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Dedicated to Prof. J. Fraser Stoddart on the occasion of his 65th birthday

1. Introduction

Rotaxanes are a family of interlocked molecules with one or more rings encircling a dumbbell-shaped component. As prime candidates for the construction of artificial molecular machines, rotaxanes have become the subject of intense investigations.[1] In many cases, [2]rotaxanes contain two recognition sites (D1 and D2) and one cyclic moiety (A) (Scheme 1). Moiety A can encircle D1 or D2 and it can be switched between the two stations upon external stimuli such as redox reactions and light irradiations. In other words, moiety A can shuttle between the D1 and D2 stations in response to external stimuli. A number of rotaxanes, in which D1 and D2 are electron donors or acceptors and correspondingly the cyclic moiety A is an electron acceptor or donor, have been described.[2] Recently, Leigh and coworkers have successfully developed a new type of rotaxanes, in which D1 and D2 are associated non-covalently with A through H-bonds.[3] Rotaxanes featuring cyclodextrins and molecular logic gates based on them have been reported.[4,5]

The [2]rotaxanes, which contain tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP), and cyclobis(paraquat-p-phenylene) (CBPQT4+) with cyclohexyl and alkyl chains as the spacers, have been comprehensively investigated by Stoddart and coworkers.[6] The following mechanism is proposed to explain the shuttling of CBPQT4+ between TTF and DNP stations: 1) The TTF moiety can be oxidized into the corresponding TTF=C46+ chemically or electrochemically and the resulting electronic repulsion between TTF=C46+ and CBPQT4+ will drive the latter to the DNP station. 2) Transformation of TTF=C46+ back to the neutral TTF state by either chemical or electrochemical reduction would bring CBPQT4+ from the DNP station to the initial TTF station.[6,7] Apart from studies in solution, the electrical bistability behavior of these TTF-DNP-CBPQT4+[2]rotaxanes has been also examined in the solid state (e.g., in two-terminal junctions with LB films).[8] Solid-state switchable tunnel junction devices have been successfully fabricated using these [2]rotaxanes.[8]

The TTF moieties employed in the construction of switchable [2]rotaxanes are D11, D12, D13, and D14 (Scheme 1). The spacers that link TTF and DNP moieties are usually oligoethyl-
lene glycol chains for most switchable [2]rotaxanes, in which the hydrogen bonds are formed between \( \alpha \)-bipyridinium protons and polyether oxygen atoms. It is anticipated that structural modification of the TTF moiety would change its electron-donating ability and accordingly the interaction between TTF and CBPQT\(^{4+}\) would be affected. Thus, it would be interesting to prepare switchable [2]rotaxanes with new TTF derivatives. In this paper we report two new TTF-DNP-CBPQT\(^{4+}\) [2]rotaxanes 1 and 2 (Scheme 2). In these two [2]rotaxanes, the TTF moiety is the 4,4\(^{\prime}\) (5\(^{\prime}\))-dialkylthiotetrathiafulvalene (D15 in Scheme 1) that is rather easily accessible based on the synthetic procedure developed by us previously, and two different spacers are used: cyclohexyl and alkyl chains. The two stopper units are G2-dendritic moieties. The results show that 1) the CBPQT\(^{4+}\) can be switched between the TTF and DNP stations of [2]rotaxanes 1 and 2 upon oxidation and reduction; 2) stable monolayers of 1 and 2 can be formed at the air–water interface and the corresponding multilayer LB films can be fabricated with the normal LB technique; 3) the LB films show electrical bistability behavior. A preliminary report about the application of [2]rotaxanes 2 in nanorecording has been described by us recently.

Scheme 1. Schematic illustration of a typical [2]rotaxane containing two recognition sites (D\(_1\) and D\(_2\)) and one cyclic moiety (A), and the chemical structures of tetrathiafulvalene (TTF) derivatives employed in [2]rotaxanes.

Scheme 2. The chemical structures of [2]rotaxane 1 and [2]rotaxane 2; the corresponding TTF units are enriched by the CBPQT\(^{4+}\) ring.
2. Results and Discussion

2.1. Synthesis and Characterization

For the preparation of [2]rotaxanes 1 and 2, the corresponding dumbbell-shaped compounds 3 and 4 were synthesized first as shown in Scheme 3. The TTF moiety with the dendritic stopper 5 was obtained by the reaction of compound 6, which was accessible based on the procedure developed by our group, and the dendritic compound 7 in the presence of CsOH·H2O. The DNP derivatives 8 and 9 were synthesized by stepwise reaction with compound 7 and the 1,4-dibromomethylcyclohexane/1,5-dibromopentane in good yields. Further reaction of compound 5 with compounds 8 and 9, respectively, afforded the dumbbell-shaped compounds 3 and 4 after purification in relatively high yields.

By using the dumbbell-shaped compounds 3 and 4 as the templates, reaction of the dicationic precursor 10 and 1,4-bis(bromomethyl) benzene (11) led to the formation of CBPQT4+ which encircled the compounds 3 and 4, and as a result, [2]rotaxanes 1 and 2 were constructed. After purification with column chromatography using a mixture solution of NH4PF6 in CH3NO2/CH2Cl2 as the eluent, analytically pure green powders of [2]rotaxanes 1 and 2 were obtained in 1–3 % yield. The yields of [2]rotaxanes 1 and 2 were rather low, which may be due to the fact that the spacers of [2]rotaxanes 1 and 2 are cyclohexyl and alkyl chains, rather than the glycol chains such as in the TTF-DNP-CBPQT4+ [2]rotaxanes reported by Stoddart et al., and thus the TTF-CBPQT4+ complex in [2]rotaxanes 1 and 2 would not be stabilized by the hydrogen bonds with α-bipyridinium protons and polyether oxygen atoms.[9] These two new [2]rotaxanes were characterized by 1H-NMR, matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry and elemental analysis. As an example, Figure 1 shows the part of the mass spectrum of [2]rotaxane 2, in which the peaks correspond to the [M – PF6]−, [M – 2PF6 + e]−, [M – 3PF6 + 2e]−, and [M – 4PF6 + 3e]−, respectively. A comparison of the 1H-NMR spectra (CD3COCD3, 298 K) of compound 4 and the [2]rotaxane 2 revealed significant changes in the chemical shift of the signals associated with the protons located closely to the TTF unit: the proton signals of the two SCH2 groups downshift from 2.76 and 3.91 ppm in compound 4 to 3.15 and 4.25 ppm in the [2]rotaxane 2, respectively.

2.2. Absorption Spectral Studies in Solution

Absorption spectral studies showed that the CBPQT4+ moiety could switch between the TTF and DNP stations of [2]rotaxanes 1 and 2 as observed for other switchable [2]rotaxanes.[6] As an example, Figure 2 shows the absorption spectrum of [2]rotaxane 2 before and after oxidation with Fe(CIO4)3 and further reduction.
with ascorbic acid. A broad absorption band (curve a in Fig. 2) with \( \lambda_{\text{max}} = 840 \) nm, which is due to the charge-transfer (CT) absorption of the TTF-CBPQT\(^{4+}\) complex, was observed, while the CT absorption band in the 500–600 nm region, which is associated with the DNP-CBPQT\(^{4+}\) complex, was not detected for [2]rotaxane 2. Similar absorption spectral features were observed for [2]rotaxane 1. These absorption spectral results revealed that CBPQT\(^{4+}\) moiety of [2]rotaxanes 1 and 2 preferentially resided by the TTF station.

Curve b corresponds to the absorption spectrum of the solution of [2]rotaxane 2 after addition of 1.0 equiv. of Fe(ClO\(_4\))\(_3\). Characteristic absorption bands of TTF\(^+/C_{46}\) with \( \lambda_{\text{max}} = 435 \) nm and 660 nm were detected. Concomitantly, the intensity of the CT band of the TTF-CBPQT\(^{4+}\) complex at 840 nm decreased and a new absorption shoulder band at 530 nm appeared. According to previous studies this new absorption shoulder band at 530 nm is generally associated with the DNP-CBPQT\(^{4+}\) complex. Such spectral variation of [2]rotaxane 2 after addition of Fe\(^{3+}\) indicated the transformation of TTF into TTF\(^+/C_{46}\) and the shifting of CBPQT\(^{4+}\) from the TTF station to the DNP station. Further addition of 1.0 equiv. of the ascorbic acid to the solution of [2]rotaxane 2 that had been treated with 1.0 equiv. of Fe(ClO\(_4\))\(_3\) led to nearly the original spectrum as shown in Figure 2 (curve c). Similar absorption spectral changes were observed for [2]rotaxane 1 after sequential reaction with Fe(ClO\(_4\))\(_3\) and ascorbic acid. These absorption spectral changes revealed that the switching of CBPQT\(^{4+}\) between the TTF and DNP stations could be reversibly controlled by oxidation and reduction for [2]rotaxanes 1 and 2.

2.3. LB Films

Figure 3 shows the surface pressure (\( \pi \))–area (\( A \)) isotherms of [2]rotaxanes 1 and 2 on a pure water surface, which were obtained by spreading 40–100 \( \mu \)L CHCl\(_3\) solutions of [2]rotaxanes 1 (0.1954 m) and 2 (0.4848 m) onto the surface of a Langmuir trough. The two \( \pi \)–A curves indicate that stable monolayers of [2]rotaxanes 1 and 2 can be formed at the air–water interface. [2]Rotaxanes 1 and 2 contain hydrophobic dendritic stoppers, TTF with CBPQT\(^{4+}\) and DNP. They are not typical amphiphilic molecules for the formation of LB films. However, it has been reported previously that these atypical amphiphilic molecules could form stable monolayers at the air–water interface and corresponding LB films could be prepared. The extrapolated molecular areas from the linear part of the isotherms were 134 A\(^2\) and 212 A\(^2\) for 1 and 2, respectively. The molecular area of the complex of CBPQT\(^{4+}\) and TTF moiety was estimated to be ca. 170 A\(^2\), thus it may be concluded that the hydrophilic part of 2, CBPQT\(^{4+}\) with TTF, was almost lying on the surface, while that of 1 was tilted relative to the surface.

The formed monolayers of [2]rotaxanes 1 and 2 at the air–water interface can be transferred onto the substrates by using the normal LB technique. As to be discussed below, multilayer LB films of [2]rotaxanes 1 and 2 can also be fabricated. The LB
films of [2]rotaxanes 1 were prepared at a surface pressure of 21 mN m⁻¹ and a lifting speed of 1–3 mm min⁻¹, and the transfer ratio was in the range of 0.9–1.0. The LB films of [2]rotaxanes 2 was prepared similarly at a surface pressure of 20 mN m⁻¹ and a lifting speed of 1–2 mm min⁻¹, and the transfer ratio was in the range of 0.8–1.0. The LB films of [2]rotaxanes 1 and 2 were characterized by atomic force microscopy (AFM) and scanning tunneling microscopy (STM). The AFM (tapping mode) and STM images of the 7-layer LB films of [2]rotaxanes 1 and 2 deposited on highly oriented pyrolytic graphite (HOPG) are provided in the Supporting information. Aggregation of [2]rotaxanes 1 and 2 to form domains was observed.

2.4. Electrical Bistability Behavior

Seven-layer LB films of [2]rotaxane 1 were deposited onto the surface of HOPG. The conducting behavior of the LB films was studied with conducting AFM. The measurements were conducted over 50 times on different sample positions, and typical I–V curves are shown in Figure 4. When the applied voltage was lower than 1.4 V, the conductivity of the LB films was rather small. Interestingly, a sudden conductivity enhancement was observed when the voltage was higher than 1.4 V. The conducting behavior of the LB films was also studied by STM, and it was found that the conductivity increased largely after applying an electric field pulse (ca. 2.0 V and 5 ms) to the LB films. These results indicated that LB films showed electrical bistability behavior, and the low-conductivity state could be transformed into the high-conductivity state by applying an electrical voltage. Seven-layer LB films of [2]rotaxane 2 were also studied with conducting AFM and STM, and a similar conductance transition was observed after applying an electrical voltage to the LB films.

The conducting behavior of the LB films of [2]rotaxanes 1 was also studied with a two-terminal junction device. For this purpose, the 50-layer LB films (with a thickness of ca. 70 nm) of [2]rotaxanes 1 were transferred onto the surface of indium tin oxide (ITO) and the top of the LB films made contact with a freshly cleaved HOPG surface. The macroscopic I–V properties of the LB films were measured with a standard I–V characterization system (Keithley Model 4200SCS). The measurement started from 0 voltage and increase in steps of 0.025 V; the data were collected 5 s after setting the voltage. As shown in Figure 5, the conductivity of the LB films of [2]rotaxane 1 was rather small when the applied voltage was lower than 1.4 V. The conductivity of the LB films increased largely when the applying voltage was over 1.4 V, again implying the transition of a low-conductivity state into a high-conductivity state (curve 1). The conductance between the two states differs by two orders of magnitude. Curve 2 was recorded for LB films that had been left for 12 h in a container at room temperature after application of 1.4 V. This result clearly showed that the high-conductivity state of the LB films of [2]rotaxane 1 was stable. Curves 3, 4, and 5 corresponded to the I–V curves of the LB films measured after applying a negative voltage. As a reverse voltage was applied, the LB films of [2]rotaxane 1 went back to the original low-conductivity state (curves 4 and 5 of Fig. 5). These results indicate that for the LB films of [2]rotaxane 1 the conductance transition can be reversibly controlled by the external voltage. This conclusion is in agreement with that deduced from conducting AFM and STM studies as discussed above.

The conducting behavior of the LB films of [2]rotaxane 2 was also studied with conducting AFM, STM, and the two-terminal junction device. A similar electrical bistability behavior was observed, and stable/reproducible nanorecording with LB films of [2]rotaxane 2 has successfully been realized.\(^{51}\) Plenty of experimental results have provided support for the following mechanism explaining the switchable electrical bistability behavior observed for TTF-DNP-CBPQT\(^{4+}\) [2]rotaxanes:\(^{6,14}\) 1) By applying a positive pulse voltage the TTF unit is oxidized into the TTF\(^{2+}\) state, and as a result CBPQT\(^{4+}\) moves to the DNP station owing to the electronic repulsion. Theoretical-calculation results indicate that the complex DNP–CBPQT\(^{4+}\) exhibits a higher conductivity than the TTF-CBPQT\(^{4+}\) complex.\(^{7}\) Therefore, it is understandable that the conductivity of the LB
fils of TTF-DNP-CBPQT\textsuperscript{+} \[2\]rotaxanes is enhanced when CBPQT\textsuperscript{+} is shifted to the DNP station. 2) Then, by applying a negative pulse voltage TTF\textsuperscript{−} is reduced to the neutral TTF unit and CBPQT\textsuperscript{+} moves back to the TTF station, and accordingly the low-conductivity state is restored. Therefore, it is reasonable to assume that the same mechanism can also account for the electrical bistability exhibited by the LB films of \[2\]rotaxanes 1 and 2. It should be mentioned that no significant difference was observed in the electrical bistability properties between \[2\]rotaxanes 1 and 2 LB films, although they had different spacers (cyclohexyl and alkyl chains) exhibiting different conformational flexibility. This is likely because molecules of \[2\]rotaxanes 1 and 2 would become more rigid in the LB films and thus the conformational flexibility would largely be reduced and no longer play a role in the electrical bistability.

3. Conclusions

The synthesis and characterization of two new TTF-DNP-CBPQT\textsuperscript{+} \[2\]rotaxanes 1 and 2 with cyclohexyl and alkyl chains as the spacers were described. Stable monolayers of \[2\]rotaxanes 1 and 2 can be formed at the air–water interface and, moreover, multilayer LB films can be prepared. Conducting AFM, STM, and two-terminal junction device studies indicate that the LB films of \[2\]rotaxanes 1 and 2 show electrical bistability behavior. It is also assumed that the movement of the CBPQT\textsuperscript{+} ring upon oxidation/reduction of TTF moiety is responsible for the electrical bistability behavior as was reported previously for other TTF-DNP-CBPQT\textsuperscript{+} \[2\]rotaxanes\textsuperscript{[8]} Although the TTF moiety (D\textsubscript{15}, Scheme 1) employed in \[2\]rotaxanes 1 and 2 is different from the TTF moieties (D\textsubscript{11,16,14}, Scheme 1) in other TTF-DNP-CBPQT\textsuperscript{+} \[2\]rotaxanes\textsuperscript{[8]} similar switching behavior of CBPQT\textsuperscript{+} between the TTF and DNP stations is realized. The present results hint that proper modification of the chemical structures of the TTF unit and the spacer has a negligible effect on the electrical bistability behavior of TTF-DNP-CBPQT\textsuperscript{+} \[2\]rotaxanes. This finding will enable us to design and prepare new multifunctional TTF-DNP-CBPQT\textsuperscript{+} \[2\]rotaxanes in the future.

4. Experimental

Chemical Reagents: Tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately prior to use. Dimethylformamide (DMF) was pre-dried over molecular sieves (4 Å) for at least 3 days before use. 1,5-dibromopentane, 1,5-dihydroxylnaphthalene, and 1,4-cyclohexanedibromomethane was prepared from 1,4-cyclohexanedimethanol were purchased from Acros Chemicals. 1,4-Cyclohexanedimethanol was pre-dried over molecular sieves (4 Å) for at least 3 days before use. 1,5-dibromopentane, 1,5-dihydroxylnaphthalene, and 1,4-cyclohexane di bromomethane was prepared from 1,4-cyclohexanedimethanol. All other reagents and solvents (standard grade) were used as received unless otherwise stated. All reactions involving compounds containing TTF units were carried out under an atmosphere of dry N\textsubscript{2}.

Characterization Techniques: Melting points were measured with an XT\textsubscript{3}-100X apparatus and used uncorrected. \textsuperscript{1}H-NMR spectra were recorded with a Bruker 300 MHz spectrometer. All chemical shifts were quoted in ppm relative to tetramethylsilane (TMS). Mass spectra were determined by MALDI-TOF-MS (BIF LEX III). Elemental analysis was performed on a Carlo-Erba-1106 instrument. Absorption spectra were measured with a Hitachi (model U-3010) UV-vis spectrophotometer.
Synthesis of [2]Rotaxane 2: A solution of 4 (0.31 g, 0.16 mmol), 10 (0.45 g, 0.63 mmol), and p-xylene dibromide (11, 0.17 g, 0.63 mmol) in dry, degassed DMF (45 mL) was stirred under N₂ for 10 days. Then the solvent was removed in vacuum to afford a residue, which was subjected to column chromatography on silica gel using a mixture solution of CH₂Cl₂ and CH₃OH (1:3, v/v) containing NH₄PF₆ (1%) as eluent. After the solvent was evaporated off, the [2]rotaxane 2 was collected as a green solid (20 mg) in 3% yield: mp 161–162 °C. ¹H-NMR (300 MHz, CD₃COCD₃) δ [ppm]: 7.90 (8H, s, Ar-H), 7.41 (44H, m, Ar-H + olefinic), 6.61–6.83 (20H, m, Ar-H), 9.55 (8H, br, Ar-H), 8.52 (8H, br, Ar-H), 7.94 (8H, s, Ar-H), 7.74 (2H, 8CH₂), 5.19 (2H, s, 4CH₂), 4.20 (2H, m, CH₂), 4.00 (2H, m, CH₂), 3.05 (2H, s, CH₂), 2.79 (16H, s, 2CH₂), 1.85–2.01 (16H, s, 3CH₃); MS (MALDI-TOF) m/z 2930.6 ([M–PF₆]⁺), 2758.7 ([M–2PF₆+e⁺]), 2613.6 ([M–3PF₆+2e⁺]), 1948.7 ([M–4PF₆+3e⁺]). Anal. calc. for C₁₅₈H₁₄₀N₄O₁₄S₆.4PF₆: C, 61.38; H, 4.57; N, 1.81.

