ORGANIC LETTERS

2012
Vol. 14, No. 23
5900–5903

A Switchable Ferrocene-Based [1]Rotaxane with an Electrochemical Signal Output

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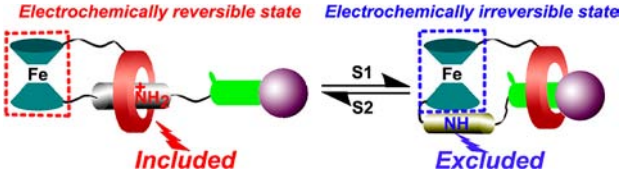
Received October 14, 2012

ABSTRACT



A [1]rotaxane, in which a linear rod is attached to one cyclopentadienyl (Cp) ring of a ferrocene unit and threaded into a dibenzo-24-crown-8 connected to the other Cp ring, was prepared. The mechanical motion of the rod-like part relative to the macrocycle has been demonstrated using ^{1}H NMR spectroscopy. Cyclic voltammetry (CV) showed that the system can be chemically switched between electrochemically reversible and irreversible states, depending on the inclusion and exclusion of the ammonium/amine group from the macrocycle.

Bistable rotaxanes, as the most common species of mechanically interlocked molecules (MIMs),[1] have received considerable attention because of their applications in molecular devices and as components of molecular machinery.[1−3] Until now, there has been much work aimed at the design and construction of multifunctional [2]rotaxanes[4] with two distinguishable states that can be recognized by various output signals, such as UV/vis absorption,[4,5] fluorescence,[5,6] electrochemical signals,[7] and circular dichroism.[8]

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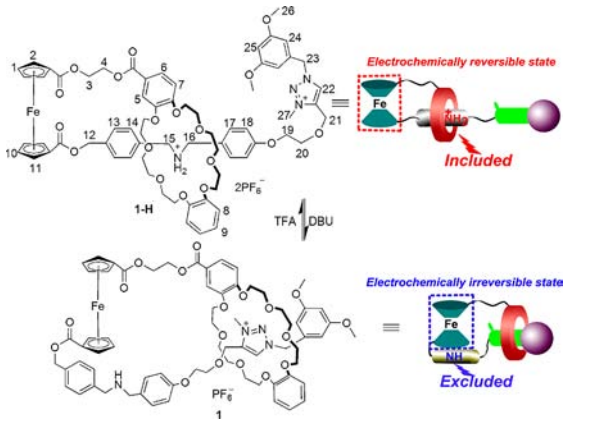
10.1021/ol302826g
Published on Web 11/12/2012

A [1]rotaxane,[9] in which the macrocycle and the axle part are bound covalently and closely, is also an important member of the family of MIMs. The architecture of this kind of interlocked system is rather unique and appealing, and their syntheses and functions also merit extensive attention. However, until now, only few [1]rotaxane systems[9] have been reported, most of which do not employ two well-separated recognition sites.[10] We believe that introduction of two recognizable stations in such a structure is the key for the design of a switchable system that can convert between two different states with remarkable output changes.

In this paper, we report the synthesis and switching property of a bistable ferrocene-based [1]rotaxane **1-H**, which can switch between two different states, namely, an electrochemically reversible state and an electrochemically irreversible state, caused by chemically driven inclusion and exclusion of an ammonium/amine group by the dibenzo-24-crown-8 (DB24C8) macrocycle. As shown in Scheme 1, [1]rotaxane **1-H** employs a ferrocene unit[7] as an axle, and an electrochemically active center is covalently attached with a DB24C8 macrocycle and a rod-like thread at each cyclopentadienyl (Cp) ring, respectively. The rod part, which contains two distinguishable recognition sites, namely, a dibenzylammonium site (DBA) and a *N*-methyltriazolium (MTA)[11] site, was threaded into the macrocycle with a bulky 3,5-dimethoxybenzene stopper situated at the end of the rod part to form an interlocked [1]rotaxane structure. In the original state, the DB24C8 macrocycle encircles the DBA station, which makes the amine group "included"; as a result, cyclic voltammetry (CV) showed a reversible oxidation−reduction curve of the free ferrocene unit. After deprotonation with a base, the macrocycle allowed the amine group to be "excluded" because of its movement and its location at the MTA station, which showed an irreversible oxidation−reduction curve. Thus, the system can switch between an electrochemically reversible state and an electrochemically irreversible state, which gives insight for the design of smart materials with switchable properties.

The syntheses of [1]rotaxane **1-H**, reference compound **3-H**, and the key intermediates are shown in Scheme 2. We designed compound **4**, containing a dibenzo-24-crown-8-based macrocycle and a Boc-protected DBA station with a terminal alkyne attached to each Cp ring of the ferrocene unit, respectively. After removal of the Boc group by treatment with TFA, it can form a predominantly self-complexing [1]pseudorotaxane in less polar solvent such as

Scheme 1. Switching Process and Schematic Representation of the bistable Ferrocene-Based [1]Rotaxane **1-H** That Can Switch between Two Different States



CH_2Cl_2, which was converted into [1]rotaxane **2-H** in a moderate yield through the well-known copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction with 3,5-dimethoxybenzyl azide **5**. [1]Rotaxane **2-H** was treated with methyl iodine, which was then followed by anion exchange with saturated NH_4PF_6 to yield [1]rotaxane **1-H** with primary DBA and secondary MTA recognition sites for the DB24C8 macrocycle. The noninterlocked reference compound **3-H** was prepared using two different strategies, as shown in Schemes 2 and S3, respectively. The first strategy, shown in Scheme 2, contains a "click" reaction between alkyl **4** and azide **5** in 54% yield to generate compound **3-Boc**, which was treated with TFA to remove the Boc group, and then followed by anion exchange to afford compound **3-H** in 76% yield. In the other strategy, compound **4** was first treated with TFA to remove the Boc group to obtain an intermediate with a DBA station that has a noncomplexing structure in polar solvent such as DMF, which was converted into compound **3-H** in a moderate yield (40%) through the "click" reaction with azide **5**. The two different synthetic strategies can yield the same product, as evidenced by the same ^{1}H NMR spectrum and the same molecular weight.

[1]Rotaxane **2-H** and compound **3-H** were all characterized by ^{1}H NMR spectroscopy and high-resolution electrospray ionization (HR-ESI) mass spectrometry. The HR-ESI mass spectra of **2-H** and **3-H** showed the major peaks at m/z 1293.4583 and 1293.4580, respectively, which can be assigned to the loss of PF_6^-, i.e. $[M\text{-}PF_6]^+$. This result supports the different isomers of **2-H** and **3-H** with the same molecular weight. However, the ^{1}H NMR spectra (Figure 1) of **2-H** and **3-H** showed different patterns in CD_3COCD_3. Compared with those of compound **3-H** (Figure 1a), the peaks for the methylene protons H_{15} and H_{16} on the DBA recognition site (Figure 1b) in rotaxane **2-H** are integrated and shifted downfield ($\Delta\delta$ = 0.20, 0.29 ppm). Meanwhile, the chemical shifts for the phenyl protons H_{13}, H_{14}, H_{17} adjacent to the DBA center are also changed with $\Delta\delta$ of −0.24, 0.14, and −0.20 ppm, respectively. The protons

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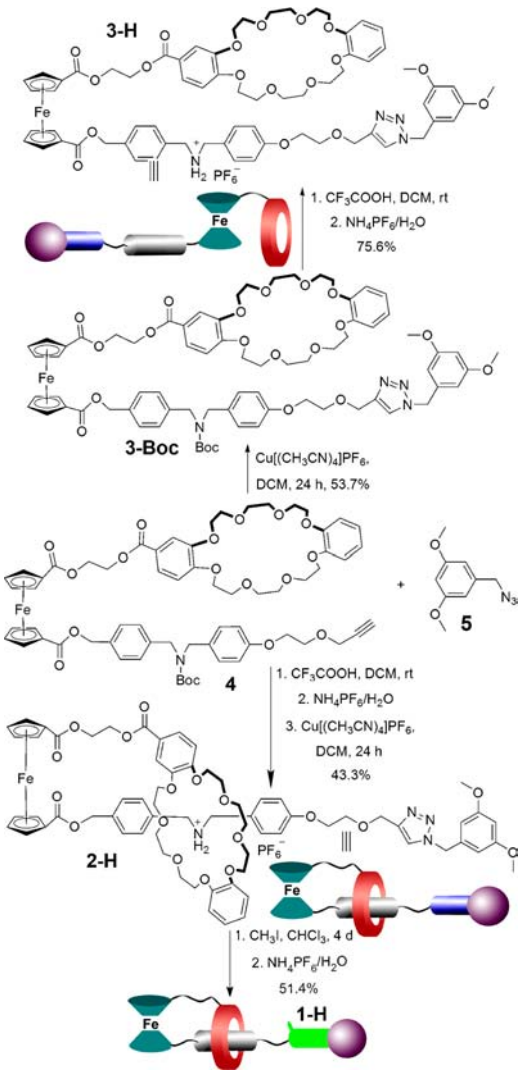
Scheme 2. Preparation of [1]Rotaxane **1-H**, **2-H** and Compound **3-H**[a]



[a] The assignments for protons of **2-H** or **3-H** are the same as these for rotaxane **1-H** shown in Scheme 1.

H_{12} neighboring the DBA station in the rod part emerged as a doublet in [1]rotaxane **2-H**, in comparison with a singlet in compound **3-H**. All the evidence confirmed that compound **2-H** has an interlocked structure, and the DB24C8 ring encircles at the DBA recognition site.

The structure of the target compound [1]rotaxane **1-H** obtained by the methylation of [1]rotaxane **2-H** was also confirmed. The HR-ESI mass spectrum of [1]rotaxane **1-H** showed that the most intense peak emerges at m/z 654.2414 as a doubly charged peak, corresponding to the consecutive loss of two PF_6^- counterions. The ^{1}H NMR spectrum (Figure 2a) of [1]rotaxane **1-H** also proved that the DB24C8 macrocycle was encircling at the DBA binding site, similar to the structure of **2-H** (Figure 1). Moreover, 2D Roesy NMR spectrum of rotaxane **1-H** (Supporting Information (SI), Figure S3) provided good evidence for the formation of the rotaxane **1-H** and the fact that the

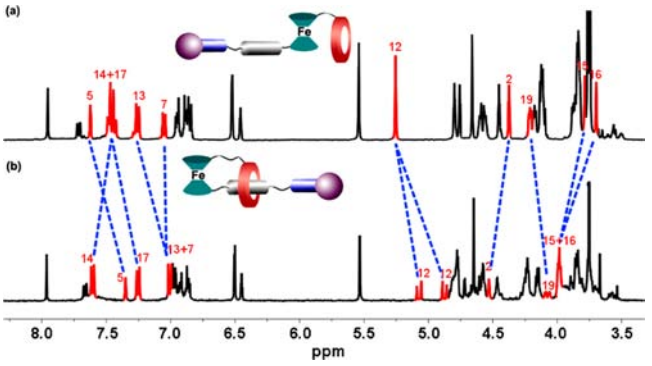


Figure 1. Partial ^{1}H NMR spectra (400 MHz, CD_3COCD_3, 298 K) of (a) **3-H** and (b) **2-H**.

DBA station resides inside the DB24C8 ring. Using HR-ESI mass spectrometry, ^{1}H NMR spectroscopy, and 2D Roesy NMR spectroscopies, we confirmed compound **1-H** existing as an interlocked [1]rotaxane structure as shown in Scheme 1.

Next we focused on the reversible acid−base-driven mechanical motion of **1-H**. Addition of 1.0 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to the CD_3COCD_3 solution of rotaxane **1-H** can deprotonate the DBA moiety, generating [1]rotaxane **1** (Scheme 1); as a result, the macrocycle was changed to reside over the MTA station, and remarkable ^{1}H NMR spectral changes were observed. As shown in Figure 2b, the protons H_{22} and H_{27} on the MTA recognition site are dramatically shifted ($\Delta\delta$ = 0.55 and −0.45 ppm, respectively), which indicates the migration of the MTA recognition site into the DB24C8 ring.

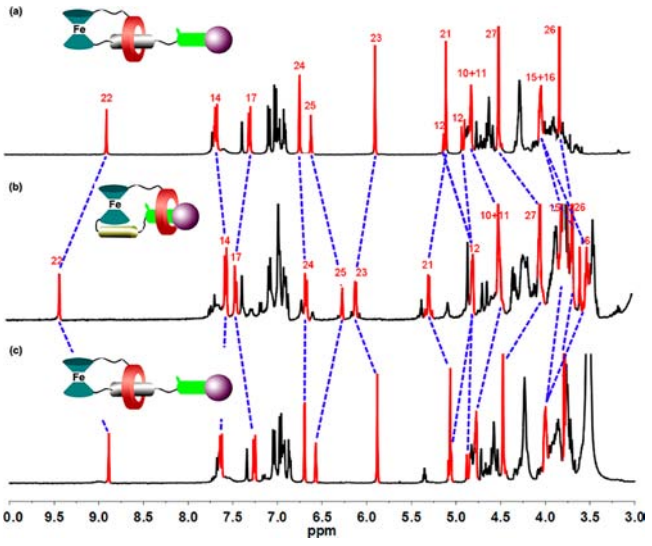


Figure 2. Partial ^{1}H NMR spectra (400 MHz, CD_3COCD_3, 298 K) of (a) **1-H**, (b) deprotonation with addition of 1.0 equiv of DBU to sample a, and (c) reprotonation with addition of 2.5 equiv of TFA to sample b.

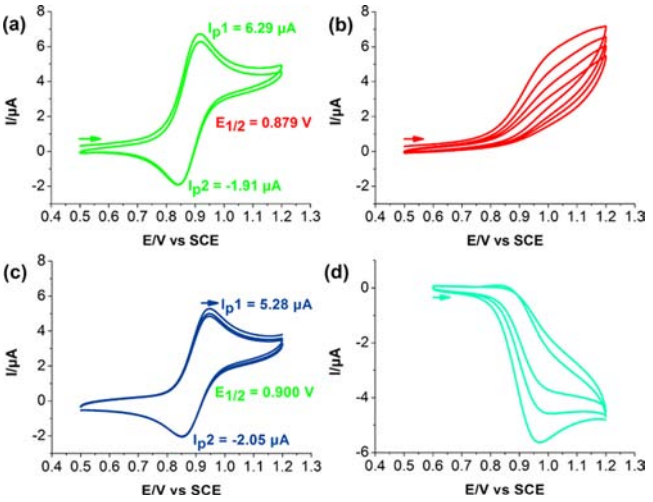


Figure 3. Evolution of the cyclic voltammetric curves of (a) **1-H**, (b) **1**, (c) **2-H**, and (d) **3-H** in CH_3CN with $[(n\text{-}Bu)_4N]PF_6$ (0.1 M) as supporting electrolyte, scanned at 20 mV s^{-1}. The contentration of each compound is 1×10^{-3} M.

Moreover, a key change was observed in the peak of the protons H_{12} neighboring the DBA station, which was changed from one doublet into two doublets with $\Delta\delta$ of -0.31 and -0.09 ppm, respectively. The 2D Roesy NMR spectrum of rotaxane **1-H** after addition of DBU (ESI, Figure S4) showed clear correlation peaks between the phenyl protons H_5, H_7, H_6, H_8, and H_9 on the DB24C8 ring, and the protons H_{27} (peak A), H_{26} (peak B), H_{21} (peak C), H_{23} (peak D), and H_{14} (peak E) on the thread also confirmed that the MTA recognition site resides in the DB24C8 ring. Upon addition of 2.5 equiv of CF_3COOH, the original ^1H NMR spectrum was regenerated (Figure 2c), which suggested that the system was recovered completely to its original state. In short, using ^1H NMR and 2D Roesy NMR spectroscopies, we proved the reversible translational motion of the molecular rod relative to the macrocycle. It should be noted that the structural difference between **2-H** (lack of a methyl group in the triazole unit) and **1-H** makes **2-H** a system that has only one recognition site, which can also be deprotonated with DBU; however, no obvious shuttling motion is observed (SI, Figure S2).

In this system, the reversible inclusion and exclusion of the macrocycle on the amine group in the rod-like thread can be adjusted by external acid–base stimuli, which can be used to construct a molecular device that can be switched between an electrochemically reversible state and an electrochemically irreversible state. Based on electrochemical properties of ferrocene (Fc), the cyclic voltammetric (CV) curves of [1]rotaxane **1-H** in CH_3CN containing 0.1 M $[(n\text{-}Bu)_4N]PF_6$ as a supporting electrolyte (Figure 3) were investigated. In the original state, [1]rotaxane **1-H** has a reversible CV curve of the **Fc** unit. The half-wave potential ($E_{1/2}$) of **1-H** is detected by a shift in $E_{1/2}$ = 0.879 V (Figure 3a) to a more positive value ($\Delta E_{1/2}$ = +0.455 V), compared with that of **Fc** ($E_{1/2}$ = 0.424 V) (SI, Figure S5a), and by a decrease in the peak currents (Ip). After deprotonated with DBU, the CV curve (Figure 3b) of [1]rotaxane **1**[12] exhibits an irreversible feature in that the oxidation and reduction peaks gradually became lower. We deduced that this CV signal change in the two states of [1]rotaxane **1-H** is ascribed to the conformation change, i.e., the inclusion or exclusion of the DBA site by the macrocycle. Control experiments with [1]rotaxane **2-H** and compound **3-H** were performed to confirm this deduction. [1]Rotaxane **2-H** in which the DBA site is also included showed a very similar CV curve (Figure 3c) with that of rotaxane **1-H**, whereas compound **3-H** showed an irreversible CV curve (Figure 3d). Further control experiments showed that the addition of 1.0 equiv of dibenzylamine to **1-H** or **Fc** (SI, Figure S5b-S5c) also yielded irreversible CV curves, indicating an interaction between the amine and the oxidized or reduced ferrocene species, which results in the irreversible oxidation and reduction processes of ferrocene.[13]

In conclusion, we have designed and constructed a ferrocene-based [1]rotaxane with two recognition sites, which can perform reversible shuttling motion and show distinguishable electrochemical signals in the two states. The system can switch between an electrochemically reversible state and an electrochemically irreversible state, which holds potential for the design and construction of switchable molecular systems.

Acknowledgment. We thank the NSFC/China (20902024, 21272073 and 21190033), National Basic Research 973 Program (2011CB808400), the Foundation for the Author of National Excellent Doctoral Dissertation of China (200957), the Fok Ying Tong Education Foundation (121069), the Fundamental Research Funds for the Central Universities (WJ1014001, WJ1213007), and the Innovation Program of Shanghai Municipal Education Commission for financial support.

Supporting Information Available. Full experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

(12) [1]Rotaxane **1** was obtained in a following procedure: [1]Rotaxane **1-H** was treated with excess DBU in CH_2Cl_2 and then washed with deionized water five times to remove DBU, followed by flash column chromatography to yield [1]rotaxane **1** for CV measurement.

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The authors declare no competing financial interest.