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PAPER

Construction of a functional [2]rotaxane with multilevel fluorescence responses†

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A rotaxane incorporating three different stations and fluorescent states (output) was prepared. The movement of the macrocycle can be easily detected by fluorescence change as an output signal and the macrocycle could be easily controlled to locate on three different stations of the thread by the tuning of acid/base (input).

Introduction

Rotaxanes and catenanes have received a great deal of attention due to their challenging construction and potential application as mechanical or electronic molecular devices for molecular electronics and nanochemistry.[1] The rotaxanes are remarkable precursors in supramolecular chemistry, and the rapid development of this chemistry led to smart assemblies possessing various architectures and properties. This new area of chemistry has promoted the understanding of the concepts of design and strategies of self-assembly of rotaxane structures based on energy input for supplying their work. They can be controllably and reversibly switched between two or more states[2] and moved by their components. Various stimuli have been applied to induce such switches, including acid/base,[3] photochemical,[4] electrochemical,[5] solvent,[6] metal binding,[7] configurational changes[8] and so on.

The movements of the macrocycles within the rotaxanes are also able to result in changes in their conformations or configurations. These changes are usually accompanied by the alteration of physical properties of the molecular rotaxane such as conductivity,[9] circular dichroism[10] and fluorescence.[11] We have reported recently the examples of a click-reaction-based synthesis of rotaxanes[12] and catenanes.[13] The 1,2,3-triazole generated by the click reaction can also be used as a molecular station.[12,14] Besides, phenolate anions can also act as an anion station,[15] and the fluorescence based on the systems can be changed in response to external acid/base stimuli. However, the rotaxane molecular machines incorporating three different stations and fluorescent states (output) for expanding the functionality of the system were seldom reported. In our hypothesis, the fluorescent hydroxy-substituted tetraphenylimidazole' derivatives were chosen as a third station. The intramolecular H-bonding interactions result in photophysical processes based on excited-state intramolecular proton transfer (ESIPT),[16] indicating the intramolecular H-bonding interactions can also play as a fluorescence switch. The results showed that a multifunctional stopper can be fabricated by associated supramolecular interactions in the three processes of movement in the supramolecular system.

Here we describe a three-station [2]rotaxane with multilevel fluorescence responses by acid/base tuning shuttling of the macrocycle along the thread. The [2]rotaxane in which one ring moves sequentially among three different binding sites ('stations') of the thread is shown schematically in Scheme 1. The three noncovalently binding states were predicted to have different binding affinities with the macrocycle: (i) a secondary dialkylammonium ($-NH_2^+-$) center, should bind strongly with the macrocycle because of the strong hydrogen bonding interactions between the macrocycle ether and cationic moieties. (ii) the 1,2,3-triazole ring, should bind less well than (i) through the hydrogen bonding interaction between the amide units in the macrocycle and the 1,2,3-triazole nitrogen atoms; (iii) a phenolate anion, can form hydrogen bonding with the amide units which interact much more strongly compared to (ii). In addition, the movement of the macrocycle could influence the intermolecular vibronic interactions of the fluorescent stopper, accompanied by the alteration of fluorescence intensity. The rotaxane shows different fluorescent responses when the macrocycle located on three stations. Thus, a new approach using fluorescence to detect the movement of the macrocycle has been developed.

Results and discussion

[2]Rotaxane **4** and compound **5** were synthesized according to Scheme 2. Compound **1** and **3** were synthesized in accordance with literature procedures.[12] The synthesis of compound **2** was shown in the supporting information. A pseudorotaxane containing half-dumbbell **1** and macrocyle **3** was formed first. Covalent capture of

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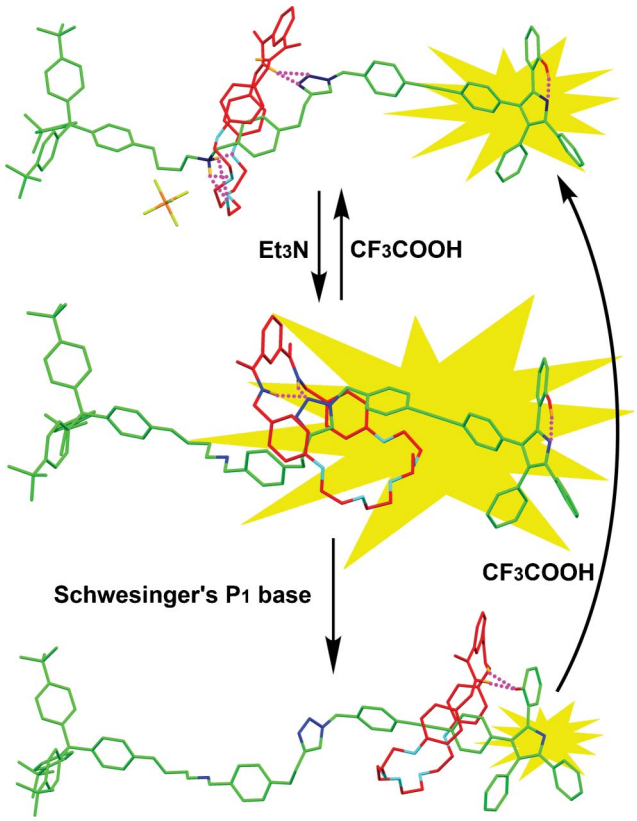
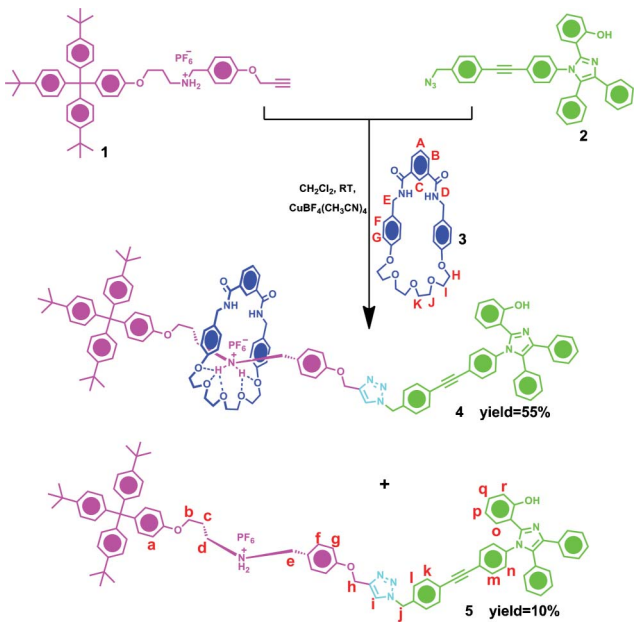


Scheme 1 The shuttling movement process of the [2]rotaxane under different stimuli (optimized by Spartan 08).



Scheme 2 Synthesis of **4** and **5**.

the threaded intermediate by a click reaction afforded [2]rotaxane **4** and dumbbell **5** in 55% and 10% yields respectively. The MALDI-TOF spectrum of **4** gave sharp peaks at *m*/*z*: 1784.7 (see the ESI†) which revealed the feature of an interlocked molecule.

As shown in Fig. 1 (a, a′, d), the ^{1}H NMR spectra of **3**, **4**, **5** in d3-acetonitrile readily confirm the interlocked structure and show that macrocycle **3** in **4** is largely localized on the alkyl ammonium region of the thread and the isophthalamide group in macrocycle **3** can interact with the triazole ring due to the hydrogen bonds between them under acidic conditions. The signals corresponding to phenylene protons (H_f: $\Delta\delta = 0.20$ and H_g: $\Delta\delta = 0.32$ ppm) and the macrocycle benzyl groups (H_F: $\Delta\delta = 0.19$ and H_G: 0.28 ppm) experience a significant upfield shift as a result of the aromatic shielding effect between them. The polyether protons (H_H–H_K) shift upfield by $\Delta\delta = 0.1$ ppm roughly as a result of a combination of C–H$\cdots$O and N^+–$H_2\cdots$O hydrogen bonds. Additionally, a shielding effect is observed for the proton adjacent to the 1,2,3-triazole ring ($\Delta\delta(H_h)$ = 0.22 ppm). Moreover, the ring amide protons H_D experience a downfield shift of $\Delta\delta = 0.21$ ppm in **4** with respect to **3**, which is attributed to hydrogen bonding to the triazole nitrogen atoms. The ^{1}H NMR spectra showed that the macrocycle **3** in rotaxane **4** was localized on the alkyl ammonium and also had hydrogen-bond interaction with the 1,2,3-triazole region of the dumbbell under acidic conditions (Scheme 1).

Upon addition of 1.2 equivalents of Et_3N to **4**, the dialkylammonium group was neutralized and the hydrogen bonds between macrocycle and ammonium group were switched off (Fig. 1b and b′). The signals for the protons near the 1,2,3-triazole ring H_h and H_j shifted upfield by 0.32 and 0.18 ppm which should be attributed to the aromatic shielding effect by **3**. The amide protons H_D experience a significant downfield shift ($\Delta\delta$ = 0.4) with respect to **3** due to hydrogen bonding with the triazole nitrogen atoms. The signal for H_e also shifted upfield by 0.15 ppm, which indicated deprotonation of the neighboring ammonium center. In addition, the 0.11 ppm upfield shift of the triazole ring proton H_i is characteristic of aromatic shielding effects. All these features indicate that the macrocycle can migrate from the dialkylammonium center to the triazole recognition site upon addition of Et_3N in acetonitrile.

Deprotonation of the phenol groups in **4** and **5** could be accomplished with Schwesinger's P_1 base. ^{1}H NMR confirms that deprotonation of the phenol group provides the third hydrogen-bonding station for the macrocycle (Fig. 1c and c′). The signals of –OH disappeared when 10 eq. of Schwesinger's P_1 base was added. The shielding of the protons in **4** shows the ring is located near the phenolate anion. The signals for H_m and H_n shifted upfield by 0.19 and 0.22 ppm, which should be attributed to the aromatic shielding effect by **3**. Compared to the deprotonated **4** by Et_3N, the signals for the protons H_g and H_h shifted downfield by 0.12 and 0.06 ppm in $\mathbf{4}^-$ (Fig. 1b′ and c′). These results indicate that the macrocycle moves to the phenolate anion recognition site due to the hydrogen bonds between them. The movement process was monitored by 2D NMR (ESI Part 6†). The shuttling is readily reversible: protonation of $\mathbf{4}^-$ with CF_3COOH smoothly regenerates **4**, which returns the macrocycle back to the original station (Scheme 1, Figure S2†).

The absorption features of the dumbbell **5** are similar to those of rotaxane **4**. When 1.2 equivalents of Et_3N were added, no change in the absorption spectra was observed. But when 10 equivalents of P_1 base were introduced, the absorption peak at 289 nm and 307 nm decreased (Figure S3†). This indicated that Et_3N could not influence the fluorescent stopper but the P_1 base could accomplish the deprotonation of the phenolate. This is in accordance with the ^{1}H-NMR analysis.

Compared with the UV-vis spectra, more significant changes happened in the fluorescence spectra. Fig. 2 demonstrates that

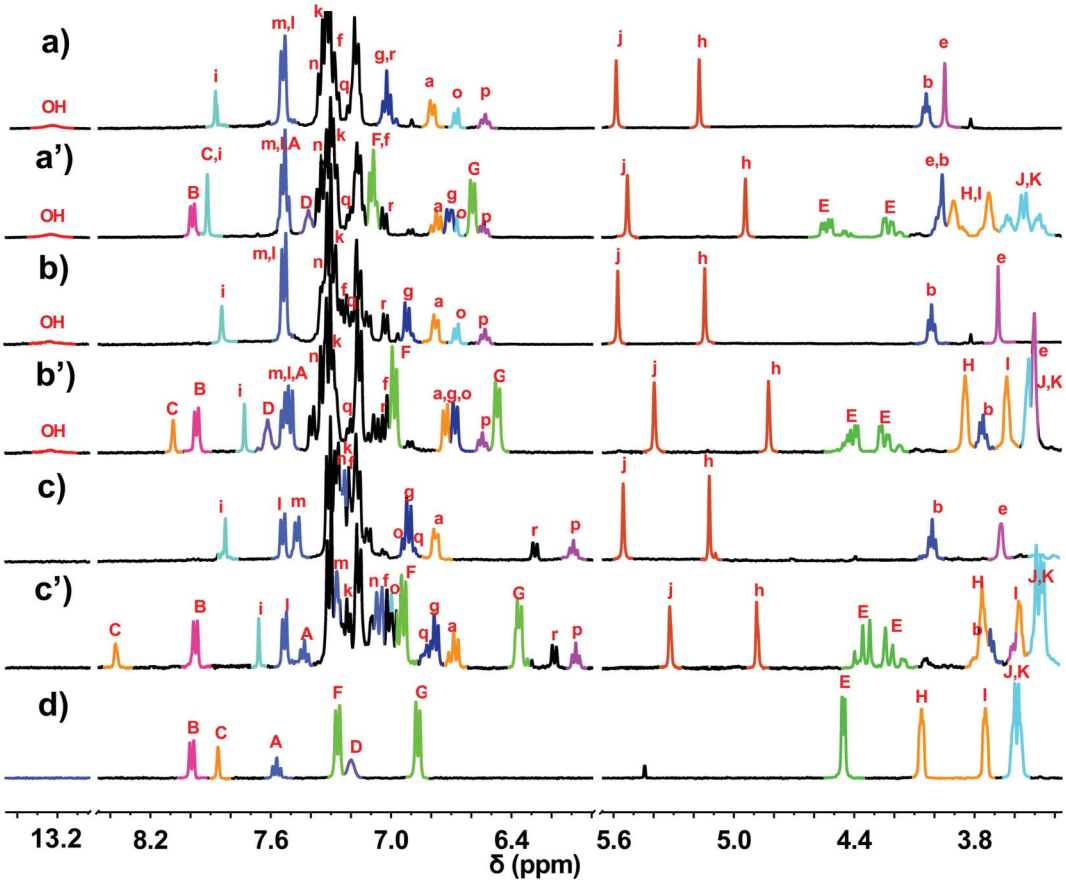


Fig. 1 Partial ^{1}H NMR spectra (400 MHz, 298 K, CD_3CN) of **3**, **4** and **5**. (a) **5**, (a′) **4**, (b) **5**+1.2 equiv Et_3N, (b′) **4**+1.2 equiv Et_3N, (c) **5**+1.2 equiv Et_3N+10 equiv Schwesinger's P_1 base, (c′) **4**+1.2 equiv Et_3N+10 equiv Schwesinger's P_1 base, (d) **3**.

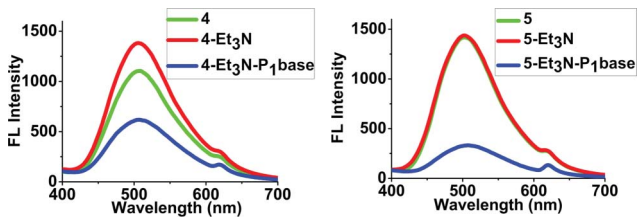


Fig. 2 Fluorescence emission spectra changes (λ_{ex} = 310 nm) of **4** and **5** upon the addition of 1.2 equiv Et_3N and 10 equiv Schwesinger's P_1 base in CH_3CN (2×10^{-5} M).

the motion of the macrocycle greatly affects the fluorescence of **4**. A comparison of the emission behavior of **4** and **5** upon the addition of Et_3N and P_1 base in CH_3CN is shown in Fig. 2. **4** and **5** both displays an emission maximum centred at 505 nm. The fluorescence intensity of **4** centred at 505 nm increased by 25% upon the addition of 1.2 equivalents of Et_3N into the solution, while there is no similar change in the emission spectra of **5** at all. It was initially considered that when the macrocycle moved to the triazole recognition site, the rotational motion of the fluorescent stopper was restricted. The restriction encumbered the radiationless rotation which induced the increase of the fluorescence.[17] In order to prove this, effect of temperature on the fluorescence intensity was investigated for **5**. Figure S4 showed the fluorescence emission spectra from 293 to 308 K.† The fluorescence intensity increases with the decreasing of temperature. This temperature effect is related to the restriction of intramolecular rotation that accompanies cooling of the solvent.[18] The decrease of the temperature and the macrocycle play the same role. They both influence the intramolecular rotation of the fluorescent stopper which result in the enhancement of the fluorescence. When 10 equivalents of P_1 base was introduced, the fluorescence of **5** was quenched (~80%), which is much stronger than that in the case of **4** (~40%). The deprotonation of the fluorescent stopper by P_1 base suppresses the ESIPT process and thus the emission was decreased. Interestingly, the emission of **4** was decreased in a smaller degree compared with that of **5**. This could be attributed to the restriction of the intermolecular vibronic caused by the macrocycle.

Conclusion

We have synthesized a multistable molecular rotaxane with three successive movement processes driven by acid/base stimuli, which are all accompanied with fluorescent responses. The macrocycle can be easily controlled to locate on three different stations of the thread by the different strengths of the three sets of noncovalent bonding interactions. The fluorescent emission intensity of the [2]rotaxane can be tuned by the movement of the macrocycle. The approach using fluorescence to detect the movement of the macrocycle was developed. In addition, this artificial multilevel molecular shuttle provides a model for interconnection of different hydrogen bonding interactions, to achieve multistable controllable systems with tunable responses.

Experimental

Synthesis of 4 and 5

A mixture of **1** (620 mg, 0.73 mmol), **2** (435 mg, 0.8 mmol), **3** (425 mg, 0.8 mmol), and $CuBF_4$ $(CH_3CN)_4$ (250 mg, 0.8 mmol) was stirred in dry CH_2Cl_2 at room temperature under nitrogen for 24 h. After removal of the solvent, the crude product was purified by column chromatography to afford **4** (770 mg, 55%) and **5** (100 mg, 10%).

4: ^{1}H NMR (400 MHz, CD_3CN) δ 13.24 (s, 1H), 7.99 (d, J = 7.8 Hz, 2H), 7.92 (s, 2H), 7.53 (m, 5H), 7.41 (s, 2H), 7.27–7.37 (m, 20H), 7.21–7.13 (m, 9H), 7.07–7.11 (m, 6H), 7.04 (d, J = 8.0 Hz, 1H), 6.77 (m, 2H), 6.71 (m, 3H), 6.59 (d, J = 8.0 Hz, 4H), 6.56–6.49 (t, 1H), 5.53 (s, 2H), 4.94 (s, 2H), 4.60–4.49 (m, 2H), 4.29–4.18 (m, 2H), 3.96 (s, 4H), 3.91 (s, 4H), 3.73 (s, 4H), 3.45–3.65 (m, 8H), 3.14 (s, 2H), 2.11 (m, 2H), 1.29 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.77, 158.95, 158.50, 156.87, 155.94, 148.54, 145.00, 144.15, 143.49, 140.74, 137.09, 135.59, 135.15, 134.66, 133.07, 132.93, 132.51, 132.40, 131.81, 131.59, 131.43, 130.73, 130.48, 130.28, 129.70, 129.34, 128.85, 128.78, 128.43, 127.24, 127.03, 126.23, 124.27, 124.14, 124.00, 123.31, 123.17, 122.83, 118.20, 117.88, 115.24, 114.24, 113.08, 112.94, 90.70, 89.10, 70.74, 70.56, 67.13, 64.26, 63.22, 61.21, 53.87, 52.05, 46.05, 43.47, 34.42, 31.50, 29.81 ppm; MALDI-TOF: m/z: 1784.7 $[M\text{-}PF_6]^+$; Elemental Analysis calcd (%) for $C_{116}H_{119}F_6N_8O_{10}P$: C, 72.18; H, 6.21; N, 5.81; found: C, 72.09; H, 6.31; N, 5.86.

5: ^{1}H NMR (400 MHz, CD_3CN) δ 13.25 (s, 1H), δ 7.87 (s, 1H), 7.54 (d, J = 7.8 Hz, 4H), 7.26–7.36 (m, 24H), 7.14–7.22 (m, 7H), 7.02 (m, 3H), 6.80 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 6.8 Hz, 1H), 6.53 (t, J = 8.0 Hz, 1H), 5.59 (s, 2H), 5.17 (s, 2H), 4.07–3.99 (m, 2H), 3.95 (s, 2H), 3.04–2.95 (m, 2H), 2.11 (m, 2H), 1.29 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.98, 159.32, 156.78, 149.31, 145.81, 145.01, 144.85, 144.13, 142.63, 141.44, 137.92, 136.43, 135.76, 133.88, 133.73, 133.24, 132.55, 132.24, 131.59, 131.26, 131.03, 130.53, 129.66, 129.58, 129.24, 129.16, 128.05, 127.86, 127.64, 127.03, 125.95, 125.04, 124.91, 124.29, 124.19, 123.45, 120.79, 118.99, 118.71, 116.35, 113.91, 113.74, 91.44, 89.96, 66.45, 64.61, 64.00, 62.38, 54.82, 47.32, 35.21, 32.30, 30.63; MALDI-TOF: m/z: 1249.5 $[M\text{-}PF_6]^+$; Elemental Analysis calcd (%) for $C_{116}H_{119}F_6N_8O_{10}P$: C 74.01, H 6.14, N 6.02; found: C 74.13, H 6.21, N 5.95.

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