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# Preparation and Properties of Rotaxanes Formed by Dimethyl-β-cyclodextrin and Oligo(thiophene)s with β-Cyclodextrin Stoppers

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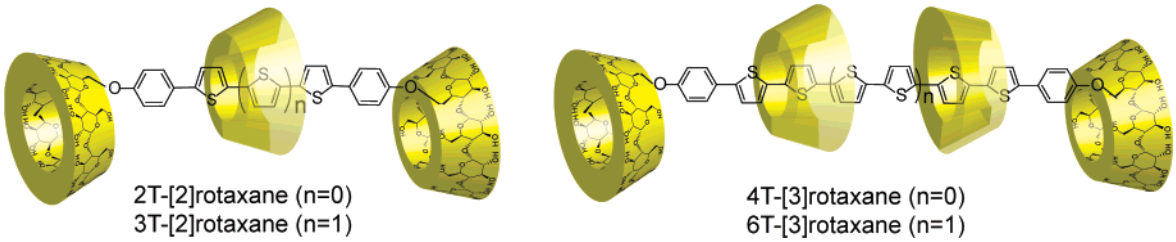


Novel cyclodextrin rotaxanes with oligothiophene as an axis molecule have been prepared by the Suzuki coupling reaction of 6-*O*-(4-iodophenyl)-β-CD (6-I-Ph-β-CD) with di(1,3,2-dioxaborolan-2-yl)-oligothiophene (oligothiophene diboric ethylene glycol esters) in aqueous solutions of dimethyl-β-cyclodextrin (DM-β-CD). These reactions gave [2]rotaxanes and [3]rotaxanes, which were isolated by reversed phase chromatography. The fluorescence intensities of rotaxanes are higher than those of dumbbell-shaped molecules (without DM-β-CD) in aqueous solutions. The inclusion ratio and chain length of rotaxanes have been found to relate to the emission properties and emission intensities of oligothiophene. In aqueous solutions, fluorescence quantum yields of rotaxanes are higher than those of dumbbell-shaped molecules. The increase in the fluorescence efficiency of rotaxane is caused by suppression of intermolecular interactions, indicating the effect of insulated oligothiophene with DM-β-CD. β-CD at the both ends of rotaxanes functions not only as bulky stoppers but also as the recognition site for guest molecules, as verified by fluorescence quenching experiments.

## Introduction

Poly(thiophene)s (PTs) and oligo(thiophene)s have attracted widespread interest due to their applications as single-molecule electronics devices and light-emitting diodes,[1] whereas mechanically interlocked molecules, rotaxanes and catenanes, are expected to become the prototype for the design and construction of controllable molecular switches and actuators.[2] Previously, we prepared cyclodextrin (CD)-based poly(rotaxane)s by capping ends of CDs−polymer complex with covalently bound stoppers.[3] Recently, conjugated poly(rotaxane)s, in which the conjugated polymer backbone is covered at the molecular level by wrapping macrocyclic molecules, such as cyclophanes,[4] CDs,[5,6] and zeolites,[7] have been studied as insulated molecular

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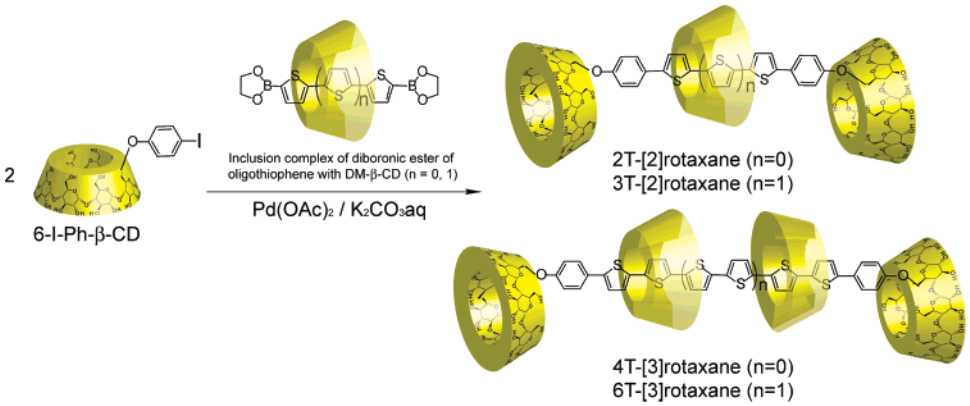
**SCHEME 1. Preparation of DM-β-CD-Oligothiophene-Based Rotaxanes with the End Stopper of β-CDs**




wires by many research groups. We also reported the formation and crystal structure of the β-cyclodextrin (β-CD)−bithiophene inclusion complex and polymerization of the corresponding inclusion complexes in a selective way to give *pseudo*-poly(rotaxane)s.[8] Although a few poly(rotaxane)s containing π-conjugated polymer have been reported, discussion on the use of monodisperse poly(rotaxane)s has not been reported yet.[9] Here we prepare 2,6-dimethyl-β-cyclodextrin (DM-β-CD)-based poly(rotaxane)s using oligothiophene as an axis molecule and isolated rotaxanes having various contents of DM-β-CD and oligothiophene. These poly(rotaxane)s have β-CD as bulky stoppers at the end of oligothiophene axis molecules to prevent DM-β-CD from slipping off the axis molecules. We investigated the fluorescence of these poly(rotaxane)s with different polymer chain lengths and CD coverages.

## Results and Discussion

**Preparation of Rotaxanes with Oligothiophenes.** Bithiophene-[2]rotaxane (2T-[2]rotaxane) and terthiophene-[2]rotaxane (3T-[2]rotaxane) were prepared by the Suzuki coupling reaction of 6-*O*-(4-iodophenyl)-β-CD (6-I-Ph-β-CD) with di(1,3,2-dioxaborolan-2-yl)-oligothiophene **(**oligothiophene diboric ethylene glycol esters) in an aqueous solution of DM-β-CD (Scheme 1). The crude product was found to contain dumbbell-shaped molecules, [2]rotaxanes, and [3]rotaxanes by MALDI-TOF mass spectroscopy. 4T-[3]Rotaxane and 6T-[3]rotaxane were produced at the same time during the preparation of 2T-[2]-rotaxane and 3T-[2]rotaxane, respectively. Dumbbell-shaped molecules, 2T-dumbbell and 3T-dumbbell, were prepared in DMF. These rotaxanes and dumbbell-shaped molecules were purified by preparative reversed phase chromatography.

**NMR Studies of Rotaxanes with Oligothiophene.** Figure 1 shows the $^1$H NMR spectra of 2T-dumbbell, 2T-[2]rotaxane, 3T-dumbbell, and 3T-[2]rotaxane in DMSO-$d_6$. The aromatic protons of dumbbell-shaped molecules showed simple peaks, indicating formation of symmetric structure. However, the aromatic protons of [2]rotaxanes showed splitting and peak shifts, caused by the asymmetric structure included in the DM-β-CD cavity. The ROESY NMR spectra of rotaxanes showed that the peaks of thienylene protons correlated with the inner protons (C(3)-*H* and C(5)-*H*) of DM-β-CD in DMSO-$d_6$ (Figures 2 and S12). *pseudo*-Rotaxane did not show any correlation peaks between inner protons of CDs and the protons of axis molecules because of dethreading in DMSO-$d_6$. These results show formation of [2]rotaxane with interlocked DM-β-CD. The aromatic protons of [3]rotaxanes, 4T-[3]rotaxane and 6T-[3]rotaxane (Figure 1e and f), gave more complicated peaks which can be ascribed to the inclusion complex of two DM-β-CDs with an axis molecule. These [3]rotaxanes have three isomers which have different direction of threading DM-β-CDs or head-to-head, head-to-tail, and tail-to-tail fashioned isomers.

**Absorption and Fluorescence Properties of Dumbbell-Shaped Molecules and Rotaxanes.** The absorption and fluorescence spectra of dumbbell-shaped molecules and rotaxanes were measured in aqueous solutions at 15 μM (Figure 3). The absorption spectra of [2]rotaxanes showed higher absorption than those of dumbbell-shaped molecules. The fluorescence intensities of [2]rotaxanes in aqueous solutions are stronger than those of dumbbell-shaped molecules. The intensities of [2]rotaxane and dumbbell-shaped molecule of 3T as an axis molecule showed greater difference than that of 2T. The fluorescence intensities of dumbbell-shaped molecules and [2]rotaxanes were comparable in methanol (Figure S13). It was suggested that in comparison to dumbbell-shaped molecules, the greater absorption and fluorescence intensities of rotaxanes in aqueous solutions were due to suppression of the intermolecular interactions of oligothiophenes by insulation of oligothiophene with DM-β-CD.

Figure 4 shows the absorption and fluorescence spectra of rotaxanes with various lengths of thiophenes. The absorption maximum wavelength ($\lambda_{max}$) and fluorescence maximum wavelength shifted to a longer wavelength with an increase in the conjugation length ($\lambda_{max}$ = 378 (2T), 407 (3T), 438 (4T), and 449 nm (6T); fluorescence maxima = 423 (2T), 481 (3T), 500 (4T), and 539 nm (6T)). Table 1 shows the quantum yields of

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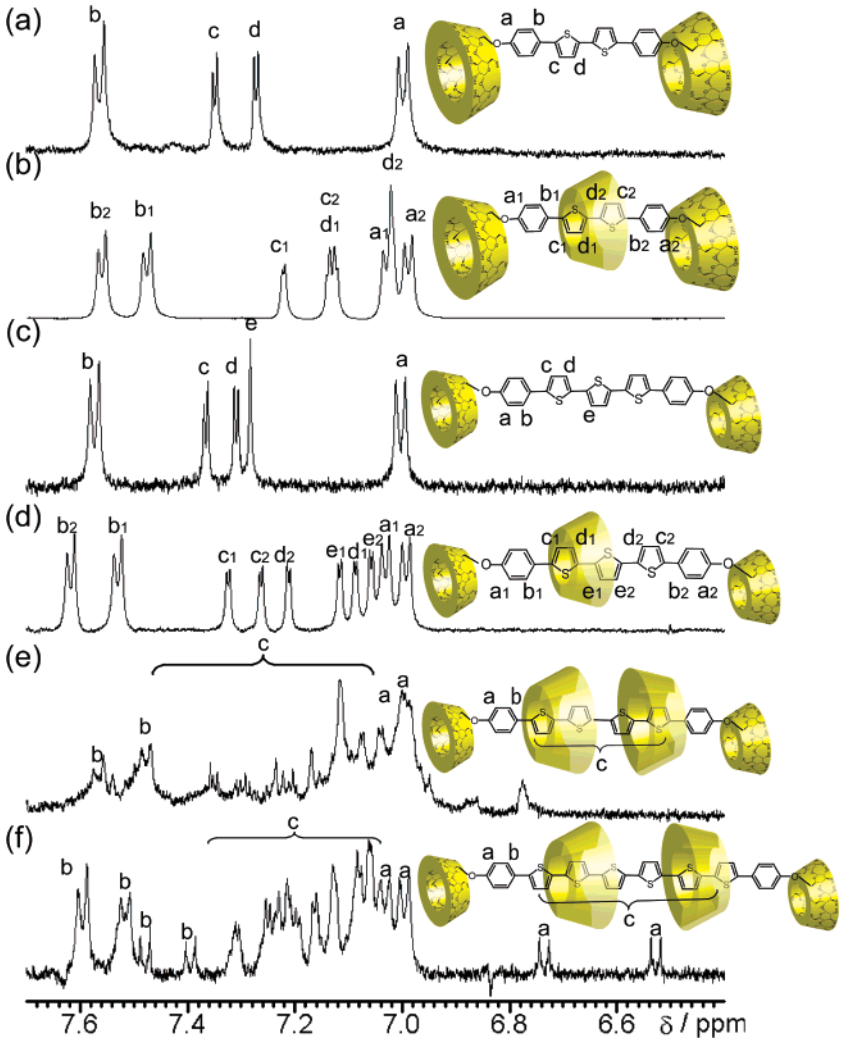


**FIGURE 1.** $^1$H NMR spectra of (a) 2T-dumbbell, (b) 2T-[2]rotaxane, (c) 3T-dumbbell, (d) 3T-[2]rotaxane, (e) 4T-[3]rotaxane, and (f) 6T-[3]-rotaxane in DMSO-$d_6$ at 30 °C.

rotaxanes and dumbbell-shaped molecules in aqueous solutions calculated using 0.1 N $H_2SO_4$ solution of quinine sulfate as a standard.[10] The inclusion ratios of DM-$\beta$-CD were calculated from the space-filling models. The quantum yields of rotaxanes increased with an increase in the inclusion ratio of DM-$\beta$-CD. The absorption and fluorescence spectra of phenyl end-capped $\beta$-nonsubstituted oligothiophene (T, 2T, 3T, 4T)[11] (in $CH_2Cl_2$) are similar in shape to the spectra of the series of rotaxanes in aqueous solutions. The spectrum of phenyl end-capped 6T could not be measured because of the poor solubility of this compound.[12] Cyclophane end-capped 6T[13] was reported as the only example of spectroscopic measurement of phenyl end-capped $\beta$-nonsubstituted 6T derivative. 6T-[3]Rotaxane was dissolved in an aqueous solution as well as in an organic solvent like methanol. It was the first example of a water-soluble long oligothiophene rotaxane.

**Fluorescence Quenching Using TNBS.** The recognition ability of $\beta$-CD in the rotaxanes was investigated by fluorescence

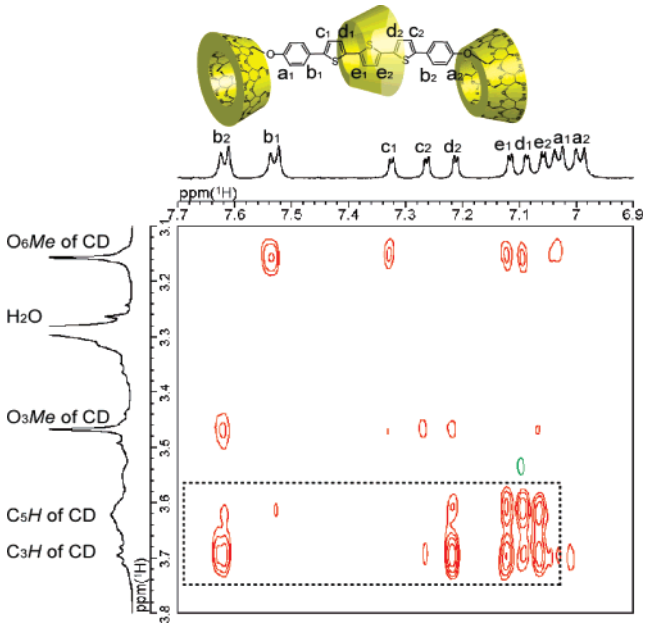


**FIGURE 2.** 2D ROESY NMR spectrum of 3T-[2]rotaxane in DMSO-$d_6$.

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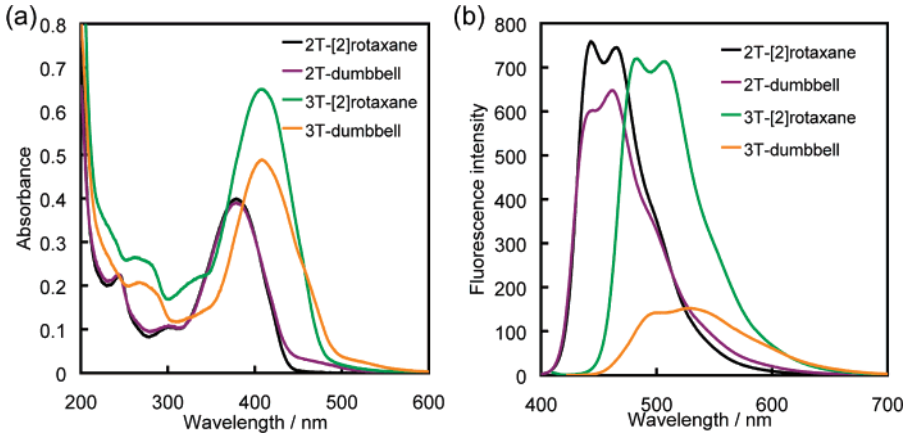



**FIGURE 3.** Absorption (a) and fluorescence (b) spectra of dumbbell-shaped molecules and rotaxanes in 15 $\mu$M aqueous solution ($\lambda_{ex}$ = 378 nm for 2T and 407 nm for 3T).

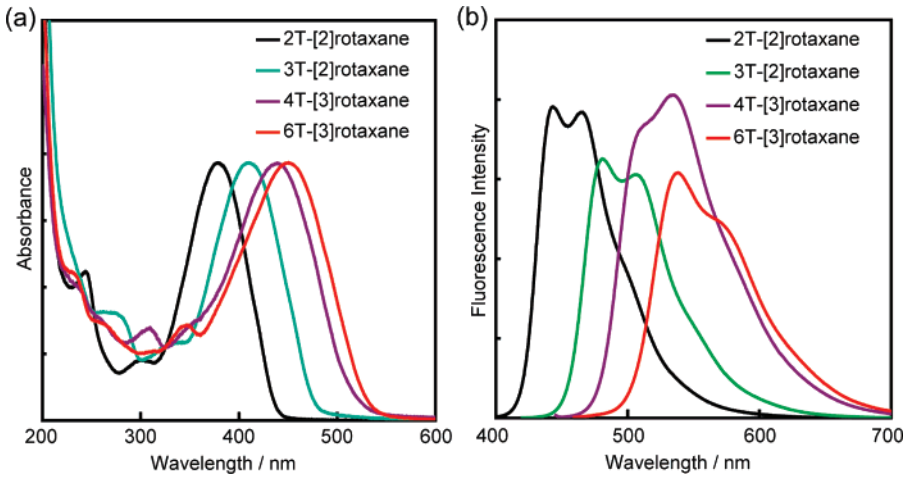



**FIGURE 4.** Absorption (a) and fluorescence (b) spectra of rotaxanes with various conjugation lengths ($\lambda_{max}$ = 378 nm for 2T, 407 nm for 3T, 438 nm for 4T, 449 nm for 6T).

**TABLE 1. Quantum Yields of Rotaxanes and Dumbbell-Shaped Molecules and Inclusion Ratio of Rotaxanes**

| | 2T-[2]rotaxane | 3T-[2]rotaxane | 4T-[3]rotaxane | 6T-[3]rotaxane | 2T-dumbbell | 3T-dumbbell |
|---|---|---|---|---|---|---|
| $\Phi_{H2O}$[a] | 0.21 | 0.15 | 0.24 | 0.17 | 0.15 | 0.06 |
| inclusion ratio/%[b] | 63 | 50 | 83 | 61 | | |

[a] Calculated using 0.1 N $H_2SO_4$ solution of quinine sulfate as a standard. [b] Calculated from 3D models.

quenching measurements. We chose 2,4,6-trinitrobenzene sulfonic acid sodium salt (TNBS Na) as a quencher because TNBS Na could be included in the $\beta$-CD cavity.[14] The $^1$H NMR spectra of the mixture of rotaxane and TNBS Na showed that the aromatic protons of TNBS Na shifted upfield, indicating formation of the inclusion complex between $\beta$-CD and TNBS Na (Figure S14). Figure 5 shows the Stern−Volmer plots for the fluorescence quenching of 2T-[2]rotaxane with TNBS Na. Fluorescence intensity dependence on quencher concentration is given by the Stern−Volmer equation (eq 1)

$$I_0/I = 1 + k_{sv}[Q] \quad (1)$$

where [Q] is the quencher concentration, $I_0$ and $I$ are the fluorescence intensities in the absence and presence of a quencher, respectively, and $k_{sv}$ is the Stern−Volmer constant.

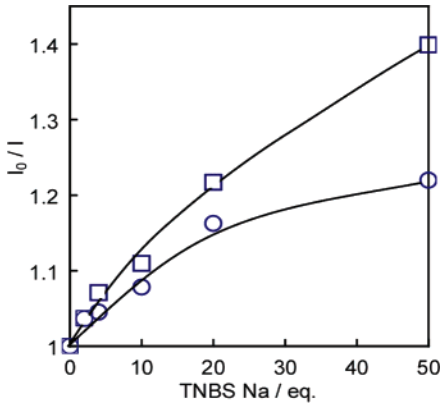



**FIGURE 5.** Stern−Volmer plots for the fluorescence quenching of 2T-[2]rotaxane with TNBS Na in the absence of AdCA (□) and presence of excess (50 equiv) AdCA (○) (in $H_2O$, 15 $\mu$M).

(14) Miyauchi, M.; Hoshino, T.; Yamaguchi, H.; Kamitori, S.; Harada, A. *J. Am. Chem. Soc.* **2005**, *127*, 2034−2035.

Upon addition of TNBS Na to the solution of 2T-[2]rotaxane, fluorescence intensities decreased with an increase in the concentration of TNBS Na. When 50 equiv of adamantane carboxylic acid (AdCA) per $\beta$-CD moiety, which is strongly bound to the $\beta$-CD cavity,[15] was added to the solution of rotaxanes with TNBS Na, the fluorescence quenching of the mixture of 2T-[2]rotaxane, TNBS Na, and AdCA was suppressed as compared with that of the mixture of 2T-[2]rotaxane and TNBS Na. Suppression of the fluorescence quenching in the mixture of 2T-[2]rotaxane, TNBS Na, and AdCA is caused by formation of the inclusion complex between $\beta$-CD and AdCA.

## Conclusion

A series of novel DM-$\beta$-CD-oligothiophene-based rotaxanes has been prepared by the palladium-catalyzed coupling reaction. [2]Rotaxanes and [3]rotaxanes which have various chain lengths and inclusion ratios of DM-$\beta$-CD were isolated from the crude products using preparative reversed phase chromatography. Their photochemical properties have been investigated by UV−vis and fluorescence measurements. The inclusion ratio and chain length of rotaxanes have been found to relate to the emission properties and emission intensities of oligothiophene. In aqueous solutions, fluorescence quantum yields of rotaxanes were higher than those of dumbbell-shaped molecules. The increase in the fluorescence efficiency of rotaxane is caused by suppression of intermolecular interactions, indicating the effect of insulated oligothiophene with DM-$\beta$-CD. We studied the ability of $\beta$-CD stoppers of the rotaxanes with TNBS Na to form inclusion complexes by the fluorescence quenching experiment. Quenching by the inclusion complex formation of 2T-[2]rotaxane with TNBS Na was observed. Now, we are investigating the preparation of supramolecular polymers using the CD-oligothiophene rotaxanes as ditopic host molecules. The supramolecular polymers will cause an increase in the conjugation length. Application of the supramolecular polymers as extended molecular wires is expected.

## Experimental Section

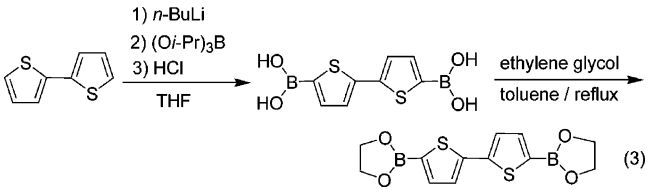
**Preparation of 6-*O*-(4-Iodophenyl)-$\beta$-cyclodextrin (eq 2).** A

(2)

solution of potassium carbonate (10.0 g, 72.4 mmol) and 4-iodophenol (10.0 g, 45.5 mmol) in 40 mL of DMF was stirred at room temperature. After 2 h, 6-*O*-toluenesulfonyl-$\beta$-CD (9.77 g, 7.89 mmol) in 40 mL of DMF was added to the reaction mixture and stirred for 24 h at 80 °C. After the prescribed time, the reaction mixture was neutralized by 250 mL of 1 N HCl. Ethyl acetate (250 mL) was added to the reaction mixture. White powder was collected by filtration. The crude product was recrystallized with hot water to give 6-*O*-(4-iodophenyl)-$\beta$-cyclodextrin in a yield of 44.9% (4.59 g).

$^1$H NMR (500 MHz, in DMSO-$d_6$, 30 °C) $\delta$ 7.55 (d, 2H, $C_2H$ of Ph, $J$ = 9.0 Hz), 6.79 (d, 2H, $C_3H$ of Ph, $J$ = 9.0 Hz), 5.76−5.62 (m, 14H, $O_{2,3}H$ of $\beta$-CD), 4.87 (d, 1H, phenyl-substituted $C_1H$ of glucopyranose, $J$ = 3.2 Hz), 4.78−4.75 (m, 6H, $C_1H$ of $\beta$-CD), 4.45−4.34 (m, 5H, $O_6H$ of $\beta$-CD), 4.32−3.90 (m, 4H, phenyl-substituted $C_{3,4,5,6}H$ of glucopyranose), 3.74−3.47 (m, $C_{3,4,5,6}H$ of $\beta$-CD). $^{13}$C NMR (125 MHz, in DMSO-$d_6$, 30 °C) $\delta$ 158.4 ($C_1$ of Ph), 137.8 ($C_2$ of Ph), 117.4 ($C_3$ of Ph), 102.0 ($C_1$ of $\beta$-CD), 83.1 ($C_4$ of Ph), 81.6 ($C_4$ of $\beta$-CD), 73.1 ($C_6$ of $\beta$-CD), 72.5 ($C_2$ of $\beta$-CD), 72.0 ($C_5$ of $\beta$-CD), 60.0 ($C_3$ of $\beta$-CD). MALDI-TOF MS (matrix: DHBA) $[M + K]^+$ = 1376.0 (calcd 1376.1). Anal. Calcd for $(C_{48}H_{73}O_{35}I)(H_2O)_3$: C, 41.45; H, 5.72. Found: C, 41.37; H, 5.64.

**Preparation of 5,5′-Di-(1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene (2T Diboric Ethylene Glycol Ester)[16] (eq 3).** At −78 °C,

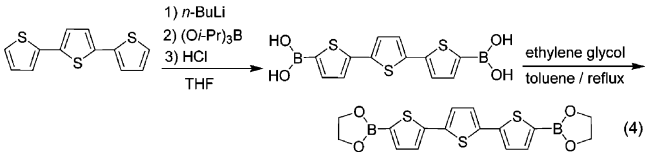


(3)

*n*-butyllithium (*n*-hexane solution, 20.4 mL, 49.9 mmol) was added dropwise to 2,2′-bithiophene (3.62 g, 21.8 mmol) in 50 mL of THF. The reaction mixture was stirred for 1 h at −78 °C and allowed to stir for 2 h at room temperature. After the prescribed time, tri-*O*-isopropyl borate (20.5 g, 109 mmol) in 20 mL of THF was added to the reaction mixture quickly via cannula and stirred for 1 h at −78 °C. After additional stirring for 12 h, the reaction mixture was neutralized with 150 mL of 2 N HCl. After separation of the aqueous phase, the aqueous phase was washed twice with diethyl ether. The combined organic phase was evaporated and dissolved in 100 mL of toluene. Ethylene glycol (20 mL) was added to the solution, and the mixture was stirred overnight at 80 °C. The organic phase was evaporated, and the residue was recrystallized with hot toluene to give 2T diboric ethylene glycol ester as green crystalline solid in a yield of 53.0% (3.60 g).

$^1$H NMR (500 M Hz, in $CDCl_3$, 30 °C) $\delta$ 7.53 (d, 2H, $C_{4,4'}H$, $J$ = 3.6 Hz), 7.53 (d, 2H, $C_{3,3'}H$, $J$ = 3.6 Hz), 4.37 (s, 8H, $-CH_2-$). MALDI-TOF MS (nonmatrix) $[M + H]^+$ = 306.9 (calcd 307.0). Anal. Calcd for $C_{12}H_{12}B_2O_4S_2$: C, 47.10; H, 3.95. Found: C, 47.29; H, 3.85.

**Preparation of 5,5″-Di-(1,3,2-dioxaborolan-2-yl)-2,2′-5,2″-terthiophene (3T Diboric Ethylene Glycol Ester) (eq 4).** 3T



(4)

diboroic ethylene glycol ester was prepared in a manner similar to 2T diboroic ethylene glycol ester using 2,2′-5,2″-terthiophene (2.00 g, 8.05 mmol), *n*-butyllithium (*n*-hexane solution, 7.56 mL, 18.4 mmol), tri-*O*-isopropyl borate (7.57 g, 40.3 mmol), and ethylene glycol (25 mL). 3T diboric ethylene glycol ester was obtained as a yellowish green crystalline solid in a yield of 34.0% (1.06 g). mp 190−191 °C.

$^1$H NMR (500 MHz, in $CDCl_3$, 30 °C) $\delta$ 7.53 (d, 2H, $C_{4,4''}H$, $J$ = 3.6 Hz), 7.53 (d, 2H, $C_{3,3''}H$, $J$ = 3.6 Hz), 7.15 (s, 2H, $C_{3',4'}H$), 4.35 (s, 8H, $-CH_2-$). MALDI-TOF MS (nonmatrix) $[M + H]^+$ = 390.0 (calcd 389.0). Anal. Calcd for $C_{16}H_{14}B_2O_4S_3$: C, 49.52; H, 3.64. Found; C, 49.40; H, 3.52.

**Preparation of Dumbbell-Shaped Molecules (eq 5). (a) 2T-Dumbbell Molecule ($n$ = 0).** Palladium acetate (8.40 mg, 0.0374 mmol), potassium carbonate (138 mg, 1.12 mmol), and 6-*O*-(4-

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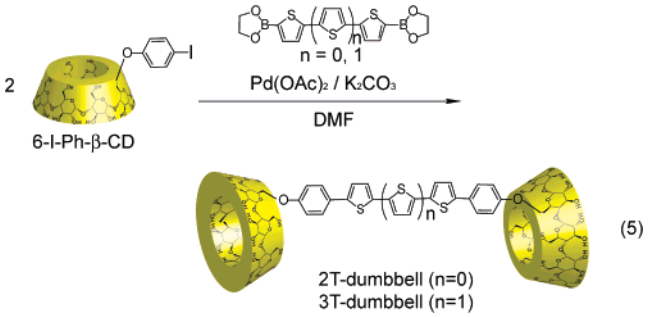


(5)

iodophenyl)-*β*-cyclodextrin (500 mg, 0.374 mmol) dissolved in 20 mL of DMF were stirred for 2 h. 2T diboric ethylene glycol ester (57.2 mg, 0.187 mmol) in 10 mL of DMF was added dropwise to the reaction mixture and stirred for 24 h at 80 °C. After neutralization by 1 N HCl, the reaction mixture was centrifuged (3500 rpm, 10 min) and the supernatant evaporated to give the crude product. The crude product was purified by HPLC (eluent; water: acetonitrile) to give 2T-dumbbell molecule in a yield of 10.6% (51.6 mg).

$^1$H NMR (500 MHz, 30 °C, in DMSO-$d_6$) $\delta$ 7.56 (d, 4H, Ph on thienylene side, $J$ = 8.5 Hz), 7.35 (d, 2H, C$_4$*H* of thienylene, $J$ = 3.8 Hz), 7.27 (d, 2H, C$_3$*H* of thienylene, $J$ = 3.7 Hz), 7.00 (d, 4H, Ph on ether side, $J$ = 9.0 Hz), 5.78−5.60 (m, 28H, O$_{2,3}$*H* of *β*-CD), 4.96−4.82 (m, 14H, C$_1$*H* of *β*-CD), 4.50−3.90 (m, 6H, phenyl substituted glucopyranose of *β*-CD), 3.75−3.50 (m, C$_{3,4,5,6}$*H* of *β*-CD). MALDI-TOF MS (matrix: DHBA) $[M + K]^+$ = 2625.6 (calcd 2623.8). Anal. Calcd for $(C_{104}H_{150}O_{70}S_2)(H_2O)_{18}$: C, 42.95; H, 6.45. Found: C, 42.92; H, 6.27.

**(b) 3T-Dumbbell Molecule (*n* = 1).** 3T-Dumbbell molecule was prepared in the a manner similar to 2T-dumbbell molecules using 3T diboric ethylene glycol ester (72.5 mg, 0.187 mmol), after purification by HPLC (eluent; water:acetonitrile) to give 3T-dumbbell molecule in a yield of 20.1% (100.2 mg).

$^1$H NMR (500 MHz, in DMSO-$d_6$,30 °C) $\delta$ 7.57 (d, 4H, Ph on thienylene side, $J$ = 8.6 Hz), 7.37 (d, 2H, C$_{4,4''}$*H* of thienylene, $J$ = 3.9 Hz), 7.31 (d, 2H, C$_{3,3''}$*H* of thienylene, $J$ = 3.7 Hz), 7.28 (s, 2H, C$_{3',4'}$*H* of thienylene), 7.00 (d, 4H, Ph on ether side, $J$ = 9.0 Hz), 5.74−5.63 (m, 28H, O$_{2,3}$*H* of *β*-CD), 4.92−4.79 (m, 14H, C$_1$*H* of *β*-CD), 4.46−3.94 (m, 6H, phenyl substituted glucopyranose unit of *β*-CD), 3.78−3.52 (m, C$_{3,4,5,6}$*H* of *β*-CD). MALDI-TOF MS (matrix: DHBA) $[M + Na]^+$ = 2688.5 (calcd 2689.5). Anal. Calcd for $(C_{108}H_{152}O_{70}S_3)(H_2O)_{16}$: C, 43.90; H, 6.28. Found: C, 43.83; H, 6.06.

**Preparation of 2T-[2]Rotaxane and 4T-[3]Rotaxane.** Palladium acetate (8.40 mg, 0.0374 mmol), potassium carbonate (138 mg, 1.12 mmol), and 6-*O*-(4-iodophenyl)-*β*-cyclodextrin (500 mg, 0.374 mmol) dissolved in 50 mL of water were stirred for 2 h. An aqueous solution (5 mL) of the inclusion complex between 2T diboric ethylene glycol ester (57.2 mg, 0.187 mmol) and DM-*β*-CD (996 mg, 0.748 mmol) was added dropwise to the reaction mixture. The reaction mixture was allowed to stir for 24 h at room temperature. After neutralization by 1 N HCl, the reaction mixture was centrifuged (3500 rpm, 10 min) and the supernatant solution evaporated to give the crude product. The crude product was purified by HPLC (eluent; water:acetonitrile) to give 2T-[2]rotaxane and 4T-[3]rotaxane in a yield of 22.7% (166.9 mg) and 3.0% (15.2 mg), respectively.

**(a) 2T-[2]Rotaxane.** $^1$H NMR (500 MHz, in DMSO-$d_6$, 30 °C) $\delta$ 7.55 (d, 2H, phenyl proton next to thienylene ring at CD second rim, $J$ = 6.9 Hz), 7.48 (d, 2H, phenyl proton next to thienylene ring at CD first rim, $J$ = 6.6 Hz), 7.22 (d, 1H, C$_4$*H* of thienylene at CD first rim, $J$ = 3.0 Hz), 7.14 (m, 1H, C$_{4'}$*H* of thienylene at CD second rim), 7.12 (m, 1H, C$_3$*H* of thienylene at CD first rim), 7.03 (d, 2H, phenyl proton next to ether bond at CD first rim, $J$ = 7.1 Hz), 7.02 (m, 1H, C$_{3'}$*H* of thienylene at CD second rim), 6.99 (d, 2H, phenyl proton next to ether bond at CD second rim, $J$ = 7.1 Hz), 5.68 (m, 28H, O$_{2,3}$*H* of *β*-CD), 4.92 (d, 7H, C$_1$*H* of DM-*β*-CD, $J$ = 2.1 Hz), 4.88 (s, 7H, O$_3$*H* of DM-*β*-CD), 4.82 (d, 14H, C$_1$*H* of *β*-CD, $J$ = 3.0 Hz), 4.42 (m, 14H, O$_6$*H* of *β*-CD), 4.42−4.13 (m, 8H, C$_{3',4',5',6'}$*H* of *β*-CD), 3.96 (bs, 2H, C$_{2'}$*H* of *β*-CD), 3.8−3.5 (m, C$_{3,4,5,6}$*H* of CDs), 3.47 (s, 21H, O$_2$Me of DM-*β*-CD), 3.15 (s, 21H, O$_6$Me of DM-*β*-CD). $^{13}$C NMR (125 MHz, in DMSO-$d_6$, 30 °C) $\delta$ 158.5 (*p*-phenyl carbon next to thienylene ring at CD second rim), 158.3 (*p*-phenyl carbon next to thienylene ring at CD first rim), 142.6 ($C_5$ of thienylene at CD first rim), 141.8 ($C_{5'}$ of thienylene at CD second rim), 134.9 ($C_{2'}$ of thienylene at CD second rim), 134.5 ($C_2$ of thienylene at CD first rim), 126.6 (*o*-phenyl carbon thienylene side at CD second rim), 126.1 (*o*-phenyl carbon thienylene side at CD first rim), 126.0 (*p*-phenyl carbon next to ether bond), 123.9 ($C_3$ of thienylene at CD first rim), 123.6 ($C_{3'}$ of thienylene at CD second rim), 122.6 ($C_4$ of thienylene at CD first rim), 122.4 ($C_{4'}$ of thienylene at CD second rim), 115.1 (*m*-phenyl carbon ether bond side at CD first rim), 115.0 (*m*-phenyl carbon ether bond side at CD second rim), 102.3 ($C_{1'}$ of *β*-CD), 101.9 ($C_1$ of *β*-CD), 100.0 ($C_1$ of DM-*β*-CD), 82.6 ($C_4$ of DM-*β*-CD), 81.9 ($C_{4'}$ of *β*-CD), 81.7 ($C_4$ of *β*-CD), 73.0 ($C_3$ of DM-*β*-CD), 72.7 ($C_3$ of *β*-CD), 72.4 ($C_2$ of *β*-CD), 72.0 ($C_5$ of *β*-CD), 70.5 ($C_6$ of DM-*β*-CD), 69.9 ($C_5$ of DM-*β*-CD), 69.7 ($C_{3'}$ of *β*-CD), 59.9 ($C_6$ of *β*-CD), 59.6 (O$_2$Me of DM-*β*-CD), 58.0 (O$_6$Me of DM-*β*-CD). MALDI-TOF MS (matrix: DHBA) $[M + Na]^+$ = 3954.8 (calcd 3955.2). Anal. Calcd for $(C_{160}H_{248}O_{105}S_2)(H_2O)_{19}$: C, 45.13; H, 6.77. Found: C, 45.04; H, 6.70. UV−vis: $\lambda_{max}$ = 378 nm.

**(b) 4T-[3]Rotaxane.** $^1$H NMR (500 MHz, in DMSO-$d_6$, 30 °C) $\delta$ 7.55 (m, 4H, phenyl proton next to thienylene ring), 7.11−7.00 (m, 12H, thienylene proton and phenyl proton next to ether bond), 5.77 (m, 28H, O$_{2,3}$*H* of *β*-CD), 4.96 (m, 14H, C$_1$*H* of DM-*β*-CD), 4.93 (s, 14H, O$_3$*H* of DM-*β*-CD), 4.82 (bs, 14H, C$_1$*H* of *β*-CD), 4.41 (m, 14H, O$_6$*H* of *β*-CD), 4.32−4.10 (m, 8H, C$_{3',4',5',6'}$*H* of *β*-CD), 3.99 (bs, 2H, C$_{2'}$*H* of *β*-CD), 3.8−3.5 (m, C$_{3,4,5,6}$*H* of CDs), 3.48 (s, 42H, O$_2$Me of DM-*β*-CD), 3.13 (m, 42H, O$_6$Me of DM-*β*-CD). MALDI-TOF MS (matrix: DHBA) $[M + Na]^+$ = 5421.9 (calcd 5433.8). Anal. Calcd for $(C_{224}H_{350}O_{140}S_4)(H_2O)_{28}$: C, 45.48; H, 6.92. Found: C, 45.09; H, 6.62. UV−vis: $\lambda_{max}$= 438 nm.

**Preparation of 3T-[2]Rotaxane and 6T-[3]Rotaxane.** 3T-[2]-rotaxane and 6T-[3]rotaxane were synthesized in the same manner as 2T-[2]rotaxane and 4T-[3]rotaxane using 5.00 mL of an aqueous solution of the inclusion complex between 3T diboric ethylene glycol ester (72.5 mg, 0.187 mmol) and DM-*β*-CD (1340 mg, 1.00 mmol). The crude product was purified by HPLC (eluent; water: acetonitrile) to give 3T-[2]rotaxane and 6T-[2]rotaxane in a yield of 23.2% (173.4 mg) and 2.8% (15.1 mg), respectively.

**(a) 3T-[2]Rotaxane.** $^1$H NMR (500 MHz, in DMSO-$d_6$, 30 °C) $\delta$ 7.62 (d, 2H, phenyl proton next to thienylene ring at CD first rim, $J$ = 7.0 Hz), 7.53 (d, 2H, phenyl proton next to thienylene ring at CD second rim, $J$ = 7.0 Hz), 7.32 (d, 1H, C$_{4''}$*H* of thienylene at CD second rim, $J$ = 2.9 Hz), 7.26 (d, 1H, C$_4$*H* of thienylene at CD first rim, $J$ = 2.9 Hz), 7.21 (d, 1H, C$_3$*H* of thienylene at CD first rim, $J$ = 2.9 Hz), 7.12 (d, 1H, C$_{3''}$*H* of thienylene at CD first rim, $J$ = 2.8 Hz), 7.09 (d, 1H, C$_{3'}$*H* of thienylene at CD second rim, $J$ = 2.7 Hz), 7.06 (d, 1H, C$_{4'}$*H* of thienylene at CD second rim, $J$ = 2.9 Hz), 7.03 (d, 2H, phenyl proton next to ether bond at CD second rim, $J$ = 7.2 Hz), 6.99 (d, 2H, phenyl proton next to ether bond at CD first rim, $J$=7.2 Hz), 5.8−5.6 (m, 28H, O$_{2,3}$*H* of *β*-CD), 4.93 (d, 7H, C$_1$*H* of DM-*β*-CD, $J$ = 2.5 Hz), 4.88 (s, 7H, O$_3$*H* of DM-*β*-CD), 4.82 (d, 14H, C$_1$*H* of *β*-CD, $J$ = 3.1 Hz), 4.41 (m, 14H, O$_6$*H* of *β*-CD), 4.32−4.14 (m, 8H, C$_{3',4',5',6'}$*H* of *β*-CD), 3.97 (bs, 2H, C$_{2'}$*H* of *β*-CD), 3.8−3.5 (m, C$_{3,4,5,6}$*H* of CDs), 3.47 (s, 21H, O$_2$Me of DM-*β*-CD), 3.16 (s, 21H, O$_6$Me of DM-*β*-CD). $^{13}$C NMR (125 MHz, in DMSO-$d_6$, 30 °C) $\delta$ 158.4 (*p*-phenyl carbon next to thienylene ring at CD second rim), 158.3 (*p*-phenyl carbon next to thienylene ring at CD first rim), 143.0 ($C_5$ of thienylene at CD first rim), 142.3 ($C_{5''}$ of thienylene at CD second rim), 135.5 ($C_{2'}$ of thienylene at CD first rim), 134.9 ($C_{5'}$ of thienylene at CD second rim), 134.2 ($C_{2''}$ of thienylene at CD second rim), 133.9 ($C_2$ of thienylene at CD first rim), 126.6 (*o*-phenyl carbon thienylene

side at CD second rim), 126.2 (*o*-phenyl carbon thienylene side at CD first rim), 125.9 (*p*-phenyl carbon next to ether bond), 124.7 ($C_3$ of thienylene at CD first rim), 124.3 ($C_{3''}$ of thienylene at CD second rim), 123.6 ($C_{3'}$ of thienylene at CD first rim), 123.4 ($C_{4'}$ of thienylene at CD second rim), 122.9 ($C_{4''}$ of thienylene at CD second rim), 122.8 ($C_4$ of thienylene at CD first rim), 115.1 (*m*-phenyl carbon ether bond side at CD second rim), 115.0 (*m*-phenyl carbon ether bond side at CD first rim), 102.2 ($C_{1'}$ of $\beta$-CD), 101.9 ($C_1$ of $\beta$-CD), 100.0 ($C_1$ of DM-$\beta$-CD), 82.6 ($C_4$ of DM-$\beta$-CD), 81.9 ($C_{4'}$ of $\beta$-CD), 81.6 ($C_4$ of $\beta$-CD), 73.0 ($C_3$ of DM-$\beta$-CD), 72.7 ($C_3$ of $\beta$-CD), 72.4 ($C_2$ of $\beta$-CD), 72.0 ($C_5$ of $\beta$-CD), 70.5 ($C_6$ of DM-$\beta$-CD), 69.9 ($C_5$ of DM-$\beta$-CD), 69.6 ($C_{3'}$ of $\beta$-CD), 59.9 ($C_6$ of $\beta$-CD), 59.5 ($O_2$Me of DM-$\beta$-CD), 58.0 ($O_6$Me of DM-$\beta$-CD). MALDI-TOF MS (matrix: DHBA) $[M + Na]^+ = 4020.9$ (calcd 4020.9). Anal. Calcd for $(C_{164}H_{250}O_{105}S_3)(H_2O)_{21}$: C, 45.01; H, 6.73. Found: C, 44.59; H, 6.29. UV−vis: $\lambda_{max} = 407$ nm.

**(b) 6T-[3]Rotaxane.** $^1$H NMR (500 MHz, in DMSO-$d_6$, 30 °C) $\delta$ 7.60 (d, 3H, Ph, $J = 8.7$ Hz), 7.52 (d, 3H, Ph, $J = 7.8$ Hz), 7.48 (d, 1H, Ph, $J = 8.7$ Hz), 7.40 (d, 1H, Ph, $J = 8.6$ Hz), 7.33−6.97 (m, 30H, thienylene and phenyl protons), 6.74 (d, 1H, Ph, $J = 9.0$ Hz), 6.53 (d, 1H, Ph, $J = 9.0$ Hz), 5.79−5.62 (m, 56H, $O_{2,3}H$ of $\beta$-CD), 4.93 (d, 28H, $C_1H$ of DM-$\beta$-CD, $J = 5.3$ Hz), 4.89 (s, 28H, $O_3H$ of DM-$\beta$-CD), 4.84 (d, 28H, $C_1H$ of $\beta$-CD, $J = 5.3$ Hz), 4.44−4.34 (m, 28H, $O_6H$ of $\beta$-CD), 4.31−4.15 (m, 16H, $C_{3',4',5',6'}H$ of $\beta$-CD), 3.97 (bs, 4H, $C_{2'}H$ of $\beta$-CD), 3.8−3.5 (m, $C_{3,4,5,6}H$ of CDs), 3.47 (s, 84H, $O_2$Me of DM-$\beta$-CD), 3.17 (m, 84H, $O_6$Me of DM-$\beta$-CD). MALDI-TOF MS (matrix: DHBA) $[M + K]^+ = 5614.8$ (calcd 5610.9). Anal. Calcd for $(C_{242}H_{348}O_{146}S_6)(H_2O)_{36}$: C, 45.17; H, 6.58. Found: C, 45.25; H, 6.66. UV−vis: $\lambda_{max} = 449$ nm.

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**Supporting Information Available:** General experimental details, $^1$H and $^{13}$C NMR spectra of compounds, MALDI TOF mass spectra of rotaxanes, 2D ROESY NMR spectrum of 2T-[2]rotaxane, absorption and fluorescence spectra of [2]rotaxanes and dumbbell-shaped molecules, and $^1$H NMR spectrum of mixture of TNBS Na and 2T-[2]rotaxane. This material is available free of charge via the Internet at http://pubs.acs.org.

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