

Ru(II)-centred porphyrin pentamers as coordination building blocks for large porphyrin arrays

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Ru(II)-centred porphyrin pentamers have been synthesised with Ni or Zn porphyrins at the peripheral sites; these elaborate systems have been used as building blocks for large porphyrin arrays through their coordination chemistry with bidentate and tetradentate ligands; coordination of a sterically unhindered pentamer to a free-base tetrapyrrolylporphyrin yields a 21 porphyrin array.

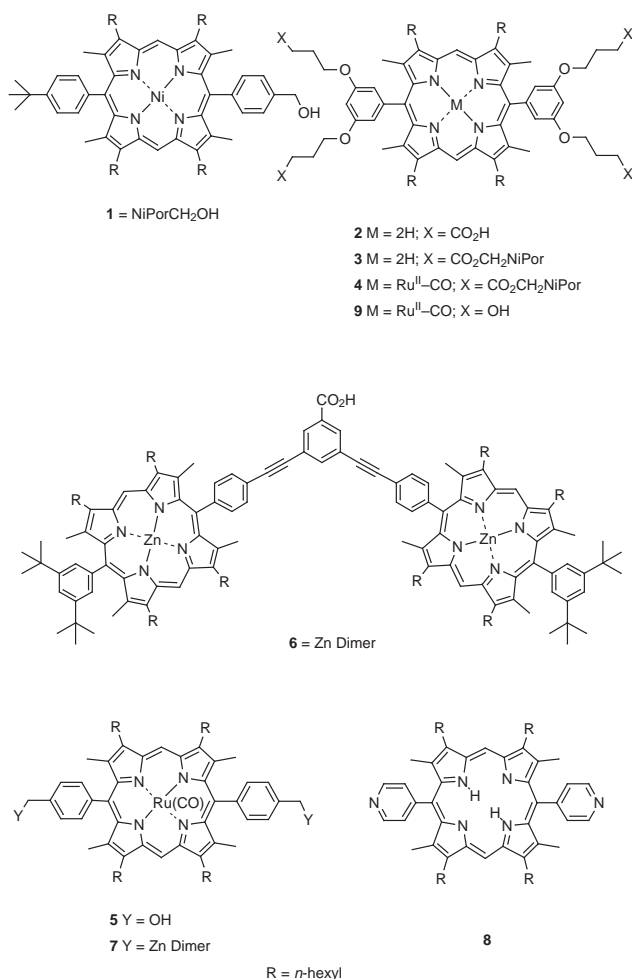
We report here the preparation of covalent Ru-centred porphyrin pentamers which can then be assembled into larger arrays by coordination to multidentate ligands.^{1,2} This highly convergent and efficient approach is illustrated with the preparation of an array of 21 porphyrins that contains units in three different metallation states; it is complementary to the fully covalent³ and photochemical⁴ approaches we have reported elsewhere.

Mitsunobu condensation⁵ of Ni-porphyrin **1** with porphyrin tetra-acid **2** (0.25 equiv.) in THF afforded the core free-base porphyrin pentamer **3** in 58% yield as a purple solid.† This

multiple Mitsunobu strategy ensures that the desired fully-coupled pentamer is the only non-polar product; it is therefore readily isolated and purified. The MALDI-TOF mass spectrum of **1** gave the anticipated MH⁺ ion at *m/z* 5185. Metallation of **3** with Ru₃(CO)₁₂ in refluxing toluene⁷ provided the Ru-centred pentamer **4** as a deep red solid in 66% yield. The lack of reactive functional groups in **3** avoids any significant Ru-mediated side reactions during metallation. The ¹H NMR properties and the presence of new peaks at *m/z* 5283 and 10566 in the MALDI mass spectrum corresponding to [(M – CO)⁺]^{8,9} and [(2M – 2CO)⁺],⁹ confirmed the successful metallation. In an inverted Mitsunobu approach, the core Ru-porphyrin diol **5**¹⁰ was esterified with 2 equiv. of the acid dimer **6**¹¹ to give the more rigid pentamer **7** in 21% yield. The MALDI-TOF spectrum revealed the expected peaks at *m/z* 5432 [(M – CO)⁺] and 10950 [(2M – 2CO)⁺].

The central Ru-ion dominates the coordination chemistry of pentamers **4** and **7**, with the strength of binding to N-ligands decreasing in the order Ru ≫ Zn ≫ Ni. Pyridyl ligands, such as those presented in this work, bind very tightly to ruthenium porphyrins, forming rigid well characterisable complexes.⁴ However, the extremely high binding affinities make NMR and UV titrations impractical. With this in mind, addition of <0.5 equiv. of diazabicyclo[2.2.2]octane (DABCO) to a 4–7 mM solution of **4** in CDCl₃ leads to exclusive Ru-coordination as shown in Fig. 1(a), where the sharp DABCO chemical shifts in the ¹H NMR spectrum are characteristic of the equilibrium between mono- and bi-nuclear porphyrin complexes, in slow exchange on the NMR chemical shift timescale. DABCO is a sufficiently small ligand that steric interaction between the peripheral porphyrins on the two porphyrin pentamers inhibits complete formation of a 10-porphyrin array. Titration of 0.5 equiv. of the larger bridging dipyrrolyl porphyrin ligand **8** with **4** results in exclusive formation of the 11-porphyrin array **4-8-4** as judged by the upfield shifts of the NH and pyridyl protons of **8** (as the 2,6-pyridyl protons of **8** shift upfield from δ 9.00 to 1.60, any 1 : 1 complex would be immediately apparent in the spectrum).

Adding a tetra-aryl ruthenium monomer to free-base tetrapyrrolyl porphyrin indicated that the 0.5 ppm highfield shift of the NH resonance is additive with each coordinated ruthenium monomer (free base δ_{NH} = –2.90, mono-coordinated δ_{NH} = –3.35, di-coordinated δ_{NH} = –3.87, tri-coordinated δ_{NH} = –4.30, tetra-coordinated δ_{NH} = –4.92). The chemical shift of the porphyrin inner NH protons is therefore diagnostic of the number of porphyrins coordinating to the tetradentate porphyrin ligand, so that binding 4 equiv. of monomer **9** shifts the NH signal from δ –2.90 to –4.91, by about 0.5 ppm per equivalent of **9** [Fig. 2(a)]. Reaction of 4 equiv. of rigid pentamer **7** with tetrapyrrolyl porphyrin gives rise to a high-field resonance at δ –4.75 (Fig. 2(b)) suggesting the formation of a 21-porphyrin array [Fig. 1(b)]. The steric congestion associated with coordination of the more flexible pentamer **4** however, is so great that the product distribution is dominated by the coordination of only three such pentamers about the tetrapyrrolyl porphyrin, as is apparent by the shift of the NH protons [δ –4.25, Fig. 2(c)]. Preliminary experiments with an extended analogue of tetrapyrrolyl porphyrin show that, four molecules of



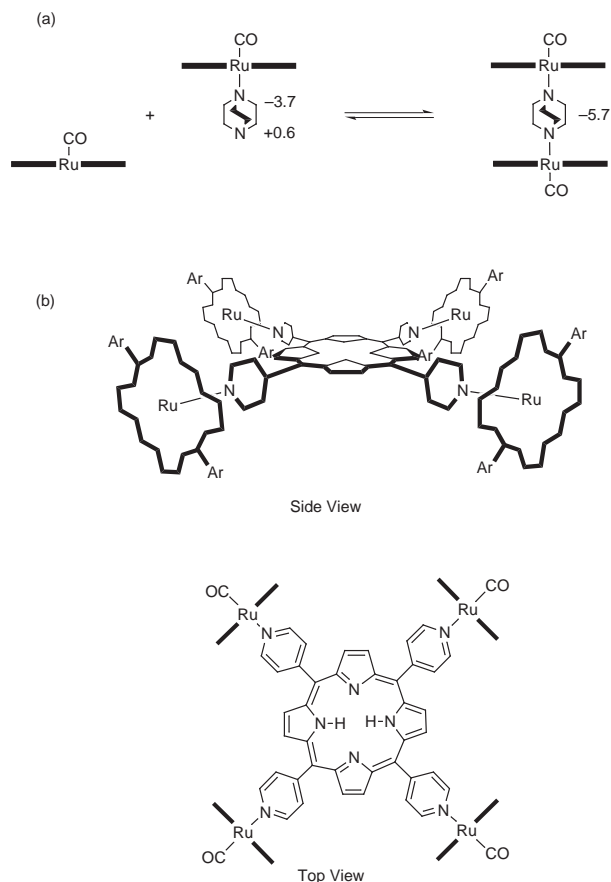


Fig. 1 (a) Equilibria and characteristic chemical shifts observed when Ru(II)-porphyrins bind DABCO; (b) cartoon representations of the assembly formed by coordination of four Ru-porphyrins to tetrapyrrolylporphyrin.

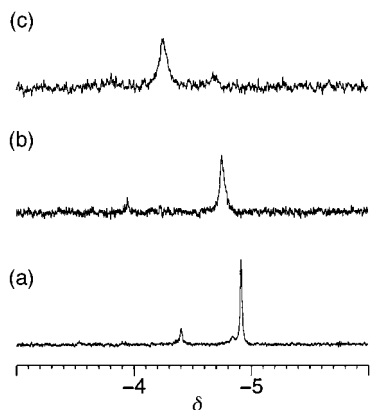


Fig. 2 Selected region of the ^1H NMR spectrum (500 MHz, CDCl_3 , 300 K) showing the NH protons of tetrapyrrolylporphyrin in the presence of: (a) 4 equiv. of monomer **9**, (b) 4 equiv. of pentamer **7**, (c) 4 equiv. of pentamer **4**.

4 can now be accommodated if the steric constraints can be released, resulting in a NH resonance at δ ca. -4.90 . The

remote porphyrins of **4** and **7** appear to have little effect on the NH chemical shift of the coordinating pyridyl porphyrins.

In summary we have demonstrated that a combination of covalent and coordination chemistry provides a versatile approach for the assembly of very large porphyrin arrays. Elsewhere we show how photolytic removal of the Ru-bound CO ligand, followed by additional ligation can produce even more elaborate arrays.⁴

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Notes and references

† All new compounds gave satisfactory ^1H and ^{13}C NMR spectra, MALDI-TOF mass spectra and analytical values. In particular, the ^1H NMR spectra of pentamers gave the correct integrated intensities for the four peripheral vs. single core porphyrin.

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