Tetrahedron 67 (2011) 3046–3052

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of thiophene-capped [2]rotaxanes

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ARTICLE INFO

Article history:
Received 30 January 2011
Received in revised form 1 March 2011
Accepted 2 March 2011

Keywords:
Rotaxanes
Thiophenes
Charge transfer complex
Electrochemistry

ABSTRACT

Two types of thiophene-capped [2]rotaxanes, i.e., bithienyl (**2T**)- and bis(3,4-ethylenedioxythiophene)-yl (**BEDOT**)-capped [2]rotaxanes, were synthesized. The electron-deficient cyclophane of cyclobis(paraquat-*p*-phenylene) (**CBPQT**$^{4+}$) was used as a macrocycle. Association constants for inclusion complexation of **2T**- and **BEDOT**-derivatives with **CBPQT**$^{4+}$ were obtained by ^{1}H NMR titration. Due to the donor–acceptor charge transfer absorption band, **2T**- and **BEDOT**-capped [2]rotaxanes have red and green colors, respectively. On the basis of electrochemical analysis, we confirmed that only **BEDOT**-capped [2]rotaxane is a promising candidate for [3]rotaxane synthesis through oxidation coupling of the thiophene unit.

1. Introduction

Synthesis of [*n*]rotaxanes, which consists of a dumbbell-shaped compound and [*n*−1] macrocycles, has been developed in last two decades.[1] Now, [*n*]rotaxanes are attracting much attention as the components for new materials, such as mechanically-tough gel,[2] molecular machines,[3] insulated molecular wires[4] etc. In the family of [*n*]rotaxanes, [3]rotaxane is an attractive structural motif, because it is applicable to the linear molecular motors[5] and adaptable receptors.[6] Although we can find many examples of [3]rotaxane synthesis based on the crown ether derivatives,[7] cyclodextrins[8] or other macrocycles,[9] only a few examples of cyclobis(paraquat-*p*-phenylene) (**CBPQT**$^{4+}$)-based [3]rotaxane synthesis have been reported so far.[5,10] **CBPQT**$^{4+}$ is an electron-deficient cyclophane and forms inclusion complex with the electron-rich compounds.[11] In the synthesis of **CBPQT**$^{4+}$-based rotaxanes, we have often faced difficulties due to the decomposition of **CBPQT**$^{4+}$ under reductive conditions.[12] Since **CBPQT**$^{4+}$-based [*n*]rotaxanes afford fascinating nano-electromechanical systems and electronics devices,[3a] development of new synthetic pathway is quite important. In our previous study on polythiophene polyrotaxane synthesis,[13] we found out that the electrochemical oxidation coupling of the thiophene derivatives is available for the synthesis of **CBPQT**$^{4+}$-based [*n*]rotaxanes. In this study, we synthesized two types of thiophene-capped [2]rotaxanes (Fig. 1). These [2]rotaxanes have electrochemically-reactive thiophene terminal at one end. Therefore we can expect to obtain [3]rotaxane through electrochemical oxidation coupling of the terminal thiophene units. The objective of this study is to clarify whether thiophene-capped [2]rotaxane can be a precursor for [3]rotaxane synthesis.

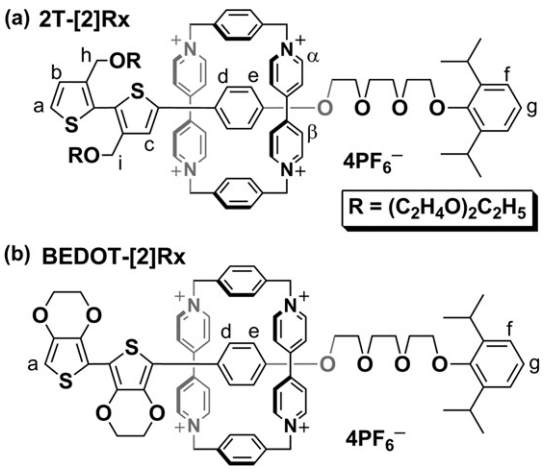

Fig. 1. Chemical structures of thiophene-capped [2]rotaxanes. (a) **2T**-[**2**]**Rx** and (b) **BEDOT**-[**2**]**Rx**. Labeling scheme for NMR assignment is also depicted.

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doi:10.1016/j.tet.2011.03.009

2. Results and discussion

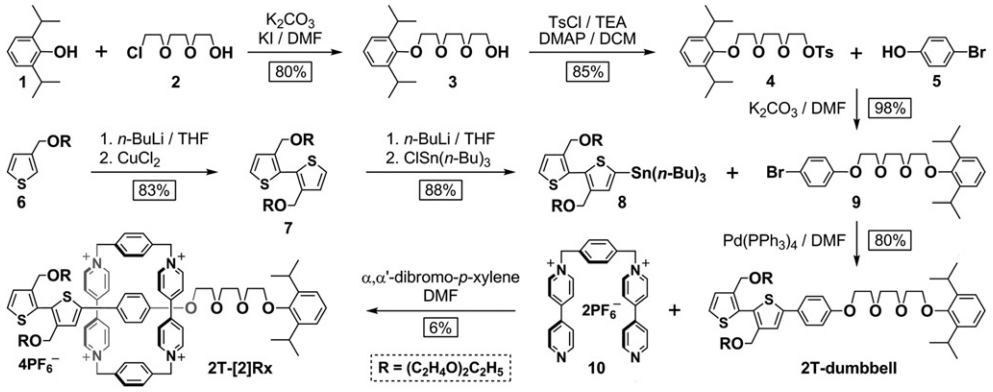
2.1. Synthesis of thiophene-capped [2]rotaxanes

Synthetic route of bithienyl-capped [2]rotaxane (**2T**-[**2**]**Rx**) is shown in Scheme 1. Tosylated product **4** was synthesized according to the literature.[14] The half-dumbbell compound **9** was obtained quantitatively by the alkylation reaction of 4-bromophenol (**5**) with **4**. 3,3′-Disubstituted-2,2′-bithiophene was synthesized from the corresponding 3-substituted thiophene (**6**) by lithiation with *n*-BuLi followed by the oxidative coupling with $CuCl_2$. After the stannylation of **7**, monostannylated bithiophene (**8**) was purified using a preparative HPLC. The dumbbell-shaped compound (**2T-dumbbell**) was synthesized using palladium-catalyzed Stille coupling with **8** and **9**.[15] **2T-dumbbell** was obtained in the yield of 80%. **2T**-[**2**]**Rx** was prepared through the clipping reaction of **CBPQT**$^{4+}$ on **2T-dumbbell** in DMF under ambient condition. Pure **2T**-[**2**]**Rx** was recovered after silica gel chromatography in the yield of 6%. Free **2T-dumbbell** was recovered after the purification process (yield: 91%) and reusable for **2T**-[**2**]**Rx** synthesis.

CBPQT^{4+} affinities to **2T**- and **BEDOT-dumbbells**. From ^{1}H NMR titration experiment,[18] the association constants (K_a) of **CBPQT**$^{4+}$ inclusion complexation were determined to be 900 and 1400 M^{-1} for **2T-thread** and **BEDOT-thread**, respectively (Fig. 2). Although ethylene glycol modification of the electron-rich component often increases the K_a value,[18,19] the side chains of the bithiophene unit contribute little to enhance affinity.

2.2. Characterization by ^{1}H NMR spectroscopy

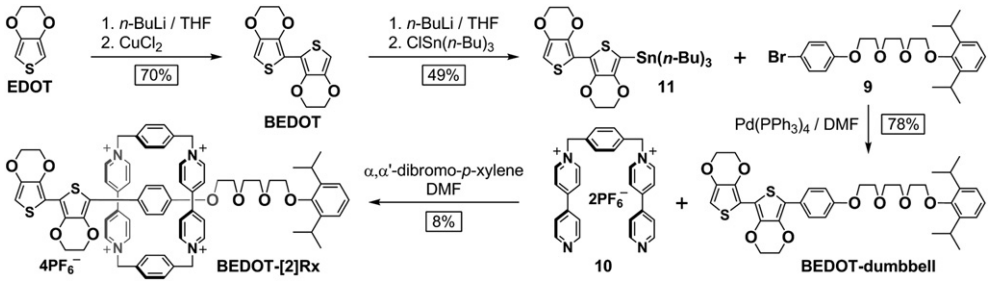
We characterized thiophene-capped [2]rotaxanes (**2T**-[**2**]**Rx** and **BEDOT**-[**2**]**Rx**) by ^{1}H NMR spectroscopy. Fig. 3 shows ^{1}H NMR spectra of **2T-dumbbell** and **2T**-[**2**]**Rx**. We assigned the aromatic protons with the help of 2D ROESY spectrum (Fig. 3c). The methylene protons (h) and (i) were assignable from the cross-peaks with the thiophene protons (b) and (c), respectively. The phenyl proton (e) was assignable from the cross-peaks with the phenyl proton (d) and the ethylene glycol proton. Compared to free dumbbell, the signals of the aromatic protons (c), (d), (e) and the methylene protons (i) in [2]rotaxane shift to higher magnetic field. These



Scheme 1. Synthesis of **2T-dumbbell** and 2T-capped [2]rotaxane (**2T**-[**2**]**Rx**).

The synthetic route of bis(3,4-ethylenedioxythiophene)-yl-capped [2]rotaxane (**BEDOT**-[**2**]**Rx**) is shown in Scheme 2. 2,2′-Bis (3,4-ethylenedioxythiophene) (**BEDOT**)[16] and its monostannylated product (**11**)[17] was synthesized from 3,4-ethylenedioxythiophene (**EDOT**) according to the literatures. Since monostannylated **BEDOT** is unstable, the palladium-catalyzed Stille coupling was carried out just after the purification of **11** using a preparative HPLC. **BEDOT-dumbbell** was obtained in the yield of 78%. **BEDOT**-[**2**]**Rx** was prepared through the clipping reaction of **CBPQT**$^{4+}$ on **BEDOT-dumbbell** in DMF under ambient condition. The yield of **BEDOT**-[**2**]**Rx** synthesis was 8%. Free **BEDOT-dumbbell** was recovered after the purification process (yield: 85%) and reusable for **BEDOT**-[**2**]**Rx** synthesis. Better yield of **BEDOT**-[**2**]**Rx** synthesis (8%) in compared with **2T**-[**2**]**Rx** synthesis (6%) is attributable to the difference in protons are affected by the shielding effect of the **CBPQT**$^{4+}$ aromatic rings due to the encapsulation inside **CBPQT**$^{4+}$ cavity.[18,19] Large chemical shift changes of the aromatic protons (c) and (d) indicate that the **CBPQT**$^{4+}$ macrocycle preferentially stays between the thiophene and phenyl groups in the dumbbell component. On the contrary, the signals of the aromatic protons (a), (b) and methylene protons (h) shift to lower magnetic field. These protons are not encapsulated by **CBPQT**$^{4+}$ but affected by the deshielding effect on the periphery of the **CBPQT**$^{4+}$ aromatic rings.[19]

Similar results were obtained for ^{1}H NMR spectra of **BEDOT-dumbbell** and **BEDOT**-[**2**]**Rx**. Namely, the aromatic protons encapsulated inside the **CBPQT**$^{4+}$ cavity, i.e., protons (d) and (e), show large chemical shift change toward higher magnetic field, and the terminal aromatic proton (a) shifts to lower magnetic field after



Scheme 2. Synthesis of **BEDOT-dumbbell** and **BEDOT**-capped [2]rotaxane (**BEDOT**-[**2**]**Rx**).

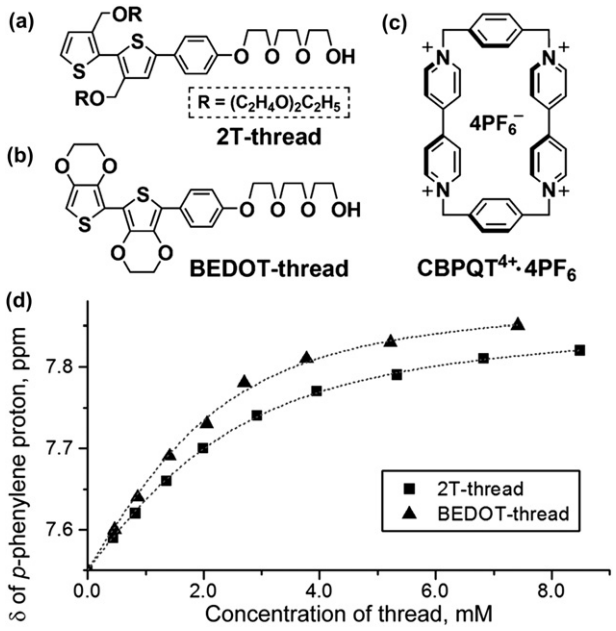


Fig. 2. Chemical structures of thiophene threads (a) **2T-thread**, (b) **BEDOT-thread** and (c) macrocycle $\mathbf{CBPQT^{4+}}\cdot 4PF_6^-$. (d) Chemical shift change in ^{1}H NMR titration experiments (CD_3CN, room temperature). The dotted lines show the curves fitted with calculation based on the K_a values.

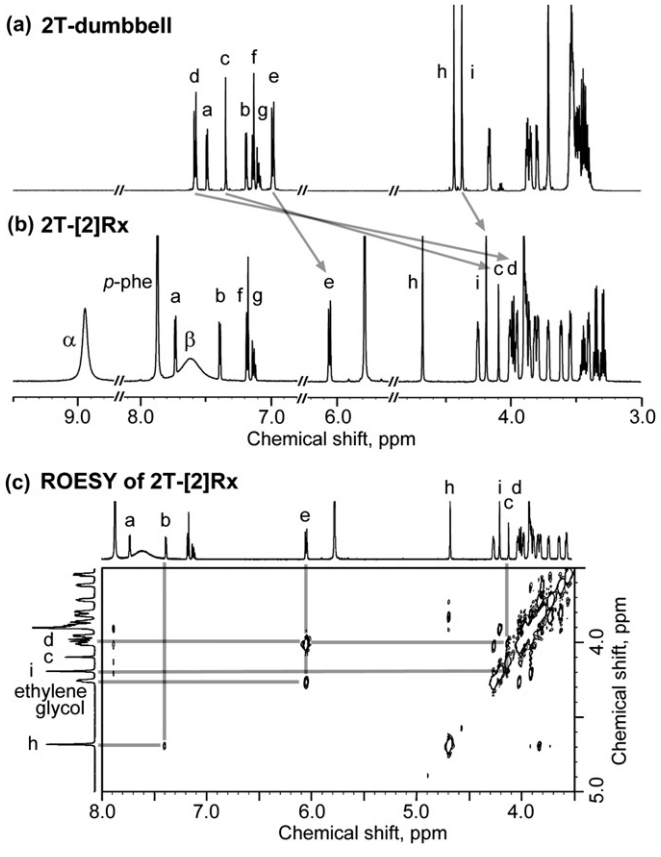


Fig. 3. ^{1}H NMR spectra of (a) **2T-dumbbell**, (b) **2T-[2]Rx** and partial ROESY spectrum of **2T-[2]Rx**. (600 MHz, CD_3CN, room temperature).

rotaxanation. We confirmed whether **BEDOT-[2]Rx** is rotaxane or *pseudo*-rotaxane. No ^{1}H NMR spectrum change was confirmed when the solution of [2]rotaxane was heated at 70 °C for 24 h. Therefore, the **BEDOT** unit is bulky enough to interlock the $\mathbf{CBPQT^{4+}}$ macrocycle.

2.3. Characterization by UV/vis spectroscopy

We characterized thiophene-capped [2]rotaxanes (**2T-[2]Rx** and **BEDOT-[2]Rx**) by UV/vis spectroscopy. The optical data are summarized in Table 1. The maximum absorption wavelength of the π–π* band for **2T-dumbbell** (λ_{Thio}=314 nm, see the Supplementary data) lies between those for the model compounds of bithiophene (302 nm)[20] and phenyl-capped bithiophene (374 nm).[21] This result is reasonable because only one end of the bithiophene unit is capped by the phenyl group in the case of **2T-dumbbell**. The same trend was confirmed for **BEDOT-dumbbell**, namely, the maximum absorption wavelength of the π–π* band for **BEDOT-dumbbell** (λ_{Thio}=363 nm) lies between those for the model compounds of **BEDOT** (320 nm)[22] and phenyl-capped **BEDOT** (398 nm).[21]

Table 1
Optical data of thiophene dumbbells and thiophene-capped [2]rotaxanes in MeCN at room temperature

Compound	λ_{CBPQT}[a] nm	ε_{CBPQT}[b] M^{-1} cm^{-1}	λ_{Thio}[c] nm	ε_{Thio}[d] M^{-1} cm^{-1}	λ_{CT}[e] nm	ε_{CT}[f] M^{-1} cm^{-1}
2T-dumbbell	—	—	314	22,000	—	—
BEDOT-dumbbell	—	—	363	34,000	—	—
2T-[2]Rx	259	39,000	(320)[g]	(19,000)[g]	485	530
BEDOT-[2]Rx	263	39,000	371	27,000	625	300

[a] Maximum absorption wavelength of $\mathbf{CBPQT^{4+}}$.
[b] Molar extinction coefficient at λ_{CBPQT}.
[c] Maximum absorption wavelength of phenyl–thiophene unit π–π* band.
[d] Molar extinction coefficient at λ_{Thio}.
[e] Maximum absorption wavelength of CT band.
[f] Molar extinction coefficient at λ_{CT}.
[g] Data was calculated from peak fitting to overlapped peaks.

Fig. 4 shows UV/vis spectra of thiophene-capped [2]rotaxanes. The peak around 260 nm mainly originates from the absorption of the $\mathbf{CBPQT^{4+}}$ macrocycle.[19] In the case of **BEDOT-[2]Rx**, we can confirm a vibronic fine structure in the π–π* band due to the rigid structure of the **BEDOT** unit.[21,23] Thiophene-capped [2]rotaxane has an additional absorption band in the visible region due to charge transfer (CT) from the electron-rich phenyl–thiophene unit to the electron-deficient bipyridinium unit in $\mathbf{CBPQT^{4+}}$.[11b,18,19] The maximum absorption wavelength of the CT bands (λ_{CT}) for **2T-[2]Rx** and **BEDOT-[2]Rx** were 485 nm and 625 nm, respectively. These absorption bands afford red and green colors to **2T-[2]Rx** and **BEDOT-[2]Rx**, respectively. Compared with free dumbbell compounds, we confirmed red-shift of the π–π* band (λ_{Thio}) for the thiophene-capped [2]rotaxanes (Table 1). This result supports that an electronic interaction exists between the phenyl–thiophene unit and bipyridinium unit.[18,19]

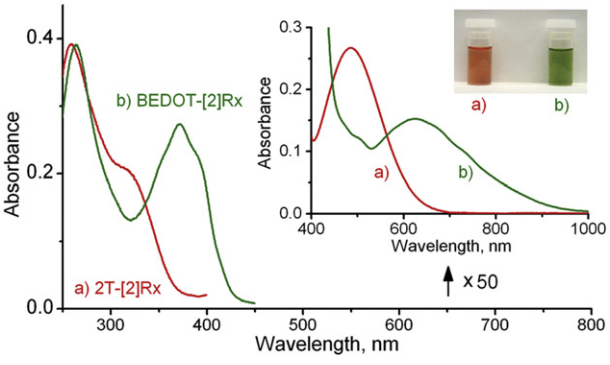


Fig. 4. UV/vis spectrum of (a) **2T-[2]Rx** and (b) **BEDOT-[2]Rx** (MeCN, 1.0×10^{-5} M, room temperature). Inset is photograph of solutions (a) **2T-[2]Rx** and (b) **BEDOT-[2]Rx**.

2.4. Electrochemical characterization

Electrochemical properties of the thiophene dumbbells and thiophene-capped [2]rotaxanes were analyzed using cyclic voltammetry (CV) and differential pulse voltammetry (DPV).[24] CV traces and half-wave potentials ($E_{1/2}$) are summarized in Fig. 5 and Table 2, respectively.

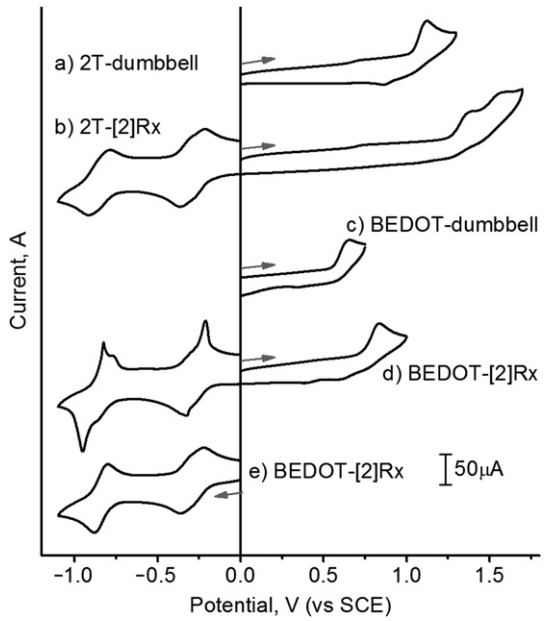


Fig. 5. Cyclic voltammetry traces recorded at 200 mV s^{-1} in argon-purged MeCN at room temperature. Sample concentration: 1.0 mM.

Table 2
Electrochemical data of thiophene dumbbells and thiophene-capped [2]rotaxanes

Compound	Half-wave potentials versus SCE (V)	
	Oxidation	Reduction
2T-dumbbell	(+1.07)[a]	—
BEDOT-dumbbell	(+0.61)[a]	—
2T-[2]Rx	+1.32[b], +1.52[b]	−0.24[c], −0.33[c], −0.85[d]
BEDOT-[2]Rx	(+0.80)[a]	−0.22[c], −0.30[c], −0.82[d]

[a] Irreversible one-electron process.
[b] Quasi-reversible one-electron process.
[c] Reversible one-electron process.
[d] Reversible two-electron process.

In CV analysis of **2T-dumbbell**, we confirmed an oxidation peak at $E_{1/2}$=+1.07 V (Fig. 5a). This oxidation peak corresponds to the radical cation formation.[21] No second oxidation peak attributable to the dication formation was observable. The redox process was irreversible, because we confirmed new peak around +0.85 V in the cathodic scan. This result suggests that the electrochemical oxidation coupling of **2T-dumbbell** takes place around +1.1 V. Compared with **2T-dummbell**, **2T-[2]Rx** showed two oxidation peaks at higher potential ($E_{1/2}$=+1.32 and +1.52 V, Fig. 5b). The electrochemically-active unit encapsulated by the **CBPQT^{4+}** macrocycle always has higher oxidation potential, because the tetracationic cyclophane **CBPQT^{4+}** suppress the formation of additional cation charge.[25] The first and second oxidation peaks in Fig. 5b correspond to the radical cation and dication formation. We could confirm the reduction peak of the radical cation and dication, but the intensity of peaks in the cathodic scan was smaller than that in the anodic scan. We found no additional peak in the cathodic scan. Therefore, we concluded these redox processes are quasi-reversible. This result suggests that the oxidation coupling of the terminal thiophene unit does not take place due to the steric and electrostatic repulsive forces between the **CBPQT^{4+}** macrocycles.[25] In the reduction part of CV (E<0), two successive two-electron reduction peaks based on the process of **CBPQT^{4+}**→**CBPQT^{2+}**→**CBPQT^{0}** were observed. We confirmed small splitting of the first two-electron reduction peak. This splitting is characteristic for **CBPQT^{4+}**-based [2]rotaxanes.[25]

In CV analysis of **BEDOT-dumbbell**, we confirmed an irreversible oxidation peak at $E_{1/2}$=+0.61 V (Fig. 5c) corresponding to the radical cation formation. No second oxidation peak was observable. This result suggests that the electrochemical oxidation coupling of **BEDOT-dumbbell** takes place around +0.6 V. Compared with **BEDOT-dumbbell**, the first oxidation of **BEDOT-[2]Rx** took place at higher oxidation potential ($E_{1/2}$=+0.80 V, Fig. 5d). The first oxidation peak of **BEDOT-[2]Rx** was also irreversible and we confirmed small new peaks in the cathodic scan (around +0.40 and +0.60 V). Furthermore, we observed the spike peaks in the reduction part of CV (E<0, Fig. 5d). These spike peaks were not observed when we scanned the potential only in the negative region (Fig. 5e). These results suggest the formation of [3]rotaxane through the electrochemical oxidation coupling of **BEDOT-[2]Rx**. Presumably, higher reactivity of the bis(3,4-ethylenedioxythiophene) unit contributes to the oxidation coupling of **BEDOT-[2]Rx**.[26] The spike peaks in the reduction region is attributable to the deposition of [3]rotaxane on the electrode surface due to low solubility of reduced [3]rotaxane. Similar spike peaks have been reported by Stoddart et al. in the CV traces of **CBPQT^{4+}**-based [3]rotaxane.[5]

3. Conclusion

We successfully synthesized two kinds of thiophene-capped [2]rotaxanes. Electrochemical analysis suggested that **BEDOT-[2]Rx** is a promising candidate for [3]rotaxane synthesis through the oxidation coupling of the terminal thiophene unit. On the other hand, we cannot expect [3]rotaxane synthesis from **2T-[2]Rx**. This result is also important for the design of polythiophene polyrotaxane. In order to obtain much amount of [3]rotaxane, we have to improve the yield in the step of rotaxanation. The improved synthesis of thiophene-capped [2]rotaxane and [3]rotaxane synthesis through oxidation coupling of the thiophene unit are now in progress.

4. Experimental section

4.1. General information

All of the reagents and solvents were purchased from the commercial source used without further purification. Compounds **4**,[14] **6**,[13] **10**,[19] **BEDOT**,[16] and **CBPQT$_4$**·4PF$_6$[19] were prepared according to literature procedures. Thread compounds **2T-thread** and **BEDOT-thread** were synthesized through the same route with the synthesis of the dumbbell-shaped components. Column chromatography was carried out using Biotage® SNAP cartridge with SP1TM FLASH purification system (Biotage). Some compounds were purified by LC-9104 recycling preparative HPLC system equipped with the linearly connected JAIGEL-1H and JAIGEL-2H columns (Japan Analytical Industry Co.). NMR spectra were recorded on a Bruker DRX600 (600 MHz and 150 MHz for ^{1}H and ^{13}C nuclei, respectively) with residual solvent as the internal standard. In ^{1}H NMR titration, the concentration of **CBPQT^{4+}**·4PF$_6^-$ was 2.11 mM in both cases. The detailed procedure of ^{1}H NMR titration was written in our previous papers.[18] High resolution electrospray ionization (HR-ESI) mass spectra were obtained on a mass spectrometer equipped in the LCMS-IT-TOF system (Shimadzu, Co.). UV/vis spectra were recorded at room temperature on a UV-2550 UV/vis spectrophotometer (Shimadzu Co.). Electrochemical

measurements were carried out at room temperature in argon-purged MeCN, with an ALS Electrochemical Analyzer, Model 612B (ALS Co.). Cyclic voltammetry (CV) was performed using a glassy carbon working electrode (0.07 cm^2, ALS Co.); its surface was polished routinely with 0.05-μm alumina/water slurry on a felt surface before use. The counter and reference electrodes were a platinum wire and a saturated calomel electrode (SCE), respectively (ALS Co.). TBA·PF_6 (0.1 M) was used as a supporting electrolyte. The half-wave potential ($E_{1/2}$) was calculated from the differential pulse voltammetry (DPV) peak top (E_{max}) and pulse height (ΔE) by using the equation of $E_{1/2}=E_{max}+\Delta E/2$.[24] ΔE was set to 50 mV.

4.2. Synthesis

Compound **7**: The compound **6** (2.3 g, 10 mmol) was dissolved in dry THF (20 mL) under Ar. The solution was cooled to −60 °C using a liquid N_2/$CHCl_3$ bath. The hexane solution of *n*-BuLi (4.0 mL, 10 mmol) was added dropwise with the gas-tight syringe. The reaction mixture was stirred for 2.5 h under dark at −60 °C. $CuCl_2$ (1.5 g, 11 mmol) was added to the reaction mixture. The reaction temperature was gradually raised to room temperature by removing the liquid N_2/$CHCl_3$ bath. After 2 h, CH_2Cl_2 (150 mL) was added to the reaction mixture and washed with 0.5 N HCl (200 mL×2) and 1 N $NaHCO_3$ (200 mL) aqueous solutions. The organic layer was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by column chromatography (SNAP Cartridge silica 100 g, hexane/AcOEt: 50%=2 column, 50→80%=6 column) to give the compound **7** as a colorless oil. Yield: 1.9 g (83%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ=1.20 (t, *J*=7.2 Hz, 6H), 3.49–3.59 (m, 12H), 3.62 (m, 8H), 4.42 (s, 4H), 7.17 (d, *J*=5.4 Hz, 2H), 7.33 (d, *J*=5.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=15.5, 67.0, 69.8, 70.2, 70.9, 71.0, 126.6, 129.1, 131.0, 138.9 ppm; IR (KBr): 3095, 2972, 2864, 1452, 1346, 1240, 1109, 1038, 941, 881, 833, 742, 696 cm^{-1}; HRMS (ESI): found *m*/*z*=481.1659 $[M+Na]^+$; $C_{22}H_{34}O_6S_2Na$ requires 481.1695.

Compound **8**: The compound **7** (1.0 g, 2.2 mmol) was dissolved in dry THF (10 mL) under Ar. The solution was cooled to −60 °C using a liquid N_2/$CHCl_3$ bath. The hexane solution of *n*-BuLi (0.85 mL, 2.2 mmol) was added dropwise with the gas-tight syringe. The reaction mixture was stirred under dark. The reaction temperature was gradually raised without refilling liquid N_2 in the $CHCl_3$ bath. After 1 h, the reaction mixture was cooled to −60 °C again using a liquid N_2/$CHCl_3$ bath. Tri-*n*-butyltin chloride ($ClSn(n\text{-}Bu)_3$, 0.58 mL, 2.1 mmol) was added dropwise to the reaction mixture. The reaction temperature was gradually raised to room temperature by removing the liquid N_2/$CHCl_3$ bath. After 1 h, CH_2Cl_2 (150 mL) was added to the reaction mixture and washed with 1 N $NaHCO_3$ (200 mL) aqueous solution. The organic layer was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, $CHCl_3$) to give the compound **8** as a colorless oil. Yield: 1.4 g (88%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ=0.90 (t, *J*=7.3 Hz, 12H), 1.12 (m, 6H), 1.20 (t, *J*=7.0 Hz, 6H), 1.35 (m, 6H), 1.58 (m, 6H), 3.49–3.59 (m, 12H), 3.62 (m, 8H), 4.44 (d, *J*=4.7 Hz, 4H), 7.17 (d, *J*=5.2 Hz, 1H), 7.19 (s, 1H), 7.31 (d, *J*=5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=11.2, 14.0, 15.5, 27.6 29.3, 67.0, 67.1, 69.7, 70.2, 70.9, 71.0, 126.3, 129.0, 131.7, 136.9, 137.4, 138.2, 138.8, 139.5 ppm; HRMS (ESI): found *m*/*z*=771.2715 $[M+Na]^+$; $C_{34}H_{60}O_6S_2SnNa$ requires 771.2755.

Compound **9**: The compounds **4** (4.6 g, 9.9 mmol), **5** (1.0 g, 5.8 mmol), and K_2CO_3 were mixed in dry DMF (20 mL). The reaction mixture was stirred at 100 °C under Ar atmosphere for 16 h. The solvent was removed by evaporation. The residue was dissolved in CH_2Cl_2 (200 mL) and washed with 1 N $NaHCO_3$ (200 mL) and 1 N NaCl (200 mL) aqueous solutions. The organic layer was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by column chromatography (SNAP Cartridge silica 100 g, hexane/AcOEt: 25%=4 column) to give the compound **9** as a colorless oil. Yield: 2.6 g (98%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ=1.22 (d, *J*=6.9 Hz, 12H), 3.39 (m, 2H), 3.79 (s, 4H), 3.85–3.94 (m, 6H), 4.11 (t, *J*=5.4 Hz, 2H), 6.80 (d, *J*=9.0 Hz, 2H), 7.10 (s, 3H), 7.36 (d, *J*=9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=24.5, 26.6, 68.1, 70.1, 71.0, 71.4, 74.2, 113.4, 116.8, 124.3, 125.0, 132.6, 142.2, 153.4, 158.3 ppm; IR (KBr): 3068, 2960, 2924, 2868, 1591, 1489, 1452, 1325, 1286, 1247, 1186, 1130, 1058, 937, 823, 796, 760, 646, 507 cm^{-1}; HRMS (ESI): found *m*/*z*=487.1469 $[M+Na]^+$; $C_{24}H_{33}BrO_4Na$ requires 487.1460.

2T-dumbbell: The compounds **8** (1.5 g, 2.0 mmol), **9** (0.95 g, 2.0 mmol), and $Pd(PPh_3)_4$ (50 mg, 4.3×10^{-5} mol) were mixed in dry DMF (10 mL). The solution was deaerated three times. The reaction mixture was stirred at 65 °C under dark and Ar atmosphere for 14 h. The solvent was removed in vacuo. The residue was directly subjected to the column chromatography (SNAP Cartridge silica 100 g, CH_2Cl_2/AcOEt: 10%=2 column, 10%→50%=6 column, 50%=4 column). The recovered fraction containing the product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, $CHCl_3$) to give **2T-dumbbell** as a colorless oil. Yield: 1.4 g (80%). ^{1}H NMR (CD_3CN, 600 MHz): δ=1.13 (m, 6H), 1.21 (d, *J*=6.9 Hz, 12H), 3.38–3.57 (m, 22H), 3.71 (s, 4H), 3.80 (m, 2H), 3.85 (m, 2H), 3.87 (m, 4H), 4.17 (m, 2H), 4.38 (s, 2H), 4.44 (s, 2H), 6.98 (d, *J*=8.8 Hz, 2H), 7.07–7.15 (m, 3H), 7.19 (d, *J*=6.0 Hz, 1H), 7.35 (s, 1H), 7.49 (d, *J*=6.0 Hz, 1H), 7.58 (d, *J*=8.8 Hz); ^{13}C NMR (CD_3CN, 150 MHz): δ=15.6, 24.3, 26.9, 66.9, 67.1, 67.2, 68.7, 70.4, 70.5, 71.1, 71.2, 71.5, 75.0, 116.0, 125.0, 125.7, 127.4, 127.5, 127.8, 129.7, 130.2, 131.4, 139.8, 140.8, 142.9, 145.2, 154.1, 159.9 ppm; IR (KBr): 3068, 2962, 2868, 1606, 1508, 1458, 1350, 1288, 1253, 1180, 1109, 937, 829, 794, 760 cm^{-1}; HRMS (ESI): found *m*/*z*=865.3969 $[M+Na]^+$; $C_{46}H_{66}O_{10}S_2Na$ requires 865.3995.

2T-[2]Rx: **2T-dumbbell** (0.42 g, 0.50 mmol), **10** (1.0 g, 1.4 mmol), and α,α′-dibromo-*p*-xylene (0.37 g, 1.4 mmol) were dissolved in dry DMF (10 mL). The mixture was stirred at room temperature under dark and Ar atmosphere for 7 days. AcOEt was added to the solution. The solution and the precipitate were directly subjected to the column chromatography (SiO_2). **2T-dumbbell** and other impurities were eluted out by AcOEt, and then CH_2Cl_2/MeOH=9:1. The product was eluted out the mixed solvent (MeOH/2 N NH_4Cl aq/$MeNO_2$=6:3:1). The recovered red solution was concentrated, then the residue was subjected to the column chromatography again (SiO_2, MeOH/2 N NH_4Cl aq/$MeNO_2$=6:3:1). The recovered red solution was concentrated to the half volume by the evaporation. An aqueous solution of NH_4PF_6 was added until no further precipitation occurred. The pink-color precipitate was recovered by filtration. The precipitate was dissolved in Me_2CO and the solution was added to the NH_4PF_6 aqueous solution to complete the counter-ion exchange. The precipitate was recovered by filtration, washed with small amount of pure water, and dissolved in Me_2CO. After the evaporation, the product **2T-[2]Rx** was obtained as a red solid. Yield: 58 mg (6%). Mp: >280 °C; ^{1}H NMR (CD_3CN, 600 MHz): δ=0.88 (t, *J*=7.0 Hz, 3H), 0.93 (t, 3H), 1.25 (d, *J*=7.0 Hz, 12H), 3.29 (q, *J*=7.0 Hz, 2H), 3.35 (q, *J*=7.0 Hz, 2H), 3.40 (m, 2H), 3.44 (m, 2H), 3.54 (m, 2H), 3.62 (m, 2H), 3.71 (m, 2H), 3.78–3.83 (m, 4H), 3.83–3.92 (m, 10H), 3.94–4.02 (m, 6H), 4.10 (s, 1H), 4.19 (s, 2H), 4.25 (m, 2H), 4.68 (s, 2H), 5.78 (s, 8H), 6.05 (d, *J*=9.0 Hz, 2H), 7.10–7.20 (m, 3H), 7.39 (d, *J*=5.2 Hz, 1H), 7.62 (br, 8H), 7.73 (d, *J*=5.2 Hz, 1H), 7.87 (s, 8H), 8.95 (br, 8H); ^{13}C NMR (CD_3CN, 150 MHz): δ=15.3, 24.4, 27.0, 65.7, 66.7, 66.8, 67.1, 69.0, 70.0, 70.1, 70.5, 70.7, 71.0, 71.1, 71.2, 71.5, 71.6, 71.7, 74.9, 115.9, 123.2, 124.3, 125.1, 125.7, 125.8, 127.8, 128.3, 130.5, 131.5, 131.7, 131.8, 138.2, 139.2, 139.5, 141.0, 142.8, 145.9, 148.7, 154.0, 160.4 ppm; IR (KBr): 3132, 3064, 2964, 2926, 2870, 1637, 1560, 1508, 1448, 1348, 1298, 1257, 1107, 840, 790, 640, 557 cm^{-1}; HRMS (ESI): found *m*/*z*=502.5465 $[M-3PF_6]^{3+}$; $C_{82}H_{98}F_6N_4O_{10}PS_2$ requires 502.5455.

Compound **11**: **BEDOT** (1.5 g, 5.3 mmol) was dissolved in dry THF (30 mL) under Ar. The solution was cooled to −60 °C using a liquid

N_2/$CHCl_3$ bath. The hexane solution of *n*-BuLi (2.0 mL, 5.5 mmol) was added dropwise with the gas-tight syringe. The reaction mixture was stirred under dark. The reaction temperature was gradually raised to −15 °C using an ice bath. After 1 h, the reaction mixture was cooled to −60 °C again using a liquid N_2/$CHCl_3$ bath. Tri-*n*-butyltin chloride ($ClSn(n\text{-}Bu)_3$, 1.4 mL, 5.2 mmol) was added dropwise to the reaction mixture. The reaction temperature was gradually raised to room temperature by removing the liquid N_2/$CHCl_3$ bath. After 1 h, CH_2Cl_2 (200 mL) was added to the reaction mixture and washed with 1 N $NaHCO_3$ (200 mL) aqueous solution. The organic layer was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, $CHCl_3$) to give the compound **11** as a dark green oil. Yield: 1.5 g (49%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ=0.90 (t, *J*=7.3 Hz, 9H), 1.12 (t, *J*=7.8 Hz, 6H), 1.34 (m, 6H), 1.56 (m, 6H), 4.18 (m, 2H), 4.24 (m, 2H), 4.27 (m, 2H), 4.33 (m, 2H), 6.24 (s, 1H).

BEDOT-dumbbell: The compounds **9** (0.65 g, 1.8 mmol), **11** (0.75 g, 1.8 mmol), and $Pd(PPh_3)_4$ (30 mg, 3.5×10^{-5} mol) were dissolved in dry DMF (5 mL). The solution was deaerated three times. The reaction mixture was stirred under dark and Ar atmosphere at 65 °C for 16 h. The solvent was removed in vacuo. The residue was directly subjected to the column chromatography (SNAP Cartridge silica 50 g, CH_2Cl_2/AcOEt: 3%=2 column, 3→15%=4 column, 15%=4 column). The recovered fraction containing the product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, $CHCl_3$) to give **BEDOT-dumbbell** as a pale yellow oil. Yield: 0.68 g (78%). ^{1}H NMR (CD_3CN, 600 MHz): δ=1.20 (d, *J*=7.2 Hz, 12H), 3.41 (m, 2H), 3.71 (m, 4H), 3.80 (m, 2H), 3.85 (m, 2H), 3.88 (m, 2H), 4.16 (m, 2H), 4.25 (m, 2H), 4.32–4.36 (m, 6H), 6.36 (s, 1H), 6.96 (d, *J*=8.6 Hz, 2H), 7.08–7.16 (m, 3H), 7.63 (d, *J*=8.6 Hz, 2H); ^{13}C NMR (CD_3CN, 150 MHz): δ=24.3, 26.9, 65.6, 65.7, 65.8, 66.0, 68.5, 70.4, 71.2, 71.5, 75.0, 98.5, 107.6, 110.3, 115.0, 115.8, 125.0, 125.6, 126.8, 127.9, 138.1, 138.2, 138.7, 142.5, 142.9, 154.1, 158.6 ppm; IR (KBr): 3105, 2960, 2924, 2868, 1602, 1572, 1521, 1504, 1473, 1438, 1361, 1282, 1249, 1186, 1120, 1087, 1066, 945, 904, 829, 796, 761, 713, 675, 636, 522, 418 cm^{-1}; HRMS (ESI): found *m*/*z*=689.2190 $[M+Na]^+$; $C_{36}H_{42}O_8S_2Na$ requires 689.2219.

BEDOT-[2]Rx: **BEDOT-dumbbell** (0.35 g, 0.52 mmol), **10** (1.1 g, 1.6 mmol), and α,α′-dibromo-*p*-xylene (0.41 g, 1.6 mmol) were dissolved in dry DMF (10 mL). The mixture was stirred at room temperature under dark and Ar atmosphere for 7 days. AcOEt was added to the solution. The solution and the precipitate were directly subjected to the column chromatography (SiO_2). **BEDOT-dumbbell** and other impurities were eluted out by AcOEt, and then CH_2Cl_2/MeOH=9:1. The product was eluted out the mixed solvent (MeOH/2 N NH_4Cl aq/$MeNO_2$=6:3:1). The recovered green solution was concentrated, then the residue was subjected to the column chromatography again (SiO_2, MeOH/2 N NH_4Cl aq/$MeNO_2$=6:3:1). The recovered green solution was concentrated to the half volume by the evaporation. An aqueous solution of NH_4PF_6 was added until no further precipitation occurred. The green-color precipitate was recovered by filtration. The precipitate was dissolved in Me_2CO and the solution was added to the NH_4PF_6 aqueous solution to complete the counter-ion exchange. The precipitate was recovered by filtration, washed with small amount of pure water, and dissolved in Me_2CO. After the evaporation, the product **BEDOT-[2]Rx** was obtained as a green solid. Yield: 74 mg (8%). Mp: >280 °C; ^{1}H NMR (CD_3CN, 600 MHz): δ=1.20 (d, *J*=6.9 Hz, 12H), 3.34 (m, 2H), 3.78 (m, 2H), 3.83 (d, *J*=8.4 Hz, 2H), 3.89–3.97 (m, 10H), 4.01 (d, *J*=8.4 Hz), 4.47 (m, 2H), 4.57–4.61 (m, 4H), 4.74 (m, 2H), 5.78 (br, 8H), 6.55 (s, 1H), 7.09–7.16 (m, 3H), 7.86 (br, 8H), 7.91 (s, 8H), 8.91 (br, 8H); ^{13}C NMR (CD_3CN, 150 MHz): δ=24.4, 26.9, 30.8, 65.6, 65.7, 65.9, 66.2, 66.6, 68.7, 70.5, 71.1, 71.5, 71.6, 74.9, 99.4, 108.9, 110.4, 110.8, 114.3, 124.5, 125.2, 125.9, 127.5, 131.7, 138.1, 138.6, 138.7, 139.1, 142.7, 142.8, 145.7, 147.9, 153.8, 155.9 ppm; IR (KBr): 3128, 3064, 2964, 2929, 2872, 1635, 1560, 1518, 1473, 1442, 1363, 1280, 1253, 1180, 1157, 1089, 1066, 945, 839, 789, 740, 640, 559, 519, 418 cm^{-1}; HRMS (ESI): found *m*/*z*=443.8200 $[M-3PF_6]^{3+}$; $C_{72}H_{74}F_6N_4O_8PS_2$ requires 443.8197.

2T-dumbbell: ^{1}H NMR (CD_3CN, 600 MHz): δ=1.21 (t, *J*=7.0 Hz, 6H), 3.51 (m, 4H), 3.54–3.61 (m, 8H), 3.61–3.67 (m, 10H), 3.72–3.78 (m, 6H), 3.89 (t, *J*=4.8 Hz, 2H), 4.17 (t, *J*=4.8 Hz, 2H), 4.41 (s, 2H), 4.48 (s, 2H), 6.93 (d, *J*=9.0 Hz, 2H), 7.18 (d, *J*=4.8 Hz, 1H), 7.28 (s, 1H), 7.33 (d, *J*=5.4 Hz, 1H), 7.51 (d, *J*=9.0 Hz, 2H); ^{13}C NMR (CD_3CN, 150 MHz): δ=15.5, 62.1, 67.0, 67.1, 67.2, 67.8, 69.8, 70.1, 70.2, 70.7, 70.9, 71.0, 71.2, 72.8, 115.4, 124.0, 126.6, 127.3, 129.2, 131.1, 138.8, 139.7, 145.1, 158.9; IR (KBr): 3088, 2970, 2866, 1606, 1508, 1458, 1348, 1292, 1251, 1179, 1111, 937, 889, 827, 748, 698 cm^{-1}; HRMS (ESI): found *m*/*z*=705.2752 $[M+Na]^+$; $C_{34}H_{50}O_{10}S_2Na$ requires 705.2743.

BEDOT-dumbbell: ^{1}H NMR (CD_3CN, 600 MHz): δ=2.87 (t, *J*=5.8 Hz, 1H), 3.52 (t, *J*=5.5 Hz, 2H), 3.58–3.63 (m, 4H), 3.65 (m, 2H), 3.80 (m, 2H), 4.13 (m, 2H), 4.24 (m, 2H), 4.32–4.36 (m, 6H), 6.36 (s, 1H), 6.96 (d, *J*=9.0 Hz, 2H), 7.64 (d, *J*=9.0 Hz, 2H); ^{13}C NMR (CD_3CN, 150 MHz): δ=61.9, 65.5, 65.7, 65.8, 66.0, 68.4, 70.2, 71.0, 71.3, 73.3, 98.5, 107.6, 110.2, 114.9, 115.8, 126.8, 127.9, 138.1, 138.2, 138.7, 142.4, 158.5; IR (KBr): 3107, 2918, 2874, 1602, 1572, 1521, 1502, 1471, 1437, 1361, 1282, 1247, 1170, 1114, 1085, 1066, 1028, 945, 904, 856, 831, 744, 675, 636, 522, 416 cm^{-1}; HRMS (ESI): found *m*/*z*=529.0931 $[M+Na]^+$; $C_{24}H_{26}O_8S_2Na$ requires 529.0967.

Acknowledgements

This work was financially supported by Grant-in-Aid for Young Scientists B, 22750175. The authors thank Bio-Organic Materials Facility of Nanotechnology Innovation Center in NIMS for the NMR measurement.

Supplementary data

^{1}H and ^{13}C NMR spectra, 2D ROESY spectra, high-resolution ESI-MS spectra of key compounds, and UV/vis spectrum of the dumbbell-shaped compounds are available. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.03.009. These data include MOL files and InChIKeys of the most important compounds described in this article.

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