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The metal-directed self-assembly of three-dimensional porphyrin arrays†

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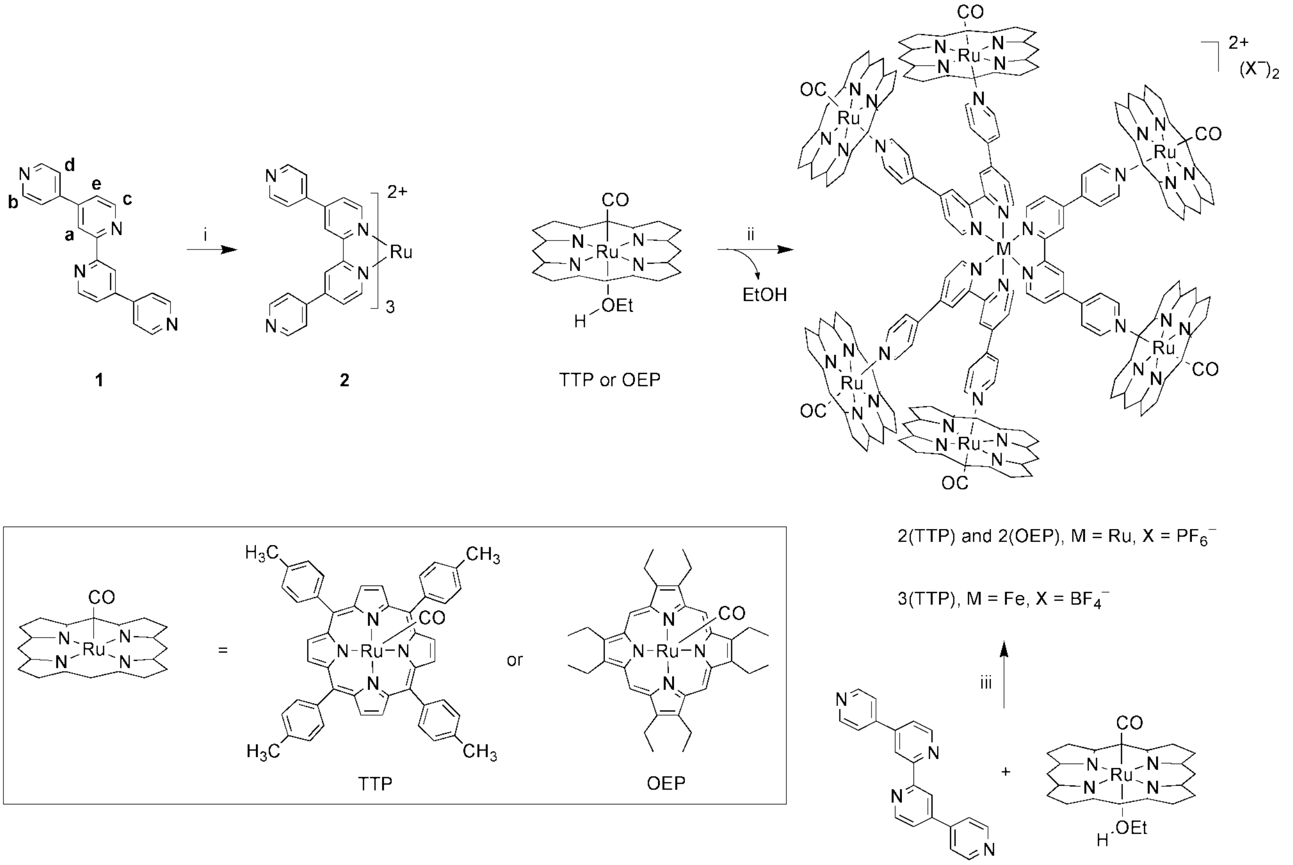
Six metalloporphyrins spontaneously assemble into octahedral arrays through a metal-directed synthesis; ^{1}H NMR provides a convenient means for tracking the progress of the self-assembly process and highlights that the rates in which the octahedral complexes form are influenced by the steric demands of the building blocks.

The power of self-assembly synthesis lies in its ability to rapidly generate large and sophisticated molecular architectures from readily accessible building blocks with maximum efficiency. Extensive hands-on synthetic steps are minimized because the pathway to the formation of the assemblies is guided by the nature of the recognition surfaces programmed into the components. This provides access to high yields under thermodynamic control. Self-assembly synthesis has been applied to the area of coordination chemistry to produce a variety of elegant structures including helicates,[1] squares,[2] closed-shell capsules,[3] linear ribbons, two-dimensional nets and three-dimensional weaves.[4] We are taking advantage of this strategy to create molecular arrays with well-defined architectures based on metalloporphyrins and other transition metal complexes.[5] Porphyrins are particularly attractive supramolecular building blocks as they have rich photo- and redox properties and, to date, numerous polymolecular assemblies held together by covalent or non-covalent interactions have been used to model solar energy capture and transfer in naturally occurring photosystems, as well as to create artificial photoactive molecular devices.[6]

We recently reported the preparation of linear multicomponent porphyrin arrays in which a central metal atom positions two pyridyl Lewis bases that, in turn, axially coordinate to ruthenium-based metalloporphyrins.[5,7] The terpyridine scaffold, however, is restricted in its use. Only linear arrays can be conveniently synthesized. A ligand displaying multiple, divergent Lewis basic sites provides a means to extend the self-assembly strategy to three-dimensional metal-templated porphyrin arrays. The tetrapyridyl ligand [4,4′-di(4″-pyridyl)-2,2′-bipyridine, **1**][8] is ideal for this purpose. We report here the spontaneous assembly of three-dimensional ruthenium arrays **2**(TTP) and **2**(OEP) *via* axial coordination of ruthenium(II) porphyrin building blocks to a modified tris(bipyridine)ruthenium(II) metal template where the Lewis basic lone pair vectors are extensions of the octahedral geometry of the central metal–ligand complexes. We also describe a one-pot



Scheme 1 *Reagents and conditions*: i, $RuCl_3 \cdot xH_2O$, ethylene glycol, reflux, then excess NH_4PF_6; ii, **2**, acetone, room temp; iii, $FeBF_4 \cdot 6H_2O$, acetone–methylene chloride, room temp.

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† Electronic supplementary information (ESI) available: synthesis and spectral data for **2**, **2**(TTP), **2**(OEP) and **3**(TTP). See http://www.rsc.org/suppdata/cc/b0/b002562n/

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synthesis of an octahedral iron analog **3**(TTP) from its simplest molecular components.

Multigram quantities of ligand **1** can be conveniently prepared in one step by dehydrogenating 4,4′-bipyridine according to known methods.[8] The octahedral ruthenium core unit **2** was prepared by heating $RuCl_3 \cdot xH_2O$ with three molar equivalents of **1** and was isolated as its hexafluorophosphate salt (Scheme 1). Arrays **2**(TTP) and **2**(OEP) were synthesized by treating the core template with six equivalents of [Ru(TTP)(CO)(EtOH)] and [Ru(OEP)(CO)(EtOH)], respectively, in acetone with gentle heating (Scheme 1). Arrays **2**(TTP) and **2**(OEP) were isolated as air-stable red solids in yields greater than 95% and characterized by UV–VIS, IR and ^1H NMR spectroscopy, and mass spectrometry.†

All arrays exhibit significantly upfield-shifted signals in their ^1H NMR spectra, corresponding to the protons on the core unit which are completely surrounded by the shielding cones of as many as six porphyrin building blocks. The most significant shift corresponds to the protons directly adjacent to the axially directed nitrogen atoms ($\Delta\delta$ as much as 8.3 ppm upfield), as it is these hydrogen atoms that are buried deepest within each porphyrin's shielding cone and experience the greatest anisotropic effect.

The most notable feature of the self-assembly process arises from the steric bulk expressed by the porphyrinic building blocks and is highlighted by the different rates at which **2**(TTP) and **2**(OEP) form in solution. ^1H NMR studies of **2**(TTP) reveal that the self-assembling process is slow on the NMR time scale and sharp peaks for the statistical mixture of fully assembled and lower-generation arrays were clearly visible, even when six molar equivalents of [Ru(TTP)(CO)(EtOH)] were added [Fig. 1(b)]. Only upon heating to 45 °C did the spectrum simplify to signals that correspond to **2**(TTP) alone [Fig. 1(c)].‡ On the other hand, despite the fact that the ruthenium atom in the octaethylporphyrin is a weaker Lewis acid,[9] complex **2**(OEP) assembles at a significantly greater rate than **2**(TTP), as illustrated by the immediate appearance of major signals for the fully assembled array [Fig. 1(d)]. We attribute these phenomena to the relative steric bulk of the tolyl and ethyl groups. The need to input additional energy in the case of **2**(TTP) was not unexpected as the tetratolylporphyrin traces out a circle of a diameter that is significantly larger than that inscribed by the octaethyl analog (18.5 *vs.* 12.7 Å). The result is that the CH_3 groups on the tolyl overlap with those on adjacent porphyrin rings in **2**(TTP).

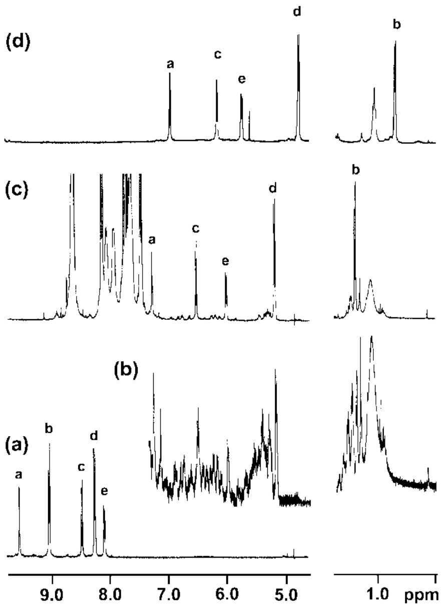

Fig. 1. ^1H NMR (300 MHz, acetone-d_6) spectra of (a) **2**, (b) **2** + 6 equiv. [Ru(TTP)(CO)(EtOH)] before and (c) after heating at 45 °C for 2 h, and (d) **2** + 6 equiv. [Ru(OEP)(CO)(EtOH)] at room temperature. Peak assignments correspond to the atom labels in Scheme 1.

The octahedral iron analog **3**(TTP) is readily synthesized in greater than 70% isolated yield in one step when a 1 : 2 mixture of solid **1** and solid [Ru(TTP)(CO)(EtOH)] is dissolved in a acetone-d_6/CD_2Cl_2 solution of $Fe(BF_4)_2 \cdot 6H_2O$ with gentle heating. This particular iron synthon was chosen for these studies because the highly labile nature of the metal's ligands allows for the rapid generation of the octahedral core fragment in high purity at room temperature, avoiding the harsh conditions required to form the ruthenate counterpart. Here, ten molecular species must organize and form twelve dative metal–ligand bonds in this assembly pathway. It is clear that, under these conditions, the self-assembly process results from the reading of both ruthenium and iron's inherent coordination algorithms and from the binding information stored in ligand **1**.

The absorption spectra in the UV–VIS region of **2**(TTP) and **2**(OEP) are essentially the sums of the spectra of the arrays' constituents. Initial steady-state emission spectra of these complexes, however, argue that there is a significant difference between the excited states of each array and their building blocks. Detailed results of the photophysical studies will be described elsewhere.

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Notes and references

‡ The spectra of both **2**(TTP) and **2**(OEP) generated *in situ* are identical to those of the corresponding isolated compounds.

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