Title: [3]Rotaxane synthesized via covalent bond formation can recognize cations forming a sandwich structure
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Content
Fluorescence spectra of 3 with cesium ion.
Synthesis of bridged Crownophane 2: To 25 ml of THF solution of crownophane 1 (300 mg, 0.52 mmol), potassium t-butoxide (64 mg, 0.57 mmol) was added and stirred for 5 h at room temperature. The solution became turbid gradually. After 50 ml of THF were added to it, 1,3-diphenylenediacetic acid dichloride (60 mg, 0.26 mmol) was then added to make the mixture clear at once. The solution was stirred overnight at room temperature. After the solvent was removed by evaporation, the residue was extracted with chloroform and the chloroform layer was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed and the residue was subjected to a preparative GPC with chloroform as an eluent to give 0.12 g of bridged crownophane 2 together with the reactant (1).

**Compound 2**: yield 35.1 %; 1H NMR (500.1 MHz, CDCl₃, ppm): 3.47- 4.29 (40H, -O-CH₂CH₂-O-), 3.82, 3.94 (8H, ArCH₂C=CH₂), 4.48, 4.58 (4H, H₂C=C), 3.73, 3.81 (4H, Ar-CH₂-CO), 7.09 - 7.85 (26H, Ar-H and OH).
IR (KBr, cm⁻¹): 3448, 2922, 1760, 1626, 1118, 743.
ESI mass (CH₃CN): calcd for C₇₈H₈₂O₁₈ 1307.47, found 1329.8 (+Na⁺).

Synthesis of [3]rotaxane 3 via covalent bond formation: To the solution of 120 mg (0.09 mmol) of 2 in 5 ml of dimethylformamide(DMF), 95 mg (0.46 mmol) of 9-aminomethylanthracene was added. Then the solution was stirred at room temperature for 5 days. After DMF was evaporated under vacuum by Kugelrohr apparatus, the residue was subjected to a preparative GPC with chloroform as an eluent to give [3]rotaxane 3 and [2]rotaxane 4.

**Compound 3**: yield 20.3 %; 1H NMR (500.1 MHz, CD₂Cl₂:CD₃CN=9:1, ppm): Assignments were performed by several two dimensional NMR techniques such as DQF-COSY, NOESY, HMQC, and HMBC. 2.39, 2.79, 2.87, 3.12, 3.41, 3.48, 3.83, 4.01, 4.15 (40H, -O-CH₂CH₂-O-), 3.69 (4H, Ar-CH₂-CO), 3.91, 3.98 (8H, ArCH₂C=CH₂), 3.93 (4H, H₂C=C), 5.13 (4H, Ar-CH₂-NH), 6.91, 7.10, 7.24, 7.29, 7.31, 7.34, 7.50, 7.61, 7.86, 7.87, 8.27, 8.30 (42H, Ar-H). 7.58 (2H, NH), 8.59 (4H, OH)
IR (KBr, cm⁻¹): 3393, 2924, 1647, 1524, 1110, 739.
Compound 4: yield 25.9 %; ¹H NMR (500.1 MHz, CD₂Cl₂:CD₃CN=9:1, ppm): Assignments were performed by several two dimensional NMR techniques such as DQF-COSY, NOESY, HMQC, and HMBC. 2.69, 2.81, 3.05, 3.10, 3.44 (20H, -O-CH₂CH₂-O-), 3.27 (4H, ArCH₂-CO), 3.79 (4H, ArCH₂C=CH₂), 3.91 (2H, H₂C=C), 5.24 (4H, ArCH₂-NH), 6.43, 6.80, 6.92, 7.23, 7.24, 7.30, 7.44, 7.50, 7.53, 7.90, 8.03, 8.27, 8.46 (32H, Ar-H), 7.10 (2H, NH), 8.12 (2H, OH).

IR (KBr, Cm⁻¹): 3418, 2922, 1647, 1114, 737.

ESI mass (CH₃CN): calcd for C₁₈₂H₁₈₀N₂O₉ 3418.72, found 3441.6 (+Na⁺).
Figure 1  Fluorescence spectra of 3 (2.2 X 10^{-6} M) in CH$_2$Cl$_2$/CH$_3$CN (9:1) with cesium ion; excitation wavelength = 285 nm.