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A Light-Driven Rotaxane Molecular Shuttle with Dual Fluorescence Addresses

Da-Hui Qu, Qiao-Chun Wang, Jun Ren, and He Tian*

Lab for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, P.R. China

tianhe@ecust.edu.cn

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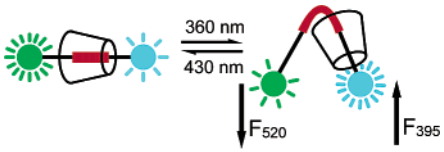
ABSTRACT



A molecular shuttle containing an α-CD macrocycle, an azobenzene unit, and two different fluorescent naphthalimide units was synthesized. The cis–trans photoisomerization of the azobenzene unit resulted in the motion of the CD macrocycle on the track. Because of the easy regulation and full reversibility of the fluorescence change of the two stopper units, the molecular shuttle could be used as a molecular storage medium or switch with all-optical inputs and outputs.

A rotaxane[1] is described as a molecular system in which a macrocycle threads a linear subunit with two bulky stoppers. Rotaxanes have attracted more and more attention because of their challenging constructions and potential applications in areas such as molecular switches,[2] molecular logic gates,[3] and molecular wires.[4] To realize their full potential, rotaxanes must have two basic properties. On one hand, the binary states, namely, the "0" state and "1" state, must be reversible. On the other hand, as output signals, they must be easily recognizable. In previous studies, the binary states of most molecular machines were distinguished by NMR spectra,[5,6] cyclic voltammetry,[7] complexation ability differences of certain ions of the two states,[8] or circular dichroism. It is rather inconvenient to transform these spectral signals into easily detected output codes, however. Using fluorescence change as an output is attractive because the signal can be

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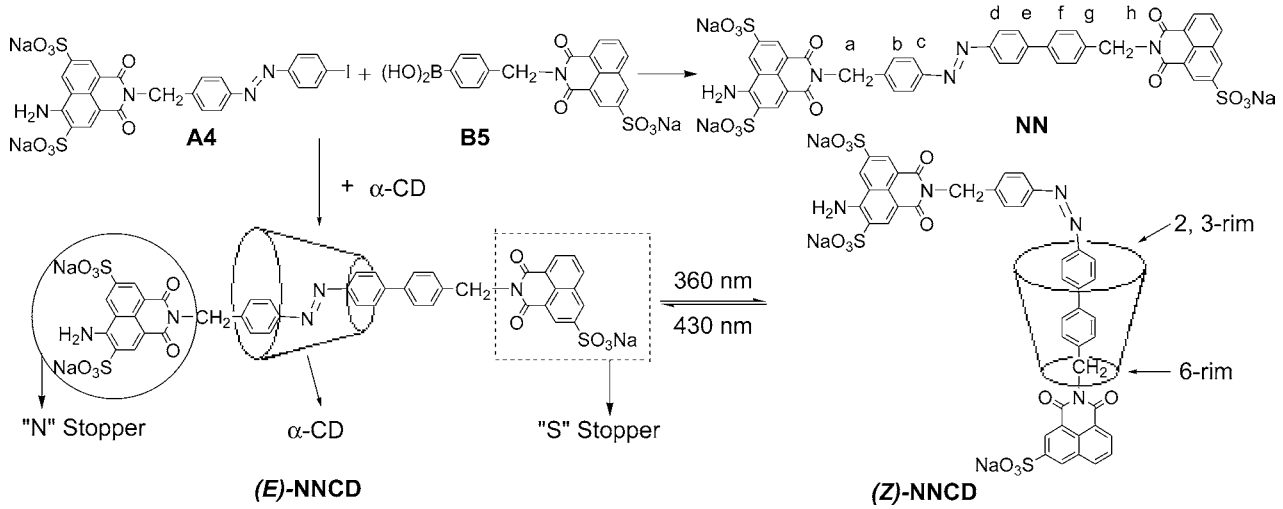

Figure 1. A4, **B5**, dumbbell **NN**, and [2]rotaxane **NNCD** studied in this work.

easily and remotely detected with low cost. However, reports on induction of a rotaxane to switch between different fluorescent states (output) as a response to a clean input are rare.[9]

In this report, we designed and synthesized an unsymmetrical light-driven molecular shuttle based on a [2]rotaxane **NNCD** (Figure 1) with an α-CD as the ring, azobenzene and biphenyl chain as the threading molecular chain, and two different fluorescent naphthalimide moieties: 4-amino-1,8-naphthalimide-3,6-disulfonic disodium salt (the "**N**" stopper) and 1,8-naphthalimide-5-sulfonic sodium salt (the "**S**" stopper) as the two bulky terminal stoppers. In this [2]rotaxane **NNCD**, reversible motion of the α-CD macrocycle between two stations (azobenzene station and biphenyl station) takes place after UV irradiation at 360 and 430 nm, respectively. This motion affects the fluorescence spectra of the two naphthalimide stoppers. When the azobenzene unit is in the trans form, the α-CD ring is located here. After a 2 min of irradiation with 360 nm UV light, the trans form ((*E*)-**NNCD**) changes to the cis form ((*Z*)-**NNCD**) and the α-CD moves to the biphenyl station. Irradiation with 430 nm light converts the (*Z*)-**NNCD** back to (*E*)-**NNCD** (Figure 1). The [2]rotaxane **NNCD** was synthesized by Pd-catalyzed Suzuki coupling where phenyl boronic acid **B5** reacted with azobenzene phenyl halide **A4** in the presence of α-CD in an Ar-saturated Na_2CO_3 aqueous solution according to Anderson's method.[10] As shown in Figure 1, treating equal equivalents of **A4** and **B5** with 2.5 equiv of α-CD for 20 h at 80 °C in an Ar-saturated 0.2 M Na_2CO_3 aqueous solution with 0.05 equiv of $Pd(OAc)_2$ catalyst led to the formation of [2]rotaxane **NNCD**. Chromatography (silica gel, the upper layer was 1.3:2:5 acetic acid/*n*-butanol/water) gave pure **NNCD** with a yield of 15%. The non-CD dumbbell **NN** was also prepared using the same conditions, in the absence of α-CD, with a yield of 30%.

Both rotaxane **NNCD** and dumbbell **NN** can be characterized by ^{1}H NMR spectra. Because of the low solubility of dumbbell **NN** in D_2O, the measurements were conducted in DMSO-d_6 (298 K). Figure 2 shows the ^{1}H NMR spectra of

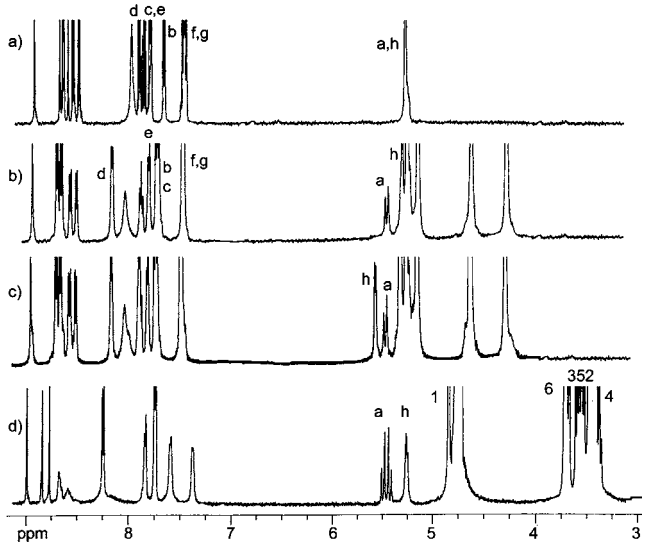

Figure 2. ^{1}H NMR spectra (500 MHz in DMSO-d_6 at 298 K) of (a) dumbbell **NN**, (b) rotaxane (*E*)-**NNCD**, and (c) the same b solution after irradiation at 360 nm for 30 min ((*Z*)-**NNCD**) and (d) ^{1}H NMR spectra (500 MHz in D_2O at 298 K) of rotaxane (*E*)-**NNCD**.

NN and **NNCD** in DMSO-d_6 (298 K). Because of the influence of α-CD, the chemical shifts of the protons b−e of the thread shown in Figure 1 have different changes: H_b ($\Delta\delta$ = 0.06 ppm), H_c ($\Delta\delta$ = −0.09 ppm), H_d ($\Delta\delta$ = 0.24 ppm), H_e ($\Delta\delta$ = −0.02 ppm). Compared to the methylene

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resonance of **NN** for $H_{a,h}$ (a singlet at δ 5.31), the methylene resonance of (*E*)-**NNCD** is split into a doublet at δ 5.48 (H_a, $\Delta\delta$ = 0.17 ppm) and a singlet at δ 5.37 (H_h, $\Delta\delta$ = 0.06 ppm) due to the influence of α-CD that is near the methylene of H_a and far from the methylene of H_h. The measurement of **NNCD** was also conducted in D_2O at 298 K (Figure 2d). Compared to neat α-CD, an obvious upfield shift of H_3 ($\Delta\delta$ = 0.15 ppm) and H_5 ($\Delta\delta$ = 0.11 ppm) of the α-CD macrocycle in **NNCD** was observed. This is a result of the aromatic shielding effect of the threaded benzene rings in the cavity of the α-CD, suggesting that the α-CD ring is threaded by dumbbell **NN**.

At the same time, the resonance peaks of the two methylenes are split completely. The resonance of H_a splits into multiplets, while the resonance of H_h is a singlet. The two-dimensional ROESY NMR of **NNCD** in DMSO-d_6 reveals the relativity of the protons of the aromatic regions and α-CD. As shown in Figure 3, strong NOEs are observed

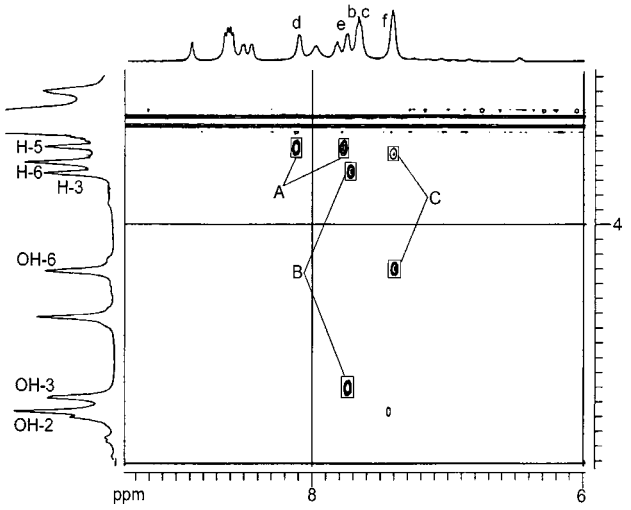

Figure 3. Two-dimensional ROESY NMR spectrum of **NNCD** (500 MHz in DMSO-d_6 at 298 K) after a mixing time of 300 ms.

from the H_b and H_c to positions on the 2,3-rim of the α-CD (mostly H-3, point B) and from the H_d,H_e to positions on the 6-rim of the α-CD (mostly H-5, point A). Simultaneously, relatively strong NOEs are observed from H_f to the H-6 and OH-6 of the α-CD (point C in Figure 3) and from H_a to the OH-2 of α-CD (Figure 4, point A). No NOE was found between H_a and the OH-6 of α-CD, demonstrating that the rotaxane **NNCD** exists as a single isomer. The orientation of the α-CD on the thread was confirmed as that shown in Figure 1.

After UV irradiation by 360 nm for 30 min, there was very little change in the resonance of the aromatic positions of **NNCD** in DMSO-d_6, while change in the resonance of the methylene protons was more profound. The latter was split into two doublets and one singlet as compared to one doublet and one singlet before the irradiation. A new signal was found at δ 5.57 (H_h of the cis form shown in Figure 2).

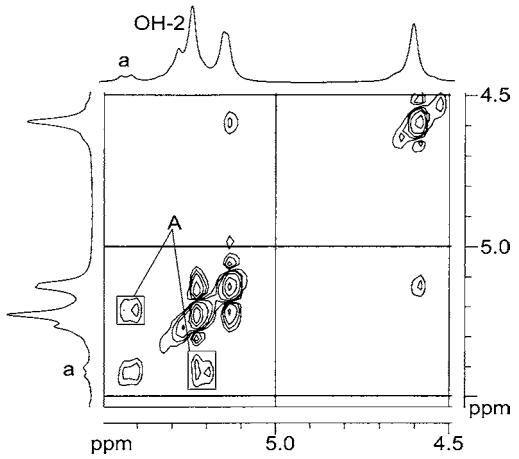

Figure 4. High-field portions of the two-dimensional ROESY NMR spectrum of **NNCD** under the same conditions as Figure 3.

This is attributed to the deshielding effect of α-CD due to the shifting of the ring away from the azobenzene unit to the biphenyl unit. The two signals at δ 5.57 (H_h of the cis form) and δ 5.48 (H_a of the trans form) appear at a 10:7 ratio. This suggests that, at the photostationary state, about 59% of (*E*)-**NNCD** was transformed to its cis form (*Z*)-**NNCD**.

Similar to Nakashima's rotaxane,[5c] both compounds **NNCD** and **NN** in this work showed photoisomerization. UV light (360 nm) irradiation of the DMF solution of **NNCD** (1.0×10^{-5} M) caused photoisomerization from the trans to cis configuration of the azobenzene unit in **NNCD**, which returned to the trans configuration following irradiation at 430 nm for 2 min. The change is characterized by an increase in absorption at around 275 nm (ΔA = 0.08) and a decrease in absorption at 350 nm (ΔA = 0.07), characteristic of the photoisomerization of the azobenzene units (shown in Supporting Information). Prolonging irradiation beyond 2 min under this experimental condition does not result in any change in the absorption and the fluorescence spectra.

A phenomenon was found in the fluorescence spectra of compound **NNCD**. UV light (360 nm) irradiation of **NNCD** in DMF (1.0×10^{-5} M) makes the fluorescence at around 520 nm (due to the "**N**" stopper) weaker and the fluorescence at around 395 nm (due to the "**S**" stopper) stronger, as illustrated in Figure 5a. As the α-CD ring is shifting away from the azobenzene unit toward the biphenyl unit, the biphenyl unit becomes more rigid. The vibration and the rotation of the bonds in the methylene and azobenzene units are enhanced, and the vibration and the rotation of the bonds in the methylene and biphenyl units are hindered. This is confirmed by the fluorescent intensity of **NN**. The fluorescence of **NN** at around 395 nm is weaker than that of (*Z*)-**NNCD** after irradiation, and the fluorescence at around 520 nm is weaker than that of (*E*)-**NNCD**. The vibration and rotation of the bonds in **NN** is facilitated by the absence of the macrocycle. Additionally, there is little change in the fluorescence of **NN** before and after UV irradiation, as is

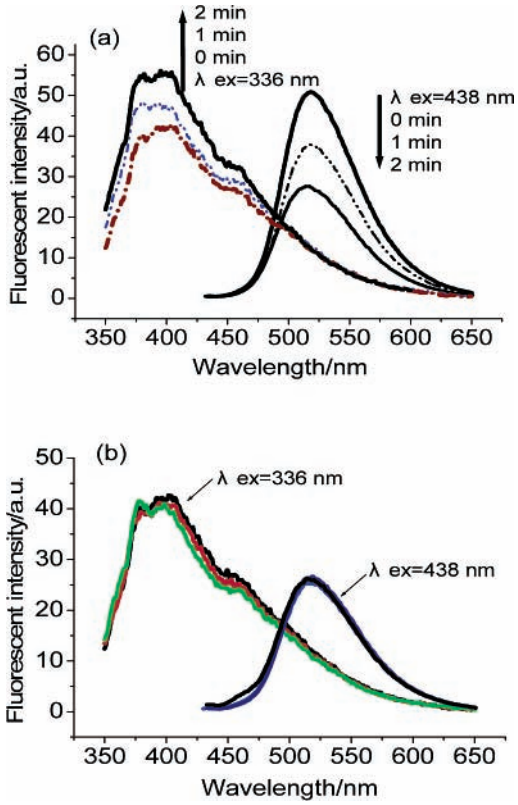

Figure 5. Fluorescence spectra of [2]rotaxane (a) **NNCD** and (b) **NN** in DMF (1×10^{-5} M) at 25 °C after irradiation with UV light 360 nm for different times.

shown in Figure 5b. Figure 5 also demonstrates that the motion of the CD in **NNCD** greatly affects the fluorescence of the two stoppers. Similar to the absorption spectra of **NNCD**, the fluorescence spectra of **NNCD** could be repeated over many cycles with UV irradiation alternating between 360 and 430 nm in 2 min intervals. The relative fluorescence quantum yields of compound **NNCD** and **NN** are listed in Table S1 of the Supporting Information. The fluorescent quantum yield ratio between (*Z*)-**NNCD** and (*E*)-**NNCD** is close to 2 at 395 nm and 0.65 at 520 nm. The fluorescence of the dumbbell **NN** did not change after UV irradiation, further proving that the α-CD strongly affects the fluorescence of the stoppers.

Figure 6 shows changes in the fluorescence intensity of **NNCD** following irradiation. In Figure 6, the upper line is the fluorescence intensity change of the "**S**" stopper (λ_{ex} = 336 nm) and the lower line is for the fluorescence intensity change of the "**N**" stopper (λ_{ex} = 438 nm). As shown in Figure 6, the rotaxane has excellent recovery properties, which is useful for studying information storage and molecular logic gates. The two kinds of fluorescence signal

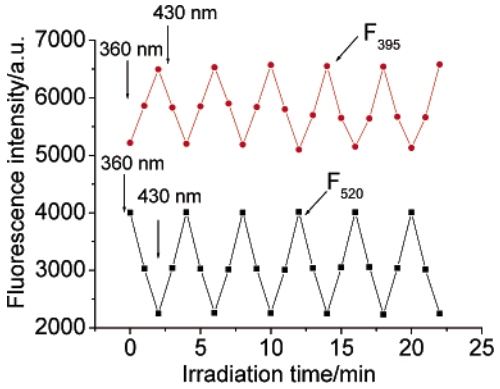

Figure 6. Changes in the fluorescence intensity of **NNCD** in DMF (the upper line is the emission at λ = 395 nm, and the other line is the emission at λ = 520 nm) along with changes in irradiation time and light source. Light sources of 360 and 430 nm UV light were alternated every 2 min.

changes (blue at 395 nm and green at 520 nm) act as the "0" state and the "1" state, respectively. Alternation of the "0" state and the "1" state is accomplished completely by optical stimuli, UV light at 360 and 430 nm. Furthermore, the fluorescence signals indicating the molecular shuttle movement are very sensitive.

In summary, the [2]rotaxane **NNCD** is a light-driven molecular shuttle in which the α-CD macrocycle can be stimulated to shuttle back and forth between the azobenzene unit and biphenyl unit by irradiation. This is accompanied by reversible changes in fluorescence intensity of the two fluorescent stoppers, which make it possible for the rotaxane to be a molecular storage or a molecular logic gate. It should be noted that the output is a fluorescence signal, which can be easily detected remotely, in contrast to other spectral signals. The inputs to this system are also optical, which are superior to chemical or electrochemical inputs because of their cleanness and convenience. Finally, the complete reversibility of the state exhibited by the molecular system allows for repetitive processing of the input signals.

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Supporting Information Available: Absorption spectra and synthetic procedures of **NNCD** and **NN**. This material is available free of charge via the Internet at http://pubs.acs.org.

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