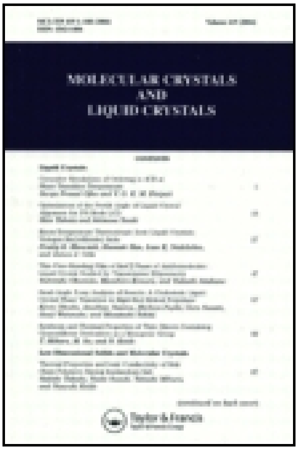

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Photodriven and Thermal-Driven Shuttling of α-Cyclodextrin on the Molecular Rotaxane Containing Azobenzene

D. H. Qu [a], Q. C. Wang [a] & H. Tian [a]

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

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Photodriven and Thermal-Driven Shuttling of α-Cyclodextrin on the Molecular Rotaxane Containing Azobenzene

D. H. Qu
Q. C. Wang
H. Tian
Lab for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai, P. R. China

A rotaxane containing an α-CD macrocycle, an azobenzene unit and two different fluorescent naphthalimide units as stoppers has been synthesized. The rotaxane can serve as a photodriven and thermal-driven molecular shuttle. The change of the temperature can make the CD macrocycle shuttle back and forth between the azobenzene and biphenyl stations, and the cis-trans photoisomerization of the azobenzene unit resulted in also the motion of the CD macrocycle on themolecular thread. The absorption and fluorescence spectra of the rotaxane in the different states were studied. The regulation and full reversibility of the fluorescence changes make the molecular shuttle serve as a molecular storage medium or switch with all clean inputs and outputs.

Keywords: α-cyclodextrin; photoisomerization; rotaxane; thermal-driven

INTRODUCTION

Rotaxanes [1,2] have attracted more and more attention in recent years because of their challenging constructions and their potential applications to serve as molecular devices [3–8]. Rotaxanes shuttling motion can be driven chemically, electrochemically or photochemically [1]. Use of light as external stimulus is now under prominent consideration because it can lead to a fast response without by-product. Heat

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Address correspondence to H. Tian, Lab for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai, 200237 P. R. China. E-mail: tianhe@ecust.edu.cn

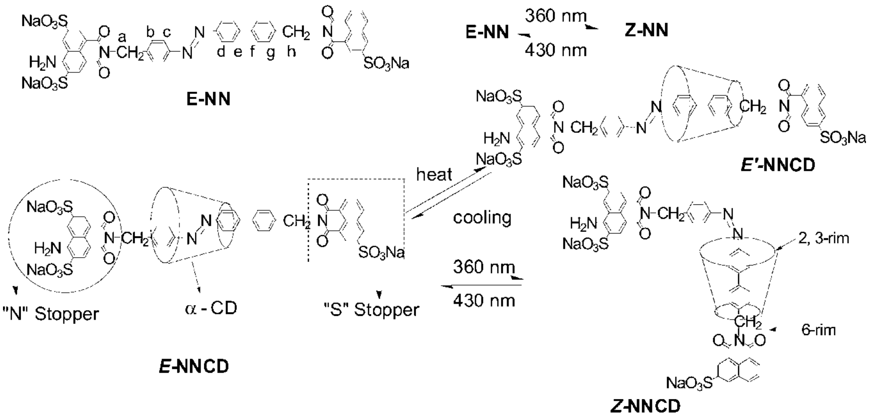

FIGURE 1 The chemical structures of the dumbbell NN and the [2]rotaxane NNCD.

(temperature change) is also a good way for external stimulus because of its convenience and cleanness [9]. In generally, the binary states of most molecular machines were distinguished by NMR spectra [10,11], cyclic voltammetry [12], complexation ability differences of certain ions of the two states [13], as well as circular dichromism. However, this is inconvenient in the future applications because of the difficulty to transform these signals into the easily detected output signals. Using fluorescence change as an output is attractive in that the signal can be easily and remotely detected and is typically low-cost.

However, reports on inducing rotaxanes to switch between different fluorescent states (output) as a response to one of the clean inputs (such as light, heat et al) are rare [14,15]. Here we report an example of [2]rotaxane molecular shuttle (Fig. 1, α-CD stands for α-Cyclodextrin), which could be driven by UV light and heat (temperature change) to bring about the easy regulation and full reversibility of the fluorescence changes of the two stopper units and to be served as a molecular storage medium or switch with all clean inputs and outputs.

EXPERIMENTAL

H NMR spectra were measured on a Brücker AM 500 spectrometer. UV/Vis spectra and fluorescent spectra were recorded on a Varian Cary500 spectrophotometer and a Varian Cary Eclipse Fluorescence Spectrophotometer (1-cm quartz cell used). The photo-irradiation was carried on a CHF-XM 500-W high-pressure mercury lamp with suitable filters (type FAL, Germany) in a sealed Ar-saturated 1 cm quartz cell. Syntheses of [2]rotaxane NNCD and NN were reported previously [15].

RESULTS AND DISCUSSION

In our previous paper [15], the chemical structure and the photoisomerization properties of the [2]rotaxane NNCD were throughly studied. Figure 2 illustrates the two dimensional ROESY NMR of the [2]rotaxane NNCD before and after UV 365 nm irradiation. As shown in Fig. 2 (left), strong NOEs are observed from the Hb and Hc to positions on the 2,3-rim of the α-CD (mostly H-3, point B) and from the Hd, He to positions on the 6-rim of the α-CD (mostly H-5, point A). Simultaneously, relatively strong NOEs are observed from Hf to the H-6 and OH-6 of the α-CD (point C in Fig. 2 (left)), which demonstrates that the rotaxane NNCD exists as a single isomer shown in Fig. 1. After UV irradiation at 360 nm for 30 min, new signals were found. As shown in Fig. 2 (right), strong NOEs are observed from the Hd to positions on the 2,3-rim of the α-CD (mostly OH-2, 3 and H-3, point A) and from the He to H-3, H-5 in the inside cavity of the α-CD (point B) and from Hg to the H-5 and OH-6 of the α-CD (point C in Fig. 2 (right)), which demonstrates the CD ring shuttle from the azobenzene unit to the biphenyl unit.

Also, the fluorescence spectra of the [2]rotaxane NNCD and dumbbell NN before and after UV 365 nm irradiation were measured. There is little change in the fluorescence of NN before and after UV 365 nm irradiation [15]. However, UV light 365 nm irradiation on NNCD in DMF (1.0×10^{-5} M) makes the fluorescence at around 520 nm

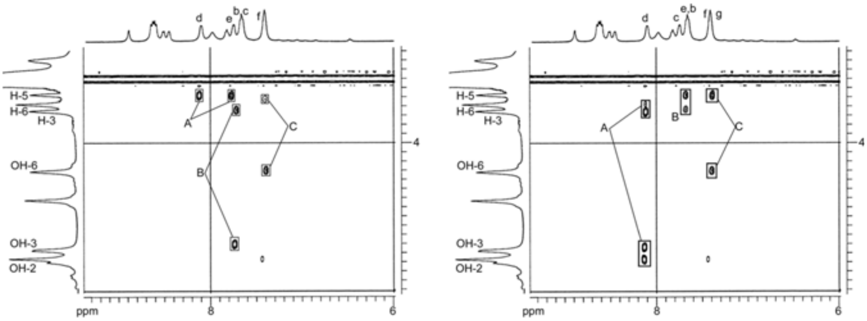

FIGURE 2 The two dimensional ROESY NMR spectrum of NNCD (500 MHz in DMSO-d6 at 298 K) at a mixing time of 300 ms (left); at the same conditions after 365 nm irradiation for 30 min (right).

(due to the "N" stopper) weaker and the fluorescence at around 395 nm (due to the "S" stopper) stronger, as illustrated in Fig. 3. So we have come to a conclusion from the fluorescence changes of the [2]rotaxane NNCD before and after UV 365 nm irradiation that the fluorescence of the fluorescent stopper becomes relatively stronger while the CD macrocycle is near the fluorescence stopper. This is probably because the vibration and the rotation of the bonds in the methylene units are hindered and enhance the fluorescence sequentially [14,15].

Now let's turn our attention to its thermo-driven phenomenon. The absorption and fluorescence spectra of dumbbell NN and rotaxane NNCD at different temperatures are measured. Temperature change has little affection on the absorption of dumbbell NN and rotaxane NNCD, except the rise in absorption at around 265 nm along with the rise of the temperature (shown in Fig. 4 left and Fig. 4 right). The absorptions at 285 nm and 350 nm did not changed, indicating that no photoisomerization of the azobenzene unit in both NN and NNCD takes place when temperature changed. However, due to the intensification of molecule movement with the increasing of temperature, the fluorescence intensity of the two stoppers of the dumbbell NN slightly declines (shown in Fig. 5).

However, in the rotaxane NNCD, the fluorescence at around 520 nm (character to the "N" stopper) become weaker and the fluorescence at around 395 nm (character to the "S" stopper) become stronger

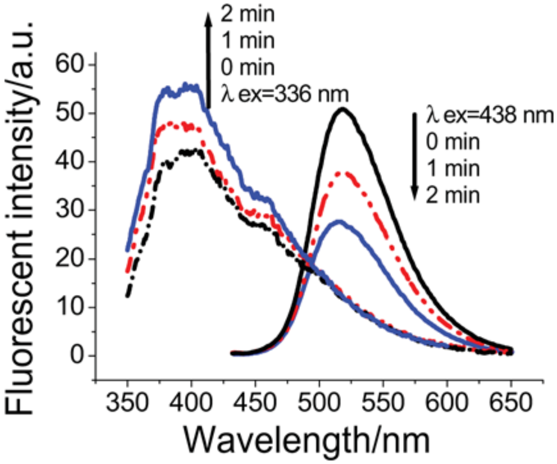

FIGURE 3 The fluorescence spectra of [2]rotaxane NNCD in DMF (1.0×10^{-5} M) at 25°C after irradiation with UV light 365 nm for different time.

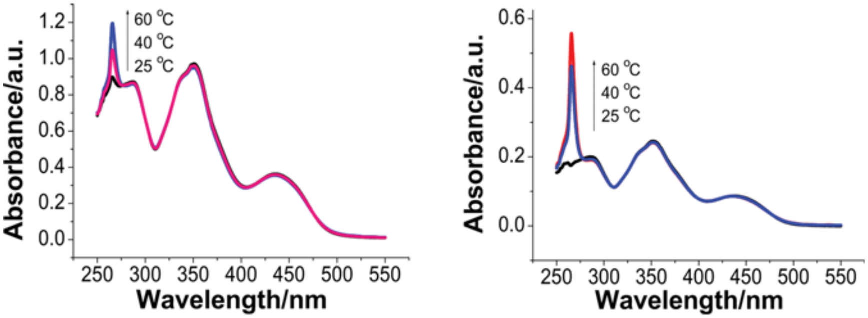

FIGURE 4 The absorption spectra of dumbbell NN (left) and NNCD (right) in DMF (5.0×10^{-5} M) at 25°C, 40°C, 60°C, respectively.

along with the rise of temperature, as illustrated in Fig. 5. Based on the observation of the fluorescence changes, we can conclude that the α-CD ring moves from the azobenzene unit to the biphenyl unit along with the rise of temperature. As the α-CD ring is shifting away from the azobenzene unit to the biphenyl unit, the biphenyl unit becomes more rigid. The vibration and the rotation of the bonds in the methylene and azobenzene units are recovered and the vibration and the rotation of the bonds in the methylene and biphenyl units are hindered. This observation is consistent with the conclusion that the fluorescence of the fluorescent stopper becomes relatively stronger

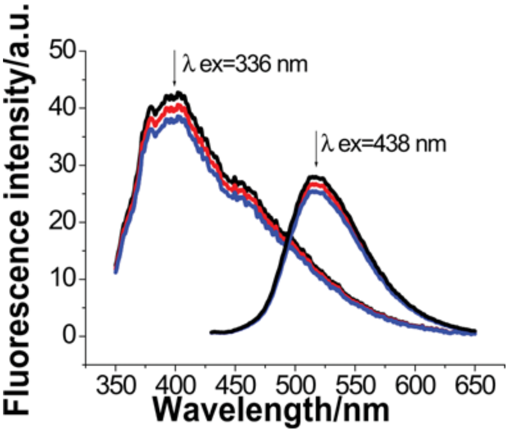

FIGURE 5 The fluorescence spectra of dumbbell NN in DMF (1×10^{-5} M) at 25°C, 40°C, 60°C, respectively. Along with the rise of the temperature, the fluorescence intensity slightly declines.

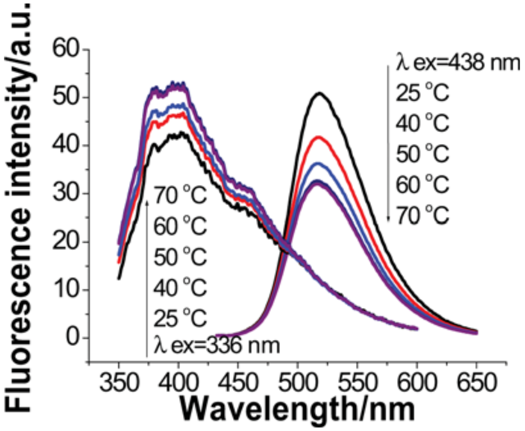

FIGURE 6 The fluorescence spectra of rotaxane NNCD in DMF (1.0×10^{-5} M) at 25°C, 40°C, 50°C, 60°C, 70°C, respectively. Along with the rise of the temperature, the fluorescence intensity at 520 nm (λex = 438 nm) gradually declines and the fluorescence intensity at 395 nm (λex = 336 nm) gradually enhances. The stationary state achieves at 60°C.

while the CD macrocycle is near the fluorescence stopper in the previous research [14,15]. Harada et al also have reported a temperature-sensitive rotaxane containing cyclodextrin, where the α-CD ring can move back and forth under the change of the system temperature [16]. Good reversibility of the fluorescence spectra of rotaxane NNCD was found along with temperature changes as illustrated in Figure 6. Based on the investigation of the absorption and fluorescence spectra it can be concluded that α-CD macrocycle could shuttle back and forth along the thread consisting of azobenzene unit and biphenyl unit with temperature change and affect the fluorescence of the stoppers greatly.

The reversible fluorescence changes of NNCD with optical stimuli or thermal stimuli is useful in application of information storage and molecular logic gates. The two codes of fluorescence signal 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 can occur completely by optical stimuli—UV light or heat. Furthermore, the fluorescence signals as an indication of the molecular shuttle movement are very sensitive.

CONCLUSION

In summary, [2]rotaxane NNCD reported here is a light-driven and thermo- driven molecular shuttle, in which the α-CD macrocycle can shuttle back and forth between the azobenzene unit and biphenyl unit by alternating UV irradiation or temperature change. This shuttle is accompanied by reversible fluorescence intensity changes of the two fluorescent stoppers. These fluorescent changes 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 read easily for its remote sensitivity, offering further advantage over other spectral signals. The inputs are photochemical energy or heat, which are superior to chemical or electrochemical means for their cleanness and convenience. Finally, the complete reversibility exhibited by the molecular system should be emphasized.

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