Self-assembly of Donor and Acceptor π-Conjugated Molecules via Complexation with γ-Cyclodextrin to Give a Pseudorotaxane Type Macromolecular Adduct with an Expanded π-Conjugation System

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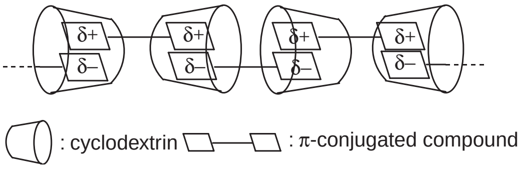
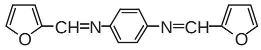
A macromolecular adduct was prepared by double-threading of donor type and acceptor type π-conjugated guest molecules into γ-cyclodextrin. According to the adduct formation, the UV-vis of the guest molecules showed a large bathochromic shift of 150 nm, suggesting formation of a new type of effectively expanded π-conjugation system. Other data supported this view.

Cyclodextrins (CDs) can include various organic guest molecules to form rotaxanes[1] and polyrotaxanes.[2] For example, β-CD and γ-CD include two aromatic molecules such as α-naphthalene[3] and styrene[4] derivatives in their cavity. The two aromatic molecules included in CD form a face-to-face packed adduct. McGown and co-workers reported double-threading of π-conjugated 1,6-diphenyl-1,3,5-hexatrienes into β- and γ-CDs to give pseudorotaxane type aggregates in which the terminal phenyl groups are also considered to assume a face-to-face packing assisted by π–π interaction.[5] Although the aggregate contained about 20–30 1,6-diphenyl-1,3,5-hexatriene molecules, expansion of effective π-conjugated length did not occur, and the aggregate showed a π–π^* absorption band at the same position as original 1,6-diphenyl-1,3,5-hexatriene. Recently, CD pseudopolyrotaxanes and rotaxanes containing π-conjugated polymers[6,7] and organic molecules[8–10] as an axle have attracted much attention because of their potential usability for electronic devices.

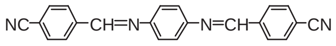
Donor-acceptor (D-A) electrostatic interaction has been utilized for construction of supramolecules[11] between sodium α-naphthyl acetate and picric acid. We thought that the stability of such a D-A interaction might be enhanced in the CD cavity and the inclusion of D-D and A-A molecules into CD would give a novel pseudorotaxane type macromolecular adduct with an expanded effective π-conjugation system.



We have tried preparation of such pseudorotaxanes by using the following π-conjugated molecules having π-electron rich furan rings (**1a**) and π-electron deficient 4-cyanophenyl groups (**1b**) at the both ends. We herein report the preparation of novel pseudorotaxane type π-conjugated adduct, its structure, and its optical and electrochemical properties.



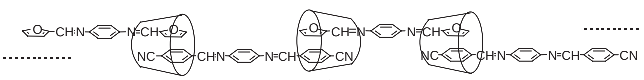
1a



1b

The π-conjugated guest molecules were synthesized by known condensation reactions of *p*-phenylenediamine with the corresponding aldehydes. The CPK molecular model indicates that **1a** and **1b** can be included in the cavity of γ-CD simultaneously.

On stirring an aqueous suspension containing the water-insoluble **1a** and **1b** and water-soluble γ-CD in a 1 : 1 : 2.5 molar ratio for 5 days at room temperature, 38% of **1a** and **1b** were solubilized according to formation of a water-soluble pseudorotaxane type π-conjugated adduct **2**. A possible structure of **2** is shown below.



2

Filtration gave an aqueous solution containing intact γ-CD and **2**, whereas 62% of added **1a** and **1b** were recovered by the filtration, respectively. These results indicate that the aqueous solution contained **2** and γ-CD in about 1 : 5.6 molar ratio based on the number of γ-CD molecule. Drying up the aqueous solution under vacuum gave a light purple powder. Separation of **2** from γ-CD was not possible. Inherent viscosity of the mixture of **2** and γ-CD in H_2O was 0.09 dL g^{-1} at 28 °C. The η_{sp}/c value was not largely dependent on c, revealing that **2** once formed was stable even in diluted conditions. Dilution of the mixture in H_2O did not give a turbid solution, which should be obtained on dissociation of **1a** and **1b** from **2**. MALDI TOF-MAS spectrum of the reaction product showed a peak due to an adduct composed of 4(**1a** + **1b**) + 5γ-CD, supporting formation of the adduct **2**. In order to determine the structure of **2**, ^{1}H NMR measurement using the ROESY technique, X-ray diffraction (XRD), and circular dichromism analyses were carried out.

In the ROESY analysis, irradiation at the signals of the CH hydrogens inside the γ-CD cavity led to appearance of positive peaks due to hydrogens of benzene and furan rings and azomethyn groups, supporting an assumption that **1a** and **1b** were included in the γ-CD cavity in **2**.

The XRD pattern of **2** showed a strong peak at 2θ (Cu Kα) of about 20°, similar to that of reported complex of γ-CD with poly(ethylene glycol)[12] having a columnar structure.

Figure 1 depicts UV-vis spectra of DMSO solutions of **1a** and **1b** and an aqueous solution of **2**. The absorption maximum and onset position of UV-vis spectrum of **2** were observed at a longer wavelength than those of DMSO solutions of **1a** and **1b** due to expansion of the effective π-conjugation length in **2**. Simple mixing of **1a** and **1b** in organic solvents did not cause such a shift

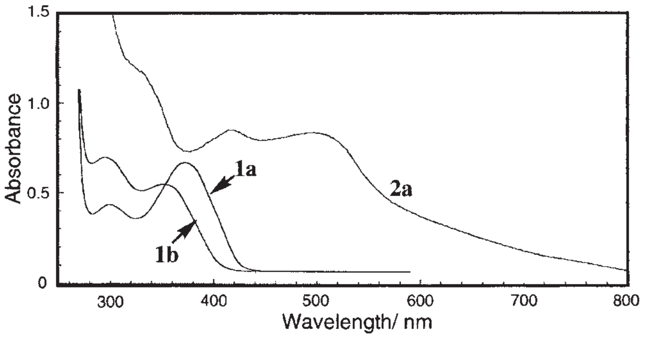


Figure 1. UV-vis. spectra of DMSO solutions of **1a** and **1b** and that of an aqueous solution of **2a**.

of the UV-vis peak. A simple mixture of **1a** and γ-CD in water did not lead to the shift of the UV-vis peak, either. The above data revealed that the postulated A-D interaction and geometrical fitness are essential for the formation of the expanded π-conjugated system.

Induced circular dichromism bands originated from interaction between the π-conjugation system and chiral CD were observed at 325, 458 and 537 nm, supporting that the guest molecules were included in the γ-CD. **2** was unstable in DMSO and the DMSO solution showed the UV-vis peaks at positions consistent with the corresponding guest molecules. The onset position of UV-vis absorption band of **2** in DMSO, however, was observed at a longer wavelength than those of **1a** and **1b**, suggesting that a part of **1a** and **1b** was still included in γ-CD and **2** in DMSO was dissociated into an adduct with a shorter effective π-conjugation length than **2** in H_2O. ^1H NMR spectrum of **2** in DMSO-d_6 showed peaks of **1a** and **1b** in a molar ratio of 1 : 1, supporting formation of **2**.

Figure 2 depicts cyclic voltammograms of **1a**, **1b**, and **2**. **2** was electrochemically active in the aqueous solution and showed an oxidation peak at a lower potential (0.33 V) than those of **1a** (0.47 V) and **1b** (0.50 V) due to expansion of the effective π-conjugation length.

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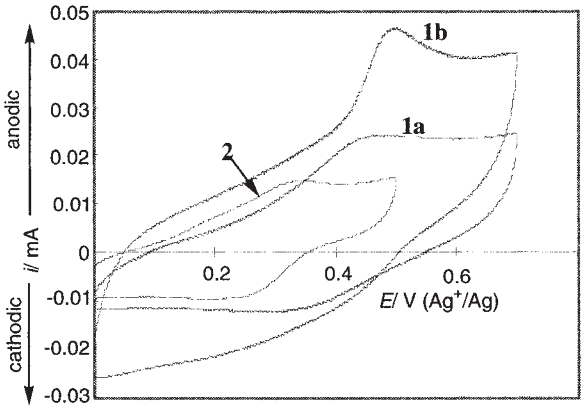

Figure 2. Cyclic voltammograms of **1a** and **1b** in CH_3CN solutions of $Bu_4N\ BF_4$ (0.10 M) and that of **2** in an aqueous solution of $NaClO_4$ (0.10 M). Sweep rate: 100 mV s^{-1}.

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