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A New Functional Bis(*m*-phenylene)-32-crown-10-Based Cryptand Host for Paraquats

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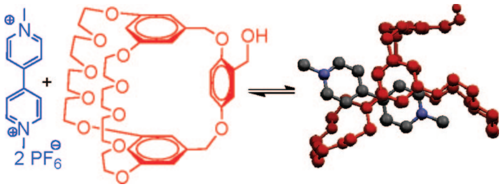
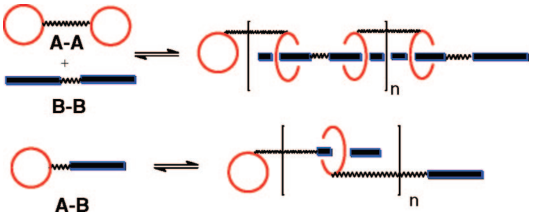


The pseudorotaxane complex of the new hydroxymethyl cryptand **3** with *N,N′*-dimethyl-4,4′-bipyridinium bis(hexafluorophosphate), $PQ(PF_6)_2$, has an association constant of $2.0(\pm0.3) \times 10^4$ M^{-1}. In the crystal structure of $\mathbf{3}\cdot PQ(PF_6)_2$ one of the bonding elements appears to be an aromatic edge-to-face interaction of a paraquat β-proton with the hydroquinone moiety; this is the first time this interaction has been reported between a cryptand and paraquat.

Crown ether-based supramolecular assemblies[1] are of great interest for many different applications.[2] We have shown that supramolecular oligomers can be synthesized from suitable building blocks containing crown ether hosts and ammonium or paraquat (*N,N′*-dialkyl-4,4′-bipyridinium) guests.[3] Crown ethers allow selective guest binding and do not exhibit self-association, which makes the synthesis of supramolecular polymers possible (Scheme 1); however, improved association constants, good solubility, and reactive functional groups are needed to afford truly polymeric supramolecular materials with degrees of polymerization, *n*, greater than or equal to 100.[3c,f,4,5] To this end we have pursued more strongly associating hosts for paraquats by incorporation of additional binding sites and preorganization of the hosts in the form of cryptands.[6] We had previously made cryptand **1**[6e] and showed that it binds *N,N′*-dimethyl-4,4′-bipyridinium bis(hexafluorophosphate), $PQ(PF_6)_2$, with an association constant (K_a) of $2.2(\pm0.2) \times 10^4$ M^{-1} in acetone-d_6 at 22 °C, but were unable to obtain a well-refined crystal structure of the complex. In the present work we prepared the functional derivative **3** (Scheme 2), studied its complexation with $PQ(PF_6)_2$, and obtained an informative crystal structure of the complex $\mathbf{3}\cdot PQ(PF_6)_2$.

SCHEME 1. A−A + B−B and A−B Building Blocks for Supramolecular Polymers



Reaction of the known bis(5-bromomethyl-1,3-phenylene)-32-crown-10[7] with 2-carbomethoxyhydroquinone under pseudo-

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(5) Since for exact 1:1 stoichiometry of A and B units, assuming that no cyclic species form, $n = [A]_c/[A]_u$ and $K_a = [A]_c/[A]_u[B]_u = [A]_c/[A]_u^2$, and thus $n = K_a[A]_u$; the subscripts 'c' and 'u' refer to complexed and uncomplexed species, respectively. Therefore, the *minimal* conditions required to produce $n = 100$ can be calculated as follows in terms of $[A]_c + [A]_u$ and K_a: 10.1 M, 10^3 M^{-1}; 1.01 M, 10^4 M^{-1}; 101 mM, 10^5 M^{-1}; 10.1 mM, 10^6 M^{-1}; 1.01 mM, 10^7 M^{-1}; 0.101 mM, 10^8 M^{-1}. In reality at lower concentrations the proportion of cyclization, primarily to the unimer, is increased and significantly lowers the actual *n* value of the linear species.[3c,f]

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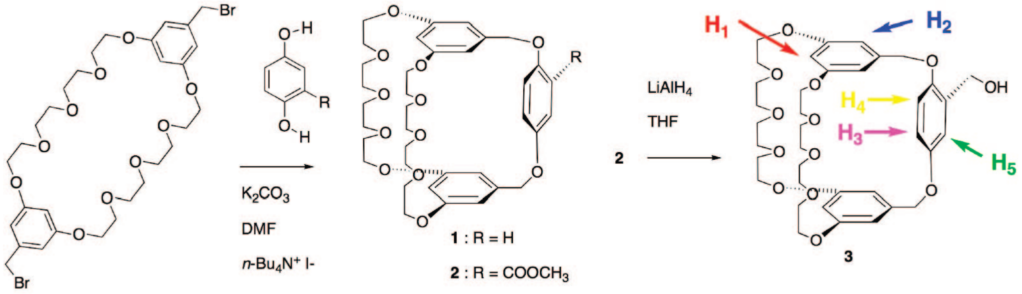
SCHEME 2. Synthesis of the Functionalized Host 3 from 2



high dilution conditions yielded cryptand **2** in 55% yield. Reduction of the ester moiety of **2** with lithium aluminum hydride produced the corresponding cryptand **3** in 90% yield.

The partial ^{1}H NMR spectra of **3**, a 1:1 mixture of **3** and $PQ(PF_6)_2$, a 1:60 mixture of **3** and $PQ(PF_6)_2$, and $PQ(PF_6)_2$, respectively, in acetone-d_6 at 23 °C are shown in Figure 1; parts b and c of Figure 1 show a single set of peaks for the constituents, **3** and $PQ(PF_6)_2$, indicating fast-exchange complexation. The aromatic proton (H_1 and H_2) signals of the cryptand were strongly shifted upfield upon complexation (Figure 1b and Figure 1c vs Figure 1d), while the signals for phenylene protons H_3, H_4, and H_5 of host **3** at 6.43, 6.53, and 7.01 ppm were shifted strongly downfield in the complex. The NMR signal of H_2 is split during complexation; this is either due to hindrance of the phenylene ring flipping[8] or because of asymmetry in the complex, which would induce drastically different chemical environments for the H_2 of each of the *m*-phenylene moieties (see the crystal structure below). All of the $PQ(PF_6)_2$ signals were shifted upfield upon complexation (Figure 1b vs Figure 1a). The Job plot[9] (Figure 2) shows the 1:1 stoichiometry of the complex $\mathbf{3}\cdot PQ(PF_6)_2$. The Δ_o value for the complex was estimated to be 0.70 ppm by measuring the peak position of H_1 in the presence of 30-, 50-, and 60-fold excess of $PQ(PF_6)_2$ and extrapolating to infinite guest concentration in a plot of $[\mathbf{3}]\Delta$, where Δ is the chemical shift change from the cryptand itself, vs the inverse of guest concentration ($1/[PQ(PF_6)_2]$). From the ^{1}H NMR data for H_1 the association constant $\{K_a = \Delta/\Delta_o/[1 - (\Delta/\Delta_o)]^2[PQ(PF_6)_2]_o\}$ was estimated to be $2.2(\pm0.2) \times 10^4$ M^{-1} in acetone-d_6 at 23 °C. This value is identical with that for the analogous unsubstituted cryptand complex $\mathbf{1}\cdot PQ(PF_6)_2$ determined previously under the same conditions.[6e]

Isothermal titration calorimetric (ITC) experiments were performed in acetone at 25 °C. Analysis of the data provided $K_a = 1.7(\pm0.1) \times 10^4$ M^{-1} and $\Delta H = -8.5(\pm0.1)$ kcal/mol.

The 1:1 nature of the complex was confirmed by Fast Atom Bombardment Mass Spectrometry (FAB-MS), using an acetone solution of **3** and $PQ(PF_6)_2$. One peak for the uncomplexed guest and three peaks for the complex $\mathbf{3}\cdot PQ(PF_6)_2$ were observed: *m/z* 331.61 (100%) $[PQ(PF_6)]^+$, 1031.4 (13%) $[\mathbf{3}\cdot PQ(PF_6]^+$, 1032.4 (8%) $[\mathbf{3}\cdot PQ(PF_6) + 1]^+$, and 1033.4 (4%) $[\mathbf{3}\cdot PQ(PF_6) + 2]^+$.

The solid state structure of inclusion complex $\mathbf{3}\cdot PQ(PF_6)_2$ was determined by X-ray crystallography.[10] The crystal structure (Figure 3) shows that the four H_α protons of the paraquat guest are unbound in the solid state. The π-stacking[15,16] of the electron-rich aromatic rings of cryptand **3** with one of the electron-poor aromatic rings of the paraquat, as evidenced by the yellow color of the crystals and solutions of the two components, is confirmed by the parallel nature (inclination angles less than 6.4°) of the aromatic rings and their spacings (3.262 and 3.432 Å, respectively). Three oxygen atoms of an ethyleneoxy arm of the host simultaneously bind two methyl protons of the guest; one H_β of the paraquat interacts with an oxygen atom of the other ethyleneoxy arm. In accord with this structure, NOE experiments verify the through space interactions of the H_α and H_β protons with the aromatic and ethyleneoxy protons of the host in the solution phase complex. We interpret the close contact between a H_β and the aromatic π-cloud of the hydroquinone moiety of host **3** as an edge-to-face interaction.[16,17] We were unable to obtain a high-quality crystal of the parent complex $\mathbf{1}\cdot PQ(PF_6)_2$ in our earlier work,[6e] although the same $C-H\cdots\pi$ interaction probably exists in that complex as well and its K_a value is the same as that of $\mathbf{3}\cdot PQ(PF_6)_2$. However,

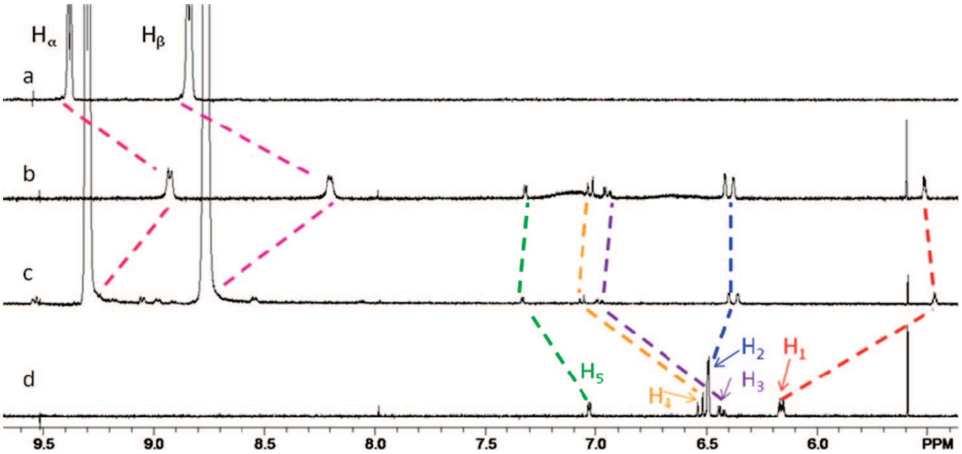


FIGURE 1. Partial ^{1}H NMR spectra (400 MHz, acetone-d_6, 23 °C) of (a) $PQ(PF_6)_2$, (b) 1.00 mM **3** and 1.00 mM $PQ(PF_6)_2$, (c) 1.00 mM **3** and 60.0 mM $PQ(PF_6)_2$, and (d) **3**.

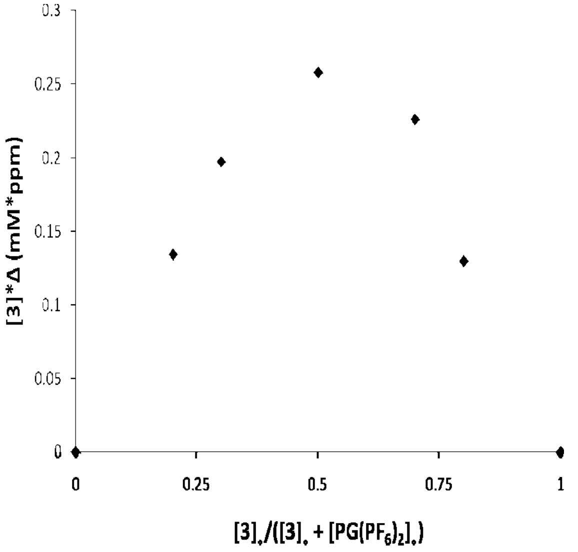


FIGURE 2. The Job plot of $3\cdot PQ(PF_6)_2$ in acetone-d_6; the total concentration $[3]_o + [PQ(PF_6)_2]_o$ was maintained at 1.00 mM. The Δ value is for proton H_1 of cryptand **3**.

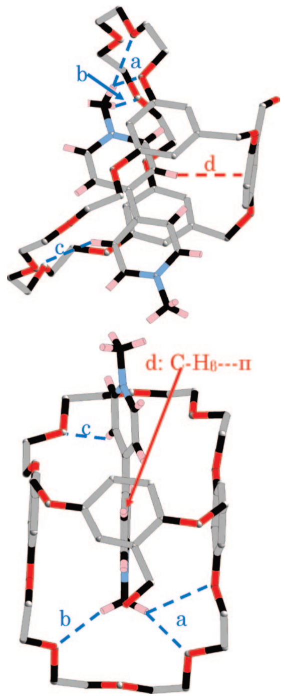
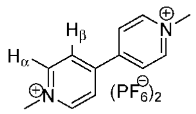
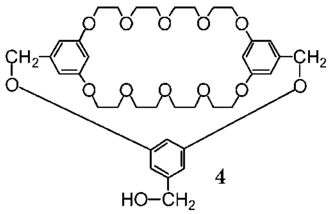


FIGURE 3. The crystal structure of $3\cdot PQ(PF_6)_2$ in top and side views. Solvent molecules and counterions were omitted. Hydrogen bonds a−c are defined by H···O distances (Å) and C−H···O angles (deg): a (bifurcated CH_3−O), 2.365, 162.3 and 2.895, 120.0; b, 2.396, 169.3; and c, 2.501, 147.6. The C−H−π edge-to-face interaction d is defined by an H···hydroquinone centroid distance of 2.905 Å and a C−H···centroid angle of 163.0°. The cryptand OH group is hydrogen bonded to an ethyleneoxy O of a neighboring molecule of **3** with an H···O distance of 2.220 Å and an O−H···O angle of 149°. The *exo*-paraquat methyl group interacts with a trapped acetone molecule. The centroid-to-centroid distance between the phenyl rings of **3** is 6.697 Å and the angle between these rings is 4.2°. The interplanar distances between the aromatic rings of the host and the *endo*-pyridinium ring are 3.262 and 3.432 Å, respectively.

in the isomeric complex $4\cdot PQ(PF_6)_2$ such an interaction was not observed; in that system the resorcinol ring was turned at an oblique angle to the paraquat ring and, presumably as a result, its K_a was lowered to 6.3×10^3 M^{-1}.[6e] Thus, $3\cdot PQ(PF_6)_2$ appears to exhibit the first edge-to-face hydrogen-bond interaction reported for a crown ether-based cryptand complex with a paraquat. If we assume that the difference in association constants between $3\cdot PQ(PF_6)_2$ and $4\cdot PQ(PF_6)_2$ is due to the C−H---π bonding in the former, it accounts for 0.77 kcal/mol or 3.2 kJ/mol toward the binding energy at room temperature. This value is in accord with other estimates[17] for this sort of intermolecular attractive force.



$PQ(PF_6)_2$



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In summary, a functionalized host, **3**, has been synthesized. It complexes $PQ(PF_6)_2$ in a 1:1 fashion as demonstrated by ^1H NMR, ITC, FAB-MS, and X-ray crystallographic studies. Due to its relatively good association constant, solubility, and functionality host **3** will allow us to synthesize building blocks for supramolecular polymers.

Experimental Section

Synthesis of Cryptand 2. Solutions of bis(5-bromomethyl-1,3-phenylene)-32-crown-10 (3.60 g, 5.00 mmol) and methyl 2,5-dihydroxbenzoate (840 mg, 5.00 mmol) in DMF (40 mL) were added via a syringe pump at 1.00 mL/h into a suspension containing

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(8) As pointed out by a reviewer.

(9) Job, P. *Ann. Chim.* **1928**, *9*, 113-2-3.

(10) A yellow prism, (0.087 × 0.088 × 0.11 mm^3), $C_{52}H_{68}F_{12}N_2O_{13}P_2$, FW = 1235.03, crystallized from acetone solution by pentane vapor diffusion at room temperature, was centered on the goniometer of an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire 2 CCD detector and operating with Mo radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.[11] The Laue symmetry was consistent with the triclinic space group $P\bar{1}$; $a = 12.466(2)$ Å, $b = 13.0591(13)$ Å, $c = 19.538(3)$ Å, $\alpha = 83.485(10)°$, $\beta = 81.194(14)°$, $\gamma = 61.214(14)°$, $V = 2751.9(8)$ $Å^3$, $Z = 2$, $D_c = 1.490$ g cm^{-3}, $T = 100$ K, $\mu = 0.187$ mm^{-1}, 9612 unique reflections $R_1 = 0.0672$, $wR_2 = 0.1892$, GOF = 0.8570. Structure solution and refinement were performed with the graphical user interface WinGX.[12] The structure was solved by direct methods using SHELXS-86[12,13] and refined using SHELXL-97.[14] The asymmetric unit of the structure comprises one crystallographically independent $3\cdot PQ(PF_6)_2$ and one acetone solvate. The final refinement model involved anisotropic displacement parameters for all non-hydrogen atoms and a riding model for all hydrogen atoms. Molecular graphics were generated with the program Crystalmaker.

(11) *CrysAlisPro*, v171.32.5; Oxford Diffraction: Wroclaw, Poland, 2007.

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potassium carbonate (32.0 g, 230 mmol) and tetrabutylammonium iodide (20.0 mg) in DMF (1.5 L) at 110 °C. After complete addition, the reaction mixture was stirred at 110 °C for 5 days. The solvent was removed by rotary evaporation. The residue was treated with chloroform and filtered. Removal of the chloroform afforded the crude product, which was purified by flash column chromatography, eluting with ethyl acetate to afford the cryptand **2** as a white solid: 2.0 g (55%) yield, mp 102.6−104.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C) δ 7.40 (1H, d, $J_3 = 3$ Hz), 6.60 (1H, dd, $J_3 = 3$ and $J_2 = 9$ Hz), 6.53 (3H, m), 6.47 (2H, m), 6.38 (2H, m), 5.13 (2H, s), 5.02 (2H, s), 4.03 (8H, m), 3.94 (3H, s), 3.78 (8H, m), 3.64 (8H, m). LR FAB MS (NBA) *m*/*z* 723.44 (30%) [**2** + K − CO_2]$^+$, 728.30 (50%) [**2**]$^+$, 729.31 (100%) [**2** + H]$^+$, 730.30 (35%) [**2** + H + 1]$^+$, 731.30 (10%) [**2** + H + 2]$^+$, 767.46 (15%) [**2** + K]$^+$, 768.48 (5%) [**2** + K + 1]$^+$. HR FAB MS (NBA/PEG) *m*/*z* calcd for [**2** + H]$^+$ $C_{38}H_{49}O_{14}$ 729.312, found 729.313, error 1.2 ppm.

Synthesis of Cryptand 3. $LiAlH_4$ (0.070 g, 1.8 mmol) was added in five portions over 1 h to a solution of **2** (1.0 g, 1.4 mmol) in THF (25 mL, distilled from Na and benzophenone) under N_2. The mixture was stirred for 12 h and worked up by using the Fieser and Fieser method.[18] The crude product was purified by alumina column chromatography, eluting with chloroform, yielding 0.86 g (90%) of colorless solid: mp 79.7−83.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C) δ 6.94 (1H, d, $J_3 = 3$ Hz), 6.48 (4H, dd, $J_3 = 3$ and $J_2 = 8$ Hz), 6.42 (3H, m), 5.07 (2H, s), 5.01 (2H, s), 4.73 (2H, d, $J_2 = 7$ Hz), 4.03 (8H, m), 3.78 (8H, m), 3.64 (16H, m), 2.61 (1H, t, $J_2 = 7$ Hz). LR FAB MS (NBA) *m*/*z* 392 (26%), 492 (9%), 562.7 (10%), 563.7 (26%) [**3** + H − $C_7H_6O_3$]$^+$, 564.7 (8%), 565.7 (1%), 682.9 (8%), 683.9 (8%), 684.9 (100%) [**3** + H − OH]$^+$, 685.9 (11%), 686.9 (5%), 687.9 (1%), 700.9 (5%) [**3**]$^+$, 701.9 (30%) [**3** + H]$^+$, 702.9 (12%), 703.9 (3%). HR FAB MS (NBA/PEG) calcd for [**3**]$^+$ $C_{37}H_{48}O_{13}$ 700.3095, found 700.3073, error 3.1 ppm.

FAB MS Determination of the Complex 3·PQ(PF_6)$_2$. LR FAB MS (NBA) *m*/*z* 331.61 (100%) [PQ(PF_6)]$^+$, 685 (8%) [**3**-OH]$^+$, 701 (4%) [**3**]$^+$, 1031.39 (13%) [**3**•PQ(PF_6)]$^+$, 1032.4 (8%) [**3**·PQ(PF_6) + 1]$^+$, 1033.4 (4%) [**3**·PQ(PF_6) + 2]$^+$. The theoretical abundance ratios for [**3**·PQ(PF_6)]$^+$, [**3**·PQ(PF_6) + 1]$^+$, and [**3**·PQ(PF_6) + 2]$^+$ are 13%, 7.4%, and 2.4%, respectively. HR FAB MS (NBA/PEG) calcd for [**3**·PQ(PF_6)]$^+$ $C_{51}H_{66}O_{15}N_2PF_6$ 1031.3888, found 1031.3903, error 0.8 ppm.

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Note Added after ASAP Publication. In the paragraph describing the solid state structure of inclusion complex 3·PQ(PF_6)$_2$, there was a change in the explanation of the through space proton interactions in the solution phase complex. The corrected version was published on June 17, 2008. Additionally, due to a production error a new version of Scheme 2 and changes to footnote 5 were published on June 26, 2008.

Supporting Information Available: Experimental details and characterizations for compounds **2** and **3**, MS, NMR, ITC, 1D NOESY, and X-ray diffraction data of the complex **3**·PQ(PF_6)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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