

Supplementary Material:

A Lamellar-ordered Poly(bi(3,4-ethylenedioxythiophene)-alt-thienyl) for efficient tuning of thermopower without degenerated conductivity

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1. EXPERIMENTAL SECTION

1.1 Chemicals

3,4-ethylenedioxythiophene (EDOT, 98%), n-butyllithium (n-BuLi, 1.6 mol L⁻¹ solution in hexanes), tetrakis (triphenylphosphine) palladium (0) (Pd(PPh₃)₄, 99.8%), 2,5-dibromothiophene (95%), and Trans-dichlorobis(triphenylphosphine)palladium(II) (Pd(PPh₃)Cl₂) were received from J&K Scientific Ltd. 2,5-Dibromothieno[3,2-b]thiophene was obtained by Aladdin. Additionally, Iron (III) p-toluenesulfonate hexahydrate (Fe(Tos)₃·6H₂O, 99%), n-butanol (n-BuOH, 99%), and propylene carbonate (99.5%, Ultra-dry) were also purchased from J&K Scientific Ltd. Chlorotributyltin (SnBu₃Cl, 98%; Energy Chemical). Lithium perchlorate (LiClO₄, 99%; Acros Organics) was vacuum-dried at 60 °C and used directly without further purification. N,N-dimethylformamide (DMF, analytical grade), tetrahydrofuran (THF, analytical grade), and dichloromethane (CHCl₃, analytical grade) were supplied by Beijing East Longshun Chemical Plant and purified by distillation with calcium hydride under a nitrogen atmosphere before use. Other chemicals and reagents (analytical grade, >98%) were all obtained from Beijing East Longshun Chemical Plant and directly used without any further purification.

1.2 Monomer synthesis

On the basis of EDOT building block, the precursors of three p-type polymers, 2,2',3,3'-tetrahydro-5,5'-bithieno[3,4-b][1,4]dioxine (BED), 2,5-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophene (BED-T) and 2,5-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thieno[3,2-b]thiophene (BED-TT) were synthesized by the introduction of thienyl group (thiophene (Th) and thieno[3,2-b]thiophene (TT)) and its synthesis routes are illustrated in **Supplementary Scheme 1**.

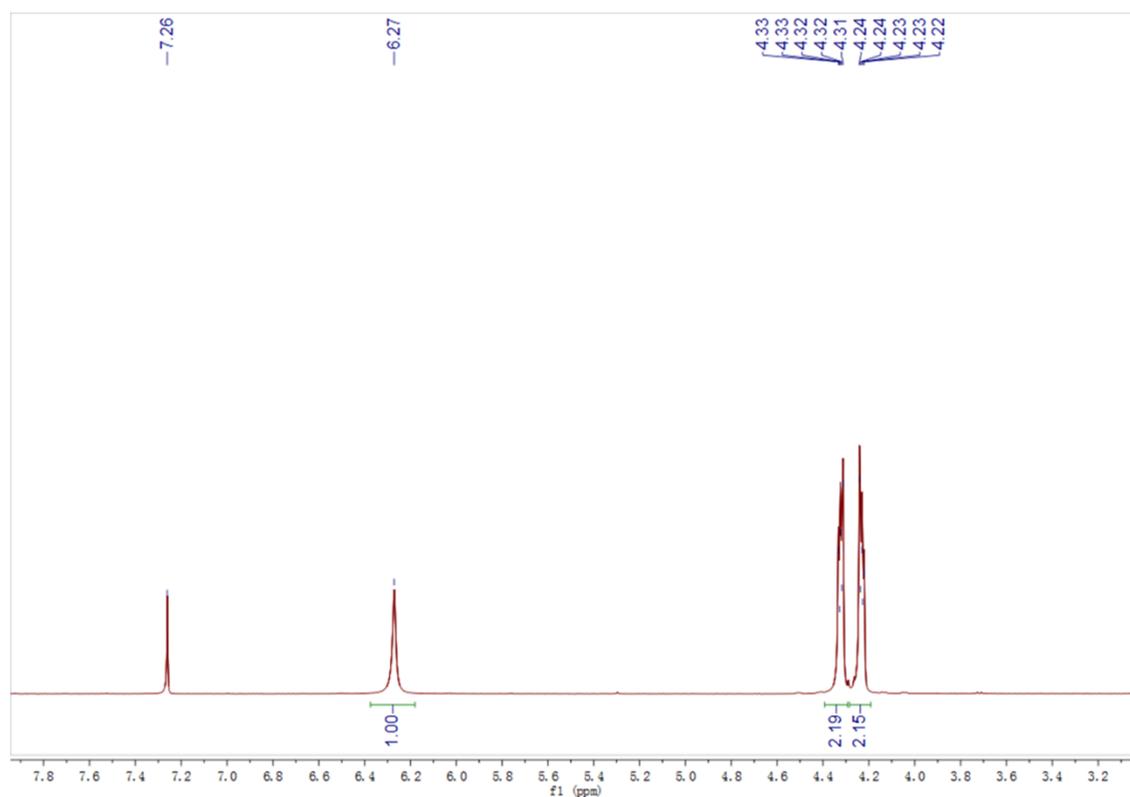
1.2.1 Tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (EDOT-SnBu₃)

The compound EDOT-SnBu₃ was synthesized according to previous reports.^[1,2] EDOT (2.84 g, 20 mmol), THF (40 mL) were added to the two necked flask in sequence with stirring and maintain temperature at -78 °C. Then purged with nitrogen and sealed. After n-BuLi (13.75 mL, 22 mmol) was injected slowly within a half hour and then the reaction was performed at in this condition and kept for 2 h under a nitrogen atmosphere. After the temp to -40 °C, 5.96 mL, 22 mmol SnBu₃Cl was added

to the flask and kept for 0.5 h under this temp and then slowly warmed to room temp, kept for 8 h under continued stirring. The resultant mixture was filtered, and the solution were removed by rotary evaporation. The remained crude product was directly used the next step experiment.

1.2.2 BED

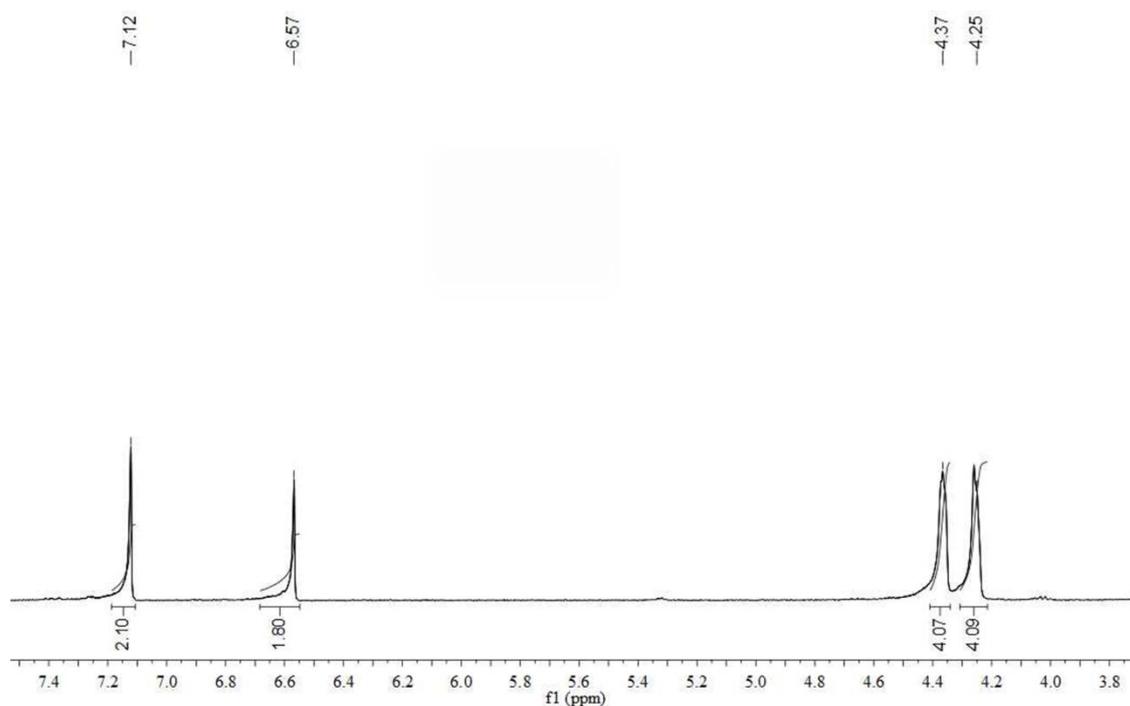
EDOT (5g, 0.035 mol) was treated at -78 °C with 150 mL refined tetrahydrofuran solution. The 28.5 ml n-BuLi (1.6 mol L⁻¹) was injected into the constant pressure drop funnel with a syringe and slowly dropped into the reactor within half an hour. The solution turned milky white and turbid after two hours of reaction at this temperature. The system was slowly warmed to 0 °C, and after stirring at this temperature for 30 min, CuCl₂ (5 g, 0.037 mol) was added, then continue to react under this condition for six hours. The mixed system was filtered to remove the filter slag after completed reaction. The filtrate was then poured into an ice bath and extracted three times with methylene chloride (DCM). And the organic layer was taken out, washed once with saturated sodium hydrogen carbonate solution, washed three times with water. The obtained organic phase was dried with anhydrous magnesium sulfate (MgSO₄) and then recrystallized after removing the excess organic solvent. **BED ¹H NMR (400 MHz, CDCl₃, Supplementary Figure 1): δ 6.27 (d, 2H), 4.32 (m, 4H), 4.23 (m, 4H).**



Supplementary Figure 1 ^1H NMR spectrum of BED in CDCl_3

1.2.3 BED-T

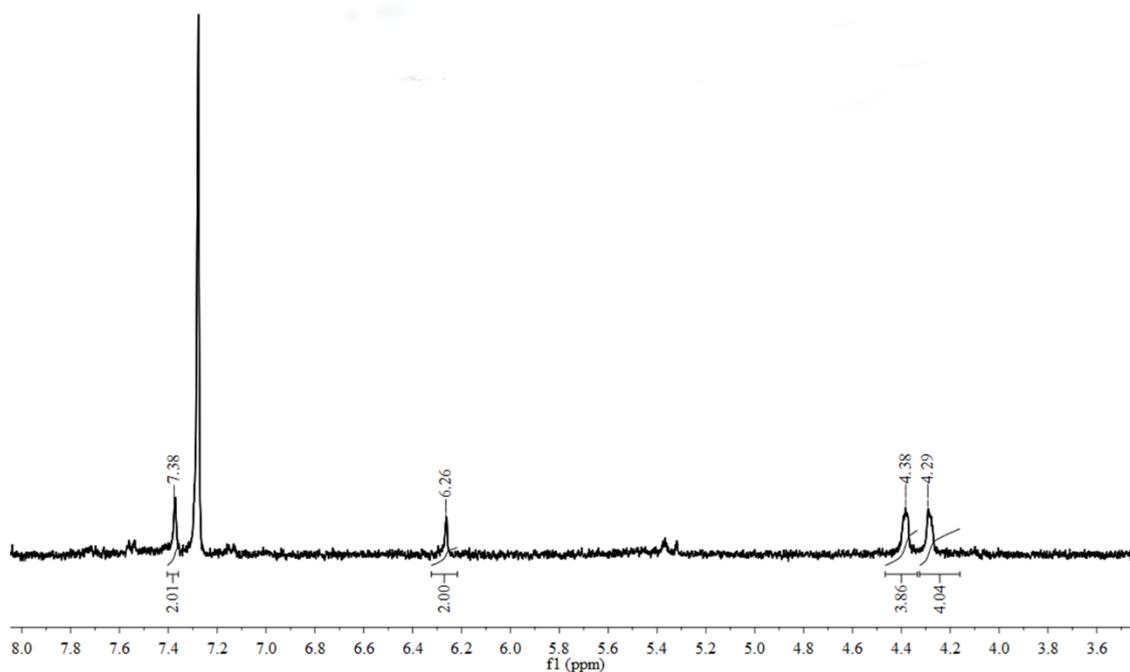
A mixture of EDOT-SnBu₃ (4.31 g, 10 mmol), 2,5-bibromothiophene (1.21 g, 5 mmol), and Pd(PPh₃)₄ (0.1152 g, 0.1 mmol) in DMF (50 ml) was stirred at reflux in 110 °C under nitrogen atmosphere for 24 h. After the temp of 110 °C to room temp, the mixture was added to into water (50 mL) and extracted with DCM (3×100). The organic phase was separated, washed with water and brine solution, dried over anhydrous MgSO₄, filtered, and the solutions were removed. Purification by column chromatography using silica gel eluting with petroleum ether and ethyl acetate gave a yellow powder. **BED-T** ^1H NMR (400 MHz, DMSO-*d*₆, Supplementary Figure 2) δ 7.12 (s, 2H), 6.57 (s, 2H), 4.37 (s, 4H), 4.25 (s, 4H).



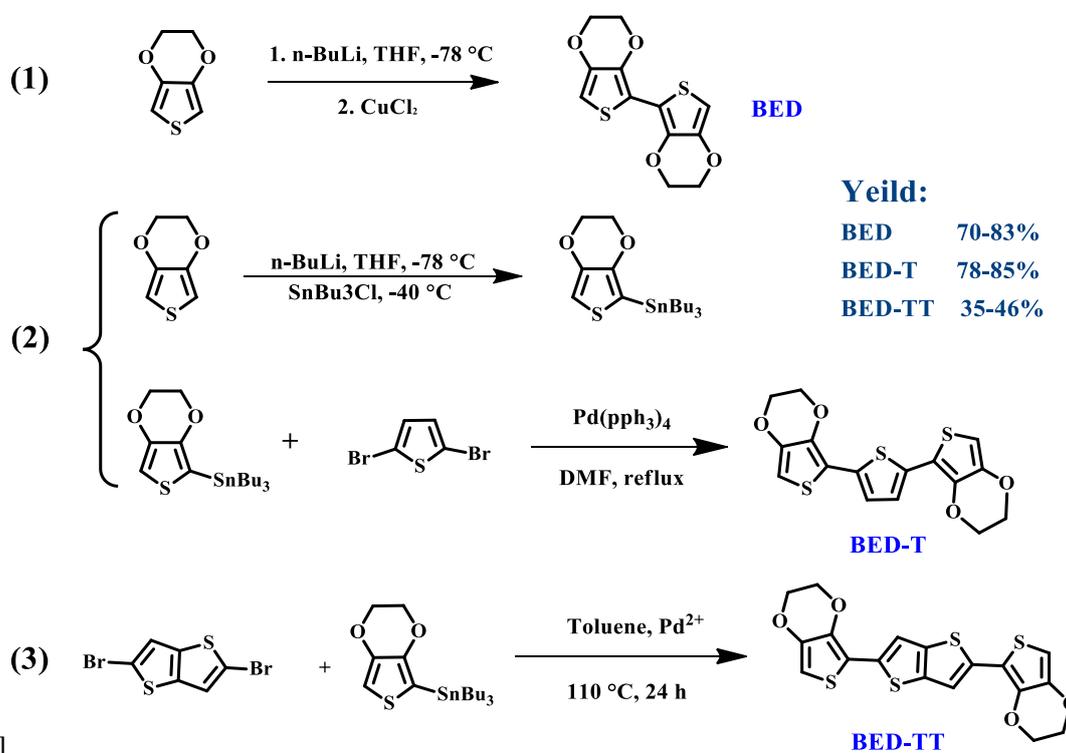
Supplementary Figure 2 ^1H NMR spectrum of BED-T in $\text{DMSO-}d_6$

1.2.4 BED-TT

BEDT-TT was synthesized by replaced $\text{Pd}(\text{PPh}_3)_4$ and 2,5-bibromothiophene with $\text{PdCl}_2(\text{PPh}_3)_2$ and 2,5-dibromothieno[3,2-b]thiophene as well as others produce of synthesis is similar the synthesis route of BED-T. After purification by silica gel column, we obtained a yellow solid powder. **BED-TT ^1H NMR (400 MHz, CDCl_3 , Supplementary Figure 3) δ 7.36 (s, 2H), 6.26 (s, 2H), 4.38 (s, 4H), 4.29 (s, 4H).**



Supplementary Figure 3 ^1H NMR spectrum of BED-TT in $\text{DMSO-}d_6$



Supplementary Scheme 1. Synthetic routes of BED, BED-T, BED-TT and the corresponding intermediate products.

1.3 Polymerization of BEDs monomers and polymer films preparation

In this study, we employed a simple and high-quality in-situ polymerization method, namely the spray-spin coating polymerization method, which has been previously reported by our group.^[4-7] Compared to traditional direct chemical oxidation methods, this method enables the preparation of polymer films through a single step of in-situ polymerization of the monomers. The specific steps for fabricating the polymer films are as follows.

According to the literature report, 2 g $\text{Fe}(\text{Tos})_3 \cdot 6\text{H}_2\text{O}$ and 630 μL $[\text{BMIm}][\text{BF}_4]$ completely dissolved in 10 mL n-butanol solution by ultrasonic method, and spin-coated on the common glass substrate pre-treated. Then the solvent evaporation was performed at 50 °C. Meanwhile, the monomer was dissolved in 20 mL of chloroform with concentration of 5 mmol L^{-1} . The use of chloroform as solvent is mainly due to the volatilization of chloroform, low boiling point and low vapor pressure (21.28 Kpa. at 20 °C). These properties guarantee the preparation of high-quality polymer films. After the above monomer solution was transferred to the spray gun and sprayed on the substrate containing the oxidant. Meanwhile, the oxidant substrate was rotated at a certain speed during the spraying process, which is advantageous for obtaining a more uniform conductive polymer film. Oxidative polymerization occurred rapidly while the monomer was in contact with the oxidizing agent, and then a blue polymer film was observed. The film was repeated rinsing with ethanol to remove the residual monomer and oxidant and then dried at 50 °C for 2 h. The schematic diagram of the preparation of polymer thin films is shown in **Figure1**.

1.4 Characterization.

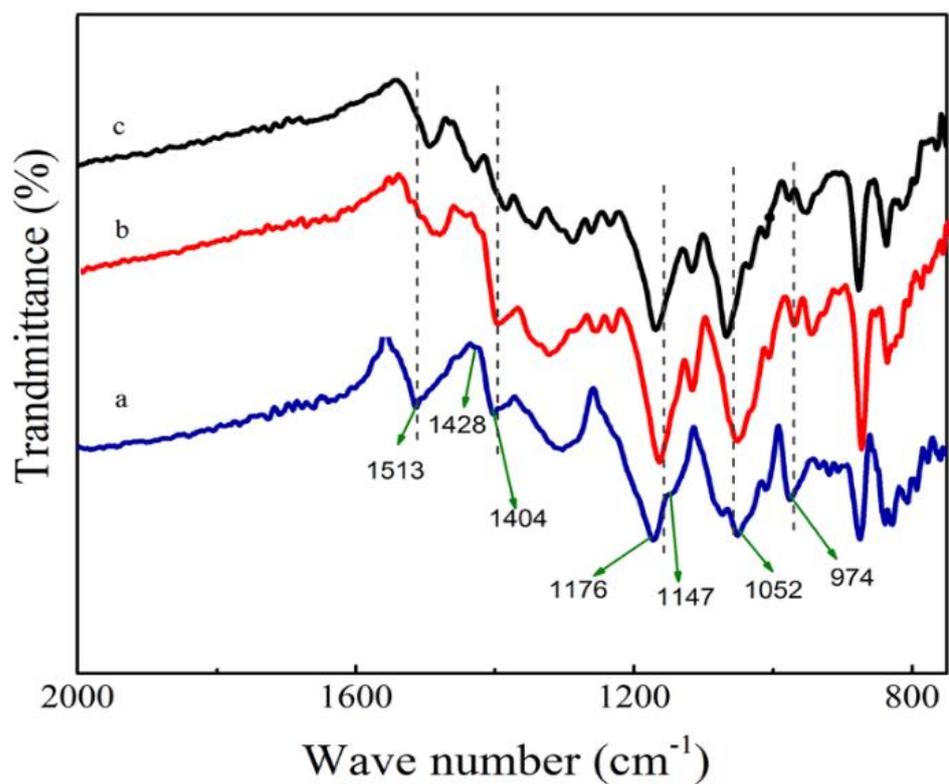
^1H NMR spectra were deuterated in $\text{CDCl}_3\text{-d}_6$ solution and recorded on a Bruker AVANCE III spectrometer and tetramethylsilane (TMS) was used as external standard. All chemical shifts were reported in ppm. Electrochemical test was performed in a one-chamber three-electrode system, and the electrochemical instrument is model V3 Princeton Applied Research. Ag/AgCl electrode as reference electrode and the ITO glass was used as working and counter electrode. In all the tests, 0.2 M LiClO_4 and propylene carbonate (PC) were used as supporting electrolyte and electrochemical solvent system, respectively. Further, the concentration of monomer in pre-test is 0.01 M. UV-Vis spectroscopy (Analytik Jena Specord 200) was used to characterize the structural information of monomer polymerization. FTIR spectra (Nicolet-460) was used to characterize the polymerization results of

monomers by the spray-spin coating polymerization method. The morphology of polymer films and the self-assembly of polymer molecules were illustrated by atomic force microscopy (AFM) and grazing-incidence wide-angle X-ray scattering (GIWAXS) pattern (Xeuss 2.0 WAXS system (Xenocs, Sassenage, France) with a PILATUS3 R 1M detector). Additionally, the sheet resistance R_s (X sq21) and the thermopower (S) (IVK21) were measured by employing the standard four-point probe technique using a Keithley 2700 Multimeter (Cleveland, OH) and a Keithley 2401 systems. S is defined as $S = -\Delta V/\Delta T$, where ΔV and ΔT (5 ± 0.5 K) are the voltage drop across the material and the temperature gradient along the voltage drop, respectively.

2. SUPPLEMENTARY DATA FIGURES

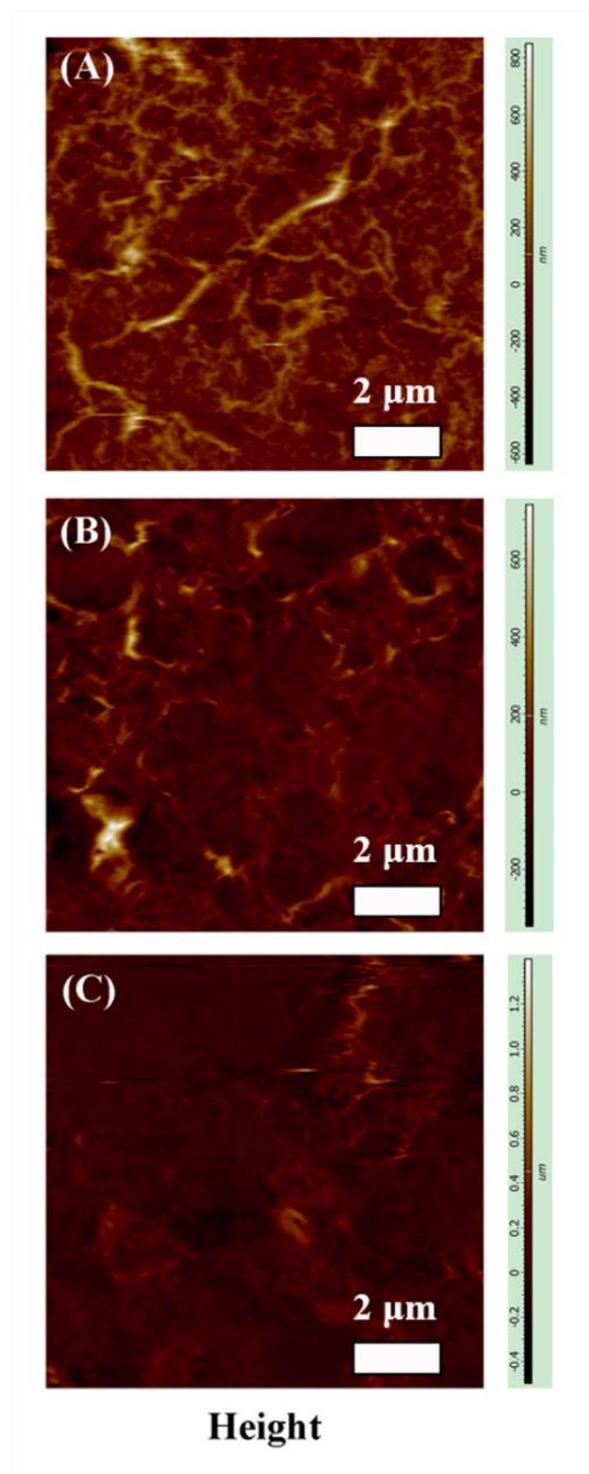
2.1 Fourier transform infrared (FTIR) spectra of PBEDs film by spray-spin coating polymerization method

Supplementary Figure 1 is the Fourier transform infrared (FTIR) spectra of PBED, P(BED-T), and P(BED-TT) films. According to the **Supplementary Figure 1**, there is a nearly absent absorption peak in the vicinity of $3000\text{--}3100\text{ cm}^{-1}$ (not depicted in the graph) that corresponds to the C-H bond vibration of the 2,5 position on the thiophene ring.^[8] This result implies that the polymerization process mainly occurs at the α -position of the thiophene ring in EDOT. The absorption bands for the stretching vibration of the C=C bond in the thiophene ring is observed at 1513 cm^{-1} .^[9] This indicates that the polymerization process does not involve any ring-opening reactions. Furthermore, the absorption bands observed at 1428 cm^{-1} correspond to the bending vibration of C-H. The absorption peaks observed at 1052 cm^{-1} , 974 cm^{-1} , and 831 cm^{-1} can be attributed to the asymmetric and symmetric stretching vibrations of C-O-C and C-S-C bonds.^[10] The absorption peaks observed in the polymer spectrum curve (b-c) of **Supplementary Figure 4** are comparable to those observed in the P(BED-T) spectrum. In short, we have obtained reliable PBEDs films.



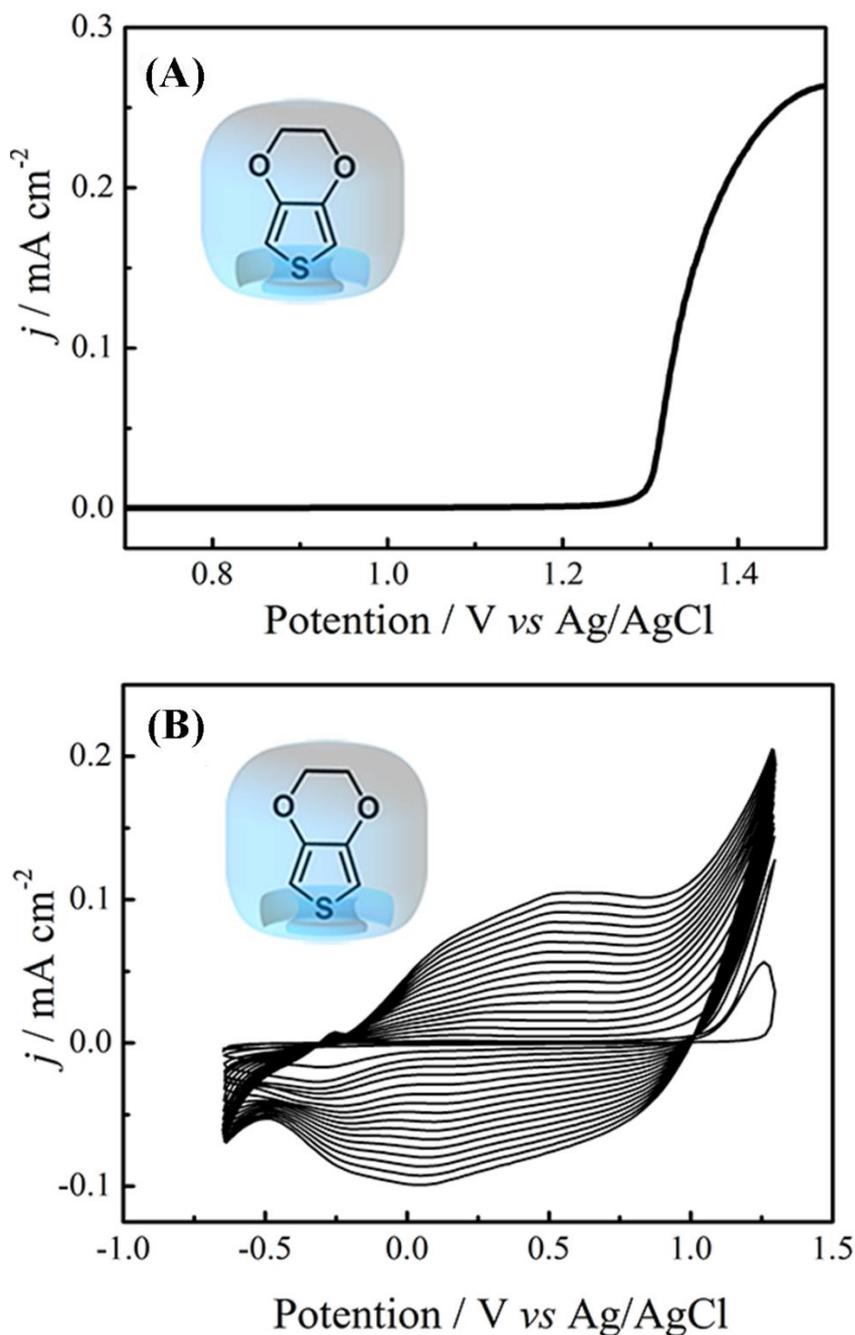
Supplementary Figure 4 FTIR spectra of (a) PBED, (b) P(BED-T), (c) P(BED-TT) films.

2.2 Atomic force microscopy (AFM) of PBEDs films.



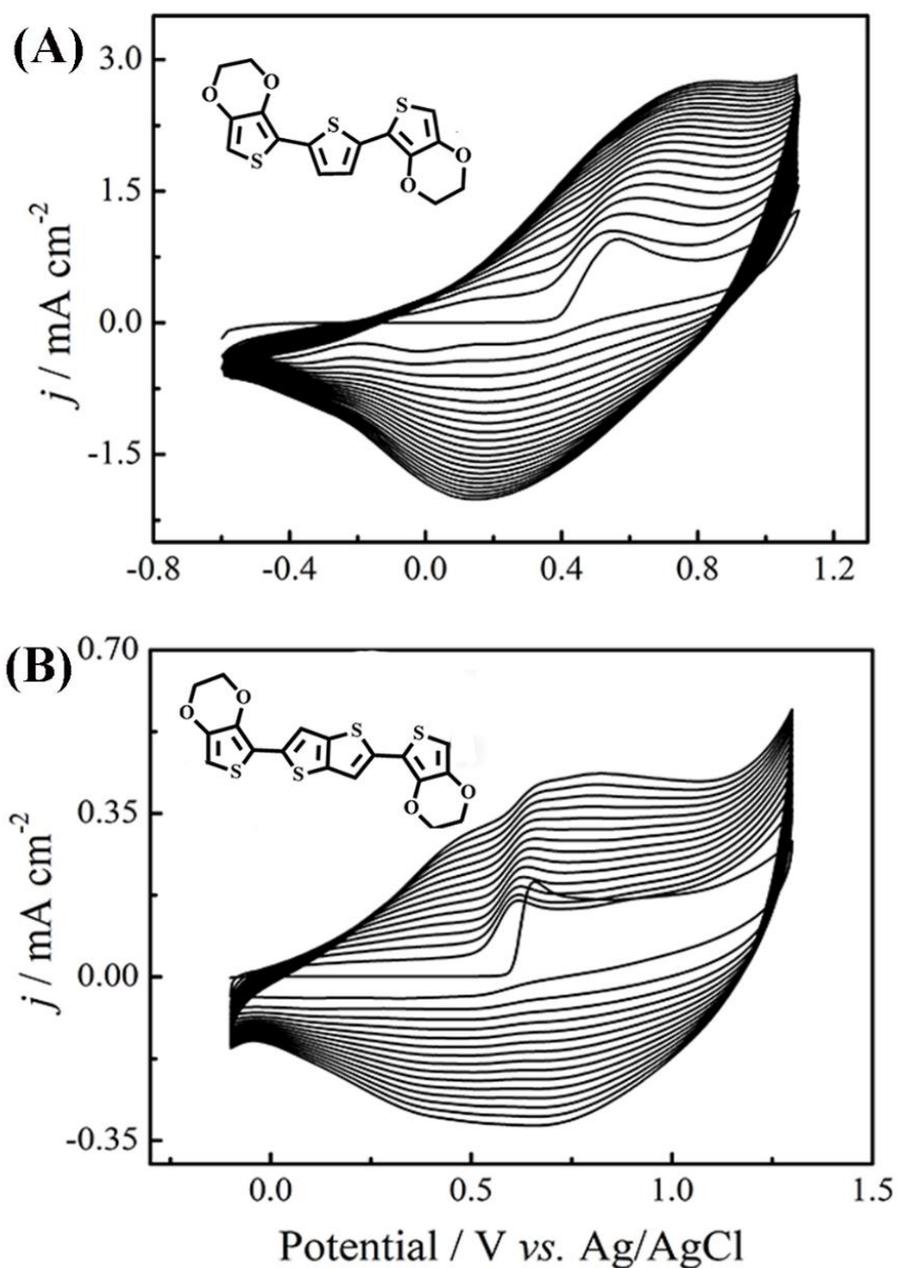
Supplementary Figure 5 Atomic force microscopy (AFM) morphology images of (A) PBED, (B) P(BED-T) and (C) P(BED-TT) films with scan area of $80 \mu\text{m} \times 80 \mu\text{m}$ prepared by spray-spin coating polymerization method.

2.3 Electrochemical Properties of EDOT



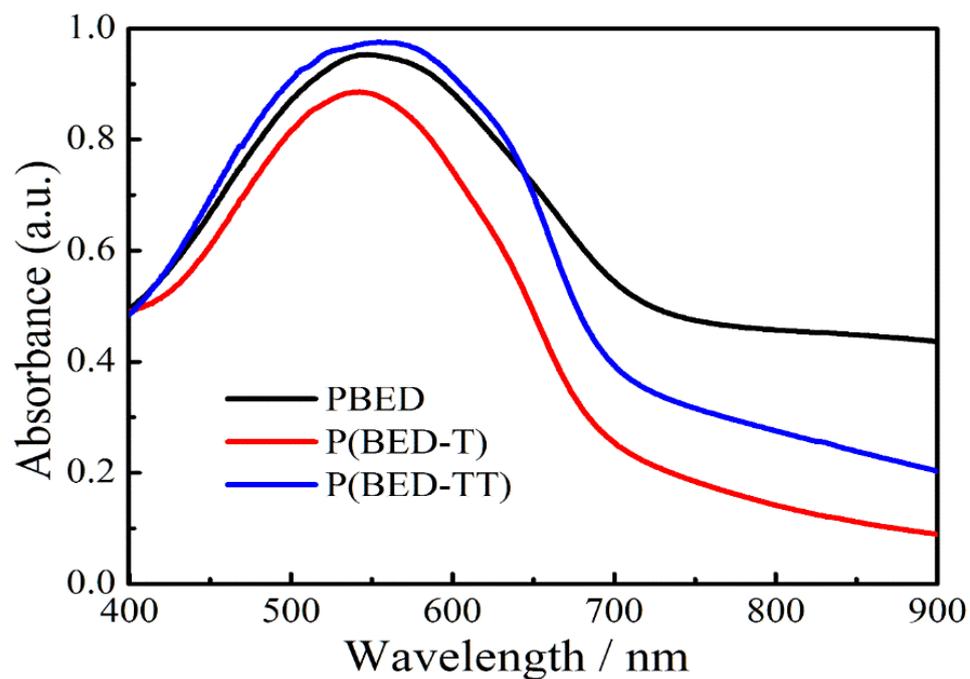
Supplementary Figure 6 (A) Anodic oxidation curves of 0.01 M EDOT in PC/LiClO₄. Potential scan rate: 10 mV s⁻¹. (B) Cyclic voltammograms of 0.01 M EDOT in PC/LiClO₄. Potential scan rate: 50 mV s⁻¹. Inset is the chemical structure of EDOT.

2.3 Cyclic voltammograms of P(BED-T) and P(BED-TT)



Supplementary Figure 7 Cyclic voltammograms of 0.01 M (A) P(BED-T) and (B) P(BED-TT) in PC/LiClO₄. Potential scan rate: 50 mV s⁻¹. Insets are the corresponding chemical structure of P(BED-T) and P(BED-TT).

2.4 UV-vis absorption spectra of de-doped PBEDs films.



Supplementary Figure 8 UV-vis absorption spectra of PBED, P(BED-T), P(BED-TT) de-doping films. Notes: The de-doping of thin films is realized by soaking in an ethanol solution containing hydrazide hydrate.

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