Templated assembly of a molecular capsule

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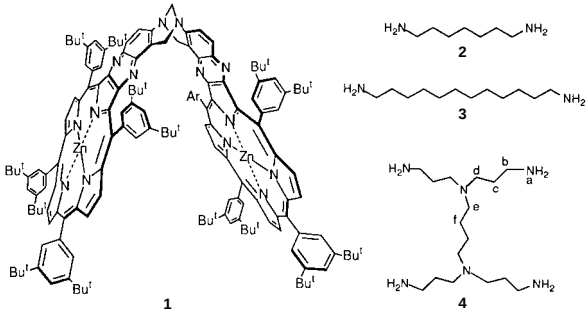
Two rigid Tröger's base dizinc(II) bis-porphyrin receptor molecules 1 and the first generation of dendrimer tetramine 4 form a 2:1 complex 5, a self-assembled spherical superstructure encapsulating the dendrimer.

Self-assembled molecular capsules have received much attention in supramolecular chemistry. Most of them are based on diphenylglycoluril building blocks in which the formation of eight (or more) hydrogen bonds favours a dimeric structure resembling a 'molecular tennis ball'.[1] These assemblies were able to reversibly encapsulate small guest molecules.[2] Recently larger dimeric structures based on calix[4]arenes have also been described, showing comparable behaviour.[3]

The use of self-assembly in the formation of porphyrin arrays to mimic some aspects of the photosynthetic machinery, has emerged in different supramolecular porphyrin structures. These porphyrin assemblies are based on hydrogen bonding,[4] metal ion coordination,[1,5] and central metal atom coordination.[6] Here, we report the formation of a self-assembled molecular capsule based on metal-to-ligand interactions of two dizinc(II) bis-porphyrins around a tetramine.

Previously we have shown that a rigid Tröger's base-like receptor strongly binds ditopic diamino ligands such as L-histidine esters[7] and α,ω-diaminoalkanes[8] in its cleft which has a Zn···Zn distance of *ca.* 8.5 Å. We have also synthesised the expanded Tröger's base dizinc(II) bis-porphyrin receptor **1**.[9] Models indicate that the Zn···Zn distance in the unbound state is *ca.* 16 Å.



Binding studies, using UV–VIS spectroscopy,† of a series of ditopic α,ω-diaminoalkanes show that 1,7-diaminoheptane **2** is the smallest guest which can bind to the receptor **1** in a ditopic manner giving a 1:1 complex with a high binding constant (1.5×10^6 dm^3 mol^{-1}). This indicates that there is some flexibility in the skeleton of **1** and that the cleft can be contracted to a Zn···Zn distance of 13 Å. The binding strength of the monodentate ligand 1-hexylamine is significantly less (5×10^4 dm^3 mol^{-1}). In the case of 1,6-diaminohexane binding is also significantly weaker and sigmoidal titration curves are observed indicating several competing modes of binding occur. Larger guests, for example 1,12-diaminododecane **3** bind significantly more strongly (7×10^7 dm^3 mol^{-1}), indicating that there is an energy penalty associated with contraction of the binding cleft.

The observation of tight binding of suitably long ditopic ligands to dizinc(II) bis-porphyrin **1** suggested to us that polyamines could be used as ligands to assemble a number of dimetallo bis-porphyrin systems around a ligand core. Dizinc(II) bis-porphyrin **1** and quatratopic ligands such as the first generation of aminodendrimer[10] **4** were expected to give a 2:1 complex by the formation of four Zn–amine bonds. Indeed, the UV–VIS titration curve of **1** with tetramine **4** showed an inflection point at 0.5 equiv. of **4** added, indicating that a 2:1 complex **5** was formed (Fig. 1). The porphyrin Q bands as well as the Soret band were shifted towards the red in the visible spectrum as ligand was added, indicating that the amines of **4** were complexed to the Zn atoms of the porphyrin units of **1**. These shifts were similar to those found for the ditopic ligands **2** and **3** upon full complexation showing that to each Zn atom of **1**, an amine was bound. The only structure which allowed a 2:1 complex and all the Zn atoms to be occupied was the molecular capsule **5** with the tetramine guest **4** inside the spherical dimer (Fig. 2). Although there are two possible forms in which the guest molecule can be bound to the tetramine, either with 9 or 14 atoms between the two Zn atoms of one unit of **1**, molecular modelling‡ studies suggest that the latter form is much more favourable, which is in line with the difference seen in binding of **2** and **3** with receptor **1**.§

In order to explore the stability of the molecular capsule **5** the titration was continued by adding further free ligand **4**. A second inflection point was observed corresponding to the addition of 1 equiv. of **4** (Fig. 1). This indicates that complex **5** dissociates to form 1:1 complexes (two Zn–amine bonds and two free amine groups per complex) at higher ligand concentration. By comparison, a titration curve of **1** with the ditopic guest **3** (or **2**) showed only one inflection point which corresponded to the addition of 1 equiv. of ligand (also two Zn–amine bonds).

To further investigate the structure of the molecular capsule **5**, 400 MHz ^{1}H NMR studies were performed (Fig. 3). To a 2.2 mmol $CDCl_3$ solution of tetramine **4** was added stepwise a 12.6 mmol solution of **1** also containing 2.2 mmol of **4**. Upon the addition of **1** the signals of **4** were broadened and upfield shifted. The NH_2 (protons a in structure **4**), α-CH_2 (protons b) and β-CH_2 (protons c) signals showed the highest shifts, being the closest protons to the porphyrin ring upon complexation. These signals shifted approximately linearly with concentration towards δ −4.68 (NH_2; total shift −5.92 ppm), −2.82 (α-CH_2; total shift −5.50 ppm) and −1.80 (β-CH_2; total shift −3.35 ppm) at 2 equiv. of **1** [Fig. 3(*c*)], indicating that all amino groups were complexed to zinc(II) porphyrins. The addition of more **1**

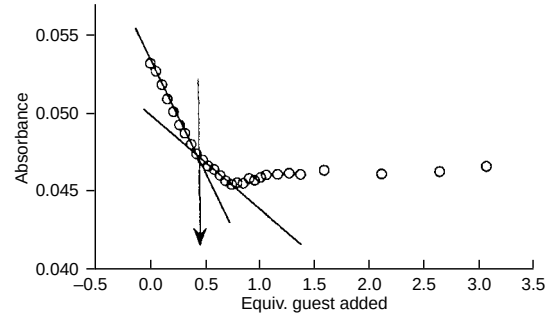


Fig. 1 UV Titration curve (616 nm) of **1** with quatratopic guest **4**

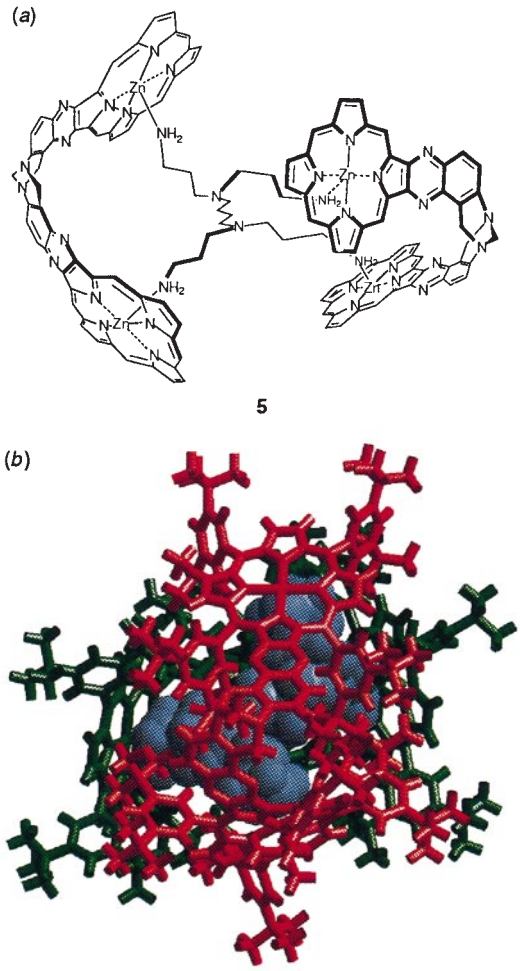


Fig. 2 (*a*) Schematic sideview with sixteen *meso* aryl groups omitted for clarity and (*b*) a modelled structure of the capsule **5** consisting of the two shape complementary receptor molecules **1** assembled around the core guest **4**. The encapsulated guest is in blue (space-filling), the receptors are in dark green and red (stick).

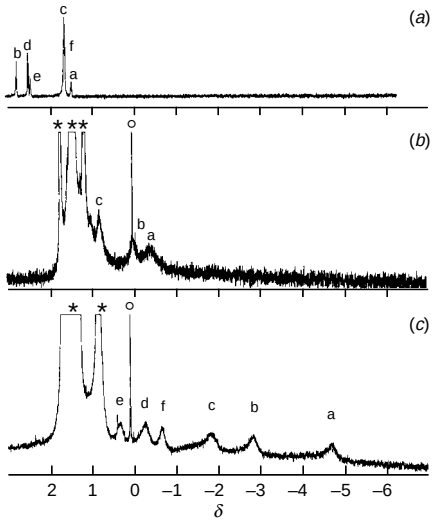


Fig. 3 ^{1}H NMR spectra of (*a*) **4**, (*b*) a 1 : 1 complex of **4** and **1**, (c) molecular capsule **5**. Peaks marked with an asterisk are from the *tert*-butyl protons of the receptor molecule and the $SiMe_4$ resonance is marked with a circle.

(up to 5.4 equiv.) did not result in significant change of chemical shifts of the protons of **4**, indicating that at these concentrations the 2 : 1 complex is stable and no higher complexes are formed. Upon the addition of just 1 equiv. of **1** the shifts of protons a, b and c of **4** [Fig. 3(*b*)] were in between the signals of free **4** [Fig. 3(*a*)] and fully complexed **4** [Fig. 3(*c*)], suggesting that a 1 : 1 complex is formed as an intermediate.

The signals of receptor **1** shifted as well. The signals of the bridging methyl groups and the β-pyrrolic protons of the porphyrin rings shifted to higher field, upon complexation. Adding more than 2 equiv. of **1** resulted in broadening of the signals of the receptor and signals of the bridging methyl groups and the β-pyrrolic protons of the porphyrin rings shifted back to lower field. These data clearly show that a 2 : 1 complex between receptor **1** and quatratopic guest **4** is formed, and that the exchange between the free components and the complex is at coalescence on the NMR timescale. At −50 °C, this equilibrium is slow and the ^{1}H NMR spectrum of a 1 : 4 mixture of **4** and **1** showed signals of the free and the complexed receptor **1**. Although the spectrum was complicated and could not be completely assigned, large downfield shifts were observed for the β-pyrrolic protons of the porphyrin rings and the other aromatic protons of the receptor. These large shifts, which were not observed for ditopic ligands, are in agreement with the structure of molecular capsule **5**.

Studies of porphyrin arrays assembled around larger dendrimers are in progress.

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Footnotes and References

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† Spectrophotometric titrations were carried out in toluene at 25.0 °C (receptor concentration 2×10^{-6} mol dm^{-3}). The absorption was followed at different wavelengths and the obtained curves were analysed using a Simplex least-squares curve-fitting procedure.[11]

‡ SPARTAN version 4.0, Wavefunction, Inc, Irvine, CA, USA, 1995 and Cerius^{2TM}, which was developed by BIOSYM/Molecular Simulations, were used.

§ The energy difference on the basis of the binding difference of **2** and **3** is estimated to be 19 kJ mol^{-1}.

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