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A Three-Level Luminescent Response in a Pyrene/Ferrocene Rotaxane

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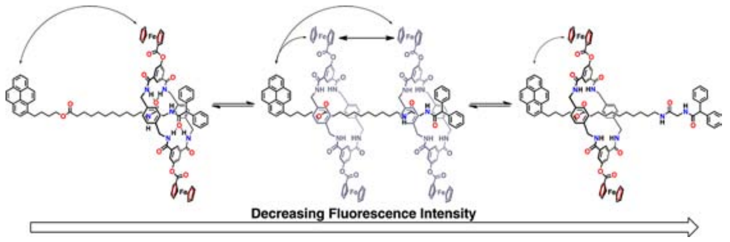
ABSTRACT



A solvent switchable rotaxane equipped with a pyrene stopper and with two ferrocenyl units on the macrocycle is reported, in which three different states, two nondegenerate and one degenerate, can be obtained in different solvents at room temperature. This is accompanied by high contrast changes in fluorescence intensity of the pyrene stopper by the presence of the ferrocenyl moieties on the macrocycle, which quench the emission of pyrene more efficiently with proximity.

Synthetic fluorescent switches and probes able to provide distinct emissive responses to different environments[1] have attracted much attention because of the great potential of application in different fields which are relevant to materials science and biology, such as molecular logic, imaging, sensing, and characterizing microenvironments, among others.[1a,2] Bistable rotaxanes provide an excellent framework to develop switches and probes, since the

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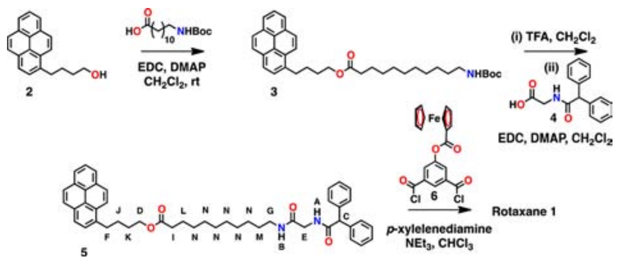
controlled motion of the macrocycle from one recognition site on the thread ("station") to another can be used to develop a distinct environmental emissive response[2,3] that can be detected with a wide variety of accessible spectroscopic techniques, both locally and remotely, and in some cases even with the naked eye.[2c,3a,3m] Herein we report a solvent switchable molecular shuttle (rotaxane **1**) with a pyrene stopper and with two ferrocenyl units on the macrocycle, in which three different states, two nondegenerate and one degenerate, can be obtained in different solvents at room temperature. This is accompanied by high contrast changes in fluorescence intensity of the pyrene stopper by the presence of the ferrocenyl moieties on the macrocycle, which quench the emission of pyrene more efficiently with proximity.

Rotaxane **1** consists of a macrocycle, functionalized with two ferrocenyl units, interlocked to a thread, equipped with (i) a pyrene unit, which acts as both a fluorophore and a stopper; (ii) an alkyl station; (iii) a 1,4-diamide station; and (iv) a diphenyl stopper.

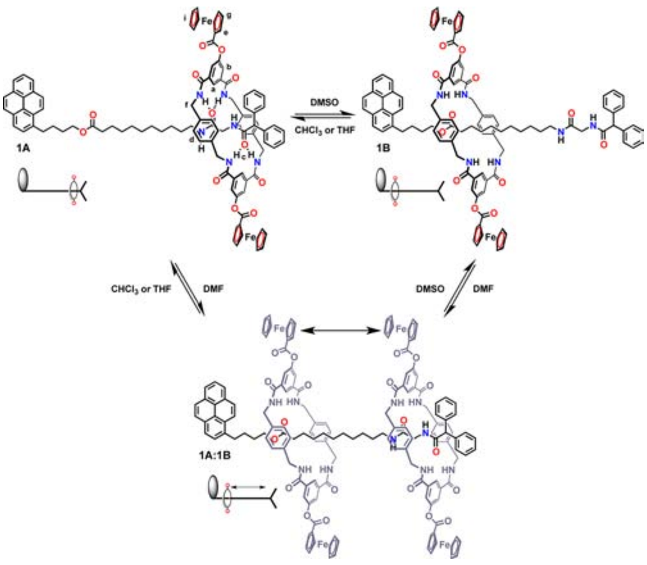
Scheme 1. Synthesis of Rotaxane **1**



Thread **5** was synthesized from 1-pyrenebutanol (**2**) as shown in Scheme 1. First, compound **2** was esterified with 11-Boc-aminoundecanoic acid in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) and 4-(dimethylamino)pyridine (DMAP). The terminal amine of **3** was deprotected in the presence of trifluoroacetic acid (TFA) and subsequently acylated with **4**[4] upon activation with EDC and DMAP to yield thread **5**. Rotaxane **1** was synthesized employing a modification[3j,5] of Leigh's protocol[6] by adding 5-ferroceneacetoxyisophthaloyl chloride **6**[5] and *p*-xylylenediamine to thread **5** under high dilution conditions.

Rotaxane **1** presents two different translational isomers in different solvents as observed by NMR spectroscopy (see Scheme 2 and Figure 1). In relative nonpolar solvents (i.e., $CDCl_3$, THF-d_8), the macrocycle is located primarily over the 1,4-diamide station (translational isomer **1A**) confirmed by the shielding of protons E and A with those of thread **5** due to the anisotropy of the aromatic rings on the macrocycle. Conversely, in DMSO-d_6, the macrocycle decomplexes from the 1,4-diamide station and switched to sit on top of the alkyl chain (translational isomer **1B**); as a consequence, the protons N of the alkyl chain are shielded for as much as 1.0 ppm, while protons E and A and are nearly deshielded (Figure 1, Table 1). The situation is different in DMF-d_7 where the macrocycle shuttles back and forth between the two stations that become energetically degenerate, as reflected by the simultaneous and less efficient shielding of the protons of the alkyl chain (M and N) and of the 1,4-diamide station (E and A) (Figure 1, Table 1).

Scheme 2. Solvent Switchable Behavior of Rotaxane **1** in Different Solvents at Room Temperature



Absorption measurements carried out on thread **5** and rotaxane **1** are dominated by the absorption of 1-substituted pyrene with matching maxima for both compounds in the same solvent. In the case of rotaxane **1**, an additional broad absorption band (400−550 nm) was observed that corresponds to the ferrocenyl moieties (Figure S9).

On the other hand, steady-state fluorescence measurements reveal an interesting trend (Figure 2, Table 2). The pyrene fluorescence (325 nm excitation), which seems to be unaffected in thread **5** (i.e., 100%), is heavily quenched in rotaxane **1** (i.e., 13% in $CHCl_3$; 9% in THF). Time-resolved fluorescence measurements (295 nm excitation) further confirm this, since for the major emitting components lifetimes were detected on the order of hundreds of nanoseconds for thread **5** (i.e., 194 ns) and of tenths of nanoseconds for rotaxane **1** (i.e., 54 ns) in Ar-saturated THF. The situation changes completely in polar solvents, and the emission is quenched more strongly with increasing hydrogen bond basicity (i.e., 8% in DMF; 4% in DMSO). In time-resolved fluorescence measurements

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(7) In addition, a 125 ns long-lived component is seen. This is attributed to slow conformational changes due to the increased viscosity of the solvent and the flexibility of the butyl linker.

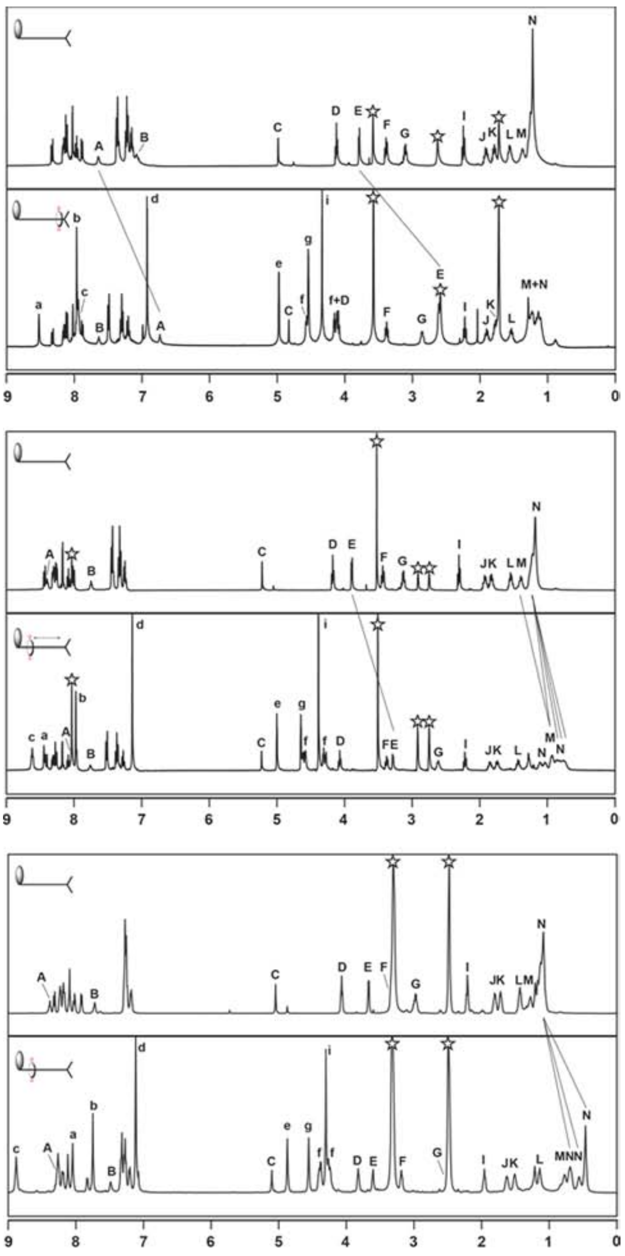

Figure 1. NMR of thread **5**, and rotaxane **1** in THF-d_8 (top), DMF-d_7 (center), and DMSO-d_6 (bottom). The assignments correspond to the lettering shown in Schemes 1 and 2.

Table 1. Shielding ($\Delta\delta$) of the Indicated Protons of Rotaxane **1** versus Thread **5**

solvent	$\Delta\delta_E$ (ppm)	$\Delta\delta_A$ (ppm)	$\Delta\delta_N$ (ppm)
$CDCl_3$	−1.3	−0.9	−0.1
THF-d_8	−1.2	−0.9	−0.2
DMF-d_7	−0.6	−0.3	−0.6
DMSO-d_6	−0.1	−0.1	−1.0

carried out in Ar-saturated DMSO, thread **5** gives rise to a fairly long-lived component (i.e., 118 ns) while the 54 ns shorter-lived component for rotaxane **1** in THF is reduced to 8.7 ns in DMSO.[7]

To ensure that any effect observed is undoubtedly owed to shuttling and not related to the solvent, 1-pyrenebutylferroceneacetate **7**[8] was synthesized and used as a reference to explore the impact of shuttling on the emissive properties (Scheme S1). The effects of the solvent can be deduced by examination of the fluorescence intensities of reference **7** since the relative position of the ferrocene and pyrene moieties is maintained, irrespective of the solvent used because of the covalent linkage bridging both units. The fluorescence intensities of **7** decrease with increasing hydrogen bond basicity except for DMF (Table 2). However a larger emission intensity is observed for **1** than for **7** in both $CHCl_3$ and THF. This is consistent with the larger relative separation in $CHCl_3$ and THF between pyrene and ferrocene, where translational isomer **1A** is mainly present, in contrast to the relative shorter separation in **7**.

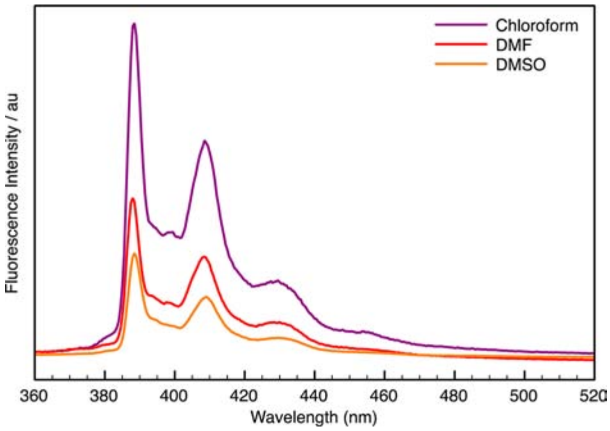

Figure 2. Comparison of the fluorescence intensities of rotaxane **1** in different solvents with matching absorbance at the excitation wavelength (325 nm).

Conversely, in DMSO the emission intensity of **1** (4%) is remarkably lower than in $CHCl_3$ and closer to the values measured for **7** (i.e., 1%) (Table 2). Such differences in emission intensity cannot be rationalized solely on the basis of the solvent without taking into account the effects derived from shuttling. The reduction in the positional integrity of the macrocycle at the 1,4-diamide station, which occurs as the hydrogen bonds are weakened by an incremental increase in hydrogen-bond basicity, causes an increase in the shuttling rate toward the formation of **1B**. This is in strong agreement with the NMR experiments. In fact, the low emission intensities observed in DMSO, where

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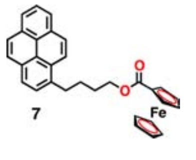
(8) Structure of reference 7 (additional details in Supporting Information).



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translational isomer **1B** exists preferentially, confirm a much closer pyrene–ferrocene separation, which is in between that of **1A** and **7** as expected. Although at first glance the emission of **1** in DMF is closer to that of THF, the measurements carried out on reference **7** indicate that emission is particularly higher in relative terms in DMF, which justifies the relative high fluorescence intensity of **1** and is also consistent with a degenerate state and, thus, with a relative separation between pyrene and ferrocene and a emission intensity that falls in between **1A** and **1B**. This is also supported by time-resolved emission experiments, where shorter-lived and similar lifetimes were observed for reference **7** in Ar-saturated THF (i.e., 10.7 and 2.1 ns in 34% and 66%, respectively) and DMSO (i.e., 3.3 and 0.5 ns in 26% and 74%, respectively), in contrast to the lifetimes measured for rotaxane **1** in THF (i.e., 54 ns) and DMSO (i.e., 8.7 ns).

Table 2. Integrated Fluorescence Intensities of Rotaxane **1** Referenced to Thread **5**

solvent	thread **5**		rotaxane **1**		reference **7**	
$CHCl_3$	2.56×10^7	100%	3.39×10^6	13%	8.05×10^5	3%
THF	6.82×10^7	100%	6.09×10^6	9%	1.38×10^6	2%
DMF	4.68×10^7	100%	3.93×10^6	8%	3.20×10^6	7%
DMSO	1.06×10^8	100%	4.29×10^6	4%	1.24×10^6	1%

In conclusion, we have reported the synthesis of a solvent switchable rotaxane equipped with a pyrene stopper and with two ferrocenyl units on the macrocycle that exists in three states in different solvents at room temperature: two nondegenerate and one degenerate. The observed high contrast changes in the fluorescence intensity of the pyrene stopper are undoubtly owed to the relative position of the macrocycle with the two ferrocenyl units along the thread, as demonstrated by a combination of NMR, steady-state, and time-resolved emission assays that verify the strong pyrene/ferrocene interactions and their tunability through a systematic change of the environment (i.e., solvent polarity and/or hydrogen bond basicity). The quenching mechanism is very complex and cannot be simplified solely in terms of electron transfer or energy transfer, since it involves the motion of the macrocycle, different solvents, and heavy atoms. Further time-resolved absorption spectroscopy studies (femto- and nanosecond), which are currently underway, will shine light on such a complex mechanism and will be reported in due time. In any case, we believe that this emission trend is essential to develop future ultrasensitive and multiresponsive luminescent molecular systems to probe different nano-, micro-, and macroenvironments.

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Supporting Information Available. Full synthetic procedures, including structural and photophysical characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.