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[2]Pseudorotaxanes and [2]Catenanes Constructed by Oxacalixcrowns/Viologen Molecular Recognition Motifs

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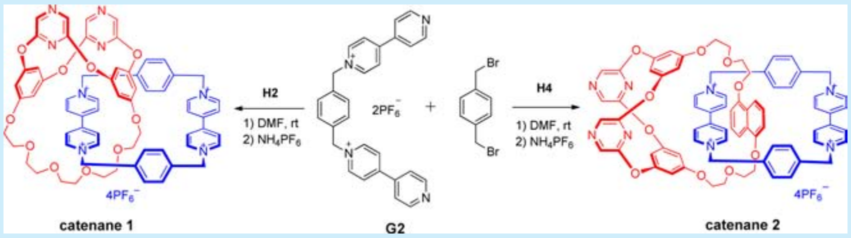
Supporting Information



ABSTRACT: Oxacalix[2]arene[2]pyrazine and functional polyether derived oxacalixcrown-6, -7, and -8 were synthesized, and their host−guest complexation with paraquat to form [2]pseudorotaxanes was studied. The [2]pseudorotaxanes were then successfully used in the construction of two oxacalixcrown-tetracationic cyclophane [$CBPQT^{4+}$] based [2]catenanes.

[2]Pseudorotaxanes, characterized by a macrocyclic host component encircling a threaded guest axle, have been intensively studied and employed as fundamental building blocks in the preparation of advanced mechanically interlocked molecules (MIMs), such as rotaxanes and catenanes.[1] Crown ethers have played a leading role in the assembly of pseudorotaxanes via host−guest interactions with different types of threaded axles. A wide variety of structurally distinct crown ethers have been developed for the preparation of functionalized MIMs over the past few decades.[2] Given the increasing interest in developing MIMs with structural complexity and advanced functionality, there continues to be a need to develop new functional crown ether hosts to recognize specific guest axles for the construction of advanced functional MIMs.[3]

Calixcrowns,[4] combining calixarene and crown ether moieties, are an attractive family of fused macrocycles which possess the conformational properties and the cavity features of both calixarenes and crown ethers. Calixcrowns have shown remarkable ionophoric properties as hosts for alkali metal ions[5] and have been used to construct mechanically interlocked molecules (MIMs).[6] Oxa(aza)calixarenes,[7] the O(N)-bridged calixarenes, emerged as a new generation of macrocyclic host molecules due to their synthetic accessibility, tunable conformations and cavities, complexability with neutral and charged guest species, and ability to assemble various topologically fascinating supramolecular architectures.[8] Oxa(aza)calixcrowns, the fused macrocycles composed of oxa(aza)calixarenes and crown ethers, are much less studied compared to their parent oxa(aza)calixarenes. Tetraoxacalix[2]arene[2]triazine azacrowns,[9] the first reported oxacalixcrowns, possessed an 1,3-alternate conformation with the capability to interact with fluoride anion. However, oxacalixcrowns have not been used to construct mechanically interlocked molecules (MIMs). We have previously reported a class of oxacalix[2]arene[2]pyrazine- and xylyl-derived oxacalixcrowns.[10] Due to the rigidities and sizes of xylyls, these oxacalixcrowns possess small cavity spaces and are incapable of binding guest molecules. We envisioned by replacing the xylyl groups with longer and more flexible oligo-ethylene glycol chains, the cavity spaces of the resulting oxacalixcrowns could be fine-tuned to host small guest molecules via the expansion of the dihedral angle between the two face-to-face oriented arene rings in the oxacalix[4]arene scaffold. Herein, we report several oxacalix[2]arene[2]pyrazine and functional polyether derived oxacalixcrowns, their formation of [2]-pseudorotaxanes with paraquat via host−guest interactions, and their application in the construction of oxacalixcrown-tetracationic cyclophane [**$CBPQT^{4+}$**] based [2]catenanes.

The synthesis of the oxacalix[2]arene[2]pyrazine-derived oxacalixcrowns **H1**−**H5** is shown in Scheme 1. Oxacalixcrown-5, -6, and -7 (**H1**, **H2**, and **H3**), which possess a cryptand-like structure,[11] were obtained by macrocyclization of dihydroxyoxacalix[2]arene[2]pyrazine **1**,[10] with bistosylated oligo-ethylene glycols under basic conditions. Similarly, oxacalixcrown-6 (**H4**) and -8 (**H5**), which contain a π-electron-rich 1,5-dioxynaphthalene unit in their oligo-ethylene

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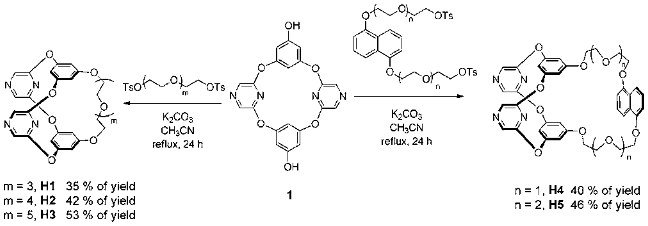
Scheme 1. Synthesis of Oxacalixcrowns H1−H5



glycol linkers, were obtained by macrocyclization of **1** with the corresponding bistosylated 1,5-dioxynaphthalene-containing oligo-ethylene glycols. All oxacalix[2]arene[2]-pyrazine derived oxacalixcrowns **H1**−**H5** were characterized by ^{1}H, ^{13}C NMR spectroscopies and HRMS spectrometry (Supporting Information).

The complexation of the oxacalixcrowns **H1**−**H5** with paraquat **G1** was investigated with 1D, 2D ^{1}H NMR spectroscopies, mass spectrometry, and single-crystal X-ray diffraction analysis. Mixing equimolar oxacalixcrown-5(**H1**) with paraquat **G1** in actone-d_6 (10 mM) at room temperature resulted in precipitation of the oxacalixcrowns. The ^{1}H NMR spectrum of the resulting mixed actone-d_6 solution (**H1** and **G1**) showed no change in the chemical shifts compared to those of free **H1** and **G1** (Supporting Information, Figure S1), suggesting no complexation occurred between **H1** and **G1**, possibly due to the limited cavity space of **H1**. However, mixing equimolar oxacalixcrown-6 **H2** (or oxacalixcrown-7, **H3**) with **G1** (10 mM) in actone-d_6 at room temperature resulted in a slightly yellow solution, suggesting the formation of charge-transfer complex between **H2** (or **H3**) and **G1**. The ^{1}H NMR spectrum of an equimolar mixture of **H2** and **G1** in actone-d_6 (10 mM) revealed significant changes in chemical shifts compared to those of free **H2** and **G1** (Figure 1). The addition of 1.0 equiv of **G1** to a solution of **H2** in acetone-d_6 caused the signals of α- and β-pyridinium and N-methyl protons of **G1** to shift upfield by 0.24, 0.27, and 0.12 ppm, respectively (Figure 1), indicating a fast complexation between **H2** and **G1** in acetone-d_6. Upon complexation of **H2** and **G1**, downfield shifts were observed for signals of the pyrazine protons (H_c, 0.11 ppm) and the phenyl protons (H_b, 0.17 ppm) in the oxacalixarene scaffold of **H2**, which possibly resulted from the hydrogen-bonding interactions between pyridinium protons of **G1** and the lower rim nitrogen atoms of oxacalixcrown-6 **H2**, as well as electron-withdrawing effect from the positively charged guest **G1**. The upfield shifts for signals of protons H_a, H_d, and H_e (−0.17, −0.38, and −0.18 ppm) of **H2** suggested the possible existence of shielding correlations. 2D ^{1}H NMR NOESY spectrum of an equimolar mixture of **H2** and **G1** (10 mM) in actone-d_6 (Supporting Information, Figure S2) clearly showed the correlations of the pyridinium and N-methyl protons of **G1** with the phenyl proton H_a and the oxyethylene protons of oxacalixcrown-6 **H2**, which provided strong evidence for the formation of a threaded complex **H2⊃G1**.

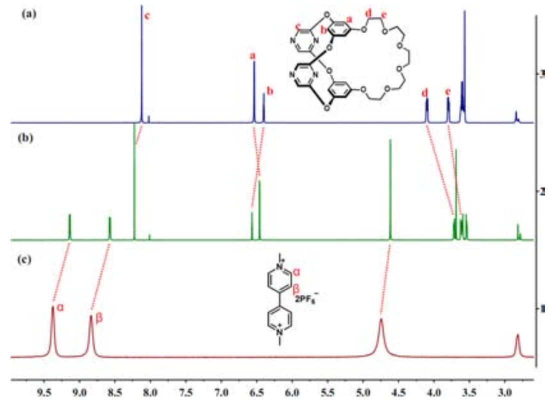


Figure 1. Partial ^{1}H NMR spectra (400 MHz, acetone-d_6, 298 K): (a) **H2**; (b) **H2** + **G1**; (c) **G1**. c = 10.00 mM.

A Job plot (Supporting Information, Figure S3) based on ^{1}H NMR data demonstrated that **H2** and **G1** formed a 1:1 complex in actone-d_6, which was further confirmed by ESI-MS spectrometry: m/z: 937.62 and 396.48 (Supporting Information, Figure S4), assigned to [**H2⊃G1**-PF_6]$^+$ and [**H2⊃G1**-2PF_6]$^{2+}$, respectively. The associate constant (K_a) of the complex **H2⊃G1** in actone-d_6 was determined to be $(1.1 \pm 0.3) \times 10^3$ M^{-1} with a ^{1}H NMR titration method (Supporting Information, Figures S5 and S6).

Single crystals of the complex **H2⊃G1** suitable for X-ray diffraction analysis were obtained by slow evaporation of the complex solution in acetonitrile and acetone. Structure analysis unambiguously established the formation of a [2]-pseudorotaxane structure **H2⊃G1** (Figure 2). In order to facilitate the threading guest **G1** in the crown-6 cavity, the dihedral angle between the two phenyl rings in the oxacalix[4]-arene scaffold of **H2** is expanded to 47° in the complex **H2⊃G1**, much larger than most of the reported values between the two face-to-face oriented arene rings in oxacalixaromatics.[7,8] The complex is stabilized by the cooperative effects of π−π stacking and C−H···O and C−H···N hydrogen bonding, consistent with the data obtained by ^{1}H NMR spectroscopy.

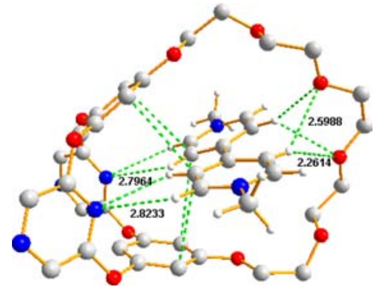


Figure 2. Crystal structure of complex **H2⊃G1**.

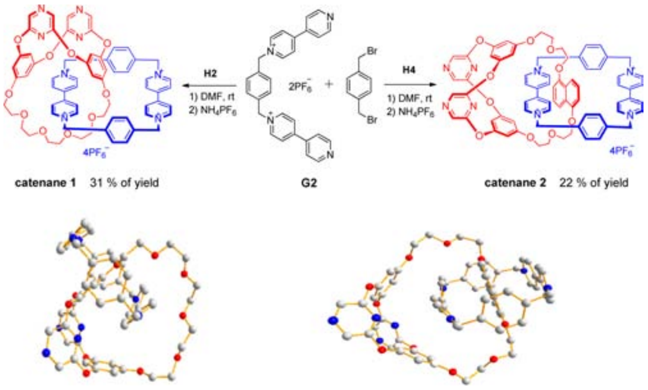
Analogously, the complexation behaviors between oxacalixcrown-7 **H3** with **G1** (10 mM) were studied in actone-d_6 at room temperature. 1D, 2D ^{1}H NMR spectra and ESI-MS spectrometry and a Job plot based on ^{1}H NMR data indicated the formation of a 1:1 complex **H3⊃G1** (Supporting Information, Figures S7−S10). The associate constant (K_a) of the complex **H3⊃G1** in actone-d_6 was determined to be $(3.0 \pm 0.4) \times 10^2$ M^{-1} (Supporting Information, Figures S11 and S12), which is weaker than that of **H2⊃G1**. The weaker binding affinity of **H3⊃G1** might be due to relatively larger cavity of oxacalixcrown-7 **H3**, which weakens the supramolecular interactions between **H3** and **G1**. Attempts to grow single crystals of complex **H3⊃G1** were unsuccessful.

The complexation of π-electron-rich 1,5-dioxynaphthalene-coorporated oxacalixcrown-6 (**H4**) and -8 (**H5**) with paraquat **G1** was also examined in actone-d_6. Mixing the colorless acetone solutions (10.00 mM) of **H4** (or **H5**) and **G1** resulted in a slight brown solution immediately, implying possible formation of a charge-transfer complex. The ^{1}H NMR spectrum of an equimolar mixture of **H4** and **G1** showed obvious upfield shifts of *α*-, *β*-pyridinium and *N*-methyl proton signals of **G1** (−0.25, −0.32, and −0.13 ppm). However, the chemical shift change of the proton signals of **H4** were small (Supporting Information, Figure S13), suggesting a weak supramolecular interaction between the crown-6 cavity of **H4** and bipyridinium guest **G1**. 2D ^{1}H NMR NOESY spectrum of an equimolar mixture of **H4** and **G1** showed weak correlations between the pyridinium protons of **G1** and the phenyl proton (H_a) of **H4** as well as correlations between the *N*-methyl protons of **G1** and oxyethylene protons of **H4**. No correlations between the pyridinium protons of **G1** and 1,5-dioxynaphthalene protons of **H4** (H_d, H_e, H_f) were observed (Supporting Information, Figure S14). Similar ^{1}H NMR data were obtained for the equimolar mixture of **H5** and **G1** (Supporting Information, Figure S15). 2D ^{1}H NMR NOESY spectrum of an equimolar mixture of **H5** and **G1** showed strong correlations between the *β*-pyridinium protons of **G1** and the phenyl protons (H_a, H_b), as well as the 1,5-dioxynaphthalene protons (H_d) on **H5**, which indicate the existence of supramolecular interactions between the bipyridinium plane of **G1** and the phenyl planes of the oxacalix[4]arene subunit, as well as the *π*-electron-rich 1,5-dioxynaphthalene plane in the polyether chain of **H5** (Supporting Information, Figure S16). The longer polyether linker in **H5** possibly renders the 1,5-dioxynaphthalene plane in a suitable position to interact with the bipyridinium plane of **G1**.

MS (ESI) spectra and Job plots based on ^{1}H NMR data indicated the formation of complexes **H4⊃G1** and **H5⊃G1** in a 1:1 stoichiometry (Supporting Information, Figures S17−S20). The associate constants (K_a) of the complexes **H4⊃G1** and **H5⊃G1** in actone-d_6 were determined to be $(1.3 \pm 0.1) \times 10^2$ M^{-1} and $(4.0 \pm 0.3) \times 10^2$ M^{-1}, respectively (Supporting Information, Figure S21−S24). Attempts to grow single crystals of complexes **H4⊃G1** and **H5⊃G1** were unsuccessful.

With the oxacalixcrowns **H2** and **H4** in hand, we made attempts to synthesize tetracationic cyclophane [**CBPQT**$^{4+}$ or cyclobis(paraquat-*p*-phenylene)]-oxacalixcrowns based [2]-catenanes by utilizing the host−guest interaction between the oxacalixcrown-6 **H2** (or **H4**) and bipyridinium dication, as shown in Scheme 2. The *π*-electron-deficient aromatic diparaquat **G2** could thread through the oxacalixcrown-6 **H2** (or **H4**) directed by the supramolecular interactions between the oxacalixcrown-6 **H2** (or **H4**) and pyridinium cation. Subsequent coupling of the complexes **H2⊃G2** and **H4⊃G2** with a *p*-xylylene moiety afforded two [**CBPQT**$^{4+}$]-oxacalixcrown-6 based [2]catenanes **C1** and **C2**, respectively.

Scheme 2. Synthesis of [2]Catenenes C1, C2, and Their Crystal Structures



The ^{1}H NMR spectra of the [2]catenanes **C1** and **C2** in actone-d_6 showed broad proton signals, which possibly resulted from the rotational restriction imposed by their rigid and crowded structures. The oxyethylene proton signals in **C1** were upfield shifted compared to those of free **H2**, suggesting the inclusion of the ethylene glycol chain inside the [**CBPQT**$^{4+}$] ring. While oxyethylene proton signals in **C2** were downfield shifted compared to those of free **H4**, hinting at the existence of hydrogen-bonding interactions between the bipyridinium protons and oxygen atoms in the polyether chain. ESI-MS also supports the formation of [**CBPQT**$^{4+}$]-oxacalixcrown-6 based [2]catenanes **C1** and **C2** by the presence of peaks at *m/z:* 1562.03 ($[\mathbf{M_{C1}}\text{-}\mathbf{PF_6}]^+$) (Supporting Information, Figure S25) and 1660.17 ($[\mathbf{M_{C2}}\text{-}\mathbf{PF_6^-}]^+$) (Supporting Information, Figure S26), respectively. Single crystals of [2]catenanes **C1** and **C2** suitable for X-ray diffraction analysis were obtained by slow diffusion of toluene into their corresponding acetonitrile sample solutions. As shown in Scheme 2, the threading bipyridinium plane of the **CBPQT**$^{4+}$ ring in **C1** is oriented similar to that in the complex **H2⊃G1**, and a dihedral angle of 49° is observed between the two phenyl rings of the **H2** subunit. One phenyl ring in the oxaclixcrown-6 (**H2**) subunit of **C1** is partly encircled by the **CBPQT**$^{4+}$ ring via mechanical linkage. The structure is stabilized by *π*−*π* stacking and C−H···*π* and hydrogen-bonding interactions. However, in the structure of [2]catenane **C2**, the 1,5-dioxynaphthalene plane of oxacalix-crown-6 (**H4**) subunit is encircled by the **CBPQT**$^{4+}$ ring. The dihedral angle between the two phenyl rings in the **H4** subunit is expanded to 84° to facilitate face-to-edge arrangement between the phenyl rings of the **H4** subunit and the threading pyridinium planes of the **CBPQT**$^{4+}$ ring. The two oxacalix-crown-6 (**H4**) encapsulated pyridinium planes are twisted by 37° in order to maximize the *π*−*π* stacking and C−H···*π* and hydrogen-bonding interactions and, thus, stabilize the mechanically linked structure.

In summary, we have developed a series of oxacalixcrowns derived from oxacalix[2]arene[2]pyrazine and functional polyether chains. Their tunable conformational structures make them efficient hosts for paraquat even with the polyether linker as short as five ethylene glycol units. The complexation study revealed that the paraquat guest threads into the oxacalixcrown cavities and the supramolecular complexes are stabilized by the cooperative effects of *π*−*π* stacking and C−H···*π* and hydrogen-bond interactions. The complexation between the oxacalixcrown and paraquat was successfully employed to template the formation of [**CBPQT**$^{4+}$]-oxacalixcrowns based [2]catenanes. Investigations on the oxacalixcrown related coordination-driven self-assembly and cooperative bindings are currently ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis and NMR of new compounds, NOESY spectra, and electrospray ionization spectra. X-ray data for new compounds (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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