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Photo-Responsive [2]Catenanes: Synthesis and Properties

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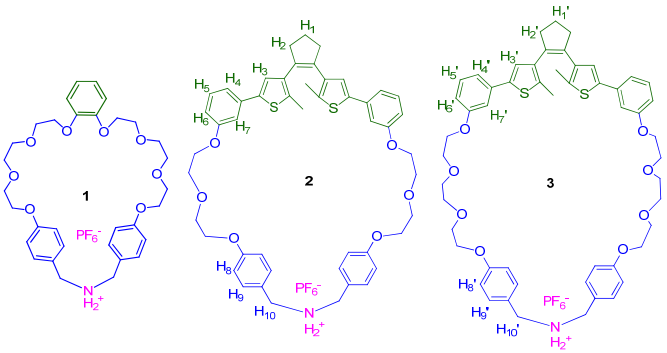
A series of novel dithienylethene-based macrocycles containing ammonium moieties has been synthesized. They have been employed as templates to construct [2]catenanes showing photoisomerization properties by means of a dynamic covalent chemistry approach. Their structures have been reliably confirmed by NMR, ESI-MS or MALDI-QTOF-MS, and elemental analysis, and their energy-minimized structures of open-and closed-ring isomers were investigated by the theoretical calculation. Investigation of the photochromic properties of these dithienylethene-based [2]catenanes has revealed good reversibility and excellent fatigue resistance upon irradiation with UV or visible light. Notably, formation of the [2]catenanes enhanced the photochromic properties compared with those of the corresponding macrocyclic ammonium salt, implying that the non-covalently interacting components of the [2]catenanes could affect the photoswitchable properties.

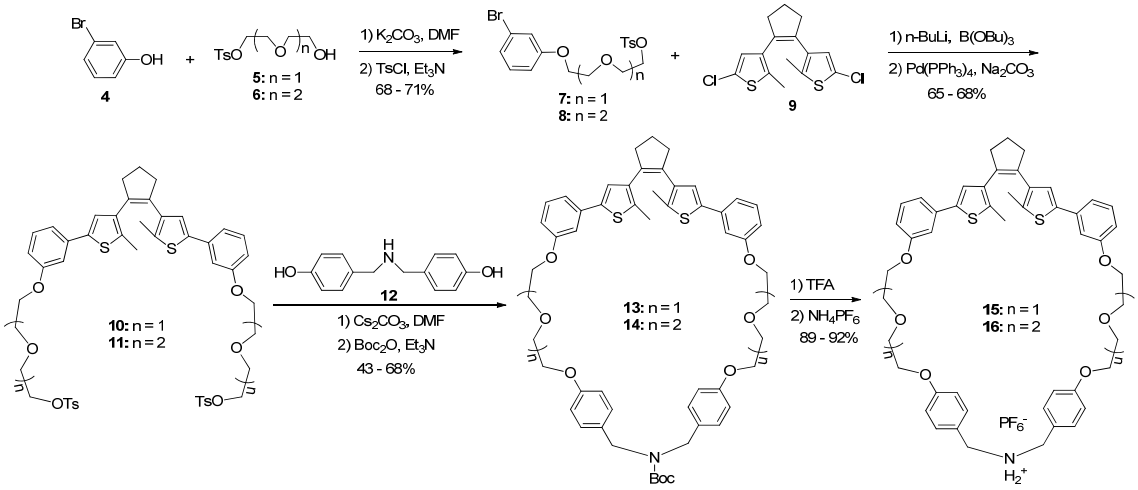
Introduction

Recently, research on mechanically interlocked molecules, better known as rotaxanes and catenanes, has grown to an unprecedented level of activity, due not only to their topological importance but also their potential applications in many fields.[1]Catenanes, topologically unique structures possessing two or more mechanically interlocked rings, have been known for nearly half a century.[2] In the meantime, the rapid development of catenanes has promoted an understanding of design strategies and approaches for the functionalization of synthetic supramolecular systems. Currently, the photoswitchable interlocked molecules have attracted some attention.[3] Photochromism is a reversible transformation between two isomers with different absorption spectra induced by alternating irradiation with UV and visible light. During the past few decades, photochromic materials have received much attention because of their potential applications in photoswitchable molecular devices and optical memory storage media.[4] Of the various types of photochromic compounds, dithienylethenes are among the most promising candidates for technological applications by virtue of their excellent thermally irreversible properties, high photoisomerization quantum yields, and remarkable fatigue resistance.[5] The incorporation of a photochromic dithienylethene unit into a mechanically interlocked system was thus expected to be beneficial for obtaining photo-responsive mechanically interlocked molecular materials. As early as in 1997, Irie found that inclusion in a cyclodextrin cavity could enhance the photocyclization quantum yield.[6] Tian et al found that the dithienylethene unit dould be used as a stopper in the construction of rotaxane.[7] Subsequently, they reported a multi-state [2]rotaxane based on dithienylethene unit which could alter intercomponent interactions in a photochromic multi-state[2]rotaxane.[8] Recently, Liu and co-workers reported a [2]pseudorotaxane formed from an unsymmetrical diarylperfluorocyclopentene and a Eu^{3+} complex of terpyridinyldibenzo-24-crown-8, which revealed dual-stimulus luminescent lanthanide molecular switching behavior modulated by host-guest interaction and optical stimuli.[9]

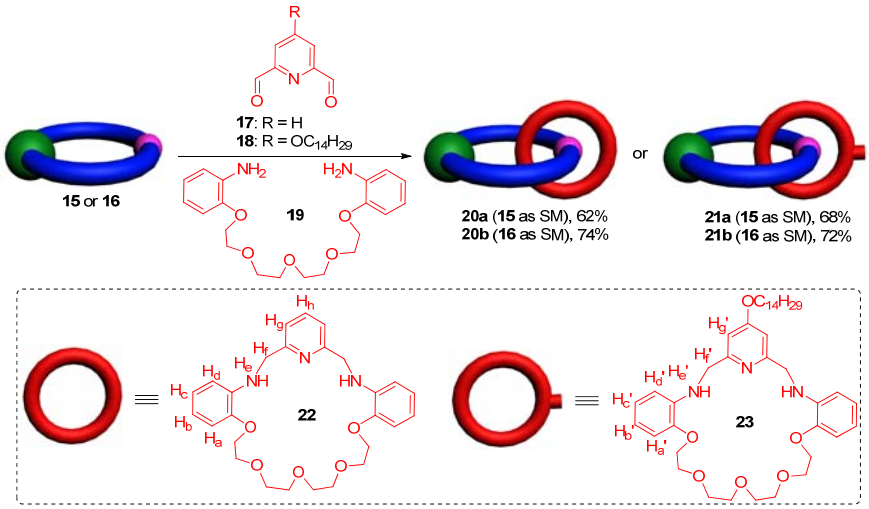


Scheme 1. The structures of macrocyclic ammoniums.

The template-directed clipping approach based on 2,6-pyridinedicarboxaldehyde and tetraethylene glycol bis(2-aminophenyl)ether is considered an efficient strategy for the synthesis of the various MIMs, such as linear [2]rotaxanes, oligomers and polymers,[10] rectangular [4]rotaxanes,[11] pH induced switchable rotaxanes,[1m] daisy chains,[12] heterorotaxanes,[13] and dendritic [2]rotaxanes.[14] Besides, our group utilized the same method to construct a series of [2]catenanes based on macrocyclic ammonium salt **1**, as shown in Scheme 1.[15] Herein, on the basis of ammonium 1, we introduced the dithienylethene and synthesized two novel macrocyclic ammonium salts **2** and **3**, which we proceeded to use to successfully construct a series of photoswitchable [2]catenanes showing photo-responsive character.



Scheme 2. Synthesis of dithienylethene-based macrocyclic ammoniums**15** and **16.**



Scheme 3. Synthesis of dithienylethene-based [2]catenanes.

Studies on their photochromic properties revealed that these photoswitchable [2]catenanes displayed good reversibility and excellent fatigue resistance upon irradiation with UV or visible light. Furthermore, it was found that the formation of [2]catenanes could enhance the photochromic properties, which indicated that the non-covalently interacting components of the [2]catenanes could affect the photoswitchable properties.

Results and discussion

Synthesisof dithienylethene-based macrocyclic ammoniums. The stepwise synthesis of photo-switchable macrocyclic alkyl ammonium salts **15** and**16**was outlined in Scheme 2. 1,2-Bis(5-chloro-2-methylthiophen-3-yl)cyclopent-1-ene (**9**) was selected as the starting material to introduce the photoswitchable unit.[16] Compounds **7** and **8**,which were synthesized by reactions of 3-bromophenol(**4**) with **5**and **6**,[17] respectively, were subjected to Suzuki coupling reactions with the boronic acid derived from the borate of compound **9**, affording the corresponding compounds**10** and **11**, respectively, in 65–68% yields. The cyclizations were performed by reactions of 4,4'-[azanediylbis(methylene)]diphenol (**12**)[15]with the pseudo crown ethers **10** and **11** in the presence of Cs_2CO_3, whereby the Cs^+ simultaneously served as a template for the cyclization. For a more convenient purification, the NH groups of the free amines were first protected with Boc_2O. The Boc-protected macrocyclic amines **13** and **14** were thereby obtained in 43–68% yields over the two steps. Their Boc protective groups were removed with excess trifluoroacetic acid (TFA) in dry dichloromethane, and the as-formed amines were simultaneously protonated. Subsequent counter-ion exchange with saturated NH_4PF_6 afforded the macrocyclic alkyl ammonium salts **15** and **16** in 89–92% yields. Additionally, N-hetero crown ethers **22** and **23**, selected to aid spectroscopic analysis, were also synthesized according to reported literature procedures.[15]The chemical structures of all new compounds were reliably confirmed by standard spectroscopic characterizations, namely by ^1H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis (see the Supporting Information).

Synthesis and characterization of photoswitchable [2]catenanes. The clipping reaction was firstly investigated for the macrocyclic ammonium salt **15** by mixing together equimolar amounts of **17** and **19** (Scheme 3) in CD_3CN, where upon alight-yellow solution was observed due to the formation of imines. Subsequently, the clipping process was followed by ^1H NMR spectroscopy. A complicated mixture containing imine oligomers was thereby observed after one day. Simultaneously, a broad singlet at δ=9.68 ppm due to the ammonium NH_2^+ protons as well as a singlet at δ=8.20 ppm due to the imine (CH=N) proton were detected (Figure S1B), which implied the presence of a dynamic [2]catenane. The mixture was then treated with BH_3·THF to reduce carbon-nitrogen double bonds to kinetically stable C-NH bonds, whereupon the [2]catenane **20a** could be separated by column chromatography in 62% yield. Comparing the ^1H NMR spectra, the resonance of the ammonium NH_2^+ protons in the kinetically stable [2]catenane **20a** showed an obvious upfield shift (singlet at δ=8.57 ppm) with respect to that of the dynamic [2]catenane, as shown in Figure 1B. To further confirm the formation of the [2]catenane, the ^1H NMR spectra of N-hetero crown ether **22**, [2]catenane**20a**, and ammonium salt**15** were studied in detail. For instance, the resonance of the protons (H_{10}) of the methylene units of macrocyclic ammonium salt **15** showed an obvious downfield shift owing to the influence of the hetero crown ether component. Moreover, the aromatic proton signals (H_8 and H_9) of ammonium salt **15** were found to be significantly upfield shifted, as a result of the hetero crown ether **22** encircling the template site of the dithienylethene ammonium salt. The observed shifts in proton resonances were in good agreement with those noted in previous studies.[11b,13, 15] In our previous work, we confirmed that the N-hetero crown ether **23** having a long alkoxyl chain could be used as one component of catenanes.[15] Therefore, the same strategy was employed to prepare [2]catenane **21a**. As presented in Figure 1, some similar shifts in the proton resonance signals were observed (Figure S1D). Additional evidence supporting this conclusion was provided by analysis of the electrospray ionization mass spectra (ESI-MS) in acetonitrile, which featured peaks at *m/z* 1293.5645 for **20a** and 1505.7800 for **21a**, attributable to the respective $[M - PF_6^-]^+$ species (Figures 2C and 2D).

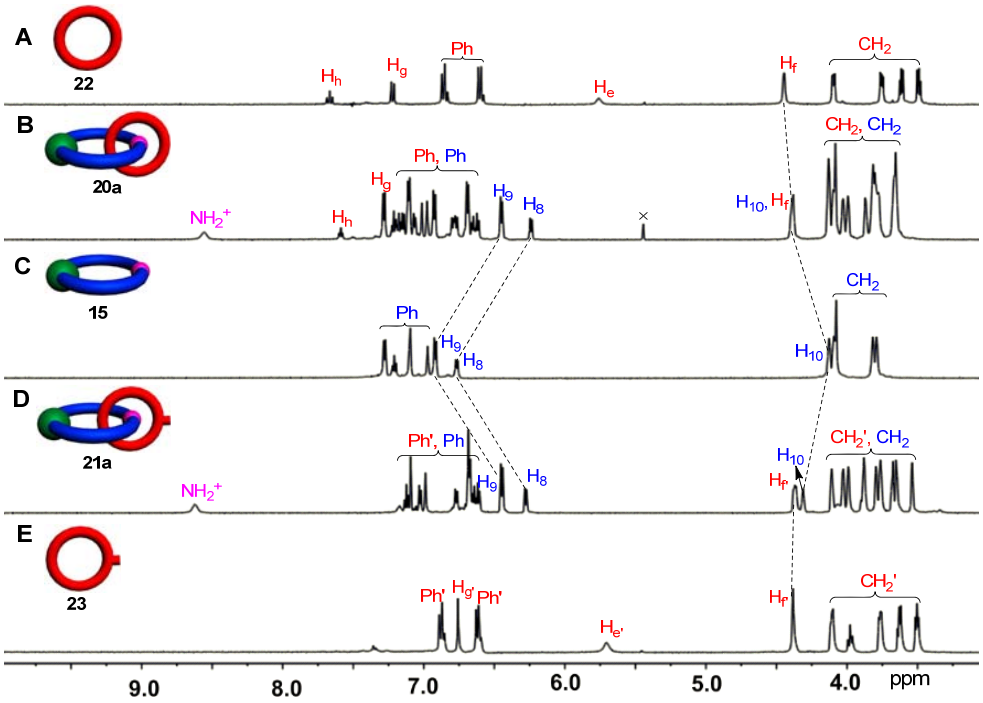


Figure 1. Partial ^1H NMR spectra (400 MHz, CD_3CN, 298 K) of **22** (A); **20a** (B); **15** (C); **21a** (D) and **23** (E).

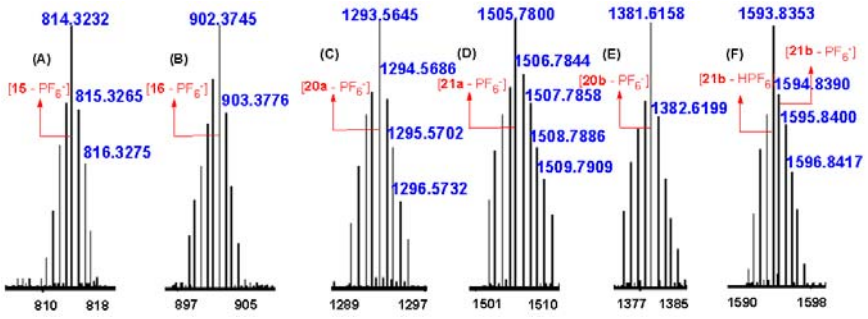


Figure 2. The MALDI-QTOF mass spectra of compounds**15** (A), **16** (B), **20a** (C), **21a** (D), **20b** (E) and**21b** (F).

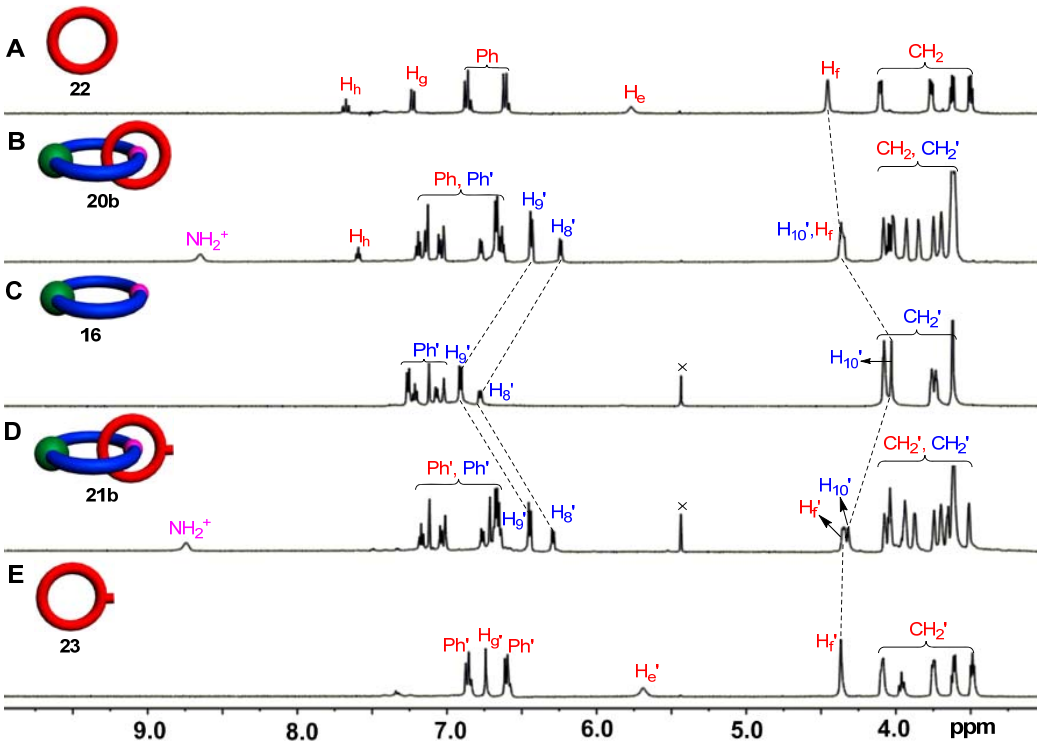


Figure 3. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of **22** (A); **20b** (B); **16** (C);**21b** (D) and **23** (E).

Subsequently, the larger macrocyclic ammonium salt **16** was employed to construct photoswitchable [2]catenanes by a similar synthetic method. The dithienylethene-based [2]catenanes **20b** and **21b** were obtained in pure form by the template-directed clipping approach shown in Scheme 3. Similarly, the formation process of these [2]catenanes could be monitored by ^{1}H NMR spectroscopy. According to the obtained data (Figures S2 and Figure 3), similar chemical shift changes to those for the characteristic protons of [2]catenanes **20a** and **21a** were also observed for [2]catenanes **20b** and **21b**. ESI mass spectra further confirmed the formation of [2]catenanes **20b** and **21b**. As can be seen in Figures 2E and 2F, peaks at *m/z* 1381.6158 and 1594.8390 attributable to $[M - PF_6^-]^+$ species with *M* corresponding to the masses of [2]catenanes **20b** and **21b**, respectively, were detected.

Photochromic properties of switchable [2]catenanes. Owing to the introduction of the dithienylethene unit, the photoisomerization behavior of the switchable [2]catenanes **20** and **21** in acetonitrile were investigated at room temperature. These switchable [2]catenanes underwent photoisomerization between ring-open isomers and ring-closed isomers upon alternating irradiation with UV light (λ = 254 nm) and visible light (λ>402 nm), as illustrated in Scheme 4. As shown in Figure 4B, the absorption maximum of **20a** was observed at 278 nm ($\varepsilon = 2.97 \times 10^4$ L mol^{-1} cm^{-1}) as a result of a π-π* transition.[18] Upon irradiation with UV light at 254 nm, the colorless solution turned purple and a new absorption band at 528 nm ($\varepsilon = 1.08 \times 10^4$ L mol^{-1} cm^{-1}) appeared due to the formation of the corresponding ring-closed isomer. Moreover, a well-defined isosbestic point was observed at 329 nm, which indicated that compound **20a** was cleanly converted into the photocyclized product. Upon irradiation with visible light (λ > 402 nm), the colored isomer underwent a cycloreversion process and returned to the initial colorless ring-opened isomer. In particular, **20a** showed very good reversibility and no apparent deterioration was observed after repeating the above process eight times, indicating excellent fatigue resistance (Figure 4B inside). Similar photochromic properties were obtained when solutions of the macrocyclic ammonium salt **15**and alkoxyl-substituted [2]catenane **21a** in acetonitrile were irradiated with the same UV/vis light, as shown in Figure 4A and 4C.Furthermore, the response rate to light for **15**, **20a** and **21a** were compared, it was found that the response rate for the alkoxyl-substituted [2]catenane**21a** was the fastest and the free macrocyclic ammonium salt **15** was the slowest, and **20a** and **21a** reached photostationary states more efficiently than **15** (Figure S3). The photochromic parameters of dithienylethenes **15**, **20a** and **21a** in acetonitrile were summarized in Table 1. From these data, it was found that the formation of photoswitchable [2]catenanes had a remarkable effect on their photochromic properties, mainly including molar absorption coefficients and quantum yields, while the change of absorption wavelength was not observed. Among these dithienylethenes, the molar absorption coefficients of both the open-ring isomer and the closed-ring isomer of alkoxyl-substituted [2]catenane **21a** were the largest ($\varepsilon = 3.79 \times 10^4$ L mol^{-1} cm^{-1}, 1.21×10^4 L mol^{-1} cm^{-1}), while those of the free macrocyclic ammonium salt **15** were the smallest ($\varepsilon = 2.51 \times 10^4$ L mol^{-1} cm^{-1}, 0.98×10^4 L mol^{-1} cm^{-1}). From these data, it is clearly evident that the mechanically interlocked molecules displayed higher quantum yields, not only cyclization quantum yields ($\varphi_{o\text{-}c}$) but also cycloreversion quantum yields ($\varphi_{c\text{-}o}$), compared to those of ammonium salt **15**. And for the cyclization quantum yields, **21a** was also the biggest ($\varphi_{o\text{-}c}$ = 0.213) and **15** was the smallest ($\varphi_{o\text{-}c}$ = 0.172) among all the dithienylethene derivatives. So it was obvious that the formation of photoswitchable [2]catenanes enhanced effectively the photochromic properties.

Subsequently, the photochromic properties of larger macrocyclic ammonium salt **16**, [2]catenane **20b** and **21b** in acetonitrile at room

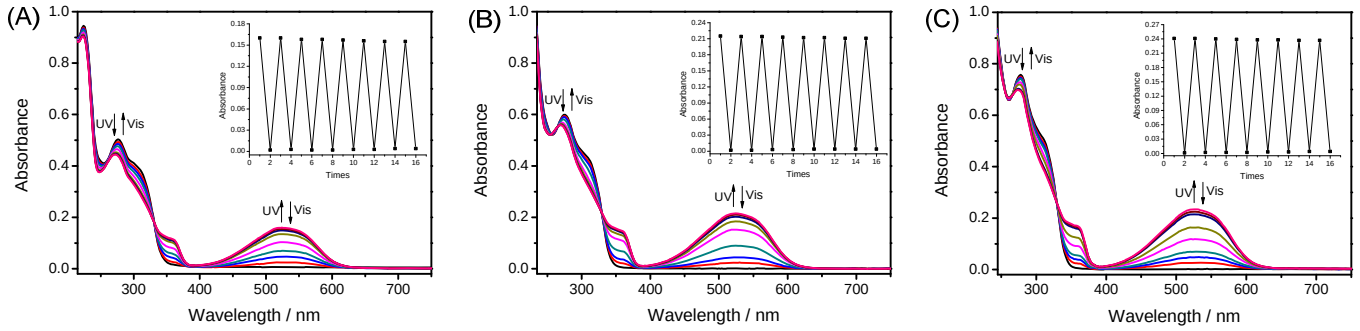


Figure 4. Absorption spectral changes of **15**, **20a** and **21a** with 254 nm UV and >402 nm Vis light irradiation in CH_3CN (2.0×10^{-5} mol/L), (A) spectral changes for **15**; (B) spectral changes for **20a**; (C) spectral changes for**21a**. (Inside) Fatigue resistance of **15**, **20a** and **21a** in CD_3CN, respectively.

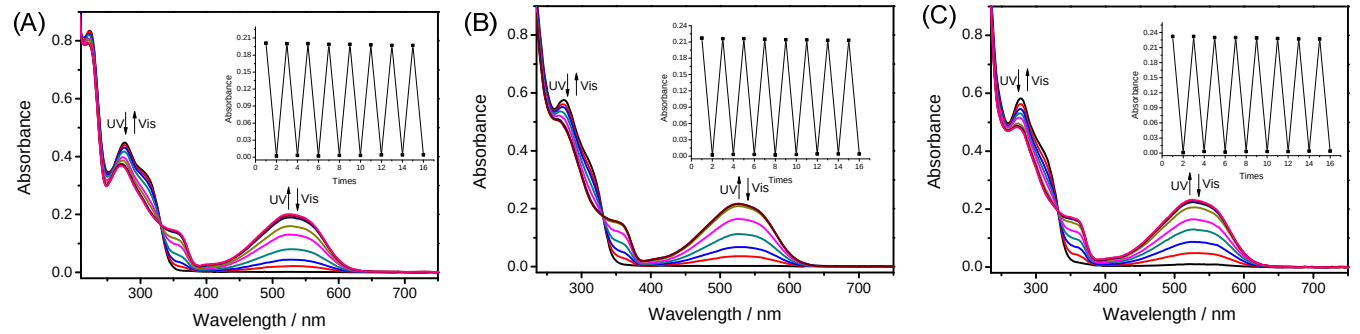
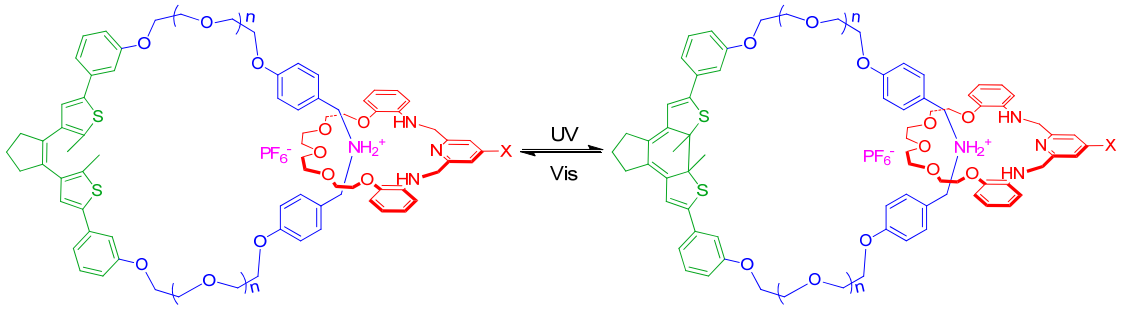


Figure 5. Absorption spectral changes of **16**, **20b** and **21b** with 254 nm UV and >402 nm Vis light irradiation in CH_3CN (2.0×10^{-5} mol/L), (A) spectral changes for **16**; (B) spectral changes for **20b**; (C) spectral changes for **21b**. (Inside) Fatigue resistance of dithienylethenes **16**, **20b** and **21b** in CD_3CN, respectively.



20a-b, 21a-b (open-ring) **20a-b, 21a-b** (closed-ring)

Scheme 4. Photochromism of switchable [2]catenanes.

temperature were also investigated. Similar photochromic properties to those described above for [2]catenanes **20a** and **21a** with smaller macrocyclic ammonium salt were observed when their solutions in CH_3CN were irradiated with UV/vis light, as shown in Figure 5. In addition, the two mechanically interlocked molecules **20b** and **21b** also attained photostationary states more rapidly than ammonium salt**16** and they also showed higher molar absorption coefficients, cyclization and cycloreversion quantum yields, as summarized in Table 1. For the macrocyclic ammonium salts of different sizes, only minor changes in their cyclization and cycloreversion quantum yields were found, which suggested that the size of the macrocyclic ammonium salt had only a small influence in this system. These experiments further proved that the mechanically interlocked molecules can promote the photochromic behavior.

Additionally, the compounds **20b** and **21b** displayed light higher quantum yields compared with the compounds **20a** and **21a** possible owing to larger cavity of ammonium component **16**. For that, the energy-minimized structures of open-ring and closed-ring isomers of [2]catenanes **20** and **21** were optimized by density functional theory (DFT) calculations at the B3LYP/6-31G* level by using Gaussian 09 programs. As shown in Figure 6, the open-ring isomers (the distances between sulfur atoms and ammonium were 14.08-14.59 Å) of **20b** and **21b** had a larger cavity in comparison to the **20a** and **21a** (the distances between sulfur atoms and ammonium were 11.14-11.20 Å). For the closed isomers of **20b** and **21b**, the distances between sulfur atoms and ammonium were 10.34-10.69Å, which was longer than that of **20a** and **21a** (8.37-8.76 Å). Accordingly, the compounds having larger cavity present a more flexible configuration, which was helpful to the photoisomerization.

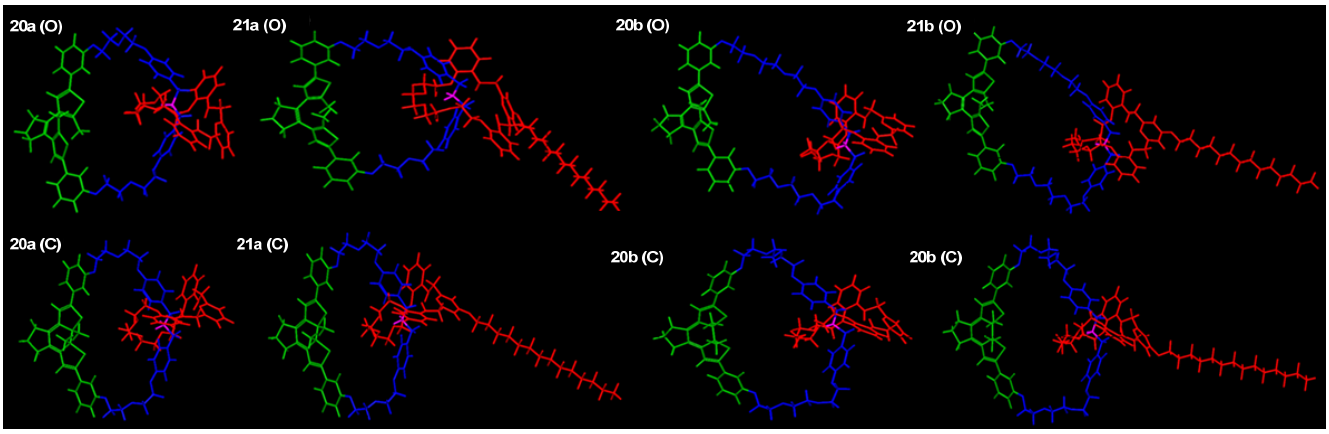


Figure 6. The energy-minimized structures of open-ring and closed-ring isomers of [2]catenanes **20** and **21** based on density functional theory (DFT) calculations at the B3LYP/6-31G* level by using Gaussian 09 programs.

Table 1. Photochromic parameters of **15**, **16**, **20** and **21** in CH_3CN (2.0×10^{-5} mol/L).

Comps	λ_{max}/nm [a] ($\varepsilon\times10^{-4}$)	λ_{max}/nm [b] ($\varepsilon\times10^{-4}$)	Φ [c]	
	(Open)	(PSS)	$\varphi_{o\text{-}c}$ (λ/nm)	$\varphi_{c\text{-}o}$ (λ/nm)
15	278(2.51)	528(0.98)	0.172	0.0015
16	276(2.25)	526(1.01)	0.160	0.0032
20a	278(2.97)	528(1.08)	0.190	0.0039
21a	278(3.79)	528(1.21)	0.213	0.0032
20b	276(2.88)	526(1.09)	0.263	0.0056
21b	276(2.91)	526(1.16)	0.278	0.0064

[a] Absorption maxima of open-ring isomers.[b] Absorption maxima of closed-ring isomers.[c] Quantum yields of open-ring ($\varphi_{c\text{-}o}$) and closed-ring isomers ($\varphi_{o\text{-}c}$), respectively.

Conclusions

In summary, macrocyclic ammonium salts incorporating dithienylethene moieties have been efficiently assembled to [2]catenanes showing photoisomerization properties by a template-directed clipping approach. These photo-responsive, mechanically interlocked molecules showed good reversibility and excellent fatigue resistance upon irradiation with light of various wavelengths. The photochromism of these [2]catenanes showed them to have superior photoisomerization properties to those of the corresponding ammonium salts, which indicated that the non-covalently interacting components of the [2]catenanes could influence the photoswitching properties. More importantly, this research provides an alternative route for the design of photo-responsive materials with excellent properties, and it is expected that more and more mechanically interlocked molecules incorporating photo-switchable blocks will be applied in optoelectronic materials in the future.

Experimental

Materials and methods. All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques, unless otherwise stated. THF was distilled under nitrogen from sodium-benzophenone. DMF was dried with magnesium sulfate then distilled under vacuum. CH_3CN was dried with calcium hydride then distilled.All other starting materials were obtained commercially as analytical-grade and used without further purification. ^1H and ^{13}C NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz) or 600 MHz.^1H and ^{13}C NMR chemical shifts are relative to TMS. Mass spectra were measured in the ESI or MALDI mode. Mass spectra were recorded on the Agilent 1100 series spectrometer with ESI ionization and Bruker ultrafle Xtreme (Ⅱ) MALDI-TOF spectrometer. UV-Vis spectra were obtained on U-3310 UV Spectrophotometer. UV light was irradiated using ZF5UV lamp (254 nm), and visible light irradiation (λ> 402 nm) was carried out by using a LZG 220 V 500W tungsten lamp with cutoff filters.

Synthesis of 7: To a solution of 3-bromophenol **4** (346 mg, 2.0 mmol) and 2-(2-hydroxyethoxy)ethyl 4-methyl–benzenesulfonate **5** (520 mg, 2.0 mmol) in DMF potassium carbonate (420 mg, 3.0 mmol) was added under vigorous stirring. After stirring the solution for 24 h at 50 ℃ under anitrogen atmosphere, the resulting mixture was allowed to cool to room temperature, the solvent were removed under vacuum, and the residue was extracted by ethyl acetate, and then dried over anhydrous sodium sulfate. The unpurified mixture above and Et_3N (1.5 mL) was dissolved in dry DCM (20 mL) and was cooled down to 0 ℃ and then p-tosyl chloride (950 mg, 5.0 mmol) in dry DCM (30 mL) were added dropwise over a 1 h period. The reaction mixture was then allowed to ambient temperature and stirred overnight. 5N HCl (4 mL) was then added and organic phase was separated and washed with saturated brine (30 mL), the organic phase was dried over $MgSO_4$. Upon removed of solvent under reduced pressure and purified on a silica gel column using petroleum ether / ethyl acetate (2:1) as the eluent to obtain the **7** as a yellow oil. Yield: 588 mg, 71%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.16-7.08 (m, 2H), 7.03 (s, 1H), 6.82 (d, J = 7.9 Hz, 1H), 4.19 (t, J = 4.6 Hz, 2H), 4.02 (t, J = 4.5 Hz, 2H), 3.78-3.74 (m, 4H), 2.42 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 144.8, 132.9, 130.5, 129.8, 127.9, 124.0, 122.7, 117.8, 113.5, 69.6, 69.2, 68.9, 67.6, 21.6. ESI MS: m/z = 437.6 [M + Na^+]; calculated mass: 437.0 [M + Na^+]. Anal.

Calcd for: $C_{17}H_{19}BrO_5S$: C, 49.17; H, 4.61. Found: C, 49.28; H, 4.73.

Synthesis of 8: Compound **8** was prepared by an analogous method similar to that used for **7** and was obtained. Yield: 623 mg, 68%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.12 (t, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 9.4 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 4.15 (t, *J* = 6.0 Hz, 2H), 4.08 (t, *J* = 6.0 Hz, 2H), 3.80 (t, *J* = 6.0 Hz, 2H), 3.69 (t, *J* = 6.0 Hz, 2H), 3.65 (br, 2H), 3.61 (br, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 144.6, 132.7, 130.4, 129.6, 127.7, 123.7, 122.5, 117.7, 113.4, 70.5, 69.4, 69.1, 68.5, 68.0, 67.4, 21.4. ESI MS: m/z = 481.1 [M + Na^+]; calculated mass: 481.0 [M + Na^+]. Anal. Calcd for: $C_{19}H_{23}BrO_6S$: C, 49.68; H, 5.05. Found: C, 49.54; H, 5.14.

Synthesis of 10: To the anhydrous THF solution (10 mL) of **9** (330 mg, 1.0 mmol), *n*-BuLi (0.9 mL of 2.5 M solution in hexane, 2.2 mmol) was added under a nitrogen atmosphereat room temperature in 10 portions using a syringe. This solution was stirred for 1 h at room temperature, then $B(OBu)_3$ (0.81 mL, 3.0 mmol) was added in one portion. This reddish solution was stirred for 5 h at room temperature and was then used in the Suzuki cross coupling reaction without any workup. And then the above reddish solution was added dropwise to a flask containing**7** (725 mg, 1.75 mmol), $Pd(PPh_3)_4$ (70 mg, 0.057 mmol) and Na_2CO_3 solution (10 mL, 2 M) at 60 ℃. Subsequently the mixture was refluxed for 24 h and cooled to room temperature, after which CH_2Cl_2 (100 mL) and H_2O (30 mL) were added. The organic layer was separated and dried (Na_2SO_4). After concentration, the compound was purified on a silica gel column using petroleum ether / ethyl acetate (2:1) as the eluent to obtain **10** as brown oil. Yield: 603 mg, 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 4H), 7.32 (d, *J* = 8.3 Hz, 4H), 7.26 (t, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.05 (s, 2H), 7.04-6.99 (m, 2H), 6.78 (dd, *J* = 8.2, 1.6 Hz, 2H), 4.24-4.21 (m, 4H), 4.07-4.05 (m, 4H), 3.78 (t, *J* = 4.0 Hz, 8H), 2.88 (t, *J* = 6.0 Hz, 4H), 2.42 (s, 6H), 2.18-2.08 (m, 2H), 2.04 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 144.7, 139.2, 136.6, 135.7, 134.6, 134.6, 132.8, 129.7, 127.9, 124.3, 118.1, 113.1, 111.4, 69.7, 69.2, 68.8, 67.3, 38.3, 23.0, 21.5, 14.4. ESI MS: m/z = 951.4 [M + Na^+]; calculated mass: 951.2 [M + Na^+]. Anal. Calcd for: $C_{49}H_{52}O_{10}S_4$: C, 63.34; H, 5.64. Found: C, 63.41; H, 5.60.

Synthesis of 11: Compound **11** was prepared by an analogous method similar to that used for **10** and was obtained as brown oil. Yield: 691 mg, 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 7.27-7.20 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.06-7.01 (m, 4H), 6.78 (d, *J* = 8.0 Hz, 2H), 4.17-4.10 (m, 8H), 3.80 (t, *J* = 4.0 Hz, 4H), 3.70-3.62 (m, 12H), 2.84 (t, *J*= 6.0 Hz, 4H), 2.41 (s, 6H), 2.08-2.01 (m, 2H), 1.98 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 144.8, 139.3, 136.5, 135.7, 134.5, 129.8, 127.9, 124.2, 118.0, 113.1, 111.4, 70.7, 69.7, 69.2, 68.7, 67.2, 38.3, 22.9, 21.6, 14.4. ESI MS: m/z = 1039.5 [M + Na^+], 1055.8 [M + K^+]; calculated mass: 1039.3 [M + Na^+], 1055.3 [M + K^+]. Anal. Calcd for: $C_{53}H_{60}O_{12}S_4$: C, 62.57; H, 5.94. Found: C, 62.51; H, 5.88.

Synthesis of 13: A mixture of **10** (930 mg, 1.0mmol) and **12** (230 mg, 1.0mmol) in dry DMF (300 mL) was added dropwise over a period of 12 h to a stirred suspension of Cs_2CO_3 (1.3 g, 4.0 mmol) at 80℃ under a nitrogen atmosphere. After the addition was completed, the mixture was stirred at 80 ℃for a further 3 d. The resulting mixture was allowed to cool to room temperature, and filtered. After that, the solvent were removed under vacuum, and the residue was extracted by ethyl ether, and then dried over anhydrous sodium sulfate. Upon removed of solvent under reduced pressure and dried. The unpurified product was dissolved in dry chloroform (40 mL) and then Boc_2O (0.88 g, 4.0mmol) and triethylamine (0.86 mL) were added. The mixture was stirred at room temperature for 24 h. Upon removed of solvent under reduced pressure and purified on a silica gel column using petroleum ether/ethyl acetate (2:1) as the eluent to obtain the Boc-protected switchable macrocycle **13** as a brown solid. Yield: 393 mg, 43%.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.01 (br, 4H), 6.97 (s, 2H), 6.91 (s, 2H), 6.77 (d, *J* = 6.4 Hz, 6H), 4.34 (s, 2H), 4.24 (s, 2H), 4.14-4.10 (m, 8H), 3.87-3.84 (m, 8H), 2.82 (t, *J* = 6.0 Hz, 4H), 2.11-2.05 (m, 2H), 2.02 (s, 6H), 1.49 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 159.07 (s), 157.75 (s), 155.88 (s), 139.26 (s), 136.51 (s), 135.73 (s), 134.78 (s), 134.56 (s), 130.55 (s), 129.69 (s), 124.33 (s), 117.91 (s), 114.58 (s), 113.47 (s), 111.72 (s), 79.81 (s), 69.88 (s), 69.80 (s), 67.62 (s), 67.56 (s), 49.39 (s), 38.05 (s), 28.45 (s), 23.04 (s), 14.37 (s). MALDI-TOF MS: m/z = 913.32 [M], 936.32 [M + Na^+], 952.29 [M + K^+]; calculated mass: 913.4 [M], 936.4 [M + Na^+], 952.3 [M + K^+]. Anal. Calcd for: $C_{54}H_{59}NO_8S_2$: C, 70.95; H, 6.51; N, 1.53. Found: C, 70.87; H, 6.60; N, 1.59.

Synthesis of 14: Compound **14** was prepared by an analogous method similar to that used for **13** and was obtained as a brown solid. Yield: 681 mg, 68%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 8.0 Hz, 2H), 7.10-7.00 (m, 10H), 6.82-6.77 (m, 6H), 4.29 (s, 2H), 4.18 (s, 2H), 4.15-4.12 (m, 4H), 4.10-4.06 (m, 4H), 3.85 (t, *J* = 4.0 Hz, 8H), 3.75 (s, 8H), 2.81 (t, *J* = 6.0 Hz, 4H), 2.08-2.02 (m, 2H), 1.95 (s, 6H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 157.9, 139.3, 136.5, 135.7, 134.6, 130.1, 129.7, 129.4, 124.1, 117.9, 114.5, 113.1, 111.6, 79.8, 70.9, 70.9, 69.7, 67.4, 67.3, 65.2, 41.9, 38.3, 28.4, 23.3, 14.4. ESI MS: m/z = 1024.8 [M + Na^+], 1040.7 [M + K^+]; calculated mass: 1024.4 [M + Na^+], 1040.4 [M + K^+]. Anal. Calcd for: $C_{58}H_{67}NO_{10}S_2$: C, 69.50; H, 6.74; N, 1.40. Found: C, 69.45; H, 6.79; N, 1.36.

Synthesis of 15: To a solution of **13** (457 mg, 0.5 mmol) in dry DCM (20 mL), TFA (0.16 mL, 2.5 mmol) was added at room temperature. After stirring for 2 h under anitrogen atmosphere, the solvent was removed under vacuum. The residue was dissolved in MeOH (3 mL), and then saturated NH_4PF_6 (6 mL, aq) was added to yield a brown precipitate. After filtering, washing with H_2O and dry under vacuum, the title compound was obtained. Yield: 441 mg, 92%. ^{1}H NMR (600 MHz, CD_3CN) δ 7.30 (d, *J* = 6.0 Hz, 4H), 7.23 (t, *J* = 6.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 4H), 6.99 (s, 2H), 6.94 (d, *J* = 8.0 Hz, 4H), 6.79 (d, *J* = 8.0 Hz, 2H), 4.15 (t, *J* = 8.0 Hz, 4H), 4.11 (t, *J* = 8.0 Hz, 4H), 4.10 (s, 4H), 3.85-3.83 (m, 4H), 3.82-3.79 (m, 4H), 2.82 (t, *J* = 6.0 Hz, 4H), 2.09-2.05 (m, 2H), 1.98 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 159.2, 139.4, 136.7, 135.9, 134.9, 134.7, 131.2, 129.8, 124.5, 121.8, 118.1, 115.8, 113.5, 112.2, 77.0, 69.8, 67.8, 67.8, 50.6, 38.2, 14.3. MALDI-QTOF-MS: m/z = 814.3232 [M - PF_6^-]; calculated mass: 814.3236 [M - PF_6^-]. Anal. Calcd for: $C_{49}H_{52}F_6NO_6PS_2$: C, 61.30; H, 5.46; N, 1.46. Found: C, 61.36; H, 5.39; N, 1.43.

Synthesis of 16: Compound **16** was prepared by an analogous method similar to that used for **15**and was obtained. Yield: 466 mg, 89%. ^{1}H NMR (600 MHz, CD_3CN) δ 7.28 (d, *J* = 12.0 Hz, 4H), 7.23 (t, *J* = 6.0 Hz, 2H), 7.14 (s, 2H), 7.09 (d, *J* = 12 Hz, 2H), 7.04 (s, 2H), 6.93 (d, *J* = 12.0 Hz, 4H), 6.80 (d, *J* = 12.0 Hz, 2H), 4.10 (t, *J* = 6.0 Hz, 8H), 4.05 (s, 4H), 3.78 (t, *J* = 6.0 Hz 4H), 3.75 (t, *J* = 6.0 Hz 4H), 3.64 (s, 8H), 2.82 (t, *J* = 6.0

Hz, 4H), 2.07-2.03 (m, 2H), 1.96 (s, 6H).^{13}C NMR (100 MHz, CD_3CN) δ 160.5, 160.0, 139.8, 137.6, 136.2, 135.5, 135.1, 132.4, 130.8, 125.4, 122.9, 119.6, 115.6, 113.9, 112.0, 71.1, 69.9, 68.4, 68.2, 51.0, 38.7, 32.0, 23.4, 23.0, 14.2. MALDI-QTOF-MS: m/z = 902.3745 [M - PF_6^-]; calculated mass: 902.3760 [M - PF_6^-]. Anal. Calcd for: $C_{53}H_{60}F_6NO_8PS_2$: C, 60.73; H, 5.77; N, 1.34. Found: C, 60.78; H, 5.83; N, 1.29.

Synthesis of 20a: A mixture of **15** (144 mg, 0.15 mmol), pyridine-2,6-dicarbaldehyde **17** (20 mg, 0.15 mmol) and tetraethyleneglycolbis (2-aminophenyl) ether **19** (56 mg, 0.15 mmol) were stirred for 10 d in dry CH_3CN (15 mL) under a nitrogen atmosphere at room temperature. Then BH_3·THF solution (1.2 mL of 1.0 M solution in THF) was added and the mixture was further stirred overnight. The solvents were removed under vacuum and the residue was purified by column chromatography (silica gel, DCM / MeOH = 100:0 ~ 50:1) to obtain the [2]catenane **20a** as a light brown solid. Yield: 134 mg, 62%. ^{1}H NMR (600 MHz, CD_3CN) δ 8.57 (s, 2H), 7.60 (t, *J* = 6.0 Hz, 1H), 7.30 (d, *J* = 6.0 Hz, 2H), 7.24-7.15 (m, 4H), 7.12 (d, *J* = 12.0 Hz, 3H), 7.08 (d, *J* = 6.0 Hz, 2H), 7.03 (s, 1H), 6.99 (s, 1H), 6.94 (d, *J* = 12.0 Hz, 3H), 6.81-6.78 (m, 3H), 6.70 (d, *J* = 6.0 Hz, 3H), 6.67-6.62 (m, 3H), 6.47 (d, *J* = 6.0 Hz, 2H), 6.26 (d, *J* = 6.0 Hz, 1H), 4.39 (s, 4H), 4.15 (s, 4H), 4.12-4.10 (m, 8H), 4.04 (br, 2H), 4.01 (br, 2H), 3.89 (br, 2H), 3.83-3.79 (m, 10H), 3.69-3.66 (m, 8H), 2.83-2.80 (m, 4H), 2.10-2.05 (m, 2H), 1.98 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, CD_3CN) δ 160.7, 160.2, 160.0, 159.3, 147.5, 139.9, 137.8, 136.4, 135.8, 135.1, 132.4, 131.2, 130.8, 125.5, 124.90, 123.4, 122.5, 120.4, 115.9, 115.5, 114.1, 113.5, 112.6, 110.9, 72.1, 71.8, 71.1, 70.3, 70.2, 68.6, 68.2, 52.5, 51.3, 50.4, 38.7, 23.5, 14.3. MALDI-QTOF-MS: m/z = 1293.5645 [M - PF_6^-]; calculated mass: 1293.5656 [M - PF_6^-]. Anal. Calcd for: $C_{76}H_{85}F_6N_4O_{11}PS_2$: C, 63.41; H, 5.95; N, 3.89. Found: C, 63.36; H, 5.89; N, 3.97.

Synthesis of 21a: [2]catenane **21a** was prepared by an analogous method similar to that used for **20a** and was obtained. Yield: 183 mg, 74%. ^{1}H NMR (600 MHz, CD_3CN) δ 8.64 (s, 2H), 7.14 (t, *J* = 6.0 Hz, 2H), 7.11 (s, 2H), 7.08-7.04 (m, 2H), 7.01 (s, 2H), 6.79 (d, *J* = 12.0 Hz, 2H), 6.73 -6.69 (m, 6H), 6.68-6.63 (m, 6H), 6.47 (d, *J* = 12.0 Hz, 4H), 6.30 (d, *J* = 12.0 Hz, 2H), 4.39 (t, *J* = 6.0 Hz, 4H), 4.33 (s, 2H), 4.13 (br, 4H), 4.05 (br, 4H), 4.01 (br, 4H), 3.92-3.90 (m, 4H), 3.82 (br, 4H), 3.78 (br, 4H), 3.70-3.66 (m, 8H), 3.56 (br, 4H), 2.80 (t, *J* = 6.0 Hz, 4H), 2.07-2.03 (m, 2H), 1.92 (s, 6H), 1.67-1.63 (m, 2H), 1.27 (m, 22H), 0.88 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, CD_3CN) δ 167.3, 161.1, 160.2, 159.9, 147.5, 139.9, 137.8, 136.4, 135.7,135.1, 131.2, 130.8, 125.4, 125.0, 122.0, 120.4, 115.5, 115.2, 113.5, 113.4, 113.0, 110.9, 108.8, 72.1, 71.8, 71.1, 70.4, 70.2, 69.1, 68.7, 68.6, 68.2, 52.5, 50.5, 38.9, 32.5, 30.2, 30.1, 29.9, 29.4, 26.4, 23.5, 23.2, 14.4, 14.2. MALDI-QTOF-MS: m/z = 1505.7800 [M - PF_6^-]; calculated mass: 1505.7796 [M - PF_6^-]. Anal. Calcd for: $C_{90}H_{113}F_6N_4O_{12}PS_2$: C, 65.43; H, 6.89; N, 3.39. Found: C, 65.51; H, 6.82; N, 3.43.

Synthesis of 20b: [2]catenane **20b** was prepared by an analogous method similar to that used for **20a** and was obtained. Yield: 156 mg, 68%. ^{1}H NMR (600 MHz, CD_3CN) δ 8.67 (s, 2H), 7.62 (t, *J* = 6.0 Hz, 1H), 7.22 (t, *J* = 6.0 Hz, 2H), 7.17 (s, 1H), 7.15 (s, 3H), 7.08 (d, *J* = 6.0 Hz, 2H), 7.05 (s, 2H), 6.80 (d, *J* = 12.0 Hz, 2H), 6.72-6.69 (m, 6H), 6.66 (t, *J* = 6.0 Hz, 4H), 6.46 (d, *J* = 6.0 Hz, 4H), 6.27 (d, *J* = 6.0 Hz, 2H), 4.40-4.37 (m, 6H), 4.11 (t, *J* = 6.0 Hz, 4H), 4.08-4.06 (m, 3H), 4.05 (d, *J* = 6.0 Hz, 4H), 3.96 (br, 4H), 3.88 (br, 4H), 3.78 (br, 4H), 3.72 (br, 4H), 3.65 (br, 4H), 3.64 (br, 4H), 3.63 (br, 6H), 2.81 (t, *J* = 6.0 Hz, 4H), 2.07-2.03 (m, 2H), 1.91 (s, 6H). ^{13}C NMR (100 MHz, CD_3CN) δ 160.1, 159.9, 159.1, 147.5, 139.9, 138.8, 137.7, 136.3, 135.6, 135.1, 131.2, 130.8, 125.4, 124.9, 122.6, 122.0, 120.4, 118.3, 115.3, 114.1, 113.4, 112.2, 110.9, 109.9, 72.0, 71.7, 71.3, 71.1, 70.2, 69.9, 68.5, 68.3, 68.2, 52.4, 50.4, 38.8, 32.1, 23.1, 14.4. MALDI-QTOF-MS: m/z = 1381.6158 [M - PF_6^-]; calculated mass: 1381.6181 [M - PF_6^-]. Anal. Calcd for: $C_{80}H_{93}F_6N_4O_{13}PS_2$: C, 62.90; H, 6.14; N, 3.67. Found: C, 62.96; H, 6.05; N, 3.60.

Synthesis of 21b: [2]catenane **21b** was prepared by an analogous method similar to that used for **20a** and was obtained. Yield: 188 mg, 72%. ^{1}H NMR (600 MHz, CD_3CN) δ 8.76 (s, 2H), 7.19 (t, *J* = 6.0 Hz, 2H), 7.14 (s, 2H), 7.06 (d, *J* = 12.0 Hz, 2H), 7.03 (s, 2H), 6.79 (d, *J* = 6.0 Hz, 2H), 6.73 (s, 2H), 6.72-6.66 (m, 10H), 6.47 (d, *J* = 6.0 Hz, 4H), 6.32 (d, *J* = 6.0 Hz, 2H), 4.38-4.35 (m, 4H), 4.34 (br, 2H), 4.10 (br, 4H), 4.06 (br, 6H), 3.98-3.95 (m, 6H), 3.90 (br, 4H), 3.77 (br, 4H), 3.72 (br, 4H), 3.67 (br, 4H), 3.65-3.63 (m, 8H), 3.54 (d, *J* = 6.0 Hz, 4H), 2.80 (t, *J* = 6.0 Hz, 4H), 2.06-2.02 (m, 2H), 1.91 (s, 6H), 1.70-1.66 (m, 2H), 1.37-1.35 m, 2H), 1.26 (br, 20H), 0.88 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, CD_3CN) δ 160.6, 160.1, 159.8, 147.5, 139.9, 137.7, 136.3, 135.6, 135.1, 132.4, 131.2, 130.8, 125.4, 124.9, 123.1, 122.0, 120.4, 115.7, 115.3, 114.0, 113.4, 112.1, 110.9, 108.8, 72.0, 71.7, 71.2, 71.1, 70.9, 70.1, 69.9, 69.3, 68.5, 68.3, 68.2, 52.4, 51.1, 50.4, 38.8, 38.7, 32.4, 32.1, 30.6, 30.1, 29.8, 29.3, 26.4, 23.5, 23.1, 23.1, 14.4, 14.3, 14.1. MALDI-QTOF-MS: m/z = 1593.8353 [M - HPF_6]; 1594.8390 [M – PF_6^-]; calculated mass: 1594.8399 [M - PF_6^-]. Anal. Calcd for: $C_{94}H_{121}F_6N_4O_{14}PS_2$: C, 64.88; H, 7.01; N, 3.22. Found: C, 64.81; H, 6.95; N, 3.17.

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†Electronic Supplementary Information (ESI) available: The ^{1}H NMR, ^{13}C NMR and MS spectra of all the new intermediates and [2]catenanes. See DOI: 10.1039/b000000x/

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