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Highlights:

1. General strategies for the synthesis of QD@MOF composites
2. Consideration of the semiconductor behaviour of MOFs
3. Applications of QD@MOF composites, including photocatalysis, light-harvesting, sensing, imaging and gas storage.
4. Future outlook for QD@MOF composites

Synthesis and applications of metal-organic framework – quantum dot (QD@MOF) composites

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Abstract

The combination of the high surface areas, microporosity and tuneable compositions of metal-organic frameworks (MOFs) with the desirable photo-physical behaviour of semiconductor nanoparticles or quantum dots (QDs), allows the preparation of composite materials with enhanced properties for applications in photocatalysis, energy, gas-storage and sensing. These QD@MOF composites are an emergent class of materials and in this review we discuss current strategies for their synthesis, consider the semiconductor behaviour of MOFs themselves and present the applications of the various materials reported this far grouped by the nature of the QD component.

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1. Introduction

1.1. Quantum Dots

Semiconductor nanocrystals in the size range 2 to 10 nm are often referred to as Quantum Dots (**QDs**) and have received significant attention in the last two decades due to their uniquely tuneable and size-dependent electronic properties, making them of interest for but not limited to biological, analytical, medical and engineering applications.[1-4] These semiconductor materials are comprised of aggregates of hundreds to a few thousands of atoms composed largely of elements from groups 12-16 (i.e. CdSe, CdSe, ZnSe, ZnO, etc.), 13-15 (InP, InAs) or 14-16 (PbSe) of the periodic table, and due to their small size being comparable to the wavelength of the electron, quantum confinement effects are often observed. [5]

QDs offer some advantages compared with conventional chromophores, including wide absorption bands, narrow and symmetrical emission bands, low photobleaching, long lifetimes and high quantum yields.[6] The characteristic UV-Vis exciton peak of QDs is strongly related to the size of the particle, with smaller QDs displaying shorter wavelengths and consequently fluorescence emission is tuneable.[7, 8] This phenomenon is often affected by the number of surface defects (referred to as trapped surface states), essentially imperfections in the crystalline structure that can lead directly to QD fluorescence quenching.[8, 9] Constant efforts to reduce the number of trapped states and increase the fluorescence quantum yield (ϕ) of the QDs are thus under investigation. Among them, passivation with a second semiconductor layer with an appropriate band gap to yield core-shell (CS) type structures seems to be one of the most promising.[10, 11] In this configuration (known as type I) the band gap of the shell is sufficiently large that it spans both the conduction and valence bands of the core where the non-radiative pathways associated with the trapping of the electron or the hole are decreased, improving the fluorescence quantum yield of the system as well as enhancing the stability of the QD against photo-oxidation. To date, many synthetic procedures to prepare these QD-CS structures, including one-pot core-shell synthesis or growing the shell around the pre-synthesized core in a two-step methodology, have been reported.[12, 13] Another important factor for applications is the dispersibility and stability of QDs in the desired media, which is readily modulated by altering the nature of the surface ligands. Different organic ligands have been used to passivate QDs during their synthesis, including phosphines, carboxylic acids, amines and thiols.[9, 14-16] Ligand exchange, derivatization or encapsulation strategies can also be employed for further surface functionalization.[17] While ligand exchange often leads to a

loss of QD fluorescence due to the creation of trapped states during the exchange process,[18] it is a suitable alternative when the desired functional group cannot be incorporated onto the QD surface directly during synthesis. Often, ligands added during the synthesis remain on the QD surface even after several ligand exchange and washing processes, which could lead to undesired behaviour in the system. Derivatization of surface groups by facile organic transformations can endow the QDs with the appropriate functionality and reduce the amount of undesired ligands (or functional groups) on the QD surface; however, a high QD stability under the organic reaction conditions is required. On the other hand, encapsulation of QDs in several media (*e.g.* polymers or micelles) could enhance the physical properties and biocompatibility of the semiconductor. It has been shown that encapsulation of QDs in phospholipid micelles for example, endows the resulting composite with biocompatibility in addition to enhancing colloidal stability, which can be subsequently employed for *in vivo* and *in vitro* studies.[19] In the same context, coating QDs with an inorganic silica shell to yield QD@SiO₂ systems, some researchers have also demonstrated these hybrids to be biocompatible, have low-toxicity and high water-dispersibility.[20] Organogelators also offer stability and good spatial distribution for metallic and semiconductor nanoparticles. Thus, QD-organogel systems have also been reported,[21] in which a symbiotic effect was observed: on one hand the critical concentration needed to form a stable organogel is reduced in the presence of the QD, and on the other the fluorescence quantum yield of the QD is enhanced when embedded in the organogel. Coating of QDs with polymers has also been widely studied in the literature and some excellent reviews have appeared during the last few years.[22] Such polymers provide long-term stability and also endow the system with additional functional groups which can be used for further transformations. In order to endow the QD with multifunctional behaviour, efforts to encapsulate these semiconductor nanoparticles in designable and tuneable hybrid matrices need to be explored.

1.2. Metal-organic frameworks

Metal-organic frameworks (MOFs), sometimes referred to as porous coordination polymers (PCPs), are a class of crystalline microporous materials formed from transition metal ions or clusters and polytopic organic linkers which assemble into topologically diverse open network type structures.[23-25] These high surface area materials have been widely employed in numerous applications including gas storage,[26] heterogeneous catalysis,[27] molecular separation [28], sensing,[29] and for therapeutics and diagnostics in biomedicine.[30, 31] Compared to wholly inorganic porous materials, MOFs offer an enormous variety of chemical composition allowing both their structure and functionality to be fine-tuned through judicious choice of building blocks. Further, their hybrid composition endows the frameworks with a

degree of flexibility where typically linker-based motions can result in dynamic guest-responsive behaviours. [32, 33]

While the discovery of new MOFs continues apace and detailed studies relating to their often unique behaviours [34] and physical properties are reported,[35] recent research efforts are becoming increasingly focussed on the growth and processing of MOFs into application-specific configurations [36], including thin films,[37] supported membranes [38, 39] and capsules.[40, 41] MOF-based composite materials are also under increasing investigation, where the combination of MOFs with other components including ceramics, biopolymers, nanoparticles and proteins are leading to the development of new functional materials with enhanced properties.[42]

In this review we focus on current progress in the preparation of QD@MOF composites, where the size-dependent electronic and optical properties of the QDs can be stabilised when encapsulated in a MOF matrix and the resulting composites exploited for selective sensing, and as scaffolds to perform photocatalysis, including water-splitting for hydrogen evolution. Additionally, the porosity of MOFs allows multifunctional systems to be prepared where the QD@MOF materials have potential to deliver cargo molecules previously encapsulated in the framework, while the composite is monitored by fluorescent techniques. For convenience we refer to all quantum dot – metal organic framework composites throughout as “QD@MOF”, although it is important to note that this does not necessarily imply a core-shell structure.

2. General synthetic methods and characterisation of QD@MOF composites

There are two well established routes that have been exploited to immobilize functional molecules or nanoscale objects within metal-organic frameworks, known as “ship in the bottle” and “bottle around the ship” methods (figure 1a,b), although they have been previously explored for other guests and matrices.[43-48]

The “ship in a bottle” method (figure 1a) consists of the immobilization of small molecules or nanoparticle precursors small enough to penetrate through the pore windows of the MOF, which by further treatment in-situ results in their transformation to the desired functional structure. Thus, the composite encloses material bigger than the pores of the framework, which remains retained inside the lattice. Some aspects of this methodology must be considered: on the one hand, it requires a sufficient level of encapsulated species, which need to be compatible with the MOF structure, and on the other the framework needs to be stable under the conditions to form the functional material or particle. It is also important to consider the possible formation of the nanoparticles on the external surface of the MOFs. Moreover, the precise control over the internal location, size and shape of the guest within the

framework structure is challenging, which could be a drawback to take into account in applications where the shape of the nanoparticle or QD is particularly important, for instance when using gold nanoparticles for SERS[49] or biomedical applications.[50] By using this methodology, several guests, such as metallic nanoparticles,[51] nanoclusters,[52] or active anticancer drugs,[53] have been successfully encapsulated inside MOFs. In the case of QD@MOF composites, the QD precursors need to be loaded into the framework, and typically treated by heating, hydrogenation or reduction to transform them into the corresponding nanoparticles. This typically involves the solution or vapour infiltration of the QD precursors into activated MOF crystals followed by a suitable hydrothermal treatment. It should be noted that bottom-up strategies to prepare QDs often rely on relatively harsh reaction conditions which can lead to local network degradation as reported for the deposition of metallic NPs into MOF matrices using this method.[54] For QDs, the MOF matrix needs to be particularly stable under high temperatures (in some cases heat treatments can exceed 300 °C) and/or redox environments; if framework-forming metal ions are susceptible to changes in oxidation state this could lead to network degradation. As previously highlighted, further consideration of this synthetic route to access MOF@QD composites, regards the location and distribution of the QDs within the pores of the framework which could potentially decrease the surface area of the MOF matrix strongly impacting on those applications where porosity is important.

The “bottle around the ship” method (figure 1b) is also known as the template synthesis method and usually occurs through an encapsulation process as previously reported for other materials.[46, 47] Firstly, the functional molecule or nanoparticle are usually stabilized by capping agents or surfactants, which are then added into a solution containing the MOF precursors. In the case of QD@MOF composites, a pre-formed semiconductor nanoparticle stabilized by an appropriate methodology (*viz.* ligand exchange, addition of surfactants) is immersed in a solution containing the MOF building blocks and the framework assembles around the QD.[55-57] By using this methodology, the QD does not occupy the pore space of the framework, but instead becomes incarcerated within the MOF matrix. Using this method, problems associated with the formation of nanoparticles on the external surface of the MOF are reduced, and the shape and size of the entrapped particles can be optimised for applications since they are pre-formed prior to framework assembly.

An alternative strategy related to the ‘bottle around the ship’ method for the incorporation of QDs into MOF matrices was presented by Buso *et al*, who report an elegant way to simultaneously achieve MOF positioning and functionalization with a range of nanoparticles, including multi-shelled CdSe/CdS/ZnS QDs.[58] α -hopeite microparticles (a poly-hydrate zinc phosphate based mineral) formed in-situ during the initial stages of framework

formation, have been found to act as efficient heterogeneous nucleation seeds for MOF-5 [MOF-5 = $\text{Zn}_4\text{O}(\text{CO}_2)_6$ clusters; 1,4-benzenedicarboxylic acid (bdc) linkers]. If the α -hopeite particles are preformed however, they can be redispersed in a range of solvents or deposited directly onto solid substrates to increase crystal growth rates or spatially localise MOF growth, respectively. The ability to decorate the α -hopeite particles with metallic and semiconductor nanoparticles further increases the power of the method enabling the controlled deposition of functional MOF-based composites. The precise positioning of MOFs onto different substrates is crucial in order to fully explore their capabilities and to begin to integrate functional MOFs and their composites into devices and this provides a step forward in this direction.[59]

Another approach to prepare QD@MOF composites that is not yet so well explored is the photochemical deposition of the semiconductor nanoparticles onto the framework surface. (Figure 1c) This procedure consists of the in-situ formation and deposition of the semiconductor nanoparticle into the surface of the support assisted by light. In the case of QD@MOF composites, the photoreduction of the metallic precursors exhibiting a suitable redox potential causes formation of the nanoparticles on the surface of the MOF.[60] The surface modification of MOFs with QDs can also be carried out by direct binding using a suitable linking group.[61] (Figure 1d) Following synthesis of the QD, its surface ligands are successively exchanged with a suitable capping group that allows direct interaction with the surface of a pre-formed MOF particle either by coordinative interactions with the metal ions that constitute the framework or through a more general physisorptive process via non-specific interactions. The main difference between this and the three previous strategies is that both materials in the resulting composite are pre-synthesized prior to their (co)-assembly, and while this should afford a greater degree of control over the size and morphology of both components any advantageous effects resulting from the porosity of the MOF (*e.g.* size-selectivity) may not be felt by the extrinsic QD.

In addition to the set of techniques usually required for the characterization of MOFs, QD@MOF composites require an optical characterization usually provided by UV-Vis and photoluminescence spectroscopy, yielding information about the size, polydispersity and fluorescent quantum yield of the QD when associated with a MOF matrix. High-resolution transmission electron microscopy (HRTEM) is one of the methods generally employed to further determine the size of the semiconductor nanoparticle. However, in order to make optimal use of this technique, a good contrast between the QD and the background is required. Additionally, the high energy provided by the electron beam can cause some disruption to many MOFs, as previously reported for MOF-5 and HKUST-1 among

others.[52, 54, 62] However, QDs often have a low contrast compared with metallic nanoparticles; thus, to provide an average of the QD size can be challenging from microscopy images alone. Nevertheless, in some cases it is possible to circumvent this problem and estimate the size of the QD from the main peak of the absorption band (exciton peak), as reported by Peng *et al.* in the case of CdSe QDs.[7] The presence of the QD inside the MOF lattice or pores can be further corroborated by energy-dispersive X-ray spectroscopy (EDX or EDS). This technique provides information about the elemental composition of the sample, since the source of X-ray excitation produce an X-ray emission spectrum characteristic of each atom. A variant of this technique is X-ray photoelectron spectroscopy (XPS), which measures the empirical formula, chemical and electronic states of the material.

Figure 1. Main methodologies used to prepare QD@MOF composites. A- Ship in bottle; B- Bottle around ship; C- Photochemical deposition; D- Direct surface functionalization.

Table 1 A summary of reported QD@MOF composites, indicating the type of QD and MOF employed, their demonstrated application where appropriate and the methodology used for their preparation.

MOF	QD	Application	Method	Ref.
Zn(bix) spheres	CdSe/ZnS	-	Bottle around ship	[63]
Amorphous CNP (Ga³⁺/AMP)	CdSe/ZnS	-	Bottle around ship	[64]
MIL-101(Al)-NH₂	CdSe	-	Ship in a bottle	[65]
MOF-5	CdSe/CdS/Cd _{0.5} Zn _{0.5} S/ZnS	Size-selective fluorescent sensing	Bottle around ship	[66]
MOF-5	CdSe/CdS/ZnS	Size-selective fluorescent sensing	Bottle around ship	[58]
EuOF	CdSe	Sensing	Bottle around ship	[56]
ZIF-8	CdTe	Size-selective fluorescent sensing	Bottle around ship	[55]
Zn₂camph₂bipy	CdTe	Enantioselective sensing	Bottle around ship	[67]
[(CdLBr)·H₂O]_n	CdS	Enantioselective sensing	Self-template	[68]
MIL-101	CdS	Hydrogen evolution	Ship in a bottle	[69]
UiO-66-NH₂	CdS	Selective photocatalysis	Photodeposition	[70]
UiO-66	CdS	Hydrogen evolution	Photodeposition	[71]
ZAVCl	CdS	Water splitting	Ship in a bottle	[72]
MIL-101(Fe)	CdS	Photocatalysis	Ship in a bottle	[73]
F-MOF, DA-MOF	CdSe/ZnS	Light harvesting	Direct functionalization	[61]
MOF-5	ZnO behaviour	-	-	[74]
MOF-5	ZnO behaviour	Photocatalysis	-	[75]
MOF-5	ZnO behaviour	MOF degradation	-	[76]

IRMOF series	ZnO behaviour	Photocatalysis	-	[77]
MOF-5	ZnO	Catalysis	Ship in a bottle	[78]
ZIF-8	ZnO	Photocatalysis	Self-template	[79]
MOF-5	ZnO	Sensing	Direct mixture	[80]
ZIF-8	ZnO	Size-selective electrochemical sensing	Self-template	[81]
ZIF-8	SnO ₂	Supercapacitor	Ship in a bottle	[82]
MOF-5	TiO ₂	-	Ship in a bottle	[83]
HKUST-1	TiO ₂	Photocatalysis	Bottle around ship	[84]
ZIF-8	GaN	-	Ship in a bottle	[85]
UMCM-1	C-dots	Sensing	Bottle around ship	[86]
ZIF-8	C-dots	Sensing	Bottle around ship	[57]
ZIF-8	C-dots	Drug delivery – fluorescence imaging	Bottle around ship	[87]
ZIF-8	Graphene QDs	-	Bottle around ship	[88]
PZn	Coordination polymers	Cellular probes	Direct synthesis	[89]

3. QD@MOF composites and their applications

A priori, it might be expected that a composite material containing embedded photoactive particles such as QDs will be used mainly in light-dependent applications such as fluorescence sensing,[3, 90] photocatalysis,[91-93] imaging[1, 4] drug release[94] and other areas where light-induced mechanisms can be exploited. However, QDs have also proven effective as pseudocapacitors or supports for other molecules.[95, 96] In this section we will discuss the preparation and current state-of-the-art in the applications of QD@MOF composites, which also provide an interesting platform to explore synergistic and/or symbiotic effects arising from the combination of the quantum confinement of semiconductor nanoparticles and the vast diversity of MOF compositions available, which can additionally confer higher stability to the nanoparticle. In this review we have grouped the reported QD@MOF composites according to the nature of the QD to facilitate presentation and discussion.

3.1 Oxide-based QD@MOF composites

Before we consider the preparation and applications of QD@MOF composites incorporating metal oxide particles using the strategies outlined in section 2, it is of value to first discuss the semiconductor properties of MOFs themselves, in particular those that contain oxide-like clusters or secondary building units (SBUs) as part of the framework.

In 2004, Zecchina and co-workers[74] described the electronic and vibrational properties of MOF-5 (sometimes referred to as IRMOF-1) which is assembled from $\text{Zn}_4\text{O}(\text{CO}_2)_6$ metal clusters (SBUs) linearly connected by 1,4-benzenedicarboxylic acid linkers into a cubic-like network. In the UV-vis diffuse reflectance spectra (DRS) of MOF-5, two main features were observed: a maximum at 290 nm that is assigned to the organic linker, and an edge at 350 nm due to the Zn_4O_{13} SBU clusters. (Figure 2a,b) This is attributed to an $\text{O}^{2-}\text{Zn}^{2+} \rightarrow \text{O}^-\text{Zn}^+$ ligand-metal charge transfer (LMCT) which is blue shifted with respect to an analogous LMCT band in ZnO due to quantum confinement effects. The authors suggest that this is indicative that the SBU clusters which form the framework behave as ZnO QDs, and MOF-5 also exhibits an intense photoluminescence at 525 nm ($\lambda_{\text{ex}} = 350$ nm), which is ascribed to an energy transfer from the photon-trapping organic linker to the Zn_4O_{13} SBU.

Figure 2. Reported semiconductor behaviour of MOF-5 and its analogues. (a) UV-vis and (b) PL spectra (excitation, grey; emission, black) of ZnO (dashed), free linker (dotted) and MOF-5 (solid). Reproduced with permission from [74]. (c) Band gap for an isorecticular series of frameworks based on the MOF-5 topology with different linkers. Reproduced with

permission from [76] (d) Photograph showing solid TiO_2 , MOF-5 and SiO_2 in an aqueous solution of methyl viologen (a-c in image) before (top) and after (bottom) irradiation at 525 W for 10 mins. Reproduced with permission from [96].

Other researchers have followed up on the semiconductor-like behaviour of MOF-5 using a range of spectroscopic methods and evaluated its potential in photocatalytic applications. Gascon *et al.* [77] employed *operando* IR spectroscopy to reveal the band gap can be readily modulated by changing the nature of the organic linker in an isorecticular series of frameworks based on MOF-5. (Figure 2c) While little to no effect on the band gap was observed regarding the size or substitution pattern of the linker, the resonance effect of the ligands plays an important role in this context, where systems with highly π -delocalized electrons show smaller band gaps. These frameworks were employed as photocatalysts for the gas phase photooxidation of propene. In this regard the IRMOF formed by a 2,6-naphthalenedicarboxylic acid linker was the most active, displaying a higher activity than ZnO and a different product distribution. Alvaro *et al.* used laser flash photolysis to investigate the semiconductor behaviour of MOF-5, which they propose arises due to transfer of a photoejected electron from the terephthalate linkers to the SBU cluster resulting in charge separation that decays on the microsecond time scale.[97] The resulting electrons and holes were demonstrated by photoinduced electron transfers under visible light irradiation from the MOF-donor to methyl viologen (figure 2d) and from the amine *N,N,N',N'*-tetramethyl-*p*-phenylenediamine to the MOF-acceptor, respectively, generating blue radicals in each case. MOF-5 was further employed for the photocatalytic degradation of phenol in aqueous solution with comparable activity to commercial P-25 TiO_2 and higher than that of ZnO .

A detailed study on the photoinduced one-electron oxidation of organics by MOF-5 was also conducted by Tachikawa *et al.*, [98] revealing the framework has a higher oxidation reaction efficiency than P-25 TiO_2 due to low hole transfer kinetics, increased lifetimes for the substrate radical cations and larger intramolecular reorganisation energies for the charge transfer system. It was postulated that the flexibility of the MOF structure and the accessibility of solvent into the porous network have an important role to play on these factors. It was also found that the presence of water affects the photoinduced reaction processes as the terephthalate linkers dissociate from the partially hydrolysed framework, indicating that the known water sensitivity of this material may limit its use.

MOF-5 has also been reported to act as a photoactive matrix for the UV-induced reduction of silver in both bulk samples and within single crystals of the framework.[75] Following adsorption of ethanolic solutions of silver nitrate into the MOF pores and exposure to UV irradiation, the Ag(I) ions are reduced to metallic silver with full retention of the framework

structure. By carrying out the experiment within a single crystal mounted on a computer controlled piezoelectric stage, a laser pulse of 780 nm could be used to photocatalytically reduce the silver ions in a highly localised manner permitting the direct writing of metallic silver patterns composed of silver dots within the single crystals. Such fine spatial control over the process allowed two QR codes to be written within the crystal separated by 10 μm as well as the deposition of high density circuit board-type pattern of 45 x 45 μm^2 suggesting the resulting metallodielectric composites could find application in microelectronics.

While the nature of the reported semiconductor behaviour of MOF-5 is undoubtedly complex, the above would appear to indicate that MOF-5 has significant potential in a diversity of photochemical applications; however, we suggest this assertion should be treated with a degree of caution at the present time. This is primarily because the purity of the MOF-5 framework is highly dependent on the synthesis route, where reduced surface areas are often reported arising from either framework interpenetration or the incorporation of organic and/or zinc species within the pore system. [99, 100] The latter issue is particularly significant since these species have the potential to manifest semiconductor-like behaviours in photoluminescence spectra which could then be attributed (rightly or wrongly) to energy or charge transfer processes in the framework itself.

Interestingly, Allendorf and co-workers have employed PL spectroscopy as a method to establish MOF-5 purity, particularly the incorporation of nanoscale ZnO impurities during synthesis.[76, 99] In this work, MOF-5 was prepared by several standard synthetic routes, and the PL spectra of the products recorded. MOF-5 obtained by direct-mixing precipitation methods possess very similar PL spectra to as-prepared 2 – 4 nm ZnO QDs, with only small blue-shifts observed from 535 nm ($\lambda_{\text{ex}} = 365 \text{ nm}$) (ZnO) to 522 nm ($\lambda_{\text{ex}} = 338 \text{ nm}$) (MOF-5) which are attributed to the slightly different particle sizes (quantum confinement effects) in the two samples. When the synthesis was carried out using solvothermal methodologies, the resulting high quality MOF-5 crystals displayed a single fluorescence emission peak at 397 nm ($\lambda_{\text{ex}} = 345 \text{ nm}$), very different from that prepared by direct precipitation. This emission is very similar to the terephthalic acid linker in dilute solutions of DMSO, indicating that the solvothermal MOF-5 possesses ligand-centred emission with no intermolecular or charge-transfer (LMCT) interactions. These results indicate that MOF-5 prepared by solvothermal methods yields a higher purity phase with respect to ZnO contaminants and the PL data is in agreement with the ligand-centred emission found for an analogous cubic MOF containing stilbenedicarboxylate linkers.[101]

Finally, fluorescence spectroscopy was also used to monitor MOF-5 degradation by water: after exposure of MOF-5 (solvothermal route) to moisture an intense blue-green emission

centred at 440 nm appears, indicating the decomposition of MOF-5 to a previously reported non-porous phase. [102, 103] This appears to be a significant observation, since appreciable luminescence is observed from decomposed MOF-5 that is otherwise phase pure by PXRD confirming the sensitivity of the method. In addition to providing a simple and sensitive means to assess overall MOF purity and degree of decomposition, this work highlights the vital need to ensure that the highest purity materials are employed when studying MOF photophysical properties in order to fully understand the observations.

The first report of loading MOFs with semiconductor metal oxide nanoparticles was by Fischer and co-workers in 2008, who prepared ZnO@MOF-5 composites by a ‘ship in the bottle’ method.[78] Using a preformed MOF-5 matrix, diethyl-Zn was adsorbed into the framework in the gas phase followed by exposure to either moist air under ambient conditions or dry oxygen to effect hydrolysis or oxidation, respectively, of the adsorbed precursor to yield the target ZnO@MOF-5 composite after annealing at 250 °C. Depending on synthesis conditions, ZnO loadings from 17.5 % to 35 % into the MOF matrix were obtained as calculated by elemental analysis, with particle sizes of ~ 4 nm as estimated from the PXRD data using the Scherrer equation and UV absorption measurements. This reveals that the ZnO QDs must occupy several cavities of MOF-5 resulting in some structural defects in the framework (Figure 3a), although some of the composites prepared using dry O₂ maintain very high surface areas in spite of this. TEM images of the composite compared to MOF-5 revealed a different contrast (figure 3b), but this was not sufficient against the matrix to permit unambiguous visualisation of loading illustrating the wider difficulty for QD@MOF composite materials. Isotopic labelling studies with ¹⁷O-enriched water indicated there was no exchange between the linker carboxylate O’s or the μ^4 -bridging oxide at the centre of the SBU cluster with the nascent ZnO species, precluding the possibility of chemical interactions of intermediate species with the MOF-5 matrix.

The ZnO@MOF-5 composite was further loaded with [CpCu(PMe₃)] yielding a Cu/ZnO@MOF-5 system following in-situ reduction of the Cu precursor under H₂ at 220 °C. Despite the rather harsh synthesis conditions, the ternary composite maintained the MOF-5 structure with a surface area of 820 m²·g⁻¹. This composite was successfully employed as a catalyst in the synthesis of methanol from synthesis gas (1atm/220°C) reaching a stable activity of 70 $\mu\text{mol}_{\text{MeOH}}\cdot\text{g}^{-1}\cdot\text{hr}^{-1}$ after an initial higher activity of 212 $\mu\text{mol}_{\text{MeOH}}\cdot\text{g}^{-1}\cdot\text{hr}^{-1}$. While this peak activity is $\sim 60\%$ of the productivity of an industrial reference catalyst, these materials were unstable after several hours under the selected conditions, causing collapse of the MOF-5 framework.

Figure 3. (a) Schematic representation of the embedding of a ZnO QD into a MOF-5 matrix and (b) TEM images of bare MOF-5 and the ZnO@MOF-5 composite. Reproduced with permission from [78].

Lv and co-workers have employed ZnO@MOF-5 composites as a fluorescent sensing system for anionic contaminants.[80] (Figure 4a) In this work, the composite sensing platform was prepared from a physical mixture of MOF-5 and ZnO QDs. Colloidal particles of MOF-5 with a zeta-potential of -6 mV were combined with positively charged ZnO QDs capped with 3-aminopropyl trimetoxysilane (APTMS), forming a flower-like composite as revealed by SEM. It was found that the MOF-5 could effectively quench the APTMS-ZnO QD fluorescence emission band at 540 nm by up to 70% through an electron-transfer process resulting from the proximity of the aggregated components due to electrostatic interactions. The addition of aqueous inorganic phosphate results in the breakdown of the MOF-5 framework through thermodynamically favourable Zn-phosphate formation and the subsequent recovery of the ZnO QD fluorescence as these are released into solution (Figure 4b). This QD-MOF system shows high selectivity and sensitivity in the presence of a range of anions and metal ions, with a detection limit for phosphate anions of $0.05\text{ }\mu\text{M}$. In addition, the determination of phosphate in tap water was successfully demonstrated. However, the necessary destruction of the composite in order to detect phosphate means the system is not recyclable.

Figure 4. (a) Schematic representation of phosphate detection using an aggregated composite of ZnO QDs and MOF-5. (b) Recovery of ZnO fluorescence with increasing amounts of phosphate added to the ZnO@MOF-5 composite dispersion. The inset shows the composite dispersion (1), the breakup of the composite after phosphate is added (2) and the composite under UV irradiation (3). Reproduced with permission from [80].

The direct transformation of metal oxides to MOFs is receiving increased attention for the facile preparation of mesostructured MOFs,[104] supported MOF membranes [38] and functional core-shell composites.[105] This typically involves the use of a metal oxide as the sole metal source which is reacted in the presence of the required linker to form the framework which typically retains the shape of the starting oxide, namely a self-templating type process. Zhan *et al.* have employed this strategy to prepare ZnO@ZIF-8 core-shell structures (where ZIF-8 is formed by Zn metal ions and 2-methylimidazole linkers) that display a size-selective photoelectrochemical response to hole scavengers.[81] Preformed ZnO nanorods were reacted with an excess of the 2-methylimidazole linker to form ZnO@ZIF-8 core-shell structures, resulting from a diffusion limited interfacial reaction between dissolved Zn^{2+} ions from the sacrificial ZnO template and the framework-forming imidazolate species. The self-templating strategy was extended to prepare ZnO@ZIF-8 nanorod and nanotube arrays supported on a FTO substrate which were subsequently employed as a photoelectrochemical sensor (Figure 5). Reductive ascorbic acid (AA) and H_2O_2 were employed as hole scavengers for the ZnO core when irradiated with light ($\lambda < 380$

nm). H_2O_2 is small compared to the aperture size of the ZIF-8 shell and can easily diffuse through where it is oxidised by the photogenerated holes on the surface of the ZnO nanorods leading to an increase in the photocurrent response of the composite array. AA on the other hand is significantly larger and does not lead to an enhancement in response due to size exclusion by the shell and AA further blocks access to water molecules that contribute to the blank response, which accounts for the slight reduction in observed photocurrent. The photocurrent response of the ZnO@ZIF-8 nanorod array is linear with respect to the concentration of the hole scavengers and thus has potential as a PEC-based sensor.

Figure 5. Schematic of a PEC sensor based on an array of ZnO@ZIF-8 nanorods. The right side of the figure shows a typical TEM image of a single nanorod and the photocurrent response curves to hydrogen peroxide and ascorbic acid (AA). Reproduced with permission from [81].

A reverse methodology to obtain QD@MOF composites by the formation of the metal oxide from MOFs has also been explored. Wee *et al* report the spontaneous room temperature transformation of ZIF-8 into ZnO induced by exposure to silver nitrate to yield a ZIF-8 matrix embedded with ZnO nanorods.[79] (Figure 6) The Langmuir surface area of the starting ZIF-8 nanocrystals was almost completely retained, reducing from $1913 \text{ m}^2\text{g}^{-1}$ (ZIF-8) to $1751 \text{ m}^2\text{g}^{-1}$ for the ZnO@ZIF-8 composite. Bright-field transmission electron microscopy (BFTEM) and high-resolution TEM reveal that the ZnO nanorods (*ca.* $100 \text{ nm} \times 10 \text{ nm}$) have a Wurtzite structure and are concentrated around the edges of the ZIF-8 particles (Figure 6a,b). It is proposed that reactions of ZnO formation on the surface of ZIF-8 result from Ag^+ ions catalytically breaking coordinative bonds in the matrix to generate a hydroxyl rich environment, followed by segregation, dehydration and condensation of the resulting Zn-hydroxyl species. In order to further demonstrate the practical utility of the transformation for film formation, ZIF-8 was coated onto carbon paper and subsequently transformed with silver nitrate solution.

Figure 6. (a) Bright-field TEM and (b) HRTEM of the ZnO@ZIF-8 composite prepared by addition of silver nitrate to the framework (the inset shows the FT of the ZnO nanorods). (c) Photocatalytic degradation of methylene blue by the composite compared with its components and TiO₂. (d) Photocatalytic recyclability of the composite. Reproduced with permission from [79].

The composite showed enhanced absorption in the visible region compared to ZIF-8, which is attributed to the charge-transfer from the valence to the conduction band of the ZnO nanorods embedded within the ZIF-8 matrix. Using a Tauc plot, the semiconductor band gap in the composite was calculated as 3.16 eV, compared to 3.28 eV for ZnO. The photocatalytic activity of the composite was evaluated for the degradation of methylene blue, giving rise to a comparable photodegradation yield to that of commercial Degussa P25 TiO₂ (78% vs 84 % of photodegradation under UV irradiation for 3 h, respectively) and the composite was reused without loss of activity or structural integrity for up to 3 cycles. (Figure 6c, d).

Supercapacitors are energy storage systems with some advantages with respect to (rechargeable) batteries, such as faster charge transfer and superior rechargeability.[106] Among them, double-layer capacitors store energy electrostatically, pseudo-capacitors store energy electrochemically, while hybrid capacitors combine both storage systems. Pseudo-capacitors usually employ metal oxides as electrodes, including SnO₂ QDs due to their desirable optical and electrical properties, low cost and chemical stability.[107] While a very limited number of MOFs have been explored as supercapacitor electrodes,[108, 109] it is expected that high surface area MOF-based composite materials could exhibit superior performance. In this context, Tang and co-workers [82] reported the preparation of SnO₂@ZIF-8 composites through an in-situ epoxide precipitation method by impregnation of ZIF-8 with the SnO₂ precursors. HRTEM images appear to reveal that 3-5 nm spherical SnO₂

particles are uniformly dispersed with the framework, although their location is not unambiguous from these data. The exceptional chemical stability of ZIF-8 under alkaline conditions led to the testing of the composite as an electrochemical capacitor using 6M KOH as the electrolyte. The specific capacitance of $\text{SnO}_2@\text{ZIF-8}$ was $931 \text{ F}\cdot\text{g}^{-1}$ at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$, which was four times higher than SnO_2 QDs alone and an order of magnitude higher than ZIF-8. (Figure 7) The improved pseudocapacitive performance of the composite is proposed to arise from the synergistic electrical behaviour of high surface area ZIF-8 and well dispersed SnO_2 QDs, which also permits good cycling stability over 500 cycles.

Figure 7. Specific capacitance as a function of scan rate for $\text{SnO}_2@\text{ZIF-8}$ composites

compared to the individual components. Reproduced with permission from [82].

Titanium dioxide (TiO_2 , titania) is a very well-known and widely used photocatalyst due to its cheap cost, high stability, easy synthetic procedures, non-toxic nature and great photoefficiency under UV light irradiation. The immobilisation of nanoscale TiO_2 in different matrices, such as polymers, zeolites or silica has been reported to increase its photocatalytic behaviour, [110] and it is expected that the tuneable functionality and high surface areas of MOFs could add additional value. Employing a similar gas phase loading strategy for $\text{ZnO}@\text{MOF-5}$, [78] Fischer *et al.* report the preparation of $\text{TiO}_2@\text{MOF-5}$ composites. [83] By carefully controlling the loading of the $\text{Ti}(\text{O}^i\text{Pr})_4$ precursor within the framework, titania:MOF ratios from 0.7:1 to 2.4:1 could be achieved. High thermal and redox stability of the host MOF-5 was required for the conversion (250°C , 48 h), which was followed by IR and ^{13}C -MAS-NMR spectroscopy. PXRD confirmed framework stability, and the intensity inversion of reflections at $2\theta = 6.9^\circ$ and 9.7° were attributed to the inclusion of titania nanoparticles inside the pores of the MOF. Although direct observation of TiO_2 nanoparticles was not possible due to the lack of contrast with the MOF, TEM and EDX show

homogeneous material without TiO₂ aggregates on the external surface of the framework; and XPS clearly confirms the presence of the semiconductor nanoparticles in the composite. Room temperature UV-vis of samples containing a 1:1 ratio of TiO₂:MOF-5 reveal onset of absorption is red-shifted compared to MOF-5 and below the absorption edge of bulk titania, and further red shifts occur with increased annealing due to sintering. The PL spectrum of the annealed composite (350 °C, 24 h) at $\lambda_{\text{exc}} = 365$ nm shows two peaks at 417 nm and 435 nm, corresponding to TiO₂ nanoparticles, while the emission of the bare MOF-5 at 525 nm was not observed, indicating a possible energy transfer from the Zn₄O₁₃ clusters of MOF-5 (acting as QDs, as described above) to the titania nanoparticles. Although these authors did not explore the photocatalytic applications of TiO₂@MOF-5, this composite is a promising material to explore solar-to-chemical energy production.

With this pretext, Xiong *et al.* [84] designed a core-shell HKUST-1@TiO₂ composite [HKUST-1 = Cu₃(benzenetricarboxylic acid)₂, btc] which shows high photocatalytic reduction efficiency of CO₂ to CH₄. (Figure 8) The key point in the two-step synthesis of this composite was the use of PVP in the conversion of Cu₂O nanocrystals into 1 μ m HKUST-1 particles, which allows the subsequent deposition of a uniform mesoporous shell (*ca.* 210 nm) of titania formed by aggregation of 10-20 nm anatase-TiO₂ nanoparticles. (Figure 8a) The nitrogen isotherm of the composite is intermediate between type I/IV indicating a clear hierarchical porosity, with a meso-/macroporous contribution arising from the textural properties of the TiO₂ shell and the inherent microporosity of the HKUST-1 core which maintains its high CO₂ adsorption capacity. This material was evaluated for the photocatalytic CH₄ production from CO₂ showing superior conversion levels (5 times over bare TiO₂) and selectivity over hydrogen in the photocatalytic reduction when compared to the individual components. (Figure 8b) This is clearly favoured by the core shell structure of the HKUST-1@TiO₂ composite for a number of reasons: i) HKUST-1 has a high storage ability for CO₂, [111, 112] ii) the photocatalytic behaviour of TiO₂ for the conversion of CO₂ into CH₄, and iii) the mesoporosity of the shell which allows the CO₂ uptake and concentration by the core. Using a range of measurements including ultrafast transient absorption spectroscopy, the authors demonstrate the highly efficient transfer of photogenerated electrons from the semiconductor to the framework, which facilitates charge separation and supplies energetic electrons to CO₂ molecules adsorbed within the cavities and onto active sites of the MOF where the reduction occurs. The design and future applications of such composites are highly promising for photocatalytic gas phase reactions and further opportunities to convert CO₂ into fuels or other value added products.

Figure 8. TEM image of HKUST-1@TiO₂ core-shell composite. (b) Production yields of CH₄ and H₂ from CO₂ using HKUST-1@TiO₂ and bare TiO₂ nanocrystals as photocatalysts following UV irradiation for 4 hrs. Reproduced with permission from [84].

3.2 S/Se/Te-based QD@MOF composites

Among the different types of semiconductor nanocrystals, chalcogenide-based QDs, generally sulphur (S), selenium (Se) and tellurium (Te) are the most promising and studied materials, not only due to their potential applications in optoelectronic and biomedicine, but also their well-known chemistry and established protocols for their preparation, which allows a meticulous control of their shape, size and structure.[113] Thus, the vast majority of QD@MOF composites are prepared from QDs formed from these chalcogenides with major applications in sensing, particularly of thiols which is also presented below.

In 2009, Maspoch *et al.*[63] reported a versatile method for the encapsulation of single or multiple functional materials into an infinite coordination polymer (ICP) lattice. Briefly, ICPs are defined as repeated ligands interconnected through metallic nodes which are generally non-crystalline network structures. Water-soluble CdSe/ZnS core-shell QDs were encapsulated within an amorphous coordination-derived matrix of composition Zn(bix) (where bix = 1,4-bis(imidazol-1-ylmethyl)benzene) using the bottle-in-ship method to yield a QD-metal organic solid composite. The pre-formed CdSe/ZnS QDs were vigorously mixed at room temperature with the Zn(II) ions and bix linkers in ethanol to entrap the nanoparticles in the Zn(bix) matrix, which took on a spherical shape as commonly observed for amorphous coordination polymers prepared by precipitation methods.[114] Fluorescence optical microscopy was used to demonstrate successful encapsulation of the QDs, with the composite displaying both red and blue emission arising from the CdSe/ZnS QD and the Zn(bix) spheres, respectively (Figure 9a,b). As outlined in section 2.1 the ‘bottle-around-the-ship’ method is a versatile strategy for the encapsulation of diverse cargoes into coordination-derived network structures, and Maspoch and co-workers were some of the first to demonstrate the simultaneous entrapment of particles and molecules into the same matrix. In this case fluorescein was co-encapsulated with the CdSe/ZnS QDs, giving rise to multi-modal

fluorescence (figure 9c) covering the red, blue and green emission bands of the QD, Zn(bix) matrix and fluorescein, respectively. Taking further advantage of the bottle around the ship method, QDs and iron oxide nanoparticles were also co-encapsulated allowing a rapid recovery of the fluorescent composite by a magnet. Although this is a non-crystalline non-porous material, the metal complex properties of Zn(bix) are fully retained after the assembly. The authors did not report any specific application for their composite, however it is noted that such broadband light emission could find utility in the laser fabrication industry.

Figure 9. (a) and (b) Fluorescence microscopy of QD/fluorescein/Zn(bix) spheres collected at different excitation wavelengths allowing the colour selective detection of fluorescence emission. (c) Fluorescence emission spectra of the composite at an excitation wavelength of 355 nm. Reproduced with permission from [63].

Following a related strategy, Kimizuka *et al.* [64] reported the embedding of anionic quantum dots into amorphous coordination networks. (Figure 10) This successful encapsulation relies on the self-assembly of adenosine monophosphate (AMP) with lanthanide ions (Gd^{3+}) on the negatively charged surface of carboxylate-functionalized CdSe/ZnS QDs to form a supramolecular structure via coordination interactions. (Figure 10a) The incorporation of the carboxyl-capped QDs was confirmed by TEM-EDX microanalysis, and crystal planes corresponding to the QDs were clearly observed in the core of the composite by HR-TEM, their visualisation likely facilitated by the amorphous nature of the shell. (Figure 10b) The shell thickness of the composite can be tailored by carefully controlling the amount of QDs in the starting AMP/ Gd^{3+} growing media. The choice of terminating ligand functionality is crucial to successful incorporation of the QDs within the composites. The ligand provides not only the desired solubility and dispersibility, but appropriate functionality at the QD surface for framework growth, in this case a hard anionic carboxylate oxygen donor for interaction with the high valent Lewis acidic Gd^{3+} cation of the coordination matrix. This was demonstrated using carboxyl-capped QDs of differing sizes which did not affect the encapsulation process; however, when the carboxylate ligands were replaced with neutral

amines significantly reduced loading levels of the QDs were incorporated into the framework (Figure 10c).

Figure 10. (a) Schematic showing the selective encapsulation of carboxylate-capped CdSe/ZnS QDs in a network of Gd³⁺ and adenosine monophosphate (AMP). (b) TEM image of the composite. (c) PL spectra of a solution of amino- and carboxylate-capped QDs before (red) and after (blue) network formation indicating selective encapsulation. Reproduced with permission from [64].

Wakaoka *et al.* [65] reported the synthesis of CdSe QDs within the pores of a MOF using the “ship in the bottle” strategy. A hot injection method [115] was employed to entrap the QD in a large-pore MIL-101(Al)-NH₂ framework (where MIL stands for Materials of Institute Lavoisier and is formed by trimeric Al clusters and 2-aminoterephthalic acid linkers, bdc-NH₂), with pores functionalised by terminal primary amine groups. The MOF was soaked in a solution containing CdO and stearic acid with the subsequent addition of the Se precursor with trioctylphosphine in octane at 230 °C. MIL-101(Al)-NH₂ decomposes at temperatures above 377 °C, [116] so under these synthetic conditions the structural integrity of the framework was not compromised. By using this methodology the formation of three sizes of CdSe QDs was observed, each giving rise to a different fluorescent emission peak (Figure 11). Relatively small QDs within the pores of the framework (1.7 and 1.8 nm) emit at 436 and 468 nm, respectively, whereas those QDs outside of the MOF pores but remaining within the framework structure perhaps within defect sites (3.3 nm) emit at 585 nm. Alongside these emissions, QDs located in the surface of the crystal of ~ 6.2 nm in size with an emission peak at 660 were also observed. This is an important demonstration of the potential difficulties in controlling QD or other nanoparticle location when employing the ‘ship in the bottle’ synthetic method for composite formation.

Figure 11. Photoluminescence spectra at 12 K from a QD@MIL-101(Al)-NH₂ composite formed by a ship in the bottle strategy clearly indicating multiple sizes of the CdSe QDs are formed. Reproduced with permission from [78].

By using scanning transmission electron microscopy (STEM) and EDS, a homogenous distribution of CdSe nanoparticles around 1.5-3.0 nm were found, corresponding to a smaller size than characterized by fluorescence spectroscopy; which match the pore size of MIL-101(Al)-NH₂. These researchers also observed that one of the dominant factors in the formation of QDs within MOFs are the pore windows, which could significantly restrict diffusion of the QD precursors from the bulk solution into the available framework porosity. This was demonstrated using MIL-100(Fe), a MOF of similar composition but with smaller pore windows (5.5 Å), which permits QD formation only on the surface of the framework when the same methodology is applied. In the ‘ship in the bottle’ method the QD synthesis necessarily occurs without surface protecting agents, but in this case could be favoured by the uncoordinated amino ligand functionality of the framework which has the potential to passivate the surface of the growing QDs within the pores.

Figure 12. (a) QD passivation strategy to increase dispersibility in DMF and DEF, common MOF-5 synthesis solvents. Reconstructed confocal microscopy stacks of the emission intensity from a QD@MOF-5 cubic crystal prepared in DEF (b) and DMF (c) showing clear QD aggregation in the latter. Reproduced with permission from [66].

As previously discussed in the introduction, an adequate surface modification of QDs with suitable ligands is necessary to prepare well-dispersed QDs in the desired solvent which is important to prevent aggregation during MOF assembly. Falcaro *et al.*, [66] reported a two step QD ligand modification (figure 12a) using yellow and red 5.2 nm and 8.3 nm CdSe/CdS/Cd_{0.5}Zn_{0.5}S/ZnS QDs, a core-shell nanoparticle designed to provide high fluorescent quantum yields (up to 70 %) and thermal stability. Such multi-shell structures are typically prepared to better passivate the QDs surface and also offer a stepwise adjustment of the lattice for improved crystallisation. The as-synthesised ligands present in the QDs (octadecylamine and (2,2,4-trimethylpentyl)-phosphonic acid) were successively exchanged by pyridine (which passivates weakly the QD surface [117]) and subsequently by 5-amino-1-pentanol (AP), to ultimately form QDs that are highly dispersible in DMF and DEF, typical solvents employed in coordination framework assembly. The AP-capped CdSe/CdS/Cd_{0.5}Zn_{0.5}S/ZnS nanoparticles were subsequently added to a DMF or DEF solution containing the Zn(NO₃)₂ and 1,4-benzenedicarboxylic acid required for MOF-5 assembly, which was heated at 100 °C for 10 h. Interestingly, as can be seen by confocal microscopy images of a single cubic crystal of QD@MOF-5, the composite obtained in DEF shows a homogenous distribution of QDs within the framework, while that prepared in DMF displayed highly aggregated QDs (Figure 12b). This was attributed to the instability of the

AP-capped QDs in DMF under the MOF growing conditions, and their subsequent agglomeration and precipitation. A possible explanation suggested by the authors relies on the stabilization of the AP-functionalized QDs by the ethyl groups present on the DEF solvent molecules. The agglomeration behaviour was further confirmed by fluorescence spectra obtained for the composites which revealed a clear red-shift following synthesis in DMF, but no such shift was detected after synthesis in DEF. In this work ICP-MS was used to determine the amount of QD in the composite, which in terms of volume was in the range 0.2 - 0.25 %.

Thiols are one of the most widely used capping groups to passivate QDs, because they bind covalently to the surface of typical chalcogenide- and sulphide-based semiconductors.[118] Due to their low stability under QD synthesis conditions however, they are often introduced via ligand exchange which results in a decrease in QD fluorescence. In the case of metal-S QDs, this quenching is due to the trapping of the hole (h^+) generated in the valence band of the QD after excitation in the HOMO of the thiol; while in the case of QDs capped with a ZnS shell, the quenching is produced by an exothermic reaction between the thiolate and Zn and/or S, which causes a significant alteration of the shell.[18] This clear and very well established interaction is thus available to evaluate the integrity and porosity of MOF matrices and hence the accessibility of semiconductor nanoparticles embedded within using thiols as molecular probes. In addition, the sensing of thiols is generally important since they are present as contaminants in fuels and petroleum products, and as markers of foodstuff deterioration. Mercaptans can also cause oxidative deterioration and alteration of the performance of various additives in finished products.[119] A number of endogenous biological thiols including cysteine, homocysteine and glutathione also play critical roles in a number of physiological and pathological processes, hence their intracellular detection may be important in disease diagnosis.[120]

With this in mind, Falcaro and co-workers evaluated their QD@MOF-5 composite for size-selective thiol sensing by the encapsulated CdSe/CdS/Cd_{0.5}Zn_{0.5}S/ZnS QDs.[58] The QD fluorescence was almost completely quenched when exposed to a solution of ethanethiol, a small S-containing molecule that is often added to odourless gaseous fuels to warn of gas leaks. The ethanethiol is small enough to readily enter the pores of the surrounding MOF matrix where it can freely diffuse through the network to reach and react with the surface of the embedded QDs resulting in the observed quenching behaviour. On the other hand, the thiol-containing polymer n-isopropyl acrylamide/acrylic acid/t-butyl acrylamide mercaptane did not show any effect on the fluorescence properties of the QDs, attributed to its large size (1700 molecular units) and thus total exclusion from the MOF pores. Similar results were obtained by the same group when α -hopeite particles decorated with CdSe/CdS/ZnS QDs were employed as a route to encapsulate these highly luminescent species into MOF-5

matrices (Figure 13): ethanethiol almost completely quenched the QD fluorescence emission after 200 min, whereas a molecule such as 2-amino-6-mercaptapurine riboside that is comparable in size to the MOF-5 cavities quenched ~ 30 % of the luminescence after 1200 min, indicating an increased diffusion barrier through the framework.[58] As expected, the large thiol containing polymer (n-isopropyl acrylamide/acrylic acid/t-butyl acrylamide mercaptane) did not quench the fluorescence, even after 50 hrs exposure.

Figure 13. Sensing of thiols by QDs encapsulated in a MOF-5 matrix using QD-decorated α -hopeite particles in a modified bottle around the ship procedure. (a-c) Emission quenching of QDs only when exposed to thiols of all sizes. (d-f) Size-selective thiol sensing by QD@MOF-5 composites, where emission quenching decreases as the size of the thiol approaches the dimensions of the pores of the framework. Reproduced with permission from [58].

Enveloping nanoparticles with surfactants and polymers allows the preparation of well-dispersed particles where the solution stability is governed largely by the functional groups on the amphiphiles or macromolecules. Polyvinylpyrrolidone (PVP) is one such example, where its polar pyrrolidone pendant groups and aliphatic backbone ensure it is soluble in water and organic solvents and has the potential to interact strongly with a variety of materials and surfaces.

Taking advantage of these properties, Huo *et al.*[55] reported a methodology to incorporate a diverse range of PVP-capped nanoparticles, including CdSe and CdTe QDs in a matrix of ZIF-8. The dual role of the amphiphilic polymer in stabilizing nanoparticles in polar media besides acting as capping agent in order to maintain their shape and size during framework assembly is crucial, as is the absolute amount of PVP needed. The key point of this methodology is the spatial control of the nanoparticles in the lattice of the ZIF-8 framework, which is readily modulated by the addition time of the nanoparticle during the synthesis. Oleic acid-capped CdSe QDs were firstly synthesised through a hot injection methodology and subsequently coated in PVP by soaking the nanoparticle in an excess of the polymer for 24 h, followed by washing with hexane and chloroform. In the case of 3-MPA-capped CdTe QDs (3-MPA = 3-mercaptopropionic acid), the PVP encapsulation was carried out in situ after the synthesis of the nanoparticle followed by the above-mentioned washing procedure. The PVP-capped QDs were subsequently soaked at r.t. for 24 h in a solution containing the ZIF-8 precursors, and the microporous framework readily assembles around them. (Figure 14a,b) The small blue-shift of the CdTe@ZIF-8 with respect to the free CdTe QD (529 vs. 532 nm) indicates a change in the surrounding environment upon matrix confinement as previously reported.[12] The size-selective properties of the CdSe@ZIF-8 composite were successfully evaluated, where the observed fluorescence was quenched on exposure to small thiols such as 2-mercaptoethanol, but showed no response to cyclohexanethiol as expected when using a small pore framework such as ZIF-8 that is known for its molecular sieving properties (Figure 14c,d).

Extending this work Huo and co-workers [121] employed a two-step growth and spin-coating method to deposit MOF thin films containing catalytic, magnetic and semiconductor nanoparticles. In the case of the latter, 4 nm PVP-capped CdSe QDs were spin coated onto a thin film of ZIF-8 deposited onto a glass substrate, followed by further matrix growth and spin coating steps to successively build up an orange multi-layered CdSe@ZIF-8 hybrid thin film (Figure 14e) with a sandwich-like structure. The presence of the PVP facilitated adsorption of the QDs onto the ZIF-8 films and provided a fresh hydrophilic surface for subsequent framework growth, enabling efficient encapsulation of the QDs. It is noteworthy that this simple combination of repeated growth and spin coating permits co-deposition of different types of nanoparticles both within the same layer and in adjacent layers within the film allowing multiple functionalities to be captured and localised. The resulting CdSe@ZIF-8 thin films display the same fluorescence behaviour on addition of thiols of different sizes as the non-anchored composite. (Figure 14f) This additional processing step allows the configuration of functional QD@MOF composites into supported and easy to handle optical sensors which is a key factor and a necessary step toward future commercialization.[36]

Figure 14. (a) TEM image of CdSe@ZIF-8 composite particles. (b) Photograph of the dispersed composites irradiated with ambient light (left) and 354 nm UV (right). (c) and (d) Size-selecting sensing of thiols via CdSe emission quenching. Reproduced with permission from [55]. (e) PL spectra of CdSe@ZIF-8 composites configured as a thin film. (f) normalized PL intensity of the CdSe@ZIF-8 thin films following addition of thiols. Reproduced with permission from [121].

As sensory materials, luminescent MOFs have great potential to be used in the detection of explosive and related substances.[122] The detection of these energetic materials is highly important, due to their risk to human life and civilian security. However, one of the reported issues associated with MOFs for the detection of nitroaromatic compounds is an apparent lack of measurement reproducibility between batches.[56] To circumvent this problem, Deep and co-workers reported the encapsulation of CdSe QDs in a europium-based MOF (EuOF, formed by Eu(III) and 1,3,5-tris(4-carboxyphenyl) benzene organic ligands) to yield a CdSe@EuOF composite, which allows the detection of small concentrations of trinitrotoluene (TNT). To prepare the composite CdSe QDs capped with thioglycolic acid were added to the growing media of EuOF [europium nitrate and 1,3,5-tris(4-carboxylphenyl)benzene]. PXRD of the composite revealed three weak additional peaks in addition to those for EuOF

corresponding to CdSe of zinc blende structure and a reduction in Langmuir surface area from 990 to 730 $\text{m}^2\cdot\text{g}^{-1}$ further confirmed the inclusion of the QDs in the framework. Curiously, TEM images of the obtained composite consisted of rod-like particles assembled into a flower-like morphology with the QDs apparently at the centre, rather than the 30 – 40 nm particles observed for EuOF prepared in the absence of the QDs.

The fluorescence properties of this composite were explored: a single emission band for the CdSe QDs at *ca.* 550 nm was observed, while 4 characteristic emissions for the Eu^{3+} in the EuOF framework were detected at 590 ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), 615 ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), 650 ($^5\text{D}_0 \rightarrow ^7\text{F}_3$), 700 ($^5\text{D}_0 \rightarrow ^7\text{F}_4$) nm following excitation at 300 nm. The composite was later examined for the detection of nitroaromatic explosives, in which the emission bands at 615 and 700 nm were partially quenched on exposure to ethanolic solutions of TNT in the concentration range 5-1000 ppb, with a detection limit of 3 ppb. This is lower than EuOF alone (22 ppb), and the coefficient of variation is reduced from 5% to 1% when the composite is employed indicating greater reproducibility in the measurements. Quenching of the emission intensity for CdSe@EuOF is attributed only to specific interactions between the analyte and the organic ligands of the EuOF framework. Although the QDs do not show any direct sensing properties towards TNT, their absence of quenching could have been used as an internal reference in this work. In this case, the improved stability and reproducibility compared to EuOF is proposed to arise from the interwoven and reinforced structure of the nanocomposite. In addition, the composite shows high selectivity for TNT over other aromatic compounds including phenol, o-cresol, toluene and nitrobenzene.

Enantioselective sensing by QD@MOF composites has also been explored. Hou *et al.*[67] prepared water-soluble CdTe QDs capped with 3-MPA and encased these in $[\text{Zn}_2(\text{camph})_2\text{bipy}]$ (camph = (+)-camphoric acid, and bipy = 4,4'-bipyridyl), a homochiral framework built from Zn(II)-camphorate layers pillared by 4,4'-bipyridyl ligands.[123] The use of a microwave synthesis platform allows a rapid encapsulation (150 min) procedure and the formation of very small and homogeneous particle sizes. PXRD of the composite remains unvaried after the encapsulation process, indicating the preservation of the chiral network structure following QD wrapping. After excitation at 365 nm, the composite shows two emission bands at 463 nm and 615 nm, which are blue-shifted when compared to the individual components (472 nm, MOF; 643 nm, QD). The composite shows a specific, selective and visible colorimetric response to L-tartaric acid, where the solution changes from red to blue, corresponding to the quenching of the QD. The composite is sensitive both to the overall concentration of L-tartaric acid and its enantiomeric excess, and while the QD fluorescence is quenched that attributed to the MOF is enhanced. The increase in framework fluorescence was attributed to the substitution of DMF molecules in the pores (which is

reported to act as a collisional quencher [124]) by the L-tartaric acid, and a subsequent reduction in non-radiative decay pathways due to restricted framework motions in the presence of guests which are a good match to the size and shape of the pore cavity. No response for D-tartaric acid, D- and L-dimethyl tartrate or D- and L-mandelic acid was observed, most probably because they are not able to diffuse (or diffuse more slowly at least) through the MOF pores to the CdTe QD. This is a clear example of how the properties of the homochiral microporous MOF matrix can enhance those of the QD, since enantioselective sensing would not be possible for the QD alone without some degree of chiral induction either through processing or the attachment of chiral ligands directly to the semiconductor surface. [125]

Over the last few years MOFs have increasingly been used as templates for the preparation of porous carbons and their composites,[126, 127] polymers,[128] gels [129] and hollow structures [130] facilitated by their well-defined crystal shapes, regular pore structures and relative ease of disassembly. In a related work, homochiral MOFs have recently been employed as a template to direct formation of chiral CdS nanotubes. By using a rod-shaped homochiral Cd-MOF, [(CdLBr)H₂O], where L stands for the (D- or L-) chiral ligand [*N*-(4-pyridylmethyl)-_{L/D}-leucine HBr]), Tang *et al.* [68] developed a novel strategy to synthesise an inorganic helical semiconductor which shows enantioselective sensing towards _{L/D}-aspartic acid. (Figure 15) This one-step methodology relies on the use of the MOF as both template and Cd²⁺ source, which in the presence of thioacetamide (as the source of S²⁻) forms chiral CdS nanotubes arising from nucleation of small CdS particles on the surface of the MOF crystals. As the reaction proceeds, the surfaces of the MOF template gradually collapse and open CdS tubes of average diameter 300 nm are formed, as supported by SEM images of the products formed at different times. By the addition of higher concentrations of Cd²⁺ ions and thioacetamide to the growing media of the Cd-MOF, well-defined helical nanotubes with 95 nm of internal diameter and thicker walls are accessible. The recognition properties of chiral CdS were investigated by a solid-state fluorescence titration with L- and D-aspartic acid. (Figure 15) CdS derived from the L-form of the MOF was more sensitive to D-aspartate and vice versa for CdS originating from the D-form of the framework. The design of such chiral semiconductor sensors is of great interest and given the structural diversity of MOFs and their ability to act as templates, it is highly likely that other examples of chiral functional inorganic and semiconductor nanomaterials will be derived in this manner.

Figure 15. Room temperature solid-state emission spectra demonstrating enantioselective sensing by helical chiral CdS nanotubes (inset, f) templated by a homochiral MOF. In this case, the nanotubes are more sensitive to D-aspartic acid (D-Asp). Reproduced with permission from [68].

While many applications of QD@MOF composites focus on sensing, there are also many reports in which these materials have been used for photocatalytic purposes, including hydrogen production from water splitting.[91, 92, 131, 132] In these materials the relative position of the semiconductor band gap must be adequately positioned to reduce or/and oxidise water using UV/visible light. In addition to this, these materials are also reported as generators of free radicals (such as hydroxyls or superoxide radicals) upon UV-Vis irradiation in aqueous solution, [133] which can be used for further radical-based reaction chemistry.

In order to improve the hydrogen production of QDs, some efforts synthesising QD-composites have been reported, such as QD-TiO₂,[132] CdSe and CdS – ZnO nanowires[134] or N-doped graphene/CdS nanocomposites,[135] among others. A promising alternative is to encapsulate these QDs in a coordination chemistry-derived framework of high surface area to increase the number of photoactive surface sites. Further, the composition of the MOF matrix may enhance charge-carrier transport by reducing recombination rates.

By preparing 2-3 nm CdS QDs in a pre-synthesised MIL-101-Cr (Cr₃F(H₂O)₂O(bdc)₃) using the ship in a bottle method, Sun *et al.*[69] reported a CdS/MIL-101 composite in which the amount of QD embedded in the resulting material can be directly tuned by adjusting the amount of CdS in the synthetic procedure. TEM images clearly show aggregated CdS embedded within the external surfaces of the octahedral MIL-101 crystals (figure 16a,b) only rather than being distributed throughout the interior, indicating that the Cd(Ac)₂ and DMSO QD precursors do not penetrate the framework fully. The presence of the semiconductor was

further confirmed by PXRD measurement, which indicated it had a cubic structure in agreement with lattice spacings derived from HRTEM. The N₂ adsorption-desorption isotherm shows the retention of the porous framework structure and high specific surface area, although the BET surface area and pore volume expectedly decrease with increasing amounts of CdS in the composite. The intensity of the UV-vis absorption bands associated with MIL-101 in the composite decreased following incorporation of CdS, and the absorption edges displayed clear red shifts toward pure CdS, in agreement with the colour changes of the samples from green to yellow with increasing amounts of the semiconductor. (Figure 16d,e)

Figure 16. TEM image of CdS@MIL-101(10) and (b) the HRTEM image of embedded CdS aggregates. c) Photocatalytic H₂ production for CdS@MIL-101 composites embedded with different amounts of CdS under visible light irradiation (20 mg of the catalyst, 0.5 wt% Pt loaded). d) UV-Vis diffuse reflectance spectra and e) photographs of pure MIL-101, CdS@MIL-101(X) (X = 5, 10, 20, 50%) and pure CdS. Reproduced with permission from [69].

CdS/MIL-101 was photodeposited with 0.5 wt% Pt particles (acting as co-catalyst) to obtain a ternary Pt@CdS/MIL-101 composite system which was examined for photocatalytic hydrogen evolution in lactic acid aqueous solution under visible light irradiation. (Figure 16c) MIL-101 itself did not act as an effective semiconductor photocatalyst, but a maximum hydrogen production of $\sim 150 \mu\text{mol}\cdot\text{hr}^{-1}$ was obtained for composites containing c.a. 10 %

(w/w) of embedded CdS. PXRD indicated stability of the composite during the photocatalytic reaction and durability over 4 cycles was demonstrated. By contrast, CdS modified MOF-5 does not show any activity for hydrogen evolution under the same conditions, which was rationalised due to the collapse of MOF-5 after embedding CdS, and the low stability of this framework in air and water indicating the importance of compatibility between the components not just for composite synthesis but also their practical utility in applications.

In the same context, Wu *et al.*[70] reported the photodeposition of CdS nanorods onto the surface of the Zr-based MOF UiO-66-NH₂ (where UiO stands for University of Oslo, and is composed by Zr₆O₄(OH)₄ clusters and bdc-NH₂ struts). UiO-66 and its family are well known highly stable frameworks which have been postulated to display semiconductor behaviour.[136] The methodology for the photodeposition is based on visible light irradiation ($\lambda \geq 420$ nm) of a mixture of UiO-66-NH₂ and CdCl₂ in an ethanolic solution containing S₈ under a nitrogen atmosphere. The PXRD pattern show the corresponding peaks of the framework which do not shift with increasing amounts of photodeposited hexagonal CdS, suggesting this is not incorporated into the MOF lattice. TEM images of the composites reveal CdS nanorods decorate the surfaces of the UiO-66-NH₂ crystals, and that the rods increase in size with increasing irradiation time as further confirmed by a red shift in their absorption energy. An atomic deposition route for the semiconductor based on the reaction of Cd⁰ with S₈ was proposed based on electrochemical data.

The CdS/UiO-66-NH₂ composite was successfully used in the selective visible light oxidation of benzyl alcohol to benzaldehyde using molecular oxygen as the oxidant. (Figure 17a) It was found that the optimum photocatalytic performance occurs for CdS/UiO-66-NH₂ composites prepared using a photodeposition time of 6hr, where 31% conversion and almost 100% benzaldehyde selectivity is observed. The photoactivity of the composite is higher than the bare framework, commercial CdS and their physical mixture indicating that an excellent interface between the two components is critical in enhancing the photocatalytic activity of CdS. The composite photocatalyst was also investigated for the selective oxidation of a range of benzylic alcohols with different ring substituents. While 100% aldehyde selectivity was observed in many cases, it is noted that highly electron-accepting groups generally display lower conversions and substrate alcohols bearing electron-donating groups such as *p*-methoxy benzyl alcohol have much higher conversions but experience a small loss in selectivity. The CdS/UiO-66-NH₂ composite photocatalyst is highly stable and was demonstrably recycled 5 times without loss of conversion or selectivity.

A mechanism for the selective photocatalytic oxidation of alcohols with the nanocomposite was proposed on the basis of electrochemical measurements coupled with quenching and spin trapping studies (Figure 17b). Under visible light irradiation, both the CdS and UiO-66-NH₂ support are photoexcited to generate charge carriers. The photogenerated electrons from CdS transfer to UiO-66-NH₂ facilitated by their excellent interfacial contact, matched band potentials and the high surface area of the composite. Oxygen reacts with the electrons to form highly reactive O₂^{•-}, and the hole generated in the CdS oxidise organic substances adsorbed on the surface of the catalyst. The superoxide radicals further react with carbocations to generate the final products.

Figure 17. (a) Enhanced and highly selective visible light photocatalytic oxidation of benzyl alcohol to benzaldehyde by CdS@UiO-66-NH₂ when compared to the individual components and a physical mixture (λ_{ex} ≥ 420 nm, 4 hours). (b) Possible mechanism of photocatalytic oxidation of alcohols to their corresponding aldehydes using the CdS@UiO-66-NH₂ nanocomposite. Reproduced with permission from [70].

The same group also reported the use of reduced graphene oxide (RGO) to produce the ternary composite UiO-66/CdS/RGO (UiO-66 is made up of Zr₆O₄(OH)₄ clusters and bdc linkers),[71] where the RGO was employed to suppress the fast recombination of charge carriers in CdS and the high surface area MOF to increase the number of catalytic sites. The UiO-66/CdS/1%RGO composite containing 1 wt% of RGO demonstrated excellent activity

for photocatalytic hydrogen evolution, which was 13.8 times higher than commercial CdS and double that observed for an analogous composite of P25/CdS/1%RGO (where P25 is Degussa P25, a commercial source of TiO₂). The improved activity over P25/CdS/1%RGO results from a higher surface area, improved homogeneous distribution of CdS and more efficient interface charge separation. The mechanism is likely to be similar to that observed for CdS/UiO-66-NH₂, [70] where the photogenerated electron is transferred from the CdS QDs to the UiO-66 framework and subsequently migrates to the RGO.

Further, Zhu *et al.* [73] reported the synthesis of CdS@MIL-101(Fe) nanocomposites and also investigated their use for the selective oxidation of benzyl alcohol to benzaldehyde using visible light under mild conditions. To prepare the composite the pre-formed framework was homogeneously dispersed in DMSO (as both solvent and S²⁻ source), followed by addition of cadmium acetate and heating of the mixture to 180 °C. By using varying amounts of the MIL-101(Fe) framework, nanocomposites containing different loadings of CdS were readily prepared. TEM images show well-dispersed ~ 5 nm CdS nanoparticles on the surface of the framework when sufficient levels of the MOF are employed in composite formation. If the amount of MIL-100(Fe) is significantly reduced, CdS QDs self-assemble into spherical particles as previously observed for the bulk semiconductor, clearly indicating that the amount of added framework is critical to achieve a homogeneous distribution of CdS on the crystalline microporous matrix. BET surface areas of the composites are in accordance with the amount of CdS, varying from 71.3 m²/g for high QD:MOF ratios to 1536.2 m²/g when small QD:MOF ratios were used, allowing the number of surface active sites and charge carrying ability to be modulated.

When the CdS@MIL-101(Fe) composites were characterized by UV-Vis diffuse reflectance spectroscopy, a red-shift in the absorption band of CdS in the composites and an enhanced absorbance in the visible region (> 500 nm) with respect to pure CdS were observed. However, it is noted that above a certain QD:MOF ratio the absorbance drops hence it is important to optimize the composition to achieve maximum visible light absorption. The band gap energies of the composites are tuneable in the range 2.16-2.37 eV, indicating addition of the MOF narrows the band gap of the CdS (bulk CdS = 2.44 eV) likely arising from strong interactions between the two components. The photocatalytic activity of CdS@MIL-101(Fe) nanocomposites were evaluated for the selective oxidation of benzyl alcohol to benzaldehyde, and displayed an enhanced performance compared to the MIL-101(Fe) framework and bare QDs reaching a maximum conversion of 54.3 % and almost 100 % selectivity when the optimal composite was employed. It is postulated that the porous matrix enhances adsorption of the benzyl alcohol substrate allowing this to accumulate at the surface of the CdS QDs, where the increase in effective concentration accelerates the photocatalysis. However, if too

much MOF is present the photocatalytic activity deteriorates as the effective surface of the active CdS is reduced which manifests the important role of the MOF. The CdS@MIL-101(Fe) composite was also stable to reuse, and no decrease in the conversion grade of benzyl alcohol was observed after 5 reaction cycles. Following further experiments including electrochemical analysis, PL spectroscopy and ESR, the authors conclude that the enhancement in the heterogeneous photocatalytic organic transformation using the composite is due to the combined effect of enhanced light absorption, efficient charge separation and high surface area.

Banerjee *et al.*[72] reported the in-situ synthesis of small CdS QDs within a Zn(II)-based low molecular weight hydrogel (ZAVA), which was subsequently transformed under mild conditions to a crystalline QD@MOF composite for photocatalytic water splitting under visible light irradiation. (Figure 18) The CdS@ZAVA hydrogel is obtained in a one-pot reaction and does not require any capping agent for the CdS nanoparticles, since they are generated in situ within the hydrogel. The CdS@ZAVA hydrogels display a tuneable luminescence emission from white to yellow and finally orange with ageing, arising from slow aggregation of the CdS particles within the matrix. Drying of the composite gels results in the corresponding xerogels, where the fluorescence properties of the initial hydrogels are retained; white emitting hydrogels give white emitting xerogels and so on. It is noted however, that once solidified the luminescence of the xerogel becomes persistent and does not change any further.

Remarkably, upon addition of chloride salts at room temperature the CdS@ZAVA hydrogel transforms directly into millimetre sized rod-shaped crystals of a ZAVA-Cl MOF embedded with CdS QDs. (Figure 18a) (HR)-TEM images reveal that the CdS particles are larger than the pore size of the framework (5-9 nm vs. 1.2 nm, respectively), and indicates they are most likely sandwiched between MOF crystallites rather than adsorbed on the MOF surfaces supported by the fact their photoluminescence does not change following multiple washes. While the degradation of QD loaded gels is an elegant and seemingly facile strategy to access QD@MOF composites, it will in all likelihood be limited to those systems that are capable of gel-network to crystalline framework transformations.

As with the xerogels, the CdS@ZAVA-Cl MOFs fully retain the fluorescent properties of the starting hydrogel and their colour is attributed to a possible energy transfer between the donor MOF and the acceptor CdS QDs. The photocatalytic ability of the CdS@ZAVA-Cl MOF to generate H₂ was determined under visible light irradiation using Pt as a cocatalyst and ethanol as a sacrificial reagent. The composite showed H₂ production of 398 – 418 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ when irradiated with visible light (figure 18b,c); significantly higher than thioglycolic acid-capped CdS QDs (100 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) and pristine ZAVCl MOF (18 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) which is transparent to visible light and essentially inactive under the tested conditions. This is a noteworthy performance for CdS@ZAVA-Cl considering the very small loading of CdS (~ 1 wt%), and the composite also displays stable photocatalytic activity over 12 cycles. In the absence of Pt however, the CdS@ZAVA-Cl MOF alone is not able to split water due to very slow reaction kinetics on the surface of the photocatalyst.[137]

Figure 18. (a) Conversion of a CdS@ZAVA composite hydrogel into MOF crystals embedded with the CdS QDs on addition of salt. (b) Photocatalytic H₂ evolution of the CdS@ZAVA-Cl composite under visible light irradiation in the presence of a Pt co-catalyst (0.5 wt%). (c) Proposed mechanism of water splitting using the CdS@ZAVA-Cl composite. Reproduced with permission from [72].

A small number of MOFs have been reported for light harvesting, where solar energy is converted to electrical or chemical energy.[138, 139] A promising class of materials in this

regard are metalloporphyrin MOFs,[140] whose porphyrin-derived linkers are structurally similar to naturally occurring pigments and light harvesting moieties. The efficiency of these components is dependent on the amount of photons absorbed in the solar spectrum, and metalloporphyrins typically provide only limited coverage of the visible region due to their narrow absorption bands. Semiconductor NPs on the other hand have been widely used to harvest visible light energy due to their narrow band gaps and significantly broader absorption spectra,[141] and Jin *et al.* report a strategy to prepare QD@MOF composites with enhanced MOF light-harvesting via energy transfer from a semiconductor QD.[61] Two Zn/porphyrin-based MOFs (by combining $\text{Zn}(\text{NO}_3)_2$ and 1,2,4,5-tetrakis(4-carboxyphenyl) benzene with (5,15-dipyridyl-10,20-bis(pentafluorophenyl))porphyrin to yield F-MOF; or with (5,15-bis(4-(pyridyl)ethynyl)-10,20-diphenyl porphyrin to yield DA-MOF) were surface-functionalised with amine-capped CdSe/ZnS core-shell QDs.[61] (Figure 19a) The QD emission band overlaps the MOF absorption band, indicating that a resonant energy transfer from the QD donor to the MOF acceptor is possible in the QD@MOF composite system, which was probed by time-resolved fluorescence spectroscopy. It was observed that the fluorescence lifetimes of the QD were shortened after its deposition on the surface of the MOF, which was directly related to the degree of spectral overlap between the components as determined for the two Zn/porphyrin MOFs in combination with two QDs with different emission bands (QD550 and QD620). (Figure 19b) It is noted that the MOF component of the QD@DA-MOF composites emit when excited at wavelengths where the MOF has no absorption, confirming the light harvesting and energy transfer. By fitting the fluorescence decay profiles energy transfer times between 1.7 and 10 ns were determined, with quantum yields as high as 84% being reached. This indicates that light harvesting efficiency is tuneable by modulating the MOF composition or QD size which both influence the spectral overlap. It was expected that the highly efficient energy transfer was facilitated by the close proximity of the QD and the MOF likely arising from a strong coordination interaction between the terminating amine groups on the semiconductor and free Zn sites on the MOF surface, which was confirmed by using QDs without amine groups where energy transfer times increased by a factor of 4.

Figure 19. (a) Schematic of the structure and light harvesting of a QD@MOF composite formed by surface modification of a porphyrin containing framework with CdSe/ZnS core-shell QDs. (b) Emission spectra of the porphyrin MOFs (a1, a2) and their composites (b1/2, c1/2) with QDs when excited at 400 nm confirming light-harvesting behaviour by energy transfer for the semiconductor. Reproduced with permission from [61].

3.3 Nitride-based QD@MOF composites

Fischer and co-workers reported the first and currently only synthesis of nitride semiconductor QDs within MOF crystals by chemical vapour infiltration of the micropores of ZIF-8 with trimethylamine gallane, which was subsequently reacted in the presence of ammonia to form GaN.[85] (Figure 20) ZIF-8 is thermally and chemically stable and was selected in this case as it is not reactive toward the ammonia required to prepare the target nitride, demonstrating the need to carefully match the chemistry of the host with that of the often harsh QD syntheses. Reaction of the inclusion compound with gaseous ammonia at 323 K led to a remarkable trimerization of the trimethyl gallane precursor to form a spectroscopically characterised cyclotrigallazane within the sodalite cavities of the ZIF-8. The reaction chemistry which forms the trimer is clearly facilitated by the confinement of the trimethyl gallane within the pores of the framework. The entrapped cyclotrigallazane was immobilised within the ZIF-8 matrix, and its confinement led to a demonstrable enhancement

in its thermal stability when compared to the neat compound. Cyclotrigallazane is known to act as a suitable precursor for the preparation of GaN, and this was exploited here by Fischer and co-workers to form GaN@ZIF-8 composites following further heat treatment with ammonia and thermal annealing under dynamic vacuum. The resulting GaN@ZIF-8 retains ~60% of the porosity of ZIF-8 itself, and contains a 13 wt% loading of the GaN semiconductor. Annular dark-field scanning transmission electron microscopy (ADF-STEM) images reveal very small GaN QDs homogeneously dispersed throughout the ZIF-8 matrix (figure 20), which was corroborated by EELS Ga-mapping. The optical properties were probed by photoluminescence spectroscopy, revealing a broad UV emission maximum at 340 nm assigned to the near-band gap emission of the GaN QDs. (Figure 20) The emission band is blue shifted compared to bulk GaN as a result of the band-gap increase due to the quantum confinement effect resulting from the very small particle sizes, which were calculated from the energy shift to be an average 2.3 ± 0.5 nm. This work nicely demonstrates the ability of robust MOF cavities to direct interesting chemistry on confined inorganic molecules, which in this case permits the in-situ formation of an active QD precursor complex within the matrix. While no applications for the GaN@ZIF-8 composite were explicitly reported, such materials could be promising for optoelectronic applications, spintronics and as photocatalysts.

Figure 20. Conceptual representation of the confined formation of GaN QDs in a ZIF-8 matrix. The images on the right show the corresponding PL spectra of the GaN@ZIF-8 composite vs. the components (upper) and the ADF-STEM image where the bright spots correspond to the QDs. Reproduced with permission from [85].

3.4 Carbon-based QD@MOF composites

Carbon QDs (CQDs) [142] are small carbon particles typically < 10 nm in size, which offer some advantages over traditional semiconductor QDs including high aqueous solubility and chemical inertness. In addition, they are less toxic and have greater biocompatibility than their semiconductor counterparts making them especially attractive for biomedical applications and imaging. The electronic properties of CQDs as electron donors and acceptors resulting in chemiluminescence further ensures they have significant potential in optronics, photocatalysis

and sensing. As a result it is not surprising that there are an increasing number of reports of CQD@MOF composites.

Lan *et al.*[86] recently reported a CQD@UMCM-1 (UMCM-1 stands for University of Michigan Crystalline Material-1 and formula $\text{Zn}_4\text{O}(\text{bdc})(\text{btb})_{4/3}$, where btb = 1,3,5-tris(4-carboxyphenyl)benzene) composite through an encapsulation process ('bottle around the ship' strategy) by adding < 6nm CQDs to a supersaturated crystallisation solution containing the MOF precursors.[143] (Figure 21a) Although the presence of the CQDs do not affect the needle-like morphology of the MOF crystals, they do appear to attenuate their size since the composite crystals are twenty times smaller than UMCM-1 prepared under otherwise identical conditions. PL spectroscopy of CQD@UMCM-1 displays an intense emission band at 500 nm (λ_{exc} = 420 nm), and the observed green luminescence is comparable to the CQDs themselves indicating they are not aggregated within the MOF matrix.

Figure 21. (A) Illustration of the bottle around the ship methodology to form CQD@UMCM-1 composites. (B) H_2 isotherms determined at 77K (samples 1a and 1b are prepared under slightly different conditions). (C) PL spectra showing quenching of the emission intensity from the composite on addition of nitro aromatic compounds (inset highlights the colour change that occurs). Reproduced with permission from [86].

The hydrogen storage capacity of the composite was evaluated under cryogenic conditions up to 1 bar, where an increase in hydrogen uptake of 9% was recorded when compared to bulk UMCM-1 despite a decrease in apparent surface area. (Figure 21b) The authors attribute this observation to specific interactions between the H_2 adsorbate and polar groups located on the

surface of the C-dots (i.e. -COOH and -OH), as evidenced by a modest increase in isosteric heat of adsorption for the composite. Such behaviour has been previously observed by Bandosz and co-workers for ammonia adsorption on GO@MOF composites (GO = graphite oxide), [144-146] which are typically obtained by dispersing GO during the MOF synthesis.

The optical properties of the CQD@UMCM-1 composite has also been successfully used for sensing of nitroaromatic compounds through an electron transfer process from the amino groups on the surface of the embedded CQDs to the electron deficient nitrobenzene and 2,4,6-trinitrophenol (TNP) analytes resulting in efficient fluorescence quenching. (Figure 21c) In the case of TNP a colour change of the solution from green to orange was observed, demonstrating a facile colorimetric detection process that is easily visualised by the naked eye. Additionally, the CQD@UMCM-1 composite shows enhanced sensitivity toward energetic analytes when compared to the bare CQDs. Such composites are a step-forward not only for its application in green fluorescence sensing, but also for its enhanced hydrogen storage capacity.

Lin *et al.* reported a CQD@ZIF-8 composite prepared through an encapsulation process of poly(ethylenimine)-capped CQDs (BPEI-CQDs) into a matrix of the MOF.[57] To this end, 4 - 8 nm BPEI-capped C-dots were prepared by one-step pyrolysis of citric acid in the presence of BPEI [147] and subsequently added to a solution containing 2-methylimidazole and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, which was stored for 24 h without stirring to yield the BPEI-CQD@ZIF-8 composite. TEM images of the composite show rhombic dodecahedral particles of ~ 400 nm consistent with bulk ZIF-8, which is confirmed by PXRD; however, due to the small size of the CQDs they are not observed. Nitrogen adsorption of the composite reveals the microporosity and high surface area associated with the ZIF-8 matrix are fully retained.

BPEI-CQD@ZIF-8 is highly water-dispersible with a strong blue fluorescent emission (figure 22) centred at 440 nm ($\lambda_{\text{ex}} = 365$ nm), which is not-shifted with respect to the BPEI-CQDs indicating retention of the optical properties of the CQDs. On addition of Cu^{2+} , adsorption of the cations into the ZIF-8 matrix concentrates these around the embedded BPEI-CQDs where Cu^{2+} reacts with their surface amino groups forming a fluorescently inactive complex which results in significant quenching of the emission (Figure 22). Surprisingly, this quenching effect is higher for the composite than the BPEI-CQDs alone, indicating a synergistic effect of accumulation and quenching. Time and pH parameters were investigated, and the optimum fluorescent quenching response was observed after 30 min in weakly alkaline media, reaching a maximum sensitivity at pH 8. Under acidic conditions it is proposed the amine groups on the BPEI-CQDs are protonated and thus unable to complex with the Cu^{2+} ions.

Figure 22. PL spectra (emission spectra, a, b; excitation spectra, c, d) and UV absorption spectra (e, f) of 0.15 mg/mL BPEI CQD@ZIF-8 solution in the absence (a, c, e) and presence (b, d, f) of 100 μM Cu^{2+} ions. The inset shows a dispersion of 0.15 mg/mL BPEI-CQD@ZIF-8 in the absence (left) and presence (right) of 100 μM Cu^{2+} ions. Reproduced with permission from [57].

The composite shows high selectivity towards Cu^{2+} , with no further effect on the quenching behaviour in the presence of other metal cations, anions or organic components tested. The limit of detection was calculated to be as small as 80 pM. Finally, the composite sensor was employed to determine the concentration of Cu^{2+} ions in water from the Min River (China), which was found to be $2.201 \pm 0.084 \mu\text{M}$ and entirely consistent with results obtained by ICPMS.

Wang and coworkers have also reported a CQD@ZIF-8 composite prepared through an identical encapsulation process to Lin, which they employ for simultaneous drug delivery and imaging.[87] (Figure 23) Water-soluble green-fluorescent C-dots ($\lambda_{\text{ex}} = 365 \text{ nm}$; $\lambda_{\text{em}} = 497 \text{ nm}$) were first embedded in a ZIF-8 matrix with full retention of their optical properties, and the resulting CQD@ZIF-8 composite was subsequently loaded with 5-fluorouracil (5-FU), a representative anticancer drug. Release experiments of 5-FU-loaded CQD@ZIF-8 composites in phosphate-buffered saline at biologically relevant pH values (7.4 and 5.5) revealed a 67% 5-FU release in neutral PBS and 92% in acidic PBS after 48hrs indicating the composite could act as a pH responsive drug delivery vehicle consistent with previous reports.[148] In-vitro cytotoxicity studies of CQD@ZIF-8 toward HELA, prostate and fibroblast cells were carried out, and in all cases 90% cell viability was observed up to a composite concentration of 25 $\mu\text{g/mL}$, revealing good biocompatibility. (Figure 23a) Following Incubation of Hela

cells with 5-FU loaded CQD@ZIF-8 for 24 hrs, fluorescent microscopy shows a distinct green fluorescence in the cells cytoplasm arising from the uptake of the composite (figure 23b,c), possibly via an endocytotic pathway. Due to the pH sensitivity of the ZIF-8 matrix, the 5-FU is slowly released following cellular uptake, and maintains its pharmacological efficacy when compared to free 5-FU at the same concentration. (Figure 23d) This work strongly indicates that QD@MOF composites have potential to be used in theranostics and personalised healthcare applications where the efficacy of drug action could be monitored in real time, allowing dosing to be optimised to the response.

Figure 23. (a) Cytotoxicity of HeLa, prostate (DU145) and fibroblast (L929) cells incubated with various concentrations of CQD@ZIF-8 composites. (b) Differential contrast and (c) CLSM images of HeLa cells incubated with 5-FU loaded CQD@ZIF-8 composites. (d) In-vitro cytotoxicity of HeLa cells with 5-FU loaded CQD@ZIF-8 composite against free 5-FU. Reproduced with permission from [87].

Related to the CQDs are graphene quantum dots (GQDs), fragments of graphene typically < 20 nm in size which display similar exciton confinement and quantum size effects. However, due to their molecular-like character, these nanoparticles are easier to handle than inorganic semiconductor QDs and are readily functionalised at their edges to modulate their photoluminescence properties.[149] However, since GQDs do not typically have any capping agents, their stabilization in solid supports is quite a challenge.

Banerjee *et al.* reported the first example of GQDs encapsulated in a ZIF-8 matrix.[88] Bare GQDs prepared *via* an electrochemical method were dispersed in propylene carbonate and suspended and added to a methanolic solution containing ZIF-8 precursors and allowed to react for 24 h. By adjusting the GQDs concentration in the reaction mixture, different % in weight of GQDs@ZIF-8 were synthesised. SEM images show spherical particles with a size of 36 nm for a 0.4 wt% GQD@ZIF-8 composite dropping to less than 30 nm for a loading of 1.2 wt%. This contrasts with the rhombic dodecahedral morphology of ZIF-8 synthesised in the absence of GQDs, which reveals the strong effect of the GQDs on the size and shape of ZIF-8 nanocrystals. HRTEM was used to reveal the location of the GQDs in the composite, which appear concentrated around the edges of the spherical ZIF-8 nanocrystals rather than homogeneously distributed throughout the centre. (Figure 24) The composite was further characterized by a suite of techniques including infrared (FT-IR), Raman, PXRD, X-ray photoelectron spectroscopy, TGA and N₂ adsorption isotherms, which corroborate the successful encapsulation of the GQDs within the ZIF-8 matrix.

Figure 24. TEM image of GQD@ZIF-8 composites (left) and water adsorption isotherms determined at STP for the composite vs. more hydrophobic ZIF-8 (right). Reproduced with permission from [88].

Successful encapsulation is partly dependent on the presence of polar surface groups on the GQD surface providing a nucleation site for ZIF-8 growth, and this functionality also increases the water adsorption capacity of the composite when compared to ZIF-8 itself. (Figure 24) This is a recurring feature of nanoscale carbon-based QD@MOF composite materials, as previously demonstrated for increased H₂ storage capacity by CQD@UMCM-1.[86] When the optical properties of the material were explored, a bathochromic shift of *ca.* 32 nm was found which was not observed in the physical mixture (GQDs + ZIF-8), indicating

fluorescence tuning due to the strong interactions between the two components. Further, the GQD@ZIF-8 composite remains stable after 3 months under normal conditions exhibiting an identical photoluminescence profile.

3.5 Coordination polymers as QDs

Coordination polymers (CPs) themselves have also been configured as QDs (CPQDs), providing a further alternative to heavy-metal based QDs. Given the modular nature and the enormous range of metal ions and linkers to choose from, such materials constitute a highly tuneable fluorescent detection platform. Li *et al.*[89] recently described for the first time the preparation of 3 nm particles of a water-dispersible coordination polymer prepared from the organic building block 3,4,9,10-perylenetetracarboxylate as linker and Zn^{2+} in a methanol solution containing KOH for 12 h at 60 °C. TEM and HRTEM images of the CPQDs show an average particle diameter of 3 ± 0.5 nm with a lattice spacing of 0.23 nm (figure 25b) consistent with PXRD data. By simply reducing the amount of KOH used during the synthesis the authors could control the size of the particles and hence their optical properties are tuneable. The CPQDs show two characteristic absorption maxima at 440 and 466 nm, which are blue shifted compared to the free ligand, and the particle also display a strong green photoluminescent response with a quantum yield of 21%, 13 times higher than the bulk CP. The emission peaks at 487 and 510 nm are attributed to Y- and E-type perylene excimers, respectively, and the relative intensity of these peaks indicate they coexist in equal amounts. (Figure 25a) The photoluminescence of the CPQDs is particularly stable and even after storage for 120 days over 90% of the emission was retained, which is apparently not quenched by solvent or oxidation.

Figure 25. (a) PL spectra of CPQDs (PZn) compared to the bulk, nanoparticles and the sodium salt of the perylene linker (PK). (b) HRTEM image of the CPQDs. (c) Fluorescence microscopy image demonstrating the ability of CPQDs in cellular imaging. Reproduced with permission from [89].

These CPQDs were used successfully as a cellular probe for A498 living cells, which revealed clear and intense photoluminescence from the intracellular region. (Figure 25c) Remarkably strong anti-bleaching behaviour was also observed, maintaining emission intensity for 3 min of irradiation at 455 nm and remaining intense even after 10 mins. This is significantly better performance than organic dyes which tend to photobleach very quickly and is comparable to more traditional inorganic semiconductor QDs. Given their desirable optoelectronic properties and demonstrable biocompatibility, CPQDs would appear to be promising candidates for fluorescent probes in biology and medicine although their stability under physiological conditions and hence intracellular fate requires further investigation.

4. Conclusions and outlook

MOFs have enormous structural and chemical diversity that can be fine-tuned for applications, making them very attractive materials for the preparation of composites with enhanced properties. In particular, the versatility of MOFs in combination with the exceptional photophysical and photochemical properties of QDs ensures the resulting composite materials are of significant interest in wide ranging fields, including photocatalysis, gas-storage, supercapacitors, sensing and light-driven water splitting for hydrogen evolution. Many of the applications discussed in this article benefit from the favourable combination of the semiconductor-like behaviour of QDs with the high surface area and porosity afforded by a MOF matrix. The MOF can play a number of roles, including stabilising and dispersing the QDs, modulating electron-hole recombination rates via effective charge separation, increasing the number of active sites and accumulating reactive species at the semiconductor surface in a size-selective manner. In turn, the QD endows the frameworks with desirable optoelectronic properties, light-harvesting capability and a fluorescent readout. The MOF matrix itself can also act as a template by which to form structured semiconductor particles, which is likely to be explored further given their size and shape dependent optoelectronic properties. Although several types of inorganic QDs have rather toxic compositions and contain heavy metals, developments in the synthesis of carbon and graphene-based QDs are likely to see these incorporated with MOFs to a greater degree especially given the potential of MOFs in biomedicine. It is envisaged for example, that CQD@MOF composites have significant potential in combined therapy and diagnostics and combining MOFs with graphene fragments could open up a whole range of new and exciting applications ranging from optoelectronics to nanoseparation.

Despite this potential there remain some challenges regarding the synthesis of QD@MOF composites, in particular using the ‘ship-in-the-bottle’ strategy where precise control over the size and location of the QD is especially difficult. Further, it is important to balance

dispersibility of the QDs in solution with the need to provide a good interface with the MOF component in order to fully benefit from the properties of the composite and it is expected that new ligands and functionalisation strategies will be developed along these lines. It may also be desirable in future to encapsulate QDs into specific compartments within MOF matrices as a step toward hierarchically functional composites, but this presents an entirely new set of synthetic challenges.

In summary, QD@MOF composites are an emerging class of material that clearly have a bright future and the potential for high impact contributions across several fields of applied research.

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5. References

- [1] X. Michalet, F.F. Pinaud, L.A. Bentolila, J.M. Tsay, S. Doose, J.J. Li, G. Sundaresan, A.M. Wu, S.S. Gambhir, S. Weiss, *Science*, 307 (2005) 538.
- [2] P. Alivisatos, *Nat Biotech*, 22 (2004) 47.
- [3] R.C. Somers, M.G. Bawendi, D.G. Nocera, *Chem. Soc. Rev.*, 36 (2007) 579.
- [4] F. Chen, D. Gerion, *Nano Lett.*, 4 (2004) 1827.
- [5] M.G. Bawendi, M.L. Steigerwald, L.E. Brus, *Annu. Rev. Phys. Chem.*, 41 (1990) 477.
- [6] U. Resch-Genger, M. Grabolle, S. Cavaliere-Jaricot, R. Nitschke, T. Nann, *Nat Meth*, 5 (2008) 763.
- [7] W.W. Yu, L. Qu, W. Guo, X. Peng, *Chem. Mater.*, 15 (2003) 2854.
- [8] H. Fu, A. Zunger, *Phys. Rev. B*, 56 (1997) 1496.
- [9] D.V. Talapin, A.L. Rogach, A. Kornowski, M. Haase, H. Weller, *Nano Lett.*, 1 (2001) 207.
- [10] C. Carrillo-Carrion, S. Cardenas, B.M. Simonet, M. Valcarcel, *Chem. Commun.*, (2009) 5214.
- [11] H. Borchert, D.V. Talapin, C. McGinley, S. Adam, A. Lobo, A.R.B. de Castro, T. Möller, H. Weller, *J. Chem. Phys.*, 119 (2003) 1800.
- [12] B.O. Dabbousi, J. Rodriguez-Viejo, F.V. Mikulec, J.R. Heine, H. Mattoussi, R. Ober, K.F. Jensen, M.G. Bawendi, *J. Phys. Chem. B*, 101 (1997) 9463.
- [13] M.A. Hines, P. Guyot-Sionnest, *J. Phys. Chem.*, 100 (1996) 468.
- [14] C.B. Murray, D.J. Norris, M.G. Bawendi, *J. Am. Chem. Soc.*, 115 (1993) 8706.
- [15] H. Shen, H. Wang, Z. Tang, J.Z. Niu, S. Lou, Z. Du, L.S. Li, *CrystEngComm*, 11 (2009) 1733.

- [16] J. Aguilera-Sigalat, S. Rocton, J.F. Sanchez-Royo, R.E. Galian, J. Perez-Prieto, *RSC Adv.*, 2 (2012) 1632.
- [17] N.I. Hammer, T. Emrick, M.D. Barnes, *Nanoscale Res. Lett.*, 2 (2007) 282.
- [18] B.-K. Pong, B.L. Trout, J.-Y. Lee, *Langmuir*, 24 (2008) 5270.
- [19] B. Dubertret, P. Skourides, D.J. Norris, V. Noireaux, A.H. Brivanlou, A. Libchaber, *Science*, 298 (2002) 1759.
- [20] S.T. Selvan, *Biointerphases*, 5 (2010) FA110.
- [21] P.D. Wadhavane, R.E. Galian, M. Angeles Izquierdo, J. Aguilera-Sigalat, F. Galindo, L. Schmidt, M.I. Burguete, J. Perez-Prieto, S.V. Luis, *J. Am. Chem. Soc.*, 134 (2012) 20554.
- [22] N. Tomczak, R. Liu, J.G. Vancso, *Nanoscale*, 5 (2013) 12018.
- [23] S. Kitagawa, R. Kitaura, S.-i. Noro, *Angew. Chem. Int. Ed.*, 43 (2004) 2334.
- [24] H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, *Nature*, 402 (1999) 276.
- [25] A.K. Cheetham, C.N.R. Rao, R.K. Feller, *Chem. Commun.*, (2006) 4780.
- [26] J.-R. Li, R.J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.*, 38 (2009) 1477.
- [27] J. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, *Chem. Soc. Rev.*, 38 (2009) 1450.
- [28] J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.*, 112 (2011) 869.
- [29] L.E. Kreno, K. Leong, O.K. Farha, M. Allendorf, R.P. Van Duyne, J.T. Hupp, *Chem. Rev.*, 112 (2011) 1105.
- [30] P. Juzenas, W. Chen, Y.-P. Sun, M.A.N. Coelho, R. Generalov, N. Generalova, I.L. Christensen, *Adv. Drug Deliver. Rev.*, 60 (2008) 1600.
- [31] C.E. Probst, P. Zrazhevskiy, V. Bagalkot, X. Gao, *Adv. Drug Deliver. Rev.*, 65 (2013) 703.
- [32] J. Rabone, Y.-F. Yue, S.Y. Chong, K.C. Stylianou, J. Bacsá, D. Bradshaw, G.R. Darling, N.G. Berry, Y.Z. Khimyak, A.Y. Ganin, P. Wiper, J.B. Claridge, M.J. Rosseinsky, *Science*, 329 (2010) 1053.
- [33] A. Ghoufi, A. Subercaze, Q. Ma, P.G. Yot, Y. Ke, I. Puente-Orench, T. Devic, V. Guillermin, C. Zhong, C. Serre, G. Férey, G. Maurin, *J. Phys. Chem. C*, 116 (2012) 13289.
- [34] Y. Sakata, S. Furukawa, M. Kondo, K. Hirai, N. Horike, Y. Takashima, H. Uehara, N. Louvain, M. Meilikhov, T. Tsuruoka, S. Isoda, W. Kosaka, O. Sakata, S. Kitagawa, *Science*, 339 (2013) 193.
- [35] T.D. Bennett, J. Sotelo, J.-C. Tan, S.A. Moggach, *CrystEngComm*, 17 (2015) 286.
- [36] D. Bradshaw, A. Garai, J. Huo, *Chem. Soc. Rev.*, 41 (2012) 2344.
- [37] A. Bétard, R.A. Fischer, *Chem. Rev.*, 112 (2012) 1055.
- [38] Y. Hu, X. Dong, J. Nan, W. Jin, X. Ren, N. Xu, Y.M. Lee, *Chem. Commun.*, 47 (2011) 737.

- [39] M.S. Denny, S.M. Cohen, *Angew. Chem. Int. Ed.*, (2015) n/a.
- [40] J. Huo, J. Aguilera-Sigalat, S. El-Hankari, D. Bradshaw, *Chem. Sci.*, 6 (2015) 1938.
- [41] A. Carné-Sánchez, I. Imaz, M. Cano-Sarabia, D. Maspoch, *Nat Chem*, 5 (2013) 203.
- [42] Q.-L. Zhu, Q. Xu, *Chem. Soc. Rev.*, 43 (2014) 5468.
- [43] C. Xu, D. Mochizuki, Y. Hashimoto, T. Honda, Y. Tsukahara, T. Yamauchi, Y. Wada, *Eur. J. Inorg. Chem.*, 2012 (2012) 3113.
- [44] S.R. Mukai, M. Shimoda, L. Lin, H. Tamon, T. Masuda, *Appl. Catal. A-General*, 256 (2003) 107.
- [45] Y. Yu, J. Mai, L. Wang, X. Li, Z. Jiang, F. Wang, *Sci. Rep.*, 4 (2014).
- [46] S. Urrego, E. Serra, V. Alfredsson, R.M. Blanco, I. Díaz, *Micropor. Mesopor. Mater.*, 129 (2010) 173.
- [47] B.-Z. Zhan, X.-Y. Li, *Chem. Commun.*, (1998) 349.
- [48] N. Herron, *Inorg. Chem.*, 25 (1986) 4714.
- [49] L. Rodríguez-Lorenzo, R.A. Álvarez-Puebla, F.J.G. de Abajo, L.M. Liz-Marzán, *J. Phys. Chem. C*, 114 (2010) 7336.
- [50] K.C.L. Black, Y. Wang, H.P. Luehmann, X. Cai, W. Xing, B. Pang, Y. Zhao, C.S. Cutler, L.V. Wang, Y. Liu, Y. Xia, *ACS Nano*, 8 (2014) 4385.
- [51] J. Liu, D.M. Strachan, P.K. Thallapally, *Chem. Commun.*, 50 (2014) 466.
- [52] R.J.T. Houk, B.W. Jacobs, F.E. Gabaly, N.N. Chang, A.A. Talin, D.D. Graham, S.D. House, I.M. Robertson, M.D. Allendorf, *Nano Lett.*, 9 (2009) 3413.
- [53] N. Maria Rosaria di, A. Valentina, C. Boiko, G. Ruxandra, D. Abderrazzak, *J. Med. Chem.*, 57 (2014) 411.
- [54] S. Turner, O.I. Lebedev, F. Schröder, D. Esken, R.A. Fischer, G.V. Tendeloo, *Chem. Mater.*, 20 (2008) 5622.
- [55] G. Lu, S. Li, Z. Guo, O.K. Farha, B.G. Hauser, X. Qi, Y. Wang, X. Wang, S. Han, X. Liu, J.S. DuChene, H. Zhang, Q. Zhang, X. Chen, J. Ma, S.C.J. Loo, W.D. Wei, Y. Yang, J.T. Hupp, F. Huo, *Nat Chem*, 4 (2012) 310.
- [56] R. Kaur, A.K. Paul, A. Deep, *Forensic Sci. Int.*, 242 (2014) 88.
- [57] X. Lin, G. Gao, L. Zheng, Y. Chi, G. Chen, *Anal. Chem.*, 86 (2013) 1223.
- [58] P. Falcaro, A.J. Hill, K.M. Nairn, J. Jasieniak, J.I. Mardel, T.J. Bastow, S.C. Mayo, M. Gimona, D. Gomez, H.J. Whitfield, R. Riccò, A. Patelli, B. Marmiroli, H. Amenitsch, T. Colson, L. Villanova, D. Buso, *Nat Commun*, 2 (2011) 237.
- [59] P. Falcaro, R. Ricco, C.M. Doherty, K. Liang, A.J. Hill, M.J. Styles, *Chem. Soc. Rev.*, (2014).
- [60] Y. Wang, Y. Wang, R. Xu, *J. Phys. Chem. C*, 117 (2013) 783.

- [61] S. Jin, H.-J. Son, O.K. Farha, G.P. Wiederrecht, J.T. Hupp, *J. Am. Chem. Soc.*, 135 (2013) 955.
- [62] M.E. Silvestre, M. Franzreb, P.G. Weidler, O. Shekhah, C. Wöll, *Adv. Funct. Mater.*, 23 (2013) 1210.
- [63] I. Imaz, J. Hernando, D. Ruiz-Molina, D. Maspoch, *Angew. Chem. Int. Ed.*, 48 (2009) 2325.
- [64] R. Nishiyabu, C. Aime, R. Gondo, K. Kaneko, N. Kimizuka, *Chem. Commun.*, 46 (2010) 4333.
- [65] T. Wakaoka, K. Hirai, K. Murayama, Y. Takano, H. Takagi, S. Furukawa, S. Kitagawa, *J. Mater. Chem. C*, 2 (2014) 7173.
- [66] D. Buso, J. Jasieniak, M.D.H. Lay, P. Schiavuta, P. Scopece, J. Laird, H. Amenitsch, A.J. Hill, P. Falcaro, *Small*, 8 (2012) 80.
- [67] L. Zhou, J. Jia, W. Shanling, K. Lu, H. Xiandeng, J.S. Michael, *Microchem. J.*, 110 (2013) 764.
- [68] X. Kuang, Y. Ma, C. Zhang, H. Su, J. Zhang, B. Tang, *Chem. Commun.*, 51 (2015) 5955.
- [69] J. He, Z. Yan, J. Wang, J. Xie, L. Jiang, Y. Shi, F. Yuan, F. Yu, Y. Sun, *Chem. Commun.*, 49 (2013) 6761.
- [70] L. Shen, S. Liang, W. Wu, R. Liang, L. Wu, *J. Mater. Chem. A*, 1 (2013) 11473.
- [71] R. Lin, L. Shen, Z. Ren, W. Wu, Y. Tan, H. Fu, J. Zhang, L. Wu, *Chem. Commun.*, 50 (2014) 8533.
- [72] S. Saha, G. Das, J. Thote, R. Banerjee, *J. Am. Chem. Soc.*, 136 (2014) 14845.
- [73] F. Ke, L. Wang, J. Zhu, *Nano Res.*, (2015) 1.
- [74] S. Bordiga, C. Lamberti, G. Ricchiardi, L. Regli, F. Bonino, A. Damin, K.P. Lillerud, M. Bjorgen, A. Zecchina, *Chem. Commun.*, (2004) 2300.
- [75] R. Ameloot, M.B.J. Roelfsaers, G. De Cremer, F. Vermoortele, J. Hofkens, B.F. Sels, D.E. De Vos, *Adv. Mater.*, 23 (2011) 1788.
- [76] P.L. Feng, J.J. Perry Iv, S. Nikodemski, B.W. Jacobs, S.T. Meek, M.D. Allendorf, *J. Am. Chem. Soc.*, 132 (2010) 15487.
- [77] J. Gascon, M.D. Alonso, A. Almeida, G.P.M. Klink, F. Kapteijn, G. Mul, *ChemSusChem*, 1 (2008) 981.
- [78] M. Müller, S. Hermes, K. Kähler, M.W.E. van den Berg, M. Muhler, R.A. Fischer, *Chem. Mater.*, 20 (2008) 4576.
- [79] L.H. Wee, N. Janssens, S.P. Sree, C. Wiktor, E. Gobechiya, R.A. Fischer, C.E.A. Kirschhock, J.A. Martens, *Nanoscale*, 6 (2014) 2056.

- [80] D. Zhao, X. Wan, H. Song, L. Hao, Y. Su, Y. Lv, *Sensors and Actuators B: Chemical*, 197 (2014) 50.
- [81] W.-w. Zhan, Q. Kuang, J.-z. Zhou, X.-j. Kong, Z.-x. Xie, L.-s. Zheng, *J. Am. Chem. Soc.*, 135 (2013) 1926.
- [82] Y. Gao, J. Wu, W. Zhang, Y. Tan, J. Zhao, B. Tang, *Mater. Lett.*, 128 (2014) 208.
- [83] M. Muller, X. Zhang, Y. Wang, R.A. Fischer, *Chem. Commun.*, (2009) 119.
- [84] R. Li, J. Hu, M. Deng, H. Wang, X. Wang, Y. Hu, H.-L. Jiang, J. Jiang, Q. Zhang, Y. Xie, Y. Xiong, *Adv. Mater.*, 26 (2014) 4783.
- [85] D. Esken, S. Turner, C. Wiktor, S.B. Kalidindi, G. Van Tendeloo, R.A. Fischer, *J. Am. Chem. Soc.*, 133 (2011) 16370.
- [86] L. Ji-Sen, T. Yu-Jia, L. Shun-Li, Z. Shu-Ran, D. Zhi-Hui, S. Ling, L. Ya-Qian, *CrystEngComm*, 17 (2014) 1080.
- [87] L. He, T. Wang, J. An, X. Li, L. Zhang, L. Li, G. Li, X. Wu, Z. Su, C. Wang, *CrystEngComm*, 16 (2014) 3259.
- [88] B.P. Biswal, D.B. Shinde, V.K. Pillai, R. Banerjee, *Nanoscale*, 5 (2013) 10556.
- [89] L. Zhang, X. Qian, L. Liu, Z. Shi, Y. Li, S. Wang, H. Liu, Y. Li, *Chem. Commun.*, 48 (2012) 6166.
- [90] J. Aguilera-Sigalat, J.M. Casas-Solvas, M.C. Morant-Minana, A. Vargas-Berenguel, R.E. Galian, J. Perez-Prieto, *Chem. Commun.*, 48 (2012) 2573.
- [91] C.-I. Wang, Z. Yang, A.P. Periasamy, H.-T. Chang, *J. Mater.*, 2013 (2013) 7.
- [92] A. Das, Z. Han, M.G. Haghighi, R. Eisenberg, *Proc. Nat. Acad. Sci.*, 110 (2013) 16716.
- [93] A. Henglein, *Pure Appl. Chem.*, 56 (2009) 9.
- [94] Y.-J. Yang, X. Tao, Q. Hou, J.-F. Chen, *Acta Biomaterialia*, 5 (2009) 3488.
- [95] H. Cui, Y. Liu, W. Ren, M. Wang, Y. Zhao, *Nanotechnology*, (2013) 345602.
- [96] J. Aguilera-Sigalat, J. Sanchez-SanMartin, C.E. Agudelo-Morales, E. Zaballos, R.E. Galian, J. Perez-Prieto, *Chemphyschem*, 13 (2012) 835.
- [97] M. Alvaro, E. Carbonell, B. Ferrer, F.X. Xamena, H. Garcia, *Chem. Eur. J.*, 13 (2007) 5106.
- [98] T. Tachikawa, J.R. Choi, M. Fujitsuka, T. Majima, *J. Phys. Chem. C*, 112 (2008) 14090.
- [99] J. Hafizovic, M. Bjørgen, U. Olsbye, P.D.C. Dietzel, S. Bordiga, C. Prestipino, C. Lamberti, K. Lillerud, *J. Am. Chem. Soc.*, 129 (2007) 3612.
- [100] G. Calleja, J. Botas, M.G. Orcajo, M. Sánchez-Sánchez, *J. Porous Mater.*, 17 (2010) 91.
- [101] C.A. Bauer, T.V. Timofeeva, T.B. Settersten, B.D. Patterson, V.H. Liu, B.A. Simmons, M.D. Allendorf, *J. Am. Chem. Soc.*, 129 (2007) 7136.
- [102] J.A. Greathouse, M.D. Allendorf, *J. Am. Chem. Soc.*, 128 (2006) 10678.

- [103] S.S. Kaye, A. Dailly, O.M. Yaghi, J.R. Long, *J. Am. Chem. Soc.*, 129 (2007) 14176.
- [104] J. Reboul, S. Furukawa, N. Horike, M. Tsotsalas, K. Hirai, H. Uehara, M. Kondo, N. Louvain, O. Sakata, S. Kitagawa, *Nat Mater*, 11 (2012) 717.
- [105] K. Khaletskaya, J. Reboul, M. Meilikhov, M. Nakahama, S. Diring, M. Tsujimoto, S. Isoda, F. Kim, K.-i. Kamei, R.A. Fischer, S. Kitagawa, S. Furukawa, *J. Am. Chem. Soc.*, 135 (2013) 10998.
- [106] M. Winter, R.J. Brodd, *Chem. Rev.*, 104 (2004) 4245.
- [107] L. Fenghua, S. Jiangfeng, Y. Huafeng, G. Shiyu, Z. Qixian, H. Dongxue, I. Ari, N. Li, *Nanotechnology*, 20 (2009) 455602.
- [108] K.M. Choi, H.M. Jeong, J.H. Park, Y.-B. Zhang, J.K. Kang, O.M. Yaghi, *ACS Nano*, 8 (2014) 7451.
- [109] R. Díaz, M.G. Orcajo, J.A. Botas, G. Calleja, J. Palma, *Mater. Lett.*, 68 (2012) 126.
- [110] C. Aprile, A. Corma, H. Garcia, *Phys. Chem. Chem. Phys.*, 10 (2008) 769.
- [111] S. Bordiga, L. Regli, F. Bonino, E. Groppo, C. Lamberti, B. Xiao, P.S. Wheatley, R.E. Morris, A. Zecchina, *Phys. Chem. Chem. Phys.*, 9 (2007) 2676.
- [112] J. Liu, Y. Wang, A.I. Benin, P. Jakubczak, R.R. Willis, M.D. LeVan, *Langmuir*, 26 (2010) 14301.
- [113] A. Valizadeh, H. Mikaeili, M. Samiei, S. Farkhani, N. Zarghami, M. kouhi, A. Akbarzadeh, S. Davaran, *Nanoscale Res. Lett.*, 7 (2012) 480.
- [114] M. Oh, C.A. Mirkin, *Nature*, 438 (2005) 651.
- [115] C. de Mello Donegá, P. Liljeroth, D. Vanmaekelbergh, *Small*, 1 (2005) 1152.
- [116] P. Serra-Crespo, E.V. Ramos-Fernandez, J. Gascon, F. Kapteijn, *Chem. Mater.*, 23 (2011) 2565.
- [117] X. Ji, D. Copenhaver, C. Sichmeller, X. Peng, *J. Am. Chem. Soc.*, 130 (2008) 5726.
- [118] R.E. Galian, M.d.I. Guardia, *TrAC, Trends Anal. Chem.*, 28 (2009) 279.
- [119] B. Basu, S. Satapathy, A.K. Bhatnagar, *Catal. Rev.*, 35 (1993) 571.
- [120] H.S. Jung, X. Chen, J.S. Kim, J. Yoon, *Chem. Soc. Rev.*, 42 (2013) 6019.
- [121] W. Zhang, G. Lu, S. Li, Y. Liu, H. Xu, C. Cui, W. Yan, Y. Yang, F. Huo, *Chem. Commun.*, 50 (2014) 4296.
- [122] Z. Hu, B.J. Deibert, J. Li, *Chem. Soc. Rev.*, 43 (2014) 5815.
- [123] D.N. Dybtsev, M.P. Yutkin, E.V. Peresypkina, A.V. Virovets, C. Serre, G. Férey, V.P. Fedin, *Inorg. Chem.*, 46 (2007) 6843.
- [124] H. Wang, W. Yang, Z.-M. Sun, *Chem. Asian J.*, 8 (2013) 982.

- [125] T. Delgado-Pérez, L.M. Bouchet, M. de la Guardia, R.E. Galian, J. Pérez-Prieto, *Chem. Eur. J.*, 19 (2013) 11068.
- [126] W. Bak, H.S. Kim, H. Chun, W.C. Yoo, *Chem. Commun.*, 51 (2015) 7238.
- [127] B. Liu, H. Shioyama, H. Jiang, X. Zhang, Q. Xu, *Carbon*, 48 (2010) 456.
- [128] H. Ejima, N. Yanai, J.P. Best, M. Sindoro, S. Granick, F. Caruso, *Adv. Mater.*, 25 (2013) 5767.
- [129] T. Ishiwata, Y. Furukawa, K. Sugikawa, K. Kokado, K. Sada, *J. Am. Chem. Soc.*, 135 (2013) 5427.
- [130] Z. Zhang, Y. Chen, X. Xu, J. Zhang, G. Xiang, W. He, X. Wang, *Angew. Chem. Int. Ed.*, 53 (2014) 429.
- [131] M.A. Holmes, T.K. Townsend, F.E. Osterloh, *Chem. Commun.*, 48 (2012) 371.
- [132] K. Kim, M.-J. Kim, S.-I. Kim, J.-H. Jang, *Sci. Rep.*, 3 (2013).
- [133] B.I. Ipe, M. Lehnig, C.M. Niemeyer, *Small*, 1 (2005) 706.
- [134] G. Wang, X. Yang, F. Qian, J.Z. Zhang, Y. Li, *Nano Lett.*, 10 (2010) 1088.
- [135] L. Jia, D.-H. Wang, Y.-X. Huang, A.-W. Xu, H.-Q. Yu, *J. Phys. Chem. C*, 115 (2011) 11466.
- [136] C. Gomes Silva, I. Luz, F.X. Llabrés i Xamena, A. Corma, H. García, *Chem. Eur. J.*, 16 (2010) 11133.
- [137] J. Ran, J. Zhang, J. Yu, M. Jaroniec, S.Z. Qiao, *Chem. Soc. Rev.*, 43 (2014) 7787.
- [138] C.Y. Lee, O.K. Farha, B.J. Hong, A.A. Sarjeant, S.T. Nguyen, J.T. Hupp, *J. Am. Chem. Soc.*, 133 (2011) 15858.
- [139] M.C. So, G.P. Wiederrecht, J.E. Mondloch, J.T. Hupp, O.K. Farha, *Chem. Commun.*, 51 (2015) 3501.
- [140] W.-Y. Gao, M. Chrzanowski, S. Ma, *Chem. Soc. Rev.*, 43 (2014) 5841.
- [141] P.V. Kamat, *J. Phys. Chem. C*, 112 (2008) 18737.
- [142] Y. Wang, A. Hu, *J. Mater. Chem. C*, 2 (2014) 6921.
- [143] K. Koh, A.G. Wong-Foy, A.J. Matzger, *Angew. Chem. Int. Ed.*, 47 (2008) 677.
- [144] C. Petit, T.J. Bandosz, *Adv. Mater.*, 21 (2009) 4753.
- [145] C. Petit, B. Mendoza, T.J. Bandosz, *Langmuir*, 26 (2010) 15302.
- [146] C. Petit, T.J. Bandosz, *Adv. Funct. Mater.*, 21 (2011) 2108.
- [147] Y. Dong, R. Wang, H. Li, J. Shao, Y. Chi, X. Lin, G. Chen, *Carbon*, 50 (2012) 2810.
- [148] L. Zhang, T. Wang, L. Yang, C. Liu, C. Wang, H. Liu, Y.A. Wang, Z. Su, *Chem. Eur. J.*, 18 (2012) 12512.
- [149] M. Bacon, S.J. Bradley, T. Nann, *Part. Part. Syst. Char.*, 31 (2014) 415.