

Supporting Information

‘A Cyclodextrin-Based Molecular Shuttle Containing Energetically Favored and Disfavored Portions in its Dumbbell Component’

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Experimental Section

Materials.

α -Cyclodextrin (α -CD) was kindly supplied by Nihon Shokuhin Kako Co., Ltd. and/or obtained from Wako Pure Chemical Industries, Ltd., and was used after drying in vacuum. 4,4'-Dipyridyl and 1,12-dibromododecane were obtained from Tokyo Kasei Kogyo Co., Ltd. Sodium perchlorate, 4-bromoethylamine hydrobromide, 2,6-dimethylpyridine, ammonium hexafluorophosphate, triethylamine hydrochloride, and 2,4-dinitro-1-fluorobenzene(DNFB) were obtained from Nacalai Tesque Inc. 3-(Trimethylsilyl)-propanesulfonic acid, sodium salt was purchased from Merck. DMSO- d_6 and D₂O used as solvents in the NMR measurements were obtained from Aldrich.

Measurements.

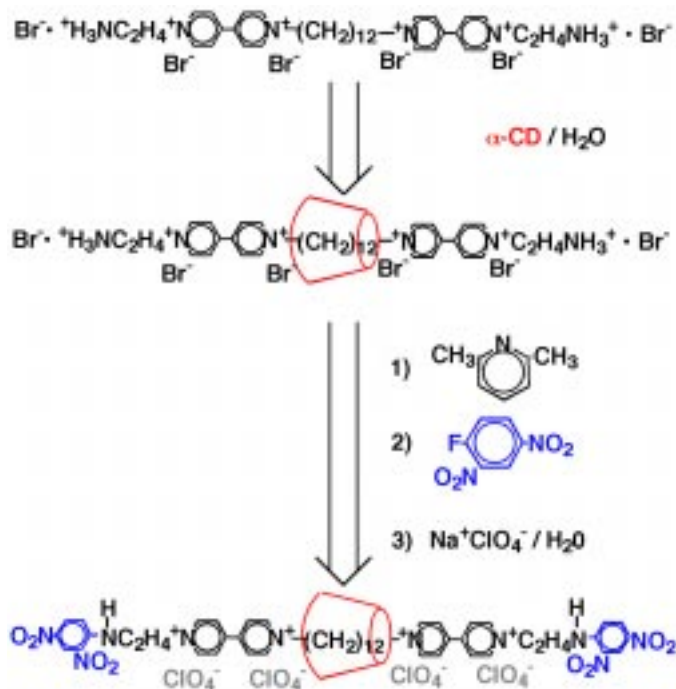
¹H NMR spectra were recorded at 270 MHz in D₂O on a JEOL JNM EX-270 spectrometer. Chemical shifts were referenced to the solvent values (δ = 4.70 ppm for HOD; δ = 2.50 ppm for DMSO- d_6) or to DSS: 3-(Trimethylsilyl)-propanesulfonic acid, sodium salt using as an external standard. Absorption spectra were recorded on a Shimadzu UV-2500PC spectrometer at room temperature. FT-IR spectra were observed on a JASCO FT/IR-410 spectrometer at room temperature by KBr method.

Preparation of rotaxanes and model compounds.

1s-[2]-rotaxane: 3. 4,4'-Dipyridyl (6.2 g, 40 mmol) and 1,12-dibromododecane (1.3 g, 4 mmol) were allowed to react in DMF (160 mL) at 80 °C for 2 days. After the evaporation of the solvent, the residue was washed with diethyl ether to yield 2.4 g of $[\text{bpy}-(\text{CH}_2)_{12}\text{-bpy}]^{2+}\cdot 2\text{Br}^-$, (90%) as a yellow solid.

$[\text{bpy}-(\text{CH}_2)_{12}\text{-bpy}]^{2+}\cdot 2\text{Br}^-$ (1.8 g, 28 mmol), 2-bromoethylamine hydrobromide (15.5 g, 76 mmol) and water (25 mL) were heated to reflux for 2 days. After the concentration of this solution, it was slowly poured into ethanol (400 mL). The yellow precipitate was purified by reprecipitation from water to ethanol to yield 2.4 g of $[\text{H}_3\text{N}-(\text{CH}_2)_2\text{-bpy}-(\text{CH}_2)_{12}\text{-bpy}-(\text{CH}_2)_2\text{-NH}_3]^{6+}\cdot 6\text{Br}^-$: 1s-aminoVO (**2**), (82%) as a yellow solid.

1s-aminoVO (**2**) (250 mg, 0.2 mmol) and α -CD (580 mg, 0.6 mmol) were dissolved in water (2 mL), and allowed to stand overnight at room temperature. After the addition of 2,6-dimethylpyridine (0.5 mL, 4 mmol) to the solution, 2,4-dinitro-1-fluorobenzene (0.3 mL, 2 mmol) was introduced and stirred for 5 hours at room temperature. After the evaporation of this solvent, the residue was washed with diethyl ether and then dissolved in water (300 mL). The addition of an excess amount of sodium perchlorate to the solution caused a precipitate. After the removal of the solvent, the product was collected, washed with water, and dried under high vacuum to give the 1s-[2]-rotaxane **3** (280 mg). The yield based on compound **2** was 55 %.



molecular shuttle (2s-[2]-rotaxane): 1. 4,4'-Dipyridyl (2.6 g, 16 mmol) and 1,12-

dibromododecane (26.0 g, 80 mmol) were allowed to react in DMF (250 mL) at 80 °C for 2 days. A precipitate produced was centrifuged and washed with diethyl ether to yield 7.1 g of $[\text{Br}-(\text{CH}_2)_{12}\text{-bpy}-(\text{CH}_2)_{12}\text{-Br}]^{2+}\cdot 2\text{Br}^-$, (60 %) as a yellow solid.

Mixed solution of DMF and methanol (v/v = 1:5, 120 mL) of $[\text{Br}-(\text{CH}_2)_{12}\text{-bpy}-(\text{CH}_2)_{12}\text{-Br}]^{2+}\cdot 2\text{Br}^-$ (4.1 g, 5 mmol) was slowly poured into DMF solution (80 mL) of 4,4'-bipyridyl (9.7 g, 62 mmol) at 60 °C, and then heated to reflux for 2 days. After the evaporation of the solvent, the residue was washed with diethyl ether to yield 5.0 g of $[\text{bpy}-(\text{CH}_2)_{12}\text{-bpy}-(\text{CH}_2)_{12}\text{-bpy}]^{4+}\cdot 4\text{Br}^-$, (88 %) as a yellow solid.

$[\text{bpy}-(\text{CH}_2)_{12}\text{-bpy}-(\text{CH}_2)_{12}\text{-bpy}]^{4+}\cdot 4\text{Br}^-$ (1.1 g, 10 mmol), 2-bromoethylamine hydrobromide (11.5 g, 57 mmol) and water (75 mL) were heated to reflux for 4 days. After the concentration of this solution, it was slowly poured into ethanol (500 mL). The yellow precipitate was purified by fractional precipitation using methanol and diethyl ether to yield 2.4 g of $[\text{H}_3\text{N}-(\text{CH}_2)_2\text{-bpy}-(\text{CH}_2)_{12}\text{-bpy}-(\text{CH}_2)_{12}\text{-bpy}-(\text{CH}_2)_2\text{-NH}_3]^{8+}\cdot 8\text{Br}^-$: 2s-aminoVO (**4**), (20 %) as a yellow solid.

2s-aminoVO (**4**) (1 g, 0.7 mmol) and α -CD (810 mg, 0.8 mmol) were dissolved in water (10 mL), and allowed to stand overnight at room temperature. After the addition of 2,6-dimethylpyridine (1.2 mL, 10 mmol) to the solution, 2,4-dinitro-1-fluorobenzene (0.8 mL, 7 mmol) was introduced and stirred for 5 hours at room temperature. After the evaporation of the solvent, the residue was washed with diethyl ether and then dissolved in water (500 mL). The addition of an excess amount of sodium perchlorate to the solution caused a precipitate. After the removal of the solvent, the residue was collected and washed with water. It was purified by fractional extraction using acetonitrile. The addition of an excess amount of triethylamine hydrochloride to the acetonitrile solution caused a precipitate as a yellow solid. This product was dissolved in water (25 mL). The addition of an excess amount of sodium perchlorate to the solution caused a precipitate. After the removal of the solvent, the product was collected, washed with water, and dried under high vacuum to give the molecular dottle (2s-[2]-rotaxane: **1**) (190 mg). The yield based on compound **4** was 11 %.

