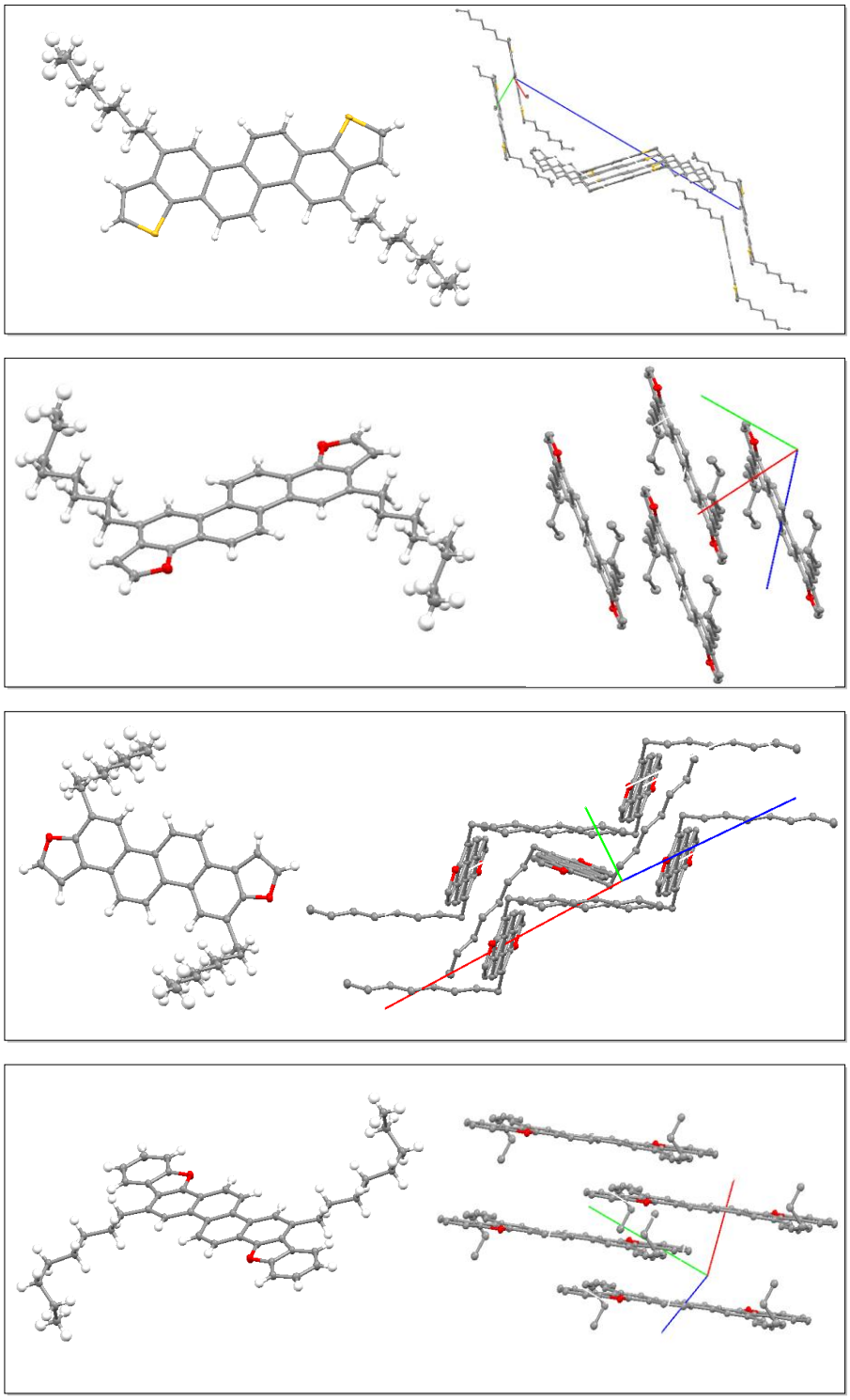


Figure 32: from top to bottom, crystal structures of 50, 54, 55 and 56, and packing. Yellow = S, red = O.

Similarly to compounds **12-15** (figure 27), C-H…π contacts were the shortest found in these systems, around 2.8-2.9 Å compared to the closest π-π contacts of 3.3-3.4 Å. Interestingly, in compound **54**, one of these short contacts was between two oxygen atoms, whereas the other three systems showed chalcogen-chalcogen contacts of 4.6 Å or over. **54** and **56** show a degree of stacking, but this occurs with aromatic portions on top of the aliphatic chains and therefore not efficiently π-stacked. **50** is fairly similar as stacked layers are observed, but these are separated by a substantial aliphatic layer, while **55** shows a typical herringbone structure.

2.1.8 Photophysical characterisation

All materials, purified by recrystallisation, were taken to Caen, France where photophysical measurements were carried out under the supervision of Prof. Bernhard Witulski.

2.1.8.1 UV-vis spectroscopy

Band gaps (E_{opt}) were determined by the onset wavelength (λ_{onset}) of the lowest-energy absorption band (λ_{max}) from UV-vis spectroscopy, using the equation ($E_{opt} = 1239.95 / \lambda_{onset}$).

Compound	**λ_{max} / nm**	**ε / dm^3 mol^{-1} cm^{-1}**	**λ_{onset} / nm**	**Observed E_{opt} / eV**	**Calculated E_{opt} / eV**
12	400	7300	408	3.04	3.07
13	386	13400	402	3.08	3.11
33	422	-	431	2.88	2.83
14	416	15200	427	2.90	2.88
15	389	15000	403	3.08	3.07
16	408	9200	417	2.97	2.94
17	416	17300	427	2.90	2.81
36	415	4400	424	2.92	2.88
38	415	7100	427	2.90	2.88
40	454	53300	471	2.63	2.53

Compound	λ_{max} / nm	ε / dm^3 mol^{-1} cm^{-1}	λ_{onset} / nm	Observed E_{opt} / eV	Calculated E_{opt} / eV
50	386	4100	392	3.16	3.39
51	373	2200	378	3.28	3.48
52	394	2800	402	3.08	3.29
53	388	4100	393	3.15	3.34
54	379	1200	384	3.23	3.48
55	366	3900	373	3.32	3.45
56	388	9100	393	3.15	3.36
57	378	12100	386	3.21	3.23

Table 8: photophysical properties of all polyaromatic heterocycles.

UV-vis spectra of the compounds shown in table 8 are shown in chapter **3.2.1**. Although not reported, **33** is included in table 8 to complete the series. ε was not calculated for **33** due to its particularly low solubility, and a saturated solution was used for UV-vis spectroscopy.

'Calculated E_{opt}' refers to TDDFT-calculated values carried out by Prof. Richard J. Whitby.[133] Correlation between determined and calculated values was good, and the results were consistent with the chrysene series (**50**-**57**) having wider band gaps than the anthracene series (figure 33).

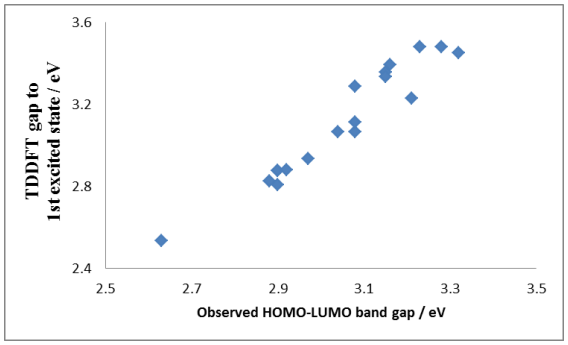


Figure 33: graph showing the correlation between observed and calculated band gap values for polyaromatic heterocyles.

Use of the same substituent in going from a benzene-derived system to a naphthalene-derived one resulted in a hypsochromic shift of λ_{max} (figure 34) increasing E_{opt} by anything from 0.1-0.3 eV.

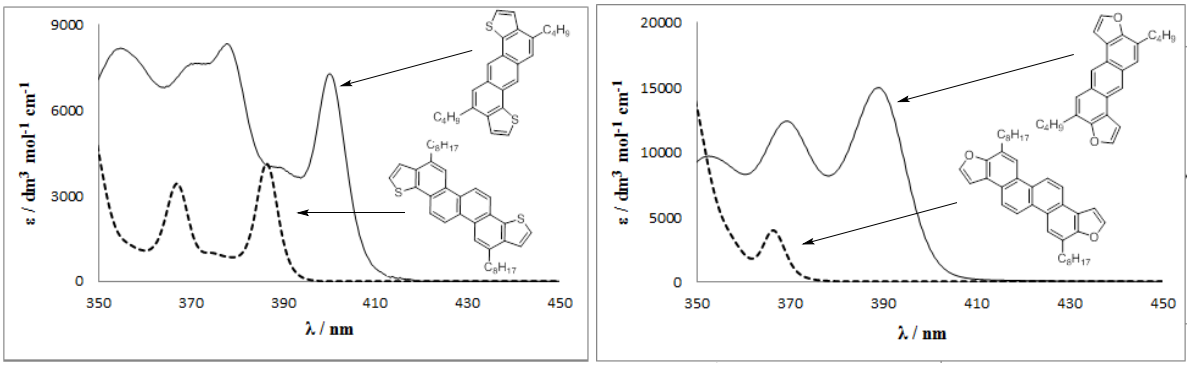


Figure 34: hypsochromic shift in going from benzene-derived to naphthalene-derived compounds.

An expected pattern was that extension of compounds by addition of an extra benzene ring on either end gave a bathochromic shift of λ_{max} and lowered the band gap (figure 35). In the anthracene series (for example in going from **13** to **14**), this lowered the band gap by around 0.2 eV while the same kind of extension in the chrysene series (for example in going from **54** to **56**) generally gave a decrease of around 0.1 eV.

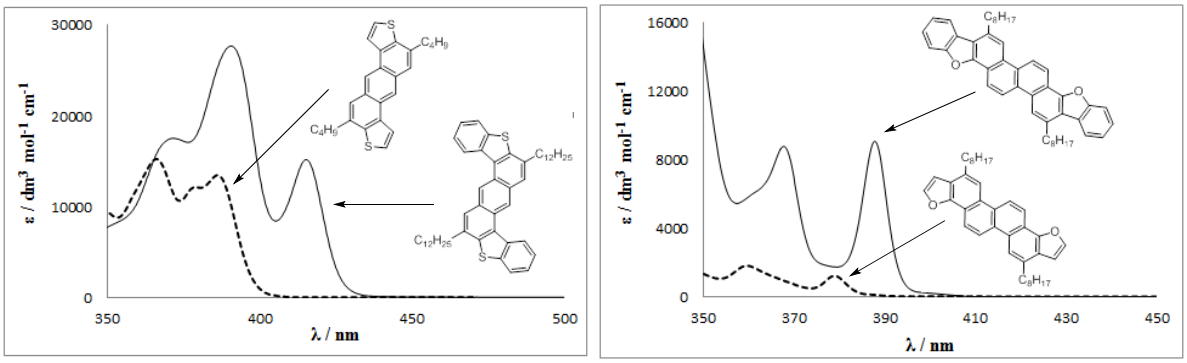


Figure 35: bathochromic shift of λ_{max} resulting from extended π-conjugation.

The effect of changing from sulphur to oxygen was studied separately within the two series. In isoelectronic benzene-derived molecules, this effect was very little except for the difference of 0.09 eV seen between **33** and **17**. The effect of type and position of heteroatom in the chrysene series **50**-**57** was much more apparent and showed a clear trend. For regioisomeric molecules, systems derived from '2-heteroaryl' substituents (**50**, **52**, **54** and **56**) gave a bathochromic shift of λ_{max} compared to their '3-heteroaryl' isomers (**51**, **53**, **55** and **57** respectively), figure 36, resulting in a band gap around 0.1 eV lower.

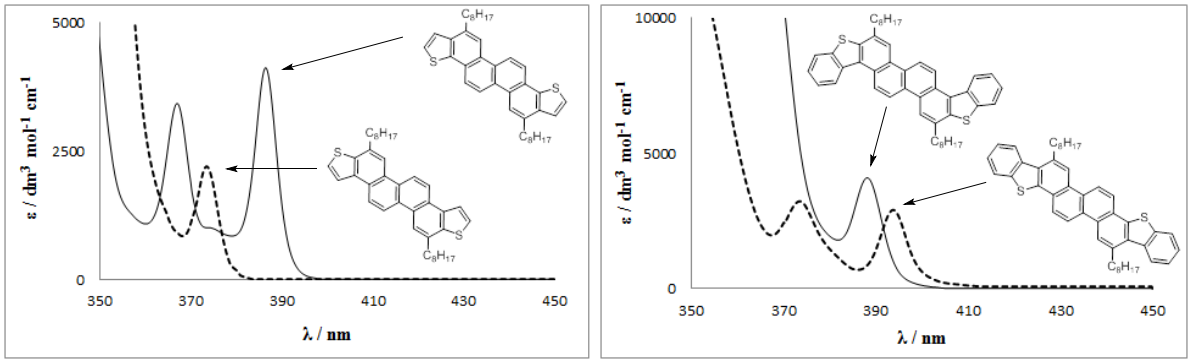


Figure 36: effect of heteroatom position on λ_{max} in isomeric molecules.

In isoelectronic molecules within the chrysene series **50-57**, incorporation of oxygen widened the HOMO-LUMO gap. Figure 37 shows how replacement of a furan unit with analogous thiophene units resulted in a bathochromic shift of λ_{max}.

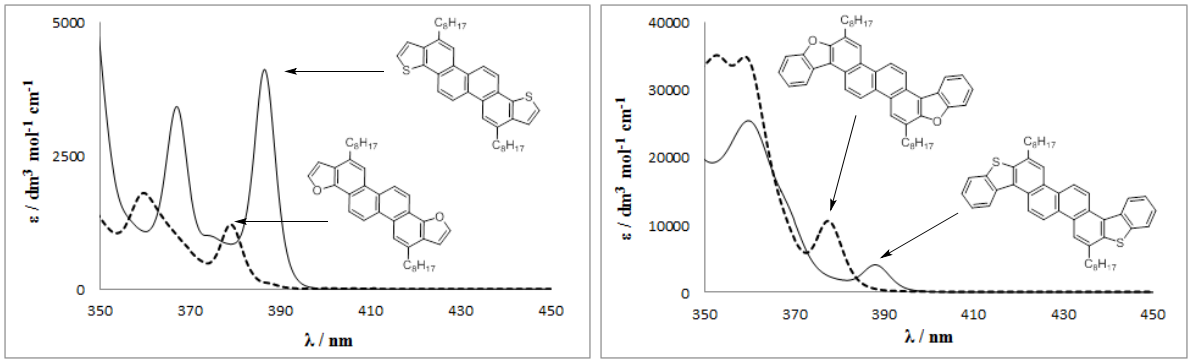


Figure 37: effect of heteroatom on λ_{max} in isoelectronic molecules.

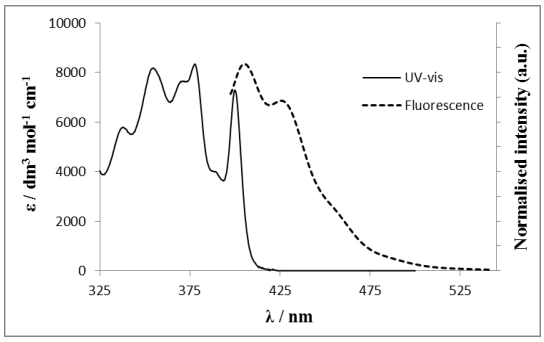
2.1.8.2 Fluorescence spectroscopy

Fluorescence emission spectra were measured for all polyaromatic heterocycles. Table 9 reports the complementary fluorescence wavelength (λ_F) for the absorption maxima (λ_{max}) reported in table 8, for each compound. The chrysene series **50-57** generally gave lower Stokes shifts than the anthracene series.

Compound	λ_{max} / nm	λ_F / nm	Compound	λ_{max} / nm	λ_F / nm
12	400	405	**50**	386	387
13	386	397	**51**	373	375
33	422	429	**52**	394	395
14	416	424	**53**	388	389
15	389	400	**54**	379	384
16	408	412	**55**	366	369
17	416	425	**56**	388	390
36	415	421	**57**	378	381
38	415	425			
40	454	468			

Table 9: complementary absorption and emission maxima from UV-vis and fluorescence spectroscopy.

Spectra of complementary absorption and emission are shown in the experimental section **3.2.1**, such as the example of **12** (figure 38).



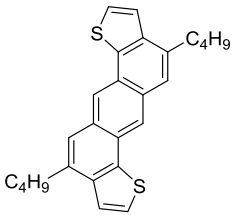


Figure 38: UV-vis and fluorescence spectra of 12.

2.1.8.3 Quantum yields

Quantum yields for all polyaromatic heterocycles were measured in rigorously degassed solutions in DCM, and the results are given in table 10. This unitless measurement can be given by the equation (Φ_F = number of photons emitted / number of photons absorbed).

Compound	Φ_F solution	Compound	Φ_F solution
12	0.08 (380 nm)	**50**	0.02 (330 nm)
13	0.16 (370 nm)	**51**	0.05 (330 nm)
33	0.08 (360 nm)	**52**	0.05 (350 nm)
14	0.11 (380 nm)	**53**	0.06 (340 nm)
15	0.48 (330 nm)	**54**	0.09 (310 nm)
16	0.41 (370 nm)	**55**	0.38 (330 nm)
17	0.67 (370 nm)	**56**	0.30 (340 nm)
36	0.10 (380 nm)	**57**	0.45 (340 nm)
38	0.09 (370 nm)		
40	0.27 (420 nm)		

Table 10: quantum yields for polyaromatic heterocycles.

Fluorescence occurs when a molecule returns from an excited state to a vibrational level associated with its ground state, emitting a photon in the process. Molecules in an excited electronic state can be deactivated by a number of other mechanisms such as internal or external conversion. Fluorescence quantum yield measures the probability of an excited molecule undergoing fluorescence emission and not a different relaxation mechanism.

Furyl-fused systems gave higher quantum yields than their thiophene analogues, and compounds derived from a '3-benzofuryl' substituent, **17** and **57**, gave among the highest values. The chrysene series **50-57** generally showed lower values than the anthracene series. Extended π-conjugation generally led to an increased quantum yield, for example the fifteen-ring thienoacene **40** which has the highest value for any sulphur-containing system.

2.1.8.4 Cyclic voltammetry

Cyclic voltammetry of polyaromatic compounds was carried out in dry DCM, using tetrabutylammonium hexafluorophosphate as the supporting electrolyte. With a ferrocene reference used, HOMO energy levels were determined from the onset of the oxidation peaks,

using the equation [HOMO = - (E^{ox}_{onset} + 4.93) eV].[134] LUMO levels were also calculated, using observed band gap values (table 8), by the equation (LUMO = HOMO + E_{opt}).

Compound	HOMO / eV	LUMO / eV
12	-6.06	-3.02
13	-5.99	-2.91
15	-5.91	-2.83
17	-5.96	-3.06
36	-6.00	-3.08
50	-6.23	-3.07

Table 11: HOMO and LUMO energies of polyaromatic heterocycles.

Cyclic voltammograms are shown in experimental section **3.2.2**, such as the example of **13** (figure 39), which also shows the ferrocene reference.

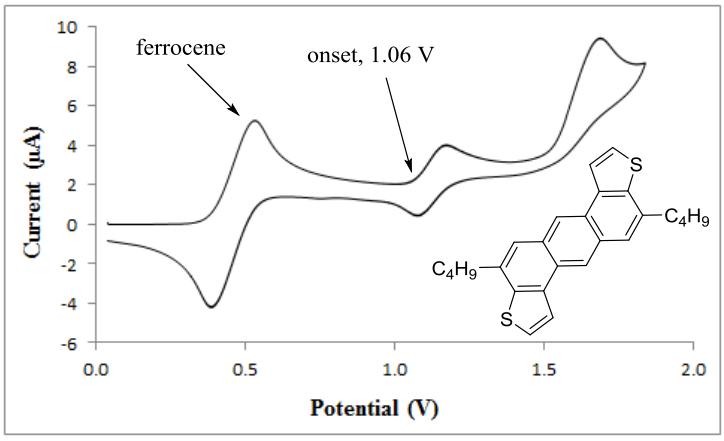


Figure 39: cyclic voltammogram of 13.

2.1.9 Conclusions

Syntheses of polyaromatic heterocycles **12-17** demonstrated the benefits of the synthetic sequence employed, with a variety of sulphur- and oxygen-containing systems produced by only changing the reagent used for C-C biaryl coupling. This also highlighted the importance of successful optimisation and scale-up of the first two steps (scheme 39). Once this was achieved, only two reactions were required for synthesis of a novel polyaromatic molecule.

A Diels-Alder side-reaction was reported in the base-catalysed reactions of **6** and **19**. Efforts were made, unsuccessfully, to negate this reaction by the introduction of potentially sterically hindering methyl and phenyl groups. Although the full mechanism of its formation remains unclear, the suspected side-product **21** was isolated and characterised.

More synthetically challenging unsymmetrical polyheterocylic compounds **36** and **38** were isolated. This required an unsymmetrical precursor **31**, which was initially synthesised in yields of 20-30%. However, mono-iodination of starting material **3** allowed for more selective mono-Suzuki coupling to give higher yields of **31**, from which two more steps furnished the targets **36** and **38**.

A fifteen-ring thienoacene **40** was synthesised by using the five-ring thienoacene **13** as a building block. This was soluble enough for optical studies and elevated temperature NMR characterisation, and was obtained as a stable compound consistent with its HOMO-LUMO band gap of 2.63 eV, substantiating the theory that more angular systems can be significantly extended unlike linear acenes, acenedithiophenes or acenedifurans.

Polyaromatic heterocycles of a different architecture, **50-57**, were synthesised by using a naphthalene starting material. Again using palladium-catalysed cross-couplings and a final base-catalysed cyclisation, these systems all contained a central chrysene unit, and gave wider optical band gaps than those containing a central anthracene unit.

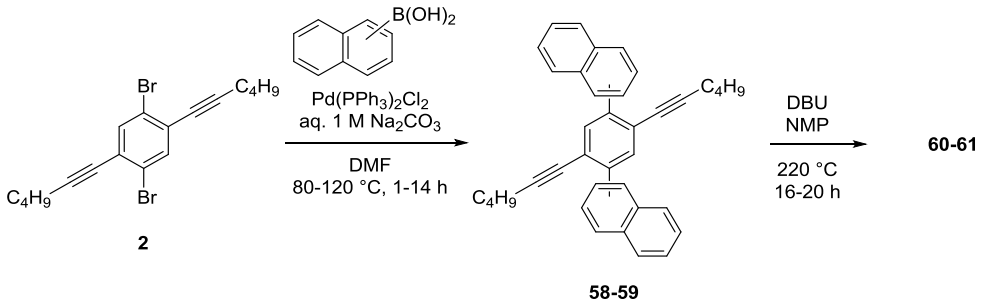
All polyheterocyclic compounds were characterised by UV-vis and fluorescence spectroscopy. Determination of the HOMO-LUMO band gaps gave good correlation with computationally calculated values, meaning that future work could aim at the synthesis of specific targets to accurately tune this band gap.

2.2 Polycyclic aromatic hydrocarbons

The synthesis of a series of PAHs was the next project, and was a continuation and elaboration of the work of Jason Howe[135] and Alexandre Debacker.[136] Some of the compounds synthesised have previously been reported, or reported but with different alkyl chains, and scaled up repeats were often necessary to provide more material for photophysical studies.

2.2.1 Synthesis of PAHs

Like the heterocycles project, use of both a benzene and naphthalene core and coupling with phenyl and naphthyl substituents gave a variety of structures. Seven-ring PAHs were synthesised using the starting material **2**, *via* Suzuki cross-couplings and base-catalysed cyclisations (scheme 68, table 12).



Scheme 68: syntheses of 60-61 in two steps from 2.

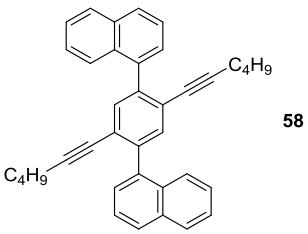
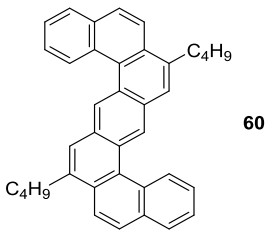
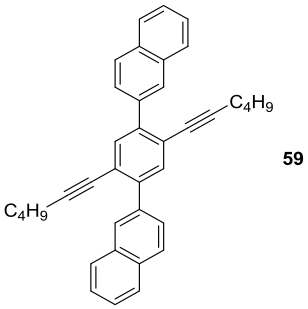
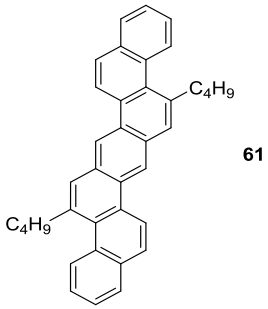
Entry	Precursor	% yield	Final compound	% yield
1	 **58**	54	 **60**	14
2	 **59**	52	 **61**	71

Table 12: syntheses of 58-61 (scheme 68) and yields.

Table 12 reveals that **60** was synthesised in low yield, and this was thought to be due to a steric 1,5 hydrogen clash (figure 40).

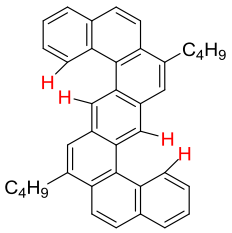
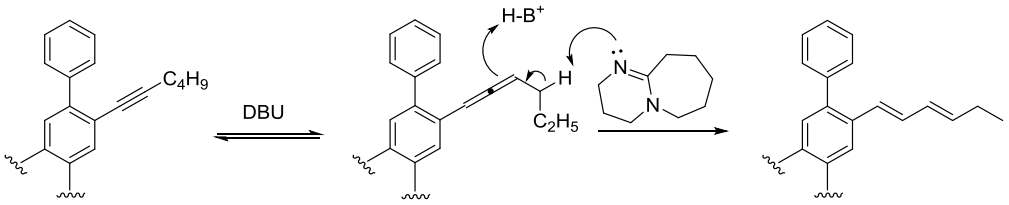


Figure 40: steric 1,5 hydrogen clash in 60.

As a result, cyclisation was probably relatively slow and encouraged formation of diene side-products. These dienes could be formed from the allene intermediate (scheme 69) in competition with the desired electrocyclisation, the full mechanism of which is shown in **2.1.3** (scheme 46).



Scheme 69: formation of possible diene side-products from the synthesis of 60.

Unlike the majority of polyaromatic compounds reported throughout this project, **60** did not precipitate from the reaction mixture upon cooling to room temperature, and once isolated showed relatively high solubility (over 20 mg was soluble in 2 mL $CHCl_3$ for recrystallisation). Crude NMR revealed, as expected, alkene peaks (5.5-6.7 ppm) but **60** was the major product although the real yield was difficult to estimate due to overlapping NMR peaks. The low yield reported is more due to the need for isolation by chromatography and recrystallisation. In the first synthesis of **60**, which gave only 7% yield, a crystal structure was resolved after recrystallisation in 2:1 pentane/chloroform (figure 41).

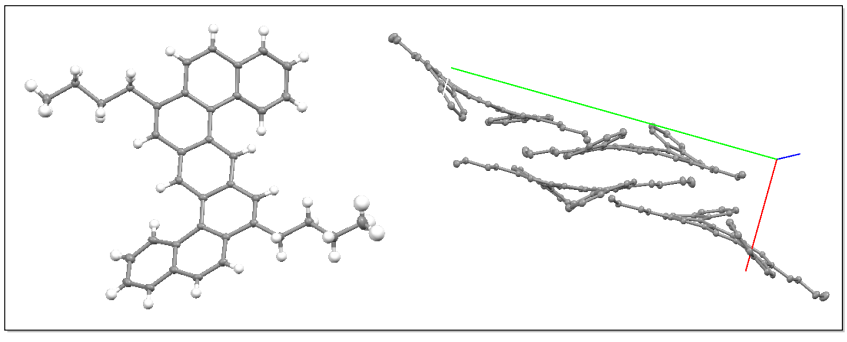
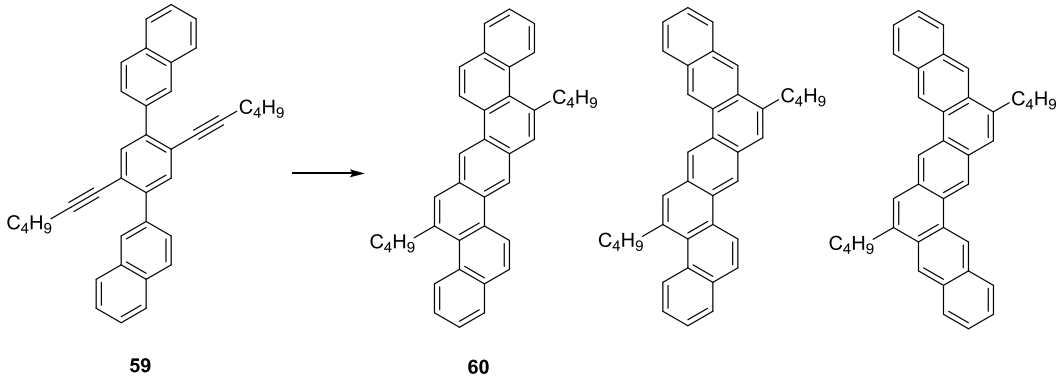


Figure 41: crystal structure of 60 and packing.

X-ray crystallography revealed a helicene-like structure, with the terminal benzene rings twisting away to avoid the steric clash. No π-π contacts lower than the sum of the Van der Waals radii (2.90 Å) were calculated for this system, with 3.4 Å as the shortest.

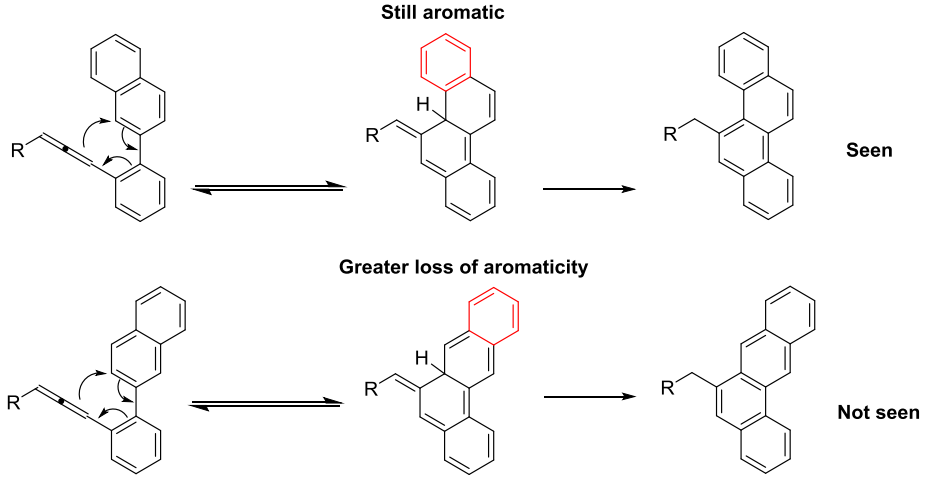
A repeat and scale-up of the synthesis of **60** gave 14% yield and 150 mg of pure compound.

Unlike its regioisomer, synthesis of **61** proceeded much more cleanly and in a higher yield of 71%. Given the structure of the precursor **59**, one might initially expect a mixture of compounds based upon the fact that the allene intermediate can conceivably cyclise onto two different sites of the naphthalene substituent (scheme 70).



Scheme 70: possible regioisomers formed from the cyclisation of 59.

However, NMR characterisation of the material obtained from the reaction was consistent with the structure of **61**, distinguishable from other structures, and showed good purity. Formation of only one compound could be supported by a mechanistic explanation (scheme 71).



Scheme 71: mechanistic explanation of cyclisation of the '2-naphthalene' substituent.

The '2-naphthalene' substituent would always cyclise to break the 1,2- (and not the 2,3-) double bond as this results in a lower loss of aromaticity in the intermediate leading to the final fused aromatic system. This observation was seen throughout the project in other examples. The structure of **61** was fully confirmed by obtention of a crystal structure after recrystallisation by slow cooling in toluene (figure 42).

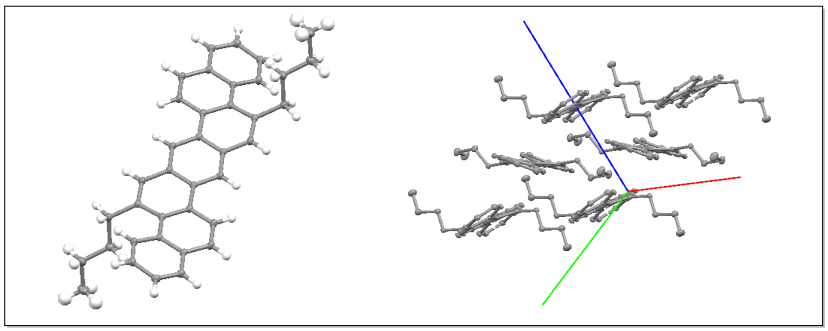
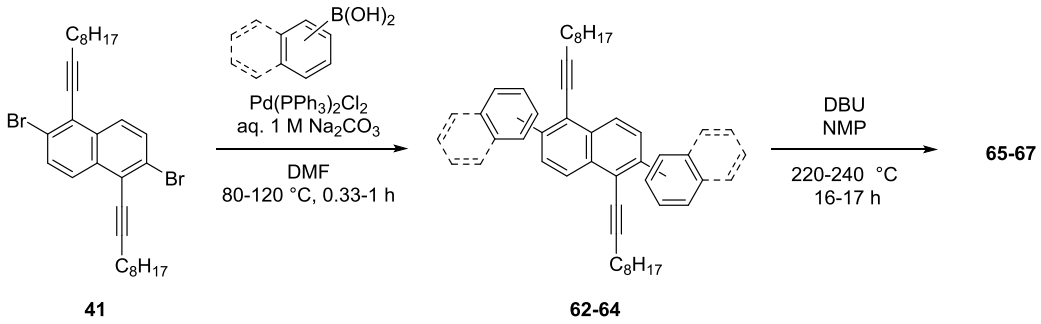


Figure 42: crystal structure of 61 and packing.

This revealed a promising degree of π-stacking, and one π-π contact (3.26 Å) less than the sum of Van der Waals radii was calculated.

As with the heterocycles, coupling of substituents onto the naphthyl core **41** followed by cyclisation provided a useful extension to this project, giving molecules with a central chrysene unit (scheme 72). Yields are given in table 13.



Scheme 72: syntheses of 65-67. Structures and yields are given in table 13.

For photophysical studies, samples of **65-67** were purified by recrystallisation in toluene (slow cooling), and crystal structures were resolved for all three (figure 43), the latter of which, **67**, was previously obtained by Alexandre Debacker.[136]

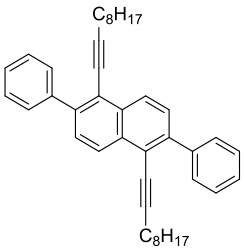
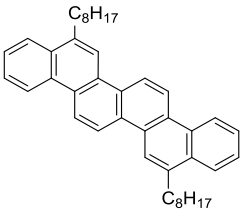
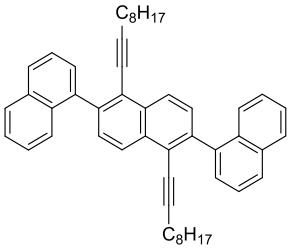
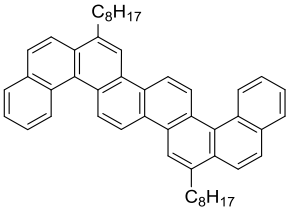
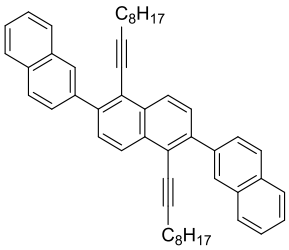
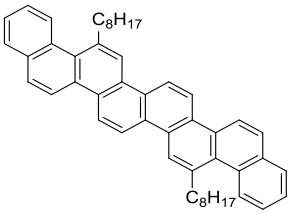
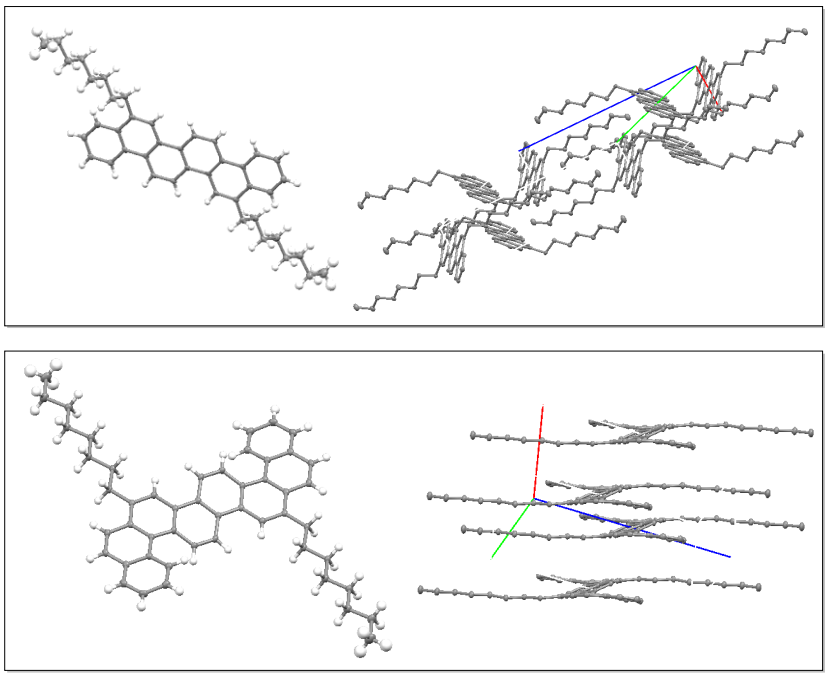
Precursor	% yield	Final compound	% yield
 **62**	64	 **65**	86
 **63**	55	 **66**	52
 **64**	71	 **67**	78

Table 13: syntheses of 62-67 (scheme 72) and yields.



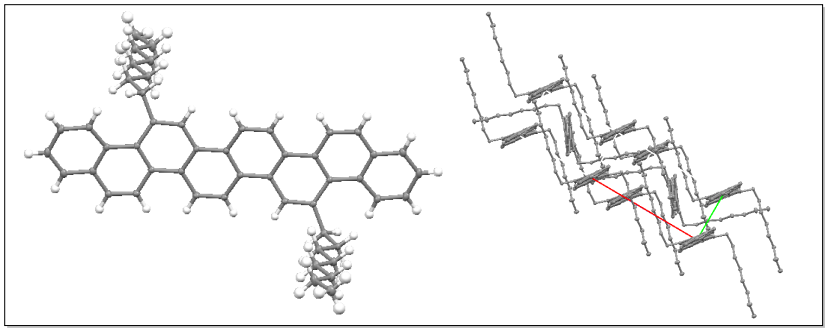


Figure 43: crystal structures of 65-67 and packing.

65 and **67** showed a mixture of edge-to-face and face-to-face interactions, while **66** showed layers of slipped π-stacks. In all three compounds, the shortest contact between sp2 carbon atoms in all three was calculated to be around 3.3 Å, shorter than the sum of the Van der Waals radii. As with **60** (scheme 68), cyclisation of the '1-naphthalene' substituent to give **66** resulted in a non-linear structure as the terminal benzene rings twisted slightly to avoid a steric 1,5 hydrogen clash (figure 44).

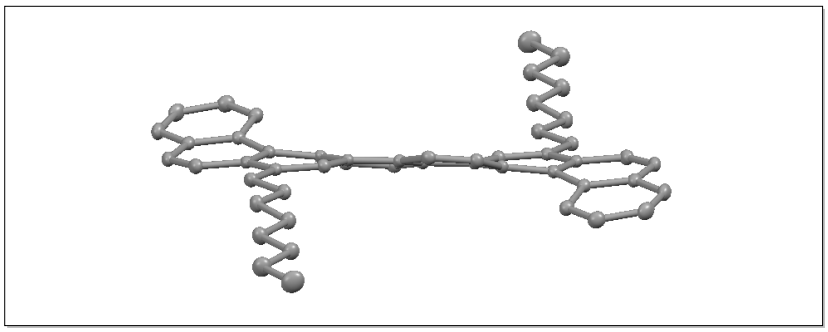
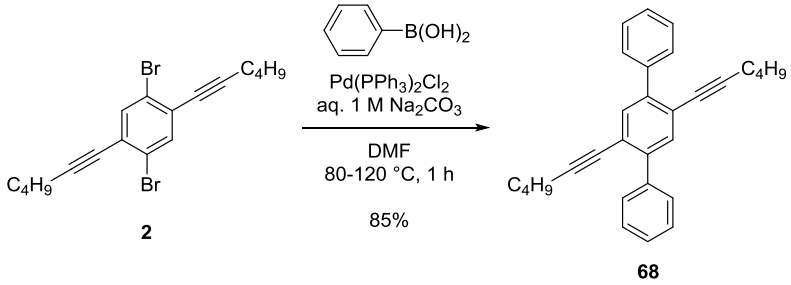


Figure 44: twisted structure of 66.

Fortunately, compound **66** precipitated from the reaction mixture upon cooling to room temperature and the superior yield of **66** compared to **60** is most likely due to its lower solubility, although the solubility was just high enough to obtain a ^{13}C-NMR spectrum at room temperature in $CDCl_3$. The compound was obtained in good purity, with the expected diene side-products left dissolved in the reaction mixture.

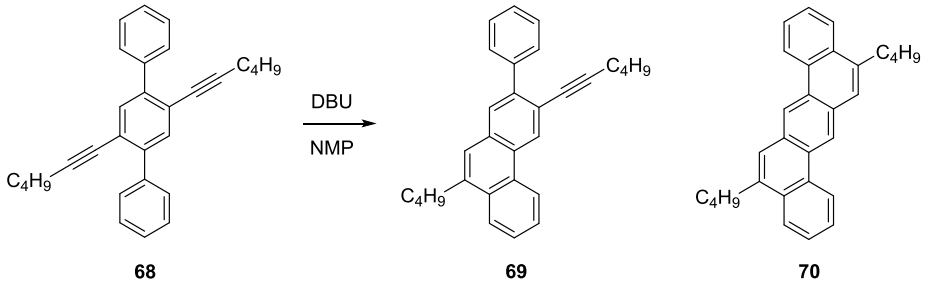
2.2.2 Study of different conditions on the base-catalysed cyclisation step

68, synthesised *via* a Suzuki cross-coupling (scheme 73) was used for a study of the effect of different temperatures, bases and solvents on the final cycloisomerisation step.



Scheme 73: synthesis of 68.

Yields up until this point, of polyaromatic heterocycles and PAHs, were quite varied, and the reactions were rarely monitored due to the low solubility of final compounds and reluctance to regularly open the sealed vessels and allow air to enter. Cyclisation of **68** was an ideal reaction for these studies as the substituted dibenz[*a,h*]anthtracene **70** (scheme 74) was synthesised by Jason Howe in 78% yield,[135] fully characterised and showed better solubility than most other systems. **70** is reported to have been isolated by extraction into diethyl ether rather than precipitation, making sampling for reverse-phase HPLC and NMR easier. The series of reactions were expected to give mainly two products, **70** and the 'mono-cyclised' compound **69** (scheme 74).



Scheme 74: base-catalysed cyclisation of 68.

Reactions were monitored by reverse-phase HPLC, and a system was developed which gave good separation between peaks identified for compounds **68** and **70**, pure samples of which were readily available. **69** was identified by characteristic NMR peaks which validated its corresponding HPLC peak, and which did not overlap with NMR peaks of **68** and **70**. It was also important to look out for side-products, notably dienes formed from the allene intermediate, formed by the mechanism shown in **2.2.1** (scheme 69).

The first set of experiments was set up to try and find the lower temperature limit for this reaction. NMP and xylene were tried as solvents, and four reactions were set up at two different temperatures. 1 equivalent of DBU was used in each case, and the reactions were held for 3 days. Temperatures given in tables 14-15, and also for all base-catalysed cyclisations reported in the experimental section **3.1.10**, are those of the aluminium block used to heat up the solutions in a thick-walled glass tube sealed with a J-Young tap.

Entry	**Solvent**	**Temperature / °C**	**Ratio 68/69/70 by HPLC**	**% purity**
1	NMP	180	3:72:15	77
2	Xylene	180	98:2:0	97
3	NMP	200	5:31:64	70
4	Xylene	200	88:11:1	95

Table 14: base-catalysed cyclisations in NMP and xylene at 180-200 °C.

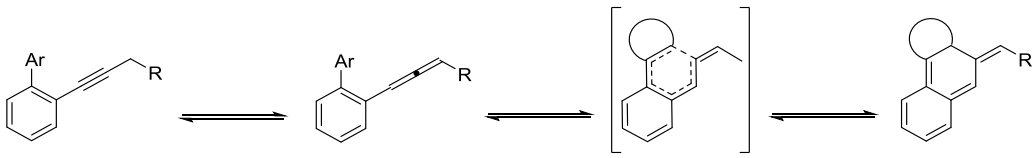
The results show that, while some conversion was observed at these temperatures, more so in NMP, a higher temperature was required for reaction completion. Meanwhile, it was clear that xylene was a much less effective solvent for the reaction at these temperatures, and any higher would be risky in a sealed tube (xylene b.p. 139 °C). Other solvents like diphenyl ether and DMPU have suitable boiling points, but NMP was used for the remainder of the reactions as this had been proven to work well so far, is regularly used in the literature[80-84] and so as not to introduce another variable into this study. Temperatures of 220-280 °C were used, and as well as DBU, inorganic bases – potassium hydroxide and potassium triphosphate basic – were tried. The results are shown in table 15, and ratios of **68**/**69**/**70** are those observed by reverse-phase HPLC.

Entry	Base, eq.	Temperature / °C	Time / h	Ratio 68/69/70	% purity
1	DBU, 1	220	3	12:64:24	85
			20	0:20:80	82
			40	0:3:97	79
2	DBU, 1	240	3	2:50:48	89
			20	0:2:98	82
3	DBU, 1	260	3	0:28:72	91
			20	0:0:100	69
4	DBU, 1	280	3	0:5:95	73
			20	0:0:100	70
5	K_3PO_4, 4	220	3	0:77:23	45
			20	0:1:99	38
6	K_3PO_4, 4	240	3	0:4:96	27
			20	0:1:99	25
7	K_3PO_4, 4	260	3	0:2:98	29
			20	0:2:98	27
8	K_3PO_4, 4	280	3	1:2:97	23
			20	0:3:97	23
9	KOH, 4	220	3	0:72:18	3
			20	0:20:80	2
10	KOH, 4	240	3	0:7:93	15
			20	0:4:96	15

Table 15: results of cyclisations using different bases at 220-280 °C.

The results in table 15 showed that inorganic bases, particularly KOH, were not suitable for this reaction. Percentage purity was generally low in entries 5-10, and it was clear that use of these bases resulted in more side-reactions. Crude NMR spectra of all entries were obtained and showed an increase in diene side-products formed when using inorganic bases.

The use of DBU at 240 °C gave the best results, and the results in table 15 showed that overnight reaction was sensible. As expected, rate of reaction increased with temperature, but the percentage purity at higher temperatures of 260 °C and 280 °C indicate that side-reactions were more likely at these higher temperatures. Previous reactions were carried out successfully at 220 °C, but calculations carried out by Professor Richard J. Whitby[137] show that the energy barrier to the cyclised transition state (scheme 75) was higher for the cyclisation of **68** than other substituents. This is because loss of aromaticity of a benzene ring costs more energy than naphthyl and heteroaryl substituents, leading to higher energy transition states (scheme 75, table 16).



Scheme 75: cyclisation mechanism showing the key transition state and loss of aromaticity of substituent.

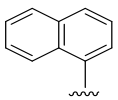
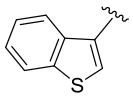
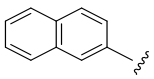
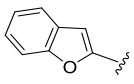
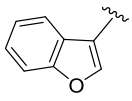
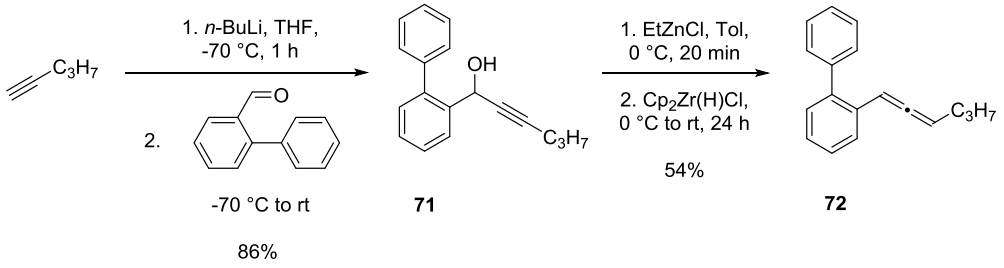
Ar	E / kJ mol^{-1}	Ar	E / kJ mol^{-1}
	137.2		104.2
	128.5		99.6
	121.7		101.2
	120.1		121.4
	96.9		

Table 16: calculated energy of the transition state shown in scheme 75 for different aryl substituents.

From this point, reactions were most commonly carried out at 240 °C overnight (14-24 h) with no monitoring. Two to four equivalents of DBU were often used rather than one, to ensure the reactions went to completion overnight. As well as lowering the yield, 'mono-cyclised' compounds like **69** could be extremely problematic, as separation from the target by column chromatography would be tricky due to the low solubility of the polyaromatics, and it was uncertain how easily they could be removed by recrystallisation.

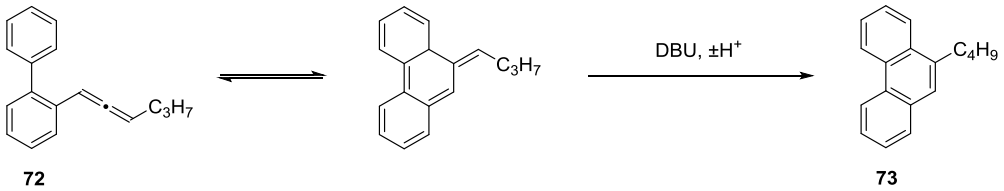
2.2.3 Synthesis and cyclisation of a model allene compound

The study in **2.2.2** prompted another investigation into the final cyclisation mechanism, in an effort to find which step in the sequence is rate-limiting. Direct reaction of an allene precursor would provide valuable information on the mechanism, and **72** was synthesised in two steps using a procedure reported by Kim and co-workers (scheme 76).[69]



Scheme 76: synthesis of 72 in two steps.

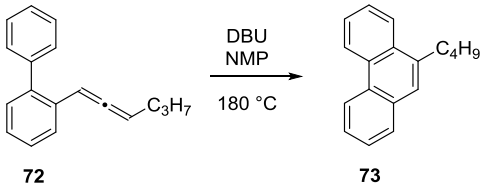
The key question in the subsequent set of experiments was whether, after cyclisation, the final and irreversible isomerisation, shown as the last step in scheme 77 to give phenanthrene **73**, was dependent on concentration of base. This step can occurs *via* a deprotonation and rearomatisation, and the results would show whether or not this is rate-limiting.



Scheme 77: mechanism of formation of 73 from allene 72.

Determination of the lower temperature limit for cyclisation of **72** was the first objective. NMR tubes are an ideal reaction vessel for monitoring the reaction progress, and the first experiments were carried out in toluene-d_8 at 110 °C but no conversion was seen. Due to the high cost of NMP-d_9, the standard J-Young tap vessels were used instead of NMR tubes, with the reactions sampled at regular intervals. No reaction was seen at 150 °C, and four reactions using variable

amounts of base were carried out at 180 °C (scheme 78). The results are shown in table 17, giving ratios calculated by NMR integration – synthesis and NMR characterisation of **73** has been reported by Burton.[79]



72 **73**

Scheme 78: cyclisation of 72 to 73.

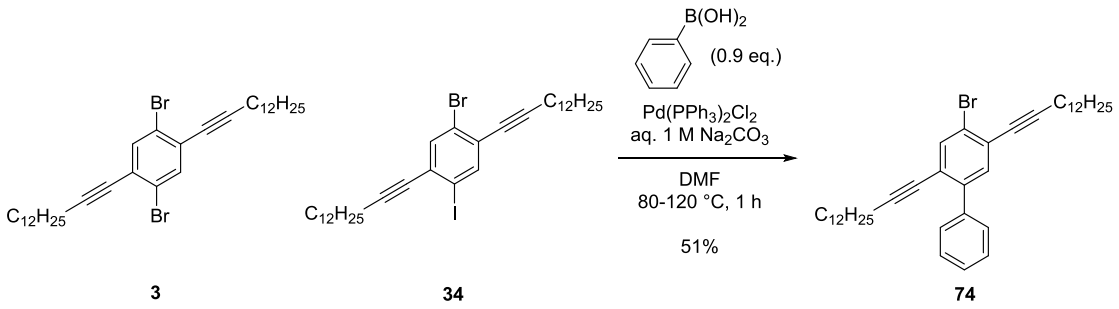
Entry	Equivs. DBU	72/73 ratio after 10 min	72/73 ratio after 0.5 h	72/73 ratio after 2 h
1	0.0	65:35	16:84	0:100
2	0.1	50:50	14:86	0:100
3	0.5	44:56	15:85	0:100
4	1.0	45:55	15:85	0:100

Table 17: reaction conversion (scheme 78) with variable amounts of base.

The experiments indicated that deprotonation of the cyclised product was not a rate limiting step, and that, at least from 0.1 to 1.0 equivalent, there was very little effect of concentration of base on the rate of reaction. Furthermore, the fact that the allene intermediate cyclised relatively fast at 180 °C, a temperature at which cyclisation of the bis-phenyl system **66** barely occurs after 3 days (see **2.2.2**, table 14), shows that it is the first deprotonation of the propargylic proton which requires the high temperatures (220-240 °C) and is rate-limiting.

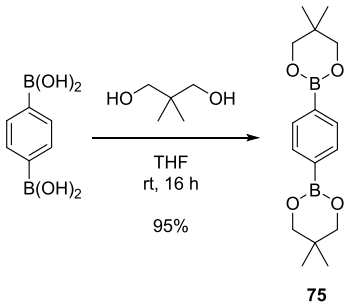
2.2.4 Synthesis of extended PAHs

Extension of existing compounds to make systems of more fused aromatic rings, *via* four cyclisations in one molecule rather than two, was a common theme throughout this research. The first extended target required precursor **74**, synthesised from a mixture of **3** and **34** (scheme 79) inseparable from a mono-iodination reaction that did not go to completion, and were present in a mass ratio of 28:72 respectively as calculated from NMR integration.



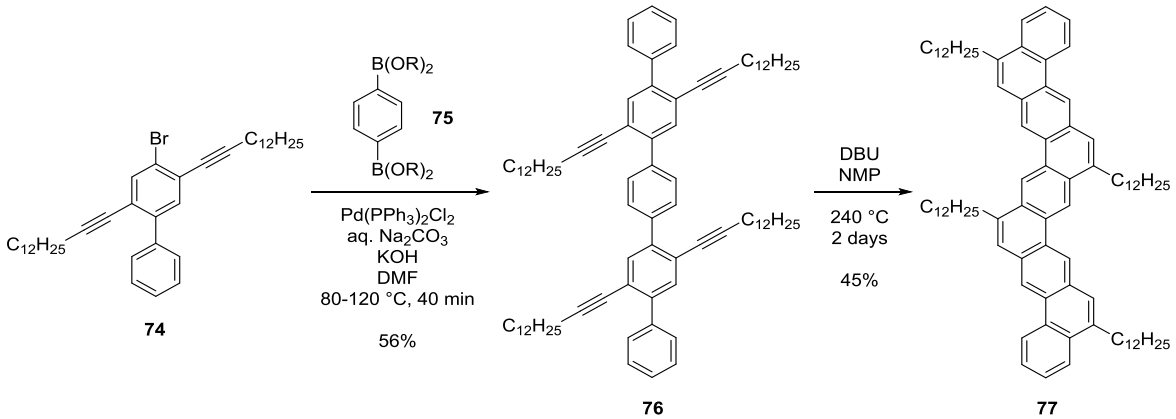
Scheme 79: synthesis of 74.

Coupling of this compound either end of a benzene-1,4-diboronate, followed by cyclisation, gave a system of nine fused rings. Commerically available 1,4-phenylenediboronic acid was converted to the neopentyl glycol ester **75**[138] in near-quantitative yield (scheme 80).



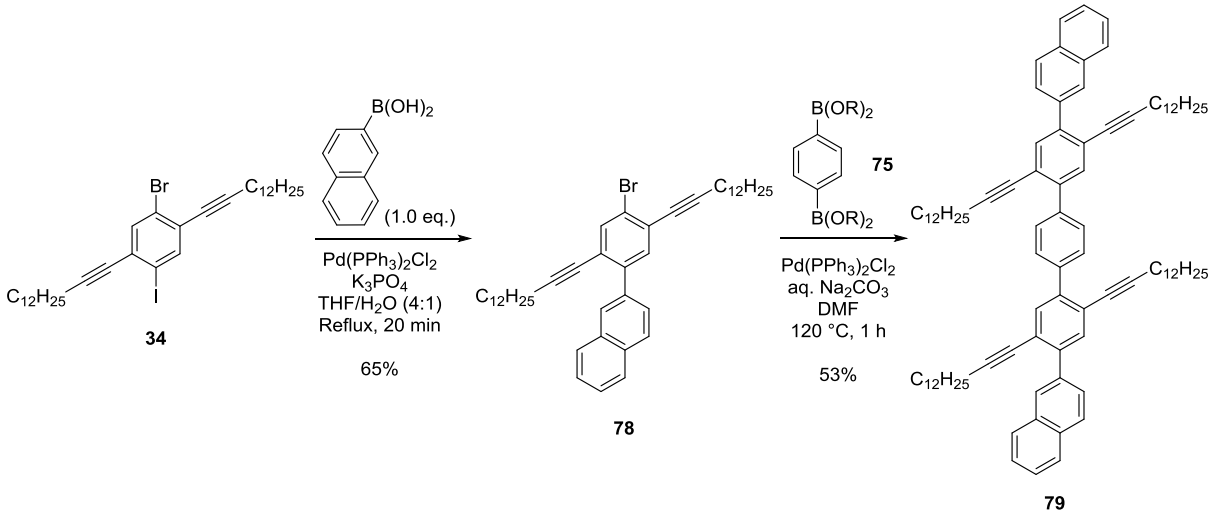
Scheme 80: synthesis of 75.

Use of a diboronic ester was considered safer than a diboronic acid in reactions like that shown in scheme 81 where the boronate, rather than the halide, was the limiting reagent and the consequences of protodeboronation would be a lot more costly than in the Suzuki reactions carried out until that point. The diboronic ester **75** was coupled with **74** and the precursor **76** cyclised, giving the target PAH **77** in 45% yield (scheme 81).



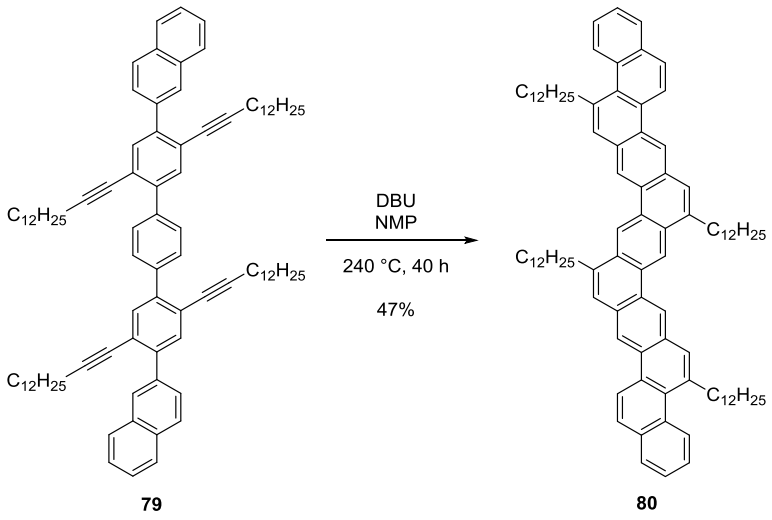
Scheme 81: synthesis of 77.

By using a naphthalene-substituted version of **74**, the same synthetic approach could be used to give an eleven-ring PAH with the same structure as **77** but for an additional benzene ring either side. The precursor **79** was synthesised in 34% yield over two steps (scheme 82).



Scheme 82: synthesis of 79.

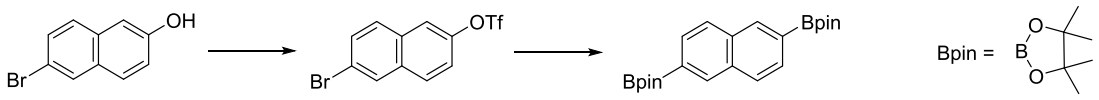
PAH **80** was synthesised from **79** in 47% yield (scheme 83).



Scheme 83: synthesis of 80.

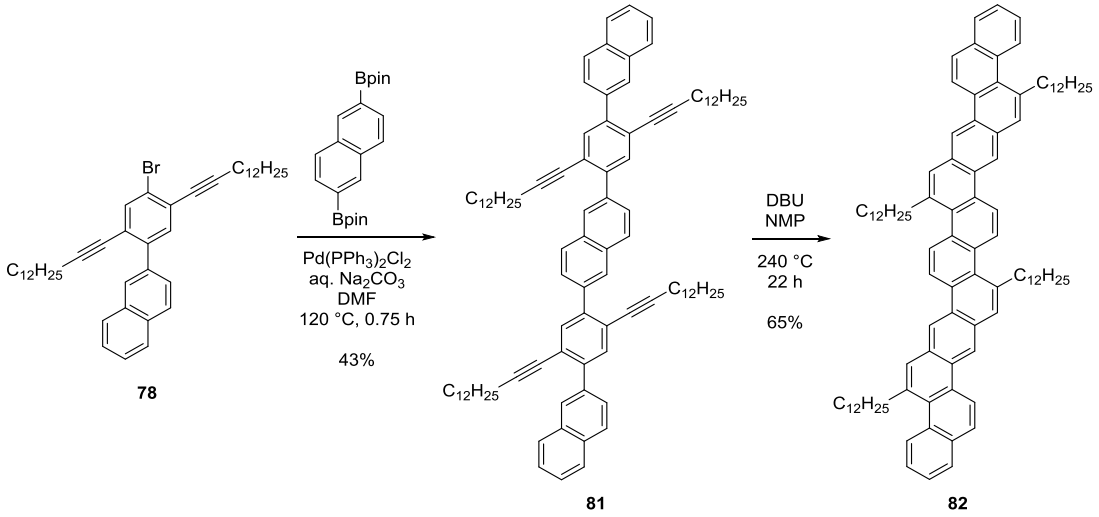
However, **80** showed extremely poor solubility. ^{1}H-NMR was obtained by using 2 mg in TCE-d_2 at 80 °C, but the material was too insoluble for ^{13}C-NMR. Both **77** and **80** appeared more amorphous in nature, and single crystals suitable for X-ray could not be grown.

One way of lengthening these PAHs was to use a naphthalene unit from which to attach the unsymmetrical precursors. 6-bromonaphthalen-2-ol was used to synthesis the diboronic acid pinacol ester, carried out by post-doctoral researcher Pawel Gawrys (scheme 84).



Scheme 84: synthesis of naphthalene-2,6-diyldiboronic acid bis(pinacol) ester.

This boronic ester was bis-coupled with **78**, and the precursor **81** cyclised, to give **82**.



Scheme 85: synthesis of 82.

To give **82**, all four alkynyl substituents cyclised to initially break the 1,2-double bond of the naphthyl unit, as in **2.2.1** (scheme 71). The regioselectivity of cyclisation and structure was confirmed by the NMR spectrum of **82**, carried out in TCE-d_2 at 60 °C (figure 45).

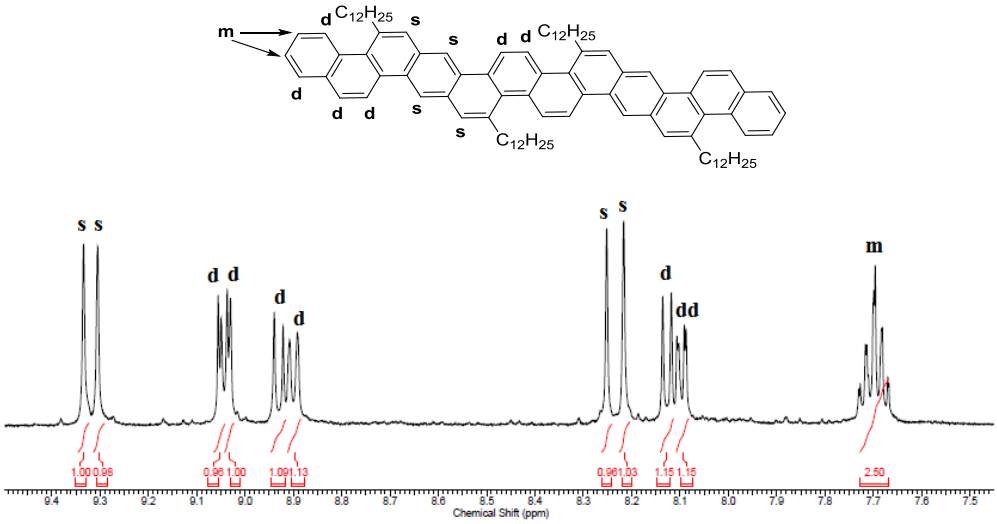


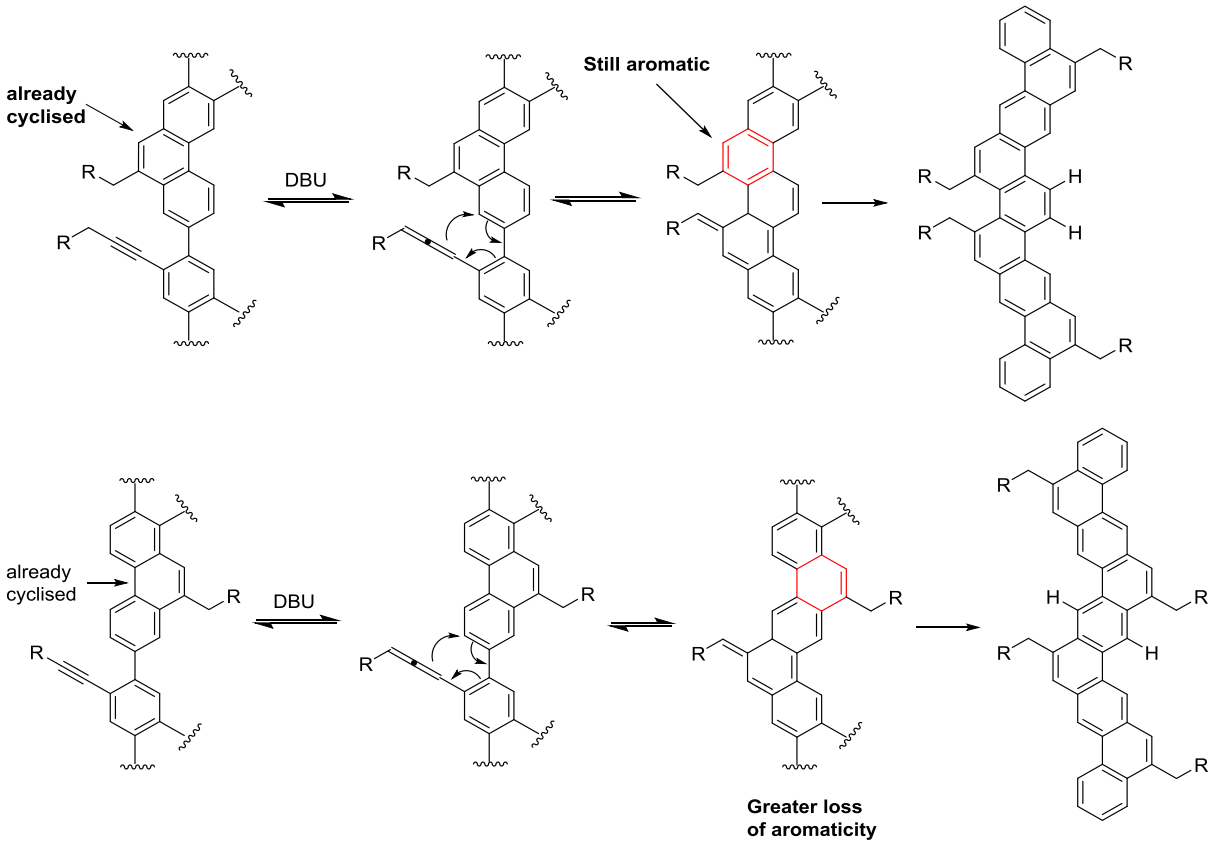
Figure 45: consistency of the NMR spectrum of 82 with its proposed structure.

As well as giving PAHs of greater length, replacement of benzene units with naphthalene should also provide greater stability to compounds upon further extension of π-conjugation.

Cyclisation of naphthalene substituents gives angular chrysene components, while cyclisation involving benzene furnishes linear anthracene units. As these polyaromatics become longer, presence of more chrysene units in place of anthracene should be conducive to achieving a more controlled decrease in HOMO-LUMO band gap, as the systems will contain a greater proportion of Clar aromatic sextets. This idea was explored further in chapter **2.3**.

2.2.5 A regioselectivity issue

Syntheses of **77** and **80** brought up an interesting regioselectivity issue. It was conceivable, especially upon discovering the regioselectivity explained in **2.2.1** (scheme 71) that these systems could cyclise to give compounds with a steric clash between two alkyl chains adjacent to the central benzene ring, and it was even suspected that these were the more likely isomers (scheme 86).

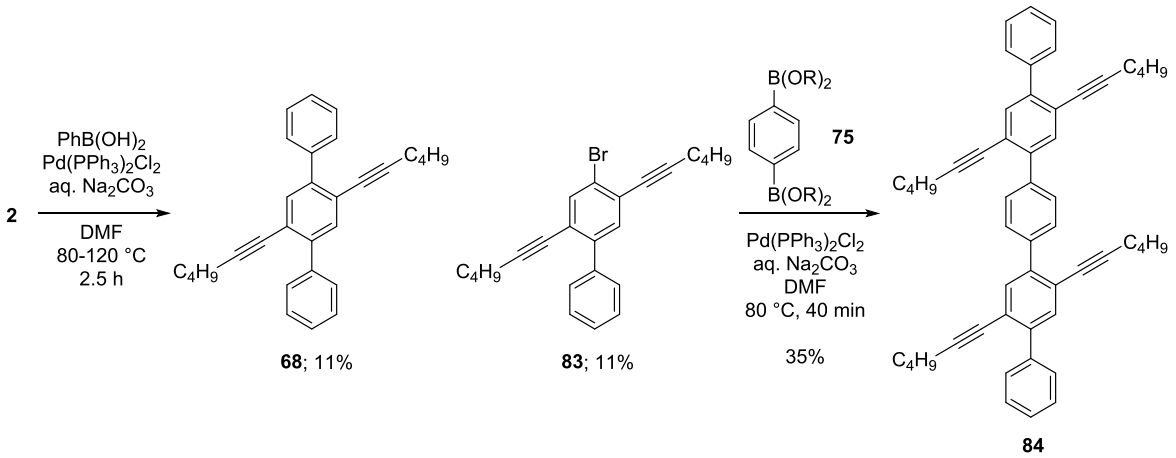


Scheme 86: cyclisation routes to two possible structures of 77.

Proving this regioselectivity was difficult, as the protons on the central benzene ring were chemically equivalent in both cases and appear as a singlet by NMR. Both compounds were too insoluble for experiments such as non-decoupled ^{13}C-NMR, and several attempts at

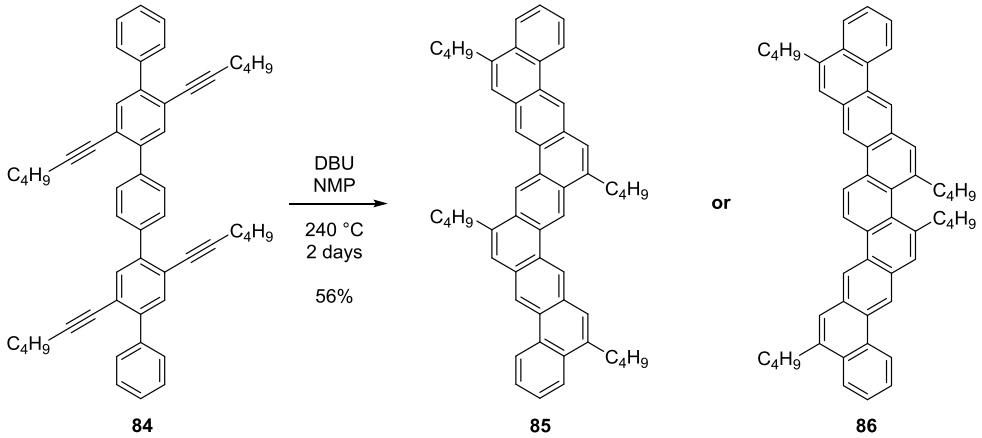
recrystallisation in solvents such as toluene, 1,1,2,2-tetrachloroethane, chloroform and xylene were unsuccessful in producing single crystals for X-ray crystallography.

84 was also synthesised (the analogue of **77** with butyl side chains), in the hope that a crystal structure would be easier to obtain. The required 'mono' precursor **83** had been previously synthesised in a mixture with the 'bis' **68**, when this had also been required (scheme 87). The statistical approach of using 1.0 equivalents of boronate was employed but this gave low yields of both compounds due to problems in separation by column chromatography. Synthesis of **68** was repeated later on (**2.2.2**, scheme 73), but a suitable quantity of **83** was synthesised and coupled to benzene-1,4-diboronic ester **75** to give **84** (scheme 87).



Scheme 87: synthesis of 84.

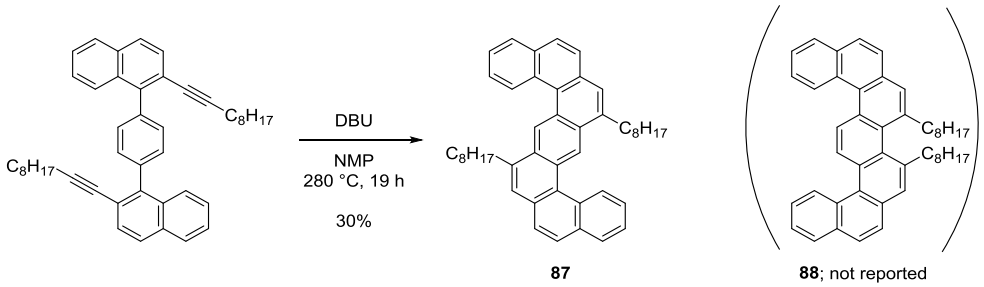
84 was cyclised to give 56% yield of a yellow solid (scheme 88). NMR showed peaks consistent with a single compound, but at this point the structure was unknown.



Scheme 88: base-catalysed cyclisation of 84.

However, like **77** and **80**, this compound did not give single crystals after several attempts. Pyridine- and nitrile-substituted compounds seen in the next chapter **2.3**, analogous in structure to **77**, were also non-crystalline.

Proving this regioselectivity by NMR studies was not a feasible option due to the insolubility of the compounds, and a lack of success in growing single crystals. The next solution was to synthesise a model system which would potentially feature the same clash of alkyl chains, and be easier to crystallise. Jason Howe reported the synthesis of **87**, the same structure as **60** but for the position of alkyl substituents, in 30% yield after recrystallization (scheme 89).[135]



Scheme 89: reported synthesis of 87.

X-ray crystallography confirmed the reported structure **87** (figure 46) despite the mechanistic explanation shown in scheme 86 supporting the synthesis of **88**.

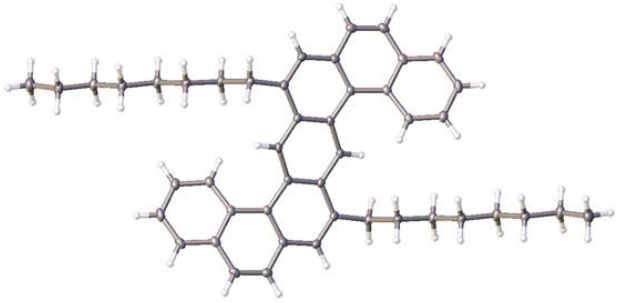
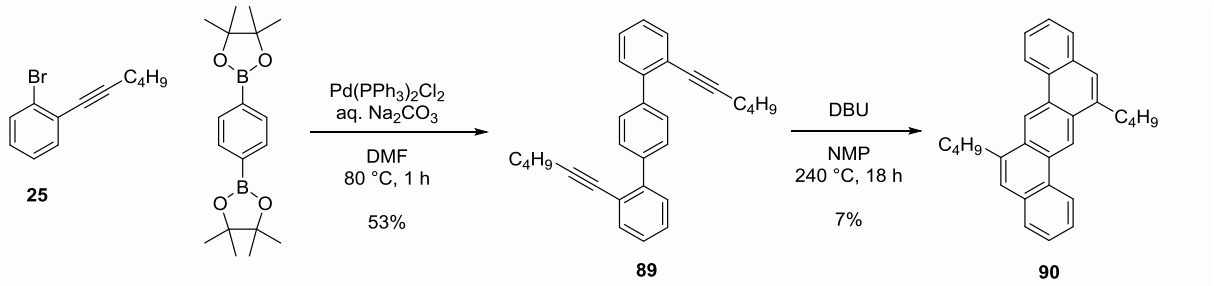


Figure 46: crystal structure of 87.

To further confirm the regioselectivity of these cyclisations, a similar synthesis of a five-ring PAH was planned. Suzuki coupling of **25** with 1,4-benzenediboronic acid bis(pinacol) ester was followed by reaction of the precursor **89** with DBU to give **90** (scheme 90).



Scheme 90: synthesis of 90 in two steps.

The very low yield of **90** can be attributed to a number of reasons. Some losses may have occurred during extraction as a large volume of water was required to wash away NMP, and crude NMR showed impurities. Mass recovery after column chromatography was around 25%, indicating possible polymerisation side-reactions. **90** was then isolated by two separate precipitations in low yield, but nonetheless the crystalline material was characterised and the structure confirmed by X-ray crystallography (figure 47).

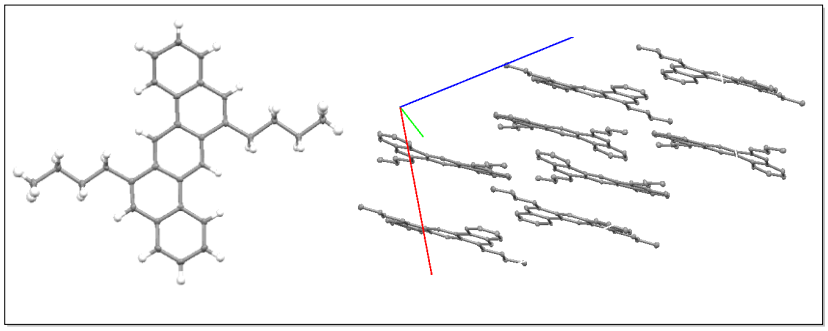


Figure 47: crystal structure of 90 and packing.

90 was isolated by precipitation from the material obtained after column chromatography. The mother liquor from these was concentrated under reduced pressure and analysed by NMR. Interestingly, this showed a fairly clean spectrum indicating one compound. Mass spectrometry analysis showed the same mass as **90**, and with no diene peaks present, this indicated the isomeric picene structure **91** (figure 48).

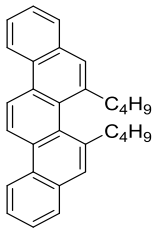


Figure 48: 6,7-dibutyl picene 91.

Although not entirely pure, the NMR spectrum was clean enough to show multiplicities and integrations consistent with **91**, and a yield of 18% has been reported. Most interestingly, two benzylic C-H signals were seen, indicating the presence of diastereotopic protons (figure 49).

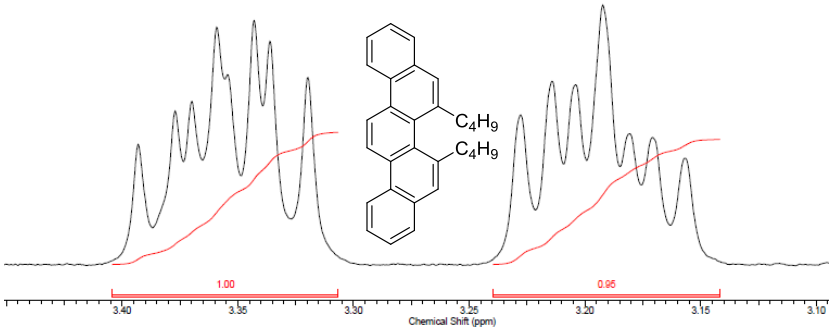


Figure 49: benzylic proton signals in 91.

Steric clash of the alkyl chains in **91** gave a twisted, chiral molecule, resulting in a complex AB system for the diastereotopic benzylic protons (figure 49). This was in contrast to **90**, where like all other planar polyaromatic systems synthesised in this project, a sharp triplet was observed (figure 50).

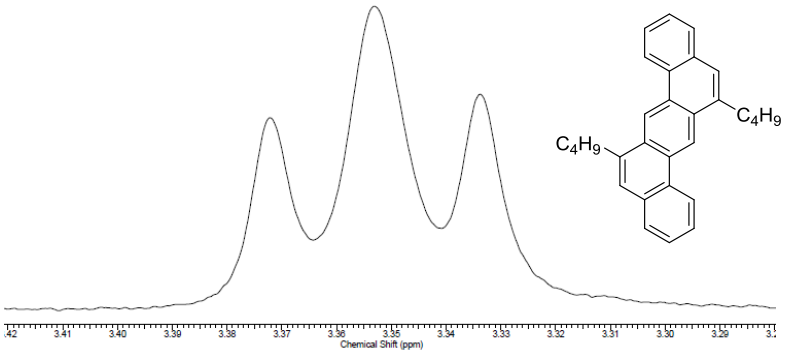


Figure 50: benzylic proton signal in 90.

Closer inspection of the crude NMR spectrum of the cyclisation reaction shown in scheme 89 also gave evidence that both structures, **87** and **88**, had been formed, with the former much easier to isolate by recrystallization, as was reported. Furthermore, literature examples of compounds which feature the same alkyl clash as **88** and **91** also report diastereotopic benzylic protons (table 18).

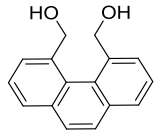
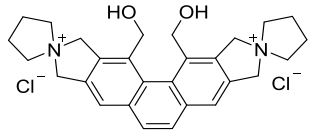
Compound	Reported chemical shifts of benzylic protons (δ, ppm)	Reference
	4.79 and 4.98	(139)
	4.63 and 4.90	(140)

Table 18: reports of diastereotopic benzylic protons in phenanthrenes featuring a steric alkyl clash.

This is consistent with the NMR spectrum of **91**. In addition, the fact that compounds **77**, **80** and **85** gave clear triplet signals for benzylic protons is strong evidence for the reported structures, which do not feature a clash of alkyl chains. It is likely that the chiral isomers of these systems were formed but left in the reaction mixture, as the reported compounds were obtained by precipitation. This may also help to explain some of the lower yields reported.

2.2.6 Photophysical characterisation

2.2.6.1 UV-vis spectroscopy

As with the heterocycles, polyaromatics with a central chrysene unit gave wider HOMO-LUMO band gaps than those with an anthracene centre (table 19) which was in agreement with calculations (figure 51).[133] Although not reported, **70** was included in table 19 for comparisons with other PAHs. Extinction coefficients for the nine- to twelve-ring systems (entries 7-10) were not measured due to the very low solubility of these compounds.

Entry	Compound	λ_{max} / nm	ε / dm^3 mol^{-1} cm^{-1}	λ_{onset} / nm	Observed E_{opt} / eV	Calculated E_{opt} / eV
1	**70**	402	1200	409	3.03	3.27
2	**60**	432	1600	444	2.79	2.86
3	**61**	424	5800	438	2.83	2.95
4	**65**	387	1900	393	3.16	3.39
5	**66**	413	1300	419	2.96	3.14
6	**67**	401	2500	410	3.02	3.22
7	**77**	443	---	456	2.72	2.90
8	**80**	453	---	467	2.66	2.78
9	**82**	443	---	455	2.73	2.67
10	**85**	444	---	456	2.72	2.90
11	**90**	398	1210	408	3.04	3.27

Table 19: photophysical properties of all PAH's.

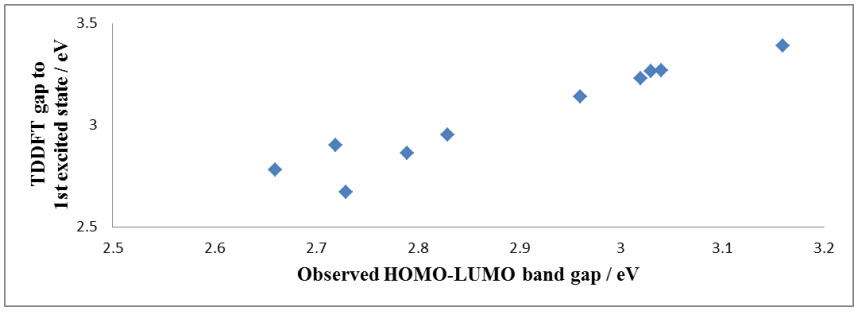


Figure 51: graph showing the correlation between observed and calculated band gap values for PAH's.

For the same substituent introduced by C-C biaryl coupling before cyclisation, use of a benzene core resulted in a bathochromic shift of λ_{max} compared to naphthalene-derived core (figure 52). This typically gave a band gap difference of around 0.2 eV.

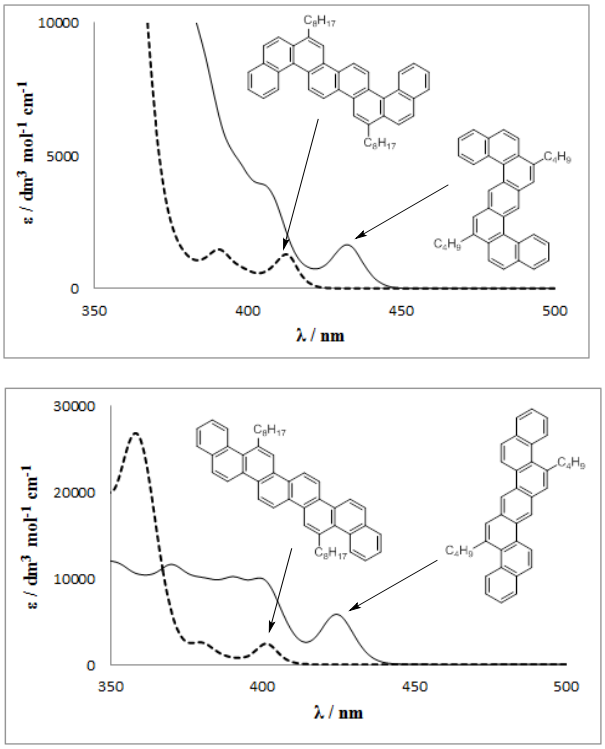


Figure 52: bathochromic shift of λ_{max} in going from chrysene- to anthracene-based systems.

Extension of PAH systems by addition of a benzene ring either side also resulted in a bathochromic shift of λ_{max} (figure 53) and a similar band gap decrease of around 0.2 eV.

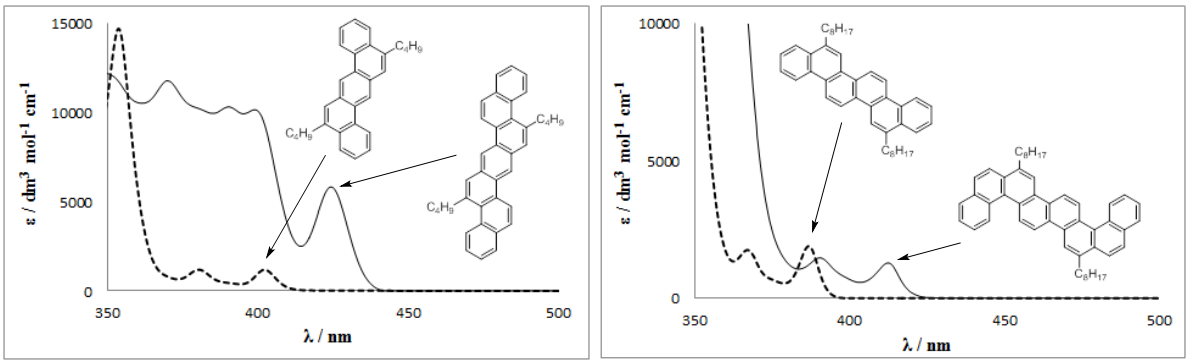


Figure 53: bathochromic shift of λ_{max} resulting from extended π-conjugation.

In compounds derived from naphthalene substituents, the 'bent' systems containing helicene-like fragments gave bathochromically shifted λ_{max} values and lower band gaps than their linear isomers (figure 54).

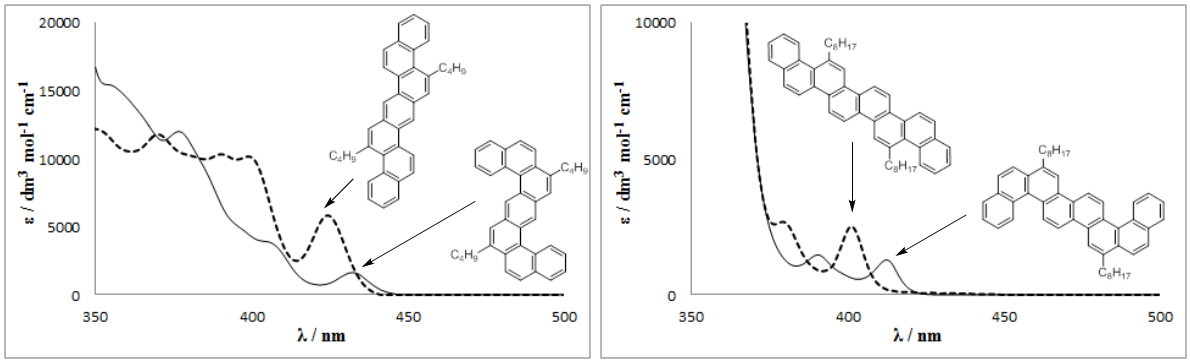


Figure 54: bathochromic shift of λ_{max} of 'bent' PAHs compared to their linear isomers.

All extended systems (table 19, entries 7-10) showed good stability in air, consistent with their band gap values of over 2.5 eV. These results showed the value of using naphthalene as a central building block for the longer compounds, as this created less linear anthracene units and, with extension, gave compounds containing a greater proportion of Clar aromatic sextets. Twelve-ring PAH **82**, derived from a naphthalene centre, gave an identical λ_{max} to the shorter nine-ring PAH **77**, derived from a benzene centre, and a very similar estimated band gap (figure 55).

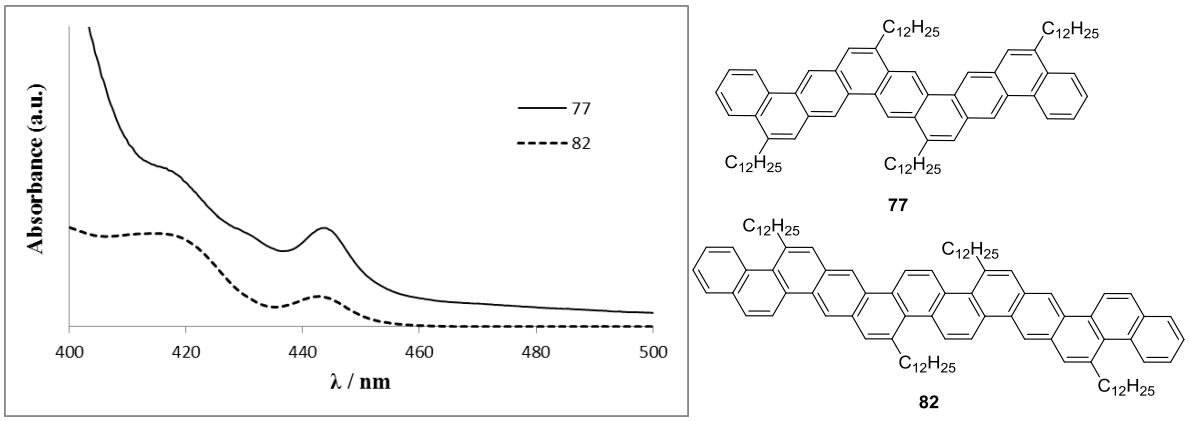


Figure 55: overlaid UV-vis spectra of PAHs 77 and 82.

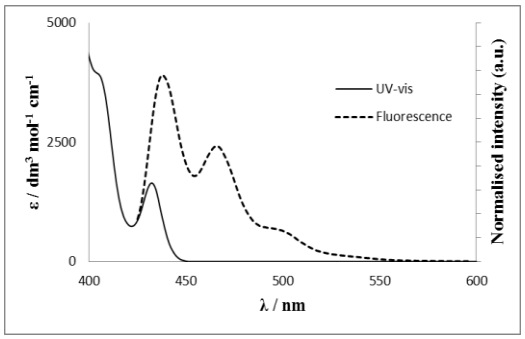
2.2.6.2 Fluorescence spectroscopy

Fluorescence emission wavelengths, λ_F, are given in table 20. The naphthalene-derived compounds **65-67** generally gave lower Stokes shifts than benzene-derived **60-61**.

Compound	λ_{max} / nm	λ_F / nm
60	432	438
61	424	433
65	387	388
66	413	415
67	401	407

Table 20: complementary absorption and emission maxima from UV-vis and fluorescence spectroscopy for PAHs.

Spectra of complementary UV-vis and fluorescence are shown in the experimental section **3.2.1**, such as the example of **60** (figure 56).



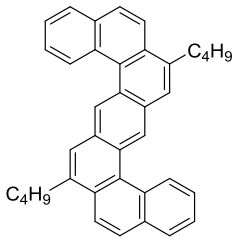


Figure 56: absorption and emission spectra of 60.

2.2.7 Conclusions

PAHs of between six and eight benzene rings were synthesised from benzene and naphthalene starting materials. Crystal structures were obtained for all of these, and in two cases, **60** and **66**, a steric 1,5 hydrogen clash resulted in twisted structures compared to other compounds, including heterocycles, which were flat molecules.

Studies on the best conditions and mechanism of the final base-catalysed cyclisation were carried out, and overnight reaction using DBU at 220-240 °C was found to be optimum. The mechanism was probed by synthesising and cyclising the model allene **72**, which found that the final deprotonation and rearomatisation was not rate-limiting or heavily dependent upon base concentration, and therefore it is the initial propargylic deprotonation which is rate-limiting and requires the high temperatures used.

Extended PAHs of nine to twelve rings were synthesised, and isolated as stable compounds with HOMO-LUMO gaps of over 2.5 eV. These syntheses revealed that the use of naphthalene units in place of benzene may give better control of the decrease of HOMO-LUMO band gap with extension of π-conjugation, an idea more thoroughly investigated in the next chapter. The initially contentious structures of **77**, **80** and **85** were solved by NMR studies as not giving a steric clash of alkyl chains.

UV-vis spectroscopy revealed a number of expected patterns, such as bathochromic shifts resulting from extension of π-conjugation or from chrysene- to anthracene-containing PAHs. The experimentally determined band gaps gave good correlation with TDDFT-calculated values. Again, this is very promising for future work, particularly in the synthesis of extended PAHs approaching graphene and their properties.

2.3 Molecular wires

2.3.1 Introduction

Having produced a number of polyheterocyclic compounds and PAHs, the final idea in this project was to apply the same chemistry to synthesise potentially highly conducting molecular wires.[141] Polyaromatic molecules were synthesised containing terminal pyridyl and nitrile groups, which can act as anchoring groups, or 'alligator clips', to provide contacts to two metal electrodes (typically gold) at either end. Other anchoring groups include amines,[142, 143] carboxylic acids,[142, 144] isonitriles,[145] thiols,[142, 146, 147] thioethers,[148, 149] thioamides[150] and trimethylsilylethynyls[151] (figure 57).

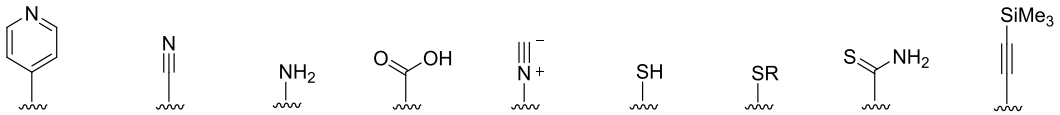


Figure 57: molecular wire anchoring groups.

Thiols are the most commonly explored anchoring group due to their high affinity for gold, achieved by formation of a strong Au-S bond *via* a thiyl (RS•) radical. However, their tendency to give disulphides can cause problems. Thioamides have been reported as an interesting and more stable alternative to thiols.[150]

After thiols, pyridines are one of the most common anchoring groups.[152-155] Studies on charge transport in a variety of tolane derivatives found that pyridine exhibited a better anchoring performance than thiol.[156] Nitriles are less studied, but have also been reported as promising alligator clips,[157] and both of these functional groups were expected to show good stability in the final base-catalysed cyclisation step of the proposed synthetic route. The nature of the anchoring group in these molecular wires in achieving good conductance is important as it heavily influences the alignment between the HOMO/LUMO energy levels in the organic molecule and the Fermi level of the gold electrode.

Like the anchoring groups, a lot of variation is seen in the molecular structure of these organic wires. Charge transport occurs through the π-conjugation of the organic compound, and typical molecular wires are π-conjugated oligomers containing aromatic rings. Examples include oligo(*p*-phenylene ethylenes) (OPEs),[158] oligo(*p*-phenylene vinylenes) (OPVs)[159] and oligothiophenes[160] (figure 58).

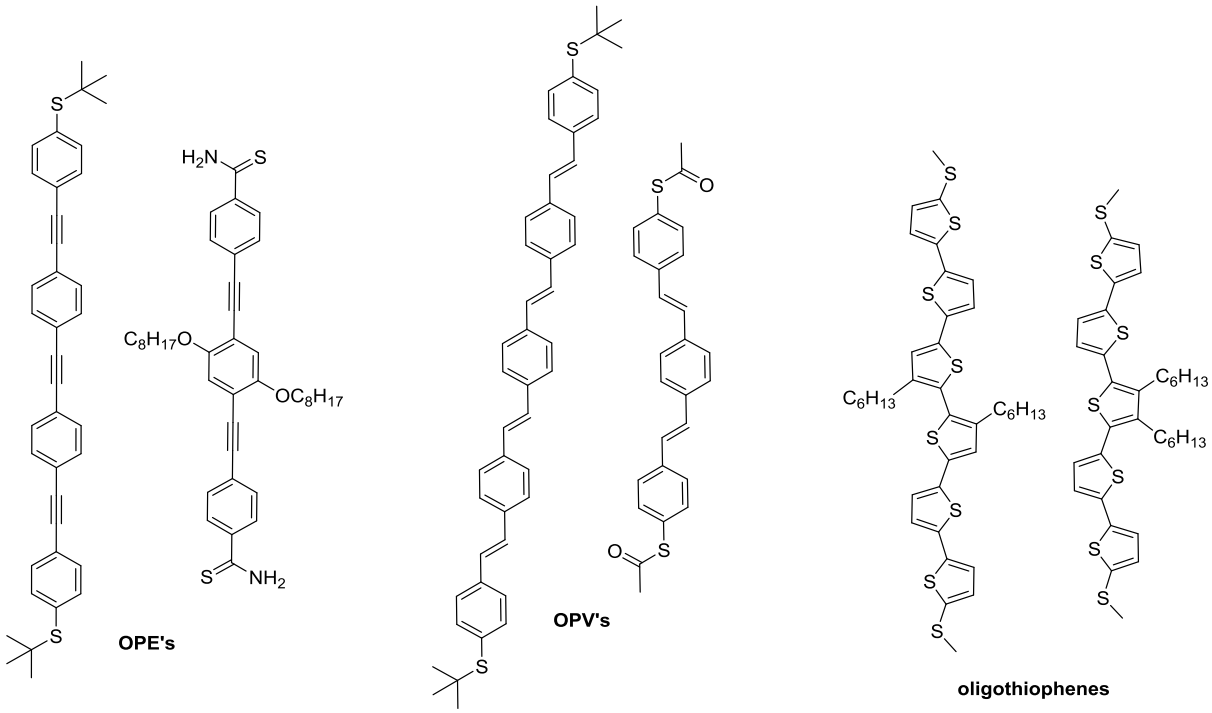
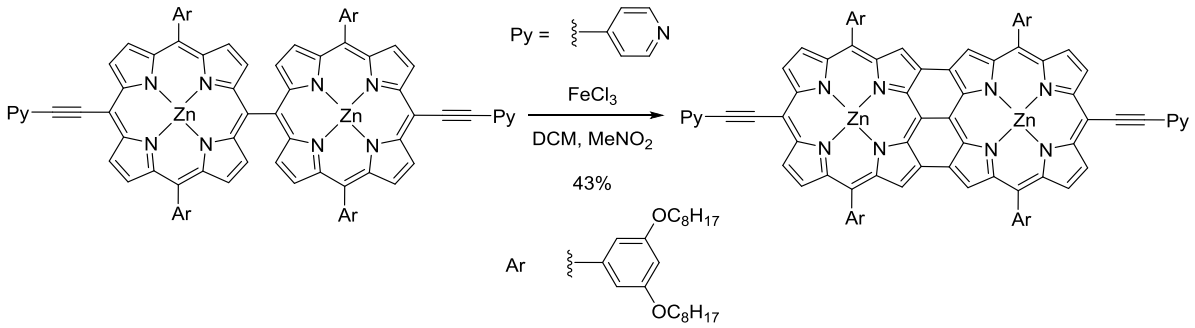


Figure 58: molecular wires.

Conductance of a molecular wire also depends on its molecular conformation. Steigerwald and co-workers demonstrated how increasing twist results in a lower degree of π-conjugation, consequently resulting in lower conductance.[161] This has also been found in zinc porphyrin-based molecular wires, which have been widely studied in the molecular electronics field.[162-165] It was found that planarisation of oligomeric porphyrins gave a very low attenuation coefficient, β.[165] Conductance in these molecular wires, containing fused porphyrins which locked the π-system in a planar conformation, was increased compared to those where porphyrin units were linked by a single bond, and therefore almost perpendicular to each other due to steric interactions. The former was synthesised from the latter in an iron-catalysed oxidative cyclisation (scheme 91).



Scheme 91: synthesis of planarised oligomeric porphyrins.

In another publication on the use of planar, rigid π-systems in molecular wires, Sukegawa et al. reported carbon-bridged OPVs which showed an 840-fold increase in electron transfer rate compared to flexible analogues.[166]

With these discoveries in mind, the synthetic chemical sequences seen so far in **2.1** and **2.2** could be applied to synthesise highly conducting molecular wires. Rigid, planar polyaromatic molecules with an effective anchoring group could show great promise in the molecular electronics field.

2.3.2 Synthesis of five- to eight-ring molecular wires

Like the previous two chapters, both benzene and naphthalene starting materials were used for molecular wire synthesis. Use of pyridinyl and 5-isoquinolinyl substituents gave molecules with a pyridine anchoring group, while 4-cyanophenyl and 6-cyanonaphthalen-2-yl substituents gave the nitrile-terminated compounds (figure 59).

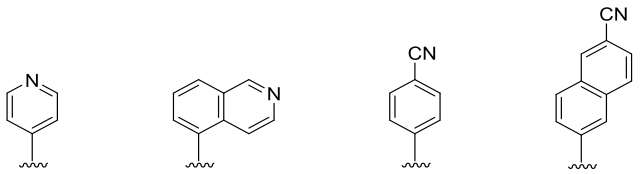
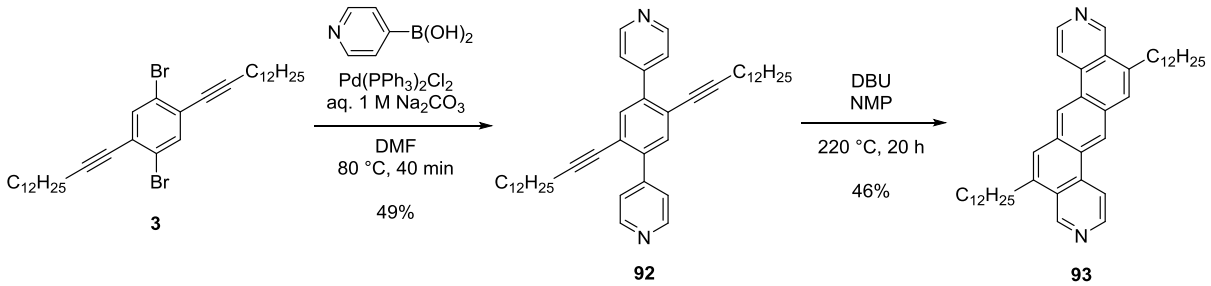
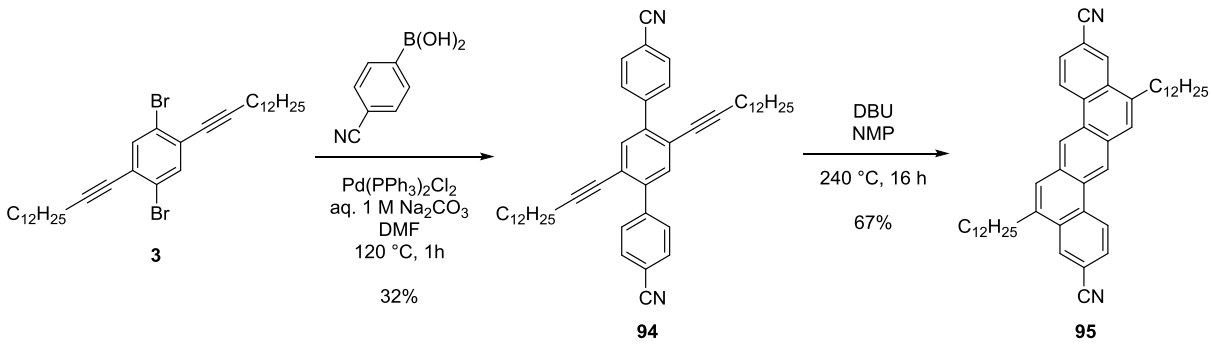


Figure 59: substituents used as terminators for molecular wire synthesis.

Use of the benzene and naphthalene cores, along with the four substituents shown in figure 59, gave eight molecules of different lengths. Those derived from the benzene core were synthesised first (schemes 92 and 93). Erring on the side of caution in terms of expected solubility of the final compounds, dodecyl side chains were used.

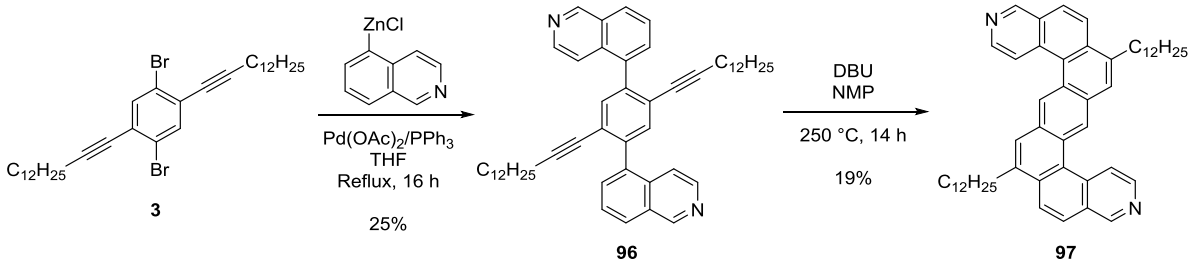


Scheme 92: synthesis of 93.



Scheme 93: synthesis of 95.

Yields of both Suzuki reactions (schemes 92 and 93) were fairly low. Problems arose mainly from column chromatography, with the need for more polar solvent systems than previously used – especially in the case of pyridine – resulting in the products eluting as mixed fractions, compromising the yields. Mass recoveries and yields for couplings of these substituents improved later on through better chromatographic methods, as gradient eluents were more commonly used. However, the two polyaromatic systems were synthesised in suitable quantities, showing good solubility with the obtention of NMR data carried out in $CDCl_3$ at room temperature. Next, synthesis of another 'bent' polyaromatic, isoelectronic to PAH **60** (**2.2.1**, scheme 68), was carried out (scheme 94).

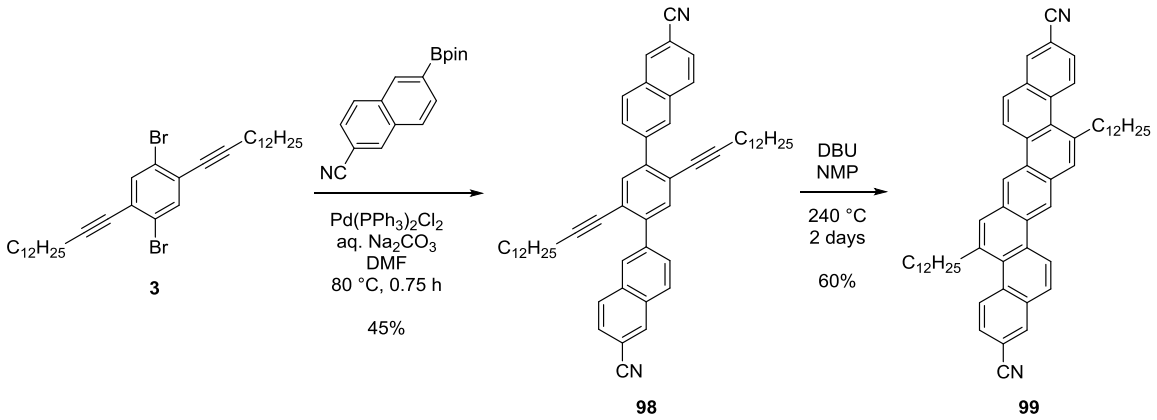


Scheme 94: synthesis of 97.

96 was made *via* a Negishi coupling, using 5-bromoisoquinoline, *n*-BuLi and zinc chloride to synthesise the organozinc reagent *in situ* at -70 °C. However, despite good literature precedent,[167, 168] coupling of this substituent was low-yielding and points to incomplete/inefficient halogen-lithium exchange. Optimisation of this reaction was planned, but not a priority, and 0.175 g of the precursor was synthesised, a suitable quantity for the next step. Like the isoelectronic PAH **60** (**2.2.1**, scheme 68), synthesis of **97** (scheme 94) was low-yielding, which could be explained by similar reasons – steric 1,5-hydrogen clash leading to more side-products, high solubility of the compound and the need for column chromatography.

However, optimisation and repeat synthesis of this system was not a priority and 30 mg of the final compound was obtained.

The readily available naphthonitrile boronic ester seen in scheme 95 was synthesised by post-doctoral researcher Pawel Gawrys and used in a Suzuki coupling with **3** to give **98**, the precursor to a seven-ring nitrile-terminated system **99**.



Scheme 95: synthesis of 99.

A crystal structure was obtained for **99** after slow cooling in toluene (figure 60).

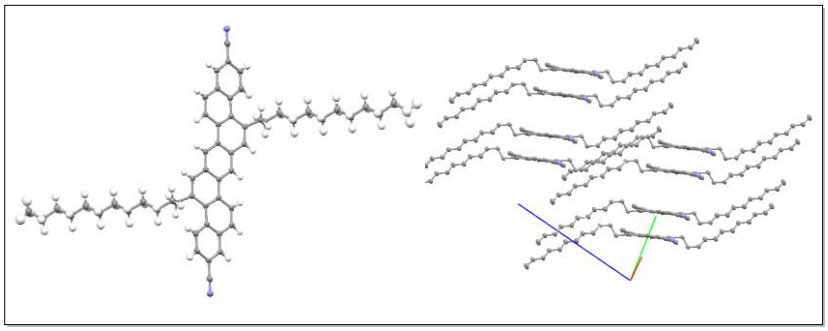
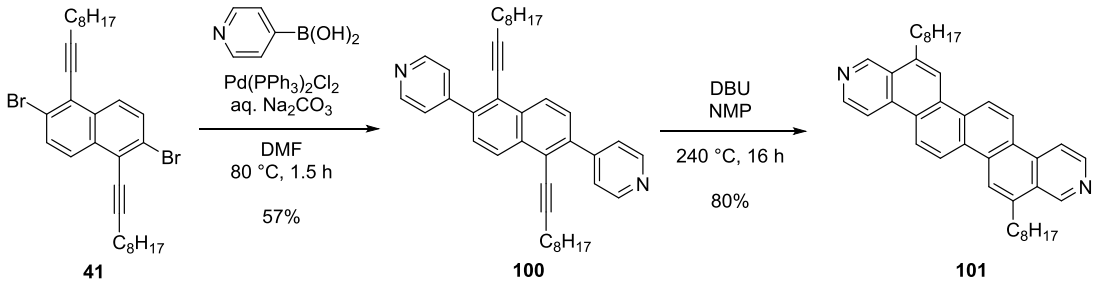


Figure 60: crystal structure of 99 and packing. Blue = N.

The same four moieties (figure 59) were substituted onto the naphthalene core **41** and cyclised, starting with pyridine to give **101** (scheme 96).



Scheme 96: synthesis of 101.

This was one of the few compounds which crystallised directly from the reaction mixture in NMP to give single crystals (figure 61).

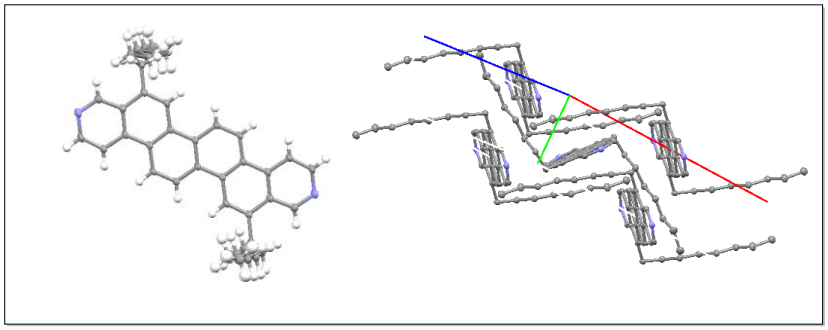
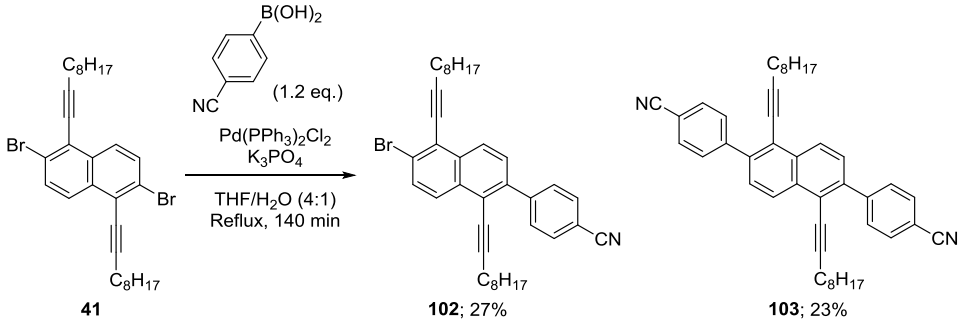


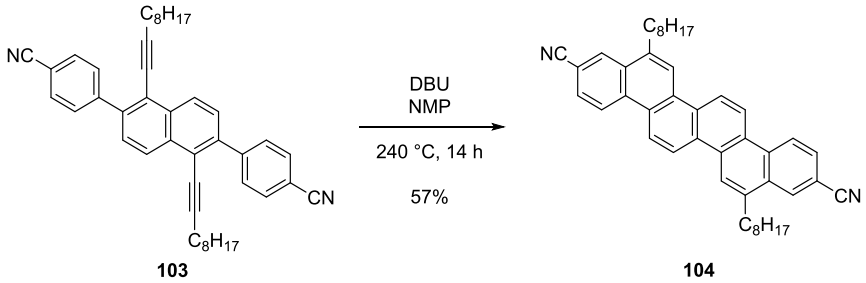
Figure 61: crystal structure of 101 and packing.

The bis-cyanophenyl-substituted precursor **103** was synthesised as part of a mixture with 'mono' **102**, which was required for later use (scheme 97).



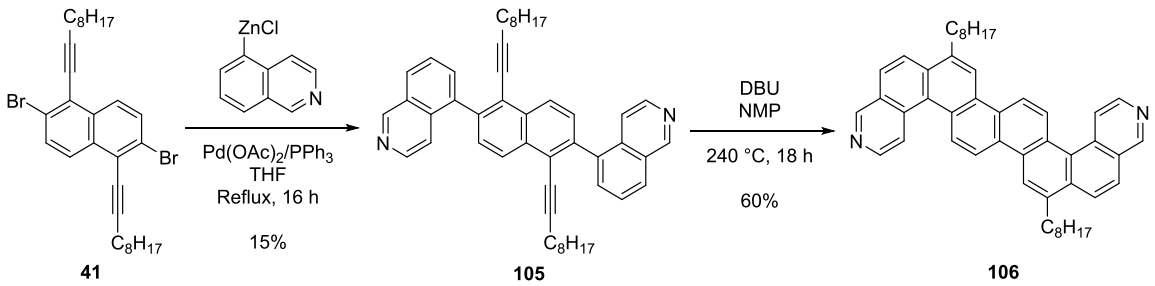
Scheme 97: synthesis of a mixture of 102 and 103.

These were separated by column chromatography, and **103** cyclised to give **104** (scheme 98).



Scheme 98: synthesis of 104.

Negishi coupling of the 5-isoquinoline substituent gave a low yield when using the naphthyl core **41**, as it did in the synthesis of **96** (scheme 94). **105** was cyclised in 60% yield to give **106** (scheme 99).



Scheme 99: synthesis of 106.

Recrystallisation of **106** by slow cooling in toluene gave single crystals, and X-ray crystallography revealed a twisted structure resulting from the steric 1,5 hydrogen clash (figure 62).

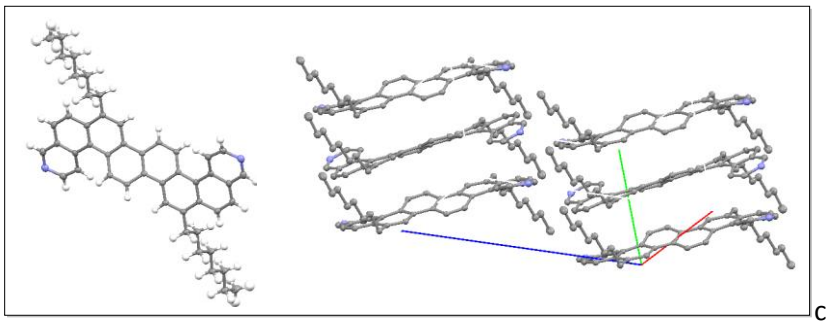
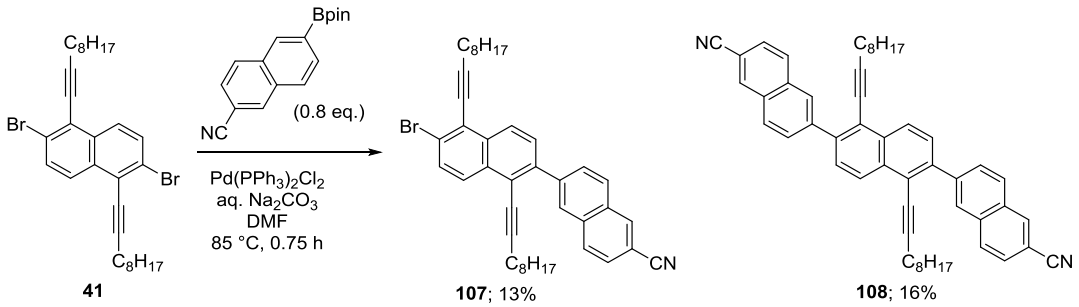


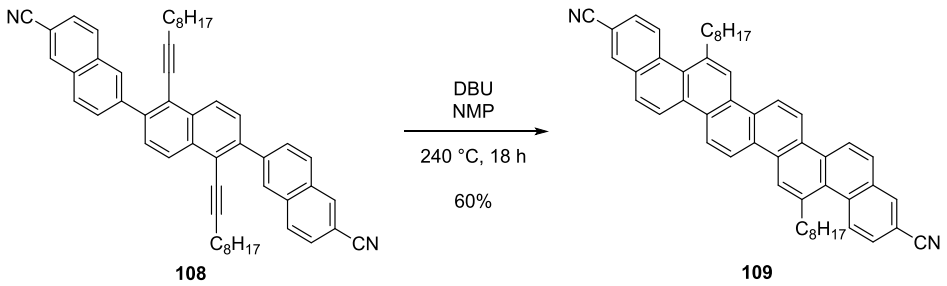
Figure 62: crystal structure of 106 and packing.

The naphthonitrile diboronic ester used in the synthesis of **98** (scheme 95) was coupled onto **41**. A mixture of mono and bis compounds, **107** and **108**, was deliberately synthesised (scheme 100) and separated by column chromatography, with the former required as a precursor for later targets.



Scheme 100: synthesis of a mixture of 107 and 108.

108 was cyclised to give an eight-ring molecular wire **109** (scheme 101).



Scheme 101: synthesis of 109.

2.3.3 Synthesis of extended molecular wires of nine or more fused rings

The polyaromatic compounds shown in **2.3.2** all follow the same chemical sequence from **3** and **41** – a palladium-catalysed Suzuki or Negishi cross-coupling to introduce two aryl substituents followed by a double cyclisation. Synthesis of longer molecular wires required extra steps, the last of which could be described as a quadruple cyclisation, such as those seen in the synthesis of extended PAHs **77**, **80** and **82** (**2.2.4**, schemes 81, 83 and 85 respectively).

The strategy towards making these extended molecular wires could be described by using a central aromatic 'core' with two boron substituents, a 'linker' with one bromide substituent and an 'end' attached to it, this 'end' containing the anchoring group. The linker, such as **102** and **107** (schemes 97 and 100 respectively), could be attached to either side of the core *via* a double Suzuki cross-coupling to give a precursor with four alkynyl substituents, and cyclisation of all of these in one reaction created a polyaromatic system of nine or more fused aromatic rings. The strategy is outlined in figure 63.

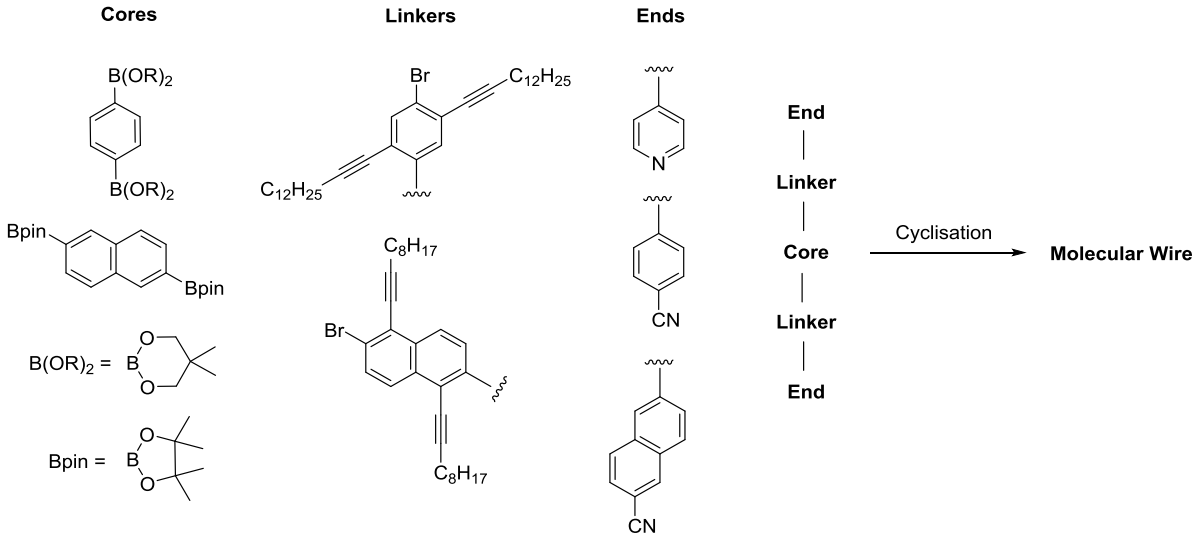
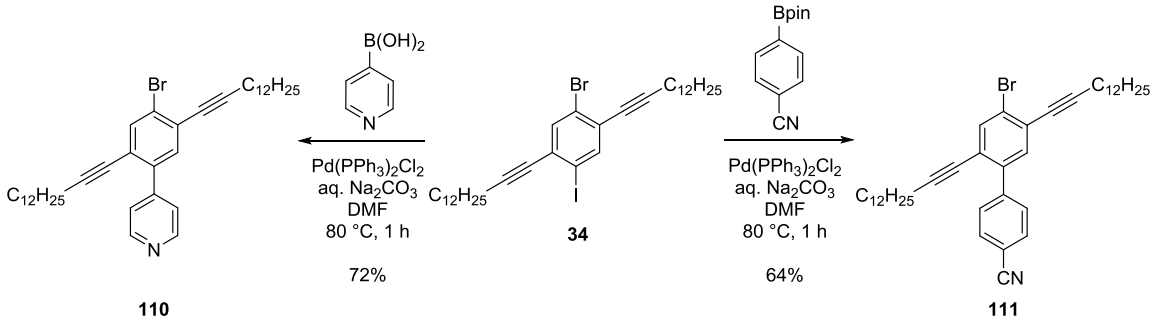


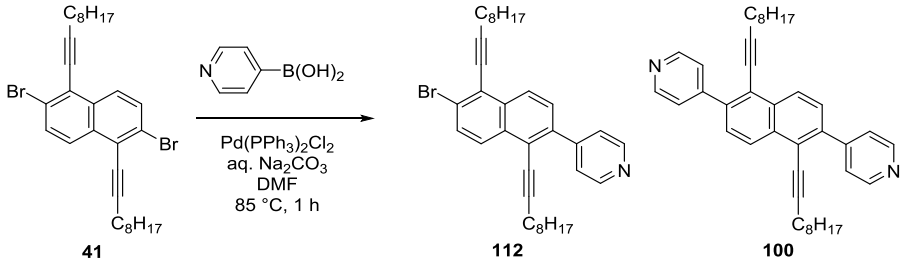
Figure 63: representation of extended molecular wire synthesis using different cores, linkers and ends.

Syntheses of the two diboronate cores are shown in **2.2.4** (schemes 80 and 84). Crucial to the success of the idea shown in figure 63 was synthesis of the linkers, as these required Suzuki reactions to attach one aromatic end where substitution of two was possible. With the benzene linkers, this problem was solved as shown in **2.1.5**, as synthesis of **34** (scheme 60) allowed for more selective mono-Suzuki coupling. The 4-pyridine and 4-cyanophenyl ends were both substituted, using 1.0 equivalent of boronate reagents with respect to **34**, to give **110** and **111** (scheme 102).



Scheme 102: mono-Suzuki couplings to give 110 and 111.

Synthesis of the naphthalene-derived linkers was more challenging. One of these, **102** with a nitrile anchoring group (**2.3.2**, scheme 97) gave a good combined yield of mono- and bis-coupled products. However, this reaction proved quite an anomaly and subsequent yields of similar reactions were not as high. A series of experiments with the naphthalene core **41** using 0.6, 0.8 and 1.0 equivalents of pyridin-4-ylboronic acid suggested that Suzuki coupling was faster once one pyridine was already substituted (scheme 103, table 21).



Scheme 103: synthesis of compounds 112 and 100 using variable amounts of pyridin-4-ylboronic acid.

Entry	Equivalents of boronic acid used	Ratio 41/112/100 by NMR	% isolated yield of 112	% isolated yield of 100	% yield of recovered starting material
1	0.6	70:16:14	10	9	44
2	0.8	60:20:20	11	12	42
3	1.0	59:12:29	7	Not isolated	24

Table 21: results of three different experiments shown in scheme 103.

These results showed that use of a sub-stoichiometric amount of boronic acid, such as 0.8 equivalents, was optimal as it gave similar yields of **112** and **100**, the former of which would be more useful as the latter was already synthesised (**2.3.2**, scheme 96). Furthermore, this would recover a useful yield of starting material **41** which could be used again in future reactions. For example, 0.8 equivalents of naphthonitrile boronic ester were used for the syntheses of **107** and **108** (**2.3.2**, scheme 100), and this gave a 36% yield of recovered starting material. Through the reactions shown in scheme 102 and table 21, over 100 mg of **112** was obtained to use in synthesis of molecular wire precursors.

To summarise, five linkers were synthesised in total (figure 64).

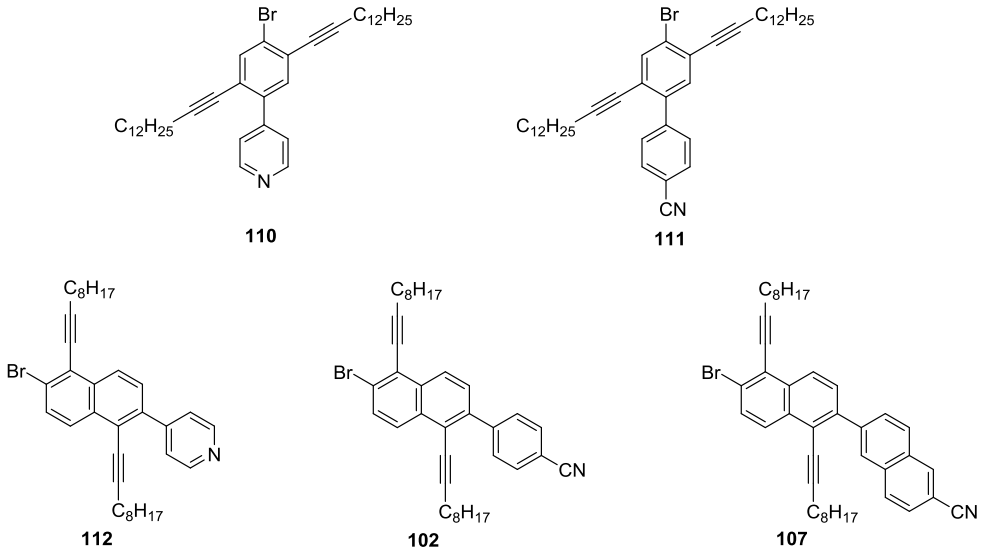
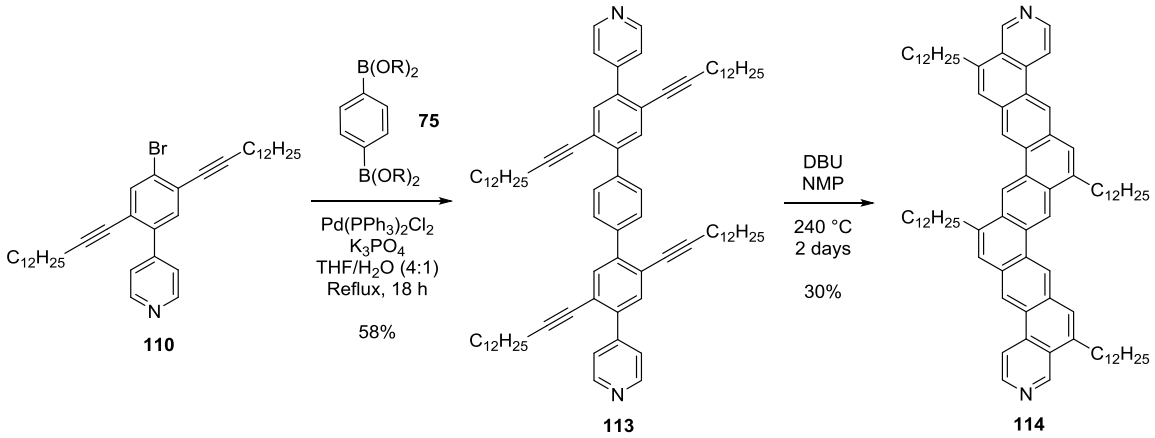


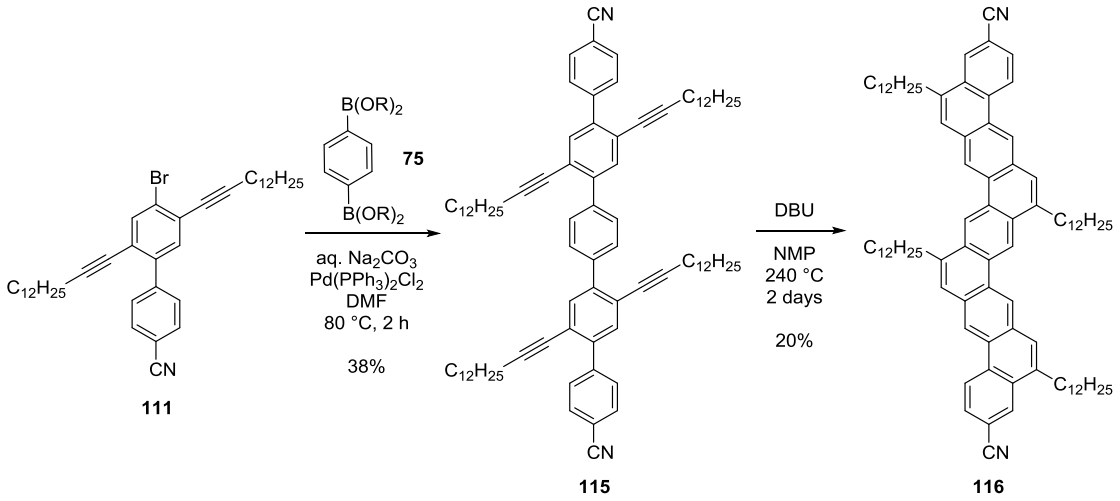
Figure 64: linker compounds for synthesis of molecular wire precursors.

Using the benzene 1,4-diboronate **75** and the two linkers **110** and **112**, two molecular wires consisting of nine fused rings were synthesised (schemes 104 and 105). NMR characterisation

of these molecular wires, **114** and **116**, both showed two sharp triplets corresponding to benzylic CH_2 protons, confirming their structures as explained in **2.2.5**.

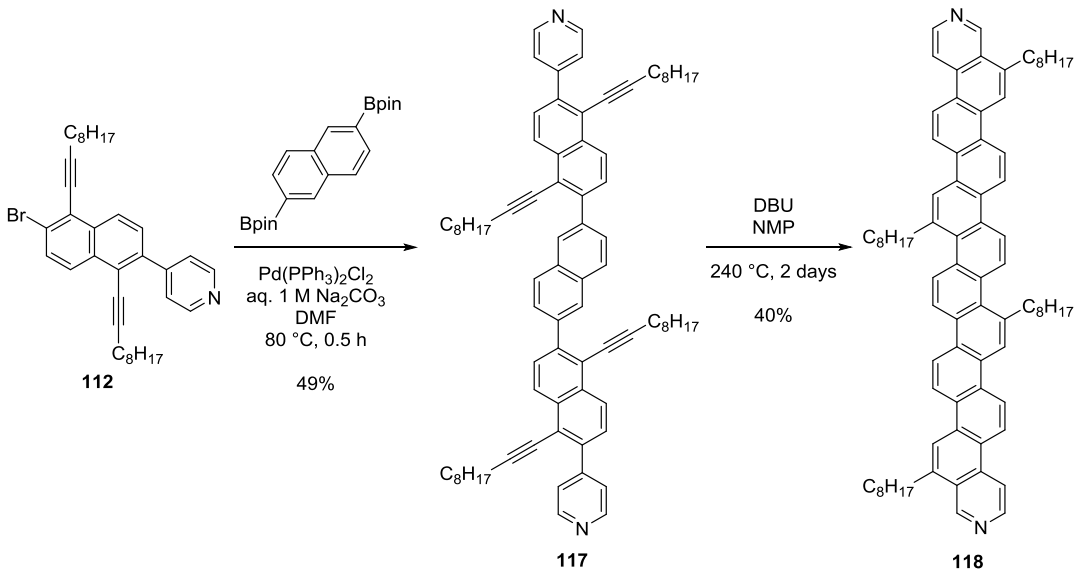


Scheme 104: synthesis of 114.

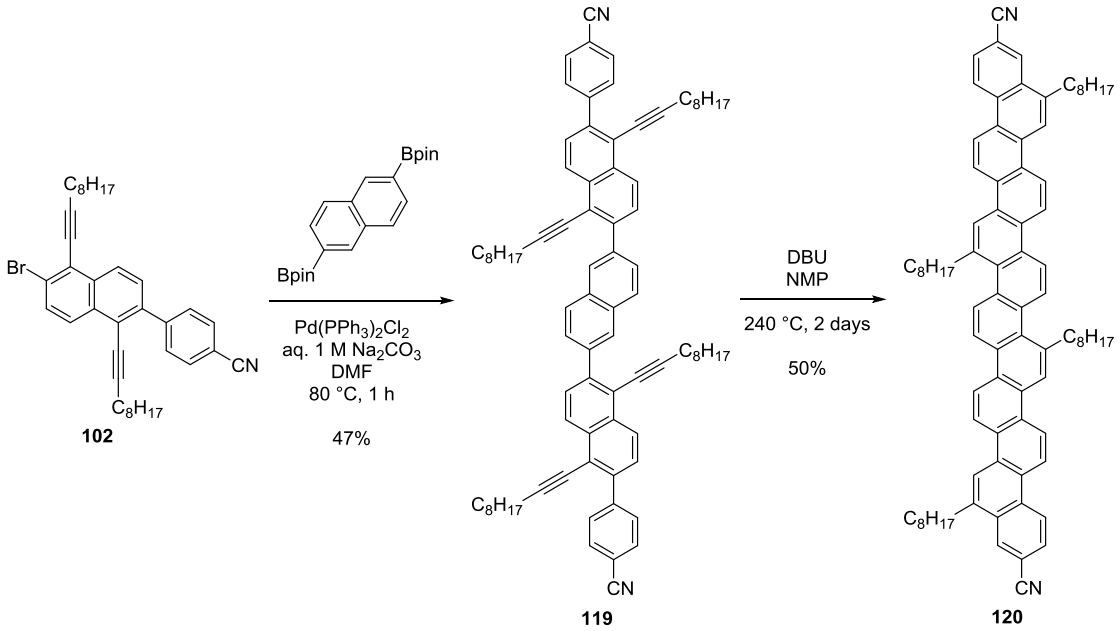


Scheme 105: synthesis of 116.

The use of naphthalene linkers **102** and **112** as well as a naphthalene core gave longer systems of extended π-conjugation, containing several chrysene moieties and no anthracene units (schemes 106 and 107).



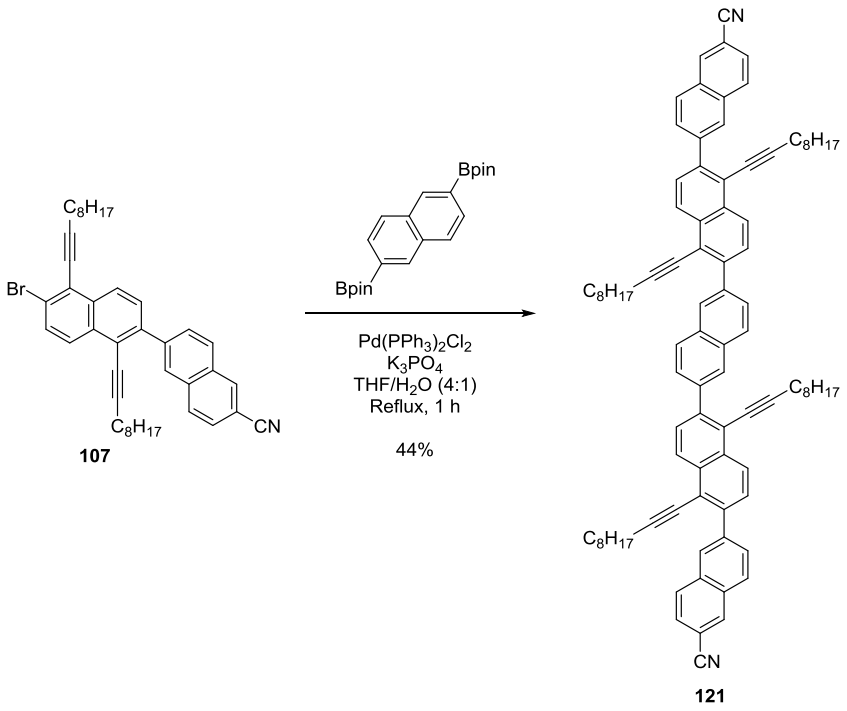
Scheme 106: synthesis of 118.



Scheme 107: synthesis of 120.

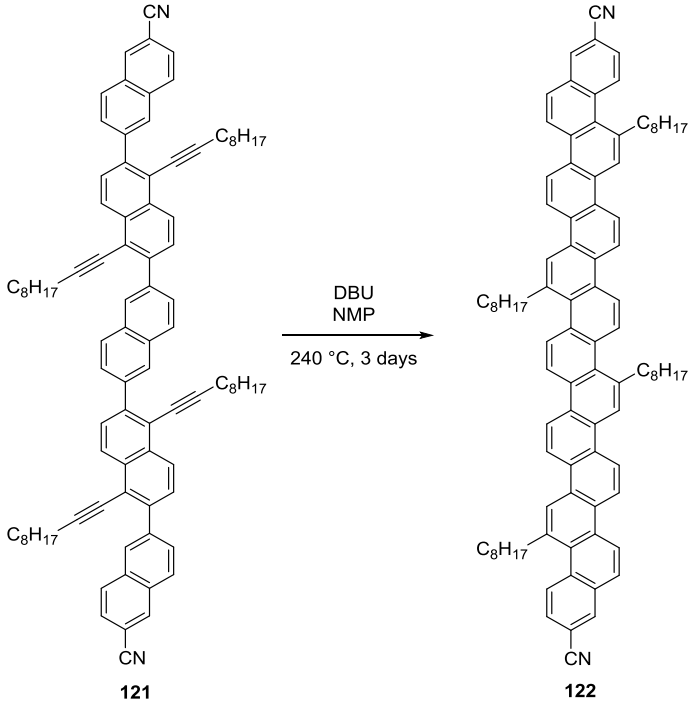
Solubility of all the extended polyaromatics shown in schemes 104-107 was very low to the point where elevated temperature was required for the obtention of NMR data. In the case of the ^{13}C-NMR of **120**, quaternary aromatic carbon atoms were barely visible in TCE-d_2, using 2 mg at 80 °C.

Despite these indications that the solubility limit was being reached with synthesis of twelve-ring systems, the fourteen-ring system created by using the naphthonitrile linker **107** was attempted. The precursor was obtained in 44% yield (scheme 108).



Scheme 108: synthesis of 121.

121 showed noticeably poor solubility of less than 1 mg/mL in toluene, and was the first non-polyaromatic compound which required elevated temperature for ^{13}C-NMR. It was therefore not surprising that the material collected from reaction of **121** in DBU and NMP at 240 °C after three days (scheme 109) was extremely insoluble and made data collection difficult.



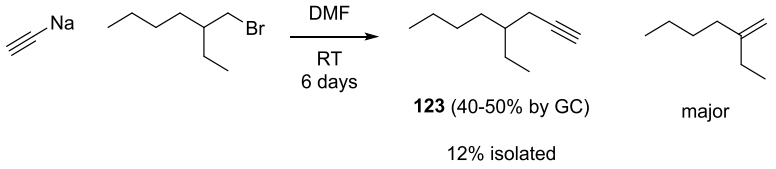
Scheme 109: attempted base-catalysed cyclisation of 121 to give 122.

No pure NMR data was collected for this material, and with only 7 mg available and considering its very low solubility, purification would have been troublesome. It appears, as expected, that the solubility limit was reached with the twelve-ring systems **118** and **120**.

2.3.4 Use of branched alkyl chains in molecular wire synthesis

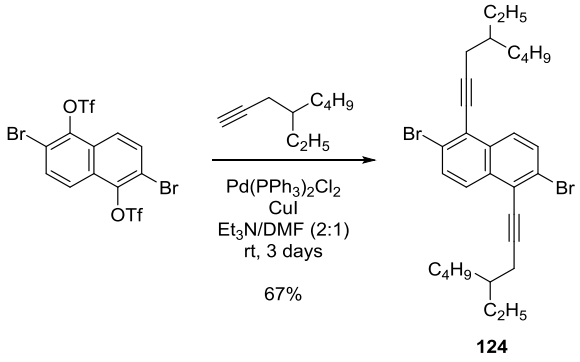
As solubility of the polyaromatic systems became lower and lower with extension, one proposed solution around this problem was the incorporation of branched alkyl chains. This eliminated the possibility of obtaining X-ray crystal structures, but in any case this was found very difficult in the cases of **114**, **116** and **118** and **120**.

The first step was to synthesise a bulk amount of 4-ethyloct-1-yne[169] **123**. Sodium acetylide, purchased from Aldrich® as an 18 weight % slurry in xylene, was reacted with 2-ethylhexyl bromide in DMF at room temperature for 6 days with GC monitoring. This was a low-yielding reaction (scheme 110) due to the formation of a significant amount of alkene *via* the competing elimination mechanism and also trouble in isolating the target alkyne by distillation.



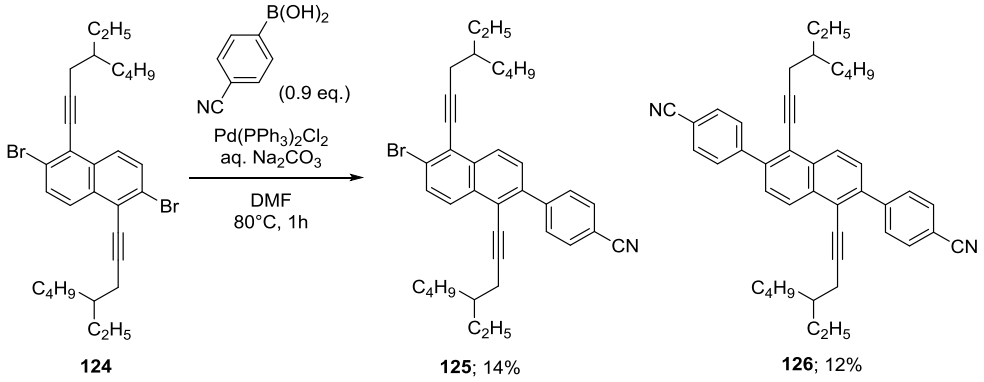
Scheme 110: synthesis of 4-ethyloct-1-yne 123.

Separation of alkyne from the alkene – as well as from xylene – was poor but just under 14 g of an alkyne/xylene mixture (37:63 calculated mass ratio by NMR) was obtained, and a 12% yield has been reported. A Sonogashira coupling gave 67% yield of **124** (scheme 111).



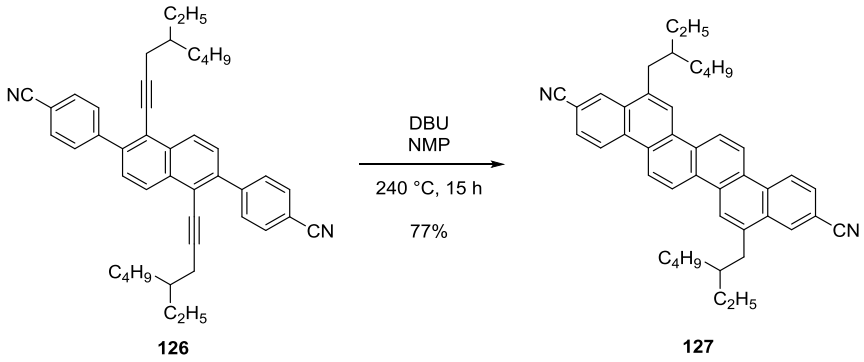
Scheme 111: Sonogashira coupling using 4-ethyloct-1-yne 121 to give 124.

A Suzuki coupling using 0.9 equivalents of 4-cyanophenylboronic acid gave similar yields of mono and bis compounds **125** and **126**, and a useful recovery (49%) of starting material (scheme 112).



Scheme 112: synthesis of a mixture of 125 and 126.

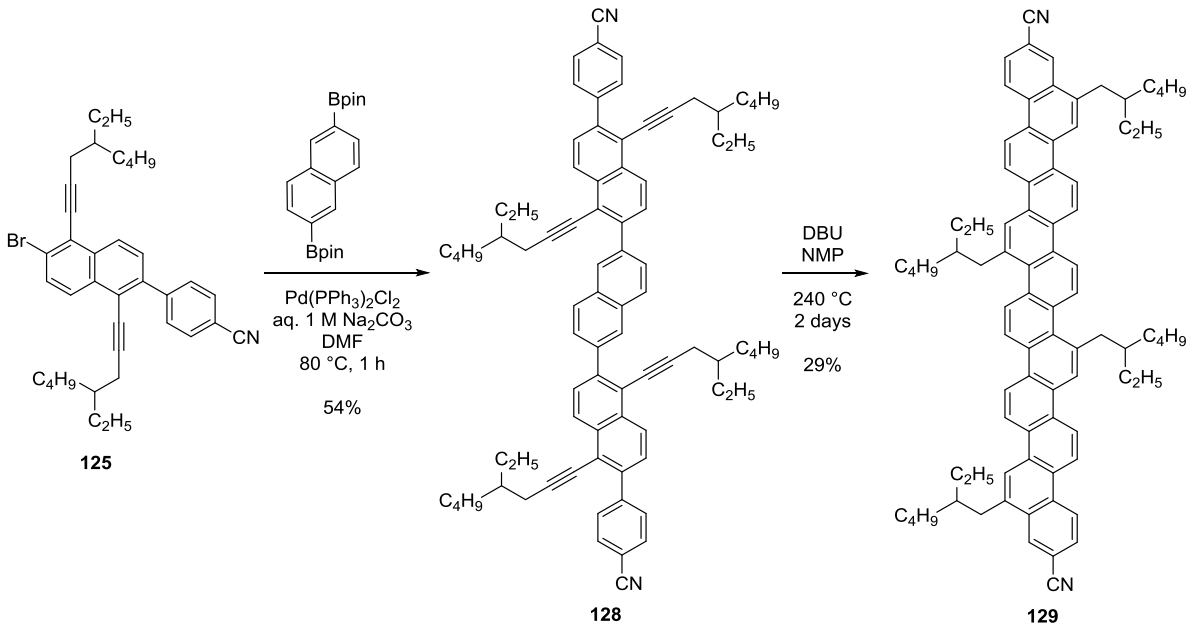
126 was reacted under the standard DBU/NMP conditions to give the branched-chain system **127** (scheme 113).



Scheme 113: synthesis of 125.

In this example, the effect of the branched alkyl chains on solubility was immediately very apparent. 2 mg of **106**, the same compound with *n*-octyl chains (**2.3.2**, scheme 98), in TCE-d_2 was used for ^{1}H-NMR while 6 mg in the same solvent at 60 °C was used for ^{13}C-NMR, and solubility in $CDCl_3$ was less than 1 mg/mL. Contrarily, NMR data for **127** was collected using a concentration of approximately 14 mg/mL in $CDCl_3$ at room temperature.

More important was the effect of these branched chains on the solubility of extended systems. The linker compound **125** was coupled with the naphthalene core and cyclised in an identical synthesis to that shown in scheme 106 except for the alkyl chains (scheme 114).



Scheme 114: synthesis of 129.

129 was obtained in 29% yield after column chromatography but did not show room temperature solubility higher than 1 mg/mL in $CDCl_3$, tol-d_8 or TCE-d_2. 6 mg of **129** was used in TCE-d_2 at 60 °C was used for ^{13}C-NMR, compared to the analogous linear-chain compound **120** (**2.3.3**, scheme 107) for which not all aromatic peaks were seen in the ^{13}C-NMR spectrum, using 2 mg at 80 °C. While not a dramatic difference in solubility, as elevated temperature NMRs were still required, in this example the use of branched alkyl chains was useful as characterisation of the polyaromatic molecular wire was easier.

Moving forward, use of branched chains may be useful for the synthesis of extended systems, particularly **122** (**2.3.3**, scheme 109) which wasn't characterised due to low solubility, but more examples are needed. In the case of the compounds with five to eight rings, this is less important as crystal structures can be obtained using linear chains, and solubility is still high enough for characterisation.

2.3.5 Photophysical characterisation

2.3.5.1 UV-vis spectroscopy

The HOMO-LUMO band gaps of all fourteen molecular wires were determined from their UV spectra (table 22). These values showed good correlation with TDDFT calculations (figure 65).[133] UV-vis spectra of all entries in table 22 are shown in experimental section **3.2.1**.

Extinction coefficients of nine- to twelve-ring systems (entries 9-12 and 14, table 22) were not calculated due to their extremely low solubility.

Entry	**Compound**	**λ_{max} / nm**	**ε / dm^3 mol^{-1} cm^{-1}**	**λ_{onset} / nm**	**Observed E_{opt} / eV**	**Calculated E_{opt} / eV**
1	**93**	417	4500	426	2.91	3.08
2	**95**	429	2900	441	2.81	2.91
3	**97**	430	3900	444	2.79	2.85
4	**99**	444	2800	461	2.69	2.68
5	**101**	397	4500	411	3.02	3.22
6	**104**	408	5500	422	2.94	3.05
7	**106**	412	4400	420	2.95	3.13
8	**109**	415	2400	429	2.89	2.99
9	**114**	450	---	461	2.69	2.81
10	**116**	455	---	469	2.64	2.71
11	**118**	419	---	428	2.90	3.03
12	**120**	421	---	432	2.88	2.93
13	**127**	408	7500	422	2.94	---
14	**129**	422	---	432	2.88	---

Table 22: photophysical properties of all molecular wires.

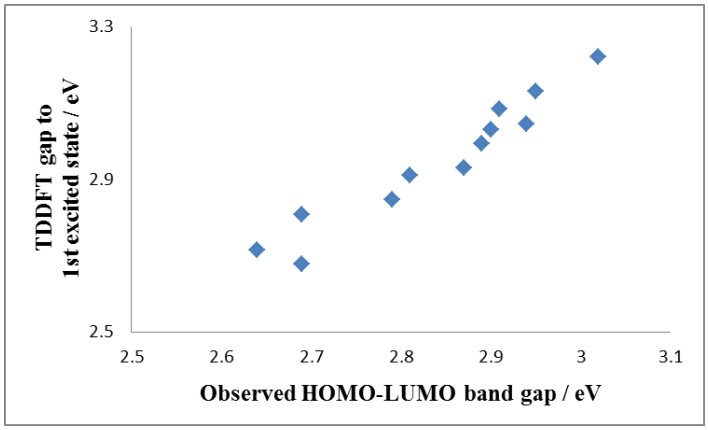


Figure 65: graph showing the correlation between observed and calculated band gap values for molecular wires.

As expected and as seen with heterocycles and PAHs, compounds containing a linear anthracene unit gave a bathochromically shifted λ_{max} compared to chrysene-based systems containing the same substituent (figure 66). This resulted in a band gap difference of 0.1-0.2 eV.

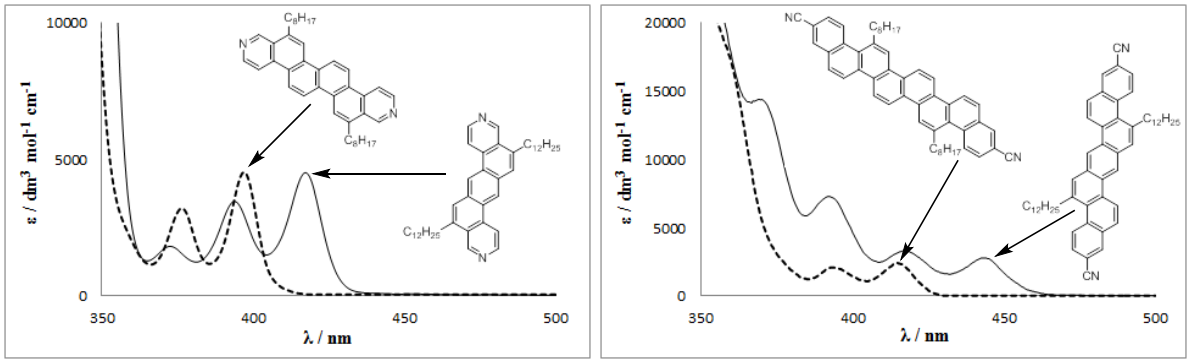


Figure 66: bathochromic shift of λ_{max} in going from chrysene-based to anthracene-based compounds.

In structurally similar molecules, a bathochromic shift of λ_{max} was observed in going from a pyridine to a nitrile anchoring group (figure 67) reducing the band gap by around 0.1 eV. This was due to the extended π-conjugation provided by the nitrile groups.

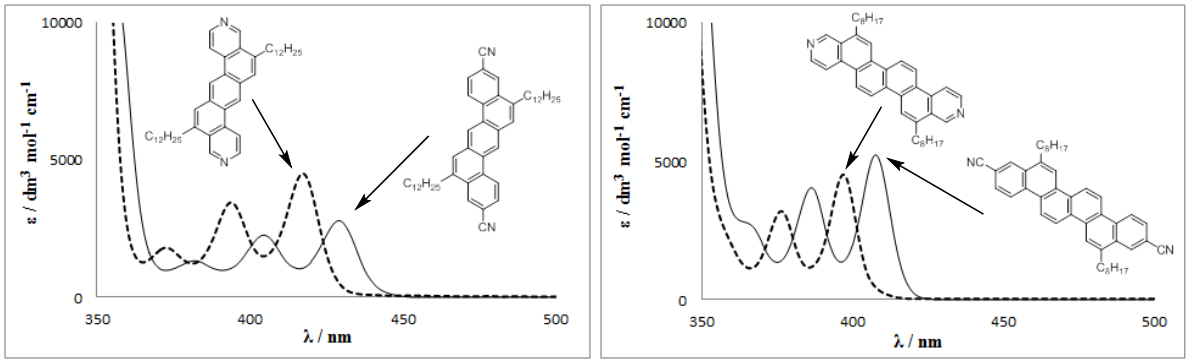


Figure 67: effect of anchoring group on λ_{max}.

Extension of compounds by using an isoquinoline or naphthonitrile substituent in place of pyridine or cyanophenyl respectively gave a bathochromic shift of λ_{max} (figure 68) and a similar band gap decrease of 0.1 eV.

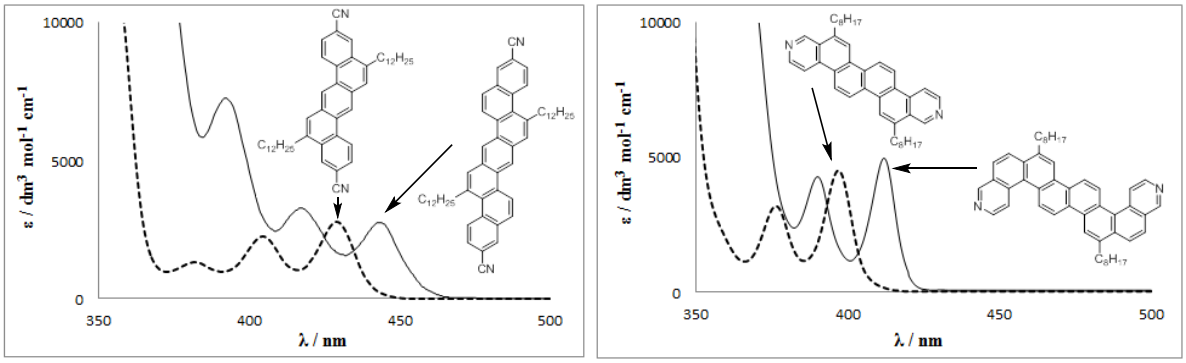


Figure 68: bathochromic shift of λ_{max} resulting from extended π-conjugation.

The results also supported the theory outlined in the conclusion **2.2.7**, that compounds synthesised using naphthalene units do not significantly lose stability as they are extended, in comparison to systems containing more linear anthracene units. This is nicely demonstrated by the band gaps determined for compounds **114**, **116**, **118** and **120** (figure 69).

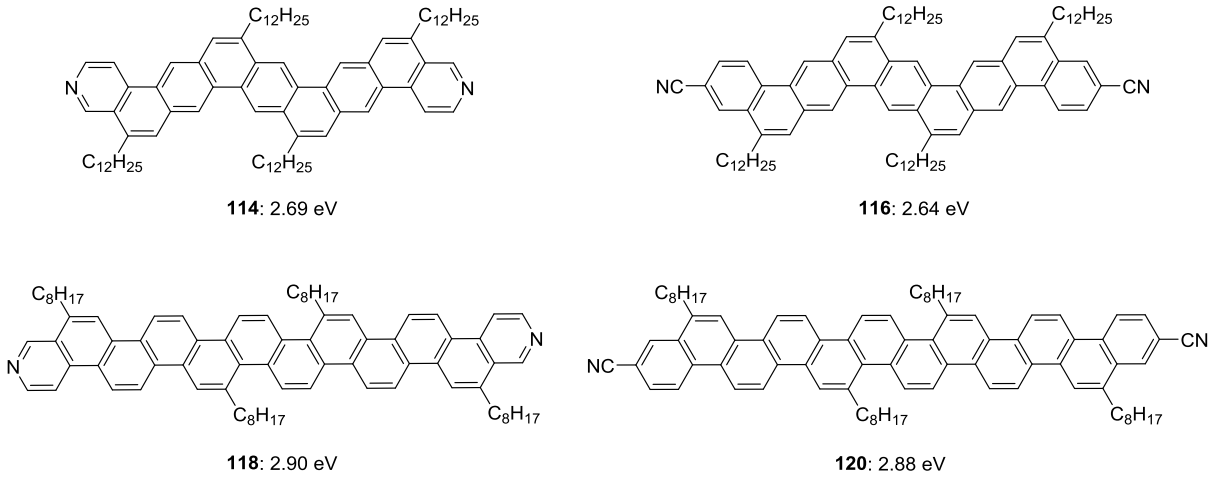


Figure 69: extended molecular wires and their band gaps.

Despite the extended π-conjugation resulting from three extra aromatic rings, **114** and **116** had significantly lower band gaps than **118** and **120**, which can be attributed to them having a larger proportion of non-aromatic Clar sextets. This is due to the presence of anthracene units in **114** and **116** not seen in **118** and **120**. Molecular wires in table 22 were divided into 'benzene-derived' and 'naphthalene-derived' and also split according to anchoring group, giving four groups. Both benzene-derived groups show a much more linear decrease in band gap as they are extended, compared to the naphthalene-derived groups (figure 70).

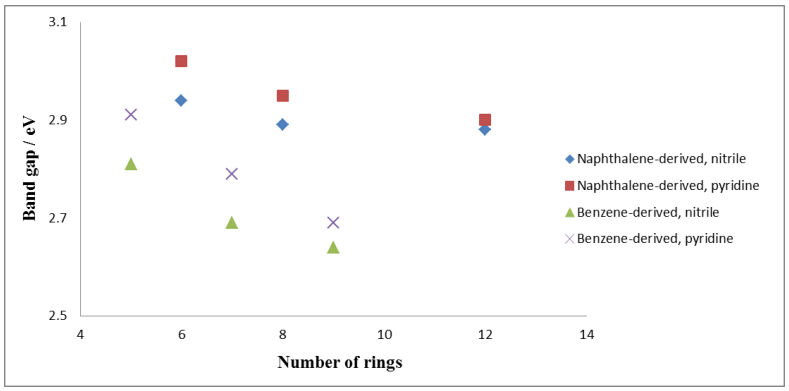


Figure 70: the difference in extension of π-conjugation in benzene- and naphthalene-derived systems.

2.3.5.2 Fluorescence spectroscopy

Fluorescence emission wavelengths, λ_F, are given in table 23 for molecular wires. Like the heterocycles and PAHs, the chrysene series (entries 4-7) gave smaller Stokes shifts than the anthracene based compounds (entries 1-3).

Entry	Compound	λ_{max} / nm	λ_F / nm
1	**93**	417	424
2	**95**	429	437
3	**97**	430	437
4	**101**	397	400
5	**104**	408	413
6	**106**	412	415
7	**127**	412	414

Table 23: complementary absorption and emission maxima from UV-vis and fluorescence spectroscopy for molecular wires.

Spectra of complementary UV-vis absorption and fluorescence emission are shown in the experimental section **3.2.1**, such as the example of **93** (figure 71).

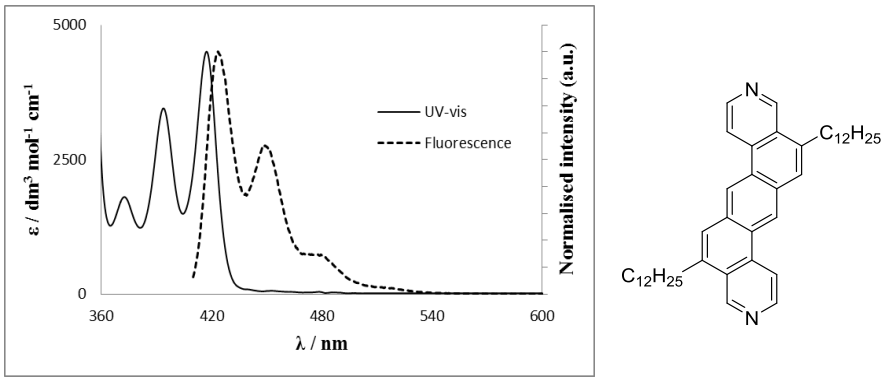


Figure 71: absorption and emission spectra of 93.

2.3.6 Conclusions

Using the benzene and naphthalene starting materials, and four different substituents, eight pyridinyl- and nitrile-terminated molecular wires were synthesised. In bringing through the precursors for these systems, several unsymmetrical molecules were also synthesised as 'linkers' for more extended molecular wires. Five of these extended systems, comprising up to twelve fused aromatic rings, were isolated. A fourteen-ring system **122** was attempted but has not been reported due to extremely low solubility.

Future work could involve a repeat synthesis of **122** using branched alkyl chains, which slightly improved the solubility of twelve-ring **120** and dramatically improved the solubility of six-ring **104**. In general, use of branched alkyl chains for the longer molecules would be favourable, as these were more amorphous and did not give single crystals in any case.

HOMO-LUMO band gaps were determined from UV-vis spectroscopy, and showed good correlation with calculated values. For structurally similar molecules, a pyridine anchoring group always gave a wider band gap than nitrile. Naphthalene-derived systems containing several chrysene moieties are good candidates for extension of π-conjugation to give longer systems, as this will not result in a significant decrease in band gap and therefore stability.

Due to the variety of possible anchoring groups, there is a lot of potential for future work in the synthesis of polyaromatic molecules as potential highly conducting molecular wires. Using the same chemistry seen in chapter **2.3**, compounds incorporating amine, carboxylic acid, nitro and thiol anchoring groups, among others, could be synthesised, particularly as the necessary boronate reagents are all commercially available. With TDDFT-calculations proving reliable, the HOMO-LUMO band gap could in theory be precisely tuned by altering both the polyaromatic architecture and the anchoring group.

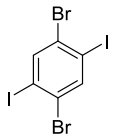
3 Experimental

3.1 Synthetic procedures and characterisation data

3.1.1 General

Reactions were carried out under an atmosphere of argon or nitrogen unless otherwise stated. For these air-sensitive reactions, solvents, liquid reagents and solutions of reagents were added *via* syringe, needle and rubber 'subaseal'. THF was distilled over sodium/benzophenone under an inert atmosphere. DCM and toluene were distilled over calcium hydride under an inert atmosphere. Other solvents (TEA, DIPA, DMF and NMP) or solutions of reagents in these solvents were degassed by simultaneously purging with argon or nitrogen and sonicating. Reactions were monitored by TLC (Merck silica gel 60 F254 plates, detecting the spots using an UV lamp), HPLC (Hewlett Packard Agilent Technologies 1100 Series HPLC system with a Hypersil ODS column (15 cm x 4.6 mm) with 254 nm detection) or GC (Hewlett Packard 6890 Series GC system with a HP-5 crosslinked methyl siloxane column (30 m x 320 μm)). Flash column chromatography was run using Merck silica gel Geduran Si60 (40-63 μm) as the stationary phase. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV300, DPX400 or DPX500 spectrometers at 298 K unless otherwise stated. Chemical shifts are recorded in parts per million (ppm) and referenced to an NMR solvent. IR spectra were recorded using Thermo Nicolet 380 FT-IR Spectrometer with a Smart Orbit Golden Gate accessory. Electron impact ionisation mass spectra (GC-EI) were recorded on a Thermo Quest TraceMS GCMS. High resolution mass spectra were recorded using a solariX (FT-ICR MS), generally using positive ion atmospheric pressure photoionisation (APPI). UV-vis spectra were recorded using an Ocean Optics USB2000+ or a JASCO V-660 spectrophotometer.

3.1.2 Synthesis of 1,4-dibromo-2,5-diiodobenzene 1



A 500 mL round-bottomed flask was charged with 1,4-dibromobenzene (20.0 g, 84.8 mmol) and iodine (53.8 g, 212.0 mmol). Concentrated sulphuric acid (250 mL) was poured into the flask and the reaction mixture was stirred at 130 °C (temperature of oil bath). Sublimed material was washed back into the flask, using a heat gun, every 0.5 h except overnight (14 h), and after 24 h, the reaction mixture was cooled to room temperature and poured into iced-water (500

mL) with stirring. This gave very little precipitate, as the large majority of product was present as a solid mass – this was triturated and dissolved in DCM (2.5 L). The solution was washed with saturated sodium bisulfite and the solvent evaporated to give a white-pink solid, which was recrystallised (toluene) to give a white solid (20.3 g). From the filtrate, two separate recrystallisations (toluene and DCM) gave a white solid (3.29 g). The solids were combined (23.6 g, 57%).

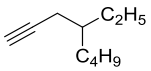
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05 (2H, s).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.32 (2CH), 129.20 (2C), 101.31 (2C).

Melting point (DCM) 165-166 °C (lit.[119] 163-165 °C).

Compound was synthesised by a variation of literature procedures.[118-120] NMR data is consistent with literature reports.[120]

3.1.3 Synthesis of 4-ethyloct-1-yne 123



A 500 mL 3-necked round-bottomed flask equipped with a stirrer bar was flushed with nitrogen for 0.5 h. Sodium acetylide, purchased from Aldrich® as a slurry in xylene (100 mL, 18 wt%, 18 g = 0.375 mol), was poured into the reaction flask. 100 mL of DMF was used to wash out the slurry from the bottle and help transfer this into the flask. 2-ethylhexyl bromide (55 mL, 59.7 g, 0.309 mol) was added over 5 minutes using a dropping funnel. After stirring for 6 days at room temperature, the reaction was stopped, diluted with water and the product extracted with pet. ether. By distilling under atmospheric pressure, 13.95 g of the target alkyne was obtained as a 37 wt% solution in xylene (by NMR); 5.16 g, 12%.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.21-2.19 (2H, m), 1.47-1.24 (10H, m), 0.94-0.88 (6H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 83.34 (C), 68.82 (CH), 38.42 (CH), 32.63 (CH_2), 28.99 (CH_2), 25.84 (CH_2), 22.92 (CH_2), 22.21 (CH_2), 14.08 (CH_3), 11.06 (CH_3).

NMR data is consistent with literature reports.[169]

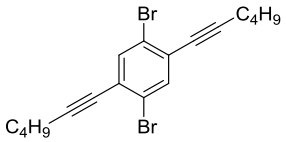
3.1.4 Sonogashira cross-coupling reactions

General

All glassware was oven-dried overnight and cooled to room temperature in a desiccator over Drierite before use. Reactions were carried out under an atmosphere of argon or nitrogen and magnetically stirred at room temperature. Copper iodide was purified by placing in the thimble of a Soxhlet apparatus, extracting with THF overnight and collecting and drying the purified

solid from the thimble. Reactions were monitored by reverse-phase HPLC and TLC, with reaction samples removed *via* syringe under argon or nitrogen.

1,4-dibromo-2,5-di(hex-1-yn-1-yl)benzene 2



A 500 mL Schlenk flask was charged with 1,4-dibromo-2,5-diiodobenzene **1** (25.0 g, 51.3 mmol), $Pd(PPh_3)_2Cl_2$ (2.2 g, 3.13 mmol) and copper iodide (1.2 g, 6.30 mmol) and evacuated/refilled with argon three times. TEA/DMF (2:1, 250 mL) was added, followed by 1-hexyne (9.5 g, 116 mmol) and the reaction was stirred at room temperature. After 22 h, the reaction mixture was diluted with saturated ammonium chloride (250 mL) and the product extracted with DCM (4 x 150 mL). The organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by recrystallisation in hot hexane (40 mL, slow cooling to room temperature and then -18 °C for 14 h) to give the target compound as a yellow solid (12.7 g, 63%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59 (2H, s), 2.47 (4H, t, *J* = 6.9 Hz), 1.66-1.47 (8H, m), 0.96 (6H, t, *J* = 7.2 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.02 (2CH), 126.48 (2C), 123.44 (2C), 98.14 (2C), 78.26 (2C), 30.44 ($2CH_2$), 21.95 ($2CH_2$), 19.30 ($2CH_2$), 13.57 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2957 (s), 2933 (s), 2868 (m), 2222 (m), 1464 (s), 1377 (m), 1065 (s), 886 (s), 729 (m).

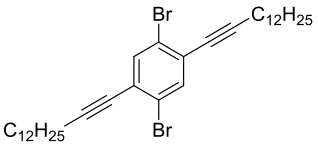
HRMS (EI) *m/z* calc. 393.99298 ($M^{+\cdot}$), found 393.99317.

UV (hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 240 (38000), 286 (40000).

Melting point 45-47 °C (lit.[135] 45-47 °C).

Data is consistent with that reported by Jason Howe.[135]

1,4-dibromo-2,5-di(tetradec-1-yn-1-yl)benzene 3



Two identical reactions were set up in which a 500 mL Schlenk flask was charged with 1,4-dibromo-2,5-diiodobenzene **1** (18.0 g, 36.9 mmol), $Pd(PPh_3)_2Cl_2$ (1.56 g, 2.22 mmol) and copper iodide (0.843 g, 4.43 mmol) and evacuated/refilled with argon three times. 1-

tetradecyne (20 mL, 15.8 g, 81.3 mmol) and TEA/DMF (2:1, 180 mL) were added and both reactions were stirred at room temperature for 14 h. Both reactions were filtered to remove precipitated material and then combined, diluted with saturated ammonium chloride (200 mL) and the product extracted with diethyl ether (4 x 100 mL). The organic layers were combined and concentrated under reduced pressure to give a dark brown oil. This was redissolved in diethyl ether (50 mL) and the solution washed with brine (2 x 300 mL), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy orange/brown solid. The product was purified by diluting the crude product with hexane (30-40 mL), filtering off undissolved solid and returning the mother liquor and repeating this process. The product was collected in six batches as a light yellow solid (40.6 g, 89%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59 (2H, s), 2.46 (4H, t, *J* = 6.9 Hz), 1.67-1.59 (4H, m), 1.52-1.45 (4H, m), 1.31-1.27 (32H, m), 0.96 (6H, t, *J* = 6.7 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.02 (2CH), 126.49 (2C), 123.47 (2C), 98.24 (2C), 78.30 (2C), 31.92 ($2CH_2$), 29.65 ($4CH_2$), 29.62 ($2CH_2$), 29.52 ($2CH_2$), 29.34 ($2CH_2$), 29.10 ($2CH_2$), 28.85 ($2CH_2$), 28.38 ($2CH_2$), 22.68 ($2CH_2$), 19.63 ($2CH_2$), 14.11 ($2CH_3$).

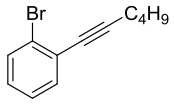
IR (neat) υ_{max}/cm^{-1} 2952 (m), 2916 (s), 2847 (s), 2224 (w), 1462 (s), 1086 (m), 889 (m), 724 (m).

HRMS (APPI) *m/z* calc. for $C_{34}H_{53}Br_2$ $(M+H)^+$ 619.25085, found 619.25152.

UV (hexane) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 240 (76000), 286 (87000).

Melting point 56-57 °C.

1-bromo-2-(hex-1-yn-1-yl)benzene 25



A 250 mL Schlenk flask was charged with $Pd(PPh_3)_2Cl_2$ (0.728 g, 1.04 mmol) and copper iodide (0.396 g, 2.08 mmol) and evacuated/refilled with argon three times. A solution of 1-bromo-2-iodobenzene (9.78 g, 34.6 mmol) and 1-hexyne (3.34 g, 40.7 mmol) in TEA/DMF (2:1, 100 mL) was added and the reaction mixture was stirred at room temperature. Extra portions of 1-hexyne were added after 50 min (2.4 mL, 20.9 mmol) and 1 h 50 min (0.3 mL, 2.61 mmol) and the reaction continued for 0.5 h after the last addition. The reaction mixture was diluted with saturated ammonium chloride (150 mL) and the product extracted with diethyl ether (4 x 100 mL). The organic layers were combined washed (brine), dried ($MgSO_4$) and

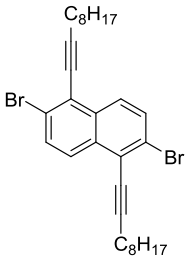
concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane) to give a brown oil (7.95 g, 97%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.56 (1H, dd, *J* = 8.1, 1.1 Hz), 7.43 (1H, dd, *J* = 7.7, 1.8 Hz), 7.23 (1H, td, *J* = 7.6, 1.1 Hz), 7.11 (1H, td, *J* = 7.7, 1.7 Hz), 2.40 (2H, t, *J* = 7.0 Hz), 1.68-1.61 (2H, m), 1.57-1.49 (2H, m), 0.97 (3H, t, *J* = 7.2 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 133.27 (CH), 132.24 (CH), 128.59 (CH), 126.84 (CH), 126.10 (C), 125.41 (C), 95.58 (C), 79.31 (C), 30.61 (CH_2), 21.95 (CH_2), 19.25 (CH_2), 13.60 (CH_3).

NMR data is consistent with literature reports.[170]

2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene 41



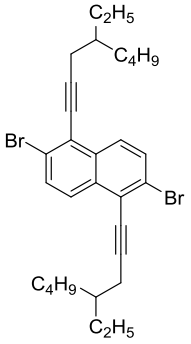
A 100 mL Schlenk flask was charged with 2,6-dibromonaphthalene-1,5-diylbis(trifluoromethanesulfonate) (4.74 g, 8.14 mmol), $Pd(PPh_3)_2Cl_2$ (0.338 g, 0.482 mmol) and copper iodide (0.181 g, 0.950 mmol) and flushed with argon for 1.5 h. A degassed mixture of DIPA/DMF (1:1, 50 mL) was added, followed by 1-decyne (3.2 mL, 2.45 g, 17.7 mmol). The reaction mixture was stirred at room temperature for 18 h, diluted with saturated ammonium chloride (100 mL) and the product extracted with diethyl ether (5 x 50 mL). The organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a dark brown oil. Pure product was obtained by diluting the crude product with hexane (25 mL) to leave a yellow solid which was then filtered off, washed with methanol and dried to give 1.78 g. After concentrating the mother liquor under reduced pressure, this process was repeated to give a further 1.26 g of material. Final yield: 3.04 g, 67%.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.11 (2H, d, *J* = 8.9 Hz), 7.68 (2H, d, *J* = 8.9 Hz), 2.63 (4H, t, *J* = 7.0 Hz), 1.77-1.73 (4H, m), 1.60-1.54 (4H, m), 1.40-1.28 (16H, m), 0.89 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 133.12 (2C), 130.97 (2CH), 127.08 (2CH), 124.95 (2C), 123.58 (2C), 101.91 (2C), 77.51 (2C), 31.83 ($2CH_2$), 29.21 ($2CH_2$), 29.10 ($2CH_2$), 28.97 ($2CH_2$), 28.62 ($2CH_2$), 22.64 ($2CH_2$), 19.90 ($2CH_2$), 14.08 ($2CH_3$).

NMR data is consistent with literature reports.[89]

2,6-dibromo-1,5-bis(4-ethyloct-1-yn-1-yl)naphthalene 124



A 250 mL Schlenk flask was charged with 2,6-dibromonaphthalene-1,5-diylbis(trifluoromethanesulfonate) (4.00 g, 6.87 mmol), $Pd(PPh_3)_2Cl_2$ (0.246 g, 0.350 mmol) and copper iodide (0.151 g, 0.793 mmol) and evacuated/refilled with argon three times. TEA (20 mL) and DMF (10 mL) were added, followed by a 37% solution of 4-ethyloct-1-yne **123** in xylene (5.26 g, 1.95 g alkyne, 14.1 mmol). The reaction mixture was stirred at room temperature for 42 h before addition of an extra portion of the 37% alkyne solution (2.75 g, 1.02 g alkyne, 7.36 mmol). The reaction was continued for 26 h, diluted with saturated ammonium chloride (150 mL) and the product extracted with diethyl ether (6 x 40 mL). The organic layers were washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, pet. ether) to give a light yellow oil, containing the target compound as a mixture with xylene and 5,12-diethylhexadeca-7,9-diyne (3.05 g, 84% product by mass, 67%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.11 (2H, d, *J* = 8.9 Hz), 7.68 (2H, d, *J* = 9.0 Hz), 2.63 (4H, d, *J* = 5.6 Hz), 1.70-1.62 (2H, m), 1.60-1.21 (16H, m), 1.00-0.86 (12H, m).

^{13}C-NMR (400 MHz, $CDCl_3$) δ 133.22 (2C), 131.00 (2CH), 127.05 (2CH), 125.01 (2C), 123.71 (2C), 100.60 (2C), 78.14 (2C), 38.91 (2CH), 32.99 ($2CH_2$), 29.13 ($2CH_2$), 26.28 ($2CH_2$), 23.08 ($2CH_2$), 23.01 ($2CH_2$), 14.14 ($2CH_3$), 11.25 ($2CH_3$).

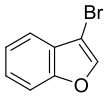
IR (neat) υ_{max}/cm^{-1} 2957 (s), 2924 (s), 2871 (m), 2857 (m), 2224 (w), 1560 (m), 1458 (m), 859 (s), 810 (s).

HRMS (APPI) calc. for $C_{30}H_{38}Br_2$ ($M^{+\cdot}$) 556.1335, found 556.1322.

UV (DCM) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 258 (70000).

3.1.5 Synthesis of boronate reagents

3-bromobenzofuran 4



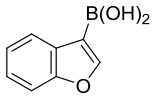
A 50 mL Schlenk flask equipped with a stirrer bar was charged with 2,3-benzofuran (0.860 g, 7.28 mmol) and flushed with argon for 0.5 h. DCM (6 mL) was added followed by a solution of bromine (1.27 g, 7.95 mmol) in DCM (6 mL), dropwise. After 40 min at room temperature, DBU (2.18 mL, 2.22 g, 14.6 mmol) was added dropwise and the reaction was continued for 1.5 h before quenching with 5% sodium thiosulphate solution (20 mL). The layers were separated and the aqueous layer was back-extracted with DCM (2 x 20 mL). All organic layers were combined, washed (2 M HCl, then brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, hexane) to give a colourless oil (0.699 g, 49%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.67 (1H, s), 7.58-7.50 (2H, m), 7.40-7.32 (2H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.39 (C), 142.60 (CH), 127.09 (C), 125.41 (CH), 123.41 (CH), 119.77 (CH), 111.71 (CH), 97.90 (C).

NMR data is consistent with literature reports.[171]

Benzofuran-3-ylboronic acid 5



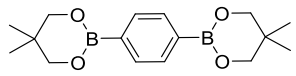
A 10 mL Schlenk flask equipped with a stirrer bar was charged with 3-bromobenzofuran **4** (0.180 g, 0.914 mmol), evacuated/refilled with argon three times and THF (2.2 mL) added. The solution was cooled using a dry ice/acetone bath to -60 °C and *n*-BuLi (2.5 M in hexanes, 0.40 mL, 1.00 mmol) added slowly. After 0.5 h, triisopropyl borate (0.63 mL, 0.513 g, 2.73 mmol) was added slowly and the reaction was continued at -60 °C for a further 0.5 h before quenching by addition of 2 M HCl (4 mL) and stirring at room temperature for 0.5 h. The product was extracted with diethyl ether (3 x 5 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy, pink solid (0.168 g, 83%). The product was used without further purification.

^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.16 (2H, s) 8.15 (1H, s), 7.91 (1H, d, J = 7.2 Hz), 7.55 (1H, d, J = 7.8 Hz), 7.29-7.21 (2H, m).

^{13}C-NMR (75 MHz, DMSO-d_6) δ 155.01 (C), 153.29 (CH), 130.31 (C), 123.86 (CH), 122.99 (CH), 122.62 (CH), 110.83 (CH).

Compound is commercially available.

1,4-bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzene 75



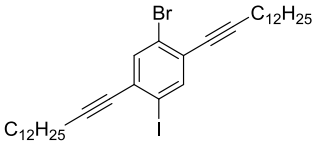
In a 250 mL round-bottomed flask under argon, a mixture of benzene-1,4-diboronic acid (1.75 g, 10.6 mmol) and neopentyl glycol (4.40 g, 42.2 mmol) in THF (50 mL) was stirred at room temperature for 16 h. The reaction mixture was diluted with water (50 mL) and stirred for 5 min, giving a white precipitate. This was filtered, washed with methanol and dried, giving 3.04 g (95%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.80 (4H, s), 3.78 (8H, s), 1.03 (12H, s).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 132.91 (4CH), 72.30 ($4CH_2$), 31.86 (2C), 21.91 ($4CH_3$).

NMR data is consistent with literature reports.[138]

3.1.6 Synthesis of 1-bromo-4-iodo-2,5-di(tetradec-1-yn-1-yl)benzene 34



An oven-dried 100 mL Schlenk flask equipped with a stirrer bar was charged with 1,4-dibromo-2,4-di(tetradec-1-yn-1-yl)benzene **3** (1.67 g, 2.69 mmol), evacuated/refilled with nitrogen three times and to it added distilled THF (50 mL). *N*-BuLi (2.5 M in hexanes, 1.11 mL, 2.78 mmol) was added slowly at -65 °C and after 0.25 h, a solution of iodine (1.33 g, 5.24 mmol) in distilled THF (10 mL) was added. The reaction mixture was warmed to room temperature, stirred for 0.25 h and quenched with saturated sodium thiosulphate. The product was extracted with diethyl ether (3 x 25 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a light brown solid (1.73 g, 96%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.84 (1H, s), 7.55 (1H, s), 2.49-2.43 (4H, m), 1.67-1.45 (8H, m), 1.31-1.27 (32H, m), 0.91-0.87 (6H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.19 (CH), 135.11 (CH), 130.93 (C), 126.57 (C), 124.66 (C), 98.17 (2C), 97.46 (C), 81.78 (C), 78.04 (C), 31.92 ($2CH_2$), 29.65 ($2CH_2$), 29.53 ($2CH_2$), 29.36 ($2CH_2$), 29.11 ($2CH_2$), 28.92 ($2CH_2$), 28.85 ($2CH_2$), 28.40 ($2CH_2$), 28.36 ($2CH_2$), 22.69 ($2CH_2$), 19.62 ($2CH_2$), 14.11 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2950 (m), 2916 (s), 2847 (s), 2224 (w), 1462 (s), 1063 (s), 889 (m), 722 (m).

UV (hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 246 (42000), 288 (38000).

HRMS (APPI) *m/z* calc. for $C_{34}H_{53}BrI$ ($M^{+\cdot}$) 666.22916, found 666.22918.

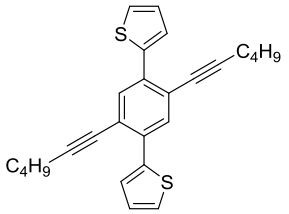
Melting point 45-46 °C.

3.1.7 Suzuki cross-coupling reactions

General

Reactions were carried out under an atmosphere of argon or nitrogen and magnetically stirred. Temperatures given refer to those of the oil baths used to heat the reaction mixtures. All boronic acids used were commercially purchased except for benzofuran-3-ylboronic acid **5** used in the synthesis of **10**.

2,2'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)dithiophene 6



A 100 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(hex-1-yn-1-yl)benzene **2** (0.600 g, 1.51 mmol), thiophen-2-ylboronic acid (0.775 g, 6.06 mmol) and $Pd(PPh_3)_2Cl_2$ (0.106 g, 0.151 mmol) and flushed with argon for 0.5 h. DMF (48 mL) and aq. Na_2CO_3 (1 M, 9.1 mL, 9.1 mmol) were added and the reaction mixture was stirred at 120 °C for 0.5 h, cooled to room temperature and diluted with water (200 mL). The product was extracted with diethyl ether (4 x 50 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, 0.5% EtOAc in hexane) to give a yellow solid (0.572 g, 94%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.69 (2H, s), 7.63 (2H, dd, *J* = 3.7, 1.1 Hz), 7.36 (2H, d, *J* = 5.1, 1.1 Hz), 7.10 (2H, dd, *J* = 5.1, 3.7 Hz), 2.47 (4H, t, *J* = 7.1 Hz), 1.65-1.59 (4H, m), 1.51-1.42 (4H, m), 0.95 (6H, t, *J* = 7.3 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 141.19 (2C), 134.08 (2C), 133.83 (2CH), 127.05 (2CH), 126.68 (2CH), 125.77 (2CH), 120.73 (2C), 96.81 (2C), 79.97 (2C), 30.35 ($2CH_2$), 22.07 ($2CH_2$), 19.54 ($2CH_2$), 13.62 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3101 (w), 2955 (m), 2928 (m), 2859 (m), 2222 (w), 1480 (m), 1460 (m), 1434 (m), 899 (s), 827 (s), 705 (s).

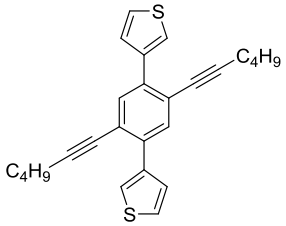
LRMS (GC/EI) *m/z* 402, 100% (M^+); 359, 36% (M^+-Pr); 317, 20% (M^+-Pr-C_3H_6); 303, 27% (M^+-Pr-C_4H_8).

HRMS (GC/EI) *m/z* calc. for $C_{26}H_{26}S_2$ ($M^{+\cdot}$) 402.14759, found 402.14863.

UV ($CHCl_3$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 282 (55000).

Melting point 77-79 °C.

3,3'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)dithiophene 7



A 250 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(hex-1-yn-1-yl)benzene **2** (1.00 g, 2.52 mmol), thiophen-3-ylboronic acid (1.29 g, 10.1 mmol) and $Pd(PPh_3)_2Cl_2$ (0.177 g, 0.252 mmol) and flushed with argon for 1 h. DMF (80 mL) and aq. Na_2CO_3 (1 M, 15 mL, 15 mmol) were added and the reaction mixture was stirred at 120 °C for 1.5 h, cooled to room temperature and diluted with water (400 mL). The product was extracted with diethyl ether (4 x 70 mL). The organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, 0.5% EtOAc in hexane) to give a yellow solid (0.823 g, 81%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.70 (2H, dd, *J* = 3.0, 1.0 Hz), 7.59 (2H, s), 7.49 (2H, dd, *J* = 5.1, 1.0 Hz), 7.35 (2H, dd, *J* = 5.1, 3.0 Hz), 2.41 (4H, t, *J* = 7.1 Hz), 1.60-1.53 (4H, m), 1.47-1.38 (4H, m), 0.93 (6H, t, *J* = 7.3 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 140.06 (2C), 136.07 (2C), 133.73 (2CH), 128.38 (2CH), 124.54 (2CH), 123.43 (2CH), 121.29 (2C), 95.20 (2C), 80.19 (2C), 30.50 ($2CH_2$), 22.00 ($2CH_2$), 19.36 ($2CH_2$), 13.60 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3101 (w), 2954 (m), 2928 (m), 2867 (m), 2222 (w), 1492 (m), 1466 (m), 1422 (m), 1365 (m), 1088 (m), 860 (m), 785 (s), 724 (m), 690 (s).

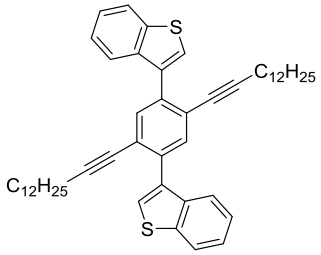
LRMS (GC/EI) *m/z* 402, 64% (M^+); 359, 100% (M^+-Pr); 317, 51% (M^+-Pr-C_3H_6); 303, 72% (M^+-Pr-C_4H_8).

HRMS (GC/EI) *m/z* calc. for $C_{26}H_{26}S_2$ ($M^{+\cdot}$) 402.14759, found 402.14874.

UV (hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 266 (47000).

Melting point 81-83 °C.

3,3'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)bis(benzo[*b*]thiophene) 8



A 100 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(tetradec-1-yn-1-yl)benzene **3** (0.500 g, 0.806 mmol), benzo[*b*]thiophen-3-ylboronic acid (0.574 g, 3.22 mmol) and $Pd(PPh_3)_2Cl_2$ (0.057 g, 0.081 mmol) and flushed with argon for 0.5 h. DMF (40 mL) and aq. Na_2CO_3 (1 M, 4.8 mL, 4.8 mmol) were added and the reaction mixture was stirred at 120 °C for 1.25 h, cooled to room temperature and diluted with water (300 mL). The product was extracted with diethyl ether (5 x 100 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown waxy solid. The crude product was purified by column chromatography (SiO_2, 1% EtOAc in hexane) to give a yellow solid (0.420 g, 72%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94-7.91 (2H, m), 7.82-7.79 (2H, m), 7.65 (2H, s), 7.59 (2H, s), 7.41-7.38 (4H, m), 2.15 (4H, t, *J* = 6.8 Hz), 1.27-1.10 (40H, m), 0.90 (6H, t, *J* = 6.8 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.34 (2C), 138.38 (2C), 136.91 (2C), 135.54 (2C), 134.16 (2CH), 125.29 (2CH), 124.20 (2CH), 123.95 (2CH), 123.66 (2CH), 123.08 (2C), 122.58 (2CH), 95.87 (2C), 79.64 (2C), 31.93 ($2CH_2$), 29.66 ($6CH_2$), 29.45 ($2CH_2$), 29.37 ($2CH_2$), 29.13 ($2CH_2$), 28.60 ($2CH_2$), 28.18 ($2CH_2$), 22.71 ($2CH_2$), 19.45 ($2CH_2$), 14.13 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3101 (w), 2915 (s), 2850 (s), 2229 (w), 1469 (m), 1453 (m), 1426 (m), 1370 (m), 1061 (m), 836 (m), 791 (m), 757 (s), 731 (s).

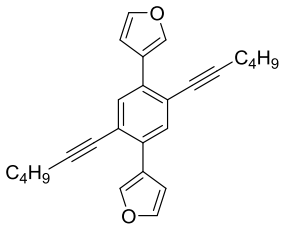
LRMS (APCI) *m/z* 727.3 $(M+H)^+$.

HRMS (APPI) *m/z* calc. for $C_{50}H_{62}S_2$ ($M^{+\cdot}$) 726.42874, found 726.42981.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 233 (50000), 274 (42000).

Melting point 77-78 °C.

3,3'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)difuran 9



A 100 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(hex-1-yn-1-yl)benzene **2** (0.300 g, 0.757 mmol), furan-3-ylboronic acid (0.339 g, 3.03 mmol) and $Pd(PPh_3)_2Cl_2$ (0.053 g, 0.076 mmol) and flushed with argon for 1 h. DMF and aq. Na_2CO_3 (1 M, 4.5 mL, 4.5 mmol) were added and the reaction mixture was stirred at 120 °C for 1.5 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with diethyl ether (4 x 20 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give an orange oil. The crude product was purified by column chromatography (SiO_2, 0.5% EtOAc in hexane) to give a yellow solid (0.193 g, 69%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.09 (2H, s), 7.54 (2H, s), 7.48 (2H, dd, *J* = 1.0, 1.0 Hz), 6.84 (2H, d, *J* = 1.0 Hz), 2.47 (4H, t, *J* = 7.1 Hz), 1.66-1.59 (4H, m), 1.53-1.44 (4H, m), 0.96 (6H, t, *J* = 7.2 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.44 (2CH), 140.99 (2CH), 132.82 (2CH), 131.90 (2C), 124.02 (2C), 120.86 (2C), 110.23 (2CH), 95.77 (2C), 80.43 (2C), 30.56 ($2CH_2$), 22.10 ($2CH_2$), 19.44 ($2CH_2$), 13.59 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2951 (m), 2930 (m), 2867 (m), 2225 (w), 1586 (m), 1454 (m), 1378 (w), 1058 (s), 1017 (s), 871 (s), 787 (s), 726 (s).

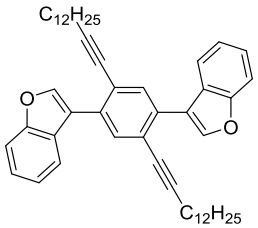
LRMS (GC/EI) *m/z* 370, 53% (M^+); 327, 61% (M^+-Pr); 271, 79% (M^+-Bu-C_3H_6); 239, 64%; 226, 100%.

HRMS (EI) *m/z* calc. for $C_{26}H_{26}O_2$ ($M^{+\cdot}$) 370.19328, found 370.19328.

UV ($CHCl_3$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 269 (60000).

Melting point 67-68 °C.

3,3'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)bis(benzofuran) 10



A 100 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(tetradec-1-yn-1-yl) benzene **3** (0.400 g, 0.645 mmol) and $Pd(PPh_3)_2Cl_2$ (0.045 g, 0.064 mmol) and evacuated/refilled with argon three times. Solutions of benzofuran-3-ylboronic acid (0.360 g, 2.22 mmol) in DMF (25 mL) and aq. Na_2CO_3 (1 M, 3.9 mL, 3.9 mmol) were added and the reaction mixture was stirred at 120 °C for 0.5 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with diethyl ether (5 x 60 mL) and the organic layers were combined, washed

(brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, 0.1% EtOAc in hexane) and recrystallization (hexane) to give a yellow solid (0.186 g, 42%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05 (2H, s), 7.80-7.78 (2H, m), 7.77 (2H, s), 7.57 (2H, d, *J* = 7.6 Hz), 7.38-7.29 (4H, m), 2.30 (4H, t, *J* = 7.0 Hz), 1.46-1.38 (4H, m), 1.33-1.22 (36H, m), 0.91-0.87 (6H, m).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 155.17 (2C), 143.61 (2CH), 133.80 (2CH), 132.34 (2C), 126.88 (2C), 124.34 (2CH), 122.69 (2CH), 122.46 (2C), 121.05 (2CH), 119.62 (2C), 111.55 (2CH), 95.98 (2C), 79.86 (2C), 31.92 ($2CH_2$), 29.62 ($6CH_2$), 29.47 ($2CH_2$), 29.35 ($2CH_2$), 29.10 ($2CH_2$), 28.83 ($2CH_2$), 28.28 ($2CH_2$), 22.69 ($2CH_2$), 19.61 ($2CH_2$), 14.10 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3056 (w), 2922 (s), 2850 (s), 2226 (w), 1466 (m), 1446 (s), 1380 (w), 1011 (m), 911 (m), 807 (m), 744 (s), 723 (s).

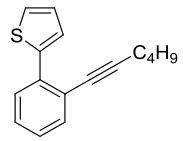
LRMS (APPI) *m/z* 695.2 $(M+H)^+$.

HRMS (APPI) *m/z* calc. for for $C_{50}H_{63}O_2$ $(M+H)^+$ 695.48226, found 695.48071.

UV (hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 270 (42000).

Melting point 88-89 °C.

2-(2-(hex-1-yn-1-yl)phenyl)thiophene 26



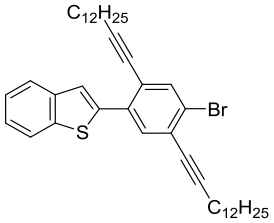
A 250 mL Schlenk flask was charged with 1-bromo-2-(hex-1-yn-1-yl)benzene **25** (1.44 g, 6.07 mmol), thiophen-2-ylboronic acid (1.54 g, 12.0 mmol) and $Pd(PPh_3)_2Cl_2$ (0.214 g, 0.305 mmol) and flushed with argon for 1 h. DMF (80 mL) and aq. Na_2CO_3 (1 M, 18 mL, 18 mmol) were added and the reaction mixture was stirred at 80 °C for 0.5 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with diethyl ether (4 x 60 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, 0.5% EtOAc in hexane) to give the compound as an orange oil (0.842 g, 58%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, dd, *J* = 3.5, 1.1), 7.56 (1H, dd, *J* = 7.8, 1.3), 7.53 (1H, dd, *J* = 7.6, 1.5), 7.36 (1H, dd, *J* = 5.3, 1.0), 7.30 (1H, td, *J* = 7.6, 1.5), 7.23 (1H, td, *J* = 7.6, 1.5), 7.12 (1H, dd, *J* = 5.1, 3.5), 2.46 (2H, t, *J* = 7.1 Hz), 1.65-1.58 (2H, m), 1.52-1.43 (2H, m), 0.96 (3H, t, *J* = 7.3 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.38 (C), 135.64 (C), 133.76 (CH), 128.79 (CH), 127.74 (CH), 126.96 (CH), 126.90 (CH), 126.45 (CH), 125.43 (CH), 121.46 (C), 95.32 (C), 80.30 (C), 30.40 (CH_2), 22.02 (CH_2), 19.42 (CH_2), 13.60 (CH_3).

NMR data is consistent with literature reports.[128]

2-(4-bromo-2,5-di(tetradec-1-yn-1-yl)phenyl)benzo[*b*]thiophene 31



A 50 mL Schlenk flask was charged with 1-bromo-4-iodo-2,5-di(tetradec-1-yn-1-yl)benzene **34** (0.250 g, 0.375 mmol), benzo[*b*]thiophen-2-ylboronic acid (0.067 g, 0.376 mmol) and $Pd(PPh_3)_2Cl_2$ (0.007 g, 0.010 mmol) and flushed with argon for 0.5 h. DMF (25 mL) and aq. Na_2CO_3 (1 M, 0.60 mL, 0.60 mmol) were added and the reaction mixture was stirred at 50 °C for 2 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with diethyl ether (4 x 40 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a red oil. The crude product was purified by column chromatography (SiO_2, 0.5% EtOAc in hexane) to give a yellow solid (0.163 g, 65%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86-7.76 (2H, m), 7.83 (1H, s), 7.73 (1H, s), 7.65 (1H, s), 7.37-7.33 (2H, m), 2.49 (2H, t, *J* = 7.0 Hz), 2.44 (2H, t, *J* = 7.0 Hz), 1.71-1.45 (8H, m), 1.34-1.24 (32H, m), 0.93-0.87 (6H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.71 (C), 140.00 (2C), 137.00 (CH), 134.56 (C), 133.56 (CH), 125.60 (C), 124.55 (CH), 124.36 (CH), 124.08 (C), 123.72 (2CH), 122.36 (C), 122.01 (CH), 98.11 (C), 97.37 (C), 79.01 (C), 77.21 (C), 31.92 ($2CH_2$), 29.64 ($6CH_2$), 29.54 (CH_2), 29.48 (CH_2), 29.36 ($2CH_2$), 29.18 (CH_2), 29.13 (CH_2), 28.99 (CH_2), 28.89 (CH_2), 28.49 (CH_2), 28.21 (CH_2), 22.69 ($2CH_2$), 19.84 (CH_2), 19.68 (CH_2), 14.10 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2955 (m), 2916 (s), 2848 (s), 2229 (w), 1463 (m), 1369 (w), 1056 (m), 889 (m), 831 (m), 745 (s), 722 (s).

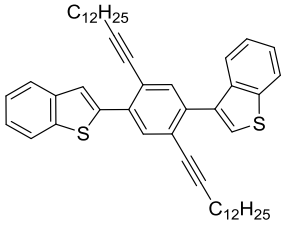
LRMS (APPI) *m/z* 673.2 $(M+H)^+$.

HRMS (APPI) *m/z* calc. for $C_{42}H_{57}BrS$ ($M^{+\cdot}$) 672.3359, found 672.3346.

UV (hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 283 (47000).

Melting point 47-48 °C.

3-(4-(benzo[*b*]thiophen-2-yl)-2,5-di(tetradec-1-yn-1-yl)phenyl)benzo[*b*]thiophene 37



A 100 mL Schlenk flask was charged with 2-(4-bromo-2,5-di(tetradec-1-yn-1-yl)phenyl)benzo[*b*]thiophene **31** (0.500 g, 0.742 mmol), benzo[*b*]thien-3-ylboronic acid (0.264 g, 1.48 mmol) and $Pd(PPh_3)_2Cl_2$ (0.026 g, 0.037 mmol) and flushed with argon for 0.5 h. DMF (40 mL) and aq. sodium carbonate (1 M, 2.2 mL, 2.2 mmol) were added and the reaction mixture was stirred at 80°C for 0.75 h, cooled to room temperature and diluted with water (75 mL). The product was extracted with diethyl ether (3 x 30 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, 0.5% EtOAc in hexane) to give the compound as a yellow solid (0.402 g, 75%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94 (1H, s), 7.92-7.90 (1H, m), 7.89-7.86 (1H, m), 7.83-7.80 (1H, m), 7.81 (1H, s), 7.77-7.75 (1H, m), 7.63 (1H, s), 7.57 (1H, s), 7.41-7.33 (4H, m), 2.45 (2H, t, *J* = 6.8 Hz), 2.17 (2H, t, *J* = 7.1 Hz), 1.65-1.57 (2H, m), 1.44-1.37 (2H, m), 1.32-1.08 (36H, m), 0.91-0.87 (6H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.50 (C), 140.14 (C), 140.06 (C), 139.90 (C), 138.26 (C), 136.98 (C), 135.28 (CH), 135.22 (C), 134.65 (C), 133.52 (CH), 125.36 (CH), 124.44 (CH), 124.31 (CH), 124.21 (CH), 123.97 (CH), 123.73 (CH), 123.58 (2CH), 123.42 (C), 122.56 (CH), 122.05 (CH), 121.13 (C), 97.19 (C), 96.10 (C), 79.98 (C), 79.44 (C), 31.93 ($2CH_2$), 29.69 ($2CH_2$), 29.66 ($4CH_2$), 29.50 (CH_2), 29.44 (CH_2), 29.37 ($2CH_2$), 29.21 (CH_2), 29.11 (CH_2), 29.02 (CH_2), 28.61 (CH_2), 28.32 (CH_2), 28.15 (CH_2), 22.69 ($2CH_2$), 19.90 (CH_2), 19.45 (CH_2), 14.11 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3063 (w), 2950 (m), 2916 (s), 2850 (m), 2226 (w), 1469 (m), 1453 (m), 1016 (m), 731 (s), 719 (s).

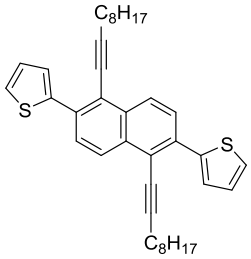
UV (hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 233 (58000), 284 (85000).

LRMS (APCI) *m/z* 727.4 $(M+H)^+$.

HRMS (APPI) *m/z* calc. for $C_{50}H_{63}S_2$ $(M+H)^+$ 727.43657, found 727.43799.

Melting point 54-56 °C.

2,2'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)dithiophene 42



A 50 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (0.330 g, 0.591 mmol), thiophen-2-ylboronic acid (0.278 g, 2.17 mmol) and $Pd(PPh_3)_2Cl_2$ (0.022 g, 0.031 mmol) and evacuated/refilled with nitrogen three times. DMF (20 mL) and aq. Na_2CO_3 (1 M, 3 mL, 3 mmol) were added and the reaction mixture was stirred at 80 °C for 0.5 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with diethyl ether (4 x 30 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 0-5% DCM in pet. ether) to give the titled compound as a yellow solid (0.235 g, 70%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.41 (2H, d, *J* = 8.8 Hz), 7.79 (2H, d, *J* = 8.8 Hz), 7.75 (2H, dd, *J* = 3.6, 0.9 Hz), 7.42 (2H, dd, *J* = 5.1, 0.9 Hz), 7.16 (2H, dd, *J* = 5.1, 3.6 Hz), 2.63 (4H, t, *J* = 7.1 Hz), 1.74 (4H, quin, *J* = 7.3 Hz), 1.57-1.49 (4H, m), 1.39-1.28 (16H, m), 0.92-0.89 (6H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.74 (2C), 134.10 (2C), 133.20 (2C), 127.74 (2CH), 127.21 (2CH), 127.02 (2CH), 126.87 (2CH), 126.08 (2CH), 117.98 (2C), 102.07 (2C), 78.20 (2C), 31.87 ($2CH_2$), 29.25 ($2CH_2$), 29.18 ($2CH_2$), 29.15 ($2CH_2$), 28.45 ($2CH_2$), 22.69 ($2CH_2$), 20.21 ($2CH_2$), 14.12 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3110 (w), 2949 (m), 2922 (s), 2840 (s), 2216 (w), 1463 (m), 1432 (m), 1055 (w), 864 (m), 815 (s), 725 (m), 693 (s).

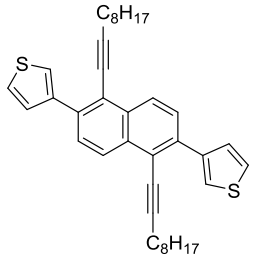
LRMS (APPI) *m/z* 564.2 ($M^{+\cdot}$).

HRMS (APPI) *m/z* calc. for $C_{38}H_{44}S_2$ ($M^{+\cdot}$) 564.28789, found 564.28711.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 306 (38000), 355 (13000), 370 (12000).

Melting point 60-62 °C.

3,3'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)dithiophene 43



A 50 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (0.250 g, 0.448 mmol), thiophen-3-ylboronic acid (0.227 g, 1.77 mmol) and $Pd(PPh_3)_2Cl_2$ (0.016 g, 0.023 mmol) and evacuated/refilled with nitrogen three times. DMF (20 mL) and aq. Na_2CO_3 (1 M, 3 mL, 3 mmol) were added and the reaction mixture was stirred at 80 °C for 0.25 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with diethyl ether (4 x 30 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown waxy solid. The crude product was purified by column chromatography (SiO_2, pet.ether) to give a yellow solid (0.183 g, 72%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.43 (2H, d, *J* = 8.7 Hz), 7.79 (2H, dd, *J* = 2.9, 1.1 Hz), 7.67 (2H, d, *J* = 8.7 Hz), 7.63 (2H, dd, *J* = 5.0, 1.1 Hz), 7.40 (2H, dd, *J* = 5.0, 2.9 Hz), 2.56 (4H, t, *J* = 7.0 Hz), 1.68 (4H, quin, *J* = 7.3 Hz), 1.48 (4H, quin, *J* = 7.2 Hz), 1.38-1.27 (16H, m), 0.91 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.43 (2C), 136.24 (2C), 133.05 (2C), 128.92 (2CH), 127.97 (2CH), 126.65 (2CH), 124.47 (2CH), 124.02 (2CH), 118.75 (2C), 99.96 (2C), 78.21 (2C), 31.86 ($2CH_2$), 29.24 ($2CH_2$), 29.18 ($2CH_2$), 29.08 ($2CH_2$), 28.60 ($2CH_2$), 22.67 ($2CH_2$), 19.97 ($2CH_2$), 14.11 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3104 (w), 2948 (m), 2924 (s), 2851 (m), 2217 (w), 1464 (m), 1454 (m), 1374 (w), 1090 (w), 849 (s), 789 (s), 722 (s).

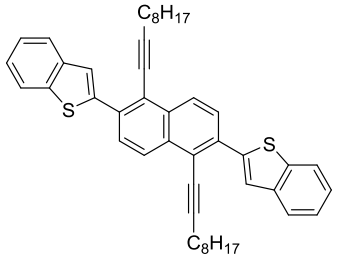
LRMS (APPI) *m/z* 564.2 ($M^{+\cdot}$), 565.3 $(M+H)^+$.

HRMS (APPI) *m/z* calc. for $C_{38}H_{44}S_2$ ($M^{+\cdot}$) 564.28789, found 564.28786.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 236 (15000), 287 (41000).

Melting point 86-88 °C.

2,2'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)bis(benzo[*b*]thiophene) 44



A 50 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (0.390 g, 0.698 mmol), benzo[*b*]thiophen-2-ylboronic acid (0.456 g, 2.56 mmol) and $Pd(PPh_3)_2Cl_2$ (0.027 g, 0.038 mmol) and evacuated/refilled with nitrogen three times. DMF (20 mL) and aq. Na_2CO_3 (1 M, 3 mL, 3 mmol) were added and the reaction mixture was stirred at 80 °C for 0.75 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with DCM (4 x 30 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown waxy solid. The crude product was purified by column chromatography (SiO_2, 0-10% DCM in pet. ether) to give a yellow solid (0.392 g, 85%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.48 (2H, d, *J* = 8.8 Hz), 8.00 (2H, s), 7.91-7.89 (2H, m), 7.86-7.83 (2H, m), 7.86 (2H, d, *J* = 8.8 Hz), 7.42-7.35 (4H, m), 2.64 (4H, t, *J* = 7.0 Hz), 1.74 (4H, quin, *J* = 7.3 Hz), 1.54-1.47 (4H, m), 1.35-1.25 (16H, m), 0.89 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.77 (2C), 140.32 (2C), 140.02 (2C), 134.42 (2C), 133.47 (2C), 128.18 (2CH), 127.00 (2CH), 124.45 (2CH), 124.31 (2CH), 124.12 (2CH), 123.72 (2CH), 122.02 (2CH), 119.22 (2C), 102.29 (2C), 77.98 (2C), 31.85 ($2CH_2$), 29.20 ($4CH_2$), 29.16 ($2CH_2$), 28.44 ($2CH_2$), 22.67 ($2CH_2$), 20.22 ($2CH_2$), 14.11 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3060 (w), 2952 (m), 2920 (s), 2849 (m), 2215 (w), 1465 (m), 1455 (m), 1377 (w), 1093 (s), 1016 (s), 871 (s), 800 (s), 740 (s), 723 (s).

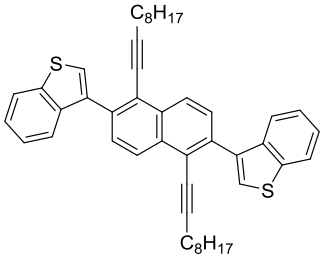
LRMS (APPI) *m/z* 664.3 ($M^{+\cdot}$).

HRMS (APPI) *m/z* calc. for $C_{46}H_{48}S_2$ ($M^{+\cdot}$) 664.31919, found 664.31861.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 241 (16000), 280 (18000), 289 (34000).

Melting point 119-120 °C.

3,3'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)bis(benzo[*b*]thiophene) 45



A 50 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (0.250 g, 0.448 mmol), benzo[*b*]thiophen-3-ylboronic acid (0.306 g, 1.72 mmol) and $Pd(PPh_3)_2Cl_2$ (0.017 g, 0.024 mmol) and evacuated/refilled with nitrogen three times. DMF (20 mL) and aq. Na_2CO_3 (1 M, 3 mL, 3 mmol) were added and the reaction mixture was stirred at 80 °C for 0.5 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with diethyl ether (4 x 30 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown waxy solid. The crude product was purified by column chromatography (SiO_2, 0-10% DCM in pet.ether), to give a yellow solid (0.189 g, 63%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.50 (2H, d, *J* = 8.6 Hz), 7.95 (2H, dd, *J* = 6.7, 2.3 Hz), 7.76-7.72 (2H, m), 7.69 (2H, d, *J* = 8.8 Hz), 7.68 (2H, s), 7.42-7.35 (4H, m), 2.33 (4H, t, *J* = 6.9 Hz), 1.37-1.18 (24H, m), 0.90 (6H, t, *J* = 7.1 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.95 (2C), 138.59 (2C), 136.77 (2C), 136.61 (2C), 133.14 (2C), 128.72 (2CH), 126.33 (2CH), 125.55 (2CH), 124.17 (2CH), 123.96 (2CH), 123.64 (2CH), 122.62 (2CH), 121.24 (2C), 100.34 (2C), 77.74 (2C), 31.87 ($2CH_2$), 29.14 ($2CH_2$), 29.12 ($2CH_2$), 28.74 ($2CH_2$), 28.37 ($2CH_2$), 22.67 ($2CH_2$), 19.73 ($2CH_2$), 14.13 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3055 (w), 2954 (m), 2922 (s), 2850 (m), 2221 (w), 1463 (m), 1455 (m), 1391 (w), 1019 (m), 837 (m), 809 (m), 793 (s), 756 (s), 732 (s).

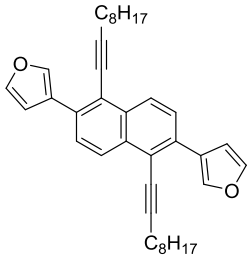
LRMS (APPI) *m/z* 664.3 ($M^{+\cdot}$).

HRMS (APPI) *m/z* calc. for $C_{46}H_{48}S_2$ ($M^{+\cdot}$) 664.31919, found 664.31797.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 242 (32000), 296 (18000), 305 (19000).

Melting point 116-118 °C.

3,3'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)difuran 47



A 50 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (0.290 g, 0.519 mmol), furanyl-3-boronic acid (0.216 g, 1.93 mmol) and $Pd(PPh_3)_2Cl_2$ (0.017 g, 0.024 mmol) and evacuated/refilled with nitrogen three times. DMF (20 mL) and aq. Na_2CO_3 (1 M, 3 mL, 3 mmol) were added and the reaction mixture was stirred at 80 °C for 0.75 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with diethyl ether (3 x 30 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown waxy solid. The crude product was purified by column chromatography (SiO_2, 0-5% DCM in pet.ether) to give a light red solid (0.198 g, 72%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.40 (2H, d, *J* = 8.7 Hz), 8.19 (2H, s), 7.64 (2H, d, *J* = 8.7 Hz), 7.54 (2H, t, *J* = 1.7 Hz), 7.01 (2H, d, *J* = 1.3 Hz), 2.63 (4H, t, *J* = 7.2 Hz), 1.74 (4H, quin, *J* = 7.3 Hz), 1.57-1.50 (4H, m), 1.40-1.30 (16H, m), 0.91 (6H, t, *J* = 6.8 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.42 (2CH), 141.56 (2CH), 133.06 (2C), 132.17 (2C), 126.96 (2CH), 126.68 (2CH), 125.27 (2C), 118.09 (2C), 110.77 (2CH), 100.74 (2C), 78.47 (2C), 31.85 ($2CH_2$), 29.23 ($2CH_2$), 29.15 ($4CH_2$), 28.67 ($2CH_2$), 22.68 ($2CH_2$), 20.03 ($2CH_2$), 14.11 ($2CH_3$).

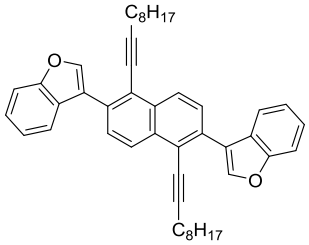
IR (neat) υ_{max}/cm^{-1} 2921 (s), 2853 (s), 2214 (w), 1583 (m), 1469 (m), 1046 (m), 1024 (m), 872 (m), 839 (m), 788 (s), 735 (m).

HRMS (APPI) *m/z* calc. for $C_{38}H_{44}O_2$ ($M^{+\cdot}$) 532.33358, found 532.33404.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 286 (34000).

Melting point 82-83 °C.

3,3'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)bis(benzofuran) 49



A 50 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (0.150 g, 0.269 mmol), 3-(benzofuran-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane (0.182 g, 0.791 mmol) and $Pd(PPh_3)_2Cl_2$ (0.012 g, 0.017 mmol) and evacuated/refilled with nitrogen three times. DMF (10 mL) and aq. Na_2CO_3 (1 M, 1.5 mL, 1.5 mmol) were added and the reaction mixture was stirred at 80 °C for 1 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with diethyl ether (5 x 20 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, 9:1 pet. ether/DCM) to give as a yellow solid (0.040 g, 24%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.52 (2H, d, *J* = 8.7 Hz), 8.14 (2H, s), 7.81 (2H, d, *J* = 8.7 Hz), 7.78 (2H, d, *J* = 7.6 Hz), 7.61 (2H, d, *J* = 8.2 Hz), 7.40-7.36 (2H, m), 7.34-7.30 (2H, m), 2.48 (4H, t, *J* = 7.0 Hz), 1.58-1.51 (4H, m), 1.37-1.25 (20H, m), 0.92-0.89 (6H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.21 (2C), 143.97 (2CH), 133.23 (2C), 132.25 (2C), 128.05 (2CH), 127.22 (2C), 126.67 (2CH), 124.31 (2CH), 122.68 (2CH), 121.10 (2CH), 120.84 (2C), 120.27 (2C), 111.60 (2CH), 100.44 (2C), 77.96 (2C), 31.83 ($2CH_2$), 29.17 ($2CH_2$), 29.11 ($2CH_2$), 28.94 ($2CH_2$), 28.48 ($2CH_2$), 22.67 ($2CH_2$), 19.87 ($2CH_2$), 14.11 ($2CH_3$).

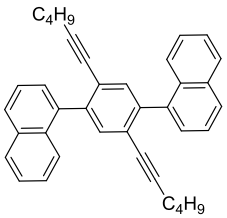
IR (neat) υ_{max}/cm^{-1} 2952 (m), 2922 (s), 2850 (m), 2216 (w), 1587 (m), 1450 (s), 1093 (s), 849 (s), 806 (s), 743 (s), 713 (s).

HRMS (APPI) *m/z* calc. for $C_{46}H_{48}O_2$ ($M^{+\cdot}$) 632.3649, found 632.3650.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 251 (43000), 288 (46000).

Melting point 111-113 °C.

1,1'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)dinaphthalene 58



A 250 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(hex-1-yn-1-yl)benzene **2** (1.00 g, 2.52 mmol), naphthalen-1-ylboronic acid (1.08 g, 6.28 mmol) and $Pd(PPh_3)_2Cl_2$ (0.088 g, 0.125 mmol) and flushed with argon for 1 h. DMF (60 mL) and aq. Na_2CO_3 (1 M, 6 mL, 6 mmol) were added and the reaction mixture was stirred at 120 °C for 70 min. An extra portion of naphthalen-1-ylboronic acid (0.200 g, 1.16 mmol) was added, and the reaction was continued at 120 °C for 0.5 h. The reaction mixture was then cooled to room temperature, diluted with water (150 mL) and the product extracted with diethyl ether (4 x 40 mL). The organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 0-2% EtOAc in pet. ether) to give a yellow solid (0.665 g, 54%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94-7.90 (4H, m), 7.84-7.76 (2H, m), 7.59 (2H, s), 7.60-7.44 (8H, m), 1.99 (4H, t, *J* = 6.7 Hz), 1.03-0.89 (4H, m), 0.86-0.77 (4H, m), 0.61 (6H, t, *J* = 7.2 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.93 (2C), 138.37 (2C), 133.94 (2CH), 133.52 (2C), 131.92 (2C), 128.04 (2CH), 127.83 (2CH), 127.24 (2CH), 126.53 (2CH), 125.77 (2CH), 125.60 (2CH), 125.10 (2CH), 123.47 (2C), 95.35 (2C), 79.68 (2C), 30.05 ($2CH_2$), 21.22 ($2CH_2$), 18.88 ($2CH_2$), 13.43 ($2CH_3$).

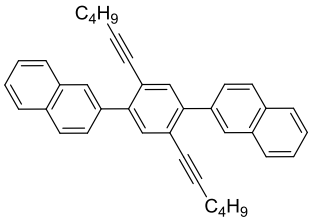
IR (neat) υ_{max}/cm^{-1} 3043 (w), 2952 (m), 2926 (m), 2865 (m), 2226 (w), 1591 (w), 1460 (m), 1372 (m), 1096 (m), 1019 (m), 799 (s), 775 (s).

HRMS (APPI) *m/z* calc. for $C_{38}H_{35}$ $(M+H)^+$ 491.27333, found 491.27311.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 287 (31000).

Melting point 135-137 °C.

2,2'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)dinaphthalene 59



A 250 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(hex-1-yn-1-yl)benzene **2** (1.00 g, 2.52 mmol), naphthalen-2-ylboronic acid (1.28 g, 7.44 mmol) and $Pd(PPh_3)_2Cl_2$ (0.085 g, 0.121 mmol) and flushed with argon for 1 h. DMF (60 mL) and aq. Na_2CO_3 (1 M, 6 mL, 6 mmol) were added and the reaction mixture was stirred at 120 °C for 1 h. Extra portions of naphthalen-2-ylboronic acid (0.300 g, 1.74 mmol) and $Pd(PPh_3)_2Cl_2$ (0.079 g, 0.113 mmol)

were added and the reaction continued overnight. After 14 h, the reaction was stopped, cooled to room temperature, diluted with water (150 mL) and the product extracted with diethyl ether (5 x 50 mL). The organic layers were combined and filtered to remove black residue, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a dark orange solid. The crude product was purified by column chromatography (SiO_2, 0.5% EtOAc in pet. ether) to give a yellow solid (0.639 g, 52%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.12 (2H, s), 7.92-7.90 (6H, m), 7.82 (2H, dd, *J* = 8.5, 1.7 Hz), 7.68 (2H, s), 7.54-7.50 (4H, m), 2.30 (4H, t, *J* = 7.0 Hz), 1.47-1.40 (4H, m), 1.32-1.23 (4H, m), 0.78 (6H, t, *J* = 7.3 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.15 (2C), 137.38 (2C), 134.24 (2CH), 133.21 (2C), 132.71 (2C), 128.21 (2CH), 128.13 (2CH), 127.62 (2CH), 127.54 (2CH), 127.24 (2CH), 126.00 (4CH), 122.07 (2C), 95.02 (2C), 80.00 (2C), 30.47 ($2CH_2$), 21.86 ($2CH_2$), 19.27 ($2CH_2$), 13.49 ($2CH_3$).

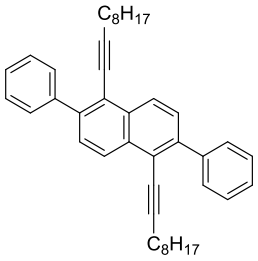
IR (neat) υ_{max}/cm^{-1} 3053 (w), 2959 (m), 2929 (m), 2859 (m), 2228 (w), 1598 (w), 1496 (m), 1461 (m), 1378 (w), 893 (m), 861 (s), 820 (s), 743 (s).

HRMS (APPI) *m/z* calc. for $C_{38}H_{35}$ $(M+H)^+$ 491.27333, found 491.27361.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 265 (94000).

Melting point 143-145 °C.

1,5-di(dec-1-yn-1-yl)-2,6-diphenylnaphthalene 62



A 250 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (1.00 g, 1.79 mmol), phenylboronic acid (0.838 g, 6.87 mmol), $Pd(PPh_3)_2Cl_2$ (0.067 g, 0.095 mmol) and flushed with argon for 40 min. DMF (50 mL) and aq. Na_2CO_3 (1 M, 7 mL, 7 mmol) were added and the reaction was stirred at 80 °C for 1 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with diethyl ether (4 x 35 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy brown solid. The crude product was purified by column chromatography (SiO_2, 0-10% DCM in pet. ether) to give a yellow solid (0.629 g, 64%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.28 (2H, d, *J* = 8.7 Hz), 7.74-7.72 (4H, m), 7.61 (2H, d, *J* = 8.6 Hz), 7.50-7.46 (4H, m), 7.42-7.38 (2H, m), 2.47 (4H, t, *J* = 7.0 Hz), 1.62-1.55 (4H, m), 1.40-1.29 (20H, m), 0.91 (6H, t, *J* = 6.8 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.11 (2C), 141.25 (2C), 132.88 (2C), 129.70 (4CH), 128.38 (2CH), 127.83 (4CH), 127.27 (2CH), 126.57 (2CH), 119.44 (2C), 99.28 (2C), 77.92 (2C), 31.87 ($2CH_2$), 29.21 ($2CH_2$), 29.18 ($2CH_2$), 28.94 ($2CH_2$), 28.55 ($2CH_2$), 22.68 ($2CH_2$), 19.85 ($2CH_2$), 14.11 ($2CH_3$).

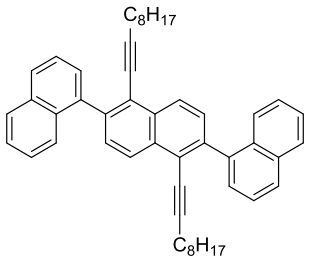
IR (neat) υ_{max}/cm^{-1} 3057 (w), 2948 (m), 2924 (s), 2851 (m), 2218 (w), 1582 (w), 1464 (m), 1442 (m), 1388 (m), 833 (s), 720 (s), 698 (s).

HRMS (APPI) *m/z* calc. for $C_{42}H_{49}$ $(M+H)^+$ 553.38288, found 553.38236.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 277 (101000).

Melting Point 90-91 °C.

1',5'-di(dec-1-yn-1-yl)-1,2':6',1''-ternaphthalene 63



A 250 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (1.67 g, 2.99 mmol), naphthalen-1-ylboronic acid (1.99 g, 11.6 mmol) and $Pd(PPh_3)_2Cl_2$ (0.103 g, 0.147 mmol) and flushed with argon for 0.75 h. DMF (60 mL) and aq. Na_2CO_3 (1 M, 10 mL, 10 mmol) were added and the reaction mixture was stirred at 120 °C for 50 min, cooled to room temperature and diluted with water (240 mL). The product was extracted with diethyl ether (5 x 40 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a dark brown oil. The crude product was first purified by adding petroleum ether (30 mL) and filtering off the undissolved solid, washing with methanol (20 mL) and petroleum ether (20 mL) and drying to give a yellow solid (0.685 g). The mother liquor was concentrated under reduced pressure and then purified by column chromatography (SiO_2, 0-10% DCM in pet. ether) to give another 0.380 g of the titled compound. Final yield: 1.07 g (55%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.51 (2H, d, *J* = 8.6 Hz), 7.95-7.91 (4H, m), 7.69 (2H, t, *J* = 8.9 Hz), 7.63 (2H, d, *J* = 8.6 Hz), 7.60-7.58 (4H, m), 7.50 (2H, t, *J* = 7.3 Hz), 7.43-7.38 (2H, m), 2.17 (4H, t, *J* = 6.8 Hz), 1.33-0.95 (24H, m), 0.90 (6H, t, *J* = 7.1 Hz).

^{13}C-NMR (400 MHz, $CDCl_3$) δ 141.67 (2C), 139.57 (2C), 133.57 (2C), 132.75 (2C), 131.95 (2C), 129.42 (2CH), 128.09 (2CH), 127.76 (2CH), 127.49 (2CH), 126.55 (2CH), 125.89 (2CH), 125.75 (2CH), 125.57 (2CH), 125.14 (2CH), 121.78 (2C), 100.06 (2C), 77.74 (2C), 31.88 ($2CH_2$), 29.06 ($2CH_2$), 29.05 ($2CH_2$), 28.43 ($2CH_2$), 28.24 ($2CH_2$), 22.68 ($2CH_2$), 19.53 ($2CH_2$), 14.12 ($2CH_3$).

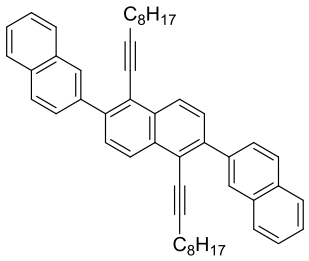
IR (neat) υ_{max}/cm^{-1} 3055 (w), 2954 (m), 2920 (s), 2851 (m), 2219 (w), 1583 (w), 1464 (m), 1389 (m), 1017 (m), 797 (s), 837 (s), 774 (s), 718 (m).

HRMS (APPI) *m/z* calc. for $C_{50}H_{52}$ ($M^{+\cdot}$) 652.40635, found 652.40618.

UV (DCM) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 244 (76000), 300 (49000).

Melting point 120-122 °C.

1',5'-di(dec-1-yn-1-yl)-2,2':6',2''-terbenzobenzene 64



A 100 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (1.00 g, 1.79 mmol), naphthalen-2-ylboronic acid (1.20 g, 6.98 mmol) and $Pd(PPh_3)_2Cl_2$ (0.062 g, 0.088 mmol) and flushed with argon for 0.5 h. DMF (50 mL) and aq. Na_2CO_3 (1 M, 5 mL, 5 mmol) were added and the reaction mixture was stirred at 120 °C for 20 min, cooled to room temperature and diluted with water (150 mL). The product was extracted with diethyl ether (5 x 70 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 0-2% EtOAc in pet. ether) to give a yellow solid (0.829 g, 71%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.55 (2H, d, *J* = 8.6 Hz), 8.21 (2H, s), 7.96-7.89 (8H, m), 7.74 (2H, d, *J* = 8.6 Hz), 7.56-7.52 (4H, m), 2.45 (4H, t, *J* = 7.0 Hz), 1.57-1.50 (4H, m), 1.31-1.15 (20H, m), 0.89 (6H, t, *J* = 7.1 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.13 (2C), 138.78 (2C), 133.23 (2C), 133.00 (2C), 132.65 (2C), 128.67 (2CH), 128.64 (2CH), 128.23 (2CH), 128.05 (2CH), 127.64 (2CH), 127.22 (2CH), 126.68 (2CH), 126.04 (4CH), 119.77 (2C), 99.53 (2C), 78.05 (2C), 31.85 ($2CH_2$), 29.13 ($4CH_2$), 28.93 ($2CH_2$), 28.59 ($2CH_2$), 22.66 ($2CH_2$), 19.88 ($2CH_2$), 14.12 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3058 (w), 2920 (s), 2853 (m), 2216 (w), 1601 (w), 1466 (m), 838 (m), 920 (s), 744 (s), 713 (s).

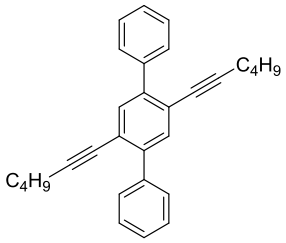
HRMS (APPI) *m/z* calc. for $C_{50}H_{53}$ $(M+H)^+$ 653.41418, found 653.41474.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 276 (103000), 293 (54000), 302 (52000).

Melting Point 109-111 °C (lit[136] 110 °C).

Data is consistent with that reported by Alexandre Debacker.[136]

2',5'-di(hex-1-yn-1-yl)-1,1':4',1''-terphenyl 68

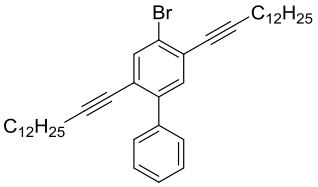


A 250 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(hex-1-yn-1yl)benzene **2** (1.60 g, 4.04 mmol), phenylboronic acid (1.73 g, 14.2 mmol) and $Pd(PPh_3)_2Cl_2$ (0.136 g, 0.194 mmol) and flushed with argon for 1 h. DMF (70 mL) and aq. Na_2CO_3 (1 M, 15 mL, 15 mmol) were added and the reaction mixture was stirred at 80-120 °C for 1 h, cooled to room temperature and diluted with water (200 mL). The product was extracted with diethyl ether (4 x 70 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, 0-30% DCM in pet. ether) to give a yellow solid (1.34 g, 85%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.64-7.62 (4H, m), 7.52 (2H, s), 7.44-7.40 (4H, m), 7.38-7.35 (2H, m), 2.31 (4H, t, *J* = 6.9 Hz), 1.50-1.43 (4H, m), 1.38-1.28 (4H, m), 0.87 (6H, t, *J* = 7.3 Hz).

NMR is consistent with that reported by Jason Howe.[135]

4-bromo-2,5-di(tetradec-1-yn-1-yl)-1,1'-biphenyl 74



A 250 mL Schlenk flask was charged with a mixture of 1,4-dibromo-2,5-di(tetradec-1-yn-1yl)benzene **3** and 1-bromo-4-iodo-2,5-di(tetradec-1-yn-1-yl)benzene **34** (1.22 g, mass ratio 28:72 respectively, 1.87 mmol), phenylboronic acid (0.197 g, 1.616 mmol) and $Pd(PPh_3)_2Cl_2$ (0.065 g, 0.093 mmol) and flushed with argon for 1 h. DMF (50 mL) and aq. Na_2CO_3 (1 M, 6 mL, 6 mmol) were added and the reaction mixture was stirred at 80-120 °C for 1 h, cooled to

room temperature and diluted with water (200 mL). The product was extracted with diethyl ether (4 x 50 mL) and the organic layers were combined, filtered to remove black residual material, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a dark brown oil. The crude product was purified by column chromatography (SiO_2, 0-10% DCM in pet. ether) to give an orange oil (0.511 g, 51%). Yield is given with respect to the boronic acid as less than 1.0 equivalent was used and the ratio of the two starting materials was an estimate from NMR.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70 (1H, s), 7.56-7.53 (2H, m), 7.42-7.35 (3H, m), 7.41 (1H, s), 2.47 (2H, t, *J* = 7.0 Hz), 2.29 (2H, t, *J* = 6.9 Hz), 1.68-1.61 (2H, m), 1.53-1.42 (4H, m), 1.31-1.25 (34H, m), 0.91-0.87 (6H, m).

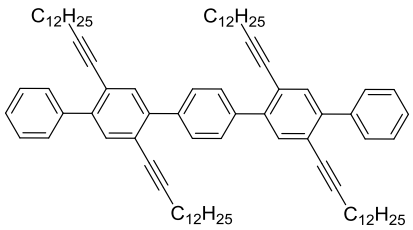
^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.39 (C), 139.17 (C), 136.18 (CH), 133.78 (CH), 129.02 (2CH), 127.88 (2CH), 127.61 (CH), 125.30 (C), 123.39 (C), 122.97 (C), 96.85 (C), 96.02 (C), 79.25 (C), 78.82 (C), 31.92 ($2CH_2$), 29.67 ($2CH_2$), 29.64 ($4CH_2$), 29.53 (CH_2), 29.50 (CH_2), 29.36 ($2CH_2$), 29.13 ($2CH_2$), 28.86 (CH_2), 28.78 (CH_2), 28.51 (CH_2), 28.26 (CH_2), 22.69 ($2CH_2$), 19.65 (CH_2), 19.53 (CH_2), 14.11 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2921 (s), 2852 (s), 2234 (w), 1472 (s), 1372 (m), 1065 (m), 897 (m), 768 (m), 723 (m), 697 (s).

HRMS (APPI) *m/z* calc. for $C_{40}H_{57}Br$ ($M^{+\cdot}$) 616.36382, found 616.36246.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 255 (30000), 289 (20000).

2',2''',5',5'''-tetrakis(tetradec-1-yn-1-yl)-1,1':4',1'':4'',1''':4''',1'''':quinquephenyl 76



A 50 mL Schlenk flask was charged with 4-bromo-2,5-di(tetradec-1-yn-1-yl)-1,1'-biphenyl **74** (0.416 g, 0.673 mmol), 1,4-bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzene **75** (0.099 g, 0.328 mmol) and $Pd(PPh_3)_2Cl_2$ (0.040 g, 0.057 mmol) and flushed with argon for 0.5 h. DMF (25 mL) and aq, Na_2CO_3 (1 M, 4 mL, 4 mmol) were added and the reaction was stirred at 80 °C. After TLC analysis showed little reaction progress, KOH (0.230 g, 4.10 mmol) and an extra portion of $Pd(PPh_3)_2Cl_2$ (0.030 g, 0.043 mmol) were added and the temperature was raised to 120 °C. The reaction was continued for 10 min, cooled to room temperature and diluted with water (100 mL). The product was extracted with diethyl ether (3 x 30 mL) and the organic

layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown waxy solid. The crude product was purified by column chromatography (SiO_2, 0-10% DCM in pet. ether) to give a yellow solid (0.211 g, 56%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.71 (4H, s), 7.65 (4H, d, *J* = 7.2 Hz), 7.59 (2H, s), 7.55 (2H, s), 7.44-7.37 (6H, m), 2.35-2.30 (8H, m), 1.55-1.45 (8H, m), 1.27-1.23 (72H, m), 0.90-0.85 (12H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.06 (2C), 141.67 (2C), 139.84 (2C), 138.82 (2C), 134.16 (2CH), 133.89 (2CH), 129.21 (4CH), 128.68 (4CH), 127.82 (4CH), 127.38 (2CH), 121.80 (2C), 121.67 (2C), 94.89 (2C), 94.78 (2C), 80.04 (2C), 79.95 (2C), 31.93 ($4CH_2$), 29.69-29.66 ($12CH_2$), 29.56 ($2CH_2$), 29.53 ($2CH_2$), 29.36 ($4CH_2$), 29.20 ($4CH_2$), 28.91 ($2CH_2$), 28.85 ($2CH_2$), 28.48 ($2CH_2$), 28.43 ($2CH_2$), 22.69 ($4CH_2$), 19.65 ($2CH_2$), 19.60 ($2CH_2$), 14.11 ($4CH_3$).

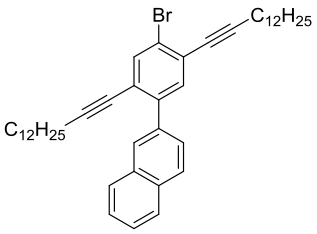
IR (neat) υ_{max}/cm^{-1} 3057 (w), 2917 (s), 2849 (s), 2230 (w), 1467 (s), 1377 (m), 1022 (w), 907 (s), 840 (s), 720 (s), 697 (s).

LRMS (APPI) *m/z* 1150.9 ($M^{+\cdot}$).

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 273 (76000).

Melting point 74-76 °C.

2-(4-bromo-2,5-di(tetradec-1-yn-1-yl)phenyl)naphthalene 78



A 100 mL Schlenk flask was charged with 1-bromo-4-iodo-2,5-di(tetradec-1-yn-1-yl)benzene **34** (1.07 g, 1.60 mmol), naphthalen-2-ylboronic acid (0.275 g, 1.60 mmol), $Pd(PPh_3)_2Cl_2$ (0.056 g, 0.080 mmol) and K_3PO_4 (1.33 g, 6.27 mmol) and evacuated/refilled with argon three times. THF (40 mL) and water (10 mL) were added and the reaction mixture was refluxed for 20 min, cooled to room temperature and THF removed under reduced pressure. Water (100 mL) was added and the product was extracted with DCM (4 x 50 mL). The organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, petroleum ether) to give a red oil (0.692 g, 65%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.01 (1H, s), 7.88-7.85 (3H, m), 7.74 (1H, s), 7.69 (1H, dd, *J* = 8.6, 1.5 Hz), 7.52 (1H, s), 7.52-7.49 (2H, m), 2.49 (2H, t, *J* = 7.0 Hz), 2.26 (2H, t, *J* = 7.0 Hz),

1.69-1.61 (2H, m), 1.54-1.46 (2H, m), 1.44-1.38 (2H, m), 1.35-1.09 (34H, m), 0.91-0.87 (6H, m).

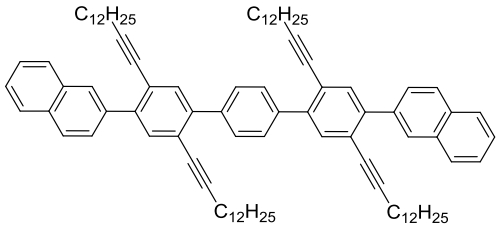
^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.36 (C), 136.70 (C), 136.23 (CH), 134.00 (CH), 133.11 (C), 132.72 (C), 128.16 (CH), 128.02 (CH), 127.61 (CH), 127.31 (CH), 127.22 (CH), 126.14 (CH), 126.10 (CH), 125.40 (C), 123.53 (C), 123.19 (C), 96.96 (C), 96.23 (C), 79.27 (C), 78.91 (C), 31.93 (CH_2), 31.91 (CH_2), 29.64 ($6CH_2$), 29.54 (CH_2), 29.41 (CH_2), 29.37 (CH_2), 29.35 (CH_2), 29.13 (CH_2), 29.10 (CH_2), 28.88 (CH_2), 28.78 (CH_2), 28.52 (CH_2), 28.29 (CH_2), 22.69 ($2CH_2$), 19.68 (CH_2), 19.54 (CH_2), 14.11 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3052 (w), 2921 (s), 2851 (s), 2232 (w), 1478 (m), 1464 (s), 1376 (w), 1063 (m), 891 (m), 856 (m), 817 (m), 748 (s), 722 (m).

HRMS *m/z* (APPI) calc. for $C_{44}H_{59}Br$ ($M^{+\cdot}$) 666.3795, found 666.3784.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 258 (62000), 289 (20000).

2,2'-(2,2'',5,5''-tetrakis(tetradec-1-yn-1-yl)-[1,1':4',1''-terphenyl]-4,4''-diyl)dinaphthalene 79

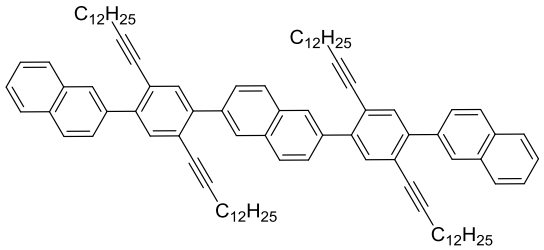


A 50 mL Schlenk flask was charged with 2-(4-bromo-2,5-di(tetradec-1-yn-1-yl)phenyl)naphthalene **78** (0.150 g, 0.225 mmol), 1,4-bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzene **75** (0.033 g, 0.109 mmol) and $Pd(PPh_3)_2Cl_2$ (0.016 g, 0.023 mmol) and evacuated/refilled with argon three times. DMF (15 mL) and aq. Na_2CO_3 (1 M, 1.5 mL, 1.5 mmol) were added and the reaction mixture was stirred at 120 °C for 1 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with diethyl ether (4 x 40 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy brown solid. The crude product was purified by column chromatography (SiO_2, 0-10% DCM in pet. ether) to give a yellow solid (0.072 g, 53%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.12 (2H, s), 7.90-7.89 (6H, m), 7.83-7.80 (2H, m), 7.75 (4H, s), 7.66 (2H, s), 7.64 (2H, s), 7.53-7.50 (4H, m), 2.36 (4H, t, *J* = 7.0 Hz), 2.29 (4H, t, *J* = 7.0 Hz), 1.58-1.50 (6H, m), 1.47-1.40 (6H, m), 1.38-1.10 (68H, m), 0.91-0.83 (12H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.02 (2C), 141.78 (2C), 138.85 (2C), 137.37 (2C), 134.43 (2CH), 134.05 (2CH), 133.21 (2C), 132.69 (2C), 128.72 (4CH), 128.21 (2CH), 128.13 (2CH), 127.61 (2CH), 127.57 (2CH), 127.20 (2CH), 125.98 (4CH), 122.03 (2C), 121.77 (2C), 95.01 (4C), 80.06 (4C), 31.93 ($4CH_2$), 29.67 ($8CH_2$), 29.65 ($4CH_2$), 29.58 ($2CH_2$), 29.45 ($2CH_2$), 29.37 ($4CH_2$), 29.21 ($2CH_2$), 29.16 ($2CH_2$), 28.94 ($2CH_2$), 28.86 ($2CH_2$), 28.49 ($2CH_2$), 28.45 ($2CH_2$), 22.69 ($2CH_2$), 22.67 ($2CH_2$), 19.69 ($2CH_2$), 19.67 ($2CH_2$), 14.12 ($2CH_3$), 14.10 ($2CH_3$).
IR (neat) υ_{max}/cm^{-1} 3052 (w), 2954 (m), 2920 (s), 2850 (s), 2230 (w), 1485 (m), 1465 (s), 1377 (w), 1022 (m), 897 (m), 862 (m), 841 (s), 742 (s), 720 (s).
LRMS (APPI) *m/z* 1250.9 ($M^{+\cdot}$), 1251.9 $(M+H)^+$.
UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 277 (112000).
Melting point 95-97 °C.

2,6-bis(4-(naphthalen-2-yl)-2,5-di(tetradec-1-yn-1-yl)phenyl)naphthalene 81



A 50 mL Schlenk flask was charged with 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (0.028 g, 0.074 mmol), 2-(4-bromo-2,5-di(tetradec-1-yn-1-yl)phenyl)naphthalene **78** (0.100 g, 0.150 mmol) and $Pd(PPh_3)_2Cl_2$ (0.006 g, 0.009 mmol) and evacuated/refilled with nitrogen three times. DMF (12 mL) and aq. Na_2CO_3 (1 M, 0.5 mL, 0.5 mmol) were added and the reaction was stirred at 80-120 °C for 1 h, cooled to room temperature and diluted with water (80 mL). The product was extracted with diethyl ether (4 x 15 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown waxy solid. The crude product was purified by column chromatography (SiO_2, 0-5% DCM in pet. ether) to give the titled compound as a yellow solid (0.041 g, 43%).
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.17 (2H, s), 8.13 (2H, s), 7.96-7.82 (12H, m), 7.70 (2H, s), 7.69 (2H, s), 7.53-7.51 (4H, m), 2.32 (4H, t, *J* = 7.1 Hz), 2.30 (4H, t, *J* = 7.1 Hz), 1.52-1.41 (8H, m), 1.33-1.12 (72H, m), 0.91-0.84 (12H, m).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.15 (2C), 142.10 (2C), 137.57 (2C), 137.39 (2C), 134.32 (2CH), 134.25 (2CH), 133.23 (2C), 132.72 (2C), 132.49 (2C), 128.22 (2CH), 128.15 (2CH), 127.90 (2CH), 127.76 (2CH), 127.62 (2CH), 127.56 (4CH), 127.22 (2CH), 126.00 (4CH),

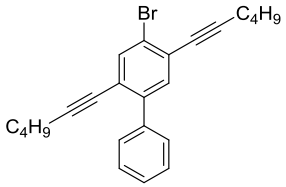
122.10 (2C), 122.05 (2C), 95.12 (2C), 95.10 (2C), 80.10 (2C), 80.06 (2C), 31.93 ($4CH_2$), 29.68 ($4CH_2$), 29.65 ($8CH_2$), 29.50 ($2CH_2$), 29.44 ($2CH_2$), 29.37 ($2CH_2$), 29.35 ($2CH_2$), 29.17 ($2CH_2$), 29.15 ($2CH_2$), 28.91 ($2CH_2$), 28.86 ($2CH_2$), 28.48 ($2CH_2$), 28.45 ($2CH_2$), 22.69 ($2CH_2$), 22.68 ($2CH_2$), 19.65 ($2CH_2$), 19.64 ($2CH_2$), 14.11 ($4CH_3$).

IR (neat) υ_{max}/cm^{-1} 3053 (w), 2919 (s), 2850 (s), 2224 (w), 1600 (w), 1484 (m), 1467 (m), 1094 (m), 1017 (m), 887 (m), 819 (s), 801 (s), 744 (s), 721 (m).

LRMS (APPI) *m/z* 1302.9 ($M^{+\cdot}$).

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 274 (85000).

4-bromo-2,5-di(hex-1-yn-1-yl)-1,1'-biphenyl 83

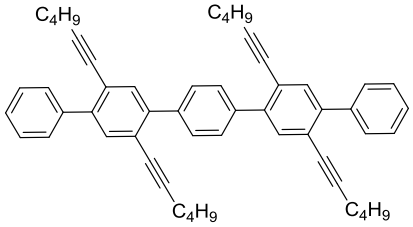


A 500 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(hex-1-yn-1-yl)benzene **2** (4.05 g, 10.1 mmol), phenylboronic acid (0.998 g, 8.19 mmol) and $Pd(PPh_3)_2Cl_2$ (0.321 g, 0.457 mmol) and flushed with argon for 1 h. DMF (100 mL) and aq. Na_2CO_3 (1 M, 15 mL, 15 mmol) were added and the reaction mixture was stirred at 80 °C. After 0.5 h, extra portions of phenylboronic acid (0.200 g, 1.64 mmol) and $Pd(PPh_3)_2Cl_2$ (0.040 g, 0.057 mmol) were added and the temperature increased to 120 °C. After 1 h at 120 °C, the reaction mixture was cooled to room temperature, diluted with water (200 mL) and the product extracted with diethyl ether (5 x 80 mL). The organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, 0-5% DCM in pet. ether) to give 4-bromo-2,5-di(hex-1-yn-1-yl)-1,1'-biphenyl as an orange oil (0.428 g, 11%). 2',5'-di(hex-1-yn-1-yl)-1,1':4',1''-terphenyl **68** was also obtained as a yellow solid (0.417 g, 11%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70 (1H, s), 7.55-7.53 (2H, m), 7.41-7.36 (4H, m), 2.49 (2H, t, *J* = 7.0 Hz), 2.30 (2H, t, *J* = 6.9 Hz), 1.67-1.60 (2H, m), 1.56-1.50 (2H, m), 1.48-1.41 (2H, m), 1.36-1.29 (2H, m), 0.96 (3H, t, *J* = 7.2 Hz), 0.89 (3H, t, *J* = 7.3 Hz).

NMR data is consistent with that reported by Jason Howe.[135]

2',2''',5',5'''-tetra(hex-1-yn-1-yl)-1,1':4',1'':4'',1''':4''',1''''-quinquephenyl 84



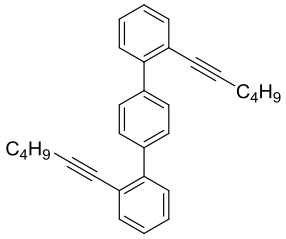
A 50 mL Schlenk flask was charged with 1,4-bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzene (0.104 g, 0.345 mmol) and $Pd(PPh_3)_2Cl_2$ (0.029 g, 0.041 mmol) and flushed with argon for 20 min. A solution of 4-bromo-2,5-di(hex-1-yn-1-yl)-1,1'-biphenyl **83** (0.285 g, 0.725 mmol) in DMF (15 mL) was added, followed by aq. Na_2CO_3 (1 M, 2 mL, 2 mmol). The reaction mixture was stirred at 80 °C for 40 min, cooled to room temperature, diluted with water (50 mL) and the product extracted with diethyl ether (4 x 20 mL). The organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy brown solid. The crude product was purified by column chromatography (SiO_2, 9:1 pet. ether/DCM) to give a yellow solid (0.085 g, 35%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.71 (4H, s), 7.65 (4H, d, *J* = 7.7 Hz), 7.59 (2H, s), 7.55 (2H, s), 7.45-7.42 (4H, m), 7.39-7.35 (2H, m), 2.35 (4H, t, *J* = 6.9 Hz), 2.33 (4H, t, *J* = 6.9 Hz), 1.55-1.44 (8H, m), 1.43-1.30 (8H, m), 0.89 (6H, t, *J* = 7.2 Hz), 0.88 (6H, t, *J* = 7.2 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.08 (2C), 141.73 (2C), 139.84 (2C), 138.85 (2C), 134.12 (2CH), 134.00 (2CH), 129.21 (4CH), 128.88 (4CH), 127.83 (4CH), 127.38 (2CH), 121.80 (2C), 121.68 (2C), 94.81 (2C), 94.72 (2C), 80.00 (2C), 79.93 (2C), 30.50 ($2CH_2$), 30.45 ($2CH_2$), 21.91 ($2CH_2$), 21.84 ($2CH_2$), 19.31 ($2CH_2$), 19.25 ($2CH_2$), 13.60 ($2CH_3$), 13.59 ($2CH_3$).

NMR data is consistent with that reported by Jason Howe.[135]

2,2''-di(hex-1-yn-1-yl)-1,1':4',1''-terphenyl 89



A 100 mL Schlenk flask was charged with 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (0.699 g, 2.12 mmol), K_3PO_4 (2.67 g, 12.6 mmol) and $Pd(PPh_3)_2Cl_2$ (0.143 g, 2.04 mmol) and evacuated/refilled with nitrogen three times. A solution of 1-dibromo-2-hex-1-yn-1-ylbenzene **25** (1.01 g, 4.26 mmol) in distilled THF (30 mL) was added *via* syringe under

nitrogen, followed by degassed water (8 mL). The reaction mixture was stirred at reflux for 1 h, cooled to room temperature, diluted with water (100 mL) and the product extracted with diethyl ether (5 x 30 mL). The organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, pet. ether) to give the titled compound as an orange oil (0.440 g, 53%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.66 (4H, s), 7.54 (2H, d, *J* = 7.6 Hz), 7.42 (2H, d, *J* = 7.6 Hz), 7.37-7.33 (2H, m), 7.30-7.26 (2H, m), 2.33 (4H, t, *J* = 6.9 Hz), 1.53-1.46 (4H, m), 1.41-1.32 (4H, m), 0.87 (6H, t, *J* = 7.3 Hz).

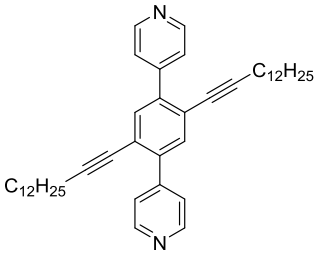
^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.29 (2C), 139.61 (2C), 133.16 (2CH), 129.41 (2CH), 128.68 (4CH), 127.68 (2CH), 126.86 (2CH), 122.34 (2C), 93.49 (2C), 80.20 (2C), 30.50 ($2CH_2$), 21.85 ($2CH_2$), 19.20 ($2CH_2$), 13.59 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3058 (w), 2955 (m), 2928 (m), 2850 (m), 2228 (w), 1474 (s), 1440 (m), 1377 (w), 1006 (m), 838 (s), 753 (s).

HRMS (APPI) *m/z* calc. for $C_{30}H_{30}$ ($M^{+\cdot}$) 390.2342, found 390.2339.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 242 (44000), 280 (20000).

4,4'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)dipyridine 92



A 100 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(tetradec-1-yn-1-yl)benzene **3** (0.600 g, 0.967 mmol), pyridin-4-ylboronic acid hydrate (0.555 g, 3.94 mmol) and $Pd(PPh_3)_2Cl_2$ (0.068 g, 0.097 mmol) and flushed with argon for 0.5 h. DMF (40 mL) and aq. Na_2CO_3 (1 M, 6 mL, 6 mmol) and the reaction mixture was stirred at 80 °C for 40 min, cooled to room temperature and diluted with water (100 mL). The product was extracted with DCM (3 x 40 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, DCM) to give a yellow/orange solid (0.295 g, 49%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.67 (4H, br), 7.54 (4H, d, *J* = 4.9 Hz), 7.52 (2H, s), 2.31 (4H, t, *J* = 7.1 Hz), 1.51-1.44 (4H, m), 1.25 (36H, m), 0.88 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.48 (2CH), 147.08 (2C), 140.35 (2C), 133.72 (2CH), 123.83 (2CH), 121.95 (2C), 96.55 (2C), 78.73 (2C), 31.86 ($2CH_2$), 29.59 ($6CH_2$), 29.46 ($2CH_2$),

29.30 ($2CH_2$), 29.04 ($2CH_2$), 28.83 ($2CH_2$), 28.21 ($2CH_2$), 22.64 ($2CH_2$), 19.48 ($2CH_2$), 14.05 ($2CH_3$).

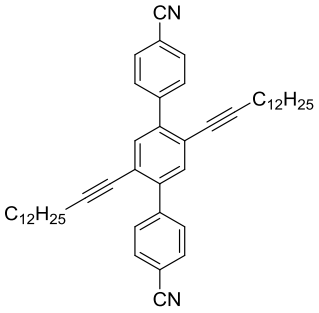
IR (neat) υ_{max}/cm^{-1} 3077 (w), 2951 (m), 2919 (s), 2850 (s), 2230 (w), 1594 (m), 1465 (m), 1088 (m), 1018 (m), 899 (m), 817 (s), 723 (s).

HRMS (APPI) *m/z* calc. for $C_{44}H_{61}N_2$ $(M+H)^+$ 617.4829, found 617.4829.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 257 (65000).

Melting point 75-77 °C.

2',5'-di(tetradec-1-yn-1-yl)-[1,1':4',1''-terphenyl]-4,4''-dicarbonitrile 94



A 50 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(tetradec-1-yn-1-yl)benzene **3** (0.600 g, 0.967 mmol), 4-cyanophenylboronic acid (0.568 g, 3.87 mmol) and $Pd(PPh_3)_2Cl_2$ (0.066 g, 0.094 mmol) and flushed with argon for 0.5 h. DMF (10 mL) and aq. Na_2CO_3 (1 M, 3 mL, 3 mmol) were added and the reaction mixture was stirred at 120 °C for 1 h, cooled to room temperature and diluted with water (50 mL). The product was extracted with diethyl ether (5 x 25 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy brown solid. The crude product was purified by column chromatography (SiO_2, 10-100% DCM in hexane) to give a yellow solid (0.204 g, 32%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.73 (8H, br), 7.50 (2H, s), 2.31 (4H, t, *J* = 7.0 Hz), 1.50-1.44 (4H, m), 1.26 (36H, m), 0.88 (6H, t, *J* = 6.8 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 144.07 (2C), 141.06 (2C), 133.82 (2CH), 131.70 (2CH), 129.86 (2CH), 121.98 (2C), 118.75 (2C), 111.41 (2CN), 96.45 (2C), 78.84 (2C), 31.87 ($2CH_2$), 29.61 ($2CH_2$), 29.59 ($2CH_2$), 29.58 ($2CH_2$), 29.49 ($2CH_2$), 29.29 ($2CH_2$), 29.06 ($2CH_2$), 28.80 ($2CH_2$), 28.22 ($2CH_2$), 22.64 ($2CH_2$), 19.46 ($2CH_2$), 14.06 ($2CH_3$).

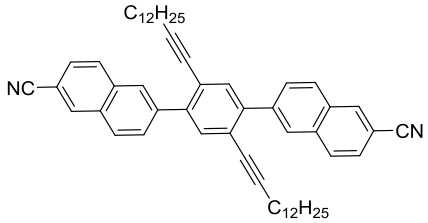
IR (neat) υ_{max}/cm^{-1} 2918 (s), 2848 (s), 2225 (m), 1604 (w), 1485 (m), 1462 (m), 1379 (w), 1019 (w), 929 (m), 839 (s), 725 (m).

HRMS (APPI) *m/z* calc. for $C_{48}H_{60}N_2$ $(M^{+\cdot})$ 664.4751, found 664.4745.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 257 (75000).

Melting point 98-100 °C.

6,6'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)bis(2-naphthonitrile) 98



A 50 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(tetradec-1-yn-1-yl)benzene **3** (0.200 g, 0.322 mmol), 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthonitrile (0.268 g, 0.960 mmol) and $Pd(PPh_3)_2Cl_2$ (0.011 g, 0.016 mmol) and evacuated/refilled with nitrogen three times. DMF (10 mL) and aq. Na_2CO_3 (1 M, 1.5 mL, 1.5 mmol) were added and the reaction mixture was stirred at 80 °C for 0.75 h, cooled to room temperature and diluted with water (80 mL). The product was extracted with diethyl ether (4 x 20 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy brown solid. The crude product was purified by column chromatography (SiO_2, 0-50% DCM in pet. ether) to give a yellow solid (0.112 g, 45%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.29 (2H, s), 8.15 (2H, s), 7.99-7.92 (6H, m), 7.67 (2H, s), 7.66 (2H, dd, *J* = 8.4, 1.5 Hz), 2.29 (4H, t, *J* = 7.0 Hz), 1.42 (4H, quin., *J* = 7.2 Hz), 1.32-1.08 (36H, m), 0.89 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.69 (2C), 140.50 (2C), 134.46 (2C), 134.22 (2CH), 133.88 (2CH), 131.53 (2C), 129.40 (2CH), 129.33 (2CH), 128.19 (2CH), 127.81 (2CH), 126.68 (2CH), 122.24 (2C), 119.23 (2C), 109.51 (2CN), 95.99 (2C), 79.46 (2C), 31.91 ($2CH_2$), 29.66 ($2CH_2$), 29.63 ($2CH_2$), 29.60 ($2CH_2$), 29.44 ($2CH_2$), 29.34 ($2CH_2$), 29.09 ($2CH_2$), 28.80 ($2CH_2$), 28.32 ($2CH_2$), 22.68 ($2CH_2$), 19.55 ($2CH_2$), 14.11 ($2CH_3$).

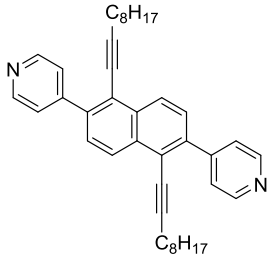
IR (neat) υ_{max}/cm^{-1} 3080 (w), 2918 (s), 2849 (s), 2225 (m), 1470 (s), 1377 (w), 901 (s), 877 (s), 825 (m), 802 (m).

HRMS (APPI) *m/z* calc. for $C_{56}H_{64}N_2$ ($M^{+\cdot}$) 764.5064, found 764.5057.

UV (DCM) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 268 (78000), 288 (43000).

Melting point 97-99 °C.

4,4'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)dipyridine 100



A 250 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (1.02 g, 1.83 mmol), pyridin-4-ylboronic acid hydrate (1.01 g, 7.17 mmol) and $Pd(PPh_3)_2Cl_2$ (0.070 g, 0.010 mmol) and evacuated/refilled with nitrogen three times. DMF (60 mL) and aq. Na_2CO_3 (1 M, 10 mL, 10 mmol) were added and the reaction mixture was stirred at 80 °C for 1.5 h, cooled to room temperature and diluted with water (200 mL). The product was extracted with diethyl ether (5 x 100 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 0-40% ethyl acetate in DCM) to give a yellow solid (0.582 g, 57%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.75 (4H, br), 8.51 (2H, d, *J* = 8.7 Hz), 7.73 (4H, d, *J* = 3.5 Hz), 7.60 (2H, d, *J* = 8.7 Hz), 2.48 (4H, t, *J* = 7.0 Hz), 1.60 (4H, quin, *J* = 7.1 Hz), 1.40 (4H, br), 1.29 (16H, br), 0.89 (6H, t, *J* = 6.6 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.21 (4CH), 148.94 (2C), 139.59 (2C), 133.33 (2C), 127.59 (2CH), 127.11 (2CH), 124.52 (4CH), 120.14 (2C), 100.85 (2C), 77.20 (2C), 31.81 ($2CH_2$), 29.18 ($2CH_2$), 29.06 ($2CH_2$), 28.97 ($2CH_2$), 28.38 ($2CH_2$), 22.63 ($2CH_2$), 19.79 ($2CH_2$), 14.08 ($2CH_3$).

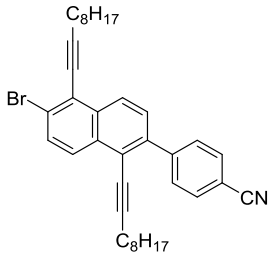
IR (neat) υ_{max}/cm^{-1} 2954 (m), 2919 (s), 2851 (m), 2221 (w), 1596 (m), 1464 (m), 1391 (m), 871 (s), 724 (m).

HRMS (ESI+) *m/z* calc. for $C_{40}H_{57}N_2$ $(M+H)^+$ 555.3734, found 555.3740.

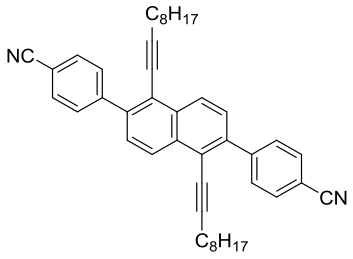
UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 276 (48000).

Melting point 144-146 °C.

4-(6-bromo-1,5-di(dec-1-yn-1-yl)naphthalen-2-yl)benzonitrile 102 and 4,4'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)dibenzonitrile 103



102



103

A 100 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (0.400 g, 0.716 mmol), 4-cyanophenylboronic acid (0.089 g, 0.606 mmol), $Pd(PPh_3)_2Cl_2$ (0.030 g, 0.043 mmol) and K_3PO_4 (0.689 g, 3.25 mmol) and evacuated/refilled with argon three times. THF (20 mL) and water (5 mL) were added and the reaction was refluxed. Extra portions of 4-cyanophenylboronic acid were added after 80 min (0.020 g, 0.136 mmol) and 110 min (0.021 g, 0.143 mmol), and after 0.5 h of the last addition, the reaction was cooled to room temperature. THF was removed under reduced pressure, the reaction mixture was diluted with water (150 mL) and the product extracted with DCM (4 x 40 mL). The organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy brown solid. The crude product was purified by column chromatography (SiO_2, 10-50% DCM in petroleum ether) to give the two titled compounds, **102** as a brown oil (0.113 g, 27%) and **103** as a light brown solid (0.100 g, 23%).

4-(6-bromo-1,5-di(dec-1-yn-1-yl)naphthalen-2-yl)benzonitrile 102

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.35 (1H, d, *J* = 8.8 Hz), 8.24 (1H, d, *J* = 9.0 Hz), 7.79 (2H, d, *J* = 8.2 Hz), 7.75 (2H, d, *J* = 8.2 Hz), 7.73 (1H, d, *J* = 9.0 Hz), 7.51 (1H, d, *J* = 8.8 Hz), 2.65 (2H, t, *J* = 7.0 Hz), 2.45 (2H, t, *J* = 7.0 Hz), 1.80-1.73 (2H, m), 1.63-1.51 (2H, m), 1.42-1.25 (20H, m), 0.92-0.89 (6H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 145.88 (C), 140.22 (C), 133.99 (C), 132.36 (C), 131.68 (2CH), 130.77 (CH), 130.38 (2CH), 128.05 (CH), 127.59 (CH), 126.54 (CH), 125.38 (C), 123.44 (C), 120.27 (C), 118.92 (C), 111.17 (CN), 101.80 (C), 100.76 (C), 77.53 (C), 77.20 (C), 31.85 (CH_2), 31.82 (CH_2), 29.23 ($2CH_2$), 29.12 (CH_2), 29.10 (CH_2), 28.99 (CH_2), 28.94 (CH_2), 28.67 (CH_2), 28.38 (CH_2), 22.66 (CH_2), 22.64 (CH_2), 19.95 (CH_2), 19.74 (CH_2), 14.09 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2922 (s), 2851 (s), 2225 (m), 1601 (m), 1463 (m), 1394 (m), 876 (m), 849 (m), 818 (s), 723 (m).

HRMS (APPI) *m/z* calc. for $C_{37}H_{42}BrN$ ($M^{+\cdot}$) 579.24951, found 579.24782.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 263 (37000), 283 (31000), 292 (33000).

4,4'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)dibenzonitrile 103

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.48 (2H, d, *J* = 8.7 Hz), 7.82 (4H, d, *J* = 8.2 Hz), 7.76 (4H, d, *J* = 8.2 Hz), 7.57 (2H, d, *J* = 8.7 Hz), 2.47 (4H, t, *J* = 7.0 Hz), 1.29 (24H, br), 0.90 (6H, t, *J* = 6.7 Hz).

^{13}C-NMR (400 MHz, $CDCl_3$) δ 145.76 (2C), 140.57 (2C), 133.20 (2C), 131.70 (4CH), 130.43 (4CH), 127.83 (2CH), 127.03 (2CH), 120.10 (2C), 118.92 (2C), 111.17 (2CN), 100.67 (2C), 77.14 (2C), 31.82 ($2CH_2$), 29.22 ($2CH_2$), 29.10 ($2CH_2$), 28.94 ($2CH_2$), 28.42 ($2CH_2$), 22.64 ($2CH_2$), 19.78 ($2CH_2$), 14.08 ($2CH_3$).

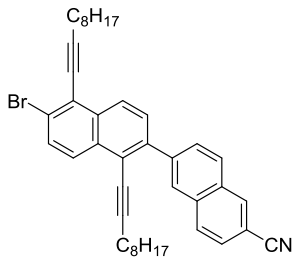
IR (neat) υ_{max}/cm^{-1} 2953 (m), 2917 (s), 2851 (m), 2224 (m), 1604 (m), 1467 (m), 1386 (m), 1019 (w), 845 (m), 821 (s), 723 (m).

HRMS (APPI) *m/z* calc. for $C_{44}H_{46}N_2$ ($M^{+\cdot}$) 602.36555, found 602.36506.

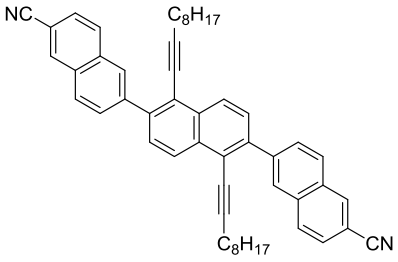
UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 292 (74000).

Melting point 175-177 °C.

6'-bromo-1',5'-di(dec-1-yn-1-yl)-[2,2'-binaphthalene]-6-carbonitrile 107 and 1',5'-di(dec-1-yn-1-yl)-[2,2':6',2''-terbenzobenzene]-6,6''-dicarbonitrile 108



107



108

A 50 mL Schlenk was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (0.595 g, 1.07 mmol), 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthonitrile (0.248 g, 0.888 mmol) and $Pd(PPh_3)_2Cl_2$ (0.035 g, 0.050 mmol) and evacuated/refilled with nitrogen three times. DMF (12 mL) and aq. Na_2CO_3 (1 M, 3 mL, 3 mmol) were added and the reaction mixture was stirred at 85 °C for 0.75 h, cooled to room temperature and diluted with water (80 mL). The product was extracted with diethyl ether (5 x 25 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy brown solid. The crude product was purified by column chromatography (SiO_2, 0-50% DCM in pet. ether) to give recovered starting material (0.212 g, 36%), **107** as a brown oil (0.088 g, 13%) and **108** as a yellow solid (0.123 g, 16%).

6'-bromo-1',5'-di(dec-1-yn-1-yl)-[2,2'-binaphthalene]-6-carbonitrile 107

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.38 (1H, d, *J* = 8.7 Hz), 8.30 (1H, s), 8.28 (1H, d, *J* = 9.2 Hz), 8.17 (1H, s), 7.99-7.97 (3H, m), 7.74 (1H, d, *J* = 9.0 Hz), 7.67-7.63 (2H, m), 2.66 (2H, t, *J* = 7.0 Hz), 2.41 (2H, t, *J* = 7.0 Hz), 1.81-1.73 (2H, m), 1.64-1.56 (2H, m), 1.50-1.43 (2H, m), 1.42-1.08 (18H, m), 0.92-0.86 (6H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.80 (C), 141.13 (C), 134.40 (C), 133.84 (CH), 133.83 (C), 132.41 (C), 131.40 (C), 130.61 (CH), 129.72 (CH), 129.35 (CH), 128.64 (CH), 128.62 (CH), 127.73 (CH), 127.56 (CH), 126.60 (CH), 126.42 (CH), 125.14 (C), 123.37 (C), 120.33 (C), 119.24 (C), 109.43 (CN), 101.67 (C), 100.38 (C), 77.61 (C), 77.21 (C), 31.84 (CH_2), 31.79 (CH_2), 29.23 (CH_2), 29.12 (CH_2), 29.09 (CH_2), 29.06 (CH_2), 28.98 (CH_2), 28.83 (CH_2), 28.67 (CH_2), 28.40 (CH_2), 22.66 (CH_2), 22.64 (CH_2), 19.95 (CH_2), 19.75 (CH_2), 14.10 (CH_3), 14.08 (CH_3).

IR (neat) υ_{max}/cm^{-1} 2953 (m), 2920 (s), 2852 (s), 2221 (m), 1568 (w), 1454 (m), 1377 (w), 895 (m), 815 (s), 724 (m).

HRMS (APPI) *m/z* calc. for $C_{41}H_{44}BrN$ ($M^{+\cdot}$) 629.2652, found 629.2655.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 265 (43000), 276 (35000).

1',5'-di(dec-1-yn-1-yl)-[2,2':6',2''-terbenzobenzene]-6,6''-dicarbonitrile 108

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.55 (2H, d, *J* = 8.6 Hz), 8.31 (2H, s), 8.23 (2H, s), 8.03-7.98 (6H, m), 7.71 (2H, d, *J* = 8.5 Hz), 7.67 (2H, d, *J* = 8.5 Hz), 2.45 (4H, t, *J* = 6.7 Hz), 1.54-1.47 (4H, m), 1.30-1.10 (20H, m), 0.89 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.02 (2C), 141.34 (2C), 134.47 (2C), 133.88 (2CH), 133.16 (2C), 131.44 (2C), 129.86 (2CH), 129.40 (2CH), 128.69 (2CH), 128.35 (2CH), 127.75 (2CH), 126.91 (2CH), 126.62 (2CH), 120.16 (2C), 119.27 (2C), 109.42 (2CN), 100.20 (2C), 77.63 (2C), 31.80 ($2CH_2$), 29.11 ($2CH_2$), 29.09 ($2CH_2$), 28.87 ($2CH_2$), 28.48 ($2CH_2$), 22.64 ($2CH_2$), 19.81 ($2CH_2$), 14.09 ($2CH_3$).

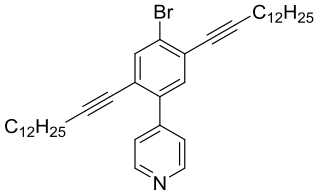
IR (neat) υ_{max}/cm^{-1} 2957 (m), 2919 (s), 2847 (m), 2226 (m), 1624 (m), 1468 (m), 1455 (m), 1372 (w), 899 (s), 890 (s), 821 (s), 769 (m), 723 (m), 672 (s).

HRMS (APPI) *m/z* calc. for $C_{52}H_{50}N_2$ ($M^{+\cdot}$) 702.3969, found 702.3978.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 279 (82000), 312 (59000).

Melting point 184-186 °C.

4-(4-bromo-2,5-di(tetradec-1-yn-1-yl)phenyl)pyridine 110



A 25 mL Schlenk flask was charged with 1-bromo-4-iodo-2,5-di(tetradec-1-yn-1-yl)benzene **34** (0.350 g, 0.524 mmol), pyridin-4-ylboronic acid hydrate (0.073 g, 0.521 mmol) and $Pd(PPh_3)_2Cl_2$ (0.007 g, 0.010 mmol) and evacuated/refilled with nitrogen three times. DMF (10 mL) and aq. Na_2CO_3 (3 mL, 3 mmol) were added and the reaction was stirred at 80 °C for 1 h, cooled to room temperature and diluted with water (60 mL). The product was extracted with diethyl ether (5 x 15 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 0-80% DCM in pet. ether) to give an orange oil (0.233 g, 72%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.65 (2H, d, *J* = 4.9 Hz), 7.73 (1H, s), 7.49-7.47 (2H, m), 7.39 (1H, s), 2.48 (2H, t, *J* = 7.0 Hz), 2.30 (2H, t, *J* = 7.0 Hz), 1.67-1.60 (2H, m), 1.52-1.44 (4H, m), 1.27 (34H, br), 0.88 (6H, t, *J* = 6.8 Hz).

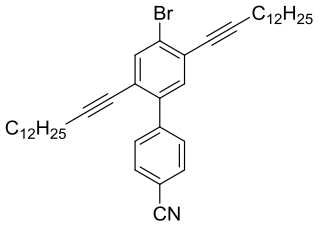
^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.48 (2CH), 146.89 (C), 139.40 (C), 136.52 (CH), 133.22 (CH), 125.78 (C), 124.95 (C), 123.73 (2CH), 122.70 (C), 97.66 (C), 97.11 (C), 78.90 (C), 78.05 (C), 31.90 ($2CH_2$), 29.62 ($4CH_2$), 29.60 ($2CH_2$), 29.51 (CH_2), 29.48 (CH_2), 29.33 ($2CH_2$), 29.10 (CH_2), 29.05 (CH_2), 28.85 (CH_2), 28.83 (CH_2), 28.44 (CH_2), 28.16 (CH_2), 22.67 ($2CH_2$), 19.63 (CH_2), 19.48 (CH_2), 14.08 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2921 (s), 2851 (s), 2231 (w), 1598 (m), 1466 (m), 1373 (w), 1066 (w), 824 (m), 720 (m).

HRMS (APPI) *m/z* calc. for $C_{39}H_{57}BrN$ $(M+H)^+$ 618.3669, found 618.3659.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 257 (27000), 253 (17000).

4'-bromo-2',5'-di(tetradec-1-yn-1-yl)-[1,1'-biphenyl]-4-carbonitrile 111



A 50 mL Schlenk flask was charged with 1-bromo-4-iodo-2,5-di(tetradec-1-yn-1-yl)benzene **34** (0.500 g, 0.749 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (0.171

g, 0.746 mmol) and $Pd(PPh_3)_2Cl_2$ (0.029 g, 0.041 mmol) and evacuated/refilled with nitrogen three times. DMF (18 mL) and aq. Na_2CO_3 (1 M, 4 mL, 4 mmol) were added and the reaction mixture was stirred at 80 °C for 1 h, cooled to room temperature and diluted with water (70 mL). The product was extracted with diethyl ether (5 x 25 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 0-20% DCM in pet. ether) to give an orange oil (0.310 g, 64%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.73 (1H, s), 7.69 (2H, d, *J* = 8.4 Hz), 7.65 (2H, d, *J* = 8.4 Hz), 7.37 (1H, s), 2.48 (2H, t, *J* = 6.9 Hz), 2.29 (2H, t, *J* = 7.0 Hz), 1.67-1.61 (2H, m), 1.52-1.42 (4H, m), 1.27 (34H, br), 0.89 (6H, t, *J* = 6.7 Hz).

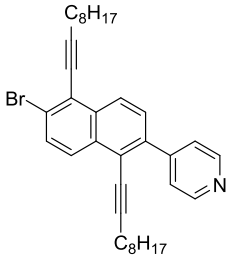
^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.85 (C), 140.29 (C), 136.48 (CH), 133.34 (CH), 131.71 (2CH), 129.79 (2CH), 125.76 (C), 124.77 (C), 122.74 (C), 118.77 (C), 111.41 (CN), 97.66 (C), 97.00 (C), 78.90 (C), 78.14 (C), 31.90 ($2CH_2$), 29.64-29.61 ($6CH_2$), 29.52 ($2CH_2$), 29.34 ($2CH_2$), 29.10 (CH_2), 29.08 (CH_2), 28.85 (CH_2), 28.81 (CH_2), 28.44 (CH_2), 28.18 (CH_2), 22.67 ($2CH_2$), 19.63 (CH_2), 19.46 (CH_2), 14.10 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2957 (m), 2917 (s), 2849 (s), 2225 (m), 1606 (w), 1470 (s), 1373 (m), 1060 (w), 879 (m), 846 (s), 719 (m).

HRMS (APPI) *m/z* calc. for $C_{41}H_{56}BrN$ ($M^{+\cdot}$) 641.3591, found 641.3603.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 269 (59000).

4-(6-bromo-1,5-di(dec-1-yn-1-yl)naphthalen-2-yl)pyridine 112



A 50 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (0.400 g, 0.716 mmol), pyridin-4-ylboronic acid hydrate (0.081 g, 0.575 mmol) and $Pd(PPh_3)_2Cl_2$ (0.027 g, 0.038 mmol) and evacuated/refilled with nitrogen three times. DMF (12 mL) and aq. Na_2CO_3 (1 M, 3 mL, 3 mmol) were added and the reaction mixture was stirred at 85 °C for 1 h, cooled to room temperature and diluted with water (80 mL). The product extracted with diethyl ether (5 x 20 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy brown solid. The crude product was purified by column chromatography (SiO_2, pet. ether then 0-20% EtOAc in DCM)

to give **112** as a dark orange oil (0.042 g, 11%) and **100** as a yellow solid (0.046 g, 12%). Starting material was also recovered by column chromatography, eluting in 100% pet. ether to give 0.168 g (42%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.70 (2H, d, *J* = 5.7 Hz), 8.35 (1H, d, *J* = 8.7 Hz), 8.24 (1H, d, *J* = 9.0 Hz), 7.73 (1H, d, *J* = 9.0 Hz), 7.60 (2H, d, *J* = 5.7 Hz), 7.52 (1H, d, *J* = 8.7 Hz), 2.65 (2H, t, *J* = 7.0 Hz), 2.45 (2H, t, *J* = 7.0 Hz), 1.79-1.72 (2H, m), 1.62-1.53 (4H, m), 1.40-1.26 (18H, m), 0.91-0.88 (6H, m).

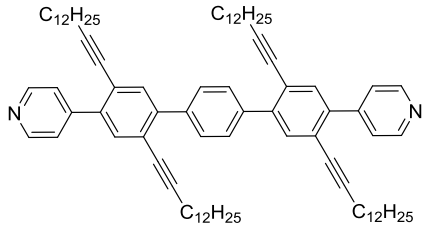
^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.42 (2CH), 148.65 (C), 139.27 (C), 134.08 (C), 132.33 (C), 130.71 (CH), 127.86 (CH), 127.62 (CH), 126.55 (CH), 125.39 (C), 124.35 (2CH), 123.41 (C), 120.27 (C), 101.78 (C), 100.87 (C), 77.52 (C), 76.81 (C), 31.84 (CH_2), 31.81 (CH_2), 29.23 (CH_2), 29.17 (CH_2), 29.11 (CH_2), 29.05 (CH_2), 28.97 (CH_2), 28.95 (CH_2), 28.65 (CH_2), 28.35 (CH_2), 22.65 (CH_2), 22.64 (CH_2), 19.93 (CH_2), 19.74 (CH_2), 14.08 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2954 (m), 2922 (s), 2852 (m), 2222 (w), 1596 (m), 1465 (m), 1439 (m), 1374 (w), 812 (s), 725 (s).

HRMS (APPI) *m/z* calc. for $C_{35}H_{42}BrN$ ($M^{+\cdot}$) 555.2495, found 555.2482.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 260 (35000), 277 (27000).

4,4'-(2,2'',5,5''-tetrakis(tetradec-1-yn-1-yl)-[1,1':4',1''-terphenyl]-4,4''-diyl)dipyridine 113



A 100 mL Schlenk flask was charged with 1,4-bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzene **75** (0.166 g, 0.550 mmol), $Pd(PPh_3)_2Cl_2$ (0.038 g, 0.054 mmol), K_3PO_4 (0.467 g, 2.20 mmol) and flushed with argon for 0.5 h. A solution of 4-(4-bromo-2,5-di(tetradec-1-yn-1-yl)phenyl)pyridine **110** (0.700 g, 1.13 mmol) in THF (20 mL) was added, followed by water (5 mL). The reaction mixture was refluxed for 18 h and cooled to room temperature. THF was removed under reduced pressure, water (100 mL) was added and the product was extracted with DCM (4 x 40 mL). The organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy brown solid. The crude product was purified by column chromatography (SiO_2, 0-10% EtOAc in DCM) to give a yellow solid (0.366 g, 58%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.68 (4H, d, *J* = 6.0 Hz), 7.71 (4H, s), 7.61 (2H, s), 7.59-7.57 (4H, m), 7.54 (2H, s), 2.34 (4H, t, *J* = 6.9 Hz), 2.33 (4H, t, *J* = 6.9 Hz), 1.55-1.47 (8H, m), 1.35-1.21 (72H, m), 0.90-0.85 (12H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.43 (4CH), 147.50 (2C), 142.87 (2C), 139.15 (2C), 138.74 (2C), 134.24 (2CH), 133.74 (2CH), 128.72 (4CH), 123.96 (4CH), 122.10 (2C), 121.66 (2C), 95.93 (2C), 95.65 (2C), 79.62 (2C), 79.15 (2C), 31.92 ($4CH_2$), 29.95 ($12CH_2$), 29.55 ($2CH_2$), 29.52 ($2CH_2$), 29.34 ($4CH_2$), 29.18 ($2CH_2$), 29.11 ($2CH_2$), 28.91 ($4CH_2$), 28.41 ($2CH_2$), 28.34 ($2CH_2$), 22.68 ($4CH_2$), 19.64 ($2CH_2$), 19.57 ($2CH_2$), 14.10 ($4CH_3$).

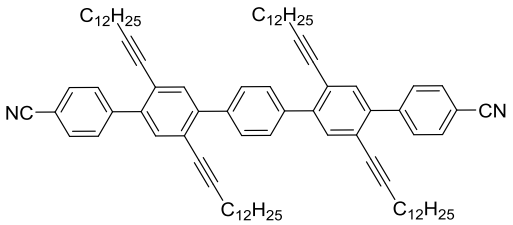
IR (neat) υ_{max}/cm^{-1} 2952 (w), 2916 (s), 2848 (s), 2230 (w), 1595 (m), 1467 (m), 1378 (w), 1090 (s), 1019 (s), 798 (s), 720 (m).

LRMS *m/z* 1152.9 ($M^{+\cdot}$), 1153.9 $(M+H)^+$.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 274 (78000), 288 (43000).

Melting point 80-82 °C.

4,4'-(2,2'',5,5''-tetrakis(tetradec-1-yn-1-yl)-[1,1':4',1''-terphenyl]-4,4''-diyl)di-4-carbonitrile 115



A 50 mL Schlenk flask was charged with 4'-bromo-2',5'-di(tetradec-1-yn-1-yl)-[1,1'-biphenyl]-4-carbonitrile **111** (0.230 g, 0.358 mmol), 1,4-bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzene **75** (0.054 g, 0.179 mmol) and $Pd(PPh_3)_2Cl_2$ (0.011 g, 0.016 mmol) and evacuated/refilled with nitrogen three times. DMF (8 mL) and aq. Na_2CO_3 (1 M, 2 mL, 2 mmol) were added and the reaction mixture was stirred 80 °C for 2 h, cooled to room temperature and diluted with water (50 mL). The product was extracted with diethyl ether (4 x 20 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 30-70% DCM in pet. ether) to give an orange oil (0.081 g, 38%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.78-7.70 (12H, m), 7.60 (2H, s), 7.52 (2H, s), 2.35-2.30 (8H, m), 1.54-1.44 (8H, m), 1.34-1.20 (72H, m), 0.90-0.84 (12H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.52 (2C), 142.69 (2C), 140.06 (2C), 138.72 (2C), 134.21 (2CH), 133.86 (2CH), 131.68 (4CH), 129.95 (4CH), 128.72 (4CH), 122.08 (2C), 121.70 (2C),

118.93 (2C), 111.17 (2CN), 95.81 (2C), 95.64 (2C), 79.62 (2C), 79.25 (2C), 31.91 ($4CH_2$), 29.64 ($12CH_2$), 29.55 ($4CH_2$), 29.34 ($4CH_2$), 29.17 ($2CH_2$), 29.13 ($2CH_2$), 28.90 ($2CH_2$), 28.88 ($2CH_2$), 28.41 ($2CH_2$), 28.35 ($2CH_2$), 22.67 ($4CH_2$), 19.63 ($2CH_2$), 19.54 ($2CH_2$), 14.09 ($4CH_3$).

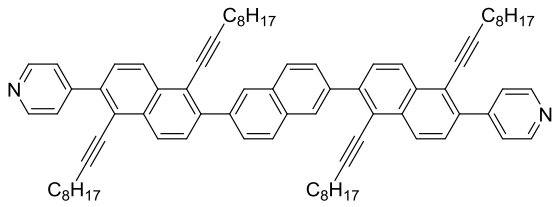
IR (neat) υ_{max}/cm^{-1} 2918 (s), 2849 (s), 2227 (w), 1607 (w), 1468 (m), 1378 (w), 1018 (w), 837 (s), 719 (m).

LRMS (APPI) *m/z* 1200.87 ($M^{+\cdot}$).

UV (DCM) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 277 (115000).

Melting point 81-83 °C.

4,4'-(1,1'',5,5''-tetra(dec-1-yn-1-yl)-[2,2':6',2''-ternaphthalene]-6,6''-diyl)dipyridine 117



A 25 mL Schlenk flask was charged with 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (0.012 g, 0.032 mmol) and $Pd(PPh_3)_2Cl_2$ (0.004 g, 0.006 mmol) and evacuated/refilled with nitrogen three times. A solution of 4-(6-bromo-1,5-di(dec-1-yn-1-yl)naphthalen-2-yl)pyridine **112** (0.037 g, 0.066 mmol) in DMF (4 mL) was added followed by aq. Na_2CO_3 (1 M, 0.4 mL, 0.4 mmol). The reaction mixture was stirred at 80 °C for 0.5 h, cooled to room temperature and diluted with water (20 mL). The product was extracted with diethyl ether (4 x 10 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a light brown solid. The crude product was purified by column chromatography (SiO_2, 0-10% EtOAc in DCM) to give a yellow solid (0.017 g, 49%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.73 (4H, d, *J* = 5.7 Hz), 8.56 (2H, d, *J* = 8.8 Hz), 8.53 (2H, d, *J* = 8.8 Hz), 8.25 (2H, s), 8.01 (2H, d, *J* = 8.6 Hz), 7.94 (2H, d, *J* = 8.6 Hz), 7.78 (2H, d, *J* = 8.7 Hz), 7.68 (4H, d, *J* = 5.9 Hz), 7.60 (2H, d, *J* = 8.7 Hz), 2.50 (4H, t, *J* = 7.0 Hz), 2.47 (4H, t, *J* = 7.0 Hz), 1.66-1.54 (8H, m), 1.45-1.19 (40H, m), 0.90 (6H, t, *J* = 6.7 Hz), 0.84 (6H, t, *J* = 6.8 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.44 (4CH), 148.99 (2C), 142.61 (2C), 139.12 (2C), 138.84 (2C), 133.57 (2C), 132.86 (2C), 132.47 (2C), 128.96 (2CH), 128.48 (2CH), 128.21 (2CH), 127.62 (2CH), 127.34 (2CH), 127.07 (2CH), 126.76 (2CH), 124.50 (4CH), 120.00 (2C), 119.87 (2C), 31.84 ($4CH_2$), 29.21 ($2CH_2$), 29.18 ($2CH_2$), 29.13 ($2CH_2$), 29.11 ($2CH_2$), 29.00

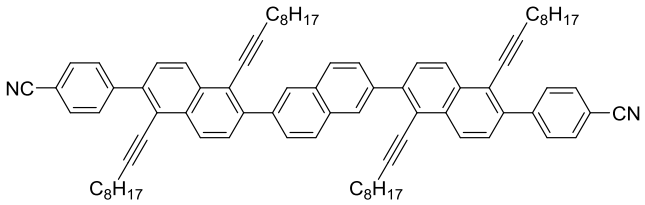
(4CH_2), 28.59 (2CH_2), 28.45 (2CH_2), 22.67 (2CH_2), 22.65 (2CH_2), 19.90 (2CH_2), 19.84 (2CH_2), 14.11 (2CH_3), 14.08 (2CH_3).

IR (neat) υ_{max}/cm^{-1} 2954 (m), 2922 (s), 2851 (m), 2217 (w), 1603 (m), 1464 (m), 1376 (w), 1029 (m), 889 (m), 816 (s), 724 (m).

LRMS (APPI) *m/z* 1078.7 ($M^{+\cdot}$), 1079.7 $(M+H)^+$.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 283 (68000), 316 (34000).

4,4'-(1,1'',5,5''-tetra(dec-1-yn-1-yl)-[2,2':6',2''-ternaphthalene]-6,6''-diyl)dibenzonitrile 119



A 50 mL Schlenk flask was charged with 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (0.025 g, 0.066 mmol) and $Pd(PPh_3)_2Cl_2$ (0.005 g, 0.007 mmol) and evacuated/refilled with argon three times. A solution of 4-(6-bromo-1,5-di(dec-1-yn-1-yl)naphthalen-2-yl)benzonitrile **102** (0.079 g, 0.136 mmol) in DMF (10 mL) was added, followed by aq. Na_2CO_3 (1 M, 0.8 mL, 0.8 mmol). The reaction mixture was stirred at 80 °C for 1 h, cooled to room temperature and diluted with water (80 mL). The product was extracted with diethyl ether (6 x 20 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 0-50% DCM in pet ether) to give a yellow solid (0.035 g, 47%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.56 (2H, d, *J* = 8.8 Hz), 8.52 (2H, d, *J* = 8.8 Hz), 8.25 (2H, s), 8.01 (2H, d, *J* = 8.5 Hz), 7.94 (2H, d, *J* = 8.5 Hz), 7.85 (4H, d, *J* = 8.2 Hz), 7.79 (2H, d, *J* = 8.7 Hz), 7.78 (4H, d, *J* = 8.2 Hz), 7.58 (2H, d, *J* = 8.7 Hz), 2.49 (4H, t, *J* = 7.3 Hz), 2.48 (4H, t, *J* = 7.3 Hz), 1.63-1.54 (8H, m), 1.42-1.19 (40H, m), 0.92 (6H, t, *J* = 7.0 Hz), 0.84 (6H, t, *J* = 6.8 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.01 (2C), 142.57 (2C), 140.04 (2C), 138.82 (2C), 133.44 (2C), 132.84 (2C), 132.46 (2C), 131.67 (4CH), 130.48 (4CH), 128.99 (2CH), 128.46 (2CH), 128.19 (2CH), 127.61 (2CH), 127.51 (2CH), 127.03 (2CH), 126.71 (2CH), 119.97 (2C), 119.86 (2C), 119.03 (2C), 110.99 (2CN), 100.34 (2C), 99.89 (2C), 77.86 (2C), 77.20 (2C), 31.85 (2CH_2), 31.83 (2CH_2), 29.24 (2CH_2), 29.17 (2CH_2), 29.13 (4CH_2), 28.99 (2CH_2), 28.97 (2CH_2), 28.59 (2CH_2), 28.47 (2CH_2), 22.67 (2CH_2), 22.64 (2CH_2), 19.89 (2CH_2), 19.81 (2CH_2), 14.11 (2CH_3), 14.08 (2CH_3).

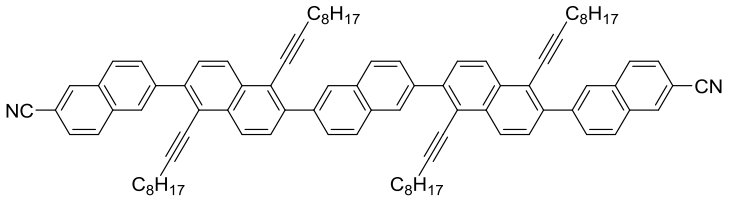
IR (neat) υ_{max}/cm^{-1} 2922 (s), 2851 (s), 2227 (m), 1604 (m), 1464 (m), 1387 (m), 1018 (w), 828 (m), 816 (s), 723 (m).

LRMS (APPI) *m/z* 1126.6 ($M^{+\cdot}$).

UV(DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 285 (53000), 296 (52000), 317 (29000).

Melting point 200-201 °C.

1',1''',5',5'''-tetra(dec-1-yn-1-yl)-[2,2':6',2'':6'',2''':6''',2''''-quinquebenzobenzene]-6,6''''-dicarbonitrile 121



A 25 mL Schlenk flask was charged with 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (0.016 g, 0.042 mmol), $Pd(PPh_3)_2Cl_2$ (0.004 g, 0.006 mmol) and K_3PO_4 (0.073 g, 0.344 mmol) and evacuated/refilled with nitrogen three times. A solution of 6'-bromo-1',5'-di(dec-1-yn-1-yl)-[2,2'-binaphthalene]-6-carbonitrile **107** (0.057 g, 0.090 mmol) in distilled THF (4 mL) was added, followed by water (1 mL). The reaction mixture was refluxed for 1 h and cooled to room temperature. THF was removed under reduced pressure, water (20 mL) was added and the product was extracted with chloroform (5 x 10 mL). The organic layers were combined, washed (water) and concentrated under reduced pressure to give a waxy brown solid. The crude product was purified by column chromatography (SiO_2, 20-50% DCM in pet. ether) to give a yellow solid (0.023 g, 44%).

^{1}H-NMR (500 MHz, tol-d_8, 353 K) δ 8.81 (2H, d, *J* = 8.6 Hz), 8.78 (2H, d, *J* = 8.6 Hz), 8.29 (2H, s), 7.99-7.96 (6H, m), 7.84 (2H, dd, *J* = 8.4, 1.2 Hz), 7.77 (2H, d, *J* = 8.7 Hz), 7.75 (2H, s), 7.59 (2H, d, *J* = 8.6 Hz), 7.55 (2H, d, *J* = 8.5 Hz), 7.50 (2H, d, *J* = 8.5 Hz), 7.22 (2H, dd, *J* = 8.4, 1.2 Hz), 2.36 (4H, t, *J* = 7.0 Hz), 2.29 (4H, t, *J* = 6.9 Hz), 1.55-1.48 (4H, m), 1.44-1.38 (4H, m), 1.36-1.18 (32H, m), 1.11 (8H, br), 0.91 (6H, t, *J* = 7.2 Hz), 0.87 (6H, t, *J* = 7.0 Hz).

^{13}C-NMR (125 MHz, tol-d_8, 353 K) δ 143.72 (2C), 142.91 (2C), 142.32 (2C), 140.12 (2C), 135.12 (2C), 134.57 (2C), 134.23 (2C), 134.11 (2CH), 133.69 (2C), 132.36 (2C), 130.28 (2CH), 129.71 (2CH), 129.67 (2CH), 129.48 (2CH), 129.45 (2CH), 129.04 (2CH), 128.85 (2CH), 128.56 (2CH), 128.34 (2CH), 127.84 (2CH), 127.57 (2CH), 127.19 (2CH), 121.36 (2C), 121.25 (2C), 119.18 (2C), 111.02 (2CN), 100.58 (2C), 100.49 (2C), 79.44 (2C), 79.19 (2C), 32.61 ($2CH_2$), 32.57 ($2CH_2$), 29.92 ($2CH_2$), 29.89 ($2CH_2$), 29.84 ($2CH_2$), 29.82 ($2CH_2$),

29.76 ($2CH_2$), 29.63 ($2CH_2$), 29.53 ($2CH_2$), 29.42 ($2CH_2$), 23.33 ($4CH_2$), 20.56 ($4CH_2$), 14.45 ($4CH_3$).

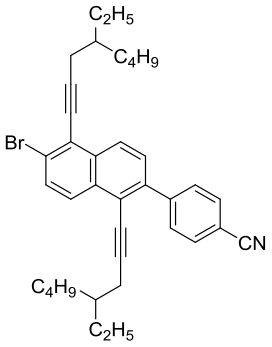
IR (neat) υ_{max}/cm^{-1} 2956 (m), 2924 (m), 2853 (m), 2228 (w), 1464 (m), 1088 (s), 1019 (s), 795 (s), 720 (m).

LRMS (APPI) *m/z* 1226.8 ($M^{+\cdot}$).

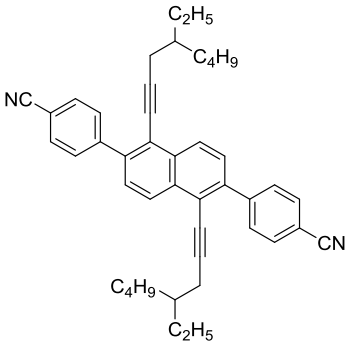
UV (DCM) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 281 (67000), 314 (45000).

Melting point 193-196 °C.

4-(6-bromo-1,5-bis(4-ethyloct-1-yn-1-yl)naphthalen-2-yl)benzonitrile 125 & 4,4'-(1,5-bis(4-ethyloct-1-yn-1-yl)naphthalene-2,6-diyl)dibenzonitrile 126



125



126

A 50 mL Schlenk flask was charged with 2,6-dibromo-1,5-bis(4-ethyloct-1-yn-1-yl)naphthalene **124** (2.54 g, 84% purity by mass, 2.13 g, 3.82 mmol), 4-cyanophenylboronic acid (0.518 g, 3.53 mmol), $Pd(PPh_3)_2Cl_2$ (0.127 g, 0.181 mmol) and Na_2CO_3 (1.68 g, 15.9 mmol) and evacuated/refilled with nitrogen three times. DMF (20 mL) and water (5 mL) were added and the reaction mixture was stirred at 80 °C for 1 h, cooled to room temperature and diluted with water (200 mL). The product was extracted with diethyl ether (5 x 40 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, 0-50% DCM in pet ether) to give **125** as an orange oil (0.318 g, 14%) and **126** (0.278 g, 12%) as a yellow solid. Starting material was recovered in 49% yield.

4-(6-bromo-1,5-bis(4-ethyloct-1-yn-1-yl)naphthalen-2-yl)benzonitrile 125

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.35 (1H, d, *J* = 8.8 Hz), 8.24 (1H, d, *J* = 9.0 Hz), 7.76-7.74 (4H, m), 7.74 (1H, d, *J* = 9.0 Hz), 7.50 (1H, d, *J* = 8.8 Hz), 2.65 (2H, d, *J* = 5.6 Hz), 2.44 (2H, dd, *J* = 5.7 Hz), 1.70-1.64 (2H, m), 1.61-1.23 (16H, m), 0.99 (3H, t, *J* = 7.3 Hz), 0.95-0.85 (9H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 145.82 (C), 140.29 (C), 134.06 (C), 132.44 (C), 131.74 (2CH), 130.79 (CH), 130.38 (2CH), 128.05 (CH), 127.52 (CH), 126.46 (CH), 125.40 (C), 123.55 (C), 120.39 (C), 118.93 (C), 111.09 (CN), 100.48 (C), 99.46 (C), 78.30 (C), 77.69 (C), 38.91 (CH), 38.71 (CH), 33.00 (CH_2), 32.90 (CH_2), 29.13 (CH_2), 29.05 (CH_2), 26.29 (CH_2), 26.11 (CH_2), 23.69 (CH_2), 23.50 (CH_2), 23.02 (CH_2), 22.94 (CH_2), 14.15 (CH_3), 14.11 (CH_3), 11.26 (CH_3), 11.15 (CH_3).

IR (neat) υ_{max}/cm^{-1} 2956 (s), 2924 (s), 2871 (m), 2857 (m), 2227 (m), 1606 (w), 1456 (m), 1378 (m), 1019 (w), 846 (m), 817 (s), 731 (m).

HRMS (APPI) *m/z* calc. for $C_{37}H_{42}BrN$ ($M^{+\cdot}$) 579.2496, found 579.2481.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 254 (16000), 261 (17000), 279 (14000), 292 (15000).

4,4'-(1,5-bis(4-ethyloct-1-yn-1-yl)naphthalene-2,6-diyl)dibenzonitrile 126

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.48 (2H, d, *J* = 8.7 Hz), 7.80 (4H, d, *J* = 8.3 Hz), 7.76 (4H, d, *J* = 8.3 Hz), 7.56 (2H, d, *J* = 8.7 Hz), 2.47 (4H, d, J = 5.3 Hz), 1.53-1.46 (2H, m), 1.41-1.25 (16H, m), 0.91 (6H, t, *J* = 6.5 Hz), 0.88 (6H, t, *J* = 7.4 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 145.90 (2C), 140.62 (2C), 133.30 (2C), 131.74 (4CH), 130.42 (4CH), 127.83 (2CH), 126.92 (2CH), 120.23 (2C), 118.94 (2C), 111.10 (2CN), 99.36 (2C), 77.87 (2C), 38.73 (2CH), 32.91 ($2CH_2$), 29.05 ($2CH_2$), 26.13 ($2CH_2$), 23.53 ($2CH_2$), 22.95 ($2CH_2$), 14.12 ($2CH_3$), 11.17 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2959 (m), 2926 (m), 2872 (m), 2858 (m), 2226 (m), 1604 (m), 1461 (m), 1385 (m), 1019 (w), 891 (m), 841 (m), 823 (s), 728 (m).

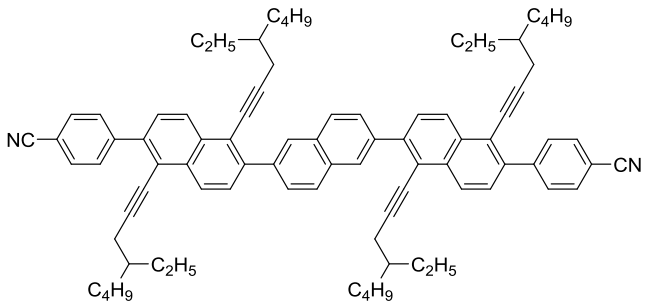
LRMS (APPI) *m/z* 602.3 ($M^{+\cdot}$).

HRMS (APPI) *m/z* calc. for $C_{44}H_{46}N_2$ ($M^{+\cdot}$) 602.36555, found 602.36635.

UV (DCM) λ_{max}/nm (ε / dm^3 mol^{-1} cm^{-1}) 291 (55000).

Melting Point 157-159 °C.

4,4'-(1,1'',5,5''-tetrakis(4-ethyloct-1-yn-1-yl)-[2,2':6',2''-ternaphthalene]-6,6''-diyl)dibenzonitrile 128



A 50 mL Schlenk flask was charged with 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (0.032 g, 0.084 mmol) and $Pd(PPh_3)_2Cl_2$ (0.008 g, 0.011 mmol) and evacuated/refilled with nitrogen three times. A solution of 4-(6-bromo-1,5-bis(4-ethyloct-1-yn-1-yl)naphthalen-2-yl)benzonitrile **125** (0.100 g, 0.172 mmol) in DMF (10 mL) followed by aq. Na_2CO_3 (1 M, 1.0 mL, 1.0 mmol). The reaction mixture was stirred at 80 °C for 1 h, cooled to room temperature and diluted with water (60 mL). The product was extracted with diethyl ether (5 x 15 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy brown solid. The crude product was purified by column chromatography (SiO_2, 20-30% DCM in pet. ether) to give a yellow solid (0.051 g, 54%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.55 (2H, d, *J* = 8.7 Hz), 8.51 (2H, d, *J* = 8.7 Hz), 8.21 (2H, s), 8.00 (2H, d, *J* = 8.5 Hz), 7.91 (2H, d, *J* = 8.5 Hz), 7.83 (4H, d, *J* = 8.1 Hz), 7.77 (4H, d, *J* = 8.1 Hz), 7.76 (2H, d, *J* = 8.7 Hz), 7.57 (2H, d, *J* = 8.7 Hz), 2.49 (4H, d, *J* = 5.6 Hz), 2.46 (4H, d, *J* = 5.7 Hz), 1.54-1.47 (4H, m), 1.43-1.18 (32H, m), 0.94-0.81 (24H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.18 (2C), 142.72 (2C), 140.13 (2C), 138.95 (2C), 133.57 (2C), 132.97 (2C), 132.52 (2C), 131.73 (4CH), 130.50 (4CH), 129.04 (2CH), 128.38 (2CH), 128.16 (2CH), 127.70 (2CH), 127.51 (2CH), 126.95 (2CH), 126.62 (2CH), 120.14 (2C), 120.03 (2C), 119.03 (2C), 110.97 (2CN), 99.05 (2C), 98.60 (2C), 78.58 (2C), 78.13 (2C), 38.83 (2CH), 38.80 (2CH), 32.95 ($2CH_2$), 32.90 ($2CH_2$), 29.10 ($2CH_2$), 29.07 ($2CH_2$), 26.17 ($2CH_2$), 26.14 ($2CH_2$), 23.69 ($2CH_2$), 23.58 ($2CH_2$), 22.98 ($2CH_2$), 22.89 ($2CH_2$), 14.13 ($2CH_3$), 14.11 ($2CH_3$), 11.20 ($2CH_3$), 11.15 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2956 (s), 2923 (s), 2856 (m), 2224 (m), 1605 (m), 1456 (m), 1378 (m), 1093 (m), 1020 (m), 820 (s), 805 (s), 732 (m).

LRMS (APPI) 1126.7 ($M^{+\cdot}$).

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 274 (103000).

Melting point 138-140 °C.

3.1.8 Negishi cross-coupling reactions

General

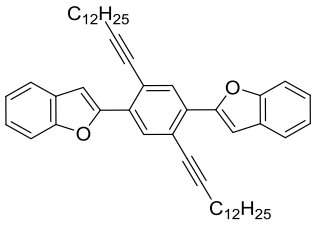
All glassware was oven-dried overnight and cooled to room temperature in a desiccator over Drierite before use. Reactions were carried out under an atmosphere of argon or nitrogen and magnetically stirred at room temperature. Furan was purified by stirring with calcium hydride overnight and distilling. Zinc chloride was dried by heating under reduced pressure (0.1 mm Hg) at 140 °C (temperature of aluminium block/oil bath) for 2-3 h in a pre-weighed Schlenk

tube or flask to give a known mass. Distilled THF was immediately added under argon or nitrogen to give a zinc chloride solution of known concentration. Reactions were monitored by TLC.

Preparation of organozinc reagents

Unless described in the procedure, all organozinc reagents were prepared in the same way. A Schlenk flask was placed under an inert atmosphere and to it added the heterocycle and THF (or a solution of the two) *via* syringe. The solution was cooled using an ice bath and 1.0-1.1 equivalents of *n*-BuLi (2.5 M in hexanes) were added slowly *via* syringe, under argon or nitrogen. The solution was warmed to room temperature, stirred for 0.5 h and then cooled again with an ice bath before slow addition of a solution of zinc chloride in THF (1.0-1.2 equivalents). The organozinc solution was stirred for 0.5 h and then transferred *via* cannula or syringe into a Schlenk flask containing all other reagents, which had been previously placed under argon or nitrogen. A quantitative conversion of the heterocycle to the corresponding organozinc chloride is assumed in the syntheses of **11**, **19**, **22**-**24**, **27**, **35**, **46** and **48**.

2,2'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)bis(benzofuran) 11



A 100 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(tetradec-1-yn-1-yl)benzene **3** (0.800 g, 1.29 mmol), palladium acetate (0.012 g, 0.053 mmol) and triphenylphosphine (0.014 g, 0.053 mmol) and flushed with argon for 1 h. A solution of benzofuran-2-ylzinc(II) chloride (5.19 mmol) in THF (38 mL) was added and the reaction mixture was refluxed for 20 h, cooled to room temperature and diluted with water (120 mL). The product was extracted with diethyl ether (3 x 50 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown waxy solid. The crude product was purified by column chromatography (SiO_2, 0.1% EtOAc in hexane) to give a yellow solid (0.350 g, 39%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.22 (2H, s), 7.82 (2H, d, *J* = 0.9 Hz), 7.63 (2H, dd, *J* = 6.9, 0.8 Hz), 7.57-7.54 (2H, m), 7.36-7.23 (4H, m), 2.62 (4H, t, *J* = 7.1 Hz), 1.80-1.71 (4H, quin, *J* = 7.3 Hz), 1.60-1.50 (4H, m), 1.26 (32H, br), 0.88 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.29 (2C), 153.05 (2C), 131.93 (2CH), 129.89 (2C), 129.20 (2C), 124.88 (2CH), 122.91 (2CH), 121.36 (2CH), 119.80 (2C), 111.06 (2CH), 106.23 (2CH), 97.73 (2C), 80.35 (2C), 31.90 ($2CH_2$), 29.68-29.63 ($6CH_2$), 29.56 ($2CH_2$), 29.34 ($2CH_2$), 29.25 ($2CH_2$), 29.15 ($2CH_2$), 28.53 ($2CH_2$), 22.68 ($2CH_2$), 20.00 ($2CH_2$), 14.11 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3060 (w), 2935 (m), 2914 (s), 2849 (s), 2221 (w), 1492 (w), 1470 (m), 1455 (m), 1010 (w), 895 (m), 803 (s), 737 (s), 718 (s).

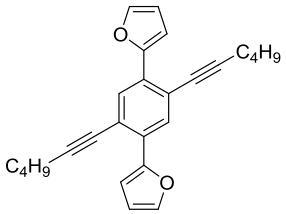
UV (hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 290 (14000).

LRMS (APPI) *m/z* 695.4 $(M+H)^+$.

HRMS (APPI) *m/z* calc. for $C_{50}H_{62}O_2$ ($M^{+\cdot}$) 694.47443, found 694.47360.

Melting point 122-124 °C.

2,2'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)difuran 19



A 100 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(hex-1-yn-1-yl)benzene **2** (0.400 g, 1.01 mmol), palladium acetate (0.016 g, 0.071 mmol) and triphenylphosphine (0.016 g, 0.061 mmol) and flushed with argon for 0.5 h. A solution of furan-2-ylzinc(II) chloride (6.05 mmol) in THF (40 mL) was added and the reaction mixture was refluxed for 18 h, cooled to room temperature and diluted with water (150 mL). The product was extracted with DCM (3 x 50 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, 0.5% EtOAc in hexane) to give the compound as a yellow solid (0.260 g, 70%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.96 (2H, s), 7.49 (2H, dd, *J* = 1.8, 0.6 Hz), 7.36 (2H, dd, *J* = 3.4, 0.6 Hz), 6.52 (2H, dd, *J* = 3.4, 1.8 Hz), 2.54 (4H, t, *J* = 7.1 Hz), 1.71-1.64 (4H, m), 1.58-1.49 (4H, m), 0.98 (6H, t, *J* = 7.3 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 151.48 (2C), 141.85 (2CH), 130.69 (2CH), 129.42 (2C), 118.46 (2C), 111.62 (2CH), 109.43 (2CH), 96.47 (2C), 80.40 (2C), 30.62 ($2CH_2$), 21.12 ($2CH_2$), 19.52 ($2CH_2$), 13.61 ($2CH_3$).

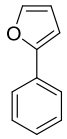
IR (neat) υ_{max}/cm^{-1} 3120 (w), 2957 (m), 2934 (m), 2865 (m), 2224 (w), 1485 (m), 1460 (m), 1377 (w), 1008 (s), 884 (m), 810 (s), 730 (s).

HRMS (APPI) *m/z* calc. for $C_{26}H_{27}O_2$ $(M+H)^+$ 371.20056, found 371.19954.

UV (hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 280 (84000).

Melting point 77-78 °C.

2-phenylfuran 22



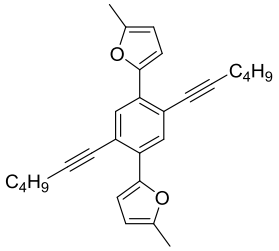
A 50 mL Schlenk flask was charged with iodobenzene (0.77 mL, 21.60 g, 6.87 mmol) and $Pd(PPh_3)_4$ (0.160 g, 0.138 mmol) and flushed with argon for 0.5 h. A solution of furan-2-ylzinc(II) chloride (28.2 mmol) in THF/hexanes (5:1, 61 mL) was added and the reaction mixture was refluxed for 2 h, cooled to room temperature and diluted with 0.5 M HCl (30 mL). The product was extracted with diethyl ether (5 x 20 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a dark orange oil. The crude product was purified by column chromatography (SiO_2, 0.5% EtOAc in hexane) to give a pale yellow oil (0.789 g, 80%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.71-7.68 (2H, m), 7.49 (1H, dd, *J* = 1.8, 0.6 Hz), 7.43-7.39 (2H, m), 7.30-7.26 (1H, m), 6.67 (1H, dd, *J* = 3.4, 0.6 Hz), 6.49 (1H, dd, *J* = 3.3, 1.8 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.00 (C), 142.03 (CH), 130.90 (C), 128.64 (2CH), 127.31 (CH), 123.79 (2CH), 111.61 (CH), 104.93 (CH).

NMR data is consistent with literature reports.[172]

5,5'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)bis(2-methylfuran) 23



A 100 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(hex-1-yn-1-yl)benzene **2** (0.300 g, 0.758 mmol), palladium acetate (0.009 g, 0.040 mmol) and triphenylphosphine (0.010 g, 0.038 mmol) and flushed with argon for 0.75 h. A solution of (5-methylfuran-2-yl)zinc(II) chloride (4.54 mmol) in THF (30 mL) was added and the reaction mixture was refluxed for 18 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with DCM (3 x 40 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$)

and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO2, 0.5% EtOAc in hexane) to give the compound as a yellow solid (0.150 g, 50%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.89 (2H, s), 7.23 (2H, d, *J* = 3.3 Hz), 6.10 (2H, d, *J* = 3.3 Hz), 2.53 (4H, t, *J* = 7.1 Hz), 2.39 (6H, s), 1.72-1.63 (4H, m), 1.58-1.46 (4H, m), 0.98 (6H, t, *J* = 7.3 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 151.82 (2C), 149.93 (2C), 130.13 (2CH), 129.18 (2C), 117.86 (2C), 110.37 (2CH), 107.81 (2CH), 96.06 (2C), 80.64 (2C), 30.67 ($2CH_2$), 22.17 ($2CH_2$), 19.57 ($2CH_2$), 13.72 ($2CH_3$), 13.63 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2952 (m), 2869 (m), 2225 (w), 1486 (m), 1451 (m), 1379 (w), 1024 (s), 809 (s), 795 (s), 741 (m).

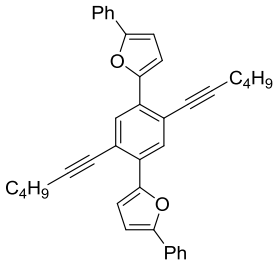
LRMS (GC/EI) *m/z* 398, 41% (M^+); 281, 34%; 207, 100%.

HRMS (APPI) *m/z* calc. for $C_{28}H_{30}O_2$ ($M^{+\cdot}$) 398.2240, found 398.2237.

UV (hexane) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 283 (60000).

Melting point 122-123 °C.

5,5'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)bis(2-phenylfuran) 24



A 50 mL Schlenk flask was charged with 1,4-dibromo-2,5-di(hex-1-yn-1-yl)benzene **2** (0.200 g, 0.505 mmol), palladium acetate (0.007 g, 0.031 mmol) and triphenylphosphine (0.007 g, 0.027 mmol) and flushed with argon for 0.75 h. A solution of (5-phenylfuran-2-yl)zinc(II) chloride (3.03 mmol) in THF (11 mL) was added and the reaction mixture was refluxed for 18 h, cooled to room temperature and diluted with water (20 mL). The product was extracted with DCM (3 x 20 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, 0.5% EtOAc in hexane) to give a yellow solid (0.146 g, 55%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05 (2H, s), 7.82-7.80 (4H, m), 7.46 (2H, d, *J* = 3.5 Hz), 7.43 (4H, d, *J* = 7.9 Hz), 7.32-7.28 (2H, m), 6.80 (2H, d, *J* = 3.5 Hz), 2.60 (4H, t, *J* = 7.1 Hz), 1.76-1.69 (4H, m), 1.61-1.52 (4H, m), 1.01 (6H, t, *J* = 7.3 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.24 (2C), 150.96 (2C), 130.64 (2CH, 2C), 129.24 (2C), 128.70 (4CH), 127.51 (2CH), 123.97 (4CH), 118.46 (2C), 111.84 (2CH), 107.32 (2CH), 96.67 (2C), 80.55 (2C), 30.67 ($2CH_2$), 22.23 ($2CH_2$), 19.67 ($2CH_2$), 13.65 ($2CH_3$).

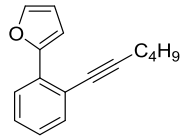
IR (neat) υ_{max}/cm^{-1} 2953 (m), 2923 (m), 2862 (m), 2230 (w), 1604 (m), 1483 (s), 1455 (m), 1371 (w), 1023 (s), 900 (m), 795 (s), 756 (s), 686 (s).

HRMS (APPI) *m/z* calc. for $C_{38}H_{34}O_2$ ($M^{+\cdot}$) 522.2553, found 522.2550.

UV (hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 382 (88000), 402 (81000).

Melting point 144-146 °C.

2-(2-(hex-1-yn-1-yl)phenyl)furan 27



A 250 mL Schlenk flask was charged with 1-bromo-2-(hex-1-yn-1-yl)benzene **25** (2.00 g, 8.43 mmol), palladium acetate (0.076 g, 0.339 mmol) and triphenylphosphine (0.088 g, 0.336 mmol) and flushed with argon for 1 h. A solution of furan-2-ylzinc(II) chloride (25.3 mmol) in THF (90 mL) was added and the reaction was refluxed for 18 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with DCM (4 x 70 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, 0.1% EtOAc in hexane) to give an orange oil (0.286 g, 15%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.84 (1H, dd, *J* = 8.1, 1.1), 7.50 (2H, td, *J* = 3.8, 1.1 Hz), 7.37-7.31 (2H, m), 7.19 (1H, td, *J* = 7.5, 1.3), 6.52 (1H, dd, *J* = 3.4, 1.8), 2.53 (2H, t, *J* = 7.1), 1.71-1.64 (2H, m), 1.58-1.49 (2H, m), 0.99 (3H, t, *J* = 7.3 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.28 (C), 141.63 (CH), 133.87 (CH), 131.51 (C), 127.74 (CH), 126.55 (CH), 125.33 (CH), 119.14 (C), 111.46 (CH), 109.03 (CH), 95.32 (C), 80.59 (C), 30.65 (CH_2), 22.08 (CH_2), 19.44 (CH_2), 13.60 (CH_3).

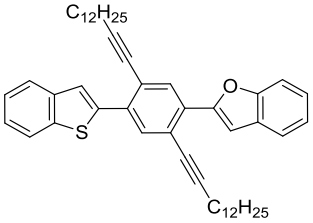
IR (neat) υ_{max}/cm^{-1} 3060 (w), 2957 (m), 2930 (m), 2869 (m), 2227 (w), 1490 (w), 1481 (m), 1439 (m), 1377 (w), 1005 (s), 810 (m), 756 (s), 732 (s).

LRMS (GC/EI) *m/z* 224 (M^+); 181 (M^+-Pr); 152 (100%).

HRMS (APPI) calc. for $C_{16}H_{16}O$ ($M^{+\cdot}$) 224.1196, found 224.1191.

UV (hexane) λ_{max}/nm (ε / dm^3 mol^{-1} cm^{-1}) 290 (10000).

2-(4-(benzo[*b*]thiophen-2-yl)-2,5-di(tetradec-1-yn-1-yl)phenyl)benzofuran 35



A 50 mL Schlenk flask was charged with 2-(4-bromo-2,5-di(tetradec-1-yn-1-yl)phenyl)benzo[*b*]thiophene **31** (0.280 g, 0.415 mmol), palladium acetate (0.004 g, 0.018 mmol) and triphenylphosphine (0.004 g, 0.015 mmol) and flushed with argon for 0.5 h. A solution of benzofuran-2-ylzinc(II) chloride (0.907 mmol) in THF (20 mL) was added and the reaction mixture was refluxed for 16 h, cooled to room temperature and diluted with water (50 mL). The product was extracted with diethyl ether (3 x 50 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown solid. The crude product was purified by column chromatography (SiO_2, 0.1% EtOAc in hexane) to give a yellow solid (0.234 g, 79%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (1H, s), 7.97 (1H, s), 7.88-7.85 (1H, m), 7.82-7.79 (3H, m), 7.63 (1H, d, *J* = 7.2 Hz), 7.55 (1H, dd, *J* = 0.6, 7.2 Hz), 7.40-7.32 (3H, m), 7.28-7.24 (1H, m), 2.60 (2H, t, *J* = 7.1 Hz), 2.51 (2H, t, *J* = 7.1 Hz), 1.78-1.63 (4H, m), 1.54-1.37 (6H, m), 1.30-1.26 (30H, br), 0.91-0.87 (6H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.29 (C), 153.01 (C), 141.23 (C), 140.11 (C), 134.79 (CH), 134.52 (C), 131.75 (CH), 129.97 (C), 129.18 (C), 124.87 (CH), 124.52 (CH), 124.34 (CH), 123.74 (2CH), 122.91 (CH), 122.02 (CH), 121.43 (C), 121.34 (CH), 119.73 (C), 111.07 (CH), 106.14 (CH), 97.84 (C), 97.28 (C), 80.17 (C), 80.04 (C), 31.91 ($2CH_2$), 29.67-29.64 ($6CH_2$), 29.55 (CH_2), 29.52 (CH_2), 29.35 ($2CH_2$), 29.23 ($2CH_2$), 29.12 (CH_2), 29.09 (CH_2), 28.49 (CH_2), 28.33 (CH_2), 22.68 ($2CH_2$), 19.94 ($2CH_2$), 14.10 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3059 (w), 2916 (s), 2848 (s), 2869 (m), 2223 (w), 1491 (w), 1468 (m), 1439 (m), 1371 (w), 1008 (w), 811 (m), 741 (s), 722 (s).

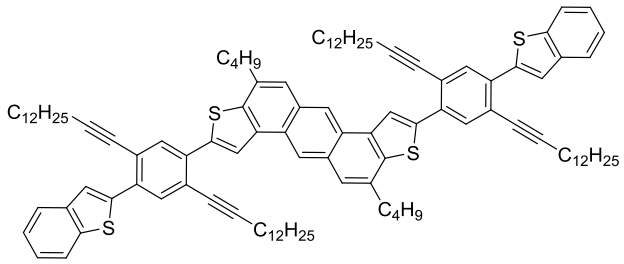
LRMS (APPI) *m/z* 711.4 $(M+H)^+$.

HRMS (APPI) calc. for $C_{50}H_{63}OS$ $(M+H)^+$ 711.45941, found 711.45825.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 290 (56000).

Melting point 82-83 °C.

2,8-bis(4-(benzo[*b*]thiophen-2-yl)-2,5-di(tetradec-1-yn-1-yl)phenyl)-4,10-dibutylanthra[2,1-*b*:6,5-*b*']dithiophene 39



A 250 mL Schlenk flask was charged with 4,10-dibutylanthra[2,1-*b*:6,5-*b*']dithiophene **13** (0.266 g, 0.661 mmol), flushed with argon for 1 h and to it added distilled THF (70 mL). The solution was cooled to -15 °C and *t*-BuLi (1.92 M in pentane, 0.86 mL, 1.65 mmol) added dropwise. After 0.5 h at -15 °C, a solution of zinc chloride in distilled THF (0.916 M, 2.9 mL, 2.66 mmol) was added dropwise and the reaction mixture was warmed to room temperature, stirred for 0.25 h and transferred *via* cannula, under argon, into a 250 mL Schlenk flask charged with a solution of 2-(4-bromo-2,5-di(tetradec-1-yn-1-yl)phenyl)benzo[*b*]thiophene **31** (0.980 g, 1.45 mmol), palladium acetate (0.008 g, 0.04 mmol) and triphenylphosphine (0.008 g, 0.03 mmol) in distilled THF (10 mL). The reaction mixture was refluxed for 16 h, cooled to room temperature and diluted with water (100 mL). The product was extracted with DCM (6 x 40 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 0-50% DCM in hexane), giving 0.295 g of a yellow solid. Fractions collected when using 1:1 DCM/hexane as the eluent gave the target compound but in poor purity. Addition of hexane gave a dark red solution which was removed, leaving 0.270 g of a yellow solid which showed good purity by TLC and NMR. Final yield: 0.565 g, 54%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (2H, s), 8.77 (2H, s), 7.97 (2H, s), 7.94 (2H, s), 7.89-7.87 (2H, m), 7.85 (2H, s), 7.82-7.80 (2H, m), 7.70 (2H, s), 7.41-7.34 (4H, m), 3.08 (4H, t, *J* = 7.7 Hz), 2.58 (4H, t, *J* = 7.2 Hz), 2.53 (4H, t, *J* = 7.1 Hz), 2.03-1.95 (4H, m), 1.80-1.73 (4H, m), 1.73-1.65 (4H, m), 1.64-1.54 (6H, m), 1.51-1.44 (8H, m), 1.32-1.14 (62H, m), 1.08 (6H, t, *J* = 7.3 Hz), 0.90 (6H, t, *J* = 6.9 Hz), 0.87 (6H, t, *J* = 6.9 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.26 (2C), 140.14 (2C), 140.02 (4C), 138.65 (2C), 135.90 (2C), 134.84 (2C), 134.66 (2CH), 134.30 (2C), 134.22 (2CH), 134.19 (2C), 130.48 (2C), 126.58 (2C), 124.47 (2CH), 124.32 (2CH), 123.72 (2CH), 123.62 (2CH), 123.44 (2CH), 122.68 (2CH), 122.01 (2CH), 121.77 (2CH), 121.41 (2C), 120.96 (2C), 97.42 (2C), 97.26 (2C), 80.24 (2C), 80.03 (2C), 34.84 ($2CH_2$), 31.90 ($6CH_2$), 31.28 ($2CH_2$), 29.65-29.14 ($24CH_2$),

28.50 ($2CH_2$), 28.37 ($2CH_2$), 22.82 ($2CH_2$), 22.68 ($6CH_2$), 20.13 ($2CH_2$), 19.99 ($2CH_2$), 14.10 ($4CH_3$), 14.05 ($2CH_3$).

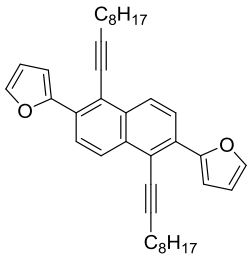
IR (neat) υ_{max}/cm^{-1} 2953 (m), 2918 (s), 2850 (s), 2227 (w), 1464 (m), 1376 (w), 1017 (w), 887 (s), 826 (s), 744 (s), 722 (s).

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 290 (107000).

LRMS (APPI) *m/z* 1587.9 $(M+H)^+$.

Melting point 151-153 °C.

2,2'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)difuran 46



A 50 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (0.100 g, 0.179 mmol), palladium acetate (0.005 g, 0.022 mmol) and triphenylphosphine (0.005 g, 0.019 mmol) and evacuated/refilled with nitrogen three times. A solution of furan-2-ylzinc(II) chloride (0.720 mmol) in THF (7 mL) was added and the reaction mixture was refluxed for 16 h, cooled to room temperature, concentrated under reduced pressure and diluted with water (50 mL). The product was extracted with DCM (5 x 15 mL) and the organic layers combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, pet. ether) to give a yellow solid (0.056 g, 59%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.43 (2H, d, *J* = 8.9 Hz), 8.06 (2H, d, *J* = 8.9 Hz), 7.57 (2H, d, *J* = 1.3 Hz), 7.53 (2H, d, *J* = 3.4 Hz), 6.58 (2H, dd, *J* = 3.4, 1.7 Hz), 2.71 (4H, t, *J* = 7.1 Hz), 1.79 (4H, quin, *J* = 7.3 Hz), 1.62-1.54 (4H, m), 1.42-1.27 (16H, m), 0.91 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.59 (2C), 142.01 (2CH), 133.06 (2C), 130.02 (2C), 126.62 (2CH), 124.25 (2CH), 115.78 (2C), 111.79 (2CH), 110.13 (2CH), 102.00 (2C), 78.43 (2C), 31.86 ($2CH_2$), 29.24 ($2CH_2$), 29.18 ($4CH_2$), 28.72 ($2CH_2$), 22.67 ($2CH_2$), 20.16 ($2CH_2$), 14.10 ($2CH_3$).

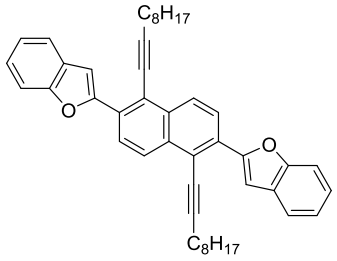
IR (neat) υ_{max}/cm^{-1} 3121 (w), 2953 (m), 2927 (s), 2850 (m), 2213 (w), 1584 (w), 1461 (m), 1371 (m), 1018 (s), 830 (m), 805 (s), 728 (s), 711 (s).

HRMS (APPI) *m/z* calc. for $C_{38}H_{44}O_2$ ($M^{+\cdot}$) 532.33358, found 532.33389.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 293 (44000), 305 (68000).

Melting point 85-87 °C.

2,2'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)bis(benzofuran) 48



A 25 mL Schlenk flask was charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (0.100 g, 0.179 mmol), palladium acetate (0.005 g, 0.022 mmol) and triphenylphosphine (0.005 g, 0.019 mmol) and evacuated/refilled with nitrogen three times. A solution of benzofuran-2-ylzinc(II) chloride (0.694 mmol) in THF (7 mL) was added and the reaction mixture was refluxed for 16 h, cooled to room temperature, concentrated under reduced pressure and diluted with water (50 mL). The product was extracted with DCM (5 x 15 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, pet. ether) to give a yellow solid (0.063 g, 56%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.53 (2H, d, *J* = 8.9 Hz), 8.26 (2H, d, *J* = 8.9 Hz), 7.92 (2H, s), 7.67 (2H, d, *J* = 7.6 Hz), 7.58 (2H, d, *J* = 8.1 Hz), 7.37-7.33 (2H, m), 7.30-7.26 (2H, m), 2.77 (4H, t, *J* = 7.1 Hz), 1.88-1.80 (4H, m), 1.65-1.59 (4H, m), 1.46-1.27 (16H, m), 0.92-0.88 (6H, m).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.36 (2C), 154.26 (2C), 133.64 (2C), 130.04 (2C), 129.29 (2C), 126.84 (2CH), 125.01 (2CH), 124.77 (2CH), 122.92 (2CH), 121.35 (2CH), 117.82 (2C), 111.11 (2CH), 106.64 (2CH), 103.04 (2C), 78.34 (2C), 31.87 ($2CH_2$), 29.25-29.23 ($6CH_2$), 28.67 ($2CH_2$), 22.68 ($2CH_2$), 20.27 ($2CH_2$), 14.11 ($2CH_3$).

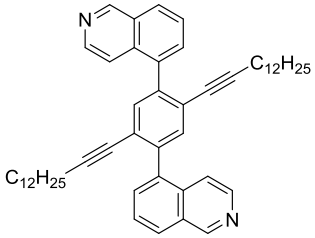
IR (neat) υ_{max}/cm^{-1} 2953 (m), 2923 (s), 2850 (m), 2216 (w), 1580 (w), 1463 (m), 1450 (m), 1373 (w), 1019 (m), 807 (s), 731 (s).

HRMS (APPI) *m/z* calc. for $C_{46}H_{48}O_2$ ($M^{+\cdot}$) 632.36488, found 632.36323.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 304 (13000), 317 (19000).

Melting point 123-126 °C.

5,5'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)diisoquinoline 96



A 25 mL Schlenk flask was charged with 5-bromoisoquinoline (0.805 g, 3.87 mmol), evacuated/refilled with argon three times and THF (8 mL) added. *N*-BuLi (2.5 M in hexanes, 1.70 mL, 4.25 mmol) was added slowly at -70 °C and the reaction mixture was stirred at this temperature. After 0.5 h, a solution of zinc chloride in THF (1.61 M, 2.64 mL, 4.25 mmol) was added slowly and the reaction mixture was warmed to room temperature. After 0.5 h at room temperature, the solution was transferred, *via* cannula, into a 50 mL Schlenk flask charged with 1,4-dibromo-2,5-di(tetradec-1-yn-1-yl)benzene **3** (0.600 g, 0.967 mmol), palladium acetate (0.011 g, 0.049 mmol) and triphenylphosphine (0.010 g, 0.038 mmol) and flushed with argon for 0.5 h. The reaction mixture was refluxed for 16 h and cooled to room temperature. THF was removed from the reaction mixture under reduced pressure, water (15 mL) was added and the product was extracted with chloroform (3 x 10 mL). The organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified twice by column chromatography (SiO_2, 0-5% EtOAc in chloroform) to give an orange oil (0.175 g, 25%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.33 (2H, s), 8.54 (2H, dd, *J* = 12.3, 5.9 Hz), 8.04 (2H, d, *J* = 8.0 Hz), 7.80-7.59 (6H, m), 7.57 (2H, s), 1.98 (4H, t, *J* = 6.8 Hz), 1.26 (32H, br), 1.11-0.95 (8H, m), 0.91-0.87 (6H, m).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 152.66 (2CH), 143.07 (2CH), 140.59 (2C), 137.18 (2C), 134.33 (2C), 134.04 (2CH), 131.42 (2CH), 128.61 (2C), 127.56 (2CH), 126.56 (2CH), 123.57 (2C), 119.09 (2CH), 96.45 (2C), 79.17 (2C), 31.88 ($2CH_2$), 29.62 ($2CH_2$), 29.61 ($2CH_2$), 29.58 ($2CH_2$), 29.33 ($2CH_2$), 29.32 ($2CH_2$), 28.91 ($2CH_2$), 28.28 ($2CH_2$), 27.92 ($2CH_2$), 22.65 ($2CH_2$), 19.12 ($2CH_2$), 14.08 ($2CH_3$).

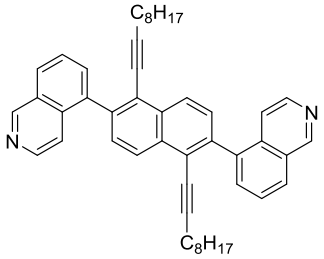
IR (neat) υ_{max}/cm^{-1} 3032 (w), 2921 (s), 2851 (s), 2228 (w), 1585 (w), 1484 (m), 1458 (m), 1374 (w), 1033 (w), 827 (s), 810 (m), 758 (s), 726 (m).

LRMS (ESI+) *m/z* 717.4 $(M+H)^+$.

HRMS (APPI) *m/z* calc. for $C_{52}H_{65}N_2$ $(M+H)^+$ 717.5142, found 717.5124.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 277 (37000).

5,5'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)diisoquinoline 105



A 25 mL Schlenk flask was charged with 5-bromoisoquinoline (0.788 g, 3.79 mmol), evacuated/refilled with argon three times and distilled THF (10 mL) was added. *N*-BuLi (2.5 M in hexanes, 1.67 mL, 4.18 mmol) was added slowly at -60 °C and the reaction mixture was stirred at this temperature. After 0.5 h, a solution of zinc chloride in THF (1.02 M, 4.10 mL, 4.18 mmol) was added slowly and the reaction mixture was warmed to room temperature. After 0.5 h at room temperature, the solution was transferred, *via* cannula, into a 50 mL Schlenk flask charged with 2,6-dibromo-1,5-di(dec-1-yn-1-yl)naphthalene **41** (0.700 g, 1.25 mmol), palladium acetate (0.012 g, 0.053 mmol) and triphenylphosphine (0.011 g, 0.042 mmol) and evacuated/refilled with argon three times. The reaction mixture was refluxed for 20 h and cooled to room temperature. THF was removed under reduced pressure, water (100 mL) was added and the product was extracted with DCM (4 x 30 mL). The organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 0-50% EtOAc in DCM) to give 0.180 g of material containing the target compound. This was purified by recrystallisation in refluxing hexane (5 mL, room temperature for 3 days) to give a yellow solid (0.126 g, 15%). No further purification was carried out.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.38 (2H, br), 8.53 (2H, dd, *J* = 8.4, 1.0 Hz), 8.47 (2H, br), 8.08 (2H, d, *J* = 8.1 Hz), 7.85 (2H, ddd, *J* = 7.0, 3.9. 1.0 Hz), 7.78-7.74 (2H, m), 7.60 (2H, d, *J* = 8.4 Hz), 7.56-7.52 (2H, m), 2.17 (4H, t, *J* = 6.8 Hz), 1.32-0.94 (24H, m), 0.88 (6H, t, *J* = 7.2 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.30 (2CH), 142.35 (2CH), 139.93 (2C), 138.63 (2C), 134.57 (2C), 132.93 (2C), 132.02-131.97 (2CH), 129.15 (2CH), 128.69 (2C), 127.56 (2CH), 126.87-126.84 (2CH), 126.31 (2CH), 122.03 (2C), 119.46 (2CH), 100.91 (2C), 77.20 (2C), 31.82 ($2CH_2$), 29.06 ($2CH_2$), 28.95 ($2CH_2$), 28.44 ($2CH_2$), 28.16 ($2CH_2$), 22.64 ($2CH_2$), 19.46 ($2CH_2$), 14.10 ($2CH_3$).

HRMS (ESI) *m/z* calc. for $C_{48}H_{51}N_2$ $(M+H)^+$ 655.4047, found 655.4050.

IR (neat) υ_{max}/cm^{-1} 3126 (w), 2953 (m), 2921 (s), 2851 (s), 2217 (w), 1615 (m), 1485 (m), 1464 (m), 1455 (m), 1384 (m), 1031 (m), 833 (s), 811 (s), 799 (m), 758 (s), 718 (s).

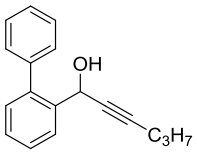
UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 244 (31000), 298 (21000).

Melting point 121-122 °C.

3.1.9 Allene synthesis

71 and **72** were synthesised using a variation of a literature procedure.[69]

1-([1,1'-biphenyl]-2-yl)hex-2-yn-1-ol 71



A 50 mL Schlenk flask equipped with a stirrer bar was evacuated/refilled with nitrogen three times. THF (8 mL) was added and 1-pentyne (1.00 mL, 0.691 g, 10.1 mmol) was added at -70 °C, followed by slow addition of *n*-BuLi (2.5 M in hexanes, 3.9 mL, 9.75 mmol). After stirring for 1 h, a solution of biphenyl-2-carboxaldehyde (0.87 mL, 0.983 g, 5.39 mmol) in distilled THF (2 mL) was added dropwise at -70 °C and the reaction was warmed to room temperature, quenched with saturated ammonium chloride (50 mL) and the product extracted with ethyl acetate (3 x 15 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 1:1 pet. ether/DCM) to give the titled compound as a colourless oil (1.16 g, 86%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86 (1H, dd, *J* = 7.8, 1.0 Hz), 7.44-7.33 (7H, m), 7.27-7.24 (1H, m), 5.44 (1H, s), 2.20 (2H, td, *J* = 7.1, 2.0 Hz), 1.53 (2H, sxt, *J* = 7.2 Hz), 0.96 (3H, t, *J* = 7.3 Hz).

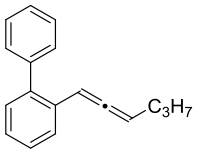
^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.77 (C), 140.26 (C), 138.95 (C), 130.09 (CH), 129.45 (2CH), 128.13 (2CH), 128.08 (CH), 127.95 (CH), 127.31 (CH), 127.29 (CH), 87.23 (C), 80.92 (C), 61.83 (CH), 21.96 (CH_2), 20.80 (CH_2), 13.49 (CH_3).

IR (neat) υ_{max}/cm^{-1} 3365 (br), 2961 (m), 2931 (m), 2221 (w), 1478 (m), 986 (s), 725 (s).

HRMS (APPI) *m/z* calc. for $C_{18}H_{18}O$ ($M^{+\cdot}$) 250.1352, found 250.1345.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 241 (41000).

2-(hexa-1,2-dien-1-yl)-1,1'-biphenyl 72



A 25 mL Schlenk flask equipped with a stirrer bar was evacuated/refilled with nitrogen three times. A solution of zinc chloride in THF (0.5 M, 1.28 mL, 0.64 mmol) was added followed by diethyl zinc solution (1.0 M in hexanes, 0.64 mL, 0.64 mmol). The reaction mixture was stirred at room temperature for 0.5 h and distilled toluene (2 mL) was added. The alkylzinc solution was cooled to 0° C, and a solution of 1-([1,1'-biphenyl]-2-yl)hex-2-yn-1-ol **71** (0.320 g, 1.28 mmol) in distilled toluene (4 mL) was added. After 20 min, $Cp_2Zr(H)Cl$ (2 mmol) was added in one portion and the reaction mixture was warmed to room temperature, stirred for 24 h and diluted with saturated sodium hydrogen carbonate (20 mL). The product was extracted with ethyl acetate (3 x 5 mL) and the organic layers were combined washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, pet. ether) to give a colourless oil (0.162 g, 54%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, d, *J* = 7.6 Hz), 7.45-7.22 (8H, m), 6.19 (1H, dt, *J* = 6.3, 3.0 Hz), 5.52 (1H, q, *J* = 6.7 Hz), 2.10 (2H, qd, *J* = 7.3, 3.1 Hz), 1.51 (2H, sxt, *J* = 7.3 Hz), 0.97 (3H, t, *J* = 7.3 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 205.61 (C), 140.94 (C), 140.12 (C), 132.44 (C), 130.17 (CH), 129.70 (2CH), 128.08 (2CH), 127.40 (CH), 127.14 (CH), 126.95 (CH), 126.42 (CH), 94.42 (CH), 92.60 (CH), 30.81 (CH_2), 22.45 (CH_2), 13.74 (CH_3).

IR (neat) υ_{max}/cm^{-1} 2959 (m), 2930 (m), 2872 (m), 1729 (m), 1691 (m), 1477 (m), 1452 (m), 1435 (m), 1379 (w), 1008 (w), 745 (s), 701 (s).

LRMS (GC/EI) *m/z* 234.1, 13% (M^+); 205.1, 42% (M^+-Et); 191.1, 100% (M^+-Pr); 178.0, 41% (M^+-C_4H_8).

HRMS (APPI) *m/z* calc. for $C_{18}H_{18}$ ($M^{+\cdot}$) 234.1403, found 234.1400.

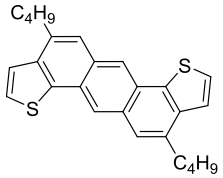
UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 243 (13000), 262 (12000).

3.1.10 Base-catalysed cyclisations

General

All base-catalysed cyclisations were carried out using DBU and NMP in a J-Young tap vessel heated by an aluminium block at 220-250 °C. Temperatures given refer to the temperature of the aluminium block. All reactions were carried out under an atmosphere of argon or nitrogen, and degassing methods are given for each procedure. The reactions were not magnetically stirred. Some ^{13}C NMR spectra carried out in tol-d_8 or odcb-d_4 may have aromatic peaks not reported as these were obscured by the solvent peaks.

4,10-dibutylanthra[1,2-*b*:5,6-*b*']dithiophene 12



Two identical reactions were set up in which a solution of 2,2'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)dithiophene **6** (0.400 g, 0.994 mmol) and DBU (0.303 g, 1.99 mmol) in NMP (32 mL) was added to a J-Young tap vessel. Both solutions were degassed by sonicating whilst under high vacuum (0.1 mm Hg) and the reaction tubes were sealed under argon, heated to 220 °C and held at this temperature for 24 h. The two reaction mixtures were cooled to room temperature and combined, diluted with 2 M HCl (40 mL) and the product extracted with DCM (4 x 40 mL). The organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown solid. The crude product was purified by column chromatography (SiO_2, hexane) and then successive recrystallisations (3:1 hexane/toluene, then 3:2 hexane/DCM) to give a yellow solid (0.153 g, 19%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.61 (2H, s), 7.67 (2H, s), 7.59 (2H, d, *J* = 5.3 Hz), 7.56 (2H, d, *J* = 5.3 Hz), 3.08 (4H, t, *J* = 7.6 Hz), 1.88-1.81 (4H, m), 1.57-1.48 (4H, m), 1.02 (6H, t, *J* = 7.3 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.37 (2C), 137.26 (2C), 135.84 (2C), 129.97 (2C), 126.56 (2C), 124.51 (2CH), 123.64 (2CH), 123.30 (2CH), 121.56 (2CH), 34.03 ($2CH_2$), 32.31 ($2CH_2$), 22.72 ($2CH_2$), 14.04 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2948 (m), 2921 (m), 2860 (m), 1451 (m), 1433, 1371 (m), 883 (s), 764 (s), 690 (s).

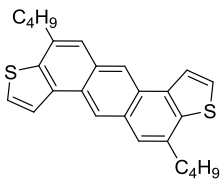
LRMS (APPI) *m/z* 403.1 $(M+H)^+$.

HRMS (APPI) *m/z* calc. for $C_{26}H_{27}S_2$ $(M+H)^+$ 403.15400, found 403.15371.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 294 (83400), 307 (198800), 338 (5800), 355 (8200), 372 (7600), 378 (8300), 400 (7300).

Melting point (hexane/DCM) 188-189 °C.

4,10-dibutylanthra[2,1-*b*:6,5-*b*']dithiophene 13



Two identical reactions were set up in which a solution of 3,3'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)dithiophene **7** (0.500 g, 1.24 mmol) and DBU (0.378 g, 2.48 mmol) in NMP (40 mL) was added to a J-Young tap vessel. Both solutions were degassed by sonicating whilst under high vacuum (0.1 mm Hg) and the reaction tubes were sealed under argon, heated to 220 °C and held at this temperature for 48 h. The two reaction mixtures were cooled to room temperature and combined, diluted with 2 M HCl (50 mL) and the product extracted with DCM (4 x 50 mL). The organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow-brown solid. The crude product was purified by column chromatography (SiO_2, hexane) and recrystallisation (hexane/DCM, 1:2) to give a yellow solid (0.675 g, 68%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.84 (2H, s), 8.19 (2H, d, *J* = 5.3 Hz), 7.75 (2H, s), 7.64 (2H, d, *J* = 5.3 Hz), 3.06 (4H, t, *J* = 7.7 Hz), 1.98-1.91 (4H, m), 1.59-1.50 (4H, m), 1.04 (6H, t, *J* = 7.4 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.35 (2C), 135.63 (2C), 134.59 (2C), 130.39 (2C), 126.58 (2C), 124.91 (2CH), 123.01 (2CH), 122.97 (2CH), 121.66 (2CH), 34.81 ($2CH_2$), 31.25 ($2CH_2$), 22.72 ($2CH_2$), 14.01 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2969 (m), 2952 (m), 2933 (m), 1463 (m), 1420 (m), 1374 (w), 1091 (m), 891 (s), 769 (m), 698 (s).

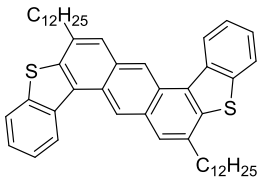
LRMS (APPI) *m/z* 403.1 $(M+H)^+$.

HRMS (APPI) *m/* calc. for $C_{26}H_{27}S_2$ $(M+H)^+$ 403.15400, found 403.15371.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 283 (93300), 292 (143500), 334 (4900), 348 (9600), 366 (15200), 379 (12100), 386 (13400).

Melting point (hexane/DCM) 213-214 °C.

4,10-didodecylanthra[2,1-*b*:6,5-*b*']dibenzothiophene 14



A solution of 3,3'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)bis(benzo[*b*]thiophene) **8** (0.200 g, 0.275 mmol) and DBU (0.084 g, 0.552 mmol) in NMP (30 mL) was added to a J-Young tap vessel and degassed by sonicating whilst under high vacuum. The tube was sealed under argon and the solution was heated to 220 °C and held at this temperature for 20 h followed by addition of extra DBU (0.084 g, 0.552 mmol) under argon and continued reaction for 48 h. The reaction

mixture was cooled to room temperature, giving a precipitate which was filtered off and dissolved in chloroform (60 mL). The solution was washed with 2 M HCl (50 mL) and then brine, dried ($MgSO_4$) and the solvent evaporated to give a yellow solid which was purified by recrystallisation (1:1 hexane/DCM) to give a yellow solid (0.066 g, 33%).

^{1}H-NMR (500 MHz, tol-d_8, 333 K) δ 9.61 (2H, s), 9.05 (2H, d, *J* = 8.2 Hz), 7.89 (2H, s), 7.82 (2H, d, *J* = 7.6 Hz), 7.48 (2H, ddd, *J* = 8.2, 7.1, 1.1 Hz), 7.29 (2H, ddd, *J* = 7.6, 7.1, 1.1 Hz), 3.08 (4H, t, *J* = 7.8 Hz), 2.03-1.97 (4H, m), 1.59-1.53 (4H, m), 1.49-1.43 (4H, m), 1.39-1.28 (28H, m), 0.90 (6H, *t*, J = 7.0 Hz).

^{13}C-NMR (500 MHz, tol-d_8, 333 K) δ 141.09 (2C), 140.41 (2C), 138.62 (2C), 135.54 (2C), 132.62 (2C), 127.15 (2CH), 125.52 (2CH), 125.49 (2CH), 125.32 (2CH), 123.84 (2CH), 123.41 (2CH), 36.08 ($2CH_2$), 32.71 ($2CH_2$), 30.57 ($2CH_2$), 30.54 ($4CH_2$), 30.49 ($4CH_2$), 30.41 ($2CH_2$), 30.17 ($2CH_2$), 30.11 ($2CH_2$), 23.42 ($2CH_2$), 14.55 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2916 (s), 2848 (s), 1463 (m), 1397 (w), 1033 (m), 895 (s), 776 (m), 734 (s), 716 (s).

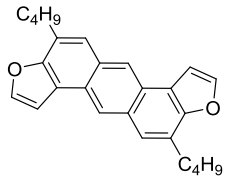
LRMS (APPI) *m/z* 726.3 ($M^{+\cdot}$), 727.3 $(M+H)^+$.

HRMS (APPI) *m/z* calc. for $C_{50}H_{63}S_2$ $(M+H)^+$ 727.43657, found 727.43619.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 298 (74300), 315 (83100), 372 (17500), 391 (27700), 416 (15200).

Melting point (hexane/DCM) 154-155 °C.

4,10-dibutylanthra[2,1-*b*:6,5-*b*']difuran 15



A solution of 3,3'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)difuran **9** (0.150 g, 0.405 mmol) and DBU (0.123 g, 0.808 mmol) in NMP (12 mL) was transferred into a J-Young tap vessel and degassed by sonicating whilst under high vacuum. The tube was sealed under argon and the solution was heated to 220 °C, held at this temperature for 48 h, cooled to room temperature and diluted with 2 M HCl (30 mL). The product was extracted with diethyl ether (4 x 20 mL) and the organic layers were combined, washed (brine), dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow-brown solid. The crude product was purified by column chromatography (hexane) and recrystallisation (hexane/DCM, 5:1) to give a yellow solid (0.100 g, 67%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.64 (2H, s), 7.81 (2H, d, *J* = 1.8 Hz), 7.68 (2H, s), 7.40 (2H, d, *J* = 1.8 Hz), 3.09 (4H, t, *J* = 7.6 Hz), 1.91-1.87 (4H, m), 1.55-1.45 (4H, m), 1.02 (6H, t, *J* = 7.3 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 151.84 (2C), 143.41 (2CH), 129.48 (2C), 128.38 (2C), 124.63 (2C), 123.33 (2CH), 121.55 (2C), 121.38 (2CH), 106.16 (2CH), 31.71 ($2CH_2$), 30.29 ($2CH_2$), 22.63 ($2CH_2$), 13.98 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2969 (m), 2952 (m), 2933 (m), 2858 (w), 1464 (m), 1367 (m), 1037 (m), 890 (s), 774 (m), 730 (s).

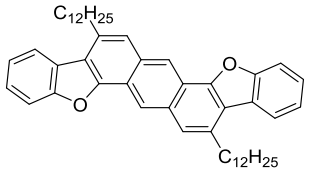
LRMS (APPI) *m/z* 371.1 $(M+H)^+$.

HRMS (APPI) *m/z* calc. for $C_{26}H_{26}O_2$ ($M^{+\cdot}$) 370.19273, found 370.19256.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 266 (105000), 338 (6100), 353 (9700), 370 (12300), 389 (15000).

Melting point (hexane/DCM) 200-202 °C.

4,10-dibutylanthra[1,2-*b*:5,6-*b*']dibenzofuran 16



A solution of 2,2'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)bis(benzofuran) **11** (0.070 g, 0.101 mmol) and DBU (0.031 g, 0.204 mmol) in NMP (8 mL) was transferred into a J-Young tap vessel and degassed by sonicating whilst under high vacuum. The tube was sealed under argon and the solution was heated to 230 °C, held at this temperature for 18 h, cooled to room temperature and diluted with methanol to give a precipitate which was filtered, washed (methanol) and dried. This was purified by recrystallisation (chloroform, 6 mL, reflux, 3 °C overnight) to give a yellow solid. The filtrate was concentrated under reduced pressure and purified by recrystallisation (toluene, 10 mL, 70 °C, room temperature overnight) to give another batch of yellow solid (0.022 g). Final yield: 0.038 g, 54%.

^{1}H-NMR (500 MHz, tol-d_8, 333 K) δ 9.08 (2H, s), 8.04-8.02 (2H, m), 7.67-7.65 (2H, m), 7.66 (2H, s), 7.29-7.27 (4H, m), 3.21 (4H, t, *J* = 7.6 Hz), 1.94 (4H, quin., *J* = 7.6 Hz), 1.60-1.54 (4H, m), 1.45-1.41 (4H, m), 1.35-1.31 (28H, m), 0.92-0.89 (6H, m).

^{13}C-NMR (125 MHz, tol-d_8, 333 K) δ 157.15 (2C), 153.38 (2C), 136.56 (2C), 132.28 (2C), 126.46 (2C), 126.22 (2CH), 123.78 (2CH), 122.90 (2CH), 122.58 (2CH), 120.92 (2C), 120.23

(2CH), 118.88 (2C), 112.56 (2CH), 35.15 ($2CH_2$), 32.76 ($2CH_2$), 30.57 ($4CH_2$), 30.53 ($8CH_2$), 30.49 ($2CH_2$), 30.21 ($2CH_2$), 23.46 ($2CH_2$), 14.59 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2956 (m), 2916 (s), 2848 (s), 1451 (m), 1398 (w), 1016 (w), 877 (m), 817 (m), 728 (s).

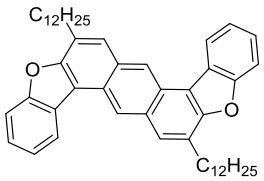
LRMS (APPI) *m/z* 694.2 ($M^{+\cdot}$), 695.2 $(M+H)^+$.

HRMS (APPI) *m/z* calc. for $C_{50}H_{63}O_2$ $(M+H)^+$ 695.48226, found 695.48311.

UV (DCM) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 286 (30400), 305 (47700), 318 (132100), 346 (7000), 366 (10100), 386 (12000), 408 (9200).

Melting point (tol) 143-144 °C.

4,10-didodecylanthra[2,1-*b*:6,5-*b*']dibenzofuran 17



A solution of 3,3'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)bis(benzofuran) **10** (0.090 g, 0.129 mmol) and DBU (0.079 g, 0.519 mmol) in NMP (8 mL) was transferred into a J-Young tap vessel and degassed by sonicating whilst under high vacuum. The tube was sealed under argon and the solution was heated to 220 °C, held at this temperature for 14 h and cooled to room temperature to give a precipitate which was filtered, washed with methanol and purified by recrystallisation (toluene, 15 mL, 70 °C, room temperature overnight) to give a yellow solid (0.060 g, 67%).

^{1}H-NMR (500 MHz, tol-d_8, 333 K) δ 9.20 (2H, s), 8.49 (2H, d, *J* = 7.5 Hz), 7.92 (2H, s), 7.61 (2H, d, *J* = 8.1 Hz), 7.40-7.36 (2H, m), 7.32-7.28 (2H, m), 3.22 (4H, t, *J* = 7.7 Hz), 2.06-2.00 (4H, m), 1.60-1.54 (4H, m), 1.49-1.43 (4H, m), 1.38-1.26 (28H, m), 0.90 (6H, t, *J* = 7.0 Hz).

^{13}C-NMR (125 MHz, tol-d_8, 333 K) δ 156.78 (2C), 154.81 (2C), 131.16 (2C), 127.98 (2CH), 126.65 (2C), 126.04 (2CH), 123.88 (2CH), 123.24 (2CH), 122.60 (2CH), 117.18 (2C), 112.57 (2CH), 32.71 ($2CH_2$), 31.49 ($2CH_2$), 30.56-30.54 ($6CH_2$), 30.51-30.49 ($6CH_2$), 30.41 ($2CH_2$), 30.16 ($2CH_2$), 23.42 ($2CH_2$), 14.54 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2953 (m), 2914 (m), 2848 (m), 1469 (m), 1438 (m), 1365 (w), 1087 (s), 1017 (s), 880 (m), 797 (s), 721 (s).

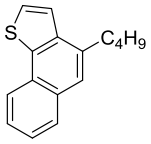
LRMS (APPI) *m/z* 694.3 ($M^{+\cdot}$), 695.4 $(M+H)^+$.

HRMS (APPI) *m/z* calc. for $C_{50}H_{63}O_2$ $(M+H)^+$ 695.48226, found 695.48261.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 264 (43700), 272 (63600), 296 (53300), 347 (8500), 366 (15100), 392 (14600), 416 (17300).

Melting point (tol) 142-143 °C.

4-butylnaphtho[1,2-*b*]thiophene 28



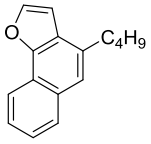
A J-Young tap vessel was charged with 2-(2-hex-1-yn-1-yl)phenyl)thiophene **26** (0.200 g, 0.832 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.120 g, 0.788 mmol) in NMP (2 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 16 h, cooled to room temperature and diluted with 1 M HCl (100 mL). The product was extracted with diethyl ether (3 x 30 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, petroleum ether) to give a yellow oil (0.147 g, 74%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.14-8.12 (1H, m), 7.90-7.87 (1H, m), 7.59-7.48 (5H, m), 3.07 (2H, t, *J* = 7.7 Hz), 1.85-1.77 (2H, m), 1.55-1.46 (2H, m), 1.01 (3H, t, *J* = 7.3 Hz).

13C-NMR (100 MHz, $CDCl_3$) δ 137.61 (C), 137.46 (C), 135.91 (C), 131.29 (C), 128.17 (CH), 127.83 (C), 125.65 (CH), 125.57 (CH), 124.66 (CH), 123.55 (CH), 123.42 (CH), 123.13 (CH), 33.89 (CH_2), 32.52 (CH_2), 22.67 (CH_2), 13.99 (CH_3).

NMR data is consistent with literature reports.[128]

4-butylnaphtho[1,2-*b*]furan 29



A J-Young tap vessel was charged with 2-(2-hex-1-yn-1-yl)phenyl)furan **27** (0.200 g, 0.892 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.137 g, 0.900 mmol) in NMP (2 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 18 h, cooled to room temperature and diluted with 1 M HCl (100 mL). The product was extracted with diethyl ether (3 x 30 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced

pressure. The crude product was purified by column chromatography (SiO_2, petroleum ether) to give an orange oil (0.116 g, 58%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.28 (1H, d, *J* = 8.2 Hz), 7.88 (1H, d, *J* = 8.1 Hz), 7.78 (1H, d, *J* = 2.1 Hz), 7.54 (1H, td, *J* = 7.5, 1.2 Hz), 7.48 (1H, dd, *J* = 8.0, 1.2 Hz), 7.45 (1H, s), 6.95 (1H, d, *J* = 2.1 Hz), 2.97 (2H, t, *J* = 7.8 Hz), 1.83-1.75 (2H, m), 1.46 (2H, sxt, *J* = 7.4 Hz), 0.99 (3H, t, *J* = 7.3 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.43 (C), 143.77 (CH), 134.44 (C), 131.68 (C), 127.72 (CH), 125.36 (CH), 125.07 (CH), 123.38 (C), 121.27 (CH), 120.19 (C), 119.86 (CH), 106.20 (CH), 33.36 (CH_2), 32.44 (CH_2), 22.58 (CH_2), 13.98 (CH_3).

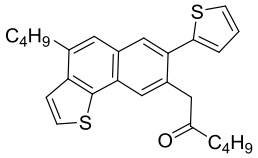
IR (neat) υ_{max}/cm^{-1} 2954 (m), 2927 (m), 2858 (m), 1588 (w), 1465 (m), 1439 (m), 1377 (w), 1026 (w), 879 (m), 811 (m), 780 (s), 744 (s), 683 (s).

LRMS (GC/EI) *m/z* 224, 37% (M^+); 181, 100% (M^+-Pr); 152, 44%.

HRMS (APPI) *m/z* calc. for $C_{16}H_{16}O$ ($M^{+\cdot}$) 224.1196, found 224.1190.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 250 (33000).

1-(4-butyl-7-(thiophen-2-yl)naphtho[1,2-*b*]thiophen-8-yl)hexan-2-one 30



A solution of 2,2'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)dithiophene **6** (0.300 g, 0.745 mmol) and DBU (0.224 g, 1.47 mmol) in NMP (4 mL) in a J-Young tap vessel was degassed by sonicating whilst under high vacuum. The tube was sealed under argon and the reaction mixture was heated to 220 °C, held at this temperature for 16 h, cooled to room temperature and diluted with 2 M HCl (25 mL). The product was extracted with diethyl ether (10 mL) and the aqueous layer was diluted with water (100 mL). More product was extracted with diethyl ether (3 x 40 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy brown solid (0.281 g). 0.033 g of the titled compound was obtained by column chromatography (SiO_2, 0-100% DCM in hexane), eluting in 100% DCM. Yield: 11%.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94 (1H, s), 7.93 (1H, s), 7.57 (1H, d, *J* = 5.5 Hz), 7.56 (1H, d, *J* = 5.5 Hz), 7.48 (1H, s), 7.39 (1H, dd, *J* = 5.2, 1.0 Hz), 7.12 (1H, dd, *J* = 5.1, 3.4 Hz), 7.03 (1H, dd, *J* = 3.4, 1.1 Hz), 4.01 (2H, s), 3.04 (2H, t, *J* = 7.6 Hz), 2.37 (2H, t, *J* = 7.4 Hz), 1.82-

1.75 (2H, m), 1.54-1.43 (4H, m), 1.30-1.21 (2H, m), 0.99 (3H, t, *J* = 7.3 Hz), 0.87 (3H, t, *J* = 7.4 Hz).

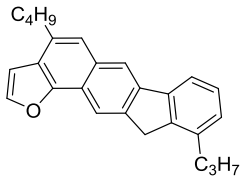
^{13}C-NMR (100 MHz, $CDCl_3$) δ 208.55 (C=O), 142.41 (C), 138.04 (C), 136.97 (C), 136.50 (C), 132.37 (C), 131.31 (C), 130.75 (CH), 130.18 (C), 127.52 (C), 127.19 (CH), 127.11 (CH), 125.73 (CH), 125.56 (CH), 125.20 (CH), 123.24 (2CH), 48.23 (CH_2), 42.15 (CH_2), 33.89 (CH_2), 32.50 (CH_2), 25.84 (CH_2), 22.63 (CH_2), 22.23 (CH_2), 13.97 (CH_3), 13.82 (CH_3).

IR (neat) υ_{max}/cm^{-1} 3117 (w), 3077 (w), 2952 (m), 2927 (m), 2866 (m), 1708 (s), 1455 (m), 1376 (m), 1052 (m), 900 (s), 830 (s), 697 (s).

HRMS (APPI) *m/z* calc. for $C_{26}H_{28}OS_2$ ($M^{+\cdot}$) 420.15761, found 420.15812.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 274 (17000).

4-butyl-10-propyl-11*H*-indeno[1',2':6,7]naphtho[1,2-*b*]furan 21



A J-Young tap vessel was charged with 2,2'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)difuran **19** (0.190 g, 0.513 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.039 g, 0.256 mmol) in NMP (2 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 24 h, cooled to room temperature and diluted with 1 M HCl (30 mL). The product was extracted with diethyl ether (5 x 10 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give 0.140 g. The crude product was purified by column chromatography (SiO_2, 0-30% DCM in pet. ether). 0.013 g of the titled compound was obtained in 90-95% purity. Yield: 7%.

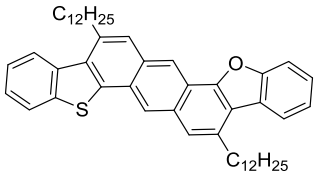
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.40 (1H, s), 8.23 (1H, s). 7.80-7.78 (2H, m), 7.54 (1H, s), 7.41-7.37 (1H, t, *J* = 7.5 Hz), 7.19 (1H, d, *J* = 7.5 Hz), 6.96 (1H, d, *J* = 2.0 Hz), 4.07 (2H, s), 2.99 (2H, t, *J* = 7.6 Hz), 2.78 (2H, t, *J* = 7.7 Hz), 1.85-1.74 (4H, m), 1.48 (2H, sxt, *J* = 7.5 Hz), 1.06 (3H, t, *J* = 7.3 Hz), 1.01 (3H, t, *J* = 7.3 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.75 (C), 143.53 (CH), 142.15 (C), 141.24 (C), 140.81 (C), 140.15 (C), 139.14 (C), 133.72 (C), 131.36 (C), 127.30 (CH), 127.27 (CH), 123.07 (C), 121.70 (CH), 119.59 (C), 118.01 (CH), 117.85 (CH), 115.47 (CH), 106.32 (CH), 35.41 (CH_2), 35.32 (CH_2), 33.35 (CH_2), 32.46 (CH_2), 23.20 (CH_2), 22.62 (CH_2), 14.20 (CH_3), 14.02 (CH_3).

IR (neat) υ_{max}/cm^{-1} 2954 (s), 2927 (s), 2856 (m), 1502 (m), 1455 (m), 1440 (m), 1375 (w), 1043 (m), 892 (m), 870 (m), 799 (s), 737 (s).

HRMS (APPI) *m/z* calc. for $C_{26}H_{26}O$ ($M^{+\cdot}$) 354.1978, found 354.1976.

2,10-didodecylbenzo[4',5']thieno[2',3':5,6]anthra[1,2-*b*]benzofuran 36



A solution of 2-(4-(benzo[*b*]thiophen-2-yl)-2,5-di(tetradec-1-yn-1-yl)phenyl)benzofuran **35** (0.140 g, 0.197 mmol) and DBU (0.060 g, 0.396 mmol) in NMP (20 mL) was transferred into a J-Young tap vessel and degassed by sonicating whilst under high vacuum. The tube was sealed under argon and the solution was heated to 220 °C, held at this temperature for 2 days and cooled to room temperature to give a precipitate which was filtered and dissolved in chloroform (200 mL). The solution was washed successively with 2 M HCl and brine, dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow solid (0.098 g, 70%).

^{1}H-NMR (500 MHz, odcb-d_4, 333 K) δ 8.97 (1H, s), 8.75 (1H, s), 8.40 (1H, d, *J* = 8.1 Hz), 8.06 (1H, d, *J* = 7.5 Hz), 7.95 (1H, d, *J* = 7.5 Hz), 7.84 (1H, s), 7.76 (1H, d, *J* = 8.1 Hz), 7.71 (1H, s), 7.50-7.37 (4H, m), 3.41 (2H, t, *J* = 7.5 Hz), 3.29 (2H, t, *J* = 7.6 Hz), 2.00-1.94 (4H, m), 1.66-1.59 (4H, m), 1.48-1.41 (4H, m), 1.37-1.23 (28H, m), 0.88-0.85 (6H, m).

^{13}C-NMR (125 MHz, odcb-d_4, 333 K) δ 156.01 (C), 152.05 (C), 139.39 (C), 138.45 (C), 137.27 (C), 137.20 (C), 136.01 (C), 134.72 (C), 131.43 (C), 131.38 (C), 125.53 (CH), 125.44 (CH), 125.32 (C), 125.15 (CH), 124.64 (CH), 124.55 (CH), 123.13 (CH), 122.83 (CH), 122.13 (CH), 121.79 (CH), 121.61 (CH), 119.98 (C), 119.37 (CH), 118.02 (C), 111.69 (CH), 35.56 (CH_2), 34.33 (CH_2), 31.89 ($2CH_2$), 29.81 (CH_2), 29.71 ($8CH_2$), 29.67 ($5CH_2$), 29.35 ($2CH_2$), 22.65 ($2CH_2$), 13.92 ($2CH_3$).

LRMS (APPI) *m/z* 711.2 $(M+H)^+$.

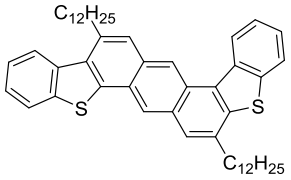
HRMS (APPI) *m/z* calc. for $C_{50}H_{63}OS$ $(M+H)^+$ 711.45941, found 711.45970.

IR (neat) υ_{max}/cm^{-1} 2961 (m), 2916 (s), 2850 (m), 1470 (m), 1450 (w), 1087 (s), 1018 (s), 898 (m), 797 (s), 730 (s), 718 (s).

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 316 (96000), 334 (25600), 371 (7600), 392 (7100), 415 (4400).

Melting point (tol) 133-134 °C.

38



A solution of 3-(4-(benzo[*b*]thiophen-2-yl)-2,5-di(tetradec-1-yn-1-yl)phenyl)benzo[*b*]thiophene **37** (0.380 g, 0.523 mmol) and DBU (0.318 g, 2.09 mmol) in NMP (30 mL) was added to a J-Young tap vessel and degassed by sonicating whilst under high vacuum. The tube was sealed under argon and the solution was heated to 220 °C and held at this temperature for 18 h followed by addition of extra DBU (0.31 mL, 2.07 mmol) and continued reaction for 22 h. The reaction mixture was cooled to room temperature, giving a precipitate which was filtered, washed with methanol and recrystallised in refluxing toluene (35 mL, room temperature for 6 h) to give a yellow solid (0.267 g, 70%).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.49 (1H, s), 9.08 (1H, d, *J* = 8.4 Hz), 8.74 (1H, s), 8.40 (1H, d, *J* = 8.0 Hz), 8.08-8.05 (2H, m), 7.91 (1H, s), 7.89 (1H, s), 7.72-7.68 (1H, m), 7.56-7.48 (3H, m), 3.43 (2H, t, *J* = 7.8 Hz), 3.06 (2H, t, *J* = 7.8 Hz), 1.97 (4H, quin., *J* = 7.7 Hz), 1.66-1.60 (2H, m), 1.56-1.50 (2H, m), 1.48-1.40 (4H, m), 1.28 (28H, br), 0.90-0.87 (6H, m).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 140.56 (C), 139.29 (2C), 138.11 (C), 137.48 (C), 137.38 (C), 137.22 (C), 134.76 (C), 131.12 (C), 131.08 (C), 130.29 (C), 128.35 (C), 128.32 (C), 125.71 (2CH), 125.36 (C), 125.11 (CH), 124.96 (CH), 124.89 (CH), 124.66 (CH), 124.59 (CH), 124.51 (CH), 123.22 (2CH), 123.06 (CH), 121.35 (CH), 35.75 (CH_2), 35.05 (CH_2), 31.92 ($2CH_2$), 29.91 (CH_2), 29.78 (CH_2), 29.69-29.65 ($10CH_2$), 29.55 (CH_2), 29.36 ($2CH_2$), 29.08 (CH_2), 22.68 ($2CH_2$), 14.11 ($2CH_3$).

LRMS (APPI) *m/z* 726.4 ($M^{+\cdot}$), 727.3 $(M+H)^+$.

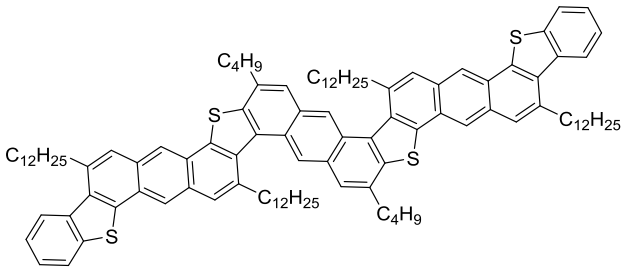
HRMS (APPI) *m/z* calc. for $C_{50}H_{63}S_2$ $(M+H)^+$ 727.43657, found 727.43598.

IR (neat) υ_{max}/cm^{-1} 2915 (s), 2847 (s), 1463 (m), 896 (m), 886 (m), 747 (s), 720 (s).

UV (DCM) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 286 (36000), 298 (47200), 313 (62700), 322 (78700), 333 (74400), 355 (6800), 373 (9500), 393 (11300), 415 (7100).

Melting point (tol) 124-125 °C.

40



A J-Young tap vessel was charged with 2,8-bis(4-(benzo[*b*]thiophen-2-yl)-2,5-di(tetradec-1-yn-1-yl)phenyl)-4,10-dibutylanthra[2,1-*b*:6,5-*b*']dithiophene **39** (0.160 g, 1.01 mmol) and flushed with argon for 0.5 h. NMP (2 mL) and DBU (0.06 mL, 0.06 g, 0.401 mmol) were added, the tube was sealed under argon and the reaction mixture was heated to 220 °C, held at this temperature for 15 h and then cooled to room temperature to give a precipitate which was filtered, washed with methanol and dried to give 0.086 g of a brown solid. More product was obtained by exhaustive extraction (DCM) from the mother liquor after dilution with 2 M HCl. The two samples were combined and purified by column chromatography (SiO_2, 10% DCM in hexane) to give a yellow solid (0.040 g, 25%).

^{1}H-NMR (500 MHz, tol-d_8, 333 K) δ 8.96 (2H, s), 8.85 (4H, m), 8.38 (2H, d, *J* = 7.6 Hz), 7.98 (2H, s), 7.90 (2H, s), 7.79 (2H, d, *J* = 7.9 Hz), 7.69 (2H, s), 7.37-7.34 (2H, m), 7.23 (2H, t, *J* = 7.3 Hz), 3.62 (4H, t, *J* = 7.5 Hz), 3.31 (4H, t, *J* = 6.9 Hz), 3.25 (4H, t, *J* = 7.5 Hz), 1.95-1.92 (4H, m), 1.81 (4H, br), 1.68-1.61 (8H, m), 1.45 (4H, br), 1.36-1.10 (74H, m), 0.92-0.89 (6H, m), 0.82 (6H, t, *J* = 6.4 Hz).

^{13}C-NMR (125 MHz, TCE-d_2, 333 K) δ 139.11 (2C), 139.07 (2C), 138.10 (2C), 137.57 (2C), 137.55 (2C), 137.29 (2C), 137.11 (2C), 134.59 (2C), 133.70 (2C), 132.06 (2C), 131.14 (2C), 130.01 (2C), 129.98 (2C), 129.49 (2C), 126.92 (2C), 126.46 (2C), 126.37 (2C), 126.06 (2CH), 125.23 (2CH), 125.17 (2CH), 125.08 (2CH), 125.04 (2CH), 124.63 (4CH), 122.97 (2CH), 122.00 (2CH), 121.58 (2CH), 35.76 ($2CH_2$), 35.41 ($2CH_2$), 34.66 ($2CH_2$), 31.75 ($2CH_2$), 31.72 ($2CH_2$), 31.69 ($2CH_2$), 31.39 ($2CH_2$), 29.61 ($2CH_2$), 29.54-29.41 ($24CH_2$), 29.18 ($2CH_2$), 29.09 ($2CH_2$), 22.75 ($2CH_2$), 22.52 ($2CH_2$), 22.45 ($2CH_2$), 13.99 ($2CH_3$), 13.93 ($2CH_3$), 13.91 ($2CH_3$).

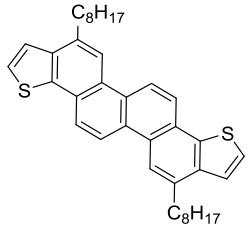
IR (neat) υ_{max}/cm^{-1} 2954 (m), 2918 (s), 2849 (s), 1461 (m), 1374 (w), 1090 (s), 1017 (s), 880 (m), 797 (s), 721 (s).

LRMS (APPI) *m/z* 1588.1 $(M+H)^+$.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 309 (103100), 330 (98900), 355 (61800), 384 (33700), 398 (34100), 427 (37700), 454 (53300).

Melting point > 250 °C.

7,14-dioctylchryseno[1,2-b:7,8-*b*']dithiophene 50



A J-Young tap vessel was charged with 2,2'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)dithiophene **42** (0.180 g, 0.319 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.101 g, 0.663 mmol) in degassed NMP (2 mL) was added and the tube sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 18 h and cooled to room temperature to give a precipitate which was filtered, washed (methanol) and dried. The titled compound was obtained as a yellow solid (0.151 g, 84%).

^{1}H-NMR (500 MHz, TCE-d_2, 333 K) δ 8.85 (2H, d, *J* = 9.2 Hz), 8.51 (2H, s), 8.32 (2H, d, *J* = 8.9 Hz), 7.67 (2H, d, *J* = 5.3 Hz), 7.65 (2H, d, *J* = 5.3 Hz), 3.22 (4H, t, *J* = 7.8 Hz), 1.94 (4H, quin, *J* = 7.6 Hz), 1.60-1.54 (4H, m), 1.49-1.44 (4H, m), 1.41-1.31 (12H, m), 0.94 (6H, t, *J* = 6.8 Hz).

^{13}C-NMR (125 MHz, TCE-d_2, 333 K) δ 138.46 (2C), 137.56 (2C), 136.75 (2C), 128.42 (2C), 127.76 (2C), 125.61 (2C), 125.46 (2CH), 123.12 (2CH), 123.07 (2CH), 121.46 (2CH), 118.88 (2CH), 34.74 ($2CH_2$), 31.74 ($2CH_2$), 30.72 ($2CH_2$), 29.63 ($2CH_2$), 29.38 ($2CH_2$), 29.12 ($2CH_2$), 22.52 ($2CH_2$), 13.99 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2949 (m), 2915 (s), 2849 (m), 1456 (m), 1378 (w), 865 (m), 813 (s), 801 (s), 696 (s).

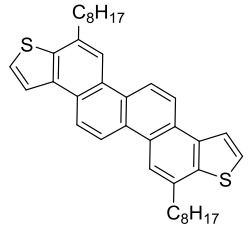
LRMS (APPI) *m/z* 564.2 ($M^{+\cdot}$).

HRMS (APPI) *m/z* calc. for $C_{38}H_{44}S_2$ ($M^{+\cdot}$) 564.28789, found 564.28729.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 303 (108400), 321 (42900), 328 (38400), 341 (12000), 367 (3400), 386 (4100).

Melting point (tol) 148-150 °C.

7,14-dioctylchryseno[2,1-*b*:8,7-*b*']dithiophene 51



A J-Young tap vessel was charged with 3,3'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)dithiophene **43** (0.120 g, 0.212 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.033 g, 0.217 mmol) in NMP (2 mL) was added and the tube sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 20 h and cooled to room temperature to give a precipitate which was washed (methanol) and dried. The titled compound was obtained as a yellow solid (0.102 g, 85%).

^{1}H-NMR (500 MHz, TCE-d_2, 353 K) δ 8.93 (2H, d, J = 9.2 Hz), 8.61 (2H, s), 8.57 (2H, d, J = 9.1 Hz), 8.19 (2H, d, J = 5.5 Hz), 7.72 (2H, d, J = 5.3 Hz), 3.22 (4H, t, J = 7.8 Hz), 2.06 (4H, quin, J = 7.6 Hz), 1.64-1.58 (4H, m), 1.53-1.47 (4H, m), 1.45-1.36 (12H, m), 0.95 (6H, t, J = 7.0 Hz).

^{13}C-NMR (500 MHz, TCE-d_2, 353 K) δ 138.72 (2C), 136.65 (2C), 135.60 (2C), 128.38 (2C), 128.07 (2C), 126.05 (2C), 125.79 (2CH), 122.86 (2CH), 122.58 (2CH), 121.18 (2CH), 118.33 (2CH), 35.67 ($2CH_2$), 31.68 ($2CH_2$), 29.54 ($2CH_2$), 29.31 ($2CH_2$), 29.26 ($2CH_2$), 29.02 ($2CH_2$), 22.43 ($2CH_2$), 13.85 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2951 (m), 2921 (s), 2851 (m), 1467 (m), 1454 (m), 1092 (m), 826 (s), 761 (s), 704 (s).

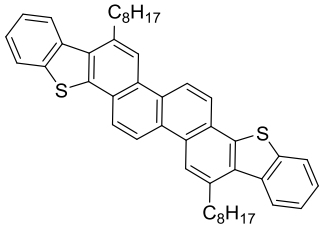
LRMS (APPI) *m/z* 564.2 ($M^{+\cdot}$).

HRMS (APPI) *m/z* calc. for $C_{38}H_{44}S_2$ ($M^{+\cdot}$) 564.28789, found 564.28660.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 260 (38800), 269 (46700), 278 (61300), 289 (98100), 330 (22000), 345 (21300), 373 (2200).

Melting point (tol) > 250 °C.

7,14-dioctylchryseno[1,2-b:7,8-*b*']dibenzothiophene 52



A J-Young tap vessel was charged with 2,2'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)bis(benzo[*b*]thiophene) **44** (0.200 g, 0.301 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.091 g, 0.598 mmol) in degassed NMP (2 mL) was added and tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 20 h and then cooled to room temperature to give a precipitate which was

filtered, washed (methanol) and dried. The titled compound was obtained as a yellow solid (0.138 g, 69%).

^{1}H-NMR (500 MHz, TCE-d_2, 353 K) δ 8.93 (2H, d, *J* = 9.2 Hz), 8.63 (2H, s), 8.47 (2H, d, *J* = 8.0 Hz), 8.38 (2H, d, *J* = 9.0 Hz), 8.09 (2H, d, *J* = 7.6 Hz), 7.63-7.59 (2H, m), 7.58-7.55 (2H, m), 3.58 (4H, t, *J* = 7.7 Hz), 2.07 (4H, quin, *J* = 7.7 Hz), 1.75-1.69 (4H, m), 1.57-1.51 (4H, m), 1.47-1.37 (12H, m), 0.96 (6H, t, *J* = 7.0 Hz).

^{13}C-NMR (125 MHz, TCE-d_2, 353 K) δ 139.44 (2C), 139.10 (2C), 138.28 (2C), 136.64 (2C), 131.89 (2C), 128.55 (2C), 128.52 (2C), 125.66 (2C), 125.57 (2CH), 124.78 (2CH), 124.58 (2CH), 123.62 (2CH), 122.90 (2CH), 121.53 (2CH), 120.93 (2CH), 35.81 ($2CH_2$), 31.68 ($2CH_2$), 29.88 ($2CH_2$), 29.56 ($2CH_2$), 29.36 ($2CH_2$), 29.07 ($2CH_2$), 22.44 ($2CH_2$), 13.86 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2953 (m), 2916 (s), 2848 (m), 1604 (w), 1467 (m), 1435 (m), 869 (s), 819 (s), 733 (s), 721 (s).

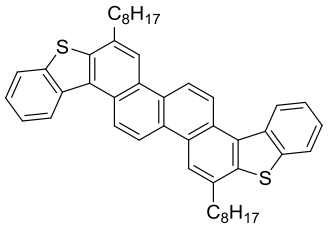
LRMS (APPI) *m/z* 664.2 ($M^{+\cdot}$).

HRMS (APPI) *m/z* calc. for $C_{46}H_{48}S_2$ ($M^{+\cdot}$) 664.31919, found 664.31942.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 259 (40300), 290 (25000), 320 (95500), 342 (53700), 373 (3100), 394 (2800).

Melting point (NMP) > 250 °C.

7,14-dioctylchryseno[2,1-*b*:8,7-*b*']dibenzothiophene 53



A J-Young tap vessel was charged with 3,3'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)bis(benzo[*b*]thiophene) **45** (0.070 g, 0.105 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.032 g, 0.210 mmol) in degassed NMP (1 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 16 h and then cooled to room temperature to give a precipitate which was filtered, washed (methanol) and dried. The titled compound was obtained as a yellow solid (0.065 g, 93%).

^{1}H-NMR (500 MHz, TCE-d_2, 333 K) δ 9.26 (2H, d, *J* = 9.5 Hz), 9.03 (2H, d, *J* = 9.5 Hz), 9.01 (2H, d, *J* = 8.4 Hz), 8.78 (2H, s), 8.10 (2H, d, *J* = 7.6 Hz), 7.71-7.68 (2H, m), 7.61-7.58 (2H,

m), 3.22 (4H, t, *J* = 7.9 Hz), 2.10-2.04 (4H, m), 1.65-1.59 (4H, m), 1.53-1.48 (4H, m), 1.45-1.36 (12H, m), 0.95 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (125 MHz, TCE-d_2, 333 K) δ 139.75 (2C), 139.57 (2C), 137.04 (2C), 135.47 (2C), 130.05 (2C), 128.82 (2C), 127.67 (2C), 127.40 (2C), 125.44 (2CH), 124.82 (2CH), 124.79 (2CH), 123.24 (2CH), 122.36 (2CH), 121.87 (2CH), 120.75 (2CH), 35.71 ($2CH_2$), 31.75 ($2CH_2$), 29.58 ($2CH_2$), 29.35 ($2CH_2$), 29.26 ($2CH_2$), 29.12 ($2CH_2$), 22.53 ($2CH_2$), 14.00 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2951 (m), 2916 (s), 2849 (m), 1463 (m), 1455 (m), 1380 (w), 1026 (m), 873 (s), 813 (s), 733 (s).

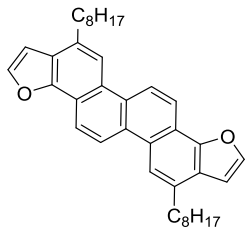
LRMS (APPI) *m/z* 664.4 ($M^{+\cdot}$).

HRMS (APPI) *m/z* calc. for $C_{46}H_{48}S_2$ ($M^{+\cdot}$) 664.31919, found 664.31926.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 264 (31100), 278 (39400), 300 (67000), 316 (52100), 343 (26400), 360 (25000), 388 (4100).

Melting point (tol) 211-215 °C.

7,14-dioctylchryseno[1,2-*b*:7,8-*b*']difuran 54



A J-Young tap vessel was charged with 2,2'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)difuran **46** (0.040 g, 0.075 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.027 g, 0.177 mmol) in degassed NMP (1 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 16 h and then cooled to room temperature and diluted with 1 M HCl (100 mL). The product was extracted with diethyl ether (7 x 20 mL) and the organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. The crude product was purified by column chromatography (SiO_2, pet. ether) to give the titled compound as a yellow solid (0.014 g, 35%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.85 (2H, d, *J* = 9.2 Hz), 8.50 (2H, d, *J* = 9.0 Hz), 8.43 (2H, s), 7.85 (2H, d, *J* = 2.0 Hz), 7.02 (2H, d, *J* = 2.0 Hz), 3.11 (4H, t, *J* = 7.8 Hz), 1.89 (4H, quin, *J* = 7.6 Hz), 1.53-1.27 (20H, m), 0.91-0.88 (6H, m).

^{13}C-NMR (400 MHz, $CDCl_3$) δ 151.34 (2C), 144.29 (2CH), 134.94 (2C), 128.34 (2C), 127.94 (2C), 123.79 (2C), 121.22 (2CH), 119.30 (2CH), 117.72 (2C), 116.91 (2CH), 106.11 (2CH),

34.44 ($2CH_2$), 31.90 ($2CH_2$), 30.82 ($2CH_2$), 29.67 ($2CH_2$), 29.55 ($2CH_2$), 29.29 ($2CH_2$), 22.67 ($2CH_2$), 14.11 ($2CH_3$).

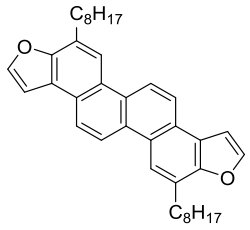
IR (neat) υ_{max}/cm^{-1} 2953 (m), 2924 (s), 2852 (m), 1484 (m), 1467 (m), 1378 (w), 1038 (m), 884 (m), 821 (s), 723 (s).

HRMS (APPI) *m/z* calc. for $C_{38}H_{44}O_2$ ($M^{+\cdot}$) 532.33358, found 532.33289.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 294 (121000), 312 (37600), 319 (33800), 334 (11200), 360 (1800), 379 (1200).

Melting point (hexane/DCM) 107-109 °C.

7,14-dioctylchryseno[2,1-*b*:8,7-*b*']difuran 55



A J-Young tap vessel was charged with 3,3'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)difuran **47** (0.130 g, 0.244 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.073 g, 0.480 mmol) in degassed NMP (2 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 20 h and then cooled to room temperature to give a precipitate which was filtered, washed (methanol) and dried. The titled compound was obtained as a yellow solid (0.104 g, 80%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.85 (2H, d, *J* = 9.0 Hz), 8.52 (2H, s), 8.31 (2H, d, *J* = 9.0 Hz), 7.84 (2H, d, *J* = 2.1 Hz), 7.39 (2H, d, *J* = 2.1 Hz), 3.18 (4H, t, *J* = 7.8 Hz), 1.94 (4H, quin, *J* = 7.6 Hz), 1.55-1.47 (4H, m), 1.45-1.38 (4H, m), 1.37-1.27 (12H, m), 0.89 (6H, t, *J* = 6.8 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.37 (2C), 144.35 (2CH), 127.93 (2C), 127.38 (2C), 127.22 (2C), 124.47 (2C), 123.40 (2C), 122.75 (2CH), 121.16 (2CH), 119.15 (2CH), 105.81 (2CH), 31.91 ($2CH_2$), 31.06 ($2CH_2$), 30.16 ($2CH_2$), 29.67 ($2CH_2$), 29.50 ($2CH_2$), 29.30 ($2CH_2$), 22.67 ($2CH_2$), 14.11 ($2CH_3$).

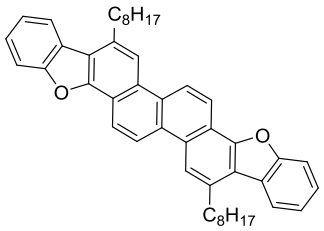
IR (neat) υ_{max}/cm^{-1} 3110 (w), 2954 (m), 2920 (s), 2850 (s), 1467 (m), 1439 (m), 1378 (w), 1037 (m), 881 (s), 826 (s), 763 (s), 732 (s).

HRMS (APPI) *m/z* calc. for $C_{38}H_{44}O_2$ ($M^{+\cdot}$) 532.3336, found 532.3322.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 258 (74600), 277 (98900), 300 (10900), 314 (14900), 328 (22800), 341 (20400), 348 (15400), 366 (3900).

Melting point (tol) 196-198 °C.

7,14-dioctylchryseno[1,2-*b*:7,8-*b*']dibenzofuran 56



A J-Young tap vessel was charged with 2,2'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)bis(benzofuran) **48** (0.040 g, 0.063 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.021 g, 0.138 mmol) in degassed NMP (1 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 20 h and then cooled to room temperature to give a precipitate which was filtered, washed (methanol) and dried. The titled compound was obtained as a yellow solid (0.028 g, 70%).

^{1}H-NMR (500 MHz, TCE-d_2, 333 K) δ 8.92 (2H, d, *J* = 9.2 Hz), 8.68 (2H, d, *J* = 9.0 Hz), 8.53 (2H, s), 8.12 (2H, d, *J* = 7.6 Hz), 7.83 (2H, d, *J* = 8.1 Hz), 7.59-7.55 (2H, m), 7.52-7.47 (2H, m), 3.43 (4H, t, *J* = 7.9 Hz), 2.03 (4H, quin, *J* = 7.6 Hz), 1.66 (4H, quin, *J* = 7.6 Hz), 1.53-1.47 (4H, m), 1.44-1.34 (12H, m), 0.94 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (125 MHz, TCE-d_2, 333 K) δ 156.08 (2C), 125.68 (2C), 136.69 (2C), 129.75 (2C), 128.14 (2C), 126.01 (2CH), 124.62 (2C), 122.94 (2CH), 121.97 (2CH), 121.12 (2CH), 119.91 (2CH), 119.07 (2C), 117.48 (2C), 117.27 (2CH), 111.70 (2CH), 34.60 ($2CH_2$), 31.64 ($2CH_2$), 29.94 ($2CH_2$), 29.55 ($2CH_2$), 29.33 ($2CH_2$), 29.05 ($2CH_2$), 22.43 ($2CH_2$), 13.90 ($2CH_3$).

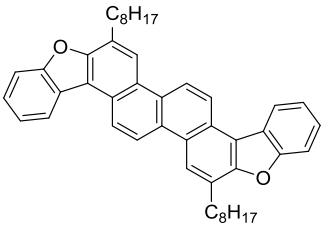
IR (neat) υ_{max}/cm^{-1} 2918 (s), 2850 (m), 1588 (w), 1464 (m), 1449 (m), 1372 (w), 1018 (m), 854 (m), 822 (s), 741 (s), 722 (s).

HRMS (APPI) *m/z* calc. for $C_{46}H_{48}O_2$ ($M^{+\cdot}$) 632.36488, found 632.36498.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 300 (65800), 311 (82200), 319 (79800), 337 (60900), 368 (7700), 388 (9100).

Melting point (tol) 218-220 °C.

7,14-dioctylchryseno[2,1-*b*:8,7-*b*']dibenzofuran 57



A J-Young tap vessel was charged with 3,3'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)bis(benzofuran) **49** (0.035 g, 0.055 mmol) and evacuated/refilled with nitrogen three times.

A solution of DBU (0.017 g, 0.112 mmol) in degassed NMP (1 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 24 h and then cooled to room temperature to give a precipitate which was filtered, washed (methanol) and dried. The titled compound was obtained as a yellow solid (0.021 g, 60%).

^{1}H-NMR (500 MHz, tol-d_8, 353 K) δ 8.89 (2H, d, *J* = 9.2 Hz), 8.76 (2H, s), 8.73 (2H, d, *J* = 9.2 Hz), 8.39 (2H, d, *J* = 7.3 Hz), 7.59 (2H, d, *J* = 7.8 Hz), 7.35-7.28 (4H, m), 3.29 (4H, t, *J* = 7.8 Hz), 2.06 (4H, quin, *J* = 7.6 Hz), 1.58 (4H, quin, *J* = 7.4 Hz), 1.49-1.43 (4H, m), 1.39-1.30 (12H, m), 0.91 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (125 MHz, tol-d_8, 353 K) δ 157.25 (2C), 155.01 (2C), 128.18 (2C), 127.32 (2C), 126.63 (2CH), 126.41 (2C), 123.71 (2CH), 123.57 (2CH), 123.12 (2CH), 122.93 (2CH), 122.82 (2CH), 119.27 (2C), 112.57 (2CH), 32.67 ($2CH_2$), 31.74 ($2CH_2$), 30.88 ($2CH_2$), 30.46 ($2CH_2$), 30.30 ($2CH_2$), 30.05 ($2CH_2$), 23.35 ($2CH_2$), 14.45 ($2CH_3$).

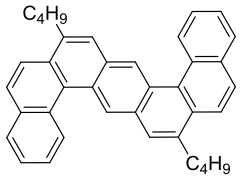
IR (neat) υ_{max}/cm^{-1} 2941 (m), 2917 (s), 2849 (m), 1465 (m), 1456 (m), 1375 (w), 1090 (m), 871 (m), 816 (s), 749 (s), 725 (s).

HRMS (APPI) *m/z* calc. for $C_{46}H_{48}O_2$ ($M^{+\cdot}$) 632.3649, found 632.3644.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 281 (116200), 292 (97200), 327 (28800), 342 (42100), 353 (35200), 359 (35000), 378 (12100).

Melting point (tol) 205-207 °C.

7,16-dibutylbenzo[*a*]naphtho[1,2-*k*]tetraphene 60



1,1'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)dinaphthalene **58** (1.10 g, 2.24 mmol) was split over two J-Young tap vessels which were both evacuated/refilled with nitrogen three times. A solution of DBU (0.750 g, 4.93 mmol) in NMP (8 mL) was split over the two reactions and both tubes were sealed under nitrogen. The reaction mixtures were heated to 240 °C, held at this temperature for 20 h, cooled to room temperature and then diluted with water (20 mL each). This gave dark yellow precipitates which were filtered, combined and dried. The crude product was purified by column chromatography (SiO_2, pet. ether) to give a yellow solid (0.475 g). Recrystallisation (2:1 hexane/DCM, 18 mL, room temperature to 3 °C overnight) gave 0.090 g of a yellow solid. The mother liquor was concentrated under reduced pressure, and a second recrystallisation gave 0.060 g. Final yield: 0.150 g, 14%.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.49 (2H, s), 9.34 (2H, d, *J* = 8.6 Hz), 8.16 (2H, d, *J* = 8.9 Hz), 8.10 (2H, d, *J* = 7.3 Hz), 8.03 (2H, d, *J* = 8.8 Hz), 7.91 (2H, s), 7.79-7.75 (2H, m), 7.70-7.66 (2H, m), 3.23 (4H, t, *J* = 7.9 Hz), 1.92-1.84 (4H, m), 1.60-1.51 (4H, m), 1.03 (6H, t, *J* = 7.3 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.61 (2C), 132.92 (2C), 130.96 (2C), 130.69 (2C), 130.23 (2C), 128.29 (2CH), 128.17 (2CH), 128.09 (2C), 128.01 (2C), 127.42 (2CH), 127.20 (2CH), 127.04 (2CH), 126.35 (2CH), 125.76 (2CH), 122.45 (2CH), 33.64 ($2CH_2$), 32.77 ($2CH_2$), 22.93 ($2CH_2$), 14.06 ($2CH_3$).

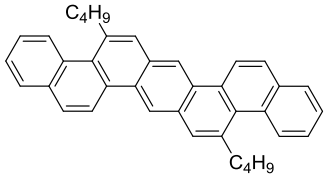
IR (neat) υ_{max}/cm^{-1} 2955 (m), 2919 (m), 2854 (m), 1595 (w), 1451 (m), 1089 (m), 1019 (m), 822 (s), 790 (s), 746 (s).

HRMS (APPI) *m/z* calc. for $C_{38}H_{34}$ ($M^{+\cdot}$) 490.2655, found 490.2656.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 296 (20400), 308 (30100), 321 (82000), 336 (170000), 355 (15400), 377 (12000), 405 (3900), 432 (1600).

Melting point (pentane/$CHCl_3$) 181-183 °C.

5,14-dibutylbenzo[*c*]naphtho[2,1-*k*]tetraphene 61



A J-Young tap vessel was charged with 2,2'-(2,5-di(hex-1-yn-1-yl)-1,4-phenylene)dinaphthalene **59** (0.140 g, 0.285 mmol) and flushed with argon for 0.5 h. NMP (2 mL) and DBU (0.18 mL, 0.183 g, 1.20 mmol) were added and the tube was sealed under argon. The reaction mixture was heated to 220 °C, held at this temperature for 16 h and cooled to room temperature to give a precipitate which was filtered, washed (methanol) and dried to give a yellow solid (0.087 g). A second batch of pure material was collected from the filtrate by the same method after 1 h at room temperature, giving 0.013 g. Final yield: 0.100 g, 71%.

^{1}H-NMR (odcb-d_4, 500 MHz, 333 K) δ 9.19 (2H, s), 8.93 (2H, d, *J* = 9.1 Hz), 8.85 (2H, d, *J* = 8.5 Hz), 8.11 (2H, s), 8.01 (2H, d, *J* = 9.0 Hz), 7.96 (2H, d, *J* = 7.9 Hz), 7.63-7.60 (2H, m), 7.57-7.54 (2H, m), 3.58-3.54 (4H, m), 1.96 (4H, quin, *J* = 7.7 Hz), 1.56 (4H, sxt, *J* = 7.4 Hz), 1.01 (6H, t, *J* = 7.4 Hz).

^{13}C-NMR (odcb-d_4, 125 MHz, 333 K) δ 137.57 (2C), 133.80 (2C), 131.27 (2C), 130.49 (2C), 130.28 (2CH), 129.24 (2C), 129.21 (2C), 129.01 (2C), 128.79 (2CH), 127.71 (2CH), 127.50

(2CH), 125.76 (2CH), 125.47 (2CH), 122.02 (2CH), 121.57 (2CH), 38.52 ($2CH_2$), 33.37 ($2CH_2$), 23.13 ($2CH_2$), 14.02 ($2CH_3$).

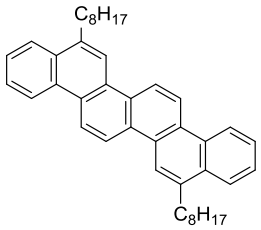
IR (neat) υ_{max}/cm^{-1} 2955 (m), 2921 (m), 2868 (m), 2853 (m), 1592 (w), 1458 (m), 1028 (w), 818 (s), 749 (s), 725 (s).

HRMS (APPI) *m/z* calc. for $C_{38}H_{35}$ $(M+H)^+$ 491.27333, found 491.27248.

UV (DCM) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 262 (35300), 286 (25800), 300 (57400), 310 (127900), 323 (190500), 351 (11900), 370 (11800), 391 (10300), 400 (10200), 424 (5800).

Melting point (tol) > 250 °C.

8,16-dioctylbenzo[*c*]picene 65



A J-Young tap vessel was charged with 1,5-di(dec-1-yn-1-yl)-2,6-diphenylnaphthalene **62** (0.200 g, 0.362 mmol) and flushed with argon for 0.5 h. NMP (2 mL) and DBU (0.40 mL, 0.408 g, 2.67 mmol) were added and the tube was sealed under nitrogen. The reaction mixture was heated to 220 °C, held at this temperature for 17 h and cooled to room temperature to give a precipitate which was filtered, washed (methanol) and dried. The titled compound was obtained as a light yellow solid (0.172 g, 86%).

^{1}H-NMR (500 MHz, TCE-d_2, 333 K) δ 9.01 (2H, d, *J* = 9.4 Hz), 8.96 (2H, d, *J* = 10.8 Hz), 8.93 (2H, d, *J* = 8.0 Hz), 8.72 (2H, s), 8.28 (2H, dd, *J* = 8.0, 1.0 Hz), 7.81-7.73 (4H, m), 3.34 (4H, t, *J* = 7.9 Hz), 2.01-1.95 (4H, m), 1.65-1.59 (4H, m), 1.52-1.46 (4H, m), 1.42-1.34 (12H, m), 0.94 (6H, t, *J* = 6.8 Hz).

^{13}C-NMR (125 MHz, TCE-d_2, 333 K) δ 138.06 (2C), 131.05 (2C), 130.68 (2C), 128.55 (2C), 128.19 (2C), 127.27 (2C), 126.42 (2CH), 126.29 (2CH), 124.45 (2CH), 123.01 (2CH), 121.43 (2CH), 121.26 (2CH), 120.83 (2CH), 34.02 ($2CH_2$), 31.75 ($2CH_2$), 30.64 ($2CH_2$), 29.84 ($2CH_2$), 29.41 ($2CH_2$), 29.15 ($2CH_2$), 22.52 ($2CH_2$), 13.99 ($2CH_3$).

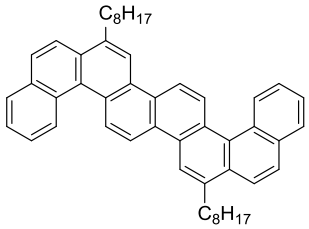
IR (neat) υ_{max}/cm^{-1} 2948 (m), 2924 (s), 2852 (m), 1582 (w), 1485 (m), 1464 (m), 1442 (m), 1388 (w), 1076 (w), 833 (s), 760 (s), 698 (s).

HRMS (APPI) *m/z* calc. for $C_{42}H_{49}$ $(M+H)^+$ 553.38288, found 553.38306.

UV (DCM) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 269 (37400), 287 (75400), 297 (106400), 330 (19700), 346 (21100), 367 (1800), 387 (1900).

Melting point (tol) > 250 °C.

8,18-dioctylbenzo[*a*]naphtho[1,2-*m*]picene 66



A J-Young tap vessel was charged with 1',5'-di(dec-1-yn-1-yl)-1,2':6',1''-ternaphthalene **63** (0.054 g, 0.083 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.027 g, 0.177 mmol) in NMP (1 mL) was added and the tube was sealed under nitrogen. The reaction was heated to 240 °C, held at this temperature for 16 h and cooled to room temperature to give a precipitate which was filtered, washed (methanol) and dried. The titled compound was obtained as a light red solid (0.028 g, 52%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.24 (2H, d, *J* = 9.3 Hz), 9.18 (2H, d, *J* = 8.2 Hz), 8.95 (2H, d, *J* = 9.5 Hz), 8.84 (2H, s), 8.19 (2H, d, *J* = 8.9 Hz), 8.07 (2H, dd, *J* = 8.9, 1.3 Hz), 8.00 (2H, d, *J* = 8.8 Hz), 7.75-7.66 (4H, m), 3.38 (4H, t, *J* = 7.9 Hz), 2.00-1.93 (4H, m), 1.64-1.56 (4H, m), 1.49-1.42 (4H, m), 1.40-1.29 (12H, m), 0.91 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.73 (2C), 133.15 (2C), 130.53 (2C), 129.84 (2C), 129.72 (2C), 129.03 (2CH), 128.68 (2C), 128.18 (2CH), 128.05 (2C), 127.48 (2C), 127.28 (2CH), 127.06 (2CH), 126.07 (2CH), 125.83 (2CH), 122.40 (2CH), 122.26 (2CH), 120.40 (2CH), 34.54 ($2CH_2$), 31.94 ($2CH_2$), 31.36 ($2CH_2$), 29.98 ($2CH_2$), 29.60 ($2CH_2$), 29.35 ($2CH_2$), 22.69 ($2CH_2$), 14.12 ($2CH_3$).

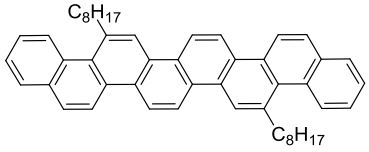
IR (neat) υ_{max}/cm^{-1} 2917 (s), 2848 (m), 1464 (m), 1434 (m), 1372 (w), 1034 (m), 870 (s), 835 (s), 754 (s), 723 (s).

HRMS (APPI) *m/z* calc. for $C_{50}H_{52}$ ($M^{+\cdot}$) 652.4064, found 652.4055.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 274 (18200), 324 (82700), 331 (89500), 350 (62300), 390 (1500), 413 (1300).

Melting point (tol) 173-176 °C.

5,15-dioctylbenzo[*c*]naphtho[2,1-*m*]picene 67



A J-Young tap vessel was charged with 1',5'-di(dec-1-yn-1-yl)-2,2':6',2''-terbenzobenzene **64** (0.180 g, 0.276 mmol) and flushed with argon for 0.5 h. NMP (2 mL) and DBU (0.17 mL, 0.173 g, 1.14 mmol) were added and the tube was sealed under nitrogen. The reaction mixture was heated to 220 °C, held at this temperature for 16 h and cooled to room temperature to give a precipitate which was filtered, washed (methanol) and dried. The compound was obtained as a yellow solid (0.140 g, 78%).

^{1}H-NMR (500 MHz, tol-d_8, 333 K) δ 8.95 (2H, d, *J* = 9.1 Hz), 8.94 (2H, s), 8.92 (2H, d, *J* = 8.6 Hz), 8.82 (2H, d, *J* = 9.3 Hz), 8.76 (2H, d, *J* = 9.1 Hz), 7.86-7.83 (4H, m), 7.56-7.53 (2H, m), 7.48-7.45 (2H, m), 3.68-3.65 (4H, m), 2.08-2.02 (4H, m), 1.58-1.52 (4H, m), 1.42-1.37 (4H, m), 1.35-1.28 (12H, m), 0.91 (6H, t, *J* = 6.8 Hz).

^{13}C-NMR (125 MHz, TCE-d_2, 333 K) δ 138.79 (2C), 133.07 (2C), 130.78 (2C), 130.07 (2C), 129.03 (2C), 128.50 (2CH), 128.17 (2C), 127.92 (2C), 127.61 (2CH), 127.53 (2CH), 127.49 (2C), 125.97 (2CH), 125.55 (2CH), 124.59 (2CH), 122.20 (2CH), 122.01 (2CH), 121.47 (2CH), 38.89 ($2CH_2$), 31.71 ($2CH_2$), 31.30 ($2CH_2$), 29.80 ($2CH_2$), 29.34 ($2CH_2$), 29.15 ($2CH_2$), 22.52 ($2CH_2$), 14.00 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2918 (s), 2849 (m), 1603 (w), 1455 (m), 1376 (w), 1040 (w), 805 (s), 743 (s), 721 (m).

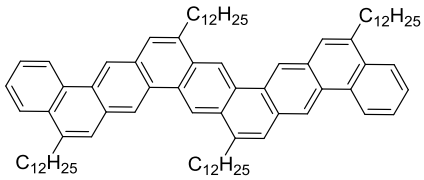
HRMS (APPI) *m/z* calc. for $C_{50}H_{53}$ $(M+H)^+$ 653.41418, found 653.41546.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 266 (32300), 301 (109800), 312 (160900), 328 (98500), 341 (37200), 358 (38900), 379 (2700), 401 (2500).

Melting point (tol) > 250 °C.

^{1}H-NMR, IR and melting point consistent with those reported by Alexandre Debacker.[136]

5,9,16,20-tetradodecylbenzo[*c*]phenanthro[2,3-*m*]pentaphene 77



A J-Young tap vessel was charged with 2',2''',5',5'''-tetrakis(tetradec-1-yn-1-yl)-1,1':4',1'':4'',1''':4''',1''''-quinquephenyl **76** (0.065 g, 0.056 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.033 g, 0.217 mmol) in degassed NMP (1.5 mL) was added and the tube was sealed under argon. The reaction mixture was heated to 240 °C, held at this temperature for 2 days and cooled to room temperature, giving a precipitate which

was filtered, washed with methanol and dried. The titled compound was obtained as a yellow solid (0.029 g, 45%).

^{1}H-NMR (500 MHz, TCE-d_2, 333 K) δ 9.57 (2H, s), 9.19 (2H, s), 9.09 (2H, s), 8.96 (2H, d, *J* = 7.8 Hz), 8.18 (2H, d, *J* = 7.8 Hz), 7.91 (2H, s), 7.87 (2H, s), 7.78-7.72 (4H, m), 3.46 (4H, t, *J* = 7.5 Hz), 3.22 (4H, t, *J* = 7.7 Hz), 2.17-2.11 (4H, m), 1.99-1.92 (4H, m), 1.78-1.72 (4H, m), 1.63-1.29 (68H, m), 0.93-0.88 (12H, m).

^{13}C-NMR (125 MHz, TCE-d_2, 333 K) δ 137.11 (2C), 136.79 (2C), 131.52 (2C), 130.46 (4C), 130.42 (2C), 129.85 (2C), 129.28 (2C), 128.87 (2C), 128.82 (2C), 126.83 (2CH), 126.50 (2CH), 126.24 (2CH), 126.15 (2CH), 124.53 (2CH), 123.34 (2CH), 121.41 (2CH), 121.20 (2CH), 118.72 (2CH), 33.54 ($2CH_2$), 33.33 ($2CH_2$), 31.74 ($2CH_2$), 31.72 ($2CH_2$), 30.23 ($2CH_2$), 29.90 ($2CH_2$), 29.87 ($2CH_2$), 29.85 ($2CH_2$), 29.62-29.48 ($20CH_2$), 29.18 ($2CH_2$), 29.15 ($2CH_2$), 22.51 ($2CH_2$), 22.49 ($2CH_2$), 13.97 ($2CH_3$), 13.95 ($2CH_3$).

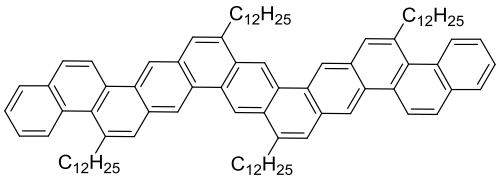
IR (neat) υ_{max}/cm^{-1} 2950 (m), 2920 (s), 2848 (s), 1467 (s), 1376 (w), 1044 (w), 900 (s), 888 (s), 750 (m), 723 (s).

LRMS (APPI) *m/z* 1150.9 ($M^{+\cdot}$).

UV (DCM) λ_{max}/nm 280, 295, 315, 329, 345, 362, 387, 418, 443.

Melting point (tol) > 250 °C.

5,9,18,22-tetradodecylchryseno[3,2-*c*]naphtho[2,1-*m*]pentaphene 80



A J-Young tap vessel was charged with 2,2'-(2,2",5,5" tetrakis(tetradec-1-yn-1-yl)-[1,1':4',1"-terphenyl]-4,4"-diyl)dinaphthalene **79** (0.030 g, 0.024 mmol) and evacuated/refilled with argon three times. A solution of DBU (0.014 g, 0.092 mmol) in degassed NMP (1 mL) was added and the tube was sealed under argon. The reaction mixture was heated to 240 °C, held at this temperature for 40 h and cooled to room temperature, giving a precipitate which was filtered, washed with methanol and dried. The titled compound was obtained as a yellow solid (0.014 g, 47%).

^{1}H-NMR (500 MHz, TCE-d_2, 333 K) δ 9.62 (2H, s), 9.29 (2H, s), 9.18 (2H, s), 9.00 (2H, d, *J* = 9.2 Hz), 8.89 (2H, d, *J* = 8.9 Hz), 8.23 (2H, s), 8.11-8.07 (4H, m), 7.93 (2H, s), 7.73-7.66 (4H, m), 3.68-3.65 (4H, m), 3.51-3.48 (4H, m), 2.21-2.15 (4H, m), 2.11-2.05 (4H, m), 1.81-1.75 (4H, m), 1.67-1.25 (68H, m), 0.93-0.91 (6H, m), 0.89 (6H, t, *J* = 7.0 Hz).

Solubility of compound was too low for obtention of ^{13}C-NMR.

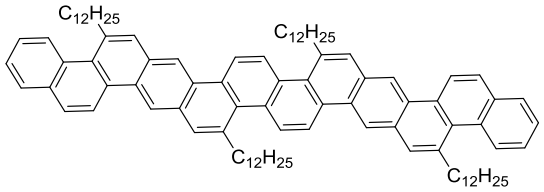
IR (neat) υ_{max}/cm^{-1} 2950 (m), 2916 (s), 2847 (m), 1464 (m), 1376 (w), 1024 (w), 820 (s), 749 (s), 722 (s).

LRMS (APPI) *m/z* 1252.0 $(M+H)^+$.

UV (TCE) λ_{max}/nm 344, 358, 374, 403, 426, 453.

Melting point (tol) > 250 °C

5,10,19,24-tetradodecylchryseno[2,3-*m*]phenanthro[2,1-*b*]picene 82



A J-Young tap vessel was charged with 2,6-bis(4-(naphthalen-2-yl)-2,5-di(tetradec-1-yn-1-yl)phenyl)naphthalene **81** (0.020 g, 0.015 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.009 g, 0.059 mmol) in NMP (0.8 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 22 h and cooled to room temperature, giving a precipitate which was filtered, washed (methanol) and dried. The titled compound was obtained as a yellow solid (0.013 g, 65%).

^{1}H-NMR (500 MHz, TCE-d_2, 333 K) δ 9.33 (2H, s), 9.30 (2H, s), 9.05 (2H, d, *J* = 3.2 Hz), 9.03 (2H, d, *J* = 3.4 Hz), 8.93 (2H, d, *J* = 9.2 Hz), 8.90 (2H, d, *J* = 8.3 Hz), 8.25 (2H, s), 8.22 (2H, s), 8.13 (2H, d, *J* = 9.0 Hz), 8.10 (2H, dd, *J* = 7.5, 1.9 Hz), 7.73-7.67 (4H, m), 3.67 (4H, t, *J* = 9.3 Hz), 3.65 (4H, t, *J* = 9.1 Hz), 2.13-2.04 (8H, m), 1.66-1.56 (8H, m), 1.52-1.45 (8H, m), 1.42-1.26 (56H, m), 0.93-0.87 (12H, m).

^{13}C-NMR (500 MHz, TCE-d_2, 333 K) δ 137.74 (2C), 137.64 (2C), 133.47 (2C), 131.31 (2C), 130.97 (2C), 130.32 (2C), 130.29 (2C), 129.83 (2CH), 129.72 (2C), 129.64 (2C), 129.51 (2CH), 129.08 (2C), 128.76 (2C), 128.70 (2C), 128.60 (2CH), 128.17 (2C), 127.54 (2CH), 127.42 (2CH), 126.79 (2CH), 125.72 (2CH), 125.42 (2CH), 121.90 (2CH), 121.53 (2CH), 121.16 (2CH), 119.68 (2CH), 38.56 ($2CH_2$), 37.63 ($2CH_2$), 31.75 ($2CH_2$), 31.73 ($2CH_2$), 31.44 ($2CH_2$), 31.01 ($2CH_2$), 29.82 ($2CH_2$), 29.73 ($2CH_2$), 29.55-29.47 ($16CH_2$), 29.40 ($2CH_2$), 29.37 ($2CH_2$), 29.16 ($4CH_2$), 22.52 ($2CH_2$), 22.50 ($2CH_2$), 13.99 ($2CH_2$), 13.96 ($2CH_3$).

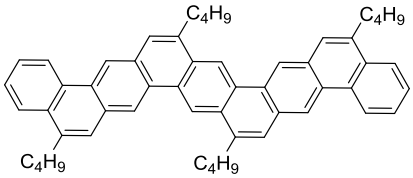
IR (neat) υ_{max}/cm^{-1} 2916 (s), 2847 (s), 1466 (m), 898 (m), 819 (m), 745 (s), 721 (m).

LRMS (APPI) *m/z* 1300.9 $(M^{+\cdot})$, 1302.0 $(M+H)^+$.

UV (DCM) λ_{max}/nm 353, 410, 443.

Melting point (tol) > 250 °C.

5,9,16,20-tetrabutylbenzo[*c*]phenanthro[2,3-*m*]pentaphene 85



A J-Young tap vessel was charged with 2',2''',5',5'''-tetra(hex-1-yn-1-yl)-1,1':4',1'':4'',1''':4''',1''''-quinquephenyl **84** (0.018 g, 0.026 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.015 g, 0.099 mmol) in NMP (1 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 2 days and cooled to room temperature, giving a precipitate which was filtered, washed with methanol and dried. The titled compound was obtained as a yellow solid (0.010 g, 56%).

^{1}H-NMR (500 MHz, TCE-d_2, 353 K) δ 9.63 (2H, s), 9.22 (2H, s), 9.12 (2H, s), 8.98 (2H, d, *J* = 7.8 Hz), 8.21 (2H, d, *J* = 7.7 Hz), 7.93 (2H, s), 7.91 (2H, s), 7.79-7.73 (4H, m), 3.51 (4H, t, *J* = 7.6 Hz), 3.25 (4H, t, *J* = 7.7 Hz), 2.19-2.14 (4H, m), 2.06-1.95 (4H, m), 1.79 (4H, sxt, *J* = 7.3 Hz), 1.66 (4H, sxt, *J* = 7.4 Hz), 1.24 (6H, t, *J* = 7.4 Hz), 1.12 (6H, t, *J* = 7.4 Hz).

^{13}C-NMR (125 MHz, TCE-d_2, 353 K) δ 137.05 (2C), 136.74 (2C), 131.60 (2C), 130.55 (2C), 130.53 (2C), 130.50 (2C), 129.94 (2C), 129.38 (2C), 128.97 (2C), 128.91 (2C), 126.78 (2CH), 126.53 (2CH), 126.20 (2CH), 126.16 (2CH), 124.48 (2CH), 123.34 (2CH), 121.41 (2CH), 121.20 (2CH), 118.74 (2CH), 33.08 ($2CH_2$), 32.91 ($2CH_2$), 32.28 ($2CH_2$), 32.01 ($2CH_2$), 29.46 ($2CH_2$), 22.83 ($2CH_2$), 13.98 ($2CH_3$), 13.83 ($2CH_3$).

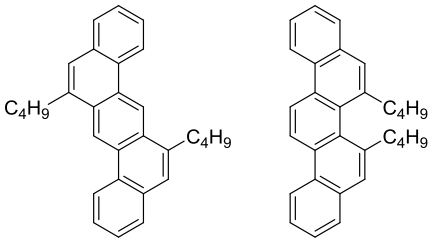
IR (neat) υ_{max}/cm^{-1} 2953 (m), 2921 (s), 2872 (m), 1463 (m), 1445 (m), 1379 (w), 1032 (w), 898 (s), 823 (s), 720 (s).

HRMS (APPI) *m/z* calc. 702.4220 ($M^{+\cdot}$), found 702.4214.

UV (DCM) λ_{max}/nm 280, 295, 317, 334, 343, 360, 386, 418, 444.

Melting point (tol) > 250 °C.

6,13-dibutylbenzo[*k*]tetraphene 90 and 6,7-dibutylpicene 91



90 **91**

A solution of 2,2''-di(hex-1-yn-1-yl)-1,1':4',1''-terphenyl **89** (0.400 g, 1.02 mmol) and DBU (0.306 g, 2.01 mmol) in NMP (4 mL) was transferred to a J-Young tap vessel and degassed by simultaneously evacuating and sonicating. The tube was sealed under nitrogen and the solution was heated to 240 °C, held at this temperature for 18 h, cooled to room temperature and diluted with 1 M HCl (50 mL). The product was extracted with diethyl ether (20 mL) and the aqueous layer then diluted with water and the product again extracted with diethyl ether several times. The organic layers were combined, washed (water), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 0-10% DCM in pet. ether) to give a waxy yellow solid (0.098 g). **90** was isolated by diluting this crude product with hexane, removing the mother liquor and drying the remaining white solid to give 0.028 g (7%). The mother liquor was concentrated under reduced pressure to give **91** (0.070 g, 18%).

6,13-dibutylbenzo[*k*]tetraphene 90

^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.45 (2H, s), 8.84 (2H, d, *J* = 8.2 Hz), 7.87 (2H, d, *J* = 7.7 Hz), 7.71-7.67 (2H, m), 7.65-7.61 (2H, m), 7.62 (2H, s), 3.35 (4H, t, *J* = 7.7 Hz), 1.98 (4H, quin, *J* = 7.6 Hz), 1.67-1.58 (4H, m), 1.08 (6H, t, *J* = 7.3 Hz).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 137.04 (2C), 132.13 (2C), 129.89 (2C), 129.55 (2C), 129.21 (2C), 128.18 (2CH), 126.90 (2CH), 126.11 (4CH), 122.47 (2CH), 118.54 (2CH), 33.23 ($2CH_2$), 32.30 ($2CH_2$), 22.98 ($2CH_2$), 14.12 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2954 (m), 2925 (m), 2853 (m), 1453 (m), 1375 (w), 1021 (w), 885 (s), 744 (s), 722 (s).

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 282 (49600), 292 (99200), 302 (131100), 326 (20100), 341 (17000), 356 (12100), 376 (1310), 398 (1210).

HRMS (APPI) *m/z* calc. for $C_{30}H_{30}$ ($M^{+\cdot}$) 390.2342, found 390.2336.

Melting point (tol) 194-196 °C.

6,7-dibutylpicene 91

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.74-8.71 (4H, m), 7.97-7.95 (2H, m), 7.75 (2H, s), 7.69-7.62 (4H, m), 3.42-3.35 (2H, m), 3.25-3.18 (2H, m), 1.28-1.18 (4H, m), 1.07-0.97 (4H, m), 0.58 (6H, t, *J* = 7.3 Hz).

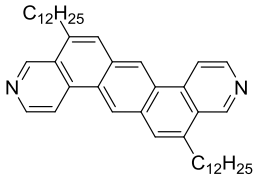
^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.27 (2C), 132.38 (2C), 129.59 (2C), 128.94 (2C), 128.32 (2C), 127.59 (2CH), 126.33 (2CH), 125.70 (2CH), 125.48 (2CH), 122.99 (2CH), 121.08 (2CH), 36.04 ($2CH_2$), 35.47 ($2CH_2$), 22.12 ($2CH_2$), 13.92 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 2954 (m), 2925 (m), 2857 (m), 1463 (m), 1455 (m), 1375 (w), 1017 (w), 879 (m), 848 (m), 743 (s).

UV (DCM) λ_{max}/nm 295, 340, 354.

HRMS (APPI) *m/z* calc. for $C_{30}H_{30}$ ($M^{+\cdot}$) 390.2342, found 390.2338.

5,12-didodecylbenzo[1,2-*f*:4,5-*f*']diisoquinoline 93



A solution of 4,4'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)dipyridine **92** (0.170 g, 0.276 mmol) and DBU (0.165 g, 1.08 mmol) in NMP (11 mL) was added to a J-Young tap vessel and degassed by sonicating whilst under high vacuum. The tube was sealed under argon and the solution heated to 220 °C and held at this temperature for 20 h. The reaction mixture was cooled to room temperature, giving a precipitate which was filtered, washed with methanol and dried. The titled compound was obtained as a yellow solid (0.078 g, 46%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.49 (2H, s), 9.01 (2H, s), 8.85 (2H, d, *J* = 5.6 Hz), 8.58 (2H, d, *J* = 5.6 Hz), 7.80 (2H, s), 3.20 (4H, t, *J* = 7.7 Hz), 1.93-1.85 (4H, m), 1.57-1.50 (4H, m), 1.45-1.38 (4H, m), 1.27 (28H, br), 0.88 (6H, t, *J* = 0.88 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.21 (2CH), 145.43 (2CH), 136.35 (2C), 135.51 (2C), 131.35 (2C), 128.11 (2C), 127.28 (2CH), 126.48 (2C), 122.32 (2CH), 116.61 (2CH), 32.73 ($2CH_2$), 31.90 ($2CH_2$), 30.33 ($2CH_2$), 29.78 ($2CH_2$), 29.66 ($4CH_2$), 29.62 ($4CH_2$), 29.55 ($2CH_2$), 29.33 ($2CH_2$), 22.66 ($2CH_2$), 14.08 ($2CH_3$).

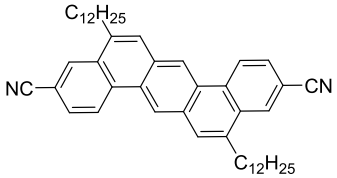
IR (neat) υ_{max}/cm^{-1} 2957 (m), 2917 (s), 2847 (s), 1586 (m), 1469 (s), 1387 (w), 1039 (w), 824 (s), 721 (m), 700 (m).

HRMS (APPI) *m/z* calc. for $C_{44}H_{60}N_2$ ($M^{+\cdot}$) 616.47510, found 616.47430.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 287 (79400), 298 (123800), 319 (23700), 333 (22200), 349 (27100), 372 (2000), 394 (3400), 417 (4500).

Melting point (hexane/$CHCl_3$) 132-135 °C.

5,12-didodecylbenzo[*k*]tetraphene-3,10-dicarbonitrile 95



A J-Young tap vessel was charged with 2',5'-di(tetradec-1-yn-1-yl)-[1,1':4',1''-terphenyl]-4,4''-dicarbonitrile **94** (0.015 g, 0.023 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.008 g, 0.053 mmol) in NMP (0.5 mL) was added and the tube was sealed under nitrogen. The reaction was heated to 240 °C, held at this temperature for 16 h, cooled to room temperature and diluted with methanol (15 mL). This was cooled at 3 °C for 8 h and the precipitate filtered, washed with methanol and dried. The titled compound was obtained as a yellow solid (0.010 g, 67%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.05 (2H, s), 8.95 (2H, d, *J* = 8.6 Hz), 8.44 (2H, s), 7.92 (2H, dd, *J* = 8.7 Hz), 7.87 (2H, s), 3.13 (4H, t, *J* = 7.6 Hz), 1.90-1.82 (4H, m), 1.58-1.50 (4H, m), 1.45-1.39 (4H, m), 1.27 (28H, br), 0.88 (6H, t, *J* = 6.5 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.50 (2C), 133.32 (2C), 131.73 (2C), 131.14 (2C), 129.71 (2CH), 128.60 (2C), 128.13 (2CH), 127.86 (2CH), 124.50 (2CH), 122.56 (2CH), 119.39 (2C), 110.62 (2CN), 33.22 ($2CH_2$), 31.91 ($2CH_2$), 29.97 ($2CH_2$), 29.77 ($2CH_2$), 29.67 ($4CH_2$), 29.64 ($4CH_2$), 29.56 ($2CH_2$), 29.34 ($2CH_2$), 22.67 ($2CH_2$), 14.11 ($2CH_3$).

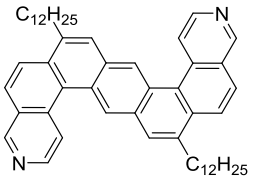
IR (neat) υ_{max}/cm^{-1} 2914 (s), 2849 (s), 2227 (m), 1491 (m), 1469 (w), 1377 (w), 1027 (w), 896 (m), 827 (m), 716 (m).

HRMS (APPI) *m/z* calc. for $C_{48}H_{60}N_2$ ($M^{+\cdot}$) 664.4751, found 664.4744.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 302 (66300), 314 (123800), 330 (36900), 343 (30500), 356 (8400), 382 (1500), 404 (2400), 429 (2900).

Melting point (tol) 149-151 °C.

7,16-didodecylanthra[1,2-*f*:5,6-*f*']diisoquinoline 97



A solution of 5,5'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)diisoquinoline **96** (0.160 g, 0.223 mmol) and DBU (0.135 g, 0.887 mmol) in NMP (4 mL) was transferred to a J-Young tap vessel and degassed by sonicating whilst under high vacuum. The tube was sealed under argon and

the solution heated to 250 °C and held at this temperature for 14 h. The reaction mixture was cooled to room temperature, diluted with methanol (5 mL) and cooled at -18 °C for 2 h to give a black solid which was filtered off. This was purified by column chromatography (SiO_2, 20% EtOAc in chloroform) to give a yellow solid (0.030 g, 19%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.46 (2H, s), 9.40 (2H, s), 9.04 (2H, d, *J* = 6.0 Hz), 8.81 (2H, d, *J* = 5.9 Hz), 8.24 (2H, d, *J* = 8.8 Hz), 8.11 (2H, d, *J* = 8.8 Hz), 7.98 (2H, s), 3.20 (4H, t, *J* = 7.8 Hz), 1.91-1.94 (4H, m), 1.57-1.50 (4H, m), 1.44-1.38 (4H, m), 1.26 (28H, br), 0.87 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.49 (2CH), 144.48 (2CH), 137.03 (2C), 133.93 (2C), 133.02 (2C), 131.04 (2C), 129.08 (2CH), 128.00 (2C), 127.68 (2C), 126.70 (2CH), 126.40 (2CH), 126.08 (2C), 124.01 (2CH), 120.49 (2CH), 33.89 ($2CH_2$), 31.89 ($2CH_2$), 30.55 ($2CH_2$), 29.86 ($2CH_2$), 29.66 ($4CH_2$), 29.63 ($2CH_2$), 29.61 ($2CH_2$), 29.57 ($2CH_2$), 29.32 ($2CH_2$), 22.66 ($2CH_2$), 14.08 ($2CH_3$).

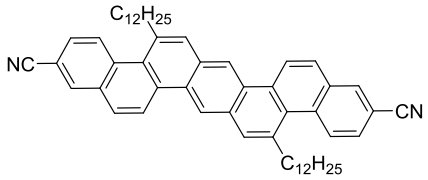
IR (neat) υ_{max}/cm^{-1} 2916 (s), 2850 (s), 1597 (s), 1468 (m), 1368 (m), 843 (m), 734 (m).

HRMS (APPI) *m/z* calc. for $C_{52}H_{64}N_2$ ($M^{+\cdot}$) 716.5066, found 716.5064.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 295 (28300), 322 (73800), 336 (129600), 367 (12500), 382 (10800), 405 (7100), 430 (3900).

Melting point (hexane/tol) 128-130 °C.

5,14-didodecylbenzo[*c*]naphtho[2,1-*k*]tetraphene-2,11-dicarbonitrile 99



A J-Young tap vessel was charged with 6,6'-(2,5-di(tetradec-1-yn-1-yl)-1,4-phenylene)bis(2-naphthonitrile) **98** (0.080 g, 0.105 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.030 g, 0.197 mmol) in NMP (2 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 2 days and cooled to room temperature to give a precipitate which was filtered, washed with methanol and dried. The titled compound was obtained as a yellow solid (0.048 g, 60%).

^{1}H-NMR (500 MHz, TCE-d_2, 333 K) δ 9.25 (2H, s), 9.09 (2H, d, *J* = 9.0 Hz), 8.93 (2H, d, *J* = 9.0 Hz), 8.42 (2H, d, *J* = 1.6 Hz), 8.21 (2H, s), 8.11 (2H, d, *J* = 8.9 Hz), 7.83 (2H, dd, *J* = 8.9, 1.7 Hz), 3.57 (4H, t, *J* = 7.8 Hz), 2.04-1.97 (4H, m), 1.61-1.55 (4H, m), 1.45 (4H, quin, *J* = 7.0 Hz), 1.38-1.28 (28H, m), 0.91 (6H, t, *J* = 6.9 Hz).

^{13}C-NMR (125 MHz, TCE-d_2, 333 K) δ 137.48 (2C), 133.81 (2CH), 132.79 (2C), 132.63 (2C), 131.43 (2C), 130.66 (2CH), 130.52 (2C), 128.85 (2C), 128.71 (2C), 128.37 (2CH), 127.03 (2CH), 126.12 (2CH), 123.72 (2CH), 122.00 (2CH), 118.98 (2C), 108.97 (2CN), 38.35 ($2CH_2$), 31.73 ($2CH_2$), 30.86 ($2CH_2$), 29.63 ($2CH_2$), 29.50 ($2CH_2$), 29.46 ($4CH_2$), 29.44 ($2CH_2$), 29.31 ($2CH_2$), 29.15 ($2CH_2$), 22.50 ($2CH_2$), 13.97 ($2CH_3$).

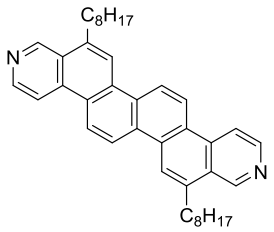
IR (neat) υ_{max}/cm^{-1} 2950 (w), 2916 (s), 2847 (s), 2225 (m), 1619 (w), 1466 (m), 1454 (m), 1370 (w), 892 (s), 824 (s), 725 (s).

HRMS (APPI) *m/z* calc. for $C_{56}H_{64}N_2$ ($M^{+\cdot}$) 764.5064, found 764.5067.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 266 (25500), 280 (20800), 305 (35100), 321 (76600), 335 (141500), 370 (14300), 393 (7200), 417 (3300), 444 (2800).

Melting point (tol) 235-237 °C.

8,16-dioctylnaphtho[2,1-*f*:6,5-*f*']diisoquinoline 101



A J-Young tap vessel was charged with 4,4'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)dipyridine **100** (0.500 g, 0.901 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.267 g, 1.75 mmol) in NMP (4 mL) was added and the tube was sealed under nitrogen. The reaction was heated to 240 °C, held at this temperature for 16 h and cooled to room temperature to give a precipitate which was filtered, washed with methanol and dried. The titled compound was obtained as a light yellow solid (0.398 g, 80%).

^{1}H-NMR (500 MHz, TCE-d_2, 333 K) δ 9.65 (2H, s), 9.04 (2H, d, *J* = 9.2 Hz), 8.90 (2H, d, *J* = 9.2 Hz), 8.86 (2H, d, *J* = 4.8 Hz), 8.73 (2H, s), 8.65 (2H, d, *J* = 5.3 Hz), 3.40 (4H, t, *J* = 7.7 Hz), 1.99 (4H, quin, *J* = 7.6 Hz), 1.61 (4H, quin, *J* = 7.4 Hz), 1.51-1.45 (4H, m), 1.40-1.35 (12H, m), 0.93 (6H, t, *J* = 6.7 Hz).

^{13}C-NMR (125 MHz, TCE-d_2, 333 K) δ 148.42 (2CH), 144.13 (2CH), 138.13 (2C), 135.02 (2C), 130.47 (2C), 129.49 (2C), 126.06 (2C), 125.88 (2C), 122.33 (2CH), 122.01 (2CH), 121.61 (2CH), 116.75 (2CH), 33.16 ($2CH_2$), 31.71 ($2CH_2$), 31.13 ($2CH_2$), 29.71 ($2CH_2$), 29.35 ($2CH_2$), 29.10 ($2CH_2$), 22.49 ($2CH_2$), 13.97 ($2CH_3$).

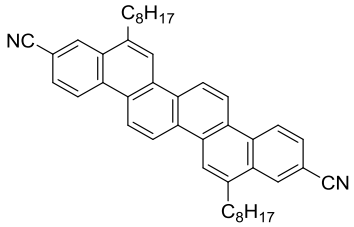
IR (neat) υ_{max}/cm^{-1} 2955 (m), 2920 (s), 2851 (s), 1615 (m), 1454 (s), 1376 (w), 1027 (w), 887 (m), 813 (s), 777 (m), 700 (m).

HRMS (ESI+) *m/z* calc. for 555.3734 $(M+H)^+$ $C_{40}H_{47}N_2$, found 555.3743.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 287 (70000), 295 (109300), 314 (32500), 327 (17800), 343 (18900), 376 (3200), 397 (4500).

Melting point (TCE) > 250 °C.

8,16-dioctylbenzo[*c*]picene-2,10-dicarbonitrile 104



A J-Young tap vessel was charged with 4,4'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)dibenzonitrile **103** (0.075 g, 0.124 mmol) and evacuated/refilled with argon three times. A solution of DBU (0.037 g, 0.243 mmol) in NMP (1 mL) and the tube was sealed under argon. The reaction mixture was heated to 240 °C, held at this temperature for 14 h and cooled to room temperature, giving a dark yellow precipitate which was filtered, washed with methanol and dried to give 0.072 g (96%). This was recrystallised by dissolving in 1,1,2,2-tetrachloroethane (8 mL, 60 °C) and cooling at 3 °C for 3 days. The purified material was obtained as a yellow solid (0.043 g, 57%).

^{1}H-NMR (400 MHz, TCE-d_2) δ 9.01 (2H, d, *J* = 9.5 Hz), 8.97 (2H, d, *J* = 8.9 Hz), 8.90 (2H, d, *J* = 9.5 Hz), 8.76 (2H, s), 8.57 (2H, d, *J* = 1.3 Hz), 7.93 (2H, dd, *J* = 8.6, 1.4 Hz), 3.30 (4H, t, *J* = 7.8 Hz), 1.95-1.87 (4H, m), 1.61-1.55 (4H, m), 1.48-1.41 (4H, m), 1.33 (12H, br), 0.93-0.89 (6H, m).

^{13}C-NMR (125 MHz, TCE-d_2, 333 K) δ 137.91 (2C), 132.93 (2C), 130.63 (2C), 129.95 (2CH), 129.62 (2C), 129.07 (2C), 127.42 (2CH), 126.92 (2C), 124.86 (2CH), 122.57 (2CH), 122.08 (2CH), 121.77 (2CH), 119.42 (2C), 109.83 (2CN), 33.68 ($2CH_2$), 31.70 ($2CH_2$), 30.68 ($2CH_2$), 29.71 ($2CH_2$), 29.35 ($2CH_2$), 29.11 ($2CH_2$), 22.50 ($2CH_2$), 13.97 ($2CH_3$).

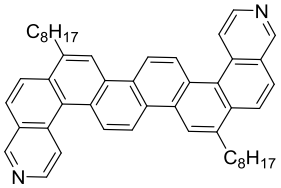
IR (neat) υ_{max}/cm^{-1} 3076 (w), 2922 (s), 2849 (s), 2222 (m), 1582 (w), 1448 (m), 1381 (w), 884 (m), 804 (s), 722 (m).

HRMS (APPI) *m/z* calc. for $C_{44}H_{46}N_2$ ($M^{+\cdot}$) 602.36555, found 602.36458.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 264 (35300), 299 (106800), 311 (170900), 325 (87400), 335 (73800), 346 (25000), 387 (3800), 408 (5500).

Melting point (TCE) > 250 °C.

8,18-dioctylchryseno[1,2-*f*:7,8-*f*']diisoquinoline 106



A J-Young tap vessel was charged with 5,5'-(1,5-di(dec-1-yn-1-yl)naphthalene-2,6-diyl)diisoquinoline **105** (0.080 g, 0.122 mmol) and evacuated/refilled with argon three times. A solution of DBU (0.020 g, 0.131 mmol) in NMP (2 mL) was added and the tube was sealed under argon. The reaction mixture was heated to 240 °C, held at this temperature for 18 h and cooled to room temperature to give a precipitate which was filtered, washed with methanol and dried. The titled compound was obtained as a yellow solid (0.048 g, 60%).

^{1}H-NMR (500 MHz, TCE-d_2) δ 9.43 (2H, s), 9.19 (2H, d, J = 9.3 Hz), 9.01 (2H, d, J = 9.7 Hz), 8.95 (2H, d, J = 6.0 Hz), 8.92 (2H, s), 8.79 (2H, d, J = 6.0 Hz), 8.31 (2H, d, J = 9.0 Hz), 8.11 (2H, d, J = 8.9 Hz), 3.37 (4H, t, J = 7.9 Hz), 1.95 (4H, quin, J = 7.7 Hz), 1.61 (4H, quin, J = 7.5 Hz), 1.49-1.43 (4H, m), 1.40-1.31 (12H, m), 0.91 (6H, t, J = 6.9 Hz).

^{13}C-NMR (125 MHz, TCE-d_2) δ 151.98 (2CH), 144.10 (2CH), 138.02 (2C), 134.09 (2C), 131.85 (2C), 129.69 (2C), 127.97 (2C), 127.72 (2C), 127.48 (2C), 126.37 (2C), 126.19 (2CH), 125.73 (2CH), 124.00 (4CH), 121.30 (2CH), 121.19 (2CH), 34.30 ($2CH_2$), 31.81 ($2CH_2$), 31.17 ($2CH_2$), 29.86 ($2CH_2$), 29.47 ($2CH_2$), 29.25 ($2CH_2$), 22.62 ($2CH_2$), 14.16 ($2CH_3$).

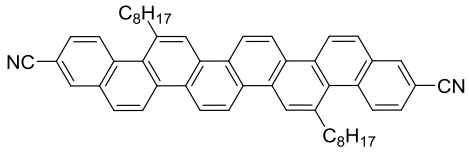
IR (neat) υ_{max}/cm^{-1} 2947 (m), 2914 (s), 2846 (m), 1464 (m), 1454 (m), 1373 (w), 1058 (w), 836 (s), 789 (s), 741 (s), 725 (m).

HRMS (ESI+) *m/z* calc. for $C_{48}H_{51}N_2$ $(M+H)^+$ 655.4047, found 655.4055.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 272 (32600), 327 (103100), 345 (62300), 361 (20700), 390 (3800), 412 (4400).

Melting point (tol) > 250 °C.

5,15-dioctylbenzo[*c*]naphtho[2,1-*m*]picene-2,12-dicarbonitrile 109



A J-Young tap vessel was charged with 1',5' di(dec-1-yn-1-yl)-[2,2':6',2''-terbenzobenzene]-6,6''-dicarbonitrile **108** (0.040 g, 0.057 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.020 g, 0.131 mmol) in NMP (1.5 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 18 h

and cooled to room temperature to give a precipitate which was filtered, washed with methanol and dried. The titled compound was obtained as a yellow solid (0.024 g, 60%).

^{1}H-NMR (500 MHz, TCE-d_2, 353 K) δ 9.08 (2H, d, *J* = 9.5 Hz), 9.02 (2H, s), 9.01-8.97 (6H, m), 8.41 (2H, d, *J* = 1.6 Hz), 8.08 (2H, d, *J* = 9.0 Hz), 7.88 (2H, dd, J = 8.8, 1.6 Hz), 3.73 (4H, t, *J* = 7.8 Hz), 2.11 (4H, quin., *J* = 7.7 Hz), 1.66 (4H, quin., *J* = 7.4 Hz), 1.54-1.49 (4H, m), 1.45-1.36 (12H, m), 0.96 (6H, t, *J* = 7.0 Hz).

^{13}C-NMR (125 MHz, TCE-d_2, 353 K) δ 138.71 (2C), 133.41 (2CH), 132.95 (2C), 132.42 (2C), 131.52 (2C), 128.94 (2C), 128.49 (2C), 128.40 (2CH), 128.27 (2C), 127.54 (2C), 126.76 (2CH), 126.41 (2CH), 125.43 (2CH), 123.95 (2CH), 122.26 (2CH), 121.90 (2CH), 118.82 (2C), 109.29 (2CN), 38.73 ($2CH_2$), 31.63 ($2CH_2$), 31.12 ($2CH_2$), 29.67 ($2CH_2$), 29.24 ($2CH_2$), 29.05 ($2CH_2$), 22.43 ($2CH_2$), 13.85 ($2CH_3$).

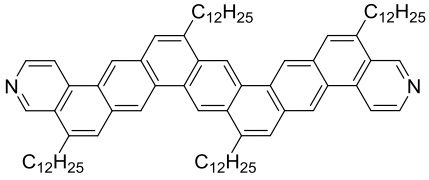
IR (neat) υ_{max}/cm^{-1} 2919 (s), 2849 (m), 2225 (m), 1619 (m), 1455 (m), 1386 (m), 895 (s), 816 (s), 719 (m).

HRMS (APPI) *m/z* calc. for $C_{50}H_{52}N_2$ ($M^{+\cdot}$) 702.3969, found 702.3955.

UV (DCM) λ_{max} /nm 293 (36700), 304 (42500), 325 (60700), 339 (51600), 393 (2100), 415 (2400).

Melting point (TCE) > 250 °C.

114



A J-Young tap vessel was charged with 4,4'-(2,2",5,5"-tetrakis(tetradec-1-yn-1-yl)-[1,1':4',1"-terphenyl]-4,4"-diyl)dipyridine **113** (0.050 g, 0.043 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.014 g, 0.092 mmol) in NMP (1 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 2 days and cooled to room temperature to give a yellow precipitate which was filtered, washed with methanol and pet. ether and dried. The titled compound was obtained as a yellow solid (0.015 g, 30%).

^{1}H-NMR (500 MHz, tol-d_8, 353 K) δ 9.71 (2H, s), 9.63 (2H, s), 9.28 (2H, s), 8.89 (2H, s), 8.88 (2H, d, *J* = 5.4 Hz), 8.31 (2H, d, *J* = 5.4 Hz), 7.81 (2H, s), 7.80 (2H, s), 3.44 (4H, t, *J* = 7.6 Hz), 3.09 (4H, t, *J* = 7.7 Hz), 2.21-2.13 (4H, m), 1.89-1.83 (4H, m), 1.76-1.70 (4H, m), 1.63-1.57 (4H, m), 1.54-1.25 (64H, m), 0.93-0.87 (12H, m).

^{13}C-NMR (125 MHz, tol-d_8, 353 K) δ 149.11 (2CH), 146.51 (2CH), 138.05 (2C), 137.06 (2C), 136.32 (2C), 132.62 (2C), 131.84 (2C), 131.56 (2C), 131.28 (2C), 130.71 (2C), 129.58 (2CH), 127.39 (2CH), 123.21 (2CH), 122.33 (2CH), 120.07 (2CH), 116.95 (2CH), 34.34 ($2CH_2$), 33.49 ($2CH_2$), 32.67 ($2CH_2$), 32.65 ($2CH_2$), 31.29 ($2CH_2$), 30.90 ($2CH_2$), 30.84 ($2CH_2$), 30.64 ($2CH_2$), 30.59 ($2CH_2$), 30.54-30.48 ($16CH_2$), 30.45 ($2CH_2$), 30.36 ($2CH_2$), 30.11 ($2CH_2$), 23.36 ($2CH_2$), 23.33 ($2CH_2$), 14.45 ($2CH_3$), 14.42 ($2CH_3$).

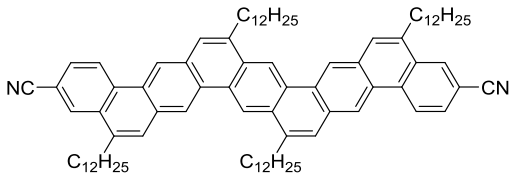
IR (neat) υ_{max}/cm^{-1} 2948 (m), 2916 (s), 2847 (s), 1468 (m), 1453 (m), 1374 (w), 1040 (m), 893 (s), 820 (m), 717 (s).

LRMS (APPI) *m/z* 1152.91 ($M^{+\cdot}$).

UV (DCM) λ_{max}/nm 273, 294, 344, 361, 385, 450.

Melting point (tol) > 250 °C.

5,9,16,20-tetrabutylbenzo[*c*]phenanthro[2,3-*m*]pentaphene-3,14-dicarbonitrile 116



A J-Young tap vessel was charged with 2,2'",5,5'"-tetrakis(tetradec-1-yn-1-yl)-[1,1':4',1":4",1'":4'",1""-quinquephenyl]-4,4'"-dicarbonitrile **115** (0.060 g, 0.050 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.032 g, 0.210 mmol) in degassed NMP (1 mL) was added and the tube sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 2 days and cooled to room temperature to give a precipitate. The reaction mixture was diluted with methanol and the mother liquor carefully decanted. The solid was washed with pet. ether several times, decanting the mother liquor each time, and then dried to give 0.012 g – yield 20%.

^{1}H-NMR (500 MHz, TCE-d_2, 353 K) δ 9.56 (2H, s), 9.11 (2H, s), 9.05 (2H, s), 8.99 (2H, d, *J* = 8.7 Hz), 8.47 (2H, s), 7.98 (2H, s), 7.93 (2H, dd, *J* = 8.6, 1.2 Hz), 7.88 (2H, s), 3.49 (4H, t, *J* = 7.7 Hz), 3.21 (4H, t, *J* = 7.7 Hz), 2.20-2.14 (4H, m), 1.99-1.93 (4H, m), 1.80-1.75 (4H, m), 1.67-1.61 (8H, m), 1.48-1.28 (60H, m), 0.93 (6H, t, *J* = 7.1 Hz), 0.90 (6H, t, *J* = 7.1 Hz).

^{13}C-NMR (125 MHz, TCE-d_2, 353 K) δ 137.54 (2C), 136.01 (2C), 133.41 (2C), 131.37 (2C), 130.93 (4C), 130.08 (2C), 130.04 (2C), 129.42 (2CH), 129.31 (2C), 127.95 (2CH), 127.72 (2CH), 127.65 (2C), 126.29 (2CH), 124.27 (2CH), 122.18 (2CH), 121.54 (2CH), 119.34 (2C), 119.01 (2CH), 110.04 (2CN), 33.26 ($2CH_2$), 33.11 ($2CH_2$), 31.68 ($2CH_2$), 31.66 ($2CH_2$), 31.31

(2CH_2), 30.16 (2CH_2), 29.82 (2CH_2), 29.80 (2CH_2), 29.74 (2CH_2), 29.56-29.39 (18CH_2), 29.08 (4CH_2), 22.43 (2CH_2), 22.40 (2CH_2), 13.84 (2CH_3), 13.80 (2CH_3).

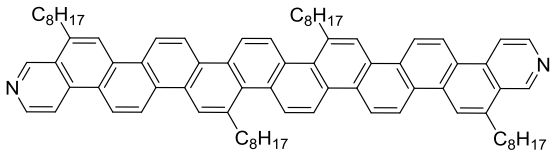
IR (neat) υ_{max}/cm^{-1} 2954 (m), 2918 (s), 2849 (s), 2226 (m), 1467 (m), 1379 (w), 899 (s), 817 (s), 720 (m).

LRMS (APPI) *m/z* 1201.91 $(M+H)^+$.

UV (DCM) λ_{max}/nm 275, 289, 358, 376, 428, 455.

Melting point (tol) > 250 °C.

8,14,22,28-tetraoctylnaphtho[1,2-*c*:5,6-*c*']dipicene-2,16-dipyridine 118



A J-Young tap vessel was charged with 4,4'-(1,1'',5,5''-tetra(dec-1-yn-1-yl)-[2,2':6',2''-ternaphthalene]-6,6''-diyl)dipyridine **117** (0.010 g, 0.009 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.007 g, 0.046 mmol) in NMP (0.5 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 2 days and cooled to room temperature, giving a precipitate which was isolated by continuous addition of methanol and removal of the mother liquor by Pasteur pipette. This gave 0.007 g of solid, which was dissolved in toluene (6 mL, 100 °C) and left at room temperature overnight for recrystallisation. The purified material was obtained as a yellow solid (0.004 g, 40%).

^{1}H-NMR (500 MHz, tol-d_8, 353 K) δ 9.71 (2H, s), 8.93-8.89 (6H, m), 8.84 (2H, d, *J* = 5.5 Hz), 8.80-8.78 (6H, m), 8.61-8.59 (4H, m), 8.26 (2H, d, *J* = 5.5 Hz), 3.74 (4H, t, *J* = 7.8 Hz), 3.19 (4H, t, *J* = 7.7 Hz), 2.13-2.07 (4H, m), 1.89 (4H, quin, *J* = 7.6 Hz), 1.59-1.53 (4H, m), 1.54-1.48 (4H, m), 1.46-1.27 (32H, m), 0.95-0.92 (6H, m), 0.88 (6H, t, *J* = 6.7 Hz).

^{13}C-NMR (125 MHz, TCE-d_2, 353 K) δ 148.36 (2CH), 144.12 (2CH), 138.69 (2C), 137.49 (2C), 134.89 (2C), 130.63 (2C), 130.26 (2C), 129.58 (2C), 129.40 (2C), 129.05 (2C), 128.09 (2C), 127.99 (2C), 127.04 (2C), 126.99 (2CH), 125.61 (2C), 125.52 (2C), 123.98 (2CH), 122.15 (2CH), 122.08 (2CH), 121.78 (2CH), 121.22 (2CH), 121.01 (2CH), 119.73 (2CH), 116.34 (2CH), 37.88 (2CH_2), 33.00 (2CH_2), 31.63 (2CH_2), 31.61 (2CH_2), 31.59 (2CH_2), 30.95 (2CH_2), 29.71 (2CH_2), 29.64 (2CH_2), 29.26 (2CH_2), 29.20 (2CH_2), 29.02 (2CH_2), 29.00 (2CH_2), 22.36 (4CH_2), 13.78 (4CH_3).

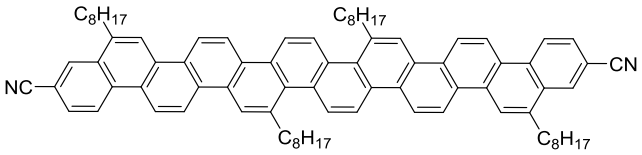
IR (neat) υ_{max} 2953 (m), 2919 (s), 2850 (s), 1582 (m), 1468 (m), 1454 (m), 1374 (w), 1092 (m), 1021 (m), 812 (s), 790 (s), 723 (m).

LRMS (APPI) 1078.7 ($M^{+\cdot}$), 1079.7 $(M+H)^+$.

UV (DCM) λ_{max}/nm 332, 347, 374, 419.

Melting point (tol) > 250 °C.

8,14,22,28-tetraoctylnaphtho[1,2-*c*:5,6-*c*']dipicene-2,16-dicarbonitrile 120



A J-Young tap vessel was charged with 4,4'-(1,3'',5,7''-tetra(dec-1-yn-1-yl)-[2,2':6',2''-ternaphthalene]-6,6''-diyl)dibenzonitrile **119** (0.030 g, 0.027 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.017 g, 0.112 mmol) in NMP (1 mL) was added and the tube was sealed under nitrogen. The reaction mixture heated to 240 °C, held at this temperature for 2 days and cooled to room temperature, giving a precipitate which was filtered, washed with methanol and dried. The titled compound was obtained as a yellow solid (0.015 g, 50%).

^{1}H-NMR (500 MHz, TCE-d_2, 353 K) δ 9.08 (2H, d, *J* = 9.5 Hz), 9.04 (2H, d, *J* = 9.5 Hz), 8.98 (2H, d, *J* = 4.8 Hz), 8.96 (2H, d, *J* = 4.0 Hz), 8.94 (2H, s), 8.91-8.89 (6H, m), 8.80 (2H, s), 8.58 (2H, s), 7.92 (2H, dd, *J* = 8.6, 1.3 Hz), 3.77 (4H, t, *J* = 7.9 Hz), 3.34 (4H, t, *J* = 7.8 Hz), 2.18-2.12 (4H, m), 2.04-1.98 (4H, m), 1.69-1.62 (8H, m), 1.46-1.35 (32H, m), 0.97 (6H, t, *J* = 7.0 Hz), 0.94 (6H, t, *J* = 7.0 Hz).

^{13}C-NMR* (125 MHz, TCE-d_2, 353 K) δ 129.82 (2CH), 127.25 (2CH), 126.86 (2CH), 124.72 (2CH), 124.08 (2CH), 122.64 (2CH), 122.39 (2CH), 122.17 (2CH), 121.33 (2CH), 121.31 (2CH), 119.87 (2CH), 109.65 (2CN), 37.09 ($2CH_2$), 33.62 ($2CH_2$), 31.70 ($2CH_2$), 31.68 ($2CH_2$), 31.66 ($2CH_2$), 30.63 ($2CH_2$), 29.77 ($2CH_2$), 29.70 ($2CH_2$), 29.33 ($2CH_2$), 29.27 ($2CH_2$), 29.07 ($4CH_2$), 22.44 ($2CH_2$), 22.43 ($2CH_2$), 13.86 ($4CH_3$).

* Only aromatic C-H are reported as not all quaternary aromatic carbon atoms were observed due to extremely low solubility of the compound.

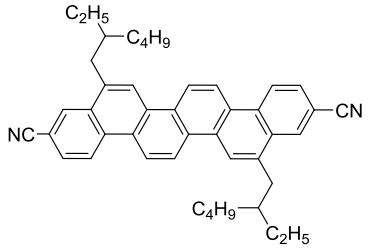
IR (neat) υ_{max}/cm^{-1} 2918 (s), 2848 (s), 2222 (m), 1616 (m), 1463 (m), 1454 (m), 1377 (w), 885 (m), 800 (s), 778 (m), 727 (m).

LRMS (APPI) *m/z* 1126.7 ($M^{+\cdot}$), 1127.7 $(M+H)^+$.

UV (DCM) λ_{max}/nm 338, 355, 421.

Melting point (tol) > 250 °C.

8,16-bis(2-ethylhexyl)benzo[*c*]picene-2,10-dicarbonitrile 127



A J-Young tap vessel was charged with 4,4'-(1,5-bis(4-ethyloct-1-yn-1-yl)naphthalene-2,6-diyl)dibenzonitrile **126** (0.125 g, 0.207 mmol) and evacuated/refilled with nitrogen three times. A solution of DBU (0.060 g, 0.394 mmol) in NMP (3 mL) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 15 h, cooled to room temperature and diluted with methanol (25 mL). This gave a precipitate which was filtered, washed with methanol and dried. The titled compound was obtained as a light yellow solid (0.096 g, 77%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.98-8.95 (4H, m), 8.89 (2H, d, *J* = 9.5 Hz), 8.70 (2H, s), 8.55 (2H, s), 7.91 (2H, d, *J* = 8.7 Hz), 3.23-3.20 (4H, m), 1.93-1.87 (2H, m), 1.52-1.26 (16H, m), 1.00 (6H, t, *J* = 7.3 Hz), 0.90 (6H, t, *J* = 7.2 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.66 (2C), 133.00 (2C), 130.88 (2C), 130.28 (2CH), 129.34 (2C), 129.02 (2C), 127.39 (2CH), 126.95 (2C), 124.85 (2CH), 123.90 (2CH), 121.90 (2CH), 121.74 (2CH), 119.40 (2C), 109.85 (2CN), 40.01 (2CH), 38.63 ($2CH_2$), 32.64 ($2CH_2$), 28.64 ($2CH_2$), 25.85 ($2CH_2$), 23.09 ($2CH_2$), 14.10 ($2CH_3$), 10.74 ($2CH_3$).

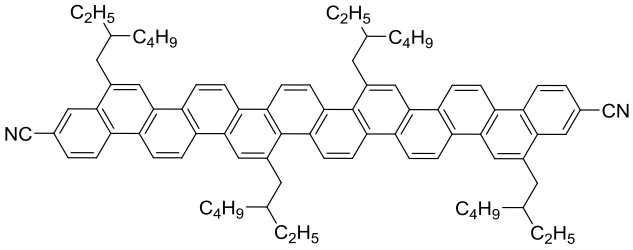
IR (neat) υ_{max}/cm^{-1} 2957 (m), 2922 (m), 2854 (m), 2222 (m), 1617 (m), 1456 (m), 1443 (m), 1378 (w), 885 (m), 804 (s), 721 (m).

HRMS (APPI) *m/z* calc. for $C_{44}H_{46}N_2$ ($M^{+\cdot}$) 602.36555, found 602.36662.

UV (DCM) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 300 (107200), 312 (166700), 326 (88300), 335 (72800), 346 (27800), 387 (6100), 408 (7500).

Melting point (hexane/DCM) > 250 °C.

8, 14, 22, 28-tetrakis(2-ethylhexyl)naphtho[1,2-*c*:5,6-*c*']dipicene-2,16-dicarbonitrile 129



A solution of 4,4'-(1,1",5,5"-tetrakis(4-ethyloct-1-yn-1-yl)-[2,2':6',2"-ternaphthalene]-6,6"-diyl)dibenzonitrile **128** (0.031 g, 0.027 mmol) in NMP (1.5 mL) was added to a J-Young tap vessel and degassed by sonicating whilst under high vacuum (0.1 mm Hg). DBU (0.03 mL, 0.031 g, 0.201 mmol) was added and the tube was sealed under nitrogen. The reaction mixture was heated to 240 °C, held at this temperature for 50 h, cooled to room temperature and diluted with methanol (20 mL) to give a precipitate which was filtered and washed with methanol. This was purified by column chromatography (SiO_2, 60-80% DCM in pet. ether) to give the titled compound as a yellow solid (0.009 g, 29%).

^{1}H-NMR (500 MHz, TCE-d_2, 333 K) δ 9.07-9.03 (4H, m), 8.96 (4H, d, *J* = 9.2 Hz), 8.94 (2H, d, *J* = 9.5 Hz), 8.90 (2H, d, *J* = 9.5 Hz), 8.87 (2H, s), 8.85 (2H, d, *J* = 9.5 Hz), 8.76 (2H, s), 8.57 (2H, s), 7.91 (2H, dd, *J* = 8.6, 1.0 Hz), 3.82-3.77 (4H, m), 3.26 (4H, t, *J* = 6.2 Hz), 1.99-1.93 (2H, m), 1.93-1.89 (2H, m), 1.58-1.50 (8H, m), 1.41-1.33 (8H, m), 1.26-1.19 (12H, m), 1.15-1.09 (4H, m), 1.05 (6H, t, *J* = 7.4 Hz), 0.96 (6H, t, *J* = 7.2 Hz), 0.78-0.74 (12H, m).

^{13}C-NMR (125 MHz, TCE-d_2, 333 K) δ 137.70 (2C), 136.27 (2C), 133.05 (2C), 130.78 (2C), 130.68 (2C), 130.03 (2CH), 129.67 (2C), 129.40 (2C), 129.11 (2C), 129.07 (2C), 128.03 (2C), 128.00 (2C), 127.15 (2C), 127.12 (2CH), 127.02 (2CH), 126.51 (2C), 124.75 (2CH), 124.68 (2CH), 123.87 (2CH), 122.38 (2CH), 122.13 (2CH), 121.31 (2CH), 121.16 (2CH), 119.47 (2CH), 119.42 (2C), 109.35 (2CN), 42.90 ($2CH_2$), 39.91 (2CH), 39.78 (2CH), 38.31 ($2CH_2$), 32.63 ($2CH_2$), 32.58 ($2CH_2$), 28.55 ($2CH_2$), 28.45 ($2CH_2$), 25.82 ($2CH_2$), 25.63 ($2CH_2$), 22.89 ($2CH_2$), 22.62 ($2CH_2$), 13.91 ($2CH_3$), 13.73 ($2CH_3$), 10.66 ($2CH_3$), 10.35 ($2CH_3$).

IR (neat) υ_{max}/cm^{-1} 3080 (w), 2955 (m), 2923 (s), 2854 (m), 2224 (m), 1616 (m), 1455 (m), 1377 (w), 1090 (m), 1018 (m), 800 (s), 726 (m).

LRMS (APPI) *m/z* 1126.8 ($M^{+\cdot}$).

UV (DCM) λ_{max}/nm 340, 356, 422.

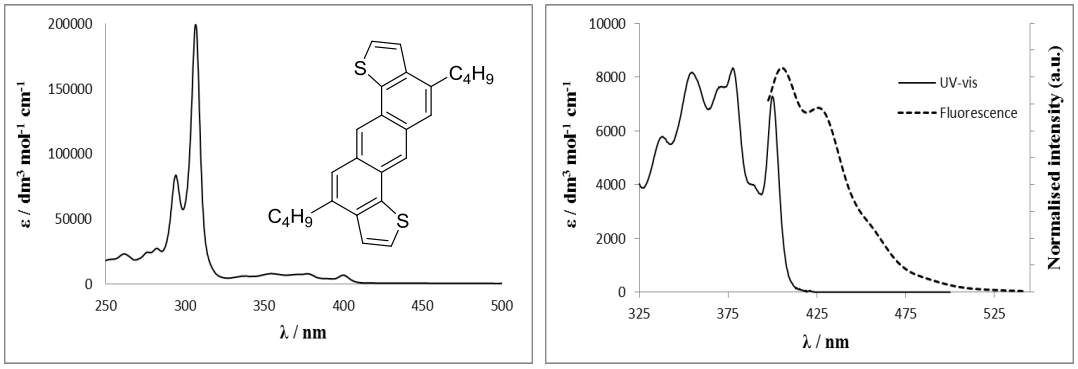
Melting point (tol) > 250 °C.

3.2 Photophysical characterisation

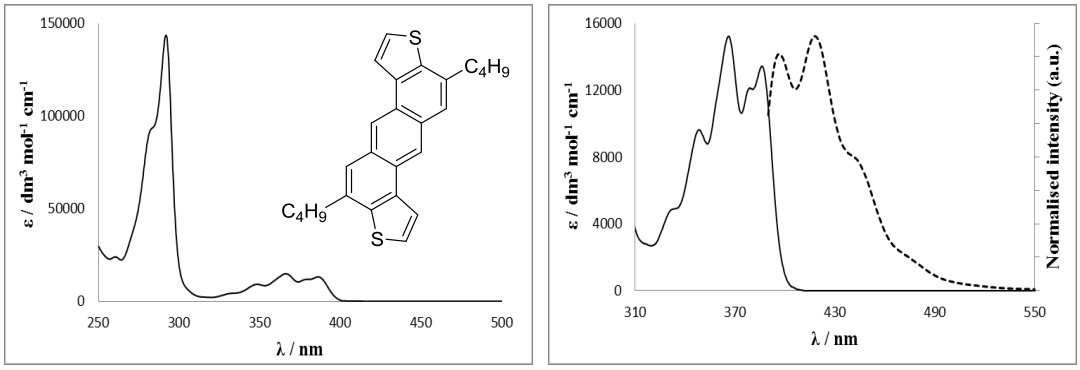
3.2.1 UV-vis and fluorescence spectra

Photophysical measurements were made at the University of Caen Basse-Normandie, France under the supervision of Prof. Bernhard Witulski. UV absorption spectra in solution were recorded with a JASCO V-660 or Ocean Optics USB2000+ spectrometer and emission spectra with a Perkin Elmer LS55 fluorescence spectrometer.

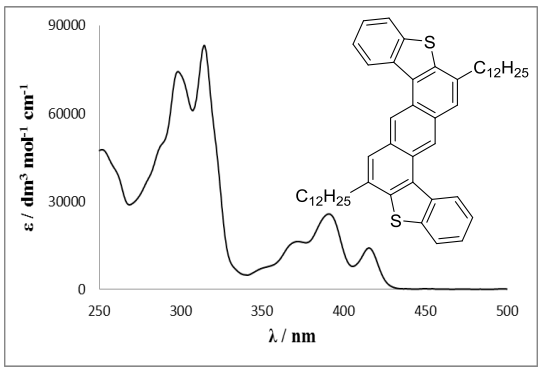
4,10-dibutylanthra[1,2-*b*:5,6 *b*']dithiophene 12

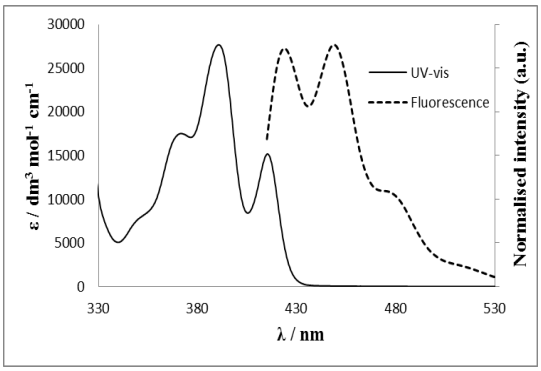


4,10-dibutylanthra[2,1-*b*:6,5-*b*']dithiophene 13

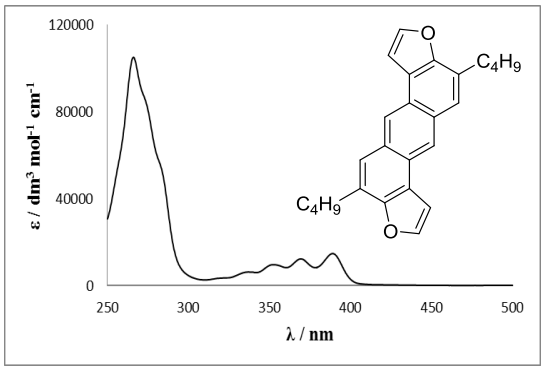


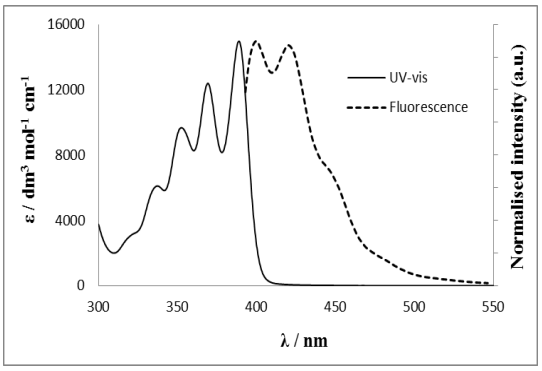
4,10-didodecylanthra[2,1-*b*:6,5-*b*']dibenzothiophene 14



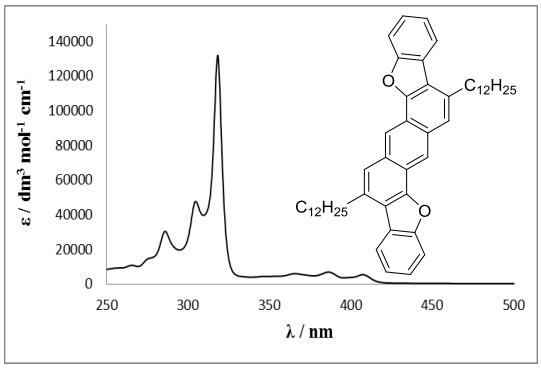


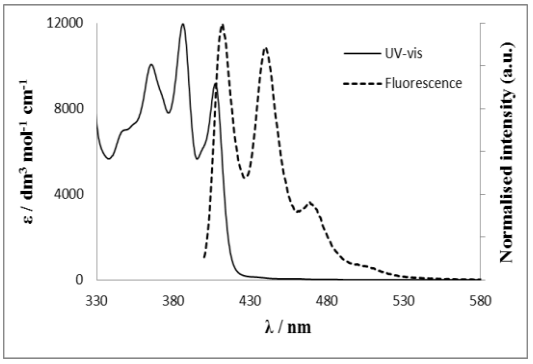
4,10-dibutylanthra[2,1-*b*:6,5-*b*']difuran 15



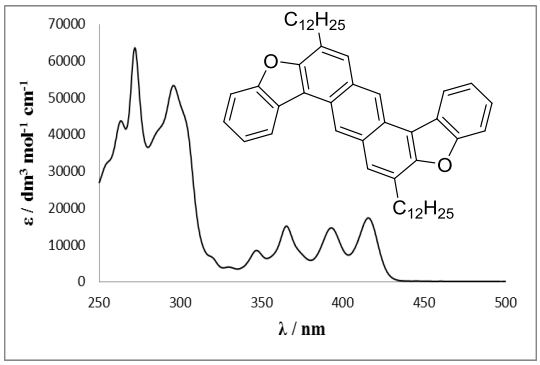


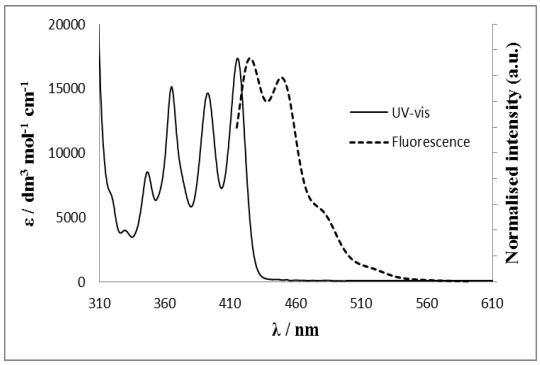
4,10-dibutylanthra[1,2-*b*:5,6-*b*']dibenzofuran 16



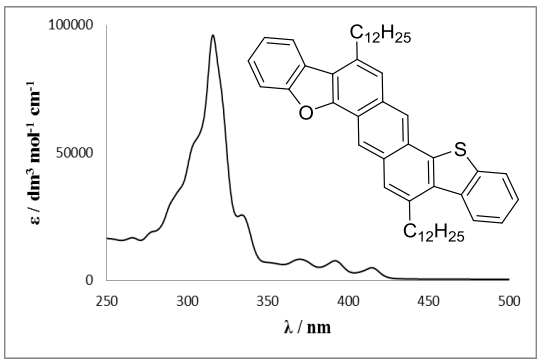


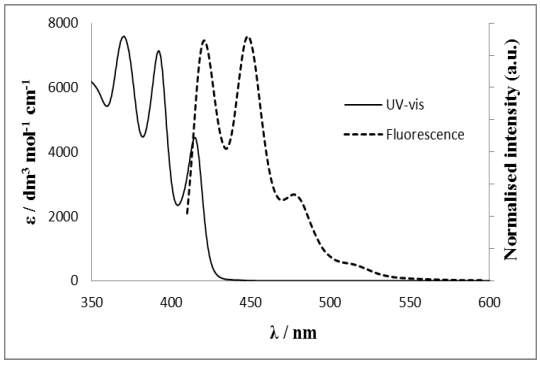
4,10-didodecylanthra[2,1-*b*:6,5-*b*']dibenzofuran 17



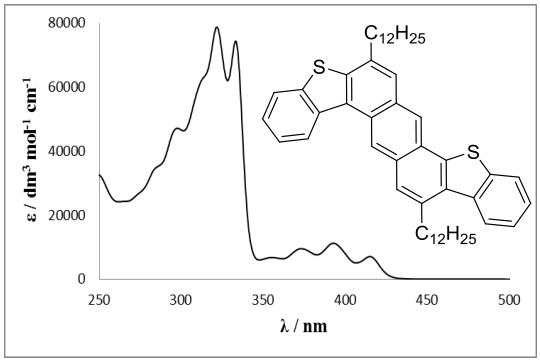


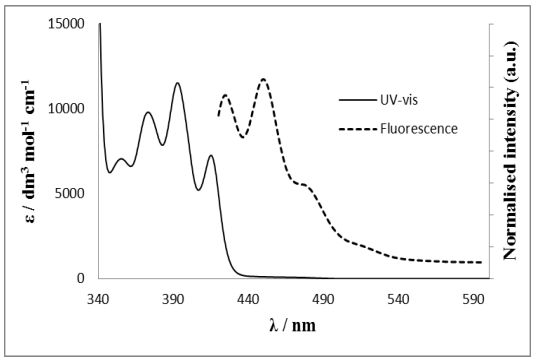
2,10-didodecylbenzo[4',5']thieno[2',3':5,6]anthra[1,2-*b*]benzofuran 36





38





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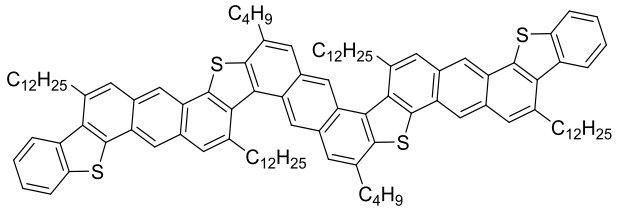
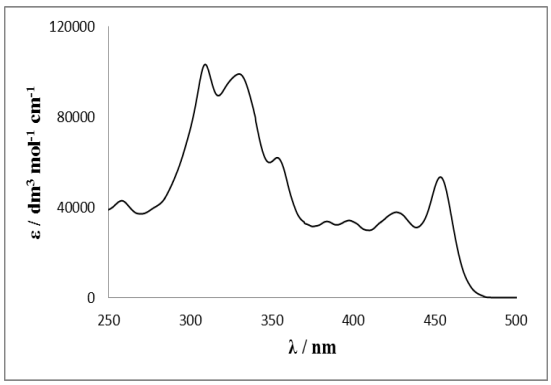
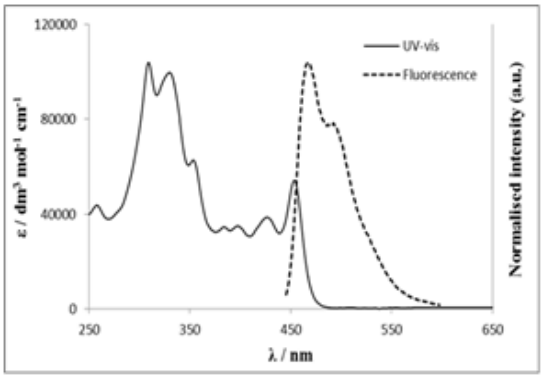
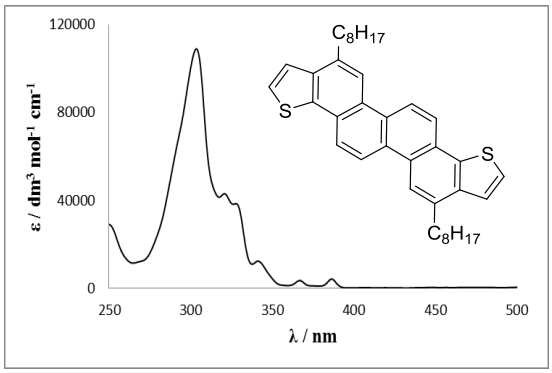
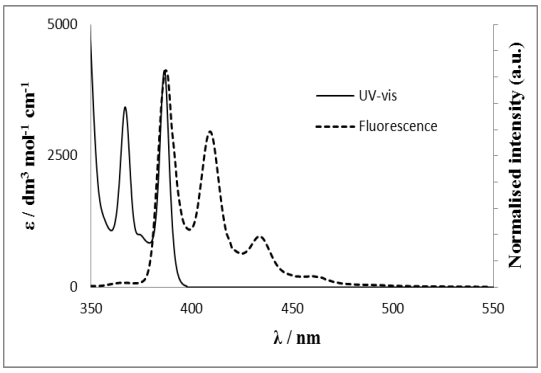




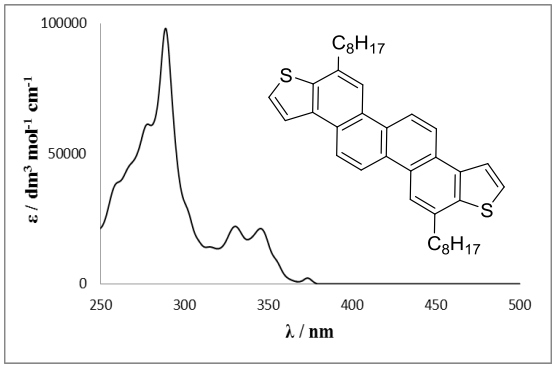


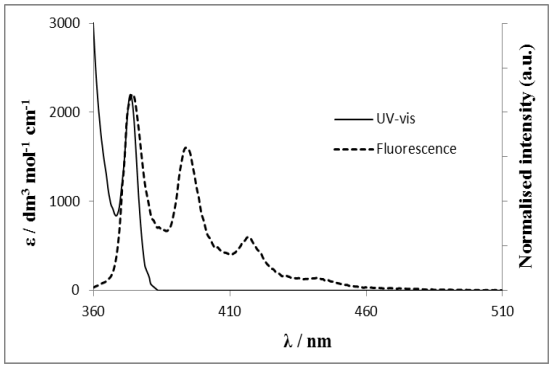
7,14-dioctylchryseno[1,2-b:7,8-*b*']dithiophene 50



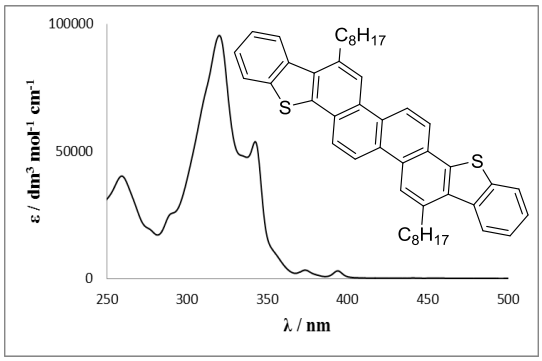


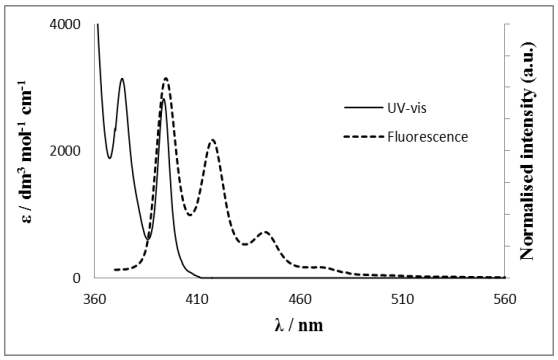
7,14-dioctylchryseno[2,1-*b*:8,7-*b*']dithiophene 51



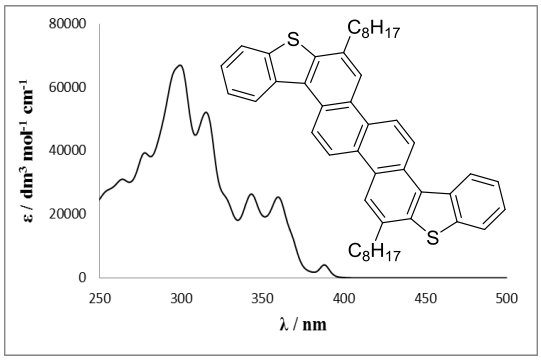


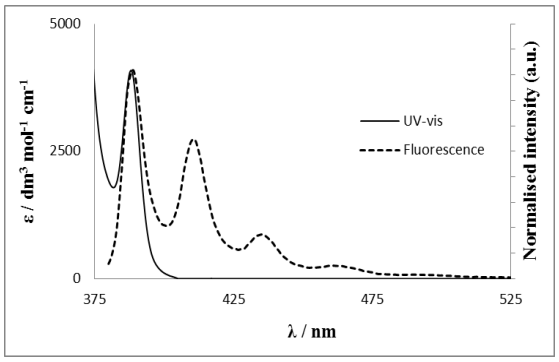
7,14-dioctylchryseno[1,2-b:7,8-*b*']dibenzothiophene 52



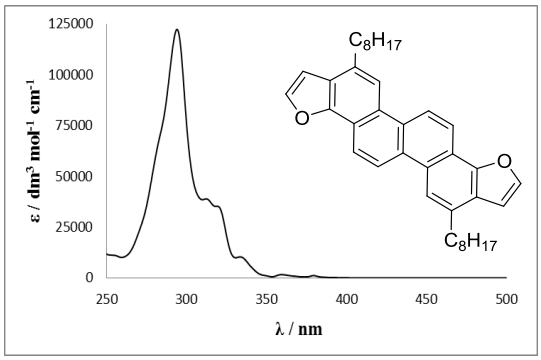


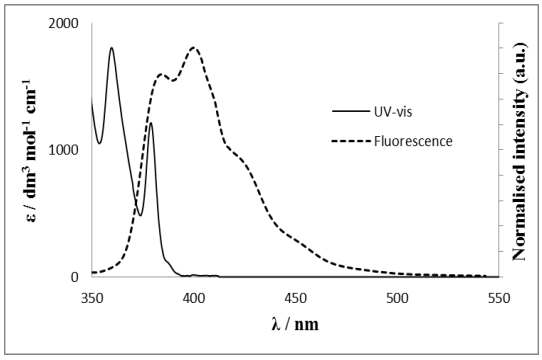
7,14-dioctylchryseno[2,1-*b*:8,7-*b*']dibenzothiophene 53



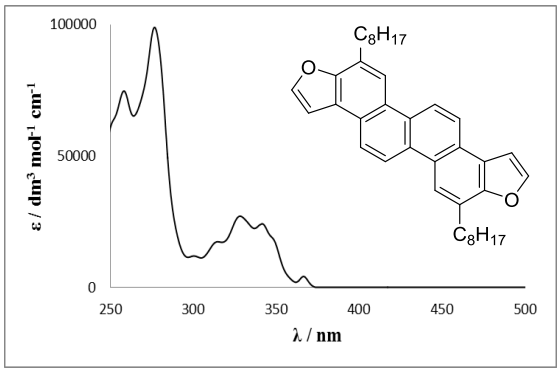


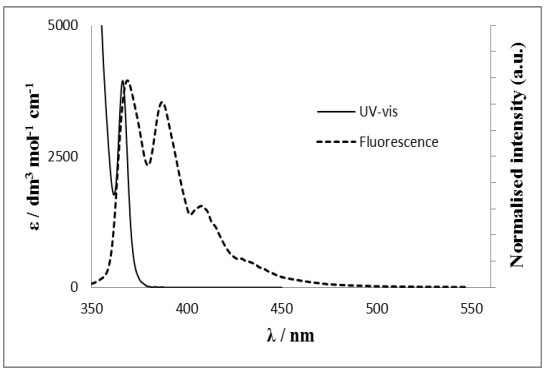
7,14-dioctylchryseno[1,2-*b*:7,8-*b*']difuran 54



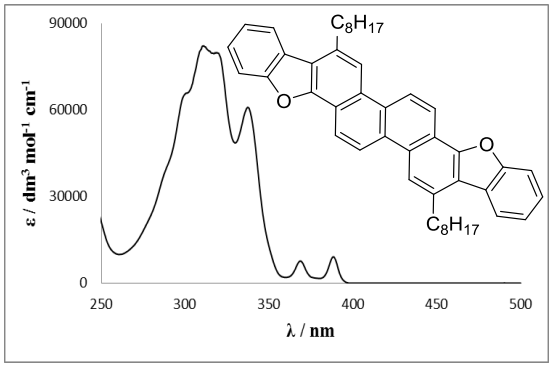


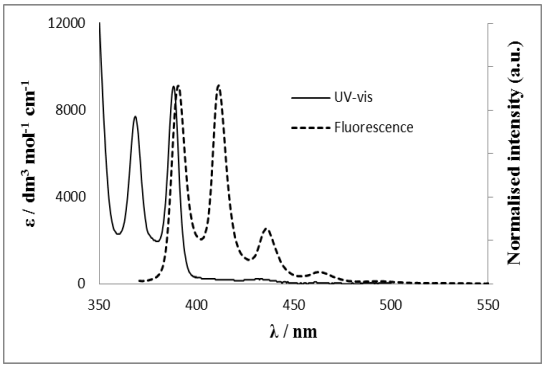
7,14-dioctylchryseno[2,1-*b*:8,7-*b*']difuran 55



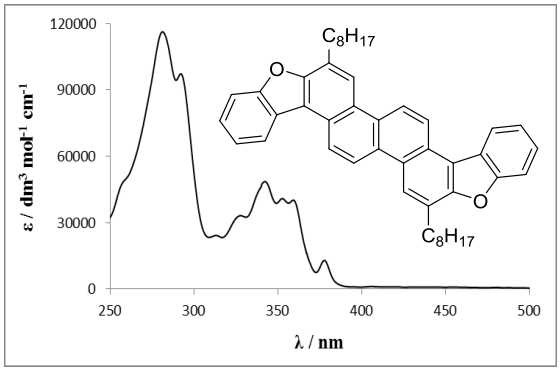


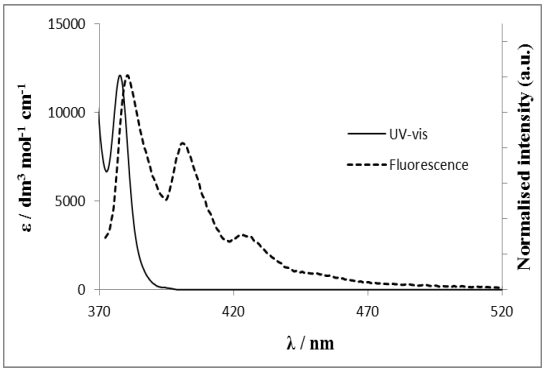
7,14-dioctylchryseno[1,2-*b*:7,8-*b*']dibenzofuran 56



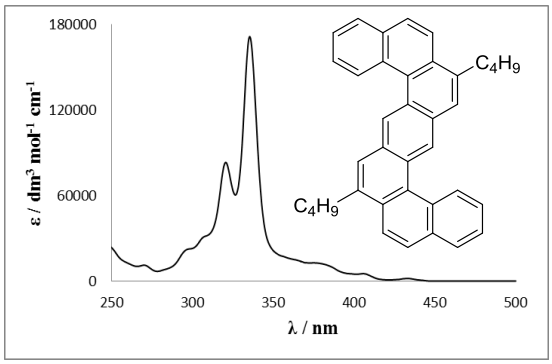


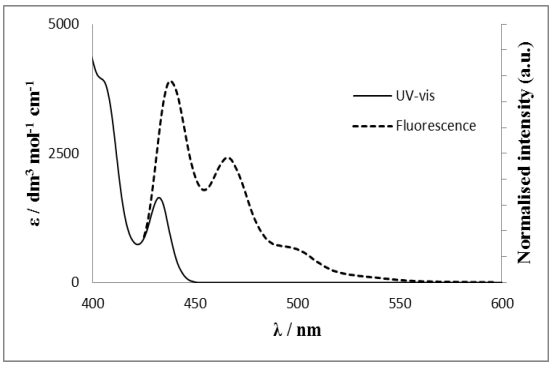
7,14-dioctylchryseno[2,1-*b*:8,7-*b*']dibenzofuran 57



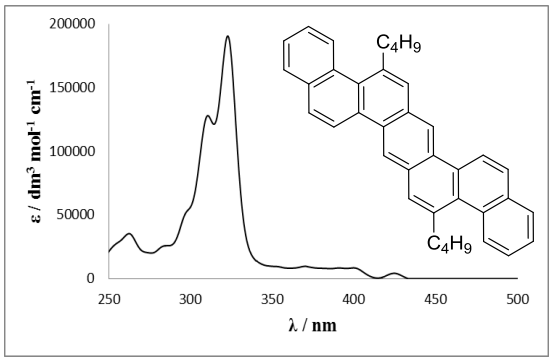


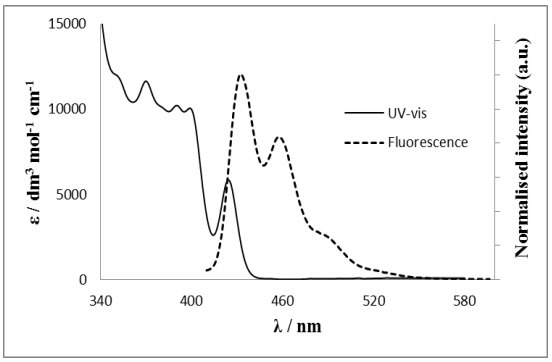
7,16-dibutylbenzo[*a*]naphtho[1,2-*k*]tetraphene 60



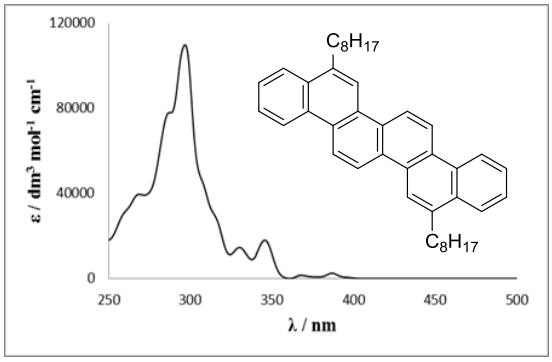


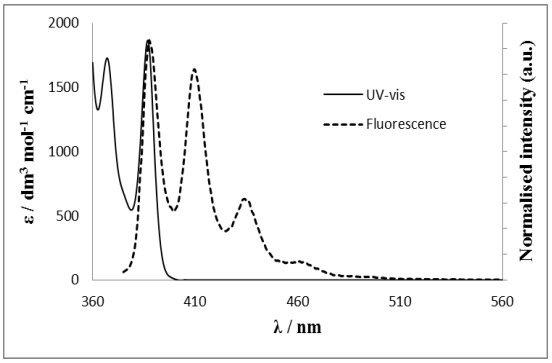
5,14-dibutylbenzo[*c*]naphtho[2,1-*k*]tetraphene 61



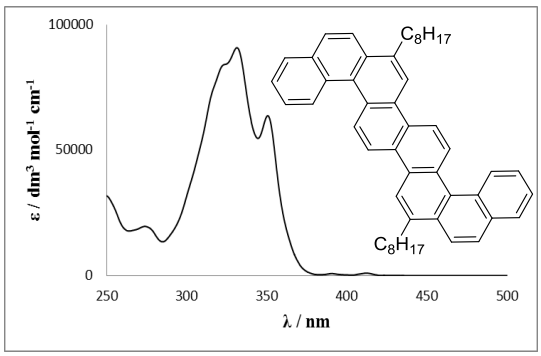


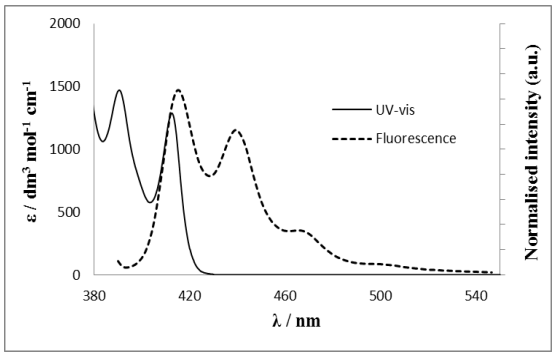
8,16-dioctylbenzo[*c*]picene 65



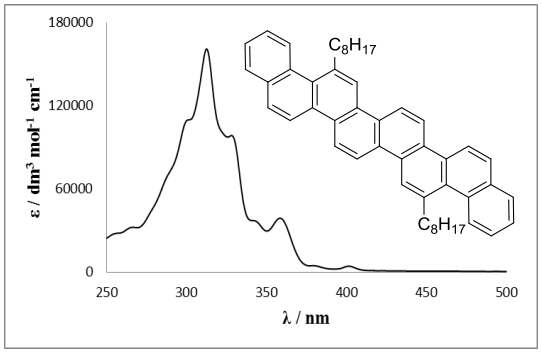


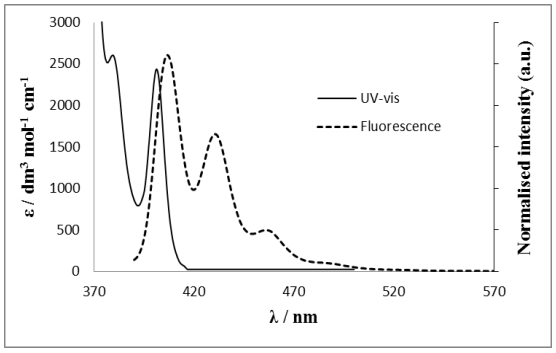
8,18-dioctylbenzo[*a*]naphtho[1,2-*m*]picene 66



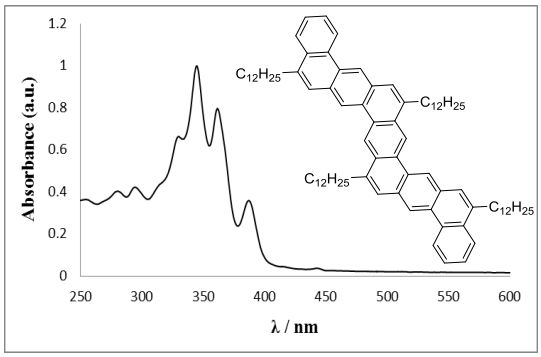


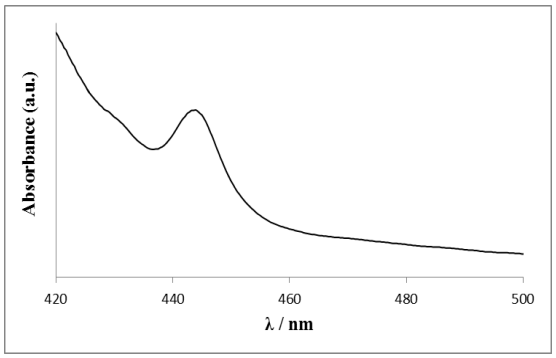
5,15-dioctylbenzo[*c*]naphtho[2,1-*m*]picene 67



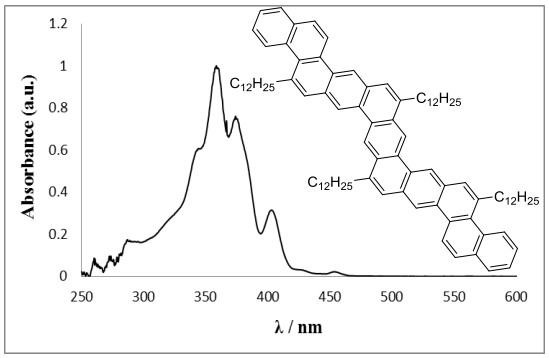


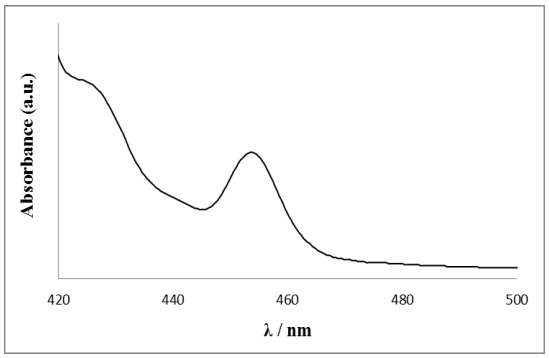
5,9,18,22-tetradodecylchryseno[3,2-*c*]naphtho[2,1-*m*]pentaphene 77



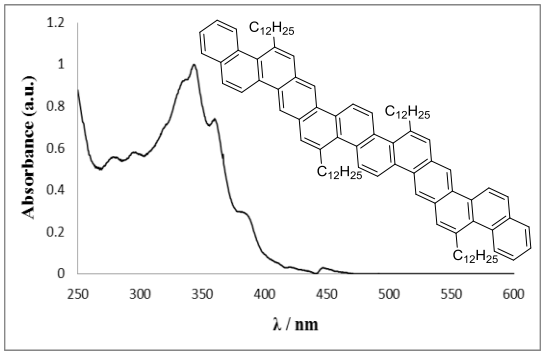


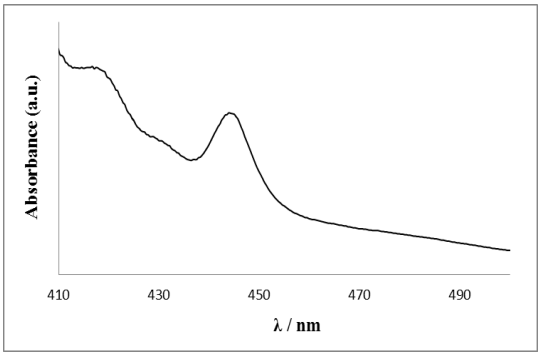
5,10,19,24-tetradodecylchryseno[2,3-*m*]phenanthro[2,1-*b*]picene 80



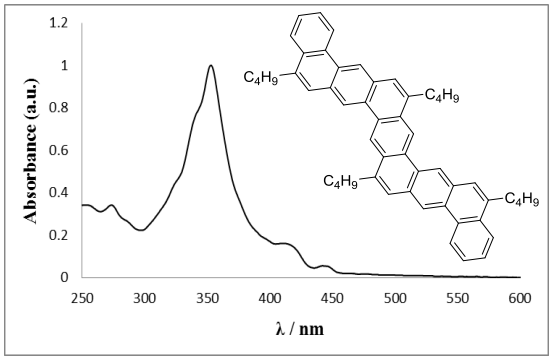


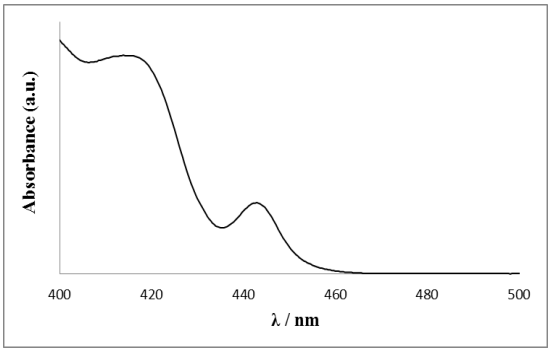
5,10,19,24-tetradodecylchryseno[2,3-*m*]phenanthro[2,1-*b*]picene 82



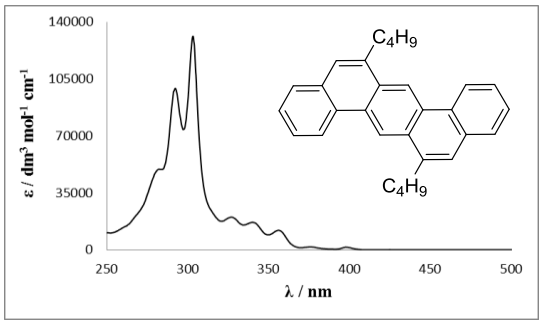


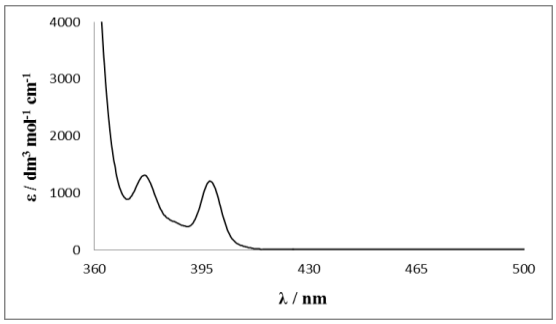
5,9,16,20-tetrabutylbenzo[*c*]phenanthro[2,3-*m*]pentaphene 85



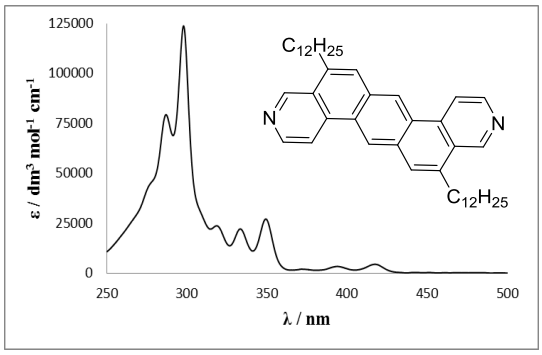


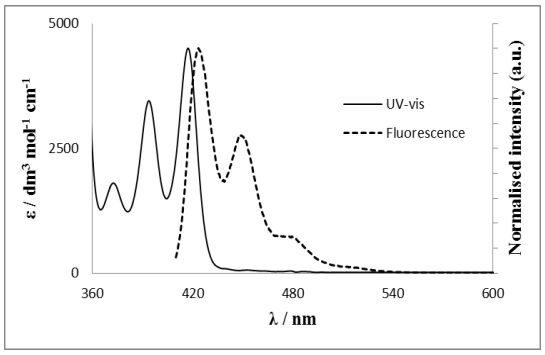
6,13-dibutylbenzo[*k*]tetraphene 90



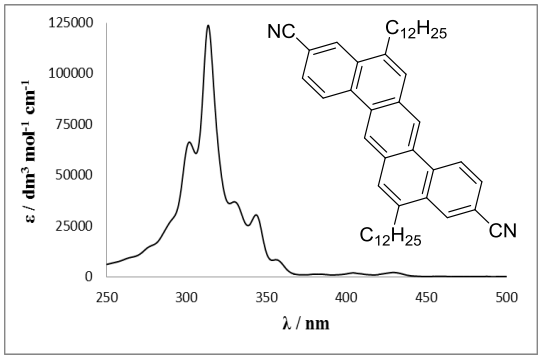


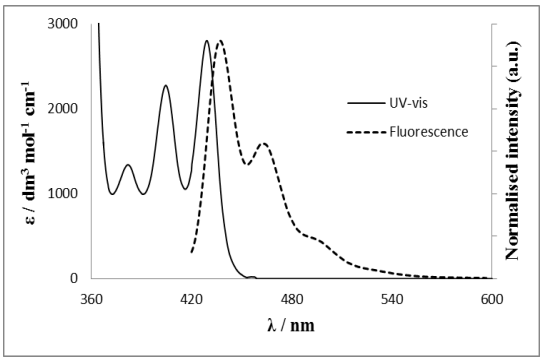
5,12-didodecylbenzo[1,2-*f*:4,5-*f*']diisoquinoline 93



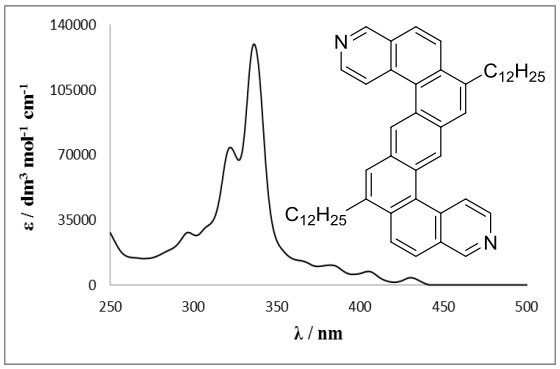


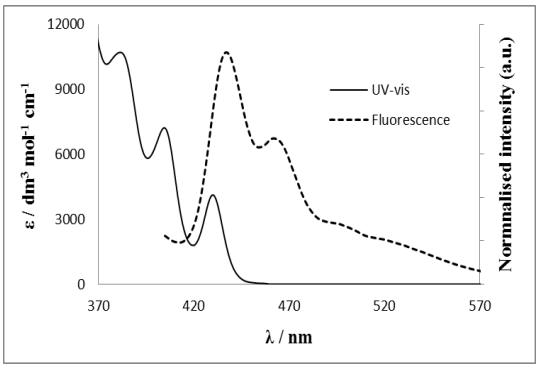
5,12-didodecylbenzo[*k*]tetraphene-3,10-dicarbonitrile 95



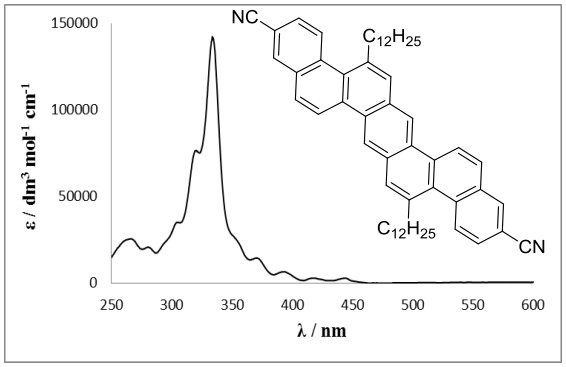


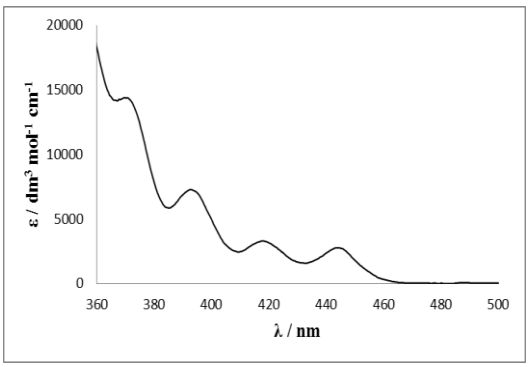
7,16-didodecylanthra[1,2-*f*:5,6-*f*']diisoquinoline 97



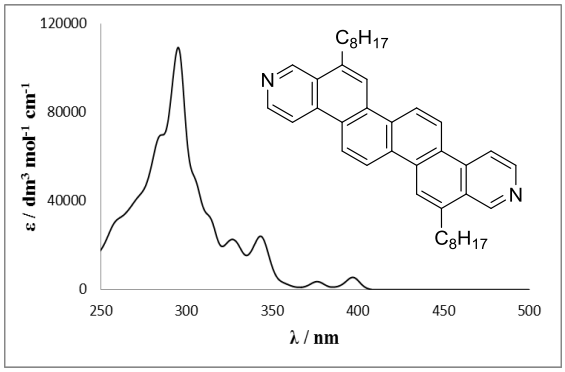


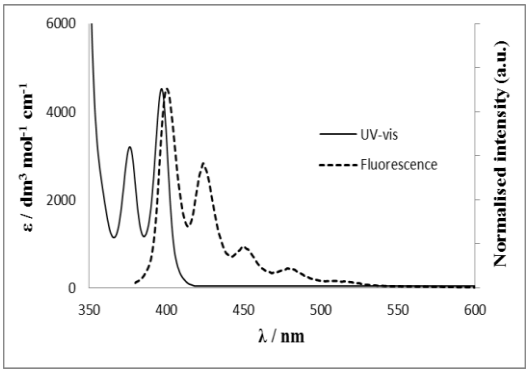
5,14-didodecylbenzo[*c*]naphtho[2,1-*k*]tetraphene-2,11-dicarbonitrile 99



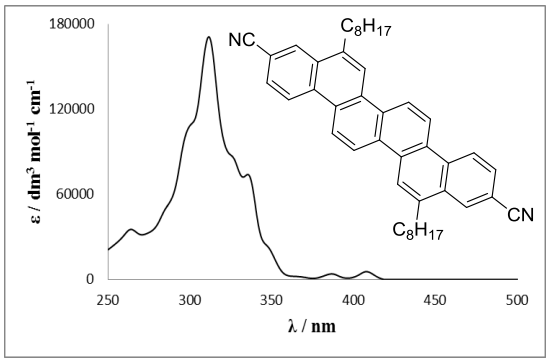


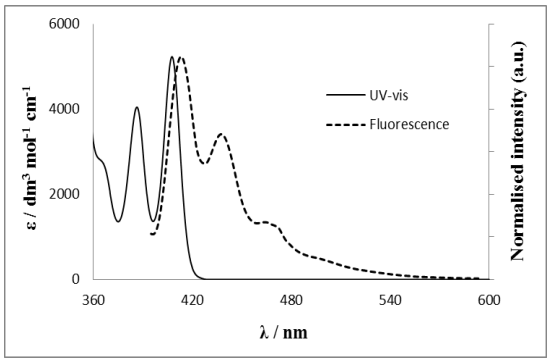
8,16-dioctylnaphtho[2,1-*f*:6,5-*f*']diisoquinoline 101



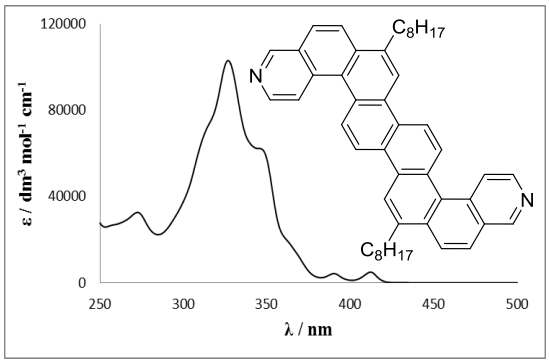


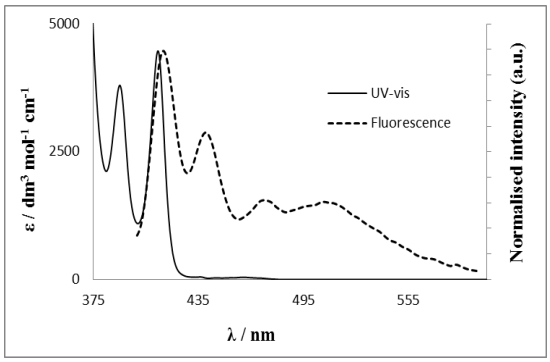
8,16-dioctylbenzo[*c*]picene-2,10-dicarbonitrile 104



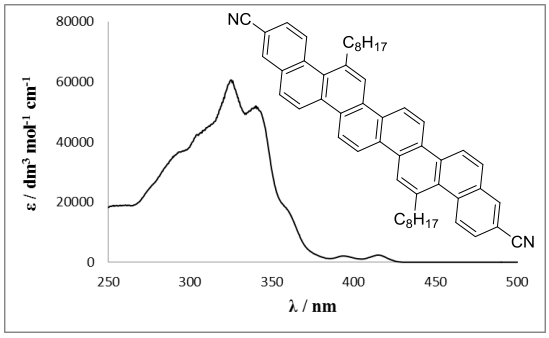


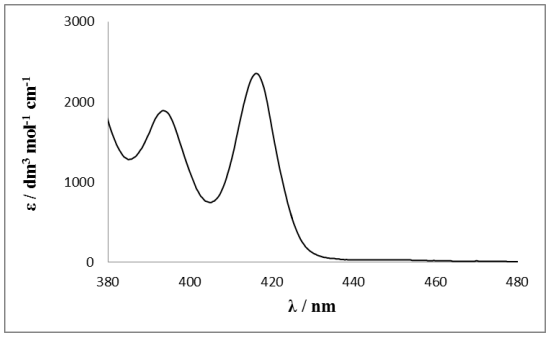
8,18-dioctylchryseno[1,2-*f*:7,8-*f*']diisoquinoline 106



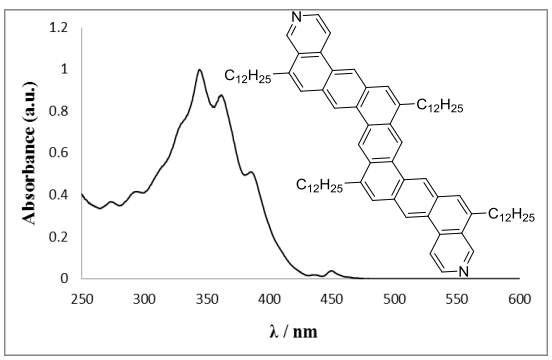


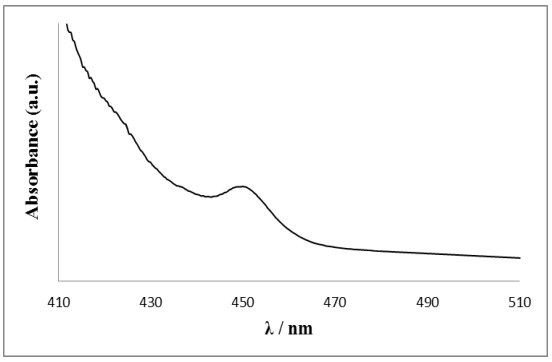
5,15-dioctylbenzo[*c*]naphtho[2,1-*m*]picene-2,12-dicarbonitrile 109



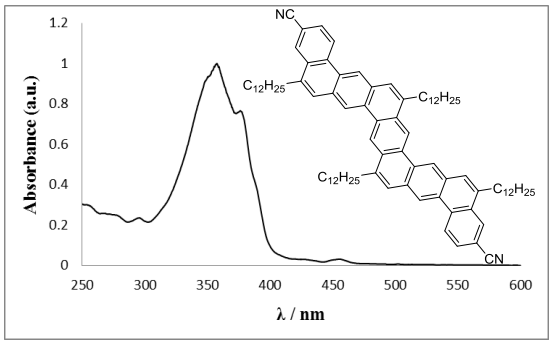


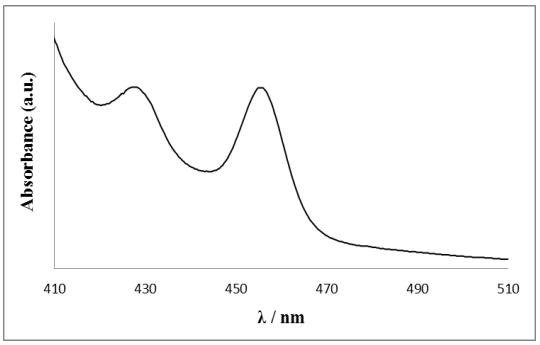
114



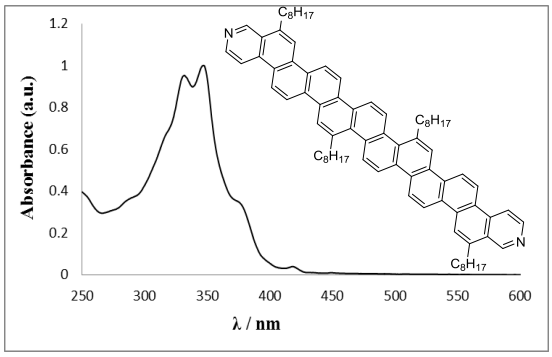


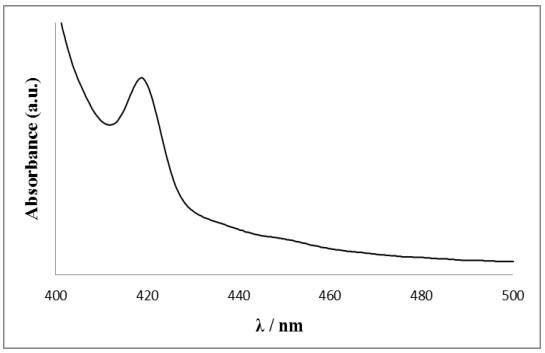
5,9,16,20-tetrabutylbenzo[*c*]phenanthro[2,3-*m*]pentaphene-3,14-dicarbonitrile 116



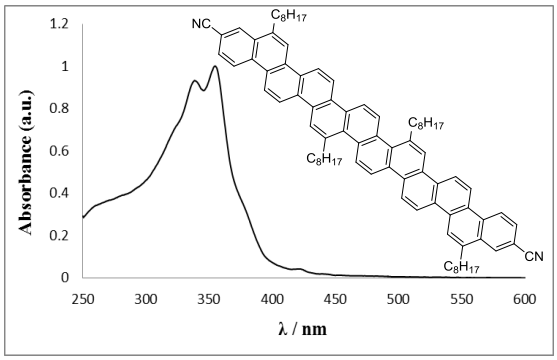


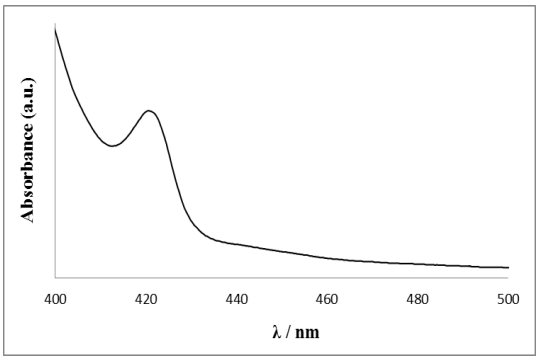
8,14,22,28-tetraoctylnaphtho[1,2-*c*:5,6-*c*']dipicene-2,16-dipyridine 118



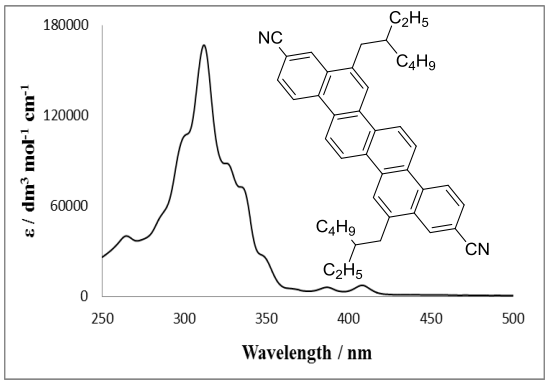


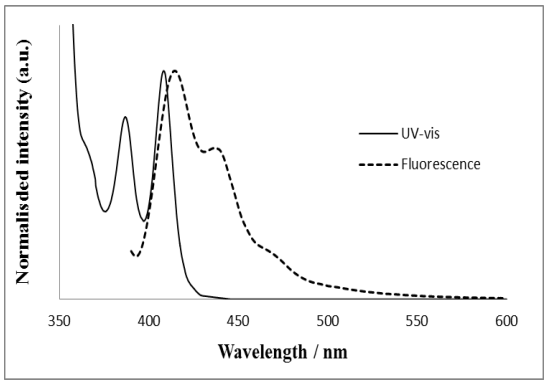
8,14,22,28-tetraoctylnaphtho[1,2-*c*:5,6-*c*']dipicene-2,16-dicarbonitrile 120



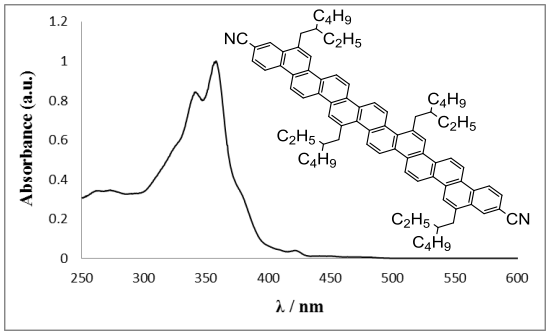


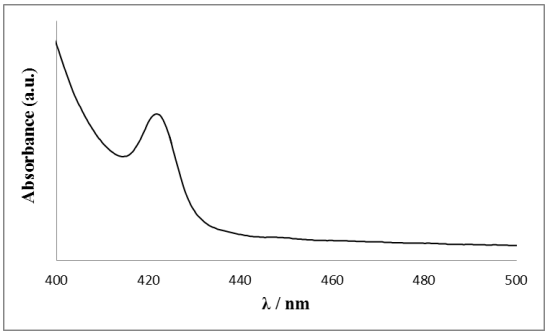
8,16-bis(2-ethylhexyl)benzo[*c*]picene-2,10-dicarbonitrile 127





8, 14, 22, 28-tetrakis(2-ethylhexyl)naphtho[1,2-*c*:5,6-*c*']dipicene-2,16-dicarbonitrile 129

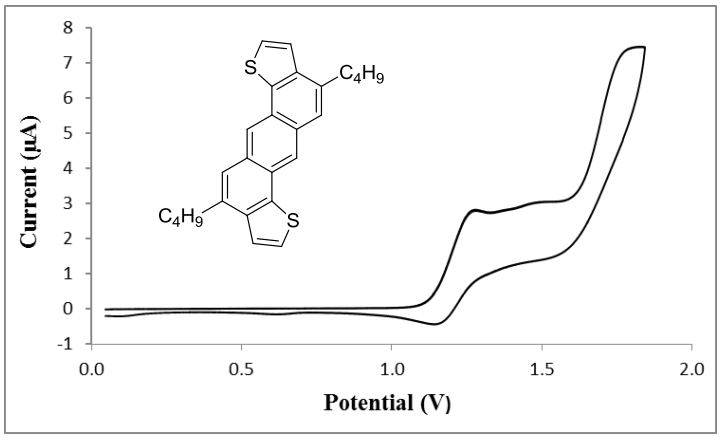




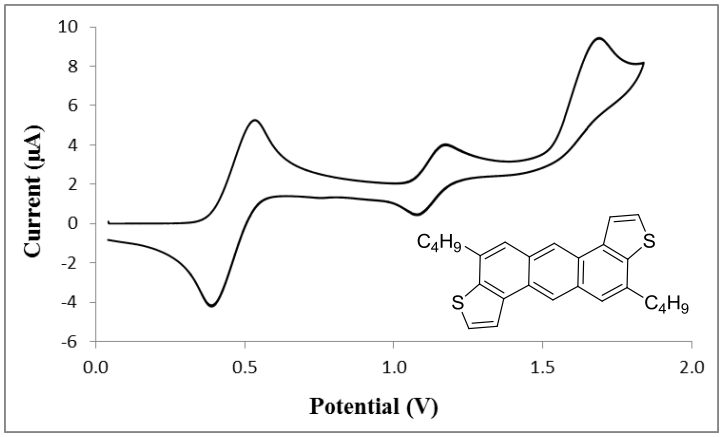
3.2.2 Cyclic voltammetry

Electrochemical studies were carried out at room temperature using a GAMRY Ref600 potentiostat. The working electrode was a platinum electrode, the auxiliary electrode a platinum wire. The reference electrode was an aqueous saturated (KCl) calomel electrode. Under the conditions used the reversible potential for the ferrocenium/ferrocene couple at 298 K is + 0.46 V in DCM. Solutions of compounds in a 0.1 M Bu_4NPF_6/CH_2Cl_2 electrolyte solution were used.

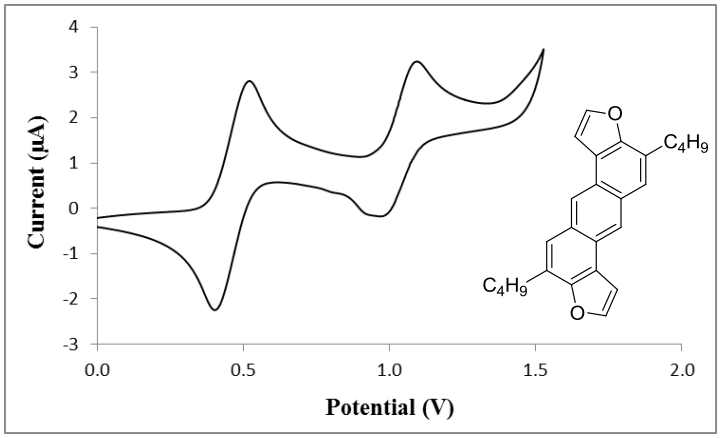
4,10-dibutylanthra[1,2-*b*:5,6 *b*']dithiophene 12



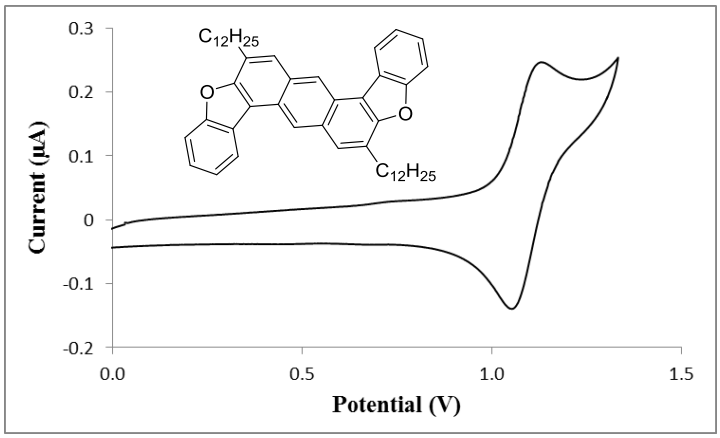
4,10-dibutylanthra[2,1-*b*:6,5-*b*']dithiophene 13



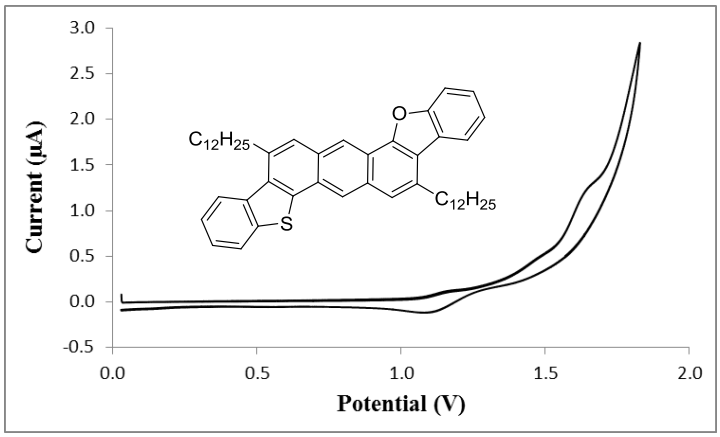
4,10-dibutylanthra[2,1-*b*:6,5-*b*']difuran 15



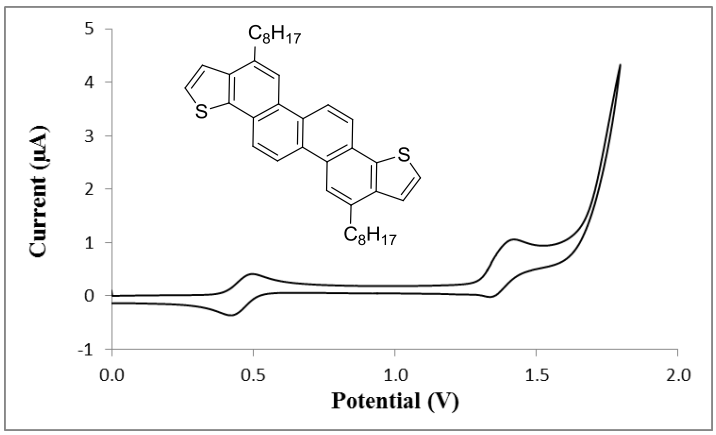
4,10-didodecylanthra[2,1-*b*:6,5-*b*']dibenzofuran 17



2,10-didodecylbenzo[4',5']thieno[2',3':5,6]anthra[1,2-*b*]benzofuran 36



7,14-dioctylchryseno[1,2-b:7,8-*b*']dithiophene 50



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5 Appendix: X-Ray crystal structure data

X-ray crystal structures were solved by Dr. Mark Light at the University of Southampton unless otherwise stated. Two different general experimentals were described in the reports. All thermal ellipsoids are drawn at the 50% probability level.

General experimental 1

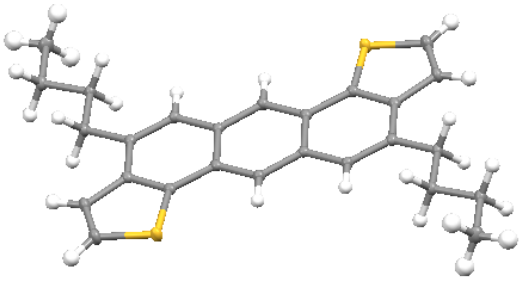
Diffractometer: Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator with HF Varimax optics (100µm focus). Cell determination, Data collection, Data reduction and cell refinement & Absorption correction: CrystalClear-SM Expert 2.0 r7 (Rigaku, 2011) , Structure solution: SHELXS97 (G. M. Sheldrick, Acta Cryst. (1990) A46 467-473). Structure refinement: SHELXL97 (G. M. Sheldrick (1997), University of Göttingen, Germany). Graphics: CrystalMaker: a crystal and molecular structures program for Mac and Windows. CrystalMaker Software Ltd, Oxford, England (www.crystalmaker.com)

Special details: All hydrogen atoms were placed in idealised positions and refined using a riding model.

General experimental 2

A single crystal was mounted on a MITIGEN holder in perfluoroether oil a Rigaku AFC12 FRE-HF diffractometer, unless otherwise stated. The crystal was kept at T = 100(2) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the ShelXT (Sheldrick, 2008 or Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with version of **ShelXL** (Sheldrick, 2008) using Least Squares minimisation.

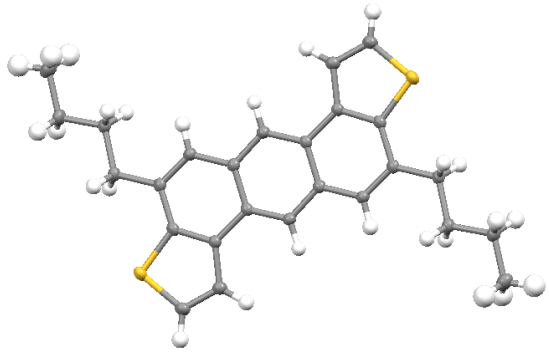
4,10-dibutylanthra[1,2-b:5,6-b']dithiophene 12



Single yellow crystals were recrystallised from 3:2 hexane/DCM at room temperature. The structure was solved by Christianne Wicking at the University of Southampton, using **general experimental 1**.

Formula	$C_{26}H_{26}S_2$	*F(000)*	214
Formula weight	402.59	Crystal	Prism; Colorless
Temperature / K	100(2)	Crystal size	0.20 × 0.20 × 0.20 mm^3
Wavelength / Å	0.71075	θ range for data collection	3.11 – 27.48°
Crystal system	Triclinic	Index ranges	$-8 \le h \le 8$, $-10 \le k \le 10$, $-12 \le l \le 13$
Space group	*P*_–1	Reflections collected	4477
a / Å	6.524(3)	Independent reflections	2296 [R_{int} = 0.0201]
b / Å	8.176(4)	Completeness to θ = 27.48 °	98.0 %
c / Å	0.786(6)	Absorption correction	Semi–empirical from equivalents
α / °	76.97(4)	Max. and min. transmission	0.9480 and 0.9480
β / °	73.46(3)	Refinement method	Full-matrix least-squares on F^2
γ / °	69.487(18)	Data / restraints / parameters	2296 / 0 / 128
V / $Å^3$	511.5(4)	Goodness-of-fit on F^2	1.161
Z	1	Final *R* indices [$F^2 > 2\sigma(F^2)$]	*R1* = 0.0341, *wR2* = 0.1029
$D_{calc.}$ / mg m^{-3}	1.307	*R* indices (all data)	*R1* = 0.0368, *wR2* = 0.1125
μ / mm^{-1}	0.270	Largest diff. peak and hole	0.495 and –0.279 e $Å^{-3}$

4,10-dibutylanthra[2,1-*b*:6,5-*b*']dithiophene 13

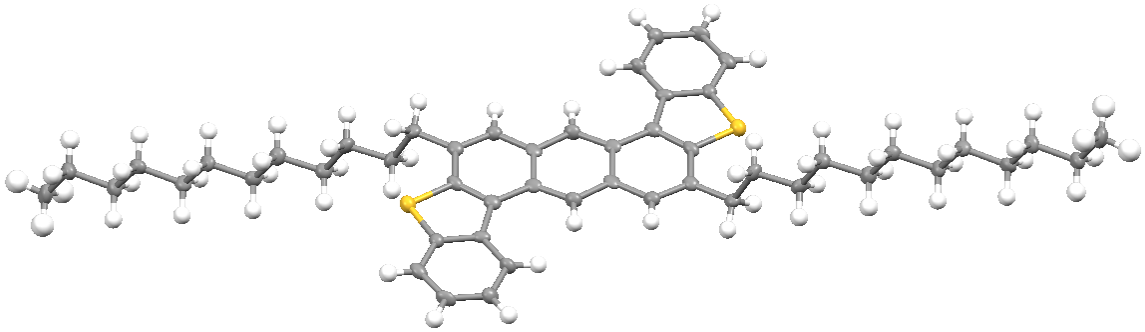


Single yellow crystals were recrystallised from 1:2 hexane/DCM at room temperature. The structure was solved by Jean-Francois Lohier at the University of Caen Lower Normandy, France. X-ray diffraction experiments on a single crystal of **13** were performed at 150 K with graphite–monochromatized Mo K_α radiation (λ = 0.71073 Å) on a Bruker–Nonius Kappa CCD area detector diffractometer.

Program(s) used to solve structure: SHELXS–97. Program(s) used to refine structure: SHELXL–97. Software used to prepare material for publication: SHELXTL–97.

Formula	$C_{26}H_{26}S_2$	α / °	90
Formula weight	402.59	β / °	106.9490(10)
Temperature / K	150	γ / °	90
Wavelength / Å	0.71075	V / Å^3	1034.36(10)
Crystal system	Monoclinic	*Z*	2
Space group	$P2_1/c$	$D_{calc.}$ / mg m^{-3}	1.293
a / Å	14.5987(8)	μ / mm^{-1}	0.267
b / Å	5.2788(3)	R_{int}	98.0 %
c / Å	14.0316(8)	$R[F^2>2\sigma(F^2)]$	0.09382

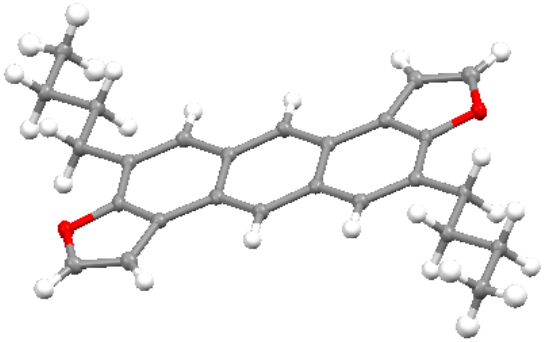
4,10-didodecylanthra[2,1-*b*:6,5-*b*']dibenzothiophene 14



Single crystals were recrystallised from 1:1 hexane/DCM at 3 °C. The structure was solved using **general experimental 1**.

Formula	$C_{50}H_{62}S_2$	*F(000)*	1576
Formula weight	727.11	Crystal	Plate; Yellow
Temperature / K	100(2)	Crystal size	0.26 × 0.05 × 0.01 mm^3
Wavelength / Å	0.71073	θ range for data collection	3.119 – 25.024 °
Crystal system	Monoclinic	Index ranges	$-25 \le h \le 62$, $-5 \le k \le 6$, $-17 \le l \le 17$
Space group	*C*2/*c*	Reflections collected	7449
a / Å	53.14(5)	Independent reflections	3336 [R_{int} = 0.0901]
b / Å	5.102(4)	Completeness to θ = 27.50 °	72.6 %
c / Å	14.953(14)	Absorption correction	Semi–empirical from equivalents
α / °	90	Max. and min. transmission	1.000 and 0.600
β / °	100.503(15)	Refinement method	Full-matrix least-squares on F^2
γ / °	90	Data / restraints / parameters	3336 / 0 / 236
V / Å^3	3986(6)	Goodness-of-fit on F^2	1.162
Z	4 (Z' = 0.5)	Final *R* indices [$F^2 > 2\sigma(F^2)$]	*R1* = 0.1074, *wR2* = 0.1687
$D_{calc.}$ / mg m^{-3}	1.212	*R* indices (all data)	*R1* = 0.1564, *wR2* = 0.1941
μ / mm^{-1}	0.168	Largest diff. peak and hole	0.306 and –0.346 e Å^{-3}

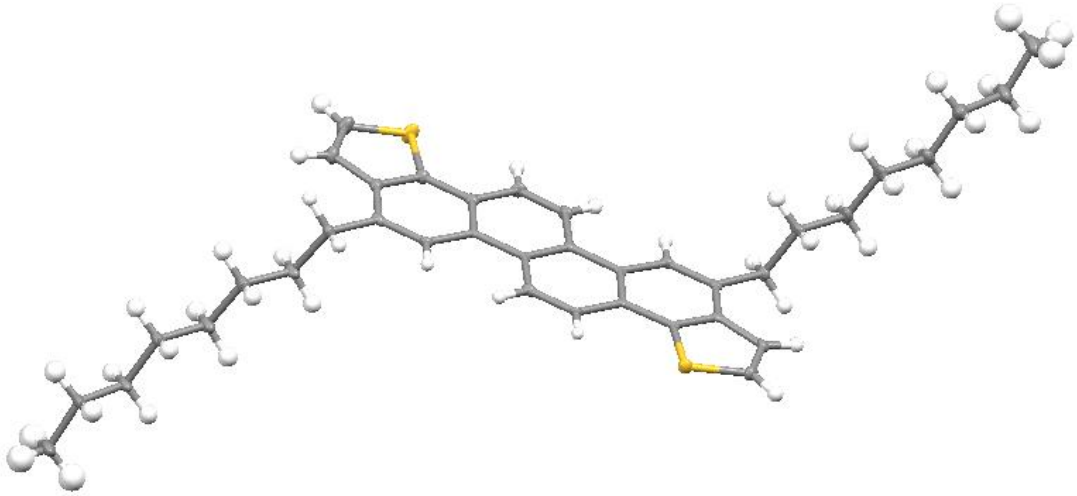
4,10-dibutylanthra[2,1-b:6,5-b']difuran 15



Single crystals were recrystallised from 5:1 hexane/DCM at 3 °C. The structure was solved by Christianne Wicking at the University of Southampton, using **general experimental 1**.

Formula	$C_{26}H_{26}O_2$	*F(000)*	396
Formula weight	370.47	Crystal	Chunk; colourless
Temperature / K	100(2)	Crystal size	0.12 × 0.10 × 0.02 mm^3
Wavelength / Å	0.71075	θ range for data collection	3.39 – 27.47 °
Crystal system	Monoclinic	Index ranges	$-14 \le h \le 17$, $-8 \le k \le 7$, $-11 \le l \le 13$
Space group	*P*_2$_1$/*c*	Reflections collected	4621
a / Å	13.514(5)	Independent reflections	2201 [R_{int} = 0.0317]
b / Å	6.701(2)	Completeness to θ = 27.47 °	99.2 %
c / Å	10.681(4)	Absorption correction	Semi–empirical from equivalents
α / °	90	Max. and min. transmission	0.9984 and 0.9906
β / °	90.629(6)	Refinement method	Full-matrix least-squares on F^2
γ / °	90	Data / restraints / parameters	2201 / 0 / 128
V / $Å^3$	967.2(6)	Goodness-of-fit on F^2	0.810
Z	2	Final *R* indices [$F^2 > 2\sigma(F^2)$]	*R1* = 0.0537, *wR2* = 0.1348
$D_{calc.}$ / mg m^{-3}	1.272	*R* indices (all data)	*R1* = 0.0679, *wR2* = 0.1477
μ / mm^{-1}	0.079	Largest diff. peak and hole	0.259 and –0.208 e $Å^{-3}$

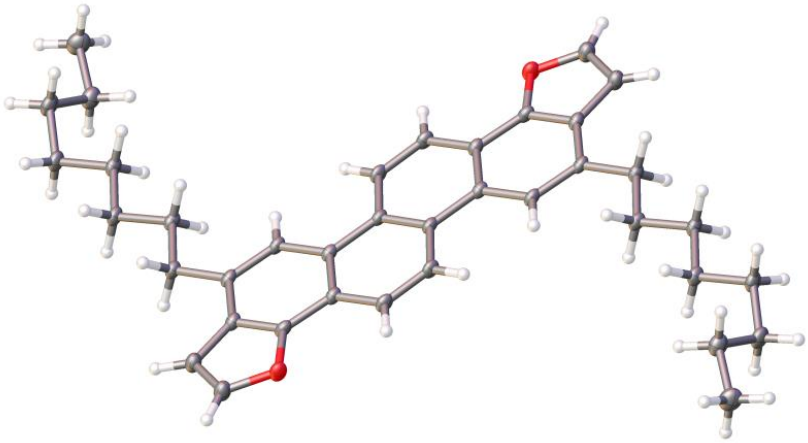
7,14-dioctylchryseno[1,2-b:7,8-*b*']dithiophene 50



Single clear colourless needle-shaped crystals were recrystallised from toluene by slow cooling (100 °C to room temperature over 2 h, and left overnight at room temperature). A suitable crystal (0.24 × 0.02 × 0.02 mm^3) was selected, and the structure was solved using **general experimental 2**. The ShelXT (Sheldrick, 2015) structure solution program was used.

Formula	$C_{38}H_{44}S_2$	V / Å^3	6168.3(4)
$D_{calc.}$ / g cm^{-3}	1.216	Z	8
μ / mm^{-1}	0.198	Z'	2
Formula Weight	564.85	Θ_{min} / °	2.929
Colour	clear colourless	Θ_{max} / °	28.698
Shape	needle	Measured Refl.	44379
Max Size / mm	0.24	Independent Refl.	15446
Mid Size / mm	0.02	Reflections Used	9119
Min Size / mm	0.02	R_{int}	0.0682
Temperature / K	100(2)	Parameters	725
Crystal System	monoclinic	Restraints	0
Space Group	$P2_1/n$	Largest Peak	1.015
a / Å	33.5348(13)	Deepest Hole	-0.545
b / Å	5.1056(3)	GooF	1.016
c / Å	36.0989(13)	*w*R_2 (all data)	0.2341
α / °	90	*w*R_2	0.2016
β / °	93.638(3)	R_1 (all data)	0.1568
γ / °	90	R_1	0.0923

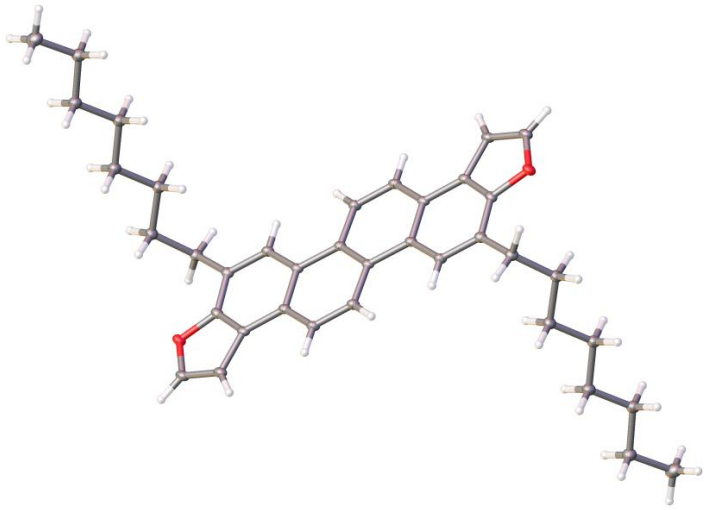
7,14-dioctylchryseno[1,2-*b*:7,8-*b*']difuran 54



Single clear colourless blade-shaped crystals were recrystallised from a mixture of hexane and DCM (6:1) after cooling at 3 °C for 24 h. A suitable crystal (0.32 × 0.08 × 0.03 mm^3) was selected and solved using **general experimental 2**. The ShelXT (Sheldrick, 2008) structure solution program was used.

Formula	$C_{38}H_{44}O_2$	V / $Å^3$	747.04(18)
$D_{calc.}$ / g cm^{-3}	1.184	Z	1
μ / mm^{-1}	0.071	Z'	0.5
Formula Weight	532.73	Θ_{min} / °	2.983
Colour	clear colourless	Θ_{max} / °	28.697
Shape	blade	Measured Refl.	11409
Max Size / mm	0.32	Independent Refl.	3344
Mid Size / mm	0.08	Reflections Used	2701
Min Size / mm	0.03	R_{int}	0.1239
Temperature / K	100(2)	Parameters	182
Crystal System	triclinic	Restraints	0
Space Group	P-1	Largest Peak	0.425
a / Å	7.5397(12)	Deepest Hole	-0.304
b / Å	8.5398(11)	GooF	1.066
c / Å	12.5684(14)	wR_2 (all data)	0.1950
α / °	71.806(11)	wR_2	0.1835
β / °	77.042(12)	R_1 (all data)	0.0775
γ / °	81.921(13)	R_1	0.0652

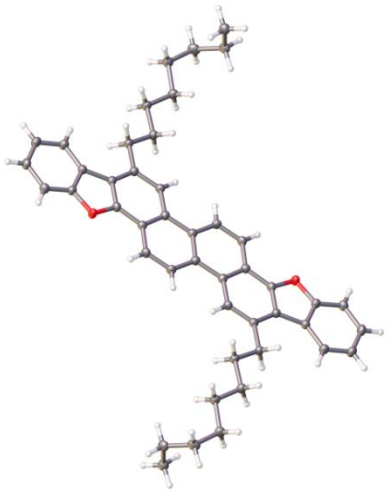
7,14-dioctylchryseno[2,1-*b*:8,7-*b*']difuran 55



Single clear colourless plate-shaped crystals were recrystallised from toluene by slow cooling (100 °C to room temperature over 2 h, and left overnight at room temperature). A suitable crystal (0.350 × 0.280 × 0.030 mm^3) was selected and the structure was solved using **general experimental 2**. The ShelXT (Sheldrick, 2008) structure solution program was used.

Formula	$C_{38}H_{44}O_2$	V / $Å^3$	1464.82(8)
$D_{calc.}$ / g cm^{-3}	1.208	Z	2
μ / mm^{-1}	0.072	Z'	0.5
Formula Weight	532.73	Θ_{min} / °	2.795
Colour	clear colourless	Θ_{max} / °	31.886
Shape	plate	Measured Refl.	17658
Max Size / mm	0.350	Independent Refl.	4668
Mid Size / mm	0.280	Reflections Used	3789
Min Size / mm	0.030	R_{int}	0.0276
Temperature / K	100(2)	Parameters	182
Crystal System	monoclinic	Restraints	0
Space Group	$P2_1/c$	Largest Peak	0.395
a / Å	22.2032(8)	Deepest Hole	-0.255
b / Å	4.83260(10)	GooF	1.043
c / Å	13.8625(4)	wR_2 (all data)	0.1381
α / °	90	wR_2	0.1293
β / °	100.003(3)	R_1 (all data)	0.0621
γ / °	90	R_1	0.0488

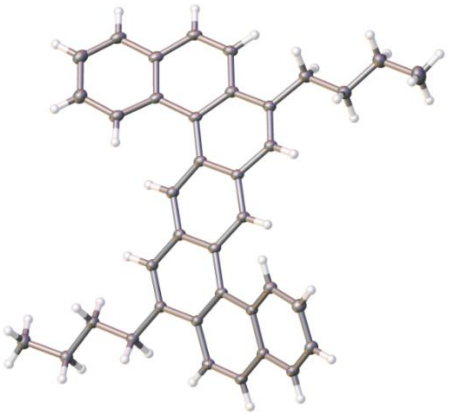
7,14-dioctylchryseno[1,2-*b*:7,8-*b*']dibenzofuran 56



Single clear colourless plate-shaped were crystallised from NMP by slow cooling (240 °C to room temperature over ~3 h). A suitable crystal (0.12 × 0.10 × 0.01 mm^3) was selected and the structure was solved using **general experimental 2**. A Rigaku AFC11 007-HF diffractometer and ShelXT (Sheldrick, 2015) structure solution program were used.

Formula	$C_{46}H_{48}O_2$	V / $Å^3$	818.61(6)
$D_{calc.}$ / g cm^{-3}	1.284	Z	1
μ / mm^{-1}	0.583	Z'	0.5
Formula Weight	632.84	Θ_{min} / °	5.114
Colour	clear colourless	Θ_{max} / °	68.851
Shape	plate	Measured Refl.	8670
Max Size / mm	0.12	Independent Refl.	2953
Mid Size / mm	0.10	Reflections Used	2764
Min Size / mm	0.01	R_{int}	0.0260
Temperature / K	100(2)	Parameters	218
Crystal System	triclinic	Restraints	0
Space Group	P-1	Largest Peak	0.309
a / Å	7.5548(3)	Deepest Hole	-0.238
b / Å	9.1645(4)	GooF	1.066
c / Å	12.6977(5)	*w*R_2 (all data)	0.1327
α / °	78.324(4)	*w*R_2	0.1300
β / °	80.633(4)	R_1 (all data)	0.0483
γ / °	73.082(4)	R_1	0.0461

7,16-dibutylbenzo[*a*]naphtho[1,2-*k*]tetraphene 60

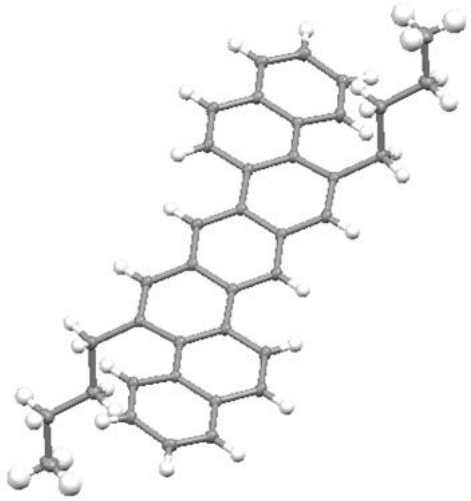


Single clear colourless prism-shaped crystals were recrystallised from a mixture of pentane and chloroform (2:1 respectively) by slow mixing. A suitable crystal (0.15 × 0.07 × 0.06 mm^3) was selected and the structure was solved using **general experimental 2**. The ShelXT (Sheldrick, 2008) structure solution program was used.

Formula	$C_{38}H_{34}$	γ / °	90
$D_{calc.}$ / g cm^{-3}	1.244	V / $Å^3$	2619.64(16)
μ / mm^{-1}	0.070	Z	4
Formula Weight	490.65	Z'	1
Colour	clear colourless	Θ_{min} / °	2.624
Shape	prism	Θ_{max} / °	32.045
Max Size / mm	0.15	Measured Refl.	16704
Mid Size / mm	0.07	Independent Refl.	5721
Min Size / mm	0.06	Reflections Used	5274
Temperature / K	100(2)	R_{int}	0.0308
Crystal System	orthorhombic	Parameters	345
Flack Parameter	-2.7(10)*	Restraints	1
Hooft Parameter	-3(2)*	Largest Peak	0.367
Space Group	$Pna2_1$	Deepest Hole	-0.251
a / Å	7.6217(3)	GooF	1.049
b / Å	22.1427(7)	wR_2 (all data)	0.1028
c / Å	15.5224(5)	wR_2	0.0997
α / °	90	R_1 (all data)	0.0437
β / °	90	R_1	0.0391

* Absolute structure not determined.

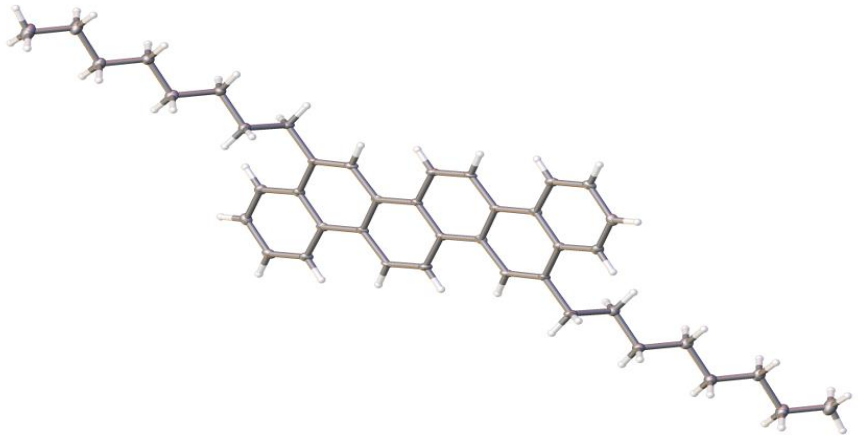
5,14-dibutylbenzo[*c*]naphtho[2,1-*k*]tetraphene 61



Single clear light yellow prism-shaped crystals were recrystallised from toluene by slow cooling (100 °C – room temperature over 2 h, and then overnight at room temperature). A suitable crystal (0.30 × 0.08 × 0.03 mm^3) was selected and the structure was solved using **general experimental 2**. The ShelXT (Sheldrick, 2015) structure solution program was used.

Formula	$C_{38}H_{34}$	V / $Å^3$	1301.61(7)
$D_{calc.}$ / g cm^{-3}	1.252	Z	2
μ / mm^{-1}	0.070	Z'	1
Formula Weight	490.65	Θ_{min} / °	2.955
Crystal colour	clear light yellow	Θ_{max} / °	30.506
Crystal shape	prism	Measured Refl.	22397
Max Size / mm	0.30	Independent Refl.	7840
Mid Size / mm	0.08	Reflections Used	6690
Min Size / mm	0.03	R_{int}	0.0203
Temperature / K	100(2)	Parameters	345
Crystal System	triclinic	Restraints	0
Space Group	P-1	Largest Peak	0.448
a / Å	9.1503(2)	Deepest Hole	-0.186
b / Å	10.4090(2)	GooF	1.028
c / Å	15.2451(5)	wR_2 (all data)	0.1310
α / °	107.806(3)	wR_2	0.1247
β / °	90.598(2)	R_1 (all data)	0.0546
γ / °	108.511(2)	R_1	0.0461

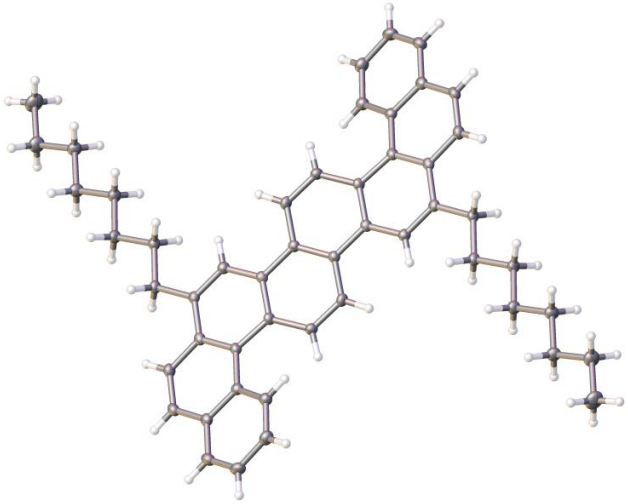
8,16-dioctylbenzo[*c*]picene 65



Single clear colourless plate-shaped crystals were recrystallised from toluene by slow cooling (100 °C – room temperature over 2 h, and then overnight at room temperature). A suitable crystal (0.220 × 0.180 × 0.020 mm^3) was selected and the structure was solved using **general experimental 2**. The ShelXT (Sheldrick, 2008) structure solution program was used.

Formula	$C_{42}H_{48}$	V / $Å^3$	1546.27(15)
$D_{calc.}$ / g cm^{-3}	1.187	Z	2
μ / mm^{-1}	0.066	Z'	1
Formula Weight	552.80	Θ_{min} / °	3.007
Crystal colour	clear colourless	Θ_{max} / °	25.026
Crystal shape	plate	Measured Refl.	13136
Max Size / mm	0.220	Independent Refl.	5279
Mid Size / mm	0.180	Reflections Used	3518
Min Size / mm	0.020	R_{int}	0.0453
Temperature / K	100(2)	Parameters	381
Crystal System	triclinic	Restraints	0
Space Group	P-1	Largest Peak	0.674
a / Å	4.8771(2)	Deepest Hole	-0.293
b / Å	14.6968(7)	GooF	1.088
c / Å	21.7866(15)	*w*R_2 (all data)	0.2702
α / °	83.278(5)	*w*R_2	0.2468
β / °	85.608(5)	R_1 (all data)	0.1344
γ / °	89.960(4)	R_1	0.0978

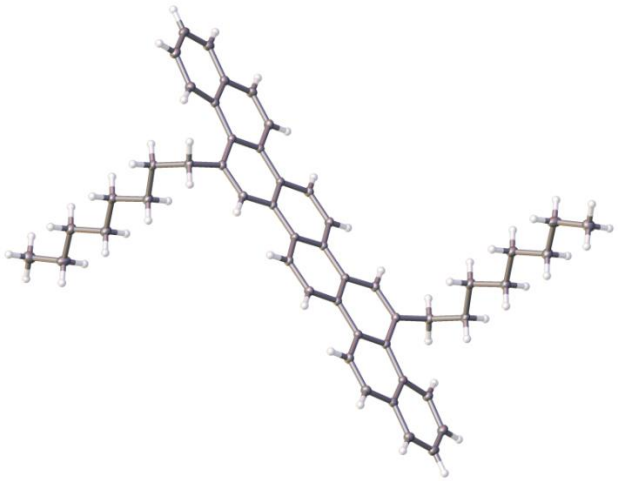
8,18-dioctylbenzo[*a*]naphtho[1,2-*m*]picene 66



Single clear colourless plate-shaped crystals were recrystallised from toluene by slow cooling (100 °C – room temperature over 2 h, and then overnight at room temperature). A suitable crystal (0.14 × 0.06 × 0.01 mm^3) was selected and the structure was solved using **general experimental 2**. The ShelXT (Sheldrick, 2008) structure solution program was used.

Formula	$C_{50}H_{52}$	V / Å^3	901.34(10)
$D_{calc.}$ / g cm^{-3}	1.203	Z	1
μ / mm^{-1}	0.067	Z'	0.5
Formula Weight	652.91	Θ_{min} / °	2.929
Crystal colour	clear colourless	Θ_{max} / °	28.699
Crystal shape	plate	Measured Refl.	12688
Max Size / mm	0.14	Independent Refl.	4647
Mid Size / mm	0.06	Reflections Used	3064
Min Size / mm	0.01	R_{int}	0.0461
Temperature / K	100(2)	Parameters	227
Crystal System	triclinic	Restraints	0
Space Group	P-1	Largest Peak	0.397
a / Å	7.6611(5)	Deepest Hole	-0.253
b/ Å	7.7652(5)	GooF	1.035
c / Å	15.5806(10)	wR_2 (all data)	0.1663
α / °	92.492(5)	wR_2	0.1457
β / °	93.004(5)	R_1 (all data)	0.1105
γ / °	102.756(5)	R_1	0.0643

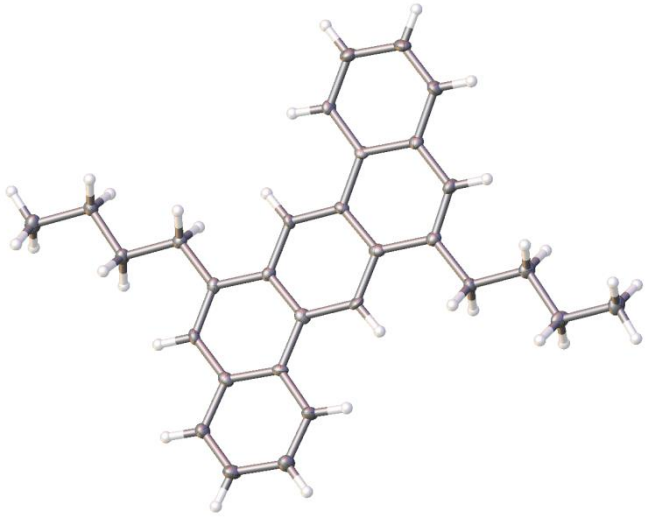
5,15-dioctylbenzo[*c*]naphtho[2,1-*m*]picene 67



Single clear colourless plate-shaped crystals were recrystallised from toluene by slow cooling (100 °C – room temperature over 2 h, and then overnight at room temperature). A suitable crystal (0.19 × 0.07 × 0.02 mm^3) and the structure was solved using **general experimental 2**. The ShelXT (Sheldrick, 2008) structure solution program was used.

Formula	$C_{50}H_{52}$	V / $Å^3$	1761.90(16)
$D_{calc.}$/ g cm^{-3}	1.231	Z	2
μ / mm^{-1}	0.069	Z'	0.5
Formula Weight	652.91	Θ_{min} / °	2.308
Crystal colour	clear colourless	Θ_{max} / °	32.279
Crystal shape	plate	Measured Refl.	21478
Max Size / mm	0.19	Independent Refl.	5913
Mid Size / mm	0.07	Reflections Used	4571
Min Size / mm	0.02	R_{int}	0.0284
Temperature / K	100(2)	Parameters	227
Crystal System	monoclinic	Restraints	0
Space Group	$P2_1/c$	Largest Peak	0.508
a / Å	18.6031(9)	Deepest Hole	-0.230
b / Å	5.4326(2)	GooF	1.031
c / Å	18.3801(10)	wR_2 (all data)	0.1385
α / °	90	wR_2	0.1271
β / °	108.466(6)	R_1 (all data)	0.0693
γ / °	90	R_1	0.0500

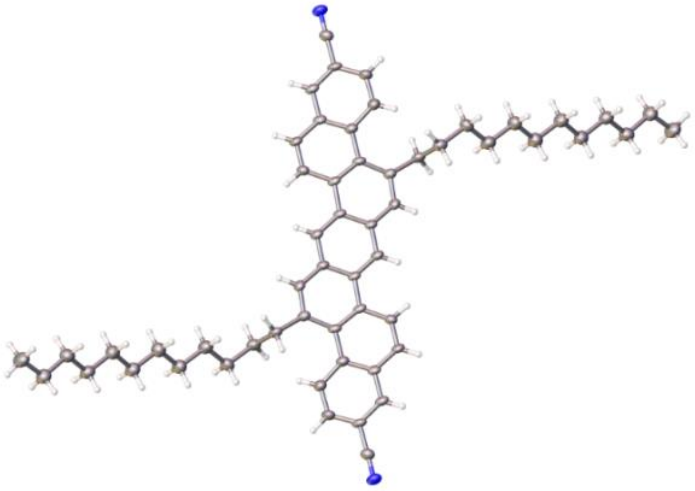
6,13-dibutylbenzo[*k*]tetraphene 90



Single clear colourless prism-shaped crystals of 6,13-dibutylbenzo[*k*]tetraphene **90** were recrystallised from toluene (3 °C overnight). A suitable crystal (0.06 × 0.04 × 0.04 mm^3) was selected and the structure was solved using **general experimental 2**. The ShelXT (Sheldrick, 2015) structure solution program was used.

Formula	$C_{30}H_{30}$	V / Å^3	4524.1(4)
$D_{calc.}$/ g cm^{-3}	1.147	Z	8
μ / mm^{-1}	0.064	Z'	1
Formula Weight	390.54	Θ_{min} / °	2.981
Crystal colour	clear colourless	Θ_{max} / °	28.700
Crystal shape	prism	Measured Refl.	28127
Max Size/mm	0.06	Independent Refl.	5815
Mid Size/mm	0.04	Reflections Used	3847
Min Size/mm	0.04	R_{int}	0.0847
Temperature / K	100(2)	Parameters	274
Crystal System	monoclinic	Restraints	0
Space Group	I2/a	Largest Peak	0.541
a / Å	14.8579(9)	Deepest Hole	-0.483
b / Å	12.4574(6)	GooF	1.058
c / Å	24.8403(11)	wR_2 (all data)	0.3241
α / °	90	wR_2	0.3005
β / °	100.266(5)	R_1 (all data)	0.1508
γ / °	90	R_1	0.1154

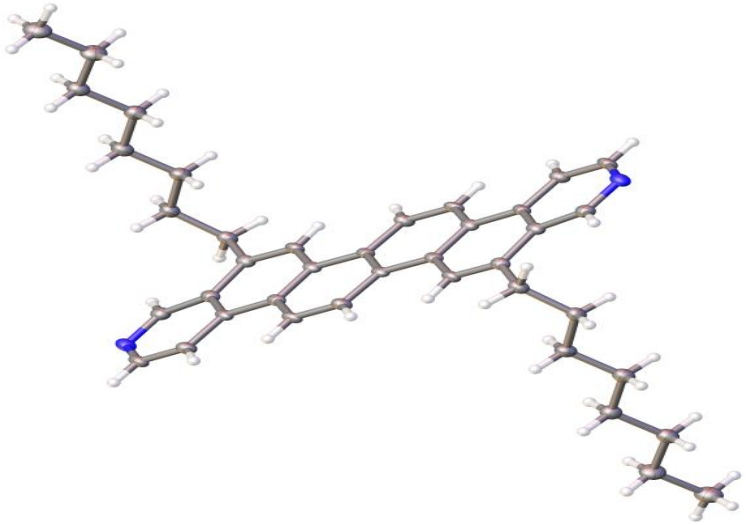
5,14-didodecylbenzo[*c*]naphtho[2,1-*k*]tetraphene-2,11-dicarbonitrile 99



Single clear yellow rod-shaped crystals were recrystallised from toluene by slow cooling (100 °C – room temperature over 2 h, and then overnight at room temperture). A suitable crystal (0.14 × 0.02 × 0.02 mm^3) was selected and the structure was solved using **general experimental 2**. The ShelXT (Sheldrick, 2015) structure solution program was used.

Formula	$C_{56}H_{64}N_2$	V / $Å^3$	1075.04(15)
$D_{calc.}$ / g cm^{-3}	1.182	Z	1
μ / mm^{-1}	0.067	Z'	0.5
Formula Weight	765.09	Θ_{min} / °	3.039
Crystal colour	clear yellow	Θ_{max} / °	26.368
Crystal shape	rod	Measured Refl.	11740
Max Size / mm	0.14	Independent Refl.	4343
Mid Size / mm	0.02	Reflections Used	2365
Min Size / mm	0.02	R_{int}	0.0701
Temperature / K	100(2)	Parameters	263
Crystal System	triclinic	Restraints	0
Space Group	P-1	Largest Peak	0.301
a / Å	4.7947(3)	Deepest Hole	-0.225
b / Å	12.5124(8)	GooF	1.037
c / Å	18.3946(18)	wR_2 (all data)	0.2397
α / °	79.188(7)	wR_2	0.2022
β / °	85.739(7)	R_1 (all data)	0.1682
γ / °	83.317(6)	R_1	0.0913

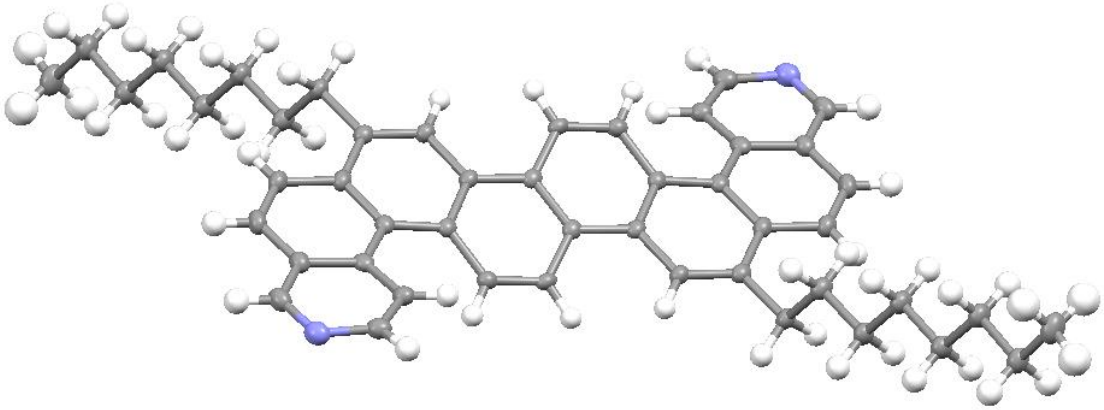
8,16-dioctylnaphtho[2,1-*f*:6,5-*f'*]diisoquinoline 101



Single clear pale yellow plate-shaped crystals were obtained by recrystallisation from NMP (240 °C – room temperature over 3 h). A suitable crystal (0.10 × 0.05 × 0.01 mm^3) was selected and the structure was solved using **general experimental 2**. The ShelXT (Sheldrick, 2015) structure solution program was used.

Formula	$C_{40}H_{46}N_2$	V / $Å^3$	1491.82(18)
$D_{calc.}$ / g cm^{-3}	1.235	Z	2
μ / mm^{-1}	0.071	Z'	0.5
Formula Weight	554.79	Θ_{min} / °	3.053
Crystal colour	clear pale yellow	Θ_{max} / °	28.699
Crystal shape	plate	Measured Refl.	9638
Max Size / mm	0.10	Independent Refl.	3825
Mid Size / mm	0.05	Reflections Used	2322
Min Size / mm	0.01	R_{int}	0.0466
Temperature / K	100(2)	Parameters	191
Crystal System	monoclinic	Restraints	0
Space Group	$P2_1/c$	Largest Peak	0.511
a / Å	20.1468(14)	Deepest Hole	-0.266
b / Å	5.1155(4)	GooF	1.043
c / Å	14.5697(9)	wR_2 (all data)	0.1919
α / °	90	wR_2	0.1664
β / °	96.535(6)	R_1 (all data)	0.1308
γ / °	90	R_1	0.0755

8,18-dioctylchryseno[1,2-*f*:7,8-*f*']diisoquinoline 106



Single clear colourless plate-shaped crystals were recrystallised from toluene by slow cooling (100 °C – room temperature over 2 h, then overnight at room temperature). A suitable crystal (0.15 × 0.02 × 0.003 mm^3) was selected and the structure was solved using **general experimental 2**. The ShelXT (Sheldrick, 2008) structure solution program was used.

Formula	$C_{48}H_{50}N_2$	V / $Å^3$	1778.36(9)
$D_{calc.}$/ g cm^{-3}	1.223	Z	2
μ / mm^{-1}	0.070	Z'	1
Formula Weight	654.90	Θ_{min} / °	2.960
Crystal colour	clear colourless	Θ_{max} / °	28.698
Crystal shape	plate	Measured Refl.	37340
Max Size / mm	0.15	Independent Refl.	9182
Mid Size / mm	0.02	Reflections Used	5744
Min Size / mm	0.003	R_{int}	0.0505
Temperature / K	100(2)	Parameters	453
Crystal System	triclinic	Restraints	0
Space Group	P-1	Largest Peak	0.327
a / Å	9.0369(3)	Deepest Hole	-0.242
b / Å	9.5664(3)	GooF	1.018
c / Å	20.6426(6)	wR_2 (all data)	0.1460
α / °	91.935(2)	wR_2	0.1262
β / °	90.822(2)	R_1 (all data)	0.1060
γ / °	94.263(2)	R_1	0.0573