

Supporting information

# Electrochromic properties of pyrene conductive polymers modified by chemical polymerization

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## S1. Testing equipment

Bruker AC400 (400 MHz) spectrometer to get <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra, Perkin-Elmer Spectrum One spectrometer to get FT-IR spectra, Shimadzu Corporation UV-2501 spectrophotometer to get UV-vis spectra, PerkinElmer Pyris 6 TGA to test thermal stability, SHL3-NanoFirst-2000-AFM to observe surface morphologies, SGI origin 350 server (Gaussian 03 software and Becke's three parameter gradient correction function (B3LYP)) to density functional theory (DFT) calculation, CHI 660A electrochemical workstation to cyclic voltammetry, UV-vis spectroscopy and electrochemical workstation to test spectroelectrochemical properties, kinetics and electrochemical impedance.

## S2. Synthesis of monomers (M1-M5)

### 1, 6- Dibromopyrene

Add pyrene (20.2 g, 10 mmol) to flask of carbon tetrachloride (500 mL), and dissolve bromine (10 mL, 195 mmol) in carbon tetrachloride (500 mL) and pour it into a constant pressure dropping funnel. The bromine carbon tetrachloride solution was added dropwise to the flask within 5 hours under stirring at room temperature. After reacting for 12 hours, the precipitate was collected by filtration. Stepwise recrystallization with toluene to obtain white needle-like crystals (15.6 g, 43.3 %).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.49 (d,  $J = 9.3$  Hz, 2H), 8.29 (d,  $J = 8.2$  Hz, 2H), 8.11 (dd,  $J = 26.4, 8.8$  Hz, 4H).

### 2, 5- Dibromothiophene

Thiophene (0.84 g, 10 mmol) and N-bromosuccinimide (3.916 g, 22 mmol) were dissolved in acetic acid (50 mL), and the reaction mixture was refluxed for 8 hours. Then, the reaction solution was poured into a mixture of 200 mL of chloroform and water and fully stirred and extracted. The organic layer was dried with anhydrous magnesium sulfate and filtered. The solvent was evaporated by rotary evaporation, and the crude product was purified by silica gel column chromatography using hexane as the eluent. Obtain colorless transparent liquid (1.989 g, 83 %).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  6.84 (s, 2H).

### 2- Tributylstannylthiophene

Dissolved 2-bromothiophene (3.24 g, 20 mmol) in a flask containing anhydrous THF (200 mL), removed the air in the system, and flushed with nitrogen, seal the flask and stir, cool the flask to  $-78$  °C, used a syringe to add n-butyl lithium (8 mL, 20 mmol, 2.5 M in hexanes) to the flask within 1 hour. After the addition was complete, kept the system at  $0$  °C and stirred for 1 hour, continued to cool to  $-78$  °C, and dropped within 30 minutes, then, added tributyltin chloride (5.87 mL, 22 mmol). After the reaction temperature returned to room temperature, stirring continued for 4 hours. Water (200 mL) was added to the reaction solution and extracted with n-hexane, dried with anhydrous magnesium sulfate and filtered, and the solvent was evaporated to obtain the crude

product that color transparent liquid (7.10 g, 95 %).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.66 (d,  $J = 4.8$  Hz, 1H), 7.27 (dd,  $J = 4.6, 1.5$  Hz, 1H), 7.21 (d,  $J = 3.2$  Hz, 1H), 1.43 – 1.28 (m, 12H), 1.13 – 1.08 (m, 6H), 0.97 – 0.87 (m, 9H).

### Bithiophene

Added 2-bromothiophene (1.62 g, 10 mmol), 2-tributylstannylthiophene (4.114 g, 11 mmol) and potassium carbonate (4.14 g, 30 mmol) into a 250 mL flask, added toluene (100 mL) and water (20 mL), added the catalyst tetrakis(triphenylphosphine)palladium (0.3467 g, 0.3 mmol), vented the flask and filled it with nitrogen, refluxed at 100 °C for 2 days under nitrogen protection, added water and ethyl acetate after cooling the reaction solution. After extraction, the organic phase was collected, and the solvent was evaporated under reduced pressure to obtain crude product, which was separated by silica gel column chromatography to obtain gray solid (1.19 g, 72 %).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.22 (d,  $J = 5.1$  Hz, 2H), 7.19 (d,  $J = 3.6$  Hz, 2H), 7.02 (dd,  $J = 5.3, 3.6$  Hz, 2H).

### $\alpha$ - Triple thiophene

It is prepared by the method of synthesizing dithiophene, using 2,5-dibromothiophene and twice the amount of 2-tributylstannylthiophene to obtain yellow-green solid (1.93 g, 78 %).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.22 – 7.08 (m, 6H), 7.02 (t,  $J = 4.5$  Hz, 2H).

### 2, 5- Bis(trimethylstannyl)thiophene (M1)

2, 5-dibromothiophene (1.2 g, 5 mmol), TMEDA (2.32 g, 20 mmol) were dissolved in a flask filled with anhydrous tetrahydrofuran (50 mL), the air in the flask was removed, the system was filled with nitrogen, and then sealed treatment and stirred, after the flask was cooled to -78 °C, slowly added n-butyllithium (8 mL, 20 mmol, 2.5 M in hexanes) with a syringe within 1 hour, raised the reaction temperature to 0 °C, kept the temperature and stirred for 2 hours, then dropped to after -78 °C, kept the temperature and added slowly trimethyltin chloride (5 g, 25 mmol) dissolved in 20 mL of THF, then continue to stirred and reacted at room temperature for 4 hours. Poured the reaction solution into ether (100 mL), added water, saturated sodium bicarbonate and

saturated brine for extraction, and poured the organic phase into saturated fluorine stir in sodium sulfide for one hour, then filtered out the insoluble matter and separated the liquids, collected the organic phase, dried with anhydrous sodium sulfate, filtered and collected the organic phase, and then rotated under reduced pressure to obtain the crude product. The silica gel column treated with triethylamine purify by column chromatography using n-hexane as the eluent to obtain a white solid (1.73 g, 84 %). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.38 (s, 2H), 0.37 (s, 18H).

#### 5, 7-bis (trimethylstannyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (M2)

EDOT (1 g, 7 mmol) and TMEDA (3.248 g, 28 mmol) were dissolved in a flask containing anhydrous tetrahydrofuran (70 mL), the air in the flask was removed, the system was filled with nitrogen, and the system was sealed and stirred. The flask was cooled to after stirring for 30 minutes at 0 °C, added LDA (14 mL, 28 mmol, 2.0 M in heptane/THF/ethylbenzene) dropwise within 30 minutes with a syringe, raise the reaction temperature to room temperature and stir for 1 hour, then cool the flask to at 0 °C, added trimethyltin chloride (6 g, 30 mmol) dissolved in 20 mL of THF dropwise within 30 minutes, stirred at room temperature for 4 hours, added water and ethyl acetate for extraction, separate the organic phase, and stirred the solution with saturated sodium fluoride for 1 hour. After filtering the insoluble matter and washing again with saturated brine, the organic phase was collected, and the solvent was evaporated under reduced pressure to obtain the crude product, which was purified by column chromatography with a neutral alumina silica gel column and petroleum ether was used as the eluent to obtain a white solid (2.38 g, 73 %). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 4.15 (s, 4H), 0.33 (s, 18H).

#### 5, 5'-bis (tributylstannyl)-2, 2'-bithiophene (M3)

Dissolved bithiophene (0.83 g, 5 mmol) in a flask containing tetrahydrofuran (50 mL), vented the flask, filled the system with nitrogen after venting, stirred in a closed container, and cooled to -78 °C for 1 hour slowly add n-butyl lithium (8 mL, 20 mmol, 2.5 M in hexanes) to the inner syringe, keep -78 °C and stirred for 20 minutes, the reaction solution gradually solidifies, heated the flask to room temperature and stirred for 2 hours, then added tintributyl chloride (7.2 mL, 25 mmol), the reaction solution was refluxed at 70 °C for 2 hours. After the reaction, it was poured

into diethyl ether, saturated sodium fluoride was added and stirred for 1 hour, filtered with celite, and the precipitate was filtered off with saturated hydrogen carbonate. Washed with sodium, collected the organic phase, dried with anhydrous magnesium sulfate, and evaporated the solvent. The crude product was obtained, which was separated by column chromatography on silica gel treated with triethylamine, using n-hexane as the eluent to obtain light blue transparent liquid (3.05 g, 82 %). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 3.3 Hz, 2H), 7.12 – 7.02 (m, 2H), 1.37 (q, *J* = 7.4 Hz, 12H), 1.22 – 1.06 (m, 12H), 0.93 (t, *J* = 7.3 Hz, 18H).

#### 5, 5''-bis (tributylstannyl)-2, 2':5', 2''-terthiophene (M4)

Synthesized by the method of synthesizing 5,5'-bis(tributylstannyl)-2,2'-bithiophene, tertiary thiophene (1.24 g, 5 mmol), anhydrous tetrahydrofuran (50 mL), n-butyllithium (8.02 mL, 21 mmol, 2.5 M in hexanes), tributyltin chloride (6 mL, 22 mmol) Obtained light green transparent liquid (3.60 g, 87 %). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.32 (t, *J* = 3.4 Hz, 2H), 7.10 (d, *J* = 3.8 Hz, 4H), 1.64 (p, *J* = 7.8 Hz, 12H), 1.40 (q, *J* = 7.3 Hz, 12H), 1.16 (ddd, *J* = 9.4, 6.5, 1.5 Hz, 12H), 0.95 (t, *J* = 7.3 Hz, 18H).

#### 4, 4' - Diaminotriphenylamine

Added ground potassium carbonate (18 g, 0.13 mol) to the flask, and added aniline (9.3 g, 0.1 mol), 1-fluoro-4-nitrobenzene (31.02 g, 0.22 mol) and DMF (50 mL) together into the flask. , The solution was heated to 135 °C and stirred for one day. After cooling, the reaction solution was poured into 1000 ml of ethanol: water (1:1), and continuously stirred to obtain yellow-brown solid, which was filtered and washed with hot water and recrystallized with acetic acid to obtain pure 4, 4-dinitrotriphenylamine.

Added 4,4-dinitrotriphenylamine (3.35 g, 10 mmol) into an Erlenmeyer flask, dissolved it with DMF (100 mL), added 1g 10 % Pd/C as a catalyst, and used a constant pressure dropping funnel to slowly dropwise hydrazine hydrate (3 mL) into the reaction flask and refluxed at 80 °C for 24 hours. After the reaction was completed, it was filtered while hot. The filtrate was added to cold water. A gray precipitate appeared. It was washed with distilled water, filtered and dried in

vacuo to obtain off-white needle-like crystals. (2.367 g, 86 %).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.07 – 7.00 (m, 2H), 6.78 (d,  $J = 8.2$  Hz, 4H), 6.66 – 6.47 (m, 7H), 4.94 (s, 4H).

#### 4-Pinacol formyl phenyl borate

Added 4-formylphenylboronic acid (10 g, 66.7 mmol) and pinacol (8.67 g, 73.4 mmol) into a middle flask containing ether (250 mL) and stirred overnight at room temperature. The solvent was removed by rotary evaporation to obtain light yellow solid. The obtained solid was poured into 100 mL of hot water. The solid melted, stirred while hot and separated. The lower layer solution was collected. After cooling, a white solid product (13.92 g, 90 %) was obtained.  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  10.05 (s, 1H), 7.99 – 7.93 (m, 2H), 7.89 – 7.83 (m, 2H), 1.36 (s, 12H).

#### 4, 4'-(Pyrene-1, 6-diyl) dibenzaldehyde (M5)

4, 4'-(pyrene-1, 6-diyl)dibenzaldehyde Combine 1,6-dibromopyrene (3.6 g, 10 mmol, 4-formylphenylboronic acid pinacol ester (6.96 g, 30 mmol), tetrakis(triphenylphosphine) palladium (0.36 g, 0.3 mmol)) and potassium carbonate ( 7.2 g, 52 mmol) was added to a 500 ml flask, added degassed 1,4-dioxane (150 mL) and water (30 mL), the system was vented three times, and finally filled with nitrogen. The closed system was heating to reflux at 100 °C for 48 hours. After cooling, the solution was poured into water and filtered, washed with water, methanol, ethyl acetate and dichloromethane successively, and finally dried under vacuum to obtain light yellow solid (2.996 g, 73 %)  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  10.18 (s, 2H), 8.26 (d,  $J = 7.8$  Hz, 2H), 8.19 – 7.99 (m, 10H), 7.83 (d,  $J = 7.9$  Hz, 4H).

### S3. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of individual monomers

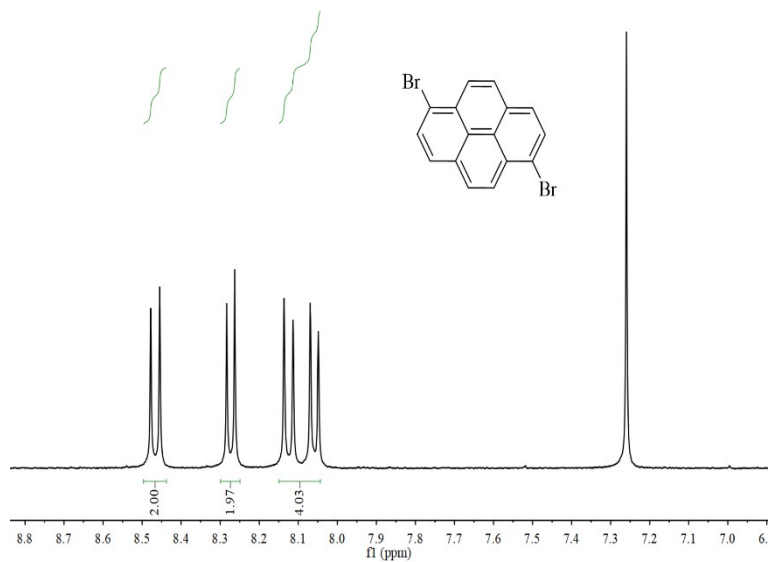


Fig. S3-1  $^1\text{H}$  NMR spectra of 1, 6- Dibromopyrene.

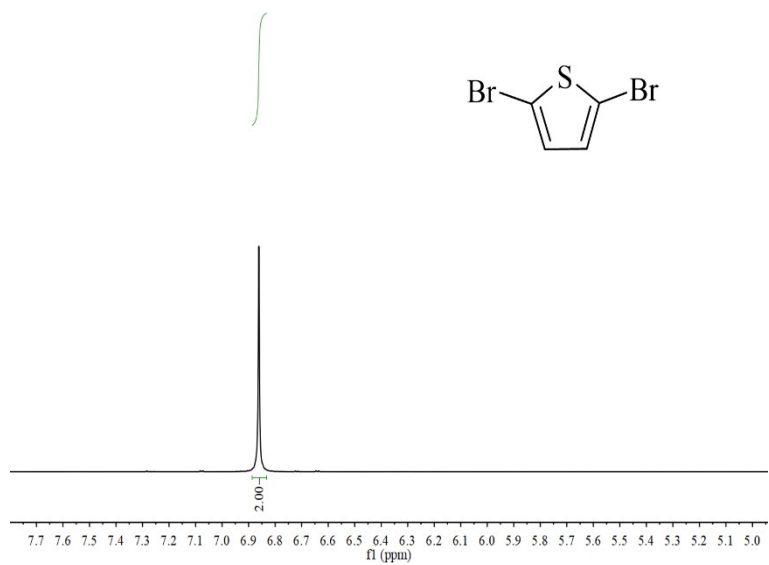
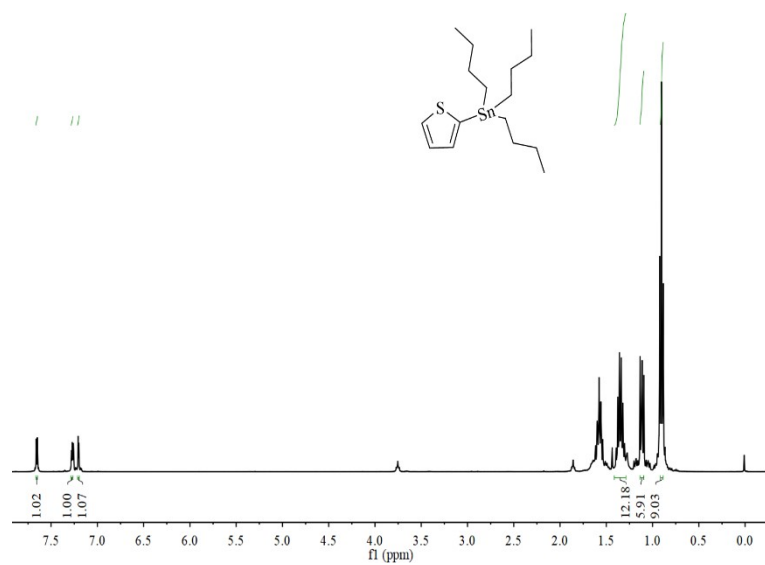
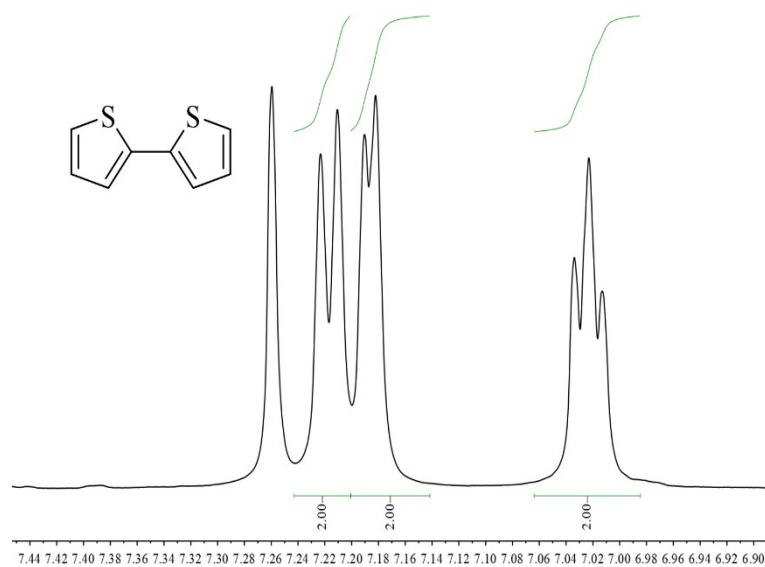


Fig. S3-2  $^1\text{H}$  NMR spectra of 2, 5- Dibromothiophene.

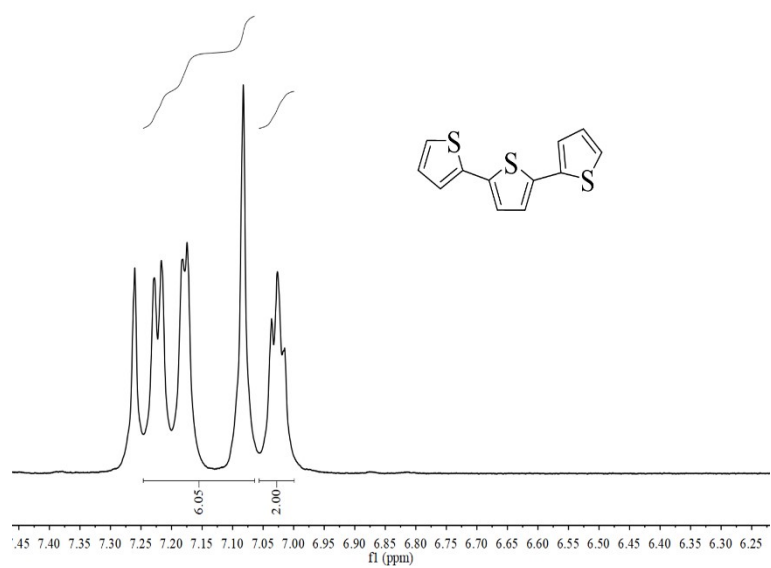


**Fig. S3-3** <sup>1</sup>H NMR spectra of 2- Tributylstannylthiophene.

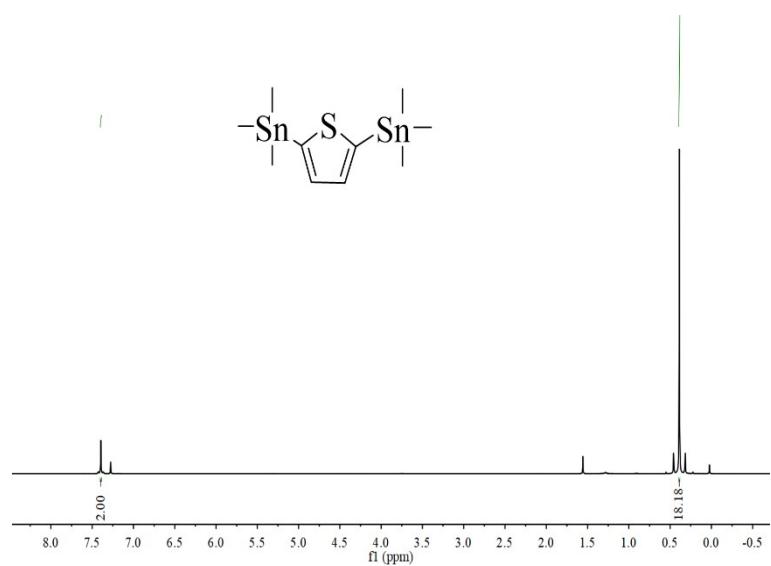


**Fig. S3-4** <sup>1</sup>H NMR spectra of Bithiophene.

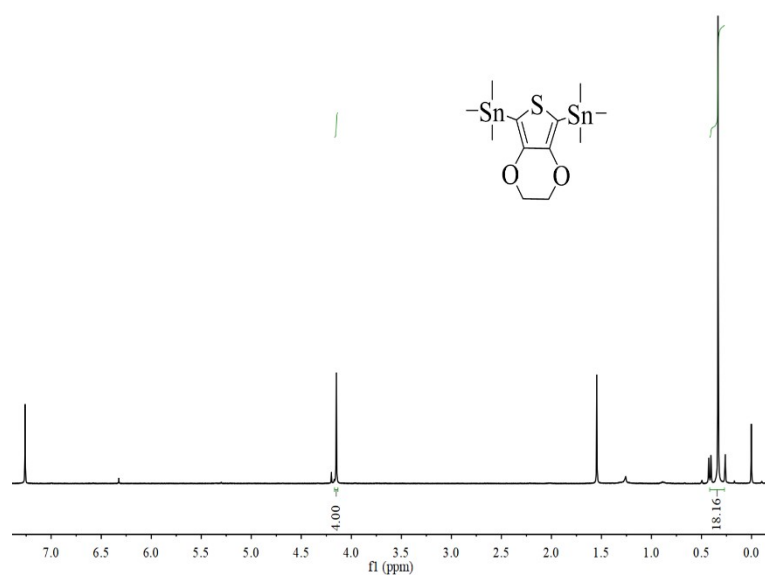




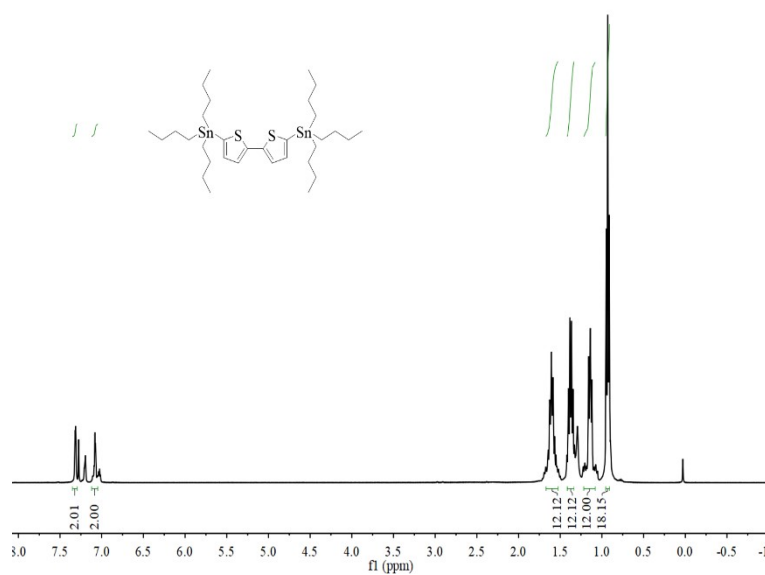
**Fig. S3-5**  $^1\text{H}$  NMR spectra of  $\alpha$ - Triple thiophene.



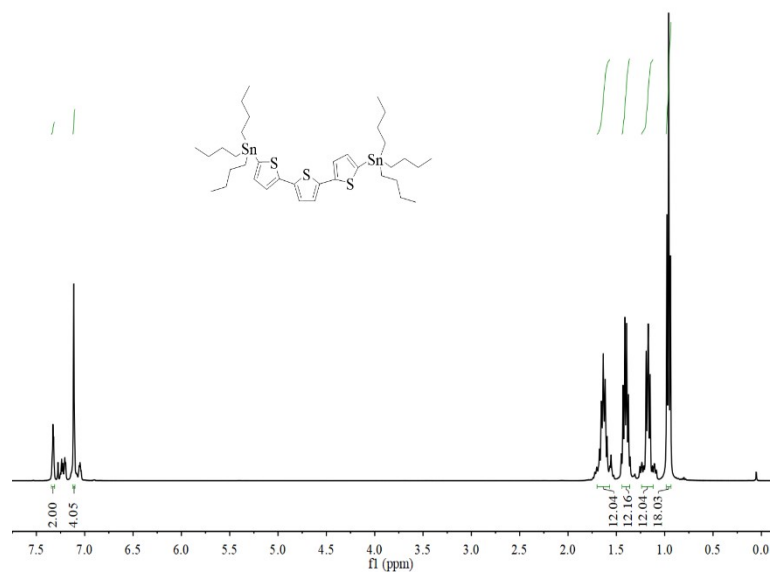
**Fig. S3-6**  $^1\text{H}$  NMR spectra of 2, 5- Bis(trimethylstannyl)thiophene.



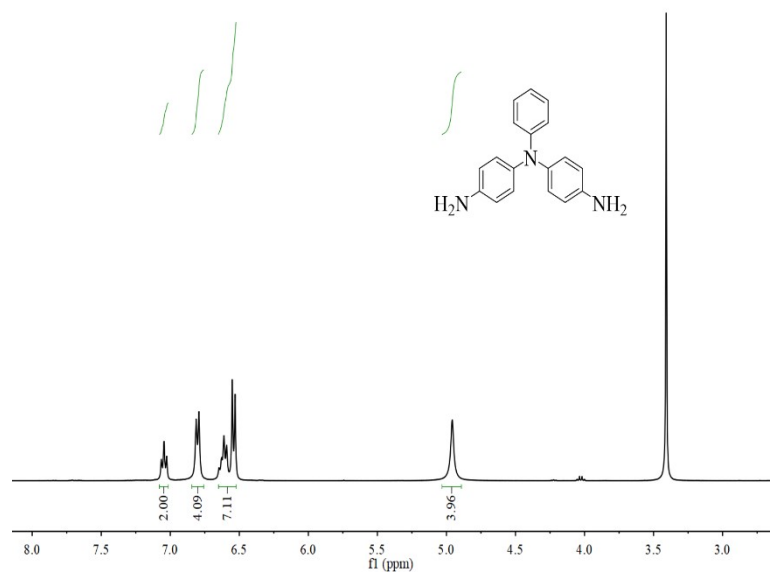
**Fig. S3-7**  $^1\text{H}$  NMR spectra of 5, 7-bis (trimethylstannyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine.



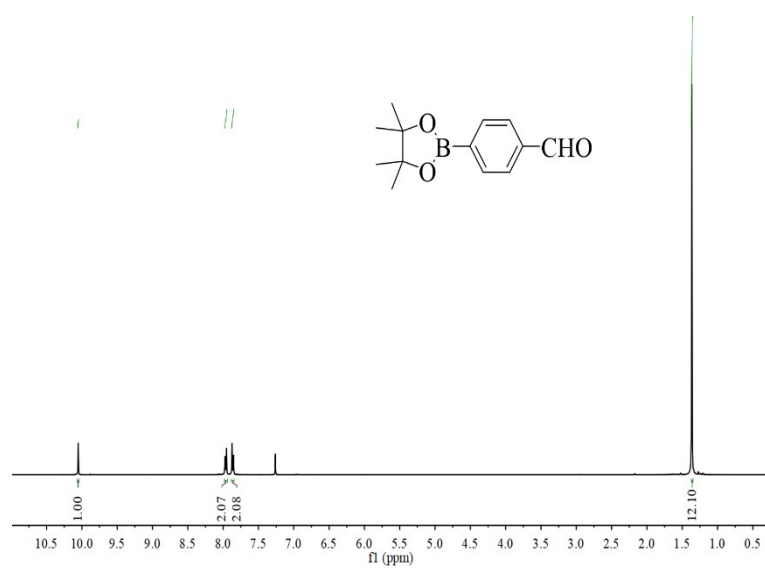
**Fig. S3-8**  $^1\text{H}$  NMR spectra of 5, 5'-bis (tributylstannyl)-2, 2'-bithiophene.



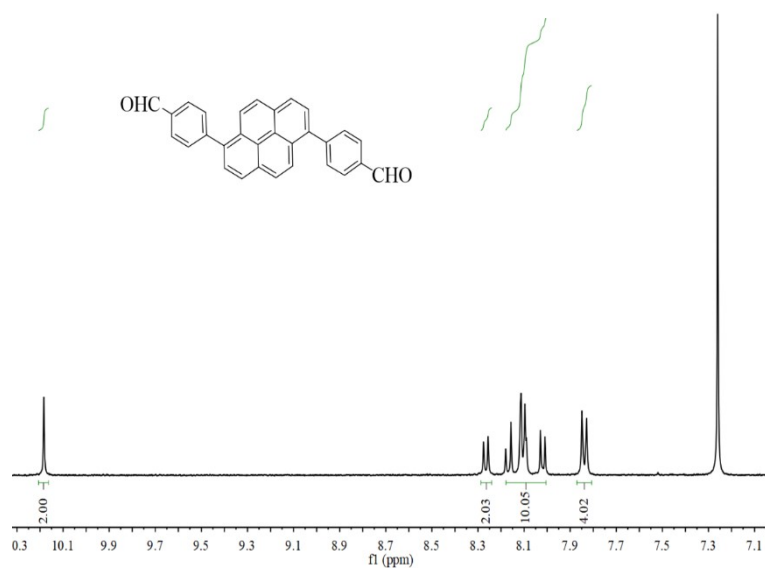
**Fig. S3-9** <sup>1</sup>H NMR spectra of 5, 5''-bis (tributylstannyl)-2, 2':5', 2''-terthiophene.



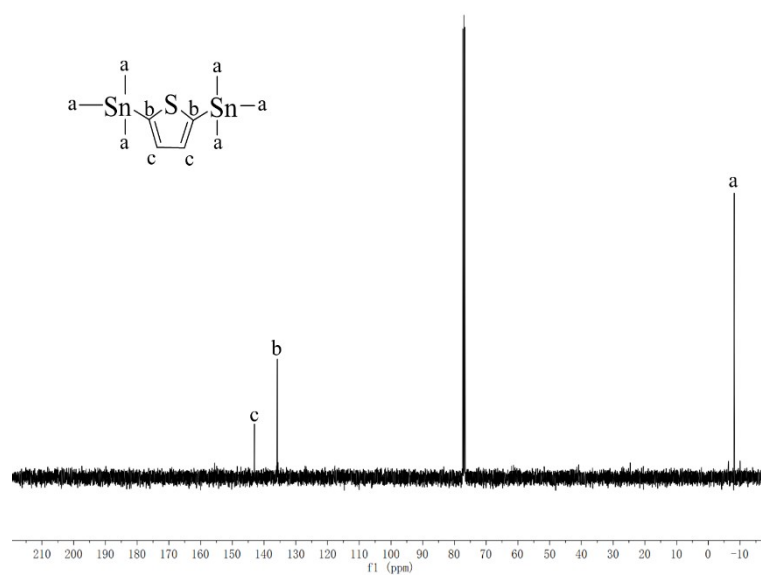
**Fig. S3-10** <sup>1</sup>H NMR spectra of 4, 4' – Diaminotriphenylamine.



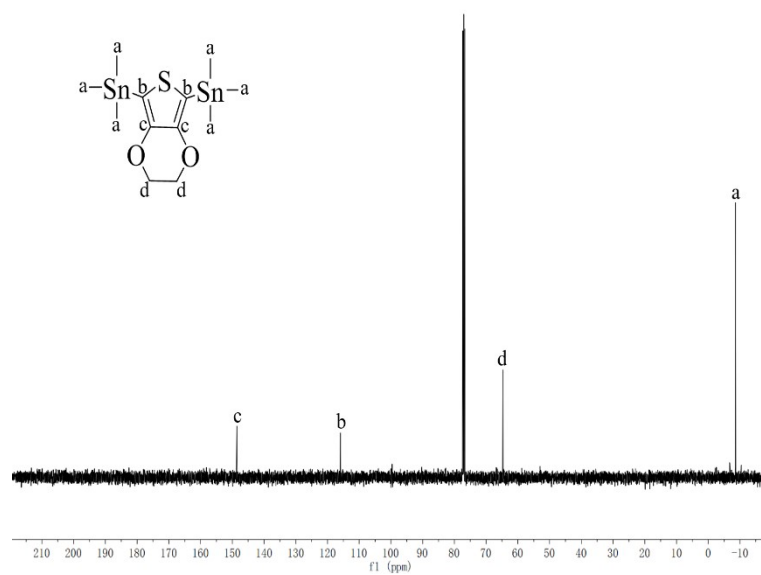
**Fig. S3-11** <sup>1</sup>H NMR spectra of 4- Pinacol formyl phenyl borate.



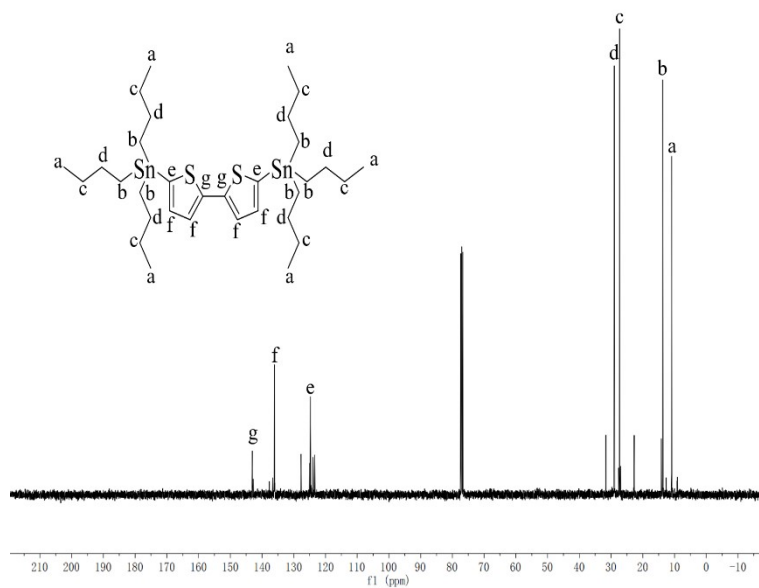
**Fig. S3-12** <sup>1</sup>H NMR spectra of 4, 4'-(Pyrene-1, 6-diyl) dibenzaldehyde.



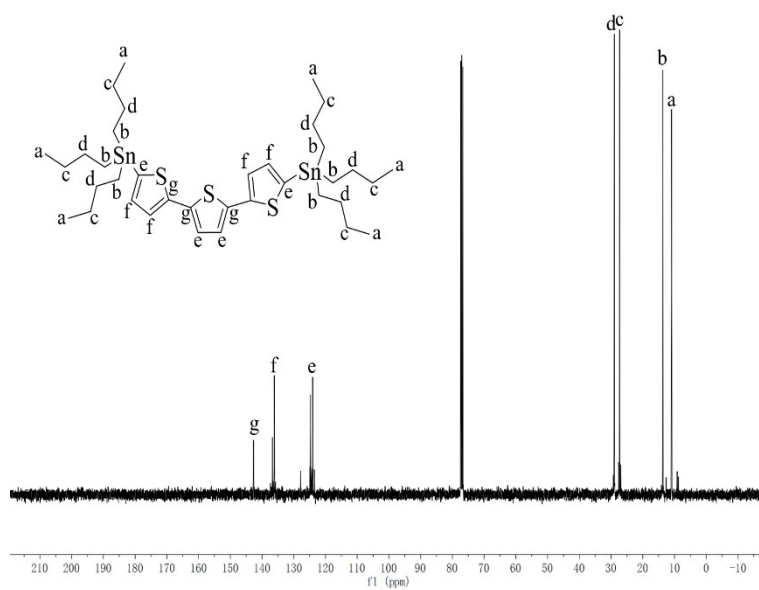
**Fig. S3-13** <sup>13</sup>C NMR spectra of M1.



**Fig. S3-14** <sup>13</sup>C NMR spectra of M2.

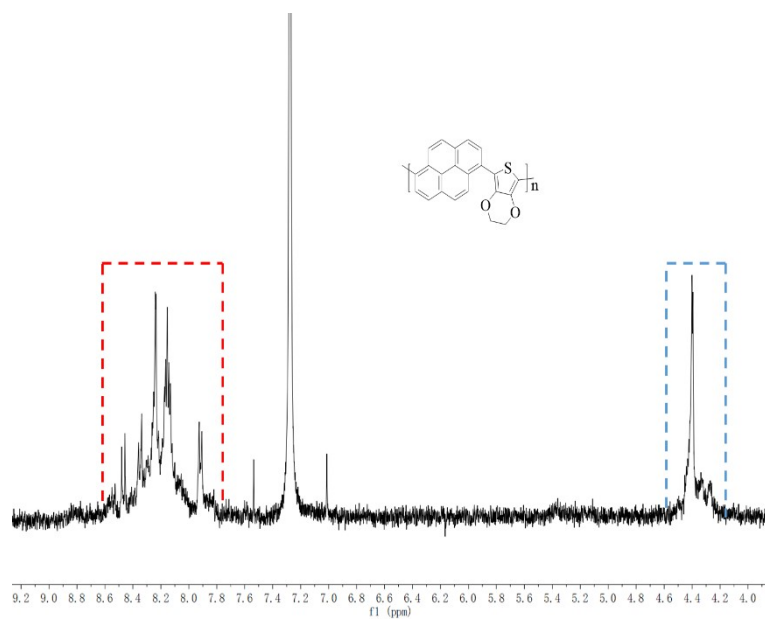


**Fig. S3-15** <sup>13</sup>C NMR spectra of M3.

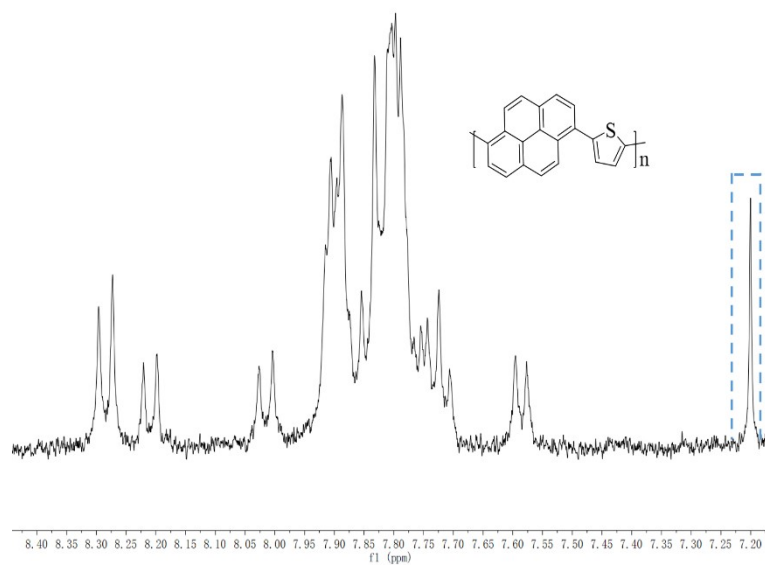


**Fig. S3-16** <sup>13</sup>C NMR spectra of M4.

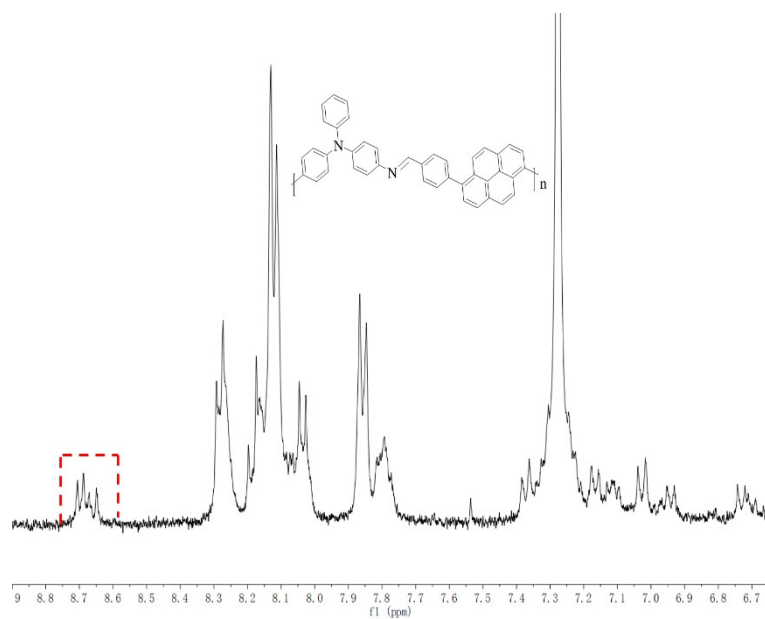
## S4. $^1\text{H}$ NMR spectra of individual polymers



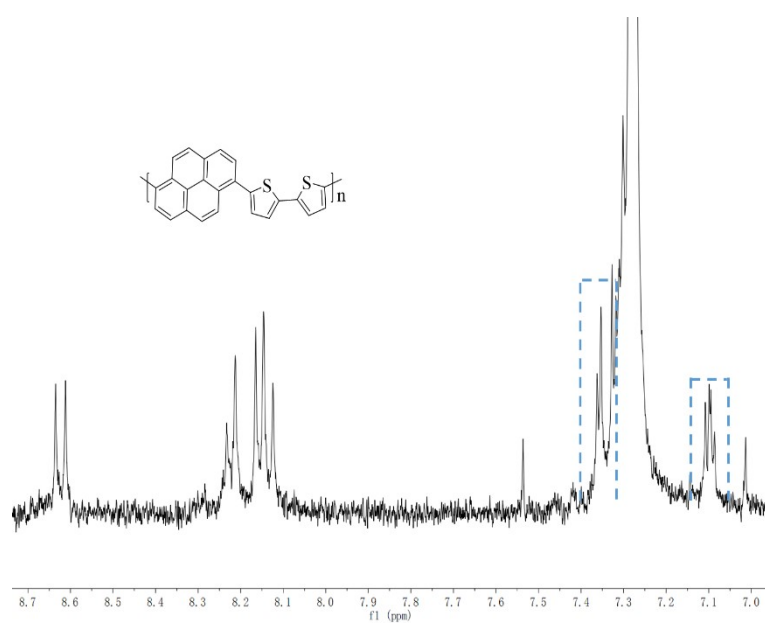
**Fig. S4-1**  $^1\text{H}$  NMR spectra of PPYEDOT.



**Fig. S4-2**  $^1\text{H}$  NMR spectra of PPYTP

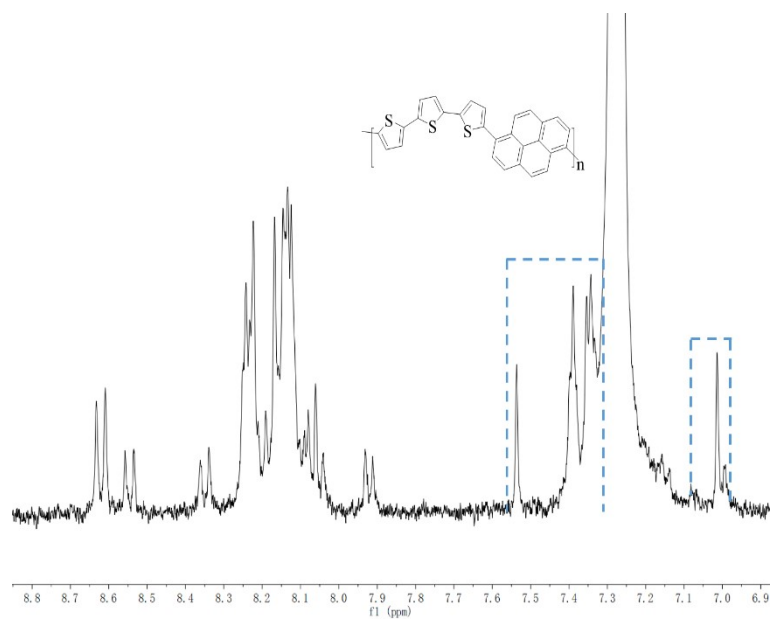


**Fig. S4-3** <sup>1</sup>H NMR spectra of PBPYTPA.



**Fig. S4-4** <sup>1</sup>H NMR spectra of PPYBTP.





**Fig. S4-5**  $^1\text{H}$  NMR spectra of PPYTTP.