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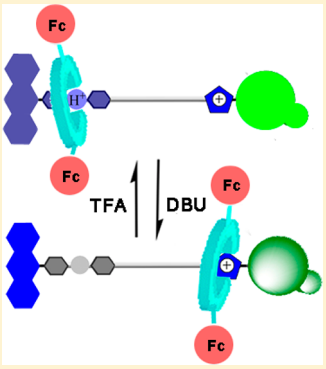
A Ferrocene-Functionalized [2]Rotaxane with Two Fluorophores as Stoppers

Hui Zhang, Bin Zhou, Hong Li, Da-Hui Qu,* and He Tian*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, P. R. China

Supporting Information

ABSTRACT: In the past few decades, bistable [2]rotaxanes have been extensively studied because of their applications in the fields of functional molecules and molecular machines. In this paper, a di-ferrocene-functionalized [2]rotaxane with two fluorophores as stoppers was designed, prepared, and studied. In this bistable [2]rotaxane, a dibenzo-24-crown-8 macrocycle functionalized with two ferrocene moieties as electron donors can reversibly shuttle between two distinct stations, namely, a dialkylammonium recognition site and a *N*-methyltriazolium recognition site, by external acid−base stimuli, which has been demonstrated using ^{1}H NMR spectroscopy. It has been shown that, by introducing two ferrocene units into the macrocycle component, the fluorescence of two fluorescent stoppers, namely, the anthracene fluorophore and the 4-morpholin-naphthalimide fluorophore, can be changed in an alternate mode by an adjustable, distance-dependent photoinduced electron transfer process that occurs between the ferrocene electron donors and each of the two fluorophores.



INTRODUCTION

Mechanically interlocked molecular architectures,[1] in particular rotaxanes and catenanes, have attracted much more attention and become the focus of research in the past few decades, because their components can move reversibly between two or more stations under the influence of various external stimuli and these assemblies are of enormous significance for the construction of nanoscale molecular machines.[2] In all reported rotaxanes, bistable [2]rotaxanes[3] were developed early and extensively studied because of their convenient and efficient synthesis. Moreover, the competitive binding ability of a macrocycle with two distinct, well-separated stations on the dumbbell-shaped component can be easily altered, and the controllable shuttling movement of the macrocycle has been widely employed to mimic machine-like action at a molecular scale. In some cases, the relative movement of the constituent parts of [2]rotaxanes can dramatically change the photophysical or electrical properties of molecules, which makes them the best candidates for the construction of molecular switches or molecular logic gates.[4] To realize this target, the introduction of various functional units into [2]rotaxanes represents a crucial step, by altering intercomponent interactions such as electron transfer,[5,6] energy transfer,[7] and charge transfer[8] interactions occurring in the mechanically interlocked structures, which can achieve specific functions that exhibit as different signal outputs, for example, absorption,[9] fluorescence,[10] and ICD changes.[11] This strategy also provides a possibility to construct more complex and multifunctional molecular platforms that can integrate several functions. In our previous work,[12] we have reported a ferrocene-functionalized [2]rotaxane in which the shuttling motion of the ferrocene-substituted macrocycle along the rotaxane thread can alter the photoinduced electron transfer process between the ferrocene electron donors and the fluorescent stopper, to give a high-contrast fluorescence output. To increase functional complexity and to construct more advanced molecular switches and machines, it is necessary to develop functional rotaxanes with dual fluoresence signal outputs. In this paper, a di-ferrocene-functionalized [2]rotaxane with two fluorophore stoppers was designed, prepared, and studied (Figure 1). By introducing two ferrocene (Fc) moieties as electron donos in the macrocycle, the fluorescence of each fluorescent stopper can be reduced and/or enhanced alternately by a tunable, distance-dependent photoinduced electron transfer (PET) process[13,14] that occurs between the Fc moieties and each of the excited fluorophores, along with remarkable fluorescence intensity changes in response to acid−base stimuli. This kind of dual-fluorescence responsive rotaxane-type molecular shuttle holds the potential to construct multilevel molecular switches with optical signals.[15]

RESULT AND DISCUSSION

Molecular Design and Syntheses. The syntheses, molecular structures, and schematic representation of [2]-rotaxane **1-H** and **2-H**, along with two reference compounds, i.e., dumbbell-shaped thread component **3-H** and ferrocene-containing crown-ether **6**, are shown in Figure 2. The target [2]rotaxane **1-H** contains a di-ferrocene-functionalized dibenzo[24]crown-8 (DB24C8) ring that is interlocked onto a dumbbell-shaped thread component bearing two terminal

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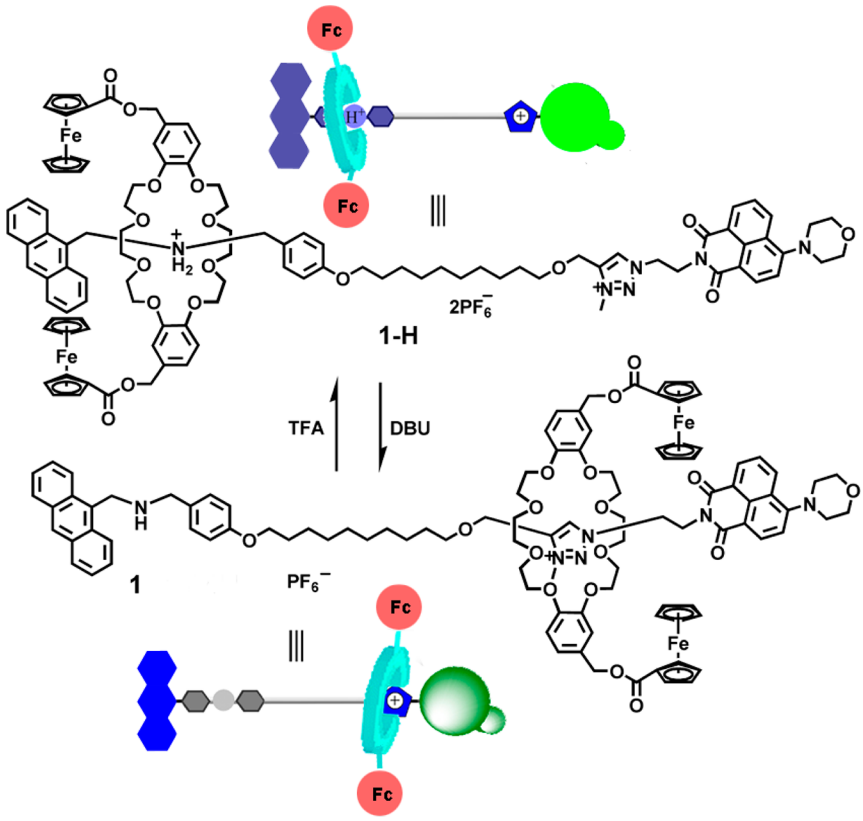

Figure 1. Schematic representation of the shuttling movement in the target rotaxane **1-H**.

fluorescent moieties, namely, 4-morpholin-naphthalimide and anthracene, as stoppers. There are two distinguishable binding sites for DB24C8, namely, dialkylammonium (DAA)[12,16−19] and *N*-methyltriazolium (MTA)[12,20,21] recognition sites. The *N*-methyltriazolium (MTA) moiety was used as a less favorable recognition site for DB24C8 upon the deprotonation of a more favorable $R_2NH_2^+$ binding site, and a long-distance alkyl chain was introduced to the thread skeleton to separate the two distinguishable binding sites. It is envisaged that, in the orginal state, the DB24C8 macrocycle is located in the DAA recognition site, which is closed to the anthracene fluorophore and far away from the 4-morpholin-naphthalimide fluorophore, and the fluorescences of the anthracene and the 4-morpholin-naphthalimide moiety are in relatively weak and strong states, respectively. Deprotonation with base can drive the macrocycle to reside in the *N*-methyltriazolium station (Figure 1). As a result, the fluorescence intensity of anthracene has an obvious increase, while on the contrary, the fluoresence intensity of 4-morpholin-naphthalimide decreases. This kind of system can function as a molecular switch that has two fluorescent signal outputs.

The alkyne **4**, incorporating a DAA unit as a primary recognition site for DB24C8 in the middle, terminated at one end by an anthracene fluorescent stopper and at the other end by a terminal alkyne group, was obtained in a 72% yield, as shown in Figure 2. The azide **5** was terminated at one end by a 4-morpholin-naphthalimide fluorescent stopper and at the other end by an azide functional group. The azide **5** and the key macrocycle ring, ferrocene-containing crown ether **6**, were synthesized according to our previously report.[12] The selective and effective interaction between a dialkylammonium ion ($R_2NH_2^+$) and a dibenzo[24]crown-8 (DB24C8) ring was chosen as the binding motif in the design of the rotaxane. The widely used "click chemistry", namely, Cu(I)-catalyzed azide−alkyne cycloaddition,[22,23] was chosen as the end-capping method in preparation of rotaxane **2-H** due to its functional group tolerance and high yield. As shown in Figure 2, alkyne **4** and crown ether **6** were mixed in dry CH_2Cl_2 at room temperature, after which azide **5** and $Cu(CH_3CN)_4PF_6$ as catalyst were added to the solution, and the mixture was stirred for 2 days to form the rotaxane **2-H** in a 65% isolated yield. The thread component **3-H** was prepared in a 90% isolated yield with the same condition as the preparation of rotaxane **2-H** in the absence of macrocycle **6**. The methylation of the triazole unit in rotaxane **2-H** followed by the anion exchange of the CH_2Cl_2 solution with saturated NH_4PF_6 solution can produce the target rotaxane **1-H** in a 90% yield. Rotaxane **1-H**, **2-H**, and compound **3-H** were well characterized using ^{1}H NMR, ^{13}C NMR, and HR-ESI mass spectrometry (Supporting Information). The reversible shuttling motion of the macrocycle between the two different recognition sites in rotaxane **1-H** was also confirmed by the ^{1}H NMR spectroscopy, as discussed below.

^{1}H NMR Measurements. Comparison of the ^{1}H NMR spectra of rotaxane **2-H** with the that of thread **3-H** reveals the interlocked architecture and the localization of the DB24C8 at the DAA station in rotaxane **2-H**. As shown in Figure 3, the ^{1}H NMR spectrum of **2-H** in $CDCl_3$ has not only all signals that appeared in the ^{1}H NMR spectrum of **3-H** (H_1−H_{25}) but also all of the peaks of protons belonging to the macrocyclic compound **6** (H_a, H_b, H_c, and H_d). Meanwhile, the HR-ESI mass spectrum of the [2]rotaxane **2-H** (Supporting Information) showed the most intense peak emerged at *m*/*z* 1791.6711 as a single charged peak with an isotope distribution that is

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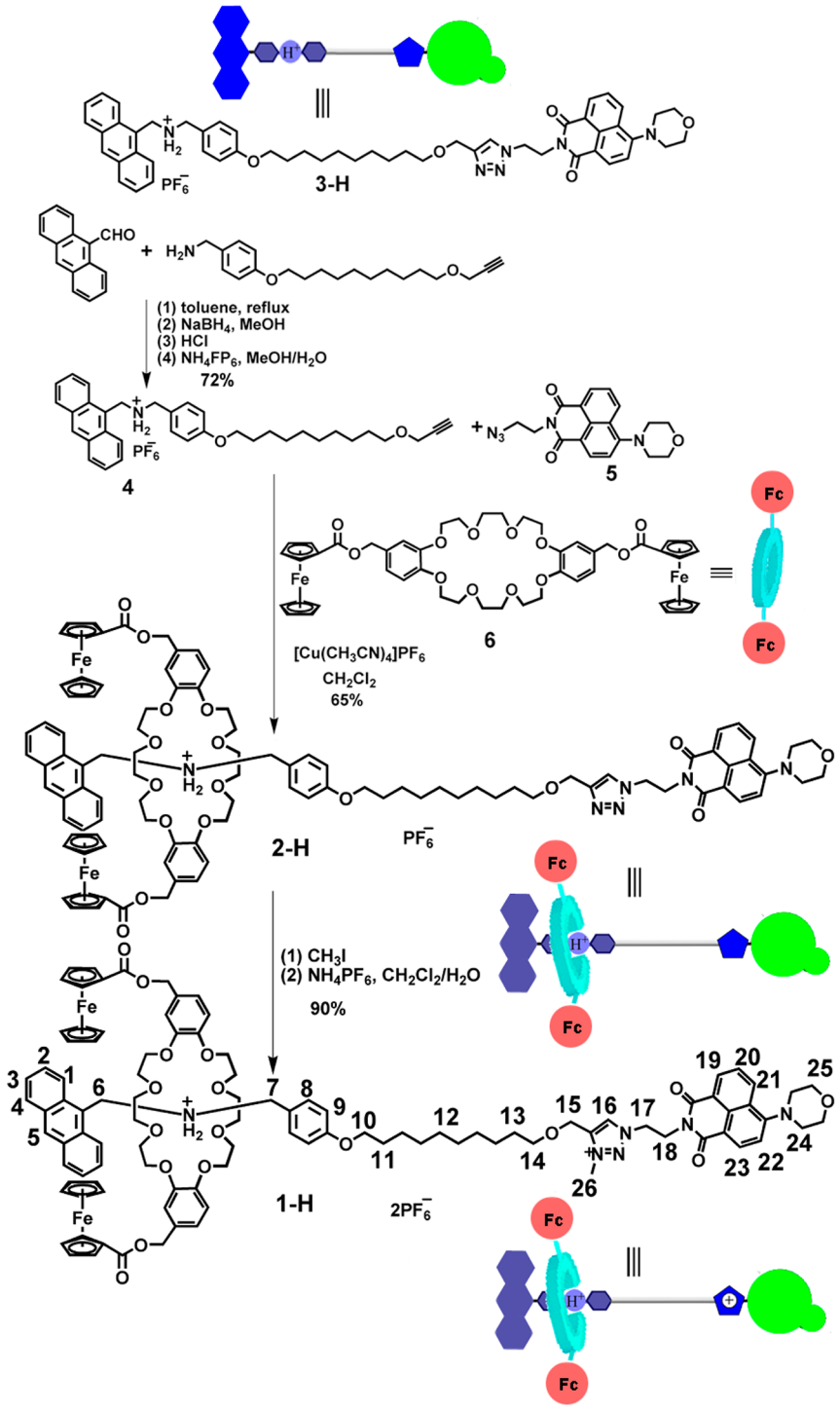

Figure 2. Syntheses and chemical structures of the target rotaxane **1-H**, **2-H**, and the dumbbell-shaped thread compound **3-H**. The assignments for protons of rotaxane **1-H** are shown, and the ones for rotaxane **2-H** and thread **3-H**, which are the same as **1-H**, are not shown.

consistent with the loss of one PF_6^- counterion, i.e., $[M - PF_6]^+$. Further comparison of the ^1H NMR spectrum of **2-H** with that of **3-H** confirmed that the macrocycle **6** predominately resides around the DAA recognition station. First, the peaks for the methylene protons H_6, H_7 on the DAA recognition site (Figure 3c) are shifted downfield tremendously ($\Delta\delta$ = 0.82, and 1.24 ppm, respectively) compared with the ones of dumbbell **3-H** (Figure 3b), suggesting that they undergo the deshielding effect of the aromatic rings of the macrocycle. Second, the peaks of protons H_1 and H_4 on the anthracene stopper and the aromatic protons H_8 also changed, and the signal of H_1 was split into two peaks, the signal of H_4 was shifted upfield ($\Delta\delta$ = −0.22 ppm), and the signal of H_8 was shifted downfield ($\Delta\delta$ = 0.25 ppm). All of this evidence confirmed the structure of rotaxane **2-H** as shown in Figure 2.

Compared with the ^1H NMR spectrum of rotaxane **2-H**, there was no significant change that was observed in the peaks that correspond to the DAA recognition site in the ^1H NMR spectrum of [2]rotaxane **1-H**, which indicated that the macrocyclic host **6** is still located at the DAA recognition site

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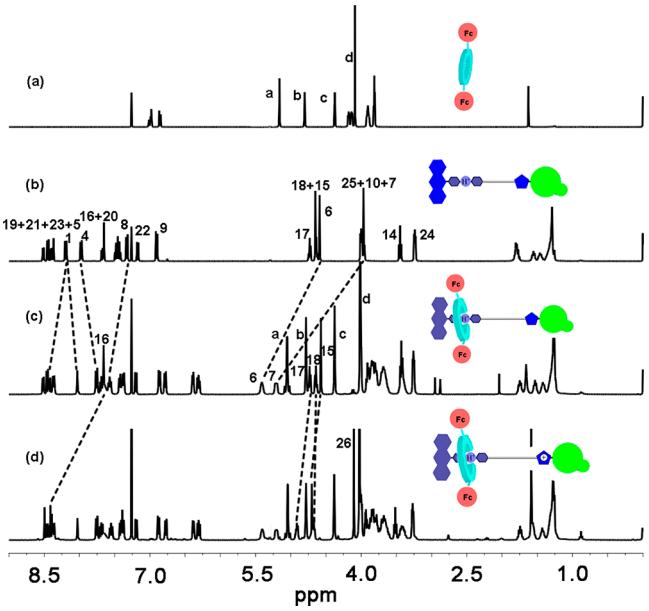

Figure 3. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (a) macrocycle **6**, (b) thread **3-H**, (c) [2]rotaxane **2-H** (d) [2]rotaxane **1-H**. The assignments correspond to the structures were shown in Figure 2.

in rotaxane **1-H**. However, the signals of protons H_{15}, H_{16}, H_{17}, and H_{18} in or neighboring to the triazole unit were shifted downfield ($\Delta\delta$ = 0.13, 0.74, 0.18, and 0.03 ppm, respectively) due to the methylation of the triazole unit. Meanwhile, the signal for the methyl proton H_{26} in the *N*-methyltriazolium part emerged at 4.10 ppm. The HR-ESI mass spectrum of the target rotaxane **1-H** also confirmed the structure as shown in Figure 2, which has the most intense peak as a doubly charged peak at m/z 903.3472, corresponding to the species that lost two PF_6^- counterions. All of this evidence confirmed that the target [2]rotaxane **1-H** was synthesized successfully as we have designed.

The shuttling motion of the macrocycle between the two distinguishable recognition sites in the molecular thread of rotaxane **1-H** was also confirmed using ^{1}H NMR spectroscopy. When the ammonium moiety was deprotonated by the addition of 2 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the CD_3COCD_3 solution of rotaxane **1-H**, the DB24C8 macrocycle migrated from the DAA station to the MTA recognition site, with the structure shown in Figure 1. As shown in Figure 4b, the methylene protons H_6 and H_7 in the DAA station moved upfield significantly ($\Delta\delta$ = −1.01 and −1.34, respectively) because of the deprotonation and the movement of the macrocycle. The peaks for the *N*-methyltriazolium protons were shifted due to association with the macrocylic compound **6**, for H_{26} with a $\Delta\delta$ of −0.18 ppm and H_{15}, H_{16}, H_{17}, and H_{18} with $\Delta\delta$ of −0.15, 0.64, 0.23, and 0.13 ppm, respectively. All of these changes indicated that the DB24C8 macrocycle moved to the MTA recognition site. After the reprotonation of the -NH- center with the addition of 4 equiv of CF_3CO_2H (TFA), the ^{1}H NMR was completely recovered (Figure 4c), indicating the return of the DB24C8 ring to the DAA station. Thus, by ^{1}H NMR spectroscopic measurements, the acid−base-induced reversible shuttling motion of the macrocycle along the rotaxane thread in [2]rotaxane **1-H** has been demonstrated.

Photophysical Properties of Rotaxane 1-H. Next we focused on the photophysical properties of rotaxane **1-H**. The

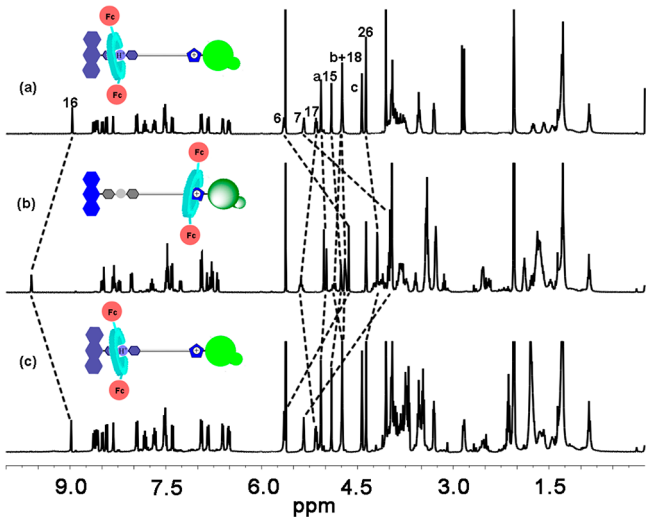

Figure 4. Partial ^{1}HNMR spectra (400 MHz, 298K, CD_3COCD_3) of (a) [2]rotaxane **1-H**, (b) the solution obtained after adding 2 equiv of DBU to the solution of (a), and (c) the solution obtained after adding 4 equiv of CF_3COOH to the solution of (b).

absorption spectrum of [2]rotaxane **1-H** in CH_2Cl_2 showed not only three characteristic absorption peaks of anthracene moiety, which has the maximum absorption wavelength at λ_{max} = 355, 373, and 393 nm, but also the absorption peak of naphthalimide (Figure 5). However, the maximum absorption

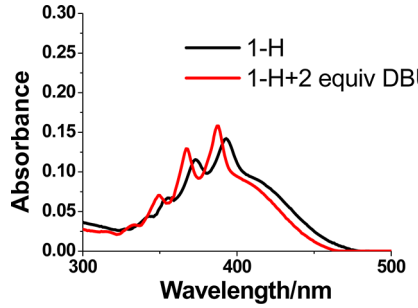

Figure 5. UV−vis absorption spectra of a dichloromethane solution of [2]rotaxane **1-H** (1×10^{-5} M) and of the mixture obtained after adding 2 equiv of DBU to the solution of **1-H**.

peak of 4-morpholin-naphthalimide was heavily overlapped with one of the absorption peak of anthracene.[24] As we previously reported,[12] the maximum absorption peak of 4-morpholin-naphthalimide appeared at 398 nm in CH_2Cl_2, which was used as one of the excited wavelengths in the fluorescence measurement. It should be noted that rotaxane **2-H** and compound **3-H** have similar absorption spectra as rotaxane **1-H**. We have also investigated into the photophysical properties of the three above-mentioned compounds in response to chemical stimuli. Upon addition of 2 equiv of DBU to the CH_2Cl_2 solutions of rotaxane **2-H** and compound **3-H**, respectively, almost no change was observed. After adding 2 equiv of DBU to the CH_2Cl_2 solution of rotaxane **1-H**, a very small spectral change was observed. Three absorption peaks arising from the anthracene unit experienced a blue shift of 6 nm, and meanwhile, the absorption peak of 4-morpholin-naphthalimide also has a blue shift. This phenomenon can be ascribed to the movement of macrocycle from DAA site to MTA site.

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Next the fluorescence spectral changes of rotaxane **1-H**, **2-H**, and compound **3-H** upon addition of DBU were determined. Very remarkable fluorescence changes were observed in rotaxane **1-H** in response to the addition of DBU (Figures 6, 7, and 8). Upon addition of 2 equiv of DBU to the dichloromethane solution of rotaxane **1-H**, the emission intensity of naphthalimide unit (λ_{em}= 517 nm) decreased 77% compared with the original spectrum when excited with 363 nm (Figure 6) and decreased 90% when excited with 398 nm (Figure 7), meanwhile, the emission intensity of the anthracene moiety has a remarkable 4.11-fold increase. This phenomenon can be attributed to the shuttling movement of the di-ferrocene-functionalized DB24C8 macrocycle. In the original state of rotaxane **1-H**, with the macrocycle residing at the DAA station, the relatively efficient PET process between ferrocene units and anthracene can result in the fluorescence quenching of the anthracene fluorophore, while the inefficient PET process between ferrocene units and 4-morpholin-naphthalimide makes the fluorescence of the 4-morpholin-naphthalimide moiety relatively strong. When DBU was added, the macrocycle moved toward the MTA station, and as a result of the association between macrocycle and MTA station, the PET process from ferrocene units to anthracene was restricted and the PET process from ferrocene units to 4-morpholin-naphthalimide was strengthened. All observations in the fluorescence experiments were in accordance with the ^{1}H NMR spectra. Most importantly, the shuttling motion of the macrocycle driven by acid−base stimuli could be repeated many times without obvious degradation, as evidenced by the reversible fluorescent change cycles of both two fluorophores (Figure 9). However, addition of 2 equiv of DBU to the solution of compound **3-H** (Supplementary Figure S2) could not result in the obvious change in the fluorescent spectrum, indicating that the di-ferrocene-functionalized macrocycle plays an important role in the design of the fluorescence-responsive rotaxane **1-H**. Addition of 2 equiv of DBU to rotaxane **2-H** (Supplementary Figure S5) also did not generate fluorescent spectral changes, which is ascribed to the fact that DBU could not result in the migration of the DB24C8 ring in rotaxane **2-H** due to the absence of MTA recognition site. It should be noted that there should be an energy transfer between the two fluorescent stoppers in rotaxane **1-H**. As shown in Figure 8, the three fluorescence emission peaks of anthracene were at 392, 414, and 439 nm, which are overlapped with the absorption band of 4-morpholin-naphthalimide (Figure 5). The excitation spectrum of [2]rotaxane **1-H** (Supplementary Figure S7), rotaxane **2-H** (Supplementary Figure S6), and dumbbell compound **3-H** (Supplementary Figure S3) confirmed that the anthracene moiety has much contribution to the fluorescence of the 4-morpholin-naphthalimide unit.

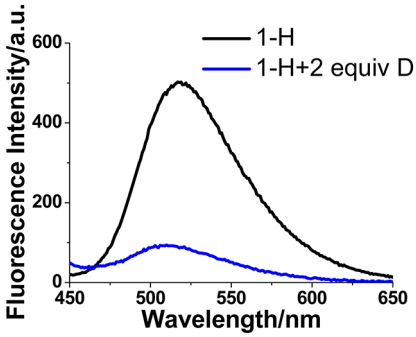

Figure 6. Fluorescence spectral changes in CH_2Cl_2 from [2]rotaxane **1-H** (1×10^{-5} M) to the mixture obtained after adding 2 equiv of DBU to the solution of **1-H**. The excitation wavelength of the fluorescent spectra is 363 nm.

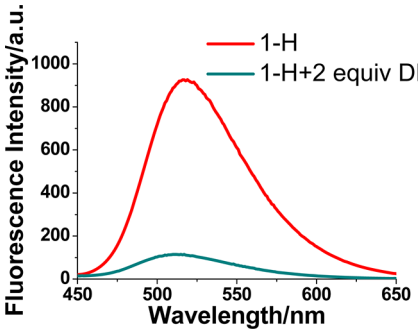

Figure 7. Fluorescence spectral changes in CH_2Cl_2 from [2]rotaxane **1-H** (1×10^{-5} M) to the mixture obtained after adding 2 equiv of DBU to the solution of **1-H**. The excitation wavelength of the fluorescent spectra is 398 nm.

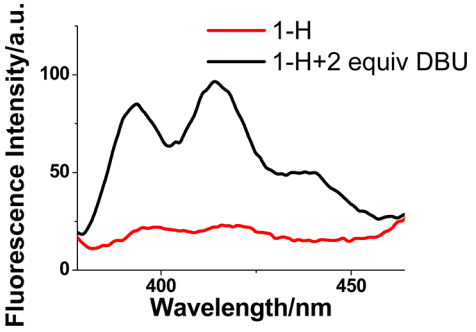

Figure 8. Fluorescence spectral changes in CH_2Cl_2 from [2]rotaxane **1-H** (1×10^{-5} M) to the mixture obtained after adding 2 equiv of DBU to the solution of **1-H**. The excitation wavelength of the fluorescent spectra is 363 nm.

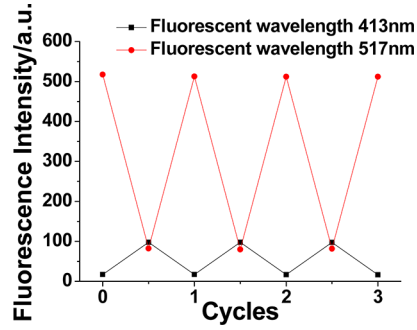

Figure 9. Fluorescence intensity of rotaxane **1-H** (10^{-5} M, CH_2Cl_2) at 517 and 413 nm upon addition of alternate external stimuli (DBU and TFA) for three cycles. The excitation wavelength is 363 nm.

CONCLUSIONS

In summary, a novel bistable [2]rotaxane, with a di-ferrocene-functionalized 24-crown-8 macrocycle interlocked onto a dumbbell-shaped component containing two fluorescent stoppers (4-morpholin-naphthalimide and anthracene) and

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two distinguishable recognition sites has been prepared and well-characterized. The shuttling motion of the functionalized DB24C8 macrocycle between the DAA station and the MTA station can be driven by external acid−base stimuli. By introducing two ferrocene moieties into the macrocycle, the fluorescence of two fluorescent stoppers can be reduced or enhanced alternately by an adjustable photoinduced electron transfer (PET) process occurring between the Fc electron donors and each of the fluorophores. This kind of system has important potential for the construction of fluorescent switches with multioutput.

EXPERIMENTAL SECTION

General. ^{1}H NMR and ^{13}C NMR spectra were measured on a 400 MHz spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz) at 298 K. The electronic spray ionization (ESI) mass spectra were tested on a TOF mass spectrometer. The UV−vis absorption spectra and fluorescence spectra were also recorded. All reagents and solvents were used as supplied, unless stated otherwise. CH_2Cl_2 was distilled over CaH_2. DMF was dried over molecular sieves, triethylamine were distilled from KOH, and THF was distilled over sodium.

Materials. All solvents were reagent grade and 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. Compounds **5**, **6**, and **7** were synthesized and purified acording to the ref 12.

Synthesis of Compound 4. A mixture of compound **7** (1 g, 3.15 mmol) and 9-anthraldehyde (0.523 g, 3.15 mmol) in dry toluene (70 mL) was refluxed overnight under argon atmosphere. The solvent was removed under vacuum, and the residue was dissolved in MeOH (50 mL). To the solution in an ice bath was added $NaBH_4$ (1.2 g, 31.5 mmol) was added in portions. After the mixture was stirred overnight, the solution was poured into water, and the mixture was extracted by DCM (3 × 50 mL). The organic layer was dried over anhydrous Na_2SO_4 and then concentrated to give the free amine compound. The residue was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH = 20:1) to give a pale solid. To a solution of the amine in MeOH (20 mL) was added HCl (6 M, 1 mL) at room temperature. After the mixture was stirred for 2 h, the solvent was removed under vacuum. The residue was redissolved in MeOH (50 mL), and then saturated NH_4PF_6 (10 mL) was added. After the mixture was stirred overnight, the solvent was removed under vacuum, water (30 mL) was added, and the mixture was extracted by DCM (3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate and then concentrated. The crude product was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH = 70:1) to give compound **4** (1.39 g, 72%) as a pale solid. Mp: 73−78 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.39 (s, 1H), 8.22 (d, J = 8.8 Hz, 2H), 8.03−7.95 (m, 2H), 7.55−7.41 (m, 4H), 7.34 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 4.68 (s, 2H), 4.13 (d, J = 2.4 Hz, 2H), 4.04−3.91 (m, 4H), 3.51 (t, J = 6.6 Hz, 2H), 2.41 (t, J = 2.4 Hz, 1H), 1.90−1.71 (m, 4H), 1.65−1.54 (m, 2H), 1.52−1.24 (m, 14H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 158.9, 131.4, 130.3, 130.0, 129.3, 127.9, 126.6, 125.1, 123.7, 114.7, 80.2, 74.2, 70.4, 68.2, 58.1, 53.2, 44.2, 29.5, 26.2. HRMS (ESI) (m/z): $[M - PF_6]^+$ calcd for $C_{35}H_{42}NO_2$, 508.3216; found, 508.3214.

Synthesis of Compound 3-H. A mixture of **4** (0.17 g, 0.28 mmol), **5** (0.1 g, 0.28 mmol), and $[Cu(CH_3CN)_4]PF_6$ (0.11 g, 0.28 mmol) was stirred in dry CH_2Cl_2 (5 mL) at room temperature for 2 days. After removal of the solvent, the residue was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH = 70:1) to give compound **3-H** (0.24 g, 90%) as a yellow powder. Mp: 64−69 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.51 (dd, J = 7.3, 1.0 Hz, 1H), 8.45 (d, J = 8.1 Hz, 1H), 8.40 (dd, J = 8.4, 1.0 Hz, 1H), 8.37 (s, 1H), 8.19 (d, J = 8.8 Hz, 2H), 8.00−7.95 (m, 2H), 7.67 (dd, J = 7.7, 6.7 Hz, 2H), 7.51−7.39 (m, 4H), 7.33 (d, J = 8.6 Hz, 2H), 7.17 (d, J = 8.1 Hz, 1H), 6.94−6.87 (m, 2H), 4.73 (t, J = 6.2 Hz, 2H), 4.67−4.61 (m, 4H), 4.59 (s, 2H), 4.03−3.93 (m, 8H), 3.45 (t, J = 6.7 Hz, 2H), 3.27−3.20 (m, 4H), 1.85−1.73 (m, 4H), 1.54 (dd, J = 13.7, 6.8 Hz, 2H), 1.50−1.24 (m, 13H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 164.1, 163.6, 155.9, 132.8, 131.4, 130.5, 129.9, 126.0, 125.8, 124.8, 122.5, 116.2, 114.9, 70.5, 68.1, 66.9, 64.2, 53.4, 47.8, 39.5, 29.5, 26.1. HRMS (ESI) (m/z): $[M - PF_6]^+$ calcd for $C_{53}H_{59}N_6O_5$, 859.4547; found, 859.4545.

Synthesis of Rotaxane 2-H. A mixture of **5** (20 mg, 0.03 mmol) and crown ether **7** (44.5 mg, 0.06 mmol) was stirred in dry CH_2Cl_2 (4 mL) at room temperature. After **6** (37.9 mg, 0.06 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 = 100:1) to give compound **2-H** (12.4 mg, 65%) as a yellow solid. Mp: 123−128 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.51 (dd, J = 7.2, 0.6 Hz, 1H), 8.46 (d, J = 8.1 Hz, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.37 (d, J = 8.7 Hz, 2H), 8.03 (s, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.72−7.53 (m, 6H), 7.46−7.33 (m, 4H), 7.20 (d, J = 8.1 Hz, 1H), 6.86 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 7.4 Hz, 2H), 6.39 (dd, J = 6.3, 1.2 Hz, 2H), 6.31 (dd, J = 8.1, 6.3 Hz, 2H), 5.41 (s, 2H), 5.25−5.16 (m, 2H), 5.11−4.99 (m, 4H), 4.78 (s, 4H), 4.73 (t, J = 6.2 Hz, 2H), 4.64 (t, J = 6.2 Hz, 2H), 4.57 (s, 2H), 4.42−4.34 (m, 4H), 4.01 (t, J = 3.4 Hz, 13H), 3.94−3.59 (m, 22H), 3.43 (t, J = 6.6 Hz, 6H), 3.31−3.20 (m, 4H), 1.79−1.69 (m, 2H), 1.59−1.49 (m, 2H), 1.46−1.20 (m, 14H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 171.7, 164.3, 163.8, 159.4, 156.2, 146.7, 145.7, 133.0, 131.6, 130.7, 130.1, 129.7, 129.4, 128.7, 127.4, 126.3, 126.0, 125.2, 124.6, 123.8, 123.1, 122.8, 121.8, 121.2, 116.4, 115.1, 114.7, 112.5, 111.8, 101.6, 101.4, 71.6, 71.5−70.8, 70.9, 70.8, 70.8, 70.2, 69.8, 68.3, 67.1, 65.5, 64.3, 53.5, 29.6, 26.2. HRMS (ESI) (m/z): $[M - PF_6]^+$ calcd for $C_{101}H_{111}N_6O_{17}Fe_2$, 1791.6705; found, 1791.6711.

Synthesis of Rotaxane 1-H. [2]Rotaxane **2-H** (0.1 g, 0.053 mmol) was dissolved in iodomethane (6 mL), and the mixture was stirred for 4 d at room temperature. The excess iodomethane was evaporated, and the solid was washed with Et_2O to give a yellow solid. To a suspension of the solid in H_2O (4 mL) were added NH_4PF_6 (0.17 g, 1.05 mmol) and CH_2Cl_2 (10 mL), respectively. The resulting mixture was vigorously stirred for 1 h. The aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was dried over Na_2SO_4 and then concentrated. The residue was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH = 100:1) to give compound **1-H** (98.1 mg, 90%) as a yellow solid. Mp: 128−132 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.42 (m, 6H), 8.03 (s, 1H), 7.76 (d, J = 8.5 Hz, 2H), 7.72−7.66 (m, 2H), 7.59−7.51 (m, 2H), 7.40 (m, 4H), 7.19 (d, J = 8.1 Hz, 1H), 6.88 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.3 Hz, 2H), 6.38 (d, J = 8.3 Hz, 2H), 6.31 (m, 2H), 5.44−5.37 (m, 2H), 5.25−5.17 (m, 2H), 5.10−4.99 (m, 4H), 4.96−4.87 (m, 2H), 4.78 (s, 4H), 4.74−4.64 (m, 4H), 4.38 (s, 4H), 4.10 (s, 4H), 4.05−3.97 (m, 14H), 3.97−3.56 (m, 24H), 3.52 (t, J = 6.5 Hz, 2H), 3.48−3.35 (m, 4H), 3.32−3.22 (m, 4H), 1.79−1.70 (m, 2H), 1.57−1.51 (m, 2H), 1.49−1.19 (m, 17H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 171.7, 164.5, 163.8, 159.3, 156.5, 146.6, 141.2, 133.2, 131.7, 131.2, 130.7, 130.0, 129.5, 128.7, 127.3, 126.1, 125.1, 124.6, 123.8, 122.2, 121.7, 121.2, 115.6, 115.1, 114.7, 112.4, 111.8, 71.6, 71.2, 70.6, 69.8, 68.2, 66.9, 65.4, 59.9, 53.5, 52.5, 45.3, 39.4, 38.4, 29.3, 25.9. HRMS (ESI) (m/z): $[M - 2PF_6]^{2+}$ calcd for $C_{102}H_{114}N_6O_{17}Fe_2$, 903.3464; found, 903.3472.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and copies of the ^{1}H and ^{13}C NMR spectra of new compounds and the absorption and fluorescence spectra of **1-H**, **2-H**, **3-H**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: dahui_qu@ecust.edu.cn; tianhe@ecust.edu.cn.

Notes

The authors declare no competing financial interest.

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