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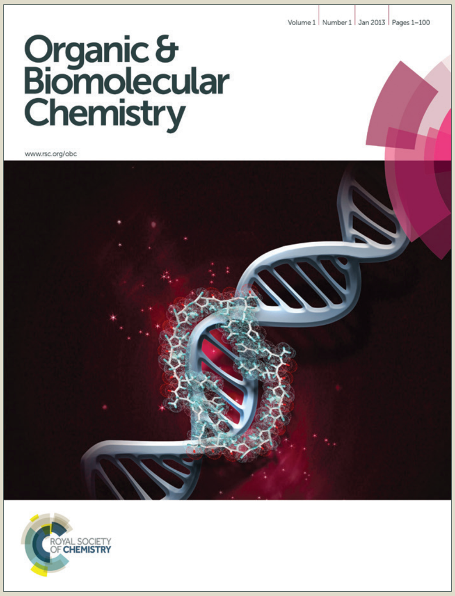

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ARTICLE

Dithienylethene-Based Rotaxanes: Synthesis, Characterization and Properties

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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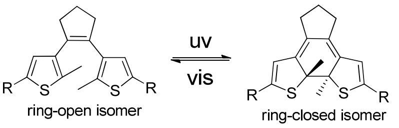
Fang Hu,[a] Juanyun Huang,[a] Meijiao Cao,[a] Zhao Chen,[a] Ying-Wei Yang,[b] Sheng Hua Liu,[a*] Jun Yin[a*]

The photochromic materials have been widely applied in the many fields. In this article, we reported a class of photochromic ammonium with dithienylethene backbone. And they were utilized as templates to construct mechanically interlocked rotaxanes and pseudorotaxane bearing photo-responsive behavior by template-directed clipping reaction and threading approach. The structures of novel rotaxanes were well defined. It was worthy to mention that the single crystal structure of [3]rotaxane containing two N-hetero crown ethers units was obtained. Their behavior of photoisomerization was investigated. These N-hetero crown ether-based rotaxanes displayed good reversibility and similar photochromic behaviors with their corresponding ammoniums when they underwent UV/vis photoirradiation. Interestingly, the cucurbit[6]uril-based pseudorotaxane showed better photoisomerization than its corresponding ammonium and those of N-hetero crown ether-based rotaxanes.

Introduction

Photochromism refers to the reversible rearrangement of a chemical species between two forms induced by alternating irradiation with UV and visible light that causes changes in the absorption spectra.[1] The application of such species in optical materials and photonic devices such as variable-transmission filters, optical information storage systems, and photoregulated molecular switches has attracted considerable interest.[1] Photochromic dithienylethene derivatives (Scheme 1) with heterocyclic aryl groups are one of the most attractive families among photochromic compounds because of their remarkable fatigue resistance, excellent thermally irreversible properties, and high sensitivity.[2]

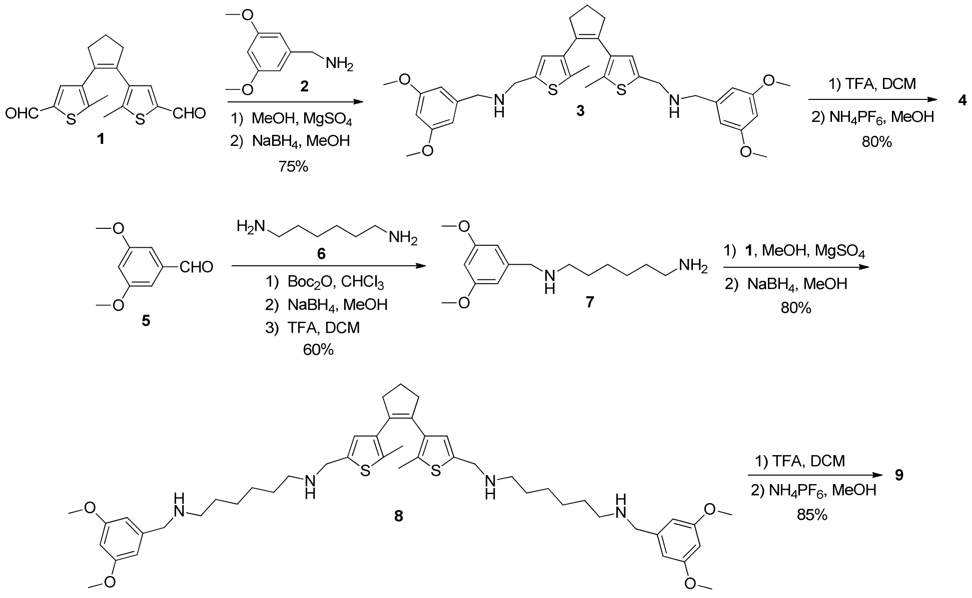
Accompanying the great development of dithienylethenes, two main strategies have been employed to design such materials with excellent photochromic behaviour. On the one hand, changing the functional groups on the R (Scheme 1) sites of the dithienylethene backbone has been a popular strategy, and various factors, such as steric hindrance, electronic effects, the length of conjugation, and so on, have been considered in the design of photochromic materials.[3] On the other hand, the bridge unit (cyclopentene) has also been substituted by other conjugated moieties.[4] Compared with covalent interaction, noncovalent interaction such as ion-dipole interaction is being increasingly considered in the design of all kinds of functional materials, and extensive research has shown that noncovalent interactions play crucial roles in determining the properties of materials.[5] Mechanically interlocked molecules (such as rotaxanes),[6] incorporating noncovalently interacting components in one molecule, provide ideal models for investigating the photochromic behaviour of dithienylethenes with mechanically interlocked backbone. To date, several studies on dithienylethene-based rotaxanes have been reported.[7] For example, Irie found that the complex of cyclodextrin and dithienylethene enhanced the photocyclization quantum yields.[8] Tian *et al* reported a multi-state [2]rotaxane based on dithienylethene unit which could alter intercomponent interactions in a photochromic multi-state[2]rotaxane.[9] Recently, Liu and co-workers reported a [2]pseudorotaxane containing a Eu^{3+} complex of terpyridinyldibenzo-24-crown-8, which revealed dual-stimulus luminescent lanthanide molecular switching behavior.[10] Herein, we present three unprecedented examples of dithienylethene-based [n]rotaxanes by installing macrocyclic moieties at the R sites of the dithienylethene backbone. Our investigations have mainly focused on their self-assembly process, structures and photoisomerization properties.



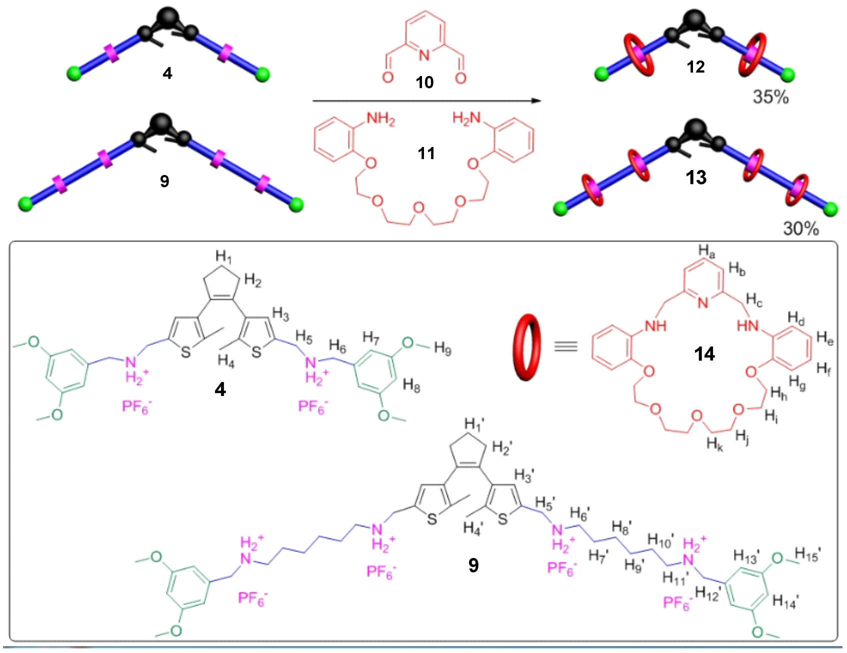
Scheme 1. Ring-open and ring-closed photoisomerization of dithienylethene.

Results and discussion

The stepwise synthesis of the dithienylethene-based ammonium salts **4** and **9** is outlined in Scheme 2. These were utilized to construct dithienylethene-based [n]rotaxanes **12** and **13** by a template-directed clipping reaction based on dialdehyde **10** and diamine **11**, as presented in Scheme 3. The clipping reaction was firstly tested for **12** and **13** by mixing equimolar amounts of dialdehyde **10**, diamine **11**, and the corresponding ammonium salts in CH_3CN. The self-assembly process was monitored by ^1H NMR. The resonances of the protons on the stopper units of [3]rotaxane **12** (H_7 and H_8, Figure 1B) displayed upfield shifts compared to those of the



Scheme 2. Synthesis of dithienylethene-based amines **3**, **8** and ammoniums **4**, **9**.



Scheme 3. The structures of dithienylethene-based ammoniums **4** and **9**, and the synthesis of [n]rotaxanes **12** and **13**.

dithienylethene-based ammonium salt **4** (Figure 1A) as a result of the shielding effect associated with the encircling crown ether macrocyclic ring. In addition, the signals of the protons (H_a and H_b) on the hetero-crown ether components were downfield-shifted relative to those of these protons in **14** itself (Figure 1C). The observed shifts in the proton resonances, which were in good agreement with those noted in our previous studies,[11] suggested that the newly installed crown ether ring system in **12** encircles the ammonium moieties of the dithienylethene-based ammonium salt **4**. Similarly, evidence for the formation of [5]rotaxane **13** by this process was provided by analysis of the relevant ^{1}H NMR spectrum. As shown in Figure 1D, obvious upfield shifts for the signals of the benzene ring protons ($H_{13'}$ and $H_{14'}$) between the spectra of **9** (Figure 1E) and **13** (Figure 1D) indicated that the crown ether units had been threaded onto the ammonium sites.

Additional evidence supporting this conclusion was provided by analysis of the respective MALDI-TOF mass spectra, which featured peaks at m/z 1577.84 attributable to $[M - HPF_6 - PF_6^-]^+$ for [3]rotaxane **12** and m/z 2735.13 attributable to $[M - 3HPF_6 - PF_6^-]^+$ for [5]rotaxane **13**, respectively (see the Electronic Supplementary Information). Gratifyingly, the

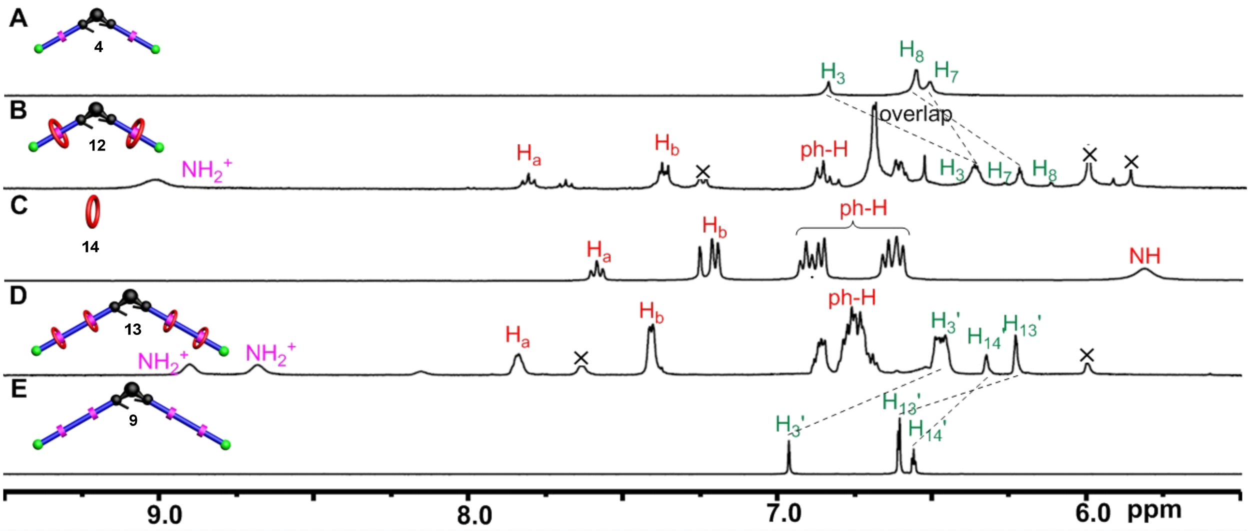


Figure 1. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of **4** (A), **12** (B), **14** (C), **13** (D), **9** (E) (resonances labeled by "×" indicate impurities in the solvents).

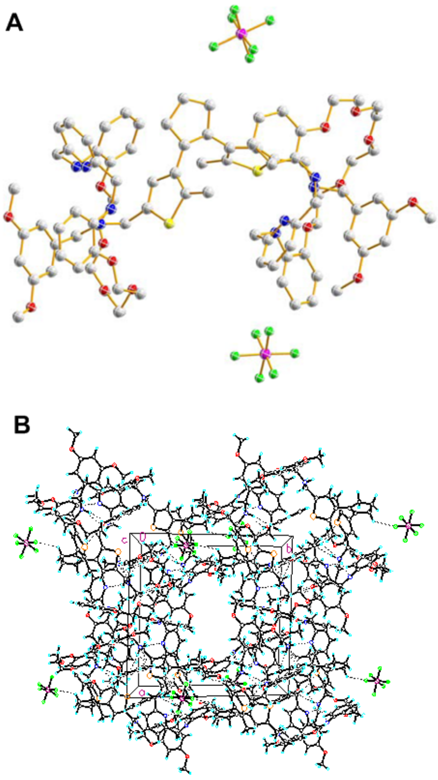


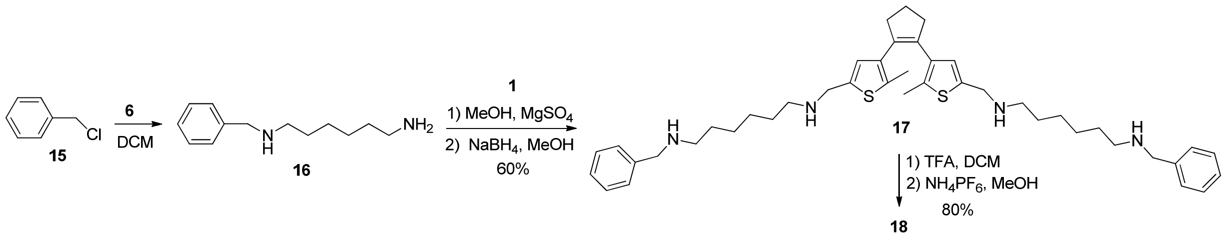
Figure 2. Single crystal structure (A) and packing views (B) of **12**.

structure of [3]rotaxane **12** could be further proved by X-ray crystallographic analysis. A single crystal of **12** suitable for X-ray diffraction analysis was grown by slow diffusion of hexane into a solution of this rotaxane in dichloromethane. The solid-state structure in Figure 2A clearly revealed that two crown ether units encircled the template sites of dithienylethene ammonium salt **4**.

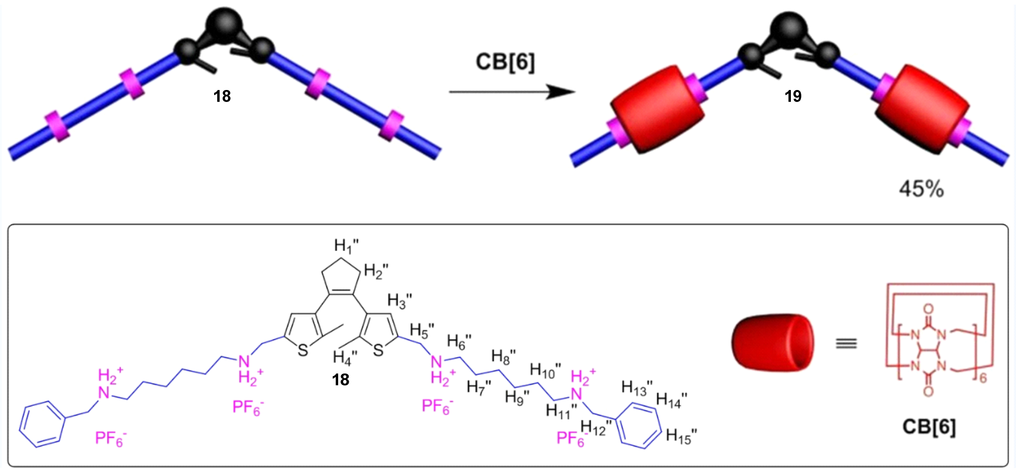
The photoisomerization behaviour of **12** and **13** induced by photoirradiation in CH_3CN was studied at room temperature. Both rotaxanes underwent photoisomerization between the ring-open isomer and the ring-closed isomer upon alternating irradiation with UV light (λ = 302 nm) and visible light (λ > 402 nm), as illustrated in Scheme 1. As shown in Figure S2A, the absorption maximum of compound **12** in CH_3CN was observed at 240 nm ($\varepsilon = 6.31 \times 10^{-4}$ L mol^{-1} cm^{-1}) as a result of a π-π* transition.[12] This colorless solution turned yellow and a new absorption band centered at 458 nm ($\varepsilon = 0.245 \times 10^{-4}$ L mol^{-1} cm^{-1}) appeared when it was irradiated with 302 nm UV light, as a result of a ring-closure reaction to give the ring-closed isomer of [3]rotaxane **12**. Upon irradiation with visible light (λ > 402 nm), the colored ring-closed isomer of [3]rotaxane **12** underwent a cycloreversion reaction to the initial colorless ring-opened isomer. The cyclization and cycloreversion quantum yields of **12** were 0.155 and 0.019, respectively. Similar photochromic behaviour was observed for [5]rotaxane **13** (Figure S2B). The photochromic parameters of N-hetero crown ether-based rotaxanes **12** and **13** were summarized in Table S1. Although the photoisomerization processes of [3]rotaxane **12** and [5]rotaxane **13** showed good reversibility, no obvious enhancements of photochromism were observed in comparison to the corresponding ammonium salts (Figure S3). It is well known that the dithienylethene is not photoreactive when it lies in the parallel conformation.[8] Therefore, it possibly derived from the similar ratio of antiparallel : parallel conformations.

Accordingly, we selected cucurbit[6]uril to construct a further dithienylethene-based rotaxane due to the bigger steric configuration.[13] The ammonium salt **18** was synthesized according to the established route (Scheme 4). The threading of cucurbit[6]uril with the dithienylethene-based ammonium salt was investigated by mixing the components in water (Scheme 5). The ^{1}H NMR spectrum of pseudo[3]rotaxane **19** (Figure S1A) showed obvious upfield shifts of the resonances of the protons on the alkyl chain ($H_{7''}$ and $H_{10''}$) with respect to the spectrum of **18** (Figure S1B).[11a] This indicated that the cucurbit[6]uril had become threaded onto the alkyl chain component between the two ammonium moieties to form a pseudo[3]rotaxane. Further proof was obtained by MALDI-TOF mass spectrometry in acetonitrile. A peak observed at m/z 2837.10 could be assigned to $[M - 2HPF_6 - PF_6^-]+$, with M being pseudo[3]rotaxane **19** (See Supporting Information).

The photochromic behaviour of **19** induced by photoirradiation in CH_3CN was measured at room temperature using the same method as above. As illustrated in Figure 3A, the absorption maximum of compound **19** in CH_3CN was observed at 237 nm ($\varepsilon = 4.82 \times 10^{-4}$ L mol^{-1} cm^{-1}). This colorless solution turned yellow and a new absorption band centered at 454 nm ($\varepsilon = 0.78 \times 10^{-4}$ L mol^{-1} cm^{-1}) appeared when it was irradiated with 302 nm UV light, as a result of a ring-closure reaction to give the ring-closed isomer of pseudo[3]rotaxane **19**. In addition, a well-defined isosbestic point was observed at 280 nm. Upon irradiation with visible light ($\lambda > 402$ nm), the ring-closed isomer underwent a cycloreversion reaction to the initial colorless ring-opened isomer. Furthermore, compound **19** had good fatigue resistance. Surprisingly, in comparison to the ammonium salt **18**, we found that the pseudo[3]rotaxane **19** had a higher degree of photoisomerization (Figure 3B) and response rate, possibly due to the increase in the ratio of antiparallel : parallel conformations.[8] Furthermore, it also showed better photochromism than those of crown ether-based dithienylethenes. These results suggested that the mechanically interlocked molecules can also be considered as a good candidate for photochromic materials with excellent photochromic behaviors.



Scheme 4. Synthesis of dithienylethene-based amine **17** and ammonium **18**.



Scheme 5. The synthesis and models of dithienylethene-based [3]rotaxanes **19**.

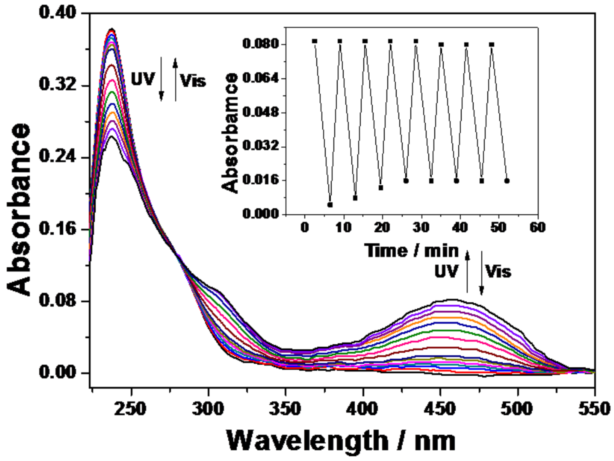


Figure 3. Absorption spectral change of pseudo[3]rotaxane **19** by photoirradiation in CH_3CN (2.0×10^{-5} mol/L). The inset shows the fatigue resistance of dithienylethene-based [n] rotaxanes ($\lambda_{UV} = 302$ nm; $\lambda_{Vis} > 402$ nm).

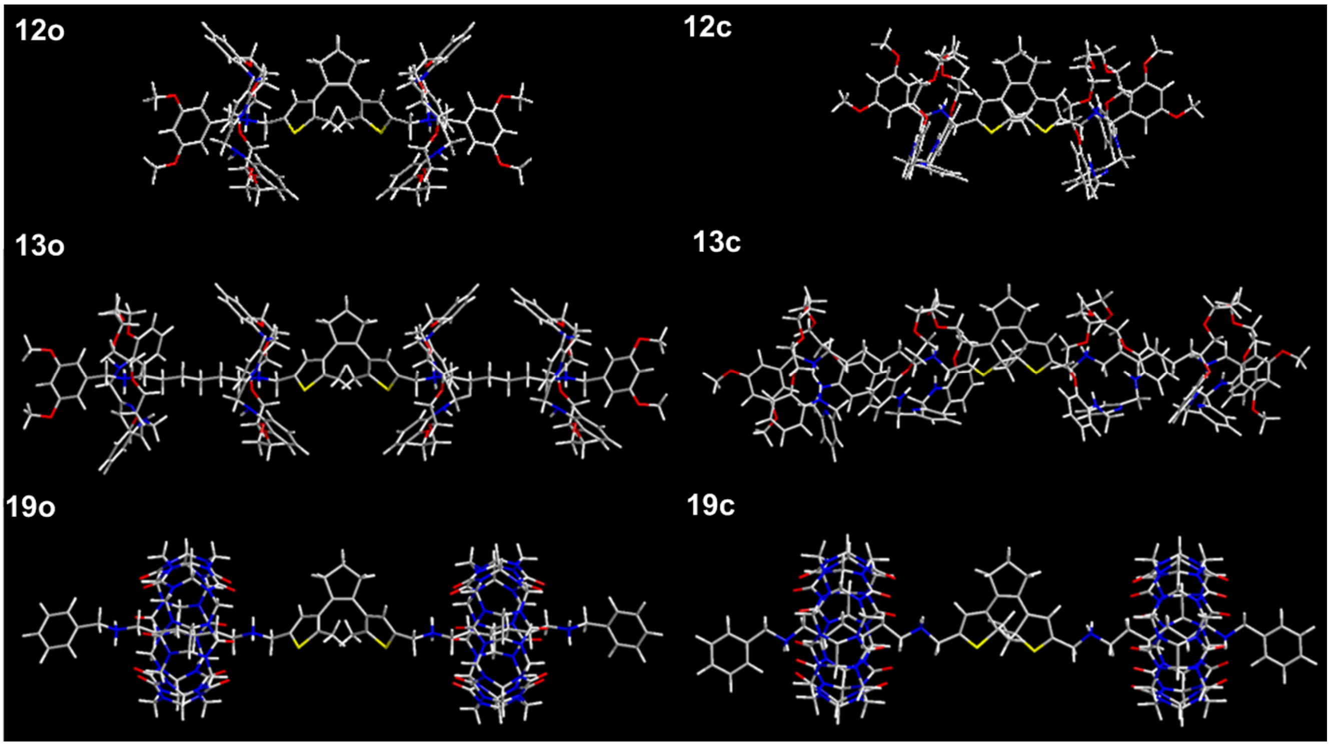


Figure 4. The optimized structures of **12**, **13** and **19** at B3LYP/6-31G* level, by using Gaussian 09 program.

Subsequently, the density functional theory (DFT) calculation had been performed to gain a deeper insight into the molecular structures of the open-ring and closed-ring forms. Details of the optimized structures were given in the Figure 4. For the open forms, the optimized structures of **12o** and **13o** showed good symmetry. The dihedral angles between the cyclopentene ring and the two thiophene rings of **12o** were 43.91(1)º and 49.15(2)º, respectively. The distance between the centers of the two thiophene rings was 5.011(1) Å. Furthermore, the unparallel confirmation of this molecule was useful to take place the photo cyclization reaction. [2a] In addition, the distance between the two reactive carbons was 3.667 Å (In the X-ray crystal structure, it was 3.998 Å), which was short enough for the cyclization reaction to take place. Photochromic reactivity usually only appears when the distance between the reactive carbon atoms is less than 4.2 Å. [14] The optimized structure of **12o** was in agreement with the X-ray crystallographic analysis. According to their strcutures in Figure 4, the corwn ether components presented obviously tortuous configuration ascribing to the flexible ethylene glycol chains. The dihedral angles between the cyclopentene ring and the two thiophene rings of **19o** were 51.16(1)º and 46.16(2)º, respectively. The distance between the centers of the two thiophene rings was 4.987(1) Å. The distance between the two reactive carbons of **19o** is 3.718 Å. For the open isomer of compound **19**, the distance between CB ring and switch unit was from 4.954(2) Å to 5.429(2) Å while the distance was 6.185(1) Å to 6.632(2) Å in the closed isomer of compound **19**. As early as 1986, Mock has reported that the dissociation constant of cucurbit[6]uril with ammonium of 1,6-diaminohexane was less than 4×10^{-7}.[15] We have also confirmed the strong affinity between cucurbituril and ammonium in our previous work.[16] This indicated that the binding is not flexible. Furthermore, from the structure of **19**, the ring of cucurbituril has bigger rigidness and steric hindrance, possibly resulting in the increase in the ratio of antiparallel : parallel conformations, which was in well agreement with previous reported by Takeshita and Irie.[8] For crown ether-based rotaxane, the binding constant between crow ether and ammonium is less than 10^3 M^{-1}.[17] Therefore, the crown ether components of rotaxanes **12** and **13** were more flexible than the cucurbituril components of rotaxane **19** in the process of transform from antiparallel to parallel conformations.

Conclusions

In summary, three novel dithienylethene-based [n]rotaxanes have been successfully synthesized, and their isomerization properties have been investigated. The photochromic activity is apparently improved by the introduction of cucurbit[6]uril. Our research has indicated that the mechanically interlocked molecules can also be considered as a good candidate for photochromic materials with excellent photoisomerization behaviors. Further work will focus on multi-responsive materials based on dithienylethene.

Experimental

Materials and methods. All manipulations were carried out under nitrogen atmosphere by using standard Schlenk techniques, unless otherwise stated. THF was distilled under nitrogen from sodium-benzophenone. 1,2-Bis(5-formyl-2-methylthien-3-yl)cyclopentene (**1**) was prepared by literature methods.[18] 2,6-pyridinedicarboxaldehyde (**10**) and Tetraethyleneglycol bis(2-aminophenyl)ether (**11**) was prepared by modified literature methods.[11c] Compound **7** was synthesized by reported method.[19] All other starting materials were obtained commercially as analytical-grade and used without further purification. The relative quantum yields were determined by comparing the reaction yield with the known yield of the compound 1, 2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene.[20] ^{1}H and ^{13}C NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz) or 600 MHz. ^{1}H and ^{13}C NMR chemical shifts are relative to TMS. UV-Vis spectra were obtained on U-3310 UV Spectrophotometer. Photoisomerization easurements were carried out under a PHK 125-W mercury lamp as an irradiation source. The ring-opening reactions were carried out using the light of a 200-W tungsten source that was passed through the appropriate cutoff filter to eliminate higher energy light. The distance between the sample and the lamp is 10 cm. The theoretical calculation in the present studies were performed at B3LYP/6-31G* level, by using Gaussian 09 program.

Synthesis of 3. To a solution of **1** (0.50 g, 1.6 mmol) in anhydrous EtOH (80 mL) was added 3,5-dimethoxybenzylamine (1.06 g, 6.32 mmol) with anhydrous magnesium sulfate acting as drying agent under nitrogen atmosphere. The mixture was refluxed for 24 h. After removing the solvent, the compound was dissolved in anhydrous MeOH (50 mL) and THF (50 mL), and sodium borohydride (605 mg, 16 mmol) was added under nitrogen atmosphere. The mixture was reacted under dark conditions overnight at room temperature. The mixture was quenched with ice water and then extracted with DCM, then dried over sodium sulfate, 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 give **3** in 65% yield as a brown gum. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 1.92 (s, 6H, CH_3), 1.96-2.04 (m, 2H, CH_2), 2.75 (t, J = 8 Hz，4H, CH_2), 3.71 (s, 4H, CH_2), 3.78 (s, 12H, CH_3), 3.82 (s, 4H, CH_2), 6.35 (s, 2H, thiophene-H), 6.48 (s, 4H, Ph-H), 6.58 (s, 2H, Ph-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 14.28, 22.91, 38.27, 47.19, 52.31, 55.27, 99.00, 105.97, 126.44, 133.61, 134.39, 135.14, 138.58, 141.96, 160.74. ESI MS m/z = 619.5 [M + H$^+$]; calculated exact mass = 618.5. Anal.calcd for $C_{35}H_{42}N_2O_4S_2$: C, 67.93; H, 6.84; N, 4.53; S, 10.36. Found: C, 67.72; H, 6.60; N, 4.25 S, 10.65.

Synthesis of 4. To a solution of **3** (0.18 g, 0.3 mmol) in dry DCM (30 mL), TFA (0.19 mL, 3 mmol) was added at room temperature. After stirring for 2 h under nitrogen atmosphere, the solvent was removed under a vacuum. The residue was dissolved in MeOH (1.0 mL), and then saturated NH_4PF_6 (2.0 mL, aq) was added to yield a pale yellow precipitate. After filtering, washing with H_2O and drying under a vacuum, the compound **4** was obtained as the pale yellow solid in 80% yield. ^{1}H NMR (400 MHz, CD_3CN): δ ppm = 1.96 (s, 6H, CH_3), 2.01-2.06 (m, 2H, CH_2), 2.76 (t, J = 8 Hz，4H, CH_2), 3.78 (s, 2H, CH_3), 3.99 (s, 4H, CH_2), 4.15 (s, 4H, CH_2), 6.52 (s, 2H, thiophene-H), 6.57 (s, 4H, Ph-H), 6.85 (sm, 2H, Ph-H). ^{13}C NMR (100 MHz, CD_3CN): δ ppm = 13.97, 22.23, 38.36, 45.55, 51.00, 55.68, 101.22, 108.14, 129.01, 132.26, 134.17, 135.35, 136.61, 137.61, 161.75. ESI MS m/z = 619.6 [M - 2HPF$_6$ + H$^+$]; calculated exact mass = 910.2. Anal.calcd for $C_{35}H_{44}F_{12}N_2O_4P_2S_2$: C, 46.15; H, 4.87; N, 3.08; S, 7.04. Found: C, 46.38; H, 4.50; N, 3.18 S, 6.95.

Synthesis of 8. To a solution of **1** (0.50 g, 1.6 mmol) in anhydrous EtOH (80 mL) was added **7** (1.68 g, 6.32 mmol) with anhydrous magnesium sulfate acting as drying agent under nitrogen atmosphere. The mixture was refluxed for 24 h. After removing the solvent, the compound was dissolved in anhydrous MeOH (50 mL) and THF (50 mL), and sodium borohydride (605 mg, 16 mmol) was added under nitrogen atmosphere. The mixture was reacted under dark conditions overnight at room temperature. The mixture was quenched with ice water and then extracted with DCM, then dried over sodium sulfate, upon removed of solvent under reduced pressure and purified on a silica gel column using ethyl acetate as the eluent to give **8** in 68% yield as a brown oil. ^{1}H NMR (400 MHz, CD_3CN): δ ppm = 1.29-1.31 (m, 8H, CH_2), 1.41-1.45 (m, 8H, CH_2), 1.95 (s, 6H, CH_3), 2.00-2.04(m, 2H, CH_2), 2.47-2.53(m, 8H, CH_2), 2.72 (t, J = 8 Hz，4H, CH_2), 3.65 (s, 4H, CH_2), 3.74 (s, 4H, CH_2), 3.75 (s, 12H, CH_3), 6.34 (t, J = 2 Hz，2H, Ph-H), 6.49 (t, J = 2 Hz，4H, Ph-H), 6.55 (s, 2H, thiophene-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 14.16, 22.83, 27.19, 29.91, 38.27, 48.36, 48.72, 48.82, 49.24, 54.03, 55.09, 55.17, 58.26, 98.52, 98.75, 106.22, 125.86, 133.21, 134.19, 134.98, 139.24, 142.53, 142.77, 160.45, 160.65. ESI MS m/z = 817.7 [M + H$^+$]; calculated exact mass = 816.7. Anal.calcd for $C_{47}H_{68}N_4O_4S_2$: C, 69.08; H, 8.39; N, 6.86; S, 7.85. Found: C, 69.43; H, 8.62; N, 6.91; S, 7.56.

Synthesis of 9. Compound **9** was prepared by an analogous method similar to that used for to **4** and was obtained as the pale yellow solid in 60% yield. ^{1}H NMR (400 MHz, CD_3CN): δ ppm = 1.35-1.37 (m, 8H, CH_2), 1.61-1.66 (m, 8H, CH_2), 1.88 (s, 6H, CH_3), 1.96-2.08 (m, 2H, CH_2), 2.77 (t, J = 7.2 Hz，4H, CH_2), 2. 94 (t, J = 7.6 Hz，4H, CH_2), 3.01 (t, J = 8 Hz，4H, CH_2), 3.81 (s, 12H, CH_3), 4.08 (s, 4H, CH_2), 4.19 (s, 4H, CH_2), 5.12 (br, 4H, NH$^+$), 6.56 (t, J = 2.4 Hz，2H, Ph-H), 6.61 (d, J = 2.4 Hz, 4H, Ph-H), 6.96 (s, 2H, thiophene-H),. ^{13}C NMR (100 MHz, CD_3CN): δ ppm = 13.93, 25.73, 45.74, 47.37, 47.99, 51.84, 55.69, 101.36, 108.18, 109.13, 128.04, 132.59, 133.48, 135.38, 136.62, 137.83, 161.76. ESI MS m/z = 817.7 [M - 3HPF$_6$ – PF$_6^-$]; calculated exact mass = 1400.4. Anal.calcd for $C_{47}H_{72}F_{24}N_4O_4P_4S_2$: C, 40.29; H, 5.18; N, 4.00; S, 4.58. Found: C, 40.11; H, 4.96; N, 3.78; S, 4.48.

Synthesis of 16. A solution of 1, 6-hexanediamine (5.80 g, 50 mmol) in DCM (100 mL) was cooled in an ice bath under nitrogen atmosphere and benzyl chloride (1.27 g, 10 mmol) in DCM (40 mL) was added dropwise to the above solution. This solution was stirred for 24 h at 0℃, After removing the solvent, the compound was dissolved in ethyl ether, After filtering, getting the filtrate, then removing the solvent to give a white solid in yield of 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 1.34 (s, 8H, CH_2), 2.64 (t, J = 7.2 Hz，4H, CH_2), 3.78 (s, 2H, CH_2), 7.28-7.31 (br, 5H, ph-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 26.77, 27.18, 33.71, 42.13, 49.37, 54.05, 126.84, 128.08, 128.34. ESI MS m/z = 207.2 [M + H$^+$]; calculated exact mass = 206.2. Anal.calcd for $C_{13}H_{22}N_2$: C, 75.68; H, 10.75; N, 13.58. Found: C, 75.58; H, 10.85; N, 13.58.

Synthesis of 17. To a solution of **1** (0.50 g, 1.6 mmol) in anhydrous EtOH (80 mL) was added **16** (1.30 g, 6.32 mmol) with anhydrous magnesium sulfate acting as drying agent under nitrogen atmosphere. The mixture was refluxed for 24 h. After removing the solvent, the compound was dissolved in anhydrous MeOH (50 mL) and THF (50 mL), and sodium borohydride (605 mg, 16 mmol) was added under nitrogen atmosphere. The mixture was reacted under dark conditions overnight at room temperature. The mixture was quenched with ice water and then extracted with DCM, then dried over sodium sulfate, upon removed of solvent under reduced pressure and purified on a silica gel column using ethyl acetate as the eluent to give **17** in 50% yield as a brown oil. ^{1}H NMR (600 MHz,

$CDCl_3$): δ ppm = 1.32-1.38 (m, 8H, CH_2), 1.48-1.49 (m, 8H, CH_2), 1.88 (s, 6H, CH_3), 2.00-2.02(m, 2H, CH_2), 2.58 (t, *J* = 6 Hz，4H, CH_2), 2.68 (t, *J* = 6 Hz，4H, CH_2), 2.74 (t, *J* = 6 Hz，4H, CH_2), 3.54 (s, 4H, NH), 3.78 (s, 4H, CH_2), 3.81 (s, 4H, CH_2), 6.56 (s, 2H, thiophene-H), 7.31 (s, 8H, Ph-H), 7.35 (s, 2H, Ph-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 14.22, 22.93, 27.25, 29.90, 30.01, 38.34, 48.43, 48.80, 49.37, 54.04, 58.25, 125.97, 126.64, 126.82, 128.06, 128.32, 128.70, 133.30, 134.33, 135.09, 139.36, 139.99, 140.42. ESI MS m/z = 697.8 [M + H^+]; calculated exact mass = 696.8. Anal.calcd for $C_{43}H_{60}N_4S_2$: C, 74.09; H, 8.68; N, 8.04; S, 9.20. Found: C, 74.20; H, 8.52; N, 8.04; S, 9.03.

Synthesis of 18. Compound **18** was prepared by an analogous method similar to that used for to **4** and was obtained as the pale yellow solid in 60% yields. ^1H NMR (600 MHz, CD_3CN): δ ppm = 1.36 (s, 8H, CH_2), 1.66 (s, 8H, CH_2), 1.95 (s, 6H, CH_3), 2.05-2.09 (m, 2H, CH_2), 2.76 (t, *J* = 6 Hz，4H, CH_2), 2.96 (t, *J* = 6 Hz，4H, CH_2), 3.02 (t, *J* = 6 Hz，4H, CH_2), 4.17 (s, 4H, CH_2), 4.20 (s, 4H, CH_2), 5.51 (br, 4H, NH^+), 6.91 (s, 2H, thiophene-H), 7.47 (s, 10H, Ph-H). ^{13}C NMR (100 MHz, CD_3CN): δ ppm = 13.97, 23.33, 25.61, 38.19, 45.71, 47.27, 47.93, 51.87, 52.35, 57.64, 128.20, 129.58, 129.77, 130.07, 130.57, 131.67, 132.56, 136.68, 137.76. ESI MS m/z = 697.6 [M - $4HPF_6$ + H^+]; calculated exact mass = 1280.6. Anal.calcd for $C_{43}H_{64}F_{24}N_4P_4S_2$: C, 40.32; H, 5.04; N, 4.37; S, 5.01. Found: C, 40.02; H, 5.02; N, 4.25; S, 5.03.

Synthesis of 12. A mixture of **4** (91 mg, 0.1 mmol), tetraethyleneglycol bis(2-aminophenyl) ether (75 mg, 0.2 mmol) and 2,2'-(pyridine-2,6-diyl)diacetaldehyde (27 mg, 0.2 mmol) was stirred for 5 d in dry CH_3CN (20 mL) under nitrogen atmosphere at room temperature. Then, $BH_3{\cdot}THF$ solution (1.6 mL) was added, and the mixture was further stirred overnight. The solvents were removed under a vacuum, and the residue was purified by column chromatography (silica gel, DCM/MeOH = 25:1) to give the **12** in 35% yield. ^1H NMR (400 MHz, CD_3CN): δ ppm = 1.95 (s, 6H, CH_3), 1.95 - 1.96 (m, 2H, CH_2), 2.19 (t, *J* = 8 Hz，4H, CH_2), 3.36 (s, 12H, CH_3), 3.41 - 3.52 (m, 4H, CH_2), 3.62 - 3.64 (m, 4H, CH_2), 3.72−3.73 (m, 8H, CH_2), 3.76−3.78 (m, 8H, CH_2), 3.79(s, 4H, CH_2), 3.87 (m, 2H, CH_2), 3.91−3.93 (m, 6H, CH_2), 3.98 (s, 2H, CH_2), 4.10−4.14 (m, 6H, CH_2), 4.47 (s, 2H, CH_2), 4.66 (s, 2H, CH_2), 4.67 (s, 2H, NH), 4.80 (s, 2H, NH), 5.87 (s, 1H, Ar), 6.01 (d, *J* = 2.4 Hz, 3H, Ar), 6.23 (d, *J* = 2 Hz, 2H, Ar), 6.38 (s, 3H, Ar), 6.54 (s, 2H, thiophene-H), 6.62 (s, 3H, Ar), 6.70 - 6.71 (m, 9H, Ar), 6.87 (s, 2H, Ar), 7.26 (d, *J* = 8.0 Hz, 1H, Ar), 7.38 (d, *J* = 8.0 Hz, 3H, Ar), 7.82 (t, *J* = 8.0 Hz, 1H, Ar), 9.02 (s, 4H, NH_2^+). The ^{13}C NMR spectrum was not collected due to the poor solubility of [3]rotaxane **12**. MALDI TOF m/z = 1577.84 [M – HPF_6 – PF_6^-]; calculated exact mass = 1868.69. Anal. Calcd for $C_{89}H_{110}F_{12}N_8O_{14}P_2S_2$: C, 57.17; H, 5.93; N, 5.99; S, 3.43. Found: C, 57.43; H, 5.57; N, 5.80; S, 3.60.

Synthesis of 13. A mixture of **9** (91 mg, 0.1 mmol), tetraethyleneglycol bis(2-aminophenyl) ether (75 mg, 0.2 mmol) and 2,2'-(pyridine-2,6-diyl)diacetaldehyde (27 mg, 0.2 mmol) was stirred for 5 d in dry CH_3CN (20 mL) under nitrogen atmosphere at room temperature. Then, $BH_3{\cdot}THF$ solution (1.6 mL) was added, and the mixture was further stirred overnight. The solvents were removed under a vacuum, and the residue was purified by column chromatography (silica gel, DCM/MeOH = 40:1) to give **13** in 30% yield. ^1H NMR (600 MHz, CD_3CN): δ ppm = 0.80 - 0.86 (m, 8H, CH_2), 1.21 - 1.28 (m, 3H, CH_2), 1.42 - 1.48 (m, 5H, CH_2), 1.95 (s, 6H, CH_3), 1.96 – 1.98 (m, 2H, CH_2), 2.09 (s, 4H, CH_2), 2.72 (s, 2H, CH_2), 2.88 (d, *J* = 5.4 Hz, 5H, CH_2), 3.37 (s, 6H, CH_2), 3.46 - 3.59 (m, 11H, CH_2), 3.63 - 3.74 (m, 34H, CH_2), 3.81−3.98 (m, 16H, CH_2), 4.00 - 4.07 (m, 6H, CH_2), 4.13−4.25 (m, 16H, CH_2), 4.40 (s, 3H, CH_2), 4.50(s, 2H, CH_2), 4.59 (s, 2H, CH_2), 4.77(s, 2H, CH_2), 4.90 (s, 3H, CH_2), 5.45 (s, 8H, NH), 6.00 (s, 2H, Ar), 6.23 (s, 3H, Ar), 6.32 (s, 2H, thiophene-H), 6.46 - 6.49 (m, 8H, Ar), 6.60 - 6.79 (m, 16H, Ar), 6.87 (d, *J* = 13.2 Hz, 6H, Ar), 7.37 - 7.40 (m, 7H, Ar), 7.63 (s, 2H, Ar), 7.84 (s, 4H, Ar), 8.15 (s, 2H, Ar), 8.68 (s, 4H, NH_2^+), 8.90 (s, 4H, NH_2^+). The ^{13}C NMR spectrum was not collected due to the poor solubility of [5]rotaxane **13**. MALDI TOF m/z = 2735.13 [M – $3HPF_6$ – PF_6^-]; calculated exact mass = 3317.32. Anal. Calcd for $C_{155}H_{204}F_{24}N_{16}O_{24}P_4S_2$: C, 56.08; H, 6.19; N, 6.75; S, 1.93. Found: C, 56.21; H, 6.06; N, 6.74; S, 1.90.

Synthesis of 19. To a solution of the **18** (0.32 g, 0.25 mmol) in H_2O, cucurbit [6] uril (0.75 g, 0.75 mmol) was added and the mixture was refluxed for 24 h under nitrogen atmosphere. After cooling, the mixture was filtered and the filtrate was treated with saturated NH_4PF_6 (2 mL, aq) to yield a white precipitate. The solid was collected by filtration, washed with water and dried under vacuum to give the title compound **19**, 0.49 g in 45% yield. ^1H NMR (600 MHz, CD_3CN): δ ppm = 0.45 (s, 8H, CH_2), 0.81 (s, 8H, CH_2), 1.95 (s, 6H, CH_3), 2.04-2.09 (m, 2H, CH_2), 2.79 (s, 4H, CH_2), 3.01 (t, 4H, CH_2), 4.16 - 4.25 (m, 24H, CB), 4.27 (s, 4H, CH_2), 5.36 (s, 4H, CH_2), 5.39 - 5.45 (m, 24H, CB), 5.51 (s, 4H, CH_2), 5.72 - 5.75 (m, 24H, CB), 7.13 (s, 2H, thiophene-H), 7.45 (s, 8H, Ph-H), 7.66 (s, 2H, Ph-H). The ^{13}C NMR spectrum was not collected due to the poor solubility of pseudo[3]rotaxane **19**. MALDI TOF m/z = 2837.10 [M – $3HPF_6$ – PF_6^-]; calculated exact mass = 3272.90. Anal. Calcd for $C_{115}H_{136}F_{24}N_{52}O_{24}P_4S_2$: C, 42.18; H, 4.19; N, 22.24; S, 1.96. Found: C, 42.48; H, 4.19; N, 24.54; S, 1.94.

Acknowledgements

We acknowledge financial support from National Natural Science Foundation of China (20931006, 21072070, 21272088) and the Program for Academic Leader in Wuhan Municipality (201271130441). The work was also supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, Ministry of Education, the Natural Science Foundation of Hubei Province (2013CFB207) and Key Laboratory of Pesticide and Chemical Biology for financial support (Grant No. 201301A01).

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] State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, 130012, P. R. China.

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

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