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Dual-Mode Operation of a Bistable [1]Rotaxane with a Fluorescence Signal

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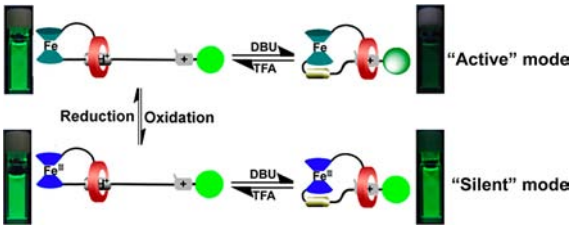
ABSTRACT



We report the operation of a ferrocene-based bistable [1]rotaxane that can work in two parallel platforms. In an "active" signal mode, the relative mechanical movement of its ring and thread in response to external acid–base-stimuli can result in a remarkable fluorescence signal output observed by the naked eye, whereas no obvious fluorescence change occurred in a "silent" signal mode after oxidation. Its fluorescence responses to the different combinations of DBU and/or $Fe(ClO_4)_3$ corresponds to an INHIBIT logic gate.

Bistable rotaxanes, in which the ring component can be switched between two distinct coconformations in response to external stimuli,[1] are of fundamental importance because of their great potential for applications in molecular switches[2] and machines.[3] Much attention has been focused on functional bistable [2]rotaxanes[4] with recognizable output signals, such as UV/vis absorption,[5] fluorescence,[6] electrochemical signals,[7] and circular dichroism.[8] However, only a few examples on functional [1]rotaxanes[9] were reported up to now. A [1]rotaxane, in which a thread part is covalently connected with and threaded into a macrocycle, is an interesting species of the family of MIMs[10] due to its rather unique and appealing architecture; for example,

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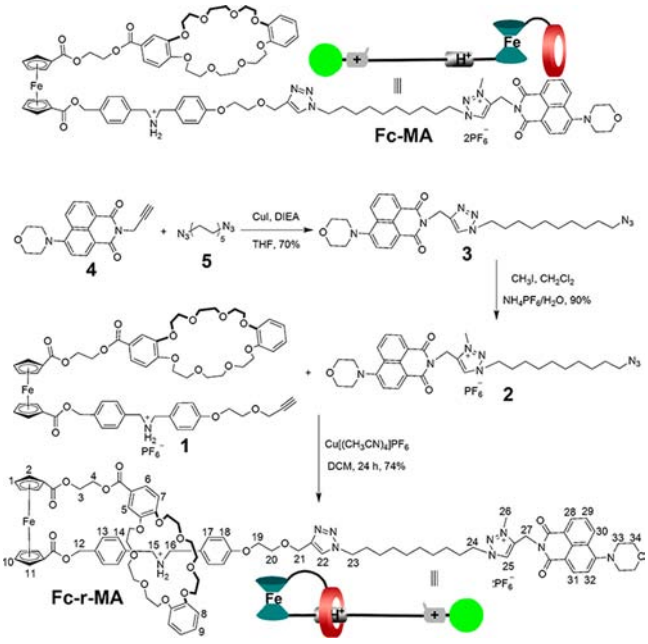
bistable [1]rotaxanes can be designed as molecular-based actuators[11] and muscles,[12] which can induce reversible extension and contraction at the molecular level. Thus, a thorough investigation and better understanding of distinct functions performed by two diastereomers, i.e. a [1]rotaxane and its corresponding noninterlocked species, are highly desired.

Here, we report the dual-mode operation of a ferrocene-based bistable [1]rotaxane that can work in two parallel platforms (see abstract graphic). It undergoes relative mechanical movements of its ring and thread in response to external acid−base stimuli and generates a remarkable fluorescence signal output monitored by the naked eye, thus working in a platform with an "active" signal mode; after oxidation by $Fe(ClO_4)_3$,[13] by which the ferrocene (Fc) unit[14] is oxidized from the di- to trivalent state, the system can "lock" its fluorescence intensity in its original level, and the relative movements of its ring and thread cannot result in an obvious fluorescence change of the system, thus working in a platform with a "silent" signal mode. This kind of system may pave the way for constructing smart switchable materials with controllable functions.

Scheme 1. Preparation of Target [1]Rotaxane **Fc-r-MA** and the Chemical Structure of Reference Compound **Fc-MA**



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The structures of [1]rotaxane **Fc-r-MA** and the corresponding noninterlocked compound **Fc-MA** are shown in Scheme 1. [1]Rotaxane **Fc-r-MA** has two key features. On one hand, a redox-active Fc unit is introduced as an axle, and its upper and lower cyclopentadienyl (Cp) rings are covalently linked with a dibenzo-24-crown-8 (DB24C8) macrocycle and a rod-like thread at each by an ester bond, respectively. On the other hand, a 4-morpholin-naphthalimide (MA) was chosen as a terminated stopper, whose fluorescence could be adjusted on and off by a distance-dependent photoinduced electron transfer (PET) process between an electron-rich Fc unit and an electron-deficient MA fluorophore.[16b] Meanwhile, the rod part, a long-distance alkyl chain, was introduced to separate two distinguishable recognition sites for DB24C8, namely a dibenzylammonium (DBA)[14b,15] station and a *N*-methyltriazolium (MTA)[15,16a] station. As shown in Scheme 1, the well-known "click" reaction between alkyne **4** and azide **5** in the presence of CuI and *N*,*N*-diisopropylethylamine (DIEA) gave **3** in a 70% yield, and then subsequent methylation with CH_3I and anion exchange with NH_4PF_6 aqueous solution can give azide **2** with a secondary MTA recognition site in a high yield (90%). Compound **1**[14b] can form a predominantly self-complexing [1]pseudorotaxane in CH_2Cl_2, and a subsequent Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction[15d] with azide **2** can produce the target [1]rotaxane in a 74% yield. The noninterlocked reference compound **Fc-MA** was prepared using a different strategy, as shown in Scheme S1.

Both **Fc-r-MA** and reference compound **Fc-MA** were characterized by ^1H, ^{13}C NMR spectroscopies and high-resolution electrospray ionization (HR-ESI) mass spectrometry. HR-ESI mass spectra supported the diastereomers of **Fc-r-MA** and **Fc-MA** with the major peaks at m/z 829.8434 and 829.8433 as doubly charged peaks for $[M-2PF_6]^{2+}$, respectively. Furthermore, the ^1H NMR spectra (Figure 1) of **Fc-r-MA** and **Fc-MA** showed different patterns in CD_3COCD_3. Compared with those of compound **Fc-MA** (Figure 1a), the peaks for the phenyl protons H_{13}, H_{14}, H_{17} neighboring the DBA station on the rod part of **Fc-r-MA** (Figure 1b) are shifted by $\Delta\delta$ of −0.24, 0.10, and −0.28 ppm, respectively. While the methylene protons H_{15} and H_{16} on the DBA recognition site are shifted downfield by $\Delta\delta$ of 0.10 ppm. Moreover, a 2D Roesy NMR spectrum of rotaxane **Fc-r-MA** (Supporting Information (SI), Figure S1) showed clear correlation peaks between the phenyl protons H_{14} (peak A) and the alkyl H_{15}, H_{16} (peak C) on the thread close to DBA recognition and methylene protons on the DB24C8 ring, as well as the phenyl protons H_7, H_8, H_9 on DB24C8 and the phenyl protons H_{14} (peak B). All the evidence confirms that the DB24C8 ring encircles at the DBA recognition site in the structure of rotaxane **Fc-r-MA**.

Next we investigated the reversible acid−base-driven shuttling motion of **Fc-r-MA**. Deprotonation of the

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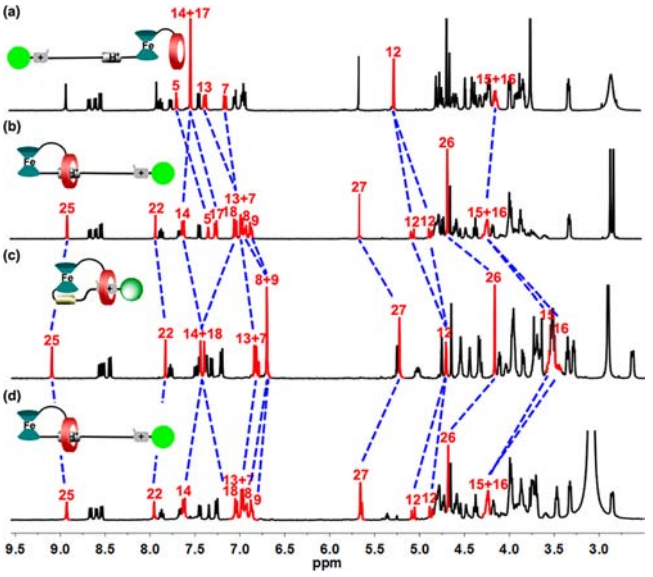

Figure 1. Partial ^{1}H NMR spectra (400 MHz, CD_3COCD_3, 298 K, 2.0×10^{-3} M) of (a) **Fc-MA**, (b) **Fc-r-MA**, (c) deprotonation with addition of 2.0 equiv of DBU to sample b and (d) reprotonation with addition of 4.0 equiv of TFA to sample c.

DBA moiety was achieved by addition of 2.0 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which can result in the migration of the MTA recognition site into the DB24C8 ring and the observation of remarkable ^{1}H NMR spectral changes. As shown in Figure 1c, the protons H_{25} and H_{26} on the MTA recognition site were shifted ($\Delta\delta$ = 0.19 and −0.52 ppm, respectively), and the protons H_{27} close to the MTA recognition site were shifted upfield ($\Delta\delta$ = −0.39 ppm), which indicated that the DB24C8 ring was encircled over the MTA station from the original DBA station. Meanwhile, the 2D Roesy NMR spectrum of the DBU-added solution of **Fc-r-MA** (SI, Figure S2) confirmed the same results. Reprotonation of the generated dibenzylamine center by the addition of 4.0 equiv of CF_3COOH resulted in regeneration of the original ^{1}H NMR spectrum (Figure 1d), which suggested that the macrocycle was recovered completely to encircle over the DBA station. Using ^{1}H NMR spectroscopy, we proved the reversible translational motion of the molecular rod relative to the macrocycle between the two stations.

Fluorescence output has been recognized as a convenient way to monitor the shuttling motion in bistable rotaxane systems.[6,16] A very remarkable fluorescence change was observed in [1]rotaxane **Fc-r-MA** in response to chemical stimuli. Compared with the original spectrum, the emission intensity at 521 nm decreased 80% upon addition of 2.0 equiv of DBU (Figure 2a). Furthermore, after adding 2.0 equiv of DBU to the solution of **Fc-r-MA**, time-resolved fluorescence (Figures S8−S9) displayed an almost constant long lifetime of 6.33 ns (56%) from the original 6.11 ns (35%) and a dramatically smaller short lifetime of 1.01 ns (44%) from the original 3.26 ns (65%). The longer lifetime is the intrinsic lifetime of the MA fluorophore, while the shorter lifetime can be attributed to electron transfer between the electron-rich Fc unit and the electron-deficient MA fluorophore. In other words, those changes could be ascribed to the closer spatial distance between the Fc unit and MA fluorophore upon addition of DBU. To obtain more information about the structures of [1]rotaxane **Fc-r-MA** at different states, we performed theoretical calculations on the two conformers (Figure S3). The optimized structure of **Fc-r-MA** in the original state shows that the macrocycle encircles on the DBA recognition site and the distance (Fe−N) between the iron atom (Fe) of the ferrocene moiety and the nitrogen atom (N) of the naphthalimide is ∼35.66 Å. After the deprotonation of the DBA station, the MTA recognition site resides in the DB24C8 ring instead, and the rod part moves toward the ferrocene unit, which leads to a closer spatial distance (12.87 Å) between the iron atom (Fe) and the nitrogen atom (N). Thus the distance-dependent PET process from the electron-rich Fc to the electron-deficient MA fluorophore became more efficient upon addition of DBU, which resulted in the fluorescence quenching. Then after adding 5.0 equiv of $Fe(ClO_4)_3$ to this solution, the emission intensity (Figure S5a) at 521 nm enhanced dramatically to its original level. This phenomenon could be attributed to the oxidation of the Fc unit; after oxidation, the electron-rich Fc unit lost its electron-donating property, and the PET process was prohibited, resulting in fluorescence enhancement. The fluorescence spectrum can also be recovered upon addition of 4.0 equiv of TFA, which can be observed by the naked eye, indicating the system is working in a platform with an "active" signal output; i.e., the acid−base-driven extraction or extension motion can generate an obvious fluorescence intensity change.

The fluorescence intensity of [1]rotaxane **Fc-r-MA** can be "locked" in its original level in the presence of $Fe(ClO_4)_3$. It should be mentioned that the ^{1}H NMR spectrum of [1]rotaxane **Fc-r-MA** upon addition of $Fe(ClO_4)_3$ showed the macrocycle still encircling on the DBA station (Figure S7). Upon addition of 5.0 equiv of $Fe(ClO_4)_3$ to the dichloromethane solution of [1]rotaxane **Fc-r-MA**, which can convert Fe(II) to Fe (III), the emission intensity at 521 nm had no obvious changes compared with the original spectrum (Figure S5b). Meanwhile, upon subsequent addition of 2.0 equiv of DBU to this solution, the emission intensity at 521 nm almost remains unchanged. It was reasonable that in this case the electron- donating abilities of the Fc unit were reduced by the oxidation, and as a result, the PET process was arrested, keeping the fluorescence intensity at a high level, even though the macrocycle was changed to reside over the MTA station upon addition of 2.0 equiv of DBU. Thus, the bistable [1]rotaxane **Fc-r-MA** can work in a platform with a "silent" signal output; i.e. the acid−base-driven extraction or extension motion cannot result in an obvious fluorescence

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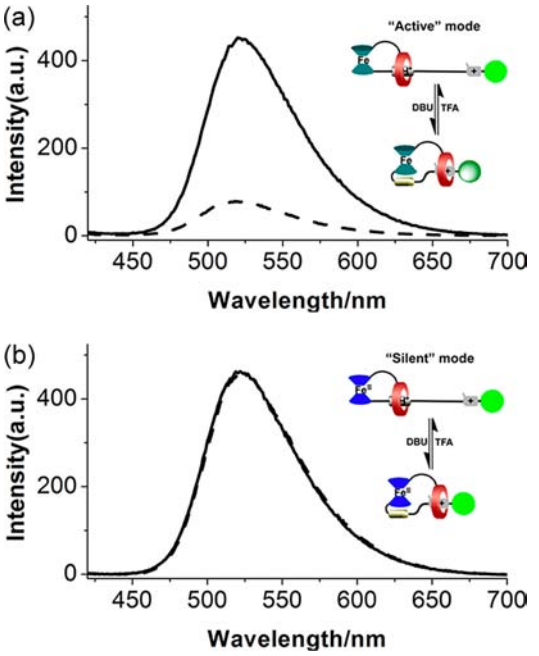
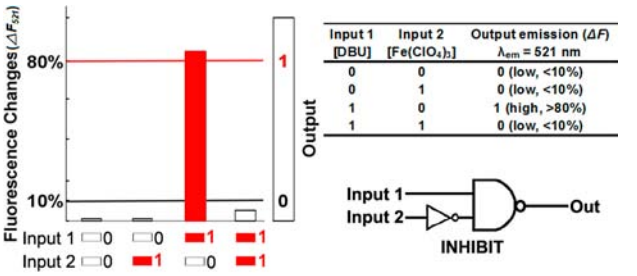


Figure 2. Fluorescence spectral changes in CH_2Cl_2 solution of (a) [1]rotaxane **Fc-r-MA** (1×10^{-5} M) (the solid line) and the mixture obtained after adding 2.0 equiv of DBU to the solution of **Fc-r-MA** (the dash line) and (b) the mixture obtained after adding 5.0 equiv of $Fe(ClO_4)_3$ to the solution of **Fc-r-MA** (the solid line) and the mixture obtained after adding 2.0 equiv of DBU to the $Fe(ClO_4)_3$-added solution of **Fc-r-MA** (the dash line). Inset: corresponding model diagrams. The excitation wavelength of all fluorescence spectra was 409 nm.

intensity change. The interconversions between the two parallel platforms are reversible using repeatable oxidation ($Fe(ClO_4)_3$) and reduction (ascorbic acid).

Interestingly, the fluorescence responses (ΔF_{521}) of [1]rotaxane **Fc-r-MA** to the different combinations of DBU (**I1**) and/or $Fe(ClO_4)_3$ (**I2**) correspond to an INHIBIT logic gate (Figure 3) with a two-input AND gate with one input carrying a NOT gate.[17] In the present INHIBIT logic gate, the input carrying NOT gate is $Fe(ClO_4)_3$ (**I2**), and the output (ΔF_{521}) is designated as "0" or "1". Importantly, the output 0 and 1 states of the current logic circuit represent several different supramolecular configurations. Because of the reversibility of the acid−base-driven and redox processes, the relative mechanical motions are



Input 1 [DBU]	Input 2 [$Fe(ClO_4)_3$]	Output emission (ΔF) λ_{em} = 521 nm
0	0	0 (low, <10%)
0	1	0 (low, <10%)
1	0	1 (high, >80%)
1	1	0 (low, <10%)

Figure 3. Output (ΔF_{521}) and the corresponding truth tables for the INHIBIT gate **Fc-r-MA** in response to external stimuli, DBU (**I1**) and/or $Fe(ClO_4)_3$ (**I2**). The solid line indicates the detection limit (80%).

repeatable and are accompanied by a reversible fluorescent output signal, and the current INHIBIT gate operates repeatedly. Furthermore, it should be noted that the corresponding noninterlocked species, **Fc-MA**, exhibited a very small magnitude of fluorescence changes in response to different orders or combinations of external stimuli DBU and/or $Fe(ClO_4)_3$, respectively (Figure S5c−S5d).

In conclusion, we have designed and constructed a bistable ferrocene-based [1]rotaxane that can work in two parallel platforms with different fluorescence response modes. The system can perform reversible mechanical motions in response to external base and acid stimuli, generating a remarkable fluorescence changes monitored by the naked eye, or has a fluorescence signal locking function upon addition of $Fe(ClO_4)_3$. The system holds important potential for the development of complicated logic circuits with memories or sequential functions.[18]

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Supporting Information Available. Full experimental procedures and characterization data of all the new compounds including [1]rotaxane **Fc-r-MA** and compound **Fc-MA**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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