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PAPER

One-pot synthesis of donor–acceptor [2]rotaxanes based on cryptand–paraquat recognition motif†

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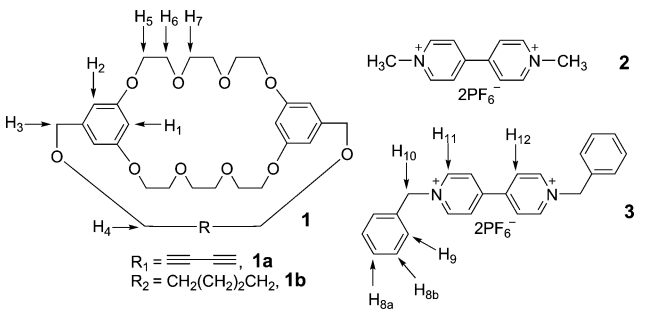
Two novel cryptand-based [2]rotaxanes were synthesized by a facile one-pot reaction from three neutral precursors: easily accessible cryptand host **1** and commercially available 4,4′-bipyridine and 3,5-di-*tert*-butylbenzyl bromide. Their structures were confirmed by ^{1}H NMR, 2D NMR, HRMS and X-ray analysis. Moreover, two [2]pseudorotaxanes based on the same cryptand hosts and dibenzyl viologen guest **3** were also demonstrated both in solution and in the solid state, which are different from previously reported [3]pseudorotaxane-like complexes formed by dimethyl viologen guest **2** and the cryptands.

Introduction

Mechanically interlocked molecules,[1-20] such as rotaxanes,[2] catenanes,[3] knots[4] and Borromean rings[5] have long been of great interest. The development of efficient, convenient, and environmentally friendly methods for the synthesis of these mechanically interlocked molecules has progressed tremendously in the past decades.[6] For example, a variety of molecular rotaxanes have been successfully constructed using a range of recognition systems. The protocols that have been applied to the synthesis of these interlocked molecules remain in general "threading-followed-by-stopping",[7] "threading-followed-by-clipping",[8] "threading-followed-by-shrinking",[9] "slippage",[10] "swelling"[11] and some miscellaneous strategies developed in recent years.[12] Although several approaches for the synthesis of these systems have been explored, they usually require several steps and expensive reagents.[11b,11c,19h] Therefore, it is highly desirable to develop more efficient and concise methods that allow the formation of several bonds in a single reaction process, cutting out the need for several purifications, minimizing chemical waste generation and saving time. Recently, Chiu's group[18a,18b] reported that molecular rotaxanes were synthesized by a one-pot synthesis method based on bis-*p*-xyly[26]-crown-6 (BPX26C6). Additionally, Takata and co-workers described that polyrotaxanes can be formed in water using a one-pot synthesis approach.[18e] However, the recognition systems that can be used for the formation of molecular rotaxanes with neutral molecules by a one-pot approach are rare.[18]

Cryptands are three-dimensional bicyclic hosts with adequate cavities that are suitable for encapsulating ions and small molecules.[19] It has been demonstrated that crown ether-based cryptands including bis(*m*-phenylene)-32-crown-10-based cryptands and bis(*m*-phenylene)-26-crown-8-based cryptands are effective hosts for binding paraquat and its derivatives to form pseudorotaxane-like complexes.[19c–19i] However, only a few examples of mechanically interlocked structures based on crown ether-based cryptands and paraquat derivatives have been reported.[8,19d–19h] Recently, we have reported a high-yielding synthesis of novel cryptands **1a** and **1b**, and demonstrated that they are powerful hosts for complexation with paraquat **2** to form [3]pseudorotaxane-like complexes with noncooperative complexation[19i] (Scheme 1). This result suggested that cryptand **1** might be able to complex to (mono)pyridinium cations in a [2]pseudorotaxane-like fashion in solution, which is crucial for preparation of [2]rotaxane by one-pot reaction. It seems reasonable to expect that [2]rotaxanes based on cryptand–pyridinium may be achieved in a one-pot method from three nonionic starting



Scheme 1 Structure and proton designations of the hosts and the guests.

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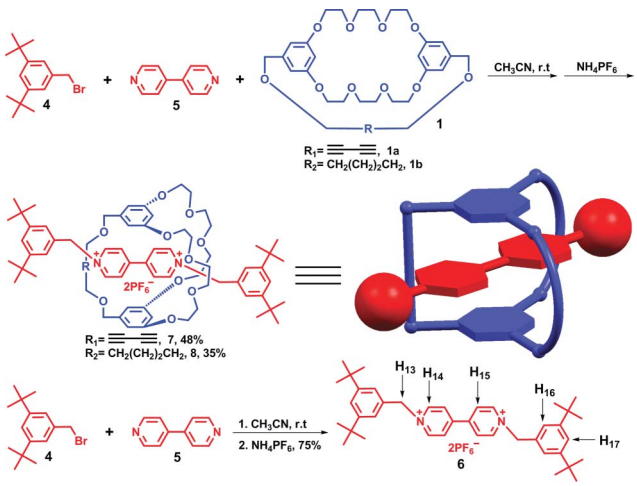
† Electronic supplementary information (ESI) available: Association constants determination, NMR spectra, mass spectra, UV–vis absorption spectra, crystal data for [2]pseudorotaxanes **1a**·**3**, **1b**·**3** and [2]rotaxane **7**. CCDC 788120, 788121 and 788122 for [2]pseudorotaxane **1a**·**3**, **1b**·**3** and [2]rotaxane **7** respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ob00629g

materials.[18a] With continuation of our interest in using these novel cryptands for construction of interlocked structures, herein, we report that (1) two novel cryptand-based [2]rotaxanes **7** and **8** were synthesized through the one-pot reactions of 3,5-di-*tert*-butylbenzyl bromide **4**, and 4,4′-bipyridine **5** and cryptand **1a**/**1b** in CH_3CN (Scheme 2). The rotaxane formation was achieved by direct reaction of easily accessible macrocycles with commercially available neutral reagents without extra-preparation of ionic thread-like precursors which are needed for most of the reported methods.[7–11] Therefore, this approach requires few steps and few purifications. (2) Unlike dimethyl viologen guest **2**, the dibenzyl viologen guest **3** binds with cryptand **1** forming a 1 : 1 complex, *i.e.* [2]pseudorotaxane both in solution and in the solid state.



Scheme 2 One-pot syntheses of [2]rotaxanes **7** and **8** based on crown ether-based cryptands.

Results and discussion

In a previous study,[19i] we have demonstrated that cryptand **1** complexes with paraquat **2** more strongly than the corresponding crown ether, as shown in Scheme 1. Consequently, a new kind of stable 2 : 1 [3]pseudorotaxane-like complex, in which two cryptands **1** encapsulated one paraquat **2**, was formed both in solution and in the solid state. To further understand the complexation between cryptand **1** and paraquat derivatives, the complexation between each of **1a** or **1b** and **3** were investigated.

Interestingly, it was found that cryptand **1** binding paraquat derivative **3** containing two benzyl groups was totally different from the case of the *N*-methyl-substituted paraquat **2**. Job plots[20a] (Fig. 1) and mole ratio plots[20b] (Fig. S3, ESI†) based on proton NMR data suggested that the complexes of either of **1a** and **1b** with **3** were of 1 : 1 stoichiometry in solution. The 1 : 1 stoichiometry of the complexation of each of cryptand **1a** and **1b** with paraquat derivative **3** was also confirmed by electrospray ionization mass spectrometric characterization of solution of cryptand **1a**/**1b** and **3** in acetonitrile. For the mass spectrum of a solution of **1a** and **3** with molar ratio 1 : 1, the base peak was at *m*/*z* 483.22, corresponding to [**3**-PF_6]$^+$. Two peaks were found for **1a**·**3** at *m*/*z* 1065.31 (73%) [**1a**·**3**-PF_6]$^+$, 460.61 (28%) [**1a**·**3**-$2PF_6$]$^{2+}$. For the mass spectrum of a solution of **1b** and **3** with molar ratio 1 : 1, the base peak was at *m*/*z* 483.28, corresponding to [**3**-PF_6]$^+$. Two peaks were found

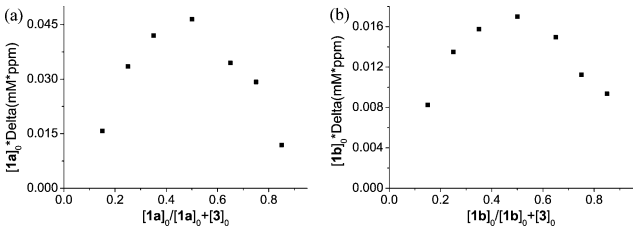


Fig. 1 Job plots of the complexes between (a) cryptand **1a** and paraquat derivative **3**, and (b) cryptand **1b** and paraquat derivative **3** in [D_6]acetone. [**1a**]$_0$ + [**3**]$_0$ = [**1b**]$_0$ + [**3**]$_0$ = 1.0 mM; Delta chemical shift change for H_2 of **1a** and **1b**.

for **1b**·**3** at *m*/*z* 1073.36 (92%) [**1b**·**3**-PF_6]$^+$, 464.56 (49%) [**1b**·**3**-$2PF_6$]$^{2+}$. Moreover, one peak was found for (**1b**)$_2$·**3** at *m*/*z* 1740.17 (6%) [(**1b**)$_2$·**3**-$C_6H_5CH_2$+Na]$^+$. However, no peaks corresponding to other stoichiometries were found in complexation of cryptand **1a** or **1b** with **3** (see ESI†).

Proton NMR spectra of an equimolar (5.00 mM) mixture of either of cryptand **1a** or **1b** with **3** in [D_6]acetone solution at ambient temperature show that the chemical shifts of the protons of the complex are significantly different from those of their free components (Fig. 2). The solution of these complexes was yellow due to charge transfer between the electron-rich aromatic ring of the host and the electron-poor aromatic ring of the guest. No signal of the free species in the spectrum was observed, suggesting that the rates of complexation and decomplexation are fast on the proton NMR time scale. Chemical shift changes of protons on cryptand **1a** and **3** are similar to those of protons on cryptand **1b** and **3** after complexation in CD_3COCD_3. Significant upfield shifts were observed for aromatic protons H_1 and H_2 on host **1**, and pyridinium protons H_{11} and H_{12} on guest **3**, indicating the formation of strong π–π stacking interaction between the π-donor (aromatic rings) and π-acceptor (bipyridinium). The benzyl protons H_3 and α-ethyleneoxy protons H_5 on **1** also moved upfield, while α-protons H_4 of alkyne/alkane, β-ethyleneoxy protons H_6 and γ- ethyleneoxy protons H_7 on **1** and aromatic protons H_8 and H_9 on **3** moved downfield.

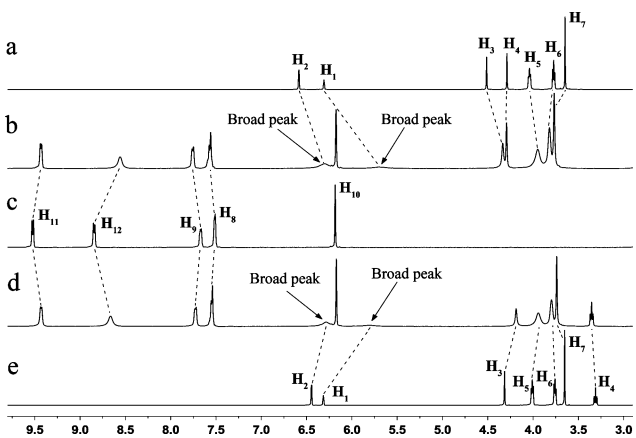


Fig. 2 Partial proton NMR spectra (400 MHz, acetone-d_6, 22 °C) of (a) 5.00 mM cryptand **1a**, (b) 5.00 mM **1a** with 5.00 mM **3**, (c) 5.00 mM paraquat derivative **3**, (d) 5.00 mM **1b** with 5.00 mM **3** and (e) 5.00 mM cryptand **1b**.

To obtain understanding of the complexation behavior of the cryptand **1a** or **1b** with paraquat derivative **3**, proton NMR characterizations were done on a series of acetone solutions for which the initial concentration of guest **3** was kept constant at 0.5 mM while the initial concentration of host **1a** or **1b** was varied systematically. Using the Benesi–Hildebrand method,[21] the association constants (K_a) were determined for these systems in CD_3COCD_3 to be K = 403 ± 27 M^{-1} and K = 186 ± 7 M^{-1}, respectively (Fig. 3). In the same way, we also determined the K_a for these systems in CD_3CN to be $K = 211 \pm 9$ M^{-1} and $K = 140 \pm 4$ M^{-1}, respectively (see ESI†). The binding affinity of cryptand **1a** or **1b** toward the paraquat derivative **3** is substantially weaker than that of paraquat **2**,[19i] possibly because of the worse geometric structure threading through the cavity of the host and less hydrogen bonding interactions as shown by the following X-ray analysis (Fig. 4 and 5).

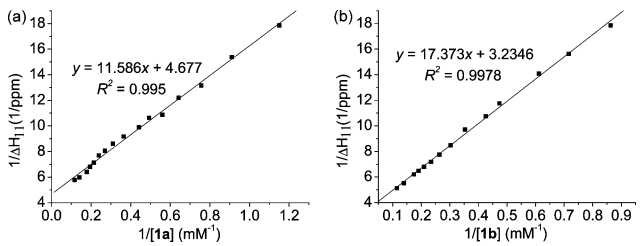


Fig. 3 Benesi–Hildebrand plots for the formation of [2]pseudorotaxanes (a) cryptand **1a** with paraquat derivative **3** and (b) cryptand **1b** with paraquat derivative **3**, based on the data for proton H_{11} at 22 °C in [D_6]acetone. $[\mathbf{3}]_0 = 0.50$ mM.

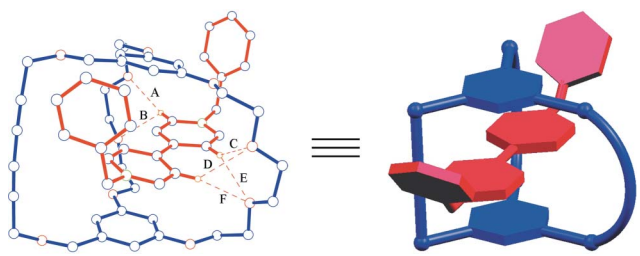


Fig. 4 Ball-and-stick representations of the X-ray structure of [2]pseudorotaxane **1a**·**3**. The PF_6 counterions and hydrogens except the ones involved in hydrogen bonding between **1a** and **3** have been omitted for clarity. Hydrogen-bond parameters: H···O distances (Å), C–H···O angles (degrees), C···O distances (Å) **A** 2.42, 151.50, 3.27; **B** 2.47, 120.97, 3.06; **C** 2.79, 147.32, 3.60; **D** 2.61, 124.02, 3.23; **E** 2.38, 148.67, 3.21; **F** 2.39, 168.18, 3.31; Face-to-face π-stacking parameters: centroid–centroid distances (Å): 4.18, 4.14, 3.61, 4.80; ring plane/ring plane inclinations (degrees): 9.37, 11.59, 8.99, 1.82; The centroid–centroid distance (Å) and dihedral angle (degrees) between the two phenylene rings of **1a**: 6.89, 10.64. The centroid–centroid distance (Å) and dihedral angle (degrees) between the two pyridinium rings of **3**: 4.27, 10.80.

Further evidence from X-ray analysis unambiguously confirmed the 1 : 1 complex formation. X-ray analysis[22] was carried out with a pale red crystal of **1a**·**3** grown by slow evaporation of an acetone solution of **3** with excess **1a**. The crystal structures obviously showed the [2]pseudorotaxane-type geometry for complex **1a**·**3** (Fig. 4). The 1 : 1 complex **1a**·**3** is stabilized in the solid state by hydrogen bonding between host and guest and face-to-face π-stacking interaction between the aromatic rings of **1a** and the

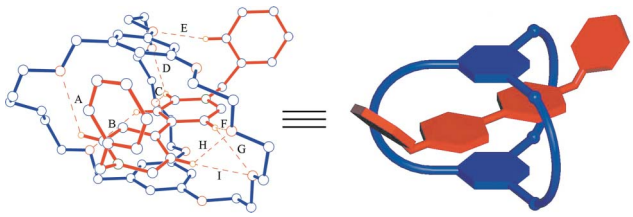


Fig. 5 Ball-and-stick representations of the X-ray structure of [2]pseudorotaxane **1b**·**3**. The PF_6 counterions and hydrogens except the ones involved in hydrogen bonding between **1b** and **3** have been omitted for clarity. Hydrogen-bond parameters: H···O distances (Å), C–H···O angles (degrees), C···O distances (Å) **A** 2.71, 125.22, 3.34; **B** 2.74, 146.78, 3.56; **C** 2.49, 147.94, 3.31; **D** 2.48, 139.06, 3.24; **E** 2.64, 146.72, 3.45; **F** 2.75, 150.95, 3.59; **G** 2.38, 142.36, 3.17; **H** 2.74, 105.81, 3.13; **I** 2.45, 169.31, 3.64; Face-to-face π-stacking parameters: centroid–centroid distances (Å): 4.29, 4.26, 4.73, 3.86; ring plane/ring plane inclinations (degrees): 17.96, 17.38, 20.68, 6.04; The centroid–centroid distance (Å) and dihedral angle (degrees) between the two phenylene rings of **1b**: 6.82, 11.87; The centroid–centroid distance (Å) and dihedral angle (degrees) between the two pyridinium rings of **3**: 4.23, 26.04.

pyridinium rings of **3**. Interestingly, in the crystal structure of **1a**·**3**, one α-pyridinium hydrogen atom of **3** is directly connected to the host through two hydrogen bonds (**A** and **B** in Fig. 4), and two β-pyridinium hydrogen atoms of **3** are directly hydrogen-bonded to ethyleneoxy oxygen atoms of **1a**, forming four hydrogen bonds (**C**, **D**, **E** and **F** in Fig. 4), unlike in the case of the complex (**1a**)$_2$·**2** which is connected by four hydrogen bonds with two α-pyridinium hydrogen atoms and six hydrogen bonds with four β-pyridinium hydrogen atoms of **2**.[19i] The value of the dihedral angle between the two pyridinium rings of **3** in **1a**·**3** is 10.80° and the two aromatic rings of the cryptand host in **1a**·**3** are almost parallel (10.64°) with a centroid–centroid distance of 6.89 Å, a value smaller than the corresponding values, 6.91 Å in complex (**1a**)$_2$·**2**, and 6.93 Å in complex (**1b**)$_2$·**2**, whose crystals are yellow.[19i] These rotational changes take place presumably in order to maximize face-to-face π-stacking interaction and charge transfer interactions between the two electron-rich phenylene rings of the cryptand and the two electron-poor pyridinium rings of the paraquat derivative guest, leading to the pale red color of crystal of **1a**·**3**.

The 1 : 1 stoichiometry of complexation between **1b** and **3** was also confirmed by its solid state structure. As in the 1 : 1 complex between **1a** and **3**, the complex **1b**·**3** has also a [2]pseudorotaxane geometry and is stabilized by several hydrogen bonds (A-I in Fig. 5) and face-to-face π-stacking interactions between the host and guest in the solid state. It is noteworthy that both the worse size fit and the less hydrogen bonding interactions between the alkyl chain of guest with the host **1a**/**1b** account for the above mentioned association constant decrease from (**1a**$_2$)·**2** to **1a**·**3** and (**1b**$_2$)·**2** to **1b**·**3**, respectively. An obvious difference between the crystal structures of complex **1a**·**3** and **1b**·**3** is the dihedral angle between the two pyridinium rings of **3** (10.80° for **1a**·**3** and 26.04° for **1b**·**3**). This twisted conformation presumably results from the maximization of hydrogen bonding interactions as well as face-to-face π-stacking interactions between the host and guest.

Based on the knowledge that (1) cryptand **1** binding **2** in 2 : 1 stoichiometry suggests that it may recognize (mono)pyridinium ions forming [2]pseudorotaxane-like geometry in solution; (2) cryptand **1** is capable of forming complexes with paraquat

derivative **3** in [2]pseudorotaxane-type complexes both in solution and in the solid state, we decided to explore a concise preparation of the desired molecular [2]rotaxanes **7** and **8** from three neutral starting compounds (*i.e.* cryptand **1a** or **1b**, 3,5-di-*tert*-butylbenzyl bromide **4**, and 4,4′-bipyridine **5**) by a one-pot reaction, as shown in Scheme 2. Gratifyingly, we have successfully prepared the [2]rotaxanes **7** and **8** from the reactions of cryptand **1a** or **1b**, 3,5-di-*tert*-butylbenzyl bromide **4**, and 4,4′-bipyridine **5**, respectively.

The synthesis of [2]rotaxane **7** was achieved by simply mixing cryptand **1a**, 3,5-di-*tert*-butylbenzyl bromide **4** and 4,4′-bipyridine **5** in a stoichiometry of 1 : 2 : 1 in CH_3CN and further stirring the reaction mixture at ambient temperature for two weeks. After column chromatography and counterion exchange, the desired [2]rotaxane **7** was obtained in 48% yield. The interlocked architecture of **7** was confirmed by comparing the ^{1}H NMR spectra of cryptand **1a**, [2]rotaxane **7** and the dumbbell-shaped component **6**[23] in CD_3COCD_3 (Fig. 6). In comparison with the free cryptand **1a**, dramatic upfield shifts were observed for the signals of the aromatic protons H_2 ($\Delta\delta_1$ = –0.05 ppm and $\Delta\delta_2$ = –1.05 ppm) and H_1 ($\Delta\delta$ = –1.25 ppm) of the cryptand **1a**. Synchronously, comparison between the spectra of the dumbbell-shaped component **6** and [2]rotaxane **7** reveals the presence and the localization of the macrocycle. The signals of pyridinium protons H_{14} and H_{15} and the *N*-methylene H_{13} on **6** moved upfield while the phenyl protons H_{16} and H_{17} moved downfield, exhibiting the formation of strong π–π stacking interaction between the π-donor (aromatic rings) and π-acceptor (bipyridinium). Most of the signals of the other hydrogens are more or less shifted in the rotaxane due to the shielding effect and hydrogen bonding. Furthermore, the proton H_2 on **1a** and protons H_{14}, H_{15} and H_{13} on **6** were all split into two sets (Fig. 6b), confirming that the threading of paraquat derivatives into the cavity of cryptand **1a** is unsymmetrical.

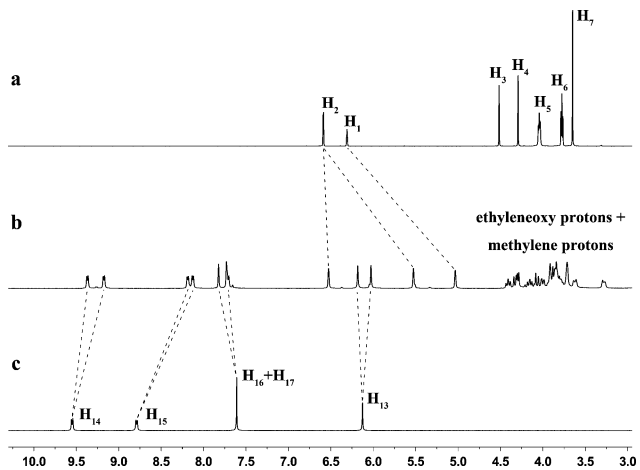


Fig. 6 Partial proton NMR spectra (400 MHz, acetone-d_6, 22 °C) of (a) cryptand **1a**, (b) [2]rotaxane **7** and (c) dumbbell-shaped compound **6**.

The formation of mechanically interlocked [2]rotaxane **7** was further confirmed by its low- and high-resolution electrospray ionization mass spectra (ESIMS). Two relevant peaks were observed in its low-resolution ESIMS: the peak at m/z = 1289.88 (74%) corresponds to $[\mathbf{7}\text{-}PF_6]^+$ and the peak at m/z = 572.69 (100%) corresponds to $[\mathbf{7}\text{-}2PF_6]^{2+}$. Three relevant peaks were observed in its high-resolution ESIMS: m/z calcd for $[\mathbf{7}\text{-}PF_6]^+$, $C_{72}H_{92}F_6N_2O_{10}P$, 1289.6388, found 1289.6435, error 3.6 ppm; calcd for $[\mathbf{7}\text{-H-}2PF_6]^+$, $C_{72}H_{91}N_2O_{10}$, 1143.6668, found 1143.6678, error 0.9 ppm and calcd for $[\mathbf{7}\text{-}2PF_6]^{2+}$, $C_{72}H_{92}N_2O_{10}$, 572.3370, found 572.3370, error 0 ppm. Moreover, the structure of [2]rotaxane **7** was also deduced from 2D NMR spectra, including H–H COSY, C–H COSY, H–H NOESY and C–H HMQC (see ESI†). The through-space correlations between the paraquat proton H_{14-15} and the aromatic H_{1-2} and as well as ethyleneoxy protons of the host were observed in the NOESY spectrum of [2]rotaxane **7**, indicating the existence of interactions between the cryptand and the dumbbell-shaped component (Fig. 7).

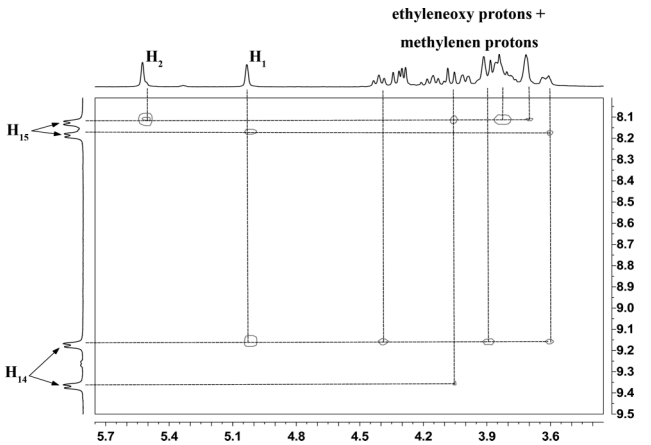


Fig. 7 Partial H–H NOESY spectrum (400 MHz, acetone-d_6, 22 °C) of [2]rotaxane **7**.

Fortunately, we obtained single crystals suitable for X-ray crystallography by vapor diffusion of isopropyl ether into an acetone solution of [2]rotaxane **7**. The solid-state structure in Fig. 8 reveals the expected [2]rotaxane geometry, confirming the threadlike unit is penetrated through two different 26-membered rings of the cryptand **1a**. Similar to the [2]pseudorotaxane between cryptand **1a** and **3**, in the solid state, [2]rotaxane **7** is stabilized by multiple noncovalent interactions, including hydrogen bonding (A–G in Fig. 8), face-to-face π-stacking interaction and

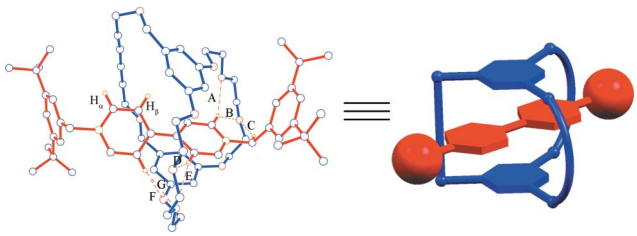


Fig. 8 Ball-and-stick representations of the X-ray structure of [2]rotaxanes **7**. The PF_6 counterions and hydrogens except the ones involved in hydrogen bonding have been omitted for clarity. Hydrogen-bond parameters: H···O distances (Å), C–H···O angles (degrees), C···O distances (Å) **A** 2.43, 146.13, 3.25; **B** 2.55, 142.83, 3.33; **C** 2.58, 154.94, 3.48; **D** 2.52, 151.89, 3.37; **E** 2.42, 139.18, 3.19; **F** 2.64, 129.57, 3.31; **G** 2.66, 159.66, 3.55; Face-to-face π-stacking parameters: centroid–centroid distances (Å): 4.58, 4.27, 5.06, 3.46; ring plane/ring plane inclinations (degrees): 40.15, 28.27, 36.43, 2.81; The centroid–centroid distance (Å) and dihedral angle (degrees) between the two phenylene rings of **1a**: 7.24, 30.31; The centroid–centroid distance (Å) and dihedral angle (degrees) between the two pyridinium rings of **6**: 4.24, 37.83.

[C–H . . . π] interactions. The two phenyl rings of the cryptand in **7** are not parallel, but adopt a dihedral angle of 30.31°, much bigger than the corresponding value, 10.64, for complex **1a**·**3**. The viologen moiety in the [2]rotaxane **7** is not coplanar, the dihedral angle of the pyridinium rings is 37.83°, which is three times greater than the corresponding value, 10.80°, for the complex **1a**·**3**. Furthermore, two [C–H . . . π] interactions can be also found between two hydrogens of the pyridinium ring (H_α and H_β) and the diacetylene unit of the cryptand; the distances between the center of the diacetylene unit and the hydrogens of the pyridinium ring are 2.88 Å and 2.98 Å, respectively.

This concise preparation of [2]rotaxane *via* a one-pot reaction was also demonstrated by the successful synthesis of [2]rotaxane **8** (35%). The mechanically interlocked structure of **8** was also fully characterized. Partial ^{1}H NMR spectra of cryptand **1b**, [2]rotaxane **8** and the dumbbell-shaped component **6** in CD_3COCD_3 are shown in Fig. 9. After the formation of [2]rotaxane **8**, similar to the [2]rotaxane **7**, the aromatic protons H_2 ($\Delta\delta_1$ = 0.06 ppm and $\Delta\delta_2$ = −0.86 ppm) and H_1 ($\Delta\delta$ = −1.18 ppm) of the cryptand **1b** moved dramatically upfield. Significant upfield shifts were also observed for the signals of pyridinium protons H_{14} and H_{15} and the *N*-methylene H_{13} on **6**, while the benzyl protons H_{16} and H_{17} moved downfield. Furthermore, the proton H_2 on **1b** and protons H_{14}, H_{15} and H_{13} on **6** were all divided into two different types (Fig. 9b), suggesting that the threading of paraquat derivatives into the cavity of cryptand **1b** is unsymmetrical.

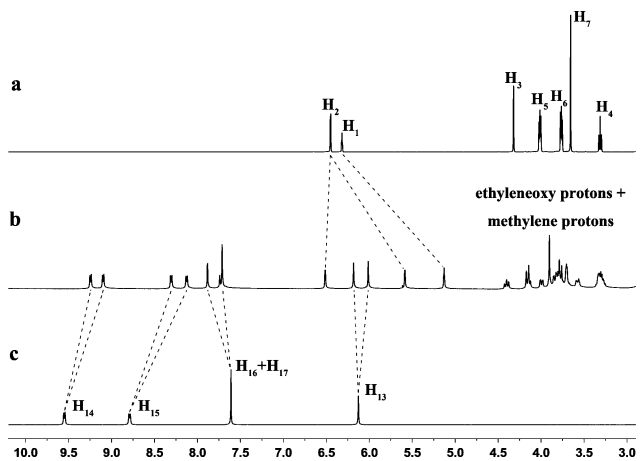


Fig. 9 Partial proton NMR spectra (400 MHz, acetone-d_6, 22 °C) of (a) cryptand **1b**, (b) [2]rotaxane **8** and (c) dumbbell-shaped compound **6**.

In its low- and high-resolution electrospray ionization mass spectra (ESIMS), three relevant peaks were observed in its low-resolution ESIMS: the peak at m/z = 1465.29 (6%) corresponds to [**8**+Na]$^+$, m/z = 1297.91 (100%) corresponds to [**8**-PF_6]$^+$ and the peak at m/z = 576.71 (38%) corresponds to [**8**-2 PF_6]$^{2+}$. Three relevant peaks were observed in its high-resolution ESIMS: m/z calcd for [**8**-PF_6]$^+$, $C_{72}H_{100}F_6N_2O_{10}P$, 1297.7014, found 1297.7056, error 3.2 ppm; calcd for [**8**-H-2PF_6]$^+$, $C_{72}H_{99}N_2O_{10}$, 1151.7294, found 1151.7331, error 3.2 ppm and calcd for [**8**-2PF_6]$^{2+}$, $C_{72}H_{100}N_2O_{10}$, 576.3684, found 576.3696, error 2.0 ppm. In addition, the structure of [2]rotaxane **8** was also deduced from 2D NMR spectra, including H–H COSY, C–H COSY, H–H NOESY and C–H HMQC (see ESI†). From two-dimensional NOESY NMR spectrum of [2]rotaxane **8** (Fig. 10), strong correlations are observed between

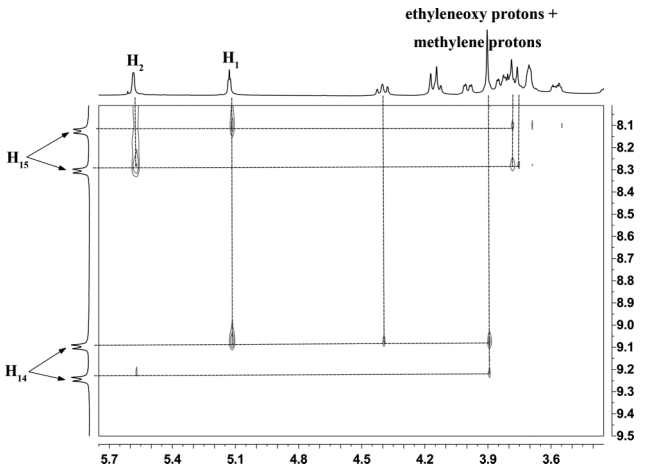


Fig. 10 Partial H–H NOESY spectrum (400 MHz, acetone-d_6, 22 °C) of [2]rotaxane **8**.

the paraquat proton H_{14-15} and the aromatic H_{1-2} as well as the ethyleneoxy protons of the guest **6**, confirming the occurrence of crown ether-based cryptand–paraquat complexation.

Finally, the absorption UV–vis spectra (Fig. S24, ESI†) of [2]rotaxanes **7** and **8** recorded in acetonitrile shown a broad charge-transfer (CT) band centered at about 380 nm (λ_{max}), a feature which is characteristic of donor–acceptor interactions involving cryptand–paraquat and is responsible for their yellow color.

Conclusions

In summary, unlike complexation with dimethyl viologen guest **2**, which forms [3]pseudorotaxane-like complexes,[19i] bis(*m*-phenylene)-26-crown-8-based cryptand **1** is capable of forming [2]pseudorotaxane-type complexes with dibenzyl viologen guest **3** both in solution and in the solid state. Especially, we have demonstrated that the cryptand-based [2]rotaxanes **7** and **8** can be easily prepared by one-pot reactions of three nonionic starting materials under mild conditions. Although the yield for rotaxane formation needs to be improved, this approach requires few steps and purifications. We believe that this current method would provide further opportunities for the assembly of incrementally more complex interlocked systems from simple neutral materials. Further work will be focused on the preparation of interlocked polymers and more intricate mechanically interlocked molecules by the polymerization of diacetylene units to generate unique π-conjugated mechanically interlocked polymers with π-conjugated backbones. Now, we intend to explore these possibilities.

Experimental

Unless specified otherwise, all reagents were purchased from commercial suppliers and used as received. CH_3CN was distilled over CaH_2. All reactions were carried out under an atmosphere of N_2. Cryptand **1a**/**1b** was prepared according to the published literature procedures.[19i] Melting points were determined on an Electrothermal x-5 melting point apparatus and are uncorrected. Thin-layer chromatography was performed on QingDao silica gel. NMR spectra were recorded at ambient temperature with Varian NMR system 400 MHz by using the deuterated solvent as the lock

and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with Thermo Finnigan LCQ Deca XP Max LC/MSn. High-resolution electrospray ionization mass spectra were recorded on Bruker Apex IV FTMS at Peking University. X-ray crystallographic was performed on Bruker SMART APEX II.

Synthesis of dumbbell-shaped compound 6

A mixture of 3,5-di-*tert*-butylbenzyl bromide **4** (187 mg, 0.66 mmol) and 4,4′-bipyridine **5** (46.9 mg, 0.3 mmol) was dissolved in CH_3CN and was stirred under N_2 for 10 days at 50–60 °C. Diethyl ether was added to the resulting light green solution and the precipitate was filtered off. This solid was dissolved in MeOH–CH_2Cl_2 and saturated aqueous NH_4PF_6 was added. The organic solvent was then evaporated under reduced pressure. The precipitate was collected and washed with H_2O to yield **6**[23] as a white solid (190 mg, 75%). Mp: >250 °C. ^{1}H NMR (400 MHz, acetone-d_6, 22 °C): δ = 9.57 (d, J = 8 Hz, 4 H), 8.81 (d, J = 4 Hz, 4 H), 7.62 (s, 6 H), 6.14 (s, 4 H), 1.32 (s, 36 H). LRESIMS: m/z = 562.62 [M-2PF_6]$^+$ and 707.39 [M-PF_6]$^+$.

Synthesis of [2]rotaxane 7

A mixture of 3,5-di-*tert*-butylbenzyl bromide **4** (59 mg, 0.2 mmol), 4,4′-bipyridine **5** (15.6 mg, 0.1 mmol) and cryptand **1a** (58 mg, 0.1 mmol) in MeCN (3 mL) was stirred under N_2 for two weeks at ambient temperature. Removal of acetonitrile afforded a pale yellow solid and the crude compound was purified by column chromatography [SiO_2; ethyl acetate–CH_2Cl_2, 3 : 7, v/v → CH_2Cl_2–MeOH, 10 : 1, v/v] to give a yellow solid. This solid was dissolved in acetone/H_2O and saturated aqueous NH_4PF_6 was added; the organic solvent was then evaporated under reduced pressure. The precipitate was collected and washed with H_2O to afford [2]rotaxane **7** (69 mg, 48%) as a yellow solid. Mp: 217–223 °C. ^{1}H NMR (400 MHz, acetone-d_6, 22 °C) δ = 9.39 (d, J = 4 Hz, 2 H), 9.19 (d, J = 8 Hz, 2 H), 8.17 (dd, J = 4, 4 Hz, 4 H), 7.84 (s, 2H), 7.73 (d, J = 12 Hz, 4 H), 6.54 (s, 2 H), 6.20 (s, 2 H), 6.04 (s, 2 H), 5.54 (s, 2 H), 5.05 (s, 2 H), 4.43 (t, J = 12 Hz, 2 H), 4.33 – 4.30 (m, 4 H), 4.17 (t, J = 12 Hz, 2 H), 4.13 – 3.98 (m, 4 H), 3.97 – 3.80 (m, 12 H), 3.73 (s, 4 H), 3.64 (d, J = 12.0 Hz, 2 H), 3.30 (d, J = 8 Hz, 2 H), 1.39 (s, 36 H). ^{13}C NMR (100 MHz, acetone-d_6, 22 °C) δ = 159.61, 158.18, 152.57, 152.52, 148.65, 147.17, 144.60, 144.56, 140.73, 132.47, 132.19, 127.05, 126.83, 125.24, 124.62, 124.41, 124.14, 105.29, 102.10, 100.05, 78.47, 71.02, 70.85, 70.38, 70.23, 69.93, 69.80, 67.30, 66.18, 66.77, 65.55, 65.44, 64.73, 58.29, 34.90, 34.86, 30.83, 30.80. LRESIMS: m/z = 1289.88 [**7**-PF_6]$^+$ and 572.69 [**7**-2PF_6]$^{2+}$. HRESIMS: m/z calcd for [**7**-PF_6]$^+$, $C_{72}H_{92}F_6N_2O_{10}P$, 1289.6388, found 1289.6435, error 3.6 ppm; calcd for [**7**-H-2PF_6]$^+$, $C_{72}H_{91}N_2O_{10}$, 1143.6668, found 1143.6678, error 0.9 ppm and calcd for [**7**-2PF_6]$^{2+}$, $C_{72}H_{92}N_2O_{10}$, 572.3370, found 572.3370, error 0 ppm.

Synthesis of [2]rotaxane 8

A mixture of 3,5-di-*tert*-butylbenzyl bromide **4** (45 mg, 0.16 mmol), 4,4′-dipyridyl **5** (12.5 mg, 0.08 mmol) and cryptand **1b** (47 mg, 0.08 mmol) in MeCN (3 mL) was stirred under N_2 for two weeks at ambient temperature. Removal of acetonitrile afforded a pale yellow solid and the crude compound was purified by column chromatography [SiO_2; ethyl acetate–CH_2Cl_2, 3 : 7, v/v → CH_2Cl_2–MeOH, 10 : 2, v/v] to give a yellow solid. This solid was dissolved in acetone/H_2O and saturated aqueous NH_4PF_6 was added; the organic solvent was then evaporated under reduced pressure. The precipitate was collected and washed with H_2O to afford [2]rotaxane **8** (41 mg, 35%) as a yellow solid. Mp: 248–250 °C. ^{1}H NMR (400 MHz, acetone-d_6, 22 °C) δ = 9.26 (d, J = 12 Hz, 2 H), 9.12 (d, J = 4 Hz, 2 H), 8.32 (d, J = 4 Hz, 2 H), 8.14 (d, J = 4 Hz, 2 H), 7.90 (d, J = 2 Hz, 2 H), 7.76 (t, J = 4 Hz, 1 H), 7.73 (s, 3 H), 6.53 (s, 2 H), 6.20 (s, 2 H), 6.03 (s, 2 H), 5.60 (s, 2 H), 5.15 (t, J = 2.0 Hz, 2 H), 4.42 (t, J = 8 Hz, 2 H), 4.17 (d, J = 12 Hz, 4 H), 4.03 (dd, J = 4, 2 Hz, 2 H), 3.92 (s, 4 H), 3.90 – 3.78 (m, 10 H), 3.72 (m, 4 H), 3.64 – 3.55 (m, 2 H), 3.44 – 3.21 (m, 8 H), 1.40 (d, J = 8 Hz, 40 H). ^{13}C NMR (100 MHz, acetone-d_6, 22 °C) δ = 159.81, 158.11, 152.71, 152.58, 148.64, 146.82, 144.40, 140.93, 132.13, 131.96, 127.60, 126.76, 125.59, 124.85, 124.48, 124.16, 107.64, 103.56, 100.23, 73.04, 71.03, 70.81, 70.39, 70.02, 69.75, 67.25, 66.74, 65.28, 64.78, 34.93, 34.85, 30.85, 29.81, 26.66. LRESIMS: m/z = 1465.29 [**8**+Na]$^+$, 1297.91 [**8**-PF_6]$^+$ and 576.71 [**8**-2 PF_6]$^{2+}$. HRESIMS: m/z calcd for [**8**-PF_6]$^+$, $C_{72}H_{100}F_6N_2O_{10}P$, 1297.7014, found 1297.7056, error 3.2 ppm; calcd for [**8**-H-2PF_6]$^+$, $C_{72}H_{99}N_2O_{10}$, 1151.7294, found 1151.7331, error 3.2 ppm and calcd for [**8**-2PF_6]$^{2+}$, $C_{72}H_{100}N_2O_{10}$, 576.3684, found 576.3696, error 2.0 ppm.

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23 P. R. Ashton, M. C. T. Fyfe, M.-V. Martínez-Díaz, S. Menzer, C. Schiavo, J. F. Stoddart, A. J. P. White and D. J. Williams, *Chem.–Eur. J.*, 1998, **4**, 1523–1534.