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Dual-Mode Control of PET Process in a Ferrocene-Functionalized [2]Rotaxane with High-Contrast Fluorescence Output

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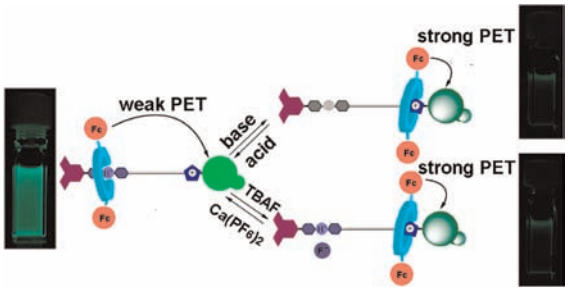
ABSTRACT



The shuttling motion of the ferrocene-functionalized macrocycle between the dibenzylammonium and the *N*-methyltriazolium recognition sites in a bistable [2]rotaxane, as well as the photoinduced electron transfer process occurring between ferrocene units and the morpholin-naphthalimide fluorescent stopper, can be adjusted not only by acid−base stimuli but also addition−removal of the fluoride anion, along with remarkable, high-contrast fluorescent intensity changes.

Bistable [2]rotaxanes, 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, have attracted much attention because of their adjustable physical and chemical properties, applications in molecular electronics, and as components of molecular machinery.[1] The shuttling motion of the macrocycle on the rotaxane thread can be driven by acid−base stimuli,[2] light,[3] electrochemical potential change,[4] or ions.[5] Recently, solution-phase counterion effects[6] have been harnessed to control submolecular motion in mechanically interlocked molecules, such as rotaxanes and catenanes. A counterion-induced switching strategy represents a very promising approach if the counterion-induced mechanical movement can be accompanied with naked-eye-based property changes, such as

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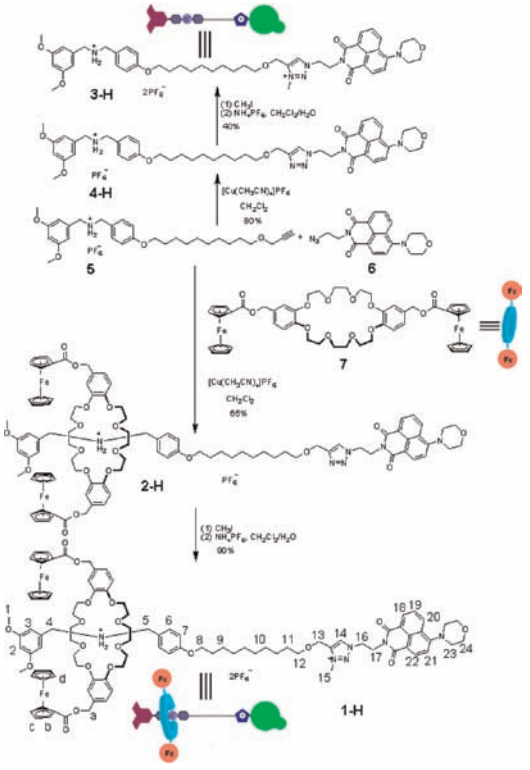
color changes[7] and fluorescence changes,[8,9] which holds the potential to function as a molecular sensing device for ions. Here, we report the design, preparation, characterization, and properties of a bistable [2]rotaxane **1-H**, in which the shuttling motion of the macrocycle on the rotaxane thread can be dual-mode-driven, i.e. by not only acid−base stimuli but also addition−removal of the fluoride anion, along with remarkable, high-contrast fluorescent intensity changes, by introducing ferrocene electron donor units into the system.

The chemical structure and preparation of rotaxane **1-H** are shown in Scheme 1. The key feature of the rotaxane-type molecular shuttle is the introduction of two ferrocene (Fc) moieties as electron donors into the dibenzo-24-crown-8 (DB24C8) ring, which can be chemically driven to shuttle between the two well-separated recognition sites, namely dibenzylammonium (DBA)[8b,c,10] and *N*-methyltriazolium (MTA) stations.[8b,c,11] As a result, the fluorescence of the 4-morpholin-naphthalimide (MA) stopper can be switched on and off by a tunable, distance-dependent photoinduced electron transfer (PET) process[12] that occurs between the Fc electron donors and the excited MA fluorophore. Using a threading-followed-by-stoppering strategy,[2,4a,8,13] rotaxane **2-H** was prepared in a moderate yield through the well-known copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction[14] between alkyne **5** and azide **6** in the presence of macrocycle **7**. Then the subsequent methylation of the triazole unit followed by anion exchange with saturated NH_4PF_6 solution afforded the target [2]rotaxane **1-H** in a high yield (90%). The dumbbell-shaped molecule **3-H** was also prepared for comparison in a similar strategy as shown in Scheme 1.

Scheme 1. Preparation and Chemical Structures of Rotaxane **1-H** and Dumbbell-Shaped Compound **3-H**



Rotaxanes **1-H**, **2-H** and dumbbell compounds **3-H**, **4-H** were well characterized using ^1H and ^{13}C NMR and HR-ESI mass spectrometry. The HR-ESI mass spectrum of the target rotaxane **1-H** revealed that the most intense peak occurred at m/z 883.8239 as a doubly charged peak, with an isotope distribution corresponding to the consecutive loss of two PF_6^- counterions, i.e. $[M-2PF_6]^{2+}$.

The ^1H NMR of **1-H** in $CDCl_3$ confirmed the location of the macrocycle to be predominantly over the DBA binding site. The peaks for the methylene protons H_4, H_5 on the DBA recognition site (Figure 1c) are shifted downfield ($\Delta\delta$ = 0.59 ppm) compared with those of dumbbell **3-H** (Figure 1b), meanwhile, the peaks of protons H_1, H_2, H_3 on the dimethoxybenzene stopper shifted upfield ($\Delta\delta$ = −0.13, −0.08, and −0.11 ppm, respectively) due to the shielding effect of macrocycle **7**. Moreover, the protons H_{14}, H_{15}, H_{16}, H_{17} on the unencircled MTA site have the same chemical shifts as those of dumbbell **3-H**. All this evidence confirmed that the DB24C8 ring exhibits a predominant selectivity for the encirclement of the DBA recognition site.

Addition of 2 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to the $CDCl_3$ solution of rotaxane **1-H** resulted in the migration of the DB24C8 ring to the MTA recognition site. As shown in Figure 1d, the methylene protons H_{16} and H_{17} neighboring the naphthalimide stopper are shifted downfield ($\Delta\delta$ = 0.48 and 0.13 ppm, respectively), and the

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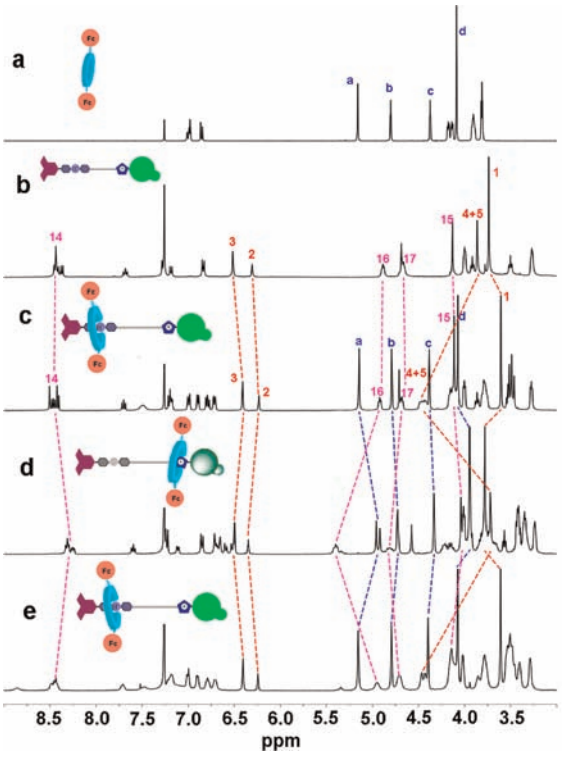

Figure 1. Partial ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of (a) macrocycle **7**, (b) dumbbell **3-H**, (c) [2]rotaxane **1-H**, (d) deprotonation with addition of 2 equiv of DBU to sample c and (e) reprotonation with addition of 4 equiv of TFA to sample d. The assignments correspond to the structures as shown in Scheme 1.

peaks for the *N*-methyltriazolium protons are shifted due to association with the DB24C8 ring, for H_{14}, H_{15} with $\Delta\delta$ of −0.19, −0.07 ppm, respectively. All these changes indicated that the macrocycle moved to the MTA recognition site. Reprotonation of the −NH− center with the addition of 4 equiv of CF_3CO_2H resulted in the return of the DB24C8 ring to the DBA station as evidenced by the regeneration of the original ^{1}H NMR spectrum (Figure 1e). Similar experiments performed in CD_3COCD_3 (Figure S1) also proved the reversible shuttling motion of the macrocycle between the two stations.

As previously studied by Chiu et al.,[15] the interactions between the DBA station and DB24C8 are affected by the nature of the counteranions. After adding 2 equiv of tetrabutylammonium fluoride (TBAF) to a $CDCl_3$ solution of **1-H**, significant changes were observed in the ^{1}H NMR changes (Figure 2b), which is similar to the spectrum obtained by addition of 2 equiv of DBU (Figure 1d), indicating the migration of the DB24C8 ring to the MTA recognition site, due to the stronger hydrogen bond between the fluoride anion and the hydrogen atom on the DBA station. Subsequent addition of 4 equiv of $Ca(PF_6)_2$ to the TBAF-added solution to remove the fluoride anion

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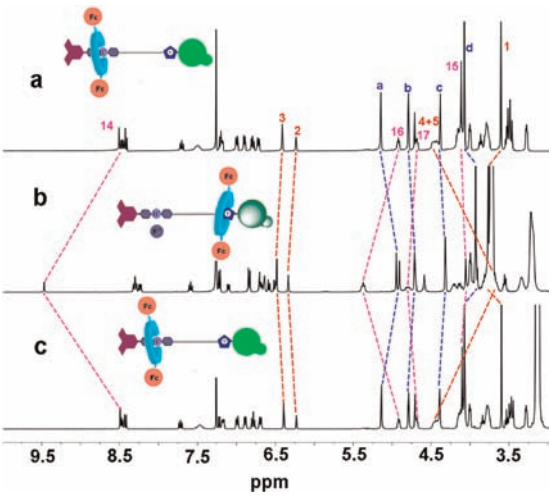

Figure 2. Partial ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of (a) [2]rotaxane **1-H**, (b) the solution obtained after adding 2 equiv of TBAF to the solution of (a), and (c) the solution obtained after adding 4 equiv of $Ca(PF_6)_2$ to the solution of (b).

through the precipitation of CaF_2 provided a spectrum identical to the original one of rotaxane **1-H** (Figure 2c), indicating the macrocycle moved back to the DBA station. To study the selectivity of rotaxane **1-H** for the fluoride anion, the ^{1}H NMR spectra in the same pattern as that of rotaxane **1-H** were obtained upon addition of TBACl, TBABr, and TBAI, indicating no shuttling movement of the macrocycle **7** and good selectivity for the fluoride anion (Figure S2). Thus, by ^{1}H NMR spectroscopic measurements, reversible acid−base-driven and fluoride-anion-driven shuttling motions of the macrocycle along the rotaxane thread have been demonstrated.

Next, we focused on the photophysical properties of **1-H** and **3-H** in response to chemical stimuli. Upon addition of 2 equiv of DBU or 2 equiv of TBAF to the solution of rotaxane **1-H** or dumbbell **3-H**, almost no absorption spectral changes were observed (Figure S3). The fluorescence intensity of dumbbell **3-H** upon addition of DBU or TBAF exhibited a small magnitude of change due to the deprotonation of the DBA moiety or the counteranion exchange from PF_6^- to F^-, respectively.

Very remarkable fluorescence changes were observed in rotaxane **1-H** in response to chemical stimuli. Upon addition of 2 equiv of DBU to the dichloromethane solution of rotaxane **1-H**, the emission intensity at 517 nm decreased 90% compared with the original spectrum (Figure 3a); furthermore, time-resolved fluorescence became a biexponential decay with a lifetime of 2.23 ns (64%) and 0.35 ns (36%) from the original monoexponential decay with a lifetime of 1.97 ns. The shorter lifetime can be attributed to electron transfer between the Fc units and MA fluorophore, while the longer lifetime is similar to the intrinsic lifetime of the MA fluorophore. Similar results were obtained when 2 equiv of TBAF were added to the dichloromethane solution of rotaxane **1-H**. The fluorescent intensity decreased

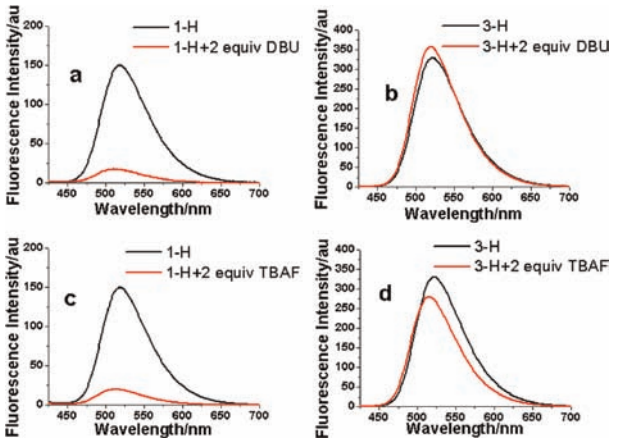

Figure 3. Fluorescence spectral changes in CH_2Cl_2 (a) from [2]rotaxane **1-H** to the mixture obtained after adding 2 equiv of DBU to the solution of **1-H**, (b) from dumbbell **3-H** to the mixture obtained after adding 2 equiv of DBU to the solution of **3-H**, (c) from [2]rotaxane **1-H** to the mixture obtained after adding 2 equiv of TBAF to the solution of **1-H**, and (d) from dumbbell **3-H** to the mixture obtained after adding 2 equiv of TBAF to the solution of **3-H**. Excitation wavelength of all fluorescence spectra was 398 nm.

88% (Figure 3c), and the fluorescent decay in this case obeyed biexponential function with lifetimes of 2.44 ns (61%) and 0.52 ns (39%). After the addition of 4 equiv of $Ca(PF_6)_2$, rotaxane **1-H** was regenerated, and the fluorescence spectra recoverd. The fluorescence changes can even be observed by the naked eye, as shown in the Supporting Information. Both of these cases indicate that the distance-dependent PET process from the Fc electron donors to the excited state of the MA fluorophore became more efficient after the functional macrocycle moved from the DBA station to the MTA station by deprotonation with DBU or addition of the fluoride anion, after which the spatial distance between the Fc units and the MA fluorophore became much closer compared with the original state. 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 (Figure S6). To further explore the influence of counteranions, we conducted experiments of addition of other halide anions to the solution of rotaxane **1-H** and dumbbell **3-H**, respectively. The same change tendencies were observed for **1-H** and **3-H** upon addition of 5 equiv of TBACl, TBABr, and TBAI, indicating that the fluorescence changes are due to the exchange of counteranions, not the movement of the macrocycle. This is in accordance with the result obtaind from the ^{1}H NMR study that Cl^-, Br^- I^- could not result in the shuttling motion of the macrocycle. In addition, the chemical oxidation of the Fc units was performed using $Fe(ClO_4)_3$ as an oxidant (Figure S8). Upon the addition of $Fe(ClO_4)_3$ to the DBU-added solution of **1-H**, the emission intensity enhanced dramatically. This phenomenon could be ascribed to the oxidation of the Fc units; after oxidation, the electron-donating abilities of the Fc units are reduced, and the PET reaction would be arrested, leading to fluorescence enhancement.

In conclusion, a novel "bright" [2]rotaxane has been prepared and well-characterized. The shuttling motion of the functionalized DB24C8 macrocycle between the DBA station and the MTA station can be driven by not only acid−base stimuli but also addition−removal of the fluoride anion. By introducing two Fc moieties into the macrocycle, the efficiency of the PET process occurring between Fc units and the MA fluorescent stopper could be altered due to the well-defined large-amplitude positional change in response to two kinds of chemical stimuli, generating remarkable, high-contrast fluorescent intensity changes observed by the naked eye. Most importantly, the system can distinguish fluoride anion from other halide anions, which holds the potential to function as a novel kind of fluorescent molecular sensing device, translating molecular recognition into mechanical movement of the subunits, and remarkable fluorescence outputs.

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Supporting Information Available. Experimental procedures and characterization data for new compounds, the absorption and fluorescence spectra of **1-H**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.