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Tunable threading/dethreading efficiency of the pseudorotaxane by ether chain length

Junbo Li [a,b], Weidong Zhou [a,b], Yuliang Li [a,*], Huibiao Liu [a], Canbin Ouyang [a,b], Xiaodong Yin [a,b], Haiyan Zheng [a,b], Zicheng Zuo [a,b]

[a] Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100190, PR China

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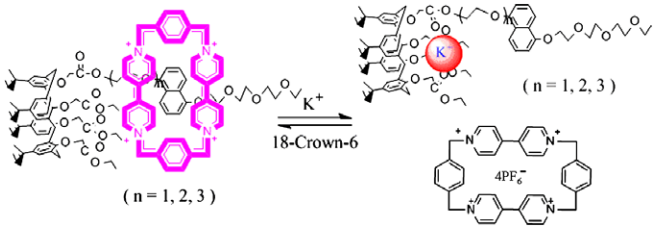
ABSTRACT

A series of axles containing the tetraethyl ester calix[4]arene derivative unit and 1,5-dioxynaphthalene (DNP) unit, with different lengths of ether chains, have been synthesized. Complexation of the axles and the cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) has been investigated by UV–vis and ^1H NMR spectra. The effect of the length of ether chain on the threading/dethreading processes has also been demonstrated, which indicated that the efficiency of threading/dethreading process decreases with the extension of ether chain.

Various molecular-level machines such as rotaxanes and catenanes have been reported over the last decade.[1] The common feature of these machines is the reversible switching between two or more states according to a given stimulus.[2] Pseudorotaxanes have been proven to be highly useful precursors for the construction of the effective artificial molecular-level machines.[3] Therefore, the design and preparation of pseudorotaxanes with this feature are necessary for the construction and development of artificial molecular-level machines.[4] This is because the threading/dethreading processes of the pseudorotaxanes can be conveniently and reversibly controlled by external stimuli such as light,[5] pH,[6] electricity,[7] etc.

Pseudorotaxanes created from the electron deficient tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) and electron-rich 1,5-dialkoxynaphthalene units have arguably become one of the most important building blocks for the synthesis of functional supramolecular systems with near-binary redox-controllable recognition properties.[8] The reduction of the $CBPQT^{4+}$ unit can induce the expulsion of the electron-rich 1,5-dialkoxynaphthalene from the cavity. Meanwhile, other stimuli such as the ions,[9] temperature[10] and pH[11] induced dethreading of the $CBPQT^{4+}$ ring had also been investigated widely. We designed and synthesized an axle which consists of a tetraethyl ester calix[4]arene derivative unit and a 1,5-dioxynaphthalene (DNP) unit. The tetraethyl ester calix[4]arene unit is a ligand for alkali metal ions and the DNP unit can complex with the $CBPQT^{4+}$ ring.[12] The designed axle is able to act both as host toward alkali metal ions and as guest toward the $CBPQT^{4+}$ ring. The [2]pseudorotaxane can be assembled from the complexation of the axle and the $CBPQT^{4+}$ ring (Scheme 1). Upon the addition of K^+ ions, the tetraethyl ester calix[4]arene complexed with the K^+ ions, which consequently induced the dethreading of the $CBPQT^{4+}$ ring due to the electrostatic repulsion.[9] 18-crown-6 is a good acceptor for K^+ ions; and the binding constant of 18-crown-6 with K^+ ions is more than ten times larger than the tetraethyl ester calix[4]arene with K^+ ions.[13] The addition of excess of 18-crown-6 can capture the K^+ ions coordinated with the calix[4]arene, which induces the $CBPQT^{4+}$ ring threading again. Furthermore, in order to suitably design molecular shuttles or molecular switches in the future with this system, a series of axles with different lengths of ether chain between the calix[4]arene derivative and 1,5-dioxynaphthalene have been synthesized and the K^+ ions induced dethreading processes have also been investigated.



Scheme 1. The threading/dethreading process of the pseudorotaxane.

* Corresponding author. Tel.: +86 10 62588934; fax: +86 10 82616576.
E-mail address: ylli@iccas.ac.cn (Y. Li).

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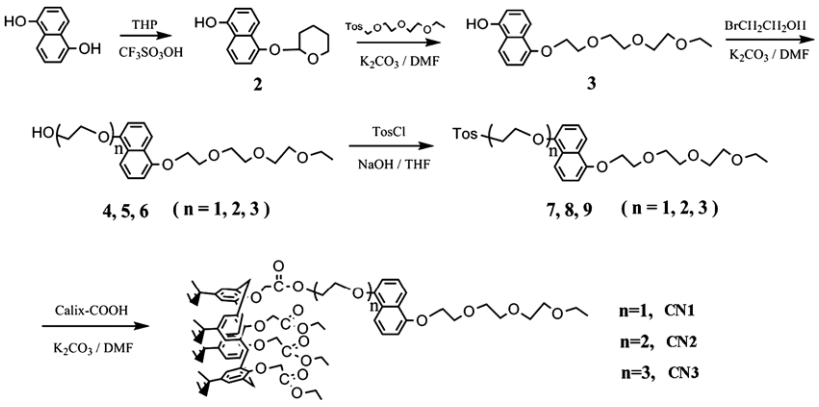

Scheme 2. Synthetic route of the CN**1**, CN**2** and CN**3**.

The tetracationic cyclophane ($CBPQT^{4+}$) was synthesized according to the literatures.[14] The synthetic routes employed in the synthesis of CN**1**, CN**2** and CN**3** are summarized in Scheme 2.[14] The mono-THP protected 1,5-dioxynaphthanlene **2** reacted with the tosylated ether chain in the presence of K_2CO_3 and 18-crown-6 in CH_3CN. The crude product was directly deprotected to afford **3** in 70% yield. Compound **3** reacted with bromoethanol in DMF to give **4**, which was tosylated subsequently to afford **5**. The synthesis of axle CN**1** was achieved by the reaction between Calix–COOH and compound **5** in 83% yield. The syntheses of the axles CN**2** and CN**3** were similar to that of the CN**1**.

Mixing equimolar proportions of CN**1** and $CBPQT^{4+}$ in CH_3CN resulted instantaneously in a deep purple color and the absorption spectra of the mixture showed a charge transfer (CT) band at 523 nm, indicating the formation of the [2]pseudorotaxane CN**1**·$CBPQT^{4+}$. Upon the addition of 5 equiv KPF_6 to the solution of [2]pseudorotaxane in CH_3CN, the purple color faded. As shown in the UV–vis absorption spectrum (Fig. 1a), the CT band absorbance at 523 nm decreased intensely. The absorbance value was reduced from 0.2 to 0.02, indicating the $CBPQT^{4+}$ ring dethreading from the CN**1**. When 10 equiv 18-crown-6 was added to the solution, the original purple color was recovered and the CT band absorbance at 523 nm was regenerated. Meanwhile, the CT band absorbance value was nearly the same as the original absorbance value, indicating that 18-crown-6 captures the K^+ ions from tetraethyl ester calix[4]arene thoroughly. Thus, the [2]pseudorotaxane CN**1**·$CBPQT^{4+}$ was formed again. Although the similar K^+/18-crown-6 induced threading/dethreading process can be clearly obtained (Fig. 1b and c) in the pseudorotaxanes CN**2**·$CBPQT^{4+}$ and CN**3**·$CBPQT^{4+}$, we can also conclude some differences: (1) the CT band absorbance values of the pseudorotaxanes increase from CN**1**·$CBPQT^{4+}$ to CN**3**·$CBPQT^{4+}$, indicating the binding constants, between the axles and $CBPQT^{4+}$ ring, increase with the extension of the ether chain; (2) after addition of 5 equiv KPF_6, the CT band absorbance values increase from CN**1**·$CBPQT^{4+}$ to CN**3**·$CBPQT^{4+}$ yet.

The ^1H NMR spectra also depicted this threading/dethreading process. Figure 2a and b shows the partial ^1H NMR spectra of the CN**1** and the $CBPQT^{4+}$ ring in CD_3CN at 25 °C, respectively. After mixing equimolar amounts of CN**1** and $CBPQT^{4+}$ in CD_3CN, the ^1H NMR spectra (Fig. 2c) showed significant changes. The protons associated with the DNP unit were appreciably shielded compared to their free analogues, indicating the encircling of the DNP moiety by the $CBPQT^{4+}$ ring.[15] The signals for protons H_b and H_c shifted upfield. At the same time, the signals for these protons broadened with some overlaps with those of protons H_d (see Supplementary data, Fig. S13). In addition, of the protons associated with the $CBPQT^{4+}$ ring, the chemical shifts for protons H_α and H_δ were almost identical, whereas those of the protons H_β and H_γ shifted upfield from 8.19 ppm to 7.73 ppm and downfield from 7.56 ppm to 7.87 ppm, respectively. These observations suggest strongly that the plane of the DNP unit in CN**1** is parallel and perpendicular, respectively, with the bipyridinium and the paraphenylene aromatic rings present in $CBPQT^{4+}$.[16] The signals of methylene protons shifted downfield: H_e ($\Delta\delta$ = +0.16 ppm), H_i ($\Delta\delta$ = +0.03 ppm), H_j ($\Delta\delta$ = +0.03 ppm), H_k ($\Delta\delta$ = +0.11 ppm). Furthermore, both protons in $CBPQT^{4+}$ and CN**1** broadened, indicating the [2]pseudorotaxane and free species were in fast exchange on the ^1H NMR timescale. Immediately upon the addition of 5 equiv KPF_6 to the NMR tube, the signals of the phenyl protons H_d shifted downfield from 6.95–7.07 ppm to 7.36–7.40 ppm, indicating K^+ ions complexed with the calix[4]arene derivative.[10] Moreover, the signals of protons H_β and H_γ shifted downfield from 7.74 ppm to 8.06 ppm and upfield from 7.83 ppm to 7.62 ppm, respectively, indicating the cyclophane $CBPQT^{4+}$ dethreaded from the axle CN**1**. Furthermore, the signals for the cyclophane $CBPQT^{4+}$ became less broad, providing further evidence for the disrupting of the pseudorotaxane CN**1**·$CBPQT^{4+}$.[17] When 10 equiv 18-crown-6 was added to the NMR tube, the ^1H NMR spectrum (Fig. 2d) recovered to Fig. 2c, indicating the K^+ ions were captured by the 18-crown-6, and the cyclophane $CBPQT^{4+}$ threaded again.

The complexation of axle with the host $CBPQT^{4+}$ was monitored by measuring the absorbance of the visible CT band that developed upon the mixing of the two components. To determine the binding constants, the 0.1 mM axles (in CH_3CN) and 0.2 mM axles (with 5 equiv KPF_6, in CH_3CN) were spectrophotometrically titrated with $CBPQT^{4+}$ (0.01 M, in CH_3CN), respectively. The binding constants were obtained by computer fitting of the experimental data points to the following equation:[18]

$$\frac{b[S]}{\Delta A} = \frac{1}{[R^0]K\Delta\varepsilon_{RS}} + \frac{[S]}{[R^0]\Delta\varepsilon_{RS}}$$

In which ΔA is the absorbance of the charge-transfer complex measured at a host concentration [S] and a guest concentration [R^0], b is the optical path length, $\Delta\varepsilon_{RS}$ is the molar absorptivity of the charge-transfer complex, and K is the equilibrium constant for the formation of the complex. The experimental data points were consistent with 1:1 stoichiometry for all the complexes. The binding constants are summarized in Table 1.

Data from Table 1 showed that the binding constants (K) of the pseudorotaxanes increased from CN**1**·$CBPQT^{4+}$ (518 M^{-1}) to CN**3**·$CBPQT^{4+}$ (10040 M^{-1}). Meanwhile, K_1/K_2 signified the K^+ ions-induced dethreading efficiency of the pseudorotaxanes, which reduced from 24.1 to 8.5, indicating that the dethreading efficiency decreased from CN**1**·$CBPQT^{4+}$ to CN**3**·$CBPQT^{4+}$. The K_{2b}/K_{2a} value (6.4) is larger than K_{1b}/K_{1a} (4.4), indicating that the electrostatic repulsion effect between the K^+ ions and $CBPQT^{4+}$ in CN**1**·$CBPQT^{4+}$

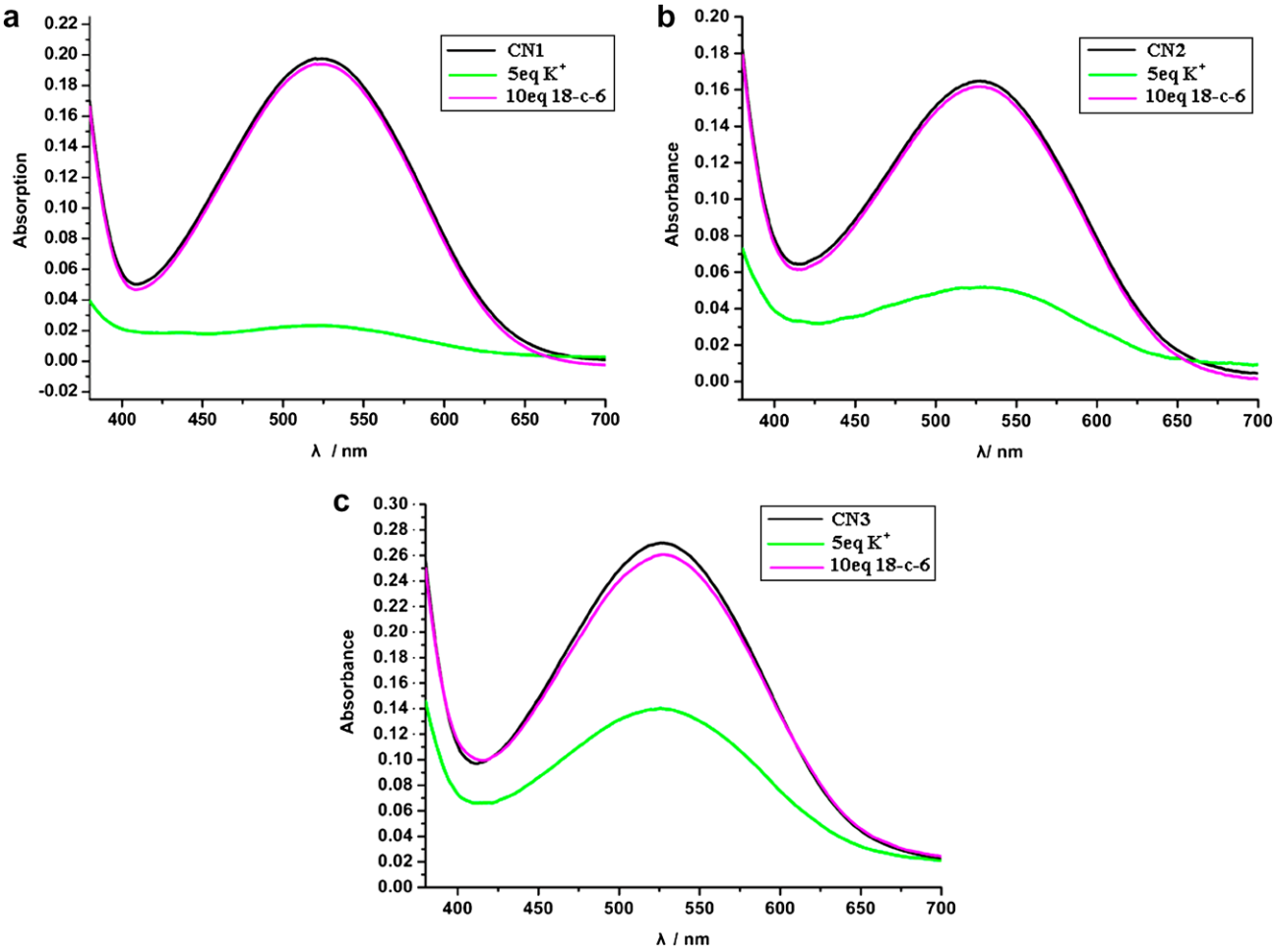

Figure 1. UV–vis spectra showing the CT bands of the pseudorotaxane (a) CN**1**·CBPQT^{4+} (1×10^{-3} M, CH_3CN), (b) CN**2**·CBPQT^{4+} (5×10^{-4} M, CH_3CN), (c) CN**3**·CBPQT^{4+} (5×10^{-4} M, CH_3CN) (black); upon the addition of 5 equiv KPF_6 (green); upon the addition of 10 equiv 18-crown-6 (magenta).

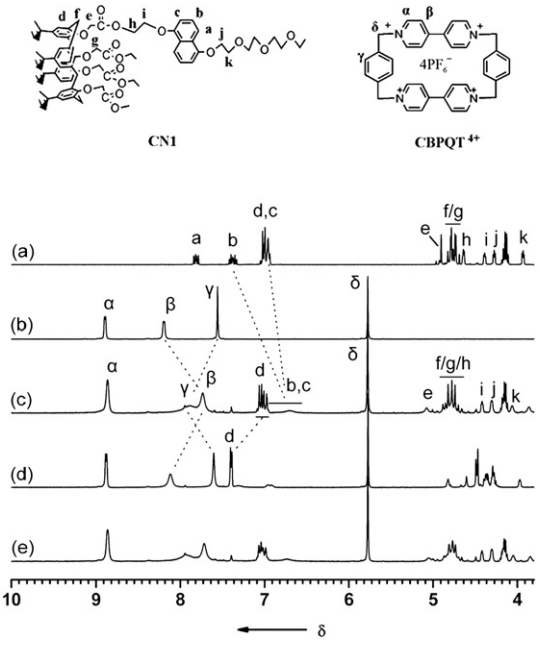

Figure 2. Partial ^{1}H NMR spectra (400 MHz, 298 K, CD_3CN) of (a) CN**1** (2×10^{-3} M); (b) CBPQT^{4+} (2×10^{-3} M); (c) CN**1**·CBPQT^{4+} (2×10^{-3} M); (d) CN**1**·CBPQT^{4+} + 5 equiv KPF_6; (e) CN**1**·CBPQT^{4+} + 5 equiv KPF_6 + 10 equiv 18-crown-6.

Table 1
A comparison of K (M^{-1}) for [2]pesudorotaxanes in CH_3CN solution

	a	b	c
K_1(without K^+ ions)	518 ± 7	2276 ± 74	10040 ± 150
K_2(with K^+ ions)	21 ± 19	137 ± 33	1186 ± 78
K_1/K_2	24.1	16.6	8.5

(a) CN**1**; (b) CN**2**; (c) CN**3**.

is stronger than that in CN**2**·CBPQT^{4+}. Meanwhile, K_{2c}/K_{2b} (8.6) is larger than K_{1c}/K_{1b} (4.4), indicating the electrostatic repulsion effect between the K^+ ions and CBPQT^{4+} in CN**2**·CBPQT^{4+} is stronger than that in CN**3**CBPQT^{4+}. So the electrostatic repulsion effect is reduced with the extension of ether chain. In other words, with the extension of ether chain, the binding constants (K) increase whereas the K^+ ions-induced dethreading efficiency decreases. The reasons are probably as follows: (a) The extended ether chain increases the [C–H···O] hydrogen bond interaction site between the ether chain and the acidic α-bipyridinium hydrogen atom;[19] (b) the steric hindrance effect between the calix[4]arene and the CBPQT^{4+} ring is reduced with the increasing distance between them; (c) the electrostatic repulsion effect between the K^+ ions and CBPQT^{4+} ring decreases with the extension of ether chain.

In conclusion, we have demonstrated a novel threading/dethreading process which can be controlled by 18-crown-6/K^+. Interestingly, the efficiency of the threading/dethreading process is

able to be tuned by extending the ether chain between the calix[4]-arene and 1,5-dioxynapathalene. Further work in our laboratory will focus on the application of this system to suitably design molecular shuttles and other molecular switches.

Acknowledgments

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Supplementary data

General methods, determination of binding constants, the original ^{1}H NMR, ^{13}C NMR, ESI, and TOF spectra of all new compounds. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.06.015.

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The solvent was evaporated and the crude product was chromatographed to give **3** (734 mg, 70%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, J = 8.5 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 6.86–6.80 (m, 2H), 5.68 (s, 1H), 4.28 (t, J = 5 Hz, 2H), 3.98 (t, J = 5 Hz, 2H), 3.85–3.79 (m, 2H), 3.73–3.66 (m, 4H), 3.61–3.58 (m, 2H), 3.52 (q, J = 7.0 Hz, 2H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.5, 151.5, 128.1, 125.5, 125.2, 125.1, 114.7, 114.1, 109.5, 105.5, 71.1, 70.8, 69.9, 67.9, 66.8, 15.2. EI-MS: m/z calcd for $C_{18}H_{24}O_5$, 320. Found 320. Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.42; H, 7.57. Compound **4**: To a solution of compound **3** (700 mg, 2.18 mmol) in DMF (10 mL), bromoethanol (186.4 μL, 2.6 mmol) and K_2CO_3 (603 mg, 4.36 mmol) was added. The solution was heated at 80 °C for 12 h. The solvent was evaporated and CH_2Cl_2 (50 mL) was added. The solution was washed with water (3 × 10 mL) and then dried over anhydrous $MgSO_4$. The crude product was chromatographed to give **4** (500 mg, 63%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90–7.83 (m, 2H), 7.38–7.32 (m, 2H), 6.85 (d, J = 7.6 Hz, 2H), 4.30–4.21 (m, 4H), 4.10–4.06 (m, 2H), 4.00–3.97 (m, 2H), 3.82–3.77 (m, 2H), 3.73–3.60 (m, 4H), 3.60–3.56 (m, 2H), 3.52 (q, J = 7.0 Hz, 2H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.4, 154.1, 126.8, 126.6, 125.2, 125.0, 114.9, 114.2, 105.8, 105.7, 71.0, 70.7, 69.8, 69.6, 67.9, 66.6, 61.6, 15.1. EI-MS m/z calcd for $C_{20}H_{28}O_6$, 364. Found 364. Anal. Calcd for $C_{20}H_{28}O_6$: C, 65.91; H, 7.74. Found: C, 65.87; H, 7.70. Compound **5**: Compound **3** (930 mg, 2.90 mmol), 2-(2′-chloroethoxy)ethanol (434 mg, 3.48 mmol), K_2CO_3 (802 mg, 5.8 mmol) were allowed to react in the same way as described for **4** and purified by column separation (silica gel) to yield **5** as a white solid (900 mg, 76%). Mp: 32–34 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89–7.84 (m, 2H), 7.38–7.32 (m, 2H), 6.86 (d, J = 7.6 Hz, 2H), 4.31–4.29 (m, 4H), 4.01–3.98 (m, 4H), 4.00–3.97 (m, 2H), 3.82–3.77 (m, 2H), 3.73–3.60 (m, 4H), 3.60–3.56 (m, 2H), 3.52 (q, J = 7.0 Hz, 2H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 154.5, 127.0, 126.9, 125.4, 125.3, 115.0, 114.7, 105.9, 72.9, 71.2, 70.9, 70.0, 69.9, 68.1, 66.8, 62.0, 15.4. EI-MS m/z calcd for $C_{22}H_{32}O_7$, 408. Found 408. Anal. Calcd for $C_{22}H_{32}O_7$: C, 64.69; H, 7.90. Found: C, 64.60; H, 7.75. Compound **7**: To a solution of compound **4** (400 mg, 1.10 mmol) and *p*-toluenesulfonyl chloride (251 mg, 1.31 mmol) in THF (20 mL), the NaOH (97 mg, 2.4 mmol) dissolved in 1 mL of H_2O was added at 0 °C; then the solution was stirred at room temperature for 12 h. After evaporation of the solvent, the crude product was dissolved in CH_2Cl_2 (50 mL) and the solution was washed with water (3 × 10 mL). The solution was dried with Na_2SO_4. The solvent was evaporated and the crude product was chromatographed to give **7** (520 mg, 91%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8 Hz, 2H), 7.62 (d, J = 8.5 Hz, 1H), 7.32–7.27 (m, 4H), 6.85 (d, J = 7.6 Hz, 1H), 6.72 (d, J = 7.6 Hz, 1H), 4.51–4.49 (m, 2H), 4.32–4.28 (m, 4H), 4.01–3.98 (m, 2H), 3.81–3.76 (m, 2H), 3.72–3.66 (m, 4H), 3.60–3.57 (m, 2H), 3.52 (q, J = 7.0 Hz, 2H), 2.41 (s, 1H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.4, 153.5, 145.0, 133.0, 130.0, 128.1, 126.9, 126.6, 125.3, 124.9, 115.3, 114.5, 105.8, 105.6, 71.1, 70.8, 69.9, 68.2, 68.0, 66.7, 65.6, 21.7, 15.3. EI-MS m/z calcd for $C_{27}H_{34}O_8S$, 518. Found 518. Anal. Calcd for $C_{27}H_{34}O_8S$: C, 62.53; H, 6.61. Found: C, 62.50; H, 6.56. Compound **8**: Compound **5** (400 mg, 0.98 mmol) and *p*-toluenesulfonyl chloride (225 mg, 1.17 mmol) were allowed to react in the same way as described for **7** and purified by column separation (silica gel) to yield **8** (520 mg, 94%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.89 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.5 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 7.6 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 4.30 (t, J = 4.7 Hz, 2H), 4.23–4.19 (m, 4H), 4.00 (t, J = 4.7 Hz, 2H), 3.91 (t, J = 4.7 Hz, 2H), 3.84–3.80 (m, 4H), 3.73–3.66 (m, 4H), 3.60–3.58 (m, 2H), 3.52 (q, J = 7.0 Hz, 2H), 2.36 (s, 1H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.5, 154.3, 145.8, 133.0, 130.0, 128.0, 126.9, 126.8, 125.3, 125.1, 114.9, 114.6, 105.8, 105.7, 71.1, 70.8, 70.0, 69.9, 69.4, 69.1, 68.0, 67.9, 66.7, 21.7, 15.3. EI-MS m/z calcd for $C_{29}H_{38}O_9S$, 562. Found 562. Anal. Calcd for $C_{29}H_{38}O_9S$: C, 61.90; H, 6.81. Found: C, 61.88; H, 6.75. Compound **9**: To a solution of compound **3** (150 mg, 0.47 mmol) in DMF (10 mL), triethyleneglycol-di(*p*-toluenesulfonate) (430 mg, 0.94 mmol) and K_2CO_3 (130 mg, 0.94 mmol) were added. The solution was heated at 80 °C for 12 h. The solvent was evaporated and CH_2Cl_2 (50 mL) was added. The solution was washed with water (3 × 10 mL) and then dried over anhydrous $MgSO_4$. The crude product was chromatographed to give **9** (200 mg, 70%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.83 (m, 4H), 7.78 (d, J = 8 Hz, 2H), 7.34 (t, J = 8 Hz, 2H), 7.29 (d, J = 8 Hz, 2H), 6.85–6.82 (m, 2H), 4.30–4.25 (m, 4H), 4.15–4.13 (m, 2H), 3.99 (t, J = 4.7 Hz, 2H), 3.94 (t, J = 4.7 Hz, 2H), 3.82–3.79 (m, 2H), 3.73–3.57 (m, 12H), 3.52 (q, J = 7.0 Hz, 2H), 2.39 (s, 1H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.5, 154.4, 144.9, 133.1, 129.9, 128.0, 126.9, 126.8, 125.2, 125.1, 114.8, 114.6, 105.8, 77.4, 77.2, 77.0, 71.1, 71.0, 70.9, 70.8,

69.9, 69.4, 68.8, 68.0, 66.7, 21.7, 15.3. EI-MS *m*/*z* calcd for $C_{31}H_{42}O_{10}S$, 606. Found 606. Anal. Calcd for $C_{31}H_{42}O_{10}S$: C, 61.37; H, 6.98. Found: C, 61.50; H, 6.90. Compound CN**1**. Compound **7** (200 mg, 0.39 mmol), Calix–COOH (310 mg, 0.32 mmol) and K_2CO_3 (45 mg, 0.64 mmol) were added to DMF (20 mL). The solution was stirred for 10 h at room temperature. Then the solvent was evaporated and CH_2Cl_2 (50 mL) was added. The solution was washed with H_2O(3 × 10 mL). The solution was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The oil product was chromatographed to obtain the CN**1** (350 mg, 83%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.33 (q, *J* = 8 Hz, 2H), 6.85–6.76 (m, 6H), 6.75–6.70 (m, 4H), 5.00–4.63 (m, 14H), 4.36–4.29 (m, 4H), 4.20–4.15 (m, 6H), 4.01 (t, *J* = 4.7 Hz, 2H), 3.83–3.81 (m, 2H), 3.73–3.67 (m, 4H), 3.61–3.59 (m, 2H), 3.52 (q, *J* = 7.0 Hz, 2H), 3.22–3.17 (m, 4H), 1.25–1.20 (m, 12H), 1.13–1.03 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.6, 170.4 154.3, 154.0, 153.1, 153.0, 152.8, 145.2, 145.1, 133.7, 133.6, 133.2, 133.1, 124.9, 114.9, 114.5, 105.7, 105.5, 71.0, 70.9, 70.7, 69.8, 67.9, 66.6, 66.2, 62.5, 60.4, 60.3, 33.8, 31.8, 31.4, 31.3, 31.0, 15.2, 14.2. MALDI-TOF *m*/*z* calcd for $C_{78}H_{102}O_{17}$, 1310.7. Found: 1333.9 $(M+Na)^+$, 1391.9 $(M+K)^+$. Anal. Calcd for $C_{78}H_{102}O_{17}$: C, 71.42; H, 7.84. Found: C, 71.33; H, 7.76. Compound CN**2**. Compound **8** (140 mg, 0.25 mmol), Calix–COOH (200 mg, 0.21 mmol) and K_2CO_3(100 mg, 0.42 mmol) were allowed to react in the same way as described for CN**1** and purified by column separation (silica gel) to yield CN**2** (200 mg, 73%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.88–7.83 (m, 2H), 7.36–7.31 (m, 2H), 6.84–6.75 (m, 10H), 4.88–4.79 (m, 12H), 4.35–4.26 (m, 6H), 4.21–4.18 (m, 6H), 4.01–3.98 (m, 4H), 3.85–3.80 (m, 4H), 3.73–3.66 (m, 4H), 3.60–3.58 (m, 2H), 3.52 (q, *J* = 7.0 Hz, 2H), 3.21–3.17 (m, 4H), 1.28–1.19 (m, 12H), 1.08–1.05 (m, 36H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7, 154.4, 153.1, 145.3, 133.6, 126.9, 125.5, 125.3, 114.9, 114.6, 105.8, 71.5, 71.2, 70.9, 70.0, 69.5, 68.0, 66.8, 63.6, 60.5, 34.0, 32.0, 31.5, 15.3, 14.4. MALDI-TOF *m*/*z* calcd for $C_{80}H_{106}O_{18}$, 1354.7. Found: 1377.9 $(M+Na)^+$, 1435.9 $(M+K)^+$. Anal. Calcd for $C_{80}H_{106}O_{18}$: C, 70.88; H, 7.88. Found: C, 71.03; H, 7.95. Compound CN**3**. Compound **9** (150 mg, 0.25 mmol), Calix–COOH (199 mg, 0.21 mmol) and K_2CO_3 (100 mg, 0.42 mmol) were allowed to react in the same way as the described for CN**1** and purified by column separation (silica gel) to yield CN**3** (210 mg, 76%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.87–7.83 (m, 2H), 7.36–7.31 (m, 2H), 6.84–6.75 (m, 10H), 4.94–4.70 (m, 12H), 4.30–4.26 (m, 6H), 4.21–4.18 (m, 6H), 4.01–3.98 (m, 4H), 3.81–3.76 (m, 4H), 3.72–3.66 (m, 8H), 3.60–3.58 (m, 2H), 3.52 (q, *J* = 7.0 Hz, 2H), 3.21–3.17 (m, 4H), 1.28–1.19 (m, 12H), 1.08–1.05 (m, 36H).^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.7, 154.6, 154.5, 153.2, 145.4, 133.7, 133.6, 133.5, 126.9, 125.6, 125.3, 125.2, 114.9,114.8, 105.9, 71.6, 71.2, 71.0, 70.1, 69.3, 68.1, 66.9, 63.6, 60.6, 34.0, 32.1, 31.6, 15.4, 14.4, 14.3. MALDI-TOF *m*/*z* calcd for $C_{82}H_{110}O_{19}$, 1398.7. Found: 1421.9 $(M+Na)^+$, 1479.9 $(M+K)^+$. Anal. Calcd for $C_{82}H_{110}O_{19}$: C, 70.36; H, 7.92. Found: C, 70.31; H, 7.90.

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