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Synthesis, Characterization and Optoelectrochemical Properties of Poly(2,5-di(thiophen-2-yl)-1-(4-(thiophen-3-yl)phenyl)-1H-pyrrole-co-EDOT)

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Abstract

A new polythiophene derivative was synthesized by electrochemical oxidative polymerization of 2,5-di(thiophen-2-yl)-1-(4-(thiophen-3-yl)phenyl)-1H-pyrrole (TTPP). The structure of the monomer was evaluated by ^{1}H-NMR and FT-IR. The polymer (P(TTPP)) and its co-polymer with 3,4-ethylenedioxythiophene (P(TTPP-co-EDOT)) were synthesized *via* potentiostatic electrochemical polymerization. The resulting polymers were characterized by cyclic voltammetry (CV), FT-IR, SEM and UV-Vis spectroscopy, and conductivity measurements. Also, the spectroelectrochemical and electrochromic properties of P(TTPP-co-EDOT) were investigated. While P(TTPP) reveals no electrochromic activity, its co-polymer with EDOT has two different colours (yellow and blue). Optical contrast, switching time, λ_{max} and band gap (E_g) of (P(TTPP-co-EDOT)) were determined.

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Keywords

Thiophene, electrochemical polymerization, EDOT, co-polymer

1. Introduction

Chemical and electronic properties of semiconductors can be combined in conducting polymers. The ability to tailor the structure of a conjugated polymer allows the rational synthesis of conducting polymers with a broad range of electronic properties. The nature of the repeating unit and the functional groups change the electronic characteristics of the polymer [1].

In recent years, the conducting polymers belonging to polyenes or polyaromatics, such as polyaniline, polypyrrole, polythiophene and poly(*p*-phenylene), have attracted great attention [2, 3]. The (hetero)aromatics polypyrrole and polythiophene are environmentally 'friendly' systems; however, they are insoluble and infusible.

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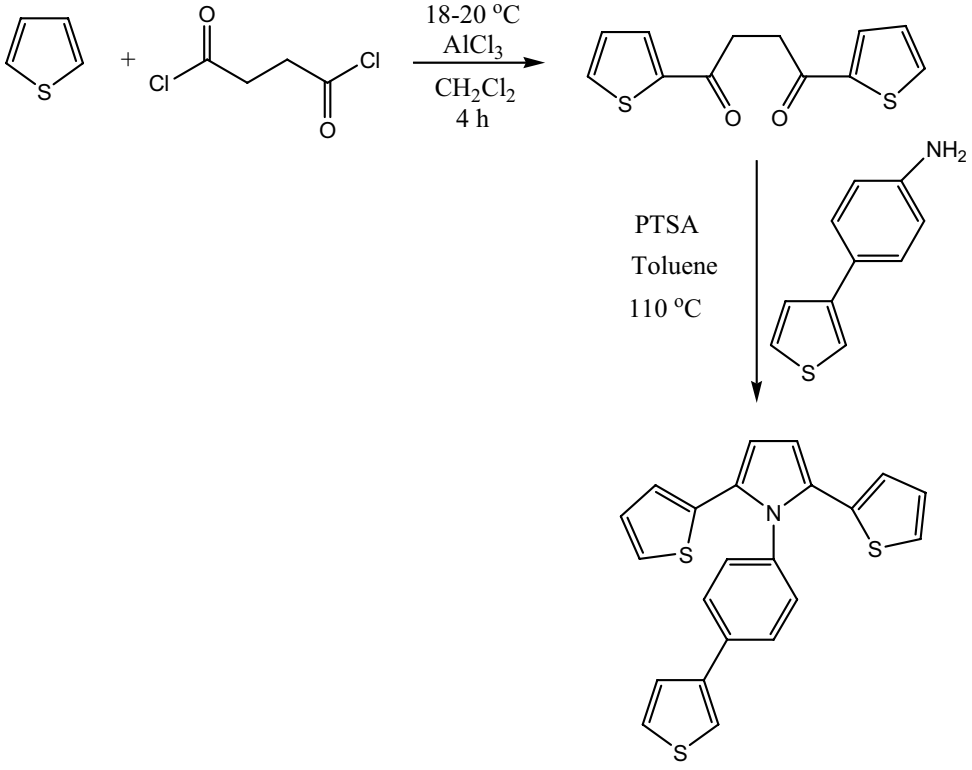
In order to overcome these problems, numerous substituted derivatives of these polymers have been developed. New chemical and physical properties are imparted to conducting polymers by the addition of an appropriate functional group to a conventional polymer [4, 5]. The characteristics and position of the side-chains can affect the properties like solubility, bandgap, ionic conductivity, morphology and miscibility with other substances [6].

The ability to dope conjugated polymers electrochemically is significant due to the easy combination of synthesis and characterization methods. Many applications of conjugated polymers, such as light emitting electrochemical cells [7, 8], microactuators [9, 10], energy storage [11], photovoltaic [12] and electrochromic devices (ECDs) [13–15], and sensors [16] are based on electrochemical transition between doped and neutral states or rely on the stability of a specific doping level.

In 1991 Jonas and Schrader [17] synthesized 3,4-ethylenedioxythiophene (EDOT) by locking the 3- and 4-positions of thiophene with an ethylenedioxy group yielding a highly electron-rich fused heterocycle which has low oxidation potential and free from the possible α,β- and β,β-linkages [18]. Poly(3,4-ethylenedioxythiophene) (PEDOT) exhibits an optical band gap of 1.6 eV. Doped PEDOT is almost transparent in the visible region and the neutral polymer is dark blue. Thus, this material is significant for its cathodically colouring electrochromic properties in device applications.

Specific monomers that have desired functionalities are required for co-polymer synthesis. Co-polymerization can lead to an interesting combination of the properties. For that matter, we have synthesized a novel co-polymer of 2,5-di(thiophen-2-yl)-1-(4-(thiophen-3-yl)phenyl)-1H-pyrrole (TTPP) with EDOT. EDOT is a popular choice as a co-monomer, since it produces a low-band-gap polymer with high stability and good conductivity [19]. EDOT and its derivatives can give rise to non-covalent intramolecular interactions with adjacent thiophenic units and, thus, induce self-rigidification of the conjugated system in which it is incorporated [20–22].

In the present work, 2,5-di(thiophen-2-yl)-1-(4-(thiophen-3-yl)phenyl)-1H-pyrrole (TTPP) (Scheme 1) was synthesized. The structure of this thiophene derivative was analyzed by spectral methods (^{1}H-NMR, FT-IR). Electrochemical polymerization of P(TTPP) was achieved using $NaClO_4$ (0.1 M) and $LiClO_4$ (0.1 M) (1:1) as the supporting electrolyte couple. In addition, the co-polymer of TTPP with EDOT was achieved *via* potentiodynamic electrolysis. The resultant co-polymer revealed electrochromism through almost the entire visible region, displaying yellow and blue colours with the variation of the applied potential. The resultant co-polymer was characterized *via* cyclic voltammetry, SEM, FT-IR, UV-Vis spectroscopies and conductivity measurements. The optoelectrochemical and electrochromic properties, such as the relative luminance, change of colour upon redox switching and switching stability of the co-polymer were determined. While P(TTPP) has no electrochromic activity, its co-polymer with EDOT has two different colours (yellow and blue).



Scheme 1. The synthetic route of TTPP.

2. Experimental

2.1. Materials

$AlCl_3$, succinyl chloride, p-toluene-sulfonic acid (PTSA), 4-(thiophen-3-yl)benzenamine, EDOT, $LiClO_4$, $NaClO_4$, thiophene, $NaHCO_3$ and $MgSO_4$ were purchased from Aldrich. Dichloromethane DCM, acetonitrile (AN) and silicagel were purchased from Merck. Toluene was purchased from Sigma. All chemicals were used as received.

2.2. Equipments

^{1}H-NMR spectra were recorded on a Bruker-Instrument NMR Spectrometer DPX-400 using DMSO as the solvent. The FT-IR spectra were recorded on a Jasco FT/IR-300E spectrometer. The FT-IR spectra were recorded using KBr discs (4000–400 cm^{-1}). Cyclic voltammograms were recorded in $NaClO_4$ (0.1 M) and $LiClO_4$ (0.1 M)/AN electrolyte/solvent couple with a system consisting of a potentiostat (CH Instruments 600), an X–Y recorder and a CV cell containing indium/tin oxide (ITO)-coated glass plate working, Pt counter electrodes, and a Ag wire pseudo-reference electrode. Measurements were carried out at room temperature. The

particle morphology of the polymer films was examined by means of scanning electron microscopy (Carl-Zeiss EVO-40) operated at 20 kV. Electrical conductivity of the co-polymer, polymer and PEDOT were measured at room temperature using a four-probe technique with a home-made instrument. Spectroelectrochemical studies were carried on Shimadzu MultiSpec-1501 UV-Vis spectrophotometer. Colourimetry measurements were done using a Minolta CS-100 spectrophotometer.

2.3. Synthesis of 1,4-Di(2-thienyl)-1,4-butanedione

From the different methods leading to 1,4-di(2-thienyl)-1,4-butanedione [23–31], the double Friedel–Crafts reaction, first suggested by Merz and Ellinger [32], was chosen. Utilizing thiophene and succinyl chloride as the reactants, aluminium chloride was used as the Lewis acid catalyst, since it is the most direct one-step procedure with good yields. We also noticed that the reaction time can be considerably reduced, the reaction mixture being refluxed for 4 h (instead of 24 h stirring at ambient temperature) without a loss in yield (78%). The synthetic route of 1,4-di(2-thienyl)-1,4-butanedione is shown in Scheme 1.

2.4. Synthesis of TTPP

The monomer (TTPP) was synthesized from 1,4-di(2-thienyl)-1,4-butanedione and 4-(thiophen-3-yl)benzenamine in the presence of catalytical amount of PTSA. A round-bottomed flask equipped with an argon inlet and magnetic stirrer was charged with 1,4-di(2-thienyl)-1,4- butanedione (0.13 g, 0.52 mmol), 4-(thiophen-3-yl)benzenamine (0.15 g, 0.86 mmol), PTSA (0.05 mmol) and toluene. The resultant mixture was stirred and refluxed for 24 h under argon. Evaporation of the toluene, followed by flash column chromatography (SiO_2 column, elution with dichloromethane), afforded the desired compound as brown powder. The synthetic route of the monomer is shown in Scheme 1.

2.5. Cyclic Voltammetry

Cyclic voltammetry (CV) was employed in order to assay the electroactivity of the polymers and to determine the oxidation–reduction peak potentials of the monomer and the polymers. The system consists of a potentiostat, an X–Y recorder and a CV cell containing indium/tin oxide ITO-coated glass plate as working electrode, platinum wire counter and Ag wire pseudo-reference electrodes. The measurements were carried out in $NaClO_4$ (0.1 M) and $LiClO_4$ (0.1 M)/acetonitrile (AN) solvent/electrolyte couple at room temperature under nitrogen atmosphere.

2.6. Synthesis of Homo-Polymer by Electrochemical Polymerization

TTPP was polymerized through constant potential electrolysis in a single-compartment cell in the presence of 0.03 M TTPP, 0.1 M $NaClO_4$/0.1 M $LiClO_4$ in AN at 1.2 V, equipped with electrodes used for CV measurements. The polymer was washed with AN in order to remove $NaClO_4$/$LiClO_4$ and unreacted monomer after the potentiodynamic electrochemical polymerization.

2.7. Co-polymer of TTPP with EDOT

TTPP (0.25 mM), dissolved in acetonitrile, and 1 μl EDOT were introduced into a single-compartment electrolysis cell. The supporting electrolyte couple was $NaClO_4/LiClO_4$. Constant potential electrolysis was run at 1.3 V for 1 min at room temperature under inert atmosphere. Resulting co-polymer films were washed with AN to remove $NaClO_4/LiClO_4$ after the electrolysis.

For the spectroelectrochemical studies, P(TTPP-co-EDOT) was synthesized in the presence of 0.25 mM monomer and 1 μl EDOT in the same solvent/electrolyte on an ITO-coated glass slide in a UV cuvette. The electrochromic measurements, spectroelectrochemistry and switching studies of the polymer film deposited on ITO-coated glass slide were carried out in the same media in the absence of monomer.

3. Results and Discussion

3.1. Cyclic Voltammetry

The cyclic voltammogram of (TTPP) in $AN/LiClO_4–NaClO_4$ indicated one oxidation peak at 0.82 V when the range between −1.0 V and +2.0 V was scanned. In the cathodic run, reduction of the deposited polymer was observed at 0.03 V (Fig. 1a). As the number of cycles increases, there is an increase in the intensity of the current. This is due to increase in the active area of the working electrode owing to electroactive polymer depositing on the electrode. A yellow cloud was also formed around the electrode due to the partial dissolution of oligomers of low molecular weight. To study the electrochemistry of the polymer a monomer-free system was used. In order to investigate the CV behaviour of the co-polymer we performed CV studies in the presence of EDOT under the same experimental conditions (Fig. 1b). There was a drastic change in the voltammogram; both the increase in the increments between consecutive cycles and the oxidation potential of the material were different from those of from both monomer and pure EDOT (Fig. 1c).

3.2. ^{1}H-NMR Spectroscopy

The structure of the monomer was confirmed by ^{1}H-NMR spectral analyses. The ^{1}H-NMR spectra of the monomer have the characteristic peaks of the structure.

^{1}H-NMR (400 MHz, 25°C, in DMSO, ppm): 8.05 (d, 1H), 7.90 (d, 1H), 7.68 (d, 1H), 7.55 (d, 1H), 7.38 (d, 1H), 7.27 (d, 1H), 6.90 (d, 2H), 6.82 (d, 2H), 6.60 (t, 4H), 5.20 (d, 2H).

3.3. FT-IR Spectroscoppy

The IR spectral characteristics of the monomer are discussed together with the electrochemically prepared polymer. The FT-IR spectrum of the TTPP shows the following absorption peaks: 3092 and 3071 cm^{-1}, assigned to C–H stretching vibration (pyrrole and thiophene); 3030 cm^{-1}, corresponding to aromatic C–H

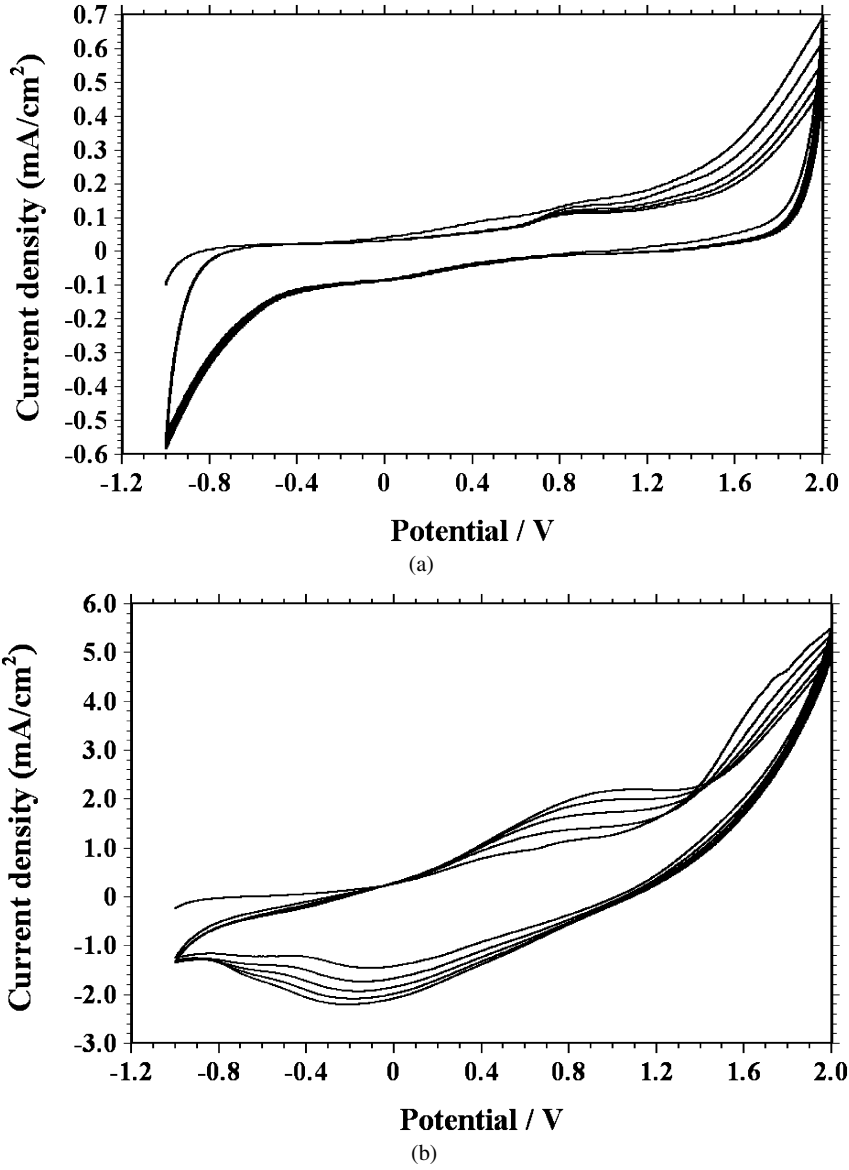
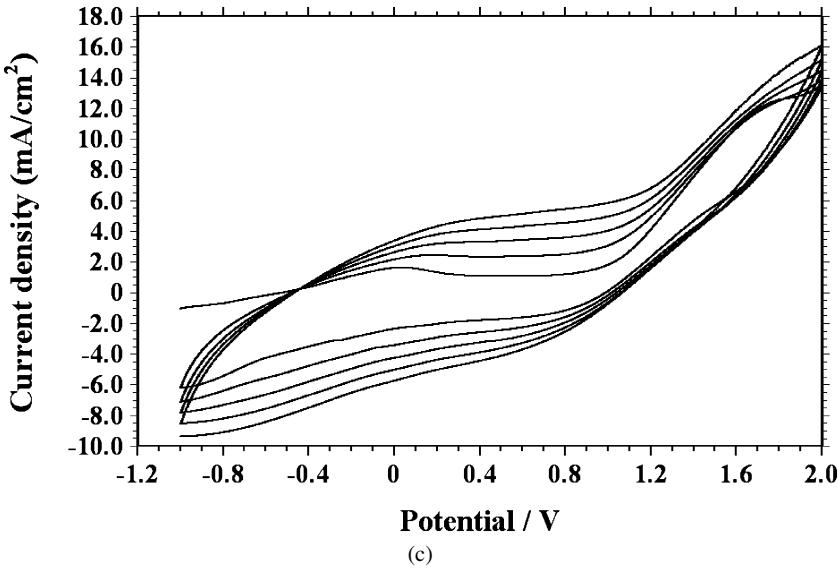


Figure 1. Cyclic voltammograms of: (a) monomer (TTPP), (b) co-polymer (TTPP-co-EDOT) and (c) EDOT in the presence of AN/$LiClO_4$/$NaClO_4$ by sweeping the potential between −1.0 V and 2.0 V. 500 mV/s (ITO).

stretching; 1625 cm^{-1}, assigned to C=N stretching vibration; 1542 and 1300 cm^{-1}, assigned to aromatic C=C, C–N stretchings due to pyrrole; 1042 cm^{-1}, assigned to C–H deformation vibration for 1-subs. pyrrole; 763 cm^{-1} C–H deformation vibration of 1,2,5-trisubstituted pyrrole [22]; and 692 cm^{-1}, assigned to C–H out-of-plane deformation vibration of thiophene. After the electrochemical



(c)

Figure 1. (Continued).

co-polymerization of TTPP with EDOT, the disappearance of peaks at 781 and 3092 cm^{-1} is evidence of the polymerization through the 2- and 5-positions of thiophene ring. The shoulder observed at 1625 cm^{-1} is due to the conjugation and the peak at 1152 cm^{-1} due to the C–O–C group indicates that EDOT is incorporated into the polymer matrix. The peaks appearing at 1095, 1121 and 640 cm^{-1} show the presence of the dopant ion, ClO_4^-.

3.4. Scan Rate Dependence of the Peak Currents

P(TTPP) and P(TTPP-co-EDOT) films were prepared by constant potential electrolysis. Their redox switching in monomer free electrolyte revealed a single, well-defined redox process. Figures 2 and 3 show cyclic voltammograms of P(TTPP) and P(TTPP-co-EDOT) at different scan rates. The current responses were directly proportional to the scan rate, indicating that the polymer films were electroactive and well adhered to the electrode [22, 33]. The scan rates for the anodic and cathodic peak currents show a linear dependence as a function of the scan rate as illustrated in the insets of Figs 2 and 3 for P(TTPP) and P(TTPP-co-EDOT), respectively. This demonstrates that the electrochemical processes are not diffusion limited and reversible, even at very high scan rates.

3.5. Conductivities of the Films

The conductivities of the films were measured using a four-probe technique. The conductivity of electrochemically prepared homo-polymer was 3.4×10^{-5} S/cm, whereas that of P(TTPP-co-EDOT) was 5.3×10^{-2} S/cm. Introducing EDOT into the polymer chain increased the conductivity.

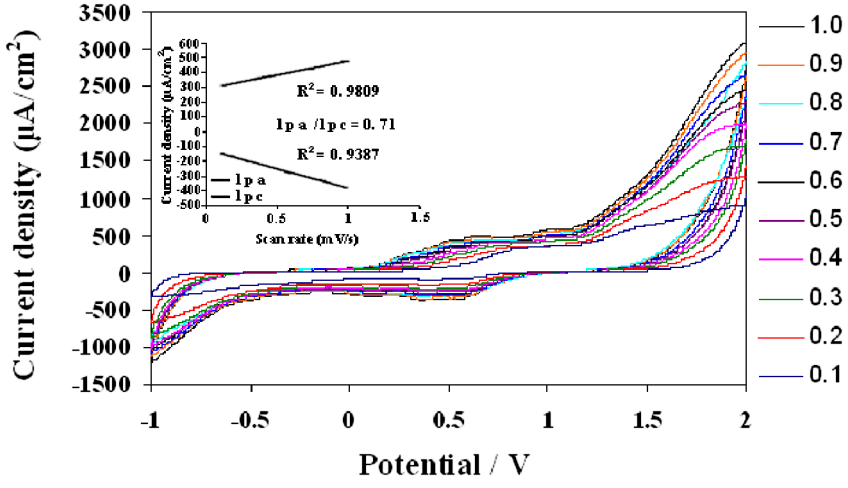


Figure 2. Cyclic voltammograms of P(TTPP) at different scan rates. Inset: Peak current *vs*. scan rate.

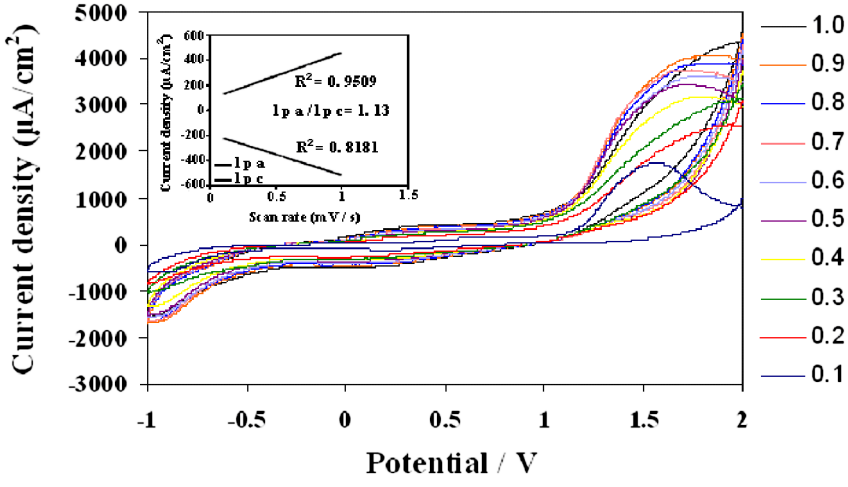


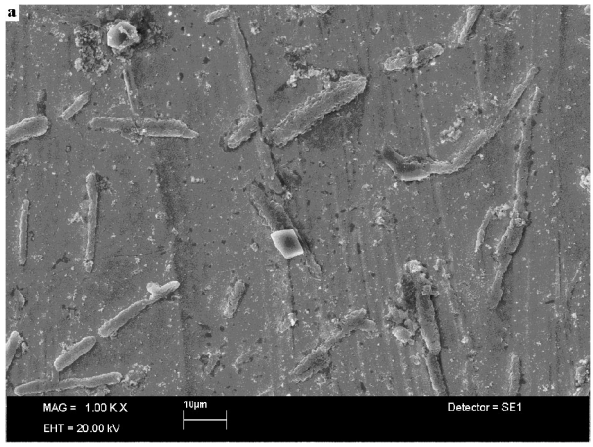
Figure 3. Cyclic voltammograms of P(TTPP-co-EDOT) at different scan rates. Inset: Peak current *vs*. scan rate.

3.6. Scanning Electron Microscopy (SEM)

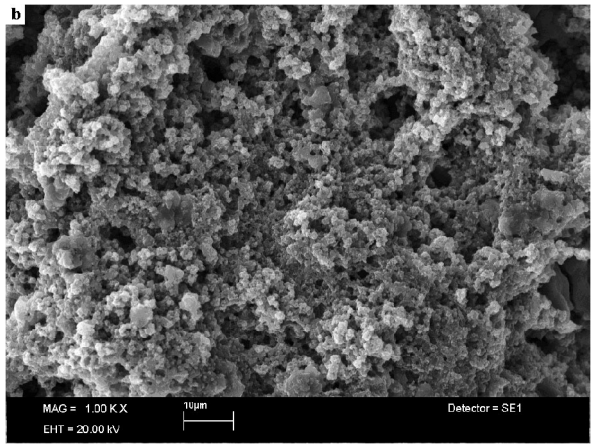
Surface morphologies of co-polymer were investigated by SEM. The SEM micrograph of P(TTPP-co-EDOT) (Fig. 4c) was different from those of from both P(TTPP) (Fig. 4a) and PEDOT (Fig. 4b). This difference could be attributed to co-polymerization.

3.7. Electrochromic Properties of the Polymer

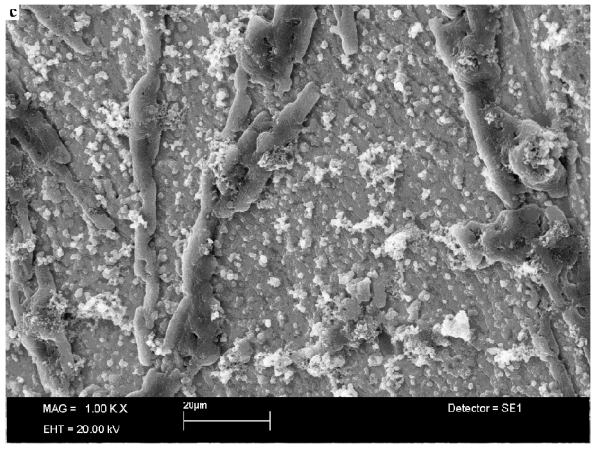
The best way of examining the changes in optical properties of conducting polymers upon voltage change is by spectroelectrochemistry. It also gives information about the electronic structure of the polymer such as band gap (E_g) and the intergap states



(a)



(b)



(c)

Figure 4. SEM micrograph of (a) P(TTPP), (b) PEDOT and (c) P((TTPP)-co-EDOT).

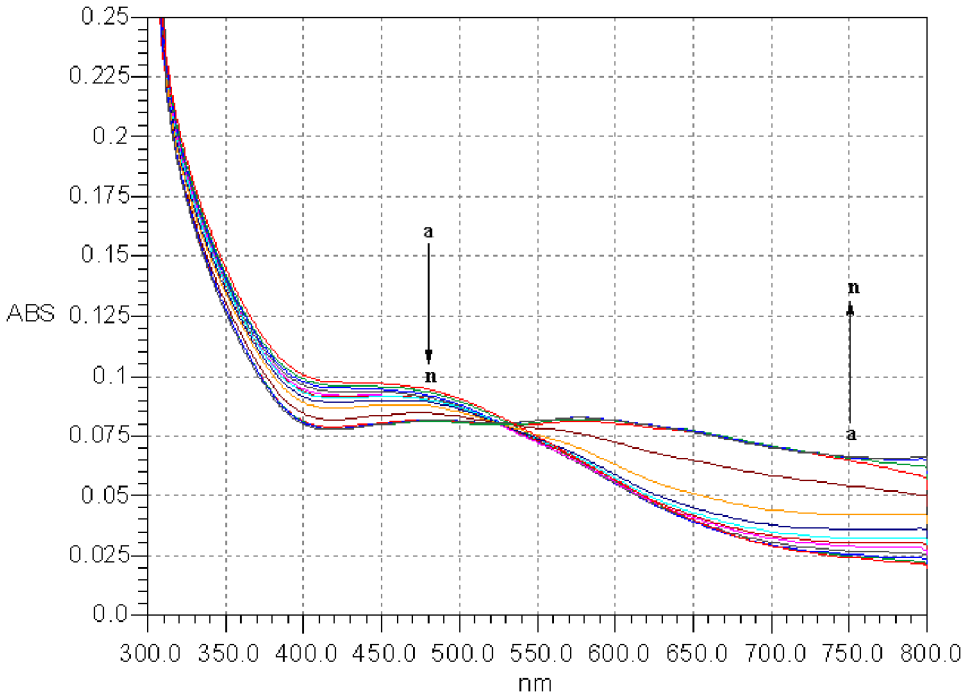


Figure 5. Spectroelectrochemistry of co-polymer at applied potentials of (a) −1.5, (b) −1.3, (c) −1.1, (d) −0.9, (e) −0.7, (f) −0.5, (g) −0.3, (h) −0.1, (i) +0.1, (j) +0.3, (k) +0.5, (l) +0.7, (m) +0.9 and (n) +1.1 V in monomer-free electrolytic solution.

that appear upon doping. P(TTPP-co-EDOT) was potentiostatically synthesized at 1.0 V on ITO electrode. The electrolyte solution was composed of 0.01 M TTPP, 0.01 M EDOT and ACN/$LiClO_4$–$NaClO_4$ (0.1 M). The spectroelectrochemical and electrochromic properties of the resultant co-polymer were studied by applying potentials between −1.5 V and +1.1 V in monomer-free ACN/$LiClO_4$–$NaClO_4$ (0.1 M) medium. In the neutral state the λ_{max} value due to the π–π^* transition of the co-polymer was found to be 480 nm and E_g was calculated as 1.67 eV (Fig. 5).

3.8. Colorimetry

The colour of an electrochromic material was defined accurately by performing colourimetry measurements. The Commission Internationale de l'Eclairage (CIE) system was employed as the quantitative scale to define and compare colours. Colorimetry measurements were performed in the same electrolyte using a Minolta CS-100 spectrophotometer. Three features of colour; hue (a), saturation (b) and luminance (L) were measured and recorded in Table 1. The P(TTPP-co-EDOT) film shows different colours in the fully reduced (−0.4 V) and oxidized states (+1.0 V). The colour of the film switches from a blue colour in the oxidized form to yellow in the reduced state.

Table 1.
Electronic and electrochromic properties of the polymers

Polymer	λ_{max} (nm)	Potential (V)	L	a	b	Colour	E_g (eV)
P(TTPP-co-EDOT)	480	−0.4	84	−5	17	Yellow	1.67
		+1.0	63	−2	−4	Blue	
PEDOT	600	+1.3	91	−8	−11	Light blue	1.60
		−1.0	40	−15	−35	Blue	

3.9. Switching

Some polymers have the ability to switch without delay and exhibit a sharp and significant colour change. Double potential step chronoamperometry was carried out to estimate the response time of the device. The potential was stepped between fully oxidized and neutral states of the polymer film with a residence time of 5 s. During the experiment, the percent transmittance (T) at the wavelength of maximum contrast was measured with a UV-Vis spectrophotometer.

For P(TTPP-co-EDOT) maximum contrast (ΔT) and switching time were measured as 26% and 1.8 s, respectively, by stepping the potential between −0.4 and +1.0 V with a residence time of 5 s.

3.10. In Situ *Electrochemical Co-polymerization*

In situ electrochemical co-polymerization of TTPP and EDOT was carried out in a solution containing 0.01 M TTPP and 0.01 M EDOT in $LiClO_4$–$NaClO_4$ (0.1 M)/ACN solvent/electrolyte couple by applying different potentials. During the electrolysis, UV-Vis spectra were recorded for every 10-s time interval. Figure 6 shows the *in situ* electrochemical co-polymerization of TTPP and EDOT.

4. Conclusion

A new thiophene derivative, 2,5-di(thiophen-2-yl)-1-(4-(thiophen-3-yl)phenyl)-1H-pyrrole (TTPP), was successfully synthesized. The structure of the monomer was evaluated by ^{1}H-NMR and FT-IR. P(TTPP) and its co-polymer with 3,4-ethylene dioxythiophene (P(TTPP-co-EDOT)) were synthesized by potentiostatic electrochemical polymerization. Characterizations of the resulting polymers were performed by CV, FT-IR, SEM, UV-Vis spectroscopy and conductivity measurements.

Electrochromic properties and switching ability of resulting co-polymer were investigated using spectroelectrochemistry, kinetic and colorimetry studies. The co-polymer displayed a full switch in 1.8 s with an optical contrast of 26%.

Scan rate dependence of the peak currents measurements show that the current responses were directly proportional to the scan rate, indicating that the electrochemical processes are not diffusion limited and reversible; even at very high scan rates and the polymer films were electro-active and adhered well to the electrode.

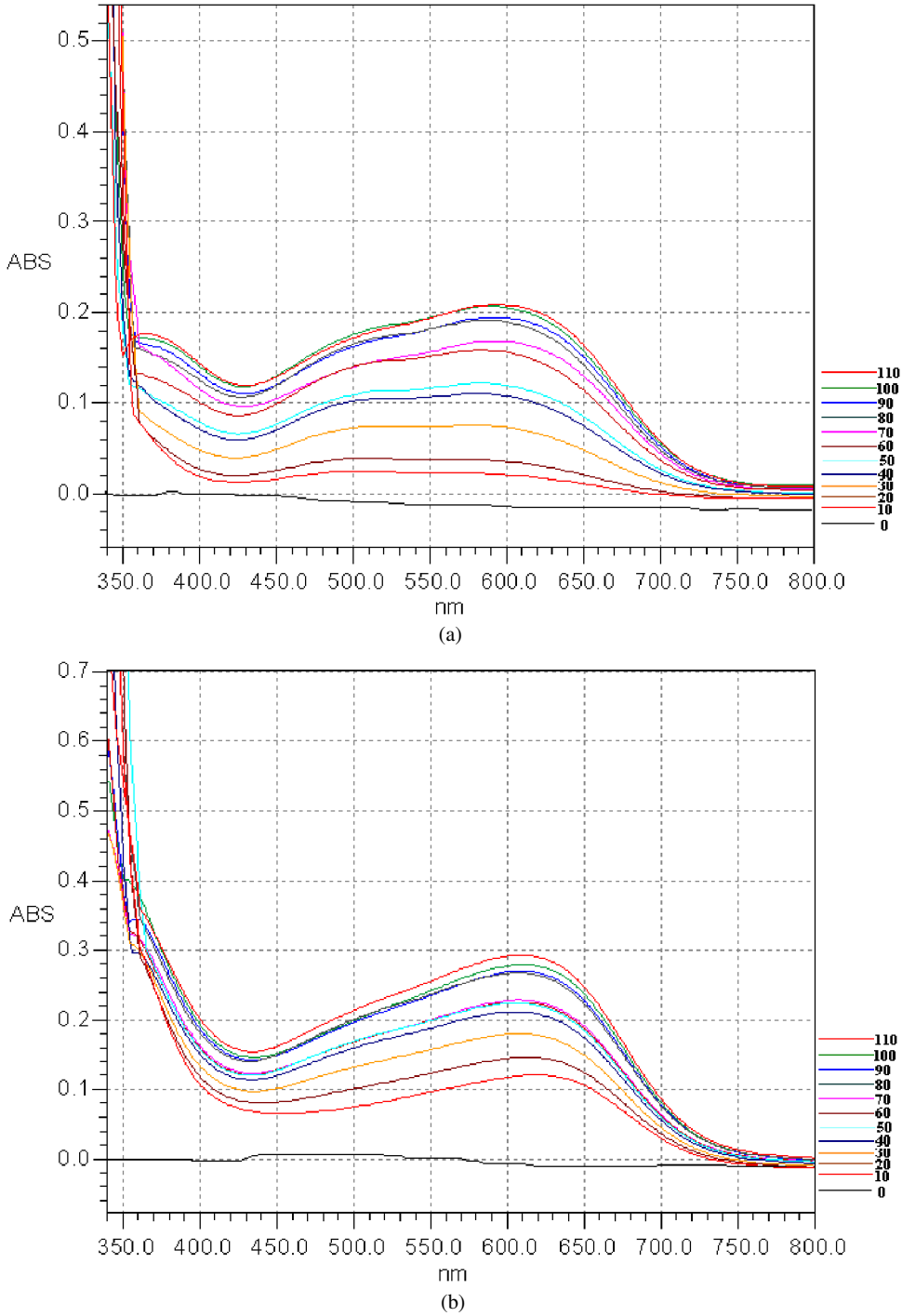
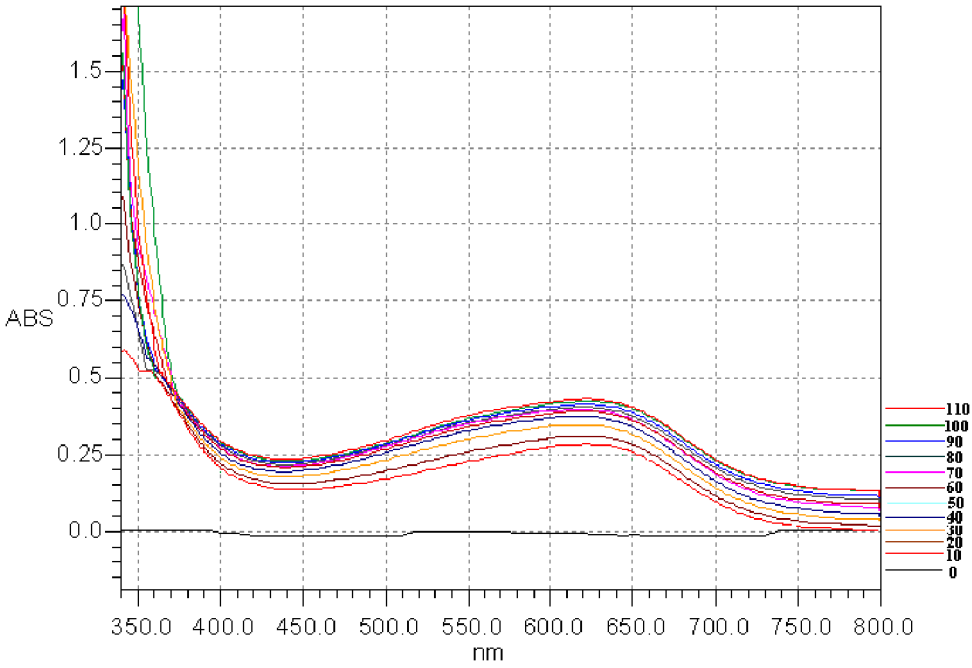
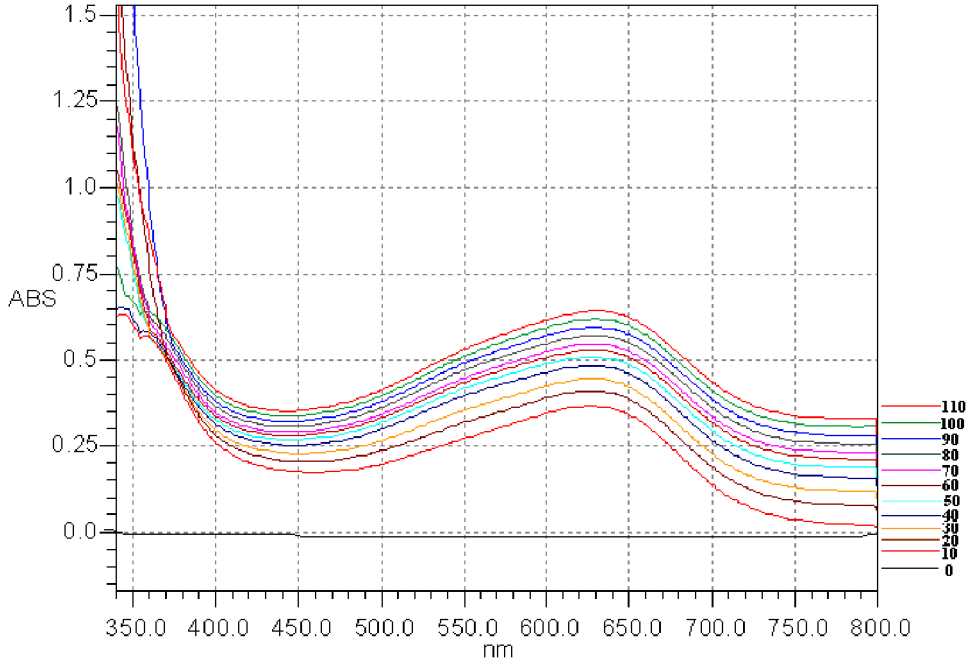


Figure 6. *In situ* electrochemical co-polymerization of TTPP and EDOT with different applied potentials: (a) 0.8, (b) 0.9, (c) 1.0, (d) 1.1 and (d) 1.2 V.

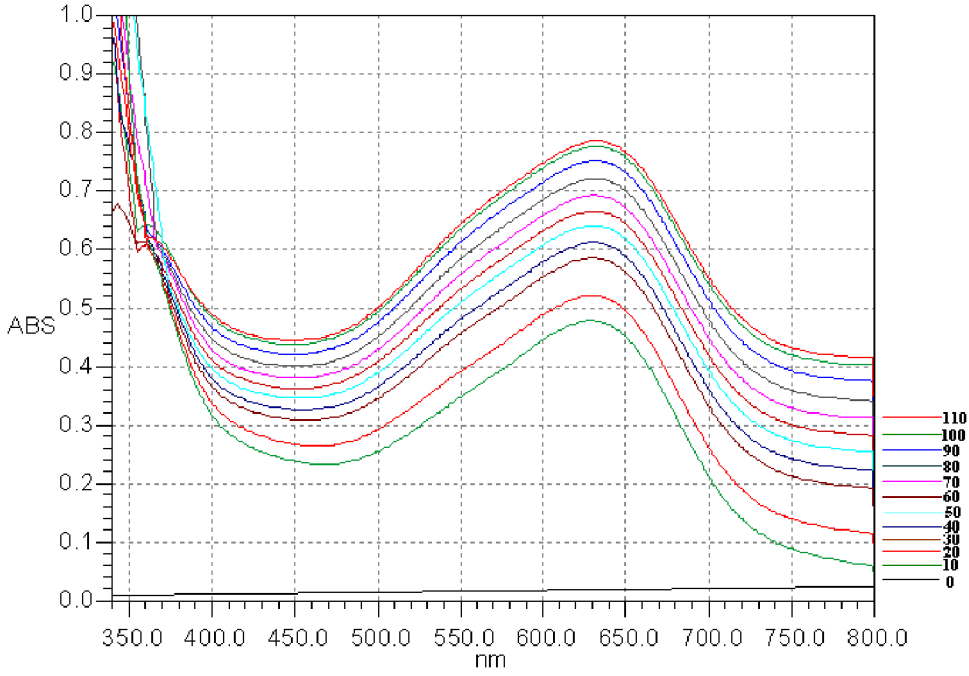


(c)



(d)

Figure 6. (Continued).



(e)

Figure 6. (Continued).

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