

## Electropolymerization and Properties of 3,4-Ethylenedioxythiophene Backbone Polymer with Tetrathiafulvalene as Pendant

Lei Zhang,<sup>1</sup> Meijiang Li,<sup>2</sup> Chengyun Wang,<sup>1</sup> Yanhong Wang,<sup>1</sup> Yongjia Shen<sup>1</sup>

<sup>1</sup>Key Laboratory for Advanced Materials, Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, People's Republic of China

<sup>2</sup>Key Lab of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 310012, People's Republic of China

Correspondence to: Y. Shen (E-mail: yjshen@ecust.edu.cn)

**ABSTRACT:** Three 3,4-ethylenedioxythiophene (EDOT) derivatives, including an EDOT-tetrathiafulvalene (TTF) derivative, were synthesized by Steglich esterification of carboxylic acids with hydroxymethyl EDOT (3,4-ethylenedioxythiophene methanol). The UV spectra showed that there was no distinctive intramolecular interaction for the EDOT–TTF monomer between the EDOT and the TTF moieties in the ground state; however, the cyclic voltammetry responses implied that such intramolecular interaction occurred. Electropolymerization in excessive potential could bring in strong overoxidation effects and degradation in the polymer film. The polymers were simulated using density functional theory with Gaussian03 package and the optimized HOMO and LUMO state were figured out. The conductivity of TTF-polymer was  $6 \text{ S}\cdot\text{cm}^{-1}$  obtained by galvano station and  $4.8 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$  obtained by potentiostatic electropolymerization after doping with 7,7,8,8-tetracyanoquinodimethane. The results indicated that this polymer was a reasonable candidate for conducting materials and it was meaningful to increase the conductive dimensions of TTF polymers by chemical doping. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** conjugated polymers; TTF; conducting polymers; electrochemistry; cyclic voltammetry

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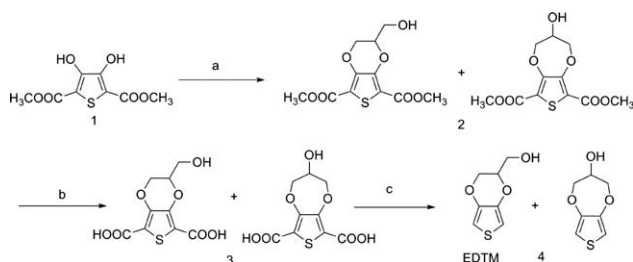
### INTRODUCTION

The conjugated thiophene polymers, such as, poly(3,4-ethylenedioxythiophene) (PEDOT), which were obtained from oxidative chemical polymerization,<sup>1–4</sup> electrochemical polymerization, or transition metal-mediated coupling of dihalo-derivative,<sup>5,6</sup> have received tremendous interesting in recent years. The combination of an especially low-oxidation potential and a relatively low-band gap gives PEDOT some unique electrochemical and spectroscopic properties not accessible in other polymers.<sup>7</sup> However, although good electric conducting properties associated with a high chemical stability have obtained, the PEDOT backbone is insoluble in common organic solution, which implies its difficulty to process. One probable resolution is to introduce a soluble functional group into the polymer.

On the other hand, tetrathiafulvalene (TTF) and its derivatives have attracted much interest as strong electron donors and they can be oxidized and reduced reversibly. It is convenient to obtain charge-transfer (C-T) complex by doping TTF with electron accepters. With this unique feature, TTF and its derivatives

have been widely employed in numerous fields.<sup>8</sup> It is meaningful to incorporate TTF group to PEDOT backbone and several efforts have been made to predict a probable application as electrical probes. Huchet et al.<sup>9,10</sup> synthesized the first polythiophene with TTF pendants (PT-TTF) by electropolymerization; the precursors  $\omega$ -bromoalkylthiophenes were good candidates for linking the TTF groups. In the similar method, Trippé et al.<sup>11</sup> and Besbes et al.<sup>12</sup> first synthesized 3,4-ethylenedioxythiophene (EDOT) derivatives, bearing an  $\omega$ -iodo-alkyl or  $\omega$ -iodo-polyether chain attached at the ethylenedioxy bridge, and they were developed as precursors for further functionalization. This method is sound for TTF substitution but it needs strict conditions (NaH, THF, 0°C), costly reagents such as a ditosylate derivative, 1,6-bromochlorohexane, or other halogenated reagents, as well as prolix reaction process. The precursor with S–CN substituting the –OH group of the hydroxymethyl EDOT (3,4-ethylenedioxythiophene methanol, EDTM) was reported recently.<sup>13</sup> It also needs several steps and the corresponding TTF derivative with iodo-alkyl functional group is not easy to gain. Furthermore, when TTF is substituted in the side

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**Scheme 1.** Synthesis of EDTM. Reagents and conditions (a) epibromohydrin, DMF, Et<sub>3</sub>N, 95°C 15 h; (b) KOH/H<sub>2</sub>O, then HCl; (c) TEA, 180°C, 3 h.

chain by the long alkyl bridge, the conformational disorder is severe as a result of these  $\sigma$ -bonds; there is a lack of description on the conductivity of the TTF polymers. Herein, we report a kind of novel soluble EDOT polymer with TTF as pendant group via facile Steglich esterification as well as its electrochemical property. The EDOT polymers are simulated using density functional theory and the optimized HOMO and LUMO states are figured out. The conductivity of the TTF polymer obtained from traditional galvanostatic doping and the C-T complex after chemical doping are measured and studied.

## EXPERIMENTAL

### Materials and Instruments

The reagents and solvents were of commercial quality and were distilled or dried using the standard procedures when necessary.

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were obtained on Bruker AVANCE 500 instrument operating at 500 and 125 MHz, respectively. Chemical shifts were quoted downfield to TMS. Mass spectra were recorded using LCQ ADVANTAGE mass spectrometer. Absorption spectra were measured with CARY 100 Conc UV-Visible (UV-Vis) spectrophotometer. The electrochemical experiments were performed with TBAPF<sub>6</sub> as the supporting electrolyte and Ag/AgCl as reference electrode. Cyclic voltammetry (CV) responses were carried out with platinum as the working and counter electrodes; the electrodes used in electropolymerization by multisweep CV, potentiostatic electropolymerization, galvanostatic station were mentioned, respectively. The geometries and electronic structures of the polymers were simulated by means of hybrid density functional theory (DFT) method, at the B3LYP level of theory with the 6-31G\* basis set performed on Gaussian 03 program package. The electric conductivity was measured using a four-probe technique with a SX1934 apparatus.

### Synthesis

EDTM (4) was synthesized according to the literature<sup>14</sup> with some modifications (Scheme 1). Dimethyl 3,4-dihydroxythiophene-2,5-carboxylate(1), which was synthesized according to the literature,<sup>15</sup> underwent etherification with epibromohydrin to yield 2 as a mixture of isomers of six and seven member ring, which was not so easy to separate even by silica column chromatography, and thus 4 was obtained as a mixture of two isomers, after saponification and decarboxylation reactions, with the ratio 6 : 1 of the six member-ring product to the seven member-ring product as shown in Scheme 1.

The functionalized TTF 1, which was synthesized according to the literature,<sup>16</sup> reacted with ethyl bromoacetate to get TTF 2, following hydrolysis in LiOH to afford TTF 3<sup>17</sup> (Scheme 2).

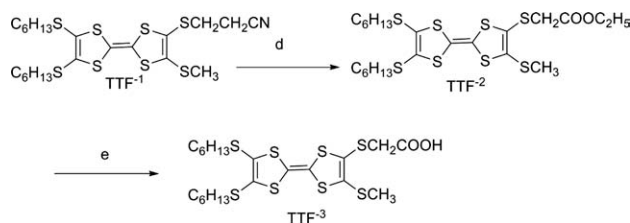
The EDOT-based monomer-containing TTF group (TTF-4) was obtained by the reaction of 4 and TTF-3 via Steglich esterification. Two other monomers (EDOT 1-2) were synthesized in the similar procedure. The EDOT-based polymers were obtained by electropolymerization as shown in Scheme 3. Both P1 and P2 were soluble in normal organic solvents, such as, dichloromethane (DCM), ethyl acetate, THF, DMF, whereas P<sub>3</sub> was insoluble in the solvents mentioned above.

### 2-Methylthio-3-ethoxycarbonylthio-6,7-bis(hexylthio)tetrathiafulvalene TTF-2

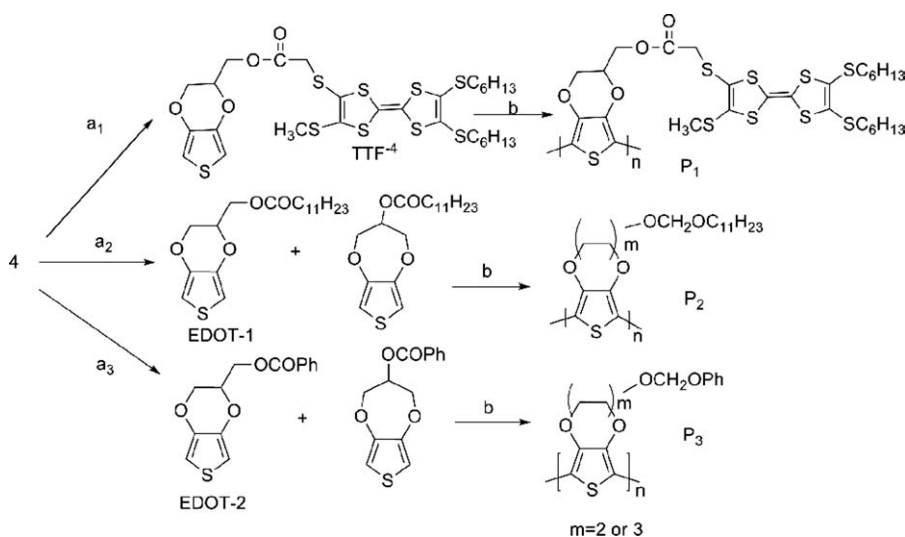
To a stirred solution of TTF 1 (1.13 g, 2 mmol) in dried DMF (60 mL), CsOH·H<sub>2</sub>O (350 mg, 2.1 mmol) in absolute MeOH (5 mL) was added over a period of 30 min under nitrogen. After stirring for 30 min, ethyl bromoacetate (0.55 mL, 5 mmol) was added and the solution turned its color from dark orange to yellow orange at once. After stirring at room temperature for 5 h, the reaction mixture was distilled under reduced pressure to remove excess ethyl bromoacetate as well as the solvent. The residue was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>-petroleum ether, 2 : 3 V/V) to give 2 as reddish orange oil (1.12 g, 93% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ : 4.21 (2 H, q,  $J = 6.9$  Hz,  $-\text{OCH}_2\text{CH}_3$ ), 3.53 (2 H, s,  $-\text{SCH}_2\text{COO}-$ ), 2.81 (4 H, t,  $J = 7.2$  Hz,  $-\text{SCH}_2\text{CH}_2-$ ), 2.46 (3 H, s,  $-\text{SCH}_3$ ), 1.68–1.58 (4 H, m,  $-\text{CH}_2-$ ), 1.45–1.36 (4 H, m,  $-\text{CH}_2-$ ), 1.33–1.28 (11 H, m,  $-\text{OCH}_2\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.89 (6 H, t,  $J = 6.6$  Hz,  $-\text{CH}_2\text{CH}_3$ ). MS (EI)  $m/z = 600$  ( $M^+$ ), 513, 482.

### 2-Methylthio-3-carboxythio-6,7-bis(hexylthio)tetrathiafulvalene TTF-3

To a stirred solution of TTF 2 (900 mg, 1.5 mmol) in 1,4-dioxane (30 mL), a solution of LiOH·H<sub>2</sub>O (420 mg, 10 mmol) in deionized H<sub>2</sub>O (5 mL) was added dropwise at room temperature. After stirring for 10 h, HCl 5M (2 mL, 10 mmol) was added dropwise and the reaction mixture was stirred for another 30 min. Diethyl ether (60 mL) and water (30 mL) were added, followed by adding 1M HCl till the pH value of water phase reached 2. The organic layer was decanted, dried over MgSO<sub>4</sub>, and evaporated under reduced pressure to afford a red solid (755 mg, 88% yield) which could be used in the next step without further purification. The crude product could be purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub> as the eluent to remove the byproduct. The residue was recrystallized with acetone to afford pure product, mp: 80–81°C. <sup>1</sup>H-



**Scheme 2.** Synthesis of TTF-3. Reagents and conditions (d) CsOH, DMF, BrCH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>, r.t; (e) LiOH, 1,4-dioxane, then HCl.



**Scheme 3.** Synthesis of EDOT-based polymers *Reagents and conditions:* (a) DCC, DMAP, HOBT in DCM, a<sub>1</sub>: TTF-3, a<sub>2</sub>: C<sub>11</sub>H<sub>23</sub>COOH, a<sub>3</sub>: PhCOOH. (b) electropolymerization.

NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ : 3.91 (2 H, s), 2.85 (4 H, t,  $J = 6.9$  Hz), 2.50 (3H, s), 1.67–1.61 (4 H, m), 1.43–1.38 (4 H, m), 1.30–1.24 (8 H, m), 0.88 (6 H, t,  $J = 6.6$  Hz). MS (EI)  $m/z = 572$  (M<sup>+</sup>) 513, 528, 482.

#### TTF-4

TTF 3 (570 mg, 1 mmol) was dissolved in fresh distilled CH<sub>2</sub>Cl<sub>2</sub> (25 mL) under argon. Dicyclohexylcarbodiimide (DCC) (230 mg, 1.1 mmol), 4-dimethylamino pyridine (DMAP) (123 mg, 1 mmol), and 1-hydroxybenzotriazole (HOBT) (135 mg, 1 mmol) were added successively. After stirring for 30 min, EDTM (0.3 g, 1.7 mmol) was added and the mixture was warmed to 40°C and reacted for 2 h. After the mixture cooled to room temperature, it was allowed to react for another 10 h. Then, the reaction mixture was washed successively with saturated NaHCO<sub>3</sub> and brine, the organic layer was decanted, dried over MgSO<sub>4</sub>, and concentrated. The residue was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>-*n*-Hexane, 2 : 1 v/v) and dried in vacuum at 40°C for 24 h to give 4 as viscous orange oil (495 mg, 68% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ : 6.34 (1 H, d,  $J = 3.6$  Hz, CHthiophene), 6.33 (1 H, d,  $J = 3.6$  Hz, CHthiophene), 4.41–4.31 (3 H, m, -OCH<sub>2</sub>CH(CH<sub>2</sub>)O-), 4.25 (1 H, dd, <sup>cis</sup> $J = 2.2$  and <sup>gem</sup> $J = 11.7$  Hz, =C(C)OCH<sub>2</sub>), 4.06 (1 H, dd, <sup>trans</sup> $J = 7.5$  and <sup>gem</sup> $J = 11.7$  Hz, =C(C)OCH<sub>2</sub>), 3.55 (2 H, s, -SCH<sub>2</sub>COO-), 2.81 (4 H, t,  $J = 6.8$  Hz, -SCH<sub>2</sub>CH<sub>2</sub>-), 2.43 (3 H, s, -SCH<sub>3</sub>), 1.65–1.58 (4 H, m, -CH<sub>2</sub>-), 1.43–1.36 (4 H, m, -CH<sub>2</sub>-), 1.33–1.28 (8 H, m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.88 (6 H, t,  $J = 6.6$  Hz, -CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 168.4, 141.1, 140.8, 134.7, 127.8, 127.6, 121.1, 112.4, 108.8, 108.6, 105.8, 100.2, 100.0, 71.1, 65.4, 63.4, 37.0, 31.3, 29.7, 28.2, 19.2, 14.0. MS (EI) =  $m/z$  726 (M<sup>+</sup>). HRMS (ESI) Calcd. for C<sub>28</sub>H<sub>38</sub>O<sub>4</sub>S<sub>9</sub> requires (M<sup>+</sup> + 1) 727.0335, Found 727.0331.

#### Electropolymerization

**Multisweep CV.** Electropolymerization of TTF-4, EDOT-1, and EDOT-2 was carried out under  $2 \times 10^{-2}$  M solution of the monomer, TBAPF<sub>6</sub> (0.1 M) as electrolyte. As the monomers are

not soluble in acetonitrile (AN), which is employed as a common solvent for electropolymerization, DCM was added to enhance the solubility. The multiplex solvent of AN : DCM = 4 : 1 was employed.

**Potentiostatic Electropolymerization.** The TTF-functionalized polymer was also obtained by potentiostatic electropolymerization. To get hundreds of milligrams of the polymers for testing their properties, a broader electrode (0.5 cm × 0.2 cm) was employed. The experiments were conducted according to the CV results, that is, the polymerization should be carried out under proper potential ( $E_{\text{appl}} = 1.8$  V), so that it would be neither too low to happen, nor too high, which causes overoxidation.

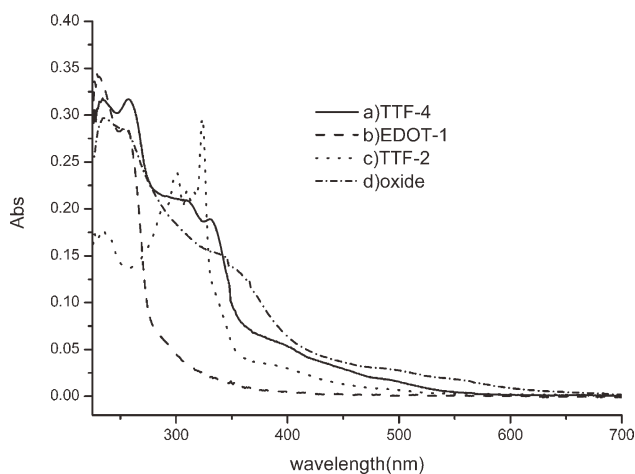
#### Galvanostatic Electropolymerization

After several failures in the mental-based electrodes such as PT or gold, we employed polished glassy carbon as electrode, and the current density was kept at 0.04 mA·cm<sup>-2</sup>, the deposition of TTF-4 was formed at around 0°C using TBAPF<sub>6</sub> as electrolyte in propylene carbonate, which acted as a plasticizer.<sup>18</sup> The deposition was carefully in progress with no environmental vibration for 20 h. The obtained film was rinsed in AN and dried overnight.

#### Preparation for Conductivity Measurements

**Electrochemical Doping.** P1 and P3 prepared in both potentiostatic electropolymerization and galvanostatic station were used for conductivity measurement.

**Chemical Doping.** As chemical doping needs much more substrate, we collected the product through the potentiostatic electropolymerization, employing two polished steel sheets (2 cm × 1 cm) as electrolysis electrodes at 1.8 V in an AN : DCM = 4 : 1 solution of 0.1 M TBAPF<sub>6</sub>. After washing and drying, a THF solution of the polymer was treated with 7,7,8,8-tetracyanoquinodimethane (TCNQ) at a molar ratio of 1 : 2 of TTF to TCNQ. The doped film with umber color was obtained from a



**Figure 1.** UV-Vis absorption spectra of TTF-2, TTF-4, EDOT-1,  $10^{-3}M$  in DCM.

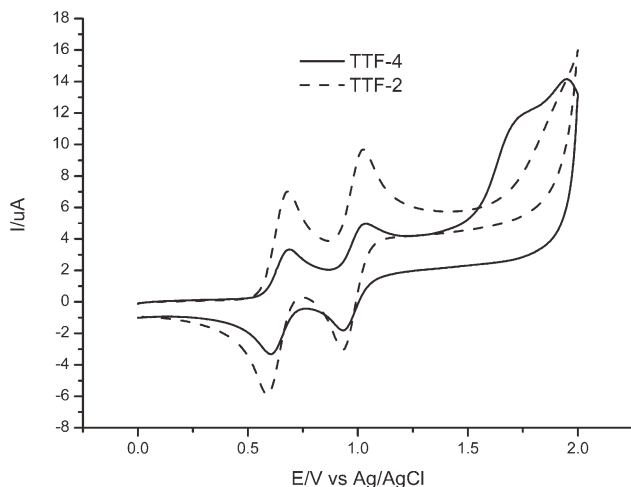
drop of concentrate solution onto an ITO glass plate<sup>19</sup> after drying in vacuum at  $40^{\circ}C$  for 24 h.

## RESULTS AND DISCUSSIONS

### Synthesis

The researchers mentioned above have converted the  $-OH$  group to  $\omega$ -halogen alkyl or  $\omega$ -halogen polyether or cyano-group. The main modifications were on the transformation of the  $-OH$  group. As the  $-OH$  group was reactive in the presence of necessary catalyst, such as, DCC, DMAP, it was meaningful to reserve it for further reaction. The esterification seemed to be feasible to obtain EDOT derivatives.

We have modified the TTF synthon (TTF-1) to yield a carboxylic TTF precursor (TTF-3). It was substituted at EDTM easily by esterification reaction. TTF-4 was obtained as a single product after work up. However, EDOT-1 and EDOT-2 were obtained as a mixture of two isomers which was very difficult to separate. The great difference may derive from the TTF group. The esterification reaction underwent an  $SN_2$  process;



**Figure 2.** CV of TTF-2 and TTF-4 in DCM  $10^{-3}M$ ,  $0.1M$  TBAPF<sub>6</sub> as electrolyte, scan rate  $50\text{ mV s}^{-1}$ .

the electron-rich TTF group enhanced the electron cloud density of the carbonyl group which gave more difficulty to the dissociation of the  $-OH$  group. On the other hand, the TTF group possesses a steric hindrance to the nucleophilic reagent, and hence the primary hydroxyl isomer is more likely to combine with it.

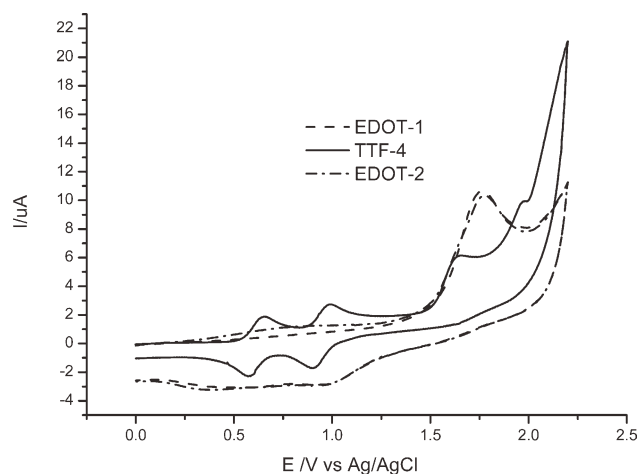
### UV-Vis Spectra

The UV-Vis absorption spectra of TTF-2, TTF-4, and EDOT-1 are shown in Figure 1. EDOT-1 (curve b) indicated two peaks at 230 and 256 nm, respectively, illustrating the  $\pi$ -conjugated thiophene ring. TTF-2 (curve c) indicated two peaks at 310 and 330 nm, respectively, illustrating the  $\pi$ - $\pi^*$  transitions of TTF moiety.<sup>20</sup> Compared with TTF-4, the two sharp-shaped peaks turned to shoulder-shaped when TTF-carboxyl group was substituted to the EDOT moiety (curve a). It could be found that the absorption of TTF-4 was an addition of TTF-2 and EDOT-1 and no new absorption band was observed.

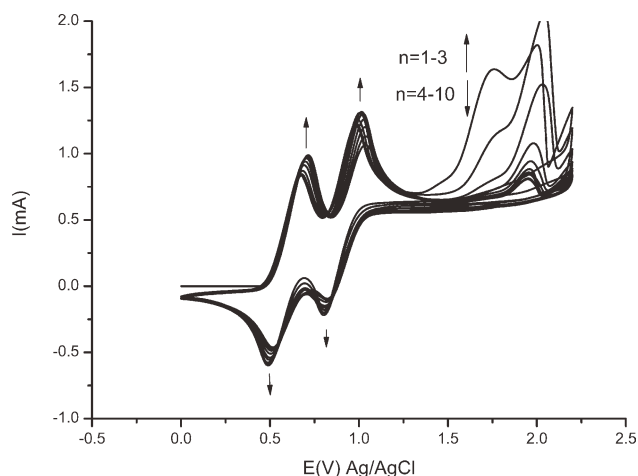
It indicated that there was no distinctive intramolecular interaction for the TTF-4 molecule between the EDOT and the TTF moieties in the ground state. When an oxidative reagent, such as  $Fe(ClO_4)_3$ , two equivalent molar ratio to TTF-4, was added, the peaks disappeared owing to the formation of  $TTF^{2+}$  as indicated by curve d.

### Cyclic Voltammetry

CV of TTF-4, TTF-2, EDOT-1, and EDOT-2 performed in DCM is shown in Figures 2 and 3. TTF-2 exhibited two reversible half peaks ( $E_{1/2\text{ox}1} = 0.65\text{ V}$ ,  $E_{1/2\text{ox}2} = 0.98\text{ V}$ ), corresponding to the successive oxidation of TTF moiety to radical cation  $TTF^+$  and dication  $TTF^{2+}$ . Compared to TTF-2, the CV of TTF-4 exhibited a new irreversible oxidation peak corresponding to the EDOT moiety ( $E_{\text{ox}}^3 = 1.66\text{ V}$ ). The cathodic 100 mV shifted from 1.76 to 1.66 V of the oxidation peak compared to EDOT-1 and EDOT-2 as shown in Figure 3, illustrating the electron interaction between TTF and EDOT moieties in TTF-4, indicating a considerable easier oxidation of the molecule. The phenomenon may be ascribed to the electron-rich character and steric hindrance effect of the TTF unit. The donor



**Figure 3.** CV of TTF-4, EDOT-1, and EDOT-2 in DCM  $10^{-3}M$ ,  $0.1M$  TBAPF<sub>6</sub> as electrolyte, scan rate  $50\text{ mV s}^{-1}$ .



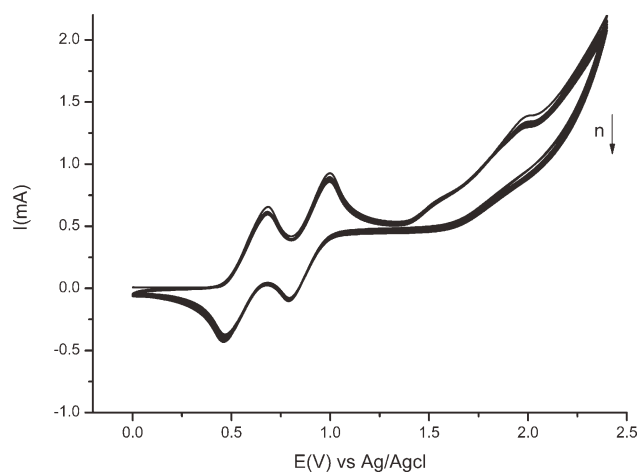
**Figure 4.** Electropolymerization of TTF-4 ( $2 \times 10^{-2}M$ ), AN : DCM (4 : 1), TBAPF6 (0.1M), 0–2.2 V  $50 \text{ mV s}^{-1}$ , 10 cycles.

effect of TTF moiety enhances the electron cloud density of the EDOT moiety. On the other hand, when the relative “powerful” TTF group with alkyl chains is substituted in the hydroxyl position, an electrostatic repulsion may occur between the neighboring TTF moieties. As a result, the framework of thiophene ring would twist and the electron would be easily lost as the descent strength of delocalization pathway of the  $\pi$ -electron system when it was electrochemically oxidized.<sup>20</sup>

#### Multisweep CV

For TTF-4, as shown in Figure 4, a brown film formed at the electrode when the scanning potential was over 1.6 V, the film grows darker with increasing potential as a result of the deposition of polymers on the anode. The reduction of TTF polymer was observed when the potential was below 1.2 V and the color of the film seemed to be a little fading. Although the potential was between 1.2 and 1.6 V, the color was not obviously changed. When the potential is in higher level, the film grows thicker and darker obviously. The potential range from 1.2 to 1.6 V could be considered as a translation region where a deposition–desorption happened. When the scanning cycle increased, the reversible peak current of TTF increased steadily as the deposition of the polymers on the anode and the increasing length of polymer backbone. Unlikely, the irreversible peak current of EDOT ring at about 1.66 V decreased because the EDOT monomer was consumed and the polymers desorbed from the anode. The current changed obviously in the first four cyclic voltammogram. As the scanning proceeded, the solution turned thicker and opaque and the deposition on the anode reached equilibrium, and hence the scanning was stopped after 10 cycles.

The overoxidation is observed with all conducting polymers when the potential exceeds specific critical values.<sup>21</sup> Overoxidation may lead to degradation of the films and result in deactivation of the redox exchange qualities of the films.<sup>22</sup> The overoxidation peak of PEDT often appears near the electropolymerization peak of EDOT<sup>23</sup>; in our case, it appeared between 2.0 and 2.2 V. To study the effect of higher potential on the polymers, the polymerization of TTF-4 was carried in 0–2.5 V scanning and the curves are shown in Figure 5.

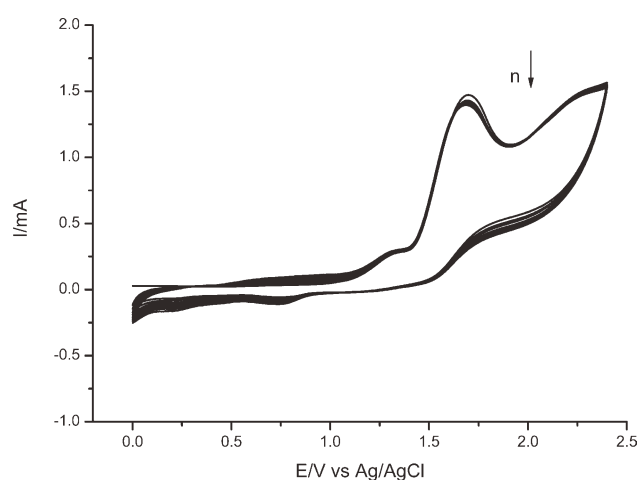


**Figure 5.** Electropolymerization of TTF-4 ( $2 \times 10^{-2}M$ ), AN : DCM (4 : 1), TBAPF6 (0.1M), 0–2.5 V  $50 \text{ mV s}^{-1}$ , 10 cycles.

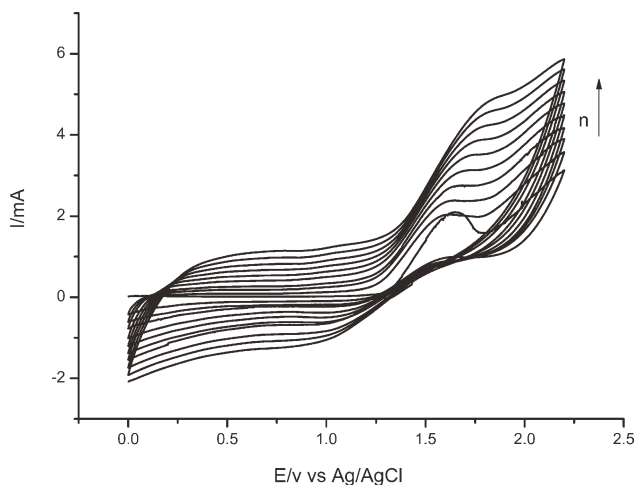
As shown in Figure 5, the TTF peaks decreased as the deactivation of the polymer films, whereas the overoxidation peak increased as high potential brought in more overoxidative products. A new peak emerged at 2.35 V, indicating that the deactivated PEDT films were reactivated by strong electron-static repulsion which was able to localize the polarons of the polymer.<sup>21</sup>

The electropolymerization of EDOT-1 was carried out in similar condition. As shown in Figure 6, unlike TTF-4, the current decreased as the cyclic voltammogram increased. The light blue film formed only when the scan potential was over 1.6 V. When the potential decreased to zero, the film even totally disappeared and no film could form till the potential was over 1.6 V again in the next scanning circle.

The colorless solution turned blue as the cyclic voltammogram increased as a reason of the formation of EDOT-1 polymer. Owing to the high solubility of the polymer, the blue solution became darker and darker and no precipitations could be observed.



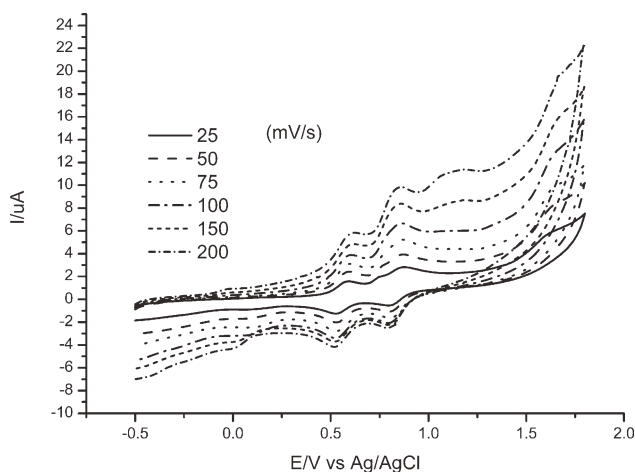
**Figure 6.** Electropolymerization of EDOT-1 ( $2 \times 10^{-2}M$ ), AN : DCM (4 : 1), TBAPF6 (0.1M),  $50 \text{ mV s}^{-1}$ , 10 cycles.



**Figure 7.** Electropolymerization of EDOT-2 ( $2 \times 10^{-2} M$ ), AN : DCM (4 : 1), TBAPF<sub>6</sub> (0.1M),  $50 \text{ mV s}^{-1}$ , 10 cycles.

Although no such problem occurred to the electropolymerization of EDOT-2, so that a dark blue film formed as the scan proceeded and the oxidation peak at 1.56 V, the polymer deposited at the electrode quickly, showing a steadily anodic growth in the current as the cyclic voltammogram increased (Figure 7). The difference might be caused by the long side alkyl chain. Owing to the solubility of the alkyl chain, the polymer became instable toward the doping procedure, meanwhile, the rate constant of forming chain-like conjugated polymer and their coupling steps with the original monomers decreased with increasing chain length.<sup>24,25</sup> In our case, the phenomenon was similar, the polymerization rate of EDOT moiety connected with long chain became slower and slower, especially when Pt was used as working electrode, as deposition of the polymer on the electrode.<sup>26</sup>

The diffusion of oligomers into the solution from the vicinity of the electrode surface did not allow them to couple further because the solution was less concentrated than the electrode



**Figure 8.** CV response of polymer-modified electrode at different scan rates in  $10^{-3} M$  monomer-free solution, AN : DCM (4 : 1), TBAPF<sub>6</sub> (0.1M).

during the electropolymerization process. The monomer/oligomer was allowed only to grow on the chain at the electrode with increasing oligomer concentrations on the surface.<sup>26</sup> Thus, after electropolymerization, we got only a solution of P2 oligomers.

### Potentiostatic Electropolymerization

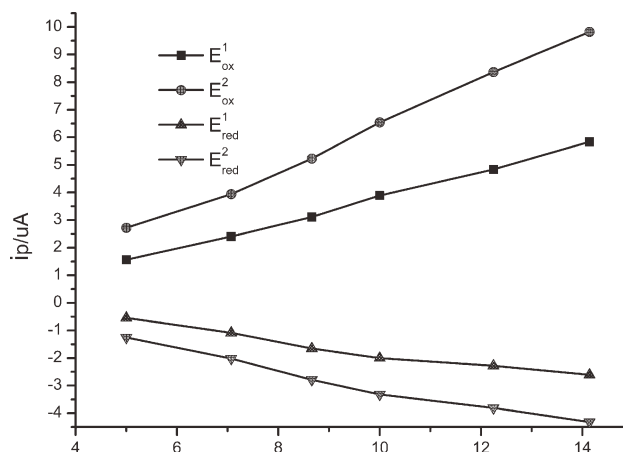
The diffusion of polymers into the bulk solution from the vicinity of the electrode surface may be resolved by employing the technique of potentiostatic electropolymerization.

The films obtained in potentiostatic electropolymerization were tested in CV scanning without removing it from the working electrode. Figure 8 shows the CV response of polymer-modified electrode at different scan rates in a monomer-free solution, illustrating the two-step reversible oxidation of the TTF moiety ( $E_1 p = 0.59 \text{ V}$ ,  $E_2 p = 0.87 \text{ V}$ ), exhibiting the TTF redox system which indicated that TTF unit constituted an internal redox-probe within the polymer film. Compared with the CV response of monomer in Figure 3, an oxidation of polythiophene at 1.18 V and a reduction peak at 0.02 V could be observed, which exhibited the redox-active PEDOT back-bone in particular. The  $i_p$  of the two redox pairs of TTF moiety had a linear relationship with square root of the scan rate as shown in Figure 9.

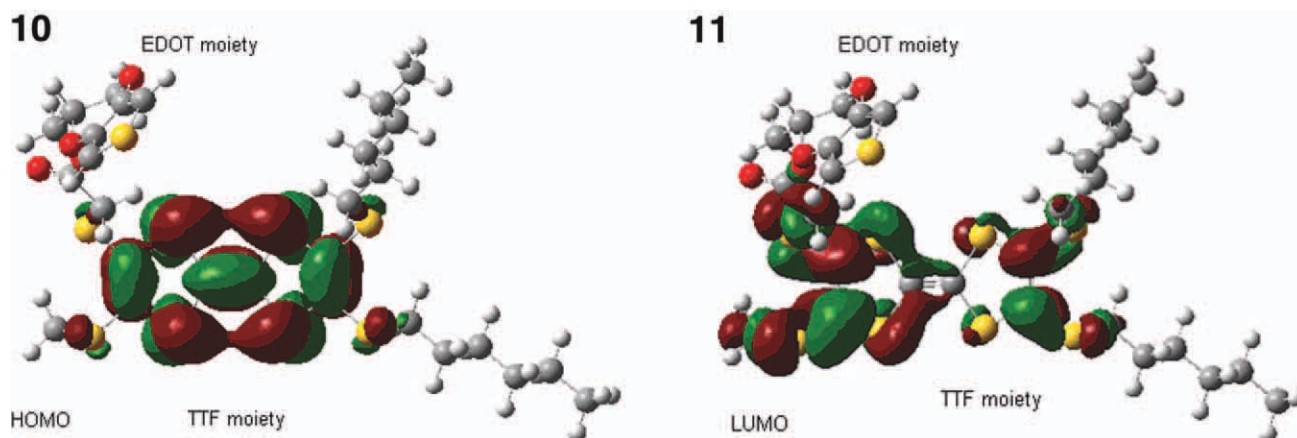
### Computational

To investigate the intramolecular interaction between the EDOT ring and the TTF group in the polymers, the polymer main cores were simulated using DFT with Gaussian03 package and the DFT was treated with the B3LYP/6-31G\* basis sets. The optimized states of HOMO and LUMO are shown in Figures 10–15 and calculated energy levels are listed in Table I.

As shown in Figures 10–15, in HOMO state, the electron cloud of P1 is mainly distributed in the TTF moiety, whereas both P2 and P3 are in EDOT moiety. It can be explained that the TTF moiety is so electron rich that it plays a dominant role in the electron cloud contribution. The calculated HOMO level of P1 is  $-4.86 \text{ eV}$ , which is different from P2 and P3, whose values are  $-5.86$  and  $-5.88 \text{ eV}$ , respectively. In LUMO state, there is



**Figure 9.** The relationship between the  $i_p$  of the two redox pairs of TTF moiety and the square root of scan rate.



**Figure 10, 11.** The optimized states of HOMO and LUMO of P1 core. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

significant difference in the electron cloud distribution for P1–P3. The electron cloud distribution of TTF in P1 (Figure 11) is biased to EDOT moiety, indicating the intramolecular charge interaction of P1. TTF group plays a slight donor role to EDOT moiety, though this molecule cannot be considered as a traditional donor–acceptor type with complete electron transfer. For P2, the electron cloud distributes in EDOT moiety both in HOMO and in LUMO state (Figures 12 and 13), indicating that the substitution of alkyl group does not have obvious effect to the electron cloud distribution. Interestingly, as shown in Figure 15, the electron cloud mainly distributes in the benzene ring in LUMO state for P3, this means that the EDOT moiety has a donor effect to the benzene ring in LUMO state.

Among the three polymers, P1 has the smallest  $E_g$  value, which can be explained by the donor effect in the polymer.<sup>27</sup> Comparing the experimental calculated values with computational values, the HOMO values agree well, it justifies the *p*-doping status of our polymers. Besides, P1 also has the smallest calculated  $E_g$  value, which is related to its donor effect as we argued above.

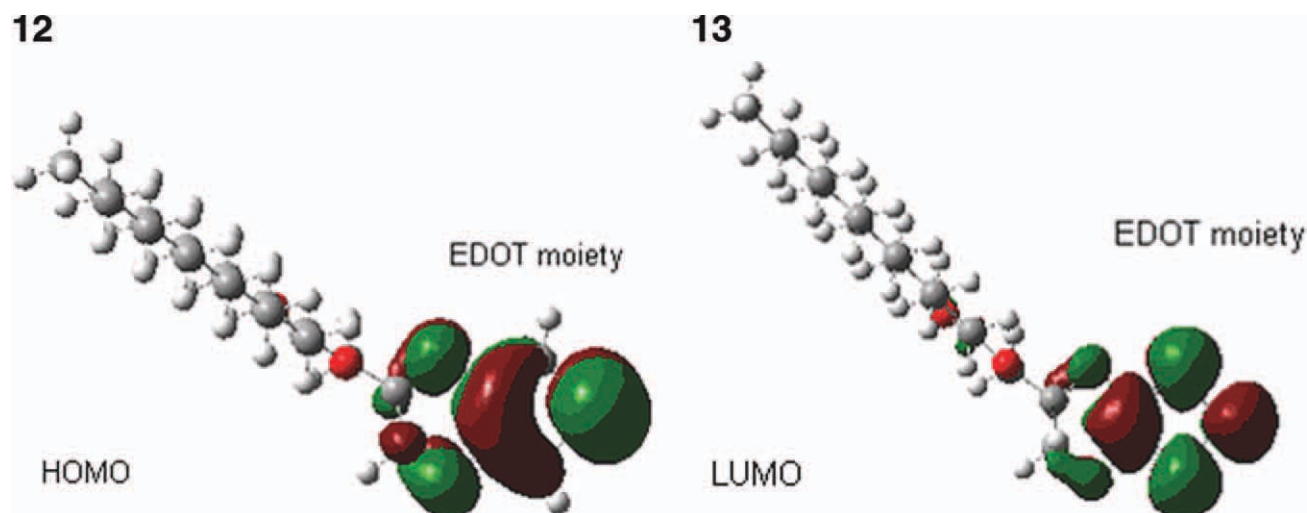
The polymer with smaller  $E_g$  value may have potential application in photovoltaic materials.<sup>28</sup>

### Conductivity

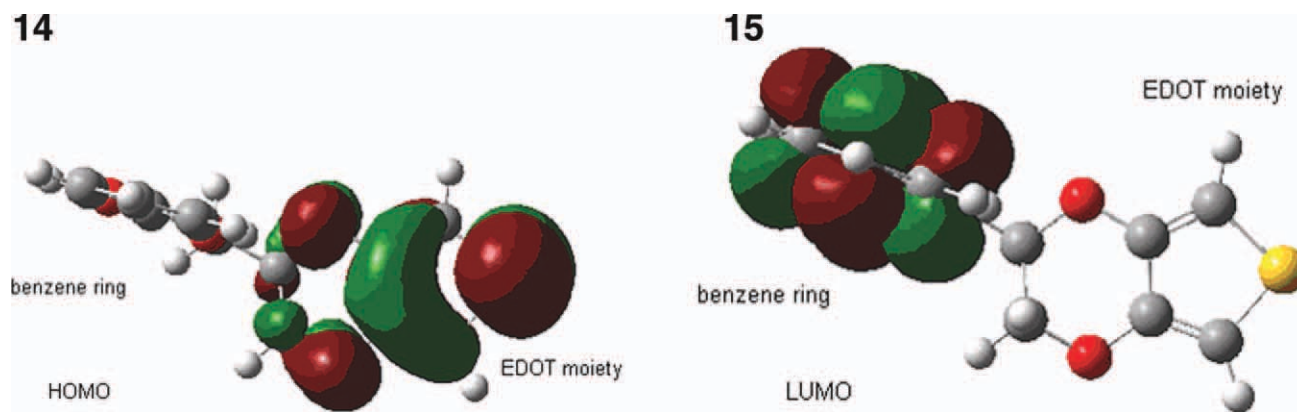
To study the electronic transport properties of the polymers, a galvanostatic procedure is employed. The conductivity of P1 and P3 obtained from both potentiostatic electropolymerization and galvanostatic station is summarized in Table II. The conductivity of P2 was not obtained because there were no qualified films for the four-probe testing owing to its instable deposition on the electrode. We measured different positions of the films and the given result was the average value.

TTF showed some metal property as a well-known organic donor, we measured the conductivity using chemical doping method with TCNQ. The conductivities of undoped and doped polymer are summarized in Table II.

As summarized in Table II, the conductivity of polymers obtained from galvanostatic station was at  $10^1$  magnitude, which was considerably larger than those from the potentiostatic



**Figure 12, 13.** The optimized states of HOMO and LUMO of P2 core. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 14, 15.** The optimized states of HOMO and LUMO of P3 core. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

electropolymerization. The large drop of conductivity emerged because the properties of polymers obtained from electrode depended on both the nature of the polymers and the electropolymerization procedure. The galvanostatic electropolymerization was found to be the function of the nature of the doping anion.<sup>29</sup> It required strict condition and long time which could be considered as a constant procedure while the potentiostatic electropolymerization was a transient procedure in which the polymers were obtained within 5 min, and the films were less tight and refined.

The conductivity of our polymers obtained in galvanostatic station was considerably lower than the unsubstituted PEDOT films in the literature.<sup>30–32</sup> This might be caused by the environment temperature and the substituted side chains. First, at lower temperature ( $-30^{\circ}\text{C}$ ) the film may grow more stably and be doped more adequately with the corresponding anion  $\text{PF}_6^-$ ; on the other hand, lower temperature could reduce the  $E_g$  value of the molecular, and thus it was more beneficial to doping and the chain increasing. Second, the asymmetric side chain may bring in disorder during the electropolymerization procedure while the ideal main chain was expected to grow in identical direction.

TTF showed some metal property as a well-known organic donor, we measured the conductivity using chemical doping method with TCNQ. The conductivities of undoped and doped polymer are listed in Table III. The conductivity of the undoped monomer could not be obtained because it could not form film that was suitable for the four-probe testing.

The chemical doping was taken out on the TTFs, it was an important interest of our research, the doping with  $\text{PF}_6^-$  was only

on the thiophene ring in the main chain to have one-dimension conductivity; the chemical doping on TTFs in the side chain could bring in another dimension conductivity. As summarized in Table III, the monomer had a conductivity at  $5.5 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$  in the doped state because the acceptance of electron from TTF to TCNQ gave rise to electron hole, which facilitated the transportation of electron. The conductivity of doped P1 was  $4.8 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ , which was 24 times higher than the undoped one and much higher than P3<sup>a</sup> (Table II). The increasing conductivity might be related to the increasing conducting dimensions<sup>33</sup> of the P1 as the two parallel charge transport mechanisms were possible: the mixed-valence interactions in  $\text{TTF}^+$  stacks as well as the conductive  $\pi$ -conjugated main chain in the doped state. It was worth noting that the linkage of TTF and EDOT was still  $\sigma$ -bond (C—O) although the conformation of TTF pendant was restricted a lot than the previous studies. The disorder in the stacks of TTF in the side chain was still one problem in obstructing the increasing of conducting dimensions. Further research was in our group such as introducing two  $\sigma$ -bonds or  $\pi$ -bond in the linkage of TTF and EDOT.

There was no evident change in conductivity of the TTF monomer and polymer after chemical doping with TCNQ in the air after 1 week. The solubility, stability, and the availability of the chemical doped TTF polymer gave a new aspect to developing conducting materials.

## CONCLUSION

We have synthesized three EDOT derivatives including an EDOT-TTF obtained by Steglich esterification of EDTM with carboxylic acids. The Steglich esterification is a feasible method

**Table I.** The Calculated Energy Levels of Polymers by B3LYP/6-31G

Polymer	HOMO (eV)	LUMO (eV)	$E_g$ (eV)	$E_g$ (eV) a (experimental)	HOMO(eV) b (experimental)	LUMO(eV) c (experimental)
P1	-4.86	-1.16	3.70	3.01	-4.89	-1.89
P2	-5.86	-1.01	4.85	3.98	-5.96	-1.98
P3	-5.88	-1.37	4.51	4.08	-5.96	-1.88

<sup>a</sup> The experimental  $E_g$  was calculated by UV-abs, <sup>b</sup> HOMO calculated by CV, <sup>c</sup> LUMO =  $E_g$  - HOMO.



**Table II.** Conductivity of Electrode Products

Polymer	Conductivity/S·cm <sup>-1</sup>	Thickness/μm
P1 <sup>a</sup>	2.0 × 10 <sup>-3</sup>	70
P3 <sup>a</sup>	3.5 × 10 <sup>-3</sup>	85
P1 <sup>b</sup>	6	40
P3 <sup>b</sup>	11	46

<sup>a</sup>Electrode product from potentiostatic electropolymerization, <sup>b</sup>Electrode product from galvanostatic station.

**Table III.** Conductivity of Undoped and Doped TTF-4 and P1

Polymer	Undoped conductivity/S·cm <sup>-1</sup>	Doped conductivity/S·cm <sup>-1</sup>
TTF-4	/	5.5 × 10 <sup>-5</sup>
P1	2.0 × 10 <sup>-3</sup>	4.8 × 10 <sup>-2</sup>

to afford EDOT derivatives. The TTF-carboxylic acid group is of high selectivity to the primary hydroxyl isomer of the EDTM mixture. The cyclic voltammetric data imply intramolecular interaction between EDOT and TTF moieties, though such interaction cannot be observed from the UV-Vis spectra. Electropolymerization in excessive potential brings in strong overoxidation effects and degradation in the polymer film. The molecule simulation of P1-P3 shows that TTF moiety may possess a donor effect toward EDOT moiety. The conductivity of P1 measured by both electrochemical doping via galvanostatic station (6 S·cm<sup>-1</sup>) and chemical doping via potentiostatic electropolymerization (4.8 × 10<sup>-2</sup> S·cm<sup>-1</sup>) indicates future application of such TTF polymers in conducting materials. The enhanced conductivity by chemical doping indicates a new way to obtain conducting polymers by increasing the conductive dimensions of the structure.

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