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Hetero-metallomacrocyclic hosts that bind molecular guests in water

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The self-assembly and energy transfer properties of metallomacrocycles that function as hosts for aromatic molecules in water is reported.

There is much current interest in metal templated self-assembly processes.[1] In particular, the self-assembly of discrete 2D and 3D geometrical entities such as squares, triangles and prisms has attracted much attention.[2] This work offers insights into the mechanism of the self-assembly process[3] and can result in functional structures that have been used as hosts and/or sensors for ionic and molecular guests.[4] Most of the complexes prepared to date are homometallic. Hupp and co-workers have reported the synthesis of a mixed Re(I)/Pd(II) macrocyclic square which display rhenium based luminescence. This square functions as a luminescent sensor for anions in organic media.[5] More recently, Lees *et al.* have reported larger macrocycles containing Re(I) corners with Os(II), Ru(II) and Fe(II) polypyridyl complexes as edges. However, only the complex incorporating osmium centres is luminescent and the steric bulk of the linker units dictates that these assemblies can not act as hosts.[6]

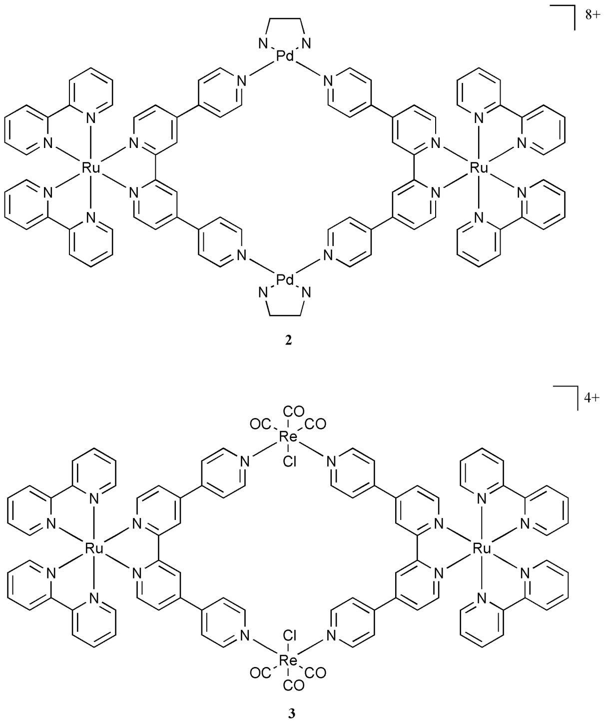
With the aim of constructing systems which incorporate the salient features from both these systems we have been investigating the self-assembly of hetero-metallic macrocycles containing 2,2′:4,4″:4′4″-quarterpyridyl,[7] L$_1$, units as linkers.

Our initial work has focused on architectures constructed from the previously reported building-block, [Ru(bpy)$_2$(L$_1$)]$^{2+}$ (**1**), which was synthesised using literature methods.[8] Using procedures reported for other self-assembly reactions[1,2] the reaction of **1** with [Pd(en)(NO$_3$)$_2$], and [Re(CO)$_5$Cl] was then investigated.† The reaction of **1** with the Pd(II) complex resulted in the isolation in good yield of an orange–red complex. While the analogous reaction between **1** and the Re(I) complex resulted in the isolation of a deep red product. The hetero-metallomacrocyclic products **2** and **3** (Scheme 1), isolated as hexafluorophosphate salts, have been characterised by ^{1}H-NMR, elemental analysis, FAB and/or ES, mass spectroscopy. Interestingly, whilst theoretical models for the isotopic distribution of peaks found in the FAB–MS of **3** showed peaks entirely consistent with monomeric **3**, the ES-MS spectra of both **2** and **3** revealed that several peaks were in fact due to **2** + **2**, and **3** + **3** dimers. However, 1-D proton NMR and 2-D COSY experiments on **2** and **3** were entirely consistent with the proposed structures (Scheme 1) and allowed a full assignment of the relevant protons. In addition, these studies showed no evidence for higher order structures such as catananes or open oligomers. Several attempts were made to obtain X-ray quality crystals, and while vapour diffusion of diethyl ether into nitromethane solutions produced small crystals of the hexafluorophosphate salts of **2** and **3** these proved to be highly unstable even at reduced temperatures.

The absorption spectra for **2** and **3** (Table 1) show high intensity, high energy bands which are consistent with intraligand π→π* transitions, while a comparison with analogous systems suggests that the less intense bands between 350 and 550 nm are due to metal-to-ligand charge-tranfer (MLCT) processes.

Both complexes display a band at 470–485 nm which is assigned to Ru(d)→L(π*) MLCT (this transition is observed at 462 nm for **1**). Again, *via* comparison with literature reports, the 370–397 nm shoulder in **2** is assigned as Pd(d)→L(π*) MLCT, while the band centred at 363 nm in **3** is assigned as a Re(d)→L(π*) MLCT.

Organic and aqueous solutions of these complexes display luminescence. For both complexes, photoexcitation results in a relatively intense emission band centred around 650–670 nm, with a shoulder around 720 nm. Given that this band is so similar for both complexes it is assigned as emission from the Ru-MLCT, which is red-shifted in comparison with **1** (λ_{em} ≈ 590 nm[9])–Fig. 1. This latter observation is consistent with the properties of other ligand-bridged oligometallic complexes.[10] Interestingly, the emission is independent of the excitation wavelength, implying that energy transfer within the macro-



2

3

Scheme 1

Table 1 Photophysical properties of **2** and **3**

Complex	UV–Vis[a] λ_{max}/nm (ε [M^{-1} cm^{-1}]/1000)	Emission[b] λ_{em}/nm
2	249 (76), 285 (81), 311 (sh), 375 (sh), 429 (19), 485 (20)	670
3	246 (63), 287 (72), 308 (sh), 363 (12), 429 (sh), 470 (16)	665

[a] Recorded in water. [b] Recorded in water, λ_{ex} = 480 nm.

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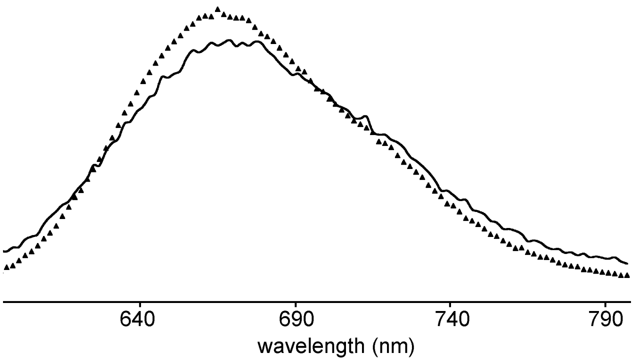

Fig. 1 Luminescence of metallomacrocyles **2** and **3**.

cyclic structure is efficient and that excitation into any MLCT or π–π* excited state results in relaxation to the lowest lying Ru-MLCT state.

Since it has been shown that related structures can bind electron-rich guest molecules,[2] the ability of the new macrocycles to function as molecular hosts in water was investigated.

Luminescence titrations with selected guests showed only very small changes in the emission intensity. However, it was found that titration of mono- and bicyclic molecules such as 1,4-dimethoxybenzene and 1-naphthol into aqueous solutions of **2** and **3** resulted in large changes in the absorption spectra of the macrocycles.‡ The changes in absorption associated with the interaction of **2** with 1-naphthol are shown in Fig. 2.

Whilst the MLCT region of the respective spectra show only small modulation, the intensity of several of the original high energy bands is greatly diminished. Most notably the band assigned to the intra-ligand π→π* diminishes accompanied by the growth of a new, higher energy band at 249 nm. These transitions are associated with several isosbestic points that are indicative of the clean formation of a 1 : 1 host–guest complex. Preliminary attempts to fit this data to a simple 1 : 1 binding curve have been hampered by aggregation of the host and more direct methods of obtaining the thermodynamic parameters for the host–guest interaction are now being explored.

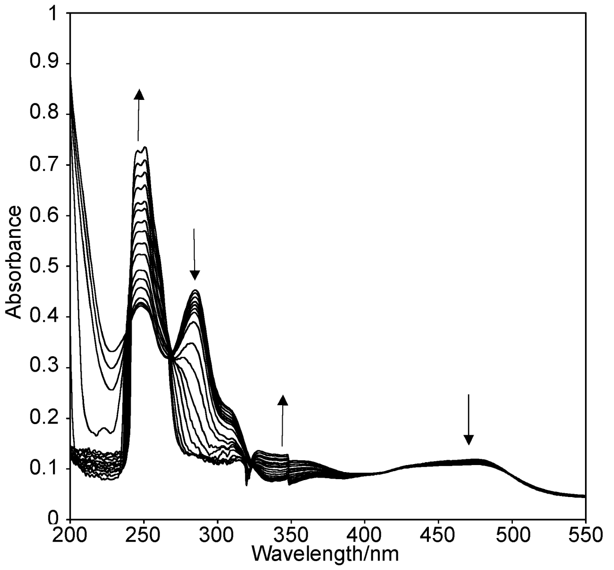

Fig. 2 Absorption titration of 1-naphthol into aqueous solutions of **2**.

We are currently investigating the interaction of **2** and **3** with a variety of other molecular guests, while modulation of the host architecture with the aim of designing specific sensing systems is also underway.

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Notes and references

† Preparation of **2**: Pd(en)Cl_2 (0.5 mmol) and $AgNO_3$ (1 mmol) were stirred overnight in a 1 : 1 MeOH : H_2O solution (10 ml). The resulting AgCl which formed was removed by filtration through Celite. To the resulting Pd(en)$(NO_3)_2$ solution was added an ethanolic solution of [Ru(bipy)$_2$(L_1)]Cl_2 (0.5 mmol), which was then stirred for 15 min at room temperature. A red–orange solid was precipitated by the addition of NH_4PF_6, which was collected by filtration and washed successively with 2 × 10 ml H_2O, 2 × 10 ml EtOH and 2 × 10 ml ether. Yield 0.6616 g (45%).^{1}H NMR (d^3-MeCN): 9.03 (d, 8H), 8.80 (s, 4H), 8.52 (m, 8H), 8.07 (m, 8H), 8.03(d, 8H), 7.90 (d, 4H), 7.70 (m, 12H), 7.43–7.36 (m, 8H), 2.85 (s, 8H). ES–MS; *m/z* (%): 1816 (70) [$(M + M) - 3PF_6]^{2+}$ 1325.5 (100) [$(M + M) - 4PF_6]^{4+}$, 1031 (80) [$(M + M) - 5PF_6]^{+}$ Anal. Calcd. for $C_{84}H_{76}N_{20}P_8F_{48}Ru_2Pd_2{\cdot}7H_2O$: C, 32.90; H, 2.96; N, 9.13. Found: C, 32.64; H, 2.82; N, 9.28%.

Preparation of **3**: [Ru(bpy)$_2$(L_1)](PF6)$_2$ (0.5 mmol) and Re(CO)$_5$Cl (0.5 mmol) were dissolved in 60 ml of 1 : 1 MeCN : THF solution. This mixture was heated to reflux for 2 days. After this time excess THF was added and a red solid precipitated out. The precipitate was collected by filtration and washed successively with 2 × 25 ml THF and 3 × 25 ml ether, then dried. Yield 1.2139 g (92%).^{1}H NMR (d^3-MeCN): 9.00 (d, 8H), 8.97 (s, 4H), 8.53 (d, 8H), 8.08 (m, 8H), 7.89 (m, 8H), 7.88 (d, 4H), 7.79–7.74 (m, 8H), 7.71 (dd, 4H), 7.43 (m, 8H). FAB–MS; *m/z* (%): 2495 (20) [$M - PF_6]^+$, 2345 (12) [$M - 2PF_6]^+$, 2203 (10) [$M - 3PF_6]^+$, 1174 (17) [$M - 2PF_6]^{2+}$. ES–MS; *m/z* (%): 2495 (22) [$M - PF_6]^+$, 1614.6 (100) [$(M + M) - 3PF_6]^+$, Anal. Calcd. for $C_{86}H_{60}N_{16}O_6Cl_2P_4F_{24}Re_2Ru_2$: C, 39.14; H, 2.29; N, 8.49. Found: C, 39.56; H, 2.47; N, 8.07%.

‡ Host–guest titration: 2000 μl of the sample solution (10^{-6} mol l^{-1}) was loaded into a 1 cm path length optical glass cuvette maintained at 25 °C. 2000 μl of water was loaded into another identical cuvette and placed in the reference cell of the spectrometer. During the titration an equimolar host solution containing guest at a concentration of 10^{-3} mol l^{-1} was added to the sample cell, whilst an equivalent titre of a solution solely containing guest at 10^{-3} mol l^{-1} was added to the reference cell. These solutions were left to equilibrate for 10–15 minutes before a spectrum was recorded.

1 J.-M. Lehn, *Chem. Eur. J.*, 2000, **6**, 2097; M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457; L. M. Greig and D. Philp, *Chem. Soc. Rev.*, 2001, **30**, 287.
2 C. J. Jones, *Chem. Soc. Rev.*, 1998, **27**, 289; M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; G. F. Swiegers and T. F. Malefetse, *Chem. Rev.*, 2000, **100**, 3483; G. F. Swiegers and T. F. Malefetse, *Coord. Chem. Rev.*, 2002, **225**, 91.
3 D. P. Funeriu, J.-M. Lehn, G. Baum and D. Fenske, *Chem. Eur. J.*, 1997, **3**, 99; P. N. W. Baxter, J.-M. Lehn, G. Baum and D. Fenske, *Chem. Eur. J.*, 1999, **5**, 102; D. P. Funeriu, J.-M. Lehn, G. Baum and D. Fenske, *Chem. Eur. J.*, 2000, **6**, 2103; S. Toyota, C. R. Woods, M. Benaglia, R. Haldimann, K. Wärnmark, K. Hardcastle and Jay S. Siegel, *Angew. Chem., Int. Ed.*, 2001, **40**, 751.
4 M. H. Keefe, K. D. Benkstein and J. T. Hupp, *Coord. Chem. Rev.*, 2000, **205**, 201.
5 R. V. Slone, D. I. Yoon, R. M. Calhoun and J. T. Hupp, *J. Am. Chem. Soc.*, 1995, **117**, 11813.
6 S.-S. Su and A. J. Lees, *Inorg. Chem.*, 2000, **39**, 134; S.-S. Sun and A. J. Lees, *Inorg. Chem.*, 2001, **40**, 3154.
7 R. J. Morgan and A. D. Baker, *J. Org. Chem.*, 1990, **55**, 1986.
8 M. A. Hayes, C. A. Meckel, E. Schatz and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1992, 703.
9 R. J. Forster and T. E. Keyes, *J. Phys. Chem., B*, 1998, **102**, 10004.
10 V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759–833.