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Formation of A_2B_2 supramolecular porphyrin co-polymers

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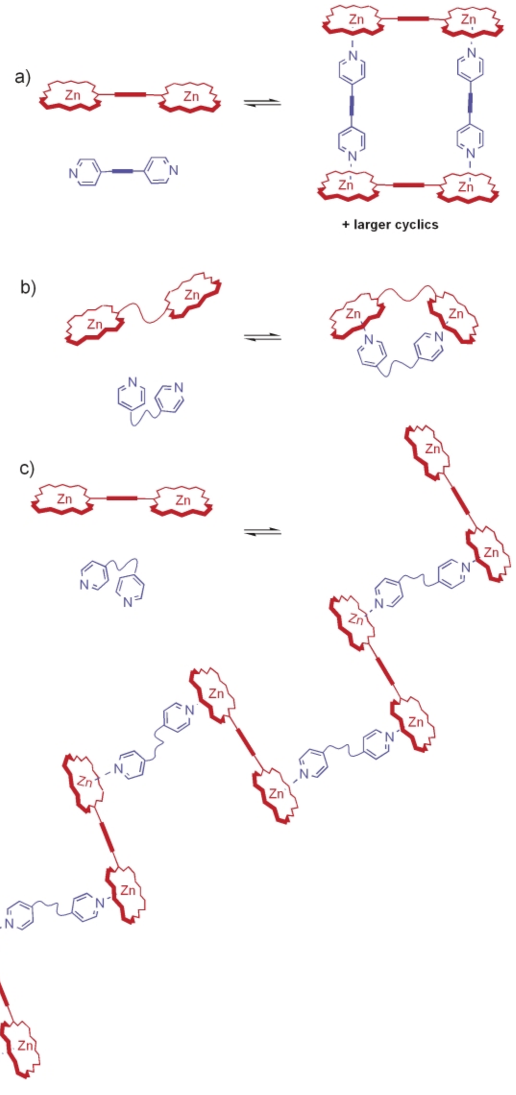
New supramolecular A_2B_2 co-polymers formed in solution from a *rigid* diporphyrin monomer (the A_2 unit) and a short *flexible* dipyridine monomer (the B_2 unit) are reported; NMR experiments show that complete binding occurs at mM concentrations; UV titrations reveal that the dipyridine unit and a monomeric control ligand have identical binding constants, confirming that linear polymers were generated (in preference to small cyclic oligomers); at 2×10^{-2} M polymers with an average molecular weight of 17 100 g mol^{-1} and containing approximately 14 porphyrin units have formed.

The ability to efficiently harvest light will ultimately lead to a number of major technological advancements. The main inspiration in developing such systems has come from nature's light harvesting complexes, which contain multiple porphyrin arrays.[1–3] These biological complexes have stimulated an enormous amount of activity towards the construction of synthetic counterparts containing multiple porphyrin arrays.[4–12] Most of this work has relied on traditional covalent chemistry,[4–8] which can often be complicated and/or time consuming. Another approach is to use supramolecular chemistry,[9–12] offering us the very real advantage of obtaining multi-porphyrin arrays using simpler chemistry that can be easily varied and modified. With some notable exceptions, the majority of supramolecular arrays are limited to the solid state or involve repeat units having both binding groups within the same molecule. The approach described within this paper uses two separate monomers each having complimentary binding groups. Our design utilises a two-component system, and is based on the application of a zinc metalated porphyrin dimer (an A_2 monomer) coordinating to a pyridine dimer (the B_2 monomer). This design is synthetically simple; meaning that either the A_2 or the B_2 unit can be varied, allowing us to enhance or change the properties of the final polymeric system. Despite the simplicity of this approach, the A_2 and B_2 monomers must meet specific design requirements (to prevent them from forming small cyclic species). For example, rigid monomer units may be predisposed to form cyclic oligomers, the size of which is controlled by thermodynamics and substrate geometry. Such predisposition results in cooperativity and is accompanied by enhanced binding, Scheme 1(a). Although completely flexible or '*scruffy*' monomeric units are not predisposed to form cyclic oligomers, it is still possible for these systems to form simple 1 + 1 dimers, as shown in Scheme 1(b). However, a balanced system utilising both rigid and flexible monomers will produce solution phase polymers (the molecular weights of these polymers will be controlled by monomer concentration and binding constant K). A final design consideration involves the length of the flexible unit; if the two end groups of the flexible unit can coordinate to both ends on the *same* rigid unit, then 1 + 1 dimers would form (Scheme 1(b)), once again the final binding (*i.e.* cyclisation) will be cooperative and therefore associated with a high binding affinity. Our approach towards supramolecular poly-porphyrins, which is shown schematically in Scheme 1(c), uses a long *rigid* porphyrin dimer **1** (Fig. 1) and a short *flexible* pyridine dimer† **2**, which is capable of adopting a variety of different conformations at room temperature (that



Scheme 1 The possible structures using various porphyrin dimers and pyridine dimers: (a) totally rigid, (b) totally flexible and (c) a combination of rigid and flexible units.

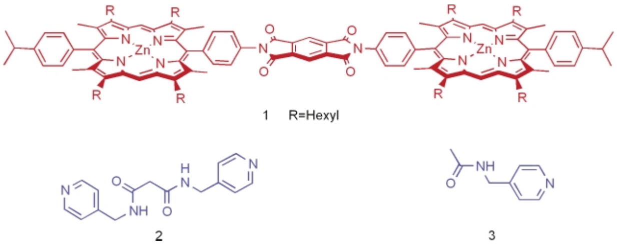


Fig. 1 The rigid porphyrin dimer, the flexible pyridine dimer and the mono-pyridine required for control experiments.

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is, pyridine dimer **2** is not predisposed to adopt any specific geometry). The pyridine dimer **2** can be synthesised, in moderate yield and high purity, by reacting malonyl chloride with two equivalents of 4-picolylamine in the presence of triethylamine. A monomeric pyridine derivative **3**, which was required for control experiments, was synthesised by reacting 4-picolylamine with acetic anhydride under basic conditions. The porphyrin dimer **1** was obtained by reacting 1,2,4,5-benzene tetracarboxylic dianhydride with two equivalents of a mono-functionalised aminoporphyrin[13,14] and an excess of acetic anhydride in DMF.[15] The crude product was a complicated mixture of components that could only be purified by repetitive column chromatography to obtain the desired product in around 40% yield. Having synthesised **2** and **3** in sufficient quantities we began investigating their potential to form supramolecular polymers.

^{1}H NMR experiments on the porphyrin dimer **1**, the pyridine dimer **2**, and an equimolar solution of **1** and **2** (all at 1.1×10^{-2} M) confirmed that complete binding had taken place. The α protons on the pyridine groups resonate at 8.55 ppm and the β protons resonate at 7.40 ppm, after addition of the porphyrin groups these protons sit within the shielded region of the porphyrin and consequently their resonances are shifted down field in the spectrum. The pyridine α protons shifted to 2.95 ppm, whilst the β protons were shifted to the area of the spectrum masked by the porphyrin's side chains (the benzyl and the $CH_2(CO)_2$ resonances were also shifted to the same masked region, nevertheless, integration confirms that 12 extra protons are now present somewhere between 0.6 and 4 ppm). In addition, the spectrum for the equimolar solution of the two monomers is noticeably broader than that obtained from the two monomers independently; this broadness is indicative of large macromolecular structures. Although these NMR experiments tell us nothing about the precise macro structure of these assemblies, they did confirm that complete binding had taken place and macromolecular structures had formed (at 1.1×10^{-2} M). Simple UV experiments (to determine the binding strength between porphyrin dimer **1** and the pyridine ligands **2** or **3**) were used to discriminate between polymerisation and cyclisation. For example, if macro-cyclisation takes place, we would predict it to occur at a significantly higher binding constant for the pyridine dimer **2** (due to cooperativity effects), compared to that obtained using the monomeric pyridine ligand **3**, which cannot form cyclics. However, if polymerisation was occurring in a linear fashion *via* a series of simple 1 : 1 binding events, then the association constants of the pyridine monomer **3** and the pyridine dimer **2** will be the same. Results from the binding assays are shown in Table 1. The monopyridyl derivative **3** forms simple 1 : 1 complexes with a binding constant of 2900 M^{-1} (this ligand cannot form cyclics). The binding constant of the dipyridine unit **2** is very similar to that obtained from the monomer **3** (2500 *vs.* 2900 M^{-1}). Thus, the similarity in the binding constants for the mono- and di-pyridine derivatives, confirms that the predominant species in solution (at mM concentrations) is a linear polymer. The average number of units in the polymer (N) can be calculated using the well established relation $N = (K[\text{monomer}])^{1/2}$, which relates binding constant and concentration.[16] Therefore, at a concentration of 2×10^{-2} M, polymers with an average molecular weight of 17 100 g mol^{-1} and 14 porphyrins were formed (K = 2500 M^{-1}).

Table 1 Binding constants of the pyridine derivatives to the porphyrin dimer **1** (calculated per pyridine unit)

Ligand	K/M^{-1}
Pyridine dimer **2**	2900 (±135)
Pyridine monomer **3**	2500 (±125)

In conclusion, by selecting repeat units with particular structural properties, we have been able to generate flexible A_2B_2 supramolecular porphyrin co-polymers in solution. From the NMR and binding constant analysis, we were able to demonstrate that these linear polymers/arrays are preferred to smaller cyclic species. Current work involves the generation of ligands/porphyrins with higher binding affinities and evaluating these systems in photophysical applications.

Notes and references

† π–π Stacking interactions between porphyrins linked *via* a flexible tether could lead to collapsed and complicated structures; the di-porphyrin unit was therefore selected as our *rigid* component.

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