Self-assembly of a multi-porphyrin supramolecular macrocycle by hydrogen bond molecular recognition

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Three triaminotriazine units bearing two appended porphyrins undergo self-assembly through multiple hydrogen-bonding with three complementary dialkylbarbituric acids yielding a supramolecular macrocycle containing six porphyrins.

Covalently bonded diads-to-pentads of porphyrins, quinones and spacers have yielded important information on the geometrical and energetical features of electron and energy transfer processes.[1] On the other hand, supramolecular architectures of functional molecules such as porphyrins may be generated by self-assembly[2] based on non-covalent interaction and molecular recognition. We have described the self-assembly of supramolecular porphyrin entities using: (*a*) hydrogen bonding,[3] (*b*) metal ion coordination[4] and (*c*) central metal coordination. Here we report the self-assembly of a circular supramolecular array **A** (Fig. 1) of six porphyrin moieties by hydrogen bond based molecular recognition;[5] it is composed of three 5,5-di(butyl)barbituric acid (diBBA) and three triaminotriazine molecules appended with either two tetraphenylporphyrins (diPT) or their zinc complexes (diZnPT).‡

Such an assembly is consistent with the solid state structure obtained by the self-assembly of three triazines bearing bulky substituents, and three 5,5-diethyl barbituric acids.[8] Electrospray mass spectrometry of a 1 : 1 solution of diZnTP and diBBA in dry CH_2Cl_2 using 1 mol% of the dimanganese(III) porphyrin triazine (diMn^{III}PT) with the acetate counter-ion as ion label,[9] yields the expected M/2+ parent peak at 2567 D. Vapour phase osmometry measurements in chloroform or toluene (molecular weights of 4956 ± 250 D and 5298 ± 276 D, respectively)§ are consistent with an assembly **A** of three diZnPT and three diBBA units (MW = 5156 D).

Incorporation of the photochemically rich porphyrin into these assemblies allows further characterization in solution. The changes observed in both the absorption and the fluorescence spectra on addition of diBBA to a solution of diZnPT, agree

Table 1 Electronic absorption bands of the assembly **A** (Fig. 1) and of reference compounds[a]

Compound[b]	Q(0,0)	Q(1,0)	B(0,0)
ZnTTolP	591 (1.00)	551 (2.2)	424 (55)
Zn5-amPP	589 (1.25)	550 (5.4)	424 (62)
diZnPT	589 (1.20)	549 (5.26)	425 (105)
A[c]	591 (1.00)	551 (4.96)	429 (80)

[a] In nm (ε = $dm^3\ mol^{-1}\ cm^{-1} \times 10^4$). [b] ZnTTolP = 5,10,15,20-tetra(4′-methylphenyl)porphyrinato zinc; Zn5-amPP = 5-(4′-aminophenyl)-10,15,20-triphenylporphyrinato zinc; diZnPT = 2-amino-4,6-bis[5-(4′-aminophenyl)-10,15,20-triphenylporphyrinato zinc]-1,3,5-triazine. [c] 122 $\mu mol\ dm^{-3}$.

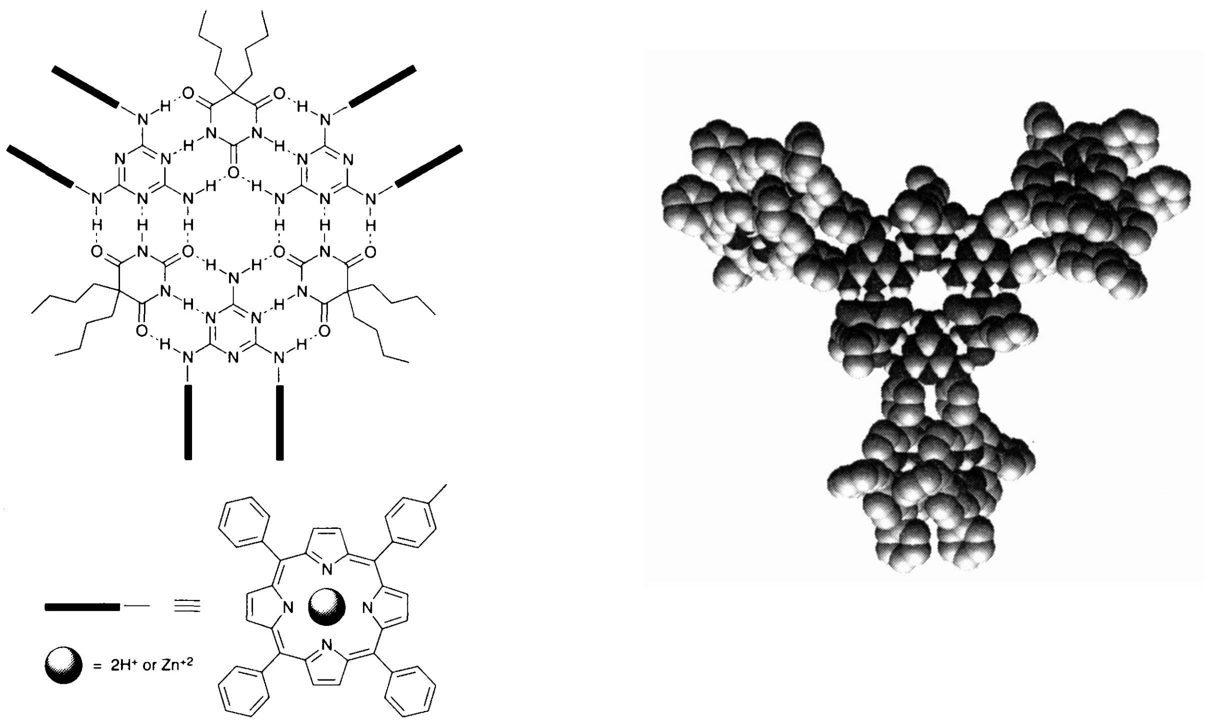

Fig. 1 A supramolecular multiporphyrin macrocycle **A** consisting of three units of 5,5-di(butyl)barbituric acid (diBBA), and of three units of 2-amino-4,6-bis[5-4′-aminophenyl)-10,15,20-triphenylporphyrinato]-1,3,5-triazine (diPT); right: computer generated MacroModel CPK representation of **A**

with the formation of a discrete cyclic structure rather than with linear assemblies of varying lengths.[¶]

The proton NMR spectrum[‖] of diZnPT in non-polar solvents such as CD_2Cl_2 and toluene-[$^2H_8$] exhibits broad bands for the porphyrin ring β-pyrrole protons and the phenyl protons with none of the fine structure normally observed for tetraphenylporphyrins. This poor resolution may be attributed to the formation of a distribution of ill-defined aggregates *via* mismatched hydrogen bonding with a variety of equilibrium constants and conformations. This was confirmed by the observation of a readily interpretable spectrum upon addition of an excess of D_2O/pyridine-[$^2H_5$] to the solution. When an equimolar amount of diBBA was added to diZnPT in CD_2Cl_2 or toluene-[$^2H_8$] there was an immediate shift of the triazine NH protons from *ca.* 7 ppm to a broad resonance (about 2 ppm width) centred at 12 ppm, consistent with earlier observations for self-assembly by hydrogen bond molecular recognition.[3] After reaching equilibrium, several of the broad resonances for the phenyl and pyrrole protons resolved into sharp multiplets. Most notably, the 2′- and 3′-protons of the 4′-aminophenyl moieties of diZnPT give a complex multiplet consisting of a doublet of doublets for the protons pointing in towards the adjacent porphyrin and a doublet of doublets for those pointing out towards the complementary diBBA. These observations agree with the formation of a defined, closed supramolecular array rather than a distribution of polymeric materials, as is also observed in other hydrogen-bond self-assembled systems.[3,8] Additionally, NOE experiments on several of the β-pyrrole protons and on the 2′- and 3′-protons of the 5-phenyl group show that each porphyrin has only one neighbouring porphyrin, whereas in a linear- or crinkled-tape with linear domains each porphyrin unit would be expected to have two neighbours. Finally, diffusion-ordered 2D NMR spectroscopy[10] indicates >90% of the two components are assembled into a supramolecular array of *ca.* 2.5 nm.[11]

The properties of porphyrins in organized media[12–14] or bound to acceptors such as quinones by H-bonding[15] have been studied. In the present assembly the barbiturate group could also serve as an acceptor, resulting in photoinduced electron transfer in an organized array of known geometry. Finally, the supramolecular cyclic architecture **A**, bearing three sets of metalloporphyrin dimers shows a striking resemblance to the ring of B850 chlorophylls found in one of the two sets of porphyrin arrays present in the light harvesting complex in photosynthetic bacteria, where the porphyrins also play an essential role in the assembly of the supramolecular protein ring.[16]

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Footnotes

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‡ All compounds and their starting materials gave satisfactory elemental analysis, ^{1}H NMR, FAB-MS, UV–VIS and fluorescence spectra. The solvents were purified by standard literature procedures. The Lindsey porphyrin synthesis[6a] was used to form the statistical mixture of *p*-nitrophenylporphyrins from a 3.2 : 1 : 4 mixture of *p*-nitrobenzaldehyde : benzaldehyde : pyrrole, where the desired 5-(4′-nitrophenyl)-10,15,20-triphenylporphyrin was the major product. This was then reduced, purified and metallated according to standard procedures.[6b,7] 2-Amino-4,6-bis[5-(4′-aminophenyl)-10,15,20-triphenyl porphyrinato zinc]-1,3,5-triazine was formed by heating a 2.1 : 1 mixture of 5-(4′-aminophenyl)-10,15,20-triphenylporphyrinato zinc and 2-amino-4,6-dichloro-1,3,5-triazine in 1,4-dioxane saturated with sodium bicarbonate for 8 h at 110 °C under argon. The zinc porphyrin was used because of its higher stability and increased nucleophilicity of the amino group. The free base diPT was obtained by demetallation in dilute HCl.

§ Addition of methanol/pyridine (5% by volume) to the assembly results in an apparent molecular weight of 852 ± 137, close to the average molecular weight of the sum of the two components (diZnPT = 1478; diBBA = 238; av. MW = 858). Membrane osmometry experiments using a cellulose acetate membrane with a lower detection limit of *ca.* 5 kd in dry toluene at 28 °C yield a molecular weight of 5400 ± 200, and, more importantly, do not give indication for the presence of higher molecular weights due to open-chain polymers.

¶ In order to probe the highest concentration ranges, absorption and front-face emission/excitation spectra were taken in 0.01–1 mm path length cells allowing concentrations up to 200 μmol dm^{-3} to be examined. Upon addition of 1 equiv. of the complementary diBBA to a 122 μmol dm^{-3} diZnPT solution the Soret band shifts to the red by *ca.* 4–5 nm and the relative intensity decreases by *ca.* 22%, with equal and concomitant broadening. This is evidence for self-assembly because the rotational conformations of the porphyrins of diZnPT are restricted to an eclipsed state such that the effective cross-section per diZnPT porphyrin is reduced. Consistent with known equilibria for these hydrogen bonding systems, the relative Soret ε per diZnPT decreases with increasing assembly concentration until it levels off at *ca.* 100 μmol dm^{-3}, in agreement with the formation of a discrete, closed 3 + 3 cyclic structure. Analogous results are found for the front-face fluorescence spectra where the relative intensity of both emission bands decrease *ca.* 25% upon formation of the assembly at 120 μmol dm^{-3}. The plots of the normalized fluorescence intensity and of the relative Soret ε *vs.* assembly concentration are remarkably similar.

‖ 500 MHz ^{1}H NMR of 120 μmol dm^{-3} diZnPT in CD_2Cl_2 or toluene [$^2H_8$] at 298 °C.

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