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# Thieno[3,2-*b*]thiophene Based Electrochromic Polymers: Experimental Cum Theoretical Appraisal of the EDOT Position

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**Keywords**: Electrochemical Polymerization Process, Electrochromism, Thieno[3,2-*b*]thiophene, EDOT, Substituent Position, Gauss Calculation , Conjugation

**ABSTRACT**: Two thieno[3,2-*b*]thiophene based polymers poly[2,5-bis(2,3-dihydro-thieno[3,4-*b*][1,4]dioxin-5-yl)thieno[3,2-*b*]thiophene] (P(2,5-BTE)) and poly[3,6-bis-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)thieno[3,2-*b*]thiophene] (P(3,6-BTE)) were synthesized by electrochemical method. By alternating 3,4-ethylenedioxythiophene (EDOT) position along the polymer backbone we studied electrochemical and optical properties by comparing 2,5- and 3,6-positions on thieno[3,2-*b*]thiophene unit. Theoretically calculated bandgaps and ultraviolet–visible spectrum (UV-Vis) peaks of the two dimers are in good agreement with the polar energy and peak range in ultraviolet–visible and near-infrared (UV–Vis–NIR) spectrum, which helps us to

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comprehend the process of electrochemical polymerization and indicates that P(2,5-BTE) has more conjugated structure than P(3,6-BTE). With the increase in voltage, both the polymers gradually transform to their quinoid structures and P(2,5-BTE) reflects color from purple to grey-blue, while P(3,6-BTE) switches from orange-red to cyan. Effective color tuning by changing the position of EDOT units are the noteworthy properties of P(2,5-BTE) and P(3,6-BTE), which make them suitable electrochromic materials.

## 1. INTRODUCTION

Though preliminarily reported in 1930s, it was until Plant first found the phenomenon of electrochromism in 1960s in his study on organic dyes, then further exploration into electrochromism started.[1] Fabrication of the first electrochromic (EC) device by S. K. Deb, using amorphous $WO_3$ thin film, by putting forward the idea of "oxygen vacancy center" mechanism,[2] opened the doors to the blossoming future of electrochromism and many scientists devoted their attention to synthesize new EC materials and fabricate new EC devices. In 1999, Stadt Sparkasse Savings Bank first used "smart window" in their new building and now a wide variety of absorptive/transmissive and reflective-type EC device applications are being studied,[3] including residential, aircraft, automotive windows/roofs, wearable vision systems (goggles, helmets)[4-6], fabrics (camouflage, chameleonic Spandex),[7-8] antiglare dimming mirrors, electronic tags, signage and e-papers.[9]

Conjugated polymers have gained much popularity, as a class of EC materials, due



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to their synthetically tunable structure, ease of processability, rapid response time and high optical contrast.[10] Thieno[3,2-*b*]thiophene based π-conjugated oligomers and polymers are being studied extensively for their use as organic semiconductors in devices such as organic field effect transistors (OFETs),[11] organic light emitting diodes (OLEDs)[12] and organic photo-voltaic cells (OPVs).[13] Thieno[3,2-*b*]thiophene has good plain symmetrical structure and functional groups can be easily modified to optimize electronic properties, making it a core unit in many useful organic optoelectronic materials.[14] On the other hand, poly(3,4-ethylenedioxythiophene) (PEDOT) has high conductivity, stable doping ability, ideal transparency and obvious color change between doping and de-doping states, making it an exceptional EC material. As an exceptional organic hole injection material, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) can greatly improve the device performance. Currently, 3,4-ethylenedioxythiophene (EDOT) and its corresponding compound PEDOT: PSS have been commercialized and are being extensively used in OLEDs,[15] OTFTs ,[16] organic electrochromics (OECs),[9] OPVs,[17] super capacitors[18] and numerous organic optoelectronic devices.

The EDOT structure in the thiophene ring augments the electron density of the ring system, effectively reducing the oxidation potential.[19] However, despite much of the research work has entailed the incorporation of the EDOT core into various aromatic moieties to study the optoelectronic properties of the new copolymers, less effort has been devoted to study such influence systematically, especially combination of the theoretical study and the experimental results. Herein, for the first time, we introduce



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two polymers poly[2,5-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)thieno[3,2-*b*]thiophene] P(2,5-BTE) and poly[3,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)thieno[3,2-*b*]thiophene] P(3,6-BTE), combine experimental results and theoretical evaluation to explore their electrochemical polymerization process and exploit the effect of EDOT substitution at 2,5- or 3,6- positions of thieno[3,2-*b*]thiophene for achieving anticipated electrochromic performance. The alternating EDOT position along the polymer backbone at different sites remarkably resulted in total different conjugations and created distinct intramolecular charge transfer.[20-21] It is noteworthy that these two novel polymers, which are synthesized by electrochemical method, have two distinct color transfer modes upon doping, this would extend the repertoire of available colors of processable electrochromics (blue, green and black etc.), which are essential for full color displays.

## 2. EXPERIMENTAL DETAILS

Except palladium catalyst which was purchased from TCI, all other chemicals were purchased from Energy chemical. Acetonitrile and dichloromethane were dried and distilled over calcium hydride under nitrogen. 2,5-dibromothieno[3,2-*b*]thiophene, tetrabromo-thienothiophene, 3,6-dibromothieno[3,2-*b*]thiophene, tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)stannane, were synthesized according to previously described methods.[22-23] All electrochemical studies were accomplished with a CHI620E electrochemical workstation. UV–Vis–NIR spectra were recorded on a Lambda 750 spectrophotometer. A three-electrode cell was utilized that consisted of

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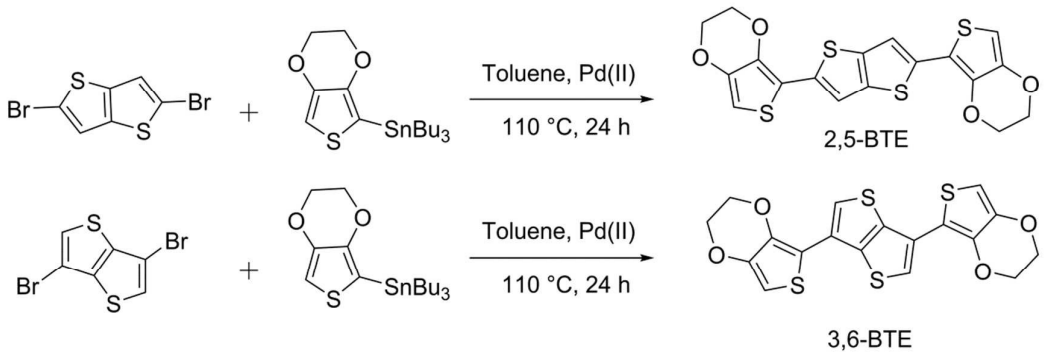
a silver (Ag) wire pseudo reference electrode, a platinum (Pt) wire counter electrode and an indium tin oxide (ITO)-coated glass or a Pt button electrode (R: 1 mm) as a working electrode. The voltage was controlled by using a CHI620E electrochemical workstation.

**2.1 Monomer Synthesis.** The synthesis of the target compounds is outlined in Scheme 1.[24]




**Scheme 1.** Synthesis route of 2,5-BTE and 3,6-BTE

*2,5-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thieno[3,2-b]thiophene* ***(2,5-BTE)***

2,5-Dibromothieno[3,2-*b*]thiophene (2.00 g, 6.70 mmol) and tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)stannane (8.70 g, 20.10 mmol) were dissolved in anhydrous toluene (75 mL). The solution was purged with argon for 30 min and $[(C_6H_5)_3P]_2PdCl_2$ (0.50 g, 0.70 mmol) was added at room temperature under an argon atmosphere. The mixture was stirred at 110 °C under argon atmosphere for 24 h, cooled and quenched by the addition of water. The mixture was then extracted with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure and then residue was subjected to



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column chromatography ($CH_2Cl_2$/ hexane, 1: 1) to get a black brown solid 1.52 g. Yield: 54%, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.35 (s, 2H), 6.24 (s, 2H), 4.37 (s, 4H), 4.26 (s, 4H). $^{13}$C NMR (400 MHz, $CDCl_3$) $\delta$ 141.98, 138.06, 136.09, 131.89, 128.40, 115.10, 97.41, 65.33, 64.65. MS (*m/z*): 421 $[M+H]^+$.

*3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thieno[3,2-b]thiophene* ***(3,6-BTE)***

The procedure is similar to the synthesis route of 2,5-BTE, and finally get a white solid 2.34 g. Yield: 83%, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.81 (s, 2H), 6.40 (s, 2H), 4.37 (s, 4H), 4.30 (s, 4H). $^{13}$C NMR (400 MHz, DMSO) $\delta$ 141.91, 138.42, 135.76, 124.83, 122.78, 109.67, 97.66, 64.35. MS (*m/z*): 421 $[M+H]^+$.

### 2.2 Electrochemical polymerization

Electrochemical polymerization was performed in a three-electrode cell that consisted of a Pt button electrode (R: 1 mm) or ITO-coated glass as the working electrode, a platinum wire as the counter electrode, and a silver (Ag) wire as the pseudo reference electrode. Electrodeposition was performed using a mixture of 0.10 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) and 2.60 mM monomer (2,5-BTE and 3,6-BTE) in dichloromethane at a scan rate of 100 $mVs^{-1}$ for 19 cycles at room temperature. Cyclic voltammograms (CV) of the polymers were obtained using the same electrode setup in monomer-free acetonitrile solution with 0.10 M $TBAPF_6$. Under repetitive cycling, a colorful film was deposited on the platinum button electrode.

## 3. RESULTS AND DISCUSSION

The electrochemical polymerization curves of the two polymers are presented in



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Figure 1.

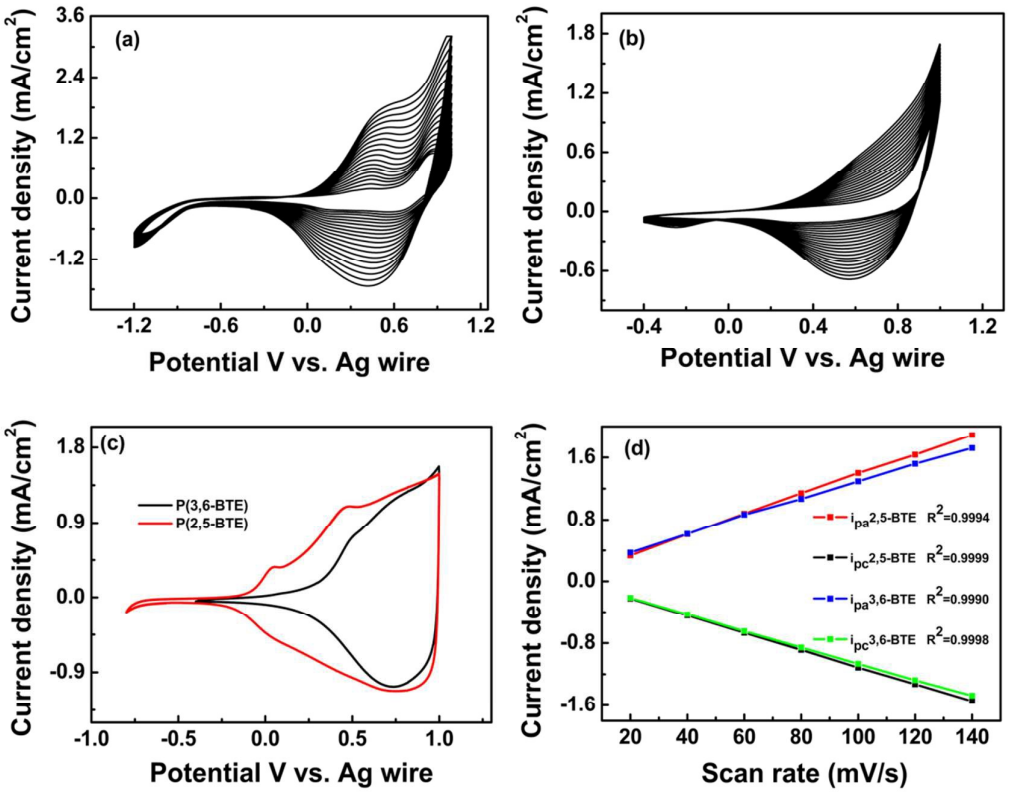


**Figure 1.** Electrochemical polymerization of (a) 2,5-BTE and (b) 3,6-BTE in 0.10 M TBAPF6/DCM via repetitive cycling at a scan rate 0.10 V/s. (c) Cyclic voltammograms of P(2,5-BTE) and P(3,6-BTE) in 0.10 M $TBAPF_6$/ ACN on a platinum button electrode at a scan rate of 0.10 V/s (d) Plot of current *versus* scan rate for P(2,5-BTE) and P(3,6-BTE)

It is evident in Figure 1(a) (b) that polymers redox processes develop rapidly and the monomers have polymerized very efficiently to form highly electroactive polymers. Polymer P(2,5-BTE) exhibits a broad oxidation/reduction peak at about +0.45 V/+0.42 V caused due to the oxidation/reduction of 2,5-EDOT substitution units and a broad reduction peak appears at +0.57 V for polymer P(3,6-BTE). The peak at +0.57 V is possibly due to the reduction of 3,6-EDOT substitution units. After



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washing with acetonitrile solution, loose film particles on the surface of P(2,5-BTE) were washed off. The onset potential values of P(2,5-BTE) and P(3,6-BTE) in Figure 1 (c) are far below the oxidation potential of thiene[3,2-*b*]thiophene (1.40 V), which confirm that EDOT units have effectively improved the conductivity.[25] Comparing the current density and potential in Figure 1 (c), the peaks caused by the oxidation of 2,5-EDOT substitution units tend to obtain lower oxidation potential and higher current density because of their more conjugated structure and electronic interactions between 2,5-EDOT substitution units and thieno[3,2-*b*]thiophene. Both polymers have a sharp current density decrease at +1.00 V in CV curves, which represents good stability of the cation radical, possibly due to a stabilizing conformational change upon oxidation.[26]

Evidently, the peak current intensities of both polymers increase steadily with the scan rate in figure 1 (d). A linear dependence of the peak anodic and cathodic currents on the scan rate is obtained having the least square fits of $R^2$ = 0.9994 and $R^2$ = 0.9999, respectively, for 2,5-BTE and $R^2$ = 0.9990 and $R^2$ = 0.9998, respectively, for 3,6-BTE, indicating that the electroactive polymer films are well-adhered to the substrate and the redox processes are non-diffusion limited.[27]

In order to characterize the colors of the deposited polymer thin films, we measured CIE color coordinates L*, a* and b*, where coordinate L* stands for lightness, a* and b* stand for two antagonistic chromatic processes; a* reveals red-green and b* reveals yellow-blue.[28] The values are measured and summarized in table 1.

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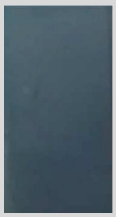
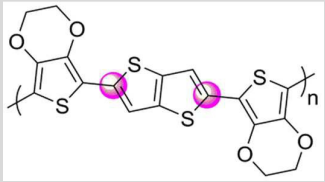
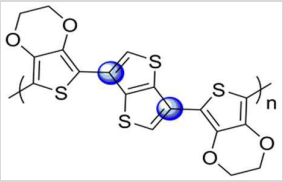
**Table 1. Colorimetric results**

| | P(2,5-BTE) | | P(3,6-BTE) | |
|---|---|---|---|---|
| Polymer's Color | |  | | |
| |  | |  | |
| Applied Potential (V) | -0.8 V | +1.0 V | -0.4 V | +1.0 V |
| L, a, b | L: 56.5<br>a: 1.1<br>b: -10.5 | L: 50.3<br>a: -1.7<br>b: -10.7 | L: 27.5<br>a: -71.1<br>b: 1.7 | L: 26.8<br>a: 30.9<br>b: 31.8 |

To investigate the optical changes in polymers P(2,5-BTE) and P(3,6-BTE), spectroelectrochemical plots are presented in Figure 2.

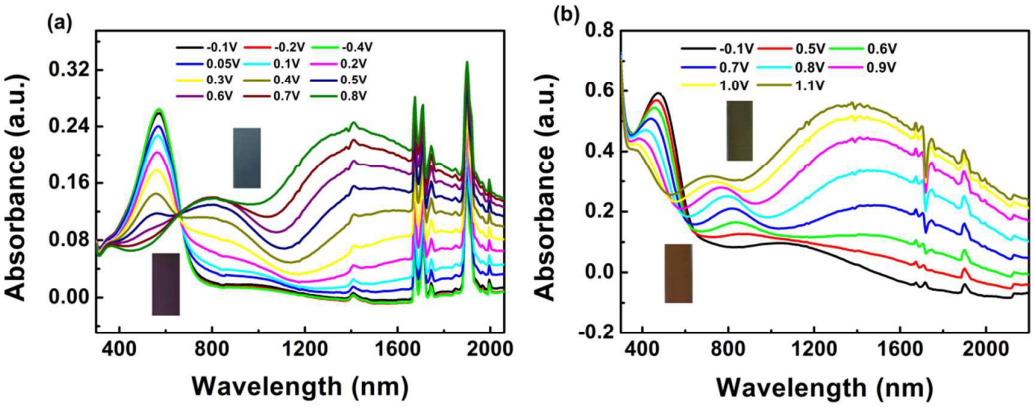



**Figure 2.** Spectroelectrochemistry of the deposited thin films of (a) P(2,5-BTE) and (b) P(2,5-BTE) in $TBAPF_6$/ACN on ITO-coated glass substrate at various applied



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potentials

Obvious optical changes can be observed by incrementally increasing the applied potential between -0.40 V and +1.20 V by UV–Vis–NIR spectrophotometer in a 0.10 M monomer-free $TBAPF_6$ /ACN solution. P(2,5-BTE) reflects purple to grey-blue color and shows π–π* transitions centered at 570 nm at -0.40 V when it is in completely reduced state. Successive oxidation of the polymer leads to decrease in intensity of the π–π* transitions with the simultaneous generation of two new broader absorption bands at 800 nm and 1410 nm which represent the generation of polarons and bipolarons in the conjugated chain.[29] When the voltage is increased to any potential between +0.60 V and +1.20 V, the polymer is completely oxidized, confirmed by the disappearing of absorption band at 570 nm. In contrast, polymer P(3,6-BTE) switches from orange-red to cyan and exhibits a totally different spectroelectrochemistry. P(3,6-BTE) shows π–π* transitions centered at 475 nm at -0.10 V when it is in completely reduced state. Successive oxidation of the polymer leads to the decrease in the intensity of the π–π* transitions with the simultaneous generation of two new broader absorption bands at 705 nm and 1370 nm which represent the generation of polarons and bipolarons in the conjugated chain. The bandgaps of two polymers P(2,5-BTE) and P(3,6-BTE), calculated from the absorption onset in their completely reduced states, are 1.82 eV and 2.00 eV respectively. Alongside, we use quantum-mechanical and molecular mechanical methods to theoretically calculate the bandgap energies and UV peaks of the two dimers 2,5-BTE and 3,6-BTE, which are 1.08 eV and 1.30 eV with maximum

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absorption peaks at 853 nm and 852 nm, respectively. The computational studies and predictions, relying on the Density Functional Theory (DFT) methods,[30] are consistent with the experimental results.

Geometries of the neutral ground state were calculated at the B3LYP/6-31 G level of the theory, followed by single-point calculations employing the 6-311 G* basis set for faster convergence as implemented in the G 09 software package.[31] The orbital energies, shown in Table 1, are calculated in two basis set respectively. The dimer structures of 2,5-BTE and 3,6-BTE are shown in Figure 3.

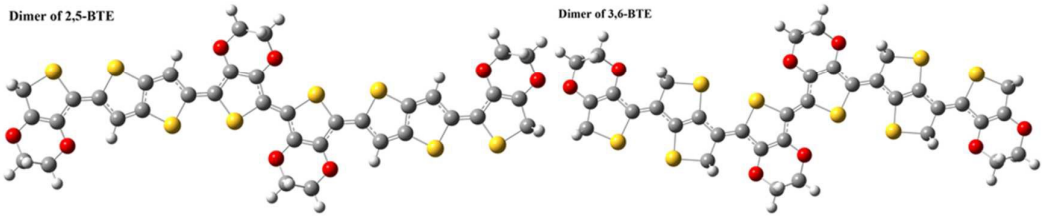


**Figure 3.** Dimer structure of 2,5-BTE and 3,6-BTE

**Table 2. HOMO/LUMO energy levels and gap ΔE calculated by DFT method**

| | B3LYP/6-31 G (eV) | | | B3LYP/6-311 G* (eV) | | |
|---|---|---|---|---|---|---|
| | HOMO | LUMO | ΔE | HOMO | LUMO | ΔE |
| Dimer (2,5-BTE) | -3.74 | -2.51 | 1.23 | -3.61 | -2.53 | 1.08 |
| Dimer (3,6-BTE) | -3.59 | -2.28 | 1.31 | -3.72 | -2.42 | 1.30 |

As shown in table 2, the calculations of HOMO and LUMO levels are carried out by density functional theory (DFT) using hybrid B3LYP functional with 6-31 G basis set for geometrical optimization and the same hybrid functional with 6-311 G* basis set for single point energy.[30, 32] All the calculations were performed in Gaussian 09



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package. Because of the dependence of properties and energy results on the accuracy of calculation methods, we choose the larger basis set for geometrical optimization (6-31 G), although the larger one took much more time. For comparison, the energy levels obtained by using both the basis sets are shown in Table 1. For Dimer 2,5-BTE, the calculated HOMO-LUMO gap, ΔE, is also in reasonable agreement with the optically observed absorption edge of 1.03-1.30 eV, given that our calculations considered an isolated molecule in vacuum, whereas the experiment is performed on a thin film. The calculated ΔE between HOMO and LUMO of 1.23 eV is in excellent agreement with the experimental results of absorption spectra. Use of the larger 6-311 G* basis set improved the orbital energy values and the ΔE is 1.08 eV that is lower than before. The calculations of UV spectrum are carried out by time-dependent density functional theory (TDDFT) using hybrid B3LYP functional with 6-31 G* basis set for geometrical optimization and the same hybrid functional with CC-PVDZ basis set for the first excited singlet state. The calculated wavelengths of the maximum absorption peak are 852.83 nm and 853.46 nm; while the experimental absorption wavelength ranges of the polarons in Figure 2 are 717 nm – 974 nm and 724 nm – 880 nm, respectively. Theoretically calculated values of the bandgap energies and maximum absorption wavelengths of the two dimers are in good agreement with the polar energy range of P(2,5-BTE) (1.03 – 1.30 eV) and P(3,6-BTE) (1.20 – 1.53 eV) and polar absorption wavelength range of P(2,5-BTE) (717 – 953 nm) and P(3,BTE) (724 – 880 nm) in UV–Vis–NIR spectrum. This helps us to understand the process of electrochemical polymerization and indicates that P(2,5-BTE) has more

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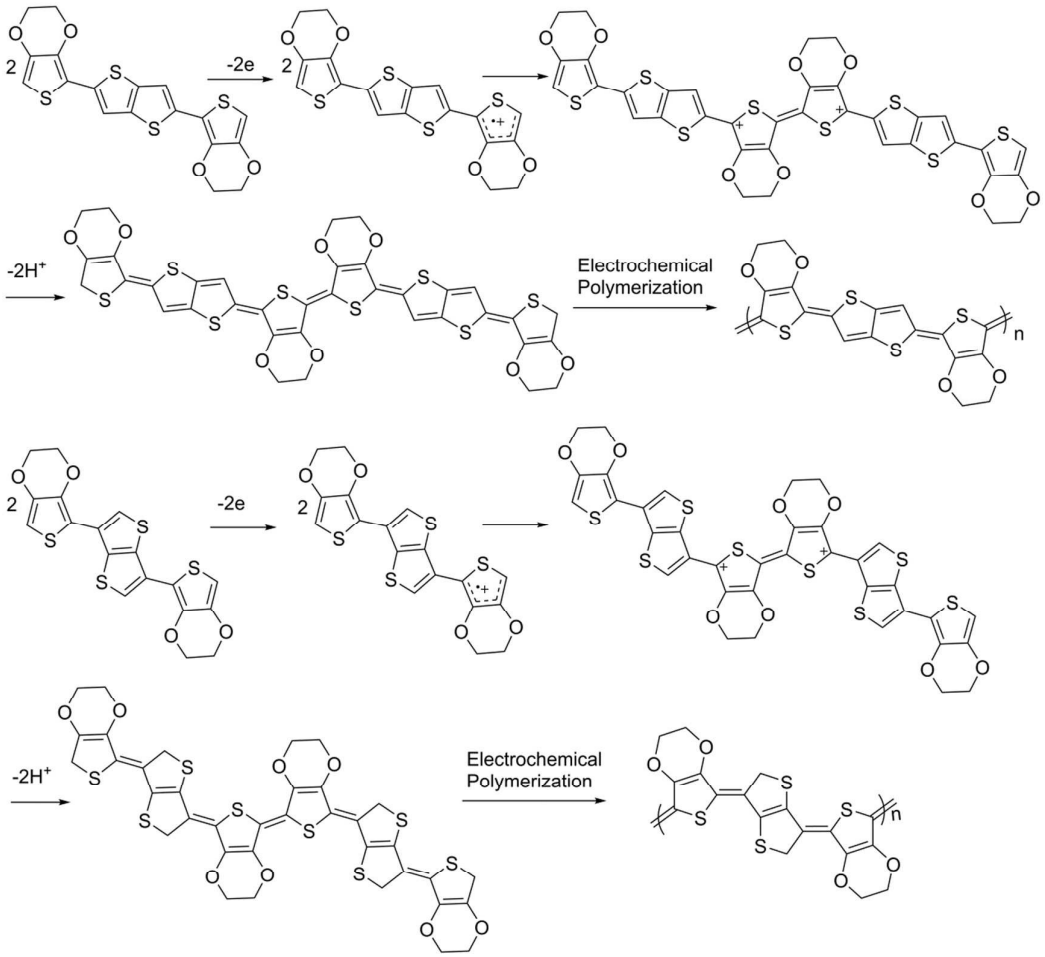
conjugated structure than P(3,6-BTE). Moreover, UV-Vis-NIR spectrum implies that different EDOT positions can dramatically change the electrochemical properties of these two polymers and their conjugation degree. Electrochemical polymerization processes are presented in Scheme 2.[33]




**Scheme 2.** Electrochemical polymerization process of P(2,5-BTE) and P(3,6-BTE)

In order to compare the surface morphology of two polymers, AFM and SEM images with 550 x 550 nm are shown in Figure 4.

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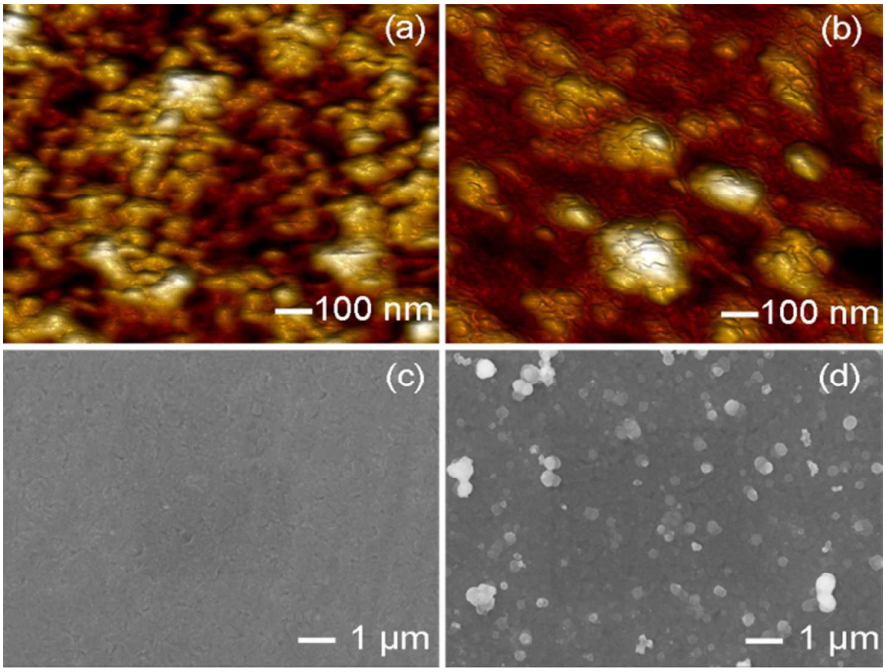


**Figure 4.** AFM images of (a) P(2,5-BTE) and (b) P(3,6-BTE). SEM images of (c) P(2,5-BTE) and (d) P(3,6-BTE)

The average root-mean-square (RMS) roughness values of the thin film surfaces of P(2,5-BTE) and P(3,6-BTE) in five different regions are 3.27 nm and 7.93 nm respectively. This reduction in roughness is attributed to the smoothing effect induced by the conjugation in P(2,5-BTE), implying that films of P(2,5-BTE) are more compact than films of P(3,6-BTE), which is also confirmed by SEM images in Figure 4 (c) and (d). No clusters or particles can be observed in the P(2,5-BTE) thin films surface, on the other hand, the films of P(3,6-BTE) contain small particles of 0.1-0.3 μm in size, and thus a less compact morphology, which confirms that P(2,5-BTE) is more conjugated than P(3,6-BTE).

The fast switching capability and a remarkable color change are essential properties of an electrochromic polymer. In order to detect the percent transmittance change (ΔT%) for the maximum optical contrast of the polymers between reduced and



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oxidized states, different potential switching of P(2,5-BTE) and P(3,6-BTE) on ITO coated glass slides was performed in 0.10 M $TBAPF_6$/ACN with a switching interval of 5 s, while percent transmittance was measured as a function of time (Figure 5).

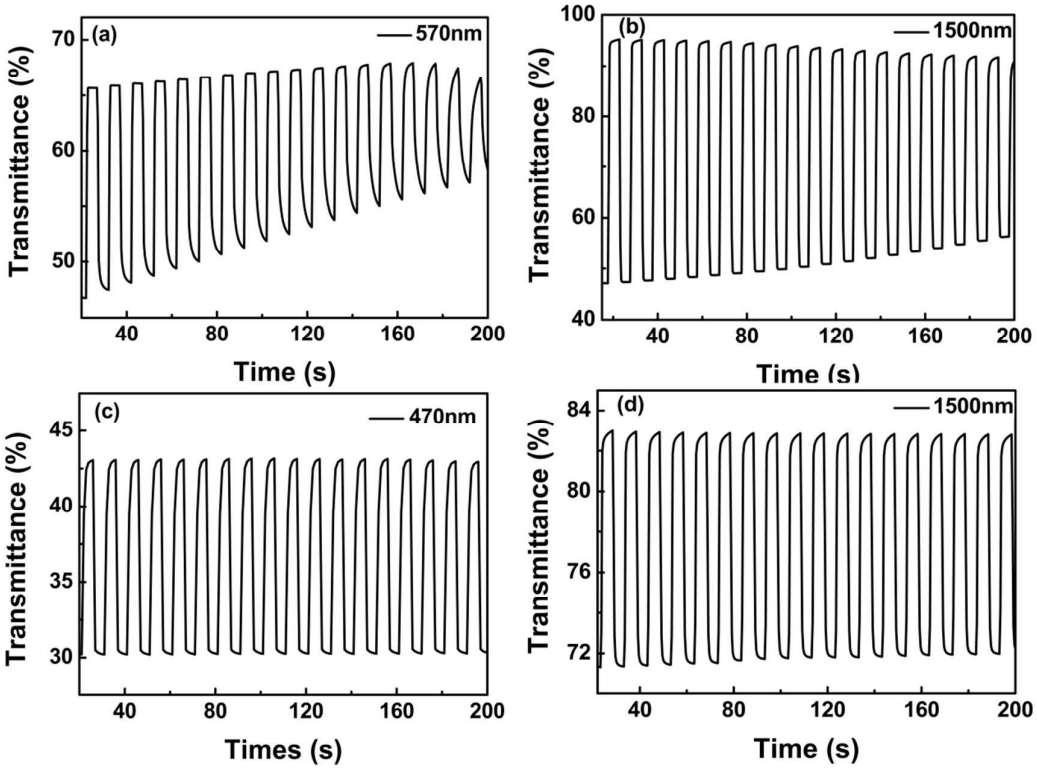


**Figure 5.** Optical transmittance change monitored at (a) 570 nm / (b) 1500 nm for P(2,5-BTE) and (c) 470 nm / (d) 1500 nm for P(3,6-BTE) on the ITO-coated glass substrate in 0.10 M $TBAPF_6$/ACN solution

The stepping potential in the range -0.80 V to +1.00 V was applied to P(2,5-BTE) polymer thin films which shows 19.15% optical contrast at 570 nm and a 48.40% optical contrast at 1500 nm with a response time of 0.57 s. Similarly, the stepped potential within the range -0.40 V to +1.00 V was applied to P(3,6-BTE) polymer thin film achieving an optical contrast of 13.36% at 470 nm and 12.00% at 1500 nm with a response time of 0.83 s. To investigate the polymers stability, films coated onplatinum



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button electrodes are investigated by using cyclic voltammograms between their reduced and oxidized states (Figure 6).

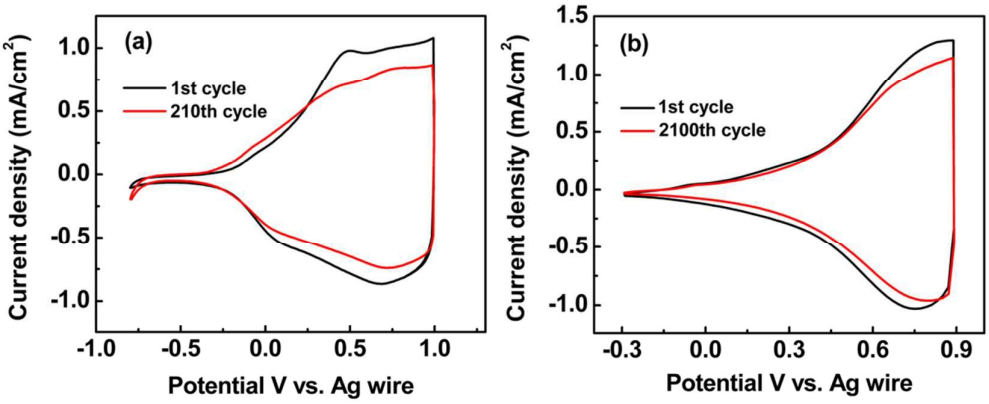


**Figure 6.** Stability test for (a) P(2,5-BTE) film and (b) P(3,6-BTE) film in 0.10 M $TBAPF_6$/ACN solution as a scan rate of 100 mV $s^{-1}$

A decrease by 18.94% for the anodic peak current ($i_{pa}$) and 14.42% for the cathodic peak current ($i_{pc}$) is observed for polymer P(2,5-BTE) after cycled between their fully oxidized state (+ 0.1 V) and fully reduced state (- 0.8 V) for 210 times; While, under the same ambient conditions, a decrease by 11.65% for the anodic peak current ($i_{pa}$) and 6.51% for the cathodic peak current ($i_{pc}$) is observed for polymer P(3,6-BTE) after cycled between their fully oxidized state (+ 0.9 V) and fully reduced state (- 0.3 V) for 2100 times. Obviously, P(3,6-BTE) thin films have better stability.

These data imply that P(2,5-BTE) can switch more quickly and has relatively more percent transmittance change than P(3,6-BTE) while P(3,6-BTE) is more stable than P(2,5-BTE).

## 4. CONCLUSION

Two novel isomer electrochromic materials, EDOT substituted thieno[3,2-*b*]thiophene, are designed and synthesized via Stille coupling. Polymer P(2,5-BTE) has lower



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oxidation potential, more compact morphology, more quick switching and more percent transmittance change than polymer P(3,6-BTE). It is assumed that the position of EDOT units in the core structure alters π-π* stacking thus making the electrochemical properties totally different. Theoretical calculations of the energy bandgaps and maximum absorption wavelength of the two dimers are in good agreement with the polar energy range and absorption wavelength range in UV–Vis–NIR spectrum, which helps us to understand the process of electrochemical polymerization and indicates that P(2,5-BTE) has more conjugated structure than P(3,6-BTE). P(2,5-BTE) switches from purple to grey-blue while P(3,6-BTE) reflects orange-red to cyan.

It can be concluded that thieno[3,2-*b*]thiophene is a suitable unit in electrochromic materials, and effective color tuning can be achieved in thieno[3,2-*b*]thiophene by substituting EDOT units at different positions which is verified by the study of electrochemical and optical properties in P(2,5-BTE) and P(3,6-BTE). Thereby, extending the repertoire of available colors of processable PECs (blue, green and black etc.), which are essential for full color displays.

## ASSOCIATED CONTENT

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**Notes**

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The authors declare no competing financial interest.

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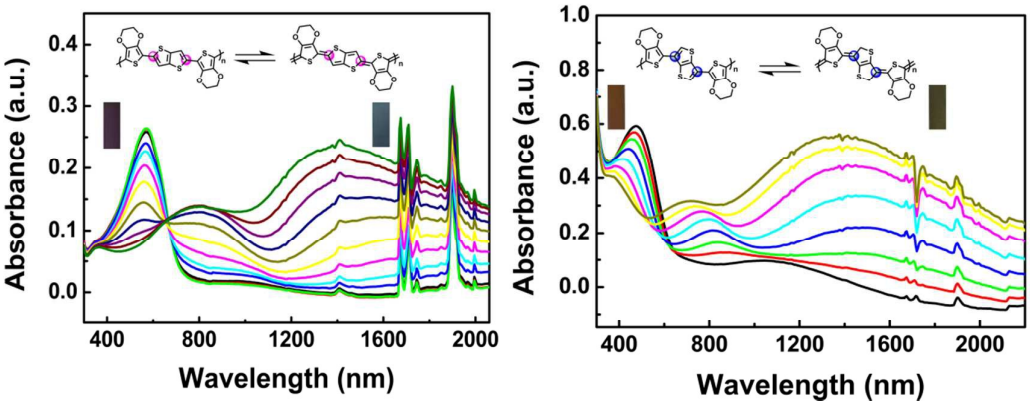


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