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From Thiophene [2]Rotaxane to Polythiophene Polyrotaxane

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Supporting Information

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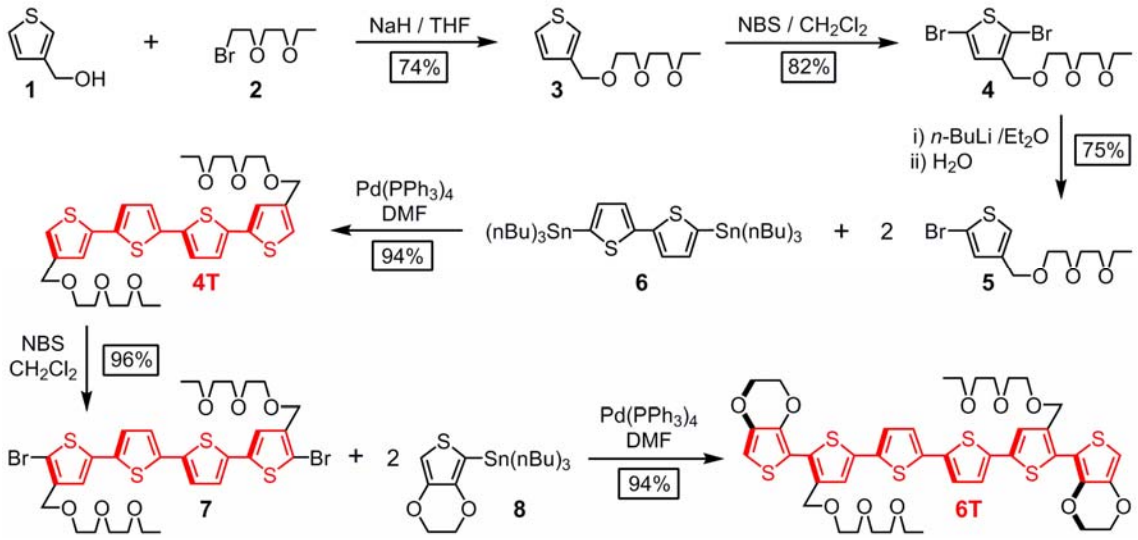
1. General

3-Thiophenemethanol, *N*-bromosuccinimide, 3,4-ethylenedioxythiophene were purchased from Sigma-Aldrich. *n*-Butyllithium in *n*-hexane was purchased from Kanto Kagaku. 2-(2-Ethoxyethoxy)ethanol, 2,2'-Bithiophene, tetrakis(triphenylphosphine) palladium(0) [$Pd(PPh_3)_4$], and α,α'-dibromo-*p*-xylene were purchased from Tokyo Chemical Industry. Sodium hydride in oil, tributyltin chloride, 4,4'-bipyridyl, ammonium chloride, ammonium hexafluorophosphate, and all of the (dry) solvents were purchased from Wako Pure Chemical Industries. All of the reagents and solvents were used without further purification. 1-Bromo-2-(2-ethoxyethoxy)ethane (**2**)[1], 5,5'-distannylated-2,2'-bithiophene (**6**)[2], 2-stannylated-3,4-ethylenedioxythiophene (**8**)[3] and cyclobis(paraquat-*p*-phenylene) tetrakis(hexafluorophosphate) (**CBPQT$_4$**•PF_6)[4] were prepared according to literature procedures. Column chromatography was carried on silica gel (Wakogel® C-400HG) or on Biotage® SNAP cartridge with SP1™ FLASH purification system (Biotage). The preparative HPLC was performed on the high resolution hydrophobic size exclusion column (JAIGEL-1H and JAIGEL-2H, Japan Analytical Industry Co. Ltd.) equipped with a controller (LC-9104, Japan Analytical Industry Co. Ltd.). Deuterated solvents for NMR analysis were purchased from Kanto Kagaku and used as received. NMR spectra were recorded on a Bruker DRX600 (600 MHz and 150 MHz for ^1H and ^{13}C nuclei, respectively) or a JEOL JNM-AL300/BZ FT NMR system (300 MHz and 75 MHz for ^1H and ^{13}C nuclei, respectively) with residual solvent as the internal standard. High resolution electrospray ionization (HR-ESI) mass spectra were obtained on a mass spectrometer equipped in the LCMS-IT-TOF system (Shimadzu, Co.). The absorption spectra were recorded at room temperature on a UV-3600 UV-Vis-NIR spectrophotometer (Shimadzu Co.). The electrochemical measurement was carried out at room temperature in argon-purged MeCN, with an ALS Electrochemical Analyzer, Model 612B (ALS Co.). The sample concentration (sexithiophene or thiophene [2]rotaxane) was set to 1.0 mM. A glassy carbon working electrode (0.07 cm^2, ALS Co.) was polished routinely with a 0.05-μm alumina/water slurry on a felt surface immediately before use. The counter and reference electrodes were a platinum wire and an SCE (ALS Co.). TBA·ClO_4 (0.1 M) was used as 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 $E_{1/2} = E_{max} + \Delta E/2$.[5] ΔE was set to 50 mV. The spectroelectrochemical measurements were performed in a quartz cell (T-5 UV10, Tosoh Co.) with immersing three electrodes in the solution. The working electrode was an ITO coated glass slide (Aldrich, Resistivity: 8−12Ω/sq). Pt and Ag wires were used as a counter electrode and a pseudo-reference electrode, respectively. The polythiophene or polythiophene polyrotaxane were prepared on the ITO coated glass slide by the potential scan from 0.0 V to +1.2V (Solvent: MeCN, Sample concentration: 1 mM, Supporting electrolyte: TBA·ClO_4,

Supporting electrolyte concentration: 0.1 M). The functionalized ITO electrode was washed thoroughly before spectroelectrochemistry measurement. The absorption spectra were recorded by UV-3600 UV-Vis-NIR spectrophotometer (Shimadzu Co.) with controlling the potential using ALS Electrochemical Analyzer, Model 612B (ALS Co.). Each spectrum was observed after applying the potential in 60 seconds. The absorption of the background including the absorptions of the solvent and ITO coated glass slide was subtracted from the original spectrum.

2. Synthesis of the dumbbell-shaped molecule 6T



Scheme S1 Synthesis of the dumbbell-shaped molecule **6T**

Compound 3: 3-Thiophenemethanol (**1**, 3.0 g, 2.6 × 10^{-2} mol) was dissolved in dry THF (20 mL). NaH in mineral oil (60 wt%, 1.5 g) was added portionwise to the solution under Ar. The solution was stirred for 30 min under nitrogen atmosphere at room temperature. 1-Bromo-2-(2-ethoxyethoxy)ethane (**2**, 10.0 g, 5.1 × 10^{-2} mol) dissolved in dry THF (10 mL) was added to the solution. The reaction mixture was stirred at 60 ºC for 14h. After cooling to 0 ºC, NaH was quenched with aqueous solution (H_2O/Me_2CO = 1:9). After removing the solvent by evaporation, the residue was dissolved in CH_2Cl_2 and washed with 1N NaCl aqueous solution. The organic layer was dried ($MgSO_4$), filtered and evaporated. The unreacted **2** was removed by column chromatography (SNAP Cartridge silica 100g, Hexane/AcOEt: 30% = 1 column, 30→80% = 6 column). The unreacted **1** was removed to by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, $CHCl_3$). The compound **3** was recovered as a colorless oil. Yield: 4.5 g (74 %). ^{1}H NMR ($CDCl_3$, 300MHz): δ = 1.21 (t, 3H), 3.48−3.68 (m, 10H), 4.57 (s, 2H), 7.07 (d, *J* = 4.7 Hz, 1H), 7.22 (s, 1H), 7.28 (d, *J* = 4.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 15.5, 67.0,

68.8, 69.6, 70.2, 71.0, 123.2, 126.2, 127.7, 139.7 ppm; HRMS (ESI): found *m/z* = 253.0882 $[M+Na]^+$; $C_{11}H_{18}O_3SNa$ requires 253.0874.

Compound 4: Compound **3** (2.3 g, 1.0×10^{-2} mol) was dissolved in CH_2Cl_2 (25 mL). After cooling to –10ºC, *N*-bromosuccineimide (NBS, 4.0 g, 2.2×10^{-2} mol) was added portionwise to the solution. The solution was gradually warm up to room temperature and kept stirring overnight. The solution was washed with 10% KOH aqueous solution. The organic layer was recovered, dried with $MgSO_4$, filtrated and evaporated. The residue was purified by column chromatography (SNAP Cartridge silica 100g, Hexane/AcOEt: 10% = 2 column, 10→30% = 6 column) to afford the compound **4** as a colorless oil. Yield: 3.2 g (82 %). ^{1}H NMR ($CDCl_3$, 600MHz): δ = 1.22 (t, 3H), 3.52 (q, 2H), 3.55−3.68 (m, 8H), 4.43 (s, 2H), 7.00 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 15.5, 67.0, 67.3, 70.0, 70.2, 70.9, 71.1, 110.2, 111.6, 131.2, 139.7 ppm; HRMS (ESI): found *m/z* = 408.9103 $[M+Na]^+$; $C_{11}H_{16}Br_2O_3SNa$ requires 408.9085.

Compound 5: The compound **4** (2.0 g, 5.2 mmol) was dissolved in dry Et_2O (40 mL). After cooling to –64 ºC, *n*-BuLi (2.7 M in hexane, 2.0 mL) was added dropwise to the solution. The solution was allowed to react under Ar atmosphere for 30 min. H_2O (2.0 mL) was added to the solution and the solution was warmed up to room temperature. Et_2O (50 mL) was added to the solution and washed with 1N $NaHCO_3$ aqueous solution. The organic layer was recovered, dried with $MgSO_4$, filtered, and evaporated. The residue was purified twice by column chromatography (SNAP Cartridge silica 100g, Hexane/AcOEt: 10% = 1 column, 10→40% = 6 column, 40% = 1 column) to afford the compound **5** as a colorless oil. Yield: 1.2 g (75 %). ^{1}H NMR ($CDCl_3$, 600MHz): δ = 1.21 (t, 3H), 3.53 (q, 2H), 3.56−3.68 (m, 8H), 4.48 (s, 2H), 7.03(d, *J* = 0.9 Hz, 1H), 7.10 (d, *J* = 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 15.5, 67.0, 68.7, 70.0, 70.2, 70.9, 71.1, 112.9, 124.5, 130.4, 140.5 ppm; HRMS (ESI): found *m/z* = 330.9988 $[M+Na]^+$; $C_{11}H_{17}BrO_3SNa$ requires 330.9979.

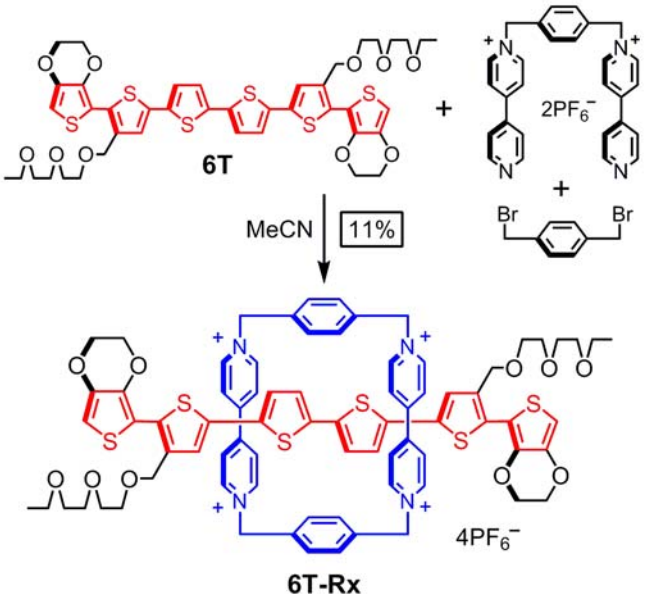
Compound 4T: The compound **5** (0.60 g, 1.9 mmol), 5,5'-distannylated-2,2'-bithiophene (**6,** 0.70 g, 9.4×10^{-4} mol), and $Pd(PPh_3)_4$ (30 mg, 2.6×10^{-5} mol) were dissolved in dry DMF (5 mL). The solution was deaerated twice. The reaction mixture was stirred at 65 ºC under Ar atmosphere for 14h. After cooling to room temperature, the solvent was removed by evaporation. The residue was dissolved in small amount of CH_2Cl_2 and directory subjected to column chromatography (SNAP Cartridge silica 50g, CH_2Cl_2/MeOH: 3→20% = 6 column). The recovered crude product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, $CHCl_3$) to give the compound **4T** as a yellow solid. Yield: 0.55 g (94 %). ^{1}H NMR ($CDCl_3$, 600MHz): δ = 1.21 (t, 6H), 3.54 (q, 4H), 3.61 (t, 4H), 3.64−3.72 (m, 12H), 4.53 (s, 4H), 7.06 (s, 4H), 7.11 (s, 2H), 7.15(s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 15.5, 67.0, 68.9, 69.8, 70.2, 71.0, 71.1,

122.3, 124.3, 124.6, 124.7, 136.3, 136.7, 137.9, 140.7 ppm; HRMS (ESI): found *m/z* = 645.1452 $[M+Na]^+$; $C_{30}H_{38}O_6S_4Na$ requires 645.1449.

Compound **7**: The compound **4T** (0.20 g, 3.2×10^{-4} mol) was dissolved in CH_2Cl_2 (10 mL). NBS (0.12 g, 6.7×10^{-4} mol) was added to the solution at –10 ºC. The solution was gradually warmed up to room temperature and kept stirring for 3 h. After adding CH_2Cl_2 (50 mL) to the solution, the solution was washed with 10% KOH aqueous solution, dried with $MgSO_4$, filtrated and evaporated. The residue was purified by column chromatography (SNAP Cartridge silica 50g, CH_2Cl_2/MeOH: 3→20% = 6 column) to afford the compound **7** as a yellow solid. Yield: 0.24 g (96 %). ^{1}H NMR ($CDCl_3$, 600MHz): δ = 1.21 (t, 6H), 3.53 (q, 4H), 3.61 (t, 4H), 3.64−3.72 (m, 12H), 4.48 (s, 4H), 7.00 (d, *J* = 4.2 Hz, 2H), 7.04 (d, *J* = 4.2 Hz, 2H), 7.07 (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 15.5, 67.0, 67.5, 70.0, 70.2, 70.9, 71.1, 110.1, 124.7, 124.8, 125.0, 135.8, 136.5, 137.5, 139.6 ppm; HRMS (ESI): found *m/z* = 800.9688 $[M+Na]^+$; $C_{30}H_{36}Br_2O_6S_4Na$ requires 800.9659.

6T: The compound **7** (0.24 g, 3.1×10^{-4} mol), 2-stannylated-3,4-ethylenedioxythiophene (**8,** 0.30 g, 7.0×10^{-4} mol), and $Pd(PPh_3)_4$ (20 mg, 1.7×10^{-5} mol) were dissolved in dry DMF (5 mL). The solution was deaerated twice. The reaction mixture was stirred at 65 ºC under Ar atmosphere for 14h. After cooling to room temperature, the solvent was removed by evaporation. The residue was dissolved in small amount of CH_2Cl_2 and directory subjected to column chromatography (SNAP Cartridge silica 50g, CH_2Cl_2/MeOH: 3→20% = 6 column). The recovered crude product was purified by the preparative HPLC (Linearly connected columns of JAIGEL-1H and JAIGEL-2H, $CHCl_3$) to give the compound **6T** as a red oil. Yield: 0.26 g (94 %). ^{1}H NMR (CD_3CN, 600MHz): δ = 1.12 (t, 6H), 3.45 (q, 4H), 3.50 (t, 4H), 3.53 (t, 4H), 3.58 (m, 8H), 4.23 (t, 4H), 4.29 (t, 4H), 4.53 (s, 4H), 6.50 (s, 2H), 7.15 (s, 4H), 7.23 (s, 2H); ^{13}C NMR (CD_3CN, 150 MHz): δ = 15.5, 65.4, 66.0, 66.9, 67.6, 70.5, 70.6, 71.1, 71.2, 100.9, 109.4, 125.6, 125.8, 126.7, 130.4, 135.9, 136.4, 136.8, 138.2, 139.9, 142.8 ppm; HRMS (ESI): found *m/z* = 925.1327 $[M+Na]^+$; $C_{42}H_{46}O_{10}S_6Na$ requires 925.1313.

3. Synthesis of the thiophene [2]rotaxane 6T-Rx



Scheme 2 Synthesis of 6T-Rotaxane

6T-Rx: The compounds **10** (130 mg, 1.4×10^{-4} M), **11**•$2PF_6$ (220 mg, 3.1×10^{-4} M) and **12** (75 mg, 2.8×10^{-4} M) were dissolved in dry MeCN (5 mL). The reaction mixture was stirred at room temperature under Ar for 7 d. AcOEt was added to the solution and the precipitate was directly subjected to the column chromatography (SiO_2). The compound **10** 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/2N NH_4Cl aq./$MeNO_2$ = 6:3:1). The recovered dark-red solution was concentrated, then the residue was subjected to the column chromatography again (SiO_2, MeOH/2N NH_4Cl aq./$MeNO_2$ = 6:3:1). The recovered dark-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 dark-green 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 dried to give the product **6T-Rx** as a green solid. Yield: 32 mg (11%).

^{1}H NMR (CD_3CN, 600MHz): δ = 1.01 (6H), 3.41 (4H), 3.58 (4H), 3.67 (4H), 3.76 (4H), 3.79 (4H), 4.38 (8H), 4.48 (4H), 5.57 (2H), 5.78 (8H), 5.89 (2H), 6.69 (2H), 6.78 (2H), 7.79 (8H), 7.88 (8H), 8.95 (8H) ; ^{13}C NMR (CD_3CN, 150 MHz): δ = 15.4, 65.5, 65.6, 66.3, 66.8, 67.5, 70.3, 71.16, 71.22, 71.4, 101.7, 108.1, 125.5, 126.3, 126.5, 127.6, 131.8, 134.4, 135.0, 136.0, 138.0, 138.2, 140.4, 143.0, 146.0, 148.5 ppm; HRMS (ESI): found *m/z* = 522.4530 $[M+PF_6]^{3+}$; $C_{78}H_{78}F_6N_4O_{10}PS_6$ requires 522.4561.

4. ^{1}H and ^{13}C spectrum of new compounds

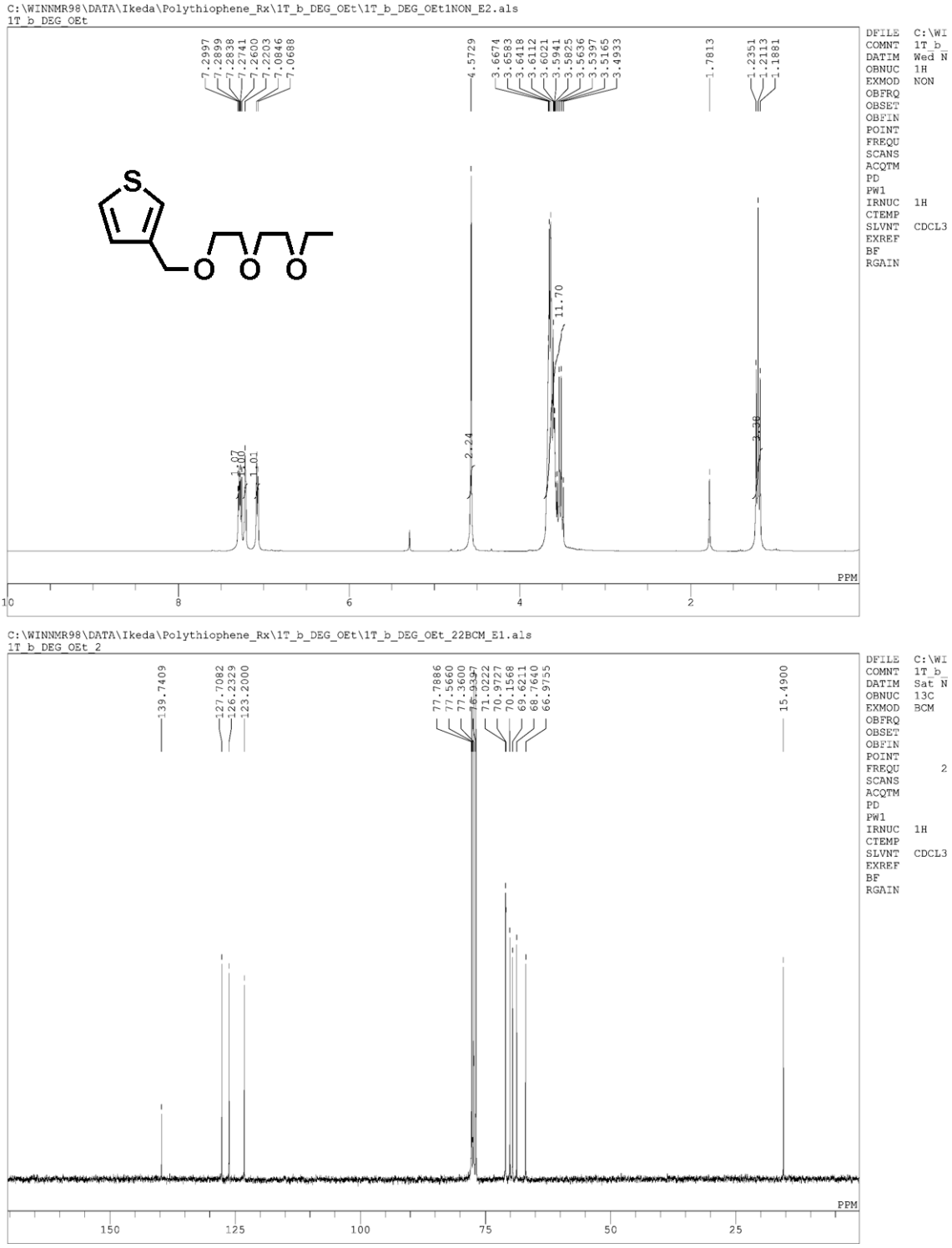


Figure S1 ^{1}H and ^{13}C NMR of the compound **3**

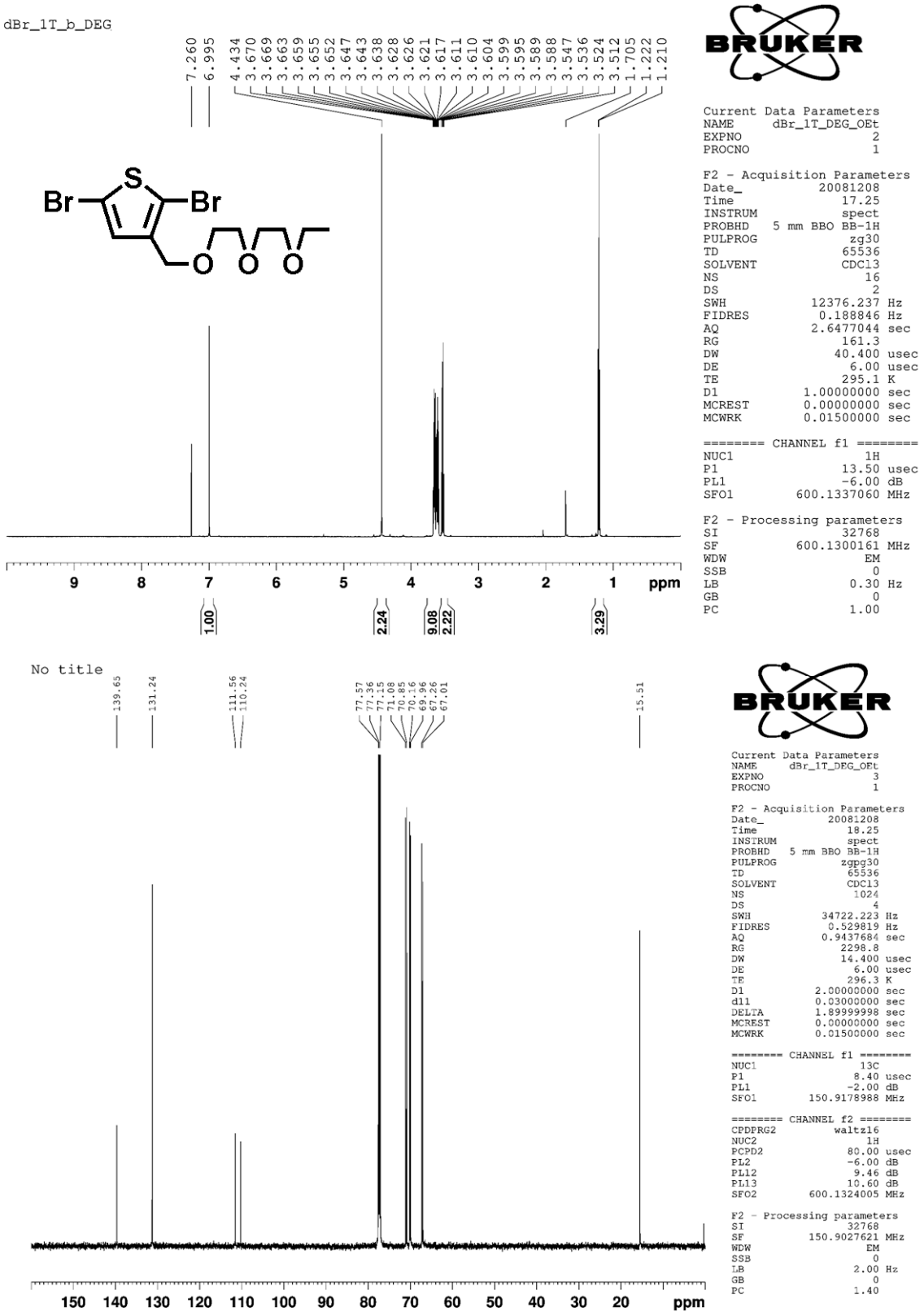


Figure S2 ^{1}H and ^{13}C NMR of the compound **4**

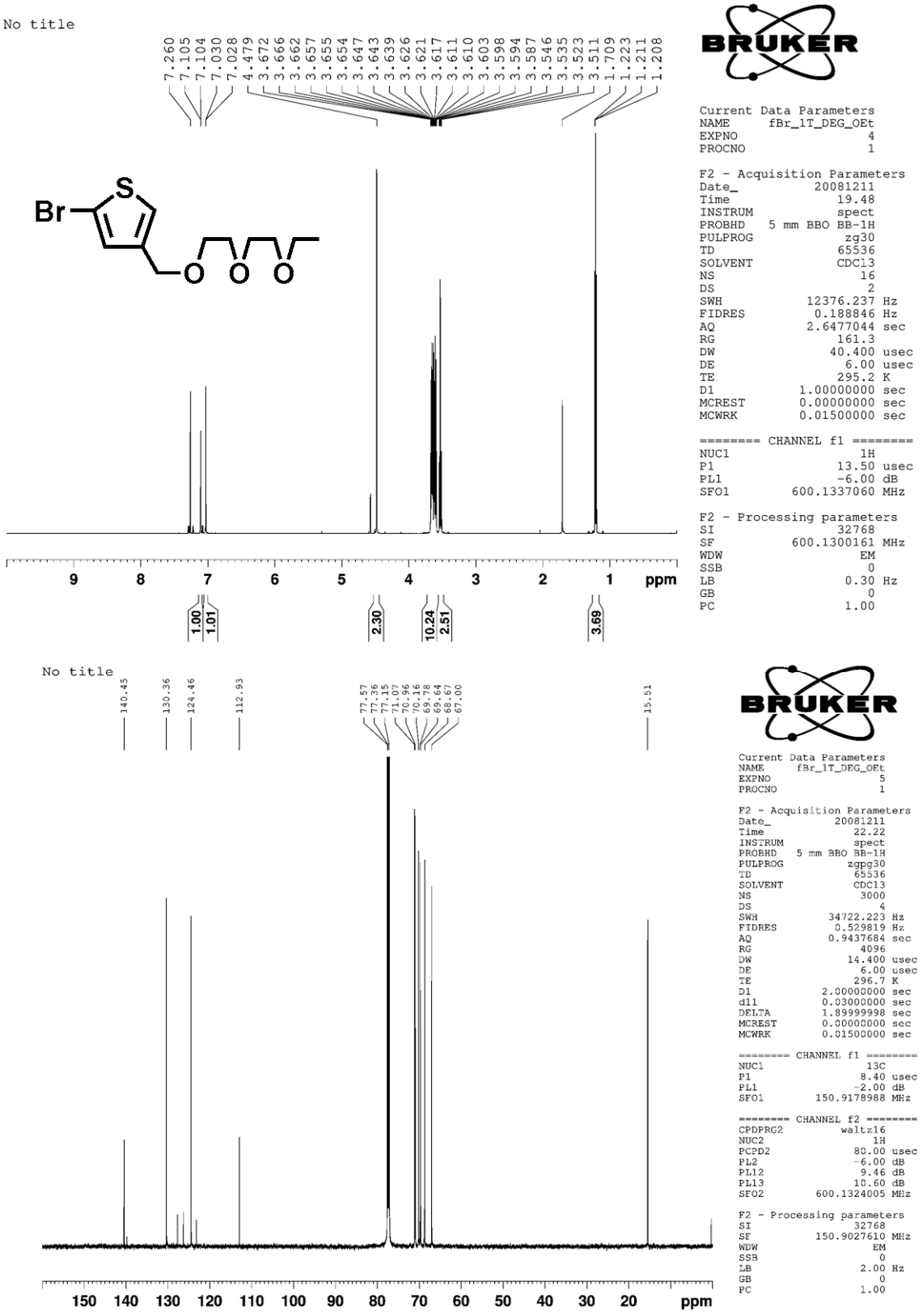


Figure S3 ^{1}H and ^{13}C NMR of the compound **5**

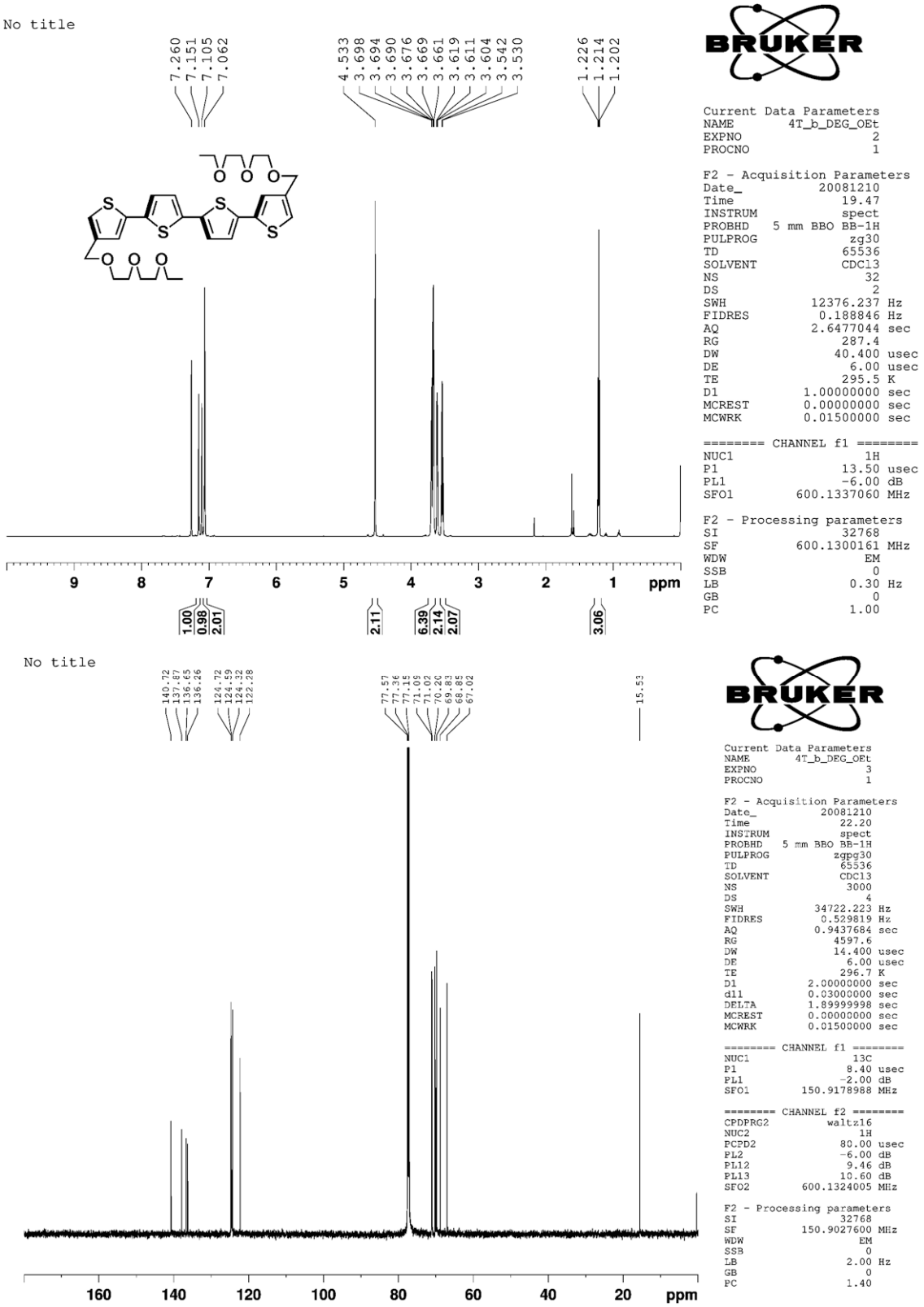


Figure S4 ^{1}H and ^{13}C NMR of the compound **4T**

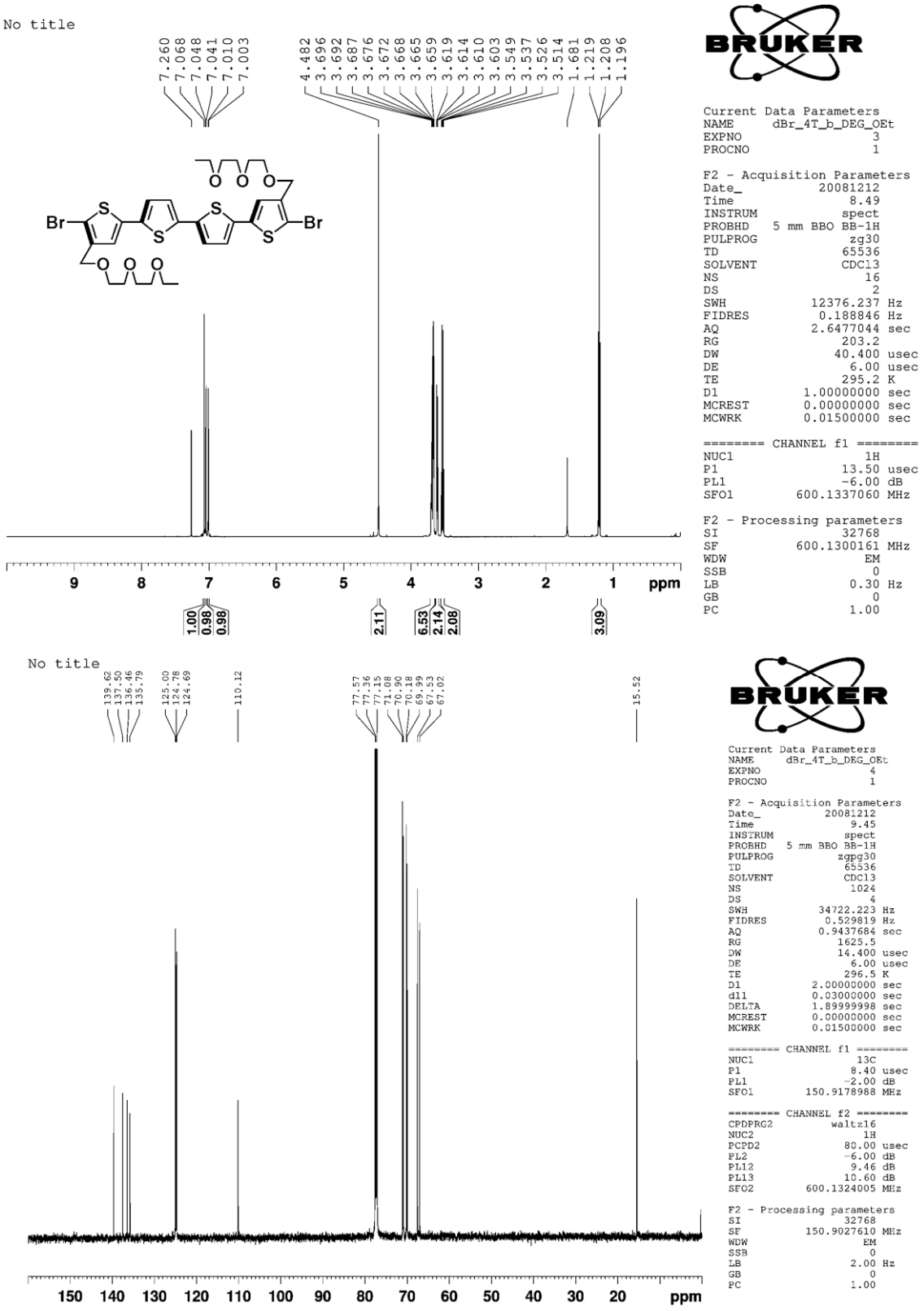


Figure S5 ^{1}H and ^{13}C NMR of the compound **7**

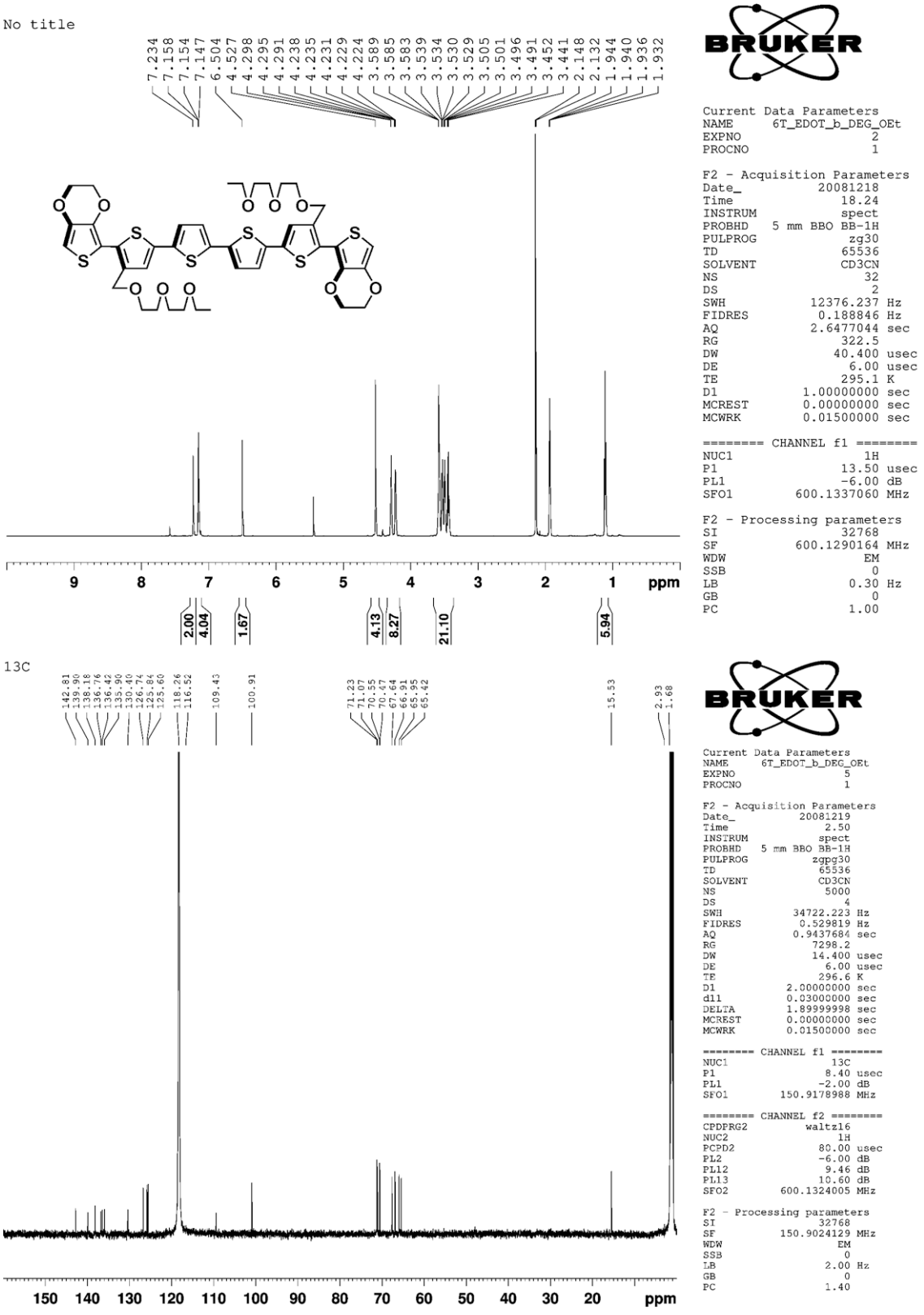


Figure S6 ^{1}H and ^{13}C NMR of the compound **6T**

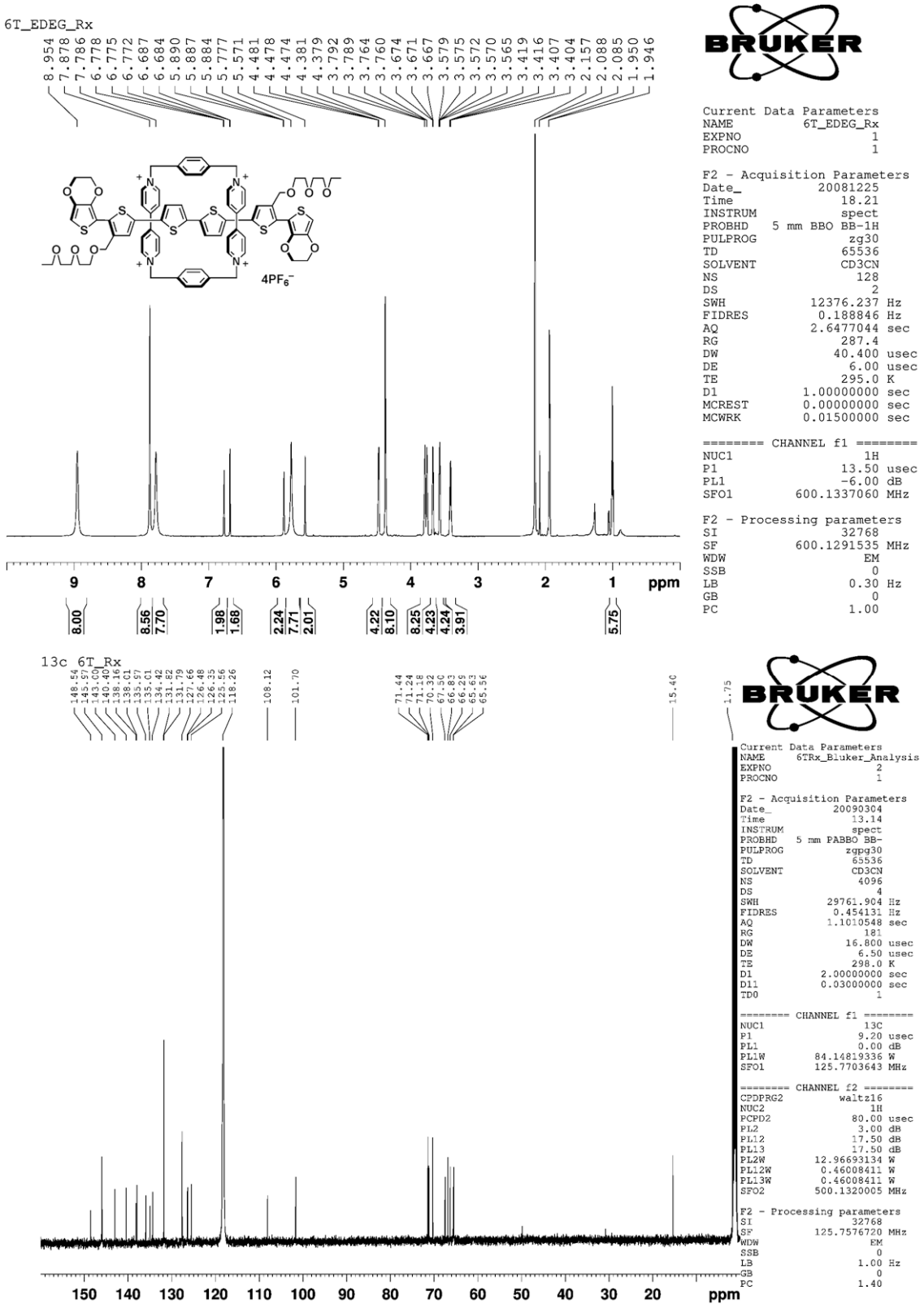
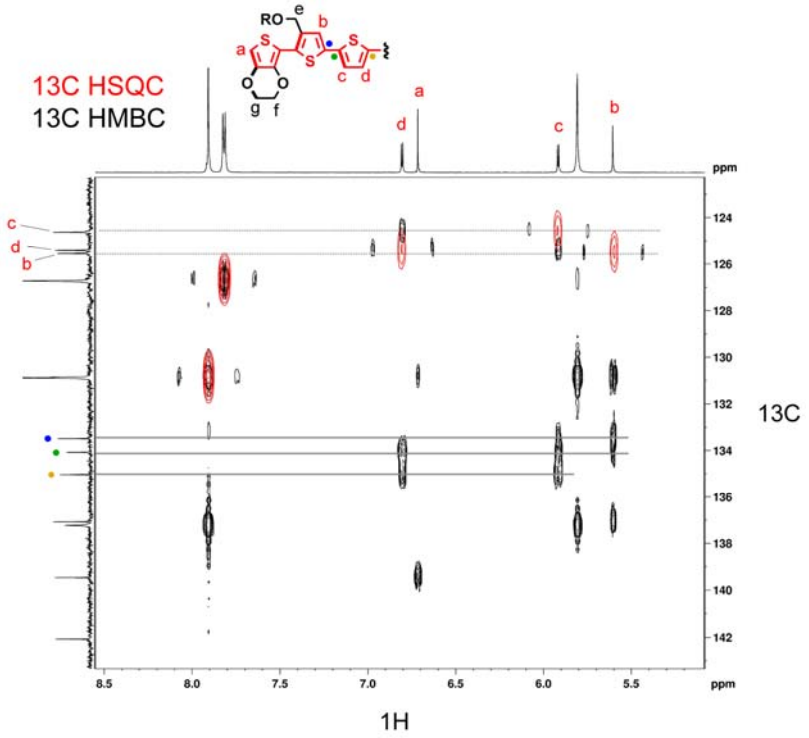
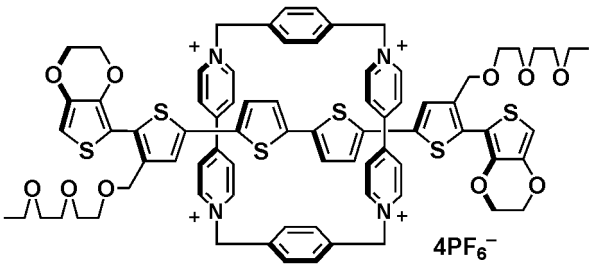


Figure S7 ^{1}H and ^{13}C NMR of the compound **6T-Rx**

5. HMQC and HMBC spectra for the ^{1}H NMR assignment of 6T-Rx



6. HR-MS of 6T-Rx



HRMS (ESI): found *m/z* = 522.4530 $[M+PF_6]^{3+}$; $C_{78}H_{78}F_6N_4O_{10}PS_6$ requires 522.4561.

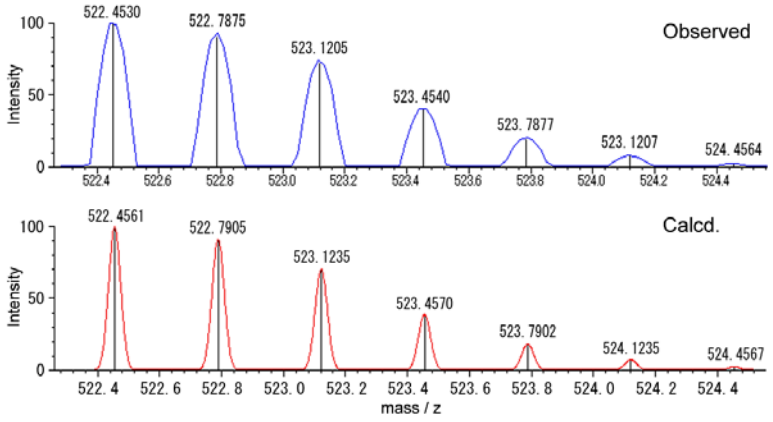


Figure S8 HR-MS of the compound **6T-Rx**

7. ^{1}H NMR titration experiment (4T vs CBPQT^{4+}·4PF$_6$)

The **CBPQT**$^{4+}$·4PF$_6$ solution (5.0 mL, 1.9 mM) was prepared using MeCN-d_3. The mixture containing **4T** (15 mM) and **CBPQT**$^{4+}$·4PF$_6$ (1.9 mM) was prepared by dissolving **4T** to the **CBPQT**$^{4+}$·4PF$_6$ solution (2.0 mL). The **CBPQT**$^{4+}$·4PF$_6$ solution (2.0 mL) was titrated by the mixture containing **4T** and **CBPQT**$^{4+}$·4PF$_6$. The chemical shift change in titration process was recorded using the NMR spectrometer at 298 K. The concentration of the guest molecule (**4T**) was calculated from the peak integral values of the α aromatic protons of **CBPQT**$^{4+}$·4PF$_6$ and the methyl protons of **4T**. The association constant K_a was calculated using a non-linear regression of the equation (1)[6] for the chemical shift change of the *p*-phenylene aromatic protons.

$$\delta_{obs} = \delta_{CBPQT} + \frac{\Delta x}{2[\mathrm{CBPQT}]}\left([\mathrm{CBPQT}] + [\mathrm{4T}] + K_a^{-1} - \sqrt{\left([\mathrm{CBPQT}] + [\mathrm{4T}] + K_a^{-1}\right)^2 - 4[\mathrm{CBPQT}][\mathrm{4T}]}\right) \qquad \text{Equation (1)}$$

δ_{CBPQT} and Δx are the chemical shift of the CBPQT^{4+} proton at [4T] = 0 and the chemical shift difference between the complexed and uncomplexed CBPQT^{4+} species, respectively.

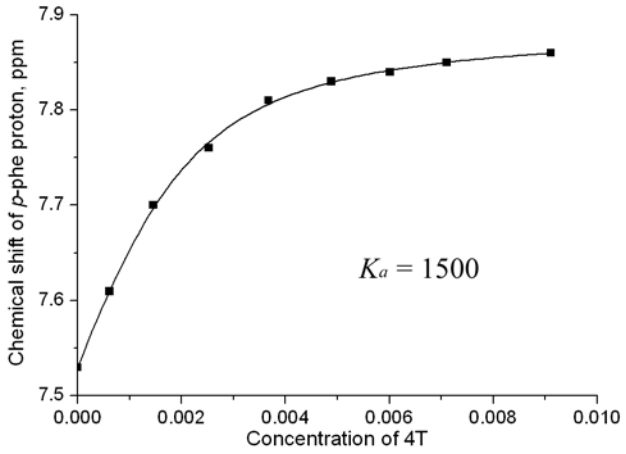


Figure S9 Chemical shift change in ^{1}H NMR titration (**4T** vs **CBPQT**$^{4+}$·4PF$_6$, MeCN, 298 K). The curve fit is depicted as solid line.

8. Complexation and Decomplexation Test – Rotaxane or Pseuro-rotaxane?

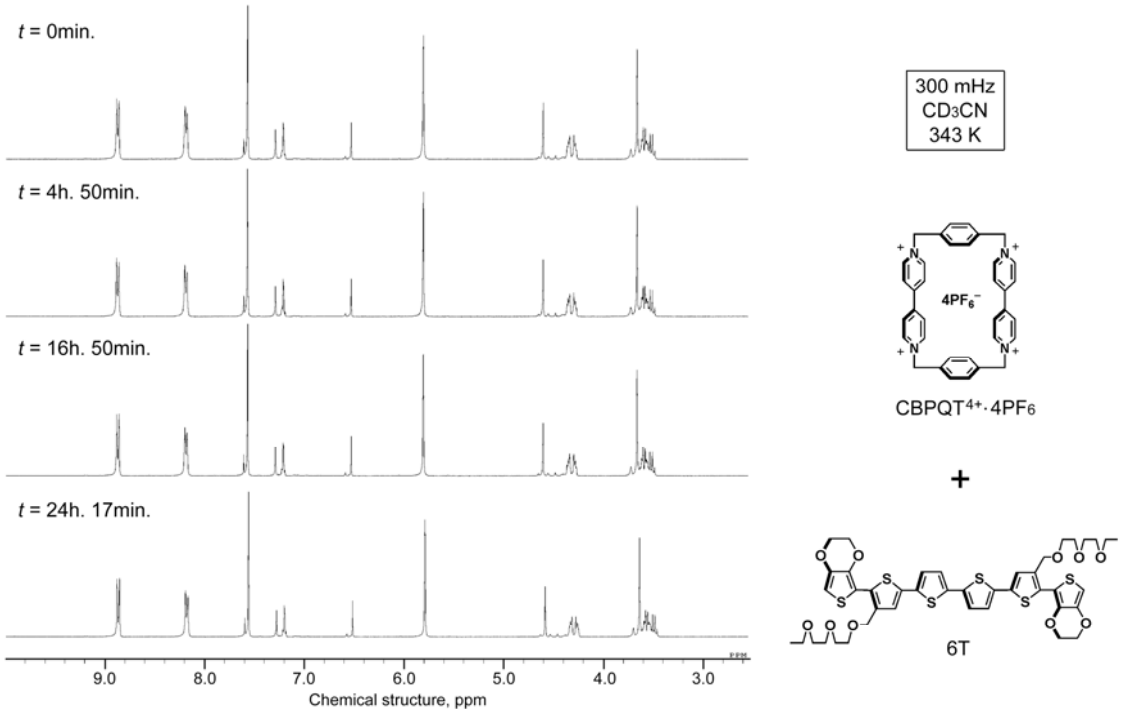


Figure S10 Time-course change in ^{1}H NMR spectrum of the mixture containing **6T** and **CBPQT**$^{4+}$·4PF$_6$ at 70ºC. *t*: Time.

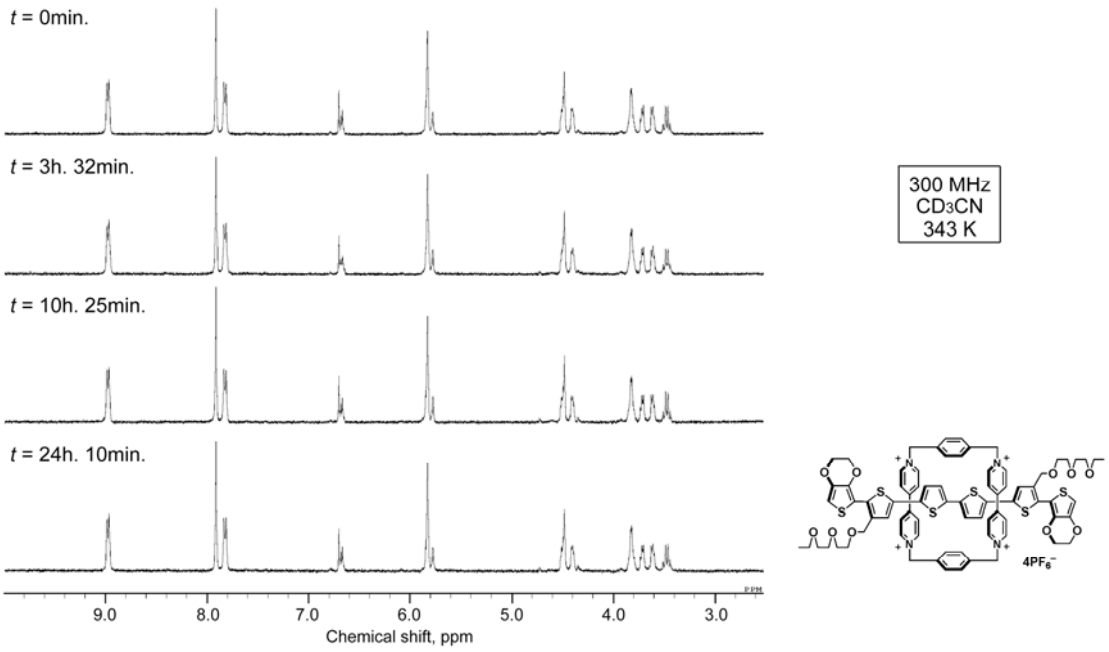


Figure S11 Time-course change in ^{1}H NMR spectrum of **6T-Rx** at 70ºC. *t*: Time.

9. UV-Vis spectra of 6T, 6T-Rx and pT-pRx

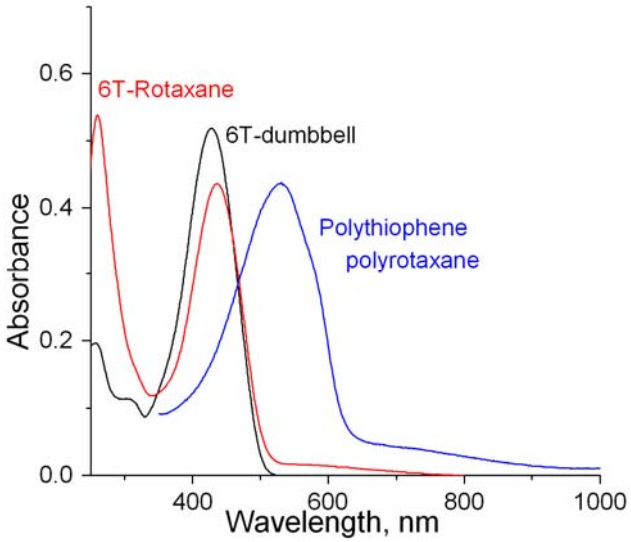


Figure S12 UV-Vis spectra of the dumbbell molecule **6T** (black), [2]rotaxane **6T-Rx** (red) solutions (Solvent: MeCN, Concentration: 1.0×10^{-5} M), and polythiophene polyrotaxane film **pT-pRx** (blue). The absorption intensity of **pT-pRx** film is normalized to that of **6T-Rx** solution.

10. Differential pulse voltammetry of 6T and 6T-Rx

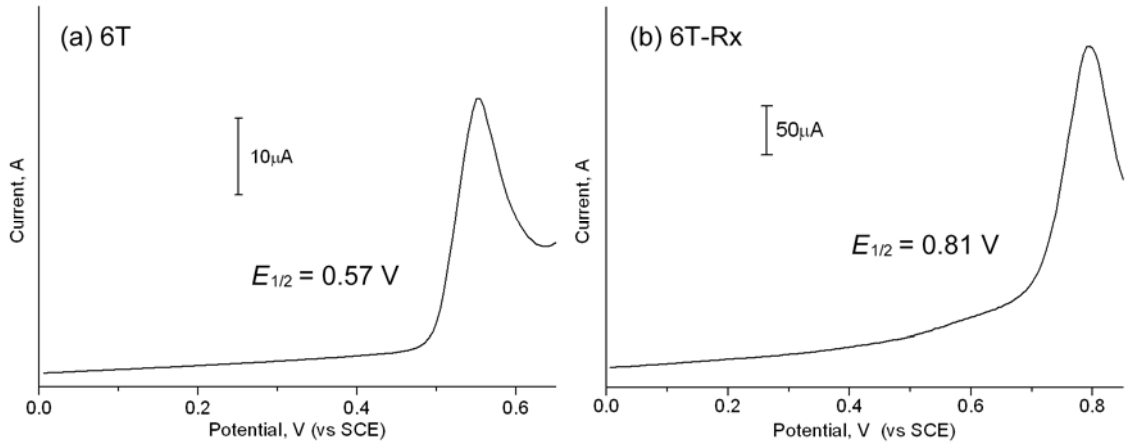


Figure S13 Differential pulse voltammograms of (a) **6T** and (b) **6T-Rx**. Solvent: argon purged MeCN, Sample concentration: 1 mM, Supporting electrolyte: 0.1 M TBA·ClO_4.

11. Change in the π-π* band in response to the applied potential

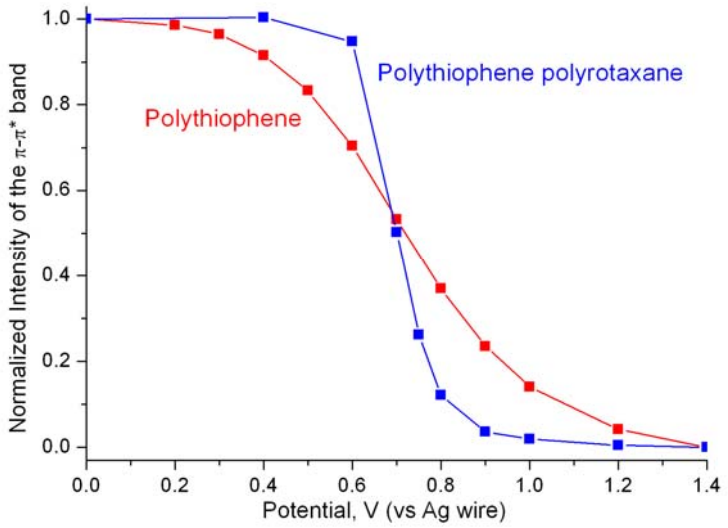


Figure S14 Relationship between the π-π* band absorption intensity and the applied potential. The absorption intensities were normalized.

12. Electrochemical reversibility of the polythiophene polyrotaxanes

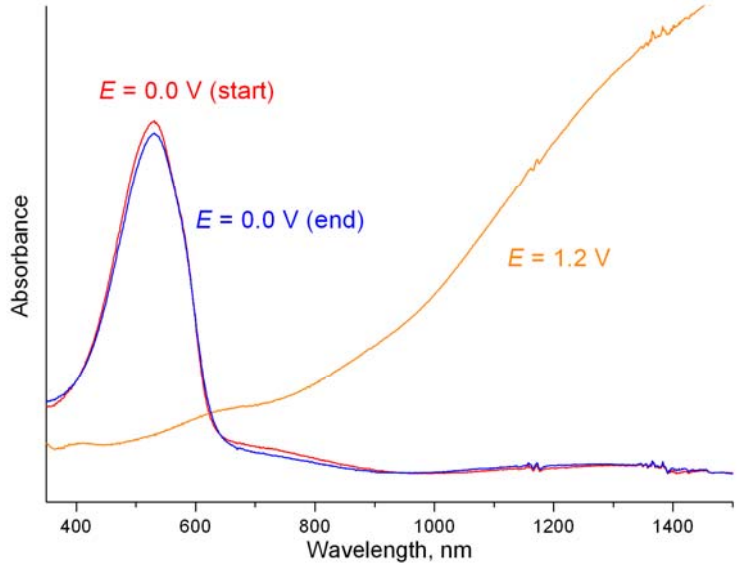


Figure S15 Comparison between the spectra before and after applying +1.2 V on the polythiophene polyrotaxane (**pT-pRx**) film

13. Peak areas in the CV trace of the polythiophene polyrotaxane film

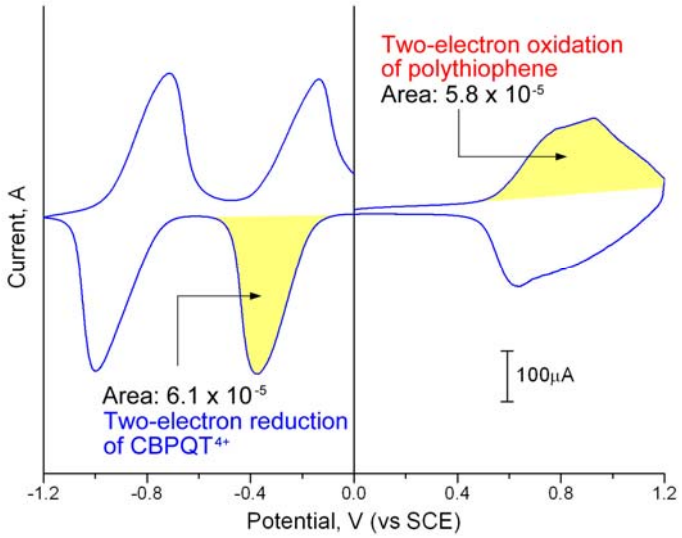


Figure S16 Peak area of the CV trace of the polythiophene polyrotaxane (**pT-pRx**) film.

14. Cyclic voltammetry of 6T and pT film

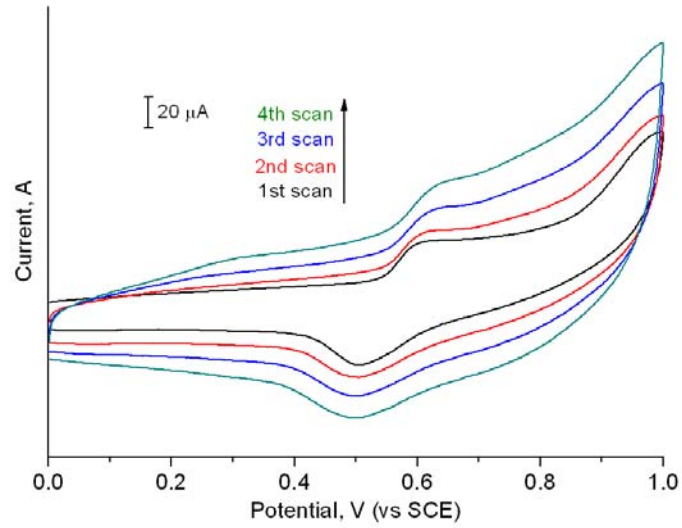


Figure S17 Cyclic voltammograms of the **6T**. Solvent: argon purged MeCN, Sample concentration: 1 mM, Supporting electrolyte: 0.1 M TBA·ClO_4. Scan rate: 200 mV s^{-1}.

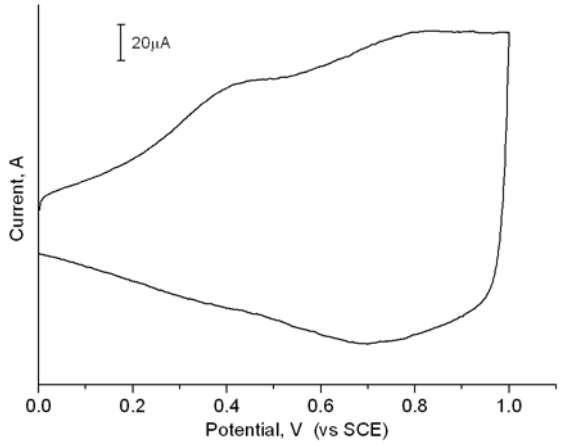


Figure S18 Cyclic voltammograms of the polythiophene **pT** film. Solvent: argon purged MeCN, Supporting electrolyte: 0.1 M TBA·ClO_4. Scan rate: 100 mV s^{-1}. The polythiophene film was prepared by the electrochemical polymerization of **6T** on ITO electrode.

15. References

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