JOC *Note*

Structure of a 4:1:4 Supramolecular Assembly of Neutral T*iiii*PO Cavitands and Tetrakis(*N*-methylpyridinium)porphyrin Iodide

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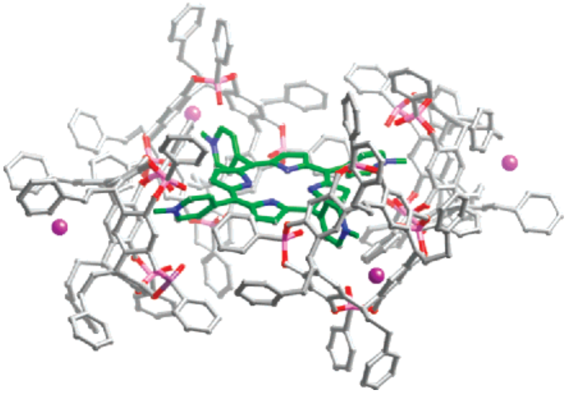

Four tetraphosphorylated T*iiii*PO cavitands **1** encapsulate the pyridinium heads of a tetrakis(*N*-methylpyridinium)porphyrin iodide to form a 4:1:4 (host)$_4$/guest^{4+}/4I$^-$ complex. The single-crystal X-ray diffraction analysis shows the arrangement of the four cavities bound to the CH_3N^+ groups of the porphyrin moiety and the four iodide anions nested between the phenethyl substituents of the hosts. ^{1}H NMR investigations show that the structure is preserved in chloroform solution and underscore the effect of the counteranions.

One of the most active fields of research in supramolecular chemistry is the design of new self-organized materials. For instance, metal coordination frameworks have been extensively studied in recent years, as they elegantly lead to the construction of materials whose properties depend on the ligand−metal arrangements and the formation of cavities and pores.[1,2] Applications in gas storage[3] or chemical catalysts are being actively investigated.[4] To reach such objectives, host−guest association using noncovalent interactions, such as H-bonding and Coulombic or van der Waals interactions, is an attractive supramolecular strategy to design new elements that will self-associate to eventually form original networks and materials. This idea prompted us to investigate the formation of self-organized, giant host−guest systems by means of host−guest interactions strong enough to ensure the stability of the assembly.

In this context the porphyrin/cavitand tandem is very attractive.[5] Recent studies by Purello, Randaccio, Sciotto, and coworkers revealed such an approach to form giant structures from tetrakis(*N*-methylpyridinium)porphyrin ($TMPyP^{4+}$) and sulfonated calix[4]arenes (calx^{n-}).[6] They reported the spectroscopic and structural study of the pH-dependent formation of multiporphyrin complexes. In this case stoichiometry and structure were easily tuned and stabilized through multiple noncovalent interactions to form controllable porphyrin arrays.[7] The all-inward orientation (*iiii*) of the P═O bonds in the T*iiii*P(O)Ph cavitand **1** is particularly interesting because of its strong propensity to form highly stable complexes with cationic guests.[8,9] Phosphato- and phosphonato-bridged cavitands present interesting host−guest properties,[10] featuring new applications in sensoring.[11−13] Besides the well-known cationic recognition properties devoted to this family of ligands,[14−16] reversible associations can be applied to the design of more sophisticated supramolecular assemblies, including supramolecular oligomers and networks. In this Note, we report the formation and the characterization of a new porphyrin-based supramolecule consisting of a $TMPyP^{4+}$ and four tetraphosphorylated cavitands **1** with active participation of the iodide counteranion in the stabilization of the complex.

Tetraphosphorylated cavitands strongly bind cationic species and are particularly suitable for ammonium cations. *N*-Methylpyridinium moieties are complementary guests, as they are bound through strong dipolar interactions between CH_3N^+ and PO groups and favorable van der Waals interactions between

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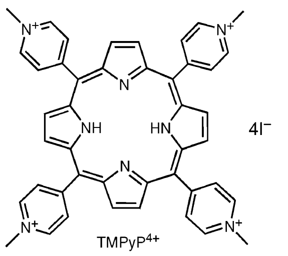
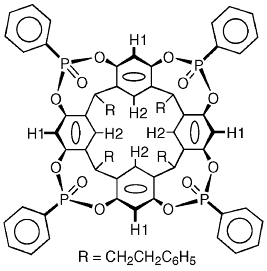


TMPyP^{4+}



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the *N*-methyl group and the resorcarene cavity.[17] In order to form highly stable associations, we used tetrakis(*N*-methylpyridinium)porphyrin tetraiodide as a template, which can then associate to four cavitand structures. The formation of the 4:1:4 (host)$_4$/guest^{4+}/4I$^-$ complex was characterized in solution and in the solid state.

Tetrakis(*N*-methylpyridinium)porphyrin compounds are generally only soluble in water or a very polar solvent such as DMSO. In the presence of cavitand **1**, TMPyP^{4+} tetraiodide is readily dissolved in chloroform to produce the supramolecule [TMPyP^{4+}][4I$^-$]·**1**$_4$ with molecular weight 6760 and was characterized by ^{1}H NMR spectroscopy. The exchange between free and bound host is slow on the proton NMR time scale, and we report in Table 1 the complexation induced shifts (CIS) of some typical protons of the complex.

The CH$_3$N$^+$ protons of the guest are high field shifted with an expected chemical shift δ(NCH$_3$) = 1.34 ppm to be compared to δ(NCH$_3$) = 4.70 ppm for the free TMPyP^{4+} (DMSO is used for the free guest, which is insoluble in CHCl$_3$), proofing the encapsulation of the methyl groups in the aromatic cavities. Mainly H(2) and CH$_2$CH$_2$ protons of the phenethyl chains ($^{\alpha}$-CH$_2$$^{\beta}CH_2$Ph), located at the narrow rim of **1**, are highly differentiated upon complexation. These important shifts are due to the encapsulation of the guest and to the peculiar localization of the counteranion. Indeed, to sustain this result, we recorded the ^{1}H NMR spectra of complexes of **1** with various ammonium salts. Changes in the ^{1}H NMR spectra were observed and showed unambiguously a behavior for chloride and iodide salts dramatically different from that observed with other salts (see Table S1 in the ESI).

The encapsulation is effective independently of the counteranion as shown by the high-field shifted resonances of the protons of the guests and of the H(1) protons in **1**. However, the H(2) and CH$_2$CH$_2$ proton resonances depend on the guest and more dramatically on the nature of the counteranion. For instance, low-field shifts from 1.47 to 2.06 ppm are observed for H(2) with chloride or iodide salts, whereas picrate or PF$_6$ salts induced lower values (0.71 to 0.97 ppm) (see ESI). Similarly, α-CH$_2$ protons of the phenethyl chains experience larger low-field shifts (0.61−0.87 ppm) with halide salts than with other salts (0.16−0.35 ppm). The β-CH$_2$ protons undergo minor effects when compared to α-CH$_2$. This is attributed to the localization of the halide anion in the pseudocavity formed by the four phenethyl groups at the narrow rim of the cavitand. This peculiar arrangement is one of the factors responsible of the stability of the 4:1:4 **1**$_4$/guest^{4+}/4I$^-$ complex in chloroform solution. This result is supported by the solid-state structure analysis described below.

TABLE 1. CIS ($\Delta\delta = \delta_{\text{bound}} - \delta_{\text{free}}$ ppm) of Guest and Host Protons in [TMPyP^{4+}][4I$^-$]·1$_4$ Complex, at 293 K in CDCl$_3$ Solution

host/guest protons	$\Delta\delta$ (ppm)
CH$_3$N$^{+\,a}$	−3.36
pyrrolicCH^a	−0.91
PyrH^a	−0.45/−0.84
H(1)	−0.09
H(2)	1.66
CH$_2$CH$_2$	0.15/0.87

[a] Free: in DMSO; bound: in CDCl$_3$.

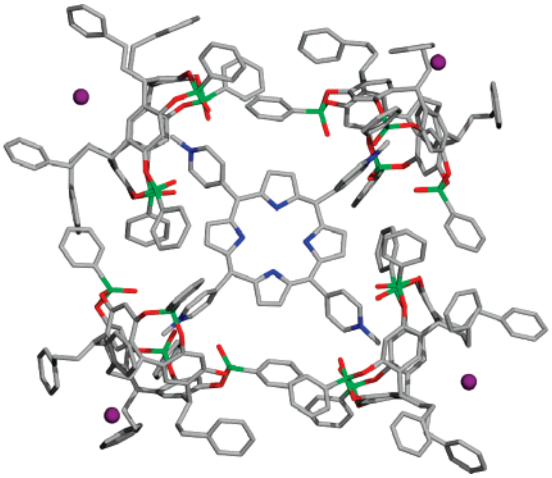

FIGURE 1. X-ray molecular structure of the [TMPyP^{4+}][4I$^-$]·**1**$_4$ complex. Solvent molecules are omitted for clarity.

In the solid-state structure of the [TMPyP^{4+}][4I$^-$]·**1**$_4$ complex, the TMPyP^{4+} porphyrin is surrounded by four cavitands **1**, each complexing a CH$_3$N$^+$group deep in the molecular cavity. The cationic supramolecule [TMPyP^{4+}]·**1**$_4$ closely resembles the basic anionic unit [TMPyP^{4+}]·[calx^{n-}]$_4$, from which the supramolecular complexes obtained by Purrello, Randaccio, Sciotto, and co-workers are formally obtained by addition of further porphyrins above and below the plane of that hosted by calx^{n-} in [TMPyP^{4+}]·[calx^{n-}]$_4$.[6,7] The supramolecule is roughly a 2 nm × 2.2 nm rectangular box with diagonal 3 nm large (estimated from the I$^-$···I$^-$ distances), each corner being occupied by a cavitand nesting a CH$_3$N$^+$ group (Figure 1). The thickness of the box was estimated to be >2 nm by measuring the distances between the more distal carbon atoms above and below the porphyrin plane. The supramolecules are closely packed without forming channels or voids.

In each cavitand, the CH$_3$N$^+$ group is stabilized by strong dipolar interactions with the four PO groups and two PO···H−C H-bonds with the *o*-CH of the pyridyl ring. Typical PO···N$^+$ and PO···C$_{\text{pyr}}$ distances are given in Figure 2. The PO···N$^+$ distances are not all equal because of the dissymmetry of the cavitands, which are elongated along one PO···OP diagonal with respect to the other.

In the four CH$_3$N$^+$−cavitand assemblies of the complex, the N$^+$ atom is coplanar with the four PO oxygen atoms, while the distance of the *N*-methyl carbons to this plane range from 1.31 Å to 1.51 Å (Figure 3). The deep encapsulation of the CH$_3$ groups inside the cavity is further stabilized by CH···π interactions. The carbon methyl groups are located at an average distance of 3.75 Å from the centroid of the phenyl groups of the resorcarene cavity.

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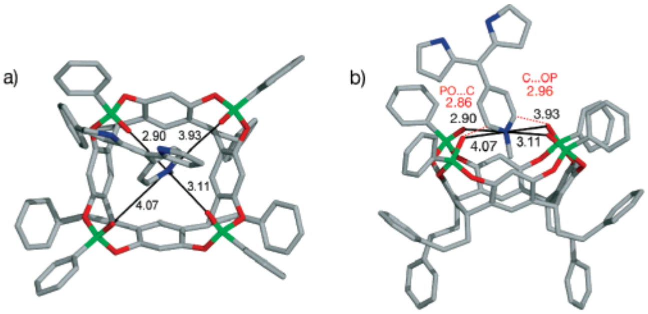

FIGURE 2. Top (a) and side (b) views of the typical coordination of the pyridinium group to the four PO groups of cavitand **1** with PO···N^+ and PO···C distances (Å).

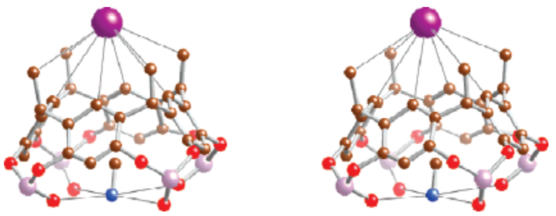

FIGURE 3. Stereoview of the localization of CH_3N^+ and I^- relatively to the molecular cavity of **1** showing the main noncovalent interactions with carbon and oxygen atoms. For clarity, only the α-CH_2 groups of the phenethyl substituents are represented.

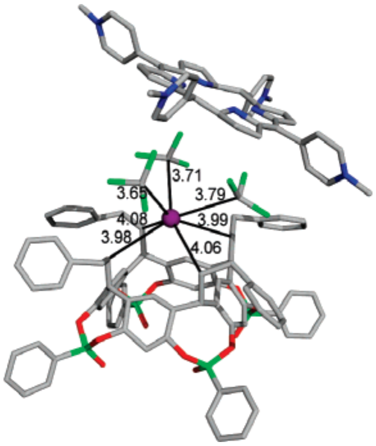

FIGURE 4. Case 1: Cavitand−iodide−porphyrin arrangement in the crystal and interactions with chloroform molecules. Example of the I(2) anion with I···C distances (Å).

There are two kinds of interaction at the narrow rim of the cavities. Both imply iodide anions, which are located in between the phenethyl chains of the hosts. In a first arrangement (case 1), present in two crystallographically independent resorcarene molecules, interacting with the central porphyrin molecule on opposite sides, the narrow rim of a cavitand faces another porphyrin guest (Figure 4). The $^{\alpha}CH_2{}^{\beta}CH_2Ph$ chains adopt a gauche conformation, which directs the CH_2Ph groups outward. The shortest distances between I^- and the cavity are observed with the α-CH_2 groups with an average I^-···C distance of 3.98 Å. This puts the iodide anion at the center of the pseudocavity defined by the lower rim substituents, and 1.75 Å from the best plane defined by the four α-CH_2 carbons (Figure 3). A complex pattern of chloroform molecules are also H-bonded to the anion and the porphyrin moiety (Figure 4).

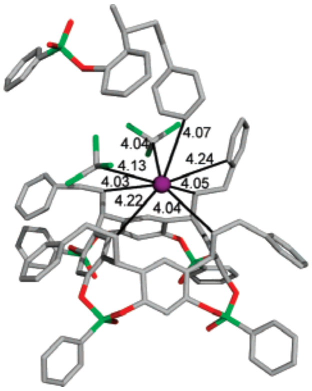

FIGURE 5. Case 2: Cavitand−iodide−cavitand arrangement in the crystal and interactions with chloroform molecules. Example of the I(4) anion with I···C distances (Å).

In the second arrangement (case 2), present in the other two crystallographically independent resorcarene molecules, the narrow rim of the cavitand is close to the phenethyl chain of a host of a neighboring supramolecule. In this case, the $^{\alpha}CH_2{}^{\beta}$-CH_2Ph chains adopt gauche or trans conformations, which introduce more interactions between iodide and the two involved cavitands. The halide anion is still located in the pseudocavity defined by the substituents at the narrow rim, with weak interactions with α-CH_2 (average I···C distances of 4.06 Å) and with nearest aromatic carbons (average I···C distances of 4.12 Å). Chloroform molecules also participate in the environment of the anion (Figure 5).

The localization of the halide anion is important and can contribute to the stability of the complex. Several articles reported on the anion effects and take into account ion-pairing and allosteric effects.[18] In general, considering what has been observed between ammonium guests and calixarene hosts, picrate salts are better than halide in calix[5]arene complexes,[19] and ammonium iodide better than ammonium tosylate in calix[4]arenes.[20] However, one should consider the balance between the ion-pair separation energy and the stabilizing forces for the ammonium ion recognition.[21,22] It thus appears that the problem is more subtle and not so obvious, and anion effects are particularly dependent on the receptor and its propensity to favor, or not, ion separation.[23] In ammonium−resorcarene complexes, Rissanen and co-workers showed that chloride or bromide anions can be localized in between the alkyl chains at the lower rim of the cavitand.[24−26] In the present case, solution NMR and solid-state studies revealed that iodide anions are located close to the narrow rim of the cavitands, a situation encountered in ammonium−cavitand complexes but seldom demonstrated in

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TABLE 2. Crystal Data and Structure Refinement for [TMPyP^{4+}][4I$^-$]$\cdot$1$_4$

molecular formula	$[(C_{84}H_{68}O_{12}P_4)_4\cdot(C_{44}H_{38}N_8)\cdot I_4]\cdot 20CHCl_3$
formula weight	6097.89
crystal system	orthorhombic
space group	$Pca2_1$
Z	4
a (Å)	28.285(1)
b (Å)	32.5755(8)
c (Å)	51.646(2)
V (Å^3)	47381.92
ρ_{calc} (gcm^{-3})	1.451
absorption coefficient (mm^{-1})	1.031
θ range (deg)	1.83−27.41
Flack parameter	0.01(2)
reflections collected/unique	373003/24077
unique reflections I > 2σ(I)	16275
data/restraints/parameters	24077/6428/4577
Goodness-of-fit on F^2	1.487
R_1 ($I > 2\sigma(I)$)	0.130
wR_2 ($I > 2\ \sigma(I)$)	0.320

solution. This behavior corresponds to the tentative re-formation of the ion-pair between charged species, and it is a consequence of the strong affinity of the tetraphosphorylated cavitand **1** for ammonium guests. In the complex, the best arrangement is the one observed in solution and in the solid state, where I$^-$ is embedded between the four chains of the narrow rim at an average distance of 7.5 Å from the N$^+$ counterion atom. A somewhat different arrangement was observed in the solid-state structure of the [4,4′-bipy(NCH$_3$)$_2$$^{2+}$][2PF$_6$$^-$]$\cdot$**1**$_2$ complex, where the two cavitands **1** are capping the CH$_3$N$^+$ groups, and the PF$_6$$^-$ anions are located at interstitial positions in the lattice,[17] in agreement with the present result. The localization of the counteranion close to the cavity side was also proposed by Böhmer et al. for the complexation of quaternary ammonium guests by calyx[5]arene hosts,[19] referring to the cation−π interactions developed by Dougherty et al.[27]

In conclusion, the strong affinity of host **1** for cationic species led to the formation of the [TMPyP^{4+}][4I$^-$]$\cdot$**1**$_4$ supramolecular complex. The molecular structure was solved in the solid state by X-ray analysis, and ^{1}H NMR studies showed that the structure is maintained in solution. The porphyrin template is surrounded by four cavitands embedding the CH$_3$N$^+$ groups, and the iodide anions are localized at the narrow rim of the cavitands in accord with observations of various ammonium@**1** complexes. The effort to recreate the ion-pair seems to be an important driving force in the structural organization of the halide salt complexes, whereas other salt guests behave differently, with consequences on the ^{1}H NMR chemical shifts. The construction of such giant supramolecular assemblies features the design of supramolecular arrays with potential applications in supramolecular oligomer based devices.

Experimental Section

Solid-State Structure Analysis. Orange-brown platelet-shaped crystals of the complex suitable for X-ray analysis were grown in chloroform/n-hexane, cavitand/porphyrin 4:1 ratio. Data collection was performed at the X-ray diffraction beamline of Elettra Synchrotron, Trieste (Italy) (monochromatic wavelength λ = 0.9 Å, Mar CCD detector), with crystals frozen at 100 K. The diffraction data were indexed and integrated using DENZO and scaled with SCALEPACK.[28] The structure was solved in $Pca2_1$ space group by direct methods using SHELXS[29] and Fourier analyses and refined by the full-matrix least-squares based on F^2 using SHELXL-97.[30] The asymmetric unit contains a supramolecular complex, formed by four phosphonato-resorcarene molecules arranged around one positive charged porphyrin, four iodide ions, and 20 chloroform molecules. During the refinement, restraints for pyridyl and phenyl groups and for chloroform molecules have been introduced in the model. In the final refinement, hydrogen atoms were included at calculated positions and non-hydrogen non-disordered atoms were treated anisotropically. The SQUEEZE function of the program PLATON[31] reveals a residual electron density of 815 electrons/cell in cell-remaining voids (10% of cell volume). A refinement using reflections modified by the SQUEEZE procedure behaved well, and the *R*-factors were significantly reduced from 0.172 to 0.130. Essential crystal data and refinement details are reported in Table 2.

Acknowledgment. Prof. Bernard Tinant is gratefully acknowledged for helpful discussion.

Supporting Information Available: Synthetic procedure; detailed solid-state structure analysis of [TMPyP^{4+}][4I$^-$]$\cdot$**1**$_4$; the ^{1}H NMR spectra of compounds **1**, TMPyP$^{4+}\cdot$4I$^-$, and complex [TMPyP^{4+}][4I$^-$]$\cdot$**1**$_4$; ^{1}H NMR data for ammonium@**1** complexes; crystallographic information file (CIF) for [TMPyP^{4+}][4I$^-$]$\cdot$**1**$_4$ complex (CCDC 631614). This material is available free of charge via the Internet at http://pubs.acs.org.

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