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Directed Synthesis of [2]Catenanes Incorporating Naphthalenediimide and Crown Ethers by Associated Interactions of Templates

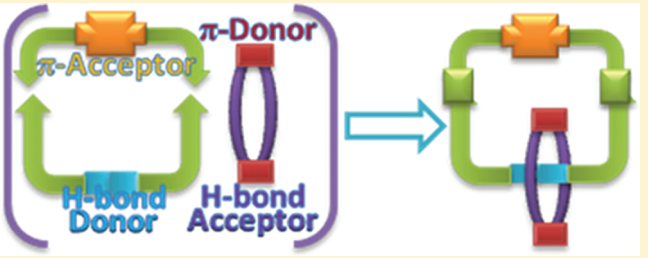
Wenlong Yang,[†,‡] Yongjun Li,[†] Jianhong Zhang,[†,‡] Nan Chen,[†,‡] Songhua Chen,[†,‡] Huibiao Liu,[†] and Yuliang Li*[,†]

[†]Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China

[‡]Graduate University of Chinese Academy of Sciences, Beijing 100080, P.R. China

Supporting Information

ABSTRACT: In this paper, we introduce a simple one-step method to synthesize [2]catenanes incorporating naphthalenediimide and crown ethers by associated interactions of templates. In this functional supermolecular system, the combined hydrogen-bond and π-donor/π-acceptor interactions led production of the [2]catenanes which exhibit reversible moving of the crown ether macrocycle on the big ring between two stations via de/reprotonation. This movement on the big ring can change the electron interaction, resulting in strong quenching of the emission of naphthalene diimide.



INTRODUCTION

The efficient preparation of mechanically interlocked structures, such as rotaxanes and catenanes, is vital for their successful applications in fabricating molecular machines, sensors, and nano materials.[1] Catenanes, topologically nontrivial molecules possessing two or more mechanically interlocked rings, have been known for nearly half a century[2] and have attracted considerable attention as synthetic targets[3] and more recently as proposed and realized components of functional molecular devices, such as switches,[4] unidirectional motors,[5] and electronic displays.[6] The synthesis of catenanes has been one of the topics where supramolecular chemistry has obtained numerous successes. The rapid development of this new area of chemistry has promoted the understanding of the concepts of design and strategies of self-assembly of structures based on inter- and intramolecular interactions to result in synthetic supramolecular systems of catenanes. The self-assembly processes guided by noncovalent forces facilitates the preorganization of the molecular components prior to the cyclization reactions, in generally via π-donor/π-acceptor complexes,[7] hydrogen bond interaction,[8] anion templation,[9] or metal complexation,[10] these strategies have been utilized frequently to construct higher order [n]catenanes by n interlocked macrocycles.[11] Recently ever more diverse methods were reported to synthesize bistable catenanes, the challenge that remains for these bistable molecules is their incorporation into an integrated functional supramolecular system, design of higher performance supramolecules and understanding the structure−function relationships that relate specifically to [2]catenanes.

The [2]catenanes synthesized by associated interaction of hydrogen-bond and π-donor/π-acceptor have not been reported. Herein, we propose a one-step hydrogen-bond and π-donor/π-acceptor template-directed self-assembly procedure for the preparation of [2]catenanes by "CuAAC click" reaction.

RESULTS AND DISCUSSION

Scheme 1 outlines the preparation of the two [2]catenanes **4A** and **4B** from the secondary dialkylammonium axle **1**, the naphthalenediimide (NDI) **2**, and crown ethers dinaphtho-24-crown-8 (DN24C8) **3A** and dibenzo-24-crown-8 (DB24C8) **3B**. A dilute equimolar amount of **2** was added dropwise to a highly dilute mixture containing an equimolar amount of compound **1**, **3**, and catalyst $[Cu(MeCN)_4]PF_6$ in dichloromethane at room temperature for 24 h. The target [2]catenanes **4A** and **4B** were obtained in 42% and 35% yield, respectively. The MALDI-TOF spectra of **4A** and **4B** gave sharp peaks at m/z 1398.7 $[M - PF_6]^+$ and 1498.5 $[M - PF_6]^+$ (see the Supporting Information), respectively, which revealed the features of an interlocked molecule. A product of [3]catenane **7** (MALDI-TOF m/z 2798.2) was obtained in 2% yield in the presence of **3B**. However, [3]catenane was not isolated when the reaction was carried out in the presence of **3A** instead. The result was similar to the Loeb[12] group's report that a series of [3]catananes was obtained using different crown ethers as the guest, which

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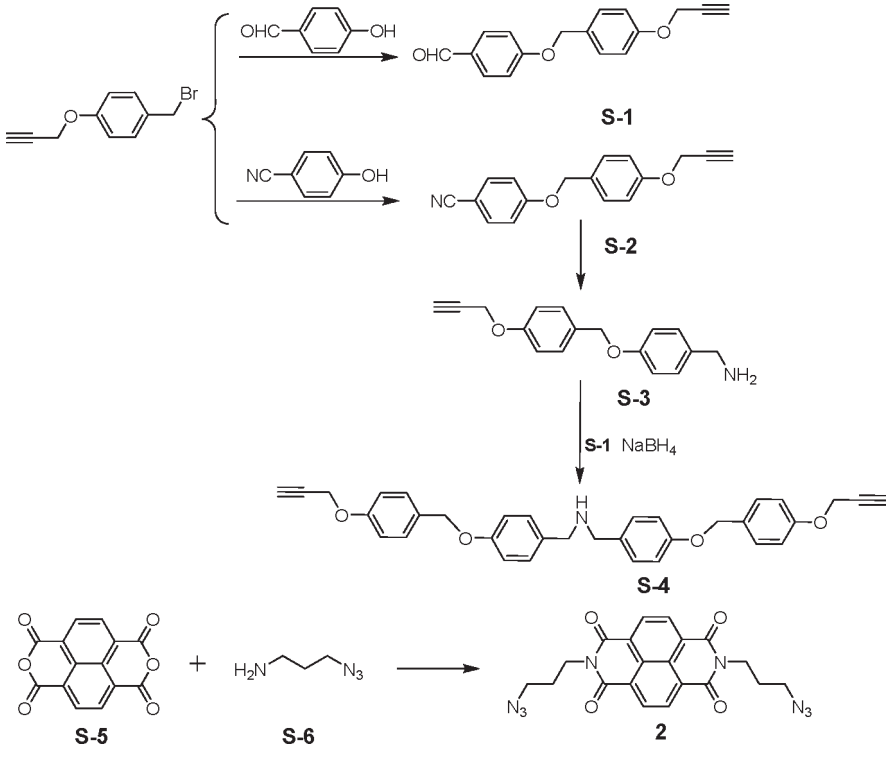
indicated formation of products with DB24C8 was 2−3 times more favorable than that with other crown ethers. Remarkably, in the same way in the absence of crown ethers **3**, the naked NDI big ring **6** (blue cycle, Scheme 1) was not observed. This is due to the electron-deficient properties of the secondary dialkylammonium axle **1** and the NDI **2** units, which enabled them to get together. Regioselective methylation of the [2]catenanes **4** was carried out in iodomethane at 40 °C overnight to afford the two-station [2]catenanes **5** by anion exchange (Scheme 1). The electrospray ionization (ESI) mass spectra of [2]catenanes **5A** and **5B** reveal triply charged peaks at m/z 476.6 and 509.9 (see the Supporting Information), respectively.

The proposed mechanism for the template-directed synthesis of the [2]catenanes **4** is shown in Figure 1, which relies on (i) the combination of N^+−H···O and C−H···O hydrogen bonds and $\pi-\pi$ stacking interactions between the dialkylammonium and the 24-crown-8 (24C8)[13]and (ii) π-donor/π-acceptor interaction between the electron-rich 24C8 and the electron-deficient NDI. The first step in this reaction is the self-assembly of 24C8 **3** with the nonstoppered secondary dialkylammonium axle **1** through hydrogen-bond interaction to form a [2]pseudorotaxane [**1** ⊂ **3**], which is dragged close to the NDI unit **2** by the π-donor/π-acceptor interaction between the electron-rich 24C8 and the electron-deficient NDI. Then closure of the ring happened by the click reaction in the presence of catalyst $[Cu(MeCN)_4]PF_6$ to afford the [2]catenanes **4**. The result indicated that the crown ethers play dual roles, not only act as the hydrogen-bond receptors for the secondary dialkylammonium but also as the essential link for the secondary dialkylammonium axle **1** and the NDI **2**.

Diisopropylethylamine (DIEA) is strong enough to deprotonate the NH_2^+ center.[14] However, due to the weak interaction between the crown ether and the triazole unit, the crown ethers did not move toward the triazole station upon addition of a slight molar excess of DIEA to the solution of **4**. The crown ethers can move toward the *N*-methyltriazolium station upon addition of DIEA to the [2]catenane **5** (Scheme 2) because of the strong interaction between the electron-rich crown ethers ring and the electron-deficient *N*-methyltriazolium station.[13] In the ^{1}H NMR spectra of the [2]catenane **5A**, the chemical shifts of the complexed crown ether hydrogens H_C and H_D are not split, indicating that they are facing a symmetrical system and the DN24C8 resides around the dialkylammonium station. Before deprotonation, the ^{1}H NMR spectra is relatively simple (Figure 2b). Upon addition of base, deprotonation of the secondary dialkylammonium moiety resulted in the moving of DN24C8 toward the *N*-methyltriazolium station, which led the [2]catenane to be a wholly nonsymmetrical system. The obvious changes can be observed from the ^{1}H NMR spectra (Figure 2c). Nearly all chemical shifts of the crown ether hydrogens are split; the peaks for the *N*-methyltriazolium C−H protons H_f and $H_{f'}$ are separated into two parts and both shifted downfield, one of which was evidently shifted downfield due to the C−H···O hydrogen-bond interaction. Obviously, an upfield shift was also observed for the signals H_a and the peak changed from singlet to multiplet, which can be attributed to the weak $\pi-\pi$-stacking interactions between the aromatic ring of DN24C8 and the naphthalene ring of NDI. All these changes indicated that the DN24C8 located at one of the *N*-methyltriazolium stations. Furthermore, upon addition of trifluoroacetic acid (TFA) to the deprotonated [2]catenane **5A**, the protons H_a appear at δ = 8.65 ppm as well as the signal for the *N*-methyltriazolium ring proton H_f which resonates at δ = 8.5 ppm, suggesting that the DN24C8 was back to the original NH_2^+ recognition site following reprotonation (Figure 2d). The signal changes of the protons H_a and H_f showed the fact that the pH-controlled switching

Scheme 1. Synthesis of [2]Catenanes 5 and [3]Catenane 7



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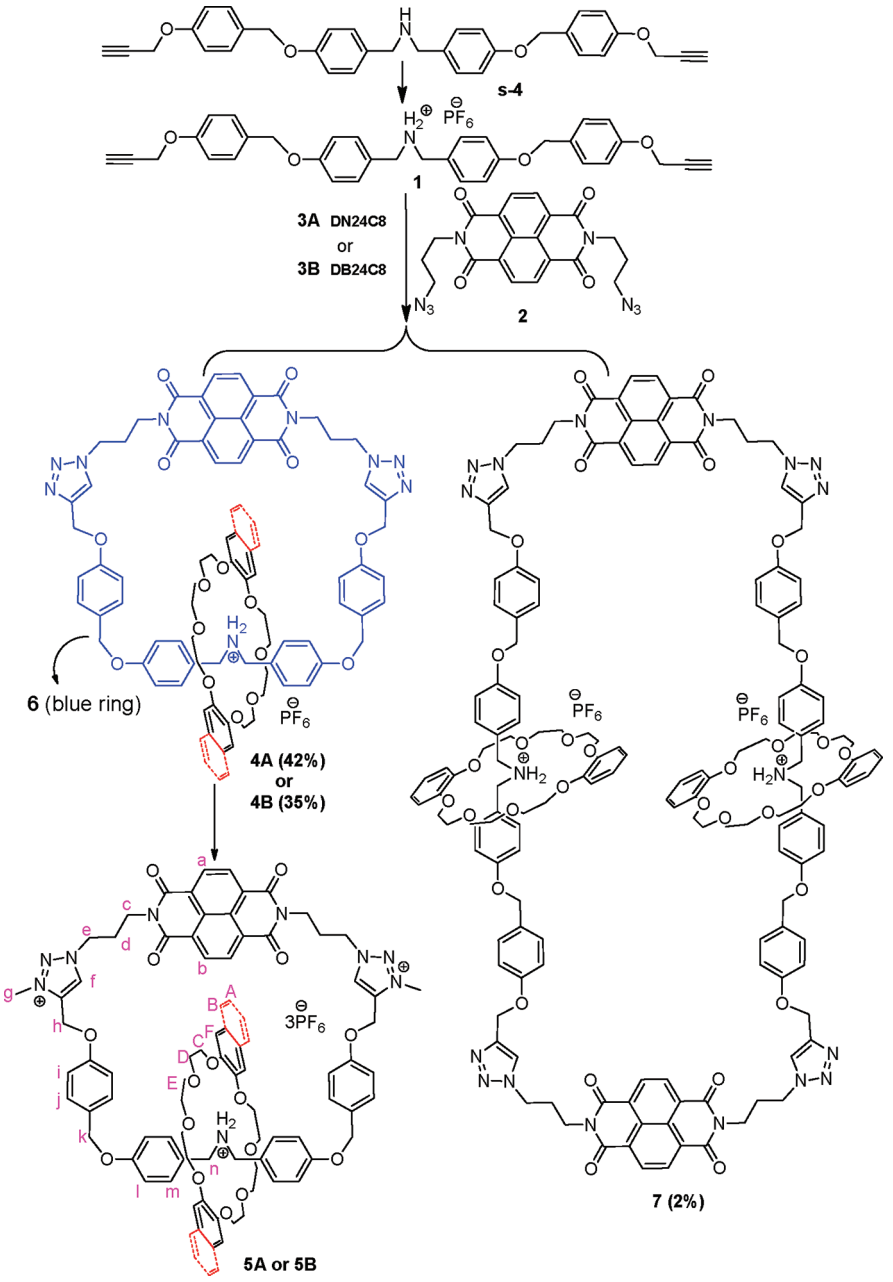
Scheme 1. Continued



process is reversible. Similar phenomena (Figure S1, Supporting Information) could also be observed when base and acid were added to the [2]catenane **5B**.

The present [2]rotaxanes **4** and **5** both display an intramolecular charge-transfer (CT) process controlled by the spacial distance between the aromatic moiety of the crown ethers and the NDI unit. UV−vis absorption spectroscopy experiments were first performed to demonstate the CT behavior. There is a CT band at about 420 nm for [2]catenane **4A** as shown in Figure 3, indicating that the CT process occurs between the naphthalene ring on DN24C8 and the NDI unit. For [2]catenane **5A**, however, the CT band decreased because of the interaction between the naphthalene ring of DN24C8 and the electron-deficient *N*-methyltriazolium unit in the ground state. When 2 equiv of DIEA was added to the solution of [2]catenane **5A**, the color of the solution changed from colorless to slightly yellow and a new CT band at about 420−450 nm was the generated. This was the result of the strong CT between the naphthalene ring of DN24C8 and the NDI unit, which indicated that DN24C8 moved toward the *N*-methyltriazolium station and was close to NDI unit. Upon addition of 4 equiv of TFA into the above system, the slightly yellow solution of **5A** turned colorless and the absorption band around 420−450 nm decreased, indicating that the CT process was restricted and the DN24C8 was back to the NH_2^+ station. Similar to the [2]catenane **5A**, an unobvious CT band around 390−400 nm was observed for [2]catenane **5B** when DIEA was added (Figure S2 Supporting Information) and the color change was hardly observed, which can be attributed to the weak CT process between the benzene ring of DB24C8 and the NDI unit and indicated that the

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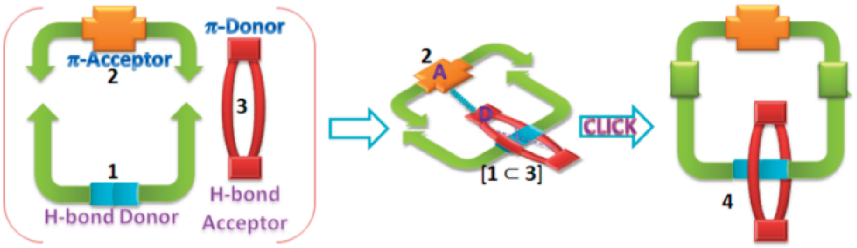
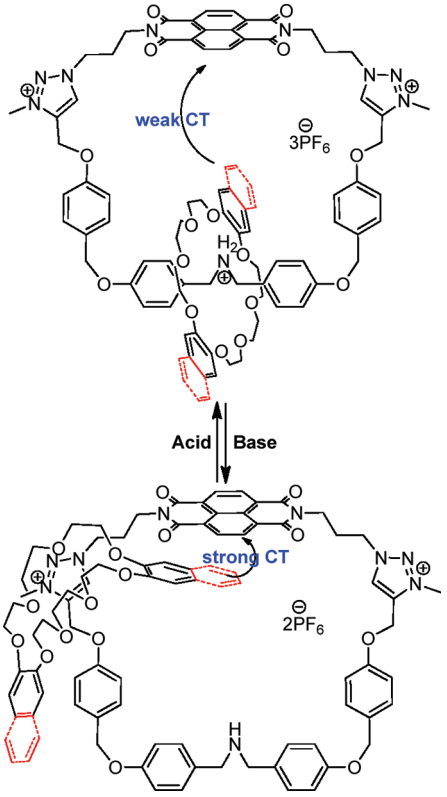


Figure 1. Proposed mechanism for synthesis of the [2]catenanes **4**.

Scheme 2. Movement Process of [2]Catenanes 5 under Acid−Base Stimuli



DB24C8 located at the *N*-methyltriazolium station. The CT band around 390−400 nm also decreased after TFA was added, suggesting that the CT process was restricted and the DB24C8 was back to the NH_2^+ site following reprotonation.

As shown in Figure 4, [2]catenanes **5A** and **5B** both exhibited strong emission at 386 nm. After addition of 2 equiv of DIEA, the emission intensity was quenched obviously, which was attributed to the CT from the electron-rich 24C8 system to the electron-deficient NDI unit and also indicated that the 24C8 moved toward the NDI unit and localized at the *N*-methyltriazolium station. The intensity can be completely recovered by addition of TFA, suggesting that the 24C8 component was back to the NH_2^+ recognition site. It is obvious that the [2]catenane **5A** showed weaker fluorescence intensity than the [2]catenane **5B** when they adopt the same conformation; this is due to the fact that DN24C8 exhibits a stronger electron-donor ability than DB24C8. The results obtained from the UV−vis absorption and fluorescence spectroscopy experiments were in accordance with the ^{1}H NMR spectra, which all indicated that the [2]catenanes **5** exhibit fully reversible switching of its crown ether between two stations via de/reprotonation (Scheme 2).

CONCLUSION

We demonstrated that the concepts of design and strategies of self-assembly of a [2]catenane structure based on associated interactions of hydrogen-bond and π-donor/π-acceptor can result in a reversible pH-controlled movement of two bistable [2]catenanes. The results demonstrate the fact that the crown ethers can function not only as an efficient hydrogen-bond acceptor for the secondary dialkylammonium but also as the essential link for the secondary dialkylammonium axle to the NDI by the π-donor/π-acceptor interaction. Such chemical reactivity of the supramolecular species expands the functionality of the system and provides a means to control the photophysical properties.

EXPERIMENTAL SECTION

Compound S-1. A solution of 1-(bromomethyl)-4-(prop-2-yn-1-yloxy)benzene (2.24 g, 10 mmol) and 4-hydroxybenzaldehyde (1.22 g, 10 mmol) in acetone (100 mL) was heated under reflux in the presence of K_2CO_3 (2.76 g, 20 mmol) under nitrogen. The reaction was monitored by TLC until it was complete. 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 (3 × 50 mL). The organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by column chromatography with CH_2Cl_2/hexane (1/1, v/v). The white solid product compound (**S-1**), 2.26 g, was obtained with a yield of 86%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.88 (s, 1 H), 7.83 (m, 2 H), 7.37 (m, 2 H), 7.0−7.06 (m, 4 H), 5.07 (s, 2H), 4.70 (s, 2 H), 2.53 ppm (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.9, 163.9, 157.8, 132.1, 130.2, 129.3, 129.1, 115.3, 78.5, 75.8, 70.1, 55.9 ppm. HRMS (EI) calcd: *m*/*z* 266.0943 for $C_{17}H_{14}O_3$. Found: *m*/*z* 266.0946.

Compound S-3. A solution of 1-(bromomethyl)-4-(prop-2-yn-1-yloxy)benzene (2.24 g, 10 mmol) and 4-hydroxybenzonitrile (1.19 g, 10 mmol) in acetone (150 mL) was heated under reflux in the presence of K_2CO_3 (2.76 g, 20 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 (3 × 50 mL). The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was reduced in volume to obtain a white solid, which was used for the next reaction without further purification. The crude product was dissolved in anhydrous THF (100 mL) and cooled in an ice bath. Excess $LiAlH_4$ (1.9 g, 50 mmol) was added in a nitrogen atmosphere. The reaction mixture was stirred overnight at ambient temperature. The reaction mixture was cooled to 0 °C, and 5 mL of water was added dropwise. After filtration, the solution was concentrated under reduced pressure to afford the crude product. Purification was accomplished by column chromatography on silica with CH_2Cl_2/MeOH (100/1, v/v) to

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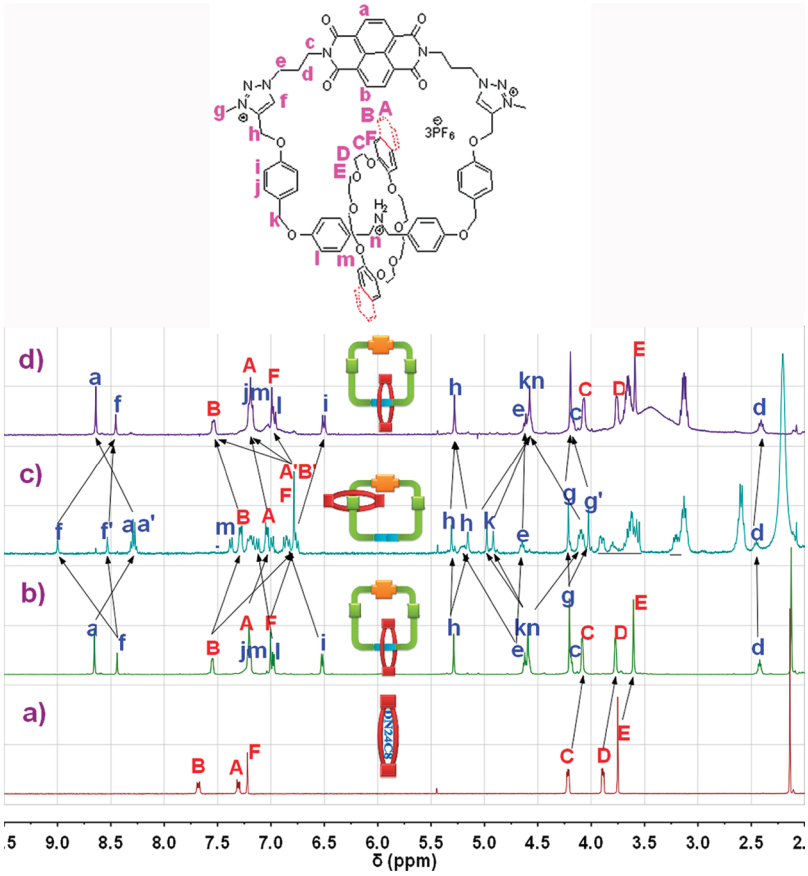

Figure 2. ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of (a) DN24C8, (b) the original spectrum of **5A**, (c) 5A after addition of 2 equiv of DIEA, and (d) **5A** further addition of 4 equiv of TFA.

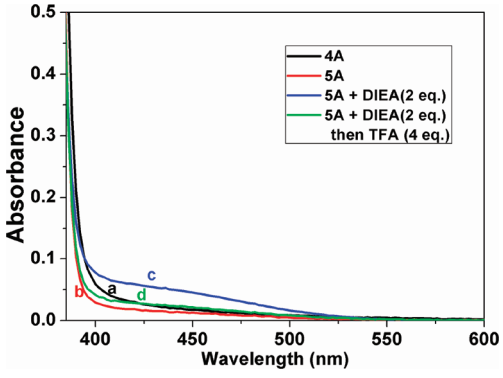

Figure 3. Absorption spectra of (a) [2]catenane **4A** (1×10^{-4} M), (b) [2]catenane **5A** (1×10^{-4} M), (c) **5A** (1×10^{-4} M) + DIEA (2 equiv), and (d) **5A** (1×10^{-4} M) + DIEA (2 equiv) then TFA (4 equiv) in CH_3CN.

give compound **S-3** (1.82 g, 68%, two steps). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.36 (m, 2 H), 7.22 (m, 2 H), 6.92−6.98 (m, 4 H), 4.98 (s, 2H), 4.69 (s, 2 H), 3.79 (s, 2 H), 2.52 (s, 1 H), 1.56 ppm (s, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.9, 157.5, 135.9, 130.2, 129.2, 128.4, 115.1, 115.0, 78.6, 75.7, 69.8, 55.9, 46.0 ppm. HRMS (EI) calcd: m/z 267.1259 for $C_{17}H_{17}NO_2$. Found: m/z 267.1263.

Compound S-4. A solution of **S-1** (2.67 g, 10 mmol) and **S-3** (2.67 g, 10 mmol) in toluene (100 mL) was heated under reflux overnight 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 THF (50 mL); then $NaBH_4$ (0.4 g, 10.5 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 THF was evaporated off, and the remaining aqueous mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried over Na_2SO_4. After being concentrated in vacuo, the crude product was purified by chromatography (SiO_2: CH_2Cl_2/MeOH, 30:1) to afford compound **S-4** as a slightly yellow solid (3.3 g, 64%): mp = 138−139 °C. ^{1}H NMR (CD_3CN, 400 MHz): δ = 7.36 (d, 4 H, J = 8.4 Hz), 7.25 (d, 4 H, J = 7.1 Hz), 6.98 (d, 4 H, J = 8.5 Hz), 6.92 (d, 4 H, J = 6.7 Hz), 4.98 (s, 4H), 4.69 (d, 4 H, J = 2.2 Hz), 3.72 (s, 4 H), 2.52 ppm (t, 2 H, J = 1.9, 2.2 Hz). ^{13}C NMR (CD_3CN, 100 MHz): δ = 158.6, 158.2, 134.3, 131.4, 130.3, 130.2, 79.7, 76.8, 70.2, 56.5, 53.6 ppm. HRMS (EI) calcd: m/z 517.2253 for $C_{34}H_{31}NO_4$. Found: m/z 517.2259.

Compound 1. TFA (1 mL) was added to the solution of compound **S-4** (2 g, 3.9 mmol) in acetone, which was stirred at room temperature for 30 min. The solvent was evaporated off, and the residue was then dissolved in acetone, followed by addition of excess NH_4PF_6 (0.82 g, 5 mmol) aqueous solution. The acetone was then removed, and the aqueous solution was extracted with CH_2Cl_2 three times (50 mL × 3). The organic extracts were dried (Na_2SO_4), and the solvent was concentrated to dryness to yield compound **1** (2.46 g, 95%), which is used for making rotaxane without further purification. ^{1}H NMR (CD_3CN, 400 MHz): δ = 7.38 (m, 8 H), 7.27 (m, 2 H), 7.00 (m, 8 H), 5.03 (s, 4 H), 4.73 (s, 4 H), 4.13 (s, 4 H), 2.8 ppm (s, 2 H). ^{13}C NMR (CD_3CN, 100 MHz): δ = 160.7, 158.4, 132.8, 130.9, 130.5, 123.7, 116.2,

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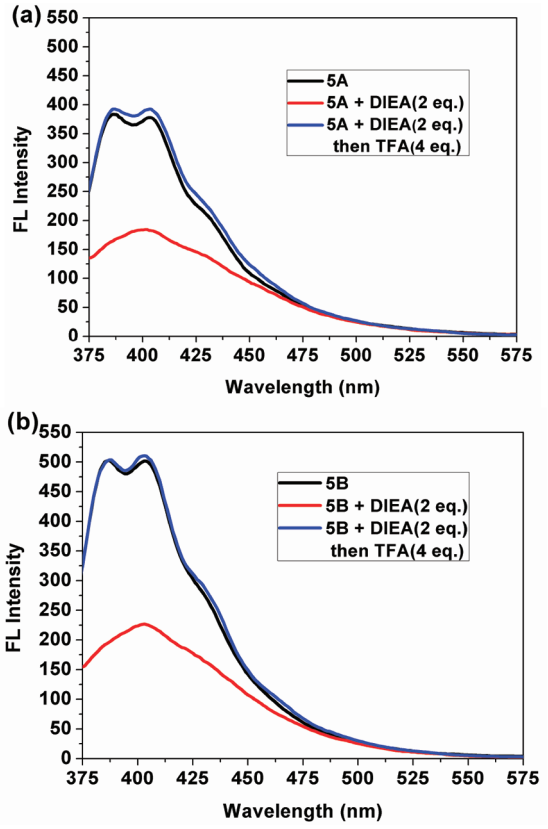

Figure 4. Fluorescence spectra of [2]catenanes **5A** and **5B** (λ_{exc} = 356 nm, 1 × 10^{-5} M, 298 K) in CH_3CN before deprotonation (black), after deprotonation with 2 equiv of DIEA (red), and reprotonation with 4 equiv of trifluoroacetic acid (TFA, blue).

115.9, 79.7, 76.9, 70.3, 56.6, 51.7 ppm. HRMS (EI) calcd: *m*/*z* 518.2326 for $C_{34}H_{32}NO_4^+$. Found: *m*/*z* 518.2318.

Compound 2. A solution of **S-5** (1.34 g, 5 mmol) and 3-azidopropan-1-amine (1 g, 10 mmol) in DMF (50 mL) was heated at 70 °C for 8 h. The product precipitated from the cooled filtrate was collected by filtration, washed with water, and dried in a vacuum, and the mixture was purified by column chromatography on silica with CH_2Cl_2/petrol (1/2, v/v) to give **2** as a pink solid (1.82 g, 84%): mp = 187−188 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.78 (s, 4 H), 4.32 (t, 4 H, *J* = 7.0, 7.1 Hz), 3.47 (t, 4 H, *J* = 6.6, 6.7 Hz), 2.06 ppm (m, 4 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.0, 131.3, 126.9, 126.7, 49.6, 38.7, 27.7 ppm. EI-MS: *m*/*z* 404 [M-N_2]. Anal. Calcd for $C_{20}H_{16}N_8O_4$: C, 55.55; H, 3.73; N, 25.91. Found: C, 55.27; H, 3.65; N, 26.13.

Compound 4A. A dilute mixture of **1** (50 mg, 0.075 mmol), **3A** (44 mg, 0.08 mmol), and $[Cu(MeCN)_4]PF_6$ (37 mg, 0.1 mmol) was stirred in dry CH_2Cl_2 (400 mL) at room temperature under nitrogen for 0.5 h. A highly dilute solution of compound **2** (32 mg, 0.075 mmol) in CH_2Cl_2 (100 mL) was added to the solution slowly over 8 h and stirred for another 24 h under nitrogen. After removal of the solvent, the crude product was purified by column chromatography (CH_2Cl_2/MeOH 30:1) to afford [2]catenane **4A** (52 mg, 42%): mp = 142−143 °C. ^{1}H NMR (CD_3CN, 400 MHz): δ = 8.54 (s, 2 H), 7.76 (s, 1 H), 7.62 (m, 2 H), 7.27 (m, 2 H), 7.11−7.16 (m, 4 H), 7.07 (s, 2 H), 6.83 (d, 2 H, *J* = 8.6 Hz), 6.55 (d, 2 H, *J* = 8.6 Hz), 4.87 (s, 2 H), 4.65 (s, 2 H), 4.55 (m, 2 H), 4.53 (t, 2 H, *J* = 6.5, 6.7 Hz), 4.19 (t, 2 H, *J* = 6.7, 6.5 Hz), 4.06 (m, 4 H), 3.67 (m, 4 H), 3.44 (s, 4 H), 2.38 ppm (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.1, 158.7, 147.7, 131.0, 130.6, 129.3, 129.2, 126.8, 126.5, 126.4, 124.9, 123.7, 115.8, 115.1, 108.4, 70.6, 69.9, 69.1, 68.7, 52.1, 42.1, 38.3 ppm. MS (MALDI-TOF): *m*/*z* 1498.5 [calcd for M^+ 1498.6]. Anal. Calcd for $C_{86}H_{84}F_6N_9O_{16}P$: C, 62.81; H, 5.15; N, 7.67. Found: C, 62.52; H, 4.96; N, 7.71.

Compound 5A. [2]Catenane **4A** (20 mg, 0.012 mmol) was dissolved in iodomethane (2 mL), and the mixture was stirred for 24 h at 40 °C. Then iodomethane was evaporated, and the solid was washed with Et_2O to give a red solid. Then, to a suspension of the previous solid in H_2O (10 mL) were added NH_4PF_6 (6.5 mg, 0.04 mmol) and CH_2Cl_2 (15 mL). The resulting bilayer solution was vigorously stirred for 3 h. After separation, the aqueous layer was extracted with CH_2Cl_2 (×3). The organic layers were combined, dried over Na_2SO_4, and concentrated to obtain quantitatively the [2]catenane **5A** (23 mg, 98%) as an orange solid: mp = 148−149 °C. ^{1}H NMR (CD_3CN, 400 MHz): δ = 8.65 (s, 2 H), 8.44 (s, 1 H), 7.55 (m, 2 H), 7.18−7.22 (m, 8 H), 6.96−6.99 (m, 4 H), 6.51 (d, 2 H, *J* = 8.5 Hz), 5.29 (s, 2 H), 4.58−4.64 (m, 6 H), 4.16−4.20 (m, 5 H), 4.08 (m, 4 H), 3.77 (m, 4 H), 3.60 (s, 4 H), 2.42 ppm (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.5, 158.7, 156.7, 147.8, 139.8, 131.3, 131.0, 130.8, 129.9, 129.5, 129.2, 126.9, 126.7, 126.3, 124.5, 124.4, 115.2, 115.1, 107.7, 70.8, 70.1, 68.5, 68.2, 58.4, 52.1, 51.8, 38.6, 37.1, 27.7 ppm. MS (ESI-MS): *m*/*z* 509.9 [calcd for M^{3+} 509.5]. Anal. Calcd for $C_{88}H_{90}F_{18}N_9O_{16}P_3$: C, 53.8; H, 4.62; N, 6.42. Found: C, 53.58; H, 4.55; N, 6.51.

Compound 4B. A dilute mixture of **1** (50 mg, 0.075 mmol), **3B** (36 mg, 0.08 mmol), and $[Cu(MeCN)_4]PF_6$ (37 mg, 0.1 mmol) was stirred in dry CH_2Cl_2 (400 mL) at room temperature under nitrogen for 0.5 h. A highly dilute solution of compound **2** (32 mg, 0.075 mmol) in CH_2Cl_2 (100 mL) was added to the solution slowly over 8 h and stirred for another 24 h under nitrogen. After removal of the solvent, the crude product was purified by column chromatography (CH_2Cl_2/MeOH 30:1) to afford [2]catenane **4B** (40 mg, 35%): mp = 145−146 °C. ^{1}H NMR (CD_3CN, 400 MHz): δ = 8.57 (s, 2 H), 7.76 (s, 1 H), 7.27 (m, 2 H), 7.14 (m, 2 H), 6.83−6.88 (m, 4 H), 6.77−6.8 (m, 2 H), 6.72 (m, 2 H), 4.98 (s, 2 H), 4.85 (s, 2 H), 4.42−4.46 (m, 4 H), 4.19 (m, 2 H), 3.95 (m, 4 H), 3.56 (m, 4 H), 3.28 (s, 4 H), 2.36 ppm (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.6, 159.2, 158.3, 148.2, 131.5, 131.3, 129.8, 127.3, 127.0, 124.4, 122.5, 116.3, 115.5, 113.7, 70.9, 70.5, 69.8, 69.2, 54.1, 52.5, 38.7, 28.9 ppm. MS (MALDI-TOF): *m*/*z* 1398.7 [calcd for M^+ 1398.6]. Anal. Calcd for $C_{78}H_{80}F_6N_9O_{16}P$: C, 60.66; H, 5.22; N, 8.16. Found: C, 60.47; H, 5.14; N, 8.25.

Compound 5B. [2]Catenane **4B** (20 mg, 0.013 mmol) was dissolved in iodomethane (2 mL), and the mixture was stirred for 24 h at 40 °C. Then iodomethane was evaporated, and the solid was washed with Et_2O to give a red solid. To a suspension of the previous solid in H_2O (10 mL) were added NH_4PF_6 (6.5 mg, 0.04 mmol) and CH_2Cl_2 (15 mL). Then the resulting bilayer solution was vigorously stirred for 3 h. After separation, the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated to obtain quantitatively the [2]catenane **5B** (23.5 mg, 97%) as a yellow solid: mp = 141−142 °C. ^{1}H NMR (CD_3CN, 400 MHz): δ = 8.69 (s, 2 H), 8.50 (s, 1 H), 7.38 (d, 2 H, *J* = 8.5 Hz), 7.18 (d, 2 H, *J* = 8.6 Hz), 7.04 (d, 2 H, *J* = 8.6 Hz), 6.80−6.83 (m, 2 H), 6.72−6.75 (m, 2 H), 6.68 (d, 2 H, *J* = 8.5 Hz), 5.32 (s, 2 H), 4.98 (s, 2 H), 4.62 (m, 2 H), 4.53 (m, 2 H), 4.22 (s, 3 H), 4.18 (m, 2 H), 3.97 (m, 4 H), 3.66 (m, 4 H), 3.45 (s, 4 H), 2.43 ppm (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 164.3, 159.5, 157.7, 148.4, 140.6, 132.1, 131.9, 131.6, 130.8, 130.4, 127.7, 127.6, 125.3, 122.1, 116.0, 115.9, 113.4, 71.4, 70.9, 69.6, 68.9, 59.2, 52.9, 52.5, 39.4, 37.9, 28.4 ppm. MS (ESI-MS): *m*/*z* 476.6 [calcd for M^{3+} 476.2]. Anal. Calcd for $C_{80}H_{86}F_{18}N_9O_{16}P_3$: C, 51.53; H, 4.65; N, 6.76. Found: C, 51.41; H, 4.59; N, 6.82.

Compound 7. In the preparation of compound **4B**, compound 7 was isolated (2.3 mg, 2%). ^{1}H NMR (CD_3CN, 400 MHz): δ = 8.50 (s, 2 H), 7.84 (s, 1 H), 7.26 (m, 3 H), 7.14 (m, 2 H), 6.92 (m, 2 H), 6.83 (m, 2 H), 6.75 (m, 2 H), 6.68 (m, 2 H), 4.96 (s, 2 H), 4.90 (s, 2 H), 4.44 (m, 5 H), 4.15 (t, 2 H, *J* = 2.6, 3.04 Hz) 3.96 (m, 4 H), 3.63 (m, 4 H), 3.41 (s, 4 H), 2.14 ppm (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.9,

158.3, 156.8, 147.5, 142.4, 130.9, 130.4, 129.3, 126.5, 121.2, 115.1, 114.8, 112.5, 70.5, 70.0, 68.9, 67.9, 61.5, 51.6, 48.1, 38.0, 27.9 ppm. MS (MALDI-TOF): m/z 2798.2 [calcd for M^+ 2797.1], 1399.6 [calcd for M^{2+} 1398.6]. Anal. Calcd for $C_{156}H_{160}F_{12}N_{18}O_{32}P_2$: C, 60.66; H, 5.22; N, 8.16. Found: C, 60.37; H, 5.13; N, 8.25.

■ ASSOCIATED CONTENT

Supporting Information. Full experimental details pertaining to the preparation and characterization of all compounds including NMR and MS spectra; COSY-NMR spectra of [2]catenanes **5A** and **5B**; absorption spectra of [2]catenanes **4B** and **5B**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: ylli@iccas.ac.cn

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