

A versatile synthetic strategy for construction of large oligomers: binding and photophysical properties of a nine-porphyrin array

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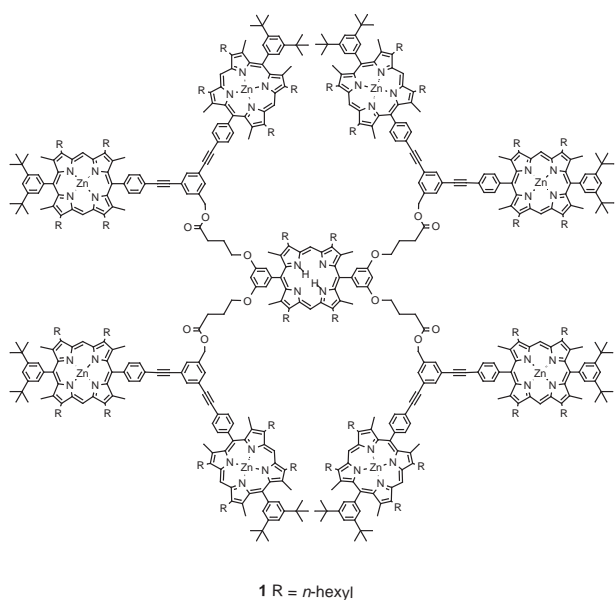
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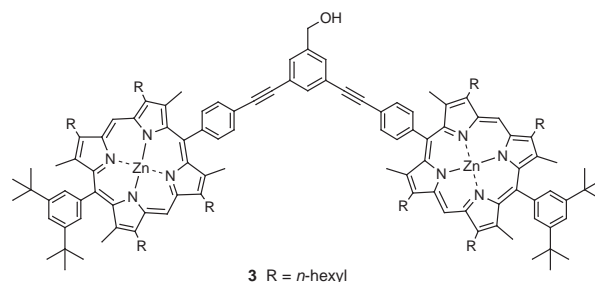
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Mitsunobu coupling of a free base porphyrin tetraacid with four equivalents of a monohydroxy metalloporphyrin dimer leads to a highly non-polar dendritic nine-porphyrin array that is readily separated from more polar products resulting from incomplete coupling; photophysical measurements reveal an energy transfer process from the peripheral metalloporphyrins to the central free-base porphyrin unit.

Covalently-linked dendritic arrays of porphyrins are of interest for their photophysical and electrochemical properties, but they present a substantial synthetic challenge.^{1,2} In particular, the chromatographic separation of successive generations, or of incomplete generations, becomes increasingly difficult. One solution has centred on the control of the chromatographic properties of the products, by varying the peripheral groups of the porphyrins between generations.² We now present a more versatile strategy based on Mitsunobu coupling of alcohols and acids to give esters.^{3,4} The key feature of this approach is the simultaneous Mitsunobu couplings of a multi-acid (or multi-alcohol) central core with several peripheral components, giving only one non-polar product; any incompletely coupled products will be significantly more polar and therefore easily separated. Here, we illustrate the strategy by describing the synthesis, binding and photophysical properties of the flexible nine-porphyrin array **1**. In the following communication⁵ we apply the same strategy to a mixed-metal 'star-shaped' porphyrin pentamer.



The key to the synthesis of **1** is the availability of the appropriately-functionalised porphyrin tetra-acid **2** and porphyrin dimer **3**. In order to avoid solubility problems, all the porphyrin units in **1** have the same hydrophobic methyl and



hexyl β -substitution pattern. Preparation of the porphyrin tetra-acid **2** involves condensation of aldehyde **4** with dipyrromethane **5** (generated *in situ*) followed by base hydrolysis. Recrystallisation from methanol gave pure **2**† in 21% overall yield. Unlike most other porphyrin acids, **2** is soluble in organic solvents such as THF or acetone. The synthesis of porphyrin dimer **3** has been reported previously.² Mitsunobu condensation of **2** with 4 equiv. of **3** in THF afforded **1**† in 69% yield as a purple solid which was easily separated from incompletely coupled side products and unreacted **2** and **3** by silica gel chromatography. Diagnostic resonances in the ¹H NMR spectrum of **1** are identified at δ -2.34 for the inner NH protons, and at δ 5.00 for the eight benzylic protons of the peripheral units. Additional confirmation for the preparation of **1** was obtained by a peak at m/z = 10045 in the MALDI-TOF spectrum (M_r C₆₆₄H₈₄₆N₃₆O₁₂Zn₈ = 10047).

As in the less flexible nine-porphyrin array that we reported earlier,² the rigid porphyrin dimer moieties in **1** can be brought together by cooperative binding to the bidentate ligand diazabicyclo[2.2.2]octane (DABCO). Titration of DABCO with **1** [Fig. 1(a)] gives a characteristic Soret maximum at 420 nm which is due to exciton coupling between the parallel porphyrin units.⁶ This exciton-coupled maximum was attained with *ca.* 10 equiv. of DABCO, which is comparable to the less-flexible nine-porphyrin array we described earlier.² However, the present flexible system is effectively unfolded again by $<10^4$ equiv. of DABCO, rather than the 10^6 -fold excess required by the rigid system. This reflects the larger number of conformations available to the more flexible system. Exciton-

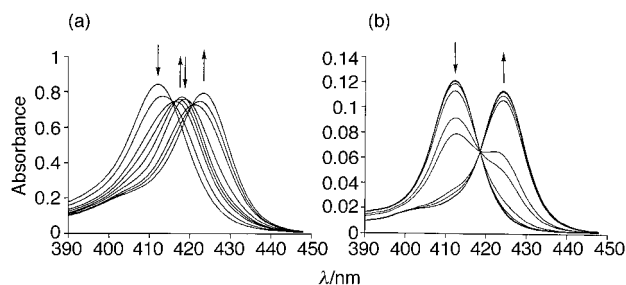
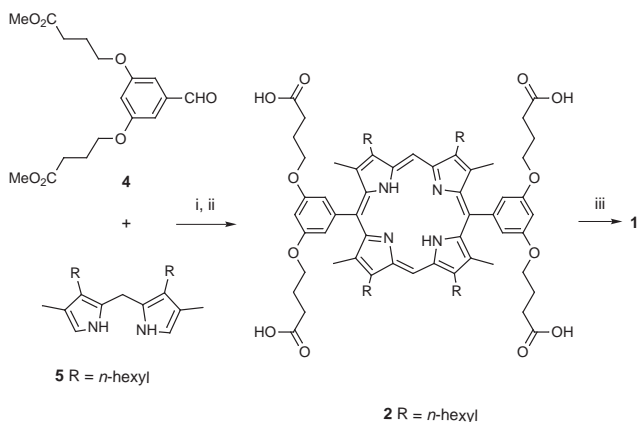


Fig. 1 UV-VIS titration (CH₂Cl₂) of DABCO (as a 2–4 $\times 10^{-4}$ M solution) vs. (a) **1** (number of equiv. added per nine-porphyrin array: 0, 1.1, 2.3, 4.0, 10.8, 22.7, 680, 1814, 7940) and (b) **3** (both as 2–5 $\times 10^{-7}$ M solutions).



Scheme 1 Reagents and conditions: i, TFA (−20 °C to room temp.), DDQ; ii, Na₂CO₃ (water–THF–ethanol), reflux; iii, **3** (4 equiv.), DEAD, PPh₃.

coupled spectra are not observed when the rigid porphyrin dimer **3** is titrated with DABCO [Fig. 1(b)].

The absorption spectrum of **1** approximates a superposition of the spectra of the constituent monomeric porphyrins, suggesting a relatively weak electronic interaction between the porphyrins. The fluorescence quantum yield of **3** ($\Phi_f = 0.035$, $\tau = 1.6$ ns, 298K) is nearly identical to that of the monomeric porphyrin precursors, indicating the absence of quenching processes. The luminescence properties of **1** indicate that both the fluorescence quantum yield and lifetime of the singlet excited state of the Zn porphyrin units are reduced 2.5 fold at 298 K relative to a monomeric Zn porphyrin. Furthermore, excitation spectra demonstrate a parallel sensitization of the fluorescence of the free base porphyrin by the Zn porphyrin. These results show that energy is transferred⁷ from the peripheral units to the core with *ca.* 60% efficiency ($k_{ET} = 9 \times 10^8$ s^{−1}). The transferred energy is subsequently emitted by the core free base porphyrin ($\Phi_f = 0.10$) with an efficiency nearly identical to that of a monomeric free base porphyrin. Calculations indicate that the most likely mechanism of energy transfer is the Förster type.⁸ The Zn porphyrin phosphorescence of **1** is completely quenched at 77 K, probably because of an energy transfer process to the triplet excited state localised on the central free base porphyrin, the phosphorescence of which is rarely observed.

In summary, we have described a synthetic strategy in which the chromatographic properties of the desired product have been designed to differ from the starting materials and side products. We have applied this approach to the preparation of a nine-porphyrin array (for which the photophysical properties have been presented), but clearly this methodology has the potential to be generalised for mixed metal systems⁴ or to other types of dendritic structures.

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Notes and references

† Selected data for **2**: anal. Found: C, 71.99; H, 7.98; N, 4.06. Calc. for C₇₆H₁₀₂N₄O₁₂: C, 72.23; H, 8.13; N, 4.43%. δ_H (250 MHz, DMSO-*d*₆) −2.62 (s, 2H, NH), 0.86 [t, *J* 7.2 Hz, 12H, (CH₂)₅CH₃], 1.25–1.55 [2 × m, 16H, (CH₂)₃(CH₂)₂CH₃], 1.70 [qnt, *J* 7.2 Hz, 8H, (CH₂)₂CH₂(CH₂)₂CH₃], 1.90–2.20 [2 × m, 16H, CH₂CH₂(CH₂)₃CH₃ and CH₂CH₂CO₂H], 2.41 (t, *J* 7.2 Hz, 8H, CH₂CH₂CO₂H), 2.62 (s, 12H, pyrrolic CH₃), 3.80–4.20 [m, 8H, CH₂(CH₂)₄CH₃], 4.15 (t, *J* 6.4 Hz, 8H, ArOCH₂CH₂), 7.00 (t, *J* 2.1 Hz, 2H, ArH), 7.21 (d, *J* 2.1 Hz, 4H, ArH), 10.18 (s, 2H, *meso*-H), 12.12 (s, 4H, CO₂H); δ_C (DMSO-*d*₆) 14.3, 22.6, 24.8, 26.4, 29.9, 30.6, 31.8, 33.4, 67.6, 96.8, 102.4, 112.8, 118.2, 136.5, 141.0, 143.3, 143.7, 144.7, 159.6, 174.5; UV–VIS (THF): positive FAB *m/z* 1265 [(M+H)⁺]; λ_{max} (log ϵ) 408 (5.44), 504 (4.77), 580 (4.69), 538 (4.64), 610 (4.55). **1**: anal. Found: C, 78.46; H, 8.41; N, 4.84. Calc. for C₆₆₄H₈₄₆N₃₆O₁₂Zn₈·3H₂O: C, 78.95; H, 8.50; N, 4.99%. δ_H (250 MHz, CDCl₃) −2.34 (s, 2H, NH), 0.85–1.00 [m, 108H, (CH₂)₅CH₃], 1.25–1.85 [3 × m, 216H, (CH₂)₂(CH₂)₃CH₃] 1.55 (s, 144H, Bu^t), 2.00–2.30 [2 × m, 80H, CH₂CH₂(CH₂)₃CH₃ and CH₂CH₂CO₂], 2.43 (s, 48H, pyrrolic CH₃), 2.49 (s, 48H, pyrrolic CH₃), 2.61 (t, *J* 7.7 Hz, 8H, CH₂CH₂CO₂), 2.78 (s, 12H, core pyrrolic CH₃), 3.60–4.30 [2 × m, 80H, CH₂(CH₂)₄CH₃ and ArOCH₂CH₂], 5.00 (s, 8H, CO₂CH₂Ar), 7.00–7.10 (m, 2H, core ArH), 7.31–7.39 (m, 4H, core ArH), 7.63–8.15 (overlapping m, 68H, ArH), 10.05 (s, 16H, *meso*-H), 10.31 (s, 2H, *meso*-H); δ_C (CDCl₃) 14.2, 14.7, 15.0, 15.6, 22.9, 24.8, 26.7, 26.9, 27.0, 30.1, 30.9, 31.8, 32.1, 33.4, 35.3, 65.3, 67.4, 89.1, 91.1, 97.6, 102.4, 112.9, 117.7, 118.0, 121.0, 122.6, 124.4, 128.1, 130.8, 133.5, 134.5, 136.3, 136.9, 137.5, 138.6, 141.6, 142.6, 143.5, 144.2, 144.6, 145.0, 146.2, 146.5, 147.3, 148.1, 149.8, 159.5, 172.9; UV–VIS (CH₂Cl₂): λ_{max} (log ϵ) 412 (6.46), 538 (5.19), 576 (4.91).

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