Selected Papers

Synthesis of Inclusion Compounds of Br–Th–Py–Br and $(RO)_2B$–Th–Py–Br (Th: Thiophene-2,5-diyl; Py: Pyridine-2,5-diyl) with γ-Cyclodextrin

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Received August 31, 2010
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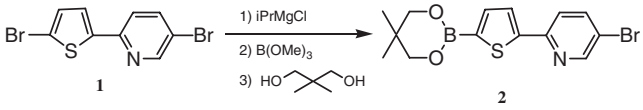
Inclusion compounds of Br–Th–Py–Br and $(RO)_2B$–Th–Py–Br ($(OR)_2$: $-OCH_2C(CH_3)_2CH_2O-$) with γ-cyclodextrin (CD), denoted by **Br–ThPy–Br–CD** and **$(RO)_2B$–ThPy–Br–CD**, respectively, were prepared. Ni(0)-promoted dehalogenative coupling of **Br–ThPy–Br–CD** gave an oligomeric inclusion product, **Oligo(ThPy–CD)**. **Oligo(ThPy–CD)** was soluble in organic solvents, and ^{1}H- and CP/MAS ^{13}C{^{1}H} NMR spectra as well as the powder XRD pattern of **Oligo(ThPy–CD)** supported the CD-encapsulated structure.

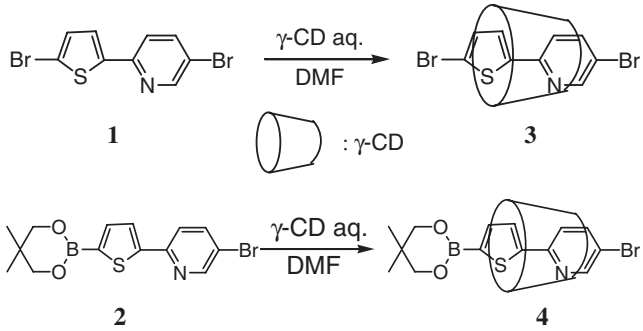
Poly(rotaxane)s and poly(pseudorotaxane)s containing a π-conjugated compound or polymer as the guest molecule are the subject of increasing interest because of their application in single molecule electronic devices.[1–4] Cyclodextrins (CDs) are typical host molecules, and CDs containing 6 to 8 glucose units recognize the guest molecule by the cavity size of CDs.

π-Conjugated polymers have received much attention because of their interesting chemical, optical, and electronic properties.[5] π-Conjugated polymers often show low solubility, and solubilization of π-conjugated polymers by forming inclusion compounds with CDs has been carried out. Synthesis of poly(pseudorotaxane)s of π-conjugated polymers from pseudorotaxane monomers has also been carried out.[2a,2d,2e] Poly[2-(2′-thienyl)pyridine-5,5′-diyl] (**P(ThPy)**)[6] is a representative donor–acceptor type (D–A) π-conjugated polymer (donor (D): thiophene unit; acceptor (A): pyridine unit), and the D–A polymers show interesting physical and chemical properties. However, **P(ThPy)** has low solubility in organic solvents. In this paper, we report the synthesis of new CD inclusion compounds of Br–Th–Py–Br and $(RO)_2B$–Th–Py–Br as well as Ni(0)-complex promoted C–C coupling of the inclusion compounds.

The new monomer **2** was prepared from 5-bromo-2-(5-bromo-2-thienyl)pyridine (**1**) (Scheme 1).[6d]



Scheme 1. Synthetic route of **2**.



Scheme 2. Preparation of pseudorotaxanes **3** and **4**.

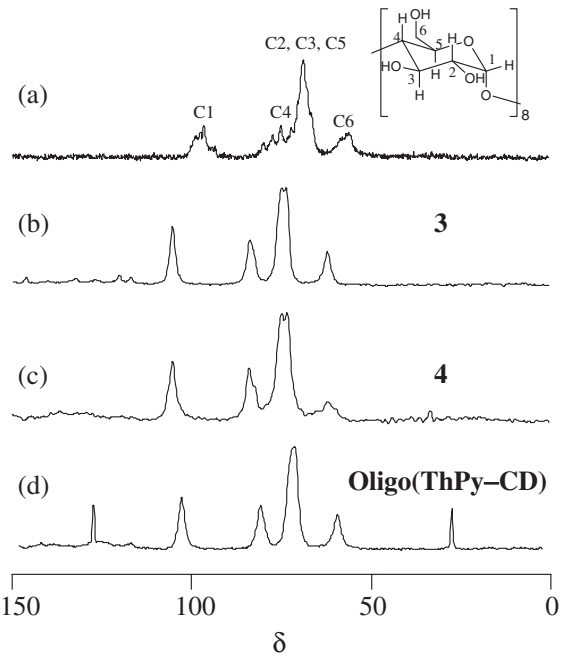


Figure 1. CP/MAS solid ^{13}C NMR spectra of (a) γ-CD, (b) **3**, (c) **4**, and (d) **Oligo(ThPy–CD)**.

Pseudorotaxanes, **3** and **4**, were prepared by reactions of **1** and **2** with γ-CD in 76% and 85% yields, respectively. In the ^{1}H NMR spectrum of **3** in DMF-d_7, the integration ratios between signals of the guest molecule and γ-CD agreed with the formation of a 1:1 inclusion compound as shown in Scheme 2. Similarly, a 1:1 included complex, **4**, was produced from **2** and γ-CD.

CP/MAS solid ^{13}C NMR spectra of γ-CD, **3**, and **4** are displayed in Figures 1a, 1b, and 1c, respectively. As shown in Figure 1a, the ^{13}C NMR spectrum of γ-CD exhibits a complex peak pattern. In Figures 1b and 1c, the γ-CD peaks appear as major peaks, and signals of thiophene and pyridine are observed as weak peaks in a range between δ 115 and 150. The peaks of γ-CD in **3** and **4** become simpler than those of original γ-CD, suggesting that γ-CD in **3** and **4** has a

Published on the web February 11, 2011; doi:10.1246/bcsj.20100247

symmetric conformation and each glucose unit has the same environment due to the inclusion of the guest molecule in the cavity of γ-CD. Such a ^{13}C NMR change has been observed with various CD-hosted poly(pseudorotaxane)s.[7] ^{1}H NMR spectra of **3** and **4** in DMF-d_7 showed the signals of γ-CD and the guest molecule, suggesting that the pseudorotaxanes **3** and **4** are in dissociative equilibria in the solution.

To prepare poly(pseudorotaxane), **P(ThPy–CD)**, reactions expressed by Method A (Ni(0) complex-promoted dehalogenative polycondensation using monomer **3**), and Method B (Pd(0)-catalyzed Suzuki–Miyaura coupling polycondensation using monomer **4**) were attempted. Direct reaction of **P(ThPy)**[6] with γ-CD (Method C) was also carried out.

The reaction expressed Method A gave an orange oligomeric powder, **Oligo(ThPy–CD)**, with an average molecular weight (M_n) of 4520 and M_w/M_n (M_w: weight average molecular weight) of 1.02 as estimated by gel permeation chromatography (GPC) in 90% yield. The M_n corresponds to degrees of polymerization of about 3. Similar dehalogenative polymerization of a CD-inclusion compound of dihalo-monomer using [Ni(0)L$_m$] has been reported.[2g] However, neither oligomeric nor polymeric products were obtained according to the C–C coupling expressed by Method B as described in the Experimental part. The direct reaction of **P(ThPy)**, which was prepared from **3** without γ-CD and had M_w of 5400,[6d] and γ-CD (Method C) did not give the inclusion compound presumably due to low solubility of **P(ThPy)**.

The orange color of **Oligo(ThPy–CD)** was different from that of **P(ThPy)** (reddish orange). **Oligo(ThPy–CD)** was soluble in DMSO, DMF, and CF_3CO_2H, and was partially soluble in $CHCl_3$, CH_2Cl_2, acetone, and THF. **P(ThPy)** has lower solubility in organic solvents.

The ^{1}H NMR spectrum (cf. Figure S2 in Supporting Information) of **Oligo(ThPy–CD)** showed γ-CD and thiophene–pyridine (Th–Py) signals and the peak pattern in the aromatic region was complex presumably because of the presence of a head-to-tail Th–Py–Th–Py unit and head-to-head and tail-to-tail Th–Py–Py–Th and Py–Th–Th–Py units. The presence of terminal units also seems to make the peak pattern complex. Peak area ratios indicated that **Oligo(ThPy–CD)** contained the Th–Py unit and γ-CD in a 1:0.8 ratio. The data indicated that a portion of γ-CD was lost during the C–C coupling. Elemental analysis of **Oligo(ThPy–CD)** supports the composition. ^{13}C NMR spectrum (Figure 1d) of **Oligo(ThPy–CD)** shows a simple peak pattern of γ-CD which indicates that the basic inclusion structure of **ThPy–CD** is maintained.

In thermogravimetric analysis, **Oligo(ThPy–CD)** showed 5% weight loss temperature ($T_{5\%}$) at 150 °C under N_2. Immediate weight loss occurred at 255 °C, and 75% weight was lost at about 400 °C. In the case of **P(ThPy)**, weight loss started at about 350 °C with about 75% residual weight at 900 °C. These data suggest that the thermal decomposition of **Oligo(ThPy–CD)** at the lower temperature occurred at the CD unit.

CDs in inclusion compounds are usually arranged in "columnar" or "cage" structures in the solid state,[8] free CDs usually take the cage packing structure. The X-ray diffraction (XRD) pattern of **Oligo(ThPy–CD)** showed two peaks at $2\theta = 17$ and 22° (Figure S3). However, the XRD pattern was much different from those of **P(ThPy)** and γ-CD, suggesting that the γ-CDs in **Oligo(ThPy–CD)** are not in the cage packing structure in the solid state.

Table 1. Optical Data of **Oligo(ThPy–CD)** and **P(ThPy)**

Polymer	UV–vis[a]	Photoluminescence[a]		
	λ_{max}/nm	λ_{EM}/nm	λ_{EX}/nm	Φ[b]/%
Oligo(ThPy–CD)	399	498	421	41.5
P(ThPy)[c]	411	488	414	50.3

a) Solvent: DMF. b) PL quantum yield (Φ) was calculated using a quinine sulfate standard (ca. 10^{-5} M solution in 0.5 M H_2SO_4 having Φ of 54.6%).[9] c) DMF-soluble part.

UV–vis and photoluminescence (PL) data of **P(ThPy)** and **Oligo(ThPy–CD)** in DMF are summarized in Table 1. **Oligo(ThPy–CD)** showed an absorption peak at a shorter wavelength by 12 nm compared with that of **P(ThPy)**, which is consistent with the lower degree of polymerization of **Oligo(ThPy–CD)**.

PL spectra of **Oligo(ThPy–CD)** showed a peak at $\lambda_{EM} =$ 498 nm, and a quantum yield of 41.5% was observed. An interesting observation in PL is that the excitation spectrum of **Oligo(ThPy–CD)** showed $\lambda_{EX} = 421$ nm, which was shifted to a longer wavelength by 22 nm from λ_{max} in the UV–vis spectrum. These results suggest the presence of electronic interaction between oligo-ThPy and CD.

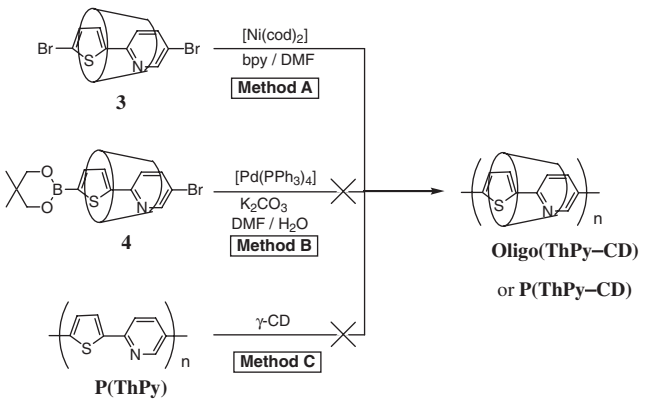
CV (cyclic voltammetry) charts of **1** and **3** show irreversible reduction peaks, as shown in Figure S5. Because the pyridine–Br (Py–Br) bond is susceptible to electrochemical reductive coupling (2Py–Br + 2e$^-$ → Py–Py + 2Br$^-$),[10] the irreversible peaks suggest occurrence of such electrochemical C–C coupling. However, electrochemical n-doping of **1** and **3** or their C–C coupling products may partly contribute to the reduction peak(s), and the anodic peak at about 0.4 V vs. Ag^+/Ag may be assigned to n-dedoping of the n-doped species. **P(ThPy)** also shows a large potential difference between n-doping and n-dedoping peaks.[6] The CV chart of **Oligo(ThPy–CD)** differs from those of **1** and **3**, and suggests a stronger contribution of the electrochemical n-doping and n-dedoping.

As described above, pseudorotaxanes of γ-CD with functionalized π-conjugated aromatic dimers, **3** and **4**, were synthesized, and oligo(pseudorotaxane), **Oligo(ThPy–CD)**, was obtained via Ni(0)-promoted dehalogenative C–C coupling of **3** without losing most of the encapsulating γ-CD.

Experimental

Preparation of Pseudorotaxane 3. To a DMF (5 mL) solution of **1**[6] (0.0638 g, 0.2 mmol) was added an aqueous solution (100 mL) of γ-CD (5 M). The formed precipitate was collected by filtration and dried in vacuo to give the pseudorotaxane **3**. Yield: 0.247 g (76%). ^{1}H NMR (400 MHz, DMF-d_7): δ 8.67 (d, $J = 2.4$ Hz, 1H), 8.13 (dd, $J = 8.5$, 2.4 Hz, 1H), 7.98 (dd, $J = 8.5$, 0.7 Hz, 1H), 7.74 (d, $J = 4.1$ Hz, 1H), 7.32 (d, $J = 4.1$ Hz, 1H), 5.86–5.85 (m, 16H, γ-CD), 5.01–5.00 (m, 8H, γ-CD), 4.67–4.64 (m, 8H, γ-CD), 3.82–3.69 (m, 32H, γ-CD), 3.54–3.43 (m, 16H, γ-CD). CP/MAS ^{13}C{^{1}H} NMR (100 MHz): δ 151.2, 146.3, 140.2, 132.2, 126.8, 120.1, 117.0, 105.3, 83.6, 74.6, 73.4, 61.9.

Preparation of Pseudorotaxane 4. Pseudorotaxane **4** was synthesized analogously from **2** (0.457 g, 1.3 mmol) and an



Scheme 3. Attempted synthesis of **Oligo(ThPy–CD)** and **P(ThPy–CD)**.

aqueous solution of γ-CD (5 mM, 100 mL). Yield: 0.714 g (85%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.66 (d, $J = 2.0$ Hz, 1H), 8.51 (s, 1H), 8.08 (dd, $J = 8.5$, 2.0 Hz, 1H), 7.93 (d, $J =$ 8.5 Hz, 1H), 7.87 (d, $J = 3.7$ Hz, 1H), 7.75 (d, $J = 3.7$ Hz, 1H), 5.86–5.85 (m, 12H, γ-CD), 5.01–5.00 (m, 6H, γ-CD), 4.67–4.64 (m, 6H, γ-CD), 3.81–3.77 (m, 22H, γ-CD), 3.51–3.44 (m, 34H, γ-CD). CP/MAS ^{13}C{^{1}H} NMR (100 MHz):δ 166.2, 150.4, 136.7, 105.3, 83.8, 74.6, 73.2, 61.7, 33.0.

Preparation of Oligo(pseudorotaxane) Oligo(ThPy–CD) (Scheme 3). Method A: Pseudorotaxane **3** (4.85 g, 3.0 mmol) was added to a dry DMF (30 mL) solution of [Ni(cod)$_2$] (0.990 g, 3.6 mmol), 1,5-cyclooctadiene (0.325 g, 3.0 mmol) and 2,2′-bipyridyl (0.562 g, 3.6 mmol), and the mixture was stirred for 0.5 h at rt and for 62 h at 60 °C. The reaction mixture was poured into ethanol (500 mL), and the orange precipitate was collected by filtration, washed with an aqueous solution of ammonia (3 times) and distilled water (3 times), and dried in vacuo. Yield: 3.95 g (90%). Anal. Calcd for [(C_9H_5NS)-$(C_{48}H_{80}O_{40})_{0.8}(H_2O)_{0.8}]_n$: C, 47.0; H, 5.9; N, 1.2; S, 2.6%. Found: C, 46.8; H, 6.3; N, 1.1; S, 2.4%.

Method B: To a dry DMF (50 mL) solution containing **4** (4.95 g, 3.00 mmol), a degassed aqueous solution of K_2CO_3 (2 M, 20 mL) and [Pd(PPh$_3$)$_4$] (0.081 g, 0.07 mmol) were added. After the mixture was stirred at 60 °C for 78 h, it was poured into an excess amount of MeOH, however, no precipitate was given.

Method C: **P(ThPy)** (32 mg, 0.20 mmol based on the repeating polymer unit) was added to an aqueous solution (10 mL) of γ-CD (0.649 g, 0.5 mmol). **P(ThPy)** was not soluble in water. The mixture was stirred at room temperature under sonication for 24 h. However, changes (e.g., color change of the aqueous solution) were not observed.

Supporting Information

Experimental details including synthetic procedures of **2**, ^{1}H NMR spectra of **3** and **Oligo(ThPy–CD)**, powder XRD pattern of γ-CD, **P(ThPy)**, and **Oligo(ThPy–CD)**, PL and excitation spectra of **P(ThPy)** and **Oligo(ThPy–CD)**, CV charts of **1**, **3**, and **Oligo(ThPy–CD)**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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