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Improved and Controlled Complexation of Paraquat Derivatives by the Formation of a Bis(*m*-phenylene)-26-Crown-8-Based Lariat Ether

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A novel bis(*m*-phenylene)-26-crown-8-based lariat ether (i.e., **3b**) was synthesized and characterized. It can bind paraquat derivatives more strongly than bis(*m*-phenylene)-26-crown-8 in solution. It forms pseudorotaxanes with two paraquat derivatives in the solid state. *N*-Methyl substitution was found to play an important role on the binding strength of lariat ether **3b**. Furthermore, due to the introduction of two benzyloxy groups, its binding to paraquat derivatives can be switched off (and back on) by adding K^+ (and then dibenzo-18-crown-6), and the disassociation percentage depends on the concentration of the added K^+ ions.

Introduction

Threaded structures, such as rotaxanes and catenanes, have been widely applied in the construction of molecular machines[1] and mechanically bonded macromolecules.[2] Paraquat derivatives (*N*,*N*′-dialkyl-4,4′-bipyridinium salts) are commonly used guests in the preparation of these self-assembled structures.[3] Bis(*p*-phenylene)-34-crown-10 (BPP34C10, Figure 1) can form pseudorotaxanes with paraquat derivatives,[4] and this recognition motif has been widely used in the construction of supramolecular systems including dendrimers with interesting electrochemical properties and guest binding properties,[5] metal–organic frameworks,[6] and supramolecular polymers.[7] Bis(*m*-phenylene)-32-crown-10 (BMP32C10) derivatives, such as **1a** and **1b**, mainly form taco complexes with paraquat derivatives,[3a,3d,8] and the related recognition motif has also been widely used in supramolecular chemistry,[9] because the symmetric nature of BMP32C10 derivatives avoids issues of isomers in the fabrication of complicated supramolecular structures. *cis*- or *trans*-Dibenzo-30-crown-10 (DB30C10) diols **2a** and **2b** can form inclusion complexes with paraquat derivatives, and the complexation can be switched by adding small molecules (KPF_6 and 18-crown-6).[10] Dibenzo-24-crown-8 (DB24C8) can also form pseudorotaxanes and rotaxanes with paraquat derivatives,[11] but the complexes based on the recognition of DB24C8 to paraquat are less stable than the complexes based on the binding of DB24C8 to secondary ammonium salts, so the DB24C8/paraquat recognition motif has usually been used as the secondary binding motif to construct pH-driven molecular machines.[12] However, up to now, the complexation of bis(*m*-phenylene)-26-crown-8 (BMP26C8, **3a**) and paraquat derivatives has been rarely explored.[3c]

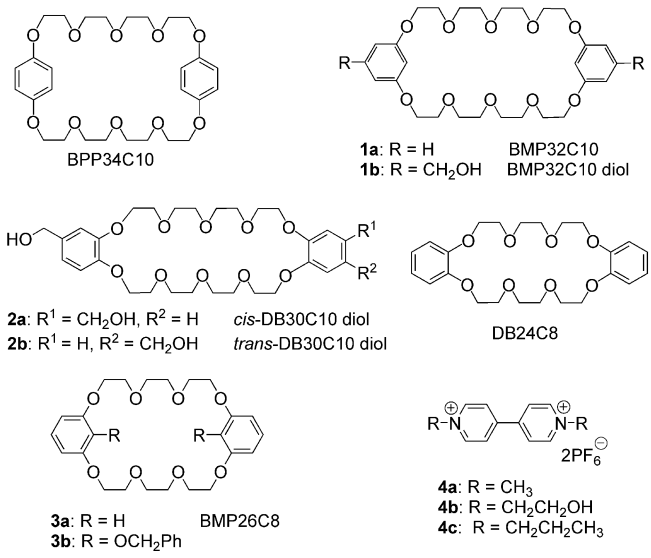

Figure 1. Chemical structures of BPP34C10, BMP32C10 derivatives **1**, *cis*- and *trans*-DB30C10 diol, DB24C8, BMP26C8 derivatives **3**, and paraquat derivatives **4**.

Lariat ethers, as "cousins" of crown ethers and cryptands, were designed to have the three dimensionality of cryptands while retaining the faster complexation dynamics of crown ethers.[13] They have been widely used in controlled transport in membranes, novel membranes, nucleotide-based molecular boxes, and cation-conducting channels.[14] However, although lariat ethers have been widely used as hosts for metal cations, the complexation of lariat ethers with paraquat derivatives has rarely been reported.

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As mentioned above, BPP34C10, BMP32C10, DB30C10, and DB24C8 can all bind paraquat derivatives, and these binding systems have been widely used in supramolecular chemistry. Naturally, we turned to the binding of paraquat using BMP26C8 derivatives. Due to their symmetric nature, BMP26C8 derivatives can be easily used in the construction of more sophisticated systems without consideration of the above-mentioned symmetry problem in the fabrication of complicated supramolecular structures. However, commonly BMP26C8 does not show good affinities with paraquat derivatives and the association constant of **3a**⊃**4a** is only 390 M^{-1} in acetone,[3c] which is not high enough for the efficient construction of mechanically interlocked threaded structures. Herein, we synthesized a new BMP26C8 derivative **3b**, which is a lariat ether with two benzyloxy groups. It forms pseudorotaxanes with paraquat derivatives **4a** and **4b**, and the complex **3b**⊃**4a** is much more stable than **3a**⊃**4a**.

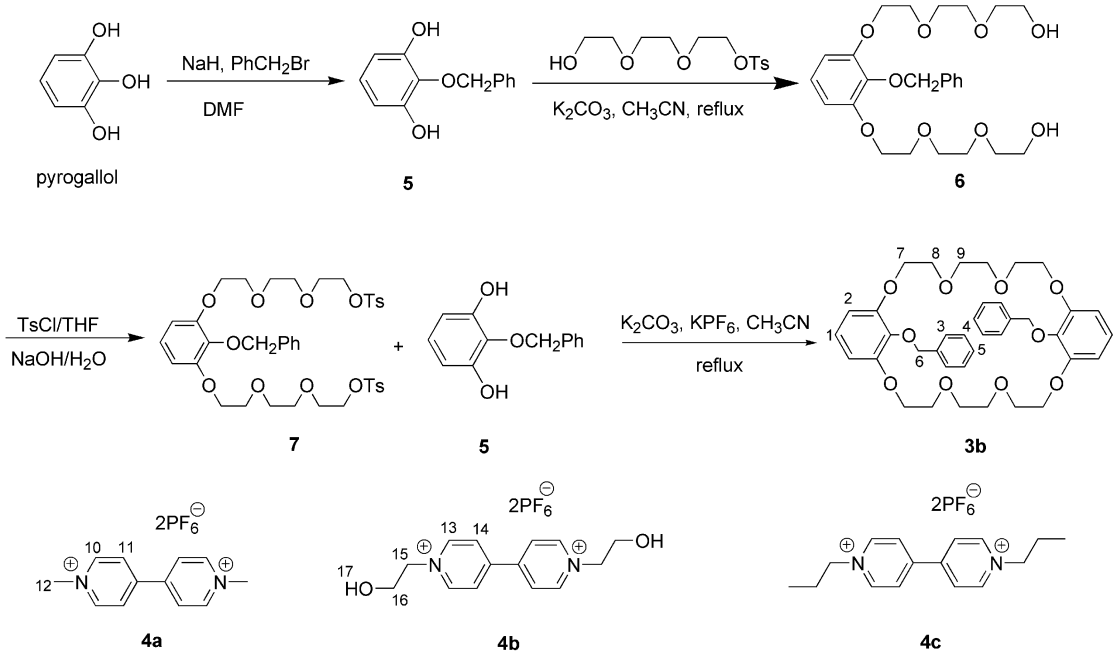
Results and Discussion

Host **3b** was synthesized from pyrogallol in four steps in good yield (Scheme 1). Then the complexations between it and two paraquat derivatives, **4a** and **4b**,[15] were studied. When equimolar (8.00 mM) acetone solutions of **3b** and either **4a** or **4b** were made, a bright yellow color appeared as a result of charge-transfer interactions between the electron-rich aromatic rings of the lariat ether host and the electron-poor pyridinium rings of the paraquat derivative guests, and it was visually observed that the yellow color of the solution containing **4b** and lariat ether **3b** was not so deep as that of the solution containing **4a** and **3b**. This difference in yellow color intensity indicated that **4a** bound lariat ether **3b** more strongly than **4b**.

Job plots[16] based on UV/Vis absorbance data for the charge-transfer band (λ = 375 nm) demonstrated that the complexes of **3b** with **4a** and **4b** were both of 1:1 stoichiometry in solution. The association constants (K_a) of complexes **3b**⊃**4a** and **3b**⊃**4b** in acetone were determined by probing the charge-transfer band of the complexes by a UV/Vis titration method to be $5.3(\pm0.5)\times10^3$ M^{-1} and $7.0(\pm0.3)\times10^2$ M^{-1}, respectively. For the investigation of the large difference in association constants of complexes **3b**⊃**4a** and **3b**⊃**4b**, the complexation between host **3b** and paraquat derivative guest **4c** was also studied as a control experiment. The association constant for **3b**⊃**4c** in acetone was determined to be $6.0(\pm0.5)\times10^2$ M^{-1}, similar with **3b**⊃**4b**, indicating that *N*-methyl substitution has an important influence on the binding strength between BMP26C8-based lariat ether **3b** and paraquat derivatives.[17] This may be due to the fact that the methyl protons of **4a** are more or less acidic and besides the pseudorotaxane geometry, the three-point binding geometry (similar to the complexation of primary alkylammonium ions and 18-crown-6)[18] can also exist for **3b**⊃**4a**, increasing the association constant.

The 1:1 stoichiometry of both **3b**⊃**4a** and **3b**⊃**4b** was confirmed by electrospray ionization mass spectrometry (ESI-MS). Peaks were found at *m*/*z* = 991.3 (9.1%) and 423.4 (100%) for **3b**⊃**4a** and at *m*/*z* = 1051.1 (3.2%) and 453.4 (100%) for **3b**⊃**4b**, corresponding to $[\mathbf{3b}\supset\mathbf{4a} - PF_6]^+$, $[\mathbf{3b}\supset\mathbf{4a} - 2PF_6]^{2+}$, $[\mathbf{3b}\supset\mathbf{4b} - PF_6]^+$, and $[\mathbf{3b}\supset\mathbf{4b} - 2PF_6]^{2+}$, respectively.

The 1:1 stoichiometry of lariat ether **3b** with paraquat derivative **4a** or **4b** was further evidenced by X-ray diffraction analysis of yellow single crystals grown by vapor diffusion of pentane into acetone solutions of **3b** with **4a** or **3b** with **4b**, respectively. The complex **3b**⊃**4a** is a [2]pseudorotaxane in the solid state (Figure 2). This is the first time



Scheme 1. Syntheses of BMP26C8-based lariat ether **3b** and chemical structures of paraquat derivatives **4a**, **4b**, and **4c**.

that threaded structures are observed between BMP26C8 and paraquat derivatives in the solid state. Interestingly, the crystal structure of **3b**⊃**4a** is quite different from those of the complexes of BPP34C10 and BMP32C10 derivatives with paraquat **4a**.[3,4,8] There are no direct hydrogen bonds between lariat ether host **3b** and paraquat guest **4a**; in sharp contrast, usually pyridinium protons of paraquat **4a** are directly hydrogen-bonded to the ether oxygen atoms of the crown ether hosts in all previously reported crown ether/**4a** complexes.[3,4,8] It is noteworthy that the two pyridinium rings of paraquat **4a** are coplanar, which was not observed in the previously reported complexes of **4a** with various crown ether hosts.[3,4,8] It seems that the solid-state structure of **3b**⊃**4a** is mostly stabilized by face-to-face π-stacking and charge-transfer interactions between the four phenylene rings of host **3b** and the two bipyridinium rings of guest **4a** (Figure 2). In the packing structure, two **3b**⊃**4a** complexes are linked by a bridge formed by two PF_6^- ions and one water molecule. Face-to-face π-stacking interactions and indirect hydrogen bonds keep the whole structure stable in the solid state.

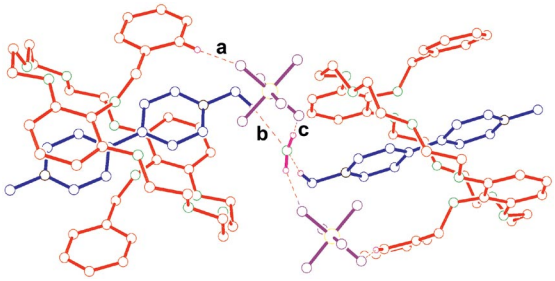


Figure 2. A ball–stick view of the X-ray packing crystal structure of **3b**⊃**4a**. Lariat ether **3b** is red, paraquat derivative **4a** is blue, PF_6^- counterions are purple, and the water molecule is magenta. Hydrogen atoms are magenta, oxygen atoms are green, nitrogen atoms are black, fluorine atoms are purple, and the phosphorus atom is yellow. The other PF_6^- counterions, solvent molecules, and hydrogen atoms except the ones involved in hydrogen bonding between lariat ether **3b** and paraquat **4a** were omitted for clarity. Hydrogen bond parameters: H···O (F) distance [Å], C(O)–H···O (F) angle [°], C(O)···O (F) distance [Å] **a**, 2.46, 170, 3.38; **b**, 2.49, 161, 3.41; **c**, 2.17, 150, 2.92. Face-to-face π-stacking parameters: centroid–centroid distances [Å] 3.78, 3.66; ring plane/ring plane inclinations [°]: 14.5, 13.4.

The complex **3b**⊃**4b** is also a [2]pseudorotaxane in the solid state (Figure 3). The same as for the complex **3b**⊃**4a**, **3b**⊃**4b** is also stabilized by face-to-face π-stacking and charge-transfer interactions between the four phenylene rings of host **3b** and the two bipyridinium rings of guest **4b**. The two pyridinium rings of paraquat **4b** are also coplanar in **3b**⊃**4b** (Figure 3). Different from the complex **3b**⊃**4a** (Figure 2), two β-pyridinium protons of paraquat **4b** are directly hydrogen-bonded to the ether oxygen atoms of lariat ether host **3b**. In the packing structure, two **3b**⊃**4b** complexes are linked by hydrogen bonds formed between the hydroxyethyl groups on two **4b** molecules and four **3b**⊃**4b** complexes are linked by a PF_6^- anion. Therefore, the whole structure is stabilized by face-to-face π-stacking and hydrogen-bonding interactions. It can be concluded from the solid-state structures of **3b**⊃**4a** and **3b**⊃**4b** that the benzyloxy groups provide good face-to-face π-stacking interactions with the pyridinium rings of the paraquat derivative guests, consistent with our design.

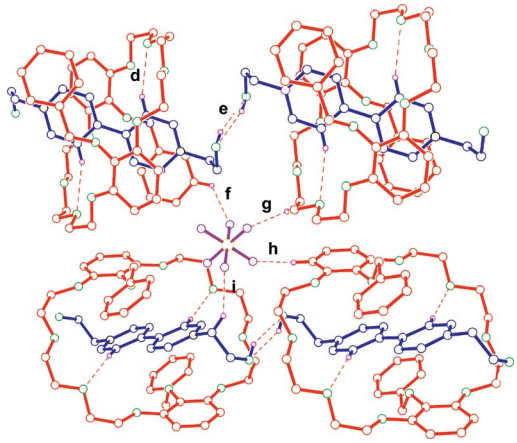


Figure 3. A ball–stick view of the X-ray packing crystal structure of **3b**⊃**4b**. Lariat ether **3b** is red, paraquat derivative **4b** is blue, and the PF_6^- ion is purple. Hydrogen atoms are magenta, oxygen atoms are green, nitrogen atoms are black, fluorine atoms are purple, and phosphorus atoms are yellow. The other PF_6^- counterions, solvent molecules, and hydrogen atoms except the ones involved in hydrogen bonding between lariat ether **3b** and paraquat derivative **4b** were omitted for clarity. Hydrogen bond parameters: H···O (F) distance [Å], C(O)–H···O (F) angle [°], C(O)···O (F) distance [Å] **d**, 2.56, 159, 3.44; **e**, 2.06, 150, 2.80; **f**, 2.54, 125, 3.16; **g**, 2.38, 166, 3.32; **h**, 2.47, 146, 3.28; **i**, 2.33, 147, 3.19. Face-to-face π-stacking parameters: centroid–centroid distances [Å] 3.84, 3.85; ring plane/ring plane inclinations [°]: 21.0, 15.4.

To further investigate the complexations between **3b** and **4a** or **4b**, ^{1}H NMR spectra of separate equimolar (8.00 mM) CD_3COCD_3 solutions of **3b** with **4a** or **4b** were examined (Figures 4 and 5). Both complexation systems **3b**⊃**4a** and **3b**⊃**4b** undergo fast exchange on the ^{1}H NMR timescale. Upfield shifts were observed for pyridinium protons H^{10} and H^{11} and *N*-methyl protons H^{12} of paraquat **4a** after complexation (Figure 4, a and b). Aromatic protons H^1, H^2, and H^3, benzyl protons H^6 and ethyleneoxy protons H^7 shifted upfield, whereas aromatic protons H^4 and H^5 and ethyleneoxy protons H^8 and H^9 of **3b** moved downfield after complexation (Figure 4, b and i). From BMP26C8 **3a** to lariat ether **3b**, two benzyloxy groups are introduced, making **3b** a good host for K^+. When KPF_6 was gradually added to an equimolar (8.00 mM) solution of **3b** and **4a** in CD_3COCD_3, the chemical shifts of protons on **4a** evolved to their uncomplexed values; correspondingly, the yellow color of the solution became lighter and lighter, indicating the dissociation of complex **3b**⊃**4a**. When 32 equiv. of KPF_6 was added, **3b**⊃**4a** was mostly disassociated (Figure 4, a, g, and i) and the solution was nearly colorless. However, when 32 equiv. of DB18C6 was subsequently added, chemical shift changes of protons on **4a** were observed again (Figure 4, a and h), and correspondingly, the yellow color of the solution returned, indicating the reformation of complex **3b**⊃**4a**.[19] Therefore, K^+ can be used as

a switch to control the association of lariat ether **3b** and paraquat **4a**, and the disassociation percentage depends on the concentration of the added K^+.

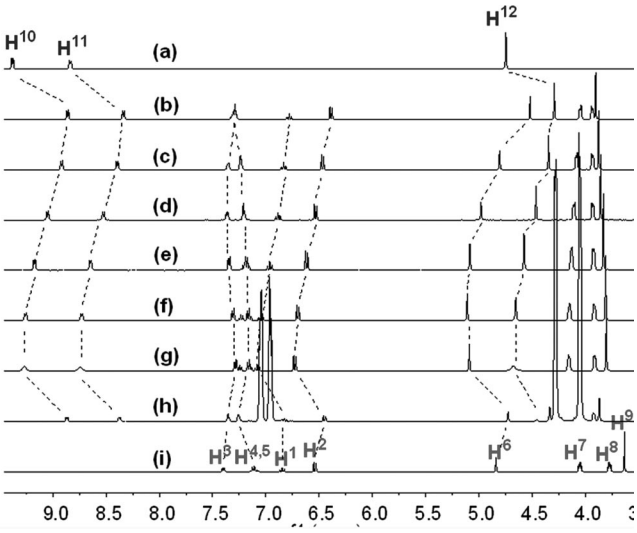


Figure 4. ^{1}H NMR spectra (400 MHz, CD_3COCD_3, 295 K) of (a) **4a**, (b) 8.00 mM **3b** and **4a**; 8.00 mM **3b** and **4a** and (c)16.0 mM KPF_6, (d) 32.0 mM KPF_6, (e) 64.0 mM KPF_6, (f) 128 mM KPF_6, (g) 256 mM KPF_6; (h) 8.00 mM **3b** and **4a** and 256 mM KPF_6 and DB18C6, and (i) **3b**.

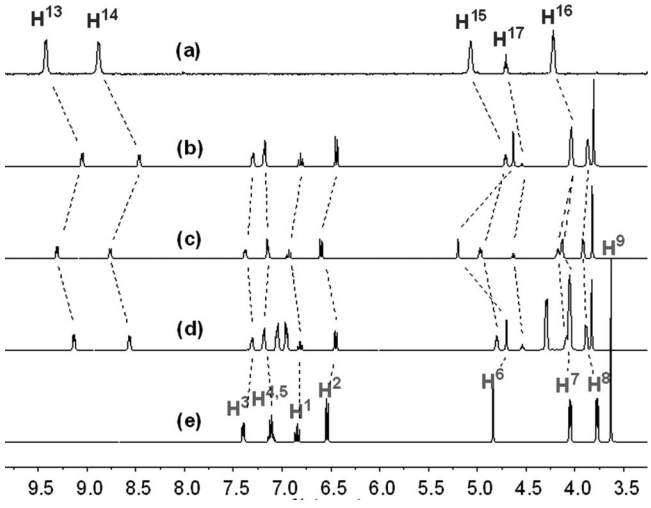


Figure 5. ^{1}H NMR spectra (400 MHz, CD_3COCD_3, 295 K) of (a) **4b**, (b) 8.00 mM **3b** and **4b**, (c) 8.00 mM **3b** and **4b** and 16.0 mM KPF_6, (d) 8.00 mM **3b** and **4b** and 16.0 mM KPF_6 and DB18C6, and (e) **3b**.

For the complexation system **3b**⊃**4b**, upfield shifts were also observed for pyridinium protons H^{13} and H^{14} and hydroxyethyl protons H^{15}, H^{16}, and H^{17} of paraquat **4b** after complexation (Figure 5, a and b). Aromatic protons H^1, H^2, and H^3, benzyl protons H^6, and ethyleneoxy protons H^7 shifted upfield, whereas aromatic protons H^4 and H^5 and ethyleneoxy protons H^8 and H^9 of **3b** moved downfield after complexation (Figure 5, b and e). Different from the complexation of **3b**⊃**4a**, less KPF_6 was required to dissociate the complex **3b**⊃**4b**, because its association constant is much smaller than that of **3b**⊃**4a**. These changes were also evidenced by ^{1}H NMR spectroscopy. When 2 equiv. of KPF_6 was added to an equimolar solution of 8.00 mM **3b** and **4b** in CD_3COCD_3, the chemical shifts of protons on **4b** returned to almost their uncomplexed values (Figure 5, a and c), and correspondingly, the yellow color of the solution disappeared, indicating the dissociation of complex **3b**⊃**4b**. However, when 2 equiv. of DB18C6 was subsequently added, chemical shift changes of protons on **4b** were observed again (Figure 5, a and d), and correspondingly, the yellow color of the solution returned, indicating the reformation of complex **3b**⊃**4b**.[19]

Conclusions

In summary, based on BMP26C8, we synthesized a lariat ether host, **3b**, for paraquat derivatives and found that it could form pseudorotaxanes with them. Due to the introduction of two benzyloxy groups, the association constant increased about 13 times from 390 (±30) M^{-1} for **3a**⊃**4a** to 5.3 (±0.5) × 10^3 M^{-1} for **3b**⊃**4a**. The *N*-methyl substitution had an important influence on the binding strength between BMP26C8-based lariat ether **3b** and paraquat derivatives. Moreover, we demonstrated that a change in the K^+ concentration could be used as a switch to control the assembly process of lariat ether **3b** and paraquat derivative guests. Further work will be the application of the recognition of **3b** to paraquat derivatives in the efficient fabrication of more complicated systems, including molecular machines.

Supporting Information (see footnote on the first page of this article): Synthetic procedures, characterizations, crystal data for **3b**⊃**4a** and **3b**⊃**4b**, Job plots, and UV/Vis data.

Acknowledgments

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[19] The chemical shift changes of the protons on the host or guest after complexation could not be fully recovered. Three possible reasons are: (1) the solution was diluted; (2) the ionic strength of the solution increased; (3) different counterions are introduced, influencing ion pairing. These factors could change the chemical shifts and/or decrease the complexation percentage.

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