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A Dual-Response [2]Rotaxane Based on a 1,2,3-Triazole Ring as a Novel Recognition Station

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Abstract: Two novel multilevel switchable [2]rotaxanes containing an ammonium and a triazole station have been constructed by a Cu^{I}-catalyzed azide–alkyne cycloaddition reaction. The macrocycle of [2]rotaxane containing a C6-chain bridge between the two hydrogen bonding stations exhibits high selectivity for the ammonium cation in the protonated form. Interestingly, the macrocycle is able to interact with the two recognition stations when the bridge between them is shortened. Upon deprotonation of both [2]rotaxanes, the macrocycle moves towards the triazole recognition site due to the hydrogen-bond interaction between the triazole nitrogen atoms and the amide groups in the macrocycle. Upon addition of chloride anion, the conformation of [2]rotaxane is changed because of the cooperative recognition of the chloride anion by a favorable hydrogen-bond donor from both the macrocycle isophthalamide and thread triazole CH proton.

Keywords: anions · click chemistry · rotaxanes · supramolecular chemistry · triazoles

Introduction

Mechanical interlocked molecules, in particular rotaxanes and catenanes, have received considerable attention due to their challenging construction and potential application in nanometer-scale molecular devices.[1] The rotaxanes that can be switched between two or more states on different stimuli have gained much more interest.[2] Various external stimuli have been employed to induce such switching, such as ion binding,[3] conformational changes,[4] and alternation of the oxidation state[5] or protonation level of the molecule.[6] Cu^{I}-catalyzed 1,3-dipolar cycloaddition reactions of organic azides and terminal alkynes also called "CuAAC click chemistry" has emerged as a powerful and appealing synthetic tool for the construction of complex materials due to its high efficiency, tolerance of sensitive functional groups, and mild reaction conditions.[7] Various complex structures, such as dendrimers,[8] polymers,[9] macrocycles,[10] molecular nanocages,[11] and derivatization of biological molecules[12] have been accomplished successfully by the click reaction. In particular, it can occur in apolar solvent at room temperature. These conditions are favorable for the hydrogen-bond recognition between macrocycle and thread in construction mechanical interlocked molecules.[13] Recently, examples of a click-reaction-based synthesis of rotaxanes and catenanes have been reported.[14] The molecular rotaxane and muscle developed by Busseron et al. also showed that the triazolium cation could be recognized by dibenzo-[24]crown-8.[15] This recognition process mainly relies on the positively charged triazolium ion. However, to the best of our knowledge, the 1,2,3-triazole generated by the click reaction as a molecular station is still rare.[16] In our system, the click reaction is not only a key step of stoppering the reaction but it also provides a potential alternative binding site, which is introduced directly by a coupling procedure.

Previous reports described the hydrogen-bond acceptor[17] and Lewis base properties of triazole nitrogen atoms[18] as well as the recognition study of anions by the polarized CH proton of triazole.[19] The large dipole (5D) of triazole, the positive end of which points toward the H atom, contributes to its unexpectedly strong hydrogen-bonding capabilities.[19a] Isophthalamide and its derivatives play an important role in

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the design of anion receptors,[20] rotaxanes,[21] and catenanes[22] because of their abilities to act as strong hydrogen-bonding donors in various solutions. With these in mind, we are very interested to examine 1) whether the 1,2,3- triazole ring system resulting from the facile cycloaddition reaction could interact with the macrocycle containing amide units by hydrogen bonding and whether a new type of molecular shuttle could be generated and, if so, 2) whether the conformation of the macrocycle can be changed by anions due to the cooperative complexation in the pocket generated by the isophthalamide group of the macrocycle and the CH proton of triazole in the thread. For these reasons, two [2]rotaxanes have been designed and synthesized that incorporate alkyl ammonium and 1,2,3-triazole "stations" in the thread and an isophthalamide group and polyether chain in the macrocycle by a click reaction. In this system, the shuttling of the macrocycle along the thread driven by acid/base and the conformational alternation of the macrocycle driven by anions has been realized.

In this contribution, we wish to highlight that the click reaction is not only a valuable tool to fabricate the functional rotaxane, but also the generated 1,2,3-triazole resulting in hydrogen-bond interactions with the macrocycle, which will be a reliable building style for the construction of novel and complex structures.

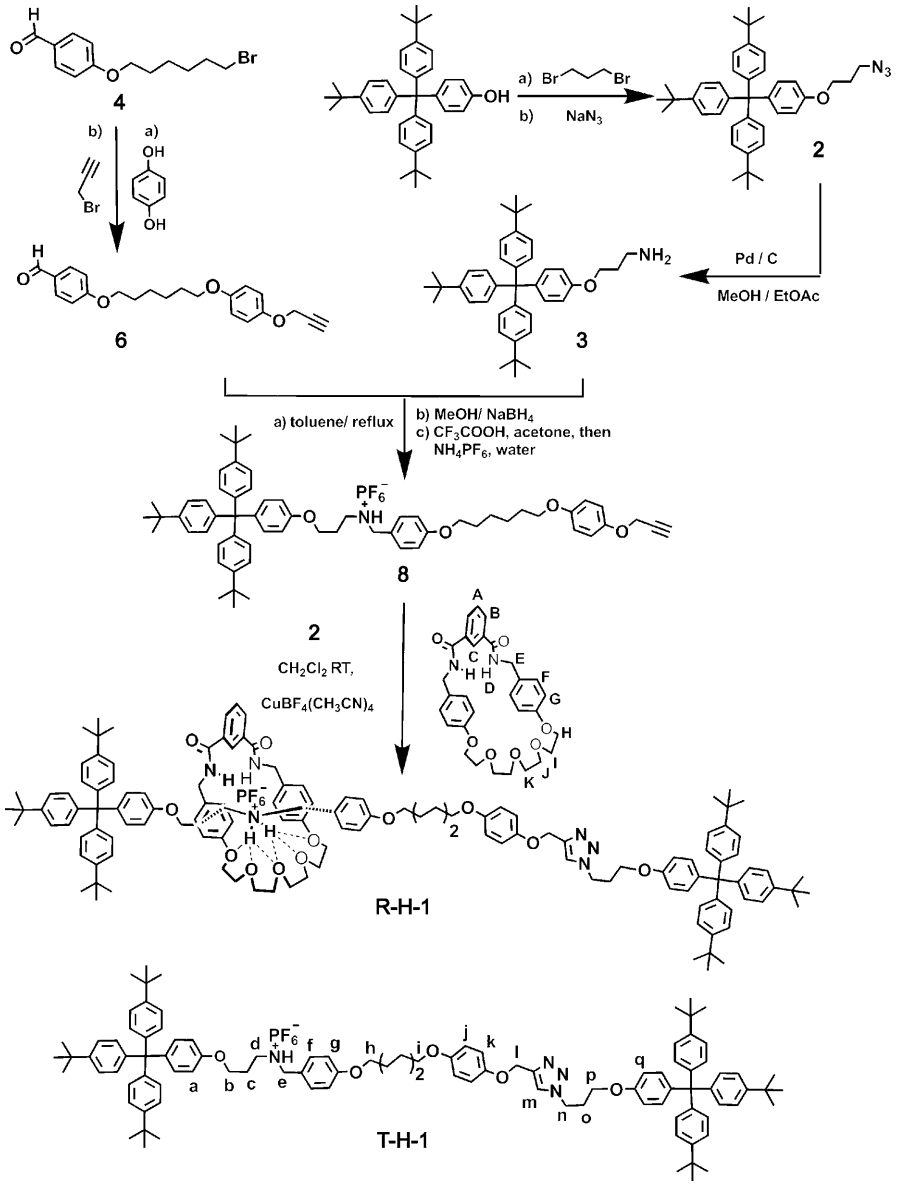
Results and Discussion

The shuttle **R-H-1** was synthesized according to Scheme 1. In CH_2Cl_2, macrocycle **M-1** assembled with the monostoppered ammonium containing compound **8** to form a pseudorotaxane.[23] Covalent capture of the threaded intermediate by a click reaction at room temperature in the presence of $[Cu(MeCN)_4]BF_4$ as the catalyst afforded the thread **T-H-1** and [2]rotaxane **R-H-1** in 50 and 35% yield after chromatographic column purification, respectively.

In our system, the azide–alkyne cycloaddition is not only a key step of the stoppering reaction, but also the generated 1,2,3-triazole can participate in hydrogen-bond interactions with the macrocycle which provides a second binding site.

The MALDI-TOF spectrum of **R-H-1** gave sharp peaks at m/z: 2041.5 $[M-PF_6-H+Na]^+$ and 2057.5 $[M-PF_6-H+K]^+$ (see the Supporting Information) which revealed the features of an interlocked molecule. The position of the macrocycle **M-1** in rotaxane could be readily determined by comparing the ^1H NMR spectra of the uncomplexed dumbbell-shaped thread and the rotaxane since the xylylene parts of the macrocycle shield the encapsulated regions of the thread.[23,13c]

As shown in Figure 1, the ^1H NMR spectra of thread **T-H-1**, rotaxane **R-H-1**, and macrocycle **M-1** in acetonitrile readily confirm the interlocked structure and show that the macrocycle **M-1** in rotaxane **R-H-1** is largely localized on the alkyl ammonium region of the thread under acidic condi-



Scheme 1. Synthesis of **R-H-1** and **T-H-1**.

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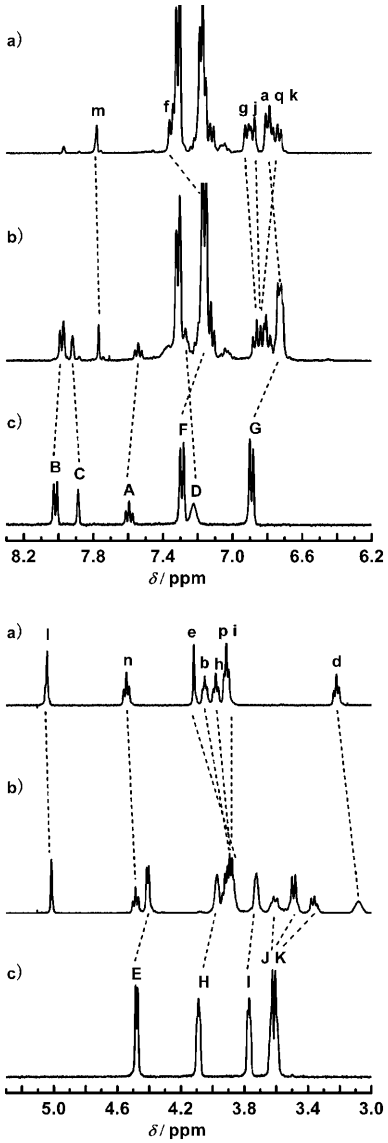

Figure 1. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 4×10^{-3} M, 298 K) of a) **T-H-1**, b) **R-H-1**, and c) **M-1**. The letters corresponding to the protons are shown in Scheme 1.

tions. As expected, the protons adjacent to the ammonium unit experience an upfield shift (H_e: $\delta=0.24$, H_d: 0.14 ppm) relative to those in free **T-H-1** due to the aromatic shielding effect of the macrocycle, whereas no variation of the protons near the triazole ring are noticed, which indicates that the macrocycle resides exclusively around the ammonium cation center. The thread phenylene protons H_f and H_g are shifted upfield in **R-H-1** as a result of the aromatic shielding effect of the macrocycle. In addition, the signals of H_F and H_G belonging to the macrocycle also experience an upfield shift, which indicates that the macrocycle is probably sandwiching the phenylene spacer so as to benefit from supplementary stabilization by means of weak π–π stacking interactions. The polyether protons H_H and H_I are shifted upfield slightly; the upfield shifts of protons H_J and H_K are more pronounced, which results from a combination of C–H–O and N^+–H–O hydrogen-bond interactions.[6]

As shown in Figure 2, upon addition of 1.2 equivalents of iPr$_2$NEt to **R-H-1**, the ammonium group was neutralized and the hydrogen bonds between the polyether moiety and the ammonium group were destroyed. Several characteristics reflect the position of the macrocycle **M-1** in rotaxane **R-1**: 1) the signals for the protons adjacent to the triazole ring exhibit a substantial upfield shift (H_l: $\delta=0.28$ and H_n: 0.26 ppm) compared with the free thread **T-1**, which could be attributed to the aromatic shielding effect by the macrocycle; 2) a significant downfield shift by $\delta=0.35$ ppm is observed for the amide protons H_D of the macrocycle **M-1**, which indicates significant hydrogen-bond interactions be-

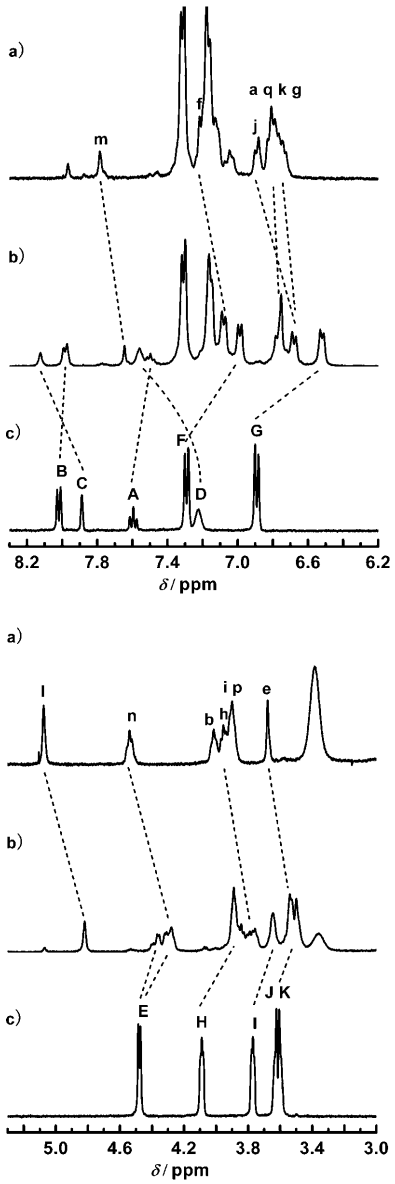

Figure 2. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 4×10^{-3} M, 298 K) of a) deprotonated thread **T-1**, b) deprotonated rotaxane **R-1**, and c) **M-1**. The letters corresponding to the protons are shown in Scheme 1.

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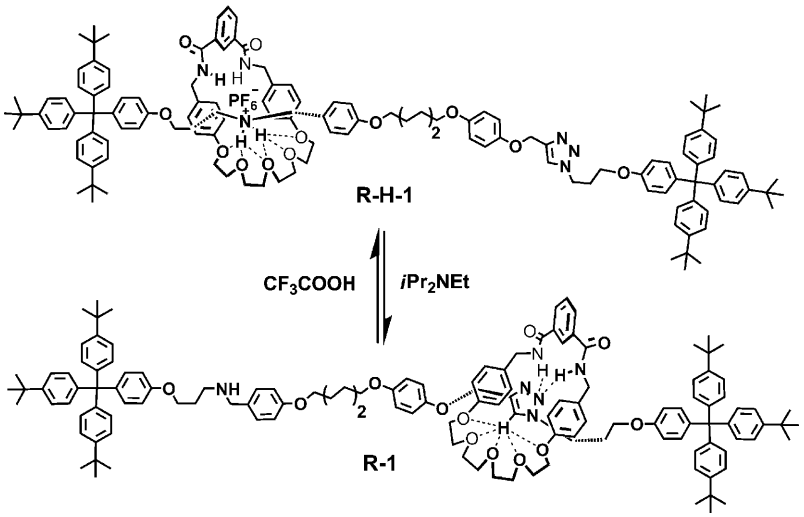
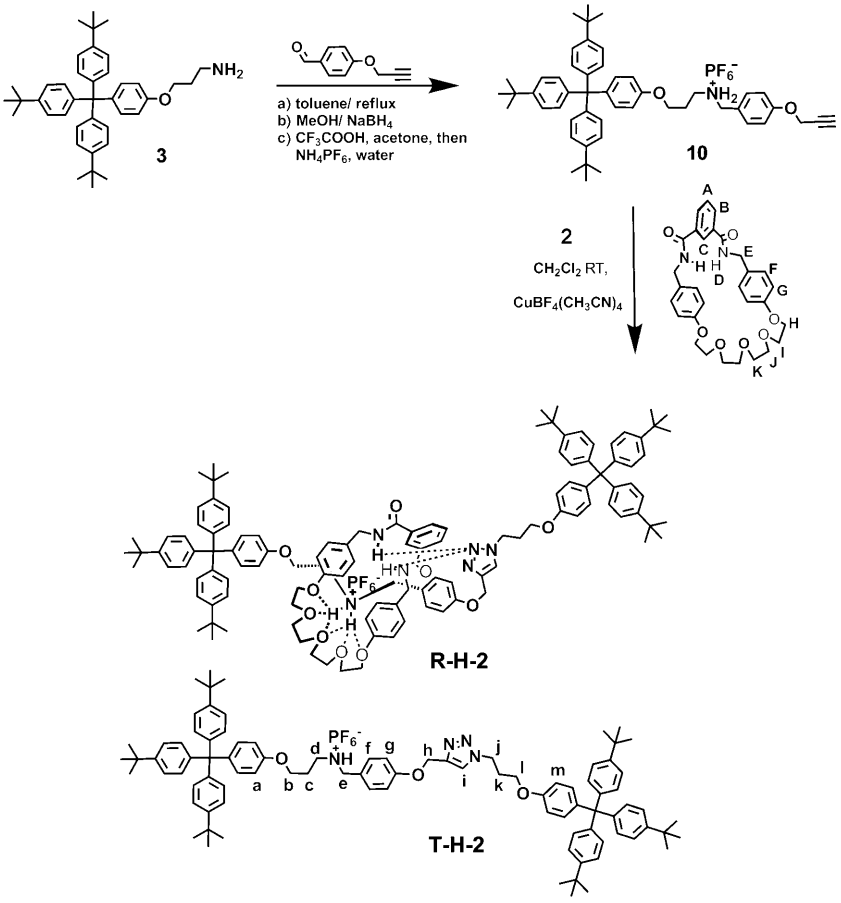
tween the amide and the hydrogen-bond acceptor of the triazole nitrogen atoms;[23] 3) the proton of the triazole ring H_m is shifted upfield by $\delta = 0.14$ ppm as a result of the aromatic shielding effect (upfield) and hydrogen bonding to the polyether (downfield). All these features confirm that the macrocycle moves to the triazole recognition site because of the hydrogen bonds between them (Scheme 2). In addition, the polyether protons (H_H–H_K) are shifted upfield by roughly $\delta = 0.1$ ppm, which indicates that the polyether oxygen atoms accept hydrogen bonds from the proton of the triazole ring. Upon addition of CF_3COOH to the deprotonated rotaxane **R-1**, the four protons H_l and H_n appear at $\delta = 4.98$ and 4.45 ppm as well as the signal for the triazole ring proton, which resonates at $\delta = 7.75$ ppm, which suggests that the **M-1** component shuttles back completely to the NH_2^+ recognition site following reprotonation (Figure S1, Supporting Information). According to the signal of the proton H_l, it is apparent that the PH-controlled switching process is reversible and can be cycled in several times (Figure S2, Supporting Information).



Scheme 2. Movement process of **R-H-1** under acid/base stimuli.



Scheme 3. Synthesis of **R-H-2** and **T-H-2**.

To verify the hydrogen-bond interactions between the macrocycle **M-1** and the 1,2,3-triazole ring, a rotaxane **R-H-2** containing a short bridge between the two recognition sites was synthesized with the by a similar reaction process (Scheme 3). The MALDI-TOF spectrum of **R-H-2** revealed a high-intensity peak at m/z: 1827.5 corresponding to **R-H-2**$^+$ after the loss of a PF_6^- unit.

Interestingly, differing from rotaxane **R-H-1**, an aromatic shielding effect is observed for the proton adjacent to the 1,2,3-triazole ring ($H_h = 0.25$ ppm) in **R-H-2** compared with it in free thread **T-H-2** (Figure 3). Moreover, the ring amide protons H_D experience a downfield shift of $\delta = 0.25$ ppm in **R-H-2** with respect to **M-1**, which is ascribed to hydrogen bonding to the hydrogen-bond acceptor, that is, the triazole nitrogen atoms. However, the proton H_i of the triazole ring and H_j close to it do not exhibit an obvious shift relative to those in thread **T-H-2**. All these features probably indicate,

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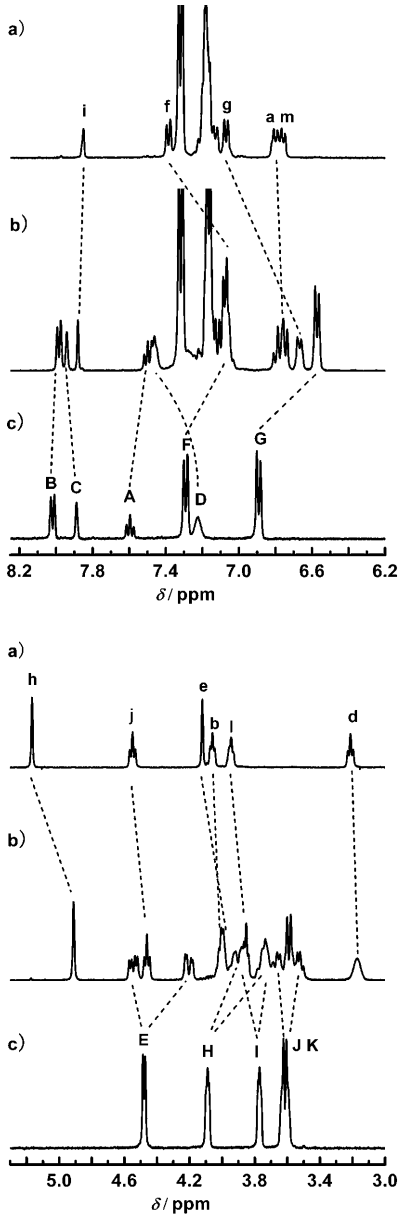
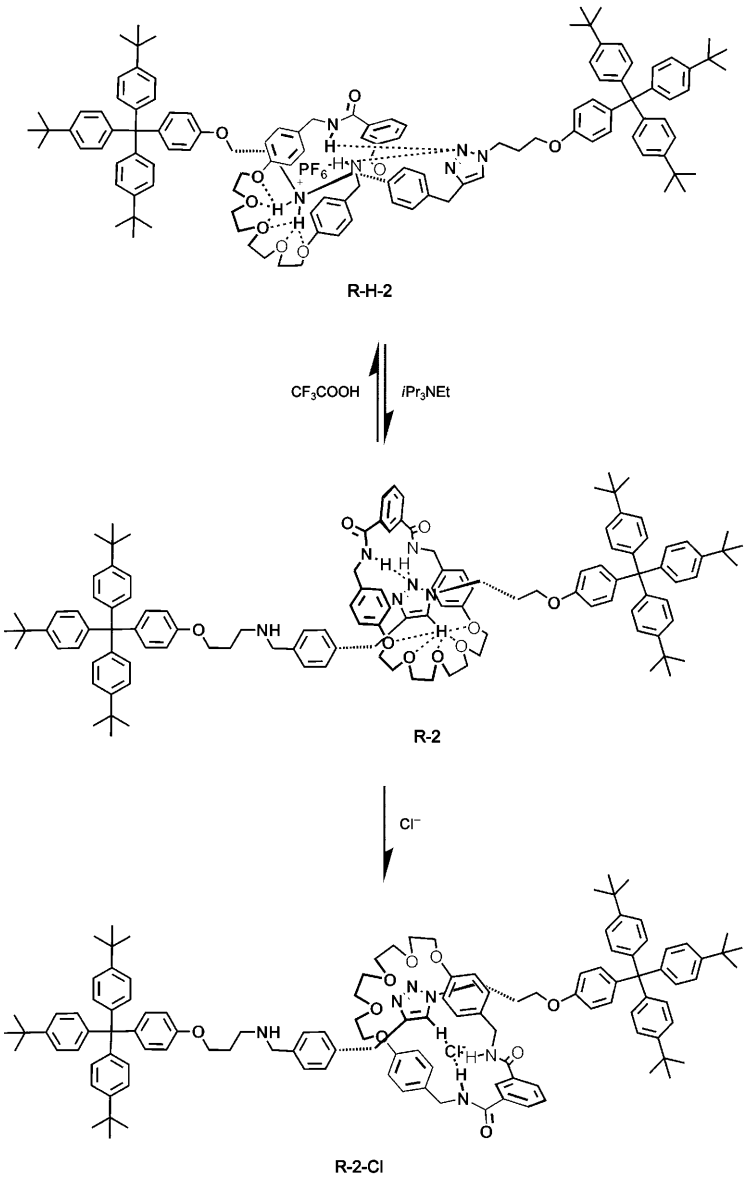


Figure 3. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 4×10^{-3} M, 298 K) of a) **T-H-2**, b) **R-H-2**, and c) **M-1**. The letters corresponding to the protons are shown in Scheme 3.

to some extent, that the isophthalamide group interacts with the triazole ring due to the hydrogen bonds between them. However, **M-1** does not reside around the triazole center completely, which arises from the ammonium cation–crown ether interaction. The signals corresponding to phenylene protons (H_f: $\delta=0.3$ and H_g: 0.4 ppm) and the macrocycle benzyl groups (H_F: $\delta=0.21$ and H_G: 0.31 ppm) experience a significant upfield shift as a result of the aromatic shielding effect between them. Based on this fact, the macrocycle **M-1** also forms the sandwiching structure with the phenylene spacer in thread **T-H-2** by means of weak π–π stacking interactions. The protons $H_{E/E'}$, $H_{H/H'}$, $H_{I/I'}$ separate into two different sets of signals as a consequence of losing the planes of symmetry orthogonal to the principal axis in the molecular shuttle.[6] The polyether protons (H_H–H_K) shift upfield by $\delta=0.1$ ppm roughly as a result of a combination of C–H–O and N^+–H–O hydrogen bonds.[6]

Thus, the ^{1}H NMR spectra support that the isophthalamide group interacts with the triazole and the polyether moiety interacts with ammonium cation. That is to say, the macrocycle spans two potential hydrogen-bonding recognition stations by a short bridge between them (see Scheme 4).

Deprotonation of **R-H-2** with 1.2 equivalents of iPr$_2$NEt resulted in significant changes to the ^{1}H NMR spectra in acetonitrile (Figure 4). The upfield shifts of the protons near the 1,2,3-triazole ring (H_h: $\delta=0.3$, H_j: 0.3 ppm) in **R-2** compared with those in free thread **T-2** should be ascribed to



Scheme 4. Movement process of multistable rotaxane **R-H-2** under different stimuli.

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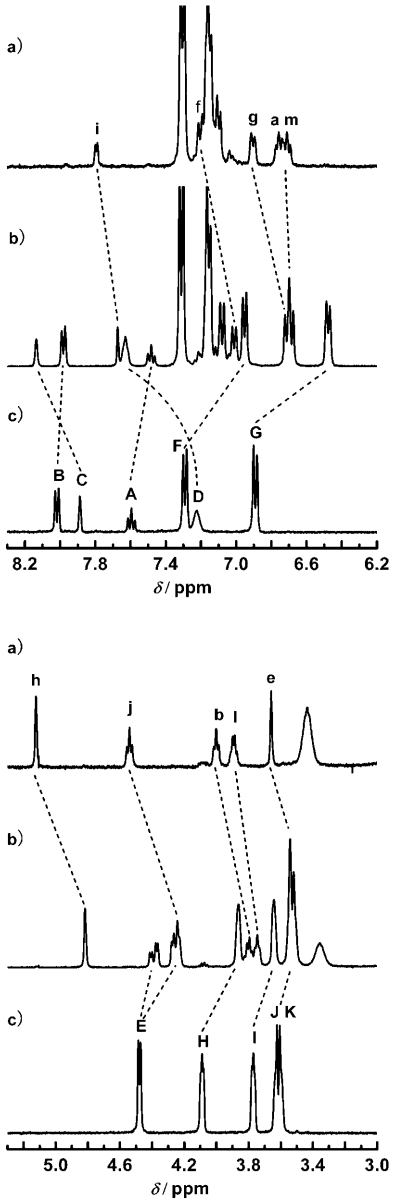

Figure 4. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 4×10^{-3} M, 298 K) of a) deprotonated thread **T-2**, b) deprotonated rotaxane **R-2**, and c) **M-1**. The letters corresponding to the protons are shown in Scheme 3.

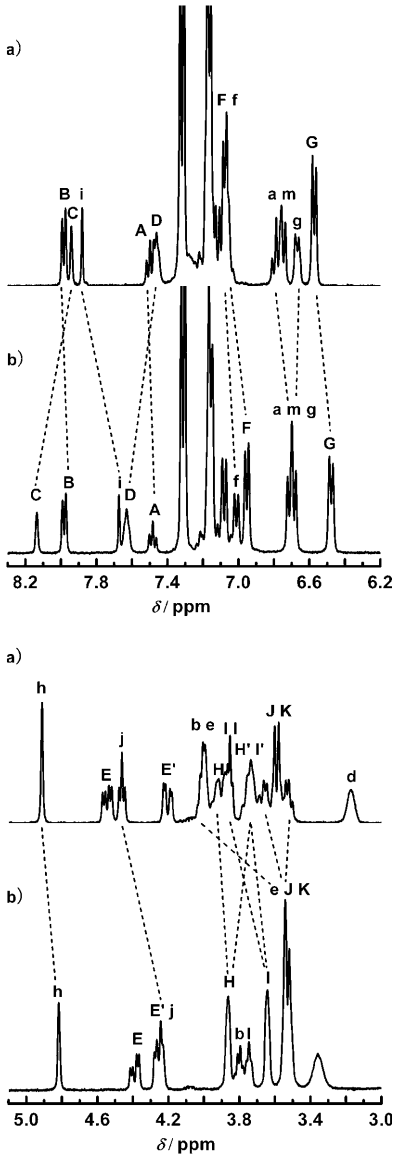

Figure 5. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 4×10^{-3} M, 298 K) of a) rotaxane **R-H-2**, and b) deprotonated rotaxane **R-2**. The letters corresponding to the protons are shown in Scheme 3.

the aromatic shielding effect by the encapsulating **M-1**. The ring amide protons H_D experience a significant downfield shift of $\delta=0.42$ ppm with respect to **M-1** due to hydrogen bonding with the hydrogen-bond acceptor of the triazole nitrogen atoms. In addition, the $\delta=0.12$ ppm upfield shift of the triazole ring proton H_i is characteristic of a combination interaction of aromatic shielding effects (upfield) and hydrogen bonding to the polyether moiety in **M-1** (downfield). All these features support the fact that the macrocycle moves towards the triazole recognition site completely where they can interact by hydrogen bonding (Scheme 4).

The ^{1}H NMR spectra of **R-H-2** and **R-2** in acetonitrile are shown in Figure 5. On addition of iPr$_2$NEt to **R-H-2**, the signal for H_e was shifted upfield by $\delta=0.46$ ppm because of deprotonation of the neighboring ammonium center and the shuttling of the macrocycle. As shown in Figure 5, when 1.2 equivalents of iPr$_2$NEt were added to the solution of **R-H-2**, the signal assigned to H_h shifted upfield ($\delta=0.1$ ppm), whereas H_D shifted downfield by $\delta=0.17$ ppm. The protons H_h and H_D shift further after the addition iPr$_2$NEt to the **R-H-2**, which confirms the **M-1** spans the two hydrogen-bond recognition sites in acidic conditions (Scheme 4). The conversion of originally separate broad signals for the protons of methylene groups in the diethylene glycol moiety of the macrocycle into the overlapping signals suggests the strong hydrogen bonding between the ammonium cation and the polyether has been destroyed after addition of iPr$_2$NEt to the solution of **R-H-2**. The upfield shifts of H_i ($\delta=0.22$ ppm) and H_j ($\delta=0.2$ ppm) of **R-H-2** indicate that the

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macrocycle mainly resides around the triazole station due to the hydrogen bonds between them. Upon addition of CF_3COOH to the fully deprotonated **R-H-2**, the signals for H_j and the triazole hydrogen H_i are shifted downfield by $\delta =$ 0.19 and 0.16 ppm relative to **R-2**, whereas slight variations were observed for the protons H_h ($\delta = 0.04$ ppm) and H_D (Figure S3, Supporting Information). All features indicate that the isophthalamide group of **M-1** interacts with the triazole and the polyether moiety switches between the two recognition sites by a de-/reprotonation process (Figure S4, Supporting Information).

We employed the deprotonated[2]rotaxane **R-2** to demonstrate the chloride anion controllable conformational changing behavior in acetonitrile solution because the ^{1}H NMR spectrum was fairly simpler than **R-1**. Upon addition of the chloride anion as its tetrabutylammonium (TBA) salt to a solution of [2]rotaxane **R-2**, dramatic changes of the ^{1}H NMR spectrum have been observed (Figure 6). As shown in Figure 6b, after the addition of 10 equivalents of chloride, the isophthalamide protons H_C and H_D are shifted downfield by $\delta = 0.68$ and 1.54 ppm, respectively, which is due to hydrogen bonds between them.[20c] The signal for the triazole proton experiences a downfield shift of $\delta = 0.2$ ppm due to hydrogen bonding to the chloride anion.[19] These phenomena can be attributed to the cooperative recognition of the chloride anion by a favorable hydrogen-bond donor from both macrocycle isophthalamide (H_C and H_D) and thread triazole proton. In addition, the proton H_h is shifted downfield by $\delta = 0.14$ ppm relative to itself in **R-2**, but still less than $\delta = 5.12$ ppm, which suggests the shielding effect of the macrocycle is reduced as a result of the conformational change on cooperative recognition of the chloride anion. However, a slight upfield shift is observed for H_j ($\delta =$ 0.1 ppm) relative to itself in **R-2**, which indicates that the shielding effect of the macrocycle is increased after conformational change. To demonstrate the chloride anion as an effective choice to alter the conformation of **R-2**, the TBA salts of bromide and iodide anions were also investigated by ^{1}H NMR spectra (Figure S5 and S6, Supporting Information). Based on the Job-plot determination of a 1:1 binding stoichiometry (Figure S7, Supporting Information), association constants for all anions (Table 1) were obtained by fitting the changes in the chemical shift of proton C to the binding isotherm (Figure S8, S9, and S10, Supporting Information).[24] The strength of anion association was observed to increase in the order $I^- < Br^- < Cl^-$. This is consistent with the increasing hydrogen-acceptor ability of the anions ($I^- < Br^- < Cl^-$). It also reflects the size and shape complementarities of the interlocked binding cavity generated by **R-2** to the chloride anion. All these features suggest that the macrocycle isophthalamide (H_C and H_D) and thread triazole proton encircle the chloride anion through cooperative hydrogen-bonding interactions, which leads the conformational alternation of the macrocycle of **R-2**.

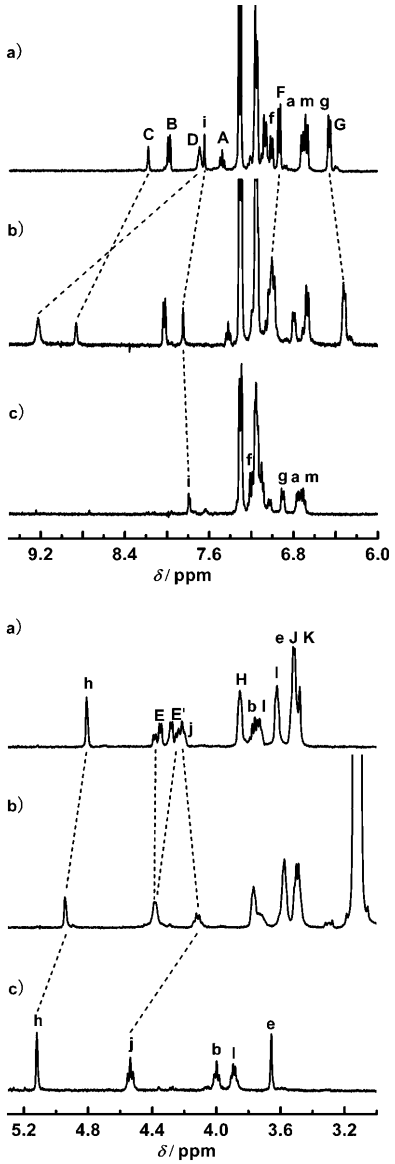

Figure 6. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 3.6×10^{-3} M, 298 K) of rotaxane **R-2** in the presence of a) 0, b) 10 equiv of TBACl (CD_3CN, 0.12 M), and c) **T-2**. The letters corresponding to the protons are shown in Scheme 3.

Table 1. Stability constants [M^{-1}] for 1:1 complexes of **R-2** with various anions in acetonitrile at 298 K.

Anion	**R-2**	
	$\Delta\delta$	K[a]
Cl^-	0.70[b]	312.07
Br^-	0.61[c]	34.50
I^-	0.16[d]	12.15

[a] Errors < 10%. [b] Changes of chemical shift [ppm] of proton C after addition of 50 equiv of the chloride anion. [c] Changes of chemical shift [ppm] of proton C after addition of 162 equiv of the bromide anion. [d] Changes of chemical shift [ppm] of proton C after the addition of 140 equiv of the iodide anion.

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Conclusions

We have successfully demonstrated an acid/base and chloride anion dual-response [2]rotaxane. In this system, the shuttling of the macrocycle along the thread driven by acid/base and the conformational alternation of the macrocycle driven by anions has been realized. Combination of the multiple hydrogen-bonding interactions with the anion-controlled translational isomerism in interlocked molecules has been well carried out. In addition, we have also demonstrated that the click reaction is not only a valuable tool to fabricate the functional rotaxane, but also the generated 1,2,3-triazole can participate in hydrogen-bond interactions with the macrocycle, which provides a novel recognition site. Interestingly, the macrocycle is able to interact with the ammonium cation and the triazole recognition station simultaneously by a short bridge under acidic conditions, whereas the macrocycle of [2]rotaxane with a longer bridge only locates on the ammonium region. Our work highlights the excellent hydrogen-bonding capacity of triazole and provides a new recognition system to construct complex structures.

Experimental Section

General methods: Unless stated otherwise, all reagents were purchased from Aldrich Chemicals and used without further purification. Solvents were purified according to the standard laboratory methods. Chromatographic separations were performed on silica gel (200–300 mesh). Reactions were monitored by TLC, which was performed on glass plates coated with SiO_2 F254 and visualized by ultraviolet (UV) light ($\lambda=254$ and $\lambda=365$ nm). ^1H and ^{13}C NMR spectra were recorded on Bruker AV 400 instruments at a constant temperature of 25 °C. All chemical shifts are reported in parts per million (ppm) from low to high field and referenced to TMS. MALDI-TOF mass spectrometric measurements were performed on Bruker Biflex III MALDI-TOF.

Compound 1: Tris(*p*-*tert*-butylphenyl)(4-hydroxyphenyl)methane[25] (2.5 g, 4.96 mmol) and 1,3-dibromopropane (3 g, 14.9 mmol) were dissolved in dry acetonitrile (100 mL) and refluxed overnight in the presence of anhydrous K_2CO_3 (2.05 g, 14.9 mmol) under nitrogen. The mixture was filtered and the solvent was removed under vacuum. The crude product was dissolved in CH_2Cl_2 and washed with water three times. The combined organic layers were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by chromatography (petroleum ether/CH_2Cl_2 2:1) to afford compound **1** as a white solid (3.0 g, 97 %). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=7.23$ (d, $J=7.79$ Hz, 6H), 7.08 (d, $J=7.93$ Hz, 8H), 6.77 (d, $J=8.21$ Hz, 2H), 4.08 (t, $J=5.72$ Hz, 2H), 3.60 (t, $J=6.4$ Hz, 2H), 2.32–2.89 (m, 2H), 1.30 ppm (s, 27H); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=156.60$, 148.43, 144.26, 140.00, 132.43, 130.88, 124.19, 113.13, 65.24, 63.20, 34.43, 32.62, 31.55, 30.26 ppm; MS (EI): m/z 626 $[M]^+$; elemental analysis calcd (%) for $C_{40}H_{49}BrO$: C 76.78, H 7.89; found: C 76.53, H 7.85.

Compound 2: A mixture of compound **1** (2.9 g, 4.64 mmol) and sodium azide (0.9 g, 13.9 mmol) in DMF was heated overnight at 80 °C. The mixture was filtered and the solvent was evaporated. The crude product was dissolved in CH_2Cl_2 and washed with water several times. The combined organic layers were dried with Na_2SO_4, and the solvents were evaporated to yield a white solid. Chromatography on silica gel (petroleum ether/CH_2Cl_2 2:1) afforded **2** in 95% yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=7.23$ (d, $J=7.81$ Hz, 6H), 7.08 (d, $J=7.68$ Hz, 8H), 6.76 (d, $J=8.09$ Hz, 2H), 4.02 (t, $J=5.78$ Hz, 2H), 3.51 (t, $J=6.68$ Hz, 2H), 2.05–2.02 (m, 2H), 1.30 ppm (s, 27H); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=156.62$, 148.44, 144.29, 140.03, 132.45, 130.90, 124.19, 113.13, 64.46, 63.23, 48.44, 34.43, 31.56, 29.01 ppm; MS (EI): m/z 587 $[M]^+$; elemental analysis calcd (%) for $C_{40}H_{49}N_3O$: C 81.73, H 8.40, N 7.15; found: C 81.68, H 8.46, N 6.91.

Compound 3: A solution of compound **2** (2.2 g, 3.8 mmol) in ethyl acetate and methanol (200 mL, acetate/methanol 1:1) was heated under reflux in the presence of Pd/C (200 mg) under hydrogen. The reaction was monitored by TLC until it was completed. The mixture was filtered and the solvent was removed under vacuum. The residue was purified by chromatography (CH_2Cl_2/MeOH 15:1) to afford compound **3** almost quantitatively. ^1H NMR (400 MHz, MeOD, 25 °C, TMS): $\delta=7.26$ (d, $J=7.79$ Hz, 6H), 7.08 (d, $J=7.25$ Hz, 8H), 6.83 (d, $J=8.44$ Hz, 2H), 4.10 (t, $J=5.49$ Hz, 2H), 3.13 (t, $J=6.24$ Hz, 2H), 2.11 (m, 2H), 1.31 ppm (s, 27H); ^{13}C NMR (400 MHz, MeOD, 25 °C, TMS): $\delta=159.23$, 151.10, 147.06, 142.82, 134.73, 133.25, 126.62, 115.66, 67.61, 65.77, 40.15, 36.57, 33.22, 29.83 ppm; MS (EI): m/z 561 $[M]^+$; elemental analysis calcd (%) for $C_{40}H_{51}NO$: C 85.51, H 9.15, N 2.49; found: C 85.77, H 8.82, N 2.22.

Compound 5: A solution of compound **4**[26] (9 g, 31.6 mmol) and hydroquinone (5.2 g, 47.2 mmol) in dried acetonitrile (250 mL) was heated under reflux in the presence of anhydrous K_2CO_3 (17.4 g 126.3 mmol) under nitrogen. The reaction was monitored by TLC until it was completed. The mixture was filtered and the solvent was removed under vacuum. The crude product was dissolved in CH_2Cl_2 and washed with water three times. The combined organic layers were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by chromatography (CH_2Cl_2/MeOH 30:1) to afford compound **5** as a white solid (4.3 g, 43 %). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=9.88$ (s, 1H), 7.83 (d, $J=8.68$ Hz, 2H), 6.99 (d, $J=8.68$ Hz, 2H), 6.79–6.74 (m, 4H), 4.05 (t, $J=6.44$ Hz, 2H), 3.91 (t, $J=6.4$ Hz, 2H), 1.89–1.76 (m, 4H), 1.58–1.53 ppm (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=$ 191.07, 164.39, 153.36, 149.68, 132.18, 129.92, 116.17, 115.76, 115.58, 114.92, 68.62, 68.40, 29.43, 29.14, 25.98, 25.93 ppm; MS (EI): m/z 314 $[M]^+$; elemental analysis calcd (%) for $C_{19}H_{22}O_4$: C 72.59, H 7.05; found: C 72.33, H 7.05.

Compound 6: A mixture of compound **5** (3 g, 9.6 mmol) and propargyl bromide (1.7 g, 14.3 mmol) in dried acetonitrile (100 mL) was heated under reflux for 6 h in the presence of anhydrous K_2CO_3 (5.3 g 38.2 mmol) under nitrogen. The mixture was filtered and the solvent was removed under vacuum. The crude product was dissolved in CH_2Cl_2 and washed with water three times. The combined organic layers were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by chromatography (CH_2Cl_2) to afford compound **6** (3.1 g, 91 %). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=9.88$ (s, 1H), 7.82 (d, $J=8.72$ Hz, 2H), 6.99 (d, $J=8.72$ Hz, 2H), 6.93–6.89 (m, 2H), 6.85–6.82 (m, 2H), 4.64 (s, 2H), 4.05 (t, $J=6.44$ Hz, 2H), 3.93 (t, $J=$ 6.4 Hz, 2H), 2.50 (s, 1H), 1.87–1.79 (m, 4H), 1.57–1.53 ppm (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=190.77$, 164.22, 153.99, 151.69, 132.00, 129.84, 116.16, 115.36, 114.79, 79.01, 75.39, 68.33, 68.28, 56.63, 29.30, 29.03, 25.88, 25.82 ppm; MS (EI): m/z 352 $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{24}O_4$: C 74.98, H 6.86; found: C 74.75, H 6.89.

Compound 7: A solution of the compound **6** (0.853 g, 2.42 mmol) and **3** (1.3 g, 2.32 mmol) in toluene (50 mL) was heated under reflux for 30 h by using a Dean–Stark apparatus. The solvent was removed under reduced pressure after the reaction was cooled to room temperature. The residue was dissolved in methanol (150 mL), then $NaBH_4$ (2 g, 52.8 mmol) was added cautiously at 0 °C. The mixture was stirred at room temperature for a further 4 h. Water was added to quench the excess $NaBH_4$. The solvent was evaporated off, and the residue was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4. After concentrated in vacuo, the crude product was purified by chromatography (CH_2Cl_2/MeOH 30:1) to afford compound **7** as slightly yellow solid (1.2 g, 58 %). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=7.22$ (d, $J=8.44$ Hz, 8H), 7.08 (d, $J=8.52$ Hz, 8H), 6.91 (d, $J=9.12$ Hz, 2H), 6.85–6.82 (m, 4H), 6.75 (d, $J=8.80$ Hz, 2H), 4.63 (s, 2H), 4.01 (t, $J=6.04$ Hz, 2H), 3.96–3.90 (m, 4H), 3.75 (s, 2H), 2.82 (t, $J=6.84$ Hz, 2H), 2.50 (s, 1H), 1.98 (t, $J=$ 6.36 Hz, 2H), 1.80–1.79 (m, 4H), 1.52 ppm (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=158.24$, 156.80, 154.03, 151.66, 149.64, 148.31, 147.02, 144.26, 139.58, 132.29, 132.08, 130.81, 129.42, 129.18, 124.12,116.16, 115.37, 114.47, 113.05, 79.01, 75.41, 68.40, 67.87, 66.20,

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63.73, 63.12, 56.62, 53.42, 46.35, 34.68, 34.35, 31.49, 31.32, 29.69, 29.37, 29.32, 25.97 ppm; MS (MALDI-TOF): *m/z*: 897.5 $[M]^+$, 920.5 $[M+Na]^+$, 936.5 $[M+K]^+$; elemental analysis calcd (%) for $C_{62}H_{75}NO_4$: C 82.90, H 8.42, N 1.56; found: C 82.65, H 8.34, N 1.52.

Compound 8: Compound **7** (500 mg, 0.56 mmol) was dissolved in acetonitrile and a few drops of trifluroacetic acid were added. After 1 hour, the solvent was removed under vacuo. The residue was dissolved in a mixture of acetone and water. Then the aqueous of NH_4PF_6 (136 mg, 0.84 mmol) was added. The mixture was stirred for 1 h and then the acetone was evaporated off. The aqueous solution was extracted with CH_2Cl_2 several times. The collected organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo to yield **8** as a yellow solid (584 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 7.30$ (d, $J = 8.40$ Hz, 2H), 7.23 (d, $J = 8.40$ Hz, 6H), 7.10–7.05 (m, 8H), 6.89–6.83 (m, 6H), 6.70 (d, $J = 8.72$ Hz, 2H), 4.63 (s, 2H), 4.06 (s, 2H), 4.03–4.02 (m, 2H), 3.91–3.88 (m, 4H), 3.15–3.13 (m, 2H), 2.49 (s, 1H), 2.17–2.16 (m, 2H), 1.79–1.76 (m, 4H), 1.50 (m, 4H), 1.29 ppm (s, 27H).

Compound 9: Compound **9** was synthesized from 4-hydroxy-1-(2′-propynyloxy)benzene and compound **3** by using the same procedure as described for the preparation of compound **7**. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 7.37$ (d, $J = 7.71$ Hz, 2H), 7.22 (d, $J = 7.73$ Hz, 6H), 7.07 (d, $J = 7.83$ Hz, 8H), 6.94 (d, $J = 7.95$ Hz, 2H), 6.71 (d, $J = 8.26$ Hz, 2H), 4.62 (s, 2H), 3.99 (m, 2H), 3.87 (s, 2H), 2.92 (t, $J = 6.08$ Hz, 2H), 2.45 (s, 1H), 2.11–2.10 (m, 2H), 1.30 ppm (s, 27H); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 157.19$, 156.67, 148.41, 144.29, 144.25, 139.83, 132.35, 130.83, 130.13, 124.14, 115.10, 113.07, 78.59, 75.65, 65.93, 63.16, 55.93, 52.60, 45.80, 34.39, 31.49, 31.32 ppm; MS (EI): *m/z* 706 $[M]^+$; elemental analysis calcd (%) for $C_{50}H_{59}NO_2$: C 85.06, H 8.42, N 1.98; found: C 85.32, H 8.29, N 2.15.

Compound 10: Compound **10** was synthesized by using the same procedure as described for the preparation of compound **8**. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 7.34$ (d, $J = 7.86$ Hz, 2H), 7.23 (d, $J = 7.87$ Hz, 6H), 7.10–7.05 (m, 8H), 6.95 (d, $J = 8.01$ Hz, 2H), 6.68 (d, $J = 8.36$ Hz, 2H), 4.63 (s, 2H), 4.17 (s, 2H), 4.02 (m, 2H), 3.24 (m, 2H), 2.42 (s, 1H), 2.18 (m, 2H), 1.30 ppm (s, 27H).

Rotaxane R-H-1 and thread T-H-1: A mixture of compound **2** (290.6 mg, 0.50 mmol), compound **8** (491 mg, 0.47 mmol) , macrocycle **1**[23] (264.3 mg, 0.49 mmol), and $[Cu(MeCN)_4]BF_6$ (148.3 mg, 0.47 mmol) was stirred in dry CH_2Cl_2 at room temperature under nitrogen for 24 h. After removal of the solvent, the crude product was purified by column chromatography (CH_2Cl_2/MeOH 30:1) to afford rotaxane **R-H-1** (356 mg, 35%) and thread **T-H-1** (383 mg, 50%).

Rotaxane ***R-H-1***: ^{1}H NMR (400 MHz, CD_3CN, 25°C, TMS): $\delta = 7.96$ (d, $J = 8.17$ Hz, 2H), 7.90 (s, 1H), 7.75 (s, 1H), 7.52 (t, $J = 7.20$ Hz, 1H), 7.35 (m, 2H), 7.29 (d, $J = 7.60$ Hz, 12H), 7.25 (m, 2H), 7.14 (m, 22H), 6.86–6.77 (m, 6H), 6.72–6.70 (m, 8H), 4.99 (s, 2H), 4.47 (t, $J = 6.80$ Hz, 2H), 4.40–4.38 (m, 4H), 3.95 (m, 4H), 3.92–3.85 (m, 10H), 3.70 (m, 4H), 3.61–3.57 (m, 2H), 3.48–3.46 (m, 4H), 3.36–3.32 (m, 2H), 3.06 (m, 2H), 2.24 (t, $J = 6.40$ Hz, 2H), 2.06 (m, 2H), 1.70 (m, 4H), 1.44 (m, 4H), 1.27 ppm (s, 54H); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 166.76$, 160.44, 156.84, 156.41, 156.03, 153.88, 152.46, 148.56, 144.26, 140.74, 140.36, 134.75, 132.55, 132.25, 131.81, 131.70, 130.91, 130.85, 130.79, 130.74, 129.39, 129.22, 128.41, 124.34, 124.25, 122.92, 122.40, 116.02, 115.64, 115.12, 114.37, 113.17, 70.90, 70.82, 70.70, 68.58, 68.30, 67.18, 64.27, 64.21, 64.11, 63.91, 63.29, 63.26, 62.78, 62.75, 52.22, 47.63, 47.57, 46.17, 43.60, 35.00, 34.86, 34.81, 34.66, 34.60, 34.48, 34.31, 31.83, 31.77, 31.58, 31.42, 30.13, 29.88, 29.44, 29.24, 27.92, 26.41, 26.05, 25.96, 25.72, 25.47, 22.83, 21.64 ppm; MS (MALDI-TOF): *m/z*: 2041.5 $[M-PF_6-H+Na]^+$, 2057.5 $[M-PF_6-H+K]^+$; elemental analysis calcd (%) for $C_{132}H_{159}N_6F_6O_{12}P$: C 73.20, H 7.35, N 3.88; found: C 73.59, H 7.19, N 4.15.

Thread ***T-H-1***: ^{1}H NMR (400 MHz, CD_3CN, 25°C, TMS): $\delta = 7.76$ (s, 1H), 7.33–7.28 (m, 14H), 7.16–7.09 (m, 16H), 6.90–6.85 (m, 4H), 6.79–6.70 (m, 6H), 5.02 (s, 2H), 4.52 (t, $J = 6.76$ Hz, 2H), 4.06 (s, 2H), 4.02 (t, $J = 4.97$ Hz, 2H), 3.95 (t, $J = 6.14$ Hz, 2H), 3.89(t, $J = 5.78$ Hz, 4H), 3.16 (t, $J = 6.8$ Hz, 2H), 2.30–2.27 (m, 2H), 2.08 (m, 2H), 1.75–1.71 (m, 4H), 1.48 (m, 4H), 1.27 ppm (s, 54H); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 159.90$, 156.32, 156.07, 153.82, 152.30, 148.48, 144.45, 144.19, 140.47, 140.29, 132.49, 132.40, 131.01, 130.84, 130.80, 124.19, 124.03, 123.46, 115.89, 115.61, 115.19, 113.08, 68.38, 67.94, 65.99, 63.96, 63.19, 62.54, 52.26, 47.50, 46.17, 34.72, 34.41, 31.76, 31.51, 31.34, 30.05, 29.29, 29.13, 26.60, 25.81, 26.78 ppm; MS (MALDI-TOF): *m/z*: 1486.9 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{102}H_{125}N_4F_6O_5P$: C 75.06, H 7.72, N 3.43; found: C 75.41, H 7.88, N 3.80.

Rotaxane R-H-2 and thread T-H-2: $[Cu(MeCN)_4]BF_6$ (177 mg, 0.56 mmol) was added to a solution of compound **2** (330 mg, 0.56 mmol), compound **10** (484.7 mg, 0.57 mmol), and macrocycle **1** (300 mg, 0.56 mmol) in dry CH_2Cl_2. The mixture was stirred at room temperature under nitrogen for 24 h. After concentration, the crude was purified by column chromatography (CH_2Cl_2/MeOH 30:1) to afford rotaxane **R-H-2** (353 mg, 32%) and thread **R-H-2** (394 mg, 49%).

Rotaxane ***R-H-2***: ^{1}H NMR (400 MHz, CD_3CN, 25°C, TMS): $\delta = 7.96$ (d, $J = 7.6$ Hz, 2H), 7.92 (s, 1H), 7.87 (s, 1H), 7.46 (m, 3H), 7.30(d, $J = 8.4$ Hz, 14H), 7.15 (m, 14H), 7.09 (d, $J = 8.8$ Hz, 2H), 7.04 (m, 6H), 6.74 (m, 4H,), 6.64 (m, 2H), 6.55 (d, $J = 8.4$ Hz, 4H), 4.88 (s, 2H), 4.55–4.50 (m, 2H), 4.44 (t, $J = 6.8$ Hz, 2H), 4.20–4.15 (m, 2H), 4.00–3.97 (m, 4H), 3.90–3.81 (m, 6H), 3.76–3.62(m, 6H), 3.58–3.48 (m, 6H), 3.14 (m, 2H), 2.20 (t, $J = 6.4$ Hz, 2H), 2.11 (m, 2H), 1.27 ppm (s, 54H); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 166.70$, 158.92, 156.89, 156.33, 155.92, 149.82, 148.44, 148.40, 146.87, 144.16, 144.12, 142.93, 140.62, 140.13, 134.64, 132.44, 132.40, 131.66, 131.49, 131.38, 130.79, 130.69, 130.20, 129.26, 124.22, 124.13, 123.21, 122.76, 115.16, 114.23, 113.07, 70.72, 70.65, 70.53, 67.18, 64.16, 64.10, 63.78, 63.16, 63.14, 61.14, 51.99, 47.53, 45.96, 43.44, 34.69, 34.36, 31.47, 31.34, 31.31, 30.05, 26.31 ppm; MS (MALDI-TOF): *m/z*: 1827.5 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{120}H_{143}N_6F_6O_{10}P$: C 73.02, H 7.25, N 4.26; found: C 73.23, H 7.20, N 4.34.

Thread ***T-H-2***: ^{1}H NMR (400 MHz, CD_3CN, 25°C, TMS): $\delta = 7.83$ (s, 1H), 7.36 (d, $J = 8.8$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 14H), 7.16 (m,18H), 7.05 (d, $J = 8.0$ Hz, 2H), 6.80–6.72 (m, 4H), 5.14 (s, 2H), 4.53 (t, $J = 6.8$ Hz, 2H), 4.11 (s, 2H), 4.03 (t, $J = 5.6$ Hz, 2H), 3.92 (m, 2H) 3.20 (t, $J = 6.4$ Hz, 2H), 2.29 (m, 2H), 2.10 (m, 2H), 1.27 ppm (s, 54H); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS):$\delta = 159.09$, 156.34, 155.99, 148.44, 144.26, 144.19, 143.37, 140.48, 14.019, 132.46, 132.33, 131.60, 130.83, 130.77, 124.23, 124.18, 123.96, 122.70, 115.40, 113.06, 64.01, 63.17, 34.71, 34.38, 31.52, 31.35, 29.96 ppm; MS (MALDI-TOF): *m/z* 1293.7 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{90}H_{109}N_4F_6O_3P$: C 75.08, H 7.63, N 3.89; found: C 74.94, H 7.80, N 4.05.

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