The First [2]Pseudorotaxane and the First Pseudocryptand-Type Poly[2]pseudorotaxane Based on Bis(*meta*-phenylene)-32-Crown-10 and Paraquat Derivatives
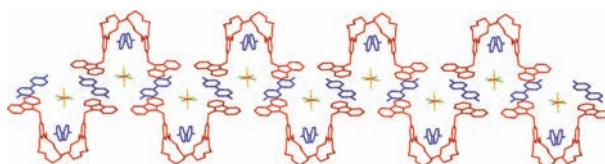
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ABSTRACT

By the self-assembly of a bis(*meta*-phenylene)-32-crown-10 bearing two electron-donating groups (carbazoles) with electron-accepting paraquat derivatives, the first [2]pseudorotaxane and the first pseudocryptand-type poly[2]pseudorotaxane based on bis(*meta*-phenylene)-32-crown-10 were isolated as crystalline solids as shown by X-ray analyses.

Pseudorotaxanes, which consist of a linear molecular component ("guest") encircled by a macrocyclic component ("host"), have been a topic of great interest and widely studied all over the world,[1] since pseudorotaxanes are the fundamental building blocks for preparation of advanced supramolecular species, such as rotaxanes, catenanes, polyrotaxanes, polypseudorotaxanes, and polycatenanes[2] with unique properties and potential applications.[1,2] Paraquat (*N*,*N*′-dialkyl-4,4′-bipyridinium) derivatives and crown

ethers have been widely employed in the construction of pseudorotaxanes.[3] Our group first demonstrated that the complexes between bis(*meta*-phenylene)-32-crown-10 (BMP32C10) (**1a**) and its diol (**1b**) and paraquat derivatives, instead of forming pseudorotaxanes, were folded into "taco" shapes (Scheme 1), as proven by their X-ray crystal structures.[4] Although it was thought that the pseudorotaxane conformation probably coexisted in solution and indirect evidence was reported,[5] nearly a quarter of a century after the first report of a BMP32C10-paraquat complex,[6] only "taco"-shaped solid state complexes have

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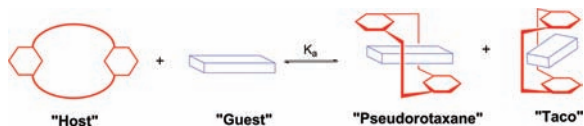
been reported.[3a,4,5,7] Here, we report the first [2]pseudorotaxane based on a BMP32C10 derivative and a paraquat derivative. Interestingly, the first pseudocryptand-type poly[2]pseudorotaxane supramolecular polymer also formed in the solid state.
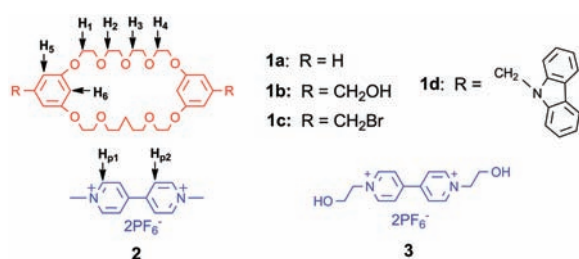

Figure 1. Structures of BMP32C10 derivatives **1a**–**d** and paraquat derivatives **2** and **3**.

Bis[5-(*N*-carbazylmethyl)-1,3-phenylene]-32-crown-10 (**1d**) (Figure 1) was prepared via the reaction between BMP32C10 dibromide (**1c**)[8] and the anion of carbazole. Solutions of **1d** and **2** in CDCl$_3$/CD$_3$CN = 1/1 < v/v >

were yellow due to the charge-transfer interaction between the electron-rich aromatic rings of **1d** and the electron-poor pyridinium rings of bisparaquat **2**, evidence for complexation. ^{1}H NMR spectra of equimolar solutions of host **1d** and guest **2** displayed only one set of peaks, indicating fast exchange (Figure 2). After complexation, peaks corresponding to H$_1$, H$_5$, and H$_6$ of **1d** and H$_{p1}$, H$_{p2}$ of **2** moved upfield, while H$_2$ and H$_3$ of **1d** moved downfield. A Job plot[9] (see Supporting Information (SI), Figure S4) based on proton NMR data demonstrated that the stoichiometry between **1d** and **2** in CDCl$_3$/CD$_3$CN = 1/1 < v/v > was 1:1, which was confirmed by High-resolution Electrospray Ionization Mass Spectrometry (HRESI-MS): *m/z* 1225.49 [**1d·2**-PF$_6$]$^+$. The association constants (K_a)[10] between **1d** and **2** and **3**[12] were determined as 440 ± 40 and 214 ± 30 M^{-1}, respectively. The K_a of **1d·2** is higher than the K_a of **1d·3**, as usually observed with these two paraquat derivatives.[13]
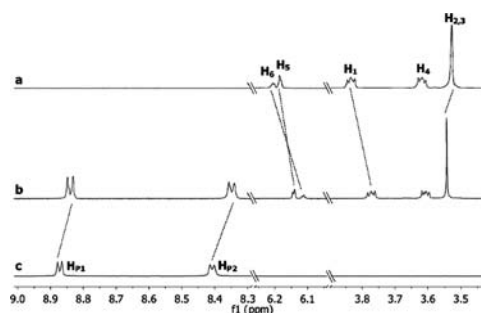

Figure 2. Partial proton NMR spectra (400 MHz, CDCl$_3$/CD$_3$CN = 1/1 < v/v >, 25 °C) of (a) 1.00 mM **1d**; (b) **1d** and **2** (1/3, mol/mol, [**1d**] + [**2**] = 1.00 mM); and (c) 1.00 mM **2**.

The X-ray analysis of a single crystal, in a form of a colorless plate, which was grown by vapor diffusion of pentane into an acetone solution of **1d**, revealed that this crown ether assumes a deformed two-stair-step structure (Figure 3a, 3b). The two phenylene rings and the two

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(10) ^{1}H NMR characterizations were done on solutions with constant [**1d**] and varied [**2**] or [**3**]. Based on these NMR data, Δ_0, the difference in δ values for protons of **1d** in the uncomplexed and fully complexed species was determined as the *y*-intercept of a plot of $\Delta = \delta - \delta_u$ vs **1d**/[**2**]$_0$ or **1d**/[**3**]$_0$ in the high initial concentration range of **2** or **3**: $\Delta_0 = 0.294$ ppm for **1d·2** and $\Delta_0 = 0.236$ ppm for **1d·3** based on H$_6$. K_a was calculated from $K_a = (\Delta/\Delta_0)/[(1 - \Delta/\Delta_0)([\mathbf{2}]_0 - \Delta/\Delta_0[\mathbf{1d}]_0)$ or its analog with [**3**]. It was found that for these systems K_a does not have the concentration dependence we found in two other systems.[5a,11]

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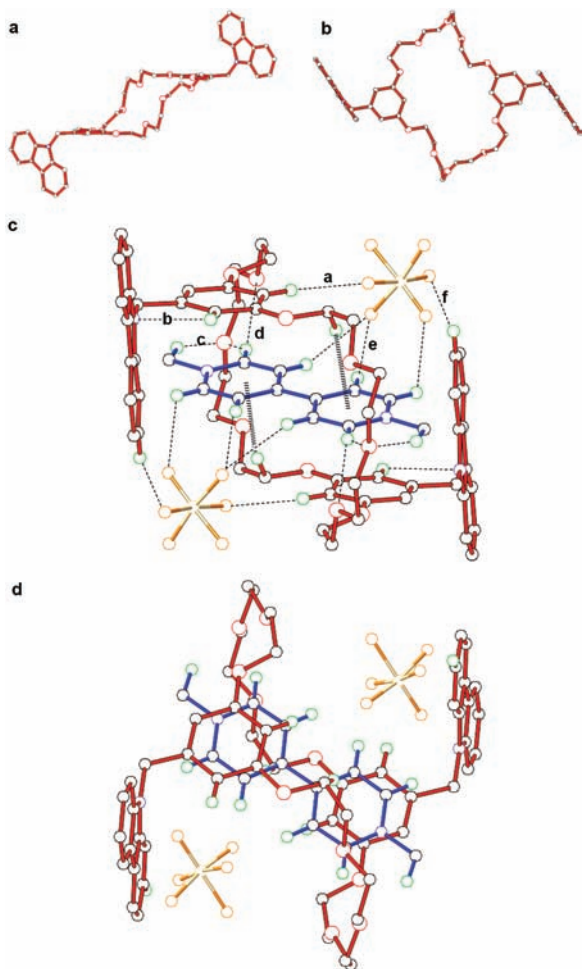
Figure 3. (**a** and **b**) Two views of the X-ray structure of **1d**. (**c** and **d**) Two views of the X-ray structure of **1d·2**. **1d** is red. **2** is blue. Oxygen atoms are red. Carbon atoms are black. Nitrogen atoms are blue. Hydrogen atoms are green. Fluorine atoms are yellow. Phosphorus atoms are brown. Dashed and hashed lines represent hydrogen bonds and CH$_2$−π interactions, respectively. The same motif is used in the following crystal structures. Solvent molecules, minor disordered carbon and hydrogen atoms, and hydrogen atoms except the ones involved in hydrogen bonding have been omitted for clarity. Hydrogen bonds in (**d**) were omitted for clarity. Selected hydrogen-bond parameters: H···O(N, F) distances (Å), C···O(N, F) distances (Å), C−H···O(N, F) angles (deg): a 2.631, 3.569, 175.6; b 2.482, 2.828, 101.4; c 2.446, 3.334, 150.6; d 2.389, 3.086, 129.9; e 2.320, 3.110, 140.2; f 2.337, 3.258, 130.8. CH$_2$−π interaction parameters: H to the centroid distance (Å): 2.799. C−H−centroid angle (deg): 152.7; face-to-face π-stacking parameters: centroid−centroid distances (Å) and dihedral angles (deg): carbazole rings and pyridinium rings: 3.808 and 9.07.

carbazole rings are parallel to each other, respectively, but as far apart as possible by extension in opposite directions,

while the phenylene and carbazole rings are almost perpendicular to each other (torsion angle = 88.5°).

However, two kinds of single crystals were obtained via the vapor diffusion of pentane into an equimolar acetone solution of **1d** and **2**: yellow rods and red rods. When a solution of **1d** and **2** in a 2:1 ratio (mol/mol) was used, the yellow rods dominated. In contrast, the red rods dominated from a solution of **1d** and **2** in a 1:2 ratio (mol/mol). X-ray analysis of a yellow rod demonstrated that the [2]pseudorotaxane structure indeed formed between **1d** and **2** (Figure 3c, 3d). In the complex **1d·2**, crown ether **1d** assumes a "zig-zig" shape. The two carbazole rings and the two phenylene rings are almost parallel to each other, respectively (torsion angle = 1.90° and 0°, respectively), while the carbazole end groups remain almost perpendicular to the phenylene rings (torsion angle = 82.9°) due to hydrogen bonds between two phenylene protons and the nitrogen atoms of the carbazole groups. The paraquat salt **2** is clearly threaded through the central cavity of host **1d**, and the resulting [2]pseudorotaxane **1d·2** complex is stabilized by hydrogen bonds, CH$_2$−π interactions[14] between **1d** and **2**, and offset π-stacking[15] between the electron-rich phenylene rings of host **1d** and the electron-poor pyridinium rings of guest **2**. This represents the first direct observation of a pseudorotaxane structure derived from a BMP32C10 derivative with a paraquat.

Interestingly, X-ray analysis of a red rod showed that one molecule of host **1d** binds two molecules of guest **2**, forming a linear pseudocryptand-type[16,17] poly[2]pseudorotaxane-poly-(**1d·2$_2$**) in the solid state (Figure 4). Similar to the other reported BMP32C10 derivatives,[3a,4,5,7] in the supramolecular polymer **1d** is folded into a "taco"-shaped structure. One paraquat molecule threads through the folded crown ether in "taco" fashion, stabilized by offset face-to-face π-stacking interactions between the aromatic rings of host **1d** and the pyridinium rings of guest **2** and hydrogen bonds between **1d** and **2**. The central PF$_6^-$ ion acts as a hydrogen bonding bridge, interacting with both host **1d** and guest **2** to close another ring, forming a pseudocryptand.[16,17] Another electron-poor paraquat molecule lies parallel and between the electron-rich carbazole rings in a face-to-face manner,[18] π-stacking (centroid-centroid distances between carbazole rings and pyridinium rings are 3.427 and 3.406 Å) and forming a "sandwich" structure which is also stabilized by the hydrogen bonds between the host, guest, and the central PF$_6^-$ ion.

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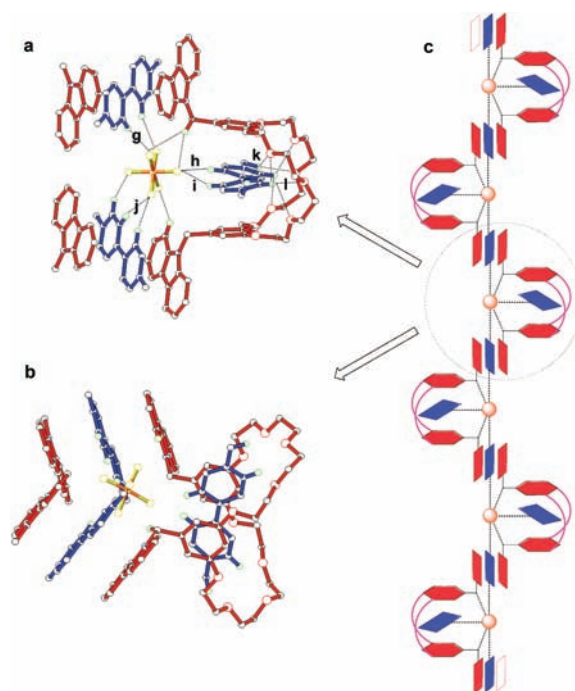(18) Yonemura, H.; Kasahara, M.; Saito, H.; Nakamura, H.; Matsuo, T. *J. Phy. Chem.* **1992**, *96*, 5765.

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Figure 4. (**a** and **b**) Two views of the X-ray structure of poly-(**1d·2₂**). **1d** is red. **2** is blue. Solvent molecules, five PF_6^- ions, and hydrogen atoms except the ones involved in hydrogen bonding have been omitted for clarity. The major disordered PF_6^- was chosen to show the hydrogen bonds. Hydrogen bonds in (**b**) were omitted for clarity. Selected hydrogen-bond parameters: $H \cdots O(F)$ distances (Å), $C \cdots O(F)$ distances (Å), $C-H \cdots O(F)$ angles (deg): g 2.265, 3.083, 143.8; h 2.423, 3.366, 172.5; I 2.433, 3.318, 155.0; j 2.409, 3.339, 166.5; k 2.438, 3.282, 144.1; l 2.432, 3.392, 166.76. Offset face-to-face π-stacking parameters: centroid-centroid distances (Å) and dihedral angles (deg.): carbazole rings and pyridinium rings: 3.427, 3.406 and 1.35, 0.60; aromatic rings of **1d** and pyridinium rings of paraquat **2**: 3.982, 3.902 and 6.54, 7.59. (**c**) Cartoon representation of the supramolecular structure.

As a result, a pseudocryptand-type poly[2]pseudorotaxane was formed, in effect because the second paraquat (**2**) acts as glue to hold the carbazole units of adjoining pseudocryptand units together in an extended chain, assisted by interactions with the counterion. To the best of our knowledge, this is the first pseudocryptand-type polypseudorotaxane to be reported.

Similarly, two kinds of crystals—yellow plates and red diamonds—resulted from diffusion of pentane into acetone solutions of host **1d** and a paraquat diol (**3**). However, due to the low quality of the red diamonds, only the crystal structure of a yellow plate was obtained (see SI, Figure S9); in the complex of **1d·3** a "taco"-shaped complex was formed, which is similar to the other reported complexes between BMP32C10 derivatives and paraquat derivatives.[3a,4,5,7] The complex **1d·3** is stabilized by offset face-to-face π-stacking interactions between the aromatic rings of host **1d** and the pyridinium rings of guest **3** and hydrogen bonds between **1d** and **3**. The hydrogen bonds between the ethylene protons of guest **3** and oxygen atoms of host **1d** possibly favor the formation of the "taco"-shaped complex over the pseudorotaxane. Based on the

results with **1d·2₂**, the red diamonds are thought possibly to be the supramolecular polymeric analog **1d·3₂**.

In summary, we demonstrated the first [2]pseudorotaxane and the first solid state[19] pseudocryptand-type poly[2]pseudorotaxane based on a BMP32C10 derivative and a paraquat derivative by X-ray analysis. Interestingly, the formation of the [2]pseudorotaxane vs the poly[2]pseudorotaxane was dependent on the ratio between the dicarbazyl BMP32C10 derivative **1d** and the paraquat. These results represent the first direct confirmation of the existence of pseudorotaxane structures in complexes between BMP32C10 derivatives and paraquat derivatives. Our present efforts are focused on using similar structures to prepare novel supramolecular polymers in solution, for example, complexation with polymers containing backbone paraquat moieties[20] to form three-dimensional networks. Likewise we expect interesting solid state structures to result from the interaction of host **1d** with polymers bearing paraquat end groups.[21]

Supporting Information Available. Synthesis of **1d**, Job plot between **1d** and **2**, ESI-MS of **1d·2**, **1d·3**, crystal structure of **1d·3**, and CIF files of **1d**, **1d·2**, **1d·2₂**, **1d·3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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