Polycationic Ru(II) Lumophores: Syntheses, Photophysics and Application in Electrostatically Driven Sensitization Of Lanthanide Luminescence

Richard C. Knighton,\*a Joseph M. Beamesb and Simon J. A. Popea\*

aSchool of Chemistry, Main Building, Cardiff University, Cardiff CF10 3AT, Cymru/Wales; bSchool of Chemistry, University of Birmingham, Birmingham B152TT. Email: popesj@cardiff.ac.uk

**Abstract**

A series of photoluminescent Ru(II) polypyridine complexes have been synthesized in a manner that varies the extent of cationic charge. Two ligand systems (L1 and L2), based upon 2,2’-bipyridine (bipy) mono- or difunctionalized at the 5- or 5,5’-positions using *N*-methylimidazolium groups, were utilized. The resulting Ru(II) species therefore carried +3, +4, +6, and +8 complex moieties based upon a [Ru(bipy)3]2+ core. Tetra-cationic [Ru(bipy)2(**L2**)][PF6]4 was characterized using XRD, revealing H-bonding interactions between two of the counter anions and the cationic unit. The ground state features of the complexes were found to closely resemble the parent unfunctionalized [Ru(bipy)3]2+ complex. In contrast, the excited state properties producing a variation in emission maxima, including a bathochromic 44 nm shift of the 3MLCT band for the tetra-cationic complex; interestingly, further increases in overall charge to +6 and +8 produced a hypsochromic shift in the 3MLCT band. Supporting DFT calculations suggest that the trend in emission behavior may, in part, be due to the precise nature of the LUMO and its localization. The utility of a photoactive polycationic Ru(II) complex was then demonstrated through the sensitization of a polyanionic Yb(III) complex in free solution. The study shows that electrostatically driven ion pairing is sufficient to facilitate energy transfer between the 3MLCT donor state of the Ru(II) complex and the accepting 2F5/2 excited state of Yb(III).

**Introduction**

The study of photoactive transition metal complexes is a rich and diverse area of chemistry and has important applications in many areas, such as light harvesting,[[1]](#endnote-1),[[2]](#endnote-2),[[3]](#endnote-3) sensing,[[4]](#endnote-4),[[5]](#endnote-5) energy upconversion,[[6]](#endnote-6),[[7]](#endnote-7),[[8]](#endnote-8) bioimaging[[9]](#endnote-9) and theranostics.[[10]](#endnote-10),[[11]](#endnote-11),[[12]](#endnote-12) While interest in earth abundant luminescent complexes[[13]](#endnote-13) has understandably, from a sustainability perspective, attracted significant attention in the last few years, the precious metals still provide an excellent basis for the rational design of efficient photoluminescent compounds.

Our interest has been drawn to the study of (poly)cationic luminescent complexes and their potential applications. In particular, cationic complexes are important in host-guest studies;[[14]](#endnote-14) as components of ionic liquids;[[15]](#endnote-15) ion-pairing;[[16]](#endnote-16) in the development of sensors and DNA binding;[[17]](#endnote-17) as photoactive components of aggregation colloids such as micelles and microemulsions;[[18]](#endnote-18) and, in membrane transport studies.[[19]](#endnote-19) However, luminescent metal complexes with high magnitudes of overall positive charge are very rare. Therefore we were interested in investigating the synthesis and physical properties of a series of cationic Ru(II) complexes that are structurally related to the archetypal triplet metal to ligand charge transfer (3MLCT) emitter [Ru(bipy)3]2+ (where bipy = 2,2’-bipyridine).

Recently, the early history of bipy has been retrospectively reviewed by Constable and Housecroft [[20]](#endnote-20) providing an important reminder of the ubiquity and ongoing application of this ligand and its close relatives. Ligand modification is the obvious route for the consideration of polycationic luminescent Ru(II) complexes and our approach, described herein, was facilitated by the use of cationic bipy ligands. Interestingly, anionic bipy ligands are more common in the literature, for example carboxylated (some of the earliest reported variants of bipy[[21]](#endnote-21)) or phosphonated[[22]](#endnote-22) derivatives of bipy are very well known and have been widely exploited in coordination chemistry.[[23]](#endnote-23) Although rarer, cationic bipys have been reported and complexed with Ru(II). Typically, these ligands incorporate terminal amine groups that can be protonated in certain media, allowing their development as luminescent sensors, or for consideration in photodynamic therapy, which exploits the inherent phototoxicity of the Ru(II) complex.[[24]](#endnote-24) Meyer and co-workers reported a series of Ru(II) complexes with quarternary alkylated amine substituents at the 4,4’ positions of the bipy framework; the complexes were studied in the context of Ru-based dye sensitized solar cells where the effect of charge and ion pairing with iodide is especially important.[[25]](#endnote-25) Similar cationic ligands have been deployed in heteroleptic Ru(II) complexes that show a very high affinity for DNA (via intercalation) and subsequent *in vitro* activity in antitumor experiments.[[26]](#endnote-26)

An additional aim of the current work on polycationic Ru(II) complexes was to investigate whether such species could be used as sensitizers of trivalent lanthanide excited states. In that context, it is now two decades since transition metal complexes were first demonstrated[[27]](#endnote-27) to be viable chromophores for sensitized lanthanide luminescence. In particular, MLCT species such as derivatives of the aforementioned [Ru(bipy)3]2+ can sensitize lanthanide ions (for example, Nd(III), Yb(III) and Er(III), all of which are near-IR emitters) which possess accepting excited states that are compatible with the donor 3MLCT energy level. Typically the lanthanide excited state is populated through energy transfer mechanisms.[[28]](#endnote-28) Generally, these mixed-metal, so-called d-f hybrids,[[29]](#endnote-29) have been obtained through covalently linked ditopic ligands,[[30]](#endnote-30) or self-assembly of complex components,[[31]](#endnote-31) including through supramolecular host-guest interactions.[[32]](#endnote-32) This current work now demonstrates that favorable electrostatic interactions in solution can be manipulated to promote energy transfer between polycationic Ru(II) and anionic Yb(III) complexes.

**Experimental Section**

1H, 13C{1H}NMR spectra were recorded on an NMR-FT Bruker 500 MHz and spectrometer and recorded in CDCl3, *,* acetonitrile-*d*3 and DMSO-*d6*. 1H and 13C{1H}NMR chemical shifts (*δ*) were determined relative to residual solvent peaks with digital locking and are given in ppm. Coupling constants are quoted in Hz. High-resolution mass spectra were obtained at Cardiff University. UV-Vis studies were performed on a Shimadzu UV-1800 spectrophotometer as MeCN solutions (1 × 10-5 M). Photophysical data were obtained on a JobinYvon–Horiba Fluorolog spectrometer fitted with a JY TBX picosecond photodetection module. A Hamamatsu R5509-73 detector (cooled to -80 ◦C using a C9940 housing) was used for near-IR measurements. Luminescence lifetime profiles were obtained using the JobinYvon–Horiba FluoroHub single photon counting module and the data fits yielded the lifetime values using the provided DAS6 deconvolution software. The pulsed source was a Nano-LED configured for 295 nm output operating at 1 MHz; for the near-IR Yb(III) lifetimes the pulsed laser source was a Continuum Minilite Nd:YAG configured for 355 nm output. Quantum yield measurements were obtained using comparative actinometry on aerated MeCN solutions of the complexes using [Ru(bpy)3](PF6)2 in aerated MeCN as a standard (*Φ* = 0.018).[[33]](#endnote-33)

**Cyclic voltammetry**

Cyclic voltammetry was performed using a PalmSens4 potentiostat. Experiments were performed using HPLC grade CH2Cl2 with an analyte concentration of 1 mM at 293 K, using triply recrystallised [nBu4N][PF6] as the supporting electrolyte at 0.1 M concentration. A three-electrode setup was used, consisting of a platinum disc working electrode, a platinum wire counter-electrode and a silver wire pseudo-reference. Solutions were spared for 10 minutes with CH2Cl2 saturated stream of nitrogen gas. Voltammograms were referenced to the ferrocene/ferrocenium redox couple measured using the same conditions.

**Computational methods**

Electronic structure calculations were performed using density functional theory within the Gaussian 09 computational chemistry suite.[[34]](#endnote-34) All calculations were performed with the Stuttgart-Dresden (SDD) effective core potential and basis set in the treatment of the iridium,[[35]](#endnote-35) in combination with a 6-31G\* basis set for all other light atoms.[[36]](#endnote-36) Geometry optimizations were performed for all cationic species, and minima were confirmed as stationary points through the computation of harmonic vibrational frequencies, each of which showed no imaginary components. These stationary points were used in single point TD-DFT calculations to compute vertical excitation energies. Calculations were performed on isolated complexes without implicit solvent due to substantial difficulties in converging both the SCF and geometry optimisation components of the higher charge complexes through the SCRF formalisation.

Phosphorescence and spin-forbidden absorption band positions are estimated using triplet inclusive TD-DFT calculations. Decomposition of the molecular orbital character was performed using the GaussSum software package. [[37]](#endnote-37)

**X-ray crystallography**

**Data collection and processing**

A suitable crystal was selected and mounted on a nylon loop with Fomblin oil and placed on a Rigaku Oxford Diffraction SuperNova diffractometer with a dual source (Cu at zero) equipped with an AtlasS2 CCD area detector at 293(2) K. The crystal was kept at a steady *T* = 293(2) K during data collection. The structure was solved with the ShelXT[[38]](#endnote-38) structure solution program using the Intrinsic Phasing solution method and by using Olex2[[39]](#endnote-39) as the graphical interface. The model was refined with ShelXL[[40]](#endnote-40) using Least Squares minimisation. CCDC 2250505 contains supplementary X-ray crystallographic data for [Ru(bipy)2(**L2**)][PF6]4. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/data\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)., or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge, CB2 1EZ; fax(+44) 1223-336-033 or email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

**Synthesis of the Ligands**

**Synthesis of** **3-([2,2'-bipyridin]-5-ylmethyl)-1-methyl-1H-imidazol-3-ium chloride (L1)**

5-chloromethyl-2,2’-bipyridine (800 mg, 3.91 mmol, 1.0 eq.) was dissolved in 1-methylimidazole (24 mL) and heated under N2 at 100 °C for 3 hours. The reaction was cooled to ambient temperature and Et2O (72 mL) was added. The mixture was cooled to 4 °C for 18 hours, filtered, and washed with Et2O (2 × 10 ml) and dried *in vacuo* to obtain the compound as a hygroscopic deliquescent off-white solid (0.870 g, 3.03 mmol, 78%). 1H NMR spectrum (500 MHz, 293 K, CD3OD): 9.17 (s, 1H, ImH, 97% deuterated in CD3OD), 8.78 (s, 1H, bipyH), 8.66 (d, 3*J*HH = 4.7, 1H, bipyH), 8.38 (d, 3*J*HH = 8.4, 1H, bipyH), 8.36 (d, 3*J*HH = 8.0, 1H, bipyH), 8.02 (d, 3*J*HH = 8.2, 4*J*HH =2.2, 1H, bipyH), 7.94 (app. t, *J*HH = 7.7, 1H, bipyH), 7.75 (s, 1H, ImH), 7.65 (s, 1H, ImH), 7.47 – 7.34 (m, 1H, bipyH), 5.60 (s, 2H, ArCH2), 3.97 (s, 3H, NCH3); 13C{1H} NMR spectrum (126 MHz, 293 K, CD3OD): 157.9 (s, bipy), 156.5 (s, bipy), 156.4 (s, bipy), 150.4 (s, bipy), 138.8 (s, bipy)138.7 (s, bipy), 138.1 (t, 1*J*CD = 34, Im - deuterated), 131.6 (s, bipy), 125.7 (s, bipy), 125.5 (s, Im), 123.7 (s, Im), 122.7 (s, bipy), 122.6 (s, bipy), 51.2 (s, ArCH2), 36.7 (s, NCH3), only the deuterated imidazolium resonance observed. ESI-MS *m/z* calcd. for [C15H15N4]+ 251.1297 found 251.1301. IR (ATR): νmax 3382, 3069, 2943, 2859, 1574, 1460, 1177, 1024, 847 cm-1.

**Synthesis of 3,3'-([2,2'-bipyridine]-5,5'-diylbis(methylene))bis(1-methyl-1H-imidazol-3-ium) dichloride (L2)**

5,5’-bischloromethyl-2,2’-bipyridine (870 mg, 3.44 mmol, 1.0 eq.) was dissolved in 1-methylimidazole (30 mL) and heated to 100 °C for 18 hours. The reaction was cooled to ambient temperature and Et2O (90 mL) was added. The reaction was stirred for 10 minutes, filtered, and the solid washed with Et2O (2 × 60 mL) to obtain the product as a hygroscopic off-white solid (1.43 g, 0.34 mmol, >99%). 1H NMR spectrum (500 MHz, 293 K, CD3OD): 9.14 – 9.11 (m, 2H, ImH, 25% deuterated), 8.80 – 8.75 (m, 2H, bipyH), 8.46 (dd, 3*J*HH = 8.2, 4*J*HH = 0.8, 2H, bipyH), 8.04 – 7.99 (m, 2H, bipyH), 7.73 (app.t, *J*HH = 1.9, 2H, ImH), 7.64 (app.t, *J*HH = 1.9, 2H, ImH), 5.58 (s, 4H, ArCH2), 3.96 (s, 6H, NCH3); 13C{1H} NMR spectrum (126 MHz, 293 K, CD3OD): 156.9 (s, bipy), 150.6 (s, bipy), 139.0 (s, bipy), 138.7 – 137.9 (m, Im- deuterated), 137.5 (s, Im – non-detuerated), 132.1 (s, bipy), 125.5 (s, Im), 123.6 (s, Im), 122.6 (s, bipy), 51.1(s, ArCH2), 36.8 (NCH3) ppm. ESI-MS *m/z* calcd. for [C20H22N6]+ 381.1595 found 381.1590. IR (ATR): νmax 3354, 3055, 2945, 2858, 1576, 1557, 1454, 1174, 1024, 785 cm-1.

**Synthesis of the Complexes**

**Synthesis of [Ru(bipy)2(L1)][PF6]3**

A Schlenk flask was charged with 3,3'-([2,2'-bipyridine]-5,5'-diylbis(methylene))bis(1-methyl-1H-imidazol-3-ium) dichloride (103.5 mg, 0.248 mmol, 1.05 eq.) and [Ru(bipy)2Cl2] (114.4 mg, 0.236 mmol, 1.0 eq.) under N2. Ethylene glycol (2 mL) was added and the solvent was sparged with N2 for 15 minutes. The reaction was heated to reflux for three hours after which time the reaction was cooled and NH4PF6(aq) (0.1 M, 10 ml) was added. The solid was filtered and the crude material purified by column chromatography (SiO2; MeCN/H2O/sat. KNO3(aq); 14:2:1 → 20:2:1). The organic solvent was removed and the product precipitated *via* the addition of NH4PF6(aq) (0.1 M, 10 ml). The solid was filtered and washed with H2O (2 × 2 mL) and dried to give the title compound as a red solid (132 mg, 0.098 mmol, 60%). 1H NMR spectrum (500 MHz, 293 K, CD3CN): 8.55-8.47 (m, 6H, bipyH), 8.43-8.40 (m, 1H, ImH), 8.11-8.02 (m, 6H, bipyH), 7.92 (dd, 3*J*HH = 8.4, 4*J*HH = 2.1, 1H, bipyH), 7.78 (ddt, 3*J*HH = 5.5, 4*J*HH = 1.5, 0.7, 1H, bipyH), 7.76-7.67 (m, 4H, bipyH), 7.52 (m, 1H, bipyH), 7.45-7.38 (m, 5H, bipyH), 5.29 (d, 2*J*HH = 16.0, 1H, ArCH2), 5.24 (d, 2*J*HH = 16.0, 1H, ArCH2), 3.83 (s, 3H, ImCH3); 13C{1H} NMR spectrum (126 MHz, 293 K, CD3CN): 158.3 (s, bipy), 158.0 (s, bipy), 158.0 (s, bipy), 157.4 (s, bipy), 153.0 (s, bipy), 153.0 (s, bipy), 152.9 (s, bipy), 152.8 (s, bipy), 152.7 (s, bipy), 152.6 (s, bipy), 151.4 (s, bipy), 138.9 (s, bipy), 138.9 (s, bipy), 138.9 (s, bipy), 138.8 (s, bipy), 138.0 (s, bipy),137.9 (s, Im), 135.1 (s, bipy), 128.9 (s, bipy), 128.6 (s, bipy), 128.6 (s, bipy), 125.8 (s, Im), 125.4 (s, bipy), 125.4 (s, Im), 125.3 (s, bipy), 125.3 (s, bipy), 125.2 (s, bipy), 123.5 (s, bipy), 118.4 (s, bipy), 50.2 (s, ArCH2), 37.1 (s, ImCH3) ppm. ESI-MS *m/z* calcd. for [C35H31F12N8P2Ru]+ 955.1008 found 955.1010. IR (ATR): νmax 1466, 1445, 758, 729, 648, 623, 556, 419 cm-1.

**Synthesis of [Ru(bipy)2(L2)][PF6]4**

A Schlenk flask was charged with 3-([2,2'-bipyridin]-5-ylmethyl)-1-methyl-1H-imidazol-3-ium chloride (34.7 mg, 0.121 mmol, 1.05 eq.) and [Ru(bipy)2Cl2] (55.8 mg, 0.115 mmol, 1.0 eq.) under N2. Ethylene glycol (1 mL) was added and the solvent was sparged with N2 for 15 minutes. The reaction was heated to reflux for three hours after which time the reaction was cooled and NH4PF6(aq) (0.1 M, 10 ml) was added. The solid was filtered and the crude material purified by column chromatography (SiO2; MeCN/H2O/sat. KNO3(aq); 14:2:1). The organic solvent was removed *in vacuo* and the product precipitated *via* the addition of NH4PF6(aq) (0.1 M, 10 ml). The solid was filtered and washed with H2O (2 × 2 mL) and dried to give the title compound as a red solid (76 mg, 0.069 mmol, 42%). 1H NMR spectrum (500 MHz, 293 K, CD3CN): 8.55 – 8.45 (m, 6H, bipyH), 8.38 (s, 2H, ImH), 8.11-8.05 (m, 4H, bipyH), 7.91 (dd, 3*J*HH = 8.5, 4*J*HH =2.0, 2H, bipyH), 7.72 (ddd, 3*J*HH = 5.6, 4*J*HH = 1.5, 0.7, 2H, bipyH), 7.65 (ddd, 3*J*HH = 5.6, 4*J*HH = 1.5, 0.7, 2H), 7.53 – 7.48 (m, 2H, bipyH), 7.43 (ddd, 3*J*HH = 7.7, 5.6, 4*J*HH =1.3, 2H), 7.39 (ddd, 3*J*HH = 7.7, 5.6, 4*J*HH = 1.3, 2H), 7.34 (app.t, *J*app = 1.8, 2H, ImH), 7.20 (app.t, *J*app = 1.9, 2H, ImH), 5.27 (d, 2*J*HH = 16.3, 2H, ArCHH), 5.23 (d, 2*J*HH = 16.3, 2H, ArCHH), 3.82 (s, 6H, ImCH3); 13C{1H} NMR spectrum (126 MHz, 293 K, CD3CN) 157.9 (s, bipy), 157.9 (s, bipy), 157.7 (s, bipy), 152.9 (s, bipy), 152.7 (s, bipy), 151.5 (s, bipy), 139.0 (s, bipy), 138.9 (s, bipy), 138.0 (s, bipy), 137.9 (s, Im), 135.4 (s, bipy), 128.7 (s, bipy), 128.6 (s, bipy), 125.6 (s, bipy), 125.4 (s, Im), 125.3 (s, bipy), 123.5 (s, Im), 50.2 (s, ArCH2), 37.1 (s, ImCH3) ppm. ESI-MS *m/z* calcd. for [C40H38N10Ru]+ 190.0584 found 190.0583. IR (ATR): νmax 1466, 1446, 1167, 759, 642, 623, 556, 470, 419 cm-1.

**Synthesis of [Ru(L2)2Cl2]Cl4**

A Schlenk flask was charged with [Ru(DMSO)4Cl2] (69.7 mg, 0.144 mmol, 1.0 eq.), LiCl (48.8 mg, 1.15 mmol, 8.0 eq.) and 3-([2,2'-bipyridin]-5-ylmethyl)-1-methyl-1H-imidazol-3-ium chloride (120 mg, 0.288 mmol, 2.0 eq.) under N2. EtOH (10 mL) was added and the solution sparged with N2 for 15 minutes. The reaction was heated to reflux for 18 hours after which time it was cooled and the solvent removed *in vacuo*. The crude material was purified by column chromatography (Al2O3; acetone/H2O; 100:0→50:50) and the solvent removed *in vacuo* to give the title compound as a purple solid (20 mg, 0.020 mmol, 14%). 1H NMR spectrum (300 MHz, 293 K, CD3OD) 9.89 (d, 4*J*HH = 2.0, 2H, bipyH), 8.66 (d, 3*J*HH = 8.6, 2H, bipyH), 8.50 (d, 3*J*HH = 8.4, 2H, bipyH), 8.13 (dd, 3*J*HH = 8.4, 4*J*HH = 2.1, 1H, bipyH), 7.91 (d, 3*J*HH = 2.0, 2H, ImH), 7.85 (d, 3*J*HH = 1.8, 2H, ImH), 7.73 (dd, 3*J*HH = 8.5, 4*J*HH = 2.0, 2H, bipyH), 7.69 (d, 3*J*HH = 2.0, 2H, ImH), 7.61 (d, 3*J*HH = 2.0, 2H, ImH), 7.56 (d, 3*J*HH = 2.0, 2H. ImH), 5.85 (d, 2*J*HH = 15.4, 2H, ArCH2), 5.76 (d, 2*J*HH = 15.4, 2H, ArCH2), 5.39 (s, 4H, ArCH2), 3.99 (s, 6H, ImCH3), 3.92 (s, 6H, ImCH3). Remaining imidazolium N-CH-N protons undetected due to deuteration. 13C{1H} NMR spectrum (126 MHz, 293 K, CD3OD): 161.8 (s, bipy), 159.9 (s, bipy), 154.0 (s, bipy), 153.7 (s, bipy), 139.0-137.9 (m, ImCD, deuterated) 136.7 (s, bipy), 135.6 (s, bipy), 125.5 (s, Im), 125.4 (s, Im), 124.9 (s, bipy), 124.7 (s, bipy), 124.2 (s, Im), 123.8 (s, Im), 51.2 (s, ArCH2), 50.2 (s, ArCH2), 36.9 (s, ImCH3), 36.8 (s, ImCH3) ppm. ESI-MS *m/z* calcd. for [C40H44Cl2N12Ru]4+ 216.0559 found 216.0572.

**Synthesis of [Ru(bipy)(L2)2][PF6]6**

A Schlenk flask was charged with [Ru(bipy)(*p*-cymene)Cl]Cl (54.5 mg, 0.114 mmol, 1.0 eq.) and 3-([2,2'-bipyridin]-5-ylmethyl)-1-methyl-1H-imidazol-3-ium chloride (100 mg, 0.239 mmol, 2.1 eq.) under N2. 2-ethoxyethanol (1 mL) was added and the reaction sparged with N2 for 15 minutes. The reaction was heated to reflux for 48 hours after which time the reaction was cooled and the compound precipitated *via* the addition of NH4PF6(aq) (0.1 M, 10 mL). The solid was filtered and washed with H2O ( 2× 5 ml). The crud mixture was purified by column chromatography (SiO2; MeCN/H2O/sat. KNO3(aq); 14:2:1→9:10:1). The organic solvent was removed *in vacuo* and the compound precipitated *via* the addition of NH4PF6(aq) (0.1 M, 10 mL). The solid was filtered and washed with H2O (2 × 5 mL) and dried *in vacuo* to give the title compound as a red solid (75 mg, 0.041 mmol, 36%). 1H NMR spectrum (500 MHz, 293 K, CD3CN) 8.54 – 8.49 (m, 4H, bipyH), 8.46 (dt, 3*J*HH = 8.1, 4*J*HH = 1.1, 2H), 8.44 – 8.40 (m, 2H, ImH), 8.37 (m, 2H, ImH), 8.10 (app.td, *J*app = 7.9, 4*J*HH = 1.5, 2H, bipyH), 7.89 (dd, 3*J*HH = 8.6, 4*J*HH = 1.9, 2H, bipyH), 7.85 (dd, 3*J*HH = 8.5, 4*J*HH = 2.0, 2H, bipyH), 7.69 – 7.66 (m, 2H, bipyH), 7.64 – 7.61 (m, 2H, bipyH), 7.52 – 7.50 (m, 2H, bipyH), 7.43 – 7.40 (m, 2H, bipyH), 7.39 (app.t, *J*app = 1.7, 2H, ImH), 7.36 (app.t, *J*app = 1.7, 2H, ImH), 5.26 (d, 2*J*HH = 16.1, 2H, ArCHH), 5.25 (s, 4H, ArCH2), 5.23 (d, 2*J*HH = 16.2, 2H, ArCHH), 3.85 (s, 6H, ImCH2), 3.83 (s, 6H, ImCH2); 13C{1H} NMR spectrum (126 MHz, 293 K, CD3CN) 157.6 (s, bipy), 157.6 (s, bipy), 157.5 (s, bipy), 153.0 (s, bipy), 151.9 (s, bipy), 151.5 (s, bipy), 139.0 (s, bipy),138.1 (s, bipy),137.9 (s, bipy),137.8 (s, Im),135.3 (s, bipy), 135.2 (s, bipy),128.7 (s, bipy), 125.7 (s, bipy), 125.5 (s, bipy), 125.3 (s, Im), 125.3 (s, Im), 125.2 (s, bipy), 123.4 (s, Im), 123.3 (s, Im), 50.1 (s, bipy), 50.0 (s, ArCH2), 50.0 (s, ArCH2), 36.7 (s, ImCH3) ppm. ESI-MS *m/z* calcd. for [C50H52F24N14P4Ru]2+ 765.1061 found 765.1061. IR (ATR): νmax 3169, 3125, 2349, 2326, 1604, 1577, 1566, 1467, 446, 1425, 1400, 1160, 760, 741, 731, 669, 648, 623, 516 cm-1.

**Synthesis of [Ru(L2)3][PF6]8**

A Schlenk flask was charged with [Ru(DMSO)4Cl2] (38.7 mg, 0.080 mmol, 1.0 eq.) and and 3-([2,2'-bipyridin]-5-ylmethyl)-1-methyl-1H-imidazol-3-ium chloride (100 mg, 0.240 mmol, 3.0 eq.) under N2. Ethylene glycol (2 mL) was added and the reaction sparged with N2 for 15 minutes. The reaction was refluxed for three hours after which time the reaction was cooled and the product precipitated as an oil *via* dropwise addition to stirring THF (100 mL). The solution was decanted and the product co-evaporated with MeOH (2 × 5 mL). The compound was purified by column chromatography (Al2O3; acetone/H2O; 100:0→50:50). The solvent was removed *in vacuo* and the oil redissolved in H2O (3 mL) and precipitated *via* the addition of NH4PF6(aq) (0.1 M, 3 mL). The solid was filtered and dried *in vacuo* to give the title compound as an orange solid (54 mg, 0.023 mmol, 31%).1H NMR spectrum (500 MHz, 293 K, CD3CN) 8.48 (d, 3*J*HH = 8.5, 6H, bipyH), 8.43 (br. s, 6H, ImH), 7.82 7.82 (dd, 3*J*HH = 8.5, 3*J*HH =2.0, 6H, bipyH), 7.63 (d, 3*J*HH = 2.0, 6H, bipyH), 7.39 (app. t, *J*HH = 1.8, 7H, ImH), 7.20 (app. t, *J*HH = 1.9, 6H, ImH), 5.25 (s, 12H, ArCH2), 3.84 (s, 18H, ImCH3); 13C{1H} NMR spectrum (126 MHz, 293 K, D2O; conducted on [Ru(L2)3]Cl8 due to solubility reasons); 156.2 (s, bipy), 151.1 (s, bipy), 137.2 (s, Im), 124.7 (s, bipy), 124.5 (s, Im), 122.6 (s, Im), 49.4 (s, ArCH2), 36.4 (s, ImCH3) ppm. ESI-MS *m/z* calcd. for [C60H64N18RuP6F36]2+ 1005.1314 found 1005.1326. IR (ATR): νmax 3169, 3126, 2349, 2324, 1664, 1578, 1564, 1477, 1446, 1425, 1400, 1167, 740, 671, 623, 470 cm-1.

**Results and Discussion**

**Synthesis**

The cationic bipy targets were chosen because they contained one or two imidazolium groups at the 5- and 5’-positions of the diimine. Therefore the precursors 5-chloromethyl-2,2’-bipyridine and 5,5’-bis-chloromethyl-2,2’-bipyridine were synthesized according to previously reported procedures (*via* the carboxylic acid, ester, and methyl alcohol intermediates; **Section S2.1**).[[41]](#endnote-41) The final ligands were obtained from alkylation of the chloromethyl derivatives using *N*-methylimidazole as reagent and solvent to give the target mono- and di-cationic analogues, **L1** and **L2**,[[42]](#endnote-42) in 78% and >99% yield respectively (**Scheme 1**). All experimental and characterization details are presented in the Supporting Information.

Despite the ubiquity of [Ru(bipy)3]2+ analogues and their syntheses in the literature,[[43]](#endnote-43) the application of relatively standard complexation procedures in our hands (*viz.* refluxing EtOH/H2O mixtures) did not give satisfactory outcomes with the cationic ligands **L1** and **L2**, resulting in incomplete complexation despite extended reaction times. This is presumably due to unfavorable electrostatic repulsion between the incoming ligands and the electropositive ruthenium center. Consequently, more forcing conditions were employed, for example using refluxing ethylene glycol as solvent. Application of this protocol to the formation of the tri-cationic and tetra-cationic complexes resulted in complete complexation within three hours, with no evidence of decomposition.

##### **Scheme 1.** Synthetic routes to the family of homologous polycationic ruthenium(II) bipyridine complexes.

After purification by column chromatography on SiO2 and anion exchange, [Ru(bipy)2(**L1**)][PF6]3, which has been previously reported and investigated in cell imaging studies,[[44]](#endnote-44) and [Ru(bipy)2(**L2**)][PF6]4 were afforded in yields of 60% and 40%, respectively. The synthesis of the hexa-cationic derivative [Ru(bipy)(**L2**)2][PF6]6 was attempted using a previously utilized two-step route *via* a [Ru(**L2**)2Cl2]Cl4 intermediate (**Scheme 2**). In this case, complexation was achieved using refluxing dimethylformamide (DMF) in the presence of excess LiCl to inhibit the formation of the tris-homoleptic [Ru(**L2**)3]8+ by-product.[[45]](#endnote-45) After chromatographic purification the target compound was isolated, albeit in low yield (14%) and the paucity of isolated compound precluded its use in the next synthetic step.



##### **Scheme 2.** Attempted synthesis of the intermediate species [Ru(**L2**)2Cl2]Cl4.

Therefore, an alternative procedure adapted from Meyer 25 was employed to promote the formation of the desired compound. Reaction of [Ru(*p*-cymene)(bipy)Cl]Cl with ligand **L2** in refluxing ethylene glycol resulted in the total consumption of starting materials, but with the formation of several products (as indicated by 1H NMR spectroscopy), which was ascribed to ligand scrambling and thus related complexes of the general formula [Ru(bipy)x(**L2**)3-x]. Conversely, reaction at 120 °C in ethylene glycol resulted in an incomplete reaction, even with extended reaction times. Gratifyingly the reaction of [Ru(*p*-cymene)(bipy)Cl]Cl with ligand **L2** in refluxing 2-ethoxyethanol produced a single species after 48 hours, with no evidence of ligand scrambling at ruthenium. After chromatography on silica and anion exchange, hexa-cationic [Ru(bipy)(**L2**)2][PF6]6 was isolated in 36% yield. The modest yields of the aforementioned complexes progressively decrease as a function of increasing charge which may be attributed to their elevated affinities to the stationary phase during chromatographic purification. Finally, the synthesis of [Ru(**L2**)3][PF6]8 was achieved using [Ru(DMSO)4Cl2] as a starting material and three equivalents of **L2** in refluxing ethylene glycol. In this case the product was purified by column chromatography of the crude [Ru(**L2**)3]Cl8using Al2O3 - due to the high affinity of the octa-cationic homologue when utilising silica– and anion exchanged thereafter to obtain [Ru(**L2**)3][PF6]8in 31% yield. The isolation of this final complex matches the record for the most highly charged mononuclear Ru(II) complex reported in the literature.25

The complexes were fully characterized using 1D and 2D NMR (298 K, CD3CN) spectroscopy (1H (**Figure 1**), 13C, COSY, HSQC, HMBC, ROESY) and mass spectrometry (**Figure S17-S32**). Complex [Ru(bipy)2(**L1**)][PF6]3exhibits *C*1 symmetry, resulting in the inequivalence of all bipyridine ligands, giving a total of six discrete pyridine moieties. The tetra- and hexa-cationic complexes [Ru(bipy)2(**L2**)][PF6]4 and [Ru(bipy)(**L2**)2][PF6]6both display time-averaged *C*2 symmetry in solution. In the case of the tetra-cationic derivative the X’ notation denotes the pyridine fragment which is closest to the imidazolium functionalized ligand as determined using through-space 1H-1H correlation. Unfortunately the highly second-order spectrum of [Ru(bipy)(**L2**)2][PF6]6 prevented absolute assignment of the unsymmetrical **L2** ligand. In the octa-cationic congener [Ru(**L2**)3][PF6]8 we observed a time-averaged *C*3 species, in agreement with the unfunctionalized parent [Ru(bipy)3][PF6]2. Other salient features of the 1H NMR spectra are the methylenic C*H*2 imidazolium resonances, which – in contrast to the uncoordinated ligands **L1** and **L2** – exhibited diasterotopicity at 298 K. This probably arises from the complexation and thus steric interference from proximate ligand systems, although subtle effects of counteranion ion-pairing cannot be ruled out. Interestingly, in the case of [Ru(bipy)(**L2**)2][PF6]6, which displays inequivalence of the two halves of complexed **L2**, one C*H*2 resonance appears as a singlet corresponding to fast bond rotation on the NMR timescale, while the other is diastereotopic resulting from slow bond rotation. Due to the resolution of the 2D spectra (298 K, 600 MHz) it was not possible to identify each C*H*2 resonance.

A graph of a person's reaction

Description automatically generated**Figure 1.** Assignment of the 1H NMR spectra (500 MHz, 298 K, CD3CN) for the family of polycationic Ru(II) complexes.

**Single crystal X-ray crystallography**

Single crystals of [Ru(bipy)2(**L2**)][PF6]4suitable for single-crystal X-ray diffraction (SCXRD) analysis (**Figure 2**, **Table S33, Figure S34, 35**) were grown from cooling of a concentrated KNO3/NH4PF6 aqueous solution. The compound crystallized in the triclinic P-1 space group with two molecules and the eight hexafluorophosphate anions in the asymmetric unit, with no additional solvent present. The three-dimensional network is perpetuated by intermolecular C-H··F hydrogen bonding interactions between the fluorine atoms of the counter anions and polarized C-H bonds in the complex. Mirroring the solution-state behavior, complex [Ru(bipy)2(**L2**)][PF6]4displays pseudo-*C*2 symmetry with an *anti*- arrangement of the flanking methyl-imidazolium groups which hydrogen-bonds intramolecularly to two nested PF6- anions, with mean C···F distances of 3.191 Å to the most acidic imidazolium N-CH-N hydrogen. This is augmented by supplementary elongated interactions to the imidazolium CH3 groups ((C···F)mean = 3.617 Å) and adjacent unfunctionalized bipyridine ligands ((C···F)mean = 3.403 Å). The coordination geometry is largely unchanged from simple heteroleptic ruthenium diimine analogues, with mean Ru-Nbipy distances of 2.071 Å and Ru-NL2 distances of 2.066 Å (*cf*. [Ru(bipy)2(bipicoline)][PF6]2; (Ru-Nbipy)mean = 2.065 Å, (Ru-Nbipicoline)mean = 2.067 Å),19 indicating that introduction of the charged imidazolium groups does not significantly alter the ligand field strength of the resultant complex.

Diagram

Description automatically generated

**Figure 2.** X-ray crystal structure of the [Ru(bipy)2(**L2**)][PF6]4 complex (ellipsoids are plotted at the 50% probability level; non-H-bonding hydrogen atoms and counter ions omitted for clarity; CCDC no. 2250505)

**Electrochemistry**

The electrochemical properties of the family of polycationic ruthenium complexes was explored using cyclic voltammetry in MeCN solution at 1 mM concentration, using [nBu4N][PF6] as the supporting electrolyte (0.1 M) and the Fc/Fc+ redox couple as a reference (**Table 1**). All complexes exhibit quasi-reversible or reversible redox waves for both the oxidation and reduction potentials of the metal center and ligand sphere respectively (**Figure S36**). The principal features of the RuII/RuIII couple is the small variance of the tri- and tetra-cationic oxidation potentials (*E*0) ([Ru(bipy)2(**L1**)][PF6]3= +0.88 V, [Ru(bipy)2(**L2**)][PF6]4 = 0.91 V) compared to the unsubstituted parent [Ru(bipy)3][PF6]2 (+0.89 V), indicating only a small effect of the increase of peripheral charge in the second coordination sphere. For the more highly charged analogues an increased perturbation is observed, manifested by an increasingly facile one-electron reduction of the RuII center. For the hexa-cationic [Ru(bipy)(**L2**)2][PF6]6 complex *E*0 shifts to +0.83 V, while for the octa-cationic derivative [Ru(**L2**)3][PF6]8*E*0 = +0.80 V. Despite the increased facility of this oxidation process, qualitative observation of the voltammograms indicate that this process became less reversible traversing down the series, which can be reconciled by the decreased stability of the generated RuIII species in solution in close proximity to the multiple pendant cationic imidazolium moieties. Three distinct negative potentials were observed in all cases corresponding to bipyridine reduction of the tris homo- and heteroleptic complexes; imidazolium groups are known to be electrochemically inert within the redox potential window studied.20 Once again the reduction waves of [Ru(bipy)2(**L1**)][PF6]3and[Ru(bipy)2(**L2**)][PF6]4 largely resembleunsubstituted [Ru(bipy)3][PF6]2, while we observed the ligand reductions becoming more difficult in the highly charged [Ru(bipy)(**L2**)2][PF6]6and[Ru(**L2**)3][PF6]8 complexes. The ease of reduction (*cf.* [Ru(bipy)3][PF6]2) correlates with the overall charge state of the [Ru(bipy)(**L2**)2][PF6]6and[Ru(**L2**)3][PF6]8complexes (Δmean = -0.14 and Δmean = -0.21 respectively). The observation of more difficult ligand reduction potentials is consistent with the more facile RuII/RuIIIredox couples although this is counterintuitive since one might expect the inverse upon introducing multiple positive charges close to the metal center. We tentatively ascribe this behavior to the presence of the multiple ion-paired hexafluorophosphate anions which may stabilize the formation of RuIII and thus destabilize the reduction of the bipyridine ligands. Indeed, the magnitude of the shift of the redox process is larger for the ligand reduction potentials and can be rationalized in the relative distance from the charged imidazolium groups (*vide* *supra*; SCXRD). Ligand reduction, and its proximity to the imidazolium moieties, is more susceptible to inductive charged effects from the hexafluorophosphate anions which are ion-paired with the imidazolium groups, when compared to the RuII/RuIII oxidation.

**Table 1.** Electrochemical oxidation and reduction potentials of the family of complexes.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Complex** | **RuII/III** | **bipy0/-1** | **bipy-1/-2** | **bipy-2/-3** |
| [Ru(bipy)3][PF6]2 | 0.89(200) | -1.76(161) | -1.94(180) | -2.18(200) |
| [Ru(bipy)2(**L1**)][PF6]3 | 0.88 (120) | -1.75(100) | -1.94(113) | -2.20(115) |
| [Ru(bipy)2(**L2**)][PF6]4 | 0.91(120) | -1.71(130) | -1.93(100) | -2.21(130) |
| [Ru(bipy)(**L2**)2][PF6]6 | 0.83(160) | -1.83(140) | -2.08(220) | -2.34(203) |
| [Ru(**L2**)3][PF6]8 | 0.80(209) | -1.95(130) | -2.15(190) | -2.41(187) |

**Photophysical Properties of the Complexes**

The UV-vis. absorption data for all complexes was obtained in aerated acetonitrile and are presented in **Table 2** and **Figure 3**. The two notable regions are high intensity UV absorptions corresponding to allowed π→π\* transitions, and weaker absorptions in the visible region, around 450 nm, due to spin allowed 1MLCT absorptions. The tri- and tetra-cationic complexes displayed high energy absorptions at 288 nm (ε ≈ 82000 M-1 cm-1), which are comparable to that of [Ru(bipy)3][PF6]2. For the hexa-cationic complex this feature is slightly shifted to lower energy (294 nm), but with an increased molar absorptivity (88000 M-1 cm-1), while the octa-cationic derivative displays the same maximum but again with a concomitantly higher absorption coefficient (101300 M-1 cm-1). The 1MLCT transition displayed only a minor variation in the wavelength position (450 - 456 nm), with the associated molar absorptivity slightly decreasing down the series of complexes. The shape of the MLCT band envelope is consistent with previous descriptions that describe the vibronic progressions associated with the transition.[[46]](#endnote-46) These results demonstrate that the pendant imidazolium groups induce a small effect on the ground state absorption properties of the Ru(II) complexes.



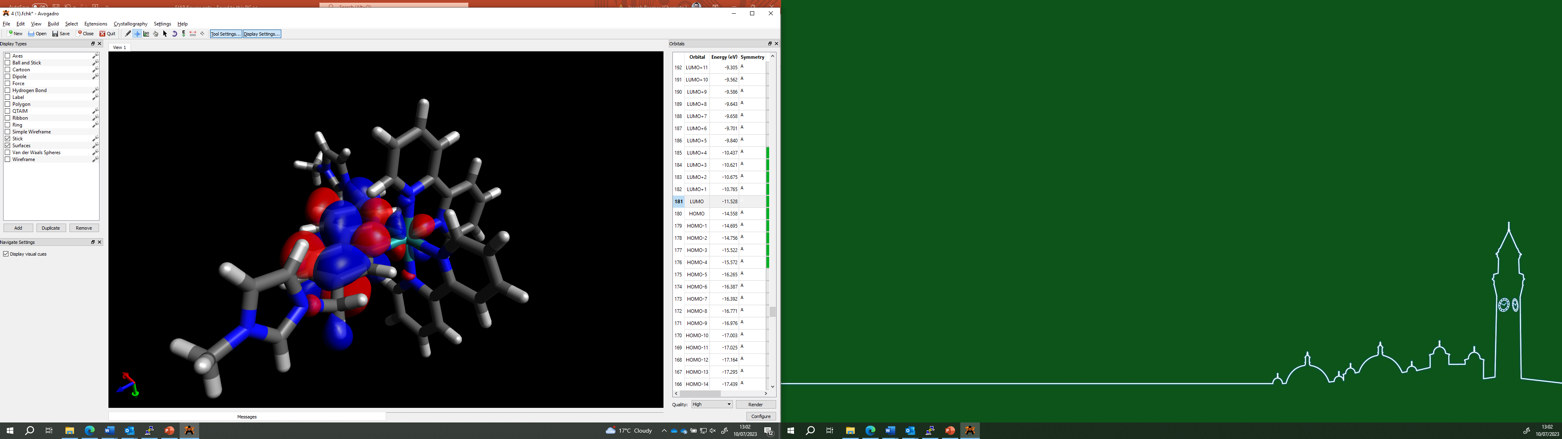
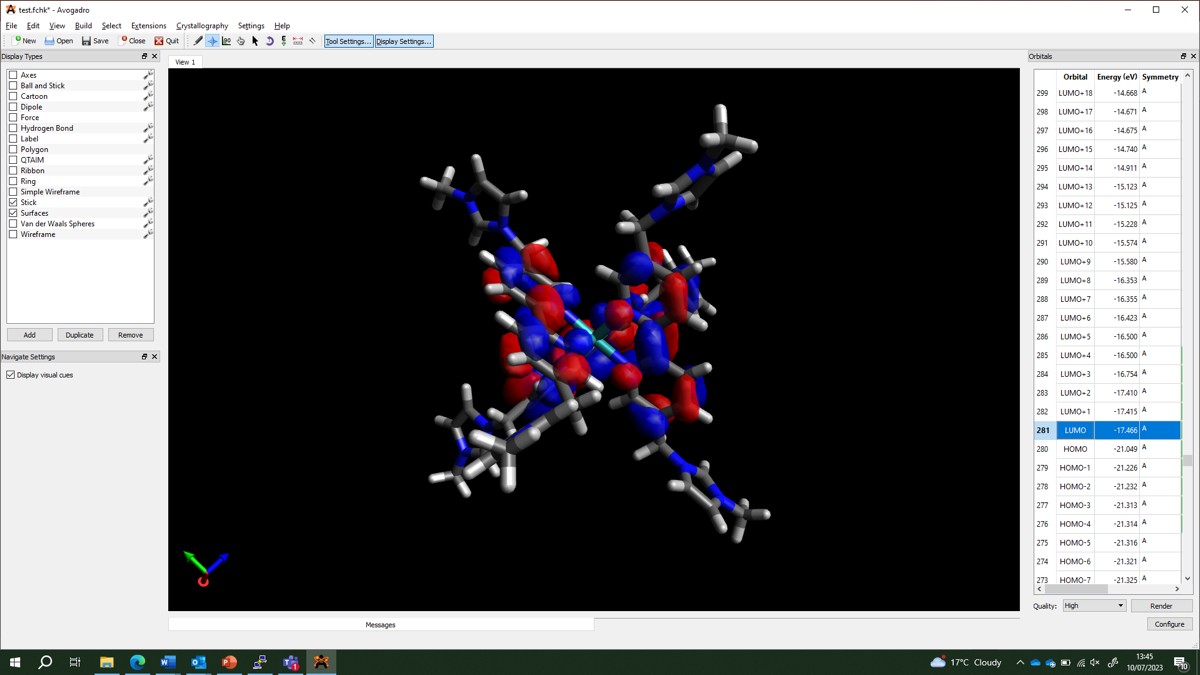
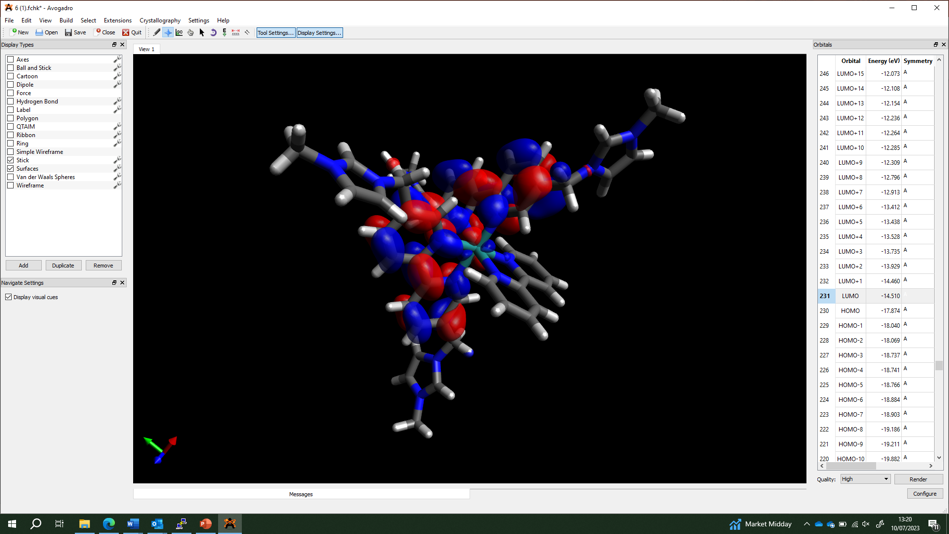
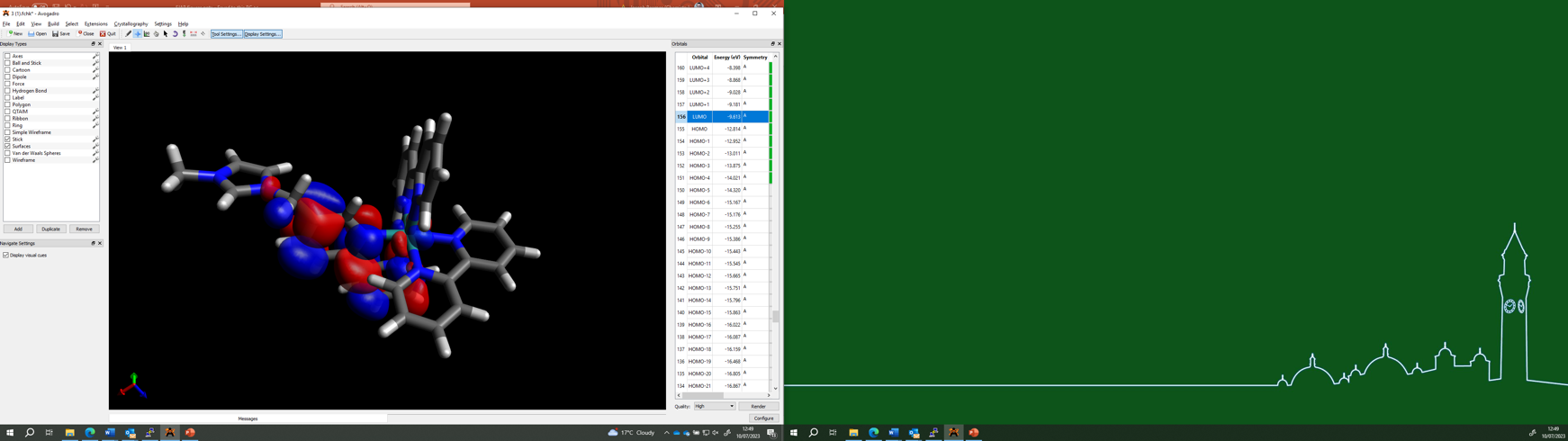
**Figure 3.** UV-vis. absorption spectra for the family of polycationic ruthenium complexes (MeCN).

The corresponding photoluminescence spectra of the complexes were initially recorded in aerated MeCN. All compounds were found to be luminescent upon excitation at 450 nm (*i.e*. directly into the 1MLCT absorption band), showing a broad featureless emission maxima at *ca*. 630 nm which clearly corresponds to 3MLCT emission. The effect of the imidazolium groups upon the excited state characteristics were found to be more pronounced than for ground state absorption (**Figure 4**). Introduction of one imidazolium group (*i.e.* [Ru(bipy)2(**L1**)][PF6]3) induced a bathochromic shift of 23 nm *vs*. unfunctionalized [Ru(bipy)3][PF6]2. This was also observed for the tetra-cationic [Ru(bipy)2(**L2**)][PF6]3complex (λem = 654 nm, ΔλMLCT = 44 nm), with the effect of the second imidazolium group being roughly additive. Strikingly, the hexa-cationic complex did not continue this trend (λem = 643 nm ΔλMLCT = 33 nm), displaying a relative hypsochromic shift *vs*. the tetra-cationic complex. Finally the emission maximum of [Ru(**L2**)3][PF6]8 (λem = 632 nm, ΔλMLCT = 21 nm) again shifted to higher energy.



**Figure 4.** Normalized emission spectra for the family of polycationic ruthenium complexes (293 K, aerated MeCN, 10-5 M).

In support of the acquisition of experimental data, supporting density functional theory (DFT) results showed that all of the transitions observed within the range 250 nm < l < 700 nm are predicted to be strongly MLCT in character (the calculated Kohn-Sham molecular orbitals are shown in **Tables S34-S41**). In all cases the transitions involved in the absorption bands observed within this window arise from occupied orbitals with 70% or greater Ru(4*d*) character, and with unoccupied character < 10% Ru(4*d*). TD-DFT calculations show a qualitative agreement with the luminescence band positions (**Tables S38-S42**), but they appear to greatly overpredict the wavelength shifts in the absorption band positions. However, the longest wavelength absorber/emitter is correctly predicted to be the [Ru(bipy)2(**L2**)]4+complex, seemingly due to a relative reduction in the energy of the LUMO.



**Figure 5.** Calculated Kohn-Sham LUMOs for (left to right) [Ru(bipy)2(**L1**)]3+ [Ru(bipy)2(**L2**)]4+ [Ru(bipy)(**L2**)2]6+ and [Ru(**L2**)3]6+.

In each complex the strongest transitions are predicted where there is significant HOMO-2/LUMO contributions and therefore the influence of the position of the LUMO is probably of great importance. For [Ru(bipy)2(**L1**)]3+ and[Ru(bipy)2(**L2**)]4+ the calculations predict that the LUMO is primarily localized on **L1**/**L2**. This is not surprising as this affords a more non-zero Franck-Condon factor with low lying **L1**/**L2**-centred unoccupied orbitals, particularly given the high localisation of many of the occupied orbitals on the metal centre. For complexes [Ru(bipy)(**L2**)2]6+ and[Ru(**L2**)3]8+ the LUMOs may become delocalized across the multiple **L2** ligands (**Figure 5**), perhaps explaining the trend noted in the experimental data.

Time-resolved photophysical measurements yielded the emission lifetimes, which increased down the series 218 to 362 ns (*cf*. 157 ns for [Ru(bipy)3][PF6]2) in aerated MeCN, possibly indicating that quenching in oxygenated solvent may be inhibited by increased the number of imidazolium moieties. Quantum yield (QY) measurements were also conducted in aerated MeCN, and also showed a break in behavior demonstrated by the λem data: in general the quantum yield reduced up to the tetra-cationic complex (Φ = 0.014) and thereafter recovered down the series to eventually surpass unfunctionalized [Ru(bipy)3][PF6]2 in the case of [Ru(**L2**)3][PF6]8(Φ = 0.021). The spectroscopic measurements were repeated under deoxygenated MeCN. Firstly, the lifetimes were increased in all cases emphasising the 3MLCT nature of the phosphorescence. The degassed lifetime and QY data now broadly replicates the same trend: a general reduction in values to [Ru(bipy)2(**L2**)][PF6]4and then a subsequent increase to [Ru(**L2**)3][PF6]8. To probe this further the relative rates of radiative and non-radiative decay were calculated and show that the values of non-radiative decay constant (*k*nr) correlate with the Energy Gap Law. Thus, the longest wavelength tetra-cationic emitter has the highest value of *k*nr.

**Table 2.** Absorption and photoluminescence data for the family of polycationic complexes.a,b

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Complex** | **λMLCT / nm (ε**  **/ M-1cm-1)** | **λem / nmc** | **τ / nsd** | **degas**  **τ / nsd** | **ΦRu** | **degas**  **ΦRu** | ***k*r / 104 s-1** | ***k*nr /105 s-1** |
| [Ru(bipy)3][PF6]2 | 450 (15,300) | 610 | 157 | 867 | 0.018[[47]](#endnote-47) | 0.09548 | - | - |
| [Ru(bipy)2(**L1**)][PF6]3 | 450 (14,000) | 633 | 218 | 907 | 0.017e | 0.069f | 0.76 | 10.3 |
| [Ru(bipy)2(**L2**)][PF6]4 | 452 (13,100) | 654 | 236 | 568 | 0.014e | 0.049f | 0.86 | 16.4 |
| [Ru(bipy)(**L2**)2][PF6]6 | 456 (12,300) | 643 | 331 | 744 | 0.018e | 0.041f | 0.55 | 12.9 |
| [Ru(**L2**)3][PF6]8 | 456 (12,500) | 632 | 362 | 841 | 0.021e | 0.054f | 0.64 | 11.2 |

a All measurements obtained in MeCN at 293 K. b 1 × 10-5 M. c λex = 450 nm. d observed lifetime, λex = 295 nm. e using [Ru(bipy)3][PF6]2 in aerated MeCN as a reference (Φ = 0.018).48 f using [Ru(bipy)3][PF6]2 in degassed MeCN as a reference (Φ = 0.095), errors are estimated at 15%.48 Estimates of *k*r and *k*nr using *k*r = Φ/τ and *k*nr = (1 − Φ)/τ.

Finally, we were interested in the potential utility of these polycationic Ru(II) complexes in further optoelectronic applications. Our hypothesis was that the increase in positive charge could be exploited in the electrostatic assembly of photoactive ion pairs. In particular, we hypothesized that the use of an anionic lanthanide complex might permit energy transfer from a Ru(II) based donor. Therefore, the polyanionic [Yb(dpa)3]3- (where dpa = pyridine-2,6-dicarboxylic acid) was identified as an ideal candidate. Initially 1H NMR studies were undertaken whereby [Yb(dpa)3]3- was added to a solution of [Ru(bipy)2(**L2**)]4+ in 0.1 M KNO3 D2O solution (**Figure S37**). Addition of the paramagnetic Yb(III) complex induced small perturbations (Δδ < 0.2 ppm) of the bipyridine resonances of [Ru(bipy)2(**L2**)]4+, although their broad nature precludes absolute assignment. More strikingly the peripheral methylenic and methyl resonances exhibit broadening and downfield shifts of 1.09 ppm and 0.68 ppm respectively, indicating interactions between the two complex units.

Photoluminescent studies were then undertaken to probe the photophysical attributes of the solution mixture. Firstly, an aerated D2O solution of the parent unfunctionalized [Ru(bipy)3]2+ was measured in the presence of 2 eq. [Yb(dpa)3]3-. An excitation wavelength of 450 nm was used and is selective for the 1MLCT band of the Ru(II) complex (note [Yb(dpa)3]3- does not absorb > 320 nm). No characteristic signal for Yb(III)-based emission was noted with only the weak tail of the 3MLCT band evident in the NIR window. We repeated the experiment using [Ru(bipy)2(**L2**)]4+ which was chosen due to its high charge and also its significantly red-shifted 3MLCT emission wavelength when compared to [Ru(bipy)3]2+ (654 nm *vs*. 610 nm). Utilizing the more highly cationic [Ru(bipy)2(**L2**)]4+ produced a remarkably different result: the characteristic emission profile of Yb(III) was immediately evident with a strong structured emission ca. 980 nm with a shoulder at 1020 nm corresponding to the Stark-split sublevels of the 2F5/2 → 2F7/2 transition (**Figure 6**). From the baseline profile it is clear that the Yb(III) emission is superimposed upon the low energy tail of the 3MLCT band. Further time-resolved NIR measurements (λem = 980 nm) revealed a decay profile that fitted well to a biexponential function giving two distinct lifetime values of 0.3 and 21.9 μs (**Figure 6**). Since [Yb(dpa)3]3- has a reported lifetime of 39 μs in D2O,[[48]](#endnote-48) the obtained values are attributed to the co-emission of the residual 3MLCT signal and the Yb-centered emission, respectively. Therefore, these measurements establish that Ru→Yb energy transfer, which we assume proceeds via a Förster mechanism, must be feasible in electrostatically assembled mixtures of ion-paired complexes in solution. Given that this behavior was not observed for [Ru(bipy)3]2+ the presence of additional charge and/or pendant hydrogen-bonding interactions may be vital in the observation of Ru→Yb energy transfer.



**Figure 6.** A comparison of the NIR emission spectra of [Ru(bipy)3]2+ (orange) and [Ru(bipy)2(**L2**)]4+ (blue) solutions in the presence of 2 eq. [Yb(dpa)3]3- (293 K, aerated D2O, 10-5 M Ru(II) complex, λex = 450 nm). Fitted decay (residual errors shown) for [Ru(bipy)2(**L2**)]4+ in the presence of 2 eq. [Yb(dpa)3]3- (293 K, aerated D2O, 10-5 M, λex = 355 nm, λem = 980 nm). The obtained lifetimes were 0.3 μs (31 % relative weighting) and 21.9 μs (69 %). The proposed photophysical pathways are shown inset.

**Conclusion**

This study has shown that a variety of synthetic approaches can be employed to isolate a series of cationic Ru(II) polypyridine-type complexes with overall charges systematically varying from +2 to +8; the octa-cationic complexes matches the highest reported magnitude of charge in the literature for Ru(II) species. Each of the complexes was demonstrated to be luminescent from a 3MLCT emitting state (610-654 nm). The interesting trend in λem shows a maximum value for the +4 species before hypsochromically shifting for +6 and +8, which may indicate the shielding effects of ion pairing in solution; degassed lifetime and quantum yield measurements support this trend. The solution state photophysical utility of polycationic Ru(II) complexes was exploited in experiments using a polyanionic Yb(III) complex. These studies show that energy transfer and subsequent sensitization of the Yb(III) excited state is possible in free solution resulting in NIR emission from Yb(III). This implies that electrostatically driven ion pairing (perhaps supported by H-bonding interactions) is possible in solution and can be used to facilitate photophysical phenomena such as through space energy transfer mechanisms.

More broadly, the development of mixed ligand complexes of Ru(II) and the study of localized versus delocalized excited states may have importance in areas of study focused upon ultrafast electron injection at semi-conductor interfaces as noted elsewhere. An investigation of inter-ligand electron transfer (electron hopping) within excited state polycationic Ru(II) species could be particularly relevant.

**Acknowledgments**

Financial support is gratefully acknowledged from the Leverhulme Trust (RPG-2021-003). We acknowledge the use of the EPSRC funded Physical Sciences Data-science Service hosted by the University of Southampton and STFC under grant number EP/S020357/1.

**Supporting Information**

Supporting Information: 1H and 13C NMR, and ESI-HRMS spectra for ligands and corresponding complexes; Single-crystal X-ray crystallography; Cyclic Voltammetry;

and Density Functional Theory

**Associated Content**

CCDC 2250505 contains supplementary X-ray crystallographic data for [Ru(bipy)2(**L2**)][PF6]4. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/data\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

**Author Information**

**Corresponding Author**

E-mail: [popesj@cardiff.ac.uk](mailto:popesj@cardiff.ac.uk)

ORCID

Present Address

S.J.A.P.: School of Chemistry, Main Building, Cardiff University, Wales, UK CF10 3AT.

Notes

The authors declare no competing financial interest.

Table of Contents ONLY



TOC text

Heteroleptic Ru(II) complexes based upon methyl imidazolium functionalised 2,2’-bipyridine ligands can be synthesized with overall charges of +3, +4, +6 and +8. Each of the complexes was photoluminescent through a 3MLCT emitting state. The utility of high overall cationic charge and light harvesting ability was demonstrated in solution through electrostatically driven d-f energy transfer to near-IR emitting Yb(III).

**References**

1. Han, W.-K.; Liu, Y.; Yan, X.; Jiang, Y.; Zhang, J.; Gu, Z.-G. Integrating Light-Harvesting Ruthenium(II)-Based Units into Three-Dimensional Metal Covalent Organic Frameworks for Photocatalytic Hydrogen Evolution. *Angew. Chem. Int. Ed.* **2022**, *61*, e202208791. [↑](#endnote-ref-1)
2. Yong, C.-K.; Parkinson, P.; Kondratuk, D. V.; Chen, W.-H.; Stannard, A.; Summerfield, A.; Sprafke, J. K.; O’Sullivan, M. C.; Beton, P. H.; Anderson, H. L.; Herz, L. M. Ultrafast Delocalization of Excitation in Synthetic Light-Harvesting Nanorings. *Chem. Sci.* **2015**, *6*, 181–189. [↑](#endnote-ref-2)
3. Cesana, P. T.; Li, B. X.; Shepard, S. G.; Ting, S. I.; Hart, S. M.; Olson, C. M.; Martinez Alvarado, J. I.; Son, M.; Steiman, T. J.; Castellano, F. N.; Doyle, A. G.; MacMillan, D. W. C.; Schlau-Cohen, G. S. A Biohybrid Strategy for Enabling Photoredox Catalysis with Low-Energy Light. *Chem* **2022**, *8*, 174–185. [↑](#endnote-ref-3)
4. Sathish, V.; Ramdass, A.; Velayudham, M.; Lu, K.-L.; Thanasekaran, P.; Rajagopal, S. Development of Luminescent Sensors Based on Transition Metal Complexes for the Detection of Nitroexplosives. *Dalton Trans.* **2017**, *46*, 16738–16769. [↑](#endnote-ref-4)
5. Knighton, R. C.; Dapin, S.; Beer, P. D. Luminescent Anion Sensing by Transition‐Metal Dipyridylbenzene Complexes Incorporated into Acyclic, Macrocyclic and Interlocked Hosts. *Chem. – Eur. J.* **2020**, *26*, 5288–5296. https://doi.org/10.1002/chem.202000661 [↑](#endnote-ref-5)
6. Bharmoria, P.; Bildirir, H.; Moth-Poulsen, K. Triplet–Triplet Annihilation Based near Infrared to Visible Molecular Photon Upconversion. *Chem. Soc. Rev.* **2020**, *49*, 6529–6554. https://doi.org/10.1039/D0CS00257G [↑](#endnote-ref-6)
7. Zhao, J.; Wu, W.; Sun, J.; Guo, S. Triplet photosensitizers: from molecular design to applications *Chem. Soc. Rev*. **2013**, *42*, 5323-5351; Elgar, C. E.; Otaif, H. Y.; Zhang, X.; Zhao, J.; Horton, P. N.; Coles, S. J.; Beames, J. M.; Pope, S. J. A. Iridium(III) Sensitisers and Energy Upconversion: The Influence of Ligand Structure upon TTA-UC Performance. *Chem. – Eur. J.* **2021**, *27*, 3427–3439. [↑](#endnote-ref-7)
8. Knighton, R. C.; Soro, L. K.; Thor, W.; Strub, J.-M.; Cianférani, S.; Mély, Y.; Lenertz, M.; Wong, K.-L.; Platas-Iglesias, C.; Przybilla, F.; Charbonnière, L. J. Upconversion in a d–f [RuYb3] Supramolecular Assembly. *J. Am. Chem. Soc.* **2022**, *144*, 13356–13365. https://doi.org/10.1021/jacs.2c05037 [↑](#endnote-ref-8)
9. Poynton, F.E.; Bright, S.A.; Blasco, S.; Williams, D.C.; Kelly, J.M.; Gunnlaugsson, T. The development of ruthenium(II) polypyridyl complexes and conjugates for: In vitro cellular and in vivo applications *Chem. Soc. Rev*. **2017**, *46*, 7706-7756; Shum, J.; Leung, P-K.; Lo, K.W. Luminescent Ruthenium(II) Polypyridine complexes for a wide variety of biomolecular and cellular applications *Inorg. Chem*. **2019**, *58*, 2231-2247; [↑](#endnote-ref-9)
10. Li, J.; Chen, T. Transition metal complexes as photosensitizers for integrated cancer theranostic applications *Coord. Chem. Rev*. **2020**, *418*, 213355; Saeed, H. K.; Sreedharan, S.; Jarman, P. J.; Archer, S. A.; Fairbanks, S. D.; Foxon, S. P.; Auty, A. J.; Chekulaev, D.; Keane, T.; Meijer, A. J. H. M.; Weinstein, J. A.; Smythe, C. G. W.; Bernardino de la Serna, J.; Thomas, J. A. Making the Right Link to Theranostics: The Photophysical and Biological Properties of Dinuclear RuII–ReI Dppz Complexes Depend on Their Tether *J. Am. Chem. Soc.* **2020**, *142*, 1101–1111. [↑](#endnote-ref-10)
11. He, L.; Tan, C.-P.; Ye, R.-R.; Zhao, Y.-Z.; Liu, Y.-H.; Zhao, Q.; Ji, L.-N.; Mao, Z.-W. Theranostic Iridium(III) Complexes as One- and Two-Photon Phosphorescent Trackers to Monitor Autophagic Lysosomes. *Angew. Chem. Int. Ed.* **2014**, *53*, 12137–12141 [↑](#endnote-ref-11)
12. Karges, J.; Kuang, S.; Maschietto, F.; Blacque, O.; Ciofini, I.; Chao, H.; Gasser, G. Rationally Designed Ruthenium Complexes for 1- and 2-Photon Photodynamic Therapy. *Nat. Commun.* **2020**, *11*, 3262; Martinez-Alonso, M.; Gasser, G. Transition metal complexes as photosensitizers for integrated cancer theranostic applications *Coord. Chem. Rev*. **2021**, *434*, 213736 [↑](#endnote-ref-12)
13. Wenger, O.S. Photoactive Complexes with Earth-Abundant Metals *J. Am. Chem. Soc*. **2018**, *140*, 13522-13533 [↑](#endnote-ref-13)
14. For example: Bruns, C.J.; Fujita, D.; Hoshino, M.; Sato, S.; Stoddart, J.FD.; Fujita, M. Emergent Ion-Gated Binding of Cationic Host–Guest Complexes within Cationic M12L24 Molecular Flasks *J. Am. Chem. Soc*. **2014**, *136*, 12027-12034; Wang, X-Y.; Sevov, S.C. Hydrogen-Bonded Host Frameworks of Cationic Metal Complexes and Anionic Disulfonate Linkers:  Effects of the Guest Molecules and the Charge of the Metal Complex *Chem. Mater*. **2007**, *19*, 4906-4912 [↑](#endnote-ref-14)
15. For example: Sitze, M.S.; Schreiter, E.R.; Patterson, E.V.; Greeman, R.G. Ionic Liquids Based on FeCl3 and FeCl2. Raman Scattering and ab Initio Calculations, *Inorg. Chem*. **2001**, *40*, 2298-2304; Chand, D.; Farooq, M.Q.; Pathak, A.K.; Li, J.; Smith, E.A.; Anderson, J.L. Magnetic ionic liquids based on transition metal complexes with N-alkylimidazole ligands *New J. Chem*. **2019**, *43*, 20-23 [↑](#endnote-ref-15)
16. Macchioni, A. Ion pairing in transition-metal organometallic chemistry *Chem. Rev*. **2005**, *105*, 2039-2073 [↑](#endnote-ref-16)
17. Komor, A.C.; Barton, J.K. The path for metal complexes to a DNA target *Chem. Commun*. **2013**, *49*, 3617-3630. [↑](#endnote-ref-17)
18. For example: Owen, T.; Butler, A. Metallosurfactants of bioinorganic interest: Coordination-induced self assembly *Coord. Chem. Rev*. **2011**, *225*, 678-687; Griffiths, P.C.; Fallis, I.A.; Chuenpratoom, T.; Watanesk, R. Metallosurfactants: interfaces and micelles *Adv. Colloid Interface Sci*. **2006**, *122*, 107-117; Donner, A.; Trepka, B.; Theiss, S.; Immler, F.; Traber, J.; Polarz, S. NHC-Metallosurfactants as Active Polymerization Catalysts *Langmuir* **2019**, *35*, 16514-16520 [↑](#endnote-ref-18)
19. Puckett, C.A.; Ernst, R.J.; Barton, J.K. Exploring the Cellular Accumulation of Metal Complexes *Dalton Trans*. **2010**, *39*, 1159-1170 [↑](#endnote-ref-19)
20. Constable, E.C.; Housecroft, C.E. The early years of 2,2’-bipyridine – a ligand in its own lifetime *Molecules* **2019**, *24*, 3951. [↑](#endnote-ref-20)
21. Willink, H.D.T., Jr.; Wibaut, J.P. Preparation of 2,2’-bipyridyl and some of its derivatives. *Recl. Trav. Chim. Pays-Bas* 1935, 54, 275–283; Smith, C.R. Skraup’s reaction applied to the phenylenediamines. Preparation of the phenanthrolines and related bipyridyls. *J. Am. Chem. Soc*. **1930**, *52*, 397–403 [↑](#endnote-ref-21)
22. Gillaizeau-Gathier, I.; Odobel, F.; Alebbi, M.; Argazzi, R.; Costa, E.; Bignozzi, C.A.; Qu, P.; Meyer, G.J. Phosphonate-Based Bipyridine Dyes for Stable Photovoltaic Devices *Inorg. Chem*. **2001**, *40*, 6073-6079. [↑](#endnote-ref-22)
23. Charbonnière, L. J.; Weibel, N.; Ziessel, R. F. 5‘-Substituted-6-Carboxylic-2,2‘-Bipyridine Acid:  A Pivotal Architecton for Building Preorganized Ligands. *J. Org. Chem.* **2002**, *67*, 3933–3936; Forato, F.; Belhboub, A.; Monot, J.; Petit, M.; Benoit, R.; Sarou-Kanian, V.; Fayon, F.; Jacquemin, D.; Queffelec, C.; Bujoli, B. Phosphonate-Mediated Immobilization of Rhodium/Bipyridine Hydrogenation Catalysts. *Chem. – Eur. J.* **2018**, *24*, 2457–2465 [↑](#endnote-ref-23)
24. Karges, J.; Kuang, S.; Maschietto, F.; Blacque, O.; Ciofini, I.; Chao, H.; Gasser, G. Rationally Designed Ruthenium Complexes for 1- and 2-Photon Photodynamic Therapy. *Nat. Commun.* **2020**, *11*, 3262. [↑](#endnote-ref-24)
25. Swords, W. B.; Li, G.; Meyer, G. J. Iodide Ion Pairing with Highly Charged Ruthenium Polypyridyl Cations in CH3CN. *Inorg. Chem.* **2015**, *54*, 4512–4519. [↑](#endnote-ref-25)
26. Gao, F.; Chen, X.; Wang, J-Q.; Chen, Y. Chao, H.; Ji, L-N. In Vitro Transcription Inhibition by Ruthenium(II) Polypyridyl Complexes with Electropositive Ancillary Ligands *Inorg. Chem*. **2009**, *48*, 5599-5601. [↑](#endnote-ref-26)
27. Klink, S.I.; Keiser, H.; van Veggel, F. C. J. M. Transition Metal Complexes as Photosensitizers for Near-Infrared Lanthanide Luminescence *Angew. Chem. Int. Ed*. **2000**, *39*, 4319-4321. [↑](#endnote-ref-27)
28. Parker, D.; Williams, J.A.G. Getting excited about lanthanide complexation chemistry J. Chem. Soc. *Dalton Trans*. **1996**, 3613-3628; Bunzlie, J-C. G. Lanthanide Luminescence for Biomedical Analyses and Imaging *Chem. Rev*. **2010**, *110*, 2729-2755; Faulkner, S.; Pope, S.J.A.; Burton-Pye, B.P. Lanthanide complexes for luminescence imaging applications *Appl. Spec. Rev*. **2005**, *40*, 1-31; Amoroso, A.J.; Pope, S.J.A. Using lanthanide ions in molecular bioimaging *Chem. Soc. Rev*. **2015**, *44*, 4723-4742 [↑](#endnote-ref-28)
29. Faulkner, S.; Natrajan, L.S.; Perry, W.S.; Sykes, D. Sensitised luminescence in lanthanide containing arrays and d–f hybrids *Dalton Trans*. **2009**, 3890-3899; Ward, M.D. Transition-metal sensitised near-infrared luminescence from lanthanides in d–f heteronuclear arrays *Coord. Chem. Rev*. **2007**, *251*, 1663-1677 [↑](#endnote-ref-29)
30. Aboshyan-Sorgho, L.; Nozary, H.; Aebischer, A.; Bunzli J-C.; Morgantini, P-Y.; Kittistved, K.R.; Hauser, A.; Eilseeva, S.V.; Petoud, S.; Piguet, C. Optimizing Millisecond Time Scale Near-Infrared Emission in Polynuclear Chrome(III)–Lanthanide(III) Complexes *J. Am. Chem. Soc*. **2012**, *134*, 12675-12684; Pope, S.J.A.; Coe, B.J.; Faulkner, S.; Laye, R.H. Metal-to-ligand charge-transfer sensitisation of near-infrared emitting lanthanides in trimetallic arrays M2Ln (M = Ru, Re or Os; Ln = Nd, Er or Yb) *Dalton Trans*. **2005**, 1482-1490; Sénéchal-David, K.; Pope, S.J.A; Quinn, S.; Faulkner, S.; Gunnlaugsson, T. Sensitized Near-Infrared Lanthanide Luminescence from Nd(III)- and Yb(III)-Based Cyclen−Ruthenium Coordination Conjugates *Inorg. Chem*. **2006**, *45*, 10040-10042; Davies, G.M.; Pope, S.J.A.; Adams, H.; Faulkner, S.; Ward, M.D. Structural and Photophysical Properties of Coordination Networks Combining [Ru(bipy)(CN)4]2- Anions and Lanthanide(III) Cations: Rates of Photoinduced Ru-to-Lanthanide Energy Transfer and Sensitized Near-Infrared Luminescence *Inorg. Chem*. **2005**, *44*, 4656-4665; Herrera, J-M.; Pope, S.J.A.; Meijer, A.J.H.M.; Easun, T.L.; Adams, H.; Alsindi, W.Z.; Sun, X-Z.; George, M.W.; Faulkner, S.; Ward. M.D. Photophysical and Structural Properties of Cyanoruthenate Complexes of Hexaazatriphenylene *J. Am. Chem. Soc*. **2007**, *129*, 11491-11504; Shavaleev, N.M.; Pope, S.J.A.; Bell, Z.R.; Faulkner, Ward, M.D. Visible-light sensitisation of near-infrared luminescence from Yb(iii), Nd(iii) and Er(iii) complexes of 3,6-bis(2-pyridyl)tetrazine *Dalton Trans*. **2003**, 808-814; Lazarides, T.; Adams, H.; Sykes, D.; Faulkner, S.; Calogero, G.; Ward, M.D. Heteronuclear bipyrimidine-bridged Ru–Ln and Os–Ln dyads: low-energy 3MLCT states as energy-donors to Yb(iii) and Nd(iii) *Dalton Trans*. *2008*, 691-698; Jones, J.E.; Jenkins, R.L.; Hicks, R.S.; Hallett, A.J.; Pope, S.J.A. Water-soluble, luminescent iridium(III)-ytterbium(III) complexes using dipyrido[3,2-a:2 ',3 '-c] phenazine derivatives as bridging units *Dalton Trans*. **2012**, *41*, 10372-10381; Shavaleev, N.M.; Moorcroft, L.P.; Pope, S.J.A.; Bell, Z.R.; Faulkner, S.; Ward, M.D. Sensitised near-infrared emission from lanthanides using a covalently-attached Pt(ii) fragment as an antenna group *Chem. Commun*. **2003**, 1134-1135; Li, L.; Zhang, S.; Xu, L.; Chen, Z-N.; Luo, J. Highly sensitized near-infrared luminescence in Ir–Ln heteronuclear coordination polymers via light-harvesting antenna of Ir(iii) unit *J. Mat. Chem. C* **2014**, *2*, 1698-1703 [↑](#endnote-ref-30)
31. Pope, S.J.A.; Coe, B.J.; Faulkner, S.; Bichenkova, E.V.; Yu, X.; Douglas, K.T. Self-Assembly of Heterobimetallic d-f Hybrid Complexes: Sensitization of Lanthanide Luminescence by d-Block Metal-to-Ligand Charge-Transfer Excited States *J. Am. Chem. Soc*. **2004**, *126*, 9490-9491. [↑](#endnote-ref-31)
32. Sambrook, M.R.; Curiel, D.; Hayes, E.J.; Beer, P.D.; Pope, S.J.A.; Faulkner, S. Sensitised near infrared emission from lanthanides via anion-templated assembly of d–f heteronuclear [2]pseudorotaxanes *New J. Chem*. **2006**, *30*, 1133-1136 [↑](#endnote-ref-32)
33. Ishida, H.; Tobita, S.; Hasegawa, Y.; Katoh, R.; Nozaki, K. Recent Advances in Instrumentation for Absolute Emission Quantum Yield Measurements. *Coord. Chem. Rev.* **2010**, *254*, 2449–2458. [↑](#endnote-ref-33)
34. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision C.01*; Gaussian Inc.: Wallingford CT, 2010. [↑](#endnote-ref-34)
35. a) Dunning Jr., T. H.; Hay, P.J. in Modern Theoretical Chemistry, Ed. Schaefer III, H.F. Vol. 3 (Plenum, New York, 1977) 1-28; b) Kuechle, W.; Dolg, M.; Stoll, H.; Preuss, H. Ab initio pseudopotentials for HG through RN. 1. Parameter sets and atomic calculations *Mol. Phys*. **1991**, *74*, 1245-1263 [↑](#endnote-ref-35)
36. Ditchfield, R.; Hehre, W.J.; Pople, J.A. Self-Consistent Molecular Orbital Methods. IX. Extended Gaussian-type basis for molecular-orbital studies of organic molecules *J. Chem. Phys*. **1971**, *54*, 724-728 [↑](#endnote-ref-36)
37. O’Boyle, N.M.; Tenderholt, A.L.; Langner, K.M. cclib: a library for package-independent computational chemistry algorithms. *J. Comput.Chem*. **2008**, *29*, 839-845 [↑](#endnote-ref-37)
38. Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst*. **2015**, *A71*, 3-8. [↑](#endnote-ref-38)
39. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst*. **2009**, *42*, 339-341 [↑](#endnote-ref-39)
40. Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst*. **2015**, *C27*, 3-8 [↑](#endnote-ref-40)
41. Charbonnière, L. J.; Weibel, N.; Ziessel, R. F. 5‘-Substituted-6-Carboxylic-2,2‘-Bipyridine Acid:  A Pivotal Architecton for Building Preorganized Ligands. *J. Org. Chem.* **2002**, *67*, 3933–3936; Forato, F.; Belhboub, A.; Monot, J.; Petit, M.; Benoit, R.; Sarou-Kanian, V.; Fayon, F.; Jacquemin, D.; Queffelec, C.; Bujoli, B. Phosphonate-Mediated Immobilization of Rhodium/Bipyridine Hydrogenation Catalysts. *Chem. – Eur. J.* **2018**, *24*, 2457–2465; Telfer, S. G.; Bernardinelli, G.; Williams, A. F. Iron and Cobalt Complexes of 5,5′-Di(Methylene-N-Aminoacidyl)-2,2′-Bipyridyl Ligands: Ligand Design for Diastereoselectivity and Anion Binding. *Dalton Trans.* **2003**, 435–440 [↑](#endnote-ref-41)
42. A crystal structure has been reported: S. Park, S-H. Moon, T.H. Kim, K-M. Park, *Acta Cryst*. **2011**, *E67*, o2392. [↑](#endnote-ref-42)
43. Balzani, V.; Ceroni, P.; Credi, A.; Venturi, M. Ruthenium Tris(Bipyridine) Complexes: Interchange between Photons and Electrons in Molecular-Scale Devices and Machines. *Coord. Chem. Rev.* **2021**, *433*, 213758; Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. Ru(II) Polypyridine Complexes: Photophysics, Photochemistry, Eletrochemistry, and Chemiluminescence. *Coord. Chem. Rev.* **1988**, *84*, 85–277 [↑](#endnote-ref-43)
44. L. Boselli, M. Carraz, S. Mazeres, L. Paloque, G. Gonzalez, F. Benoit-Vical, A. Valentin, C. Hemmert, H. Gornitzka, *Organometallics* **2015**, *34*, 1046-1055. [↑](#endnote-ref-44)
45. Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. Mixed Phosphine 2,2’-Bipyridine Complexes of Ruthenium. *Inorg. Chem.* **1978**, *17*, 3334–3341 [↑](#endnote-ref-45)
46. Dongare, P.; Myron, B.D.B.; Wang, L.; Thompson, D.W.; Meyer, T.J. [Ru(bpy)3]2+ revisited. Is it localized or delocalized? How does it decay? *Coord. Chem. Rev*. **2017**, *345*, 86-107 [↑](#endnote-ref-46)
47. Ishida, H.; Tobita, S.; Hasegawa, Y.; Katoh, R.; Nozaki, K. Recent Advances in Instrumentation for Absolute Emission Quantum Yield Measurements. *Coord. Chem. Rev.* **2010**, *254*, 2449–2458. [↑](#endnote-ref-47)
48. Sveshnikova, E.B.; Shakhverdov, P.A.; Shakhverdov, T.A.; Lanin, V.E.; Safina, R.U.; Bolotin, B.M.; Ermolaev, V.L. Luminescence of dipicolinic complexes of lanthanide ions *Optics and Spectroscopy* **2003**, *95*, 898-907 [↑](#endnote-ref-48)