Self-assembly of Macrocyclic Porphyrin Oligomers

Xianglan Chi, Andrea J. Guerin, Richard A. Haycock, Christopher A. Hunter* and Luke D. Sarson

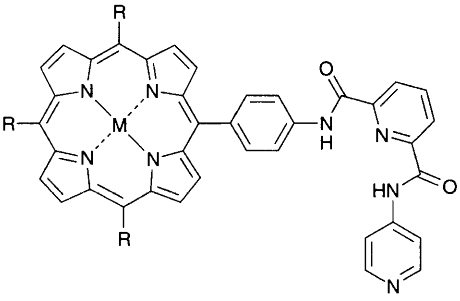
Krebs Institute for Biomolecular Science, Department of Chemistry, University of Sheffield, Sheffield, UK S3 7HF

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 catalysis[3] 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.

Zn**1** 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 Zn**1** to 150° in Zn**2** should favour the formation of a trimeric macrocycle (Fig. 1). Similarly, Zn**3** has an appropriate geometry for self-assembling as a tetramer (Fig. 2). Zn**2a**, Zn**3a** and Zn**3b** were synthesised in good yield (> 80%) from the corresponding amino porphyrins using similar procedures as reported previously for Zn**1**.†

The ^{1}H NMR spectrum of Zn**2a** in chloroform is characteristic of a complex in which the pyridyl group is coordinated to a zinc centre. The changes in ^{1}H NMR chemical shift of the signals due to the pyridyl protons of Zn**2a** relative to those for H_2**2a** are shown in Fig. 3. The α-pyridine protons experience very large upfield shifts due to their proximity to the porphyrin ring current. The ^{1}H 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



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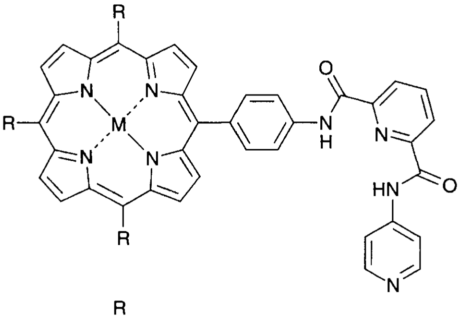

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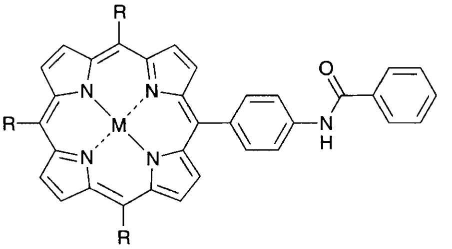
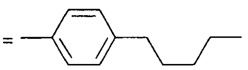
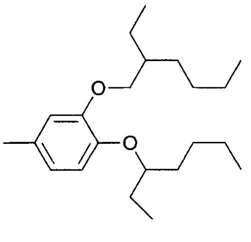


3a R = R^1
3b R = R^2

M = 2 H or Zn

R^1 = 

R^2 = 

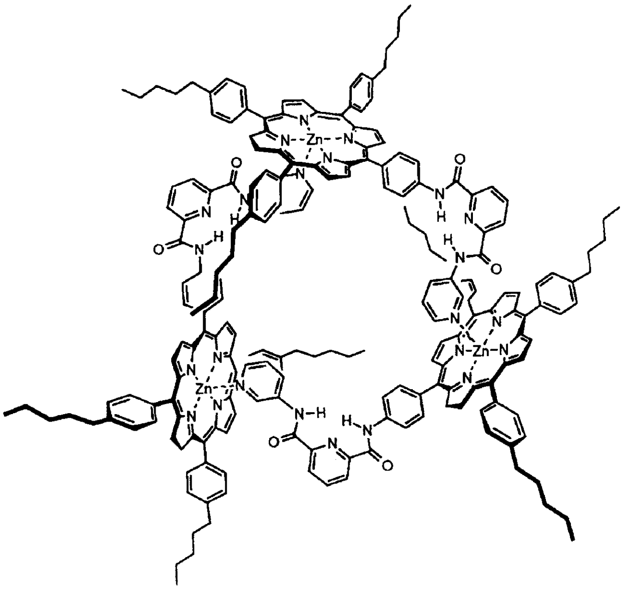


Fig. 1 The structure of the self-assembled trimer (Zn**2a**)$_3$

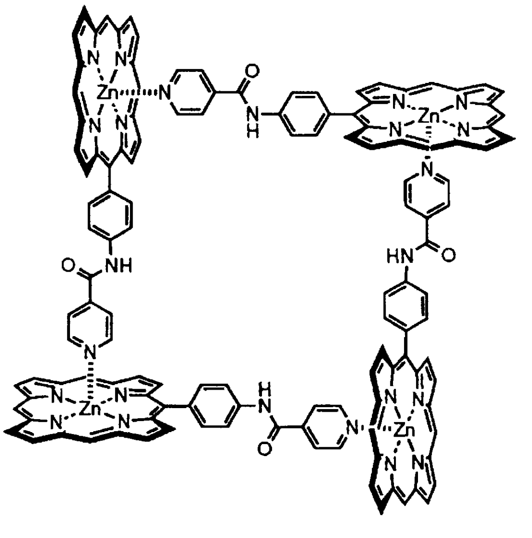


Fig. 2 The structure of the self-assembled tetramer (Zn**3**)$_4$. The *meso* substituents are omitted for clarity.

$CDCl_3$. This complex is significantly more stable than the corresponding simple Zn**4a**·**6** complex which has an association constant of 3.8 × 10^3 dm^3 mol^{-1} in dichloromethane.

Vapour phase osmometry of Zn**2a** 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 Zn**2a** 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).‡

The UV–VIS absorption spectrum of Zn**2a** in dichloromethane is strongly concentration dependent: at low concentrations (10^{-7} mol dm^{-3}), it resembles the spectrum of Zn**4a**, but at high concentrations (10^{-4} 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} mol dm^{-3}. In addition, at high concentrations the Soret absorption of Zn**2a** 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 Zn**4a**·**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 Zn**2a** 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 ± 1 × 10^{12} dm^6 mol^{-2} for formation of the trimer in dichloromethane.

Zn**3a** and Zn**3b** were characterised using the same methods. In this case, both the ^1H NMR and UV–VIS absorption spectra are strongly concentration dependent. Dilution studies in dichloromethane using both techniques indicate that self-assembly takes place at around 10^{-4} 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 Zn**3b** in chloroform solution yielded an effective molecular weight of 6470 ± 260 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.* Zn**3b** adopts a tetrameric structure in solution (Fig. 2).‡

Assuming a two state equilibrium between monomer and tetramer, curve fitting gave association constants (K_{closed} in Scheme 1) of 9 ± 1 × 10^{12} for Zn**3a** and 3.1 ± 0.4 × 10^{12} dm^9 mol^{-3} for Zn**3b** 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_{open} = 3.1 × 10^4 dm^3 mol^{-1}). If we assume that Zn**3** forms a similar open polymeric structure instead of the closed tetrameric cycle and reanalyse our dilution data, we obtain a value of 1.1 ± 0.2 × 10^4 for K_{open} for Zn**3a** and 6.2 ± 1.3 × 10^3 mol^{-1} for K_{open} for Zn**3b**. These are much larger than the values we have determined for the corresponding Zn**4a**·**7** and Zn**4b**·**7** complexes (K = 1.9 ± 0.2 × 10^3 and 1.4 ± 0.3 × 10^3 dm^3 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 contants for the Zn**4a**·**7** and Zn**4b**·**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 Zn**3a** K_{closed} = 9 ± 1 × 10^{12} and for Zn**3b** K_{closed} = 3.0 ± 0.4 × 10^{12} dm^9 mol^{-3}). A simulation of the populations of the various species present

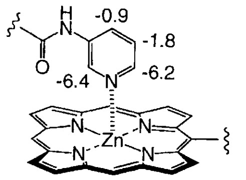
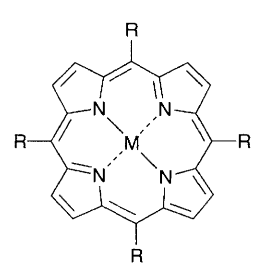
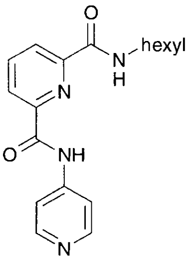


Fig. 3 The upfield changes in ^1H NMR chemical shift observed for Zn**2a** compared with H_2**2a**



4a R = R^1
4b R = R^2



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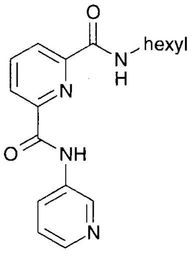

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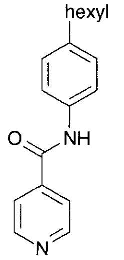

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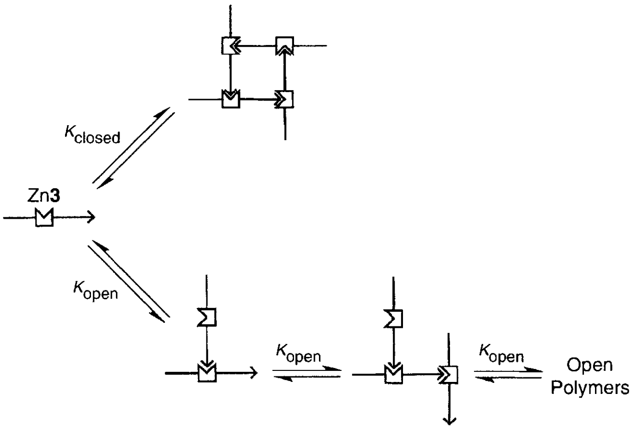

Scheme 1

shows that the amount of the open oligomeric structure is negligible over the concentration range studied experimentally but does became significant at concentrations approaching the solid state (> 1 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.

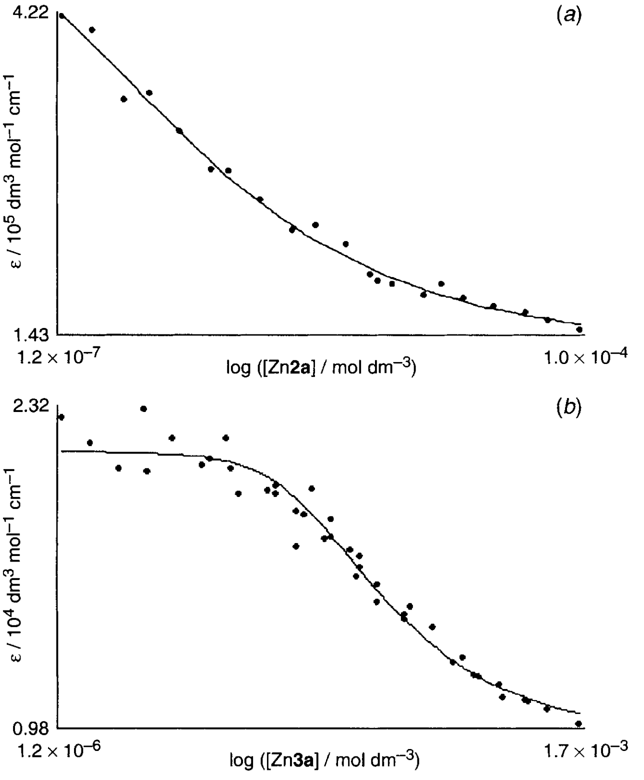

Fig. 4 UV/VIS molar extinction coefficients of (*a*) Zn**2a** at 423 nm and (*b*) Zn**3a** at 551 nm plotted as a function of concentration. Computer fits of the binding isotherms to the experimental data were used to determine the stability constants for the assemblies as described in the text and are superimposed on the experimental data points.

We thank Glaxo, the CVCP and the University of Sheffield (L. D. S.), the EPRSC (R. A. H.), Pfizer Ltd and the University of Sheffield (A. J. G.) and the Lister Institute for funding (C. A. H.).

Received, 22nd June 1995; Com. 5/04030B

Footnotes

† All new compounds gave satisfactory spectroscopic data.

‡ We have also observed the Zn**2** trimer and the Zn**3b** 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. Dorsselaer and J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 209.

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