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, logic gates, sensors, valves, and machines. 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. To avoid the over-encircling, partially overlapping the two stations is the strategy conventionally adopted. Herein we describe a novel method which generates steric


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-amino phenoxyl side arm, and the dimethylamino phenyl moiety (DMA) and p-amino phenoxyl 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 width, which is relatively larger than the distance of the two branches. 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 D2O at pH 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 D2O at pH 9.6 were thus recorded to obtain the coconformation details of DP⊂CB, as shown in Figure 2a and 2b. Compared with pure DP, the aromatic protons H3 and H8 on DMA conduct distinct shielding effects (ΔδH3 = −0.05 and ΔδH8 = −0.88 ppm) while the two vinyl protons H5 and H6 undergo deshielding effects (ΔδH5 = +0.66 and ΔδH6 = +0.20 ppm), and the chemical shift of H6 is nearly unaltered (ΔδH6 = +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 on one opening of CB[7] and the two methyl groups locate on the vicinity of the other. Those protons, H1, H2, H3, H4 on pyridinium unit, and H12, H13 on OA, are all found to move downfield (ΔδH1 = +0.08, ΔδH2 = +0.21, ΔδH3 = +0.17, ΔδH4 = +0.18, ΔδH12 = +0.57 and ΔδH13 = +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.

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

Figure 2. 1H NMR spectra (D2O, 500 MHz) of DP (a), DP⊂CB (b), ADP (c), and ADP⊂CB (d). Spectra a and b were recorded at pH 9.6 and c and d at pH 4.7.
(pH > 5.25) and protonized ADP form (OA is protonated while the cyanine arm remains intact at 2.81 < pH < 5.25). Noticing that CBs favor highly stable inclusion complexes with cationic organic guest, especially those of the --NH₃⁺ 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 pKₐ value of OA is the critical point for the pH switching. However, it should be noted that the pKₐ value of an amino group would become bigger upon complexation, which means that the pKₐ⁺ value of OA would not be less than 5.25 when forming an inclusion with CB[7]. The ¹H NMR spectra of ADP in the presence of 1.3 and 2.5 equiv of CB[7] in D₂O at pH 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 ¹H NMR measurements of ADP and ADP in the presence of 1.3 equiv of CB[7] (ADP⊂CB) in D₂O at pH 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 H₁₂, H₁₃ of the p-aminophenoxy group on ADP⊂CB are observed obviously shifted to higher field (ΔδH₁₂ = 0.15 and ΔδH₁₃ = 0.40 ppm), and the ethyl protons H₁₀ and H₁₁ exhibit downfield shift (ΔδH₁₀ = 0.16 and ΔδH₁₁ = 0.26 ppm). These facts reveal that ADP⊂CB is also a [2]pseudorotaxane where the CB[7] ring encircles the p-aminophenoxy 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—H₅, H₆, H₇, H₈ and H₉—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]

![Figure 3. Energy-minimized structure of ADP⊂CB.](image)

The electron-donating effect origins from the dimethylaminostyrene group, which can develop favorable hydrogen-bonding, ion–dipole interaction, and hydrophobic effects with CBs, it is expected that the 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 dimethylaminostyrene 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.

More importantly, the switching of the CB[7] ring from the cyanine branch of ADP⊂CB to the aminophenoxy side arm of ADP⊂CB is easily detected by a change of color. Figure 4 displays the absorption spectra of DP, ADP, DP⊂CB, and ADP⊂CB (in H₂O, 1.0 × 10⁻⁵ M). Curves a and b are relevant to the absorption of DP⊂CB and ADP⊂CB after 10 switching circles.

![Figure 4. UV–vis absorption spectra of DP, ADP, DP⊂CB, and ADP⊂CB in H₂O, 1.0 × 10⁻⁵ M. Curves a and b are relevant to the absorption of DP⊂CB and ADP⊂CB after 10 switching circles.](image)

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
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 monitoring of the absorption maximum change upon the pH variation of ADP⊂CB aqueous 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 prototating the aniline group and such inclusion exchange is accompanied with a color readout.

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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.