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PAPER

Altering intercomponent interactions in a photochromic multi-state [2]rotaxane†

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Rotaxanes have attracted much attention because of their challenging constructions and potential applications. In this paper, a multi-state [2]rotaxane, in which a dithienylethene-functionalized dibenzo-24-crown-8 macrocycle was interlocked onto a thread component bearing a 4-morpholin-naphthalimide fluorescent stopper and two distinct recognition sites, namely, dibenzylammonium and *N*-methyltriazolium recognition sites, was prepared and studied. By introducing a dithienylethene photochrome into the macrocycle component, multi-mode alteration of the intercomponent interactions, such as energy transfer, electron transfer, and charge transfer interaction between the photochrome and the fluorescent naphthalimide stopper could be altered in this multi-state rotaxane system in response to the combination of chemical and photochemical stimuli.

Introduction

During the past few decades, research on mechanically interlocked molecules, better known as rotaxanes and catenanes, has grown to an unprecedented level of activity, because of their interesting physical and chemical properties, applications in molecular electronics and smart materials with adjustable surface properties and as components of molecular machinery.[1–2] A bistable [2]rotaxane, in which the competitive binding ability of a macrocycle with two distinct, well-separated recognition sites on the thread component, can be changed in response to an external stimuli, and can function as molecular switches or molecular logic gates if functional units are introduced into a rotaxane molecule.[2] Up until now various functional units were introduced into mechanically interlocked structures to achieve specific functions[2] and to realize intercomponent interactions such as electron transfer,[3] energy transfer,[4] charge transfer[5] interactions *etc.* To develop more advanced molecular machines and to increase functional complexity, it is necessary to combine and alter the common intramolecular interactions on a unimolecular platform.[6] In this paper, we have demonstrated that the combination of multi-mode intercomponent interactions can be altered in a photochromic multi-stable [2]rotaxane, with its structure shown in Fig. 1. By introducing a dithienylethene (DTE) photochromic[7] functional group in this system, multi-mode alteration of intercomponent interactions such as energy transfer, electron transfer, charge transfer interaction *etc.*, can be realized within a controllable configuration and spatial distance (Scheme 1), along with UV/Vis absorption and fluorescence spectral changes in response to the combination of chemical and photochemical stimuli. This kind of multi-state molecular shuttle holds the potential to construct multi-level molecular machines and complicated logic gates.[6,8]

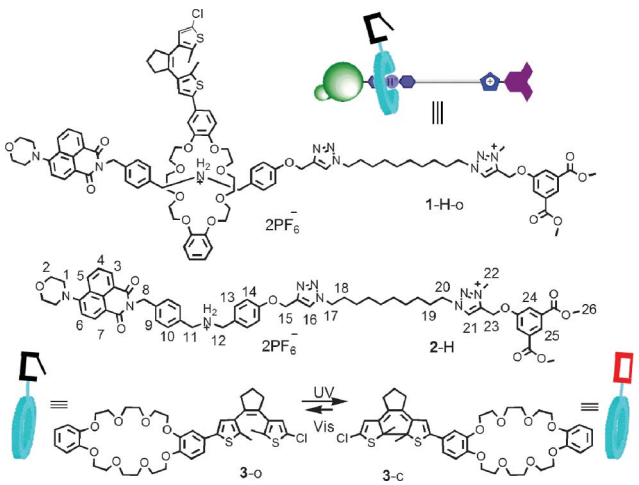

Fig. 1 The chemical structures of a photochromic rotaxane **1**-H-o, a dumbbell-shaped thread component **2**-H, dithienylethene-containing crown ether **3**-o and its photo-induced reversible interconversions between the ring-opened form (**3**-o) and the ring-closed form (**3**-c).

Results and discussion

Molecular design and syntheses

The chemical structures of the multi-state [2]rotaxane **1**-H-o, along with its dumbbell-shaped thread component **2**-H and

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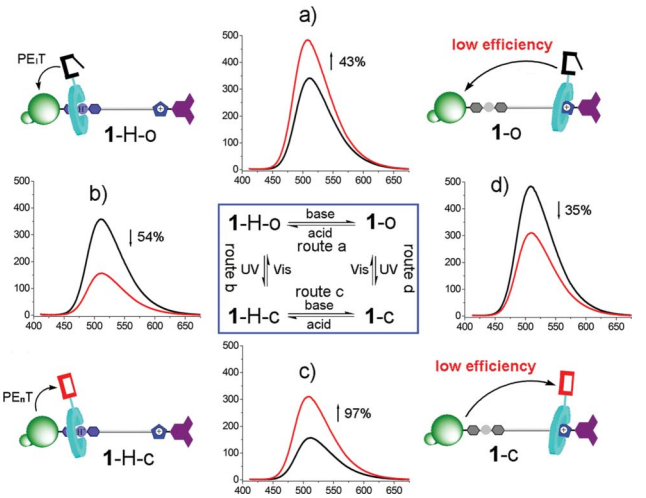

Scheme 1 Schematic representations and interconversions between the four states of rotaxane **1**-H-o, and the fluorescence spectral changes for rotaxane **1**-H-o in response to different combinations of chemical and photochemical stimuli. The fluorescence spectral changes a, b, c, d correspond to routes a, b, c, d, respectively.

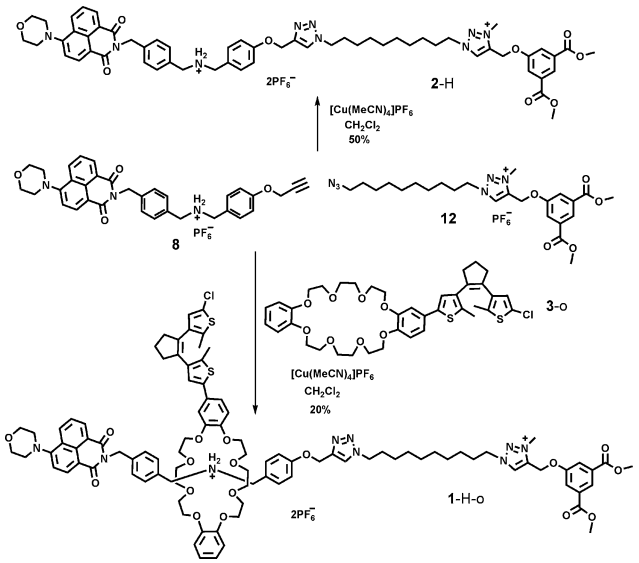

Fig. 2 Preparation of compound **2**-H and [2]rotaxane **1**-H-o.

dithienylcyclopentene-containing crown-ether **3**-o are shown in Fig. 1. Rotaxane **1**-H-o has several key features: a photochromic dithienylethene (DTE) unit was incorporated into a dibenzo-24-crown-8 ring (DB24C8) that was interlocked onto a dumbbell-shaped thread component **2**-H, bearing a 4-morpholin-naphthalimide (MA) fluorescent stopper situated at one end. Two distinguishable binding sites for DB24C8, namely dibenzylammonium (DBA)[9] and *N*-methyltriazolium (MTA)[10] recognition sites, were separated by a long-distance alkyl chain. 4-Morpholin-naphthalimide unit was chosen as a fluorescent stopper situated at one end of the thread because of its high photostability, high fluorescent quantum yield, and desirable spectroscopic properties. A mono-chloride substituted perhydrodithienylcyclopentene unit, covalently attached to a 24-crown-8 macrocycle ring, was chosen as the photochromic unit. The interaction between secondary dialkylammonium ions ($R_2NH_2^+$) and dibenzo-24-crown-8 (DB24C8) ring has been chosen as the binding motifs in our design. An 1,2,3-triazolium receptor, namely the *N*-methyltriazolium moiety, was selected as a less favorable recognition site for DB24C8 upon the deprotonation of a more favorable $R_2NH_2^+$ binding site. The well-known Cu(I)-catalyzed azide-alkyne cycloaddition, also called "click chemistry" was chosen as the stoppering strategy of rotaxane preparation due to its high efficiency and functional group tolerance.

The syntheses of the [2]rotaxanes **1**-H-o, the thread component **2**-H, dithienylcyclopentene-containing crown-ether **3**-o and the key intermediates involved in the preparation of the rotaxane system are outlined in Fig. 2, Scheme S1 and S2 (supporting information†) and described in detail in the experimental section. As shown in Scheme S1, the alkyne **8**, incorporating a DBA unit as a primary recognition site for DB24C8 in the middle of the chain, terminated at one end by a 4-morpholin-naphthalimide fluorescent stopper, and at the other by a terminal alkyne group, was obtained in high yield in three steps, starting from the known compounds **4**, **5**, and **7**. The azide **12**, containing a *N*-methyltriazolium moiety as a secondary recognition site for DB24C8, was terminated at one end by a dimethyl 5-hydroxyisophthalate stopper, and at the other end by an azide functional group. Compound **12** was obtained in high yield in two steps, starting from the known compounds **9** and **10**, as shown in Scheme S1.

The synthesis of the key macrocycle ring, dithienylcyclopentene-containing crown ether **3**-o, was illustrated in Scheme S2.† Bischlorodithienylcyclopentene **13** was treated with one equivalent *n*-butyl lithium to yield dithienylcyclopentene monoboronic acid dimethyl ester, followed by a Suzuki coupling with 4-bromo-dibenzo-24-crown-8 **14** to afford **3**-o in a moderate yield. As shown in Scheme 1, alkyne **8** and crown ether **3**-o was mixed in dry CH_2Cl_2 at room temperature, after which azide **12** and $Cu(CH_3CN)_4PF_6$ catalyst were added to the solution, and the mixture was stirred for two days to form the rotaxanes **1**-H-o in 20% isolated yield. The thread component **2**-H was prepared in 50% isolated yield under the same conditions as for the preparation of rotaxane **1**-H-o in the absence of macrocycle ring **3**-o. Rotaxane **1**-H-o and thread compound **2**-H were well characterized using ^{1}H NMR, ^{13}C NMR and HR-ESI mass spectrometry. The HR-ESI mass spectrum revealed that the most intense peak occurred at *m*/*z* 887.3704 as a doubly charged peak for rotaxane **1**-H-o, with an isotope distribution corresponding to the consecutive loss of two PF_6^- counterions, *i.e.* $[M - 2PF_6]^{2+}$.

^{1}H NMR measurements

The ^{1}H NMR of **1**-H-o in CD_3COCD_3 confirmed the location of the macrocycle to be predominantly over the DBA binding site. As shown in Fig. 3a and 3b, the peak for the methylene protons H_8 neighbouring to the naphthalimide fluorescent stopper become split, and the peak for the methylene protons H_{11}, H_{12} on the DBA recognition station are shifted downfield with a $\Delta\delta$ of 0.16 compared with the one of dumbbell **2**-H. Moreover, the protons (H_{21}, H_{22}, H_{23}) on the unencircled *N*-methyltriazolium unit have the same chemical shifts as the ones on dumbbell **2**-H, proving the fact that the DB24C8 ring exhibit a predominant

Table 1 Excitation wavelength (λ_{ex}), monitoring wavelength (λ_{em}), fluorescence lifetime (τ), and relative emission intensity (I_r) of **2**-H and **1**-H-o obtained from the time-resolved fluorescence measurement in dichloromethane solution

	λ_{ex} (nm)	λ_{em} (nm)	τ (ns)	I_r[a]
2-H	398	513	8.96	0.87
2-H + DBU	395	510	8.27	0.85
1-H-o	398	512	8.15 (78.21%), 4.38 (21.79%)	0.63
1-H-o + DBU (**1**-o)	396	510	8.44	0.90
1-H-o at PSS (**1**-H-c)	398	511	8.72 (90.70%), 3.47 (9.30%)	0.30
1-H-o + DBU at PSS (**1**-c)	398	510	8.34	0.59

[a] The relative emission intensity (I_r) was calculated using a reference compound, namely *N*-ethyl-4-morpholin-naphthalimide, whose emission intensity in a dichloromethane solution at a concentration of 1.0×10^{-5} M was defined as 1.

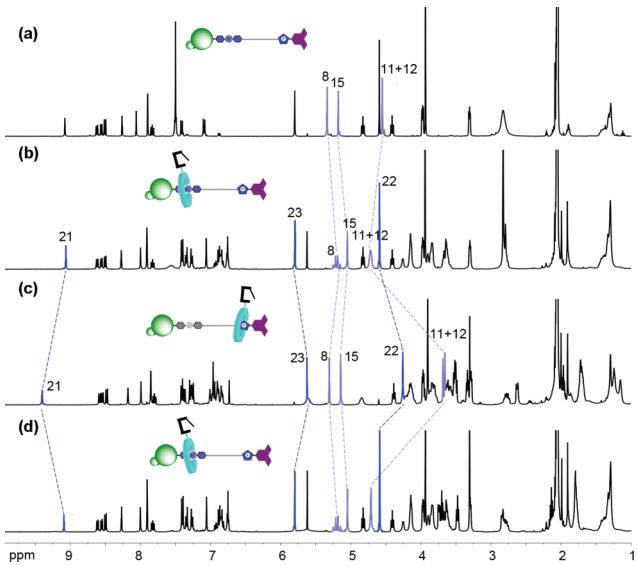

Fig. 3 ^{1}H NMR spectra (400 MHz, CD_3COCD_3, 298 K) of (a) thread **2**-H, (b) [2]rotaxane **1**-H-o, (c) deprotonation with addition of 1.2 eq. of DBU to sample b, (d) reprotonation with addition of 1.4 eq. of TFA to sample c. The assignments corresponding to the structures were shown in Fig. 1.

selectivity for the encirclement of the DBA ($R_2NH_2^+$) recognition site.

Addition of 1.2 eq. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) resulted in the migration of the DB24C8 ring to the *N*-methyltriazolium recognition site (Fig. 3c), generating **1**-o (shown in Scheme 1). The methylene protons H_{11} and H_{12} in the DBA station are shifted upfield with a $\Delta\delta$ of −1.05 ppm. The peaks for the *N*-methyltriazolium protons are shifted due to association with the DB24C8 ring, for H_{21} with a $\Delta\delta$ of 0.34 ppm and H_{22}, H_{23} with $\Delta\delta$ of −0.33, −0.17 ppm, respectively. Moreover, the peak for the methylene protons H_8 becomes singlet relative to the original multiplet because of the migration of the DB24C8 ring from the DBA recognition station to the *N*-methyltriazolium station. Reprotonation of the -NH- center with the addition of 1.4 eq. of CF_3CO_2H resulted in the return of the DB24C8 ring to the DBA recognition station as evidenced by the regeneration of the original ^{1}H NMR spectrum (Fig. 3d). Thus, by ^{1}H NMR spectroscopic measurements, chemically driven reversible shuttling motion of the [2]rotaxane **1**-H-o has been demonstrated.

The photophysical properties of 1-H-o, 2-H and 3-o

The physical properties of dithienylethene-containing crown ether **3**-o and the dumbbell **2**-H were investigated. Irradiation of a dichloromethane solution containing **3**-o with 254 nm resulted in an immediate decrease in the intensity of the absorption band at around 300 nm corresponding to the disappearance of the ring-opened isomer **3**-o along with a concomitant increase in an absorption band at 450–600 nm (Figure S3†), corresponding to the appearance of the ring-closed isomer **3**-c (Fig. 1). A clear isosbestic point was observed around 335 nm, indicating a unimolecular process. The generated red **3**-c solution returns to colorless **3**-o upon irradiation with visible light (> 450 nm). Compound **2**-H showed an absorption band with λ_{max} at 398 nm and a strong emission band with λ_{em} at 511 nm (Figure S4†). The decay profile of dumbbell **2**-H was a single exponential with a lifetime of 8.96 ns (Table 1), typical of MA fluorophore. Upon addition of 5 eq. DBU, which can deprotonate the ammonium center to a secondary amine group, a small spectral change was observed. Moreover, as shown in Table 1, the fluorescence lifetime of compound **2**-H upon addition of 5 eq. DBU almost hardly changes. It is reasonable because deprotonation of the ammonium center does not affect the fluorescent moiety and the efficiency of the PE_IT process from the free amine to the fluorescent moiety is extremely low in this case.[11,12] This also helps to study the photophysical properties of the [2]rotaxane **1**-H-o.

Next we focused on the physical properties of the [2]rotaxane **1**-H-o in response to chemical and photochemical stimuli. As shown in Scheme 1, starting from **1**-H-o, addition of excess DBU can drive the functionalized macrocycle shuttling to the *N*-methyltriazolium recognition station, generating **1**-o (route a), followed by irradiation at 254 nm to reach the photostationary state (PSS) to give **1**-c (route d), in which the DTE unit is in its ring-closed form; starting from **1**-H-o, irradiation at 254 nm results in the formation of **1**-H-c (route b), which was treated by addition of excess DBU to yield **1**-c (route d). Each route was characterized by time-resolved fluorescence spectroscopy and UV/Vis absorption spectroscopy, as discussed below.

The emission intensity of the rotaxane **1**-H-o is around 72% of that of the dumbbell **2**-H, and the time-resolved fluorescence of **1**-H-o showed a bi-exponential decay with lifetimes of 8.15 ns (78.21%) and 4.38 ns (21.79%) compared with the mono-exponential decay of dumbbell **2**-H, which is attributed to photoinduced electron transfer process (PE_IT) from the opened-form DTE photochrome to the excited state of 4-morpholin-naphthalimide fluorophore. The HOMO and LUMO values of the

fluorophore, *N*-ethyl-4-morpholin-naphthalimide, was calculated as −5.66 eV and −2.12 eV, respectively. The HOMO and LUMO values of ring-opened **3**-o, was calculated as −5.05 eV and −0.77 eV, respectively. The HOMO values of the two functional units further showed it is possible that an electron from the HOMO of the opened-form photochrome was transferred to the vacancy in the HOMO of the excited 4-morpholin-naphthalimide fluorophore, and this PE_IT process partially quenched the fluorescence of the 4-morpholin-naphthalimide moiety. After addition of 5 eq. DBU to convert **1**-H-o to **1**-o (route a in Scheme 1), the emission intensity increased 43% (Scheme 1a) and became the same value as that of dumbbell **2**-H. Moreover, time-resolved fluorescence of **1**-o exhibited a mono-exponential decay with lifetime of 8.44 ns, further proving the distance-dependent PE_IT is eliminated because of the large distance between the two functional units. Irradiating **1**-o at 254 nm to reach the PSS containing **1**-c (route d in Scheme 1), the emission intensity decreased 35% (d in Scheme 1), due to less efficient photoinduced energy transfer process (PE_nT) between naphthalimide and ring-closed DTE moieties in **1**-c.

Upon irradiation of rotaxane **1**-H-o at 254 nm (route b in Scheme 1), generating **1**-H-c, the emission intensity decreased 54% at the PSS (b in Scheme 1), indicating a conversion of an efficient PE_IT process to an efficient PE_nT process, which occurred between the excited naphthalimide fluorophore and closed-form DTE unit.[12,13] To this PSS solution, 5 eq. DBU was added to generate **1**-c, in which the closed-form dithienylethene-containing macrocycle was encircled on the *N*-methyltriazolium station (route c in Scheme 1). The emission intensity increased 97% compared to that of the PSS mixture (c in Scheme 1), and the time-resolved fluorescence became a mono-exponential decay with a lifetime of 8.34 ns from the original bi-exponential decay, both of which indicate an conversion of an efficient PE_nT process to a less efficient PE_nT process between the functional units. It should be mentioned that the two strategies to generate **1**-c, namely routes a + d and routes b + c (Scheme 1), gave the same UV/Vis absorption and fluorescence spectra, indicating the same mixture ratio at the photostationary states of both strategies.

UV/Vis absorption spectroscopy was also employed to investigate the photochromic properties of **1**-H-o and **1**-o, in which the dithienylethene-containing crown ether **3**-o was located at two different recognition stations, namely, the DBA site and the MTA site, respectively. As shown in Fig. 4, new absorption bands at 450–600 nm arose upon irradiation of the **1**-H-o and **1**-o solutions at 254 nm, indicative of the appearance of ring-closed DTE units in **1**-H-c and **1**-c, respectively. However, as shown in Fig. 4a (insert), an additional peak at around 580–700 nm was observed during the photoisomerization process of **1**-H-o, compared with that of **1**-o, which might be attributed to the intercomponent charge transfer interaction between the electron-deficient naphthalimide unit and the electron-rich closed-form dithienylethene unit. Addition of 5 eq. DBU can drive the closed-form DTE photochrome shuttling to the *N*-methyltriazolium station and eliminated the intercomponent charge transfer interaction, evident from disapearance of the absorption band at 580–700 nm (Figure S5†). Irradiation of either macrocycle **3**-o (Figure S3†), rotaxane **1**-o (Fig. 4b), or a mixture of **3**-o and **2**-H (Figure S6†) could not result in the formation of the absorption band at 580-700 nm, further proving there is an intercomponent charge transfer between the two functional units in rotaxane **1**-H-c. The photochemical conversions of both **1**-H-o and **1**-o are reversible, which are similar to the photochemical process of **3**-o.

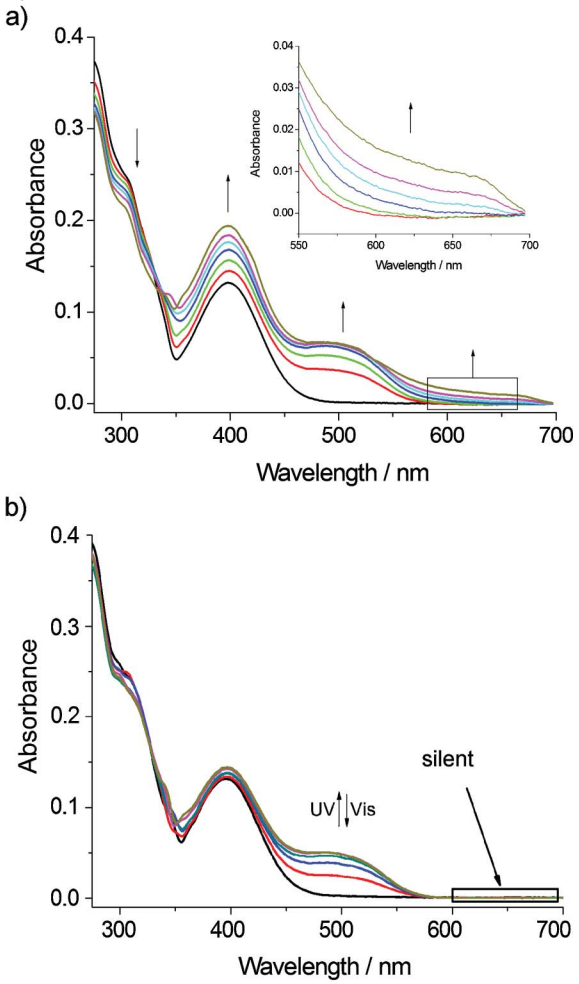

Fig. 4 UV/Vis spectra of [2]rotaxane **1**-H-o in CH_2Cl_2 (1×10^{-5} M) at room temperature, a) upon irradiation at 254 nm for 210 s to reach the PSS. Insert: enlargement of the spectra in the band of 550–700 nm; b) upon irradiation at 254 nm for 210 s to reach the PSS in the presence of 5 eq. DBU.

Experimental

General

^{1}H NMR and ^{13}C NMR spectra were measured on a Brüker AV-400 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on a LCT Premier XE mass spectrometer. The UV-Vis absorption spectra and fluorescence spectra were obtained on a Varian Cary 100 spectrometer and a Varian Cary Eclipse (1 cm quartz cell used), respectively. The fluorescence lifetime measurements were performed by using the time correlated single photon counting (TCSPC) technique following excitation by a nanosecond flash lamp (Edinburgh instruments FL920). The photoirradiation was carried out by a CHF-XM 500-W high-pressure mercury lamp in a sealed Ar-saturated 1 cm quartz cell. The distance between the lamp and the sample cell was 20 cm. Photostationary states were ensured by monitoring composition changes in time by taking UV spectra at distinct intervals until

no changes were observed. The fluorescence intensity of all compounds that contain 4-morpholin-naphthalimide was normalized.

Material

Chemicals were used as received from Acros, Aldrich, Fluka, or Merck. All solvents were reagent grade, which were dried and distilled prior to use according to standard procedures. The molecular structures were confirmed using ^{1}H NMR, ^{13}C NMR and high-resolution ESI mass spectroscopy. The syntheses of compounds **4**, **7**, **9**, **10**, **13** and **14** are described in the supporting information.†

Synthesis of compound 8

A mixture of compound **6** (0.2 g, 0.43 mmol), 4-(2-propynyloxy)benzylamine **7** (0.35 g, 2.15 mmol), K_2CO_3 (0.12 g, 0.86 mmol) in acetonitrile (15 ml) was stirred under reflux for 12 h. After the reaction mixture had been cooled to room temperature, the solvent was removed under reduced pressure. The residue was purified using column chromatography (SiO_2, CH_2Cl_2–MeOH = 30/1) to give a yellow solid. The yellow solid (0.19 g, 0.35 mmol) was dissolved in MeOH (20 ml), and HCl (6 M, 2 ml) was added. After stirring for a few minutes, the solvent was removed under reduced pressure. The residue was dissolved in MeOH (20 ml), followed by the addition of saturated NH_4PF_6 solution. After the mixture was stirred for 2 h, the mixture was extracted with CH_2Cl_2 (3 × 20 ml). The combined organic layer was evaporated, and the residue was purified using column chromatography (SiO_2, CH_2Cl_2–MeOH = 30/1) to give **8** (0.12 g, 50%) as a yellow powder. ^{1}H NMR (CD_3COCD_3, 400 MHz, 298 K): δ 8.59 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 7.2 Hz, 1H), 8.48 (d, J = 8.0 Hz, 1H), 7.81 (dd, J = 8.4 Hz, 7.3 Hz, 1H), 7.49 (br d, J = 7.2 Hz, 6H), 7.39 (d, J = 8.4 Hz, 1H), 7.03 (m, 2H), 5.32 (s, 2H), 4.80 (d, J = 2.4 Hz, 2H), 4.46 (d, J = 4.0 Hz, 4H), 3.97 (t, J = 4.4 Hz, 4H), 3.29 (t, J = 4.4 Hz, 4H), 3.10 (t, J = 2.4 Hz, 1H). ^{13}C NMR (CD_3COCD_3, 100 MHz, 298 K): δ 164.8, 164.2, 159.3, 157.1, 140.3, 133.3, 132.4, 131.8, 131.7, 130.9, 130.6, 129.4, 127.0, 126.9, 125.6, 124.0, 117.4, 116.1, 116.0, 79.5, 77.2, 67.4, 56.3, 54.3, 52.2, 43.5. HRMS (ESI) (m/z): $[M - PF_6]^+$ calcd for $C_{34}H_{32}N_3O_4$, 546.2393; found, 546.2388.

Synthesis of compound 12

A solution of **11** (1 g, 2.12 mmol) in CH_3I (15 ml) was stirred at 40 °C for 12 h. The reaction mixture was cooled to room temperature, and CH_3I was evaporated off *in vacuo*. The residue was dissolved in MeOH (15 ml), followed by the addition of a saturated NH_4PF_6 solution. After the mixture was stirred for 2 h, the mixture was extracted with CH_2Cl_2 (3 × 20 ml). The combined organic layer was evaporated, and the residue was purified using column chromatography (SiO_2, CH_2Cl_2–MeOH = 100/1) to give **12** (1.07 g, 80%) as a white powder. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.52 (s, 1H), 8.28 (s, 1H), 7.77 (s, 2H), 5.39 (s, 2H), 4.54 (t, J = 7.4 Hz, 2H), 4.34 (s, 3H), 3.91 (s, 6H), 3.25 (t, J = 6.8 Hz, 2H), 2.01 (m, 2H), 1.58 (m, 2H), 1.28 (br, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 165.5, 156.8, 139.1, 132.3, 129.9, 124.7, 119.7, 58.1, 54.4, 52.6, 51.4, 38.6, 29.2, 29.1, 29.1, 29.0, 28.8, 28.7, 26.6, 26.0. HRMS (ESI) (m/z): $[M - PF_6]^+$ calcd for $C_{24}H_{35}N_6O_5$, 487.2669; found, 487.2671.

Synthesis of compound 3-o

To the solution of 1,2-bis(5-chloro-2-methylthien-3-yl) cyclopentene **13** (0.50 g, 1.52 mmol) in anhydrous THF (10 ml), *n*-BuLi (0.5 ml of 2.5 M solution in hexane, 1.6 mmol) was added using a syringe in two portions under nitrogen at –78 °C and then stirred for 1 h. After tri-*n*-butyl borate (98%, 0.5 ml, 1.6 mmol) was added, the reddish solution was stirred for 8 h at room temperature. A mixture of 4-bromo-dibenzo-24-crown-8 **14** (0.8 g, 1.52 mmol) and $Pd(PPh_3)_4$ (0.10 g) was stirred in THF (10 ml) for 15 min at room temperature. Then aqueous Na_2CO_3 (10 ml, 2 M) was added. The reactive mixture was stirred at 50 °C, and the reddish solution of BTE-containing boronic acid dibutyl ester was added dropwise using a syringe. Subsequently, the mixture was refluxed for 24 h and cooled to room temperature. The reactive mixture was poured into H_2O and extracted with CH_2Cl_2 and dried with anhydrous Na_2SO_4. The residue was purified using column chromatography (SiO_2, CH_2Cl_2–MeOH = 50/1) to give compound **3**-o (0.3 g, 28%). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.20–7.10 (m, 2H), 7.10–7.02 (m, 5H), 6.89 (s, 1H), 6.63 (s, 1H), 4.35–4.27 (m, 8H), 3.83–3.76 (m, 8H), 3.67–3.60 (d, J = 4.9 Hz, 8H), 2.82 (t, J = 7.2 Hz, 2H), 2.74 (t, J = 7.3 Hz, 2H), 2.10–2.03 (m, 2H), 2.02 (s, 3H), 1.77 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): 148.28, 148.05, 138.40, 136.45, 135.36, 135.25, 134.56, 133.97, 133.33, 126.92, 124.83, 124.12, 123.63, 120.62, 117.16, 116.78, 116.70, 113.82, 77.34, 77.02, 76.71, 38.24, 22.93. HRMS (ESI) (m/z): $[M + Na]^+$ calcd for $C_{39}H_{45}ClNaO_8S_2$, 763.2142; found, 763.2140.

Preparation of dumbbell 2-H

A mixture of **8** (20 mg, 0.03 mmol), **12** (37.9 mg, 0.06 mmol), and $Cu(CH_3CN)_4PF_6$ (11.2 mg, 0.03 mmol) was stirred in dry CH_2Cl_2 (1 mL) at room temperature for two days. After removal of the solvent, the residue was purified using column chromatography (SiO_2, CH_2Cl_2–MeOH = 15/1) to give compound **2**-H (33.7 mg, 50%) as a yellow solid. ^{1}H NMR (CD_3COCD_3, 500 MHz, 298 K): δ 9.10 (s, 1H), 8.63 (d, J = 8.5 Hz, 1H), 8.57 (d, J = 7.5 Hz, 1H), 8.51 (d, J = 8.0 Hz, 1H), 8.27 (s, 1H), 8.07 (s, 1H), 7.90 (s, 2H), 7.84 (t, J = 7.5 Hz, 1H), 7.51 (d, J = 5.5 Hz, 6H), 7.42 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.5 Hz, 2H), 5.81 (s, 2H), 5.34 (s, 2H), 5.18 (s, 2H), 4.84 (t, J = 7.0 Hz, 2H), 4.60 (s, 3H), 4.56 (m, 4H), 4.41 (t, J = 7.3 Hz, 2H), 3.98 (t, J = 4.5 Hz, 4H), 3.94 (s, 6H), 3.31 (t, J = 4.5 Hz, 4H), 2.11 (m, 2H), 1.90 (m, 2H), 1.37 (m, 12H). ^{13}C NMR (CD_3COCD_3, 100 MHz, 298 K): δ 166.0, 164.8, 164.3, 160.4, 158.6, 157.1, 143.8, 140.6, 140.5, 133.3, 133.3, 132.7, 132.6, 131.8, 131.7, 131.1, 131.0, 130.9, 130.7, 129.8, 129.4, 128.7, 127.0, 126.9, 124.6, 124.5, 124.2, 124.0, 122.6, 120.7, 117.4, 116.6, 116.3, 116.1, 116.0, 67.4, 62.4, 59.8, 54.9, 54.3, 52.9, 52.2, 52.1, 50.6, 43.5, 39.3, 31.0, 27.0, 26.6. HRMS (ESI) (m/z): $[M - 2PF_6]^{2+}$ calcd for $C_{58}H_{67}N_9O_9$, 516.7531; found, 516.7522.

Preparation of [2]rotaxane 1-H-o

A mixture of **8** (20 mg, 0.03 mmol) and crown ether **3**-o (44.5 mg, 0.06 mmol) was stirred in dry CH_2Cl_2 (1 mL) at room temperature for 2 h. After **12** (37.9 mg, 0.06 mmol) and $Cu(CH_3CN)_4PF_6$ (11.2 mg, 0.03 mmol) were added to the solution, the mixture was stirred for two days. After removal of the solvent, the residue was purified using column chromatography (SiO_2, CH_2Cl_2–MeOH = 15/1) to give compound **1**-H-o (12.4 mg, 20%) as a yellow solid.

^{1}H NMR (CD_3COCD_3, 400 MHz, 298 K): δ 9.10 (s, 1H), 8.63 (d, J = 8.4 Hz, 1H), 8.56 (d, J = 7.2 Hz, 1H), 8.51 (d, J = 8.0 Hz, 1H), 8.27 (s, 1H), 7.99 (s, 1H), 7.90 (s, 2H), 7.83 (t, J = 7.8 Hz, 1H), 7.41 (dd, J = 8.4 Hz, 4.0 Hz, 3H), 7.34 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.05 (s, 2H), 6.95–6.70 (m, 9H), 5.81 (s, 2H), 5.20 (m, 2H), 5.04 (s, 2H), 4.84 (t, J = 7.2 Hz, 2H), 4.72 (br, 4H), 4.60 (s, 3H), 4.41 (t, J = 7.2 Hz, 2H), 4.26 (m, 2H), 4.19–4.10 (m, 6H), 3.97 (t, J = 4.4 Hz, 4H), 3.94 (s, 6H), 3.90 (m, 2H), 3.88–3.80 (m, 6H), 3.70–3.57 (m, 8H), 3.30 (t, J = 4.4 Hz, 4H), 2.11 (m, 2H), 1.99 (s, 3H), 1.91 (s, 3H), 1.89 (m, 2H), 1.30 (m, 12H). ^{13}C NMR (CD_3COCD_3, 100 MHz, 298 K): δ 166.1, 164.8, 164.3, 160.1, 158.7, 157.1, 148.9, 148.6, 148.6, 148.1, 144.0, 140.8, 140.5, 140.0, 137.4, 136.7, 136.7, 134.7, 134.4, 134.3, 133.4, 131.9, 131.9, 131.8, 130.9, 130.8, 130.4, 129.3, 128.8, 128.3, 127.1, 127.0, 125.5, 125.2, 124.7, 124.6, 124.6, 124.2, 122.2, 122.1, 120.8, 119.0, 117.6, 116.1, 115.7, 113.8, 113.5, 110.6, 71.7, 71.7, 71.3, 71.2, 69.2, 68.9, 67.5, 62.5, 59.9, 55.1, 54.4, 53.1, 53.0, 50.7, 43.6, 39.4, 39.0, 38.8, 31.2, 27.2, 26.7, 23.7, 14.5, 14.4. HRMS (ESI) (m/z): $[M - 2PF_6]^{2+}$ calcd for $C_{97}H_{112}ClN_9O_{17}S_2$, 887.3670; found, 887.3704.

Conclusions

Combining the switching processes performed by rotaxane **1**-H$_o$ in response to different combinations of chemical and photochemical stimuli, it can be summarized that the photochromic DTE unit played a very important role as a controlling unit in this multi-level molecular machine, in which multi-mode alteration of intercomponent interactions can be realized. When the DTE unit is in its open form, the PE_1T process between the open-form DTE unit and the naphthalimide fluorescent unit can be tuned by a chemically driven large-amplitude positional change of the subunit. On the other hand, when the DTE unit is in its closed-form, the PE_nT process and charge transfer interaction between the closed-form DTE unit and the naphthalimide fluorescent unit can be chemically regulated. In conclusion, we have demonstrated reversible multi-mode alteration of intercomponent interactions such as energy transfer, electron transfer, charge transfer *etc.* in a multi-state rotaxane system by taking advantage of UV/Vis absorption spectroscopy and time-resolved fluorescence spectroscopy. Most importantly, we have proved that, by introducing photochromic units to the unique structure of a rotaxane, combination of different tasks (*e.g.* memory with stable photochromic unit) can be realized in a multi-state molecular shuttle, which holds an important potential to construct multi-functional molecular machines.[1,14,15]

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