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Dithienylethene-based rotaxanes: synthesis, characterization and properties†

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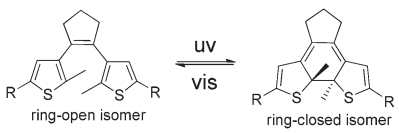
The photochromic materials have been widely applied in many fields. In this article, we report a class of photochromic ammoniums with a dithienylethene backbone. They were utilized as templates to construct mechanically interlocked rotaxanes and pseudorotaxanes showing photo-responsive behavior by template-directed clipping reaction and the threading approach. The structures of novel rotaxanes were well defined. It is worth mentioning that the single crystal structure of [3]rotaxane containing two N-hetero crown ether units was obtained. Their photoisomerization behavior was investigated. These N-hetero crown ether-based rotaxanes displayed good reversibility and similar photochromic behaviors to 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 among the most attractive families of photochromic compounds because of their remarkable fatigue resistance, excellent thermally irreversible properties, and high sensitivity.[2]



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

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 bridging unit (cyclopentene) has also been substituted by other conjugated moieties.[4] Compared with covalent interactions, noncovalent interactions such as ion–dipole interactions are 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 a 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 yield.[8] Tian *et al.* reported a multi-state [2]rotaxane based on the 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

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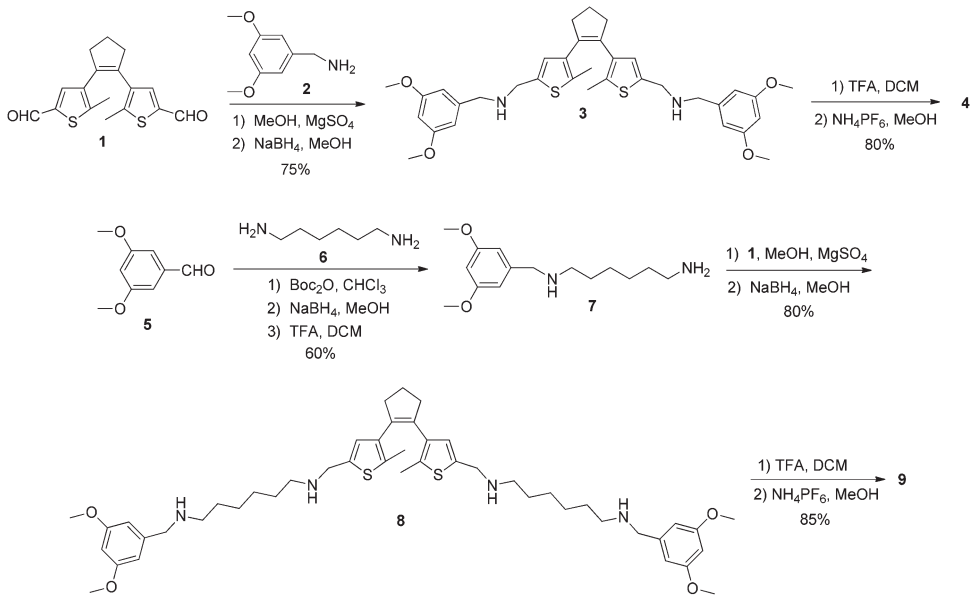
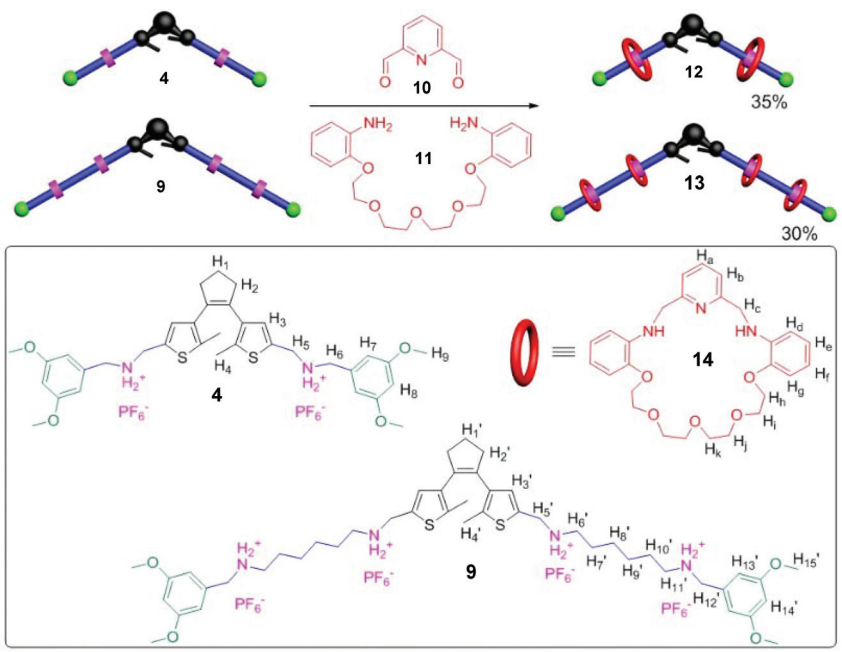
by installing macrocyclic moieties at the R sites of the dithienylethene backbone. Our investigations have mainly focused on their self-assembly process, structures and photoisomerization properties.

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 first 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, Fig. 1B) displayed upfield shifts compared to those of the dithienylethene-based ammonium salt **4** (Fig. 1A) as a result of



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**.

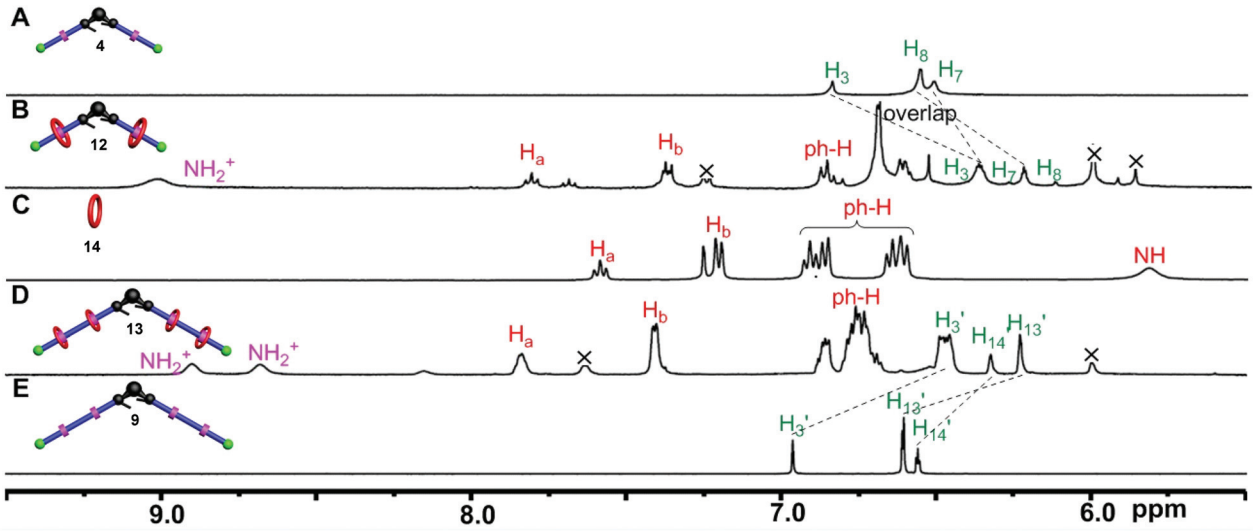


Fig. 1 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of **4** (A), **12** (B), **14** (C), **13** (D), **9** (E) (resonances labeled as "×" indicate impurities in the solvents).

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 (Fig. 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 Fig. 1D, obvious upfield shifts for the signals of the benzene ring protons ($H_{13'}$ and $H_{14'}$) between the spectra of **9** (Fig. 1E) and **13** (Fig. 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 at *m/z* 2735.13 attributable to $[M - 3HPF_6 - PF_6^-]^+$ for [5]rotaxane **13** (see the ESI†). Gratifyingly, the 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 Fig. 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 Fig. 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 the π–π*

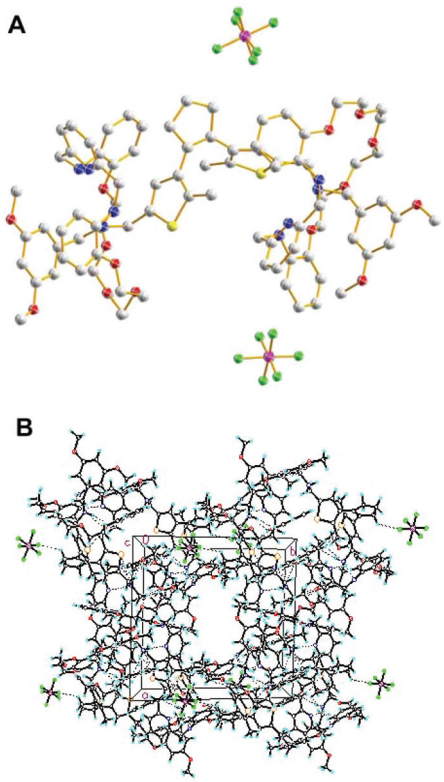


Fig. 2 Single crystal structure (A) and packing views (B) of **12**.

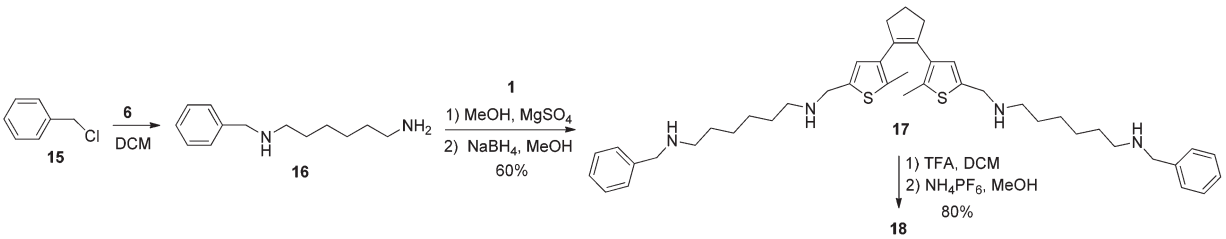
transition.[12] This colorless solution turned yellow and a new absorption band centered at 458 nm ($\varepsilon = 0.245 \times 10^{-4}$ L mol^{-1} cm^{-1}) appeared when it was irradiated with 302 nm UV light, as a result of a ring-closure reaction to give the ring-closed isomer of [3]rotaxane **12**. 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-open 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** (Fig. S2B†). The photochromic parameters of N-hetero crown ether-based rotaxanes **12** and **13** are 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 with the corresponding ammonium salts (Fig. S3†). It is well known that the dithienylethene is not photoreactive when it lies in the parallel conformation.[8] Therefore, it is possibly derived from the similar ratio of antiparallel : parallel conformations.

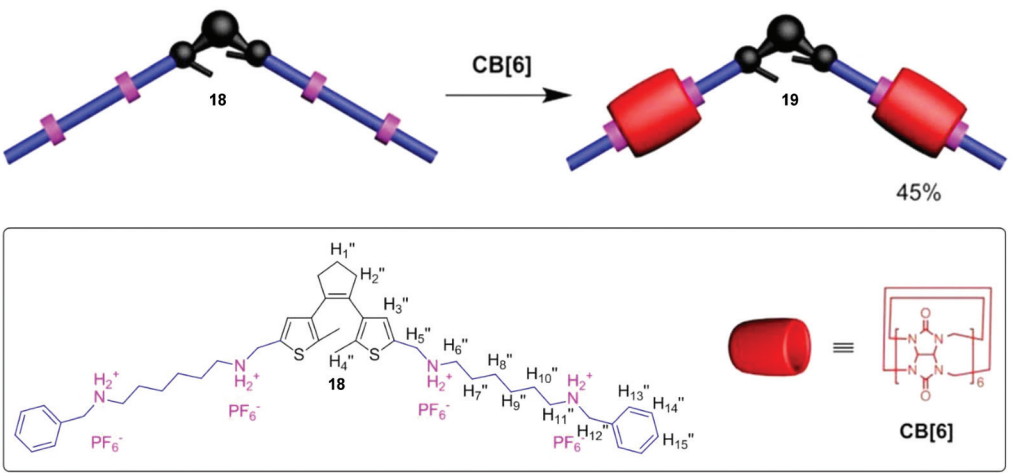
Accordingly, we selected cucurbit[6]uril to construct a further dithienylethene-based rotaxane due to the bigger steric configuration.[13] The ammonium salt **18** was synthesized according to the established route (Scheme 4). The threading of cucurbit[6]uril with the dithienylethene-based ammonium salt was investigated by mixing the components in water (Scheme 5). The ^{1}H NMR spectrum of pseudo[3]rotaxane **19** (Fig. 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** (Fig. 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 ESI†).

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 Fig. 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 (λ > 402 nm), the ring-closed isomer underwent a cycloreversion reaction to the initial colorless ring-open isomer. Furthermore, compound **19** had good fatigue resistance. Surprisingly, in comparison with the ammonium salt **18**, we found that the pseudo[3]rotaxane **19** had a higher degree of photoisomerization (Fig. 3B) and response rate, possibly due to the increase in the ratio of antiparallel : parallel conformations.[8] Furthermore, it also showed better photochromism than crown ether-based dithienylethenes. These results suggested that the mechanically interlocked molecules can also be considered as good candidates for photochromic materials with excellent photochromic behaviors.

Subsequently, the density functional theory (DFT) calculation had been performed to gain a deeper insight into the



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



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

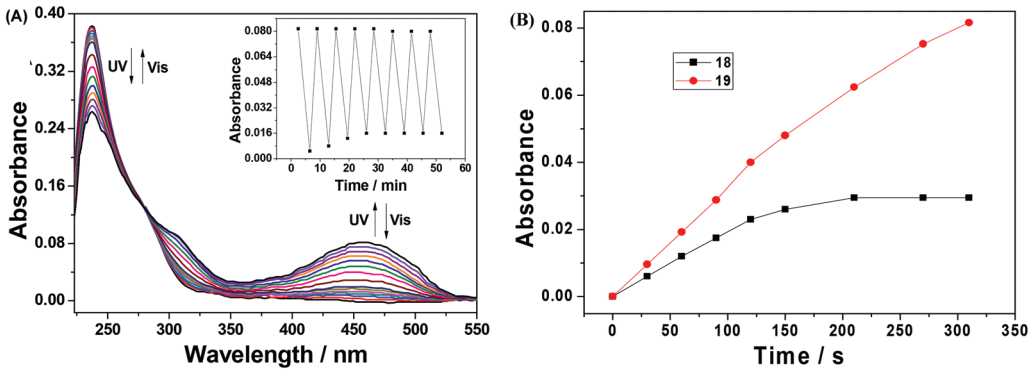


Fig. 3 (A) Absorption spectral change of pseudo[3]rotaxane **19** by photoirradiation in CH_3CN (2.0×10^{-5} mol L^{-1}). The inset shows the fatigue resistance of dithienylethene-based [*n*]rotaxanes (λ_{UV} = 302 nm; λ_{Vis} > 402 nm); (B) The cyclization kinetics of **18** and **19** in CH_3CN (2.0×10^{-5} mol L^{-1}) upon irradiation with UV light (λ = 302 nm).

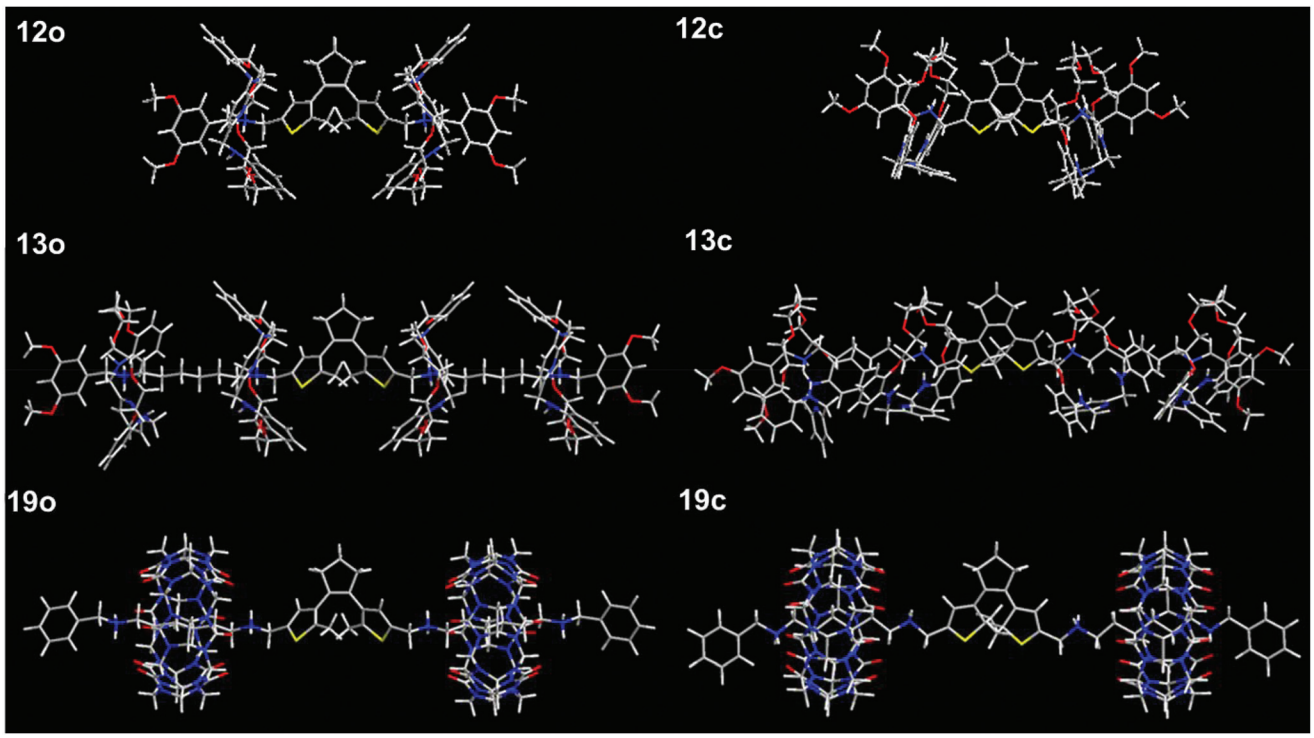


Fig. 4 The optimized structures of **12**, **13** and **19** at the B3LYP/6-31G* level, using the Gaussian 09 program.

molecular structures of the open-ring and closed-ring forms. Details of the optimized structures are given in Fig. 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)° and 49.15(2)°, 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 for the photo cyclization reaction to take place.[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 structures in Fig. 4, the crown ether components presented the 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)° and 46.16(2)°, 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 the CB ring and the switch unit was from 4.954(2) Å to 5.429(2) Å while the distance was from 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 an increase in the ratio of antiparallel : parallel conformations, which was in good agreement with a previous report by Takeshita and Irie.[8] For crown ether-based rotaxanes, 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 transformation 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 good candidates 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 a nitrogen atmosphere 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**) were prepared by modified literature methods.[11c] Compound 7 was synthesized by a 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 a 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 a U-3310 UV Spectrophotometer. Photoisomerization measurements 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 study was performed at the B3LYP/6-31G* level, using the 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 a drying agent under a 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 a nitrogen atmosphere. The mixture was reacted under dark conditions overnight at room temperature. The mixture was quenched with ice water, extracted with DCM, dried over sodium sulfate, and upon removal of the solvent under reduced pressure it was then 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 a nitrogen atmosphere, the solvent was removed under 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 vacuum, compound **4** was obtained as a 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 a drying agent under a 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 a nitrogen atmosphere. The mixture was reacted under dark conditions overnight at room

temperature. The mixture was quenched with ice water, extracted with DCM, dried over sodium sulfate, and upon removal of the solvent under reduced pressure, it was then 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 **4** and was obtained as a 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 a 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 °C. After removing the solvent, the compound was dissolved in ethyl ether. After filtering, the solvent was removed from the filtrate to give a white solid in a 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 a drying agent under a 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 a nitrogen atmosphere. The mixture was reacted under dark conditions overnight at room temperature. The mixture was quenched with ice water, extracted with DCM, dried over sodium sulfate, and upon removal of the solvent under reduced pressure, it was then 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 **4** and was obtained as a pale yellow solid in 60% yield. ^{1}H 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 a nitrogen atmosphere at room temperature. Then, BH_3·THF solution (1.6 mL) 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 = 25 : 1) to give the **12** in 35% yield. ^{1}H 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 a nitrogen atmosphere at room temperature. Then, BH_3·THF solution (1.6 mL) 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 = 40 : 1) to give **13** in 30% yield. ^{1}H 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 **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 a 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. ^{1}H 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.

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