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An Anthracene-Based Photochromic Macrocycle as a Key Ring Component To Switch a Frequency of Threading Motion

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Abstract: A concept and demonstration of a switching in frequencies of molecular motions are described using a pseudorotaxane system. The setup consists of dibenzylammonium hexafluorophosphate and a photochromic dianthrylethane-based [24]crown-8-type macrocycle, which we designed as a key ring component for the pseudorotaxane system having photocontrollable threading functionality by changing the size of ring component due to the action of light.

Keywords: crown compounds · molecular devices · noncovalent interactions · photochromism · rotaxanes

Introduction

Interlocked molecules such as catenanes and rotaxanes[1] are thought to be prime candidates for the implementation and the development of devices at the nanometer scale,[2] artificial photosynthesis,[3] construction of ion channels,[4] or the development of artificial molecular machines.[5] The mechanically interlocked components of these molecules can be induced to switch between different geometries in response to either physical or chemical stimuli, since the components of catenanes and rotaxanes can be induced to perform relative motions, such as circumrotation[6] (rotary motion) and shuttling[7] (linear motion). Based on such geometrical switching properties, molecular electronics devices have been developed.[8] On the other hand, a control of the rate of molecular motion is one way to create new devices at molecular level. Schalley and co-workers reported a control mechanism of the rate of shuttling motions in [2]rotaxanes by different solvent effects on electrostatic interactions.[9] In order to control the rate of molecular motion, pseudorotaxanes are the promising candidates for molecular machines and device components, because pseudorotaxanes are viewed as prototypes of simple molecular machines and show characteristic motion, namely slippage and deslippage motions.[10] Recently, interesting investigations on these motions have been reported including a description of the intermediate region between pseudorotaxanes and rotaxanes,[11] effects of the size of stoppers,[12] a ring shape and a stopper structure,[13] a length of dumbbell component on thermodynamic parameters of these motions.[14] In this paper, we report a new concept and a demonstration of a switching in the frequency of molecular motions using a pseudorotaxane system in which frequencies of threading and dethreading motions is reversibly and quantitatively changed in response to physical stimuli by changing the size of ring component.

Results and Discussion

Design of a switching system: In order to design a switching system controlled by a frequency of molecular motions, we chose a pseudorotaxane which consists of dibenzylammonium hexafluorophosphate (DBA) and a photochromic dianthrylethane-based macrocycle **1**.[15] We designed **1** as a key ring component of the pseudorotaxane system to include a photocontrollable threading functionality (Figure 1a).

The photodimerization and the thermal reversion of the anthracene units between open-form molecule **1** and closed-form molecule **2** would cause substantial change of the cavity size reversibly.[16] Because the cavity size of **2** should be similar to that of dibenzo-[24]crown-8, **2** would form a stable complex with a secondary ammonium salt.[17] In addition to the stabilization of closed-form crown ether and ammonium moiety, destabilization at transition state, which is presumably when the crown ether is placed on the bulky group at the ends, is also important, because the energy difference between these strategies correspond to activation

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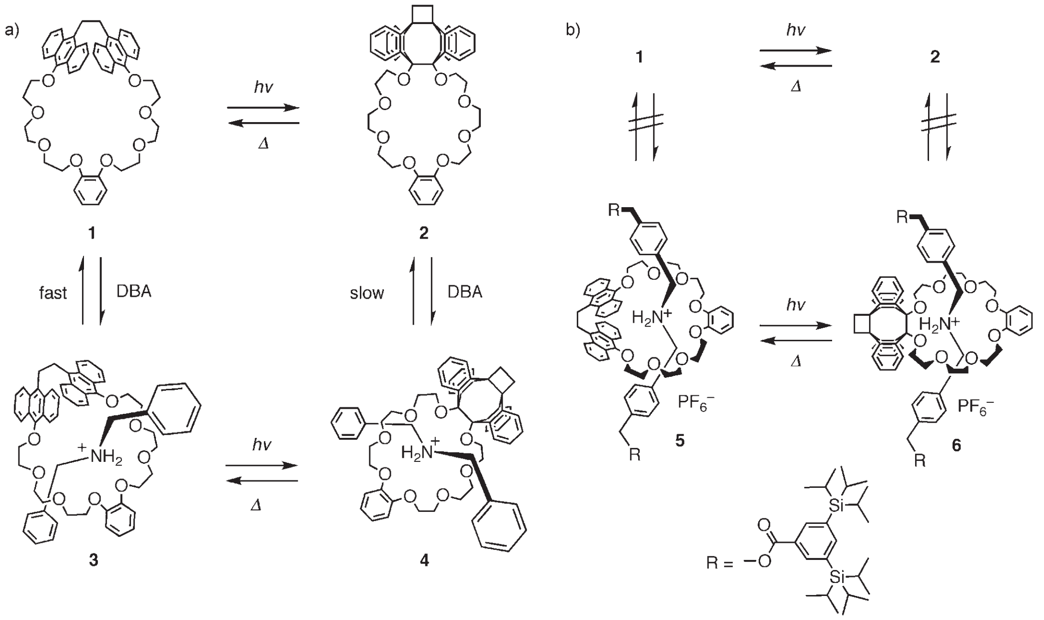


Figure 1. a) A concept of switching between fast and slow threadings in pseudorotaxane by using a photochromic anthracene-based [24]crown-8-type macrocycle and DBA. b) Ideal non-threadable supramolecules.

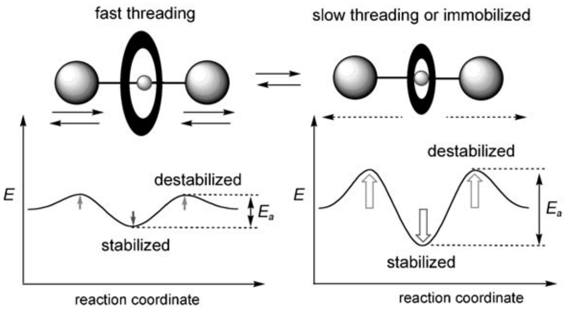
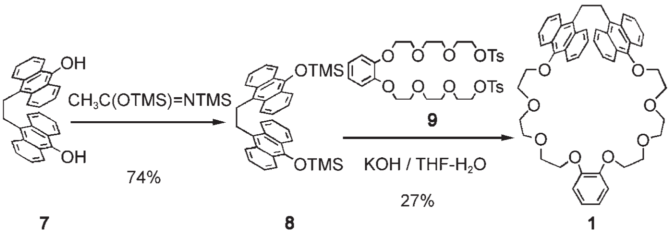


Figure 2. Concept and energy diagram of switching between fast and slow threading in pseudorotaxane.

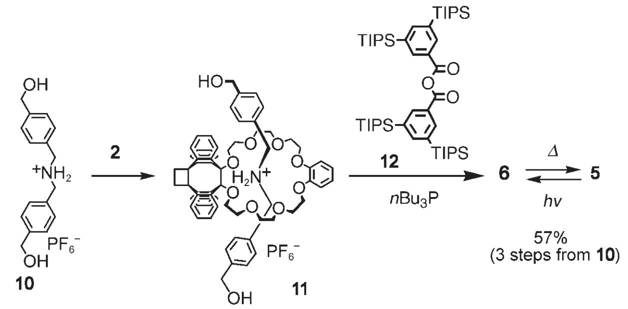
energy as shown in Figure 2. Because dibenzo-[24]crown-8 is not able to do deslippage over the 3,5-dimethylphenyl stopper, 3,5-dimethylphenyl group is expected to be large enough to prevent deslippage of the closed-form **2**. Then, we chose the phenyl group as a proper end group of axle-like component. Consequently, it is expected that the photocontrollable threading motion would be achieved using crown ether **1** as the key ring component and DBA as the proper axle-like component. For comparison, the rotaxanes **5** and **6** composed of the same crown ether as ring component and axle-like component with bulky stopper moieties at the both ends were also prepared, where the threading/dethreading motion was completely stopped.

Preparation of macrocycle 1: The previously reported preparation of the photocontrollable [18]crown-6- and [12]crown-4-type compounds[18] containing a dianthrylethane moiety from 1,2-bis(10-hydroxy-9-anthryl)ethane (**7**)[19] and corresponding oligoethyleneglycol ditosylates in the presence of sodium hydroxide resulted in low yields of the macrocyclization, partly because of the lability of diol **7**. Even though diol **7** is relatively stable in form of crystals, it decomposes rapidly in solution. For this reason, high dilution conditions, which are common for macrocyclization, could not be applied. Therefore, diol **7** obtained as fine crystals was converted to stable bis(trimethylsilyl)ether **8** using *N*,*O*-bis(trimethylsilyl)acetamide (BSA) in 74% yield. Then in situ deprotection and coupling of **8** with ditosylates **9** furnished macrocycle **1** with considerably improved yield (27%) compared with the previous syntheses of related molecules as shown in Scheme 1.[18]



Scheme 1. Synthesis of the photochromic ring component **1**.

Preparation of rotaxane 5: The synthesis of rotaxane **5** is summarized in Scheme 2. The closed-form **2** was prepared from **1** in benzene by irradiation with a 500-W high-pressure mercury lamp followed by evaporation of the solvent with cooling. Because the closed-form **2** is stable enough at low temperature to handle, the freshly prepared **2** and secondary ammonium phosphate **10** were dissolved in CH_2Cl_2/CH_3CN. The resulting pseudorotaxane **11** was treated with acid anhydride **12** in the presence of 40 mol% of $n$$Bu_3P$ under ice



Scheme 2. Synthesis of the [2]rotaxanes **5** and **6**.

cooling.[20] Thermal reversion of the rotaxane **6** to **5** occurred during the post-treatment. The open-form [2]rotaxane **5** was obtained in 57 % yield (three steps from **10**).

Quantitative interconversion of ring component 1 and 2: The photoisomerization of ring component **1** to the corresponding closed-form molecule **2** proceeded quantitatively. The solution of **1** in well-degassed CD_3CN was placed in a Pyrex NMR tube at 285 K and irradiated with the high-pressure mercury lamp for 10 min. After the irradiation, the solution was kept under 273 K in order to avoid significant thermal reversion of **2**. In the ^1H NMR spectra, a sharp singlet signal assigned to the benzylic protons (H_a) of **1** at 4.1 ppm disappeared and a singlet signal assigned to the aliphatic protons appeared at 2.9 ppm after the irradiation as shown in Figure 3. In the aromatic region, the characteristic signals at δ 8.12 and 7.55 ppm disappeared after irradiation and the corresponding aromatic protons (H_b, H_c) appeared at δ 6.8–7.0 ppm.

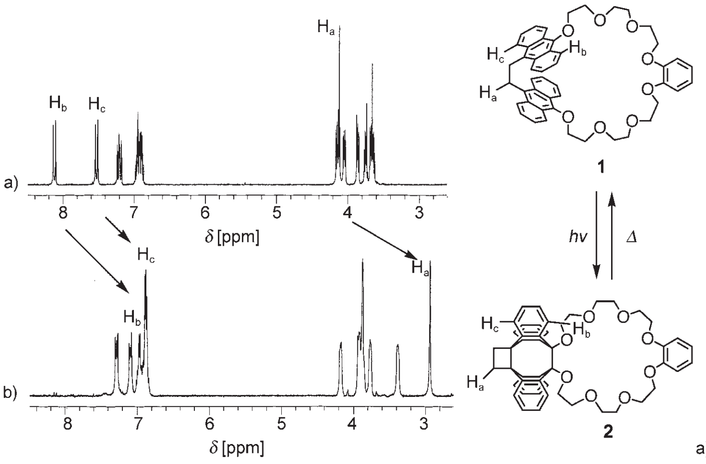


Figure 3. Partial ^1H NMR spectra (270 MHz) of a) open-form macrocycle **1** and b) closed-form **2**; recorded in CD_3CN at 243 K.

The thermal reversion of **2** to **1** involved appreciable spectral change observed in UV-visible spectroscopy. The half-life of **2** in acetonitrile was obtained based on the increase of absorbance at 383 nm by means of UV-visible spectroscopy: 10 min at 303 K, whereas 148 min at 283 K. Because of the long half-life at low temperature, the closed-form molecule **2** could be conveniently isolated and then converted reversibly at room temperature to the open-form molecule **1**.

The photoirradiation and subsequent thermolysis were performed repeatedly using the sample solution prepared in quartz cell for absorption spectra in well-degassed CH_3CN (0.1 mM). Photoreaction was carried out using the 500-W high-pressure mercury lamp through Pyrex filter for 30 s cooling with water bath, then thermal reversion was carried at 313 K for 45 min monitoring absorbance at 383 nm by means of UV/Vis spectrometer. The change of the absorbance is shown in Figure 4. After 10 times repetition, 97.4 % durability is obtained based on the difference in absorbance.

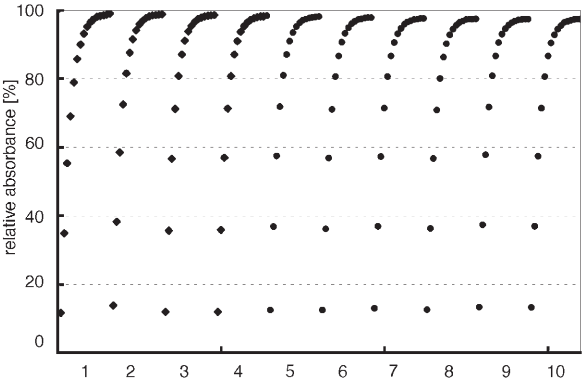


Figure 4. Ten continuous cyclical changes in relative absorbance at 383 nm during photoreaction and thermal reversion cycles between open-form **1** and closed-form **2**; recorded in CD_3CN at 313 K.

Quantitative interconversion of rotaxane 5 and 6: The photoisomerization of **5** to **6** proceeded also quantitatively. The ^1H NMR spectra of **5** at 273 K are shown in Figure 5. In the

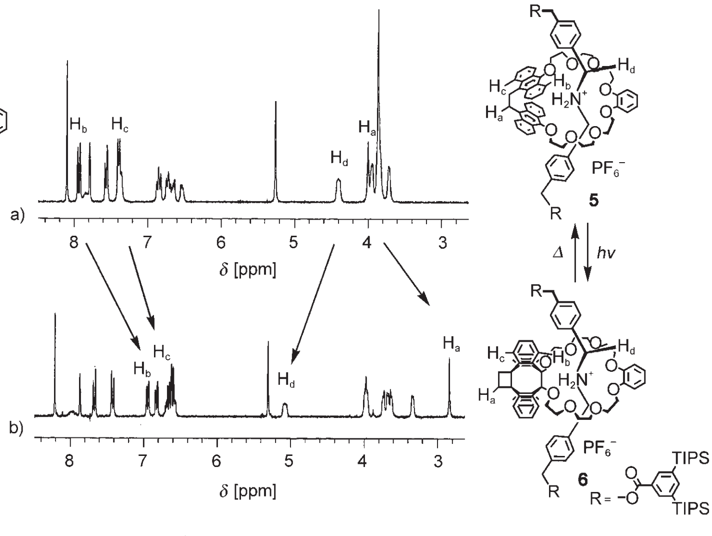


Figure 5. Partial ^1H NMR spectra (270 MHz) of a) open-form rotaxane **5** and b) closed-form **6**; recorded in CD_3CN at 273 K.

^{1}H NMR spectra, characteristic changes for the signals of the ring component protons are observed. A sharp singlet signal assigned to the benzylic protons (H_a) of **5** at δ 4.05 ppm disappeared and corresponding signal of an aliphatic proton (H_a) appeared at 2.84 ppm after the irradiation, the aromatic signals (H_b, H_c) at 8.12 and 7.55 ppm shifted to 6.92–6.75 ppm after irradiation. The signal assigned to the benzylic protons of axle-like component (H_d) of **5** at 4.42 ppm shifted to 5.08 ppm after the irradiation. The thermal reversion of **5** to **6** was observed by the ^{1}H NMR spectra and the UV-visible spectra.

The photoirradiation for 30 s and following thermolysis at 313 K for 60 min was performed repeatedly. The change of the absorbance at 382 nm by means of UV/Vis spectrometer is shown in Figure 6. After 10 times repetition, 97.5 % durability is obtained based on the difference in absorbance. The half-life of **6** in acetonitrile was determined based on the increase of absorbance at 383 nm by means of UV-visible spectroscopy: 18 min at 303 K, whereas 222 min at 283 K. Half-lives of the rotaxanes **6** to **5** are significantly longer than those of the ring components **1** to **2**. It seems very likely that the presence of the salt will increase the stability of the crown ether and slow down its retrophotodimerization.

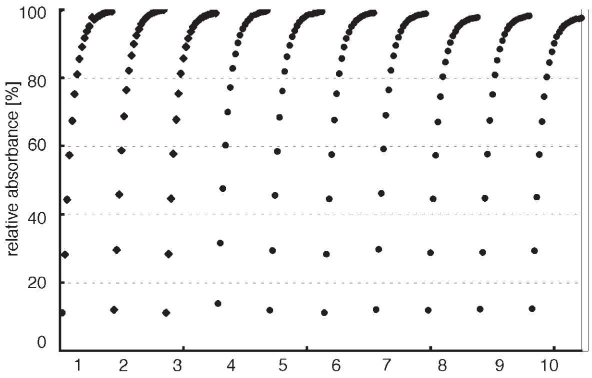


Figure 6. Ten continuous cyclical changes in relative absorbance at 382 nm during photoreaction and thermal reversion cycles between open-form **5** and closed-form **6**; recorded in CD_3CN at 313 K.

Characterization of pseudorotaxanes: The apparent half-life of **2** in the presence of DBA in acetonitrile was obtained based on the increase of absorbance at 383 nm by means of UV-visible spectroscopy: apparent half-life is 11 min at 303 K, whereas it is 160 min at 283 K (Table 1). Although the half-lives of corresponding rotaxane **6** to **5** are appreciably longer than those, apparent half-lives of **2** to **1** in the presence of DBA are slightly longer than those of the ring components **2** to **1** itself.

Table 1. Apparent half-lives of the thermal reversion of **2**, **6** and pseudorotaxane system (**2** with DBA) in CH_3CN obtained based on UV-visible spectral changes.

T [K]	$t_{1/2}$ [min]		
	2	**2** with DBA	**6**
283	148	160	222
303	10	11	18

In order to characterize the pseudorotaxane formation of the ring component **1** or **2** with the axle-like ammonium salt component ^{1}H NMR titration experiments were performed. Although kinetic and thermodynamic data at high temperatures were not obtainable because of the less thermal stability of closed-form complex, ^{1}H NMR spectroscopy at room temperature gave information both on thermodynamic stability of pseudorotaxane and kinetic information of threading and dethreading rate.

The addition of DBA to a solution of **1** in CD_3CN formed a crown ether–ammonium cation complex. The complexation equilibrium was fast on the NMR time scale and gave signals at weight averaged chemical shifts of the free and complexed host. The binding constants of this system were obtained based on the chemical shift change by the titration experiment followed by non-linear least-square data treatment method. The binding constants are listed in Table 2 in a temperature range from 273 to 233 K. In addition to the binding constants, information on the frequency of molecular motions was obtained from this experiment. Even at a low temperature of 233 K, the host–guest complexation equilibrium has a fast exchange rate compared with the NMR time scale.

Table 2. Association constants of crown ethers **1** and **2** with dibenzyl ammonium hexafluorophosphate in CD_3CN, determined by nonlinear least-squares method and single point measurement, respectively.

T [K]	K [M^{-1}]	
	1	**2**
273	23	67
263	30	82
253	42	126
243	53	184
233	63	286

In contrast, the host–guest complexation equilibrium of the closed-form complex **2** with DBA in CD_3CN has a slow exchange rate compared with the NMR time scale so that the peaks due to the complexed host and the free host are observed individually in an NMR spectrum. The ^{1}H NMR spectrum of a mixture of **2** and DBA is shown in Figure 7 together with those of **2** c) and DBA a). In Figure 7b), the signals with asterisks (*) are assigned to the pseudorotaxane and others are due to the free DBA and free **2**.

Based on the ^{1}H NMR spectra, the binding constants of **2** with DBA were obtained by the integration of the complexed and free host signals. The results are listed in Table 2 together with those of **1** with DBA. The binding constants of **2** are two to four times larger than those of the open-form **1**. The stable binding between **2** and DBA may explain the elongation of apparent half-lives of **2** and slow exchange in the presence of DBA.

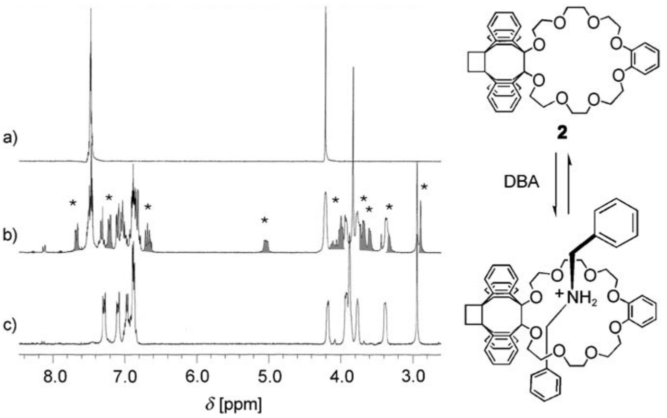


Figure 7. ^{1}H NMR spectra (270 MHz, CD_3CN, 243 K) of a 1:1 mixture (20 mM) of open-form macrocycle **1** and DBA. The descriptors "*" refer to signals representing protons of pseudorotaxane.

Conclusion

The anthracene-based photochromic molecules **1** and **2** are interconverted reversibly by photoirradiation and thermolysis. The binding constants of **1** and **2** with DBA differ considerably. In addition, considerable differences in half-lives of thermal reversions of pseudorotaxane **4** and rotaxane **6** are observed. The significant difference in frequencies of threading motions of DBA with ring components **1** or **2** in pseudorotaxane system is observed by ^{1}H NMR spectroscopy. The rate constant of **1** is higher than the NMR time scale, however, the rate constant of **2** is smaller within the temperature range between 233 and 303 K. The switching frequency of the molecular motion by the structural change of ring component is possible to produce promising new switching devices. We are currently investigating the extended application of this cavity-size changeable ring component to the syntheses of two-station [2]rotaxanes for the demonstration to stop the shuttling process by action of light and to quantify the shuttling velocity.

Experimental Section

General methods: ^{1}H NMR (270, 300, or 400 MHz) and ^{13}C NMR (67.5, 75.0, or 100 MHz) spectra were recorded on a JEOL JNM-AL-400, a Varian Mercury 300 or a JEOL JNM-GSX-270 spectrometer. The chemical shifts of ^{1}H NMR and ^{13}C NMR signals are quoted relative to tetramethylsilane. IR spectra were recorded as a KBr disk on a JASCO FTIR-410 spectrometer. Mass spectral analyses were performed on a JEOL JMS-DX303HF. Elemental analyses were carried out with a Perkin-Elmer 2400II analyzer. UV-visible spectra were recorded on a Hitachi U-3310 spectrometer in acetonitrile. Preparative HPLC separation was undertaken with a JAI LC-908 chromatograph using 600 mm × 20 mm JAIGEL-1H and 2H GPC columns with $CHCl_3$ as an eluent. Solvents were dried (drying agent in parentheses) and distilled prior to use: THF (sodium/benzophenone), CH_3CN, CH_2Cl_2 (CaH_2).

Crown ether 1: In a 1 L three-necked flask equipped with a reflux condenser, a thermometer, a Hershberg dropping funnel, and a magnetic stirrer bar were placed a saturated aqueous solution (9 mL, 130 mmol) of KOH and THF (100 mL). A solution of **8** (1.91 g, 3.42 mmol) and ditosylate **3** (2.50 g, 3.66 mmol) in THF (500 mL), which was deaerated by sonification for 30 min, was added through the dropping funnel. The solution was added dropwise into the flask during 22.5 h under reflux. After an additional 1 h stirring at 55 °C, the reaction mixture was cooled to room temperature. The resulting reddish suspension was neutralized with 6 N HCl. The mixture was extracted with Et_2O and CH_2Cl_2, washed with brine, and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, which was followed chromatography (hexane/AcOEt 1:1) gave **1** (685 mg, 27 %) as yellow foam. ^{1}H NMR (300 MHz, CD_3CN, 30 °C): $\delta = 8.12$ (d, $J = 8.6$ Hz, 4H), 7.53 (d, $J = 8.7$ Hz, 4H), 7.21 (ddd, $J =$ 1.0, 8.7, 8.6 Hz, 4H), 6.98–6.87 (m, 8H), 4.20 (t, $J = 4.8$ Hz, 4H), 4.14 (s, 4H), 4.11 (t, $J = 4.8$ Hz, 4H), 3.86 (t, $J = 6.8$ Hz, 4H), 3.75 (t, $J = 2.8$ Hz, 4H), 3.70–3.64 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 150.6$, 149.9, 131.7, 130.0, 125.6, 125.1, 125.0, 124.9, 123.4, 122.4, 115.5, 80.0, 71.7, 71.5, 70.9, 70.8, 69.9, 27.7 ppm; IR (KBr): $\tilde{\nu}$ = 3064, 3048, 2921, 2869, 1618, 1592, 1559, 1503, 1348, 1255, 1093, 771, 753 cm^{-1}; HR-MS (FAB): m/z: calcd for $C_{48}H_{48}O_8$: 752.3349; found: 752.3346 $[M^+]$.

Closed crown ether 2: A solution of crown ether **1** (14.6 mg, 19.4 mmol) in CD_3CN (1.0 mL) was placed in a Pyrex NMR tube and was well degassed by a bubbling of dry argon for 30 min. Then, the solution was irradiated using a 500-W high-pressure mercury lamp for 10 min. After irradiation, the reaction mixture was immediately chilled to 0 °C to avoid thermal reversion reaction. ^{1}H NMR (270 MHz, CD_3CN, −30 °C): $\delta =$ 7.29 (t, $J = 4.5$ Hz, 4H), 7.10 (m, 4H), 7.02–6.84 (m, 12H), 4.18 (br, 4H), 3.94–3.88 (m, 12H), 3.77 (br, 4H), 3.39 (br, 4H), 2.94 ppm (s, 4H).

Rotaxane 5: A solution of crown ether **1** (100 mg, 133 mmol) in benzene (10 mL) was placed in a Pyrex tube and was well degassed by a bubbling of dry argon. Then, the solution was irradiated using a 500 W high-pressure mercury lamp for 15 min in an ice bath. After irradiation, the solvent was evaporated off with cooling. Freshly prepared **2** in CH_2Cl_2 (600 mL) was mixed with secondary ammonium phosphate **10** (49.0 mg, 121 mmol) in CH_3CN (100 mL) and acid anhydride **12** (226 mg, 226 mmol) in CH_2Cl_2 (400 mL) in an ice-salt bath. Then, 40 mol % of nBu_3P (12 mmol) was added to the mixture solution under N_2 atmosphere and the reaction solution was stirred for 3 h in the ice-salt bath. Evaporation of the solvent followed by preparative HPLC separation (JAIGEL-1H and 2H GPC columns with $CHCl_3$) gave **5** (137 mg, 68.9 mmol, 57 %). M.p. 131.0–134.5 °C; ^{1}H NMR (270 MHz, CD_3CN, 0 °C): $\delta = 8.14$ (d, $J = 1.2$ Hz, 4H), 7.95 (d, $J = 8.3$ Hz, 4H), 7.95–7.80 (br, 2H), 7.83 (brs, 2H), 7.56 (d, $J = 8.3$ Hz, 4H), 7.44 (d, $J = 9.0$ Hz, 4H), 7.40 (d, $J = 8.3$ Hz, 4H), 6.92–6.89 (m, 4H), 6.78–6.75 (m, 4H), 6.69–6.67 (m, 2H), 6.58–6.55 (m, 2H), 5.28 (s, 4H), 4.42 (brt, $J = 6.6$ Hz, 4H), 4.05 (s, 4H), 3.97–3.95 (m, 4H), 3.86–3.84 (m, 16H), 3.71–3.70 (m, 4H), 1.39 (heptet, $J = 7.3$ Hz, 12H), 1.00 ppm (d, $J = 7.3$ Hz, 72H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 166.9$, 148.7, 147.1, 146.41, 146.40, 138.3, 136.4, 134.2, 130.6, 130.4, 129.3, 129.0, 128.1, 128.0, 124.5, 124.1, 123.6, 121.9, 121.8, 112.3, 73.9, 71.2, 70.6, 70.2, 69.6, 68.3, 65.7, 52.7, 26.6, 18.6, 10.8 ppm; IR (KBr): $\tilde{\nu}$ = 2943, 2866, 1725, 1506, 1459, 1268, 1131, 882, 842 cm^{-1}; MS (FAB): m/z: 1843.0 $[M-PF_6]^+$, elemental analysis calcd (%) for $C_{114}H_{156}F_6NO_{12}PSi_4$: C 68.81, H 7.90, N 0.70; found: C 68.65, H 8.03, N 0.69.

Closed rotaxane 6: In a manner similar to that described for **2**, a solution of rotaxane **5** (7.0 mg, 3.52 mmol) in CD_3CN (700 mL) was irradiated. After irradiation, the reaction mixture was immediately chilled to 0 °C to avoid thermal reversion reaction. ^{1}H NMR (400 MHz, CD_3CN, 30 °C): $\delta = 8.21$ (d, $J = 1.2$ Hz, 4H), 7.98 (br, 2H), 7.87 (brt, $J = 1.2$ Hz, 2H), 7.67 (d, $J = 7.9$ Hz, 4H), 7.43 (d, $J = 8.1$ Hz, 4H), 6.95 (d, $J = 7.2$ Hz, 4H), 6.84 (d, $J = 7.3$ Hz, 4H), 6.70–6.57 (m, 12H), 5.31 (s, 4H), 5.08 (br, 4H), 3.98 (br, 8H), 3.73–3.64 (m, 12H), 3.40 (br, 4H), 2.84 (s, 4H), 1.46 (heptet, $J = 7.4$ Hz, 12H), 1.04 (d, $J = 7.3$ Hz, 72H).

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