CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200500825

Noncovalent Synthesis in Aqueous Solution and Spectroscopic Characterization of Multi-Porphyrin Complexes

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Abstract: The interactions of the tetracationic *meso*-tetrakis(*N*-methyl-4-pyridyl)porphyrin (H_2TMPyP) and its metallo derivatives (MTMPyP) (where M = copper(II), zinc(II), and gold(III) with the octa-anionic form (at neutral pH) of 5,11,17,23-tetrasulfonato-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)calix[4]arene (C_4TsTc) lead to a series of complex species whose stoichiometry and porphyrin sequence can be easily tuned. Crystallographic, spectroscopic, and diffusion NMR studies converge towards a common picture in which a central 1:4 porphyrin/calixarene unit serves as a template for the formation of more complex species. These species arise by successive, stepwise addition of single porphyrin molecules above and below the plane of the 1:4 central core to ultimately give a 7:4 complex. Noticeably, the stoichiometry of the various complex species corresponds to the actual concentration ratio of porphyrins and calixarenes in solution allowing the stoichiometry of these species to be easily tuned. This behavior and the remarkable stability of these species allow homo-porphyrin and hetero-(metallo)porphyrin species to be formed with control of not only the stoichiometry but also the sequence of the porphyrin array. The flexibility and ease of this approach permit, in principle, the design and synthesis of porphyrin arrays for predetermined purposes. For example, we have shown that it is very easy to design and obtain mixed porphyrin species in which a foreseen photoinduced electron-transfer is indeed observed.

Keywords: calixarenes · noncovalent synthesis · porphyrinoids · self-assembly · template synthesis

Introduction

Porphyrins are very interesting molecules for different reasons. In addition to their quite unique (spectroscopic, electrochemical, etc.) properties, easily tunable by metallation or variation of the nature and number of peripheral substituents, they are involved in many biologically crucial reactions: from the binding and transport of small molecules to electron transfer and the capture of energy. To attain the high level of specificity entailed in biological reactions, most of these natural machineries require cooperativity between the various porphyrins and/or different functional/structural elements of the complex structure they belong to. These natural devices, if replicated in simpler model systems, could find remarkable applications in both biomedical and technological fields.

A "classical" covalent synthesis is mostly used to obtain these multi-porphyrin supramolecular species.[1] The main reason for the predominance of the covalent synthesis over the noncovalent method is that the former allows finer con-

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trol over the structure of the final species, intrinsic to the strength of the covalent bond. Noncovalent interactions are weaker and less addressable. One possible way to partly overcome the limitations inherent in the noncovalent route is to use a combined approach and begin the synthesis with covalently synthesized multipart components (as porphyrin conjugates) and then self-assemble these with the other components (or multiparts) to obtain the final species.[1a,b,2]

Only few examples of noncovalent "total" syntheses (that is, syntheses performed by starting from the simplest monomeric components) of multi-porphyrin species have been reported to date.[1a,b,2a,3,4b,c] Some of these "purely" noncovalent approaches take advantage of the high thermodynamic stability and/or kinetic inertness of the species formed by the interaction between multi-anionic and multicationic components.[3n,4]

Recently, good control was achieved over the "total" noncovalent synthesis of multi-porphyrin systems in aqueous solution.[4b,c] This self-assembly is driven by the templating action of an octa-anionic calixarene (5,11,17,23-tetrasulfonato-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)calix[4]arene (in a *cone* conformation), C_4TsTc, Figure 1a) on a tetracationic porphyrin (*meso*-tetrakis(*N*-methyl-4-pyridyl)porphyrin, H_2TMPyP, Figure 1b) and/or its metal derivatives. Starting from a central 1:4 porphyrin/calixarene species it has been shown by structural (Figure 2) and solution data[4b,c] that it is possible to pile, in a stepwise fashion, up to six porphyrins above and below the central porphyrin to form a final 7:4 species. Interestingly, the stoichiometric ratio of the complex species corresponds to the actual ratio of the components in solution.

To better assess the relationship between the porphyrin/calixarene stoichiometry in the complexes and the concentration ratio of the two components in solution we present here additional emission (obtained by irradiating the calixarene or porphyrin moieties) and diffusion NMR[5] measurements. The latter technique is a fast, reliable, and accurate way of determining the diffusion coefficients of supramolecular systems in solution.[6–11] It has also been used, inter alia, to evaluate association constants,[6] to probe encapsulation in dimeric[7] and hexameric capsules,[8] to determine dendrimer generation and structure,[9,10] and to elucidate the structure of the self-assembled supramolecular systems.[11,12]

Experimental Section

The synthesis of the 5,11,17,23-tetrasulfonato-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)calix[4]arene (*cone* conformation) (C_4TsTc) has previously been reported.[13] H_2TM4PyP and its metal derivatives were purchased from Mid-Century or obtained by metal insertion following literature procedures.[14] Absorption measurements were carried out on a Varian Cary 500 spectrophotometer. Fluorescence measurements were performed on Jasco 747 and Jobin-Yvon Fluorolog3-111-VUV instruments. To avoid photodegradation, calixarene fluorescence measurements ($\lambda_{exc}=240$ nm) were performed using a black glass filter (Melles Griot, no. 03 FCG 177) which cuts out about 50% of the intensity at this wavelength. All spectroscopic measurements have been performed in aqueous solution using ultra-pure Millipore water (without buffer) in 1×1 cm^2 quartz cuvettes.

NMR diffusion measurements were performed on a 400 MHz Avance Bruker NMR spectrometer equipped with a Great 1 gradient system capable of producing magnetic field pulse gradients of about 50 G cm^{-1} in the z direction. All experiments were carried out using a 5 mm inverse probe. Measurements were performed at least three times and the diffusion coefficients are reported as the mean ± standard deviation of at least

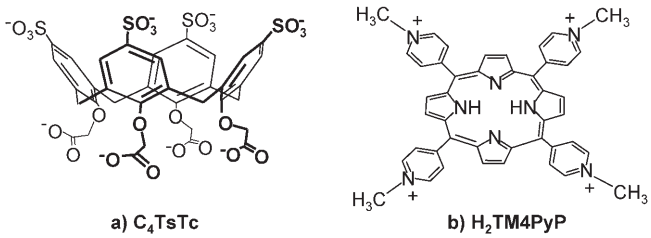

Figure 1. Schematic drawing of a) the calixarene and (b) the porphyrin used in this work.

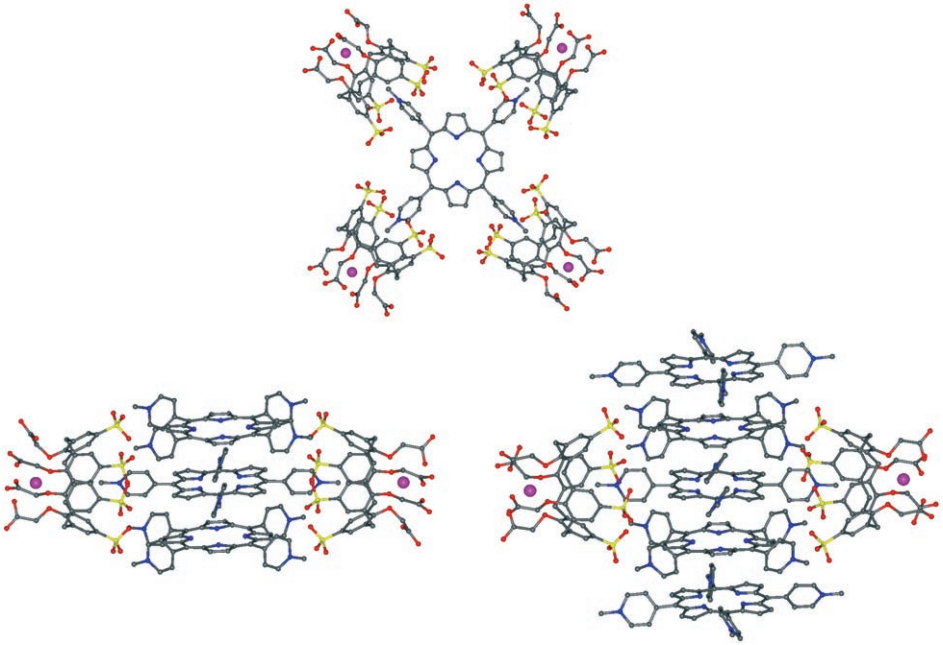

Figure 2. Top: Host–guest interactions in the unit formed by the central tetracationic porphyrin and four calixarenes as extracted from the structure of the complexes shown in the lower part of this figure. Each calixarene hosts a sodium ion (violet circles) in the lower rim.[4b] Bottom: Side view of the tri- (left) and penta-porphyrin (right) supramolecular complexes. The two calixarenes interacting with the central porphyrin above and below the figure plane have been omitted for clarity.[4b]

three experiments. Only data for which the correlation coefficients of $\ln(I/I_0)$ versus $\gamma^2\delta^2G^2(\Delta-\delta/3)$ (in which γ is the gyromagnetic ratio, G the pulsed gradient strength and Δ and δ are the time separation between the pulsed-gradients and their duration, respectively), generally termed the "diffusion weighting" and denoted as the b values, were higher than 0.999 are reported. The measurements were all performed at 298 K using LED pulse sequences[5b,c] with sine-pulsed gradients of 7 ms duration ($\delta = 7$ ms) which were incremented from 0 to 36 G cm^{-1} in 10 or 20 steps. The diffusion time was 30 ms and the echo time (TE) was 18, 22, and 26 ms depending on the linewidth of the sample. The eddy current delay (te) in the LED experiments was 50 ms. For the free porphyrin and C_4TsTc the same parameters were used, the only difference being that δ was set to 4 ms as a result of their significantly higher diffusion coefficients.

Single crystal preparation: The supramolecular complexes H_2TMPyP/C_4TsTc (**1**) and CuTMPyP/C_4TsTc (**2**) were prepared and crystallized by the vapor diffusion method with hanging-drops at 20 °C using Linbro multi-well tissue plates as containers of reservoir solutions. The stock solutions used contained C_4TsTc (7 mM) (A), H_2TMPyP (14 mM) (B), and CuTMPyP (14 mM) (C). Crystals of **1** were obtained in drops formed by mixing solution A (4 μL) with solution B (1.5 μL) and a reservoir solution (2 μL) containing poly(ethylene glycol) (PEG 300) (45–60 % v/v) as precipitant and allowing this to equilibrate against the reservoir (1 mL). Crystals suitable for X-ray diffraction experiments (dimensions $0.6\times0.6\times0.2$ mm^3) were obtained from a solution containing PEG 300 (57 % v/v). Crystals of **2** were obtained in drops formed by mixing solution A (2 μL) with solution C (2 μL), a reservoir solution (2 μL) containing poly(ethylene glycol) (PEG 300) (30–52 % v/v) as precipitant, and Tris buffer (0.1 M, pH 9.0) and allowing this to equilibrate against the reservoir (1 mL). Crystals suitable for X-ray diffraction experiments (dimensions $0.5\times0.5\times0.1$ mm^3) were obtained from a solution containing PEG 300 (50 % v/v).

X-ray data, solution, and refinement of structures: Preliminary in-house diffraction experiments using a conventional X-ray source with crystals frozen at 100 K permitted only the determination of the unit cell parameters (maximum resolution limit = 3.5 Å). Therefore, data collection was performed using synchrotron radiation (XRD1 diffraction beam-line of Elettra, Trieste) with a monochromatic X-ray beam and MarCCD detector. The crystals, dipped in their cryoprotected mother liquor, were mounted in a loop and frozen at 100 K in nitrogen. The diffraction data were indexed and integrated using MOSFLM[15] and scaled with SCALA (Collaborative Computational Project, Number 4, 1994). Crystal data are reported in Table 1. The structure of the complexes were solved by direct methods by using SIR2002[16] and anisotropically refined (hydrogen atoms at the calculated positions) with bond-length and -angle restraints by full-matrix least-squares methods on F^2 (SHELXL-97).[17] Refinement details are reported in Table 1.

CCDC-255225 and CCDC-255226 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Spectroscopic characterization of the porphyrin/calixarene complexes: The feasibility of the stepwise synthesis of noncovalent porphyrin/calixarene complexes is underlined by the results obtained by titrating a calixarene solution against increasing amounts of porphyrin (Figure 3). By using the structural data, which show that the central building block of the supramolecular complexes is the 1:4 porphyrin/calixarene unit, we have plotted the emission intensities of porphyrin (left panel) and calixarene (right panel) versus the number of porphyrins complexed to four calixarenes. Figure 3 reveals the presence of various break points corresponding to the formation of different species with stoichiometric ratios ranging from 1:4 to 7:4.

This stepwise building indicates that these species are not in equilibrium with the free components or that the equilibrium is by far shifted towards species formation. Support for this thermodynamic stability and/or kinetic inertness comes from a back-titration performed by titrating the 7:4 species against calixarene, as shown in Figure 4.

Figure 4 shows H_2TMPyP emission following the titration of a calixarene solution against increasing amounts of porphyrin (blue line) and the back-titration performed by adding increasing amounts of C_4TsTc (black line). The initial addition of calixarene to the 7:4 species (red point) led to the expected decrease in porphyrin emission (see the black curve).[18] However, the reduction in fluorescence stops at a stoichiometric ratio of 4:4 and remains constant in spite of further additions of calixarene.[19] This means that it is easier to dismantle those complexes with a high porphyrin/calixarene ratio (from 7:4 to 5:4), but, as the net negative charge of the complexes increases, the (cationic) porphyrins experience stronger electrostatic interactions and the complexes become much more stable such that they cannot be taken apart.[20]

To further corroborate the formation of the different complexes and probe their stoichiometry we performed NMR diffusion measurements. These studies, which were carried

Table 1. Crystallographic data for **1** and **2**.

Compound	**1**	**2**
molecular formula	$[(C_{44}H_{38}N_8)_5(C_{36}H_{24}NaO_{24}S_4)_4Na_8]\cdot64\,H_2O$	$[(C_{44}H_{36}CuN_8)_5(C_{36}H_{24}NaO_{24}S_4)_4Na_8]\cdot67\,H_2O$
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
Z	1	1
a [Å]	13.5055(6)	13.7984(7)
b [Å]	29.363(2)	30.051(3)
c [Å]	30.295(3)	31.151(3)
α [°]	88.122(4)	88.157(4)
β [°]	95.179(5)	94.912(6)
γ [°]	102.837(5)	102.987(6)
V [Å^3]	11665(2)	12539(2)
ρ_{calcd} [g cm^{-3}]	1.238	1.200
absorption coefficient [mm^{-1}]	0.163	0.571
resolution limit, $\lambda/2\sin\theta$ [Å]	0.97	1.07
reflections collected/unique	53460/23140	36497/18990
unique reflections $I>2\sigma(I)$	15077	11724
data/restraints/parameters	23140/13127/2664	18990/13755/2709
goodness-of-fit on F^2	1.39	1.35
R_1 $[I>2\sigma(I)]$	0.132	0.136
wR_2 $[I>2\sigma(I)]$	0.344	0.346

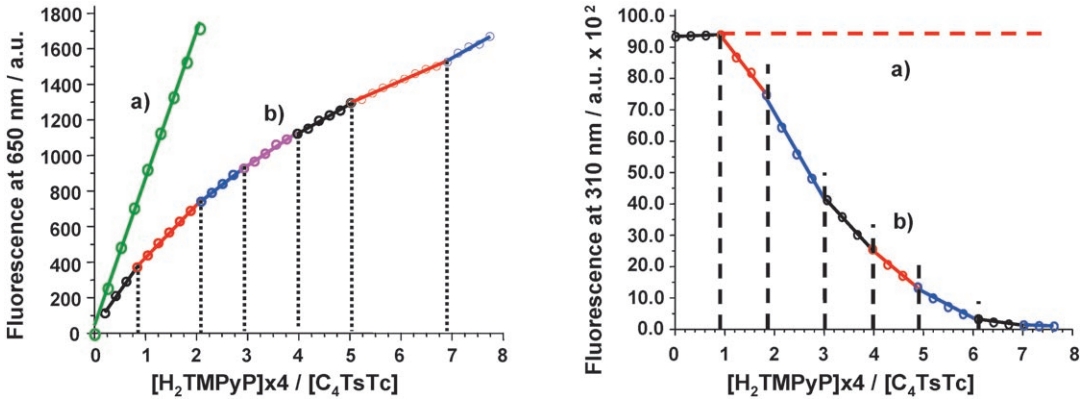

Figure 3. Left: Fluorescence of H_2TMPyP ($\lambda_{exc}=420$ nm) following the titration of a calixarene solution (1 μM) against increasing amounts of H_2TMPyP. Line a) shows H_2TMPyP emission in the absence of calixarenes. Right: Fluorescence of C_4TsTc ($\lambda_{exc}=240$ nm) following the titration of a calixarene solution (2.5 μM) against increasing amounts of H_2TMPyP. Line a) shows C_4TsTc emission in the absence of porphyrins.

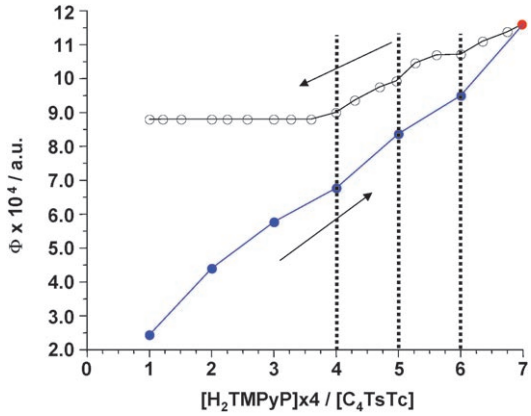

Figure 4. H_2TMPyP fluorescence at 650 nm concerning: a) the titration of an aqueous solution of calixarene against a solution containing increasing amounts of porphyrin up to the formation of the 7:4 species (blue curve, for the sake of simplicity we have reported only the break-points); b) the back-titration of the previous solution containing the 7:4 species (2.5×10^{-7} M) (red point) performed with increasing amounts of C_4TsTc. The arrow indicates the titration direction.

out at significantly higher concentrations than those used in the spectrophotometric studies, show unequivocally the formation of a 1:4 porphyrin/C_4TsTc complex. When C_4TsTc is in a large excess (beyond the 1:4 stoichiometry) two sets of NMR signals are observed for the calixarene indicating, on the NMR timescale, slow exchange between the unbound and the bound calixarenes in the complex. However, when the porphyrin/C_4TsTc stoichiometry is exactly 1:4, only one set of signals is observed for each component in the complex. The left panel of Figure 5 shows the signal decay, as a function of the gradient strength, of three peaks of the porphyrin and two peaks of the C_4TsTc in the porphyrin/C_4TsTc complex formed in D_2O solution when the porphyrin/C_4TsTc stoichiometry is exactly 1:4. Figure 5 clearly shows that all five peaks have the same signal decay, implying that they have the same diffusion coefficient and represent molecular components that diffuse as a single molecular entity. The right panel of Figure 5 shows the signal decay of the peaks of C_4TsTc and the porphyrin H_2TMPyP in the 1:4 porphyrin/C_4TsTc complex and in their free state. The diffusion coefficients extracted from these NMR diffusion experiments are summarized in Table 2.

The data clearly show that, as expected, the diffusion coefficient of C_4TsTc is somewhat smaller than that of H_2TMPyP and that both diffusion coefficients are much higher than the diffusion coefficient found for the 1:4 porphyrin/C_4TsTc complex. Importantly, the diffusion coefficients for the two molecular species in the complex are exactly the same implying that these molecular species diffuse as a single molecular entity. From this low diffusion coeffi-

Table 2. Diffusion coefficient (D) of H_2TMPyP, $C_4T_sT_c$, and the different complexes formed between them in D_2O solutions at different stoichiometric ratios at 298 K.

Entry	System	Concentration [mM]	D [10^{-5} cm^2 s^{-1}]		
			H_2TM4PyP	$C_4T_sT_c$	D_2O[a]
1	$C_4T_sT_c$	20.0	–	0.265 ± 0.001	1.940 ± 0.020
		2.0	–	0.270 ± 0.001	1.898 ± 0.004
2	H_2TMPyP	5.0	0.301 ± 0.001	–	1.937 ± 0.014
		0.5	0.316 ± 0.002	–	1.993 ± 0.011
3	H_2TMPyP/$C_4T_sT_c$ (1:4)	5.0/20.0	0.130 ± 0.002	0.129 ± 0.004	1.917 ± 0.004
4	H_2TMPyP/$C_4T_sT_c$ (1:4)	1.0/4.0	0.129 ± 0.003	0.126 ± 0.009	1.913 ± 0.006
5	H_2TMPyP/$C_4T_sT_c$ (1:4)	0.2/0.8	0.121 ± 0.007	0.120 ± 0.010	1.917 ± 0.009
6	H_2TMPyP/$C_4T_sT_c$[b] (2:4)	10.0/20.0	0.123 ± 0.003[c]	0.125 ± 0.002	1.910 ± 0.004
7	H_2TMPyP/$C_4T_sT_c$[d] (3:4)	15.0/20.0	D_{fast} 0.23 ± 0.01[c]	0.107 ± 0.001	1.907 ± 0.008
			D_{slow} 0.110 ± 0.008		

[a] Diffusion coefficient of HOD in D_2O. [b] System obtained by addition of H_2TMPyP to the system of entry 3. [c] For this system, the lines were broader than those obtained with entry 3. [d] System obtained by the addition of H_2TMPyP to the system of entry 6.

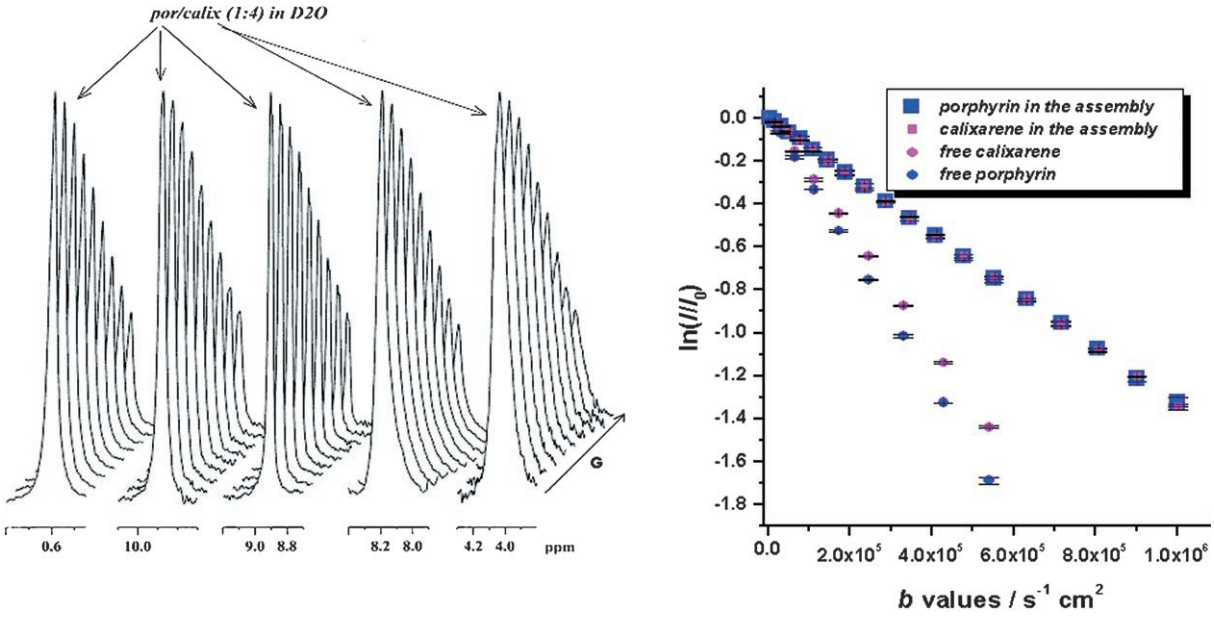

Figure 5. Left: Signal decay of three peaks of H_2TMPyP and two peaks of C_4TsTc in a 1:4 porphyrin/C_4TsTc complex as a function of the gradient strength (G). Right: Normalized signal decay of H_2TMPyP and C_4TsTc in the unbound state and in the 1:4 porphyrin/C_4TsTc complex as a function of the diffusion weighting (b).

cient a hydrodynamic radius (r_h) of 1.88 ± 0.04 nm was calculated for this complex. This radius is slightly higher than the value expected for the 1:4 complex whose dimensions are $3.0 \times 3.0 \times 1.4$ nm^3. Because of the relatively low diffusion coefficient found for the 1:4 complex and since we had to use high concentrations of the components (5 and 20 mM of H_2TMPyP and C_4TsTc, respectively) we could not rule out, a priori, aggregation of the 1:4 porphyrin/C_4TsTc complex. Therefore we repeated the diffusion experiments on this complex after dilution by a factor of 5 and 25 and in both cases no significant changes in the extracted diffusion coefficients were observed, implying that the 1:4 complex prevails in solution over this range of concentrations. These results also suggest that, over this range of concentrations, self-aggregation of the 1:4 PyP complex is not very significant.

More importantly, addition of a second equivalent of the porphyrin H_2TMPyP to the 1:4 complex resulted in a small, but noticeable reduction in the diffusion coefficients of the two components of the complex (Table 2). Addition of a third equivalent of H_2TMPyP to the complex obtained resulted in a further small, albeit significant, reduction in the diffusion coefficients of the two components of the complex, as shown in Figure 6. A plausible explanation for these results is the formation of the 2:4 and 3:4 H_2TMPyP/C_4TsTc complexes following addition of the porphyrin to the 1:4 species. Note that the NMR signals of the 3:4 complex in solution are broader than those observed for the 1:4 species. Therefore the determination of the exact ratio between the two components was difficult to obtain from simple integration and it may well be that there is an excess of H_2TMPyP beyond the 3:4 ratio. In this case, the decay (in the diffusion experiment) of the H_2TMPyP signals of the 3:4 H_2TMPyP/C_4TsTc complex was found to be non-monoexponential and

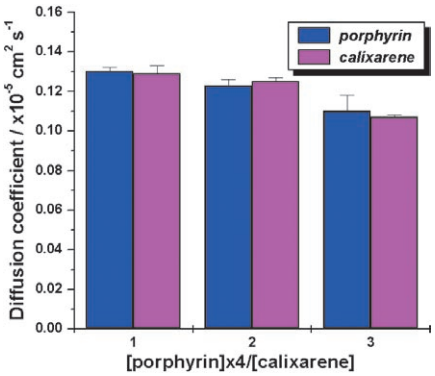

Figure 6. Graphical representation of the diffusion coefficients of H_2TMPyP and C_4TsTc in D_2O solution for porphyrin/calixarene ratios of 1:4, 2:4, and 3:4.

two diffusion coefficients, namely D_{slow} and D_{fast}, could be extracted. D_{slow} is similar to that of C_4TsTc in the complex species, while D_{fast} is higher although significantly lower than that of H_2TMPyP in the unbound state (Table 2). This may well originate from the fact that, under the experimental conditions used in the NMR diffusion experiments, additional porphyrin beyond the 3:4 ratio of H_2TMPyP/C_4TsTc can exchange with a small fraction of unbound porphyrin on the NMR timescale such that a certain fraction of H_2TMPyP have, on average, a higher diffusion coefficient than that of the 3:4 complex (see Table 2).

Therefore, the fluorescence and NMR data (Figure 3, Figure 4, Figure 5, and Figure 6) suggest that the self-assembly of the tetracationic H_2TMPyP, in the presence of the anionic calixarenes, leads to the formation of a series of dis-

crete complexes having well-defined and tunable stoichiometries derived from the piling of porphyrin macrocycles above and below the plane of a central 1:4 porphyrin/calixarene complex (Figure 2). The ditopic nature of C_4TsTc turns out to be crucial. The presence of four sulfonate and four carboxylate moieties on the upper and lower rim, respectively, shields the electrostatic repulsion between the like-charged porphyrins and provides an environment in which various types of noncovalent interactions can be arranged.

The "sharpness" of the break-points suggests that these complexes are kinetically inert and thermodynamically stable. On the other hand, the existence of a network of electrostatic interactions between net opposite charges, together with many other noncovalent interactions (from π–π to van der Waals), has been shown to be important not only to ensure thermodynamic stability but also to render such species kinetically inert.[4a]

Multi-porphyrin complexes: The distinct and quite sharp break-points observed in the fluorescence titrations of C_4TsTc against H_2TMPyP (Figure 3) suggest that it may be possible to obtain multi-porphyrin complexes. These porphyrin/calixarene species exhibit a remarkable stability and form with a stoichiometry corresponding to the stoichiometric ratio of the various components in solution and by the successive piling of porphyrins, whose sequence is governed only by the order of addition.[4c]

Therefore, for example, starting with the free calixarene, the addition of one equivalent of the porphyrin A will lead to the 1:4 species. Further addition of another equivalent of the porphyrin B will lead to the 2:4 supramolecular complex, and so forth, up to seven different porphyrins.[4c] Figure 7 shows an example of a multi-porphyrin supramolecular species built by successively piling two equivalents of AuTMPyP, two equivalents of CuTMPyP, and two equivalents of ZnTMPyP above and below the plane of a preformed 1:4 species formed by using H_2TMPyP as the central porphyrin.[21]

In order to ascertain the possible influence of the central metal on the complexation properties of porphyrins with calixarenes we have studied the structures of the systems with the free base and its copper derivative (CuTMPyP).

At buffered pH 8.2 and 9.0 we were able to obtain single crystals of both H_2TMPyP/C_4TsTc (**1**) and CuTMPyP/C_4TsTc (**2**), respectively, which are isomorphous (Table 1) and, hence, have very similar crystal structures. In both, the crystal structure may be considered as being built up by piling the porphyrin/calixarene 3:4 units (like that shown on the left side of the lower part of Figure 2) one over another and shifted by 3.9(1) Å, with the external porphyrins separated by 4.0(1) Å. A side view of the resulting pile of the copper complex **2** is shown on the left side of Figure 8. The unit cell contains one 3:4 unit which is arranged about a crystallographic symmetry center. It consists of four octaanionic calixarenes, each hosting a sodium ion, and three tetracationic porphyrins, separated by 4.1(1) Å, and, hence,

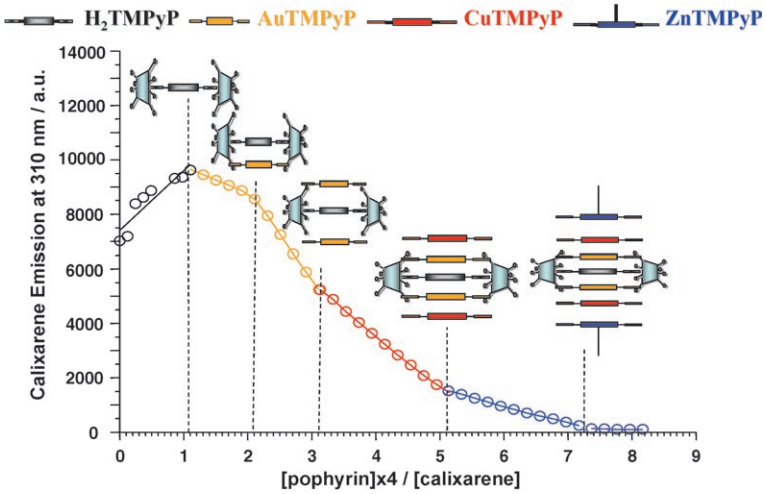

Figure 7. Fluorescence variation of C_4TsTc following the titration of a calixarene solution (2.5 μM) against increasing amounts of different porphyrins schematically presented at the top of the figure.

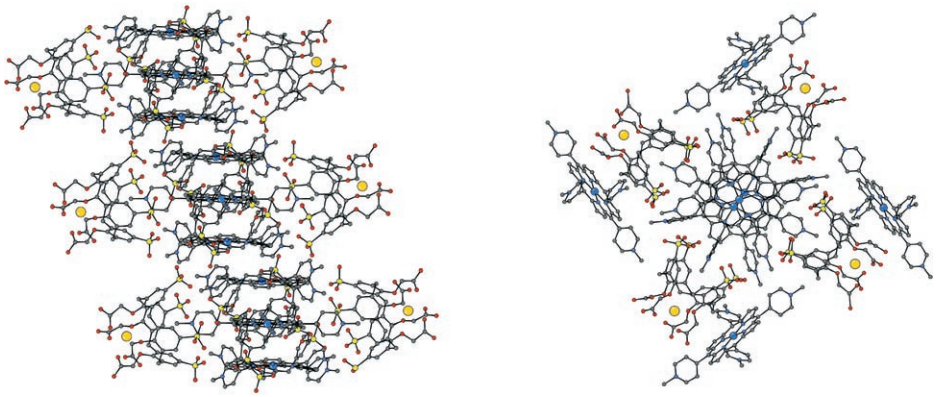

Figure 8. Left: Side view of the chain of **2** along the crystallographic *a* axis; the two calixarenes above and below the plane of the figure are not shown. Right: View of the chain projected in a plane perpendicular to the *a* axis. The cationic copper–porphyrins arranged about the symmetry centers and surrounding the chains are also shown. Blue and yellow circles represent copper and sodium ions, respectively.

has an electric charge of −16. This negative charge is compensated by two additional free porphyrins, arranged about the pile as shown on the right side of Figure 8, and eight sodium ions per unit cell. This result shows that the formation of the supramolecular complexes is not significantly influenced by the presence of metals in the porphyrin core and that the structure of the complex does not rearrange following metal insertion.

Knowledge of the complex structures and the tunability of their stoichiometry make possible a rational exploitation of these supramolecular species.

Among the different applications of these multi-porphyrin species, here we will show one concerning a species designed to activate energy-transfer processes. It is known, in fact, that, owing to the different electronegativities of the two metal centers, Zn^{II}–porphyrin/Au^{III}–porphyrin dimers give rise to the above-mentioned energy-transfer processes.[22] The following results show that it is possible to obtain various dimers and trimers with different sequences by simply "mixing and shaking" the chosen components in the right order and ratio to give the desired sequence and stoichiometry, respectively. In order to understand the importance of the molar ratio between donor and acceptor we have synthesized various complexes.

Complex formation was checked by monitoring the emission at 310 nm of a calixarene solution (2.5×10^{-6} M). The multi-porphyrin complex with a zinc(II)–porphyrin as the central moiety was synthesized by adding, first, one equivalent of ZnTMPyP (6.25×10^{-7} M). The formation of this species is clearly evidenced by the first break-point (Figure 9). Successively, two equivalents of AuTMPyP were added leading to the formation of the 2:4 and 3:4 species. Finally, the addition of another equivalent of ZnTMPyP leads to the ZnTMPyP/AuTMPyP/ZnTMPyP/AuTMPyP/$(C_4TsTc)_4$ species.

Figure 10 shows the absorption spectrum of the AuTMPyP/ZnTMPyP/AuTMPyP/$(C_4TsTc)_4$ species. Together with the absorption of AuTMPyP (at 402 nm) and ZnTMPyP (at 436 nm), a further absorption is present at about 450 nm; according to Segawa et al.[22] this band can be assigned to a $Zn^{II}\rightarrow Au^{III}$ energy-transfer process. The spectrum of ZnTMPyP/AuTMPyP/ZnTMPyP/AuTMPyP/$(C_4TsTc)_4$ is not significantly different from that observed for the trimeric species.

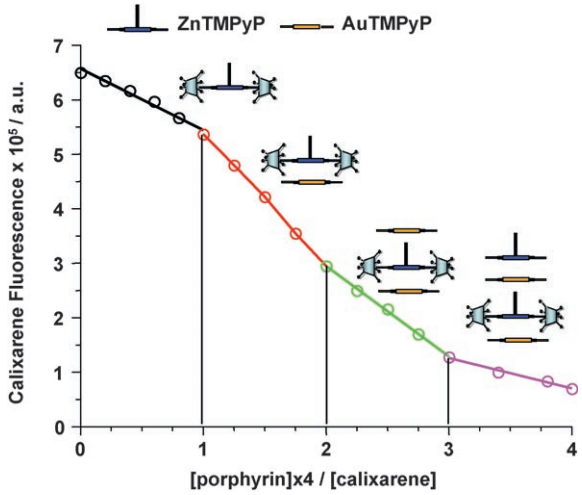

Figure 9. Fluorescence variation of C_4TsTc following the titration of a calixarene solution (2.5 μM) against increasing amounts of different porphyrins schematically represented at the top of the figure.

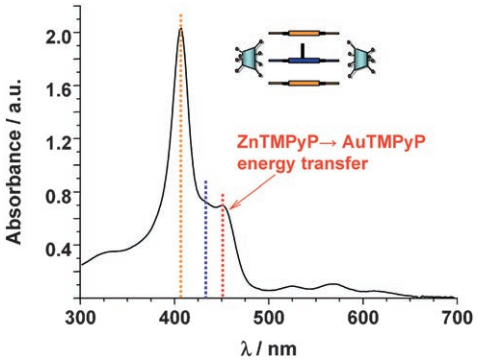

Figure 10. Absorption spectrum of an aqueous solution of the ZnTMPyP/$(AuTMPyP)_2$/$(C_4TsTc)_4$ species.

Conclusions

C_4TsTc is able to template the formation of discrete porphyrin arrays assembled by four calixarene units. Diffusion NMR measurements corroborate our hypothesis that in aqueous solution the stoichiometry of the various complexes corresponds to the actual concentration ratio of porphyrins and calixarenes. Knowledge of the structures of the complexes from crystallographic data, together with the possibility of forming in solution discrete complexes with desired porphyrin sequences, opens the way to a new rational synthesis of porphyrin arrays suitable for different applications ranging from molecular devices to simple models of haemoproteins.

Acknowledgement

We thank MURST (FIRB RBAUOIhAAAA and PRIN 2003037580) for partial financial support.

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[18] The emission of the back-titration is higher than that observed for the forward experiment (performed by adding porphyrins) owing to the higher concentration of the species.

[19] The emission remains constant for three days.

[20] The higher negative potential causes an increase in the calixarene–porphyrin attractions and more effective shielding of the positive–positive repulsions. Consequently, the π–π interactions strengthen as a result of the decreased porphyrin–porphyrin distance.

[21] Owing to the overlap or lack (CuTMPyP) of porphyrin emission these experiments could only be performed by monitoring the calixarene emission.

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Received: July 15, 2005
Please note: Minor changes have been made to this manuscript since its publication in *Chemistry–A European Journal* Early View. The Editor.
Revised: November 10, 2005
Published online: January 17, 2006

