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Self-Complementary Phosphonate Cavitands

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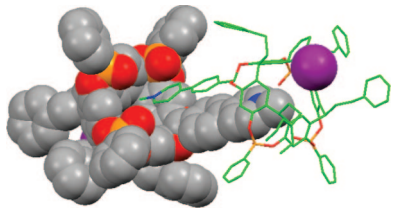
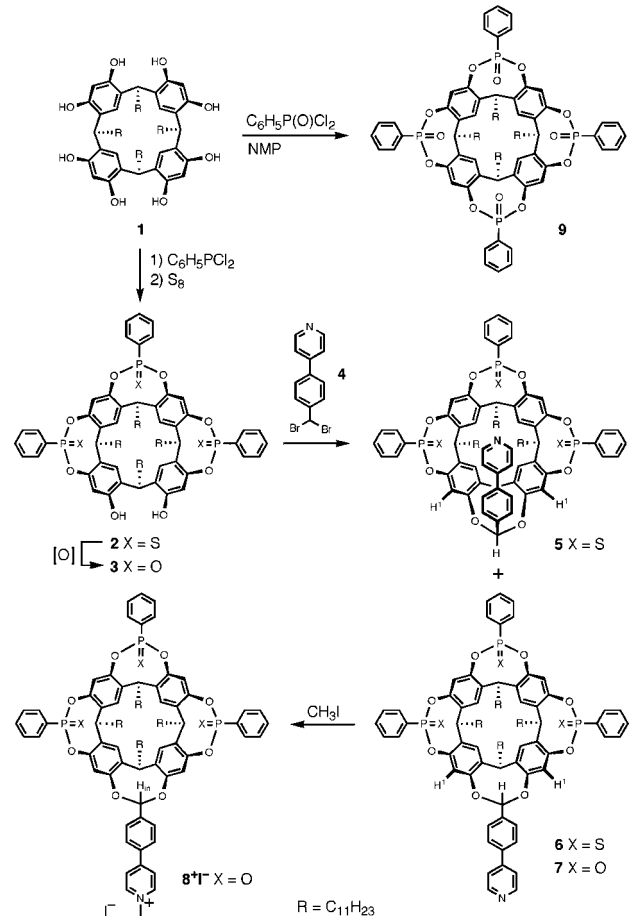


iii-Phosphorylated cavitands incorporating an *N*-methylpyridinium guest moiety as the fourth bridging unit form supramolecular associations by inclusion of the charged CH_3N^+-pyridinium head into a neighboring host cavity. The dimeric association is favored in solution and was characterized by NMR, mass spectrometry, DOSY experiments, and single crystal X-ray analysis.

The design of supramolecular host−guest assemblies requires developing efficient hosts that will provide stable associations and control over their structure and lability. For instance, the formation of supramolecular host−guest oligomers and polymers is a rapidly expanding area of research because of their potential value in organizing molecular assemblies according to targeted properties and/or architecture.[1] The phosphonate cavitands derived from the calix[4]resorcinarenes have proven to be highly efficient cation binders. They combine an aromatic cavity and an inward (*i*) orientation of four hard donor phosphonate groups at the wide rim of the calix scaffold.[2] When suitably functionalized at their narrow rim, they self-assemble to form original supramolecular polymers.[3] In the present work, we report the design of novel supramolecular associations that utilize guest-substituted hosts.[4] This involves the replacement of one of the bridging units, while maintaining three P═O binding sites to retain the stability of the complex. This is realized by substituting one phosphonate group with a tolylpyridinium bridge presenting an *N*-methylpyridinium guest unit. The remaining three P═O bonds are oriented toward the molecular cavity (*iii* or 3*i* configuration).

SCHEME 1. Synthesis of Tolylpyridinium-Bridged 3*i*-Phosphorylated Cavitand 8^+I^- and 4*i* Cavitand 9



The reaction of tetraresorcinol **1** with 3 equiv of $PhPCl_2$ followed by addition of sulfur gave the 3*i* compound **2** in 25% isolated yield (Scheme 1). The subsequent treatment of **2** with hydrogen peroxide or *m*-chloroperoxybenzoic acid (MCPBA) led to the triphosphonate derivative **3** in good yields. The NMR data of the new compounds were in agreement with the expected structures with a rigid cavity. Tolylpyridine-bridged compounds can be obtained by reaction of compounds **2** and **3** with α,α′-dibromotolylpyridine **4**[5] and K_2CO_3 in DMF. At this stage of the synthesis, it was interesting to investigate the stereoselec-

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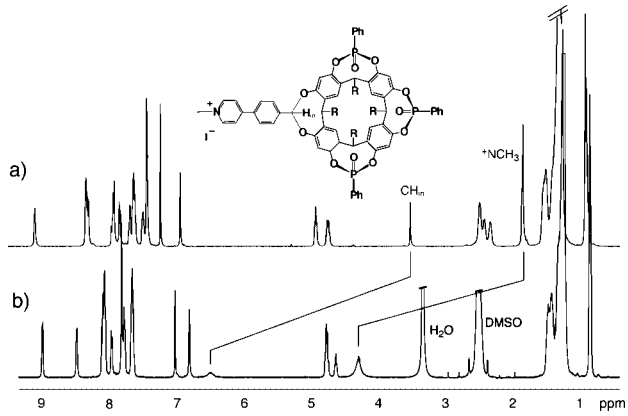

FIGURE 1. ^{1}H NMR spectra (500 MHz) of $\mathbf{8}^+\mathrm{I}^-$ in $CDCl_3$ (a) and DMSO-d_6 (b).

tivity of this last bridge installation with the PS (**2**) and PO (**3**) derivatives. Compound **2** afforded the two isomers **5** and **6** with inward and outward orientation of the tolylpyridine bridge, respectively. Both isomers **5** (25%) and **6** (40%) were fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR and HRMS. For instance, in **5** the two H^1 aromatic protons at the wide rim (Scheme 1) along with the OCHO proton were upfield and downfield shifted by 1.67 and 1.34 ppm, respectively, with respect to **6**, due to the shielding effect of the aromatic rings. Unexpectedly, starting from derivative **3**, only the desired outward isomer **7** was isolated in 41% yield. The *out*-tolylpyridine isomer **7** presents a free cavity with three P═O phosphorus binding sites oriented inward, and can be exploited for complexation of cationic species. To investigate the possible self-assembling process of **7**, the methylpyridinium salt $\mathbf{8}^+\mathrm{I}^-$ was prepared in quantitative yield by using CH_3I in CH_2Cl_2. Compound $\mathbf{8}^+\mathrm{I}^-$ was recovered as a solid that precipitated from diethyl ether and was fully characterized and studied by NMR spectroscopy.

By using the method described for the *iiii* (4*i*) isomer,[6] the preparation of the 3*i* phosphonate cavitand **3** from tetraresorcinol **1** and 3 equiv of $PhP(O)Cl_2$ was unsuccessful. The reaction of **1** with $PhP(O)Cl_2$ in the presence of *N*-methylpyrrolidine (NMP) afforded only compound **9**,[7] regardless of the number of equivalents of phosphorus reagent used (3 or 4 equiv; Scheme 1).[8]

In $CDCl_3$ solution, the ^{1}H NMR spectrum of $\mathbf{8}^+\mathrm{I}^-$ exhibited a strong upfield shift ($\Delta\delta$ = 2.4 ppm) of the CH-*in* proton of the tolylpyridine bridge with respect to **7**. At the same time, the CH_3N^+ methyl resonance at δ 1.80 ppm is indicative of the encapsulation of the methylpyridinium head into the molecular cavity of a neighboring host (Figure 1). Consequently, the supramolecular assembly should result in the formation of a dimeric structure or oligomeric species with either cyclic or linear structures. In DMSO, the ^{1}H NMR spectrum of $\mathbf{8}^+\mathrm{I}^-$ showed a different situation, in which resonances of the CH-*in* and the CH_3N^+ group were low-field shifted ($\Delta\delta$ = 3.0 and 2.48 ppm, respectively), in comparison to the $CDCl_3$ solution (Figure 1). Indeed, in polar solvent, the host−guest association

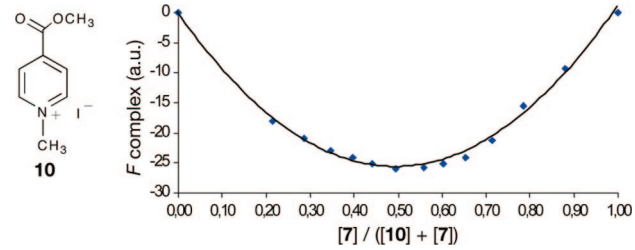

FIGURE 2. Job plot for the **10@7** complex obtained from fluorescence titration experiment.

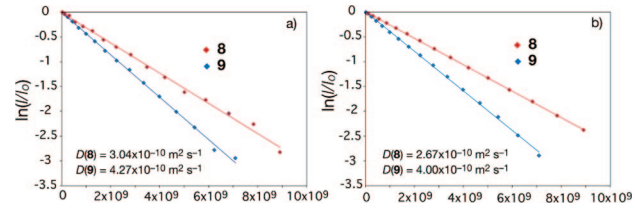

FIGURE 3. Plots of $\ln(I/I_o)$ vs. arbitrary units proportional to the square of the gradient amplitude for ^{1}H diffusion measurements on **9** and $\mathbf{8}^+\mathrm{I}^-$: (a) in $CDCl_3$ and (b) in $CDCl_3$/THF mixture.

is strongly reduced by the preferential solvation of the guest moiety. However, the broadening of these signals suggests a residual weak complexation in DMSO, demonstrating the efficiency of the PO···N^+ interactions.

To assess the stability of the inclusion of a pyridinium guest inside the 3*i* phosphonate cavitand, the binding constant K_a was determined in CH_2Cl_2 with *N*-methylmethylisonicotinate iodide salt (**10**) as model guest, and cavitand **7** as host. The Job plot obtained from fluorescence data, showed the formation of the 1:1 complex **10@7** (Figure 2). The K_a value of 1.4 ± 0.4 × 10^4 M^{-1} is similar to that calculated from UV−vis titration experiments (K_a = 1.0 ± 0.4 × 10^4 M^{-1}) in the same solvent. In ethanol, a more polar and solvating medium, the K_a value decreased to 3.9 ± 0.1 × 10^3 M^{-1}. This indicates that, under these conditions, ammonium complexation was still efficient.

Diffusion-order ^{1}H NMR spectroscopy experiments (DOSY)[9] are particularly appropriate for characterizing host−guest supramolecular assemblies. The determination of the self-diffusion coefficients *D* of the species in solution allows us to estimate their dimensions via their hydrodynamic radii.[10] Temperature effects on solvent viscosity and chemical exchanges can be important, and the use of cavitand **9** as reference (Scheme 1) allowed the direct comparison of the diffusion constants *D* extracted from the plots of $\ln(I/I_o)$ versus the square of the pulse gradient strength (Figure 3). In $CHCl_3$, the $D(\mathbf{8})/D(\mathbf{9})$ ratio gave an estimate of the hydrodynamic volumes ratio $V_H(\mathbf{8}) = 2.8V_H(\mathbf{9})$.[11] This proves that **8** possesses a larger hydrodynamic radius than **9** and that a dimeric species prevailed in $CHCl_3$ solution. Interestingly, when performed in the more polar $CHCl_3$/THF 3:2 mixture ($\mathbf{8}^+\mathrm{I}^-$ is not soluble in pure THF), on average, an estimated $V_H(\mathbf{8}) = 3.4V_H(\mathbf{9})$ was obtained, indicating that the dimer still prevails, but higher molecular weight species are formed. These data were corroborated by mass spectrometry experiments.

Electrospray and coldspray ionization mass spectrometry[12] of $\mathbf{8}^+\mathrm{I}^-$ in $CHCl_3$ solution gave a main signal at *m*/*z* 1651.90

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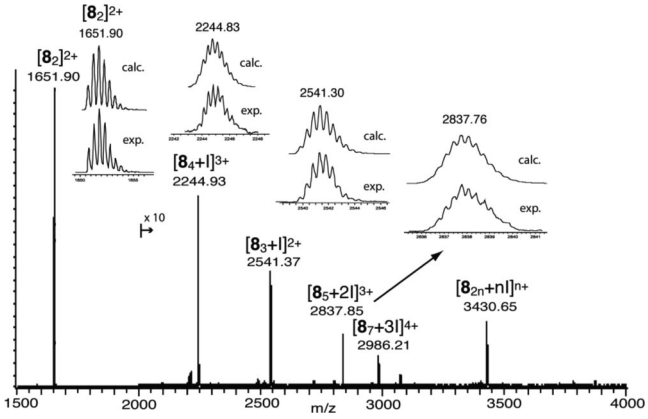

FIGURE 4. ESI-MS of a $CHCl_3$ solution of $\mathbf{8}^+I^-$.

corresponding to the dimeric structure $[\mathbf{8}_2]^{2+}$ (Figure 4). Other signals were found at *m*/*z* 2244.93 $[\mathbf{8}_4 + I]^{3+}$, 2541.37 $[\mathbf{8}_3 + I]^{2+}$, 2837.85 $[\mathbf{8}_5 + 2I]^{3+}$, and 2986.21 $[\mathbf{8}_7 + 3I]^{4+}$, which were attributable to the *n*-charged $[\mathbf{8}_{2n} + nI]^{n+}$ species detected for $n = 1-4$. The dimeric self-assembly is the main compound in solution. The sparingly soluble higher molecular weight species rapidly precipitated and did not allow further investigations. The mass spectrum of the same $CHCl_3$ solution performed after 1 h proved the predominance of the dimer (Figure S12, Supporting Information). Thus, the limiting factor in detecting higher molecular weight species is their low solubility, preventing us from investigating further concentration effects. Increasing the concentration of $\mathbf{8}^+I^-$ led to the formation of a precipitate, presumably comprising oligomeric species.

Attempts to obtain single crystals of $\mathbf{8}^+I^-$ for X-ray diffraction analysis failed, likely due to the presence of the long alkyl chains at the narrow rim. Consequently, we synthesized the tetraphenetyl cavitand $\mathbf{11}^+I^-$, which proved to be a better candidate for X-ray analysis. A synthetic scheme similar to that used for the synthesis of $\mathbf{8}^+I^-$ was followed. In solution, $\mathbf{11}^+I^-$ behaves similarly to $\mathbf{8}^+I^-$in $CHCl_3$ (see the Supporting Information). Single crystals of $\mathbf{11}^+I^-$, suitable for X-ray diffraction studies, were obtained by crystallization from CH_2Cl_2/CH_3OH. In the solid, two cavitands $\mathbf{11}^+I^-$ are complementary self-associated to form the dimeric supermolecule depicted in Figure 5. The H_3CN^+ moieties are encapsulated in the resorcinarene cavities with the carbon methyl located at 1.41 Å from the mean plane defined by the PO oxygen atoms, and at an average distance of 3.73 Å from the centroid of the aromatic groups. The two tolylpyridinium moieties are stacked with a tolylpyridine mean plane distance of 3.8 Å. In each complexation site, the N^+ nitrogen atom and the three coordinating PO oxygen atoms lie in the same plane (average PO···N^+ distance is 3.83 Å). Interestingly, the iodide ion is located in the pseudocavity defined by the four $^{\alpha}CH_2-{}^{\beta}CH_2-$Ph chains at the narrow rim, as already observed with ammonium complexes of tetraphosphonate cavitands.[13] The shortest distances between I^- and the cavity involve the $^{\alpha}CH_2$ carbons (average I···CH_2 distance is 4.12 Å) and the aromatic CH carbons (average I···CH is 4.35 Å) (see the Supporting Information).

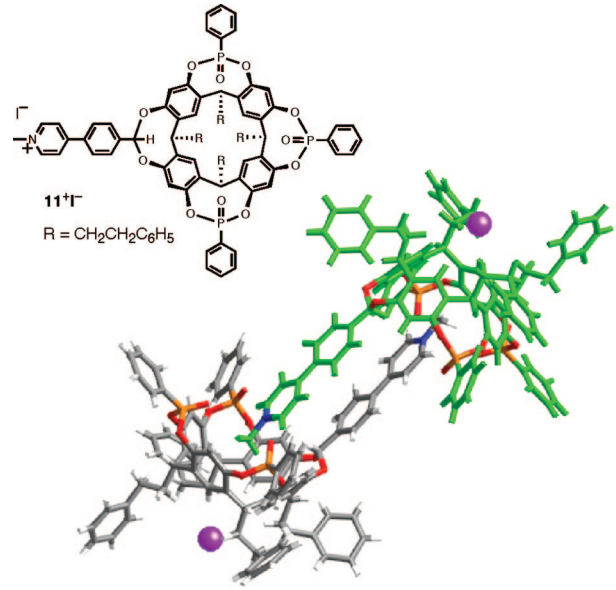

FIGURE 5. Structure of $\mathbf{11}^+I^-$ and X-ray molecular structure of the dimeric assembly $[\mathbf{11}^+I^-]_2$.

The 4*i* tetraphosphonate cavitands for which **9** is a representative member have proved to form strong associations with cationic guests in weakly polar solvent.[6] For instance, high binding constants $K_a = 10^6-10^7$ M^{-1} were determined with pyridinium guests in dichloromethane.[3,14] Although a drop in the K_a value was observed with the 3*i* cavitand **7**, its high affinity for pyridinium guests is clearly demonstrated by the self-assembly of the pyridinium salt $\mathbf{8}^+I^-$ in forming the stable dimeric association $[\mathbf{8}^+I^-]_2$. Such dimeric associations have been observed with other cavitand hosts,[15] and they are mainly due to a favorable entropic factor.[16] The low solubility of the host−guest association has been a limiting factor to observe higher molecular weight species in solution. The organization of such supramolecular assemblies will be further investigated in the solid phase to obtain new insights into their structure, geometry, and properties.

Experimental Section

Materials. The synthesis of the phosphonate cavitands **2**, **3**, **5**−**9**, and $\mathbf{11}^+I^-$ are described in detail in the Supporting Information. Typical procedures for the preparation of $\mathbf{8}^+I^-$ from its precursors are described below. All compounds were fully characterized by ^1H, ^{13}C, and ^{31}P NMR and mass spectrometry (see the Supporting Information).

Cavitand 2. Pyridine (1 mL, 12.4 mmol) and dichlorophenylphosphine (0.73 mL, 5.38 mmol) were added dropwise to a suspension of **1** (1.99 g, 1.8 mmol) in toluene (160 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 45 min and then allowed to reach room temperature. Sulfur (0.252 g, 7.8 mmol) was then added and the solution was heated at reflux temperature for 6 h. The resulting mixture was filtered at room temperature and the filtrate was concentrated under vacuum to give a beige residue (2.96 g). Silica gel column chromatography (eluent CH_2Cl_2/ethyl acetate from 98:2 to 90:10) of the residue afforded the 3*i* compound **2** (0.671 mg, 0.44 mmol, 25%). LSIMS *m*/*z* obsd

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1541.7339 ([M + Na]$^+$, calcd 1541.7334 for $C_{90}H_{121}O_8P_3S_3$). ^{31}P NMR (81.02 MHz, 300 K, CD_2Cl_2) δ 75.7, 76.7. ^{1}H NMR ($CDCl_3$, 300 K, 700.13 MHz) δ 0.87 (m, 12H, CH_3), 1.26 (m, 64H, $CH_2-CH_2-(CH_2)_8-CH_3$), 1.34 (m, 2H, $CH_2-CH_2-(CH_2)_8-CH_3$), 1,43 (m, 4H, $CH_2-CH_2-(CH_2)_8-CH_3$), 1.47 (m, 2H, $CH_2-CH_2-(CH_2)_8-CH_3$), 2.19 (m, 2H, $CH_2-CH_2-(CH_2)_8-CH_3$), 2.27 (m, 2H, $CH_2-CH_2-(CH_2)_8-CH_3$), 2.34 (m, 4H, $CH_2-CH_2-(CH_2)_8-CH_3$), 4.37 (t, 1H, CH, J = 8.0 Hz), 4.67 (t, 1H, CH, J = 7.7 Hz), 4.72 (t, 2H, CH, J = 7.7 Hz), 6.48 (s, 2H, H_{1b}), 6.66 (s, 2H, H_{1a}), 7.18 (s, 2H, $H_{2b/a}$), 7.30 (s, 2H, $H_{2a/b}$), 7.50 (m, 6H, H_{4a} and H_{4b}), 7.57 (m, 3H, H_{5a} and H_{5b}), 8.12 (m, 2H, H_{3a}), 8.16 (m, 4H, H_{3b}).

Cavitand 3. *m*-Chloroperoxybenzoic acid (1.73 g, 10 mmol) was added to a solution of cavitand **2** (0.40 g, 0.26 mmol) in $CHCl_3$ (15 mL). The mixture was stirred at room temperature for 40 min. After evaporation of the solvent, the crude compound was purified by column chromatography on neutral alumina oxide (eluent CH_2Cl_2:ethanol 95:5 v/v) to give **3** as a white solid (0.286 g, 74%), mp >350 °C. LSIMS m/z obsd 1493.8017 ([M + Na]$^+$, calcd 1493.8019 for $C_{90}H_{121}O_{11}P_3$). ^{31}P NMR (CD_2Cl_2, 300 K, 80.02 MHz) δ 9.60 (2P), 10.12 (1P). ^{1}H NMR (CD_2Cl_2, 300 K, 200.13 MHz) δ 0.87 (m, 12H, $CH_2-(CH_2)_9-CH_3$), 1.27 (m, 72H, $CH_2-(CH_2)_9-CH_3$), 2.20 (m, 2H, $CH_2-(CH_2)_9-CH_3$), 2.24 (m, 6H, $CH_2-(CH_2)_9-CH_3$), 4.31 (t, 1H, CH, J = 7.4 Hz), 4.74 (m, 3H, CH), 6,62 (br s, 2H, H_{1b}), 6,89 (br s, 2H, H_{1a}), 7.19 (s, 2H, $H_{2a/b}$), 7.35 (s, 2H, $H_{2b/a}$), 7.59 (m, 9H, $H_{4a,b,5a,b}$), 8.07 (m, 6H, $H_{3a,b}$).

Cavitand 7. *N*-Methylpyrrolidine (0.009 mL, 8.6 × 10^{-3} mmol) and K_2CO_3 (0.018 g, 0.013 mmol) were added under argon to a solution of cavitand **3** (0.126 g, 0.086 mmol) in DMF (12 mL). The mixture was heated to 75 °C and reagent **4** (0.031 g, 9.5 10^{-3} mmol) was then added. The reaction mixture was heated at 75 °C for 2 days and then poured into ethyl acetate (60 mL) at room temperature. The solution was extracted with water (10 × 10 mL), dried over Na_2SO_4, and evaporated to dryness under vacuum to give a brown residue. Silica gel column chromatography (eluent CH_2Cl_2/THF from 10:1 to 2:1) afforded cavitand **7** (0.058 g, 41% yield). LSIMS m/z obsd 1636.8769 ([M + H]$^+$, calcd 1636.8779 for $C_{102}H_{128}NO_{11}P_3$). ^{31}P NMR (CD_2Cl_2, 300 K, 81.02 MHz) δ 9.40 (2P), 10.28 (1P). ^{1}H NMR (CD_2Cl_2, 297 K, 497.81 MHz) δ 0.88 (m, 12H, $CH_2-(CH_2)_9-CH_3$), 1.28 (m, 64H, $CH_2-CH_2-(CH_2)_8-CH_3$), 1.48 (m, 8H, $CH_2-CH_2-(CH_2)_8-CH_3$), 2.37 (m, 8H, $CH_2-CH_2-(CH_2)_8-CH_3$), 4.76 (br t, 1H, CH_a, J = 8.2 Hz), 4.85 (br t, 2H, CH_b, J = 8.1 Hz), 4.93 (br t, 1H, CH_c, J = 8.1 Hz), 5.89 (s, 1H, CH), 6,88 (br s, 4H, $H_{1a,b}$), 7.31 (br s, 4H, $H_{2a,b}$), 7.54 (d, 2H, H_8), 7.58 (m, 6H, $H_{4a,b}$), 7.70 (m, 3H, $H_{5a,b}$), 7.71 (d, 2H, $H_{6/7}$), 7.81 (d, 2H, $H_{7/6}$, J = 8.2 Hz), 8.09 (m, 6H, $H_{3a,b}$), 8.62 (m, 2H, H_9).

Cavitand 8$^+$I$^-$. Iodomethane (38 10^{-3} mL, 0.6 mmol) are added to a solution of cavitand **7** (53 mg, 32.5 × 10^{-3} mmol) in CH_2Cl_2 (7.6 mL). The reaction mixture was stirred at room temperature for 3 days and then evaporated to dryness. The resulting compound is dissolved in diethyl ether (2 mL) and the precipitate that forms is filtered to give **8**$^+$I$^-$ quantitatively. MS ESI m/z 1651.90 ([M + H]$_2^{2+}$, $C_{103}H_{131}NO_{11}P_3$). ^{31}P NMR (CD_2Cl_2, 300 K, 81.02 MHz) δ 11.86 (1 P), 12.18 (2 P). ^{1}H NMR ($CDCl_3$, 297 K, 497.81 MHz) δ 0.85 (m, 12H, $CH_2-(CH_2)_9-CH_3$), 1.25 (m, 64H, $CH_2-CH_2-(CH_2)_8-CH_3$), 1.48 (m, 8H, $CH_2-CH_2-(CH_2)_8-CH_3$), 1.80 (s, 3H, N^+CH_3), 2.29 (m, 2H, $CH_2-CH_2-(CH_2)_8-CH_3$), 2.38 (m, 2H, $CH_2-CH_2-(CH_2)_8-CH_3$), 2.46 (m, 4H, $CH_2-CH_2-(CH_2)_8-CH_3$), 3.49 (s, 1H, CH), 4.73 (m, 2H, C$\underline{H}_{a,c}$), 4.91 (m, 2H, C$\underline{H}_b$), 6.95 (s, 2H, $H_{1a/b}$), 7.45 (m, 6H, $H_{1b/a}$, $H_{2a/b}$), 7.50 (m, 2H, H_{4a}), 7.63 (m, 5H, H_{4b}, H_{5a}), 7.70 (m, 2H, H_{5b}), 7.85 (d, 2H, H_6, $^3J_{HH}$ = 8.0 Hz), 7.95 (m, 6H, H_7, H_{3a}), 8.33 (m, 6H, H_{3b}, H_8), 9.12 (d, 2H, H_9, $^3J_{HH}$ = 6.5 Hz).

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Supporting Information Available: Experimental procedures; full experimental details for the synthesis and characterization of compounds **2**, **3**, **5**−**7**, **8**$^+$I$^-$, **11**$^+$I$^-$; ^{1}H NMR spectra and mass spectra; DOSY NMR; fluorescence and UV/vis titrations; and figures of the crystal structure. This material is available free of charge via the Internet at http://pubs.acs.org. Supplementary X-ray crystallographic data for **11**$^+$I$^-$ have been deposited at the Cambridge Crystallographic Data Center as CCDC-707966 and can be obtained free of charge via www.ccdc.cam.ak.uk/conts/retrieving.html or on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax +44-1233-336-033; E-mail data_request@ccdc.cam.ac.uk), on quoting the deposition number.

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