Templated formation of multi-porphyrin assemblies resembling a molecular universal joint

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The rigid bis-porphyrinic host 2 forms 1:1 complexes with rigid 5,15-bis(4-pyridyl)porphyrins and both 1:1 and 2:1 complexes with tetrapyridylporphyrin 4, with the latter complex providing a new example of a self-assembled system containing an enclosed molecular environment.

Strategies for self-assembly are receiving increasing attention for the construction of multichromophoric supramolecular arrays involving porphyrins.[1] In particular, metal ion co-ordination utilising ligation of the metallated porphyrin nucleus has proven efficient for positioning photoactive components.[2,3] Systems exerting co-operativity between two or more non-covalent interactions provide access to self-assembled arrays with increased stability compared to systems relying on a single interaction alone.[3] The construction of such porphyrinic arrays is a key to the development of synthetic models which mimic the manner in which nature assembles the photoactive components within the photosynthetic apparatus and produces charge separation in high quantum yield.[4]

Here, we show that the rigid bis-porphyrin **2** can react with rigid dipyridyl porphyrins to form 1:1 complexes, and that the tetrapyridylporphyrin component **4** can form both 1:1 and 2:1 complexes;† the latter porphyrin array **7** has a shape and mobility reminiscent of a universal joint.‡ While such a structure is novel and aesthetically intriguing, its value is conceptual; it may have interesting photophysical properties and its formation suggests similar methodologies for the assembly of other large covalent capsules.

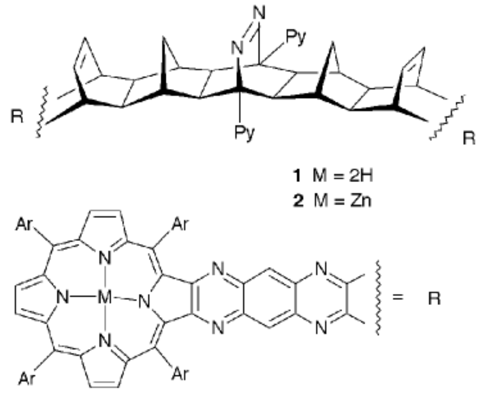
Molecular modelling (AM1) revealed that a self-assembled host–guest arrangement between bis-porphyrin **2** and rigid dipyridyl rod **3** or tetrapyridyl rod **4** should be feasible, based on the following dimensions: a porphyrin centre-to-centre distance in **2** of 22 Å (Fig. 1); pyridine N–N distances in 5,15-dipyridyl substituted porphyrins **3** and **4** of 15.7 and 15.5 Å, respectively; and an average zinc porphyrin to pyridyl bond distance of 2.2 Å.[7]

Mixing equimolar amounts of rigid bis-porphyrin **2** [formed from **1**[8] by treatment with $Zn(OAc)_2$ in CH_2Cl_2–MeOH] and dipyridyl porphyrin rod **3**§ ($CDCl_3$ or CD_2Cl_2) resulted in the formation of a 1:1 complex **5** (C_{2v}). Examination by ^{1}H NMR spectroscopy revealed sharp resonances for **3** complexed on the inside of **2** in which the resonances for **2** were slightly broadened. Such broadening has been observed previously in complexation studies involving **3**,[9] and in both cases these signals were sharpened by cooling the solution to 263 K or below.

The α- and β-pyridyl resonances of **3** within **5** are drastically affected by the host porphyrin system's magnetic anisotropy, shifting upfield by 5.74 and 1.66 ppm respectively. In contrast, the proton resonances of the fused carbocyclic framework in **5** are only slightly affected by the guest porphyrin (*ca.* $\Delta\delta$ 0.14). Such large pyridyl shifts are indicative of coordination of the bis-pyridyl porphyrin guest with the bis-zinc porphyrin host.[3]

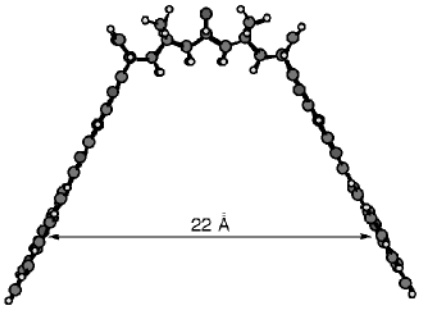
UV spectroscopic titrations carried out in CH_2Cl_2 at 298 K (424 and 433 nm) yielded a Job plot with a maximum at $x = 0.5$, confirming the 1:1 stoichiometry of complexation in **5**. Analysis of the titration data by non-linear least-squares revealed an empirical association constant of *ca.* 10^8 M^{-1}. This association constant is considerably stronger than that observed for pyridine itself with a zinc porphyrin precursor (10^4 M^{-1}) indicating strong chelation within **5**.

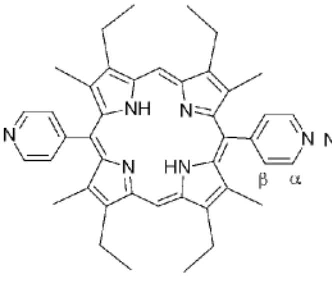
When the dipyridylporphyrin guest was replaced by the tetrapyridylporphyrin **4**,[10] the ^{1}H NMR spectrum at 303 K for a 1:1 mixture of host **2** and guest **4** in $CDCl_3$ revealed sharp



1 M = 2H
2 M = Zn

Ar = 3,5-di-*tert*-Butyl   Py = 2-pyridyl





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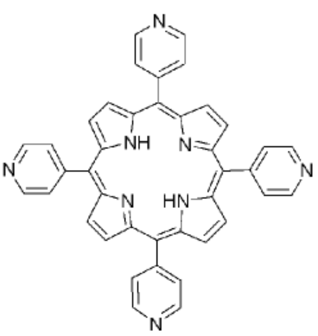

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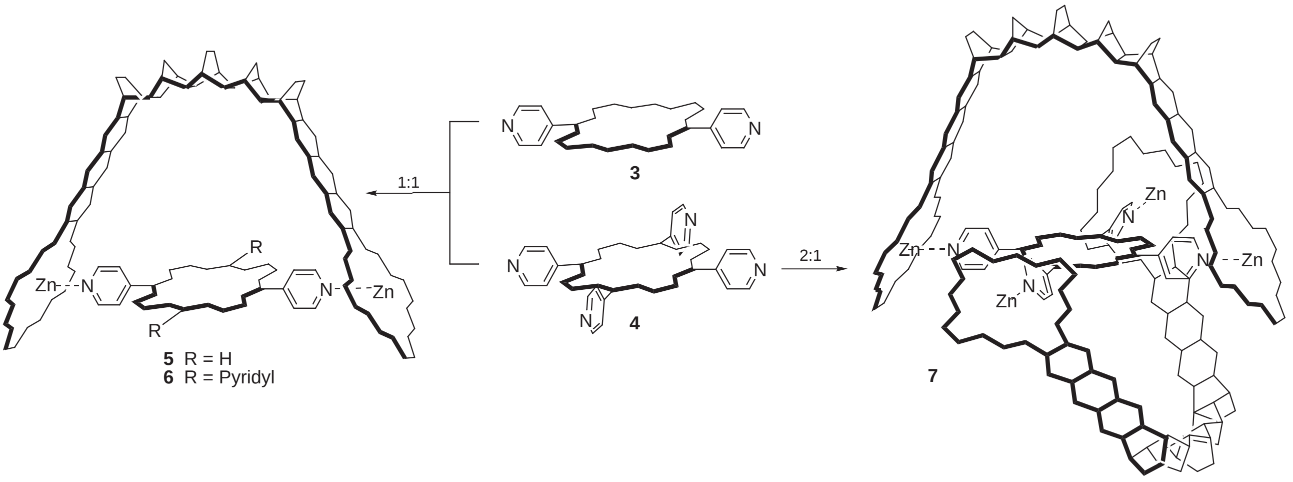
Fig. 1 Molecular modelling of the skeletal backbone of **1** reveals the overall U-type geometry.



Scheme 1

resonances for **2** and, surprisingly, only a single resonance for **4**, the pyrrole NH (δ −3.77, $\Delta\delta$ −0.89 ppm). The resonances for the protons of the norbornyl backbone of cavity molecule **2** are again only slightly affected by the addition of **4** (*ca.* $\Delta\delta$ 0.04 ppm), but the fact that those on the inside face of the backbone are most affected is consistent with the formation of an internal 1:1 complex. Cooling this solution to 233 K produced a new set of proton resonances where the resonances for α- and β-protons of **4** now reflect their new complexed environment. Two unique sets of resonances for the pyridyl ring protons were observed with the most shielded set occurring at δ 3.19 ($\Delta\delta$ −5.9 ppm) and 6.35 ($\Delta\delta$ −1.8 ppm).

The second set of pyridyl ring protons for **4** in the 1:1 complex **6** are less shielded (*viz.* α $\Delta\delta$ −0.2 ppm, β $\Delta\delta$ −0.49 ppm) from the resonances of uncomplexed **4** and this smaller shift is consistent with the uncoordinated pyridyl groups being in a complexed environment such as **6**. Saturation transfer experiments revealed that the two sets of pyridyl ring proton resonances undergo rapid exchange. The above data support **4** being complexed within the cavity of **2** yet with an uncoordinated environment for the second set of pyridyl rings, as illustrated in Scheme 1. The formation of the 1:1 complex in solution is consistent with electrospray mass spectrometry of the complex, which yielded peaks for **6** (*m/z* 1837 $[M + 2H]^{2+}$).

We were intrigued by the possibility of encapsulating the tetratopic guest **4** within two of the ditopic host units **2**. ^{1}H NMR examination at 303 K of a solution containing a 2:1 ratio of **2** to **4** revealed a similar situation to the 1:1 case, *i.e.* complete absence of any resonances for **4** except for the pyrrole NH resonance (δ −4.05 $\Delta\delta$ −1.17 ppm) and small but significant changes for the resonances of **2** (*ca.* $\Delta\delta$ 0.09 ppm). Cooling the solution to 233 K again yielded new resonances derived from guest **4**, *i.e.* two sets of resonances for the pyridyl protons of **4**, but now both sets of resonances indicate porphyrin coordination ($\Delta\delta$ α −5.76, −6.17 and β −1.67, −2.99 ppm). Furthermore, two resonances were observed for the β-pyrrole resonances of **4** in **7** compared to a single resonance for uncomplexed **4**.

We interpret these data as follows. The two α- and β-pyridyl proton resonances are a result of the assymmetry enforced by the horizontal and rotationally rigid positioning of **4** within **7**. The two β-pyrrole resonances can result from either of two effects, (a) the formation of a distorted complex (Scheme 1) where the complexation of the second equivalent of **2** is forced to adopt an eccentric position owing to the steric interactions between the *tert*-butyl substituents on the porphyrin subunits¶ and where the subunits are reciprocating slowly on the NMR timescale, or (b) the result of slow NH tautomerism in the central free-base porphyrin unit, with fast exchange between the two possible eccentric conformations of **7**.‖ We also note that free-base **2** shows evidence of NH tautomerism at similar low temperatures. In either case, the result is an intriguing arrangement resembling a molecular scale mechanical universal joint.

The concept of organising two host molecules around a central template has been successfully employed by others to create enclosed molecular environments.[5,6] The ability of **2** to act as a host for other porphyrinic guests opens the way for non-covalent positioning of photoactive components and such studies are underway in our laboratories.

Notes and references

† Crossley *et al.* have recently reported the first 2:1 complex involving the self-assembly of rigid bisporphyrins (2 equiv.) using a flexible tetratopic amine (ref. 5).

‡ This complex also bears some resemblance to the topology of the Rebek ‘ball-like’ molecules, although the latter assemble independently of guest inclusion in contrast to the templated assembly described here (ref. 6).

§ The synthesis of the dipyridylporphyrin rod **3** was achieved by the acid-catalysed condensation of 3,3′-diethyl-4,4′-dimethyldipyrromethane and pyridine-4-carbaldehyde followed by oxidation with chloranil (ref. 9).

¶ Such an off-centre arrangement is also supported by molecular modelling.

‖ We thank the referee for suggesting this alternative. Experiments are currently underway to differentiate between (a) and (b).

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