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Short communication

Synthesis and characteristics of a novel pseudorotaxane with the diarylethene as the functional stopper

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Abstract

The synthesis and characteristics of a novel pseudorotaxane formed by the diarylethene as the functional stopper, the CB[6] (cucurbit[6]uril) as the macrocycle and diprotonated diaminobutane as the 'string' were reported. The pseudorotaxane exhibited good photochromic properties and could be alternate between colorless ring-open and colored ring-closed forms by alternative irradiation with UV light of 254 nm and 365 nm because of the functional diarylethene stopper. The CB[6] bead was localized on aliphatic chain to combine N^+ of the diprotonated diaminobutane by non-covalent bonds. The molar ratio of CB[6] to the 'string' was 1:1. This character will make it potential for use in the construction of the prototype of molecular machines.

Keywords: Pseudorotaxane; Photochromic properties; Diarylethene; Supramolecule; Self-assembling

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1. Introduction

Photochromic molecules attract much attention from fundamental as well as practical points of view because of their potential for applications to optical devices, such as optical memories and switches [1]. Among the photochromic compounds, diarylethenes are regarded as the best candidates for such devices, because of their advantages such as a high efficiency of photoisomerizations, sufficient thermal stability of both the open and the close forms, a very high resistance to photofatigue, and the ease with which the reaction can be monitored by UV–vis spectroscopy [2–4].

Recently, many investigations concerning artificial molecular machines [5–8] have been carried out because of their potential applications in areas such as molecular logic gates [9–12], molecular switches [13–16], molecular wires [17,18], and information storage [19]. Pseudorotaxanes, a class of supramolecular species in which a molecular thread is encircled by a molecular bead, have been employed in the construction of prototype molecular machines because dethreading and rethreading movements of a thread through the center of a ring are reminiscent of the action of a linear motor [20–25]. Cucurbit[*n*]uril (CB, $n = 5–8$) [26,27], a macrocycle comprising glycoluril units that has a hydrophobic cavity and polar carbonyl groups surrounding the portals, can be used as a molecular 'bead' in the self-assembly of interlocked structures such as rotaxanes, pseudorotaxane, polyrotaxanes and molecular necklaces [28–30]. The stability of host–guest complexes of CB[6] with diaminoalkanes such as diaminobutane strongly depends on pH [31]. When the two nitrogen atoms of the diaminobutane are protonated at low pH, the CB[6] resides at the protonated diaminobutane site and forms a stable 1:1 complex [32–34] with the diprotonated diaminobutane.

Although lots of chemically controllable molecular switches generally operated through the sequential addition and removal of electrons, metal ions, or protons are relatively simple to design and provide significant outputs during the switching [35–37], there were by-products during the movements of

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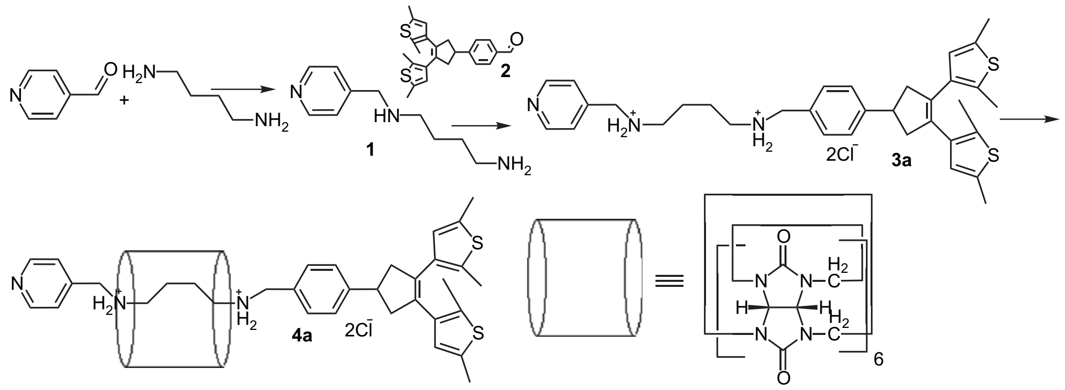


Scheme 1. Synthetic routes of the compounds.

the macrocycle between the two stations [38,39]. Here we report a novel pseudorotaxane formed by the CB as the macrocycle and diprotonated diaminobutane as the ‘string’ (Scheme 1). By introducing the diarylethene as the functional stopper to the pseudorotaxane, the pseudorotaxane exhibited good photochromic properties and could be alternate between colorless ring-open and colored ring-closed forms by alternative irradiation with UV light of 254 nm and 365 nm.

2. Experimental

^{1}H NMR spectra were recorded on a Bruker AM-500 spectrometer operating at frequencies of 500 MHz. Elemental analysis was performed on a Perkin–Elmer 2400C instrument. Mass spectra (MS) were recorded on an MA1212 instrument using standard conditions (ESI, 70 eV). UV–vis spectra were performed on a Varian Cary 100 spectrophotometer (1 cm quartz cell used). The preparation of compound **2** was reported previously [40].

*2.1. Compound **1***

1,4-Diaminobutane (5 g, 56.72 mmol) was added to the solution of pyridine-4-carbaldehyde (1.22 g, 11.34 mmol) in methanol (20 mL) dropwise at 0 °C. After the reaction mixture was stirred for 12 h 0 °C, $NaBH_4$ (0.54 g, 14.29 mmol) was added and stirred overnight. After acidified with 1 N HCl at 0 °C and then stirred for 10 h, the mixture was basified to pH 14 with solid NaOH with ice cooling and extracted with $CHC1_3$ (4 × 50 mL). After dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure, the residue was purified by column chromatography using petroleum NH_4OH/MeOH (6:100) to afford compound **1** as colorless oil, 1.67 g (82%).

^{1}H NMR (DMSO-d_6) δ: 1.31–1.35 (m, 2H, $-CH_2$), 1.36–1.44 (m, 2H, $-CH_2$), 2.40–2.41 (m, 2H, $-CH_2$), 2.46–2.49 (m, 2H, $-CH_2$), 3.67 (2H, s, $-CH_2$), 7.31 (d, 2H, $J = 6$, Ar–H), 8.45 (d, 2H, $J = 6$, Ar–H). ESI-MS: $m/z = 179.3$. Anal. Calcd for $C_{10}H_{17}N_3$: C, 67.00; H, 9.56; N, 23.44. Found: C, 67.03; H, 9.57; N, 23.45.

*2.2. Compound **3a***

A mixture of compound **1** (55 mg, 0.31 mmol) and compound **2** (100 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) and CH_3OH (10 mL) was stirred at room temperature for 12 h. $NaBH_4$ (10 mg, 0.26 mmol) was introduced with brief ice cooling. The reaction mixture was allowed to stand for 15 h

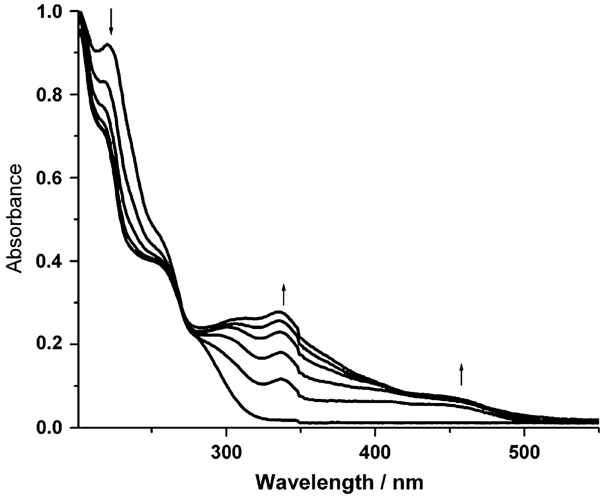


Fig. 1. Absorption changes of pseudorotaxane **4a** (3×10^{-5} M, in H_2O) upon irradiation at 254 nm; irradiation times were 1, 2, 3, 4 and 5 min.

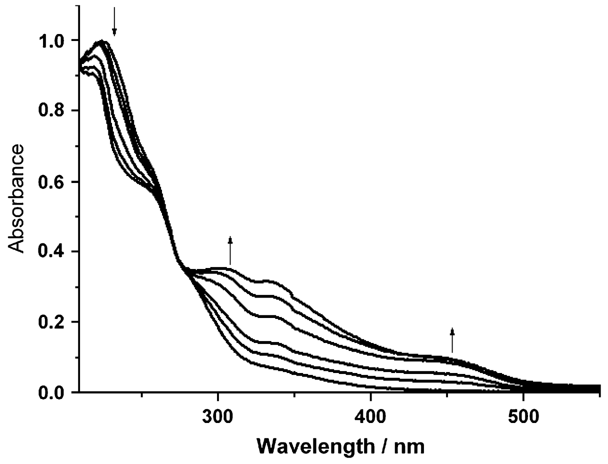


Fig. 2. Absorption changes of the diarylethene **3a** (3×10^{-5} M, in H_2O) upon irradiation at 254 nm; irradiation times were 1, 2, 3, 4 and 5 min.

at room temperature and was acidified with 1 N HCl at 0 °C and kept overnight. The mixture was basified to pH 14 with solid NaOH with ice cooling and extracted with $CHCl_3$ (4×10 mL). After dried over anhydrous $MgSO_4$ and then concentrated in vacuo, the residue was purified by column chromatography using petroleum NH_4OH/MeOH (2:100) to afford compound **3a** as colorless oil, 137 mg (86%); m.p. 145–148 °C (decomp.).

^1H NMR (D_2O) δ: 1.49 (m, 4H, $-CH_2$), 1.66 (s, 6H, $-CH_3$), 1.97 (s, 6H, $-CH_3$), 2.45 (m, 2H, $-CH_2$), 2.75 (m, 2H, $-CH_2$), 2.91–3.07 (m, 4H, $-CH_2$), 3.23 (m, 1H, $-CH$), 3.96 (2H, s, $-CH_2$), 4.35 (2H, s, $-CH_2$), 6.20 (2H, s, thiophene–H), 7.07 (d, 2H, $J = 5.4$, Ar–H), 7.24 (d, 2H, $J = 5.4$, Ar–H), 7.86 (d, 2H, $J = 6.0$, Py–H), 8.65 (d, 2H, $J = 6.0$, Py–H). ESI-MS: $m/z = 557.8$ $[M + 2H]^{2+}$. Anal. Calcd for $C_{34}H_{43}N_3S_2 \cdot 2PF_6$: C, 48.17; H, 5.11; N, 4.96. Found: C, 48.15; H, 5.09; N, 5.01%.

2.3. *Pseudorotaxane* ***4a***

The solution of compound **3a** (100 mg, 0.18 mmol) in acetone (20 mL) was protonated by adding concentrated HCl (1 mL). The solution was filtered off and the solid was redissolved in water (10 mL). To the mixture was added CB[6] (0.12 g, 0.36 mmol) and stirred overnight. After the undissolved cucurbituril was filtered off, the residue was concentrated in vacuo to about 2 mL. The aqueous solution was added to 10 mL ethanol and then filtered off. The solid was dried under vacuum overnight to give pseudorotaxane **4a**, 197 mg (95%).

^1H NMR (D_2O) δ: 0.62 (m, 4H, $-CH_2$), 1.79 (s, 6H, $-CH_3$), 2.19 (s, 6H, $-CH_3$), 2.52 (m, 8H, $-CH_2$), 3.50 (m, 1H, $-CH$), 4.31 (2H, s, $-CH_2$), 4.34 (2H, s, $-CH_2$), 4.38 (m, 12H), 5.63 (m, 24H), 6.40 (2H, s, thiophene–H), 7.40 (2H, Ar–H), 7.75 (2H, Ar–H), 8.49 (2H, Py–H), 8.93 (2H, Py–H). ESI-MS: $m/z = 1553.9$ $[M^+ + 2H]^{2+}$. Anal. Calcd for $C_{70}H_{77}N_{27}O_{12}S_2 \cdot 2PF_6 \cdot 9H_2O$: C, 41.90; H, 4.87; N, 18.85. Found: C, 41.83; H, 4.79; N, 18.76%.

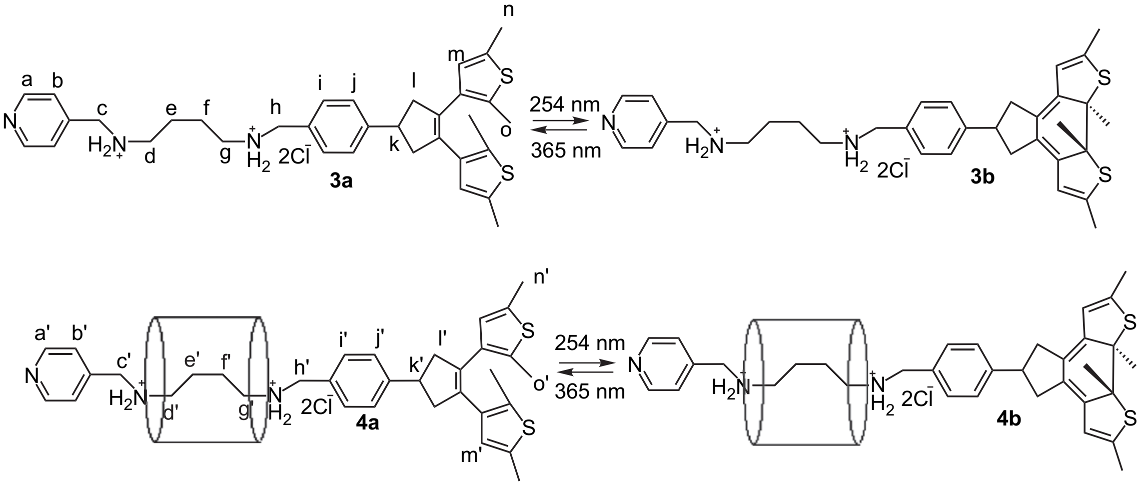
3. Results and discussion

The pseudorotaxane **4a** exhibited good photochromic properties as the diarylethene **3a** and could be alternate between colorless ring-open and colored ring-closed forms by alternate irradiation with UV light of 254 nm and 365 nm. The photochromism of the pseudorotaxane **4a** and the diarylethene **3a** in the aqueous solution is illustrated in Figs. 1, 2 and Scheme 2. Fig. 1 illustrates the absorption spectral changes of the aqueous solution of **4a** (3×10^{-5} M) upon photoirradiation. Upon UV light (254 nm) irradiation, the colorless solution turned to yellow and the absorption band appeared at 335 nm and 450 nm due to the formation of the closed form **4b**, and the peak of **4a** at 222 nm was suppressed. Upon irradiation with UV light of 365 nm, the yellow solution of **4b** was completely bleached, and the absorption spectrum returned to that of **4a**.

Obviously, there was an isosbestic point at 268 nm ($\varepsilon = 1.0 \times 10^3\ M^{-1}\ cm^{-1}$), and it indicated that the equilibrium of two isomers (ring-open and ring-closed forms) existed in isomerization upon irradiation. The cyclization and cycloreversion quantum yields of the pseudorotaxane in aqueous solution were 0.20 and 0.30, respectively. In order to evaluate the fatigue resistance properties of the pseudorotaxane **4a** in the aqueous solution, we irradiated it alternately with UV light of 254 nm and 365 nm. We found it could be stable for more than 200 irradiation cycles.

The ^1H NMR spectrum indicated that CB[6] resided at diprotonated diaminobutane unit without change when the photoisomerizations of the stopper diarylethene because of no pH change with the photoisomerizations of the diarylethene and the tight binding between CB[6] with diprotonated diaminobutane ($\log K_a/M^{-1} = 5.27$) [26]. The thermal stability of the open- and closed-ring forms of the pseudorotaxane was evaluated. The absorption spectra of **4a** and **4b** did not change after they were stored in dark for one month at room temperature.

The photochromism of the diarylethene **3a** in the aqueous solution is shown in Fig. 2. Upon UV light (254 nm)



Scheme 2. The photochromism of the diarylethene and the pseudorotaxane.

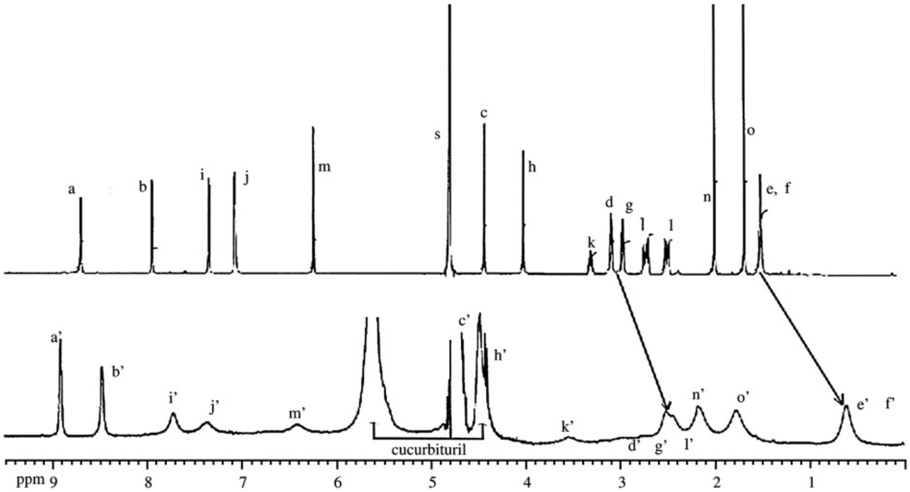


Fig. 3. The comparison of ^{1}H NMR signals of **3a** (top) and **4a** (bottom).

irradiation, the new absorption band appeared at 301 nm and 450 nm due to the formation of the closed form **3b**, and the peak of **3a** at 222 nm was suppressed. Upon irradiation with UV light of 365 nm, the absorption spectrum returned to that of **3a**.

Fig. 3 compares ^{1}H NMR spectra of **3a** and **4a**. The signals of the methylene groups (e, f and d, g) located inside CB were shifted to upfield, and the signals of the protons (a, b, i, j and h) outside CB but near were shifted to downfield. The signal of the proton c was also shifted to downfield and the chemical shift of proton c was the same as that of the solvent. The signals of the other protons (k, l, m, n and o) changed little because the distance between the protons and CB was far and the effect of the CB was little. The ^{1}H NMR spectrum of pseudorotaxane **4a** also indicated the molar ratio of CB[6] to the ‘string’ was 1:1.

4. Conclusions

In summary, a novel pseudorotaxane formed by the diarylethene as the functional stopper and CB[6] as the macrocycle was synthesized with a high yield. The pseudorotaxane exhibited good photochromic properties because of the functional stopper diarylethene. The CB[6] resided at diprotonated diaminobutane unit in the course of the photoisomerizations of the diarylethene because of the tight binding between CB[6] with diprotonated diaminobutane and no pH change with the photoisomerizations of the diarylethene. This character will make it useful in the construction of the prototype of the molecular machines for applications in areas such as optical memories, molecular logic gates, and molecular switches.

Acknowledgments

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