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The Supramolecular Assembly of Porphyrin Arrays

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Abstract. The self-assembly of porphyrin arrays containing three, seven or eleven porphyrins results from the interaction of the bis-pyridyl porphyrin **1** with the zinc porphyrins **2**, **3**, or **4**, respectively.

Key words: porphyrin, arrays, self-assembly, supramolecular.

1. Introduction

Self-assembled porphyrin arrays have attracted much attention in recent years. Supramolecular chemistry would appear to circumvent a number of synthetic problems common to the formation of large porphyrin arrays. These porphyrin assemblies have been constructed using hydrogen bonding [1], and transition metal coordination [2]. Recent work in the coordination of *meso*-pyridyl functionalised porphyrins to ruthenium tetraphenylporphyrin has provided a variety of geometrically diverse dimers, trimers, tetramers and pentamers. We considered this an excellent method for dramatically increasing the size of porphyrin arrays in a relatively straightforward fashion. Here, we present the synthesis of a number of porphyrin arrays formed by the interaction of the *bis-meso*-pyridylporphyrin **1** [3] with zinc tetraphenylporphyrin **2**, the trimeric porphyrin array **3** [4] and the pentameric array **4** [5] to give new supramolecular arrays of three **5**, seven **6** and eleven **7** porphyrins, respectively.[1]

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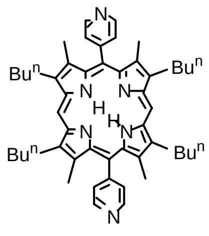
[1] Selected ^{1}H NMR (270 MHz, CDCl$_3$) data for: **5**: $\delta = -2.59$ (br s, 2H, NH), 0.977 (t, 12H, CH$_3$), 1.56–1.49 (m, 20H, CH_2 and CH$_2$CH_3), 1.95–1.79 (m, 8H, CH$_2$), 3.15 (d, 4H, ^{3}J = 5 Hz, H$_{\text{pyridyl}}$), 3.16 (t, 8H, CH_2CH$_2$CH$_2$CH$_3$), 6.29 (d, 4H, ^{3}J = 5 Hz, H$_{\text{pyridyl}}$), 7.82–7.75 (m, 24H, H$_{m,p\,\text{Ph}}$), 8.31–8.27 (m, 16H, H$_{\text{Ph}}$), 8.98 (s, 16H, H$_{\text{pyrrole, ZnTPP}}$), 9.85 (s, 2H, H$_{\text{pyrrole}}$). For **6** $\delta = -2.73$ (br s, 2H, NH), 2.58–2.67 (m, 132H, ArCH$_3$, CH$_{3\,\text{trimer}}$ CH$_{3\,\text{bis-pyridyl}}$), 3.47 (br s, 4H, H$_{\text{pyridyl}}$), 3.90 (t, 8H, CH_2CH$_2$CH$_2$CH$_{3\,\text{bis-pyridyl}}$), 4.10 (t, 16H, CH_2CH$_2$CH$_2$CH$_{3\,\text{trimer}}$), 6.89 (br s, 4H, H$_{\text{pyridyl}}$), 7.41 (dd, 8H, ^{3}J = 16 Hz, H$_{\text{ethenyl}}$), 7.45 (d, 16H, J = 2 Hz, H$_{p\text{Ar trimer}}$), 7.71 (m, 32H, H$_{\text{Ar}}$), 8.12 (d, 8H, ^{3}J = 8Hz, H$_{\text{Ar}}$), 8.82–8.68 (m, 28H, H$_{\text{pyrrole, trimer}}$), 9.08 (s, 4H, H$_{\text{pyrrole, trimer}}$), 10.03 (s, 2H, H$_{\text{pyrrole, bis-pyridyl}}$), 10.29 (s, 4H, H$_{\text{pyrrole, trimer}}$). For **7** δ = 1.07 (t, 12H, ^{3}J = 7 Hz, CH$_3$), 1.60–1.75 (m, 16H, CH$_2$), 1.98–2.08 (m, 8H, CH$_2$), 3.72–3.86 (m, 8H, CH$_2$), 2.47–2.47 (m, 204H, CH$_3$), 4.71 (br s, 4H, H$_{\text{pyridyl}}$), 7.05 (br s, 4H, H$_{\text{pyridyl}}$), 7.33 (m, 8H, H$_{\text{Ar}}$), 7.39 (s, 8H, H$_{\text{Ar}}$), 7.47 (m, 16H, H$_{\text{Ar}}$), 7.39 (q, 16H, ^{3}J =16 Hz, H$_{\text{ethenyl}}$), 7.64 (s, 32H, H$_{\text{Ar}}$), 7.70



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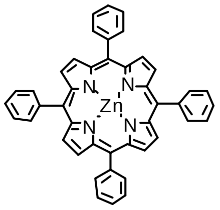

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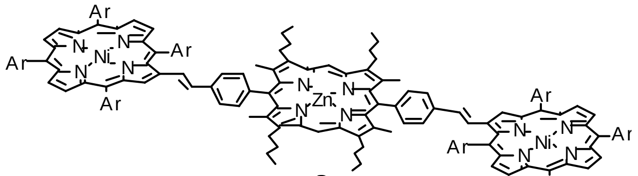

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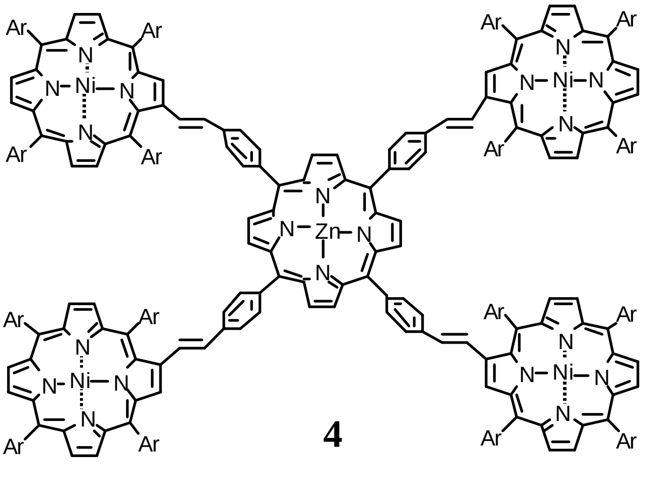

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2. Results and Discussion

In this preliminary work we have focused our attention on zinc as the coordinating metal. An NMR titration of **1** with **2** results in the formation of a symmetrical compound. Most notable is the change in chemical shifts of the pyridyl protons from 9.02 and 8.05 ppm in **1** to 3.15 and 6.29 ppm in **5** as they come under the influence of the diamagnetic ring-current of the porphyrin **2**. This result is similar to the well known chemical shift changes observed for the coordination of a pyridine to a Zn(II) ion held in a porphyrin core [6]. The predicted structure was a trimeric

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(m, 48H, H_{Ar}), 8.36 (d, 16H, ^3J = 16 Hz, H_{Ar}), 8.80–8.70 (m, 56H, $H_{pyrrole}$), 9.09 (s, 8H, $H_{pyrrole}$), 9.22 (s, 16H, $H_{pyrrole}$), 10.04 (m, 56H, $H_{pyrrole\ bis-pyridyl}$).

porphyrin **5** where both the pyridyl groups on **1** are bound to a ZnTPP. This was confirmed by a single crystal X-ray determination of **5**.[2]

Crystals of **5** were obtained from the slow diffusion of MeOH into a CH_2Cl_2 solution containing **1** and **2** in a 1 : 2 ratio. The structure of **5** is shown in Figure 1 and is confirmation that both pyridines in **1** are available for coordination. The ZnTPP groups are symmetry equivalent and are effectively perpendicular to the porphyrin core of the *bis-meso*-pyridyl porphyrin.

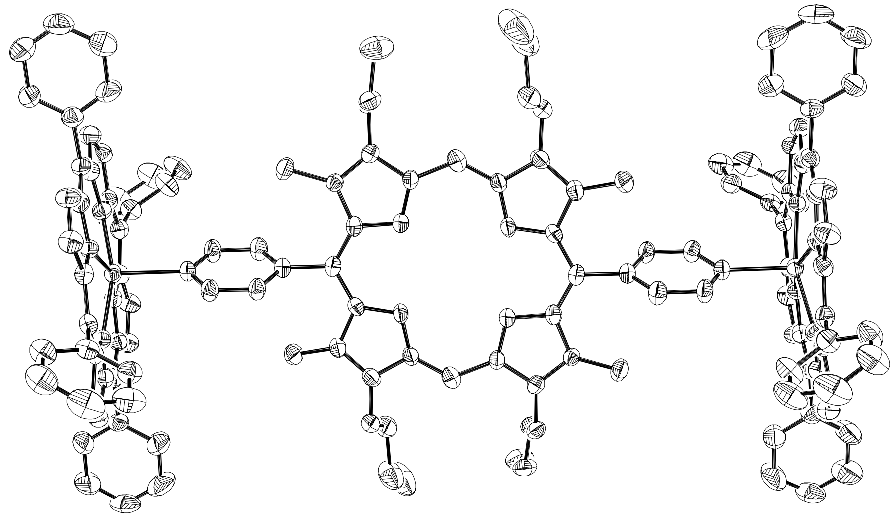

Figure 1. Molecular structure of **5**.

The formation of large porphyrin arrays can be achieved in similar fashion using **3** or **4**.[3] Once again the shifts of the pyridyl protons are indicative of the coordination of the pyridine to a zinc bound in a porphyrin core. Thus the addition of two equivalents of **3** to **1** in $CDCl_3$ results in the formation of a seven porphyrin array **6**, with the pyridyl protons shifting from 9.02 and 8.05 to 3.47 and 6.89 ppm, respectively. The potential of this reaction is most clearly demonstrated by the reaction of two equivalents of **4** with **1**. This gives rise to an eleven porphyrin

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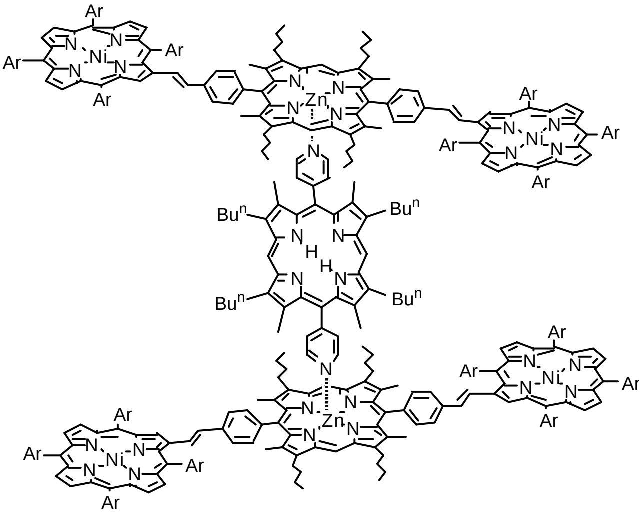
[2] *Crystal data* for **5**: C_{138} H_{122} N_{14} Zn_2, M = 2107.24, monoclinic, space group $P2_1/c$, a = 12.296(2), b = 21.057(5), c = 21.659(5) Å, β = 101.16(3)°, U = 5502(2) $Å^3$, Z = 2, D_c = 1.272 g cm^{-3}, μ = 0.496 mm^{-1}, (Mo-Kα, λ = 0.71073 Å), $F(000)$ = 2216, T = 295 K, Enraf-Nonius Cad-4 diffractometer, crystal size 34 × 0.24 × 0.21 mm, $2\theta_{max}$ 50°, 10144 reflections measured, 9662 unique (R_{int} = 0.0435). Structure solution by direct methods, full-matrix least-squares refinement F^2 for all data, with anisotropic displacement parameters, riding isotropic H atoms, no absorption correction. Final $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]_{...}\}$ = 0.2000 for all data, conventional R = 0.0468 for 4309 data having $F_o^2 > 2\sigma(F_o^2)$, S = 0.988. Final difference map between 0.332 and −0.580 e $Å^{-3}$. Programs: SHELXS-95, SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany), and ORTEP-3. CCDC-100833

[3] Porphyrins **3** and **4** have meso-3,5-dimethylphenyl substituents (Ar = 3,5-dimethylphenyl).

array **7** with an ^{1}H NMR spectrum indicative of a symmetrical compound. The pyridyl protons are shifted from 9.02 and 8.05 to 4.71 and 7.05 ppm, respectively.



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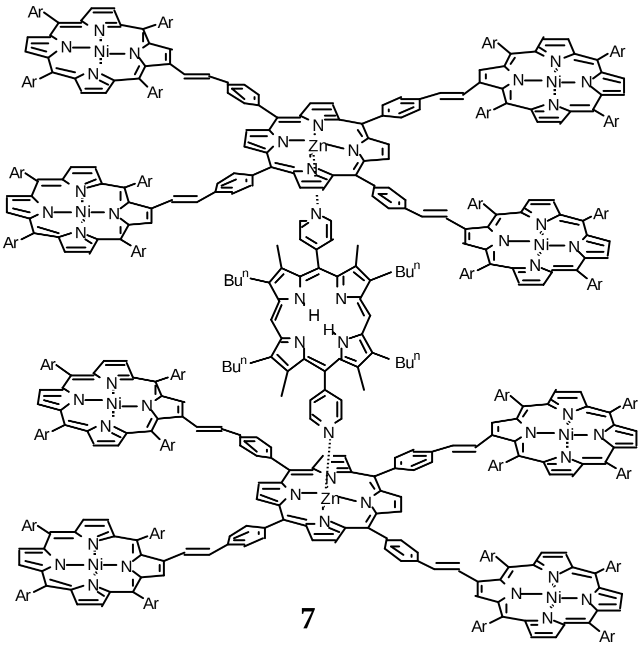

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Stepwise equilibrium constants for the formation of **5** and **6** were evaluated by consideration of the shift in ^{1}H NMR pyridyl proton signals of **1**, Figure 2. NMR experiments were conducted for total zinc porphyrin (M either **2** or **3**) to pyridyl ligand (L) **1** concentration ratios from 0 to 3.5 and constants were optimised using a SIMPLEX [7] algorithm based upon proportionality of the signal shift to the mole fraction of pyridyl ligand bound to zinc porphyrin. The formation of both **5** and **6** were found to proceed *via* an intermediary 1 : 1 complex; $K_{\mathrm{ML}} = 4.2 \times 10^3$ and $K_{\mathrm{M2L}} = 2.3 \times 10^3$ for **5** and $K_{\mathrm{ML}} = 2.7 \times 10^4$ and $K_{\mathrm{M2L}} = 1.3 \times 10^4$ for **6**. Unfortunately, the large number of protons in **4** prevents an accurate measurement of the equilibrium constant for the formation of **7**.

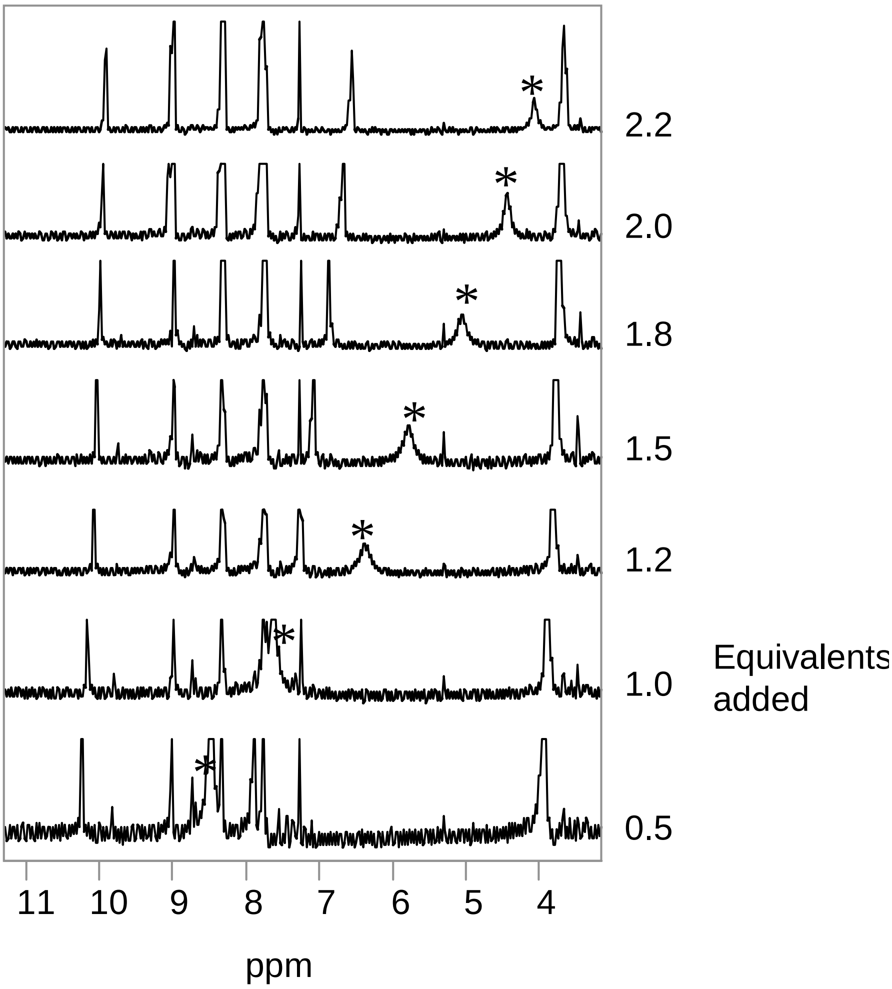

Figure 2. Some examples of the ^{1}H NMR spectra of **1** with varying equivalents of **2**. α-Pyridyl protons are marked with an asterisk.

The eleven porphyrin array, **7**, is the largest, coordinated porphyrin array currently known, testifying to the utility of this approach for the formation of porphyrin arrays. This work is continuing with other metalloporphyrins, specifically ruthenium-containing species, which have much higher binding constants enabling greater elaboration of the arrays [8].

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