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A Novel Supramolecular System: Combination of Two Switchable Processes in a [2]Rotaxane

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Abstract: A novel supramolecular system, which is made up of a dibenzo[24]crown-8 (DB24C8) ring component linked with a calix[4]arene derivative, a dumbbell component, containing a secondary ammonium center ($-NR_2H_2^+-$) and a 4,4′-bipyridinium ($BIPY^{2+}$) unit, and stoppered with two 3,5-di-*tert*-butylphenyl groups on the two termini of the dumbbell component, has been synthesized. The system displays a combination of two processes: the pH-induced shuttling of a DB24C8 ring and the complexation/decomplexation of K^+ ions. The switching process of this supramolecular system was investigated in detail by ^1H NMR spectroscopy. The results showed that the supramolecular system can only switch smoothly in CD_3CN. The two separated switchable processes can run together smoothly in this supramolecular system.

Keywords: calixarenes · rotaxanes · complexation · molecular devices · supramolecular chemistry

Introduction

With the great development of biotechnology and biochemistry in the past decades, scientists have been inspired to construct artificial molecular machines for mimicking natural motors.[1–5] Supramolecular systems such as "molecular motors",[6–12] "molecular shuttles",[13–21] "molecular muscles",[22–24] "molecular walkers",[25,26] and "molecular elevators"[27,28] have been reported. Variations in these supramolecular architectures show remarkable properties. The well-known [2]rotaxane system contains two different recognition sites in the dumbbell component while the ring unit can be moved between the two recognition sites by an external stimulus.[29,30] The controlled switching of the molecular shuttle in response to an external stimulus suggests the possibility to construct a novel [2]rotaxane-based supramolecular system for a certain function.[31–33] The Stoddart group has reported a so-called molecular elevator based on a pH-switchable [2]rotaxane.[27] The Leigh group has shown that switching of a light-controllable molecular shuttle can move small drops of low-volatility liquids.[34] The investigation of a supramolecular system, which combines two switchable processes in a [2]rotaxane is useful for the construction of molecular-level devices. Here, we report the design and synthesis of a novel [2]rotaxane-based supramolecular system, which combines two processes: the acid–base switchable shuttling of a DB24C8 ring and the controlled complexation/decomplexation of K^+ ions with the calix[4]arene derivative. Our [2]rotaxane is made up of a DB24C8-ring component linked to a calix[4]arene derivative, a dumbbell component containing a secondary ammonium center ($NR_2H_2^+$) and a 4,4′-bipyridinium^{2+} ($BIPY^{2+}$) unit stoppered with 3,5-di-*tert*-butylphenyl groups on the termini of the dumbbell (Figure 1). At low pH, the DB24C8 ring binds the $-CH_2NH_2^+CH_2-$ site preferentially. At high pH, deprotonation occurs resulting in the loss of hydrogen bonding and therefore, the macrocycle moves to the $BIPY^{2+}$ site because of the more favorable π–π stacking interactions. Shuttling of the DB24C8 ring causes movement of the calix[4]arene host linked to the DB24C8, a process which is reversible. Meanwhile, the calix[4]arene derivative can form a 1:1 complex with K^+ ions,[35] and the ability of K^+ to complex with 18-crown-6 is stronger than the ability of K^+ to complex with the calix[4]arene derivative.[36] Thus, the addition of 18-

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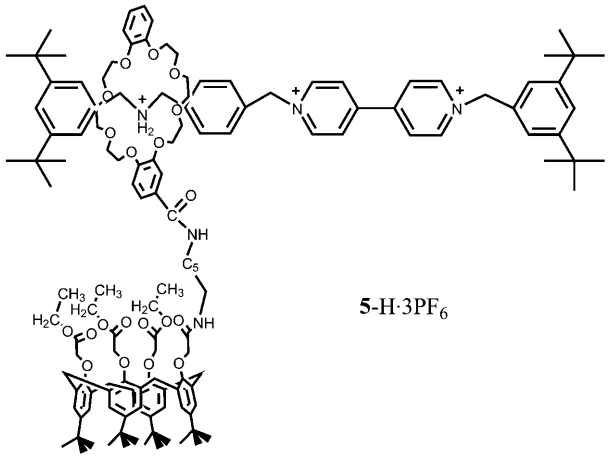


5-H·3PF$_6$

Figure 1. The molecular structure of the [2]rotaxane **5**-H·3PF$_6$.

crown-6 can capture the K^+ complexed with the calix[4]arene. As a result, the complexation/decomplexation of K^+ ions with the calix[4]arene derivative can be controlled reversibly.

Results and Discussion

The synthesis of compounds **1**, **2**, and **4**-H·2PF$_6$ was carried out according to known literature procedures.[37–39] Calix-crown **3** (74% yield) was synthesized by condensation of crown ether carboxylic acid **1** and amino-calix[4]arene **2** in the presence of 1-(3-dimethylaminopropyl)-3-ethylecarbodiimide hydrochloride (EDCI) and 4-(dimethylamino)-pyridine (DMAP) in CH_2Cl_2. The [2]rotaxane **5**-H·3PF$_6$ (26% yield) was assembled by the formation of a stable 1:1 complex of precursor **4**-H·2PF$_6$ containing the (-NH_2^+-) functionality and calix-crown **3**, followed by stoppering at the thread's open ends to interlock the ring (Scheme 1).

High-resolution electrospray ionization (HR-ESI) mass spectroscopy revealed (see Supporting Information) that the most intense signal in the spectra occurred at $m/z = 740.1167$ for the **5**-H·3PF$_6$, with an isotope distribution corresponding to $[M-3PF_6]^{3+}$. This result supports the structural assignment of the mechanically interlocked [2]rotaxane **5**-H·3PF$_6$. The ^{1}H–^{1}H-COSY spectrum of the [2]rotaxane **5**-H·3PF$_6$ is depicted in Figure 2. With the help of the ^{1}H–^{1}H-COSY spectrum, the signals in the regions of $\delta = 6$–8 ppm and $\delta =$ 3–5 ppm could be assigned clearly. As a result, two sets of signals at $\delta = 4.77$ ppm and $\delta = 4.72$ ppm were assigned to H_e and H_f adjacent to the secondary dialkylammonium center. The H_n and H_o were assigned to be $\delta = 8.00$ ppm and $\delta =$ 7.18 ppm, the signals of H_j, H_k, H_l, H_m for calix[4]arene, and H_p, H_q, H_r, H_s, H_t for the DB24C8 were all assigned in Figure 3b.

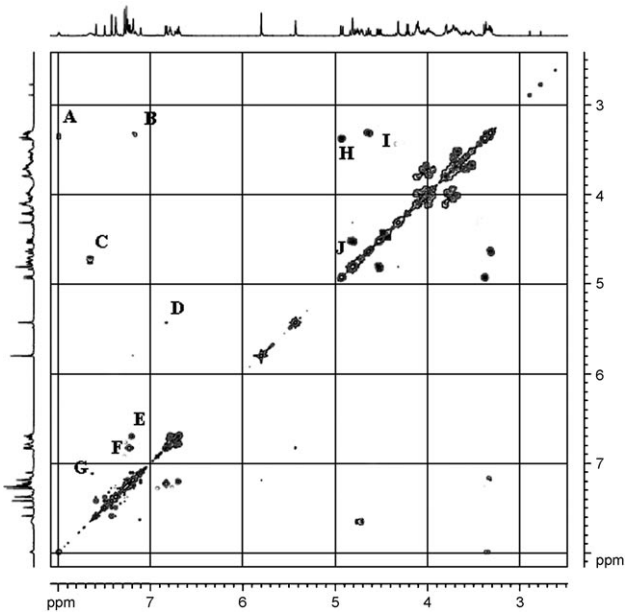


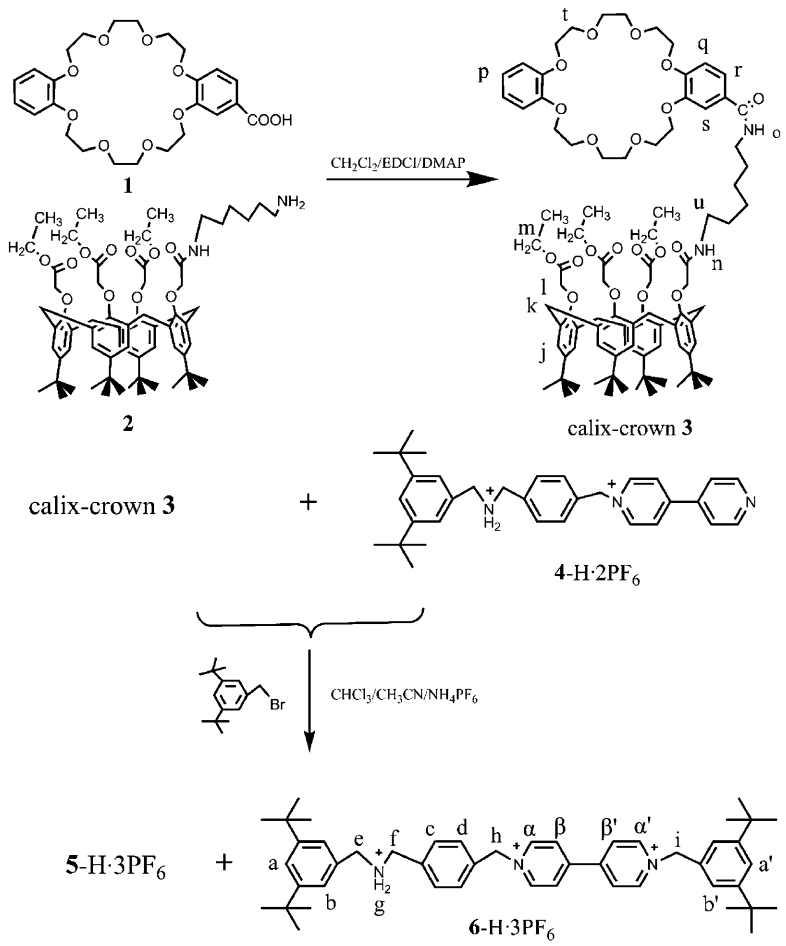
Figure 2. The ^{1}H–^{1}H COSY spectrum of **5**-H·3PF$_6$ in CD_3CN. **A**: H_n/H_u ; **B**: H_o/H_u; **C**: $H_{e,f}/H_g$; **D**: H_d/H_h; **E**: H_t/H_q; **F**: H_c/H_d; **G**: H_s/H_g; **H**: H_k/H_k; **I**: $H_k/H_{k;}$ **J**: H_l/H_l.

The ^{1}H NMR spectra of the thread **6**-H·3PF$_6$, calix-crown **3**, and the [2]rotaxane **5**-H·3PF$_6$ were recorded in CD_3CN (Figure 3). The signals between 3.8 ppm and 4.2 ppm (Figure 3c), relative to the protons H_t of *O*-methylene in DB24C8, changed from two doublets and one singlet to several multiplets in [2]rotaxane **5**-H·3PF$_6$ (Figure 3b). This is a consequence of the pairs of protons in each of the *O*-methylene groups becoming diastereotopic for the interlock.[27] The methylene protons H_e and H_f adjacent to the secondary dialkylammonium centers were shifted downfield from 4.25 ppm and 4.20 ppm in thread **6**-H·3PF$_6$ to 4.77 ppm and 4.72 ppm ($\Delta\delta = 0.52$ ppm) in [2]rotaxane **5**-H·3PF$_6$, respectively. Furthermore, the $BIPY^{2+}$ protons changed from H_α (8.94 ppm), $H_{\alpha'}$ (8.99 ppm), H_β (8.35 ppm), $H_{\beta'}$ (8.38 ppm) in **6**-H·3PF$_6$ to H_α (8.72 ppm), $H_{\alpha'}$ (9.05 ppm), H_β (8.45 ppm), $H_{\beta'}$ (8.50 ppm) in **5**-H·3PF$_6$. The ^{1}H NMR spectra supported the formation of rotaxane **5**-H·3PF$_6$ and the selective binding of DB24C8 with the -NH_2^+- site.

The Stoddart group has demonstrated that the DB24C8 ring resides exclusively on the -NH_2^+- recognition center. Bases that can cause deprotonation of these centres could act as chemical inputs, promoting the movement of the DB24C8 ring toward the bipyridinium units.[27] Since the bipyridinium unit is very sensitive to nucleophilic bases, we chose the weakly nucleophilic base *N*-ethyl diisopropyl-

Abstract in Chinese:

摘要：设计、合成了一个基于[2]轮烷的超分子体系，它由一个与四酯基杯四芳烃连接的二苯并 24-冠-8 以及一个含有亚胺及 4, 4′-联吡啶两个位点的哑铃状组分组成。此超分子体系组合了酸碱至苯并-24-冠-8 大环的移动及钾离子络合/去络合两个可逆过程，其运行情况通过氢谱的变化进行了观察。研究结果表明此超分子体系只能在乙腈溶液中有效运行，两个独立的可逆过程能很好的协同运行。



Scheme 1. Synthetic route towards [2]rotaxane **5**-H·3PF$_6$.

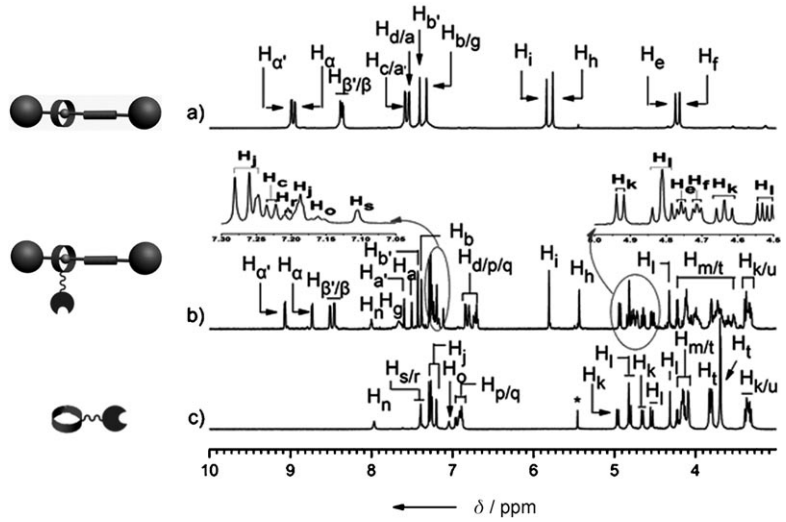


Figure 3. The partial ^{1}H NMR spectra (600 MHz, 298 K, in CD_3CN) recorded on a) **6**-H·3PF$_6$, b) **5**-H·3PF$_6$, and c) calix-crown **3**. The lettering corresponds to the proton assignments shown in Scheme 1.

amine (*i*Pr$_2$NEt). We monitored the switching process in three different solvents with the same base *i*Pr$_2$NEt. In the solvents $CDCl_3$ and CD_3COCD_3, the addition of *i*Pr$_2$NEt (1.2 equiv, or even a large excess of *i*Pr$_2$NEt) led to the incomplete deprotonation as judged from the complicated ^{1}H NMR spectrum (Figure 4), which shows that the DB24C8 ring cannot move completely to the bipyridinium units even with an excess of *i*Pr$_2$NEt. In the case of the incomplete deprotonation, subsequent addition of trifluoroacetic acid (TFA, 1.2 equiv) recovered the ^{1}H NMR spectrum of **5**-H·3PF$_6$, suggesting that the process of protonation/deprotonation is reversible. Complete deprotonation of the -NH_2^+- center can however be obtained by addition of the same base, *i*Pr$_2$NEt, to another solvent CD_3CN.

The acid–base induced shuttling process was monitored by ^{1}H NMR spectroscopy in CD_3CN. Upon addition of a slight excess of weak base, *i*Pr$_2$NEt (1.2 equiv), to a solution of **5**-H·3PF$_6$ in CD_3CN, the solution changed from colorless to pale yellow, which indicates the formation of a charge transfer (CT) complex of DB24C8 with the $BIPY^{2+}$ unit.[28] The ^{1}H NMR spectra (Figure 5) revealed that the resonance signals for the methylene protons $H_{e/f}$ in **5**-H·3PF$_6$ were shifted upfield from 4.76 and 4.71 ppm to 3.71 ppm, which indicates complete deprotonation of the -NH_2^+- site. The aromatic protons H_a/H_b shifted upfield from 7.49/7.37 ppm to 7.34/7.19 ppm, indicating the disappearance of C–H···O hydrogen bonds. Moreover, the resonance signals of $BIPY^{2+}$ protons all changed: H_α ($\Delta\delta = +0.07$ ppm), $H_{\alpha'}$ ($\Delta\delta = -0.12$ ppm), H_β ($\Delta\delta = +0.03$ ppm), $H_{\beta'}$ ($\Delta\delta = +0.15$ ppm), and the methylene protons $H_{i/h}$ shifted upfield from 5.80/5.43 ppm to 5.76/5.35 ppm. All these ^{1}H NMR spectra changes exhibit that the DB24C8 ring moves from the -NH_2^+- site to the $BIPY^{2+}$

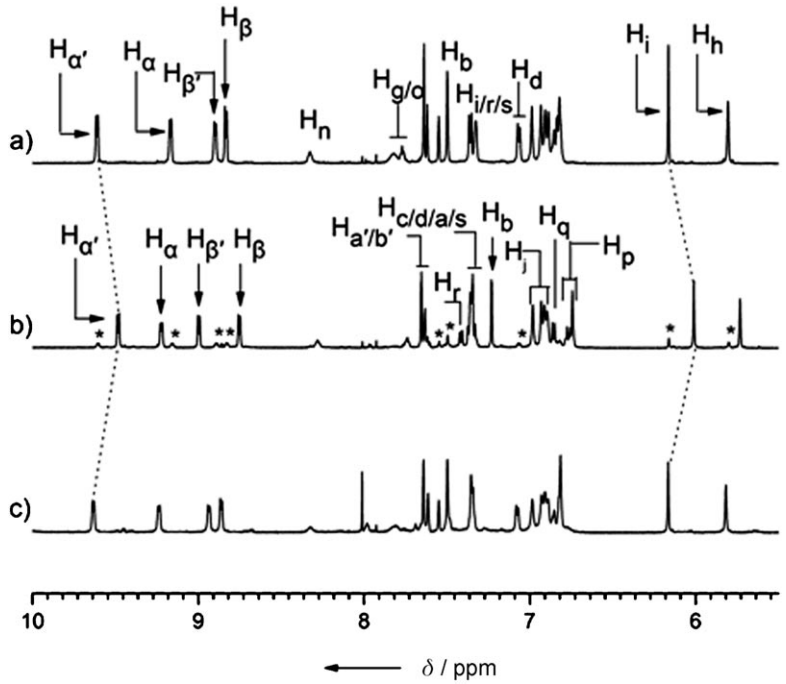


Figure 4. The partial ^{1}H NMR spectra (600 MHz, 298 K) recorded on a) **5**-H·3PF$_6$ (in CD_3COCD_3); b) after an addition of excess *i*Pr$_2$NEt, c) after an addition of excess TFA. "*" refers to the incomplete deprotonation parts of **5**-H·3PF$_6$.

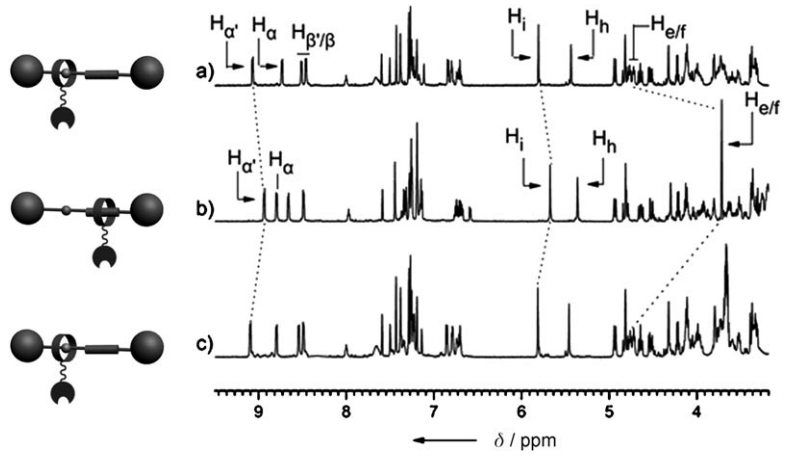


Figure 5. The partial ^{1}H NMR spectra (600 MHz, 298 K) recorded on a) **5**-H·3PF$_6$ (in CD_3CN); b) after an addition of *i*Pr$_2$NEt (1.2 equiv), c) after an addition of TFA (1.2 equiv).

unit. The original ^{1}H NMR spectra of **5**-H·3PF$_6$ were recovered upon addition of a small excess of TFA which shows the reversibility of the switching process.

The combination of the pH-induced shuttling of DB24C8 and the complexation/decomplexation of the K^+ ions with calix[4]arene derivative was also investigated by ^{1}H NMR spectroscopy (Figure 6). The data are summarized in Table S1 of the Supporting Information. Upon the addition of KPF_6 (5 equiv) to the solution of [2]rotaxane **5**-H·3PF$_6$ in CD_3CN, the resonance signals of protons H_j, H_k, H_l, H_m relative to the suspender calix[4]arene derivative changed significantly (Figure 6b). The aromatic protons H_j shifted downfield from 7.29, 7.27, 7.26, 7.20 ppm (four singlets) to 7.30–7.37 ppm (nearly a singlet); the methylene protons H_k, H_l shifted upfield and were broadened; the methylene protons H_m (multiplet) shifted downfield from 4.08-4.25 ppm to 4.20–4.31 ppm. These results indicate that the K^+ ions complex with the suspender calix[4]arene derivative in [2]rotaxane **5**-H·3PF$_6$.[40] Upon the addition of *i*Pr$_2$NEt (1.2 equiv), the DB24C8 ring moved from the -$CH_2NH_2^+CH_2$- site to the $BIPY^{2+}$ unit. The characteristic resonance for the four -$CH_2NH_2^+CH_2$- protons $H_{e/f}$ shifted upfield from 4.70-4.77 ppm to 3.71 and 3.69 ppm; the $BIPY^{2+}$ protons also changed for H_α, $H_{\alpha'}$, H_β, $H_{\beta'}$ (ppm): 8.79 [+0.04], 8.94 [-0.09], 8.51 [+0.08], 8.70 [+0.24]. At the same time, the unchanged proton signals of H_j, H_k, H_l, H_m in the calix[4]arene derivative indicates that it is still complexed with K^+ ions. After the addition of 18-crown-6 (10 equiv), the characteristic resonance signals of aromatic protons H_j and methylene protons H_k, H_l, H_m relative to the suspender calix[4]arene derivative in **5**-H·3PF$_6$ were all recovered (Figure 6d), which indicates the decomplexation of K^+ ions with the calix[4]arene derivative. The unchanged signals of methylene protons $H_{e/f}$ and $BIPY^{2+}$ protons H_α, $H_{\alpha'}$, H_β, $H_{\beta'}$ demonstrated that the DB24C8 ring is still located on the $BIPY^{2+}$ site, which indicates that the addition of the 18-crown-6 has no effect on the shuttling of the DB24C8 ring. The original ^{1}H NMR spectra of **5**-H·3PF$_6$ were regenerated upon the addition of a slight excess of TFA (1.2 equiv), which shows that the switching process is reversible.

Conclusions

We have synthesized a novel [2]rotaxane-based supramolecular system, which combines the pH-induced shuttling pro-

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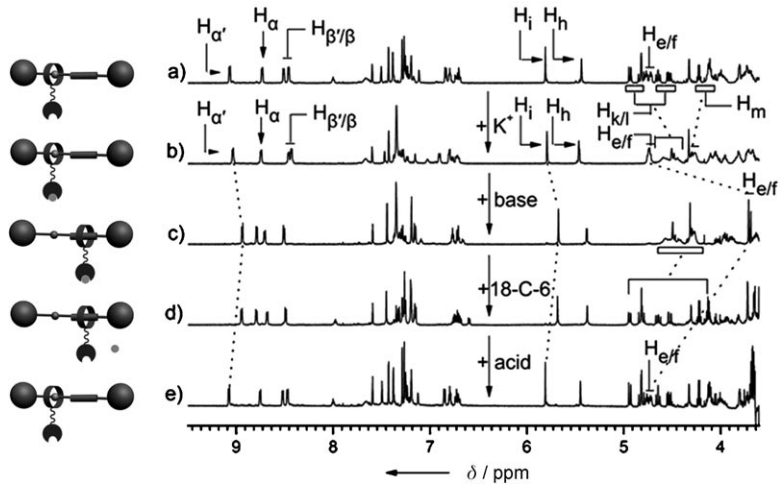

Figure 6. The partial ^{1}H NMR spectra (600 MHz, 298 K, in CD_3CN) recorded on a) **5**-H·3PF$_6$, b) addition of an excess of KPF_6, c) addition of *i*Pr$_2$NEt (1.2 equiv), d) addition of an excess of 18-crown-6, e) addition of a slight excess of TFA.

cess of the DB24C8 ring and the complexation/decomplexation process of K^+ ions with the calix[4]arene derivative. The switching processes have been monitored by ^{1}H NMR spectroscopy. The investigation of this novel supramolecular system is useful for the construction of future molecular-level devices.

Experimental Section

All solvents and reagents were used as received unless stated otherwise. All solvents were dried prior to use according to standard literature procedures. Reactions were monitored by thin-layer chromatography on glass plates coated with SiO_2 F254. The plates were inspected by UV light or in I_2 vapor. Column chromatography was performed on silica gel (160–200 mesh). ^{1}H and ^{13}C NMR spectra were recorded on either 1) a Bruker AV 600 (600 and 150 MHz, respectively) or 2) a Bruker AV 400 (400 and 100 MHz, respectively) at ambient temperature. They were referenced using their residual solvent as the internal standard. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were performed on a Bruker Biflex III MALDI-TOF spectrometer using *trans* 3-indoleacrylic acid as the matrix, observing reflector-positive ions. HR-ESI mass spectra were performed on a Bruker APEX II FT-ICRMS spectrometer. The absorption spectra were carried out in acetontrile (CH_3CN) solutions at room temperature. UV/Vis spectra were measured on a Hitachi U-3010 spectrometer with sample concentration of 2×10^{-4} M.

The binding constant of K^+ ions with the calix[4]arene derivative **10** (see Supporting Information) in acetonitrile is measured by the change of the UV/Vis absorption between 250 and 300 nm. In acetonitrile, the analytical concentration of the calix[4]arene derivative **10** was 2×10^{-4} M. A constant ionic strength (10^{-2} M) was provided by Bu_4NPF_6 (Fluka, puriss), and the cation was introduced using KPF_6 (TCI). The binding constant of calix[4]arene derivative **10** with the K^+ was calculated to be $(1.553\pm0.024)\times10^3$ M^{-1}.

Synthesis of Calix-Crown 3

To a stirred solution of **1** (150 mg, 0.14 mmol), **2** (98.4 mg, 0.2 mmol), and DMAP (25 mg, 0.2 mmol) in $CHCl_3$ (20 mL) cooled in an ice bath under N_2, was added EDCI (38 mg, 0.2 mmol), and the reaction allowed to stir overnight at room temperature. The resulting solution was washed with saturated solution of citric acid (3× 10 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed. The resulting solid was purified by silica-gel chromatography using CH_2Cl_2/CH_3CH_2OH = 60:1 at first, and then CH_2Cl_2/CH_3CH_2OH = 10:1 to obtained the desired compound as a white solid (calix-crown **3**, 160 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.4 (brs, 1H, NH), 7.44 (s, 1H, ArH), 7.32 (d, J = 8.4 Hz, 1H, ArH), 6.82–6.90 (m, 5H, ArH), 6.75, 6.78, 6.82 (s, 8H, ArH), 4.89, 4.62 (AB-q, J = 16.1 Hz, 4H, $OCH_2C(O)$), 4.72, 4.55 (s, 4H, $OCH_2C(O)$), 4.75, 4.65, 3.25, 3.23 (AB-q, J = 13.1 Hz, 8H, $ArCH_2Ar$), 4.16–4.21 (q, 6H, OCH_2CH_3), 3.81–4.21 (m, 24H, -OCH_2CH_2O-), 3.38–3.45 (m, 4H, -NCH_2-), 1.61–1.71 (m, 4H, -CH_2-), 1.43 (brs, 4H, -CH_2-), 1.27 (t, 9H, OCH_2CH_3), 1.06, 1.12 ppm (s, 36H, $C(CH_3)$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 170.2, 153.1, 152.7, 152.6, 151.2, 148.8, 148.3, 145.4, 145.3, 145.2, 133.1, 133.0, 132.8, 132.5, 127.6, 125.7, 125.5, 125.5, 125.4, 121.3, 121.3, 120.0, 114.0, 112.8, 112.3, 74.3, 71.7, 71.2, 71.1, 71.1, 69.8, 69.7, 69.6, 69.3, 69.3, 69.2, 60.6, 60.4, 39.4, 38.7, 33.8, 33.7, 33.7, 31.9, 31.4, 31.3, 31.2, 29.8, 29.3, 26.1, 26.0, 14.1 ppm; MS (MALDI-TOF): *m/z* (%): 1560.6 $[M+Na]^+$; HRMS (ESI): *m/z* (%) calcd for $C_{89}H_{120}N_2O_2Na$: 1559.8327 $[M+Na]^+$; found: 1559.8311; elemental analysis: calcd (%) for $C_{89}H_{120}N_2O_2$: C 69.51, H 7.86, N 1.82; found: C 68.63, H 7.97, N 1.98.

Synthesis of 5-H·3 PF$_6$

A solution of 3,5-di-tert-butyl benzylbromide (85 mg, 0.30 mmol) in $CHCl_3$/CH_3CN (5 mL, 3:2) was added to the solution of **4**-H·2PF$_6$ (38 mg, 0.05 mmol) and the calix-crown **3** (192 mg, 0.125 mmol) in $CHCl_3$/CH_3CN (20 mL, 3:2) under nitrogen atmosphere. The temperature was then raised to 70 °C, and the mixture was subsequently stirred for an additional two days. Upon cooling, the reaction mixture was concentrated in vacuum and the residual solid was purified by column chromatography (SiO_2, CH_2Cl_2, CH_2Cl_2/CH_3CH_2OH = 10:1, then 5:1) to afford a pale yellow solid that was dissolved in acetone (20 mL), then a saturated aqueous solution of NH_4PF_6 was added dropwise. The acetone was removed in vacuum and the remaining solid was dissolved in the solvent (CH_2Cl_2/$MeNO_2$ = 1:3, 20 mL). The organic phase was washed with H_2O (3×30 mL), dried over anhydrous $MgSO_4$, and evaporated to yield **5**-H·3PF$_6$ as a pale yellow solid (39 mg, 26%). ^{1}H NMR (600 MHz, CD_3COCD_3): δ = 9.61 (d, J = 6 Hz, 2H), 9.17 (d, J = 6 Hz , 2H), 8.90 (d, J = 6 Hz, 2H), 8.83 (d, J = 6 Hz, 2H), 8.33 (brs, 1H), 7.82 (brs, 2H), 7.77 (brs, 1H), 7.66 (s, 2H), 7.64 (s, 1H), 7.55 (s, 1H), 7.50 (s, 2H), 7.36, 7.07 (A, A', X, X', 4H), 7.32 (s, 2H), 66.88–6.98 (m, 8H), 6.82–6.85 (m, 5H), 6.16 (s, 2H), 5.80 (s, 2H), 4.75–4.95 (m, 12H), 4.66 (d, J = 15.6 Hz, 2H), 4.55 (s, 2H), 4.05–4.29 (m, 14H), 3.75–3.90 (m, 12H), 3.58–3.70 (m, 4H), 3.35–3.43 (m, 4H), 3.3(d, J=13.2 Hz 4H),1.68 (brs, 2H), 1.60 (brs, 2H), 1.40–1.44 (m, 4H), 1.31 (s, 18H), 1.31 (s, 18H), 1.26 (s, 18H), 1.23–1.28 (m, 9H), 1.08,1.11,1.16 ppm (s, 36H); ^{13}C NMR (150 MHz, CD_3COCD_3): δ = 171.1, 170.4, 167.1, 154.5, 154.0, 153.9, 153.3, 152.4, 151.4, 151.2, 150.6, 148.2, 148.2, 148.0, 146.7, 146.6, 146.1, 134.4, 134.1, 134.0, 133.4, 132.5, 132.0, 131.4, 129.2, 128.6, 128.5, 126.7, 126.7, 126.5, 126.7, 125.0, 124.8, 124.6, 124.3, 122.0, 121.5, 113.2, 112.3, 111.6, 75.4, 72.7, 72.2, 71.6, 71.4, 71.3, 71.0, 70.9, 69.0, 68.7, 68.6, 66.5, 64.8, 61.4, 61.2, 53.9, 52.7, 40.0, 39.5, 35.7, 35.6, 34.5, 32.6, 32.2, 31.8, 31.7, 31.7, 31.6, 30.8, 30.3, 27.1, 27.0, 14.6 ppm; MS (MALDI-TOF): *m/z* (%): 2365.6 $[M-2PF_6]^+$, 2217.6 $[M-3PF_6]^+$; HRMS (ESI): *m/z* (%) calcd for $C_{137}H_{184}N_5O_{20}$: 739.7839 $[M-3PF_6]^+$; found 739.7844.

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