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Molecular Shuttles

A Ferrocene-Functionalized Bistable [2]Rotaxane with Switchable Fluorescence

Li Liu, Qi Wang, Ming Cheng, Xiao-Yu Hu, Juli Jiang,* and Leyong Wang*[a]

Abstract: A switchable, bistable molecular shuttle based on dialkylammonium ion and urea functional recognition sites, and a macrocycle bearing a ferrocenyl unit has been constructed, in which the ferrocenyl macrocycle can be easily switched along the thread by addition of acid/base or by addition/removal of acetate anions. The shuttling motion of the macrocycle is accompanied with different fluorescence responses via the adjustment of the photoinduced electron transfer (PET) effect between the ferrocene electron donor and the fluorophores.

Mechanically interlocked molecules (MIMs),[1] in particular functional bistable [2]rotaxanes, have attracted much attention in the past few decades due to their challenging construction and potential applications as an excellent framework for the fabrication of molecular machines, such as molecular switches and probes.[2] The shuttling motion of the macrocycle between different recognition sites on the rotaxane thread can be driven by acid/base,[3] ion binding,[4] altering the oxidation state,[5] photochemistry,[6] and solvent changes.[7] Some of these shuttling motions are usually accompanied with remarkable changes in physical properties, such as circular dichroism,[8] conductivity,[9] and fluorescence.[10] Among them, fluorescence change is preferably used as an output signal since it can be easily and remotely detected with low cost.

Recently, some successful examples based on bistable [2]rotaxanes with excellent fluorescence responses have been developed,[10] for example, a typical [2]rotaxane with a fluorescent response toward the shuttling movements was reported by Tian and co-workers in 2004.[10a] With further research for switchable rotaxane-containing fluorophores, ferrocene-modified rotaxane attracted more and more attention.[10f,g,k–m] A pyrene/ferrocene-based [2]rotaxane with a three-level luminescent response was reported by Mateo-Alonso et al.,[10f] and a ferrocene-functionalized molecular shuttle was constructed by Qu and co-workers, in which the fluorescence of the rotaxane can be reduced or enhanced alternately by an adjustable photoinduced electron transfer (PET) process occurring between two ferrocene (Fc) units in the macrocycle and two fluorescent stoppers.[10l] However, it is still a challenge to construct systems in which the shuttling motion of the macrocycle is accompanied with different fluorescence responses, and surely this system would pave the way for constructing more complicated and delicate multilevel molecular switches with optical signals.

On the basis of the above-mentioned works and our recent work on a phosphine-oxide-based, three-station molecular shuttle,[4d] and in continuation of research on molecular shuttles, herein we describe an acid/base and anion-responsive bistable molecular shuttle bearing an anthracene stopper on the thread and a ferrocenyl unit on the macrocycle, in which two different states are obtained by using external stimuli (acid/base and anions). As a result, the fluorescence can be reduced or enhanced respectively by the distance-dependent PET effect between the electron donor moiety Fc and the anthracene stopper in response to different stimuli.[10f,g,11]

Based on the reported macrocycle designed by Chiu and co-workers,[3c,4a] we obtained a ditopicmacrocycle **4**, which contains a 2,6-pyridinediamide, a polyether chain, and a ferrocenyl unit (Scheme 1). The designed bistable [2]rotaxane [**1**-H][PF_6] incorporates the ferrocenyl macrocycle **4**[4a,10f,12] and a dialkylammonium group (DAA^+) and urea station in the thread (Scheme 1). By using different external stimuli, the [2]rotaxane exists in two possible states. Such switchable properties of the molecular shuttle can be controlled by exploiting the relative pK_a of the DAA^+ binding site and acetate-binding affinity of the urea station by acid/base regulation or the addition/removal of acetate anions (Scheme 2).

Rotaxane [**1**-H][PF_6] was prepared in 13% yield by using a threading-followed-by-stoppering strategy, with the formation of thread [**2**-H][PF_6] in 19% yield at the same time. The structure and synthetic procedure for making rotaxane [**1**-H][PF_6] and thread [**2**-H][PF_6] are shown in Scheme 1 (see Supporting Information for details). The HRMS of [2]rotaxane [**1**-H][PF_6] showed the most intense peak at $m/z = 1305.5721$ as a single charged peak with an isotope distribution, which is consistent with the loss of one PF_6^- counterion, that is, $[M-PF_6]^+$ (Figure S24). Meanwhile, the comparison of ^{1}H NMR

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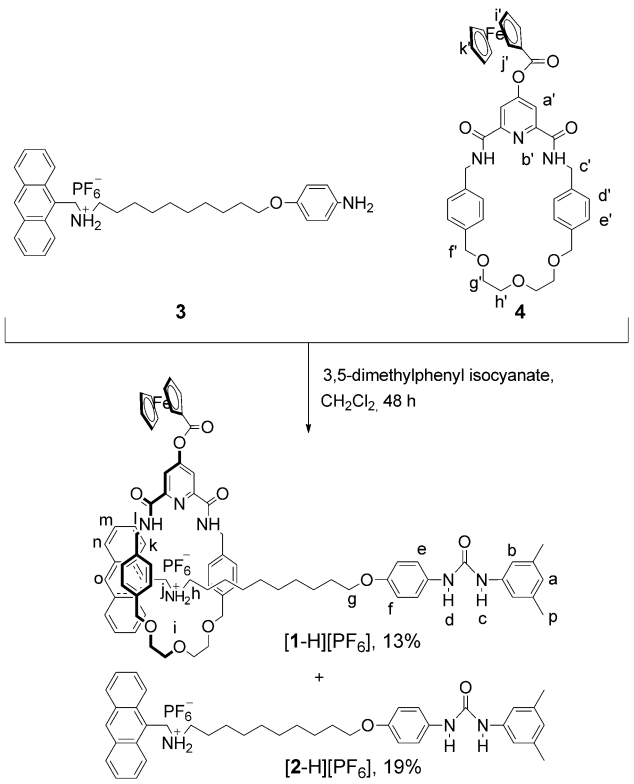
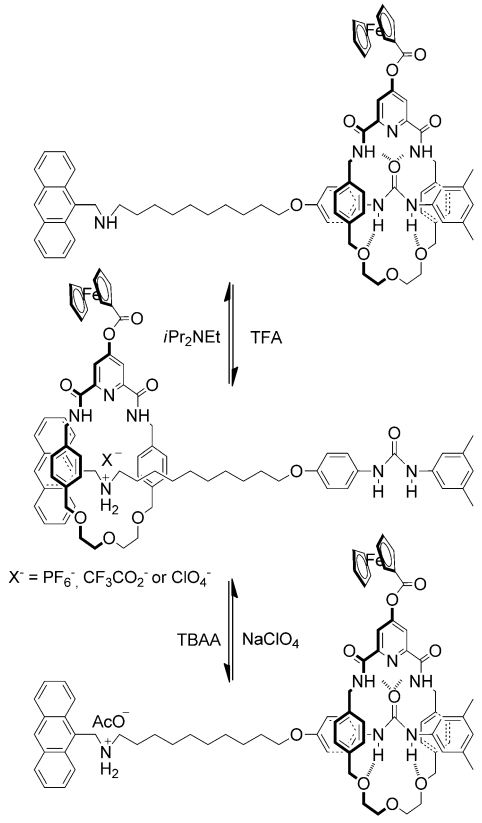


Scheme 1. Synthesis of the molecular shuttle [**1**-H][PF_6] and dumbbell-shaped thread [**2**-H][PF_6].



Scheme 2. The shuttling process of the macrocycle **4** along the rotaxane thread.

spectra of molecular shuttle [**1**-H][PF_6], dumbbell-shaped thread [**2**-H][PF_6], and the macrocycle **4** in $CDCl_3/CD_3CN$ (1:1, v/v) suggested the formation of an interlocked architecture and the macrocycle **4** stayed at the DAA^+ station in rotaxane [**1**-H][PF_6]. As shown in Figure S18, the overlapping proton signals of two methylene groups ($H_{g'}$ and $H_{h'}$) in the diethylene glycol unit of macrocycle **4** split into two broad signals and the macrocyle NH protons shifted clearly downfield ($\Delta\delta H_{b'} = 0.26$ ppm), suggesting possible dipole–dipole interaction and the formation of hydrogen bonds between the thread and the macrocycle in rotaxane [**1**-H][PF_6]. Moreover, $H_{d'}$ and $H_{e'}$ of the macrocycle in rotaxane [**1**-H][PF_6] shifted upfield compared with those of free macrocycle **4**, which was attributed to the aromatic shielding effect of the anthracene group. In addition, the signals of protons adjacent to the DAA^+ group in molecular shuttle [**1**-H][PF_6] shifted remarkably ($\Delta\delta H_j = -0.10$ ppm, $\Delta\delta H_k = -0.04$ ppm, $\Delta\delta H_n = -0.12$ ppm and $\Delta\delta H_o = 0.41$ ppm), while almost no changes for the signals adjacent to the urea group were detected compared with those of free thread [**2**-H][PF_6]. This was attributed to the interaction between the DAA^+ group and the macrocycle **4**. The above results indicate that the expected molecular shuttle was successfully obtained, where the macrocycle stayed at the DAA^+ station.

Subsequently, the shuttling properties of [**1**-H][PF_6] between the DAA^+ and urea stations were investigated by ^1H NMR spectroscopy. Upon addition of 1.5 equivalents of iPr_2NEt to neutralize the DAA^+ group of [**1**-H][PF_6], significant upfield shifts of the aromatic protons adjacent to the urea group ($\Delta\delta H_b = -0.33$ ppm, $\Delta\delta H_e = -0.31$ ppm, and $\Delta\delta H_g = -0.06$ ppm) were detected (Figure 1a and 1b), indicating the

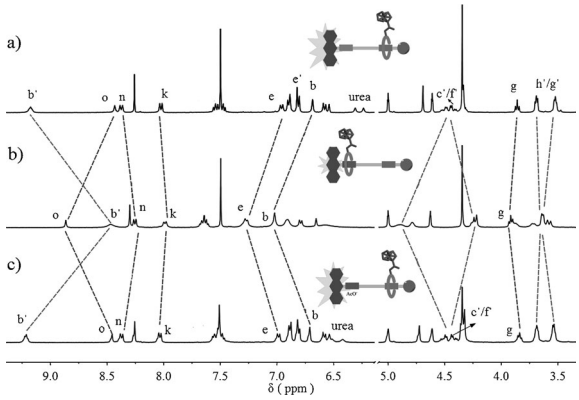


Figure 1. Shuttling of [**1**-H][PF_6] driven by base or acetate ion addition. Partial ^1H NMR spectra (400 MHz, $CDCl_3/CD_3CN = 1:1$, v/v, 298 K) of a) the mixture obtained after adding iPr_2NEt (1.5 equiv.) to [**1**-H][PF_6], b) rotaxane [**1**-H][PF_6], and c) the mixture obtained after adding TBAA (1.5 equiv.) to [**1**-H][PF_6].

aromatic shielding effect of the macrocycle at the urea station. The upfield shifts of the urea protons and the downfield shifts of the amide proton signals of macrocycle **4** ($\Delta\delta H_{b'} = 0.71$ ppm) suggested the formation of hydrogen bonds between the carbonyl group of the urea station and the macrocycle according to the literature.[3c] Clear changes were also de-

tected for the aromatic protons of the anthracene group (H_k, H_n, H_o, Figure 1a) and methylene protons of the macrocycle ($H_{c'}$, $H_{f'}$, $H_{g'}$, and $H_{h'}$). Furthermore, after the addition of iPr$_2$NEt, the chemical shift of the protons of the anthracene group in [**1**-H][PF$_6$] were similar with that of the free thread [**2**-H][PF$_6$], indicating the disappearance of the interactions between macrocycle **4** and the DAA$^+$ group (Figure S21). All of the above evidence confirmed that the macrocycle had moved to the urea group from the original DAA$^+$ station. Furthermore, when trifluoroacetic acid (TFA) was used to protonate the DAA$^+$ group, the [2]rotaxane with the macrocycle at the DAA$^+$ station was reformed again, and a similar spectrum to that of the original molecular shuttle [**1**-H][PF$_6$] was obtained (Figure S19). The above results demonstrate clearly that the switching of the molecular shuttle [**1**-H][PF$_6$] can be easily realized by acid/base control.

The anion-controllable shuttling of the molecular shuttle [**1**-H][PF$_6$] was investigated further. Tetrabutylammonium acetate (TBAA, 1.5 equiv.) was added to a $CDCl_3/CD_3CN$ (1:1, v/v) solution of the molecular shuttle with the macrocycle at the DAA$^+$ station and the ^{1}H NMR spectrum was recorded. This spectrum was similar to that of the molecular shuttle after adding 1.5 equivalents of iPr$_2$NEt, indicating that the macrocycle had switched to the urea group (Figure 1b and Figure 1c). The movement of the macrocycle was attributed to the much stronger binding affinity of the acetate anion with the DAA$^+$ center than that of the macrocycle with the DAA$^+$ center. Then, the addition of $NaClO_4$ removed the acetate ion, which translocated the macrocycle **4** back to the DAA$^+$ site efficiently (Figure S20), demonstrating the reversible movement of the macrocycle between the DAA$^+$ and urea groups.

Next, the changes of fluorescence intensity of rotaxane [**1**-H][PF$_6$] and thread [**2**-H][PF$_6$] in response to chemical stimuli were determined. Upon the addition of 1.5 equivalents of iPr$_2$NEt to a dichloromethane solution of rotaxane [**1**-H][PF$_6$] and thread [**2**-H][PF$_6$], respectively, the emission intensity of rotaxane [**1**-H][PF$_6$] increased remarkably compared with its original spectrum (Figure 2), while there was almost no response

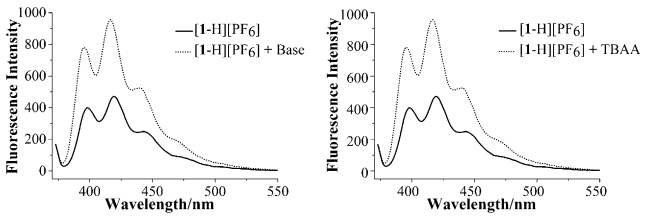


Figure 2. Changes of the fluorescence emission spectra of [**1**-H][PF$_6$] upon the addition of of iPr$_2$NEt or TBAA (1.5 equiv.) in CH_2Cl_2 (1×10^{-6} M), $\lambda_{ex}=363$ nm.

from the thread [**2**-H][PF$_6$] (Figure S31). As shown in Figure 2, when iPr$_2$NEt was added to the solution of rotaxane [**1**-H][PF$_6$], three emission peaks arising at 398, 419, and 443 nm attributable to the anthracene unit of rotaxane [**1**-H][PF$_6$] increased in intensity by 1.95-fold, 2.03-fold, and 2.11-fold, respectively, which could be attributed to the movement of the ferrocenyl macrocycle from the DAA$^+$ station to the urea site, resulting in a longer distance between the Fc and anthracene group. Consequently, the relatively efficient PET effect between Fc and the anthracene group became very weak, which led to the increase of fluorescence intensity.[10l]

Furthermore, in order to switch the macrocycle back to the DAA$^+$ group, TFA was added to protonate the DAA$^+$ moiety, and the emission intensity of the solution decreased remarkably compared with the spectrum obtained under the basic conditions due to the restoration of relatively efficient PET effect between the Fc and anthracene groups. As shown in Figure S29, when TFA was added to the solution of rotaxane [**1**-H][PF$_6$] in the presence of iPr$_2$NEt, three emission peaks attributable to the fluorophore unit decreased in intensity by 0.61-fold, 0.59-fold, and 0.57-fold, respectively, compared with the original spectrum of [**1**-H][PF$_6$]. We thought that this phenomenon was probably due to the strong PET effect between the macrocycle and fluorophore groups. Additionally, fluorescence changes were imperceptible after the addition of base and then acid to the solution of the thread [**2**-H][PF$_6$], which showed that the introduction of the ferrocenyl macrocycle can influence the output of the fluorescence signals (Figure S31). Almost identical results were obtained when 1.5 equivalents of TBAA were added to a dichloromethane solution of rotaxane [**1**-H][PF$_6$] (Figure 2), but the fluorescent decrease was not observed as expected when $NaClO_4$ was added to remove the anion AcO$^-$. Presumably, NaOAc is soluble in dichloromethane solution at a very dilute concentration (10^{-6} M was used in fluorescence analysis), so it is impractical to remove AcO$^-$ in the form of NaOAc precipitate (Figure S30).

Lots of effort was devoted to getting the crystal structure of [**1**-H][PF$_6$] but this was unsuccessful. The model thread **5**, containing only the DAA$^+$ group, was designed to further illustrate the interaction between the DAA$^+$ group and macrocycle **4**. Fortunately, single crystals suitable for X-ray crystallography were obtained through diffusion of *n*-hexane into a CH_2Cl_2 solution of macrocycle **4** and model compound **5**. The solid state structure reveals a [2]pseudorotaxane molecular geometry for the complex **4**⊃**5**, which is stabilized through N–H···O hydrogen bonds. The face-to-face π-stacking interactions of the parallel aromatic rings belonging to two adjacent macrocycle promote the stability of the crystal (Figure 3). The above results confirm that weak noncovalent interactions could be used as driving force to stabilize the complexation between the macrocycle and the DAA$^+$ site. The interlocked structure of **4**⊃**5** fixes the distance between Fc and the anthracene group within the range of effective PET effect, which caused the fluorescent decrease of **4**⊃**5** compared with that of free **5** (Figure S33).[13] Similarly, for rotaxane [**1**-H][PF$_6$], the DAA$^+$ group could stabilize the macrocycle close to the anthracene stopper which caused the weak fluorescence emission of [**1**-H][PF$_6$].

In conclusion, an acid/base and anion-responsive, bistable molecular shuttle bearing an anthracene stopper on the thread and a Fc units on the macrocycle was constructed successfully, in which two different states can be easily and reversibly obtained. The shuttling motion of the functionalized macrocycle between the DAA$^+$ station and the urea site can be

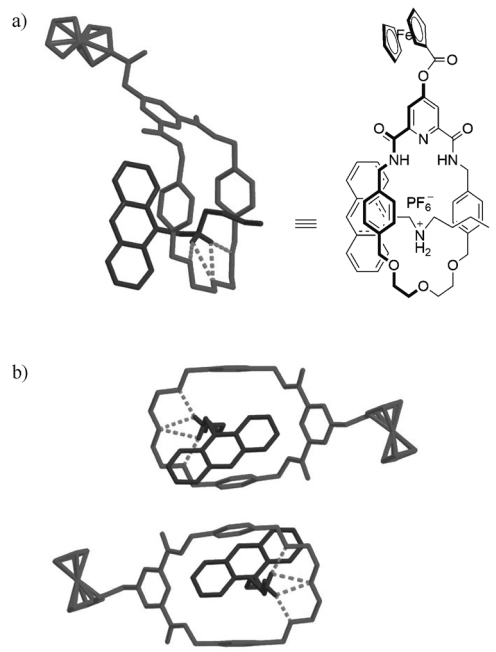


Figure 3. X-ray crystal structure of the pseudorotaxane **4**⊃**5**. a) The intramolecular H-bonds in pseudorotaxane **4**⊃**5**, b) The packing structure of pseudorotaxane **4**⊃**5**. For clarity, all PF_6 counterions have been omitted. Intramolecular hydrogen bonds are shown as dotted lines. Hydrogen bond parameters in the pseudorotaxane structure: N–H···O distances (Å): 2.040(3), 2.112(3), 2.392(4), 2.689(4). N–H···O angles (°): 151.1(3), 160.1(2), 119.3(3), 97.1(2). Face-to-face π-stacking parameter in the packing structure: centroid–centroid distance (Å): 3.733(6).

driven by external acid/base or anion stimuli. The fluorescence of anthracene group can be decreased or enhanced alternately by an adjustable PET effect between the Fc electron donor and the fluorescent stopper. This kind of molecular shuttle would have a bright future for the construction of functional fluorescent switches with multiple outputs.

Experimental Section

Experimental Details

A mixture of **3** (0.216 g, 0.36 mmol) and **4** (0.253 g, 0.36 mmol) in anhydrous CH_2Cl_2 was stirred for 1 h. Then, 3,5-dimethylphenyl isocyanate (0.077 mL, 0.54 mmol) was added, the resulting mixture was stirred at 25 °C for 48 h, and then the solvent was evaporated under reduced pressure. The residue was purified by silica-gel column chromatography (CH_2Cl_2/CH_3OH = 20:1, v/v) to afford [2]rotaxane [**1**-H][PF_6] (0.07 g, 0.048 mmol, 13%) as a yellow solid and dumbbell-shaped salt [**2**-H][PF_6] (0.05 g, 0.067 mmol, 19%) as a yellow solid. See the Supporting Information for more experimental data.

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Keywords: anthracene · fluorescence · molecular shuttle · photoinduced electron transfer · rotaxanes

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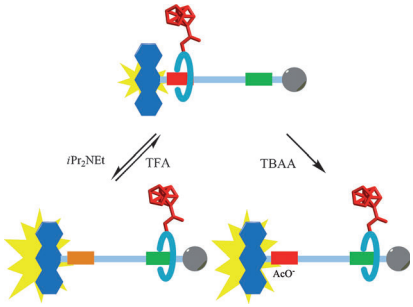
A Ferrocene-Functionalized Bistable [2]Rotaxane with Switchable Fluorescence



Stop in the name of love: An acid/base and anion-based bistable molecular shuttle with an anthracene stopper on the thread and one ferrocenyl unit (Fc) on the macrocycle has been obtained, and by external stimuli, two different states could be easily and reversibly controlled, which were accompanied with the switchable fluorescence changes due to the PET effect between the Fc electron donor moiety and anthracene stopper.