

# Pseudocryptand-Type [3]Pseudorotaxane and “Hook-Ring” Polypseudo[2]catenane Based on a Bis(*m*-phenylene)-32-crown-10 Derivative and Bisparaquat Derivatives

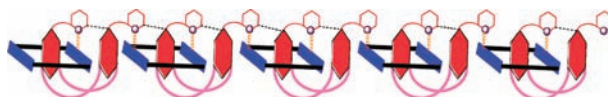
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## ABSTRACT



The first pseudocryptand-type supramolecular [3]pseudorotaxane was designed and prepared via the self-assembly of a bispicolinate BMP32C10 derivative and a bisparaquat. The complexation behavior was cooperative. In addition, the complex comprised of the BMP32C10 derivative and a cyclic bisparaquat demonstrated strong binding; interestingly, a poly[2]pseudocatenane structure was formed in the solid state for the first time.

In supramolecular chemistry, pseudorotaxanes are the supramolecular mechanically linked species constructed from linear molecular components (“Guests”) encircled by macrocyclic components (“Hosts”). Pseudorotaxanes are not only the fundamental precursors for the preparation of

novel supramolecular species, such as rotaxanes, catenanes, polyrotaxanes and polycatenanes,<sup>1</sup> but also are applied as functional materials, such as molecular machines, drug delivery devices, and so on.<sup>2</sup> Therefore, the design and preparation of pseudorotaxanes, especially with novel topologies, have been topics of current interest.<sup>3</sup> Crown ethers and derivative cryptands, such as **1**, and paraquat derivatives (*N*, *N'*-dialkyl-4,4'-bipyridinium salts),<sup>4</sup> e.g., linear bisparaquat **2** and cyclobis(paraquat-*p*-phenylene) (CBPQT) **3**, have been widely employed to construct pseudorotaxanes and catenanes (Scheme 1).<sup>5</sup> Cryptands, e.g., **1d**, have been proved to be much better hosts for paraquat derivatives compared

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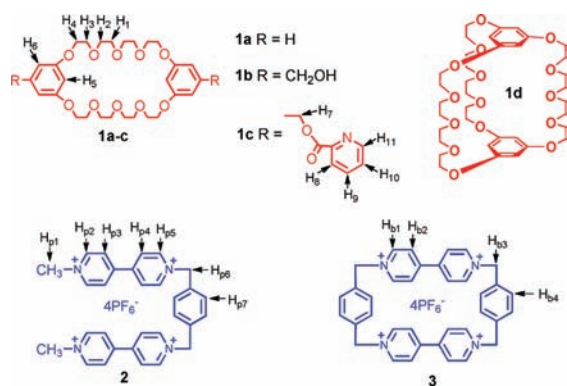
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**Scheme 1.** Structures of Crown Ethers **1a–c**, Cryptand **1d**, and Bisparaquats **2** and **3**



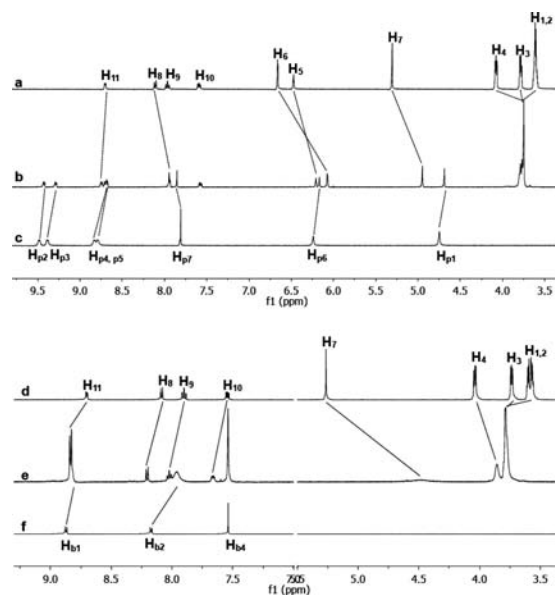
with the corresponding simple crown ethers, e.g., **1a**.<sup>6</sup> Recently, we reported the first supramolecular cryptand-type [2]pseudorotaxanes based on synthetically easily accessible bis(*m*-phenylene)-32-crown-10 (BMP32C10) derivatives, including **1c**, and a paraquat derivative with remarkably improved association constants due to the formation of pseudocryptand structures in the complexes.<sup>7</sup> Inspired by these results, here we report the design and self-assembly of a pseudocryptand-type supramolecular [3]pseudorotaxane via cooperative complexation between BMP32C10 dipicolinate derivative **1c** and bisparaquat **2**. Moreover, complexation of **1c** and cyclic bisparaquat **3** produced the first “hook-ring” poly[2]pseudocatenane in the solid state.

The individual solutions of **1c** and **2** in acetone-*d*<sub>6</sub> were colorless; however, the mixed solutions of **1c** and **2** in acetone-*d*<sub>6</sub> were deep yellow due to the charge-transfer interaction between the electron-rich aromatic rings of **1c** and the electron-poor pyridinium rings of **2**, good evidence for complexation.<sup>1</sup> <sup>1</sup>H NMR spectra of the mixed solutions of **1c** and **2** displayed only one set of peaks, indicating the complexation was a fast exchange process (Figure 1). After complexation, peaks corresponding to H<sub>3</sub>, H<sub>4</sub>, H<sub>5</sub>, H<sub>6</sub>, H<sub>7</sub>, and H<sub>8</sub> of **1c** and H<sub>p1</sub>, H<sub>p2</sub>, H<sub>p3</sub>, H<sub>p4</sub>, H<sub>p5</sub>, and H<sub>p6</sub> of **2** moved upfield, while H<sub>1</sub>, H<sub>2</sub> and H<sub>11</sub> of **1c** and H<sub>p7</sub> of **2** moved downfield, as normally observed in similar complexes.<sup>5–7</sup>

The stoichiometry of the complex between dipicolinate host **1c** and linear bisparaquat **2** was determined to be 2:1

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**Figure 1.** Partial proton NMR spectra. Upper stacked spectra (400 MHz, acetone-*d*<sub>6</sub>, 25 °C): (a) **1c**; (b) **1c** and **2** ( $[1c]_0 = 0.95$  mM,  $[2]_0 = 0.50$  mM); (c) **2**. Bottom stacked spectra (500 MHz, acetonitrile-*d*<sub>3</sub>, 25 °C): (d) **1c**; (e) **1c** and **3** ( $[1c]_0 = [3]_0 = 2.18$  mM); (f) **3**.

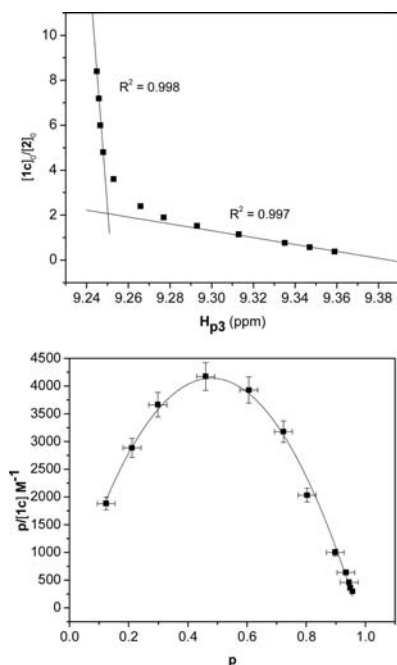
by a molar ratio plot (Figure 2)<sup>8</sup> and confirmed by an electrospray ionization mass spectrum (ESI-MS):  $m/z$  1174.84 [**1c**<sub>2</sub>·**2** – 2PF<sub>6</sub> + H]<sup>2+</sup>, 1101.73 [**1c**<sub>2</sub>·**2** – 3PF<sub>6</sub>]<sup>2+</sup>, 734.85 [**1c**<sub>2</sub>·**2** – 3PF<sub>6</sub> + H]<sup>3+</sup>, 514.94 [**1c**<sub>2</sub>·**2** – 4PF<sub>6</sub> + H]<sup>4+</sup>.<sup>9</sup> It should be noted here that the stoichiometry between the BMP32C10 diol **1b**, which is the precursor of **1c**, and **2** was reported as 1:1, while the stoichiometry between BMP32C10 cryptand **1d** and **2** was reported as 2:1 in the same solvent.<sup>5a</sup> This observation provided an indication of the formation of a cryptand-like structure in the **1c**·**2** complex.

The value of  $\Delta_0$ , the chemical shift difference for H<sub>p3</sub> of **2** between the uncomplexed and fully complexed species was determined to be 0.137 ppm by extrapolation of a plot of  $\Delta$ , the chemical shift difference for H<sub>p3</sub> between solutions of the uncomplexed and partially complexed **2**, versus  $1/[1c]_0$  in the high initial concentration range of **1c**.<sup>9</sup> The complexed fraction,  $p$ , of the bisparaquat **2** can be calculated from  $p = \Delta/\Delta_0$ . Based on a Scatchard plot,  $K_1$  was estimated to be  $6.0 \pm 0.9 \times 10^3$  M<sup>-1</sup> and  $K_2$  was determined to be  $8.1 \pm 0.7 \times 10^3$  M<sup>-1</sup> in acetone-*d*<sub>6</sub>.<sup>10</sup> The ratio  $K_2/K_1 =$

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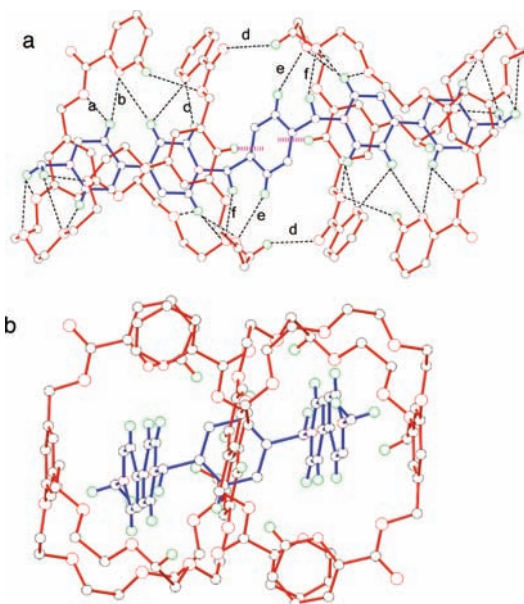
(10)  $K_1 = [1c \cdot 2]/\{[1c][2]\}$  and  $K_2 = [1c_2 \cdot 2]/\{[1c]^2[2]\}$ . The intercept of the linear fit straight line based on the first three data points for low  $p$  (Figure 2, lower plot) gave the value of  $2K_2 - K_1$ , while the slope of the last four data points for high  $p$  (Figure 2) gave the value of  $-2K_2$ .<sup>11c</sup>



**Figure 2.** Upper plot: mole ratio plot for **1c** and **2**. Bottom plot: Scatchard plot for complexation of **1c** with **2**.  $P$  = fraction of bisparaquat **2** units complexed. Error bars in  $p$ :  $\pm 0.03$  absolute. Error bars in  $p/[1c]$ :  $\pm 0.06$  relative. The polynomial fit line is simply to guide the reader's eyes. The experiment was performed in acetone- $d_6$  at 22 °C.

1.35 is much higher than the value of 0.25 expected for statistical complexation, indicating that the complexation between **1c** and **2** is cooperative.<sup>11</sup> In addition,  $K_2$  and  $K_1$  are much higher than the  $K_a$  ( $6.3 \times 10^2 \text{ M}^{-1}$ , in acetone- $d_6$ )<sup>5a</sup> between precursor **1b** and **2** due to the formation of a pseudocryptand structure in the complex, as confirmed by the X-ray analysis (see below).

X-ray diffraction analysis of a crystal of the complex of **1c** with **2** (Figure 3), which was grown via the vapor-diffusion of pentane into an acetone solution, confirmed the stoichiometry between **1c** and **2** and demonstrated the formation of a pseudocryptand-type supramolecular [3]pseudorotaxane structure. In the complex, two molecules of **1c** form a pseudocryptand structure by folding the pyridyl arms; the pyridyl rings interact via offset face-to-face  $\pi$ -stacking.<sup>12</sup> The bisparaquat molecule **2** is threaded through the central cavity of the pseudocryptand **1c**. The complex is stabilized by hydrogen bonds between pyridyl rings, ether oxygen atoms, and the hydrogen atoms of the bisparaquat, offset  $\pi$ - $\pi$  stacking between pyridyl rings, aromatic rings of **1c** and pyridinium rings of **2**, and CH- $\pi$



**Figure 3.** Two views of the X-ray structure of **1c**<sub>2</sub>·**2**. Oxygen atoms are red. Carbon atoms are black. Nitrogen atoms are purple. Hydrogen atoms are green. **1c** is red. **2** is green. The same settings are used in the following crystal structures. Solvent molecules,  $\text{PF}_6^-$  ions, and hydrogens except the ones involved in hydrogen bonds were omitted for clarity. Pink dashed lines represent the CH- $\pi$  interactions. Selected hydrogen-bond parameters: H $\cdots$ O(N) distances (Å), C $\cdots$ O(N) distances (Å), C-H $\cdots$ O(N) angles (deg): a 2.59, 3.29, 130.691; b 2.50, 3.37, 151; c 2.32, 3.10, 138; d 2.46, 3.35, 149; e 2.69, 3.55, 155; f 2.40, 3.34, 159. All the hydrogen bonds are omitted for clarity in b.

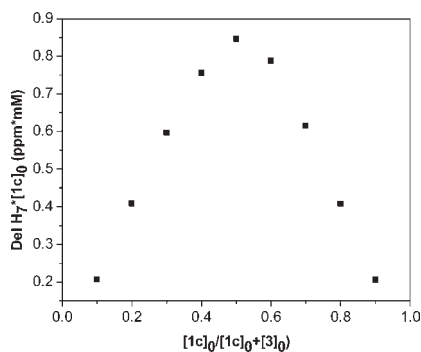
interactions. It should be noted here that the carbonyl oxygen atoms of one host **1c** form intermolecular hydrogen bonds (bond d in Figure 3) with the H<sub>1</sub> of the other threaded **1c** molecule. This favors the threading of the second **1c** molecule and leads to cooperative complexation. Another possible reason for the cooperative complexation is that the threading of the first crown ether **1c** molecule restricts the conformational freedom of bisparaquat **2** by forming hydrogen bonds (bonds e and f in Figure 3) and CH- $\pi$  interaction (CH-centroid 2.68 Å) between the first threaded crown ether **1c** and bisparaquat, thereby favoring the threading of the second host molecule.

Similarly, the mixed solutions of dipicolinate **1c** and CBPQT **3** in acetonitrile- $d_3$  were deep yellow due to the charge-transfer interaction between the electron-rich aromatic rings of **1c** and the electron-poor pyridinium rings of **3**, indicating complexation. <sup>1</sup>H NMR spectra of solutions of **1c** and **3** displayed only one set of signals (Figure 1), indicating fast exchange. Upon complexation, signals corresponding to H<sub>7</sub> and H<sub>4</sub> of **1c** and H<sub>b1</sub> and H<sub>b2</sub> of **3** moved upfield, while H<sub>1</sub>, H<sub>2</sub>, H<sub>3</sub>, H<sub>9</sub>, H<sub>10</sub>, and H<sub>11</sub> of **1c** moved downfield as normally observed in similar complexes.<sup>5-7</sup> A Job plot (Figure 4)<sup>13</sup> showed that the stoichiometry of the complex between **1c** and **3** was 1:1 and

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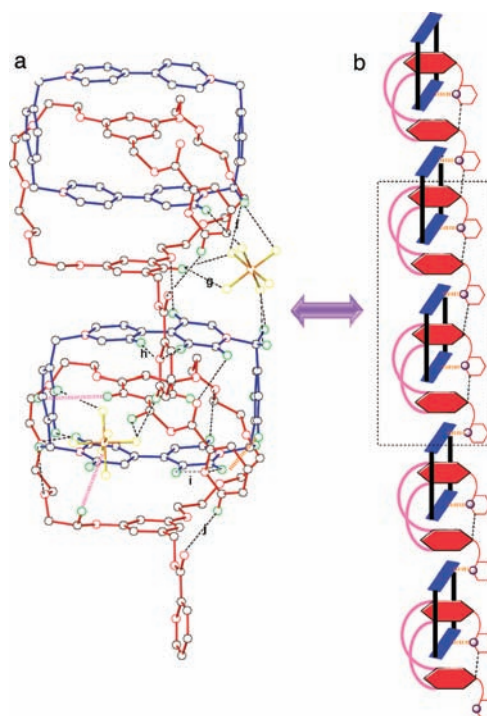
**Figure 4.** Job plot showing 1:1 stoichiometry of the complex between **1c** and **3** in acetonitrile- $d_3$ .  $[1c]_0 + [3]_0 = 2.18$  mM.

the stoichiometry was confirmed by an electrospray ionization mass spectrum (ESI-MS):  $m/z$  808.44  $[1c \cdot 3 - 2PF_6]^{2+}$ , 735.79  $[1c \cdot 3 - 3PF_6]^{2+}$ , 490.66  $[1c \cdot 3 - 3PF_6]^{3+}$ .<sup>9</sup>  $K_a$  was determined to be  $1.7 \pm 0.2 \times 10^4$   $M^{-1}$  in acetonitrile- $d_3$  based on the proton NMR data.<sup>14</sup>

Interestingly, X-ray analysis of a single crystal of the complex **1c**·**3**, which was grown via the vapor-diffusion of diisopropyl ether into an acetonitrile solution, showed that complex **1c**·**3** forms a “hook-ring” shaped poly[2]pseudocatenane structure in the solid state (Figure 5). Different from other crown ether/paraquat complexation systems in which crown ethers always are the hosts, in this system the crown ether **1c** acts as a guest and is threaded through the central cavity of CBPQT **3**, which acts as a host. A **1c**·**3** repeating unit was formed accordingly. One pyridyl arm of crown ether **1c** interacts with one paraquat side of **3** in the repeating unit and leaves the other paraquat side of **3** open. At the same time, the other pyridyl arm of **1c** acts as a “hook” to interact with the open paraquat side of host **3** ring in an adjacent repeating unit. Also, there is a hydrogen bond between **1c** and a host **3** belonging to an adjacent repeat units. Therefore, **1c**·**3** units are linked together. In addition,  $H_{11}$  of one pyridyl arm of **1c** forms a hydrogen bond with the carbonyl oxygen of the other pyridyl arm on the same **1c**. Two  $PF_6^-$  counterions act as hydrogen bonding bridges, interacting with both pyridyl arms of **1c** and a paraquat side of host **3**, forming a pseudocatenane structure.<sup>15</sup> As a result, a poly[2]pseudocatenane was formed and stabilized by hydrogen bonds, offset  $\pi$ - $\pi$  stacking between aromatic rings of **1c** and pyridinium rings of **3** and CH- $\pi$  interactions between

(14) <sup>1</sup>H NMR characterizations were done on solutions with constant **1c** and varied **3**. Based on these NMR data,  $\Delta_0$ , the difference in  $\delta$  values for proton  $H_7$  of **1c** in the uncomplexed and fully complexed species, was determined to be 0.930 ppm as the y-intercept of a plot of  $\Delta = \delta - \delta_u$  vs  $[1c]_0/[3]_0$  in the high initial concentration range of **3**.  $K_a$  was calculated from  $K_a = (\Delta/\Delta_0)/[(1 - \Delta/\Delta_0)([3]_0 - \Delta/\Delta_0 [1c]_0)]$ .  $\Delta/\Delta_0$  values between 0.2 to 0.8 were used. When the ratio of  $[3]_0/[1c]_0$  was higher than 7.9/1, no further chemical shift change was observed, and **1c** was considered to be fully complexed.

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**Figure 5.** (a) X-ray structure of poly(**1c**·**3**). **1c** is red. **3** is blue. Solvent molecules,  $PF_6^-$  ions and hydrogen atoms except the ones involved in hydrogen bonding have been omitted for clarity. Selected hydrogen-bond parameters:  $H \cdots O(F, N)$  distances (Å),  $C \cdots O(F, N)$  distances (Å),  $C-H \cdots O(F, N)$  angles (deg): f 2.58, 3.22, 122; g 2.59, 3.44, 155; h 2.41, 3.33, 166; i 2.73, 3.35, 124; j 2.46, 3.35, 134. (b) Cartoon representation of the supramolecular structure.

the  $H_6$  protons of **1c** and aromatic rings of **3** (CH-centroid 2.94 Å). To the best of our knowledge, this is the first poly[2]pseudocatenane to be reported.

In summary, for the first time, we demonstrated a pseudocryptand-type supramolecular [3]pseudorotaxane based on a BMP32C10 derivative with a linear bisparaquat. The complexation behavior was cooperative. In addition, the complex between the same BMP32C10 derivative and a cyclic bisparaquat derivative exhibits a rather high association constant and leads to the observation of a poly[2]pseudocatenane structure in the solid state for the first time. Currently, we are focusing on introducing similar structures into polymers and preparation of pseudocryptand-based polypseudorotaxanes.

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**Supporting Information Available.** Supporting Information ( $\Delta_0$  determination, mass spectra and X-ray crystallographic files (CIF) for **1c**·**2** and **1c**·**3**). This material is available free of charge via the Internet at <http://pubs.acs.org>.