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Switchable V-Type [2]Pseudorotaxanes

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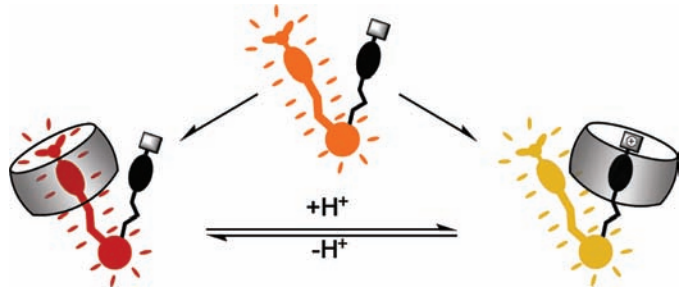
ABSTRACT



A V-type molecule comprising a 2-[2-[4-(dimethylamino)phenyl]ethenyl]pyridinium cyanine branch and a *p*-aminophenoxy ethyl side arm was synthesized and can form quite different [2]pseudorotaxanes with cucurbit[7]uril (CB[7]) as a model thread in aqueous solution. The CB[7] ring can be switched reversibly from the cyanine branch to the aminophenoxy ethyl side arm by protonation of the aniline group, and the color of the solution was changed from orange red to yellow.

A [2]pseudorotaxane is a type of supramolecular assembly where a rodlike molecule threads a cyclic molecule. In recent years, switchable [2]pseudorotaxanes become one of the hot topics for their applications on the construction of molecular devices such as switches,[1] logic gates,[2] sensors,[3] valves,[4] and machines.[5] The integrating/disintegrating behavior and the migration of the ring component between two binding stations on the thread are the two fundamental switching motions of a [2]pseudorotaxane. Compared with the disintegrating switching, the migrating switching acts more like a machine. However, in a [2]pseudorotaxane which comprises no bulky terminal groups on both ends of the axle, once the two stations are arranged separately at about 180°, the encircling of two rings on the rod to form a [3]pseudorotaxane occurs, and the switching system becomes complicated.[6] To avoid the over-encircling, partially overlapping the two stations is the strategy conventionally adopted.[7] Herein we describe a novel method which generates steric

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hindrance to prevent the over threading by settling two CB[7] binding sites on the two arms of a V-type molecule (**DP**) at an angle of about 60°. The CB[7] ring can be switched between the two stations by pH stimuli, and two different [2]pseudorotaxanes are originated.

The **DP** molecule is a 2-[2-[4-(dimethylamino)phenyl]ethenyl]pyridinium cyanine dye with a *p*-aminophenoxy ethyl side arm, and the dimethylamino phenyl moiety (**DMA**) and *p*-aminophenoxy group (**OA**) on the two branches are potential binding sites for the CB[7] macrocycle, as shown in Figure 1. CB[7] has a 9.1 Å depth and a 7.3 Å equatorial

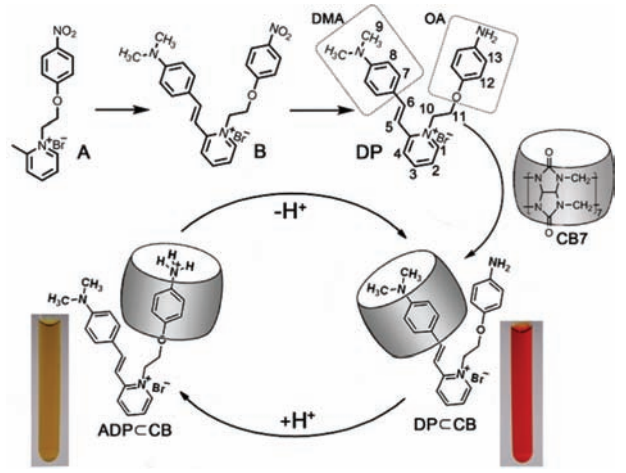

Figure 1. Formation and the switching behaviors of the two [2]pseudorotaxnes **DP⊂CB** and **ADP⊂CB**.

width,[8] which is relatively larger than the distance of the two branches.[9] So it is impossible for two CB[7] rings to encircle simultaneously both arms of **DP** because of steric hindrance. The fact that same proton resonances of **DP** were found in the presence of 1.3 and 2.5 equiv of CB[7] in D_2O at pD 9.6 (Figure S3, Supporting Information) also supports the impossibility of the formation of a [3]pseudorotaxane. The NMR integration of the appropriate proton resonances of **DP** in the presence of 0.8 equiv of CB[7] indicates that there are 79% of **DP** combine with CB[7] (Figure S3) and the formation of a [2]pseudorotaxane (**DP⊂CB**) from stoichiometric complexation was thus validated.

For the coconformational identification of cucurbituril-based inclusion complexes, it is a common rule that the protons inside the hydrophobic cucurbituril cavity undergo shielding effect while the outside ones conduct deshielding effects, and those near the carbonyl rim are scarcely affected.[10] The ^1H NMR spectra of **DP** and **DP⊂CB** (**DP** in the presence of 1.3 equiv of CB[7]) in D_2O at pD 9.6 were thus recorded to obtain the coconformation details of **DP⊂CB**, as shown in Figure 2a and 2b. Compared with pure

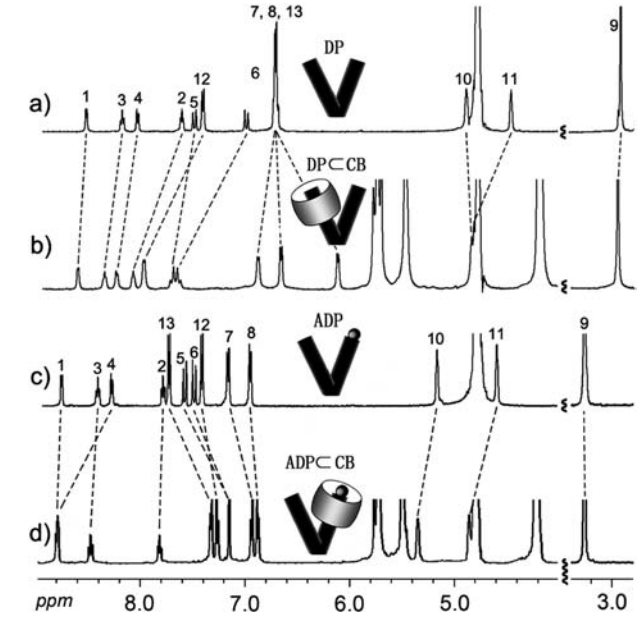

Figure 2. ^1H NMR spectra (D_2O, 500 MHz) of **DP** (a), **DP⊂CB** (b), **ADP** (c), and **ADP⊂CB** (d). Spectra a and b were recorded at pD 9.6 and c and d at pD 4.7.

DP, the aromatic protons H_7 and H_8 on **DMA** conduct distinct shielding effects ($\Delta\delta_{H7} = -0.05$ and $\Delta\delta_{H8} = -0.88$ ppm) while the two vinyl protons H_5 and H_6 undergo deshielding effects ($\Delta\delta_{H5} = +0.66$ and $\Delta\delta_{H6} = +0.20$ ppm), and the chemical shift of H_9 is nearly unaltered ($\Delta\delta_{H9} = +0.03$ ppm). These spectroscopic results indicate that, among the [2]pseudorotaxane, the CB[7] macrocycle resides over the benzene ring of the cyanine arm, the vinyl group stands out from one opening of CB[7] and the two methyl groups locate on the vicinity of the other. Those protons, H_1, H_2, H_3, H_4 on pyridinium unit, and H_{12}, H_{13} on **OA**, are all found to move downfield ($\Delta\delta_{H1} = +0.08$, $\Delta\delta_{H2} = +0.21$, $\Delta\delta_{H3} = +0.17$, $\Delta\delta_{H4} = +0.18$, $\Delta\delta_{H12} = +0.57$ and $\Delta\delta_{H13} = +0.17$ ppm), which is coincident with their location outside the CB[7] cavity. It is interesting that the CB[7] in **DP⊂CB** is away from the pyridinium and encircles the tail of the cyanine dye, which is quite different from those common CBs-based inclusion complexes where the CBs would stay around the N^+ and to the best of our knowledge is first observed.

The pK_a of **OA** is 5.25[11] and that of **DMA** is determined as 2.81,[12] so the V-type molecule could exsist in **DP** form

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(9) The distance between the two benzene rings is about 7.3 Å from the energy-minimized structure of **DP**; see Figure S2, Supporting Information.

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(pH > 5.25) and protonized **ADP** form (**OA** is protonized while the cyanine arm remains intact at 2.81 < pH < 5.25). Noticing that CBs favor highly stable inclusion complexes with cationic organic guest,[13] especially those of the $-NH_3^+$ group, which can develop favorable hydrogen-bonding, ion−dipole interaction, and hydrophobic effects with CBs, it is expected that the CB[7] macrocycle could move to the ammonium side branch of **ADP** from the original cyanine branch to form a new [2]pseudorotaxane. In this case, the pK_a value of **OA** is the critical point for the pH switching. However, it should be noted that the pK_a value of an amino group would become bigger upon complexation,[14] which means that the pK_a' value of **OA** would not be less than 5.25 when forming an inclusion with CB[7]. The ^{1}H NMR spectra of **ADP** in the presence of 1.3 and 2.5 equiv of CB[7] in D_2O at pD 4.7 were then recorded and the observed same proton signals of **ADP** again supports the non-[3]pseudorotaxane formation (Figure S4, Supporting Information).

The ^{1}H NMR measurements of **ADP** and **ADP** in the presence of 1.3 equiv of CB[7] (**ADP⊂CB**) in D_2O at pD 4.7 were then carried out for the [2]pseudorotaxane formation investigation, as shown in parts c and d, Figure 2. Compared with **ADP**, the aromatic protons H_{12}, H_{13} of the *p*-aminiumphenoxy group on **ADP⊂CB** are observed obviously shift to higher field ($\Delta\delta H_{12} = -0.15$ and $\Delta\delta H_{13} = -0.40$ ppm), and the ethyl protons H_{10} and H_{11} exhibit downfield shift ($\Delta\delta H_{10} = +0.16$ and $\Delta\delta H_{11} = +0.26$ ppm). These facts reveal that **ADP⊂CB** is also a [2]pseudorotaxane where the CB[7] ring encircles the *p*-aminiumphenoxy unit as assumed with the ethyl group staying outside.

The protons of the cyanine branch, which locate outside of the CB[7] ring, are thus expected to shift downfield as a result of the deshielding effect of the ring. However, except the downfield-shifted protons on the pyridinium, those protons on the dimethylaminostyrene unit—H_5, H_6, H_7, H_8 and H_9—shift to higher field. The energy-minimized structure of **ADP⊂CB** gives useful information, as illustrated in Figure 3. The steric exclusion of CB[7] macrocycle forces the styrene group to turn at an angle and detach the plane of pyridinium ring. Consequently, the electron-donating effect origins from the dimethylamino unit through the styrene group to the pyridinium ring is shut down, and as a result, the cloud density of the dimethylaminostyrene group increases while the pyridinium ring decreases, which are coincident with the above detected upfield shift of the protons on dimethylaminostyrene group and the downfield shift of the protons on the pyridinium ring.

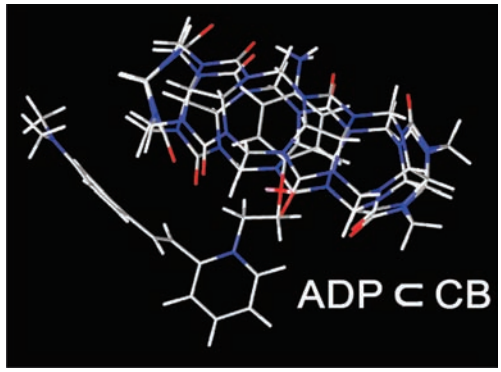

Figure 3. Energy-minimized structure of **ADP⊂CB**.

More importantly, the switching of the CB[7] ring from the cyanine branch of **DP⊂CB** to the aminiumphenoxy side arm of **ADP⊂CB** is easily detected by a change of color. Figure 4 displays the absorption spectra of **DP**, **ADP**, as well as the [2]pseudorotaxane **DP⊂CB** and **ADP⊂CB**. The colors of the aqueous solution of **DP** (at pH 9.6) and **ADP** (at pH 4.7) are orange yellow and exactly the same with the maximum absorption peaks both at 445 nm. Compared with the identical color of the two unbound molecules, the two corresponding inclusions with CB[7] ring show obvious color changes. On one hand, **DP⊂CB** conducts a color of orange red in the aqueous solution with the maximum absorption peak at 459 nm, which is a 14 nm bathochromic shift with respect to that of **DP**. This finding might be attributed to the shielding effects on the dimethyl amino group (donor) and the deshielding effects on the pyridinium ring (acceptor) when **DMA** was encapsulated inside the hydrophobic cavity of CB[7], which result in the enhancement of intramolecular charge-transfer effects among the cyanine branch. On the

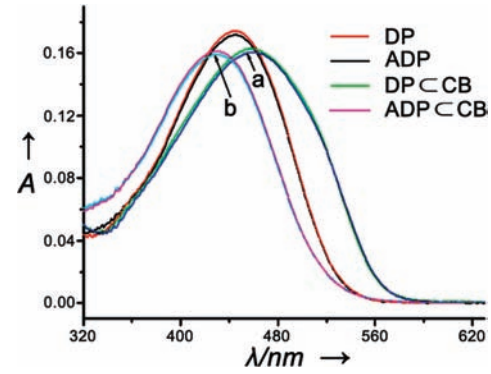

Figure 4. UV−vis absorption spectra of **DP**, **ADP**, **DP⊂CB**, and **ADP⊂CB** (in H_2O, 1.0×10^{-5} M). Curves a and b are relevant to the absorption of **DP⊂CB** and **ADP⊂CB** after 10 swithing circles.

(11) Hall, W. E.; Higuchi, T.; Pitman, I. H.; Uekama, K. *J. Am. Chem. Soc.* **1972**, *94*, 8153–8156.

(12) The pK_a value was determined by monitoring the absorption change of **DP** (2.5×10^{-5} M) at $\lambda = 327$ nm upon pH variation from 6.0 to 1.0; see the Supporting Information.

(13) (a) Eelkema, R.; Maeda, K.; Odell, B.; Anderson, H. L. *J. Am. Chem. Soc.* **2007**, *129*, 12384–12385. (b) Liu, Y.; Shi, J.; Chen, Y.; Ke, C.-F. *Angew. Chem., Int. Ed.* **2008**, *47*, 7293–7296. (c) Gadde, S.; Batchelor, E. K.; Weiss, J. P.; Ling, Y.; Kaifer, A. E. *J. Am. Chem. Soc.* **2008**, *130*, 17114–17119. (d) Rauwald, U.; Scherman, O. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 3950–3953.

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other hand, **ADP⊂CB** exhibits a 17 nm hypsochromic shift relative to **ADP** with the peak maximum at 428 nm and the color of the solution is yellow. This phenomenon should result from the reduced conjugate degree of the cyanine branch in view of the distortion mentioned above.

It should be noted that the switching between **DP⊂CB** and **ADP⊂CB** is reversible. A switching circle where **DP⊂CB** is converted to **ADP⊂CB** and then turned back to **DP⊂CB** was achieved by adjusting the pH value of **DP⊂CB** aqueous solution (1.0×10^{-5} M 250 mL, pH 9.6) to 4.7 and afterward again to 9.6 using diluted HCl and NaOH aqueous solutions (both 1.0 M). Such a switching circle can be repeated many times. As shown in Figure 4, the absorption curves of **DP⊂CB** and **ADP⊂CB** after 10 switching circles are exactly the same with their original ones. The reversibility of the switching process is thus validated.

The fact that the absorption maximum of the two [2]pseudorotaxanes are different allowed us to estimate the pK_a' value of **OA** upon complexation. The moritoring of the absorption maximum change upon the pH variation of **ADP⊂CB** aquoeus solution from 4.0 to 11.0 were carried out as illustrated in Figure 5. The pK_a' value was found to be 7.31, which is a 2.06 shift corresponding to pK_a. It can also be seen that the selected pH values for states **DP⊂CB** (pH 9.6) and **ADP⊂CB** (pH 4.7) are appropriate from this titration curve.

In conclusion, two CB[7] recognition sites were arranged on both arms of a new V-type cyanine molecule consisting of an aminophenoxy ethyl side branch. The steric hindrance between the two stations provides a novel way to prohibit the formation of a [3]pseudorotaxane but to favor [2]pseudorotaxane inclusions. It should be noted that the CB[7] ring can be switched from the cyanine branch to the aminophenoxy ethyl side branch by protonating the aniline group and such inclusion exchange is accompanied with a color readout.

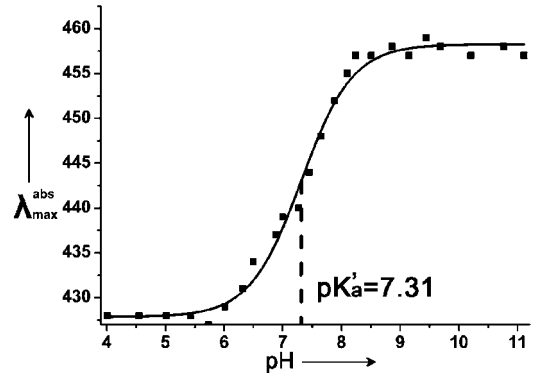

Figure 5. Change of the absorption maximum of **ADP** aqueous solution (2.5×10^{-5}M) in the presence of 1.3 equiv of CB[7] upon pH variation from 4.0 to 11.0.

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Supporting Information Available: Synthetic details, NMR spectra, figures, and curves mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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