

Self-assembly of Macrocyclic Porphyrin Oligomers

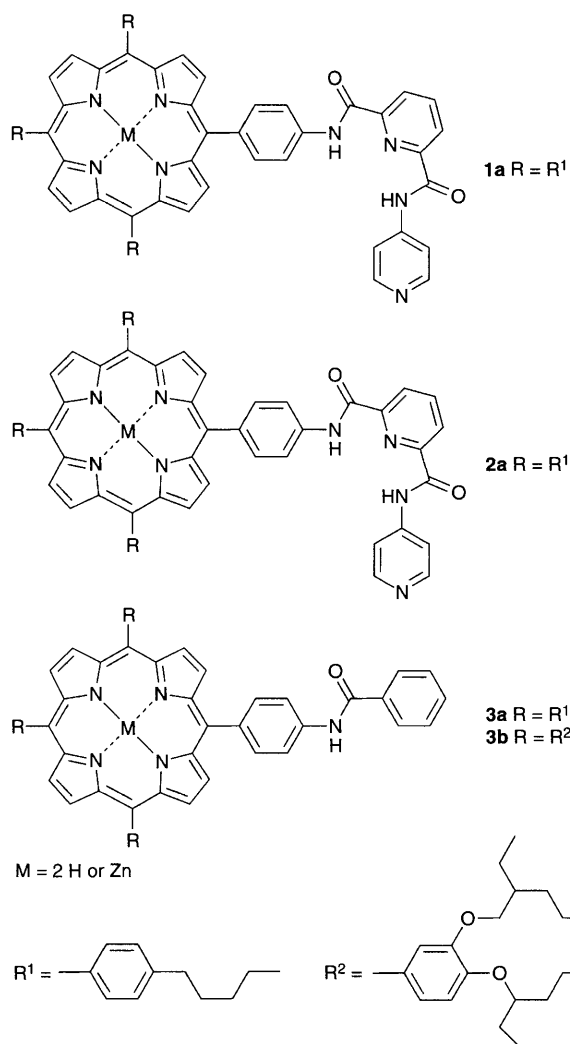
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Coordination of zinc porphyrins by pyridine ligands is used to construct macrocyclic complexes: the self-assembly properties of the cyclic oligomers depends critically on the covalent structure of the monomer units which can be selected to give stable di-, tri- or tetra-meric assemblies.

The coordination of a basic nitrogen ligand to a metalloporphyrin is an attractive interaction for probing the scope of non-covalent chemistry for controlling structure and reactivity. In recent years, this recognition motif has been exploited in the study of host-guest interactions,¹ template-directed synthesis,² enzyme-like catalysis³ and self-assembly.⁴ We have been using the coordination of pyridine ligands to zinc porphyrins to investigate the self-assembly of macrocyclic porphyrin structures which encompass large functionalised cavities capable of guest recognition.⁵ Here we extend this approach to the construction of self-assembled tri- and tetra-meric macrocycles.

Zn1 forms a remarkably stable self-assembled dimer in solution.⁵ We reasoned that changing the angle between the pyridine ligand and the plane of the porphyrin would lead to quite different self-assembly properties. Thus increasing the angle between the plane of the porphyrin and the orientation of the pyridine ligand from 90° in Zn1 to 150° in Zn2 should favour the formation of a trimeric macrocycle (Fig. 1).



Similarly, Zn3 has an appropriate geometry for self-assembling as a tetramer (Fig. 2). Zn2a, Zn3a and Zn3b were synthesised in good yield (>80%) from the corresponding amino porphyrins using similar procedures as reported previously for Zn1.[†]

The ¹H NMR spectrum of Zn2a in chloroform is characteristic of a complex in which the pyridyl group is coordinated to a zinc centre. The changes in ¹H NMR chemical shift of the signals due to the pyridyl protons of Zn2a relative to those for H₂2a are shown in Fig. 3. The α-pyridine protons experience very large upfield shifts due to their proximity to the porphyrin ring current. The ¹H NMR spectrum is essentially concentration independent, indicating the presence of a stable self-assembled complex at concentrations greater than 10⁻⁴ mol dm⁻³ in

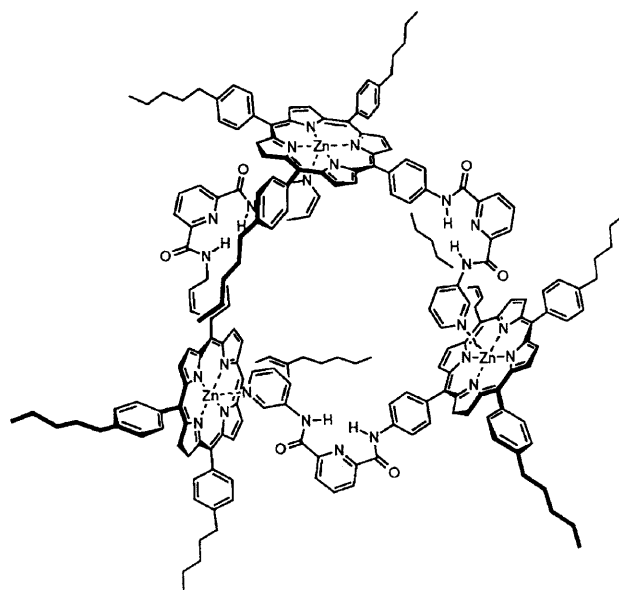


Fig. 1 The structure of the self-assembled trimer (Zn2a)₃

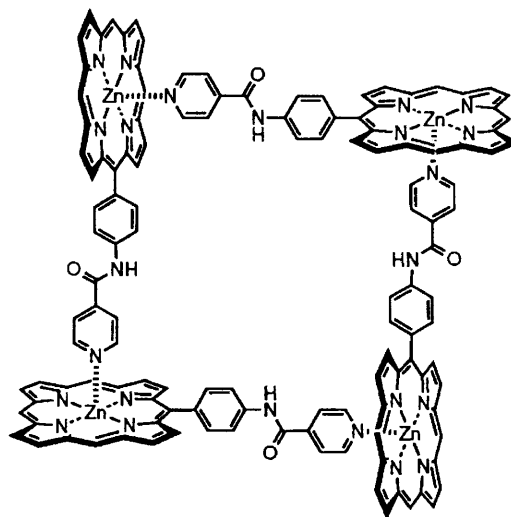


Fig. 2 The structure of the self-assembled tetramer (Zn3)₄. The meso substituents are omitted for clarity.

CDCl_3 . This complex is significantly more stable than the corresponding simple Zn4a-6 complex which has an association constant of $3.8 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ in dichloromethane.

Vapour phase osmometry of Zn2a in chloroform solution yielded an effective molecular weight of 3300 ± 300 which was constant between concentrations of 3 and 20 mmol dm^{-3} . Comparison with the molecular weight of the monomer, 1129, shows that Zn2a forms a trimeric structure in solution. Together with the NMR data which shows that each of the pyridyl groups is coordinated to a zinc porphyrin and the UV-VIS data which shows that each of the porphyrins is coordinated to a pyridyl ligand, this proves that the structure of the assembly is a macrocyclic trimer (Fig. 1). \ddagger

The UV-VIS absorption spectrum of Zn2a in dichloromethane is strongly concentration dependent: at low concentrations ($10^{-7} \text{ mol dm}^{-3}$), it resembles the spectrum of Zn4a , but at high concentrations ($10^{-4} \text{ mol dm}^{-3}$), the absorption bands are red-shifted. These changes are characteristic of a zinc porphyrin-pyridine complex at high concentrations and an uncoordinated zinc porphyrin at low concentrations, which implies that self-assembly is taking place between 10^{-7} and $10^{-5} \text{ mol dm}^{-3}$. In addition, at high concentrations the Soret absorption of Zn2a is split into two bands of equal intensity separated by 9 nm. The extinction coefficients of the two bands are approximately half that observed for the corresponding Zn4a-6 complex, and this is characteristic of an exciton coupling interaction between two porphyrins which are close in space but which are neither coplanar nor perpendicular. 6 This shows that Zn2a does not form a cyclic dimer or tetramer at these concentrations, but the splitting is consistent with the cyclic trimer structure in Fig. 1 in which the planes of the porphyrins are oriented at 60° . A UV-VIS absorption dilution study was used to determine the stability of the self-assembled macrocycle [Fig. 4(a)]. This yielded a value of $5 \pm 1 \times 10^{12} \text{ dm}^6 \text{ mol}^{-2}$ for formation of the trimer in dichloromethane.

Zn3a and Zn3b were characterised using the same methods. In this case, both the ^1H NMR and UV-VIS absorption spectra

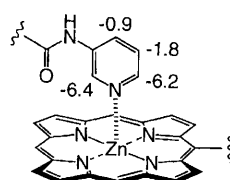
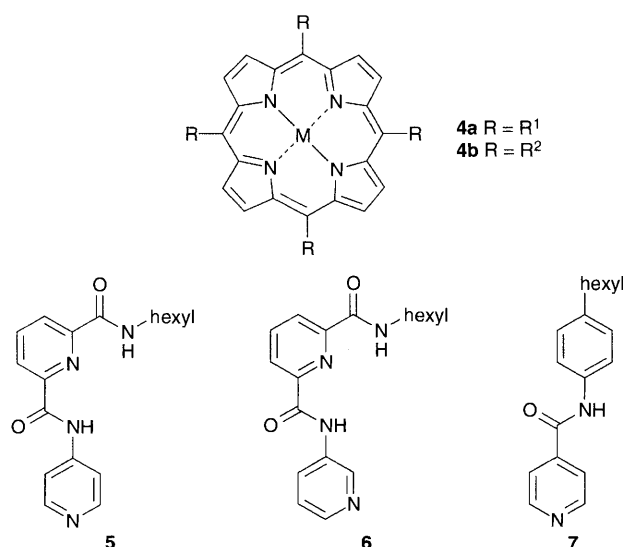


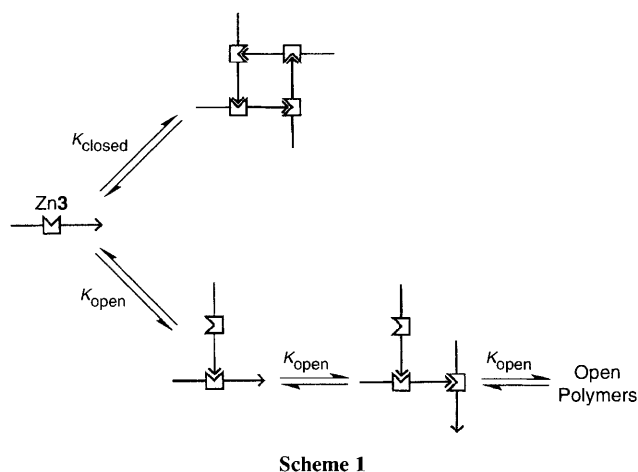
Fig. 3 The upfield changes in ^1H NMR chemical shift observed for Zn2a compared with $\text{H}_2\text{2a}$



are strongly concentration dependent. Dilution studies in dichloromethane using both techniques indicate that self-assembly takes place at around $10^{-4} \text{ mol dm}^{-3}$. Characteristic changes in the wavelengths of the Soret and Q bands in the UV-VIS spectrum are indicative of zinc coordination by pyridine at high concentrations. Changes in the ^1H NMR chemical shifts are also characteristic of this interaction: at high concentrations, the pyridine α and β protons move 5.7 and 1.8 ppm upfield respectively due to the porphyrin ring current. Vapour phase osmometry of Zn3b in chloroform solution yielded an effective molecular weight of $6470 \pm 260 \text{ g mol}^{-1}$ which was constant between concentrations of 8 and 25 mmol dm^{-3} . Since the molecular weight of the monomer is 1568, the self-assembled structure contains 4.1 ± 0.2 monomer units, *i.e.* Zn3b adopts a tetrameric structure in solution (Fig. 2). \ddagger

Assuming a two state equilibrium between monomer and tetramer, curve fitting gave association constants (K_{closed} in Scheme 1) of $9 \pm 1 \times 10^{12}$ for Zn3a and $3.1 \pm 0.4 \times 10^{12} \text{ dm}^9 \text{ mol}^{-3}$ for Zn3b using the dilution data in dichloromethane [Fig. 4(b)]. Fleischer and Shachter have previously studied a similar zinc porphyrin, and they concluded that it formed a linear polymeric aggregate in solution which was corroborated by X-ray crystallography of the solid (Scheme 1 bottom). 7 However, the stability constant for their open polymeric assembly in solution (K_{open} in Scheme 1) was unusually large for pyridine coordination of a zinc porphyrin ($K_{\text{open}} = 3.1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$). If we assume that Zn3 forms a similar open polymeric structure instead of the closed tetrameric cycle and reanalyse our dilution data, we obtain a value of $1.1 \pm 0.2 \times 10^4$ for K_{open} for Zn3a and $6.2 \pm 1.3 \times 10^3 \text{ mol}^{-1}$ for K_{open} for Zn3b . These are much larger than the values we have determined for the corresponding Zn4a-7 and Zn4b-7 complexes ($K = 1.9 \pm 0.2 \times 10^3$ and $1.4 \pm 0.3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ respectively in CH_2Cl_2) which is further evidence for the assembly of the closed structure (Zn3) $_4$ in Fig. 2 with cooperativity between the four coordination interactions. The K_{open} values above are close to the Fleischer and Shachter estimate which suggests that their porphyrin also forms closed cyclic tetramer structures in solution. How then can the X-ray data be rationalised?

It is clear that both the open linear oligomers-polymers and the closed cyclic tetramer are possible in this system (Scheme 1). We make the assumption that the association constants for the Zn4a-7 and Zn4b-7 complexes are identical to K_{open} in our system. We can therefore reanalyse the dilution data using a model which allows for the formation of open polymeric structures in competition with the cyclic tetramer. This model produces a better fit to the experimental data without using any additional variables, but has no effect on the stability constant for formation of the closed tetramer (for Zn3a $K_{\text{closed}} = 9 \pm 1 \times 10^{12}$ and for Zn3b $K_{\text{closed}} = 3.0 \pm 0.4 \times 10^{12} \text{ dm}^9 \text{ mol}^{-3}$). A simulation of the populations of the various species present



shows that the amount of the open oligomeric structure is negligible over the concentration range studied experimentally but does become significant at concentrations approaching the solid state ($> 1 \text{ mol dm}^{-3}$). Thus the closed cyclic tetramer dominates in solution, but the open polymer is favoured in the solid state, consistent with the X-ray results of Fleischer and Shachter.

In conclusion, changes in the covalent structure of the porphyrin monomers are expressed in dramatic changes in the self-assembly properties of the system. The formation of dimer, trimer or tetramer can be controlled simply by altering the

orientation of the ligand with respect to the plane of the porphyrin. This is clearly a very promising and versatile technique for the construction of a variety of large macrocyclic cavities with different dimensions and recognition properties. In addition, the ability to measure accurate association constants for these systems has enabled a thermodynamic analysis of the factors which control the efficiency of self-assembly processes, as described in the following paper.

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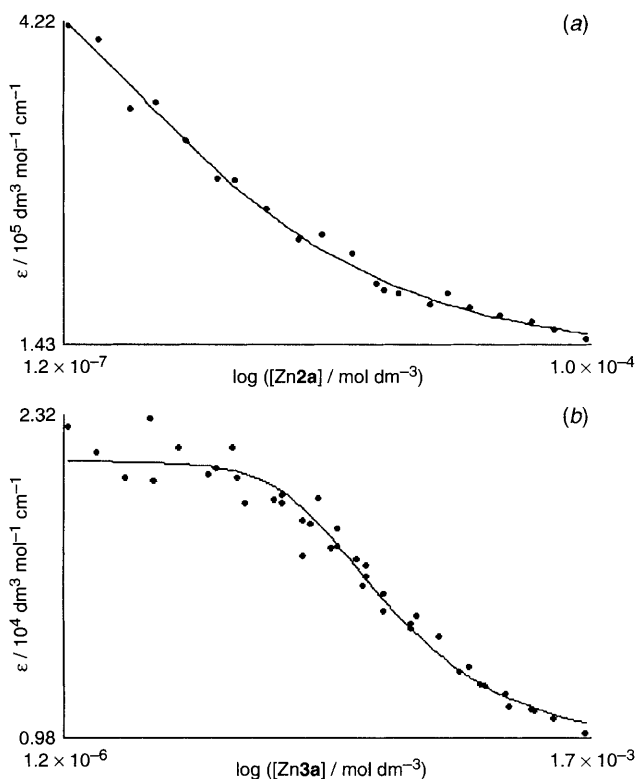


Fig. 4 UV/VIS molar extinction coefficients of (a) Zn2a at 423 nm and (b) Zn3a at 551 nm plotted as a function of concentration. Computer fits of the binding isotherms to the experimental data were used to determine the stability constants for the assemblies as described in the text and are superimposed on the experimental data points.

Footnotes

† All new compounds gave satisfactory spectroscopic data.

‡ We have also observed the Zn2 trimer and the Zn3b tetramer in the FAB mass spectra. However, the intensities of these signals are weak, and we have found that zinc porphyrin-pyridine complexes are difficult to detect using mass spectrometry: the FAB mass spectrum is not usually representative of the complexes which are present in solution as determined by other spectroscopic techniques. Ion-labelling techniques may prove useful in overcoming this problem, see K. C. Russell, E. Leize, A. V. Dorselaer and J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 209.

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