

# Self-assembly of a linear multicomponent porphyrin array through axial coordination

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The bis[4'-(4'''-pyridyl)-2,2':6',2''-terpyridine]ruthenium and osmium complexes **1a** and **1b** react with 2 equiv. of [Ru(TTP)(CO)(EtOH)] **4** to generate linear multicomponent arrays **3a** and **3b**; intramolecular phosphorescence quenching is observed for both arrays in contrast to their molecular building blocks which phosphoresce.

The rich photo- and redox chemistry of porphyrins has led to the design of sophisticated multicomponent molecular arrays held together by covalent or noncovalent interactions.<sup>1</sup> Efforts in this area have been spawned primarily by attempts to model solar energy capture and transfer in naturally occurring photosystems as well as to generate photoactive molecular devices.<sup>2</sup> One of the major concerns when designing such models is the ultimate control over the spatial organization of the chromophoric units within the arrays, where the photoinduced energy- and/or electron-transfer reactions of the resulting complexes will be governed by the supramolecular topology.

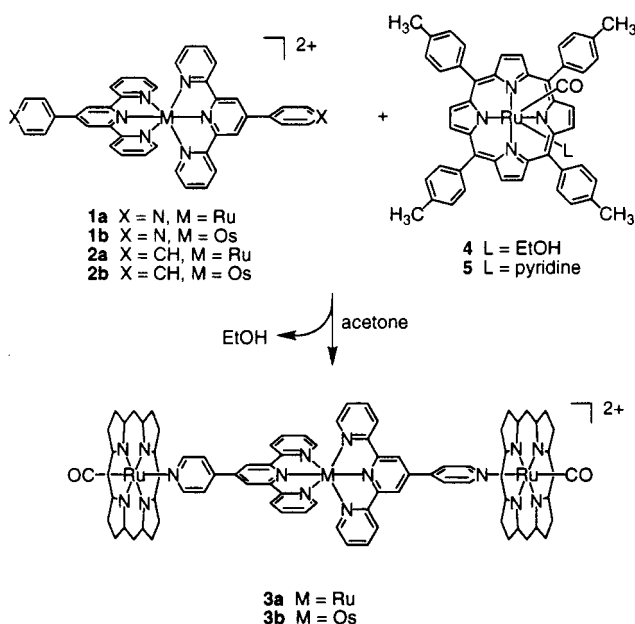
Our interests in this area are in the design and construction of molecular assemblies with well defined rigid architectures based on hybrid arrays of transition metal complexes axially coordinated to octahedral metalloporphyrins. We report here two linear multicomponent arrays **3a** and **3b** formed through the self-assembly of a central bis(terpyridine)transition metal complex linking two ruthenium(II) porphyrins *via* axial coordination.<sup>3</sup> The core units of triads **3a** and **3b** [M(pytpy)<sub>2</sub><sup>2+</sup>, pytpy = 4'-(4'''-pyridyl)-2,2':6',2''-terpyridine; M = Ru **1a**, Os **1b**] were prepared as their air-stable hexafluorophosphate salts as previously described.<sup>4</sup> The final triads **3a** and **3b** were prepared by adding 2 mol equiv. of [Ru(TTP)(CO)(EtOH)] **4**<sup>5†</sup> to 1 equiv. of [M(pytpy)<sub>2</sub>]<sup>2+</sup> in acetone and gently heating (Scheme 1). Alternatively, the triads can be prepared at room

temperature by adding an excess of the metalloporphyrin. In either case, the fully assembled triad complexes were isolated as red (Ru) and red-brown (Os) solids and characterized by UV-VIS spectroscopy, <sup>1</sup>H NMR spectroscopy and mass spectrometry.

The <sup>1</sup>H NMR spectra of both complexes **3a** and **3b** show significant upfield shifts for all hydrogen atoms of the M(pytpy)<sub>2</sub><sup>2+</sup> core unit as anticipated for protons lying within the shielding cone of the porphyrin (Fig. 1).<sup>6</sup> The anisotropic effect never completely disappears and extends over the entire distance spanned by the core unit (*ca.* 11 Å). We attribute this to an additive effect of both porphyrins forming the complex's walls. As expected, the protons immediately adjacent to the pyridine nitrogen of the core unit are the most affected and are seen to move as much as 7.5 ppm upfield upon complexation (protons H<sub>a</sub> in Fig. 1). The smallest, but still significant, shielding effect acts upon the hydrogen atoms closest to the central metal which are shifted 0.5 ppm to higher field (protons H<sub>c</sub> in Fig. 1).

The <sup>1</sup>H NMR studies reveal that, even in a competitive solvent such as acetone, coordination to the metalloporphyrin is strong and ligand-exchange is slow on the NMR timescale, and sharp, unchanging peaks for the statistical mixture of mono- and di-addition products were clearly visible when only 1 mol equiv. of [Ru(TTP)(CO)(EtOH)] **4** was added (Fig. 1, inset). This observation is useful when preparing complexes *in situ* and is utilitarian when constructing larger porphyrin arrays.<sup>‡</sup>

Initial photophysical studies show that the absorption spectra in the UV-VIS region of complexes **3a** and **3b** are essentially the sum of the absorption spectra of the triads' constituents. The steady-state emission properties of the triad complexes, however, differ greatly from those of their building blocks. In order



Scheme 1

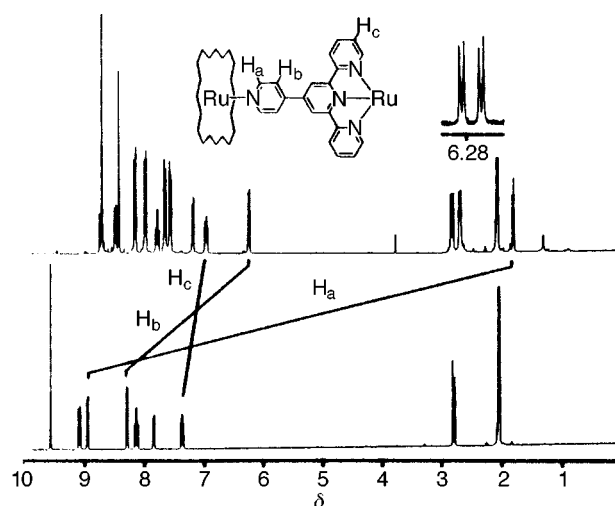
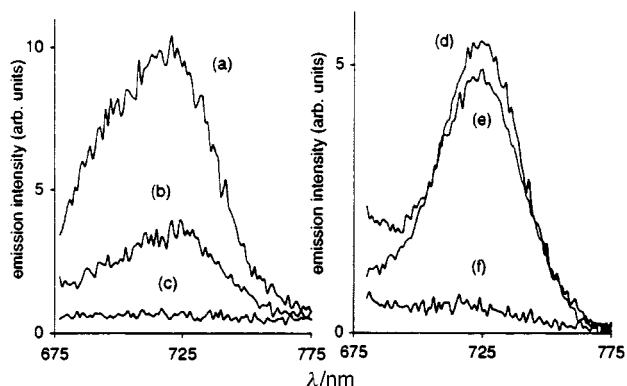


Fig. 1 <sup>1</sup>H NMR (300 MHz, acetone-d<sub>6</sub>) spectra of [Ru(pytpy)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> **1a** (bottom trace) and triad **3a** (top trace). The inset spectrum corresponds to protons H<sub>b</sub> when only 1 mol equiv. of [Ru(TTP)(CO)(EtOH)] was added showing both mono- (peaks on the left) and bis-coordination (peaks on the right) arrays.



**Fig. 2** Emission spectra (uncorrected) of  $\text{CH}_2\text{Cl}_2$  solutions of (a) **2b** ( $\lambda_{\text{ex}} = 670$  nm), (b) **1b** ( $\lambda_{\text{ex}} = 670$  nm), (c) **3b** ( $\lambda_{\text{ex}} = 670$  nm), (d) **5** ( $\lambda_{\text{ex}} = 530$  nm), (e) 2:1 mixture of **5** and **2a** ( $\lambda_{\text{ex}} = 530$  nm), (f) **3a** ( $\lambda_{\text{ex}} = 530$  nm). All spectra were run in dry deoxygenated solvent.

to evaluate the photoemission properties of each of the triads' building blocks without complications from the other luminescent species, the triads composed of the two different core units **1a** and **1b** were investigated independently. The osmium core unit **1b** phosphoresces from its triplet excited state<sup>2</sup> at room temperature in  $\text{CH}_2\text{Cl}_2$ , but the phosphorescence of the triad **3b** is significantly quenched (Fig. 2). Here, the substantial reduction in phosphorescence intensity of the core unit on going from bis(terpyridine)osmium **1b** to triad **3b** can most likely be ascribed to ligation-induced quenching, where the porphyrin is acting as a Lewis acid for the monodentate pyridine of **1b**. This claim is supported by the complete luminescence quenching of **1b** upon *in situ* protonation with 2 equiv. of trifluoroacetic acid, although, at this stage, intramolecular triplet energy transfer from the core complex to the porphyrin cannot be completely ruled out.<sup>9</sup>

The lack of room temperature photoemission of the bis(terpyridine)ruthenium core unit **1a** enabled us to study the porphyrin unit, which shows substantially weaker phosphorescence intensity at room temperature in comparison with osmium core unit **1b**.<sup>7</sup> Again, significant phosphorescence quenching was observed for triad **3a** in comparison with the free pyridine-coordinated porphyrin species  $[\text{Ru}(\text{TTP})(\text{CO})(\text{py})]$  **5** (Fig. 2). In order to rule out the existence of intermolecular phosphorescence quenching between non-coordinated chromophores, the phenyl analog of **1a**,  $[\text{Ru}(\text{phtpy})_2]^{2+}$  (phtpy = 4'-phenyl-2,2':6',2''-terpyridine) **2a**, which cannot axially coordinate to the metalloporphyrin, was prepared.<sup>8</sup> There was no observable intermolecular quenching of the excited state of porphyrin chromophore **5** when treated with 2 mol equiv. of **2a**, clearly indicating that the luminescence quenching occurs only when the metalloterpyridine complex is intimately coordinated to the porphyrin. We can conclude from these observations that there

is effective electronic communication between chromophores within the assembled triad. A possible explanation for the luminescence quenching is that photoinduced electron-transfer occurs, followed by non-radiative decay of a charge-separated species.<sup>§</sup> Identification of this charge-separated species and characterization of the phosphorescence quenching process within the arrays are currently under investigation.

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## Notes and references

† The abbreviation TTP refers to 5,10,15,20-tetratolylporphyrinato dianion.

‡ Manuscript in preparation.

§ Excited states of metalloporphyrins are known to exhibit photoredox behaviour involving both oxidative and reductive quenching. Literature precedent suggests an electron-transfer process (see ref. 9 and references cited therein), although examples of the less frequent energy-transfer process have also been documented for covalently bound porphyrin-terpyridine hybrids (see Flamigni *et al.* in ref. 1, for example).

- 1 L. Flamigni, F. Barigelletti, N. Armaroli, J.-P. Collin, J.-P. Sauvage and J. A. Gareth Williams, *Chem. Eur. J.*, 1998, **4**, 1744 and references therein; R. W. Wagner, J. Seth, S. I. Yang, D. Kim, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Org. Chem.*, 1998, **63**, 5042 and references therein; T. Arimura, C. T. Brown, S. L. Springs and J. L. Sessler, *Chem. Commun.*, 1996, 2293; C. M. Drain, K. C. Russell and J.-M. Lehn, *Chem. Commun.*, 1996, 337; C. A. Hunter and R. J. Shannon, *Chem. Commun.*, 1996, 1361; R. K. Kumar, S. Balasubramanian and I. Goldberg, *Chem. Commun.*, 1998, 1435.
- 2 J. P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993.
- 3 For representative examples of ruthenium(II) porphyrin arrays assembled through axial coordination, see: K. Funatsu, T. Imamura, A. Ichimura and Y. Sasaki, *Inorg. Chem.*, 1998, **37**, 4986; E. Alessio, M. Macchi, S. Heath and L. G. Marzilli, *Chem. Commun.*, 1996, 1411; M. Ikonen, D. Guez, V. Marvaud and D. Markovitsi, *Chem. Phys. Lett.*, 1994, **231**, 93 and references therein.
- 4 E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1994, 1409.
- 5 K. Funatsu, A. Kimura, T. Imamura, A. Ichimura and Y. Sasaki, *Inorg. Chem.*, 1997, **36**, 1625; J. P. Collman, C. E. Barnes, P. J. Brothers, T. J. Collins, T. Ozawa, J. C. Gallucci and J. A. Ibers, *J. Am. Chem. Soc.*, 1984, **106**, 5151.
- 6 For previous reports of this anisotropy, see ref. 3.
- 7 For a detailed description of the triplet state phosphorescence of both components, see: L. M. A. Levine and D. Holten, *J. Phys. Chem.*, 1988, **92**, 714 and ref. 4.
- 8 E. C. Constable, J. Lewis, M. C. Liptrot and P. R. Raithby, *Inorg. Chim. Acta*, 1990, **178**, 47.
- 9 J.-P. Collin, A. Harriman, V. Heitz, F. Odobel and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1994, **116**, 5679; A. Harriman, F. Odobel and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1995, **117**, 9461.

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