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A bis-spiropyran-containing multi-state [2]rotaxane with fluorescence output

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ABSTRACT

In this paper, a bis-spiropyran-functionalized [2]rotaxane with a 4-morpholin-naphthalimide fluorophore as stopper was designed, synthesized, and studied. The macrocycle can shuttle reversibly in response to external acid–base stimuli and the spiropyran functional group can be switched to its ring-opened merocyanine (MC) state. It has been shown that, by introducing two spiropyran units into the system, intercomponent interactions, such as electron transfer and energy transfer processes, between the SP or MC functional units and the fluorophore, can be altered in response to the combination of acid–base and photochemical stimuli, which can generate obvious UV/vis absorption and fluorescence spectral changes.

1. Introduction

Over the past few decades, mechanically interlocked molecules,[1] such as rotaxanes and catenanes, have become typical candidates in the design of artificial molecular machines. Bistable rotaxanes,[2] which can change their shapes and properties in response to external stimuli, have important potential to function as molecular switches,[3] molecular logic gates,[4] and stimuli-responsive materials[5] when functional units are introduced into the rotaxane molecule. Various photochemically and electrochemically active units have been introduced into mechanically interlocked rotaxanes to achieve specific functions and to realize intercomponent interactions, such as electron transfer,[6] energy transfer,[7] charge transfer interactions[8] etc., most of them featuring an absorption or fluorescent spectral changes as outputs that can be easily detected. On the other hand, photochromic compounds, such as diarylethenes[9] and spiropyrans,[10] can alter their ability to absorb visible radiation in response to optical stimuli and were exploited as important functional units to modulate the emission of compatible fluorophores, using the 'ON/OFF' properties of the fluorescence to store and/or transfer information in a nondestructive manner. In most cases, the specific fluorophore was covalently linked to the photochromic molecule (or linked to it through a spacer) to form the dyad or the triad, or the macromolecular constructs.[11] However, this modulation has rarely been realized in mechanically interlocked molecular systems.[12] In this paper, we report the design, preparation, characterization, and properties of a bis-spiropyran-containing [2]rotaxane **1**-H-SP, in which intercomponent transfer interactions, can be altered in response to the combination of chemical and photochemical stimuli, along with remarkable UV/vis absorption and fluorescence spectral changes.

2. Results and discussion

2.1. Molecular design and syntheses

The chemical structures and schematic representations of the multistable [2]rotaxane **1**-H-SP, bis-spiropyran-containing crown ether **2**-SP and its reversible photoswitching process, and dumbbell-shaped thread component **3**-H are shown in Scheme 1. [2]Rotaxane **1**-H-SP has several key features: a bis-spiropyran-functionalized dibenzo-24-crown-8 (DB24C8) crown ether macrocycle was interlocked into the rotaxane thread, which contains a long-distance alkyl chain that separates two distinguishable binding sites, namely dibenzylammonium (DBA)[13] and *N*-methyltriazolium (MTA)[2d,14] recognition sites for DB24C8. The stoppers are a 4-morpholin-naphthalimide fluorescent moiety on one side—employed because of its desirable spectroscopic properties—and a 3,5-dimethoxyl benzene stopper group on the other side. The DB24C8 macrocycle has been proved to have a better affinity for the DBA station than for the MTA one, and no affinity at all for the *N*-benzylamine moiety, thus allowing the shuttling movement in response to acid–base stimuli.[15] As shown in Schemes 1 and 2, UV light irradiation of spiropyran (SP) can induce heterolytic cleavage

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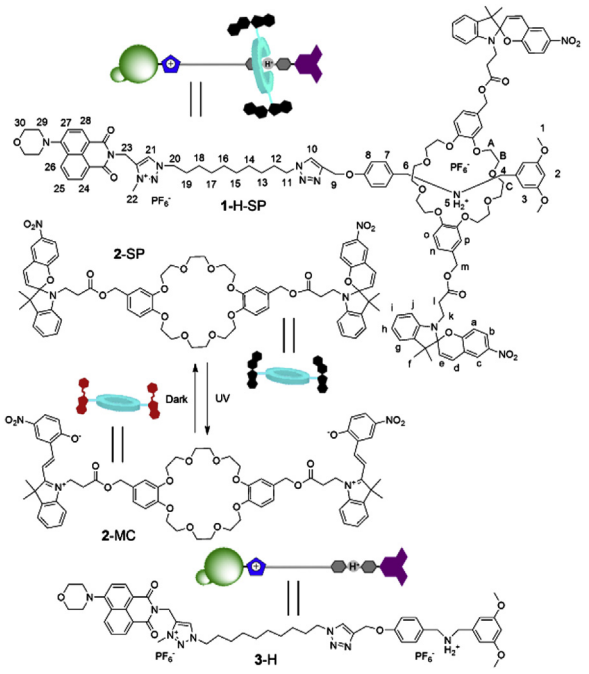
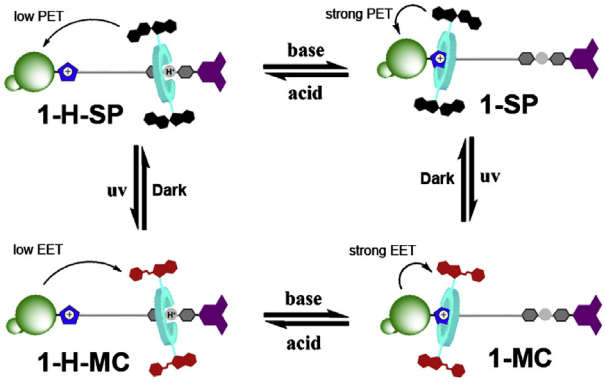


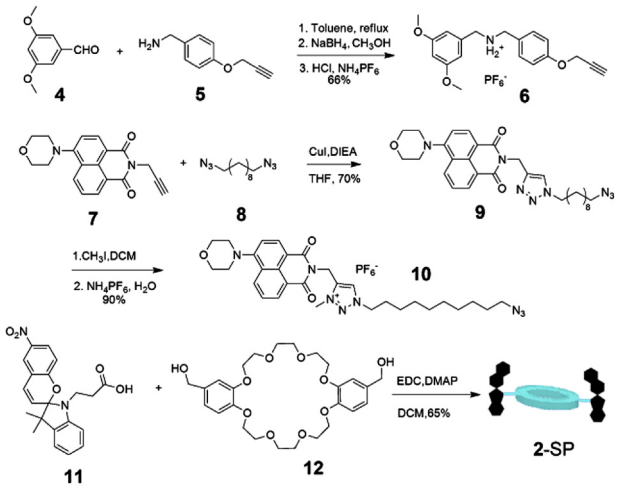
Scheme 1. The chemical structures and schematic representations of a photochromic rotaxane **1**-H-SP, a bis-spiropyran-containing crown ether **2**-SP, and a dumbbell-shaped thread component **3**-H.



Scheme 2. Schematic representations and interconversions between the four states of rotaxane **1**-H-SP in response to different combinations of chemical and photochemical stimuli.

of the spiro carbon–oxygen bond, to generate ring-opened merocyanine (MC) structure. Moreover, the acid–base stimuli can drive the reversible shuttling motion of spiropyran-functionalized DB24C8 macrocycle between two distinguishable stations. On the basis of the facts, the alterations of intercomponent interactions between the functional units, such as photoinduced electron transfer (PET) and electron energy transfer (EET) processes, can be realized in one molecular platform under different stimuli combinations of two external inputs (Scheme 2).

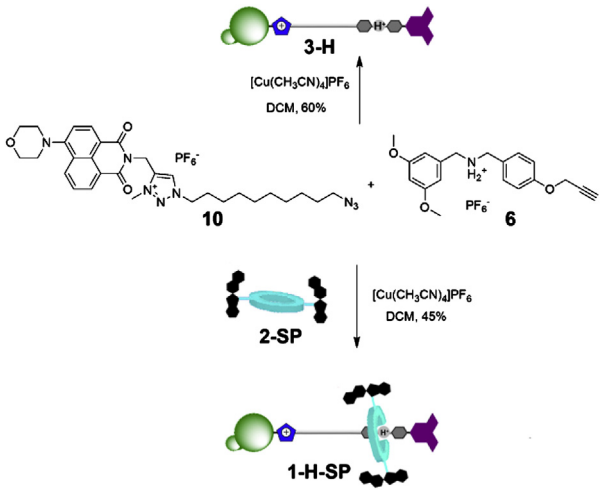
The synthetic route for key intermediates **2**-SP, **6**, and **10** was shown in Scheme 3. As described in Scheme 3, aldehyde **4** and benzylamine **5** were refluxing in toluene, and then the afforded white Schiff base was reduced with $NaBH_4$ in methanol, followed by acidification, and ion exchange to give the alkyne **6** in a 66% yield. The click reaction between the known compounds alkyne **7** and azide **8** gave **9** in a 70% yield, and subsequent methylation and ion exchange with NH_4PF_6 aqueous solution to obtain **10** with a secondary MTA recognition site in a high yield (90%). Bis-spiropyran-containing crown ether **2**-SP was prepared in



Scheme 3. Preparation of compound **6**, **10**, and **2**-SP.

a moderate yield (65%) via the esterification of spiropyran carboxylic acid **11** and benzyl alcohol **12**.

The synthesis of [2]rotaxane **1**-H-SP was illustrated in Scheme 4. Using the copper(I)-catalyzed Huisgen alkyne–azide 1,3-dipolar cycloaddition[16] as the stopping strategy of rotaxane preparation, the target [2]rotaxane **1**-H-SP was successfully obtained. A mixture of alkyne **6** and crown ether **2**-SP in dry CH_2Cl_2 was stirred for 10 min at room temperature, after which azide **10** and $[Cu(CH_3CN)_4]PF_6$ were added to the solution, and the mixture continued to stir for 24 h to form the rotaxane **1**-H-SP in 45% isolated yield. The thread component **3**-H was also prepared as a reference compound in a similar strategy in the absence of crown ether **2**-SP. [2]Rotaxane **1**-H-SP, and the thread component **3**-H were well-characterized by ^1H NMR, ^{13}C NMR spectroscopies and HR-ESI mass spectrometry (Supplementary data). The HR-ESI mass spectra of [2]rotaxane **1**-H-SP and **3**-H gave sharp peaks at *m/z* 1052.4816 $[M-2PF_6]^{2+}$ and 435.7376 $[M-2PF_6]^{2+}$, respectively, in excellent agreement with the calculated value (1052.4810 and 435.7373, respectively).



Scheme 4. Preparation of compound **3**-H and [2]rotaxane **1**-H-SP.

2.2. ^1H NMR measurements

The direct comparison of ^1H NMR spectra (Fig. 1) of crown ether **2**-SP, [2]rotaxane **1**-H-SP, and thread component **3**-H in $CDCl_3$

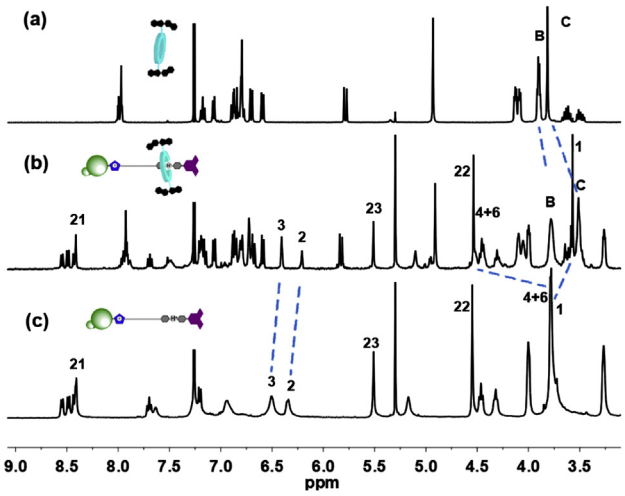


Fig. 1. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (a) crown ether **2**-SP, (b) [2]rotaxane **1**-H-SP, (c) thread component **3**-H. The assignments correspond to the structures as shown in Scheme 1.

indicates the localization of the DB24C8 at DBA station. As shown in Fig. 1, the methylene protons H_4 and H_6 in the DBA station of the rotaxane (Fig. 1b) were shifted downfield ($\Delta\delta$=0.69 ppm) compared with those of dumbbell **3**-H (Fig. 1c), meanwhile, the peaks of protons H_1, H_2, H_3 on the dimethoxybenzene stopper shifted upfield ($\Delta\delta$=−0.20, −0.16, and −0.11 ppm, respectively) due to the shielding effect of macrocycle **2**-SP. Moreover, the protons (H_{21}, H_{22}, H_{23}) on the MTA unit have the same chemical shifts as the ones on dumbbell **3**-H, and the peaks of protons H_B, H_C on the DB24C8 experienced upfield shift ($\Delta\delta$=−0.12, −0.29 ppm, respectively) compared with the ones of macrocycle **2**-SP (Fig. 1a) due to a combination of [N–H···O] and [C–H···O] hydrogen bonds. All this evidence proved the fact that the DB24C8 ring exhibited a predominant selectivity for the encirclement of the DBA recognition site.

It has been reported that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is strong enough to deprotonate the NH_2^+ center.[15] Addition of 1.1 equiv DBU resulted in the moving of the DB24C8 toward the MTA recognition site, generating **1**-SP (shown in Scheme 2). The peaks for the methylene protons H_4, H_6 on the DBA recognition site are shifted upfield (with a $\Delta\delta$ of −0.51 ppm) as a result of both the deprotonation of the neighboring ammonium and the shuttling of the macrocycle (Fig. 2b). Due to association with the DB24C8 ring,

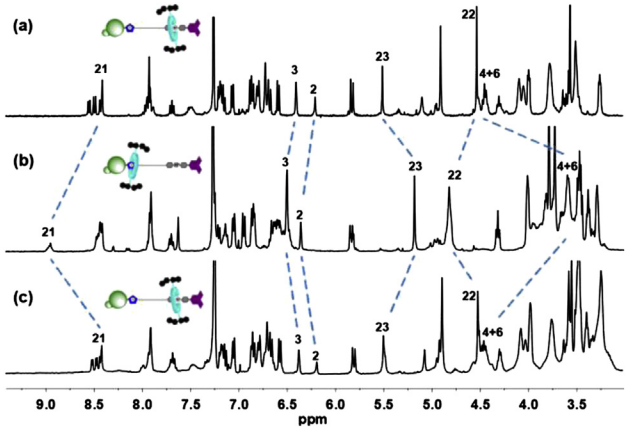


Fig. 2. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (a) [2]rotaxane **1**-H-SP (1×10^{-2} M), (b) deprotonation with addition of 1.1 equiv of DBU to sample a, (c) reprotonation with addition of 1.2 equiv of TFA to sample b.

the peaks for the MTA protons H_{21}, H_{22}, H_{23} were shifted with $\Delta\delta$=0.54, 0.21, and −0.33 ppm, respectively. Moreover, the peaks for the protons H_2, H_3 on the dimethoxybenzene stopper shifted downfield with $\Delta\delta$=0.09 and 0.14 ppm, respectively. The macrocycle shuttled back around the ammonium station upon reprotonation of the amine with the addition of 1.2 equiv CF_3CO_2H, which was evidenced by the regeneration of the original ^{1}H NMR spectrum (Fig. 2c). Thus, using the ^{1}H NMR spectroscopy, the reversible acid–base shuttling motion of the [2]rotaxane **1**-H-SP has been demonstrated.

2.3. The photophysical properties of 1-H-SP, 2-SP, and 3-H

The photophysical properties of bis-spiropyran-containing crown ether **2**-SP and the dumbbell **3**-H were investigated. Irradiation of **2**-SP in dichloromethane solution with 365 nm for 2 min can reach the photostationary state (PSS) and result in an increase in an absorption band at 500–650 nm (Fig. 3a), which indicates the appearance of the ring-opened isomer **2**-MC, with its structure shown in Scheme 1. The system can be recovered to its original SP state and the solution becomes colorless when placed in dark for 5 min.

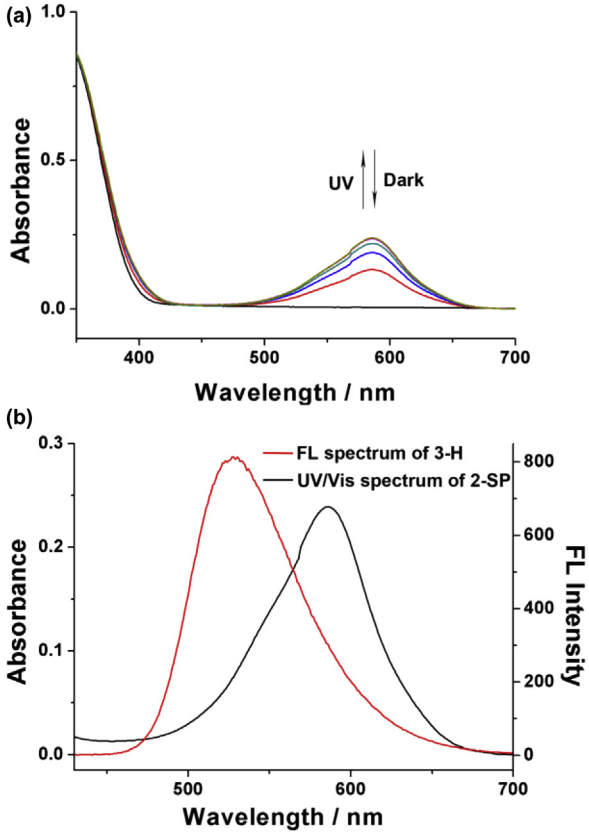
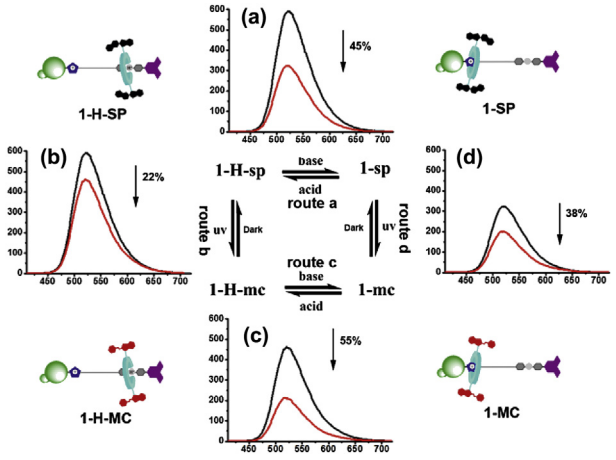


Fig. 3. (a) UV/vis spectral change of compound **2**-SP in CH_2Cl_2 (2×10^{-5} M) at room temperature upon irradiation at 365 nm to reach the PSS. (b) Partial fluorescence spectrum of **3**-H in CH_2Cl_2 (2×10^{-5} M) excited with 410 nm and UV/vis spectrum of **2**-SP in CH_2Cl_2 (2×10^{-5} M) upon irradiation at 365 nm for 2 min to reach the PSS.

The absorption spectrum of compound **3**-H showed an absorption band with λ_{max} at 410 nm and the fluorescence emission displayed a band with λ_{em} at 522 nm when excited at 410 nm (Fig. S1). The absolute fluorescence quantum of dumbbell **3**-H was 0.52, which was hardly changed upon addition of 3 equiv DBU. It is reasonable because the DBA center is far away from the fluorescent stopper and deprotonation of the ammonium center does not affect

the fluorescent moiety. This also helps to study the photophysical properties of the [2]rotaxane **1**-H-SP. It should be noted that there is obvious overlap between the emission spectrum of **3**-H and the absorption spectrum of ring-opened isomer **2**-MC (Fig. 3b), as a result, it is possible that the EET process from the excited MA fluorophore to the **2**-MC moiety could occur, if the two components are sufficiently close to each other.[17]

Then we focused on the physical properties of the [2]rotaxane **1**-H-SP in response to chemical and photochemical stimuli. The emission intensity of the rotaxane **1**-H-SP is around 92% of that of the dumbbell **3**-H, and the absolute fluorescence quantum yield of **1**-H-SP is 0.41, whereas that of **3**-H is 0.52. Presumably, the photoinduced electron transfer from the photochrome to the excited fluorophore is responsible for the decrease in quantum yield. The HOMO and LUMO values of the *N*-ethyl-4-morpholin-naphthalimide fluorophore,[12] were calculated as −5.6 eV and −2.1 eV, respectively, and the HOMO value of SP,[18] reported by several literature as −5.3 eV to −4.7 eV. Therefore, it was possible that an electron from the HOMO of the SP photochrome was transferred to the vacancy in the HOMO of the excited 4-morpholin-naphthalimide fluorophore, which partially quenched the fluorescence of the 4-morpholin-naphthalimide moiety. As shown in Scheme 5, the dichloromethane solution of **1**-H-SP was added of excess DBU, which could induce the shuttling motion of the macrocycle **2**-SP to the MTA recognition station, generating **1**-SP (route a), then irradiated the sample at 365 nm to reach the PSS to give **1**-MC isomer (route d), with the photochromic functional unit in a ring-opened merocyanine state. The other route can also generate **1**-MC. Starting from **1**-H-SP, firstly irradiation at 365 nm resulted in the formation of **1**-H-MC (route b), then followed by addition of excess DBU to the mixture to yield **1**-MC (route c). Each route was characterized using UV/vis absorption and fluorescence emission spectroscopies, as discussed below.



Scheme 5. Schematic representations and interconversions between the four states of rotaxane **1**-H-SP, and the fluorescence spectral changes for rotaxane **1**-H-SP 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. Excitation wavelength was 410 nm.

Starting from **1**-H-SP, upon addition of 1.1 equiv DBU to convert **1**-H-SP to **1**-SP (route a in Scheme 5), the absorption spectrum had no obvious change, however, the emission intensity decreased 45%, meanwhile, the absolute fluorescence quantum yield of **1**-SP dropped to 0.18. This change can be attributed to an efficient PET process from two SP photochromic groups to the excited state of 4-morpholin-naphthalimide fluorophore. Irradiation at 365 nm could convert **1**-SP into **1**-MC (route d in Scheme 5), and resulted in a new absorption band at 500–650 nm corresponding to the generation of ring-opened MC units **1**-MC. The emission intensity of 1-MC decreased 38% (d in Scheme 5), and the absolute fluorescence quantum yield was 0.09. Indeed, the MC component can activate an EET process and lead to a partial fluorescence quenching. Nonetheless, the emission spectrum of **1**-MC does not show the characteristic fluorescence of **2**-MC at 643 nm (Fig. S2). The lack of sensitized fluorescence suggests that the transfer of energy from the excited fluorophore to the MC photochrome is not particularly efficient. In fact, the HOMO value of MC,[18] reported as −5.4 eV to −4.5 eV, indicating that the photoinduced transfer of one electron from the photochrome to the excited fluorophore is exoergonic. Presumably, both of the electron transfer process and energy transfer pathway contribute to the nonradiative deactivation of the excited fluorophore.[17]

Restarting from **1**-H-SP, irradiation at 365 nm resulted in the formation of **1**-H-MC, the emission intensity decreased 22% at the PSS (b in Scheme 5), and the absolute fluorescence quantum yield of **1**-H-MC dropped to 0.28, both of which indicate a less efficient PET and EET processes between the two functional units. The less efficient PET and EET processes can be ascribed to the long distance between the naphthalimide fluorophore and opened-form MC units. To this PSS solution, 1.1 equiv DBU was added to generate **1**-MC, in which opened-form merocyanine-containing macrocycle was shuttling to the MTA recognition station (route c in Scheme 5), and the emission intensity decreased 55% compared to that of the PSS mixture (c in Scheme 5). This obvious change was due to an efficient PET and EET processes between the two functional units.

It should be mentioned that the photochemistry of photochromic spiropyran was unaffected by the addition of DBU, as evidenced by nearly the same PSS absorption spectra of **1**-H-SP and **1**-SP (Fig. S3). It should also be noted that the two strategies to generate **1**-MC from **1**-H-SP, namely route a+d and route b+c (Scheme 5), gave almost the same absorption and fluorescence spectra (Fig. 4).

3. Conclusion

In conclusion, a novel [2]rotaxane with two spiropyran photochromic functional groups has been prepared and well-characterized. The rotaxane **1**-H-SP can respond to different combinations of chemical and photochemical stimuli, and displays multiple states with distinguishable fluorescence output. In **1**-H-SP and **1**-SP, the PET process between the SP unit and the naphthalimide fluorescent unit can be tuned by acid–base stimuli. In **1**-H-MC and **1**-MC, both of the PET and EET processes interaction between the MC unit and the naphthalimide fluorescent unit can be chemically regulated. Most importantly, the reversible alteration of intercomponent interactions (such as energy transfer, electron transfer) in a rotaxane system can take advantage of UV/vis absorption spectroscopy and fluorescence emission spectroscopy, which are easy to be detected. This kind of multi-state molecular shuttle holds the potential to construct multi-level molecular machines and complicated logic gates.

4. Experimental

4.1. 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 an 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 photoirradiation was carried on 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

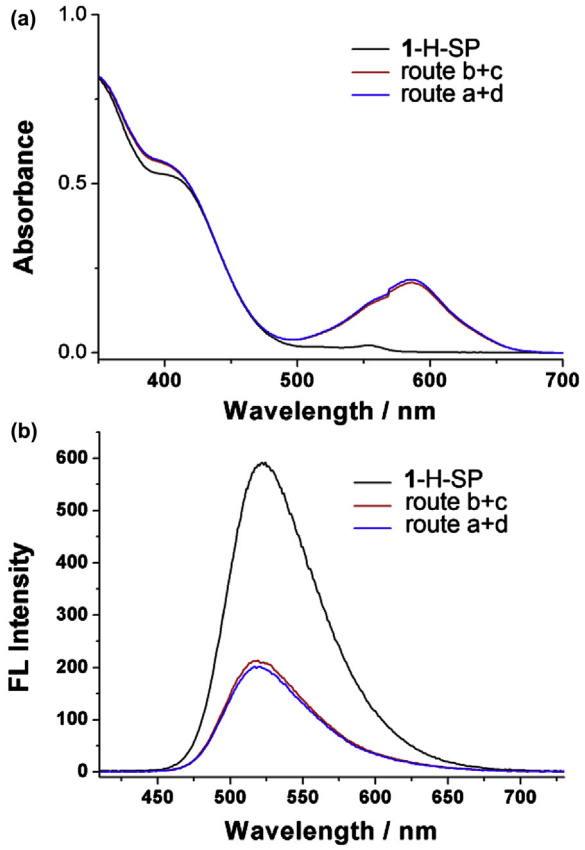


Fig. 4. (a) UV/vis spectral of **1**-H-SP, route a+d and route b+c. (b) Fluorescence spectra of **1**-H-SP, route a+d and route b+c (CH_2Cl_2, 2×10^{-5} M). Excitation wavelength was 410 nm.

monitoring composition changes in time by taking UV spectra at distinct intervals until no changes were observed. The absolute quantum yields of fluorescence were measured by using a Fluoromax-4 fluorescence spectrophotometer equipped with the quantum yield measuring accessory and report generator program.

4.2. Materials

Chemicals were used as received from Acros, Aldrich, Fluka, or Merck. All solvents were in reagent grade, which were dried and distilled prior to use according to standard procedures. The molecular structures were confirmed via ^{1}H NMR, ^{13}C NMR, and high-resolution ESI mass spectroscopy. Compounds **5**,[12] **7**,[19] **8**,[12] **11**,[11b] **12**[6c] were synthesized according to the previous reports.

4.3. Synthesis of compound 6

A mixture of compound **4** (0.4 g, 2.4 mmol) and **5** (0.39 g, 2.4 mmol) was refluxed overnight in toluene (30 mL). The solvent was removed under reduced pressure. The residue was dissolved in methanol, and $NaBH_4$ (0.29 g, 7.2 mmol) was added in small portions under ice-bath. The mixture was stirred at room temperature for a further 6 h. Water was added to quench the excess $NaBH_4$. The mixture was extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4. After concentrating in vacuo, the white solid 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 CH_2Cl_2 (20 mL), followed by the addition of saturated NH_4PF_6 aqueous solution, which resulted in a suspension. The precipitate was collected by suction filtration. Recrystallization from MeOH gave **6** (0.72 g, 66%) as a white solid: mp=160–161 °C. ^{1}H NMR (400 MHz, CD_3SOCD_3, 298 K): δ=9.07 (s, 2H), 7.43 (d, J=8.7 Hz, 2H), 7.06 (d, J=8.7 Hz, 2H), 6.67 (d, J=2.2 Hz, 2H), 6.55 (t, J=2.2 Hz, 1H), 4.84 (d, J=2.3 Hz, 2H), 4.10 (d, J=2.5 Hz, 4H), 3.76 (s, 6H), 3.58 (t, J=2.3 Hz, 1H). ^{13}C NMR (100 MHz, CD_3SOCD_3, 298 K): δ=160.5, 157.6, 133.8, 131.5, 124.3, 114.9, 107.6, 100.4, 79.0, 78.3, 55.3, 49.9, 49.5. HRMS (ESI) (m/z): $[M-PF_6^-]^+$ calcd for $C_{19}H_{22}NO_3$, 312.1600; found, 312.1596.

4.4. Synthesis of compound 9

A mixture of compound **7** (1.00 g, 3.12 mmol), 1,10-decanediazide **8** (1.4 g, 6.3 mmol), CuI (0.12 g, 0.63 mmol), and *N*,*N*-diisopropylethylamine (0.78 g, 6.3 mmol) in anhydrous THF (20 mL) was stirred at room temperature for 12 h under nitrogen atmosphere. The resulting suspension was filtered, and the filtrate was evaporated under reduced pressure. The residue was partitioned in H_2O/CH_2Cl_2. The organic layer was dried over Na_2SO_4 and filtered, and the filtrate was evaporated to dryness. The residue was purified via column chromatography (SiO_2, CH_2Cl_2/petroleum ether=5/1) to give **9** (1.68 g, 70%) as a green solid: mp=109–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ=8.61 (dd, J=7.3, 0.9 Hz, 1H), 8.55 (d, J=8.1 Hz, 1H), 8.42 (dd, J=8.4, 0.9 Hz, 1H), 7.71 (dd, J=8.3, 7.4 Hz, 1H), 7.61 (s, 1H), 7.23 (d, J=8.1 Hz, 1H), 5.50 (s, 2H), 4.27 (t, J=7.3 Hz, 2H), 4.04 (t, J=7.9 Hz, 4H), 3.21–3.29 (m, 6H), 1.80–1.89 (m, 2H), 1.53–1.62 (m, 2H), 1.20–1.37 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ=164.1, 163.6, 155.8, 143.7, 132.8, 131.4, 130.3, 129.9, 126.1, 125.8, 123.0, 116.9, 114.9, 66.9, 53.4, 51.4, 50.2, 35.1, 30.2, 29.2, 29.2, 29.0, 28.9, 28.8, 26.6, 26.4. HRMS (ESI) (m/z): $[M+H]^+$ calcd for $C_{29}H_{37}N_8O_3$, 545.2989; found, 545.2985.

4.5. Synthesis of compound 10

A solution of **9** (1 g, 1.84 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 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 via column chromatography (SiO_2, CH_2Cl_2/MeOH=100/1) to give **10** (1.16 g, 90%) as a green powder: mp=140–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ=8.56 (dd, J=7.3, 0.9 Hz, 1H), 8.50 (d, J=8.1 Hz, 1H), 8.40–8.46 (m, 2H), 7.71 (dd, J=8.3, 7.5 Hz, 1H), 7.22 (d, J=8.2 Hz, 1H), 5.50 (s, 2H), 4.56 (s, 3H), 4.44–4.55 (m, 2H), 3.95–4.08 (m, 4H), 3.15–3.36 (m, 6H), 1.99 (m, 2H), 1.52–1.60 (m, 2H), 1.19–1.42 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ=164.1, 163.5, 156.7, 140.0, 133.5, 131.9, 131.3, 130.8, 130.0, 125.9, 125.9, 122.1, 115.5, 115.0, 66.8, 54.2, 53.4, 51.4, 38.5, 31.8, 29.2, 29.0, 28.9, 28.7, 28.7, 26.6, 26.0. HRMS (ESI) (m/z): $[M-PF_6^-]^+$ calcd for $C_{30}H_{39}N_8O_3$, 559.3145; found, 559.3144.

4.6. Synthesis of compound 3-H

A mixture of **6** (30 mg, 0.04 mmol), **10** (27.4 mg, 0.06 mmol), and $[Cu(CH_3CN)_4]PF_6$ (11.2 mg, 0.03 mmol) was stirred in dry CH_2Cl_2 (1 mL) at room temperature for 24 h. After removal of the solvent, the residue was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH=15/1) to give compound **3**-H (27.8 mg, 60%) as a yellow solid: mp=105–106 °C. ^{1}H NMR (400 MHz, CD_3COCD_3, 298 K): δ=8.90 (s, 1H), 8.64 (dd, J=8.5, 1.0 Hz, 1H), 8.58 (dd, J=7.3, 1.0 Hz, 1H), 8.52 (d, J=8.1 Hz, 1H), 8.08 (s, 1H), 7.85 (dd, J=8.4, 7.4 Hz, 1H), 7.51 (d, J=8.0 Hz, 2H), 7.43 (d, J=8.1 Hz, 1H), 7.11 (d, J=8.2 Hz, 2H), 6.74 (s, 2H), 6.55 (s, 1H), 5.64 (s, 2H), 5.19 (s, 2H), 4.73 (t, J=7.2 Hz,

2H), 4.67 (s, 3H), 4.47 (m, 4H), 4.40 (t, J=7.1 Hz, 2H), 3.94–4.01 (m, 4H), 3.79 (s, 6H), 3.28–3.35 (m, 4H), 1.96–2.04 (m, 2H), 1.84–1.92 (m, 2H), 1.31 (m, 12H). ^{13}C NMR (100 MHz, CD_3COCD_3, 298 K): δ=170.9, 164.8, 164.1, 162.3, 160.4, 159.2, 157.6, 141.1, 140.7, 133.8, 132.5, 132.3, 132.1, 132.0, 130.7, 126.9, 126.8, 123.5, 116.7, 116.0, 116.0, 116.0, 108.5, 101.6, 67.3, 62.4, 55.8, 54.6, 54.3, 50.6, 39.2, 32.7, 30.9, 27.0, 26.5. HRMS (ESI) (m/z): $[M-2PF_6^-]^{2+}$ calcd for $C_{49}H_{61}N_9O_6$, 435.7373; found, 435.7376.

4.7. Synthesis of compound 2-SP

To the mixture of compound **11** (0.20 g, 0.53 mmol) and **12** (0.10 g, 0.21 mmol) in CH_2Cl_2 (100 mL), EDCI (0.12 g, 0.6 mmol) and DMAP (12.05 mg, 0.1 mmol) were added. The mixture was stirred overnight and then washed the mixture with brine (3×50 mL). The organic layer was dried over anhydrous sodium sulfate. The combined organic layer was evaporated, and the residue was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH=200/1) to give **2**-SP (0.17 g, 65%) as a brown powder: mp=75–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ=7.95–8.02 (m, 4H), 7.15–7.21 (m, 2H), 7.07 (d, J=6.5 Hz, 2H), 6.86 (m, 10H), 6.70 (d, J=8.7 Hz, 2H), 6.60 (d, J=7.7 Hz, 2H), 5.79 (d, J=10.4 Hz, 2H), 4.93 (s, 4H), 4.07–4.16 (m, 8H), 3.90 (m, 8H), 3.81 (s, 8H), 3.45–3.82 (m, 4H), 2.53–2.76 (m, 4H), 1.24 (s, 6H), 1.09 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ=171.7, 159.4, 150.7, 150.5, 146.2, 141.0, 136.0, 130.0, 128.3, 127.8, 125.8, 123.1, 122.7, 121.9, 121.9, 119.8, 118.6, 118.5, 117.7, 115.5, 106.8, 106.7, 71.8, 71.7, 71.1, 71.1, 69.8, 69.8, 66.2, 52.8, 39.3, 33.7, 25.7, 19.7. HRMS (ESI) (m/z): $[M+H]^+$ calcd for $C_{68}H_{73}N_4O_{18}$, 1233.4920; found, 1233.4924.

4.8. Synthesis of compound 1-H-SP

A mixture of **6** (20 mg, 0.04 mmol) and crown ether **2**-SP (98.6 mg, 0.08 mmol) was stirred in dry CH_2Cl_2 (1 mL) at room temperature for 2 h. After **10** (28.1 mg, 0.04 mmol) and $[Cu(CH_3CN)_4]PF_6$ (11.2 mg, 0.03 mmol) were added to the solution, the mixture was stirred for 2 days. After removal of the solvent, the residue was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH=15/1) to give compound **1**-H-SP (43 mg, 45%) as a brown solid: mp=135–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ=8.55 (d, J=7.5 Hz, 1H), 8.49 (d, J=8.2 Hz, 1H), 8.43 (m, 2H), 7.85–8.00 (m, 5H), 7.67–7.72 (m, 1H), 7.52 (s, 2H), 7.14–7.23 (m, 5H), 7.07 (d, J=7.4 Hz, 2H), 6.79–6.90 (m, 8H), 6.66–6.76 (m, 6H), 6.59 (d, J=7.7 Hz, 2H), 6.41 (s, 2H), 6.21 (s, 1H), 5.83 (d, J=10.3 Hz, 2H), 5.52 (s, 2H), 5.11 (s, 2H), 4.91 (s, 4H), 4.54 (s, 3H), 4.40–4.53 (m, 6H), 4.31 (m, 2H), 4.08 (m, 8H), 4.01 (d, J=4.2 Hz, 4H), 3.79 (s, 8H), 3.62 (m, 4H), 3.57 (s, 6H), 3.52 (s, 8H), 3.27 (d, J=4.2 Hz, 4H), 2.54–2.82 (m, 4H), 1.96 (m, 6H), 1.31 (m, 10H), 1.24 (s, 6H), 1.10 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 171.7, 164.1, 163.5, 160.8, 159.4, 156.6, 147.4, 147.3, 147.3, 146.2, 140.9, 139.9, 135.9, 133.4, 131.9, 131.2, 130.9, 130.0, 129.0, 128.2, 127.9, 125.9, 125.9, 125.7, 123.5, 122.7, 122.1, 121.9, 121.8, 119.7, 118.6, 115.5, 115.4, 115.0, 114.0, 112.9, 112.3, 106.7, 106.7, 106.6, 100.1, 70.6, 70.1, 68.2, 68.1, 66.8, 66.1, 55.0, 54.1, 53.3, 52.5, 52.2, 52.2, 39.2, 38.5, 33.8, 33.5, 31.9, 31.7, 29.7, 29.6, 29.3, 29.1, 28.9, 28.8, 28.45, 28.5, 28.2, 28.2, 25.7, 25.6, 24.3, 22.6, 19.7, 14.1. HRMS (ESI) (m/z): $[M-2PF_6^-]^{2+}$ calcd for $C_{117}H_{133}N_{13}O_{24}$, 1052.4810; found, 1052.4816.

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Supplementary data

Characterization data; UV/vis absorption and fluorescence spectra, and other materials. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.04.119.

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