anisotropically. Some disorder in one of the cyanide groups and the (*S*)-pn ligands coordinated to Mn^{2+} ions was also observed. The occupancy of the disordered atoms and the K^+ ion was determined by population anaysis. The refinement converges with $R_1 = 0.0615$ for 2520 data ($I > 4\sigma(I)$), $wR_2 = 0.1371$ for 5405 unique data ($2.81 \leq \theta \leq 28.33^\circ$), Flack parameter = 0.06(5), max/min residual electron density 0.527/ − 0.298 e Å^3. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-165941. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Calixarene – Porphyrin Supramolecular Complexes: pH-Tuning of the Complex Stoichiometry**

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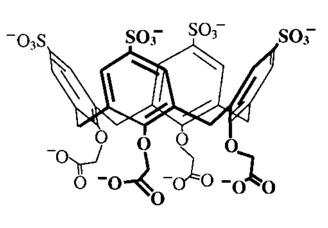
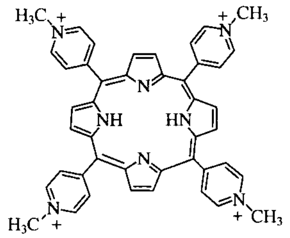
The rich chemistry of calixarenes and porphyrins as (polytopic) receptors and photoactive species, respectively, as well as the enormous possibility of functionalizing the periphery of these molecules have boosted the synthesis of their covalent conjugates for use as possible molecular devices.[1] It has recently been shown, for example, that covalent porphyrin – calixarene conjugates behave as molecular tweezers when individual specific functions are synergistically exploited.[2] Some preliminary data on the formation of noncovalent complexes have also been reported but, to date, no structural data on such supramolecular species have been presented.[3]

Here we present a spectroscopic and structural study that shows that the cationic porphyrin (H_2T4) and the anionic sulphonated calixarene (C_4TsTc) blocked in a *cone* conformation and bearing carboxylic functions[4] form quite stable supramolecular complexes, both in the solid state and in aqueous solution. Furthermore, the H_2T4:C_4TsTc molar ratio is tuned by the protonation state of the C_4TsTc carboxylate groups.



C_4TsTc



H_2T4

The absorption and fluorescence spectra of H_2T4 are characterized by an intense absorption band at 422 nm (Soret band) and an emission at 650 nm, respectively. C_4TsTc absorbs in the far UV region (about 200 nm) and, at pH 6, emits at 307 and 602 nm. However, at pH 2.2, where the four carboxylic groups of C_4TsTc are all protonated ($pK_{a1} = 3.03$, $pK_{a2} = 3.27$, $pK_{a3} = 3.97$, $pK_{a4} = 4.57$),[5] the emissions are almost completely quenched.

The interaction of H_2T4 with C_4TsTc at pH 6 and $I = 0.05\,\text{M}$ (NaCl) is accompanied by significant hypochromism and broadening of the Soret band (see inset of Figure 1) and remarkable quenching of both the porphyrin and calixarene emissions. The spectroscopic features of H_2T4 at pH 2.2 following complex formation with C_4TsTc ($I = 0.05\,\text{M}$) are very similar to those observed at pH 6.

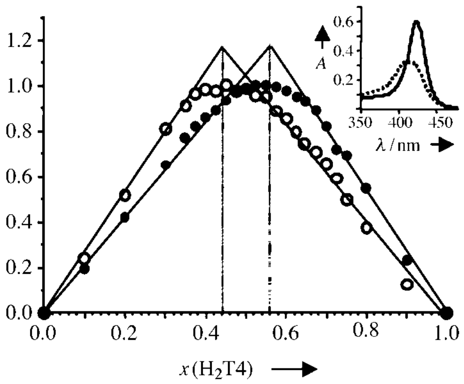


Figure 1. Normalized absorption Job plots at pH 2.2 (○) and 6 (●). The inset shows the absorption spectrum of H_2T4 (2.8 μM) before (——) and after (----) the addition of C_4TsTc (2.2 μM).

However, the Job plots performed at pH 2.2 and 6 show there is a large difference in the ratio of the complex formed (Figure 1). The maximum value at a porphyrin molar fraction of 0.44 at pH 2.2 indicates the formation of species with a 4:3 C_4TsTc:H_2T4 ratio, whereas the maximum value at a porphyrin molar fraction of 0.56 at pH 6 indicates the formation of species with a 4:5 C_4TsTc:H_2T4 ratio. We were able to obtain single crystals of the porphyrin – calixarene complexes at pH ≈ 2 (**1**) and at pH 6 (**2**).

In agreement with the results from the solution study, the H_2T4:(C_4TsTc+H_2T4) molar ratio is 0.43 (2 calixarene moieties, 1.5 porphyrin molecules, and 2 sodium ions) in the asymmetric unit of the crystals obtained at pH ≈ 2 (**1**).[6] Here,

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the "central" H_2T4 unit of a trimeric H_2T4 ensemble is arranged on a crystallographic center of symmetry (1/4, 1/4, 0), and each of its methylpyridinium moieties is inserted into a tetra-anionic C_4TsTc molecule from the sulphonate side of the calixarene (Figure 2). The ditopic nature of C_4TsTc allows it to host one sodium ion on each carboxylate side of the calixarenes. In both **1** and **2** the Na^+ ions are hepta-coordinated by oxygen atoms of the hydroxymethylmethoxy residues at distances in the range of 2.1–2.6 Å. The centrosymmetric unit is sandwiched by two porphyrin rings, which are rotated by 45° with respect to the central one. The resulting neutral supramolecular complex is characterized by a porphyrin mean plane separation of 4.2 Å between the nearly planar porphyrin rings (Figure 3a). The crystal is built up by these supramolecules in such a way as to form large channels (19 × 32 Å; Figure 4), in which the solvent molecules are disordered.

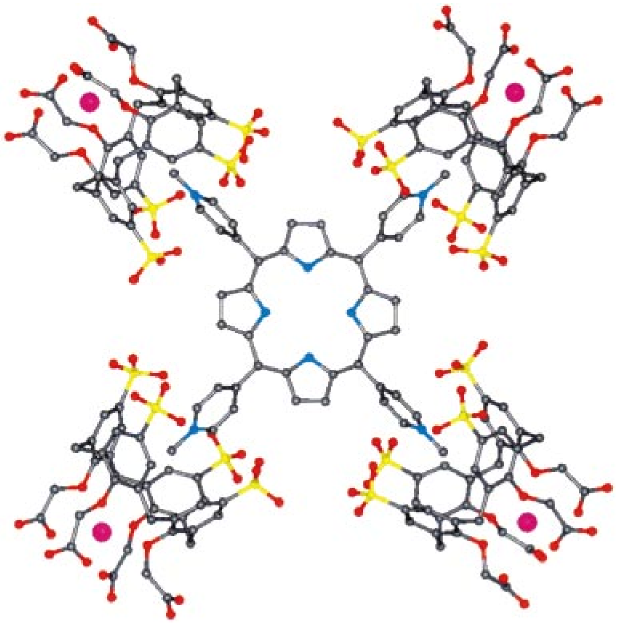

Figure 2. The host–guest interactions in the centrosymmetric unit formed by the central porphyrin cation with calixarene molecules and Na^+ ions (violet circles).

Unlike the crystals obtained at pH 2, the asymmetric unit of the crystals obtained at pH 6[6] contains two hepta-anionic calixarene molecules, three tetracationic porphyrin rings, and two sodium ions, with a H_2T4:(C_4TsTc+H_2T4) molar ratio of 0.6. This value corresponds to a C_4TsTc:H_2T4 molar ratio of 4:6. Seemingly, this result disagrees with the 4:5 ratio obtained in solution. However, a closer look at the structure of **2** readily explains the difference. In fact, the same trimeric ensemble observed in **1**, still arranged on a crystallographic center of symmetry, is also present in **2**, but now, as a result of the deprotonation of the carboxylic groups, the trimeric "core" is staked with two additional porphyrin rings, one above and one below. Each porphyrin ring is rotated by 45° with respect to the external H_2T4 molecules of the trimeric core unit and leads to the 4:5 complex of Figure 3b. The nearly planar five porphyrin rings are separated by a mean plane distance of 4.1 Å. The sixth tetracationic H_2T4 unit—arranged on the crystallographic twofold axes—is isolated with respect to the 4:5 core, and essentially balances the charge of the tetra-anionic supramolecule. The isolated porphyrin rings and the

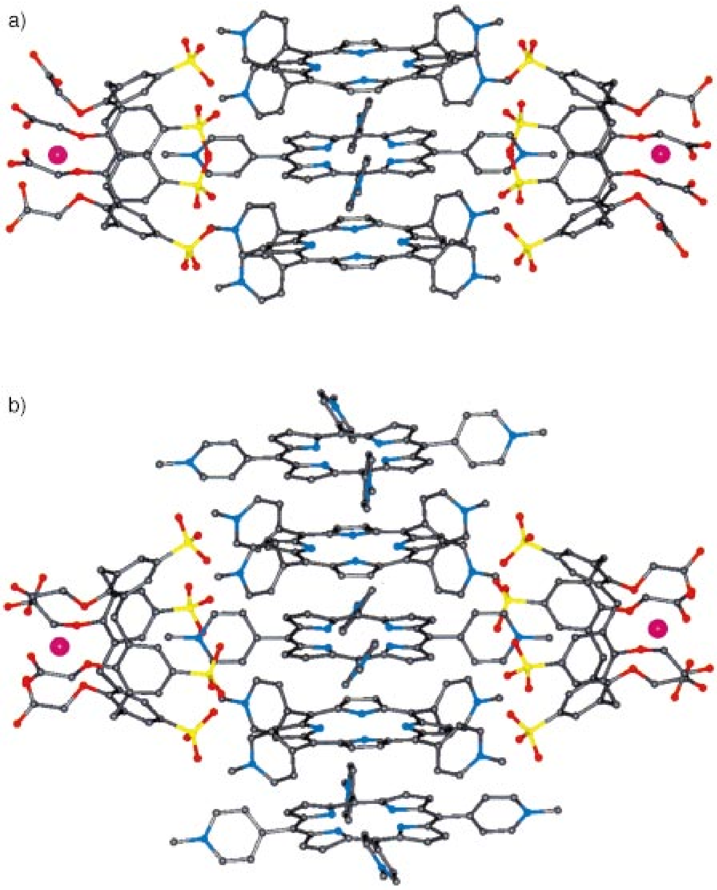

Figure 3. Side views of the neutral supramolecular complex in **1** (a) and the anionic supramolecular complex in **2** (b). In both cases the crystallagraphic centers of symmetry are at the center of the central porphyrin ring. The two calixarene molecules interacting with the central porphyrin ring above and below the plane have been omitted for clarity.

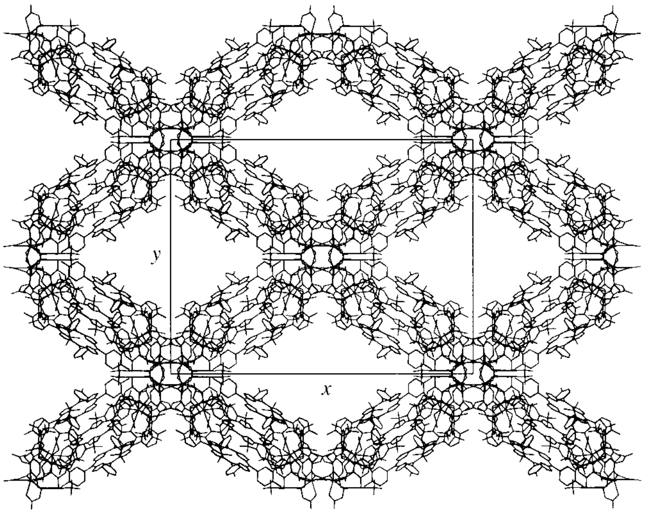

Figure 4. Crystal packing of **1** as viewed along the *z* axis. The channels containing the solvent molecules are shown. The trimeric units are arranged in such a way as to form the walls of the channels.

supramolecular anion are packed in such a way as to form two series of interconnected channels which contain the disordered solvent molecules.

Both complexes are stabilized by a synergistic network of noncovalent interactions: 1) electrostatic interactions between the positive residues on the porphyrin rings and the anionic sulphonate groups, 2) stacking interactions between the porphyrin rings, and possibly 3) $CH \cdots \pi$ interactions between the $N^+{-}CH_3$ groups and the C_4TsTc molecules. Quite intriguingly, the stoichiometry of the species in the solid state is preserved in solution.

In conclusion, the ditopic nature of C_4TsTc seems to be crucial. The presence of sulphonated and carboxylate groups on the upper and lower rim, respectively, allows for the organization of cationic porphyrins by shielding their like-charge repulsion and providing various sites (the cavity and the anionic groups) for different kinds of weak interactions, as well as the modulation of the number of assembled cationic porphyrins by changing the protonation state of the carboxylic groups.[11] The final result is the formation of stable porphyrin self-aggregates in aqueous solution having a well-defined and tunable stoichiometry. This point is relevant considering that, with few exceptions,[12] porphyrin self-aggregation in water leads to species having ill-defined stoichiometry.

Experimental Section

The supramolecular complexes were prepared and crystallized by the vapor-diffusion method with hanging drops at 18 °C by using Linbro multiwell tissue plates as containers for the reservoir solutions. The stock solutions used were 7 mM C_4TsTc (A) and 14 mM H_2T4Cl_4 (B). Crystals of **1** were obtained in drops formed by mixing solution A (4 µL) with solution B (2 µL) that were set to equilibrate against a reservoir solution of glacial acetic acid (60–70 %, 1 mL). The crystals used in the diffraction experiments (typical dimensions $0.4 \times 0.4 \times 0.3$ mm) were obtained with 65 % glacial acetic acid (pH ≈ 2). Crystals of **2** were obtained in drops formed by mixing solution A (2 µL), solution B (2 µL), and reservoir solution (2 µL) which were set to equilibrate against a reservoir solution (1 mL) containing polyethylene glycol (PEG 300, 30–40 % (v/v)) as the precipitant and 0.1M sodium acetate buffer (pH 6.0). The crystals used in the diffraction experiments (typical dimensions $0.6 \times 0.6 \times 0.4$ mm) were obtained with 35 % PEG 300. Crystals of **1** and **2** deteriorate quickly when left in air.

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[6] Data collection were performed at the X-ray diffraction beam-line of Elettra Synchrotron, Trieste (Italy) using a MAR345 Image Plate and wavelengths of 0.9300 Å for **1** and 0.7100 Å for **2**. The crystals were mounted in loops and frozen to 100 K. The crystal of **1** was cryoprotected by vaseline oil and the crystal of **2** was directly cryocooled. The diffraction data were indexed and integrated using MOSFLM[7] and scaled with SCALA (Collaborative Computational Project, No. 4, 1994). The structures of **1** and **2** were solved by direct methods (SHELXS-97[8]) and refined by full-matrix least-squares methods on F^2 (SHELXL-97[8]). Bond lengths and angles of the porphyrins and calixarenes were restrained. **1**: $C_{276}H_{204}N_{24}O_{96}S_{16}Na_4 \cdot 70\,H_2O$, $M_r = 7259$, monoclinic, space group $C2/c$; $a = 48.34$, $b = 35.47$, $c = 25.59$ Å, $\beta = 109.03°$, $V = 44\,721$ Å^3, $Z = 4$, $\rho_{calcd} = 1.078$ g cm^{-3}, $F(000) = 15\,184.0$, $\mu = 0.16$ mm^{-1}; 1030 parameters, 501 restraints; max./min. residual electron density 0.84/ – 0.72 e Å^{-3}. Total reflections collected 29111 (resolution 1.20 Å), of which 12420 were unique ($R_{merge} = 0.0101$). Final $R_1 = 0.218$ and $wR_2 = 0.480$, S(GOF) = 2.9 for 7379 observed reflections ($I > 2\sigma(I)$). **2**: $C_{408}H_{312}N_{48}O_{96}S_{16}Na_4 \cdot 97\,H_2O$, $M_r = 9775$, monoclinic, space group $C2/c$, $a = 52.05$, $b = 30.32$, $c = 36.10$ Å, $\beta = 114.05°$, $V = 51\,986$ Å^3, $Z = 4$, $\rho_{calcd} = 1.249$ g cm^{-3}, $F(000) = 20\,536$, $\mu = 0.16$ mm^{-1}. Total reflections collected 49705 (resolution 1.00 Å), of which 26167 were unique ($R_{merge} = 0.0642$). Final $R_1 = 0.256$ and $wR_2 = 0.555$, S(GOF) = 3.8 for 16461 observed reflections ($I > 2\sigma(I)$); 1402 parameters, 626 restraints; max./min. residual electron density 3.66/ – 0.78 e Å^{-3}. The large values of R_1 and wR_2 are common for supramolecular complexes having very large unit cells[9] and a large number of disordered solvent molecules. Several examples of these structures with values of R_1 of about 0.20 and above have been reported.[10] In addition, the poor quality of the single crystals and the loss of crystallinity during the X-ray exposure did not allow the collection of good diffraction patterns. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-167496 (**1**) and -167497 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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