# Electrosynthesis and Spectroelectrochemistry Properties of Copolymers Based on 3,4-Ethylenedioxythiophene and Quaterthiophenen Derivatives

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Based on quaterthiophenen, bisethyleneoxyl are appended to thiophene rings (2,5-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thieno[3,2-b]thiophene, BED-TT) for modified monomer structure and obtain a lower onset potential as well as strong electron donor properties. Different molar ratio copolymers of BED-TT with 3,4-ethylenedioxythiophene (EDOT) was electrochemically synthesized, and the effects of changes in the amount of EDOT on the electrochemical and spectrochemistry properties of the copolymers were tracked. The resultant copolymer P(BED-TT-*co*-EDOT) was characterized via cyclic voltammetry, Raman, and spectroelecrochemistry. The study found that the amount of EDOT in the mixed system of BED-TT and EDOT can regulate the oxidation potential, electrochemical activity, and redox process of polymer films to a certain extent. The spectroelectrochemical results revealed that the copolymer P(BED-TT-*co*-EDOT) has a narrower optical band gap (1.63-1.67eV) and a richer electrochromic color (from pink purple, purple to gray blue, blue).

Keywords: quaterthiophenen; EDOT; copolymer; electrochemistry; spectroelecrochemistry;

# **1. INTRODUCTION**

The development of electrochromic technology and the wide application of electrochromic devices have led to more and more research scholars working on electrochromic materials. Compared with inorganic counterparts, electrochromic conductive polymers have several key advantages, such as high contrast and speedy response times, but the most charming interest is their ability to subjectively adjust color via structural modifications.[1,2] At present, it is generally accepted that the discoloration

mechanism of conductive polymers is explained by the energy band theory.[1-3] By changing the electronic structure of the polymer by electrochemical doping, a relatively low-polarization sub-gap state is formed between the conduction band and the valence band, which effectively lowers the energy level difference. The energy absorbed by the transition of valence electrons between different energy levels is different, which leads to the change of the absorption spectrum of the film and the occurrence of electrochromic phenomenon. Therefore, the electrochemical and spectral chemical properties of materials are important cornerstones for studying electrochromic materials.[4]

To access better performance of electrochromic devices, on the one hand, researchers often need to optimize the chemical structure of polymer molecules: extending the conjugated chain backbone and introducing functional side chains as modifications. For example, thiophene attach functional side chains to the  $\beta$  positions, such as alkyl side chains,[5-7] halogen atoms,[8-10] fluorinated alkyl groups,[11] carboxylates or ester groups[12-13] to change the optical band of the polymer, and making the material exhibit different electronic structure and photoelectric performance. Although precise modification of the polymer structure can effectively optimize the electrical properties of the material itself, the precursors are often more complicated to achieve structural modification, which will greatly increase the time and cost of material preparation. On the other hand, the copolymerization of two or more prepolymers having significant electrochromic properties in a certain solvent system according to a suitable composition ratio is also considered to be an extremely important means for obtaining high performance electrochromic material.[14-16] This is mainly because compared with the structure modification method, electrochemical copolymerization is a fast and effective method to optimize the polymer's electrochromic properties, and successfully avoid the increase in material preparation time and cost caused by complex synthesis processes.

Polythiophene and its derivatives, as one of the most classic conducting polymers, also have a wide range of applications in organic electrochromic materials, because it is easy to synthesize, has a narrow band gap, good chemical stability and high electrical conductivity.[4, 17-19] As a typical thiophene derivative, EDOT, due to the introduction of a strong electron-donating dioxyethylene side chain, makes it have a low oxidation potential and its polymer has a smaller band gap, good redox reversibility and high optical contrast. Due to its unique electrical properties, EDOT is often used as a building block for some polymer molecules to optimize the material's electrochromic properties.[4, 20-23] In addition, poly (2,5-bis (3-hexadecylthiophen-2-yl) thiono[3,2-b] thiophene) (PBTTT), as a typical quaterthiophene polymer, is widely used in organic field-effect transistors owing to its good conjugate plane and large carrier mobility. Due to the unique molecular structure, narrow band gap, low filmforming potential, and good redox stability of PBTTT, it has the potential application in the field of organic electrochromic devices, but there are few efforts on this field referring to the copolymerization of quaterthiophene and EDOT monomers currently.

Thus, in this study, we successfully synthesized a quaterthiophene derivative, BED-TT, and explored the effect of the introduction of dioxyethylene side chain on the electrical properties of monomers and their polymer molecules. The copolymerization of BED-TT and EDOT with different molar ratios obtained by electrochemical methods, and the relationship between the structure and electrical properties of these polymer molecules is analyzed by techniques such as cyclic voltammetry, spectrochemistry, and Raman.

## 2. EXPERIMENTAL

## 2.1. Materials

n-Butyllithium (n-BuLi, 1.6 mol L<sup>-1</sup> solution in hexanes), 3,4-ethylenedioxythiophene (EDOT, 98%), trans-dichlorobis(triphenyl-phosphine) Palladium (II) (Pd(PPh<sub>3</sub>)Cl<sub>2</sub>), n-butanol (n-BuOH, 99%), iron (III) p-toluenesulfonate hexahydrate (Fe(Tos)<sub>3</sub>·6H<sub>2</sub>O, 99%), and propylene carbonate (PC, 99.5%, Ultra-dry) were received from J&K Scientific Ltd. 2,5-dibromothieno[3,2-b]thiophene and Chlorotributyltin (SnBu<sub>3</sub>Cl, 98%) were obtained by Aladdin. Lithium perchlorate (LiClO<sub>4</sub>, 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 trichloromethane (CHCl<sub>3</sub>, analytical grade) were supplied by Beijing East Longshun Chemical Plant and

purified by calcium hydroxide distillation in a nitrogen atmosphere. Other chemicals and reagents (analytical grade, >98%) were supplied by common chemical reagent companies and not treated further before use.

## 2.2. Synthesis of 2,5-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thieno[3,2-b]thiophene (BED-TT)

#### 2.2.1. Tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (EDOT-SnBu<sub>3</sub>)

The compound EDOT-SnBu<sub>3</sub> was synthesized according to previous reports.[24-26] EDOT (20 mmol) was added to 40 mL of calcium hydride-treated THF, and n-BuLi (22 mmol) was slowly added dropwise to remove H of  $\alpha$  position in thiophene under a N<sub>2</sub> atmosphere at -78 °C. Then the reaction was performed at in this condition and kept for 2 h. After the temp to -40 °C, 22 mmol SnBu<sub>3</sub>Cl was added to the flask and kept for 0.5 h and then slowly warmed to room temp, kept for 8 h under continued stirring. The resulting mixed system was directly removed from the solvent, then filtered to obtain a crude product, which was then used for the next coupling reaction.

#### 2.2.2. BED-TT

According to literature, the Stille Coupling reaction was used to synthesize BED-TT monomer.[27-28] 50 ml of DMF was added to a mixed solution of 10 mmol of EDOT-SnBu<sub>3</sub>, 5 mmol of 2,5-dibromothieno[3,2-b]thiophene, and 0.5 mmol of Pd(PPh<sub>3</sub>)Cl<sub>2</sub>, and placed in a N<sub>2</sub> atmosphere at 110 °C. The reaction was carried out under reflux for 12 h. When the reaction was cooled to room temp., the crude product was washed with water and then repeatedly extracted with dichloromethane. After that, the obtained mixed solution was further spun off and purified using a silica gel column. BED-TT <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (s, 2H), 6.26 (s, 2H), 4.38 (s, 4H), 4.29 (s, 4H).



**Scheme 1.** Synthetic routes of BED-TT with the corresponding intermediate products and electrochemical polymerization of P(BED-TT-*co*-EDOT).

### 2.3. Electrochemical tests

Electrochemical testing was performed using the electrochemical instrument with model Princeton V3 in a standard three-electrode systems in single compartment at room temperature. In this electrochemical test system, the working electrode and the counter electrode are both indium-tin oxide (ITO) glass, and the reference electrode is a fresh Ag/AgCl electrode prepared in 6 M hydrochloric acid solution. These ITO glasses as electrodes were ultrasonicated for 20 minutes in ITO washing lotion, acetone, and ethanol, respectively, and then rinsed with deionized water as well as dried in air before each experiment. In order to visually observe the electrochromic properties of the polymer film, the area of the ITO-coated glass on the working electrode was expanded to  $2.5 \times 0.8 \text{ cm}^2$ . A mixture of PC solution containing 0.2 M of LiClO<sub>4</sub> (LiClO<sub>4</sub>/PC) was used as the electrolyte solution in the electrochemical polymerization and analysis. These P(BED-TT) and poly(3,4-ethylenedioxythiophene) (PEDOT) films were obtained by electrodeposition on the ITO glass under constant potential in the mixture solution of the corresponding 0.01 M monomer (BED-TT, or EDOT) and 0.2 M LiClO<sub>4</sub>/PC. Their copolymer films were prepared in the same electrolyte solutions containing the different  $n_{\text{BED-TT}}$ : $n_{\text{EDOT}}$  ratio of 1:1, 1:2, 1:3, and 1:5 with the total concentration of 0.01 M. The polymer film electrochemical tests were performed in monomer-free electrolyte solutions.

## 2.4. Characterization

Using tetramethylsilane (TMS) as an external standard, the <sup>1</sup>H NMR spectrum of the monomer was tested in a CDCl<sub>3</sub> solution and recorded on a Bruker AVANCE III spectrometer. Raman spectroscopy uses a 532nm excitation light source and is presented on a Lab RAM HR Evolution Raman spectrometer (HORIBA Scientific, France). The Cary 50 spectrophotometer was used to record the

spectroelectrochemical data of the polymer film, and during the test, the film was placed in a LiClO<sub>4</sub>/PC solution without monomer.

#### **3. RESULTS AND DISCUSSION**

3.1. Electrochemical Polymerization



**Figure 1.** Anode polarization curves of (a) 0.01 M BED-TT, monomer mixture with BED-TT/EDOT= (b) 1:1, (c) 1:2, (d) 1:3, (e) 1:5 and (f) 0.01 M EDOT in the 0.1 M LiClO<sub>4</sub>/PC. Scanning rates: 10 mV s<sup>-1</sup>.

Since the oxidation potential is a characteristic phenomenon of the polymer itself, any change in the electronic energy level of the polymer due to the structural modification will affect its own oxidation potential.[29] To understand the effect of adding EDOT to the electrolyte system (0.1 M LiClO<sub>4</sub>/PC) on the onset oxidation potentials of BED-TT, a series of anode polarization curves of BED-TT and EDOT monomer with different ratios were obtained. All curves were obtained at a scanning rate of 10 mV s<sup>-1</sup>. Meanwhile, for comparison, the anode polarization curve of BED-TT and EDOT were also tested. As we can see from Figure 1. For BED-TT and EDOT, the onset oxidation potential ( $E_{onset}$ ) is 0.59 V and 1.08 V respectively, indicating that the two monomers can obtain a high quality polymer film at a low mild oxidation potential. [28, 30-32] It is expectable that the oxidation potential of BED-TT was significantly lower than that of EDOT due to the large conjugate plane of the trimer compound BED-TT. What's more, a relatively small difference of  $E_{onset}$ , 0.35V, implies that electrochemical copolymerization between BED-TT and EDOT can be easily achieved in PC with LiClO<sub>4</sub> as supporting electrolyte.[15, 33] Further, the E<sub>onset</sub> of these monomer mixed solution containing different molar ratios are significantly different from  $E_{\text{onset}}$  of (BED-TT) and (EDOT), which also means the existence of the interaction between the two monomers in the process of electrochemical polymerization. Obviously, when the amount of EDOT in the mixed system increases, the  $E_{onset}$  of the BED-TT/EDOT mixture

approaches the oxidation potential of the EDOT. Interestingly, after the introduction of EDOT, the current density of the anodic polarization curve of the monomer increased significantly, indicating that the mixed monomer has better electrochemical activity. However, with the increase of the amount of EDOT, the current density of the polarization curve gradually decreases. When BED-TT: EDOT = 1:1, the current density increases most with the voltage.



Figure 2. Electrochemical deposition of (A) 0.01 M BED-TT, monomer mixtures with BED-TT/EDOT=
(B) 1:1, (C) 1:2, (D) 1:3, (E) 1:5, and (F) 0.01 M EDOT in the LiClO<sub>4</sub>/PC solution system at 50 mV s<sup>-1</sup>.

Cyclic voltammetry (CV) is a technique commonly used to analyze the polymer growth rate during monomer redox processes.[34-35]The successive CV curves of BED-TT, different molar ratios BED-TT/EDOT mixture, and EDOT in 0.1 M LiClO<sub>4</sub>/PC at 50 mV s<sup>-1</sup> are shown in Figure 2. In these CV curves, the oxidation and reduction peak current increases with the repeated scanning, and the formation of a blue polymer film can be observed on the working electrode surface. Meanwhile, this result also demonstrates that the as-prepared conductive polymers have an admirable electrochemical activity.[18, 24] Compared with the pure BED-TT and EDOT (see Figure 2A and Figure 2F), the feature and the position of the redox peak of the CVs curve of the monomer mixture system are rather different in Figure 2(B-E), indicating that copolymerization of BED-TT and EDOT units has been obtained during electrochemical polymerization. However, although the CV curve of the monomer mixture are distinct from their neat monomer's, the CV curves of the BED-TT/EDOT mixture with different molar ratios have similar characteristics. In addition, it is worth noting that the redox potential range of the BED-TT/EDOT mixture system becomes wider with the introduction of the EDOT unit, indicating that more EDOT units are introduced into the backbone chain of the copolymer.[15] Among these CV curves of BED-TT, BED-TT/EDOT, and EDOT, fairly strong and broad redox wave can be observed from all CVs of the monomer. This is thought to be due to the wide distribution of polymer chain lengths or the conductive material on the polymer backbone from a neutral state to a metal state. [14, 24, 31]

### 3.2 Electrochemical behavior of films

These P(BED-TT), poly(3,4-ethylenedioxythiophene) (PEDOT) and their copolymer films were obtained by electrodeposition on the ITO glass under constant potential and electrochemical behaviors of the copolymers were further investigated. The P(BED-TT-co-EDOT) is used to represent the polymer obtained by copolymerization of BED-TT and EDOT (Scheme 1). After 2 minutes of de-doping, the electrochemical phenomena of the film were characterized by CVs in a monomer-free electrolyte at different scan rates of 25 mV s<sup>-1</sup> to 300 mV s<sup>-1</sup>. Unlike their monomer's, the CV curves of P(BED-TT), PEDOT and P(BED-TT-co-EDOT) have significant differences, which also illustrates the successful preparation of the copolymer film.[15, 36] It is important that P (BED-TT-co-EDOT) films with different monomer molar ratios have very distinct redox peaks, which further implies that the amount of EDOT introduced will affect the preparation of copolymer films.[31] Furthermore, there is a significant difference in the driving power of the redox polymer, when the EDOT was introduced. These differences correspond to the highest occupancy state of the molecule, [35] which can be generally observed in conductive polymers. There are many reasons for this difference, including the ease of diffusion of dopants in and out of the polymer film and the transfer of surface charge.[24,37] The polymer P(BED-TT) exhibits a satisfactory redox reversible process, which is indicated by an almost intact redox potential over the entire scan rate range.



**Figure 3.** Cyclic voltammograms of (A) P(BED-TT), P(BED-TT-*co*-EDOT) obtained with BED-TT/EDOT= (B) 1:1, (C) 1:2, (D) 1:3, (E) 1:5, and PEDOT in the monomer-free CAN/LiClO<sub>4</sub> at different scanning rates.

Interestingly, when the molar ratio of BED-TT to EDOT was 1: 1, the CV curve of the copolymer showed a narrower redox peak compared to P(BED-TT), and the position of its maximum reduction peak shifted in the direction of high voltage. However, as the molar amount of EDOT increases, the redox peak of the copolymer CV curve is significantly widened, and the position of its maximum reduction absorption peak starts to move in the low voltage direction.

#### 3.3 Spectroelectrochemistry

Spectroelectrochemistry is a very useful tool in characterizing the electronic structure of polymers and tracking changes in the polymer's spectral absorption under different doping states. As mentioned earlier, the UV-Vis-NIR spectrometer is used to record changes in the spectral absorption of polymer films under different applied voltages in a monomer-free 0.2 M LiClO<sub>4</sub> / PC solution. As shown in Figure 4A and Table 1, the maximum absorption peak of P(BED-TT) at 535 nm is assigned a  $\pi$ - $\pi$ \* transition, and the film is purple under neutral conditions.[38-39] As the potential gradually increases from -0.7~1.1 V, the maximum absorption peak at 535 nm gradually decreases and shifts to the right, as well as a new peak appears near 700 nm. The isoabsorption point at 630 nm indicates that the polymer molecule has a neutral oxidation state to a polaron state.[41] A similar trend can also be observed in the spectroelectrochemical diagram of P(BED-TT-*co*-EDOT) and PEDOT. However, the position of the maximum absorption peak of P(BED-TT-*co*-EDOT) is between 591-598 nm (Figure 4B-E), which produces a red shift of 56-63 nm relative to PBED-TT. This result mean that the introduction of EDOT can significantly increase the effective conjugate length of polymer molecules, which is conducive to carrier transport in polymers and improves the electrochemical activity of materials.



**Figure 4.** Spectroelectrochemistry of (A) P(BED-TT), P(BED-TT-*co*-EDOT) obtained with BED-TT/EDOT = (B) 1:1, (C) 1:2, (D) 1:3, (E) 1:5, and (F) EDOT on the ITO glass in monomer-free 0.2 M LiClO<sub>4</sub>/PC electrolyte.

**Table 1.** Electrochemical spectra of the as-prepared homopolymers and copolymers

Polymer	P(BED-TT) -	P(BED-TT-co-EDOT)				DEDOT
		1:1	1:2	1:3	1:5	- FEDUI
$\lambda_{max}(nm)$	535	591	598	591	593	599
$\lambda_{edge} (nm)$	708	741	741	763	751	747
$E_{\rm g}({\rm eV})$	1.75	1.67	1.67	1.63	1.65	1.66

Similarly, with the increase of the applied potential, these copolymer molecules also appear new polaron peaks after 700 nm, and at the same time, the peak of the neutral state near 590 nm gradually decreases. In the oxidized state, the absorption peak around 630-1000nm can be attributed to the increase of charge carrier delocalization and the overall stability of the oxidation state. [41] In addition, according to the film photos in Figure 4, the color of the film of the copolymer in the reduction state and the oxidation state is also significantly different with respect to the P (BED-TT) film. Wherein the color of the reducing state is gradually changed from the light purple to the dark purple, and the blue of the oxidation state is also shallow to deep, but the color change contrast of the oxidized state is relatively poor compared with the reduced state, which is more similar to that of PEDOT (Figure 4F). Because the electron absorption of the polymer will show different color changes at different potentials, the color change of the polymer from the reduced state to the oxidation state indicates that the polymer has good electrochromic properties. Using the commencement of the low energy end of the  $\pi$ - $\pi$ \* transition calculations of polymers, it was found that P (BED-TT-co-EDOT) has a narrower band gap of 1.63-1.67 eV compared to P (BED-TT) 1.74 eV. Surprisingly, the band gap of these polymers is almost equal to that of PEDOT, and the amount of EDOT in the monomer mixture has little effect on the band gap of the polymer. This result means that the copolymer has been successfully prepared, and the introduction of EDOT can regulate the band structure of polymer molecules to a certain extent.



**Figure 5.** Raman spectra of (a) P(BED-TT), and P(BED-TT-*co*-EDOT) obtained in the monomer mixtures with BED-TT/EDOT= (b) 1:1, (c) 1:2, (d) 1:3 (e) 1:5 as well as (f) PEDOT films.

Raman spectra of various P(BED-TT-*co*-EDOT) copolymers that prepared in the electrolyte system containing BED-TT and EDOT with different ratios by electrochemical copolymerization are shown in Figure 5. For comparison, Raman spectra of homopolymer P(BED-TT) and PEDOT are also presented. The wavenumbers of the observed band in these spectra are given in the Table 2.[42-45] The band at 400, 576, and 990 cm<sup>-1</sup> corresponding to the deformation of the oxyethylene ring, at 700 cm<sup>-1</sup> relating to the symmetric C-S-C deformation were found in P(BED-TT) homopolymers and copolymers

but were weak in the PEDOT film. Additionally, the peak at 1276 cm<sup>-1</sup> is assigned to the  $C_{\alpha}$ - $C_{\alpha'}$  (interring) stretching. The  $C_{\beta}$ - $C_{\beta'}$  stretching is located at 1370 cm<sup>-1</sup>.

Raman shift (cm <sup>-1</sup> )	Assignation			
440, 576, 990	Deformations of oxyethylene ring			
700	Symmetric C-S-C deformation			
1276	$C_{\alpha}$ - $C_{\alpha'}$ (inter-ring) stretching			
1370	$C_{\beta}$ - $C_{\beta'}$ stretching			
1419, 1448	Symmetric $C_{\alpha}=C_{\beta}$ stretching			
1515	Asymmetric $C_{\alpha}=C_{\beta}$ stretching			

Table 2. Typical vibrational modes of PEDOT

Importantly, three strong band of various P(BED-TT-*co*-EDOT) and P(BED-TT) films at 1419, 1448, and 1515 cm<sup>-1</sup> are corresponded to the symmetric  $C_{\alpha}=C_{\beta}$  stretching and asymmetric  $C_{\alpha}=C_{\beta}$  stretching, respectively. Especially, in these strong band, the band at 1419 cm<sup>-1</sup> is a band only appearing in the P(BED-TT) and these copolymers, and the others strong band that are appeared in the P(BED-TT) and copolymers were shown weaker and broader in the PEDOT film. These results suggest that the copolymer films were obtained by electrochemical copolymerization. Further, with the relative concentration of BED-TT decreases, the two peak intensity ratios at 1419 and 1448 cm<sup>-1</sup> also show the same trend, which indicates that the number of EDOT blocks in the copolymer increases with the relative concentration of EDOT monomer in the electrolyte system.

## **4. CONCLUSIONS**

A quaterthienyl small molecule BED-TT was successfully synthesized, which has a small oxidation potential and good redox reversibility. Several reasons to result in the phenomenon are as follow: (a) BED-TT is an oligomer of thiophene, which has a longer effective conjugate length than thiophene; (b) The introduction of a dioxyethylene side chain with strong electron-donating properties increases the density of the electron cloud in the molecule. When the mixing ratio of BED-TT and EDOT is 1: 1, 1: 2, and 1: 3, the *E*<sub>onset</sub> of the mixed monomer gradually increases compared to BED-TT. In addition, the CV of these P(BED-TT-*co*-EDOT) films also showed a narrower redox peak than P (BED-TT) and its redox peak gradually widened as the amount of EDOT increased. Moreover, these spectroelectrochemical results show that the copolymer P (BED-TT-*co*-EDOT) has a larger effective conjugated structure and narrower band gap than P (BED-TT), and the amount of EDOT has no obvious effect on the band gap of the polymer. The color changes of polymers P(BED-TT) and their copolymers from reduced to oxidized state indicate that both have better electrochromic properties.

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