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ARTICLE

Construction of Photoswitchable Rotaxanes and Catenanes Containing Dithienylethene Fragments

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Ziyong Li,[ac] Xie Han,[ac] Haiyan Chen,*[b] Di, Wu,[a] Fang Hu,[a] Sheng Hua Liu,*[a] Jun Yin*[a]

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Mechanically interlocked structures such as rotaxane and catenane provide a novel backbone for constructing the functional materials with a unique structural characterization. In this work, we design and synthesize a series of photoswitchable rotaxanes and catenanes containing photochromic dithienylethene fragments by a template-directed clipping approach based on dynamic imine chemistry. Their structures have been well-confirmed by NMR, mass spectrometry and elemental analysis. Investigation on photoisomerization indicates that these dithienylethene-based mechanically interlocked molecules have good reversibility and excellent fatigue resistance upon irradiation with UV or visible light. Interestingly, the mechanically interlocked molecules containing two dithienylethene backbone display around 2-fold molar absorption coefficients compared with that of mono dithienylethene. Furthermore, the introduction of fluorophore pyrene on the dithienylethene component authorizes these molecules can serve as the fluorescent switches.

Introduction

Rotaxane and catenane as one type of classical mechanically interlocked configuration have displayed comprehensive applications in many fields such as nanoelectronic devices, artificial smart materials, molecular machines, fluorescent sensors and biological technology etc.[1] The existence of mechanical bonds support they can be used as the components for constructing the versatile topological structures and functional materials in supramolecular chemisty. Over the past decades, numerous examples have shown that rotaxanes and catenanes can be used to construct their corresponding oligomers, polymers, dendrimers, MOFs, nanostructures and functional materials.[2, 3] In our group, we always devote to developing the novel topological structures with mechanically interlocked backbone such as heterorotaxanes, tetragonal rotaxanes, dendritic rotaxane, catenanes and rotacatenanes.[4] Recently, we found that the mechanical interaction can adjust the photoisomerization behaviors of photochromic dithienylethenes when crown ethers or cucurbituril are threaded into the dithienylethenes to form the corresponding rotaxanes or pseudorotaxanes.[5]

To obtain the full-colored photochromic materials, one of the most efficient strategy is that prepares dithienylethene derivatives with multiple photochromic units.[6] From their molecular structures, these dithienylethenes present a common feature is that every photochromism unit is linked by covalent bond, as shown in Figure 1(A). However, few reports involve in the multiple photochromic dithienylethenes in which every photochromism unit is linked by non-covalent bond (Figure 1(B)). Owing to the fact that rotaxanes and catenanes have shown the mechanical interlocked architectures with versatile topological configuration, they provide a desirable model to construct the multiple photochromic dithienylethenes linked by non-covalent mechanical bond. As mentioned above, the non-covalent mechanical interaction has become a strategy to adjust the properties of materials. Therefore, utilizing the non-covalent mechanical bond to construct multiple photochromic dithienylethenes will probably induce some novel photochromic behaviors.

In our previous works, we have constructed a series of mechanically interlocked molecules by the dynamic imine covalent chemistry based on dialdehydes **1** or **2** with tetra (ethylene glycol) bis(2-aminophenyl)ether **3**, as presented in Scheme 1. In view of the importance and structural diversity of multiple photochromic dithienylethenes, in this work, we design and synthesize a pyrene-labeled building block dialdehyde **4** containing a dithienylethene unit. Such design can completely meet the requirement of multiple photochromic dithienylethenes when it is treated with diamine **3** in the presence of diammonium **6** and dithienylethene-based macrocyclic ammoniums **8** and **9**. As a comparison, mono ammoniums **5** and **7** are also used to construct the corresponding rotaxane and catenane. Their structures have been well characterized, and their photoisomerization and emission behaviors are investigated.

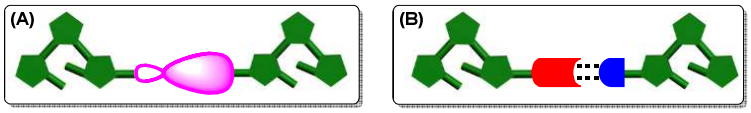
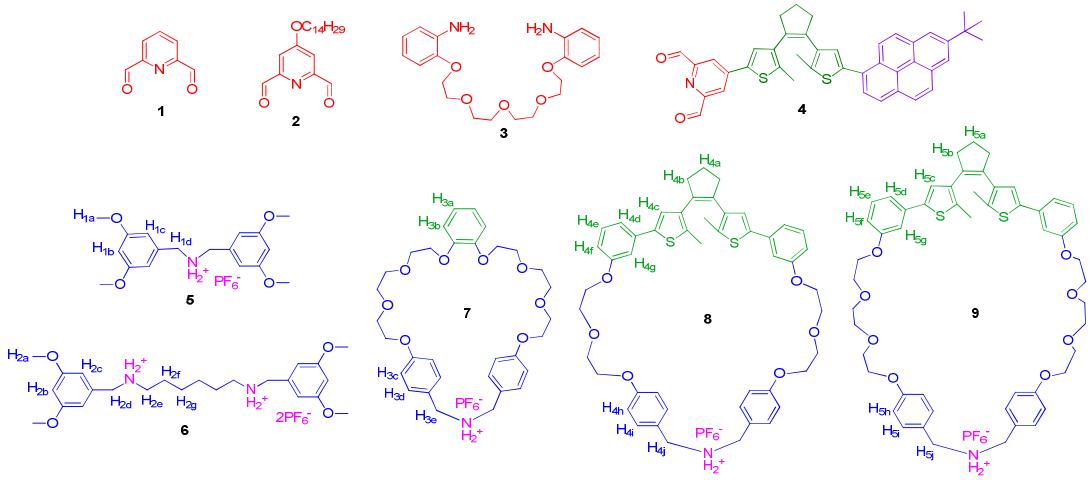


Figure 1. Schematic representation of multiple photochromic system: (A) each unit is linked by covalent bond; (B) each unit is linked by non-covalent bond.



Scheme 1. Chemical structures of compounds **1-9**.

RESULTS AND DISCUSSION

The stepwise synthesis of dithienylethene-functionalized 2, 6-pyridinedicarboxaldehyde **4** is outlined in Scheme 2. The 1, 2-bis(5-chloro-2-methylthiophen-3-yl)cyclopent-1-ene **10** as starting material is treated with butyl lithium and tributyl borate followed by the Suzuki cross-coupling reaction with 1-bromo-7-(tert-butyl) pyrene **11** to afford the corresponding intermediate **12** in 68% yields. Then reaction of **12** with 4-bromopyridine-2,6-dicarbaldehyde **13** gives the crucial intermediate **4** in 86% yield. Fortunately, a single crystal of **4** suitable for X-ray crystallographic analysis is obtained by diffusion of hexane into a dichloromethane solution at room temperature. The crystal structure confirms the structure of dithienylethene **4**, as presented in Figure 2. Its packing view, related crystal data and structure refinement parameters are listed in supporting information (Figure S1 and Table S1 in ESI). To aid spectroscopic analysis of ^{1}H NMR, dithienylethene-based N-hetero crown ether **15** is synthesized in 41% yields by the treatment of dialdehyde **4** and diamine **3** under the template of ammonium **14**, followed by reduction with BH_3·THF. The chemical structures of all new intermediates are well-confirmed by standard spectroscopic characterizations.

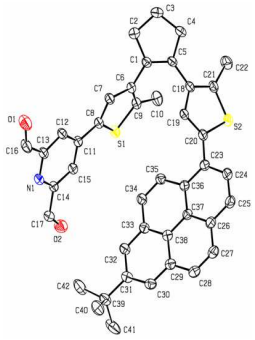
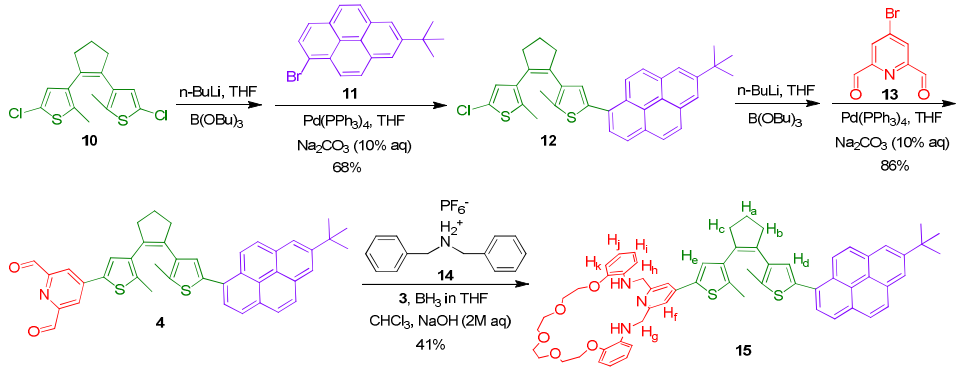


Figure 2. Single crystal structure of dialdehyde **4** (Hydrogen atoms have been omitted)

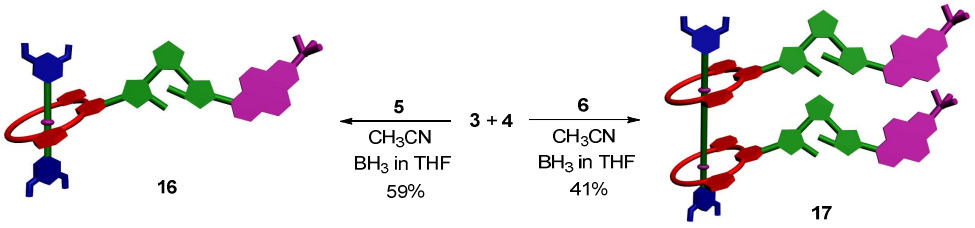


Scheme 2. Synthesis of compounds **4** and **15**.

Dithienylethene-based [2]rotaxane and [3]rotaxane.

The clipping reaction is firstly investigated for the dialkylammonium **5** by mixing together equimolar amounts of **4** and **3** in CD_3CN. The observation of a broad singlet at 9.79 ppm for ammonium NH_2^+ protons as well as a singlet at 8.32 ppm for imine (CH=N) protons in ^1H NMR spectra shows that macrocyclic imine formation has taken place in a reversible manner (Figure S2 in ESI). And then, the mixture is treated with BH_3 in THF to reduce the dynamic imine bond into the kinetically stable C-NH bonds, affording [2]rotaxane **16** in 59% yields in Scheme 3. In the ^1H NMR spectra (as shown in Figure 3B), the resonance of ammonium NH_2^+ proton in the kinetically stable [2]rotaxane **16** shows an obvious upfield shift (singlet at 8.64 ppm) compared with the corresponding dynamic [2]rotaxane. Furthermore, the data of detailed ^1H NMR studies are obtained. For example, a comparison of the corresponding spectra for **15** and **16**, compound **5** revealed considerable downfield shifts for H_{1d} protons. It suggests that these acidic protons ($-CH_2-$) exist hydrogen bonding interaction with the oxygen atom of the N-hetero crown ether **15**. And the aromatic protons H_{1b} and H_{1c} of the dialkylammonium **5** are found to be upfield shifted, ascribing to the shielding influence of the macrocycle **15**.

The synthetic procedure described above has been confirmed to be an efficient protocol for the synthesis of mono dithienylethene-based rotaxane. Subsequently, the same synthetic method is utilized to synthesize the dual photochromic dithienylethene **17**, as shown in Scheme 3. After similar process, the pure form of [3]rotaxane **17** is obtained in 41% yields. And the similar chemical shift changes for proton signals on [3]rotaxane **17** as [2]rotaxane **16** are observed, as shown in Figure 3. Further proof is performed by the electrospray ionization mass spectrometry (ESI-MS) or the matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrum. The peak at *m/z* 1311.9 and 2404.75 can be assigned to the $[M - PF_6^-]^+$ and $[M - HPF_6 - PF_6^-]^+$ species, in which M was the photoswitchable [2]rotaxane **16** and [3]rotaxane **17**, respectively (In ESI)



Scheme 3. Synthesis of [2]rotaxane **16** and [3]rotaxane **17**.

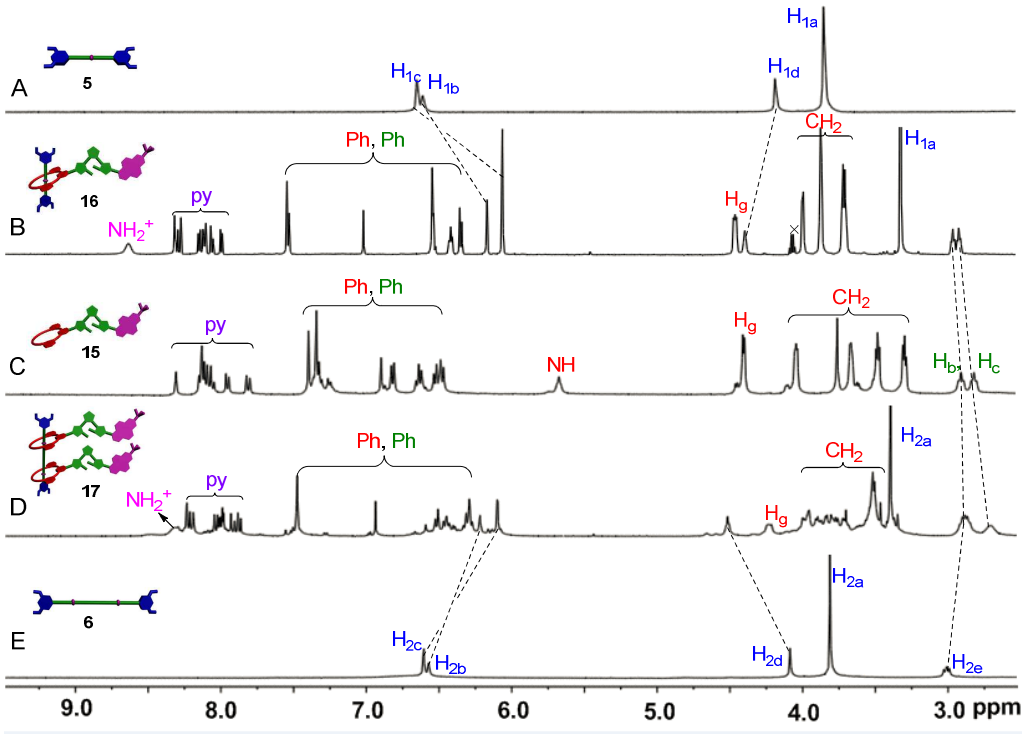


Figure 3. Partial ^1H NMR spectra (400 MHz, CD_3CN, 298 K) of **5** (A); **16** (B); **15** (C); **17** (D); **6** (E).

The introduction of dithienylethene unit enables them to have the photoswitch function. Subsequently, the photochromic behavior of [2]rotaxane **16** and [3]rotaxane **17** induced by photoirradiation in acetonitrile is investigated at room temperature, as shown in Figure 4. For [2]rotaxane **16**, three main absorption bands are observed at 240 nm (ε = 7.58 × 10^4 L mol^{-1} cm^{-1}), 282 nm (ε = 4.75 × 10^4 L mol^{-1} cm^{-1}), 346 nm (ε = 2.81 × 10^4 L mol^{-1} cm^{-1}), respectively. Upon irradiation with 254 nm UV light, the colorless solution turns purple and a new absorption band at 552 nm (ε = 1.78 × 10^4 L mol^{-1} cm^{-1}) appears due to the formation of the corresponding ring-closed isomer (Scheme S1 in ESI). Moreover, a well defined isosbestic point can be observed at 380 nm, which implies that [2]rotaxane **16** can cleanly convert to the photocyclized product. Upon irradiation with visible light (λ > 402 nm), the colored ring-closed isomer undergoes a cycloreversion reaction and returns to the initial colorless ring-open isomer. It is worth mentioning that **16** shows very good reversibility, and no apparent deterioration is observed after repeating the above process eight times, which indicates that the [2]rotaxane **16** has very excellent fatigue resistance (as shown inset in Figure 4A).

Similar photochromic behavior is obtained in Figure 4B when the CH_3CN solution of [3]rotaxane **17** is irradiated with the same UV/Vis light. Despite [3]rotaxane **17** contains two dithienylethene components, it reveals almost same UV/Vis absorption spectra and changes in comparison to [2]rotaxane **16** only having a dithienylethene unit. As expected, [3]rotaxane **17** has an around 2-fold molar absorption coefficients than [2]rotaxane **16** due to two dithienylethene components of **17**, indicating that the two dithienylethene units takes place the photochromic reaction. The quantum yields of the cyclization ($\varphi_{o\text{-}c}$) and the cycloreversion ($\varphi_{c\text{-}o}$) are shown in Table S2 (In ESI). Compared with the cycloreversion quantum yield ($\varphi_{c\text{-}o}$ for [2]rotaxane **16** and [3]rotaxane **17** are 0.0072 and 0.0032, respectively), both of the [2]rotaxane **16** and [3]rotaxane **17** exhibit higher cyclization quantum yield ($\varphi_{o\text{-}c}$ for [2]rotaxane **16** and [3]rotaxane **17** are 0.131 and 0.052, respectively). However, [2]rotaxane **16** displays higher cyclization quantum yields ($\varphi_{o\text{-}c}$) and cycloreversion quantum yields ($\varphi_{c\text{-}o}$), compared to that of [3]rotaxane **17**, possibly due to its more complicated configuration and bigger steric hindrance of **17**. The corresponding parameters are summarized in Table S2 (In ESI). Next, the fluorescence changes of **16** and **17** induced by photoirradiation in CH_3CN are investigated at room temperature. As shown in Figure 5, upon excitation with 346 nm, [2]rotaxane **16** and [3]rotaxane **17** exhibit completely similar emission around at 438 nm. Their emission intensity gradually decreases upon irradiation with 254 nm UV light until reaching the photostationary state. This phenomenon may be attribute to FRET between the pyrene moiety and ring-closed dithienylethene moiety.[7] While the photoirradiation of visible light can return the original emission as a result of the formation of ring-open isomer. These results indicate that two [2]rotaxanes can be used as the fluorescence-responsive switch in optoelectronic materials.

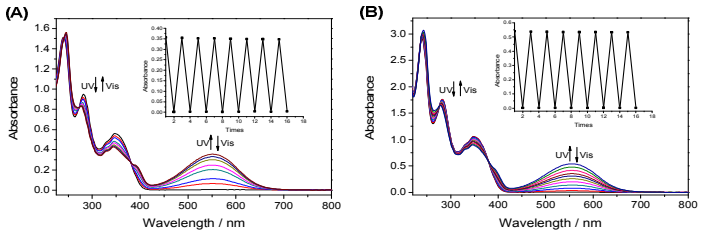


Figure 4. Absorption spectral changes of **16** (A) and **17** (B) with 254 nm UV and >402 nm visible light irradiation in CH_3CN (2.0×10^{-5} mol/L). (Inside) Fatigue resistance of **16** and **17** in CD_3CN, respectively.

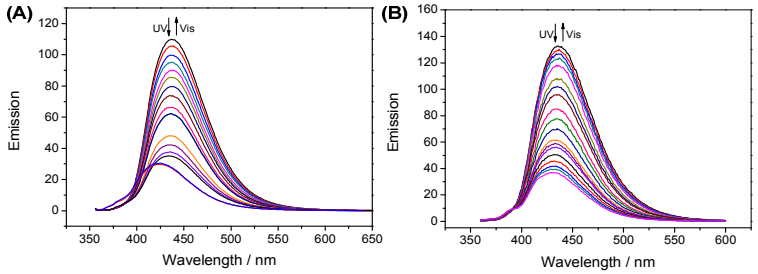


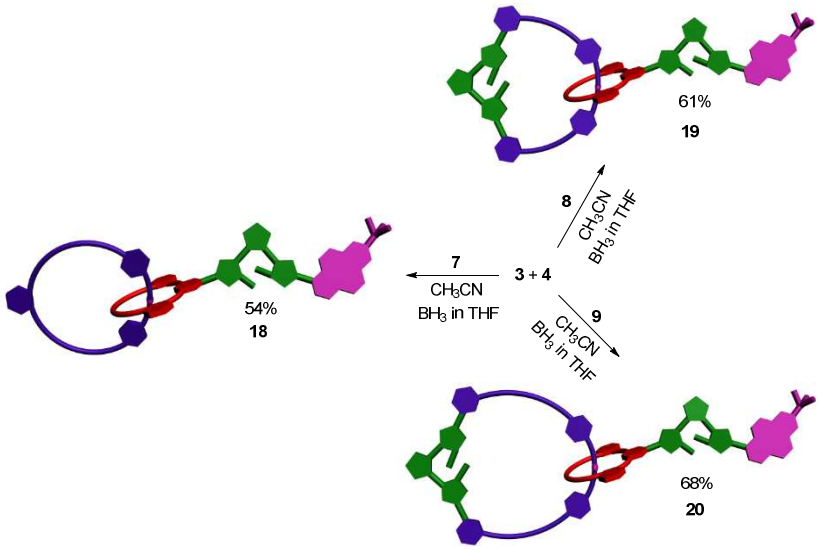
Figure 5. Emission intensity changes of **16** (A) and **17** (B) with 254 nm UV and >402 nm visible light irradiation in CH_3CN (2.0×10^{-5} mol/L) (λ_{ex} = 346 nm).

Dithienylethene-based [2]catenanes.

Subsequent researches focus on the construction of [2]catenanes containing dual dithienylethene units. Accordingly, dithienylethene-based macrocyclic alkylammoniums **8**, **9** are used to perform the clipping reaction by mixing together equimolar amounts of bisaniline **3** and dialdehyde **4** in CD_3CN, respectively. The ^1H NMR is used to record the process of clipping reaction. For example, a broad singlet at 9.56 ppm for ammonium NH_2^+ protons and a singlet at 8.09 ppm for imine (CH=N) protons can be observed, implying that the dynamic catenane has formed (Figure S3 in ESI) when ammonium **8** or **9** is employed as a template. And then, treating the dynamic imines with BH_3 in THF leads to the formation of the kinetically stable catenanes **19** and **20** in 61-68% yields, as outlined in Scheme 4. Additionally, to aid the properties

comparison, the [2]catenane **18** is synthesized by a same template-directed clipping approach in 54% yields (in Scheme 4).

In their ^{1}H NMR spectra (as shown in Figure 6B), the resonance of protons (H_{3d}, H_{3c}) on the benzene ring of [2]catenane **18** displays obvious up-field shifts in comparison to its template **7**. For other [2]catenanes, similar shifts (H_{4i} and H_{4h} for **19**; H_{5i} and H_{5h} for **20**) can be also found (Figure 5; Figure S4 in ESI). Moreover, the resonance of ammonium NH_2^+ protons in the kinetically stable [2]catenanes **18**-**20** show the abroad singlet at 8.42, 8.52 and 8.65 ppm (Figure 5; Figure S4 in ESI), respectively, and the signal corresponding to proton H_g exhibits downfield shift due to the hydrogen bonding interaction, which is well in agreement with our previous reports.[4] At the same time, the signals for protons H_e and H_f experience an upfield shift. These results clearly confirm the existence of [2]catenanes. Finally, inspection of the MALDI-TOF mass spectra shows the presence of a peak at m/z 1807.82, 1895.67 and 1561.79 that are assigned to the $[M\text{-}PF_6^-]^+$ species, in which M is [2]catenanes **19**, **20** and **18**, respectively.



Scheme 4. Synthesis of [2]catenane **18**, **19** and **20**.

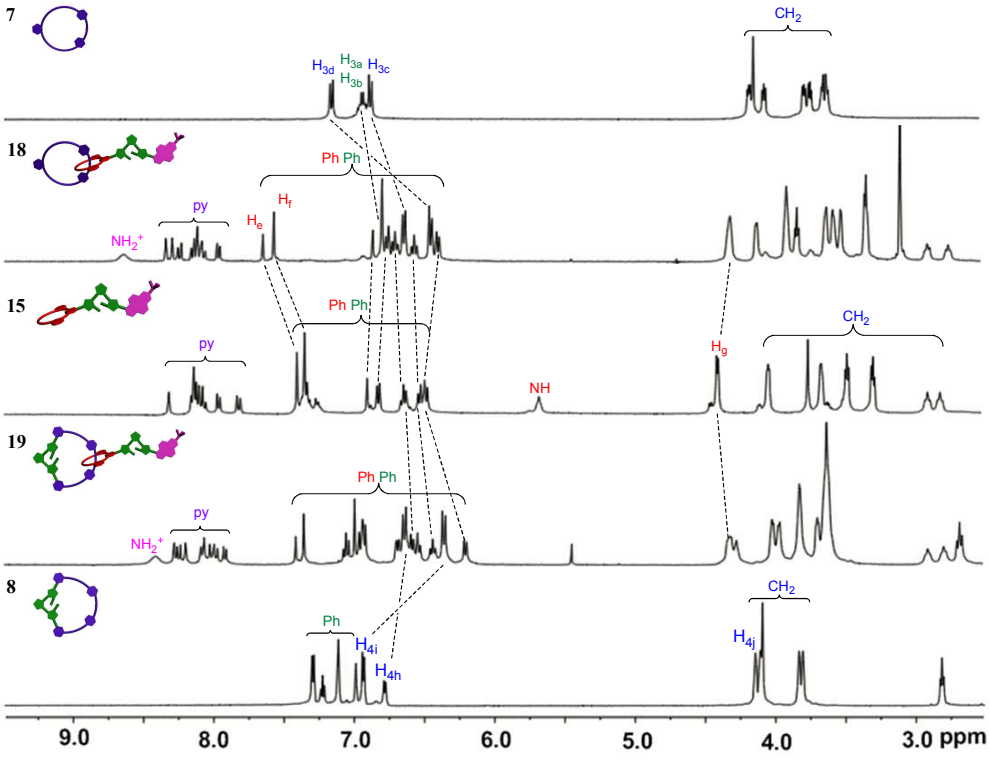


Figure 6. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of **15** (A); **19** (B); **8** (C).

Similarly, the photochromic behaviors of [2]catenanes **18**, **19** and **20** induced by photoirradiation in acetonitrile are investigated at room temperature. As shown in Figure 7, they display completely similar absorption maximum around at 236 nm and 280 nm. Upon irradiation with 254 nm UV light, their colorless solution turn purple along with the appearance of a new absorption band at 546 nm due to the formation of their corresponding ring-closed isomers (Scheme S2 and S3 in ESI). Moreover, similar isosbestic point can be observed around at 380 nm, implying that [2]catenanes can be cleanly converted to the photocyclized products. Upon irradiation with visible light (λ > 402 nm), the colored isomers undergo the cycloreversion reaction and return to the initial ring-open isomers. In particular, they show very good reversibility without apparent deterioration after repeating the above process eight times. The result indicates that the [2]catenanes **18**, **19** and **20** have very excellent fatigue resistance (in Figure 7). Interestingly, **19** and **20** also reveal 2-fold molar absorption coefficients in comparison to compound **18**, which is well in agreement with [3]rotaxane **17** containing two dithienylethene units liked by non-covalent mechanical bond. The result is completely different from those of multi-dithenylethene system linked by covalent bonds.[6] Investigation on quantum yields suggest that **19** and **20** containing two dithienylethene moieties have higher cyclization quantum yields ($\varphi_{o\text{-}c}$) than compound **18**. Compound **20** based on the macrocyclic ammonium **9** with a bigger cavity possesses higher cyclization quantum yields ($\varphi_{o\text{-}c}$) and cycloreversion quantum yields ($\varphi_{c\text{-}o}$) than compound **19**. And all of the [2]catenanes possess higher cyclization quantum yields ($\varphi_{o\text{-}c}$) compared to cycloreversion quantum yields ($\varphi_{c\text{-}o}$). The related data are summarized in Table S3 (in ESI). The fluorescence changes indicate that these [2]catenanes can be also applied in fluorescent switches (Figure S5 in ESI).

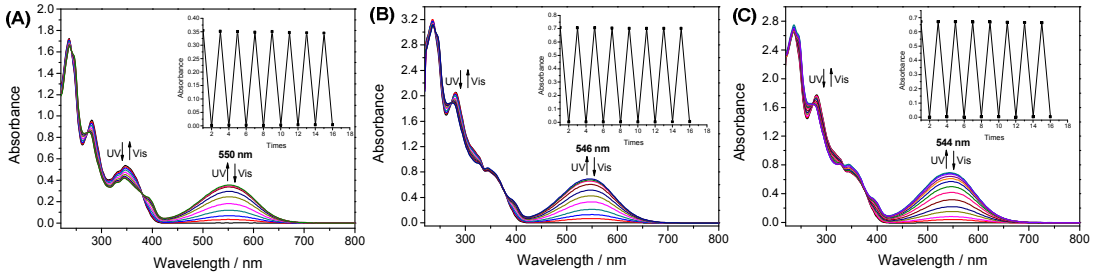


Figure 7. Absorption spectral changes of **18** (A), **19** (B) and **20** (C) with 254 nm UV and >402 nm Vis light irradiation in CH_3CN (2.0×10^{-5} mol/L). (Inside) Fatigue resistance of **18**, **19** and **20** in CD_3CN, respectively.

Conclusions

In summary, a novel building block dithienylethene-functionalized 2, 6-pyridinedicarboxaldehyde moiety is synthesized and is performed the template-directed clipping reaction to construct dithienylethen-based mechanically interlocked molecules. Investigation on photochromic properties indicates that these rotaxanes and catenanes have good reversibility and excellent fatigue resistance upon irradiation with UV or visible light. And they can be used as a fluorescent switches. It is worth mentioning that these mechanically interlocked molecules containing two dithienylethene backbone displays 2-fold molar absorption coefficients compared with mono dithienylethenes. More importantly, this research provides a novel model to design photo switches with multi dithienylethene units.

Experimental Section

General Methods. All reactions and assembly processes were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. THF was distilled under nitrogen from sodium benzophenone. CH_3CN and CH_2Cl_2 were dried with calcium hydride and then distilled. 1, 2-bis(5-chloro-2-methylthiophen-3-yl)cyclopent-1-ene **10**,[8] 1-bromo-7-(tert-butyl) pyrene **11**[9] and 4-bromopyridine-2, 6-dicarbaldehyde **13**[10] are prepared by using literature methods. All other starting materials are obtained commercially as analytical grade and used without further purification. ^1H and ^{13}C NMR spectra were collected with either a 400 or 600 MHz spectrometer. Mass spectra were measured in the EI, ESI or MALDI mode. UV-vis spectra were obtained on a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer, and fluorescence spectra were taken on a Hitachi Model F-4500 fluorescent spectrophotometer. In the photoisomerization reaction, UV light irradiation (254 nm) was carried out using a ZF5UV lamp, and visible light was irradiated using a LZG 220 V 500 W tungsten lamp (λ > 402 nm) with cutoff filters.

Synthesis of 12: To the anhydrous THF solution (10 mL) of **10**, *n*-BuLi (0.4 mL of 2.5 M solution in hexane, 1.0 mmol) was added under nitrogen at 0 ℃ in 10 portions using a syringe. This solution was stirred for 1 h at room temperature, then $B(OBu)_3$ (0.41 mL, 1.5 mmol) was added in one portion. This reddish solution was stirred for 6 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 **11** (340 mg, 1.0 mmol), $Pd(PPh_3)_4$ (50 mg, 0.041 mmol) and 10 mL Na_2CO_3 solution (2 M) at 60 ℃. Subsequently the mixture was refluxed for 24 h at N_2 atmosphere and cooled to room temperature, after which CH_2Cl_2 (60 mL) and H_2O (20 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 as the eluent to obtain the **12** as a yellow solid; yield 374 mg, 68%. ^1H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, J = 9.2 Hz, 1H), 8.21 (s, 2H), 8.10 (d, J = 7.9 Hz, 1H), 8.01-8.06 (m, 3H), 7.97 (d, J = 7.9 Hz, 1H), 6.95 (s, 1H), 6.72 (s, 1H), 2.90 (t, J = 7.2 Hz, 2H), 2.77 (t, J = 6.8 Hz, 2H), 2.24 (s, 3H), 2.18 (s, 3H),

2.07-2.11 (m, 2H), 1.59 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 138.2, 136.0, 135.7, 135.5, 135.3, 134.0, 133.3, 131.3, 130.8, 130.5, 129.6, 129.2, 128.4, 128.0, 127.7, 127.6, 127.1, 127.1, 125.1, 125.0, 124.7, 124.3, 123.0, 122.5, 122.2, 38.2, 38.1, 35.2, 31.9, 23.0, 14.4, 14.2. EI MS: m/z = 550.34 [M]; calculated exact mass: 550.16. Anal. Calcd for: $C_{35}H_{31}ClS_2$: C, 76.26; H, 5.67. Found: C, 76.35; H, 5.59.

Synthesis of 4: To the anhydrous THF solution (10 mL) of **12**, *n*-BuLi (0.48 mL of 2.5 M solution in hexane, 1.2 mmol) was added under nitrogen at 0 ℃ in 10 portions using a syringe. This solution was stirred for 1 h at room temperature, then $B(OBu)_3$ (0.41 mL, 1.5 mmol) was added in one portion. This reddish solution was stirred for 6 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 **13** (210 mg, 1.0 mmol), $Pd(PPh_3)_4$ (50 mg, 0.041 mmol) and 10 mL Na_2CO_3 solution (2 M) at 60 ℃. Subsequently the mixture was refluxed for 24 h at N_2 atmosphere and cooled to room temperature, after which CH_2Cl_2 (60 mL) and H_2O (20 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 / dichloromethane (1 : 4) as the eluent to obtain the **3** as a yellow solid; yield 558 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 2H), 8.25 (d, *J* = 9.3 Hz, 1H), 8.17 (s, 3H), 8.11 (d, *J* = 1.7 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 8.00-7.90 (m, 4H), 7.49 (s, 1H), 6.93 (s, 1H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.24 (s, 3H), 2.19 (s, 3H), 2.11-2.16 (m, 2H), 1.56 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 153.4, 149.2, 144.2, 139.7, 138.4, 138.2, 136.5, 135.9, 135.6, 134.6, 133.7, 131.2, 130.6, 130.5, 129.4, 129.0, 128.6, 128.4, 127.9, 127.7, 127.1, 124.9, 124.5, 124.3, 122.9, 122.5, 122.1, 120.1, 38.2, 35.2, 34.8, 31.9, 23.1, 14.8, 14.4. EI MS: m/z = 649.47 [M]; calculated exact mass: 649.21. Anal. Calcd for: $C_{42}H_{35}NO_2S_2$: C, 77.62; H, 5.43; N, 2.16. Found: C, 77.55; H, 5.51; N, 2.07.

Synthesis of 15: A solution of **4** (130 mg, 0.2 mmol), **3** (75 mg, 0.2 mmol), and dibenzylammonium hexafluorophosphate **14** (69 mg, 0.2 mmol) in acetonitrile (20 mL) and dichloromethane (8 mL) was stirred at room temperature for 48 h. BH_3 in THF (1.0 mol/L in THF, 1.6 mL, 1.6 mmol) was added to the reaction mixture, which was left stirring at room temperature for 24 h. The excess of solvent was removed under vacuum and the residue was dissolved in $CHCl_3$ and 2 mol/L NaOH (2 mL, aq) was added and stirred for additional 1 h. Then the residue was extracted with DCM (3 × 50 mL) and the organic layer was washed with water, dried over anhydrous sodium sulfate, and then purified by silica gel column chromatography (eluent: petroleum ether: ethyl acetate = 1 : 1) to give compound **15** as a brown solid; yield 81 mg, 41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 9.3 Hz, 1H), 8.20 (s, 1H), 8.12 (s, 1H), 8.02-8.10 (m, 3H), 7.90-7.97 (m, 2H), 7.36 (br, 3H), 7.26 (br, 3H), 6.97 (s, 1H), 6.82-6.86 (m, 4H), 6.58-6.65 (m, 4H), 5.73 (s, 2H), 4.47 (s, 4H), 4.13 (d, *J* = 2.1 Hz, 4H), 3.77-3.83 (m, 4H), 3.67 (t, *J* = 3.9 Hz, 4H), 3.45 (t, *J* = 3.9 Hz, 4H), 2.92 (t, *J* = 6.5 Hz, 2H), 2.84 (t, *J* = 6.9 Hz, 2H), 2.17 (s, 3H), 2.15 (s, 3H), 2.09-2.14 (m, 2H), 1.55 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 149.2, 146.1, 142.6, 139.9, 138.2, 137.3, 137.1, 136.8, 136.1, 135.7, 135.6, 134.4, 131.2, 130.7, 130.5, 129.6, 129.1, 128.4, 128.2, 128.0, 127.7, 127.6, 127.1, 126.9, 124.9, 124.7, 124.3, 122.9, 122.8, 122.5, 122.1, 116.4, 115.6, 114.1, 110.6, 70.8, 70.6, 70.2, 69.9, 53.2, 49.4, 38.2, 35.1, 31.8, 23.1, 14.6, 14.4. ESI MS: m/z = 994.5 [M + H^+]; calculated exact mass: 993.42. Anal. Calcd for: $C_{62}H_{63}N_3O_5S_2$: C, 74.89; H, 6.39; N, 4.23. Found: C, 74.94; H, 6.31; N, 4.16.

Synthesis of photoswitchable [2]rotaxane 16: A solution of **4** (130 mg, 0.2 mmol), the dialkylammonium **5** (93 mg, 0.2 mmol) and tetraethyleneglycol bis(2-aminophenyl) ether **3** (75 mg, 0.2 mmol) in dry CH_3CN (20 mL) and dichloromethane (6 mL) was stirred for 5 days at room temperature under an N_2 atmosphere. Then BH_3·THF (1.6 mL) was added and the solution was further stirred overnight. The solvents were removed under vacuum and the residue was purified by column chromatography (silica gel, DCM / MeCN / MeOH = 100 : 0 : 0 – 75 : 25 : 1) to obtain photoswitchable [2]rotaxane **16** as a brown solid; yield 172 mg, 59%. ^{1}H NMR (600 MHz, CD_3CN) δ 8.64 (s, 2H), 8.30-8.32 (m, 2H), 8.28 (s, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 8.10-8.13 (m, 2H), 8.07 (d, *J* = 8.9 Hz, 1H), 7.99-8.01 (m, 1H), 7.54 (d, *J* = 8.2 Hz, 3H), 7.02 (s, 1H), 6.54 (d, *J* = 5.9 Hz, 4H), 6.42 (t, *J* = 7.0 Hz, 2H), 6.35 (d, *J* = 7.9 Hz, 2H), 6.17 (s, 2H), 6.06 (s, 4H), 4.46 (t, *J* = 6.0 Hz 4H), 4.39 (s, 2H), 3.99 (d, *J* = 5.5 Hz, 4H), 3.87 (s, 8H), 3.71 (d, *J* = 6.7 Hz, 8H), 3.32 (s, 12H), 2.96 (t, *J* = 6.8 Hz, 2H), 2.92 (t, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 2.31 (s, 3H), 2.13-2.17 (m, 2H), 1.51 (s, 9H). ^{13}C NMR (100 MHz, CD_3CN) δ 166.0, 164.8, 154.8, 151.6, 151.5, 148.3, 142.8, 141.9, 141.6, 141.0, 139.2, 136.4, 135.8, 135.7, 134.5, 133.6, 133.3, 132.2, 129.6, 129.4, 127.9, 127.7, 126.3, 124.3, 122.4, 115.1, 111.9, 105.9, 76.4, 76.1, 75.4, 75.1, 74.9, 74.8, 74.5, 72.5, 60.0, 57.6, 54.8, 42.8, 40.0, 36.4, 36.2, 28.1, 27.5, 19.1, 18.7, 18.5. ESI MS: m/z = 1311.9 [M – PF_6^-]; calculated exact mass: 1456.56. Anal. Calcd for: $C_{80}H_{87}F_6N_4O_9PS_2$: C, 65.92; H, 6.02; N, 3.84. Found: C, 65.87; H, 6.11; N, 3.92.

Synthesis of photoswitchable [3]rotaxane 17: A solution of **4** (130 mg, 0.2 mmol), the dialkylammo -nium **6** (70 mg, 0.1 mmol) and tetraethyleneglycol bis(2-aminophenyl) ether **3** (75 mg, 0.2 mmol) in dry CH_3CN (20 mL) and dichloromethane (6 mL) was stirred for 10 days at room temperature under an N_2 atmosphere. Then BH_3·THF (1.6 mL) was added and the solution was further stirred overnight. The solvents were removed under vacuum and the residue was purified by column chromatography (silica gel, DCM / MeCN / MeOH = 100 : 0 : 0 – 75 : 25 : 1) to obtain photoswitchable [3]rotaxane **17** as a brown solid; yield 110 mg, 41%. ^{1}H NMR (400 MHz, CD_3CN) δ 8.33 (s, 4H), 8.20-8.27 (m, 6H), 7.98-8.06 (m, 6H), 7.88-7.95 (m, 4H), 7.49 (d, *J* = 2.0 Hz, 4H), 6.95 (s, 2H), 6.41-6.54 (m, 12H), 6.29-6.35 (m, 6H), 6.24 (t, *J* = 4.0 Hz, 2H), 6.12 (d, *J* = 4.0 Hz, 4H), 4.53 (s, 4H), 4.25 (br, 4H), 3.97-4.02 (m, 6H), 3.89-3.93 (m, 4H), 3.77-3.86 (m, 8H), 3.70-3.74 (m, 4H), 3.48-3.53 (m, 14H), 3.41 (m, 12H), 2.87-2.94 (m, 8H), 2.73 (br, 4H), 2.29 (s, 10H), 2.17 (s, 6H), 2.09-2.15 (m, 4H), 1.46 (m, 4H), 1.28 (d, *J* = 1.2 Hz, 4H), 0.89 (t, *J* = 6.8 Hz, 4H). ^{13}C NMR (100 MHz, CD_3CN) δ 161.6, 160.0, 150.2, 147.3, 143.8, 138.4, 137.4, 136.6, 136.5, 136.3, 135.2, 131.9, 131.3, 129.9, 128.8, 125.2, 123.4, 123.2, 122.9, 121.8, 120.0, 113.1, 110.6, 107.2, 101.0, 71.8, 71.4, 70.8, 68.1, 55.6, 52.3, 50.6, 48.9, 38.3, 35.5, 31.9, 31.7, 26.5, 23.6, 23.0, 18.3, 14.7, 14.3, 14.0. MALDI MS: m/z = 2404.75 [M - HPF_6 - PF_6^-]; calculated exact mass: 2695.05. Anal. Calcd for: $C_{148}H_{164}F_{12}N_8O_{14}P_2S_4$: C, 65.91; H, 6.13; N, 4.15. Found: C, 65.84; H, 6.19; N, 4.04.

Synthesis of diswitchable [2]catenane 18: A solution of **4** (65 mg, 0.1 mmol), macrocyclic dialkylammonium **8** (96 mg, 0.1 mmol) and tetraethyleneglycol bis(2-aminophenyl) ether **3** (38 mg, 0.1 mmol) in dry CH_3CN (10 mL) and dichloromethane (3 mL) was stirred for 5 days at room temperature under an N_2 atmosphere. Then BH_3·THF (0.8 mL) was added and the solution was further stirred overnight. The solvents were removed under vacuum and the residue was purified by column chromatography (silica gel, DCM / MeCN / MeOH = 100:0:0 − 75:25:1) to obtain diswitchable [2]catenane **18** as a brown solid; yield 119 mg, 61%. ^{1}H NMR (400 MHz, CD_3CN) δ 8.42 (s, 2H), 8.21 – 8.29 (m, 3H), 7.98 – 8.10 (m, 4H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.42 (s, 1H), 7.36 (s, 2H), 7.06 (t, *J* = 7.9 Hz, 2H), 7.00 (s, 2H), 6.97 (s, 1H), 6.92 – 6.85 (m, 4H), 6.54 – 6.71 (m, 10H), 6.45 (t, *J* = 7.6 Hz, 2H), 6.37 (d, *J* = 8.5 Hz, 4H), 6.21 (d, *J* = 7.7 Hz, 2H), 4.32 – 4.35 (m, 4H), 4.28 (s, 2H), 4.02 – 4.05 (m, 4H), 3.98 (d, *J* = 5.3 Hz, 4H), 3.84 (br, 8H), 3.71 (t, *J* = 4.0 Hz, 4H), 3.64 (br, 14H), 2.92 (t, *J* = 8.0 Hz, 4H), 2.81 (t, *J* = 8.0 Hz, 4H), 2.69 (t, *J* = 7.4 Hz, 4H), 2.25 (s, 3H), 2.22 (s, 3H), 2.06 – 2.13 (m, 4H), 1.77 (s, 6H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, CD_3CN) δ 160.2, 160.1, 159.9, 150.4, 147.3, 143.7, 139.9, 138.9, 138.6, 138.5, 137.6, 137.1, 136.6, 136.5, 136.3, 135.5, 135.3, 134.9, 132.1, 131.5, 131.3, 131.1, 130.7, 130.1, 128.9, 128.6, 128.4, 127.9, 125.5, 125.3, 125.2, 124.8, 124.4, 123.5, 123.4, 123.0, 122.4, 121.9, 120.3, 115.4, 113.4, 113.2, 113.0, 110.8, 72.1, 71.8, 71.0, 70.3, 70.1, 68.6, 68.5, 68.1, 52.4, 50.4, 38.8, 38.5, 35.7, 32.0, 23.7, 23.4, 14.8, 14.5, 14.4. MALDI MS: m/z = 1807.85 [M - PF_6^-]; calculated exact mass: 1952.71. Anal. Calcd for: $C_{111}H_{115}F_6N_4O_{11}PS_4$: C, 68.22; H, 5.93; N, 2.87. Found: C, 68.30; H, 6.02; N, 2.74.

Synthesis of diswitchable [2]catenane 19: [2]catenane **19** was prepared by an analogous method to that used for [2]catenane **18**; yield 139 mg, 68%. ^{1}H NMR (400 MHz, CD_3CN) δ 8.54 (s, 2H), 8.21 – 8.29 (m, 3H), 7.99 – 8.08 (m, 4H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.46 (s, 1H), 7.37 (s, 2H), 7.08 (t, *J* = 7.9 Hz, 2H), 7.01 (s, 2H), 6.94 (t, *J* = 6.7 Hz, 5H), 6.63 – 6.68 (m, 6H), 6.59 (br, 4H), 6.45 – 6.48 (m, 2H), 6.38 (d, *J* = 8.4 Hz, 4H), 6.23 (d, *J* = 7.8 Hz, 2H), 4.30 (d, *J* = 3.5 Hz, 6H), 3.99 (s, 8H), 3.79 – 3.83 (m, 8H), 3.66 (d, *J* = 3.9 Hz, 4H), 3.60 (br, 14H), 3.53 (d, *J* = 3.2 Hz, 8H), 2.88 (t, *J* = 8.0 Hz, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.68 (t, *J* = 7.2 Hz, 4H), 2.23 (s, 3H), 2.18 (s, 3H), 2.03 – 2.08 (m, 4H), 1.79 (s, 6H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, CD_3CN) δ 160.0, 159.8, 150.3, 147.4, 143.7, 139.9, 138.8, 138.5, 138.4, 137.6, 137.1, 136.5, 136.2, 135.4, 135.2, 134.9, 132.1, 131.9, 131.4, 131.2, 131.1, 130.7, 130.1, 128.9, 128.6, 128.3, 127.9, 125.4, 125.2, 125.1, 124.7, 123.4, 123.0, 121.9, 120.3, 115.3,113.8, 113.2, 112.7, 112.3, 110.8, 72.0, 71.7, 71.2, 71.0, 70.1, 69.9, 68.3, 68.2, 68.1, 52.3, 50.5, 38.8, 38.6, 35.6, 31.9, 23.7, 23.4, 14.8, 14.4. MALDI MS: m/z = 1895.67 [M - PF_6^-]; calculated exact mass: 2040.76. Anal. Calcd for: $C_{115}H_{123}F_6N_4O_{13}PS_4$: C, 67.63; H, 6.07; N, 2.74. Found: C, 67.55; H, 6.14; N, 2.79.

Synthesis of monoswitchable [2]catenane 20: [2]catenane **20** was prepared by an analogous method to that used for [2]catenane **18**; yield 92 mg, 54%. ^{1}H NMR (400 MHz, CD_3CN) δ 8.65 (s, 2H), 8.34 (d, *J* = 1.8 Hz, 1H), 8.29 (d, *J* = 1.7 Hz, 1H), 8.23 – 8.26 (m, 1H), 8.08 – 8.17 (m, 4H), 7.96 – 7.98 (m, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.57 (s, 2H), 6.87 (d, *J* = 2.1 Hz, 1H), 6.80 (s, 4H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.71 (t, *J* = 7.7 Hz, 3H), 6.63 – 6.67 (m, 4H), 6.57 (t, *J* = 7.6 Hz, 2H), 6.47 (s, 2H), 6.45 (d, *J* = 1.9 Hz, 1H), 6.40 (d, *J* = 7.9 Hz, 2H), 4.32 (br, 6H), 4.14 (d, *J* = 3.3 Hz, 4H), 3.92 (br, 8H), 3.85 (t, *J* = 5.3 Hz, 4H), 3.64 (s, 4H), 3.59 (s, 4H), 3.54 (s, 4H), 3.34 – 3.37 (m, 8H), 3.11 (s, 6H), 2.92 (t, *J* = 6.5 Hz, 2H), 2.77 (t, *J* = 6.5 Hz, 2H), 2.36 (s, 3H), 2.20 (s, 3H), 2.02 – 2.09 (m, 2H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, CD_3CN) δ 159.9, 159.8, 150.4, 149.2, 147.4, 143.7, 138.6, 138.4, 138.2, 137.8, 137.1, 136.7, 136.5, 136.5, 135.3, 132.0, 131.4, 131.3, 130.2, 130.1, 129.2, 128.9, 128.6, 128.3, 127.8, 125.4, 125.2, 125.0, 124.7, 123.5, 123.3, 123.0, 122.4, 122.1, 121.9, 120.2, 116.1, 115.1, 114.6, 113.3, 111.0, 71.9, 71.5, 71.0, 70.8, 70.7, 70.6, 70.3, 70.2, 69.9, 69.7, 69.3, 68.3, 68.2, 52.3, 50.3, 38.5, 38.3, 35.6, 32.0, 31.9, 23.6, 23.0, 14.6, 14.4, 14.1. MALDI MS: m/z = 1561.78 [M - PF_6^-]; calculated exact mass: 1706.68. Anal. Calcd for: $C_{94}H_{105}F_6N_4O_{13}PS_2$: C, 66.10; H, 6.20; N, 3.28. Found: C, 66.19; H, 6.31; N, 3.15.

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Notes and references

[a] Key Laboratory of Pesticide and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, PR China E-mail: yinj@mail.ccnu.edu.cn
[b] Department of Biomedical Engineering, School of Engineering, China Pharmaceutical University, 24 Tongjia Lane, Gulou District, Nanjing 210009, China. E-mail: chenhaiyan@cpu.edu.cn
[c] Z. L. and X. H. contributed equally to this work.

† Electronic Supplementary Information (ESI) available: Packing diagram and crystal data of **4**, partial ^{1}H NMR spectra of **16**, **19** and **20**. NMR, MS spectra of all the interminates, photochromic reaction and photochromic parameters **16**, **17**, **18**, **19** and **20**, fluorescence spectra of **18**, **19** and **20** See DOI: 10.1039/b000000x/

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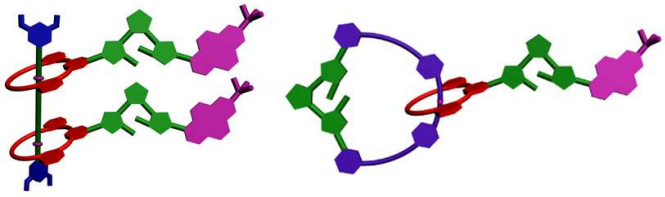
Construction of Photoswitchable Rotaxanes and Catenanes Containing Dithienylethene Fragments

Ziyong Li,[ab] Xie Han,[ab] Sheng Hua Liu,*[a] Jun Yin*[a]



Dual-dithienylethene System Based on Mechanical bonds