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A Shuttling Molecular Machine with Reversible Brake Function

Keiji Hirose,* Yoshinobu Shiba, Kazuaki Ishibashi, Yasuko Doi, and Yoshito Tobe[a]

Abstract: Design, synthesis, and demonstration of a prototype of a shuttling molecular machine with a reversible brake function are reported. It is a photochemically and thermally reactive rotaxane composed of a dianthrylethane-based macrocycle as the ring component and a dumbbell shaped molecular unit with two, secondary ammonium stations separated by a phenylene spacer as the axle component. The rate of shuttling motion was shown to be reduced to less than 1% (from 340 to $<2.5\ s^{-1}$) by reducing the size of the ring component from 30-crown-8 to 24-crown-8 macrocycles upon photoirradiation. The ring component was turned back to 30-crown-8 by thermal ring opening, thus establishing a reversible brake function that works in response to photochemical and thermal stimuli.

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

Introduction

For the implementation and the development of artificial molecular machines[1] and electronic devices at the nanometer scale,[2] rotaxanes[3] are thought to be prime candidates. The functions in these devices are based on relative motions, such as shuttling[4] and circumrotation[5] in response to either physical or chemical stimuli. For example, based on the differences in conductivity caused by changes of sites on which the ring component locates (station) in response to electrical stimuli, molecular electronic devices have been developed.[6] The positional control of ring molecules by shuttling motion has been studied most extensively, in contrast to the rate-control of shuttling motion. As a chemical approach to control the rate of shuttling motion, Schalley and co-workers reported that complexation of the phenolic moiety of the axle component of a rotaxane with a bulky base reduced its shuttling rate. Leigh and Stoddart suggested that the shuttling rates of rotaxanes can be changed by exchanging the solvents, which affects the interactions between the ring and stations. In the former approach, repetitive switching of the rates would be hindered by accumulation of products formed by the complexation/decomplexation cycle. In the latter approach, continuous switching of solvent polarity would, in practice, be difficult because a large volume of solvent would accumulate if the polarity was changed in a repetitive manner.[7]

Thus, construction of a braking system at a molecular scale capable of reversible switching of rates by physical stimuli has not been achieved.[8] Very recently, we reported a substantial change of the slippage/deslippage rates of a pseudorotaxane system caused by light and heat.[9] On the basis of these results, we designed a rotaxane system that has a reversible brake function for shuttling motion by utilizing a size-changeable crown ether as the ring component. Here we report the synthesis of the [2]rotaxane and quantitative evaluation of the change of its shuttling rates by ^{1}H NMR measurement.

Results and Discussion

Design of the rotaxane: Our concept for the control of the shuttling motion is shown in Figure 1, which includes models of [2]rotaxanes capable of changing the size of ring components and their corresponding potential energy diagrams. Figure 1a shows the larger ring (open-form) rotaxane and 1b shows the smaller ring (closed-form) state, which are reversibly interconverted. The rotaxanes possess an identical axle component that has a symmetrical structure and is composed of two stoppers, two stations, and one spacer. The potential energy of the individual rotaxane depends on the position of the ring component. The steric barrier between the ring component and the spacer is larger in the closed-form

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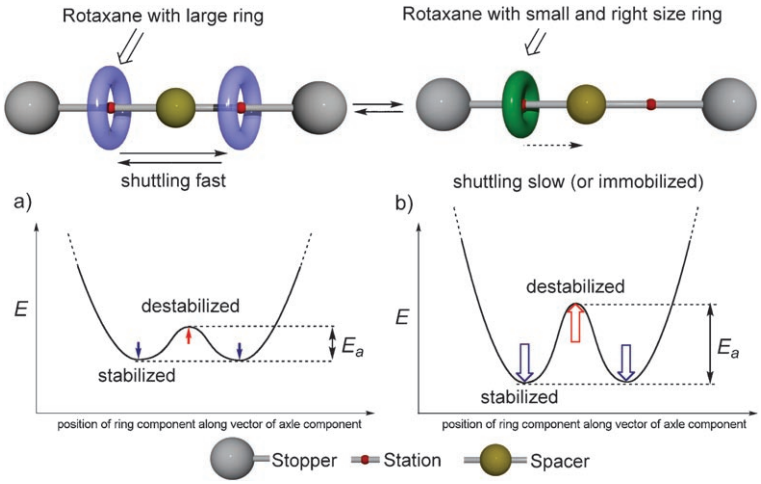
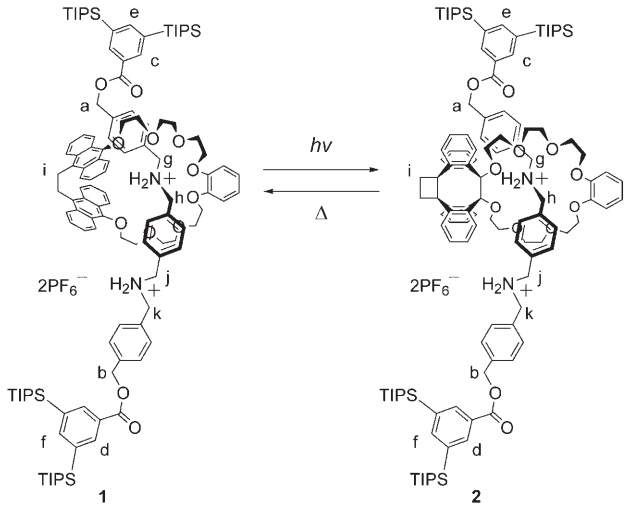


Figure 1. Models of [2]rotaxanes and the corresponding energy diagrams of a shuttling machine with effective brake function.

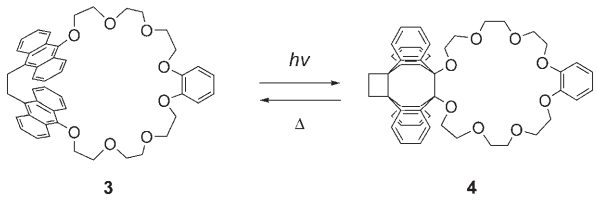
than in the open-form. Moreover, through the attractive interactions between the ring components and the stations, the closed-form rotaxane can be more stabilized than the open-form. Consequently, the shuttling rate of the closed-form rotaxane would be reduced more effectively than that of the open-form.

To build a prototype of the shuttling molecular machine with a reversible brake function, the following structural requirements should be fulfilled; 1) a size-changeable ring component, which responds to external stimuli, 2) an appropriate spacer, which acts as a small barrier to the open-form ring and a large barrier to the closed-form ring, and 3) a station, which interacts more strongly with the closed form ring molecule than the open-form. As a rotaxane system, which meets these requirements, we designed rotaxanes **1** and **2** consisting of a photochromic dianthrylethane-based ring component[10] and a dumbbell shaped axle molecule with a phenylene group and two secondary ammonium sites



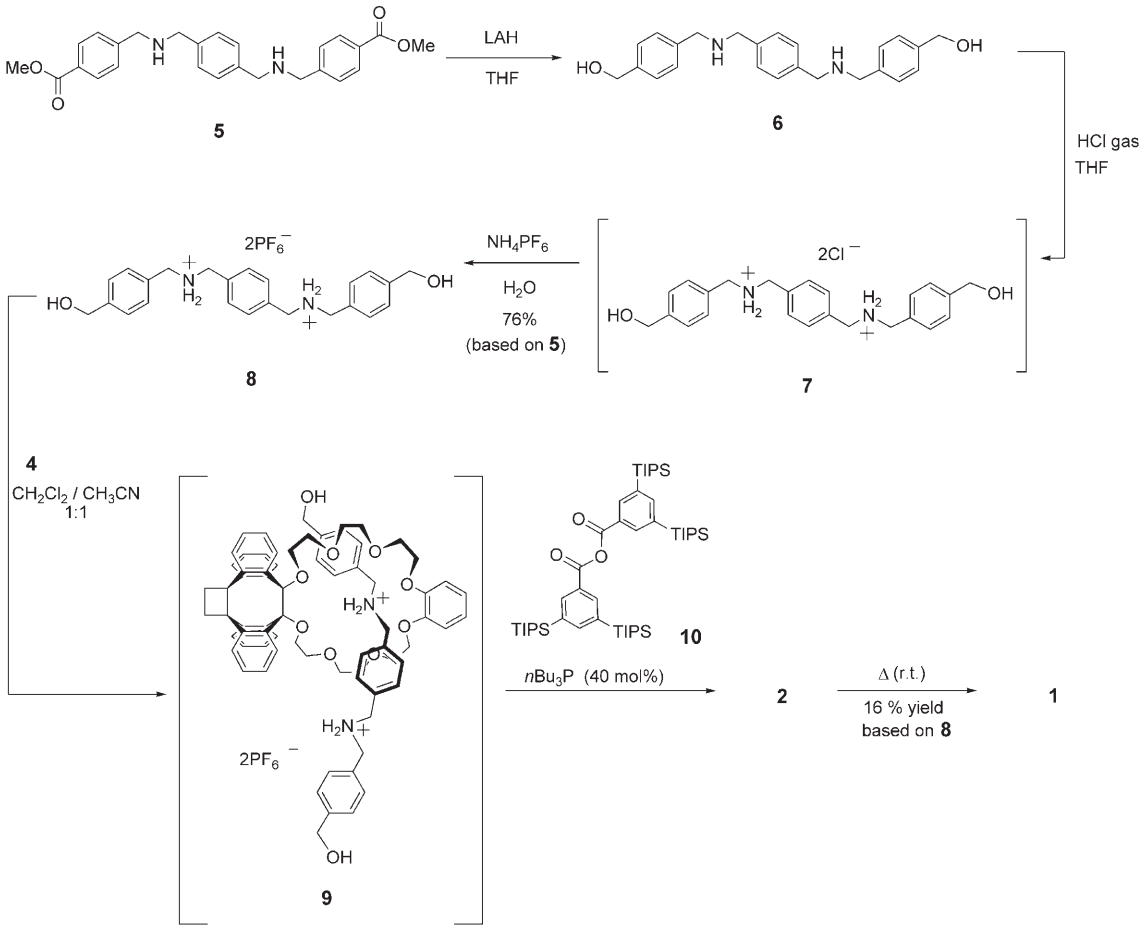
Scheme 1. The open- (**1**) and closed- (**2**) forms of the shuttling machine with reversible brake function.

(Scheme 1). In Scheme 2 the structures of open and closed-form ring molecules **3**[9] and **4**[9] corresponding to **1** and **2**, respectively, are shown. The photodimerization of the anthracene units of **3** and the thermal reversion of **4** to **3** cause a substantial change in their cavity size, which is fully reversible. The interconversion between these two isomers proceeded quantitatively and in 97.5% durability after 10 cycles. The closed-form ring molecule **4** forms a more stable complex with dibenzylammonium hexafluorophosphate than open-form molecule **3**. On the basis of these results, we adopt **3** and **4** for the ring components of rotaxanes **1** and **2**. As the stopper, 3,5-bis(triisopropylsilyl)phenyl group was selected because it is large enough to prevent deslipping of the axle component from the open-form ring molecule **3** (30-crown-8 type).



Scheme 2. Reversible isomerization between open- (**3**) and closed- (**4**) forms of ring molecules.

Preparation of rotaxane 1: The synthesis of rotaxane **1** was carried out through two different routes, which are summarized in Scheme 3 and Scheme 4. Diester **5** and the photocontrollable macrocycle **3**, which were prepared according to the literature,[7i,9] were used as starting materials in both routes. As shown in Scheme 3, ammonium hexafluorophosphate **8** was prepared from diester **5** by reduction with LAH, followed by salt formation with gaseous HCl and anion exchange with NH_4PF_6. The closed-form ring molecule **4**, freshly prepared from the open-form compound **3** by UV irradiation, was treated with **8** in CH_2Cl_2/CH_3CN (1:1) at 273 K to produce pseudorotaxane **9**. Addition of anhydride **10** and nBu$_3$P[11] at 273 K, followed by purification with preparative HPLC, furnished the open-form [2]rotaxane **1** via closed-form **2** (which opened during the isolation procedure). However, the chemical yield of **1** was not satisfactorily (<16% yield from **8**), and **1** was contaminated with a small amount of the corresponding [3]rotaxane. The reasons for the low yield are attributed to low solubility of **8** in non-polar solvents, which reduced the extent of the for-



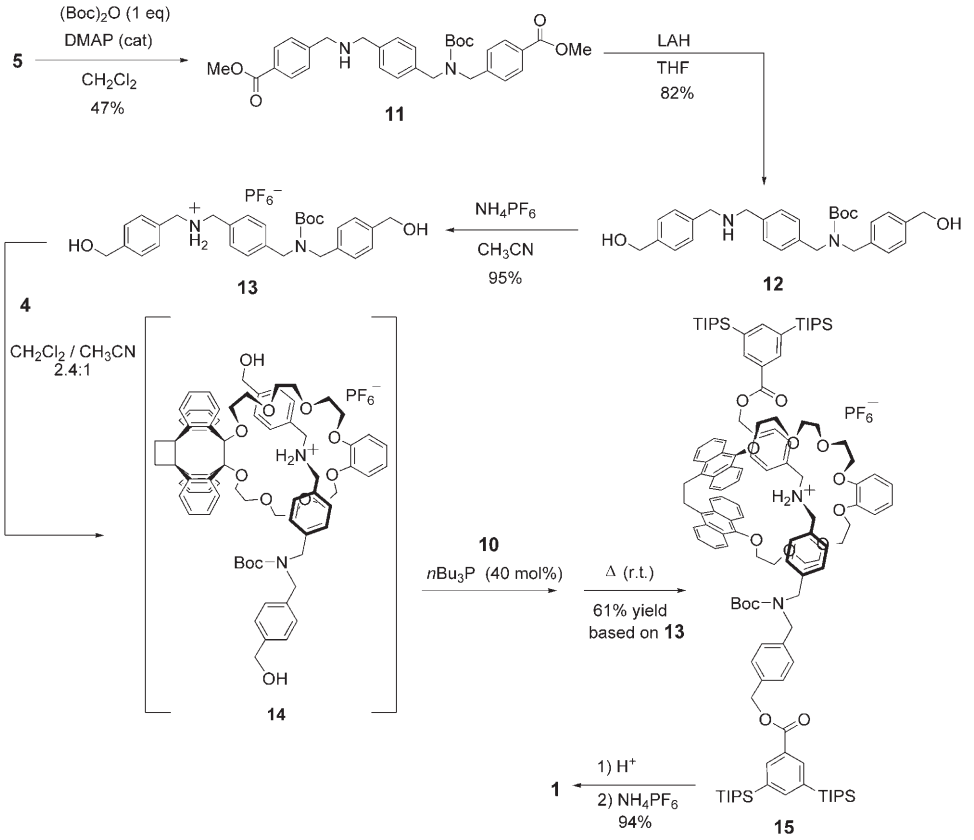
Scheme 3. Synthesis of rotaxane **1**.

mation of pseudorotaxane **9** during the capping reaction, and the formation of a [3]rotaxane.

To improve the yield of **1**, mono protected ammonium hexafluorophosphate **13** was used as an alternative axle unit, as shown in Scheme 4. Diester **5** was converted to the corresponding amine **11** (47% yield), which, in turn, was reduced with LAH to **12** (82%). Subsequent protonation gave the mono protected ammonium hexafluorophosphate **13** (95%), the solubility of which in nonpolar solvents was improved compared to **8**. The rotaxane formation was then carried out in a mixed solvent consisting of CH_2Cl_2 and CH_3CN in a ratio of 2.4:1 in a similar manner as shown in Scheme 3. After the purification by preparative HPLC, we obtained **15** (61%). Deprotection of the Boc group of **15** followed by treatment with NH_4PF_6 afforded open-form rotaxane **1**.

Interconversion between open- and closed-form rotaxanes 1 and 2: The ^{1}H NMR spectra of **1** and **2** in [D_8]THF at 303 K are shown in Figure 2. When a solution of **1** in [D_8]THF immersed in an ice bath was irradiated with a high-pressure mercury lamp, the sharp singlet signal assigned to the benzylic proton (H_i) of **1** at $\delta = 4.12$ ppm disappeared. The disappearance of this benzylic proton and the appearance of the aliphatic proton of **2** at $\delta = 2.90$ ppm indicated that the ring closure had proceeded efficiently. In addition, the signal assigned to the benzylic protons of the axle component (H_g, H_h, H_j, and H_k) of **1** appeared as a broad signal at 4.36 ppm, which was averaged on the NMR time-scale. After the irradiation, the signal split into several signals including those of H_g and H_h at 5.28 and 5.10 ppm. The signals of H_j and H_k of **2** overlapped with the ethereal signals of the ring component. The spectrum of **2** reverted to that of **1** completely after the NMR solution of **2** was left at room temperature overnight. This implies that the thermal reversion of **2** to **1** proceeds quantitatively. Hence, the evidence for reversible switching between **1** and **2** by external stimuli, photoirradiation and thermal heating, was thus established.

Determination of shuttling rates of open-form rotaxane 1 and closed-form rotaxane 2: To determine the rates of the shuttling motion of rotaxane **1**, VT-NMR spectra (Figures 3 and 4) were recorded. The rates of the shuttling motion of rotaxane **1** were determined by the line-shape analysis of their VT-NMR spectra in [D_8]toluene and [D_8]THF.[12] Figure 5 shows the partial experimental ^{1}H NMR spectra of the benzylic protons (H_a, H_b) on the axle component of open-form rotaxane **1** at different temperatures together with the simulated spectra assuming the rates shown. The ki-



Scheme 4. Alternative route for synthesis of rotaxane **1**.

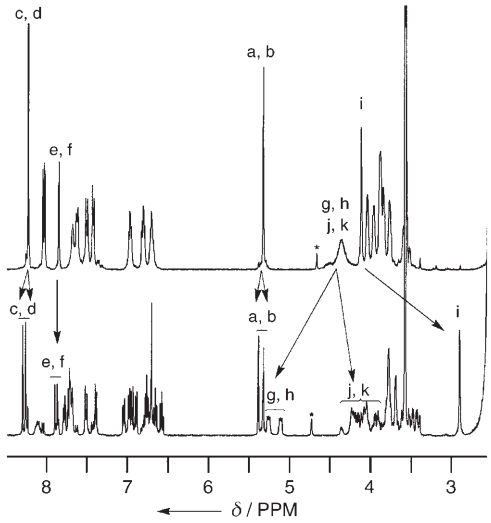


Figure 2. Partial ^{1}H NMR spectra (400 MHz) of open- (**1**, upper) and closed-form (**2**, lower) 2-station [2]rotaxanes recorded in [D_8]THF at 303 K.

netic parameters were determined from the Eyring plot listed in Table 1. On the other hand, the shuttling rates of closed-form rotaxane **2** could not be determined in the same manner. The room-temperature spectra of **2** indicate that the shuttling motion is slow on the NMR time scale and that the coalescence of the split signals was not observed when the solutions were heated to 303 K in [D_8]toluene and to 323 K in [D_8]THF, respectively.[13] Therefore, the maximum estimated rates of shuttling motion are $k_{303\,K} < 19\,s^{-1}$ and $k_{323\,K} < 86\,s^{-1}$, respectively, from the Gutowski's equation calculated from the observed $\Delta\nu$ (the smallest difference between the resonance frequencies of exchangeable protons H_a and H_b in both solvents) of **2**, as shown in Table 1.

As shown in Table 1, the rate of shuttling of open-form rotaxane **1** ($k_{303\,K} = 860\,s^{-1}$) is at least 45 times faster than that of closed-form rotaxane **2** ($k_{303\,K} < 19\,s^{-1}$) in [D_8]toluene. The switching ratio in [D_8]THF is about 50 ($k_{323\,K} = 4500\,s^{-1}$ vs. $k_{323\,K} < 86\,s^{-1}$). These results clearly demonstrate that the shuttling motion was controlled very effectively by changing the ring size of the rotaxanes by using photochemical cycloaddition and thermal reversion. In addition, the solvent does not affect significantly the ratio of shuttling rates.

The rate of shuttling of closed-form **2** was also estimated by saturation transfer experiments.[14] As a result, the shuttling rate of rotaxane **2** at 273 K in [D_8]THF was estimated to be $< 2.3\,s^{-1}$. The rate constant of **1**, $k_{273\,K} = 340\,s^{-1}$, at the same temperature in [D_8]THF was calculated from the kinetic parameters obtained from the VT-NMR shown in Table 1. These results also demonstrate that the rate of shuttling was reduced substantially to less than 1% (from 340 to

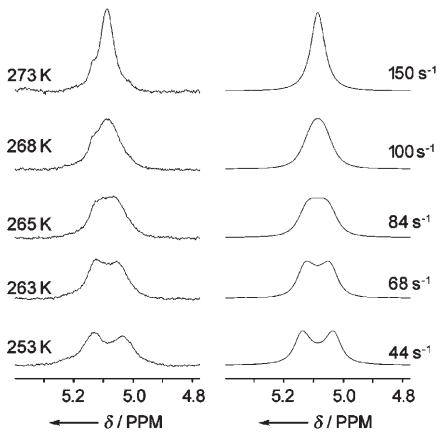


Figure 3. Experimental (left) and simulated (right) partial VT-NMR (270 MHz) spectra of protons H_a and H_b of **1** in [D_8]toluene. The corresponding temperatures and exchange rates are indicated.

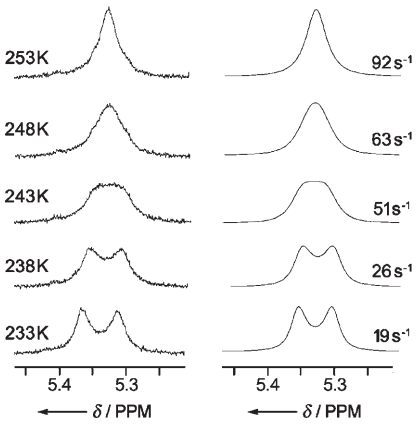


Figure 4. Experimental (left) and simulated (right) partial VT-NMR (270 MHz) spectra of protons H_a, and H_b of **1** in [D_8]THF. The corresponding temperatures and exchange rates are indicated.

Table 1. Rates of shuttling and the corresponding kinetic parameters of **1** and **2**.

	solvent	T_c [K]	$\Delta\nu$ [Hz]	$\Delta H^{\neq}$ [kJ mol^{-1}]	$\Delta S^{\neq}$ [J K^{-1} mol^{-1}]	k [s^{-1}]
1	[D_8]toluene	266	–	37 ± 4	-65 ± 17	860 ± 270[b]
2	[D_8]toluene	>303	8.4	nd[a]	nd[a]	<19[b,c]
1	[D_8]THF	243	–	36 ± 2	-65 ± 8	4500 ± 300[d]
2	[D_8]THF	>323	39	nd[a]	nd[a]	<86[d,c]

[a] Not determined. [b] at 303 K. [c] Maximum rates estimated from the Gutowski's equation, assuming that the coalescence was observed at each temperature. [d] at 323 K.

$<2.3\ s^{-1}$) by changing the size of the ring component from 30-crown-8 to 24-crown-8 type macrocycles.

Conclusion

We have synthesized 2-station [2]rotaxanes that have a dianthrylethane moiety in the ring unit of which size could be changed reversibly and quantitatively by intramolecular photochemical cycloaddition and thermal reversion. Substantial differences between the shuttling rates of the open- and closed-form rotaxanes were observed, demonstrating that the shuttling motion was controlled effectively by the external stimuli. These results clearly demonstrate the potential of the brake function of the present system for applications in the control of shuttling and other motions directed toward the construction of artificial molecular machines.[15]

Experimental Section

General: ^{1}H NMR (270, 300, or 400 MHz) and ^{13}C NMR (67.5, 75.0, 100, or 125.6 MHz) spectra were recorded by using a Varian Unity-Inova 500, 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 or residual solvent. IR spectra were recorded as a KBr disk by using a JASCO FTIR-410 spectrometer. Mass spectral analyses were performed by means of a JEOL JMS-DX303HF for EI and FAB ionization. The LD TOF mass measurements were performed by means of a Shimadzu/Kratos AXIMA-CFR spectrometer. Elemental analyses were carried out by using a Perkin–Elmer 2400II analyzer. UV-visible spectra were recorded by using a Hitachi U-3310 spectrometer in acetonitrile. Preparative HPLC separation was undertaken with a JAI LC-908 chromatograph by 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 ketyl), CH_3CN, CH_2Cl_2 (CaH_2). Compounds **3**, **5** and **10** were prepared according to the literature, respectively.[7i,9]

Synthesis of 7: To a suspension of LAH (770 mg, 20.3 mmol) in dry THF (100 mL) was added slowly a solution of **5** (2.20 g, 5.09 mmol) in dry THF (50 mL) over 13 min. After 1.5 h stirring at room temperature, water (10 mL) was added slowly at 5 °C. The reaction mixture was filtered through a pad of Celite by suction. The solvent of the combined filtrate was evaporated off. The residue was washed with aqueous solution of 20% KOH (50 mL), extracted with diethyl ether, and the extract was dried over anhydrous $MgSO_4$. The removal of the solvent under reduced pressure gave crude **6** (2.89 g) as a pale yellow oil. Introduction of a HCl gas into a solution of **6** in THF (150 mL) gave **7** as a white powder. Filtration by suction, washing with THF, and drying under reduced pressure gave **7** (2.11 g, 92% yield for 2 steps). Thus obtained **7** was employed for anion exchange reaction to **8** without further purification. m.p. 225–230 °C (decomp.); ^{1}H NMR (270 MHz, D_2O, 30 °C): $\delta=7.54$ (s, 4H), 7.48 (s, 8H), 4.68 (s, 4H), 4.32 (s, 4H), 4.31 ppm (s, 4H); IR (KBr): $\tilde{\nu}=3366$ (br), 2992, 2940, 2788, 2716, 2592, 2364, 1557, 1457, 1417, 1217, 1021, 976, 848 cm^{-1}; MS (FAB): m/z: 377.2 $(M-HCl-Cl)^+$.

Synthesis of 8: Addition of a solution of NH_4PF_6 (6.01 g, 36.9 mmol) in H_2O (10 mL) into a solution of **7** (900 mg, 2.00 mmol) in H_2O (20 mL) resulted in a suspension. The precipitates were collected by suction filtration. Recrystalization from CH_3CN/Et_2O gave **8** (1.07 g, 80% yield) as colorless crystals. m.p. 260 °C (decomp.); ^{1}H NMR (270 MHz, CD_3CN, 30 °C): $\delta=7.51$ (s, 4H), 7.43 (s, 8H), 4.61 (s, 4H), 4.26 (s, 4H), 4.24 ppm (s, 4H); ^{13}C NMR (75.5 MHz, [D_6]DMSO, 30 °C): $\delta=129.69$, 129.65, 129.5, 129.3, 127.5, 126.4, 62.5, 50.2, 49.9 ppm; IR (KBr): $\tilde{\nu}=3379$ (br), 3249, 3227, 2994, 2945, 2789, 2714, 1582, 1416, 838, 758 cm^{-1}; MS (FAB): m/z: 522.9 $(M-PF_6)^+$, 378.2 $(M-2PF_6)^+$; elemental analysis calcd (%) for $C_{24}H_{30}F_{12}N_2O_2P_2$: C 43.12, H 4.52, N 4.19; found: C 42.91, H 4.53, N 4.12.

Synthesis of rotaxane 1 from 8: A solution of crown ether **3** (70.0 mg, 93.0 μmol) in benzene (7 mL) was placed in a Pyrex tube and was well degassed by bubbling dry argon. Then, the solution was irradiated by using a 500 W high pressure mercury lamp for 10 min in an ice bath. After irradiation, the solvent was evaporated off with cooling. The freshly prepared **4** in CH_2Cl_2/CH_3CN (1:1) (400 μL) was mixed with secondary ammonium hexafluorophosphate **8** (60.1 mg, 89.9 μmol) in CH_3CN (200 μL) and acid anhydride **10** (165 mg, 194 μmol) in CH_2Cl_2 (200 μL) in an ice-salt bath. Resulted precipitates were dissolved by the addition of CH_2Cl_2 (100 μL) and CH_3CN (100 μL). Then, 40 mol% of nBu$_3$P (9 μL, 36 μmol) was added to the mixture under a N_2 atmosphere. After stirring for 5.5 h in the ice-salt bath and 0.5 h at room temperature, the solvent was evaporated. Preparative HPLC separation of the products gave **1** (33.1 mg, 16% yield) as a yellow powder. MS (MALDI-TOF): m/z: 2061.7 $(M-PF_6)^+$; 2715.9 ([3]rotaxane-HPF_6-PF_6).

Synthesis of 11: A solution of amine **5** (1.42 g, 3.28 mmol), di-*tert*-butyl dicarbonate (Boc_2O) (711 mg, 3.26 mmol), and *N*, *N*-dimethylaminopyridine (DMAP) (18 mg, 16 μmol) in CH_2Cl_2 (25 mL) was stirred at room temperature for 2 h. After evaporation of the solvent, chromatography on silica gel (eluent: hexane/ethyl acetate) gave **11** (818 mg, 47%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): $\delta=8.02$–7.97 (m, 4H), 7.42 (d, $J=8.5$ Hz, 2H), 7.30–7.17 (m, 6H), 4.44 (brs, 2H), 4.38 (brs, 2H), 3.91 (s, 3H), 3.90 (s, 3H), 3.86 (s, 2H), 3.79 (s, 2H), 1.48 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): $\delta=166.9$, 166.8, 155.8, 145.6, 139.2, 136.4, 129.8, 129.7, 129.1, 128.8, 128.3, 128.1, 127.9, 127.6, 127.1, 80.4, 52.9, 52.8, 52.1, 52.0, 49.5, 28.5 ppm; IR (neat): $\tilde{\nu}=3334$ (br), 2977, 2952, 2842, 1723, 1694, 1612, 1456, 1435, 1408, 1366, 1281, 1164, 1111,

1019, 755 cm^{-1}; MS (FAB): *m/z*: 532.9 $(M+H)^+$; HRMS (FAB): *m/z*: for $C_{31}H_{37}N_2O_6$: calcd: 533.2652; found: 533.2668.

Synthesis of 12: Into a suspension of LAH (200 mg, 5.27 mmol) in THF (30 mL) was added a solution of **11** (710 mg, 5.09 mmol) in THF (10 mL) dropwise during 3 min at −10 °C. After 30 min stirring at room temperature, water was added slowly. The solvent was evaporated off, and the residue was extracted with diethyl ether. The extract was washed with 10% KOH aqueous solution and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave **12** as a pale yellow oil (520 mg, 82%). Amine **12** was employed for anion exchange reaction to **13** without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ = 7.33 (s, 4H), 7.29–7.25 (m, 4H), 7.15 (brs, 4H), 4.67 (s, 2H), 4.64 (s, 2H), 4.39 (brs, 2H), 4.33 (brs, 2H), 3.80 (s, 2H), 3.77 (s, 2H), 1.49 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ = 155.9, 139.9, 139.8, 139.0, 138.6, 137.3, 136.8, 128.4, 128.3, 128.1, 127.6, 127.13, 127.09, 80.1, 65.1, 65.0, 52.8, 52.7, 49.3, 49.0, 28.5 ppm; IR(neat): $\tilde{\nu}$ = 3384 (br), 3054, 3009, 2977, 2928, 2867, 1682, 1457, 1411, 1365, 1245, 1163, 732 cm^{-1}; MS (FAB): *m/z*: 477.0 $(M+H)^+$; HRMS (FAB): *m/z*: for $C_{29}H_{37}N_2O_4$: calcd: 477.2753; found: 477.2621.

Synthesis of 13: Into a solution of amine **12** (340 mg, 713 μmol) and NH_4PF_6 (122 mg, 748 μmol) in CH_3CN (8 mL), argon gas was vigorously bubbled for 2 h. Then the solvent was removed by evaporation, and the residue was extracted with acetone/CH_2Cl_2 (1:1). The extract was washed with water and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave **13** (420 mg, 95%) as a colorless foam. m.p. 78–81 °C; ^{1}H NMR (270 MHz, CD_3CN, 30 °C): δ = 7.43 (s, 4H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.29–7.25 (m, 4H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.61 (d, *J* = 5.4 Hz, 2H), 4.53 (s, 2H), 4.41 (brs, 4H), 4.21 (s, 2H), 4.20 (s, 2H), 3.28 (t, *J* = 5.4 Hz, 1H), 1.43 ppm (s, 9H); ^{13}C NMR (100 MHz, CD_3CN): δ = 156.6, 144.7, 141.8, 138.0, 131.1, 131.0, 130.0, 129.9, 129.0, 128.5, 128.1, 127.9, 118.2, 80.8, 64.5, 64.1, 52.1, 52.0, 28.6 ppm; IR (KBr): $\tilde{\nu}$ = 3587, 3357 (br), 3244, 2978, 2934, 2878, 2825, 1662, 1464, 1415, 1368, 1250, 1163, 848 cm^{-1}; MS (MALDI-TOF): *m/z*: 477.1 $(M-PF_6)^+$; elemental analysis calcd (%) for $C_{29}H_{37}F_6N_2O_4P$: C 55.95, H 5.99, N 4.50; found: C 55.92, H 5.93, N 4.73.

Synthesis of rotaxane 15: A solution of crown ether **3** (130 mg, 173 μmol) in benzene (10 mL) was placed in a Pyrex tube and was well degassed by bubbling dry argon. Then, the solution was irradiated using a 500 W high pressure mercury lamp for 20 min in an ice bath. After irradiation, the solvent was evaporated off with cooling. The freshly prepared **4** in CH_2Cl_2 (300 μL) was mixed with secondary ammonium hexafluorophosphate **13** (90.1 mg, 145 μmol) in CH_3CN (125 μL), and a solution of anhydride **10** (270 mg, 319 μmol) in CH_2Cl_2 (250 μL) in an ice-salt bath. Then, 40 mol% of nBu_3P (15 μL, 58 μmol) was added to the mixture under a N_2 atmosphere. After stirring for 6.5 h in an ice-salt bath, the solvent was evaporated. Subsequent preparative HPLC separation gave **15** (194 mg, 61% yield) as a yellow foam. m.p. 115–118 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 30 °C): δ = 8.20 (s, 4H), 7.98 (br, 2H), 7.97 (d, *J* = 9.1 Hz, 4H), 7.84 (brs, 1H), 7.82 (brs, 1H), 7.55 (d, *J* = 8.7 Hz, 4H), 7.50–7.35 (m, 8H), 7.25–7.21 (m, 8H), 6.99 (br, 4H), 6.92 (br, 4H), 6.77–6.73 (m, 2H), 6.60–6.57 (m, 2H), 5.38 (s, 2H), 5.34 (s, 2H), 4.38 (br, 8H), 4.14 (br, 4H), 4.05–4.04 (m, 4H), 3.95–3.94 (m, 4H), 3.77–3.59 (m, 16H), 1.47 (s, 9H), 1.47–1.37 (m, 12H), 1.07 (d, *J* = 7.2 Hz, 36H), 1.05 ppm (d, *J* = 7.4 Hz, 36H); ^{13}C NMR (125.6 MHz): δ = 167.2, 167.0, 155.9, 148.9, 147.2, 147.0, 146.5, 140.0, 138.3, 136.5, 136.4, 135.7, 134.3, 134.1, 130.7, 130.5, 129.8, 129.4, 129.3, 129.0, 128.2, 128.1, 12803, 128.02, 127.5, 124.6, 124.2, 123.6, 121.9, 121.8, 112.3, 80.4, 73.9, 71.2, 70.5, 70.2, 69.6, 68.2, 66.0, 65.6, 52.6, 49.1, 28.4, 26.5, 18.51, 18.49, 10.8, 10.7 ppm; IR (KBr): $\tilde{\nu}$ = 3133, 3066, 2943, 2889, 2866, 1720, 1696, 1461, 1268, 1250, 1130, 882, 843 cm^{-1}; MS (MALDI-TOF): *m/z*: 2061.7 $(M-PF_6)^+$; elemental analysis calcd (%) for $C_{127}H_{173}O_{14}N_2F_6PSi_4$: C 69.05, H 7.89, N 1.27; found: C 68.96, H 7.99, N 1.37.

Synthesis of rotaxane 1: Into a solution of rotaxane **15** (151 mg, 68.4 μmol) in CH_2Cl_2 (4 mL) was added a solution of CF_3COOH (303 mg, 2.66 mmol) in CH_2Cl_2 (4 mL). After the reaction mixture was stirred for 4 h at room temperature, to the reaction mixture was added water. The reaction mixture was extracted with CH_2Cl_2 and the organic layer was washed with water and a saturated aqueous solution of NH_4PF_6 and dried over $MgSO_4$. After the solvent was removed, recrystallization of the residue from hexane/ethyl acetate gave **1** (140 mg, 94%) as a yellow powder. m.p. 137–140 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 30 °C): δ = 8.21 (d, *J* = 1.0 Hz, 4H), 7.97 (d, *J* = 8.6 Hz, 4H), 7.84 (brs, 2H), 7.63 (brs, 4H), 7.57 (d, *J* = 8.9 Hz, 4H), 7.53–7.43 (m, 8H), 7.05–7.00 (m, 4H), 6.88–6.82 (m, 4H), 6.71–6.59 (m, 4H), 5.40 (s, 4H), 4.19–3.98 (m, 20H), 3.67 (br, 8H), 3.51 (br, 4H), 3.43 (br, 4H), 1.43 (heptet, *J* = 7.3 Hz, 12H), 1.07 ppm (d, *J* = 7.3 Hz, 72H); ^{13}C NMR (100 MHz): δ = 167.0, 153.5, 148.8, 147.0, 146.5, 136.4, 134.1, 130.7, 129.1, 128.8, 128.1, 127.9, 124.5, 124.2, 124.1, 123.6, 121.9, 121.8, 112.4, 74.0, 71.1, 70.5, 70.4, 69.6, 68.4, 65.9, 31.6, 26.6, 18.6, 10.8 ppm; IR (KBr): $\tilde{\nu}$ = 3067 (br), 2944, 2866, 1720, 1505, 1459, 1268, 1131, 844 cm^{-1}; MS (FAB): *m/z*: 1963.2 $(M-2PF_6)^+$; elemental analysis calcd (%) for $C_{122}H_{166}O_{12}N_2F_{12}P_2Si_4$: C 64.98, H 7.42, N 1.24; found: C 64.92, H 7.34, N 1.17.

Synthesis of the closed-form rotaxane 2: A solution of rotaxane **1** (6.5 mg, 2.9 μmol) in [D_8]THF (700 μL) was placed in a Pyrex NMR tube and was well degassed by a bubbling of dry argon for 45 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 (400 MHz, [D_8]THF, 0 °C): δ = 8.29 (d, *J* = 1.0 Hz, 2H), 8.25 (d, *J* = 1.0 Hz, 2H), 8.12 (brs, 2H), 7.87 (d, *J* = 11 Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 4H), 7.74–7.68 (m, 8H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.05–6.94 (m, 6H), 6.87 (d, *J* = 6.8 Hz, 2H), 6.81–6.70 (m, 8H), 6.67–6.55 (m, 4H), 5.40, (s, 2H), 5.33 (s, 2H), 5.28 (br, 2H), 5.10 (br, 2H), 4.24–3.36 (m, 26H), 2.90 (s, 4H), 1.52–1.43 (m, 12H), 1.08 ppm (d, *J* = 7.6 Hz, 72H).

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[1] a) E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem.* **2007**, *119*, 72–196; *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191; b) G. S. Kottas, L. I. Clarke, D. Horinek, J. Michl, *Chem. Rev.* **2005**, *105*, 1281–1376; c) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **2000**, *112*, 3484–3530; *Angew. Chem. Int. Ed.* **2000**, *39*, 3348–3391; d) B. L. Feringa, R. A. van Delden, N. Koumura, E. M. Geertsema, *Chem. Rev.* **2000**, *100*, 1789–1816; e) T. R. Kelly, R. A. Silva, H. De Silva, S. Jasmin, Y. Zhao, *J. Am. Chem. Soc.* **2000**, *122*, 6935–6949; f) T. Muraoka1, K. Kinbara1, T. Aida, *Nature* **2006**, *440*, 512–515; g) T. Felder, C. A. Schalley, in *Highlights in Bioorganic Chemistry* (Eds.: H. Wennemers, C. Schmuck), Wiley-VCH, Weinheim, **2004**, pp. 526–539.

[2] a) A. P. de Silva, H. Q. N. Gunaratne, C. P. McCoy, *Nature* **1993**, *364*, 42–44; b) P. Ghosh, P. K. Bharadwaj, J. Roy, S. Ghosh, *J. Am. Chem. Soc.* **1997**, *119*, 11903–11909; c) D. L. Feldheim, C. D. Keating, *Chem. Soc. Rev.* **1998**, *27*, 1–12; d) W. Lu, C. M. Lieber, *Nat. Mater.* **2007**, *6*, 841–850.

[3] a) G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, New York, **1971**; b) D. M. Walba, *Tetrahedron* **1985**, *41*, 3161–3212; c) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Rev.* **1987**, *87*, 795–810; d) H. W. Gibson, H. Marand, *Adv. Mater.* **1993**, *5*, 11–21; e) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725–2828; f) R. Jäger, F. Vögtle, *Angew. Chem.* **1997**, *109*, 966–980; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 930–944; g) *Molecular Catenanes, Rotaxanes and Knots* (Eds.: J.-P. Sauvage, C. Dietrich-Buchecker), Wiley-VCH, Weinheim, **1999**; h) H. Tian, Q.-C. Wang, *Chem. Soc. Rev.* **2006**, *35*, 361–374.

[4] a) P.-L. Anelli, N. Spencer, J. F. Stoddart, *J. Am. Chem. Soc.* **1991**, *113*, 5131–5133; b) R. A. Bissell, E. Córdova, A. E. Kaifer, J. F. Stoddart, *Nature* **1994**, *369*, 133–137; c) P.-L. Anelli, M. Asakawa, P. R. Ashton, R. A. Bissell, G. Clavier, R. Górski, A. E. Kaifer, S. J. Langford, G. Mattersteig, S. Menzer, D. Philp, A. M. Z. Slawin, N.

Spencer, J. F. Stoddart, M. S. Tolley, D. J. Williams, *Chem. Eur. J.* **1997**, *3*, 1113–1135; d) D. A. Leigh, A. Troisi, F. Zerbetto, *Angew. Chem.* **2000**, *112*, 358–361; *Angew. Chem. Int. Ed.* **2000**, *39*, 350–353; e) P. R. Ashton, R. Ballardini, V. Balzani, A. Credi, R. Dress, E. Ishow, C. J. Kleverlaan, O. Kocian, J. A. Preece, N. Spencer, J. F. Stoddart, M. Venturi, S. Wenger, *Chem. Eur. J.* **2000**, *6*, 3558–3574; f) S. Saha, J. F. Stoddart, *Chem. Soc. Rev.* **2007**, *36*, 77–92.

[5] a) P.-L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. T. Gandorfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, C. Vicent, D. J. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 193–218; b) V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, **2003**, pp. 329–347.

[6] a) ref [5b], pp. 348–386; b) C. P. Collier, E. W. Wong, M. Belohradsky, F. M. Raymo, J. F. Stoddart, J. P. Kuekes, R. S. Williams, J. R. Heath, *Science* **1999**, *285*, 391–394; c) C. P. Collier, G. F. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart, J. R. Heath, *Science* **2000**, *289*, 1172–1175; J. F. Stoddart, J. R. Heath, *Science* **2000**, *289*, 1172–1175; d) F. Durola, J.-P. Sauvage, *Angew. Chem.* **2007**, *119*, 3607–3610; *Angew. Chem. Int. Ed.* **2007**, *46*, 3537–3540; e) J. E. Green, J. W. Choi1, A. Boukai1, Y. Bunimovich1, E. Johnston-Halperin, E. Delonno, Y Luo, B. A. Sheriff1, K. Xu1, Y. S. Shin, H.-R. Tseng, J. F. Stoddart, J. R. Heath, *Nature* **2007**, *445*, 414–417.

[7] Several chemical approaches have been reported. For a chemical approach by salt formation and metal coordination, see: a) P. Ghosh, G. Federwisch, M. Kogej, C. A. Schalley, D. Haase, W. Saak, A. Lützen, R. M. Gschwind, *Org. Biomol. Chem.* **2005**, *3*, 2691–2700; b) L. Jiang, J. Okano, A. Orita, J. Otera, *Angew. Chem.* **2004**, *116*, 2173–2176; *Angew. Chem. Int. Ed.* **2004**, *43*, 2121–2124; c) D. A. Leigh, P. J. Lusby, A. M. Z. Slawin, D. B. Walker, *Angew. Chem.* **2005**, *117*, 4633–4640; *Angew. Chem. Int. Ed.* **2005**, *44*, 4557–4564; for a chemical approach by covalent bond formation, see: d) A. S. Lane, D. A. Leigh, A. Murphy, *J. Am. Chem. Soc.* **1997**, *119*, 11092–11093; e) J. V. Hernandez, E. R. Kay, D. A. Leigh, Science **2004**, 306, 1532–1537; f) J. S. Hannam, S. M. Lacy, D. A. Leigh, C. G. Saiz, A. M. Z. Slawin, S. G. Stitchell, *Angew. Chem.* **2004**, *116*, 3322–3326; *Angew. Chem. Int. Ed.* **2004**, *43*, 3260–3264; g) M. N. Chatterjee, E. R. Kay, D. A. Leigh, *J. Am. Chem. Soc.* **2006**, *128*, 4058–4073; for a chemical approach by solvent exchange, see: h) D. B. Amabilino, P. R. Ashton, V. Balzani, C. L. Brown, A. Credi, J. M. J. Frechet, J. W. Leon, F. M. Raymo, N. Spencer, J. F. Stoddart, M. Venturi, *J. Am. Chem. Soc.* **1996**, *48*, 12012–12020; i) J. C. Matthew, C. T. Fyte, J. F. Stoddart, *J. Org. Chem.* **2000**, *65*, 1937–1946; j) A. S. Lane, D. A. Leigh, A. Murphy, *J. Am. Chem. Soc.* **1997**, *119*, 11092–11093.

[8] For a switchable gate against shuttling movement by light see: V. Serreli, C.-F. Lee, E. R. Kay, D. A. Leigh, *Nature*, **2007**, *445*, 523–527.

[9] K. Hirose, K. Ishibashi, Y. Shiba. Y. Doi, Y. Tobe, *Chem. Eur. J.* **2008**, *14*, 981–986.

[10] a) H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, *Pure Appl. Chem.* **1980**, *52*, 2633–2648; b) F. Moriwaki, A. Ueno, T. Osa, *Chem. Lett.* **1986**, *15*, 1865–1868; c) G. Deng, T. Sakai, Y. Kawahara, S. Shinkai, *Supramol. Chem.* **1993**, *2*, 71–76; d) J. H. R. Tucker, H. Bouas-Laurent, P. Marsau, S. W. Riley, J.-P. Desvergne, *Chem. Commun.* **1997**, 1165–1166; e) I. Yamashita, M. Fujii, T. Kaneda, S. Misumi, *Tetrahedron Lett.* **1980**, *21*, 541–544; f) J.-P. Desvergne, J. Lauret, H. Bouas-Laurent, *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 504–513.

[11] H. Kawasaki, N. Kihara, T. Takata, *Chem. Lett.* **1999**, *28*, 1015–1016.

[12] To avoid the decomposition of **1**, the solvent for the irradiation with high pressure mercury lamp was limited. For this reaction [D_8]THF and [D_8]toluene were chosen as suitable polar and less polar solvents.

[13] The temperature for the VT-NMR measurement was limited because the cycloreversion of the closed-form rotaxane **2** started to occur at higher temperatures during the measurement.

[14] Details of the saturation transfer experiment are given in Supporting Information.

[15] We have successfully applied the related braking function to the effective switching of rocking motion of [2]rotaxanes (unpublished results).

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