Complex Formation of Cyclodextrins with Various Thiophenes and their Polymerization in Water: Preparation of Poly-*pseudo*-rotaxanes Containing Poly(thiophene)s

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Abstract

Cyclodextrins (α-CD, β-CD and 2,6-di-*O*-dimethyl-β-CD (DM-β-CD)) were found to form inclusion compounds with thiophenes (thiophene (**T**), bithiophene (**2T**)) in water and in crystalline states. The structures of α-CD–**T**, β-CD–**2T**, and DM-β-CD–**2T** inclusion complexes were determined by X-ray crystallography. DM-β-CD forms a 1:1 cage type complex with **2T**. In contrast, β-CD formed 2:3 (CD:guest) complexes with thiophene and α-CD formed 2:3 complexes, both of the channel type. These inclusion complexes were found to polymerize by $FeCl_3$ in the inclusion compounds in water. The products were formed poly-*pseudo*-rotaxane between cyclodextrins and poly(thiophene) characterized by IR, ^{1}H-NMR and ^{13}C CP/MAS NMR. The molecular weights of the poly-*pseudo*-rotaxanes with poly(thiophene) were determined by the MALDI-TOF mass spectra to be 3000–5000. In comparison between poly-*pseudo*-rotaxane (DM-β-CD–poly(thiophene)), authentic poly(thiophene) and the washed DM-β-CD–poly(thiophene) which was washed with DMF to dethread DM-β-CD, these poly-*pseudo*-rotaxane was characterized by Raman, UV–vis and fluorescence spectra. The maximum emission band of DM-β-CD–poly(thiophene) shifted to a shorter wavelength. The hypsochromic shift was derived from poly-*pseudo*-rotaxane with DM-β-CD.

Introduction

The chemistry of rotaxanes has progressed well in accordance with the interest in their unique structures and the expectation to development as the parts of molecular machines and molecular device [1–19]. Previously, we prepared a number of *pseudo*-rotaxane formation between polymer, organic polymer and inorganic polymer, and cyclodextrins [20]. α-Cyclodextrin forms *pseudo*-rotaxane with PEG in an aqueous solution at room temperature, while β-cyclodextrin and γ-cyclodextrin does not form *pseudo*-rotaxane with PEG [20(a)–(h)]. Recently, we reported that β-cyclodextrin and γ-cyclodextrin formed *pseudo*-rotaxane with poly(dimethylsiloxane) and poly(dimethylsilane), a typical inorganic polymer in an aqueous solution [20(p)–(r)].

There are two methods of synthesizing rotaxanes containing CDs in water. One method is to mix the polymer with a saturated solution of cyclodextrins. Another method is that monomers were polymerized *in situ* in the cavity of cyclodextrin. π-Conjugated polymers have disadvantages in inter-chain charge-mobility and the π–π stacking interaction, both of which are essential to completing single-molecule electronic devices. However, when these polymers were the low solubility in water, it is difficult to form rotaxanes [21,22]. We reported the crystal structure of the β-CD–bithiophene inclusion complex and its polymerization using an oxidative initiator to form poly-*pseudo*-rotaxane between β-cyclodextrin and poly(thiophene) in water [23]. Around the same time, Yamamoto and Yamaguchi also reported the preparation and optical properties of β-CD poly-*pseudo*-rotaxane of poly(thiophene) and poly(3-alkylthiophene-2,5-diyl), which were prepared by mixing β-CD saturated solution and poly(thiophene)s [24]. Another group succeeded in preparing poly(ethylenedioxy thiophene) in cyclodextrin aqueous solutions, but poly-*pseudo*-rotaxanes containing poly(ethylenedioxy thiophene) was not obtained by the polymerization reaction [25]. We supposed that cyclodextrins dethread off poly(ethylenedioxy thiophene) because of steric repulsion. In this paper, we describe the synthesis and crystal structure of cyclodextrins inclusion complexes

with various thiophenes, and the polymerization of the corresponding inclusion complexes in a selective way to obtain poly-*pseudo*-rotaxanes. Moreover, optical properties of these poly-*pseudo*-rotaxane with poly(thiophene) were compared with the naked authentic poly(thiophene).

Results and discussion

Complex formation of thiophenes with α-CD, β-CD and Dimethyl-β-CD

The complexes were obtained by the addition of thiophenes to aqueous solutions of CDs at room temperature or 45 °C, and agitating by ultrasound. The solution became turbid and the complexes were formed as crystalline precipitates. α-CD and β-CD formed complexes with thiophene (T) in 42 and 37% yields, respectively. β-CD and DM-β-CD formed complexes with bithiophene (2T) in 31 and 24% yield, respectively, at 45 °C whereas α-CD formed complexes in low yield (1.3%). Although β-CD and DM-β-CD also formed complexes with terthiophene (3T) in 2.4, and 8.9% yields, respectively, α-CD did not form complexes with 2T or 3T. When 2T was added into a dilute DM-β-CD solution, crystalline complexes suitable for X-ray studies were obtained at 40 °C. α-CD also gave powder crystalline complexes with T at room temperature.

Molecular structures of α-CD–T, β-CD–2T and DM-β-CD–2T inclusion complexes by X-ray analysis

Figure 1 shows the results of the X-ray structure of a single crystal of α-CD–T inclusion complex, and the crystal packing is shown in Figure 4. The crystallographic data are listed in Table 1. α-CD formed a 2:3 inclusion complex with T regardless of the molar ratio of the host to the guest charged in the complex formation. One T was located in the cavity on the primary hydroxyl sides of its α-CD. Another two Ts were located at the center of the dimer cavity on the secondary hydroxyl sides. The dimer units of α-CD–T staked each other to form a head-to-head channel-type structure. Thiophenes, located at the rim of the secondary hydroxyl group, are alternately arranged in the channel by π–π stacking. The conformation of α-CD is stabilized by the intramolecular hydrogen-bonds connecting the secondary hydroxyl groups at position 3 with neighboring secondary hydroxyl groups at position 2 with an average distance of 2.868 Å. Supramolecular structures were formed by the three intermolecular hydrogen bonding between O2 secondary hydroxyl groups of the two α-CD with an average intermolecular distance of 2.953 Å, the two intermolecular hydrogen bonds between O3 secondary hydroxyl groups of the two α-CD with an average intermolecular distance of 2.838 Å and the seven intermolecular hydrogen bonds between O2 hydroxyl group and O3 hydroxyl groups of the two α-CD with an average intermolecular distance of

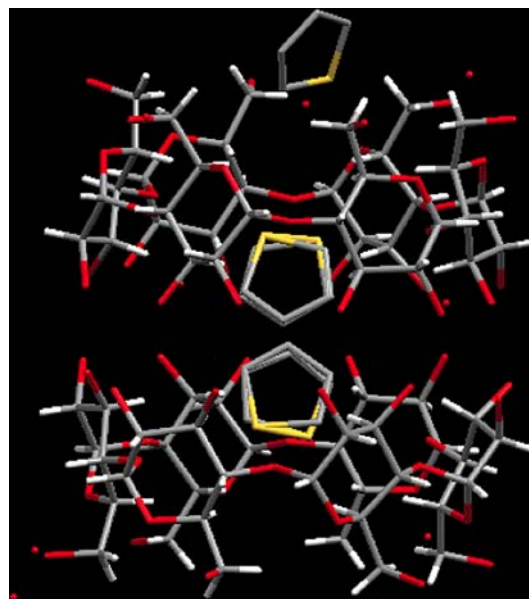*Figure 1*. The crystal structure of the α-CD–thiophene inclusion complex. Carbon and oxygen of α-CD are shown in gray and red respectively. Carbon and sulfur of thiophene are shown in gray and yellow, respectively.

2.770 Å. These structures are similar to those of the CD complexes with the cyclopentadienyl complex [26,27]. There were no intermolecular hydrogen bonds between sulfur of **T** and hydroxyl groups of α-CD.

Figures 2 and 3 show results of the X-ray studies of the single crystals of the β-CD–**2T** and DM-β-CD–**2T** inclusion complexes, respectively. The packing structures are shown in Figures 5 and 6. The crystallographic data are also listed in Table 1. β-CD formed a 2:3 inclusion complex with **2T**, one of which was located at the center of the dimer cavity on the secondary hydroxyl side of the β-CDs, which are aligned vertically with the cavity axis. The crystal structures of β-CD–**2T** classified as a channel type structure. The β-CD–**2T** inclusion complex was

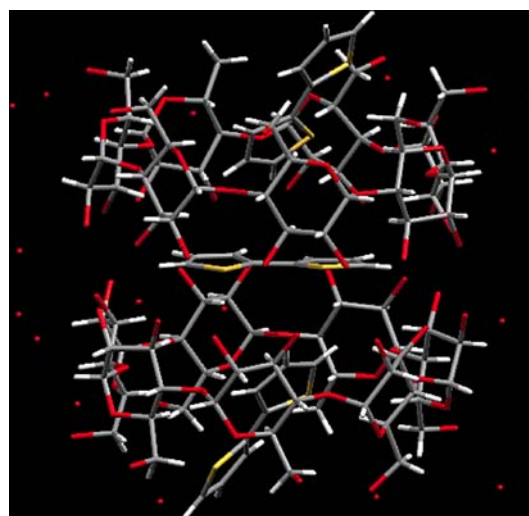*Figure 2*. The crystal structure of the β-CD–bithiophene inclusion complex. Carbon and oxygen of β-CD are shown in gray and red respectively. Carbon and sulfur of bithiophene are shown in gray and yellow, respectively.

Table 1. Crystal data and collection parameters for α-CD–**T**, β-CD–**2T**, DM-β-CD–**2T** inclusion complexes

	α-CD–**T**	β-CD–**2T**	DM-β-CD–**2T**
Formula	$C_{84}H_{84}O_{69}S_3$	$C_{108}H_{116}O_{91}S_6$	$C_{63}H_{103}O_{35}S_{2.6}$
Formula weight	2293.69	3062.43	1509.58
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$(#2)	$P2_1$(#4)	$P2_12_12_1$(#19)
a (Å)	13.728(9)	15.184(12)	11.321(14)
b (Å)	13.788(10)	32.51(2)	14.910(18)
c (Å)	15.598(10)	15.639(10)	45.19(5)
α (°)	91.32(5)	–	–
β (°)	92.88(6)	102.62(7)	–
γ (°)	118.74(5)	–	–
V (Å^3)	2582(3)	7532(9)	7629(16)
Z	1	4	4
D_{calcd} (g/cm^3)	1.475	1.350	1.314
F(000)	1188	3176	3208
μ[MoKα] (cm^{-1})	1.88	17.86	1.84
Temp (K)	150(2)	200(2)	173(2)
$2\theta_{min}$, $2\theta_{max}$ (°)	3.02, 27.49	6.57, 89.74	4.4, 27.32
No. of refl. measured (total)	11,510	16,850	8965
No. of refl. measured (unique)	10,975	9391	3355
No. of variables	1327	1591	931
wR2	0.2160	0.2937	0.2744
R	0.0595($I > 2.0\sigma(I)$)	0.1163($I > 2.0\sigma(I)$)	0.0856($I > 2.0\sigma(I)$)
GOF	0.231	1.589	1.031

reported to form a 1:1 inclusion complex [28]. One of the **2T** guest molecules, which was clipped by β-CDs, was supposed to be stabilized by some hydrogen bonds between the secondary hydroxyl groups of two β-CDs. However, when the crystals of the β-CD–**2T** inclusion complex were washed with diethyl ether, **2T** was released from the dimer cavity by the dissociation of the hydrogen bond. DM-β-CD formed a 1:1 inclusion complex with **2T** and the cage-type category. **2T** is aligned horizontally with the cavity axis. The conformation of DM-β-CD is stabilized by the intramolecular hydrogen-bonds connecting the secondary hydroxyl groups at position 3 with the neighboring methoxyl groups at position 2 with an average distance of 2.88 Å. There is no intermolecular hydrogen bonding between O3n secondary hydroxyl
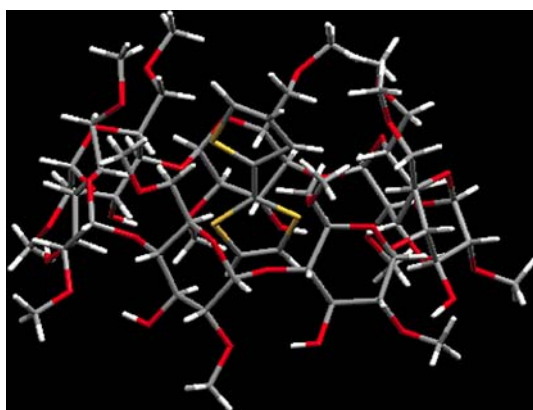
groups of DM-β-CD and between O6n primary hydroxyl groups of DM-β-CD. The β-CD–**2T** inclusion complex and the DM-β-CD–**2T** inclusion complex also did not form intermolecular hydrogen bondings between sulfur of **2T** and hydroxyl groups of β-CDs.

*Polymerization of α-CD–**T**, α-CD–**2T**, DM-β-CD–**2T** and DM-β-CD–**3T** inclusion complexes*

We tried to polymerize the α-CD–**T**, β-CD–**2T**, DM-β-CD–**2T** and DM-β-CD–**3T** inclusion complexes using FeCl$_3$ in water at 30 °C for 24 h (Scheme 1). Native

Figure 3. The crystal structure of the 2,6-*O*-dimethyl-β-CD–bithiophene inclusion complex. Carbon and oxygen of 2,6-*O*-dimethyl-β-CD are shown in gray and red respectively. Carbon and sulfur of bithiophene are shown in gray and yellow, respectively.
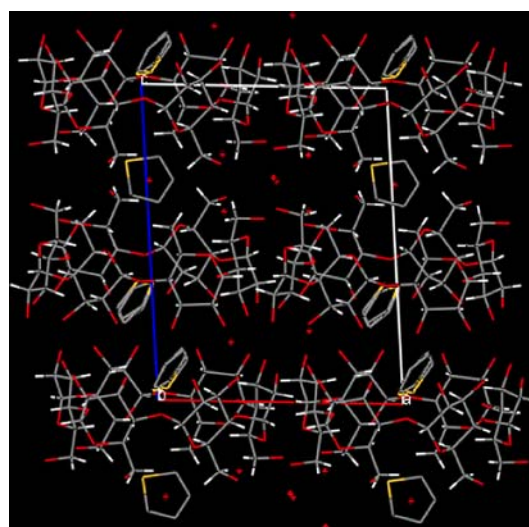

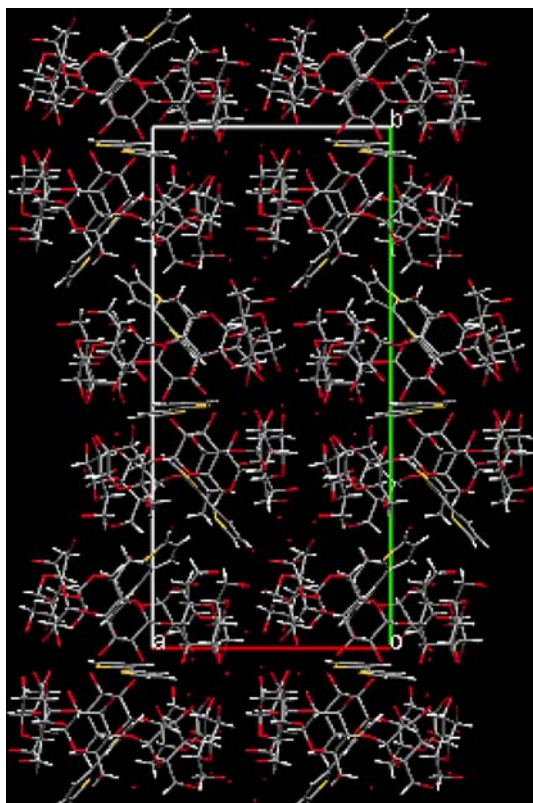*Figure 4.* The packing structure of the α-CD–thiophene inclusion complex. Cross-section of the **ac** plane.

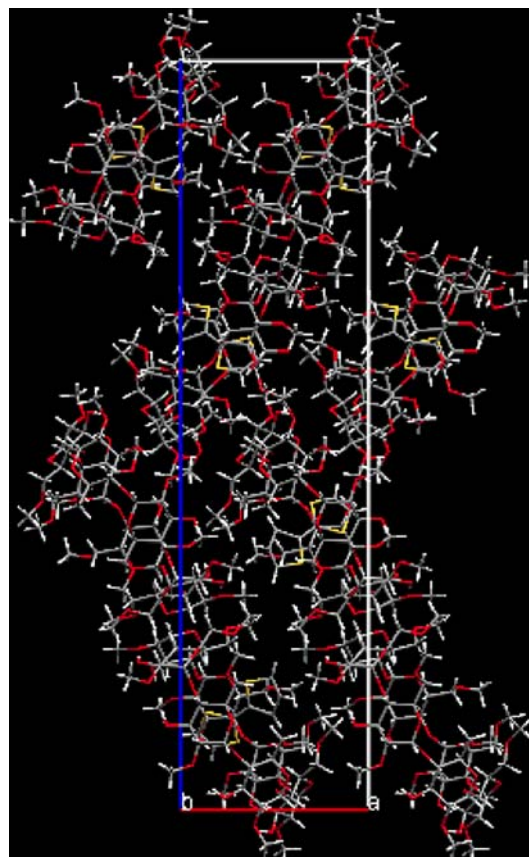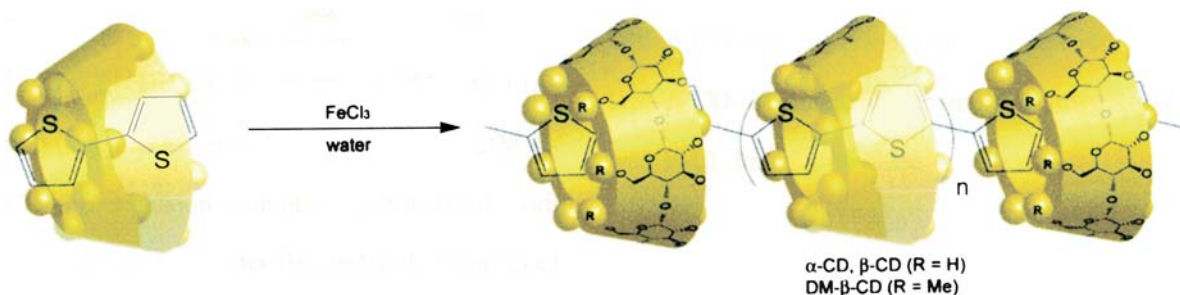*Figure 5*. The packing structure of the β-CD–bithiophene inclusion complex. Cross-section of the **ab** plane.

Figure 6. The packing structure of the 2,6-*O*-dimethyl-β-CD–bithiophene inclusion complex. Cross-section of the **bc** plane.

bithiophene and thiophene are not polymerized by FeCl$_3$ in water. The polymerization of the DM-β-CD–**2T** inclusion complex and the DM-β-CD–**3T** inclusion complexes were carried out homogeneously and produced relatively high yields (DM-β-CD–**2T**; 46.5%, DM-β-CD–**3T**; 37.5%) [29]. On the other hand, α-CD–**T** and β-CD–**2T** produced α-CD–poly(**T**) and β-CD–poly(**2T**) in 1.2 and 1.8% yield, respectively. The low yield of α-CD–**T** and β-CD–**2T** inclusion complexes were due to their heterogeneous state. In contrast, DM-β-CD–**2T** and DM-β-CD–**3T** inclusion complexes were more suitable for obtaining polymers of higher molecular weights in high yields due to their homogeneous nature.

The structures of the polymers were characterized by the IR spectrum, ^{13}C CP/MAS NMR and the mass spectrum. The FT-IR spectra of poly(thiophene), which were prepared with the DM-β-CD–**3T** inclusion complex, showed characteristic bands of authentic poly(thiophene) at 1491 and 791 cm^{-1} and strong bands at 3375, 2924, 1451 and 1368 cm^{-1}, characteristic of DM-β-CD in Figure 7b. The spectra of poly(thiophene) prepared with the DM-β-CD–**2T** inclusion complex also showed bands of poly(thiophene) and DM-β-CD. This powder was washed with water and THF three times to remove the residual DM-β-CD and **2T**. A precipitated powder still exhibits these strong bands, showing that poly-*pseudo*-rotaxane containing DM-β-CD was formed in the polymer sample. The ^{13}C CP/MAS NMR spectrum of poly(thiophene) prepared from the DM-β-CD–**2T** inclusion complex gave simpler signals than those of DM-β-CD, showing that the structure of DM-β-CD is changed to more symmetrical one by complexation with poly(**2T**) resulting in a rotaxane type structure as shown in Figure 8.

α-CD, β-CD (R = H)
DM-β-CD (R = Me)

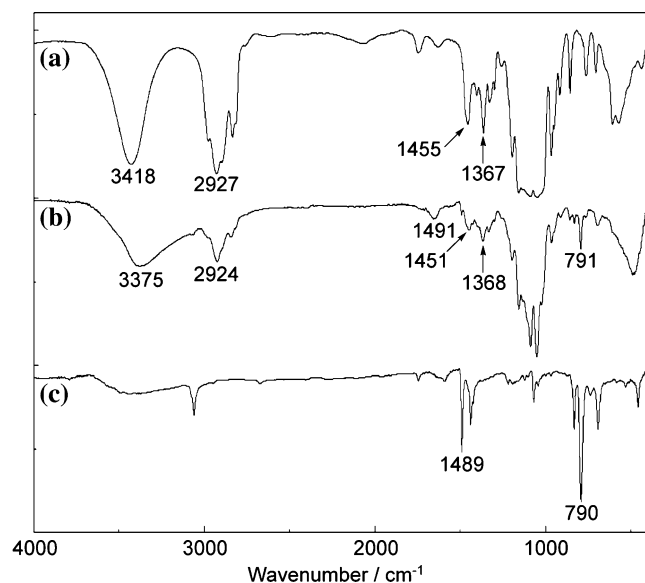*Scheme 1*. Schematic illustration of the polymerization of CDs–**2T** inclusion complex.

Figure 7. The FT-IR spectra of DM-β-CD (a), poly(thiophene) prepared from the DM-β-CD–3T inclusion complex, polymerized with FeCl₃ initiator in water (b), and poly(thiophene) prepared in organic solvent (c).

The characterization poly-pseudo-rotaxane with poly(thiophene)s

To characterize an average conjugation length of poly-*pseudo*-rotaxane, the Raman spectra of DM-β-CD–poly(**2T**) and DM-β-CD–poly(**3T**) were measured *ex situ* with an excitation wavelength of 514.2 nm in Figure 10. The symmetric stretching modes of the aromatic C=C bond appeared at 1458.0 cm^{-1}. The stretching modes of the C–C inter-ring bond were observed at 1217.8 cm^{-1}, and the bonds at 1046.7 and 700.0 cm^{-1} were assigned to the deformation modes of the C–H bond and the C–S–C aromatic bond. We focused on the bands at 1498.2 cm^{-1} in DM-β-CD–poly(**2T**) and 1505.3 cm^{-1} in DM-β-CD–poly(**3T**), which can be attributed to the antisymmetric stretching vibrations of the aromatic C=C band. In particular, the band of antisymmetric stretching vibrations of DM-β-CD–poly(**3T**) showed higher vibration shift than that of DM-β-CD–poly(**2T**), indicating that the average conjugation length of DM-β-CD–poly(**3T**) was longer than that of DM-β-CD–poly(**2T**).

In comparison between the insulated poly(thiophene) and the naked poly(thiophene), Figures 11–13 show the UV–visible and the fluorescence spectra of DM-β-CD–poly(**2T**), the naked poly(thiophene) (authentic poly(thiophene)) and another DM-β-CD–poly(**2T**) which was washed with DMF to dethread DM-β-CD. The absorption band at 480 nm in the washed DM-β-CD–poly(**2T**) complex shifted to shorter wavelengths. The absorption bands over 560 nm in the washed DM-β-CD–poly(**2T**) complex shifted to longer wavelengths and were similar to the spectrum of the authentic poly(thiophene). The fluorescence spectra were obtained with an excitation wavelength of 484 nm (λ_{max}) in a solid state. In comparison between DM-β-CD–poly(**2T**), authentic poly(thiophene) and washed DM-β-CD–poly(**2T**), the emission bands of the washed DM-β-CD–poly(**2T**) at

To evaluate the molecular weight of the polymer, the MALDI-TOF mass spectra of these polymers were measured. The signals in the MALDI-TOF mass spectrum of poly(thiophene) prepared from the DM-β-CD–**2T** inclusion complex, hereinafter called DM-β-CD–poly(**2T**), can clearly be assigned as proton adducts of poly(**2T**) and sodium or potassium cation adducts of DM-β-CD in Figure 9a. The number-average molecular weight of poly(**2T**) was up to 5000. The spectrum of poly(thiophene) prepared from DM-β-CD–**3T**, hereinafter called DM-β-CD–poly(**3T**), shows that the signals of the sodium cation adducts of poly(**3T**) were larger than that of DM-β-CD–poly(**2T**) in Figure 9b.
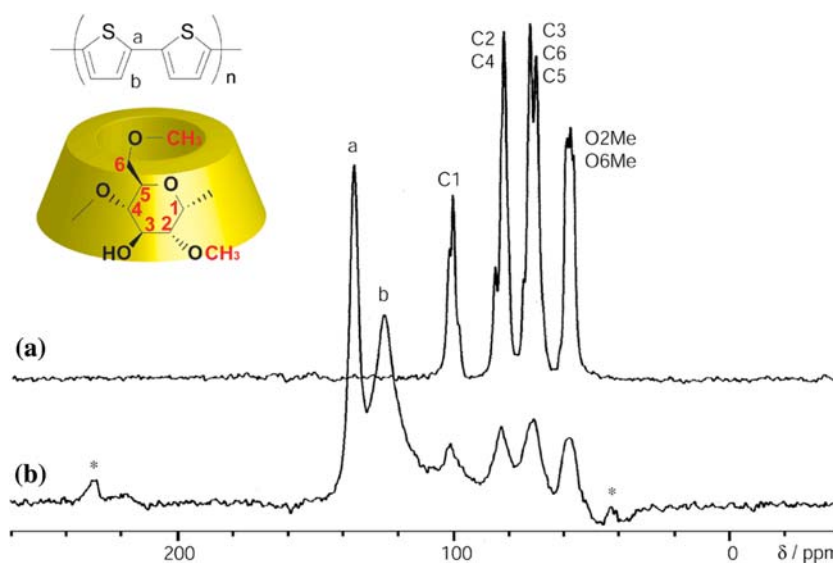

Figure 8. The ^{13}C CP/MAS NMR spectra of (a) DM-β-CD and (b) polythiophene prepared from DM-β-CD–**2T** inclusion complex, polymerized with FeCl₃ initiator in water.
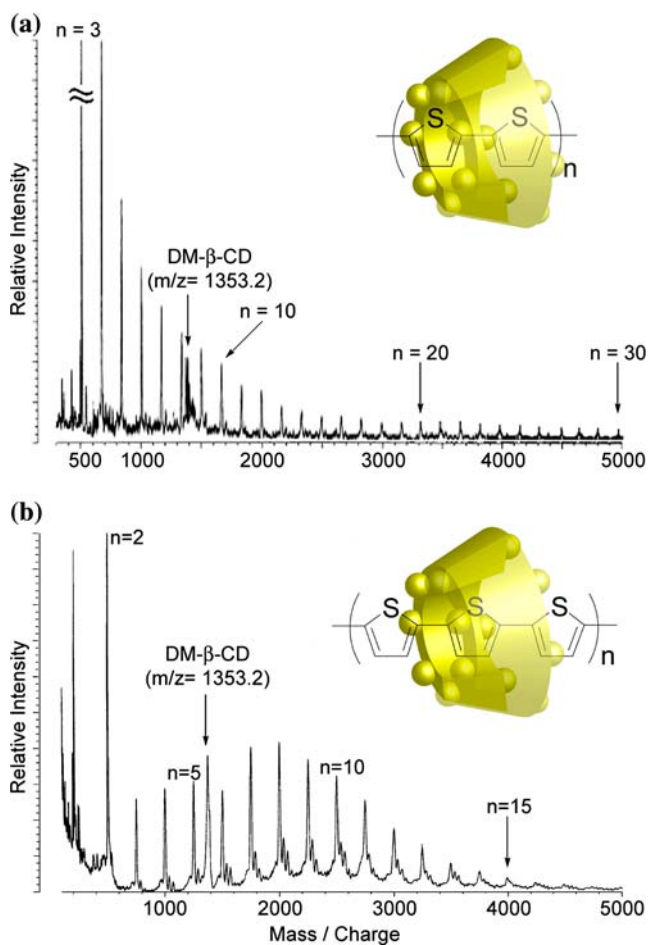
Figure 9. The MALDI-TOF mass spectra of poly(thiophene) prepared from the DM-β-CD–**2T** (a), and DM-β-CD–**3T** (b) without matrix.

620 nm shifted to a longer wavelength, as shown in Figure 12. The emission bands of the DM-β-CD–poly(**3T**) also shifted to longer wavelength, as shown in Figure 13, indicating that these blue shifts were derived from the complex formation of DM-β-CD and poly(thiophene).
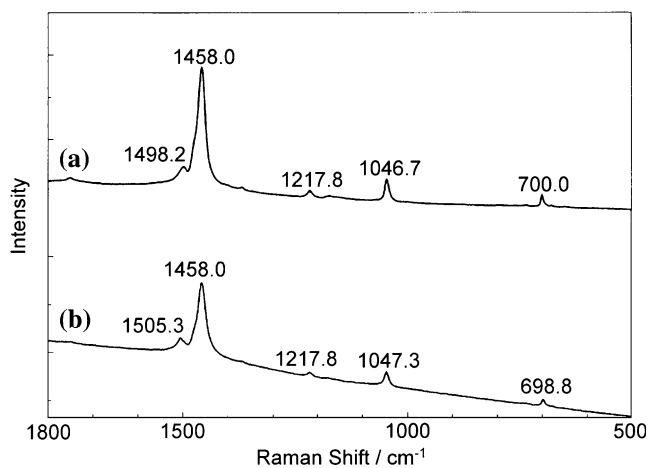

Figure 10. The Raman spectra of poly(thiophene) prepared from the DM-β-CD–**2T** inclusion complex (a), and poly(thiophene) prepared from the DM-β-CD–**3T** inclusion complex (b).
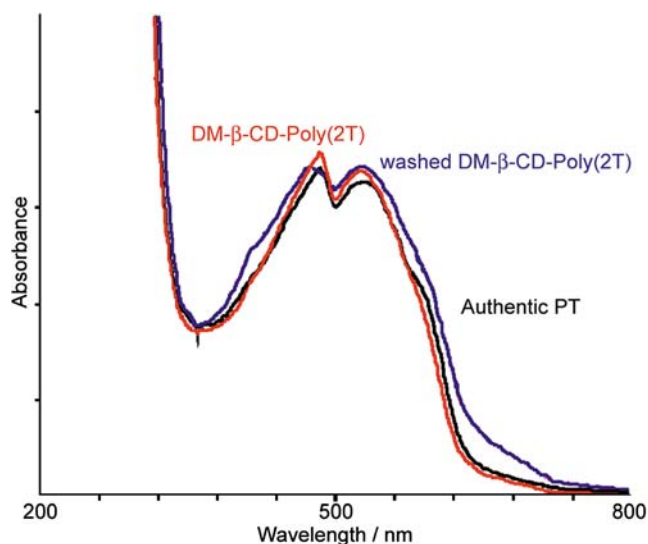

Figure 11. The UV–vis spectra of DM-β-CD–poly(**2T**) (red line), authentic poly(thiophene) (black line) and DM-β-CD–poly(**2T**) washed with DMF (blue line).

Experimental section

General considerations

2,6-Di-*O*-methyl-β-cyclodextrin (DM-β-CD) and 2,2′-bithiophene (**2T**) were purchased from Tokyo Kasei Co. β-Cyclodextrin (β-CD) was purchased from Nacalai tesque. Iron (III) chloride, 2,2′:5,2″-terthiophene (**3T**) and poly(thiophene-2,5-diyl) were purchased from Aldrich Chem. Co.

The [1]H (500 MHz), and ^{13}C (125 MHz) NMR spectra in D$_2$O were measured with a JEOL JNM-Lambda 500 spectrometer. Chemical shifts were referenced to the value (δ = 4.70 ppm for D$_2$O). The ^{13}C CP/MAS NMR spectra in a solid state were measured at 75.6 MHz with a Chemmagnetics JNM-CMX300W spectrometer with a 7.5 mm f probe using vacpX-tppm pulse sequence at room temperature. The sample spinning rate was
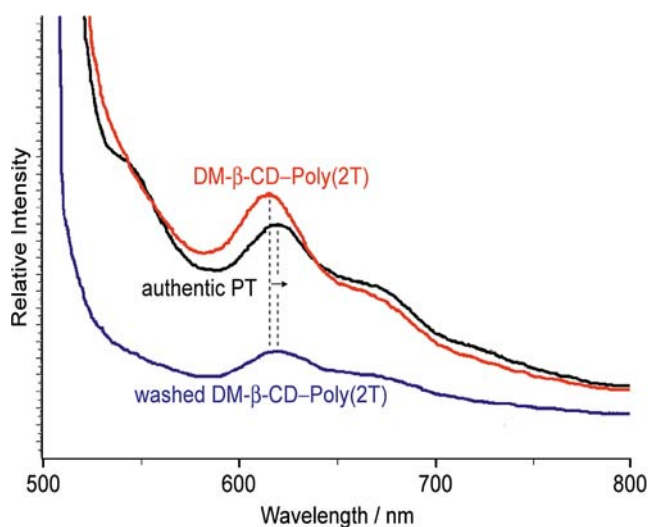

Figure 12. The fluorescence spectra of DM-β-CD–poly(**2T**) (red line), authentic poly(thiophene) (black line) and DM-β-CD–poly(**2T**) washed with DMF (blue line).
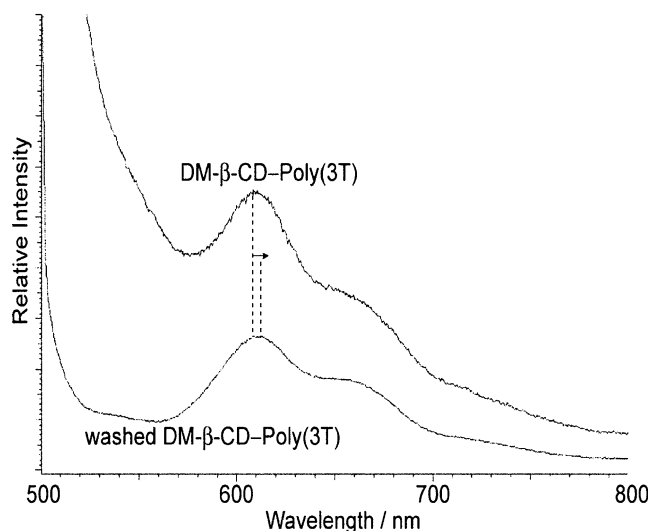
Figure 13. The fluorescence spectra of DM-β-CD–poly(**3T**) (upper line) and DM-β-CD–poly(**3T**) washed with DMF (under line).

4.0–5.0 KHz. Chemical shift was referenced to external hexamethyl benzene (δ = 17.36 ppm). FT-IR measurements were performed with a JASCO FT/IR-410 spectrometer. The Raman spectra were recorded with a JASCO NR-1800 spectrometer at room temperature. The excitation source was a 514.5 nm Ar-ion laser line and the optical power of the sample was maintained at 25 mW. The matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry experiments were performed with a Shimadzu/KRATOS AXIMA-CFR mass spectrometer. The absorption spectra were recorded with a Shimadzu UV2500 PC spectrometer at room temperature. The fluorescence spectra were recorded with a HITACHI F-2500 spectrometer at room temperature.

Preparation of α-CD–T inclusion complex

A saturated aqueous solution of α-CD (200 mL, 3.26 mmol) was added to thiophene (0.540 g, 3.26 mmol) at 60 °C. The mixture was allowed to stand at room temperature overnight. The precipitated crystal product was collected, in colorless crystal form, by centrifugation. After being filtered and washed with water and THF, the crystals were dried under a vacuum to produce the α-CD–**T** complex. Yield: 1.46 g (42.3%).

^{1}H NMR (500 MHz, 30 °C, D$_2$O): δ 7.49(m, 2H, C(2,5)H of **T**), 7.21(m, 2H, C(3,4)H of **T**), 5.00(d, J = 3.4, 6H, C(1)H of α-CD), 3.91(t, 6H, C(3)H of α-CD), 3.83(m, 12H, C(5,6)H of α-CD), 3.57(m, 6H,C(2)H of α-CD), 3.53(t, 6H, C(4)H of α-CD). ^{13}C-NMR (125 MHz, 30 °C, D$_2$O): δ 127.7(C(2,5) of **T**), 126.1(C(3,4) of **T**), 101.9(C(1) of α-CD), 81.7(C(4) of α-CD), 73.9(C(3) of α-CD), 72.6(C(5) of α-CD), 72.3(C(2) of α-CD), 61.0(C(6) of α-CD) Anal. Calcd. for (C$_{36}$H$_{60}$O$_{30}$)$_1$(C$_4$H$_4$S)$_1$(H$_2$O)$_2$: C, 43.79; H, 6.62; S, 2.92. Found: C, 43.80; H, 6.32; S, 3.11.

Preparation of β-CD–2T inclusion complex

A saturated aqueous solution of β-CD (200 mL, 3.26 mmol) was added to 2,2′-bithiophene (0.540 g, 3.26 mmol) at 60 °C. The mixture was allowed to stand at room temperature overnight. The precipitated crystal product was collected, in the form of pale blue crystals by centrifugation. After being filtered and washed with water and THF, the crystals were dried under a vacuum to produce the β-CD–**2T** complex. Yield: 2.46 g (81.8%).

^{1}H-NMR (500 MHz, 30 °C, D$_2$O): δ 7.43 (d, J = 4.7, 6H, C(5,5′)H of **2T**), 7.15 (m, 12H, C(3,3′,4,4′)H of **2T**), 5.05 (d, J = 3.5, 14H, C(1)H of β-CD), 3.92 (t, 14H, C(3)H of β-CD), 3.84 (m, 28H, C(5,6)H of β-CD), 3.64 (m, 14H,C(2)H of β-CD), 3.56 (t, 14H, C(4)H of β-CD). ^{13}C-NMR (125 MHz, 30 °C, D$_2$O): δ 136.3 (C(2,2′) of **2T**), 130.7 (C(4,4′) of **2T**), 123.8 (C(3,3′,5,5′) of **2T**), 102.3 (C(1) of β-CD), 81.5 (C(4) of β-CD), 73.6 (C(3) of β-CD), 72.5 (C(5) of β-CD), 72.2 (C(6) of β-CD), 60.6 (C(6) of β-CD). Anal. Calcd. for (C$_{42}$H$_{70}$O$_{35}$)$_2$(C$_8$H$_6$S$_2$)$_3$(H$_2$O)$_5$: C, 45.37; H, 5.92; S, 6.73. Found: C, 45.60; H, 5.94; S, 6.46.

Preparation of DM-β-CD–2T inclusion complex

A saturated aqueous solution of 2,6-di-*O*-methyl-β-CD (20 mL, 3.76 mmol) was added to 2,2′-bithiophene (0.312 g, 1.88 mmol). The mixture was cooled to 0 °C with an ice bath and stirred vigorously overnight. The solution was heated at 40 °C and the crystals were isolated as pale blue crystals. After removing supernatant carefully, these crystals were dried under a vacuum to produce the DM-β-CD–**2T** complex. Yield: 2.05 g (72.8%).

^{1}H-NMR (500 MHz, 30 °C, D$_2$O): δ 7.41 (d, J = 4.8, 2H, C(5,5′)H of **2T**), 7.08 (m, 4H, C(3,3′,4,4′)H of **2T**), 5.14 (d, J = 3.6, 7H, C(1)H of DM-β-CD), 3.84 (t, 7H, C(3)H of DM-β-CD), 3.62(s, 7H, C(5)H of DM-β-CD), 3.51(s, 21H, O(2)CH_3 of DM-β-CD), 3.30 (s, 21H, O(6)CH_3 of DM-β-CD). ^{13}C-NMR (125 MHz, 30 °C, D$_2$O): δ 137.0 (C(2,2′) of **2T**), 128.7 (C(4,4′) of **2T**), 123.8 (C(3,3′,5,5′) of **2T**), 100.0 (C(1) of DM-β-CD), 82.3 (C(4) of DM-β-CD), 81.9 (C(2) of DM-β-CD), 72.8 (C(3) of DM-β-CD), 70.9 (C(6) of DM-β-CD), 70.6 (C(5) of DM-β-CD), 59.9 (O(2)CH_3 of DM-β-CD), 58.9 (O(6)CH_3 of DM-β-CD). Anal. Calcd. for (C$_{56}$H$_{98}$O$_{35}$)$_1$(C$_8$H$_6$S$_2$)$_1$(H$_2$O)$_1$: C, 50.72; H, 7.05; S, 4.23. Found: C, 51.02; H, 7.09; S, 3.96.

Preparation of DM-β-CD–3T inclusion complex

The DM-β-CD–**3T** inclusion complex solution was synthesized in a manner similar to the DM-β-CD–**2T** inclusion complex at room temperature. 2,6-Di-*O*-methyl-β-CD (20 mL, 5.64 mmol) and 2,2′:5,2″-terthiophene (0.233 g, 0.94 mmol). Yield: 0.243 g (8.9%, pale yellow crystal).

^{1}H-NMR (500 MHz, 30 °C, D$_2$O): δ 7.49 (d, J = 5.0, 2H, C(5′,5″)H of **3T**), 7.33 (d, J = 2.7, 2H, C(3′,3″)H of

3T), 7.26 (s, 2H, $C(3,4)H$ of **3T**), 7.21 (m, 2H, $C(4',4'')H$ of **3T**), 5.25 (d, J = 3.6, 42H, $C(1)H$ of DM-β-CD), 4.04 (t, 42H, $C(3)H$ of DM-β-CD), 3.85 (s, 42H, $C(5)H$ of DM-β-CD), 3.69 (s, 126H, $O(2)CH_3$ of DM-β-CD), 3.45 (s, 126H, $O(6)CH_3$ of DM-β-CD). ^{13}C-NMR (125 MHz, 30 °C, D_2O): δ 137.0 ($C(2,5)$ of **3T**), 136.3 ($C(2',2'')$ of **3T**), 128.5 ($C(5',5'')$ of **3T**), 125.4 ($C(4',4'')$ of **3T**), 124.9 ($C(3',3'')$ of **3T**), 124.1 ($C(3,4)$ of **3T**), 100.7 ($C(1)$ of DM-β-CD), 82.2 ($C(4)$ of DM-β-CD), 81.9 ($C(2)$ of DM-β-CD), 73.5 ($C(3)$ of DM-β-CD), 71.3 ($C(6)$ of DM-β-CD), 70.3 ($C(5)$ of DM-β-CD), 60.2 ($O(2)CH_3$ of DM-β-CD), 58.5 ($O(6)CH_3$ of DM-β-CD). Anal. Calcd. for $(C_{56}H_{98}O_{35})_5(C_{12}H_8S_3)_2(H_2O)_{3.5}$: C, 50.60; H, 7.16; S, 2.67. Found: C, 50.76; H, 6.99; S, 2.48.

Inclusion polymerization of β-CDs–2T inclusion complexes a typical procedure

All manipulations were carried out by the use of standard Schlenk techniques under an argon atmosphere. Water was deoxygenated by distillation under argon. An aqueous solution of the β-CDs–**2T** inclusion complexes (5 mol) was added to FeCl$_3$ (10 mmol) via syringe at 0 °C. The vessel was kept at this temperature for the prescribed time and then the precipitated products were collected by centrifugation and dried in vacuum.

Crystallographic data collection and structure determination of α-CD–T, β-CD–2T and DM-β-CD–2T inclusion complexes

Crystals of α-CD–**T**, β-CD–**2T** and DM-β-CD–**2T** inclusion complexes suitable for X-ray diffraction studies were mounted on a cryoloop. The measurements of α-CD–**T** and β-CD–**2T** inclusion complexes were made with a Rigaku R-AXIS-RAPID Imaging Plate diffractometer with graphite monochromated MoKα radiation (λ = 0.71069) at 150 and 200 K. The relevant crystal and data statistics are summarized in Table 1. Indexing was performed from one oscillation which was exposed for 5.0 min. The camera radius was 127.40 mm. The readout was performed in 0.100 mm pixel mode. The measurements of DM-β-CD–**2T** inclusion complexes were made with a Rigaku MERCURY CCD system diffractometer with graphite monochromated MoKα radiation (λ = 0.71069) at 193 K. The readout was performed in 0.100 mm pixel mode. A symmetry-related absorption correction using the ABSCOR [30] program was applied. The data was corrected for Lorentz and polarization effects. The structures of these complexes were solved by direct methods (SHELXS-97 [31]) and refined by full-matrix least squares refinement (SHELXL-97) [31]. In subsequent refinement, the function $\sum w(|F_o|-|F_c|)^2$ was minimized, and $|F_o|$ and $|F_c|$ were the observed and calculated structure factors amplitudes. The agreement indices were defined as $R = \sum||F_o|-|F_c||/\sum|F_o|$ and $R_w = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. The positions of all non-hydrogen atoms in the complex were found with Fourier electron density

maps and refined anisotoropically. All hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and fixed. These illustrations were drawn with Mercury 1.2.

Conclusion

A series of α-CD, β-CD and DM-β-CD inclusion complexes with thiophenes were prepared. The X-ray analyses of α-CD–**T** and β-CD–**2T** revealed 2:3 inclusion complexes in the head to head channel structure. In contrast, the molecular structure of the DM-β-CD–**2T** inclusion complex was formed to have a 1:1 inclusion complex with a cage type structure. We have succeeded in obtaining polymers of β-CD–**2T**, DM-β-CD–**2T** and DM-β-CD–**3T** by FeCl$_3$ in water. Poly(thiophene)s were found to have a *pseudo*-rotaxane structure, as was proved by ^{1}H-NMR, ^{13}C CP/MAS NMR and FT-IR. These inclusion complexes have relatively high molecular weight of poly(thiophene)s, in spite of the polymerization in water, and the DM-β-CD–**3T** inclusion complex was found to produce poly-*pseudo*-rotaxane-containing a higher molecular weight poly(thiophene) of about 3000–7000 by MALDI-TOF mass spectra. The Raman band of DM-β-CD–poly(**3T**) was observed in the high vibration area, indicating that an average conjugation length of poly-*pseudo*-rotaxane, DM-β-CD–poly(**3T**) is longer than that of DM-β-CD–poly(**2T**). The fluorescence spectra of DM-β-CD–poly(**2T**) and DM-β-CD–poly(**3T**) showed a characteristic band shift ascribed to the poly-*pseudo*-rotaxane-containing DM-β-CD. Now, we are investigating the preparation of poly(rotaxane)-containing DM-β-CD using various oligothiophenes with bulky end stoppers.

Supporting Information Available

X-ray crystallographic data for crystals, α-CD–**T**, β-CD–**2T** and DM-β-CD–**2T** as CIF files.

Acknowledgements

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