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A Redox-Switchable α-Cyclodextrin-Based [2]Rotaxane

Yan-Li Zhao,[†] William R. Dichtel,[†,§,¶] Ali Trabolsi,[‡] Sourav Saha,[†,‖]

Ivan Aprahamian,[†] and J. Fraser Stoddart*[,†,‡]

[†] *Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, California 90095,* [‡] *Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208,* [§] *Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, Pasadena, California 91125*

[¶] *Current address: Department of Chemistry and Chemical Biology, Cornel University, Ithaca, New York 14853-1301*

[‖] *Current address: Department of Chemistry, Yale University, 225 Prospect Street, New Haven, Connecticut 06520-8107*

Supporting Information

Correspondence Address
Professor **J Fraser Stoddart** Department of Chemistry Northwestern University 2145 Sheridan Road Evanston, Illinois 60208-3113 Tel: (+1)-847-491-3793 Fax: (+1)-847-491-1009 Email: stoddart@northwestern.edu

General. All reagents, including α-cyclodextrin, 5-hydroxyisophthalic acid (**S2**), propargyl bromide, 2-bromoethanol (**S7**), and propargyl alcohol (**S9**) were purchased commercially and were used without further purification. The monotosylated tetrathiafulvalene derivative (**S1**) was prepared according to literature procedures.[S1] Dimethyl 5-hydroxyisophthalate (**S3**) was prepared from **S2**, according to literature procedures.[S2] 2-Azidoethanol (**S8**) was prepared from 2-bromoethanol (**S7**) and NaN_3, also according to literature procedures.[S3] Thin layer chromatography (TLC) was carried out using silica gel 60 F254 (E. Merck). Column chromatography was performed on silica gel 60F (Merck 9385, 0.040–0.063 mm). Deuterated solvents (Cambridge Isotope Laboratories) for nuclear magnetic resonance (NMR) spectroscopic analyses were used as received. NMR spectra were recorded on a Brüker Avance 500 or 600 spectrometer at 25 °C. Chemical shifts were reported in parts per million (ppm) downfield from the Me_4Si resonance which was used as the internal standard when recording ^1H NMR spectra. The addition of K_2CO_3 in the NMR experiments of the [2]rotaxane is to destroy the strong hydrogen bonds between α-cyclodextrin and stoppers, making the movement of α-cyclodextrin doable.[S4] High-resolution matrix-assisted laser desorption/ionization spectra (HR-MALDI) were measured on an AppliedBiosystems DE-STR MALDI time-of-flight mass spectrometer. The reported molecular mass (*m*/*z*) values were the most abundant monoisotopic mass. Electrochemical experiments were carried out at room temperature in argon-purged aqueous solutions, with a Princeton Applied Research 263A Multipurpose instrument interfaced to a PC. Cyclic voltammetry experiments were performed using a glassy carbon working electrode (0.018 cm^2, Cypress Systems). Its surface was polished routinely with 0.05 μm alumina-water slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was a standard calomel electrode (SCE). The concentration of the sample and

supporting electrolyte (lithium perchlorate ($LiClO_4$)) were ca. 1.0×10^{-3} and 0.1 mol L^{-1}, respectively. UV/Vis spectra were recorded at room temperature on a Varian 100 Bio instrument. Circular dichroism (CD) spectra were recorded on a Jasco J-715 Spectropolarimeter at 25 °C. The microcalorimetric titrations were performed by an isothermal titration microcalorimeter (MicroCal Inc., Model No.: VP-ITC) at the atmospheric pressure and 25 °C in potassium carbonate-potassium borate-potassium hydroxide buffer solution (pH 10). In each run, a buffer solution of α-cyclodextrin host in a 0.250 mL syringe was sequentially injected with stirring at 300 rpm into a buffer solution of guest in the sample cell (1.4 mL volume). A control experiment was performed to determine the heat of dilution by injecting a host buffer solution into a pure buffer solution, containing no guest. The dilution enthalpy was subtracted from the apparent enthalpy obtained in each titration run, and the net reaction enthalpy was analyzed by using a single-site binding model. The Origin software (MicroCal) was used to simultaneously determine the binding constant (K_a) and reaction enthalpy (ΔH^0) with the standard derivation on the basis of the scatter of data points from a single titration experiment. Three independent titration experiments were performed to afford self-consistent parameters and give the averaged values.

S4: A solution of **S1** (0.59 g, 1.00 mmol), **S3** (0.21 g, 1.00 mmol), K_2CO_3 (1.00 g, 7.24 mmol), LiBr (10.0 mg, 0.12 mmol), and [18]crown-6 (10.0 mg, 0.04 mmol) in anhydrous MeCN (50 mL) was heated under reflux and an atmosphere of argon for 16 h. After cooling, the reaction mixture was filtered and the solid was washed with Me_2CO. The combined filtrates were concentrated, and the residue was purified by column chromatography (SiO_2: CH_2Cl_2 / EtOH 99:1) to give compound **S4** (0.41 g, 65%) as a yellow oil. ^1H NMR (500 MHz, CD_2Cl_2, 25 °C, TMS): δ 3.58–3.72 (m, 14H, OCH_2), 3.98 (s, 6H, CO_2Me), 4.13–4.15 (m, 2H, Ar-OCH_2), 4.29 (s, 4H,

TTF-CH_2), 6.28–6.29 (d, 2H, TTF-H), 7.87 (s, 2H, Ar-H), 8.32 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C): δ 52.3, 62.1, 70.1, 71.2, 79.3, 117.5, 118.6, 121.5, 127.6, 131.1, 138.4, 158.3, 166.6. MS (HR-MALDI): Calcd for $C_{26}H_{32}O_{10}S_4$ *m*/*z* = 632.0878, found *m*/*z* = 632.0821.

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