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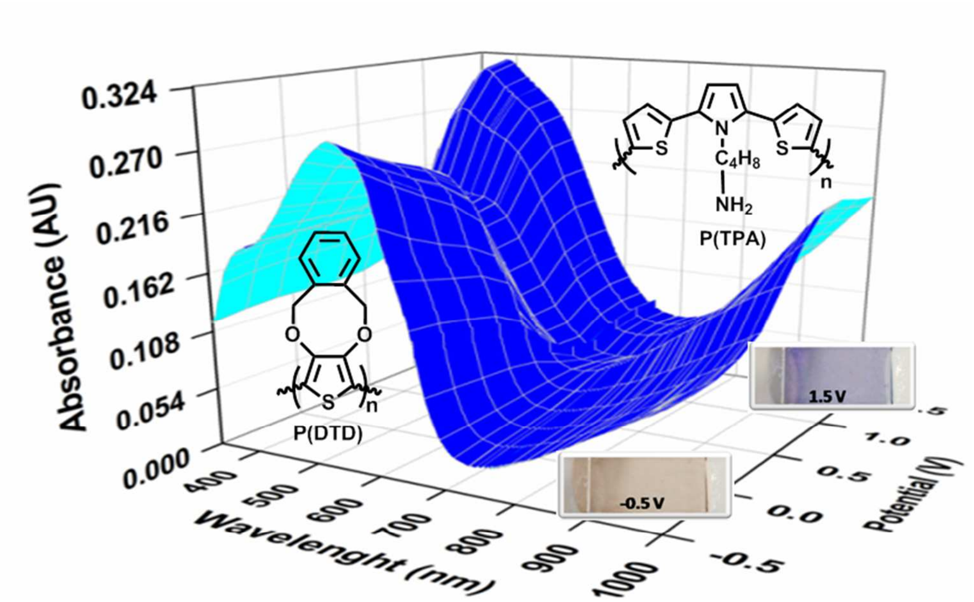

Spectroelectrochemistry graph of novel TPA/DTD electrochromic device
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Preparation of an EDOT-Based Polymer: Optoelectronic Properties and Electrochromic Device Application

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Abstract

Here we present the synthesis, characterization and electropolymerization of a new EDOT-based monomer; 5,10-dihydrobenzo[f]thieno[3,4-b][1,4]dioxocine (DTD). Electrochemical polymerization of DTD was performed potentiostatically by using dichloromethane (DCM) as solvent and tetrabutylammonium hexafluorophosphate ($TBPF_6$) as supporting electrolyte. Homopolymer [P(DTD)] films and copolymer [P(DTD-*co*-TPA)] films of DTD prepared by using 4-(2,5-di(thiophen-2-yl)-1H-pyrrole-1-yl)butane-1-amine (TPA) were characterized via CV and UV–vis spectroscopy. Spectroelectrochemical analysis of P(DTD) reflected electronic transitions at 585 nm (π-π^* transition) with an electronic band gap of 1.69 eV. Electrochromic studies revealed that P(DTD) has competitive properties to EDOT. Furthermore, dual-type complementary colored polymer electrochromic device based on P(DTD) and P(TPA) were constructed in sandwich configuration. Spectroelectrochemical studies revealed that the oxidized state of the device shows blue color whereas it shows yellow for the reduced state. Maximum contrast (Δ%T) and switching time of the device were measured as 25.5% and 0.5 s for 385 nm and 21% and 1.0 s for 550 nm.

1. Introduction

Conducting polymers (CPs) constitute an important class of materials that alternates single and double carbon–carbon bonds along their polymeric chains and they possess the properties of both organic polymers and inorganic semiconductors. They are also called as synthetic metals or intrinsically electroactive conjugated polymers.[1,2,3,4,5] The discovery of high electrical conductivity in doped polyacetylene has stimulated an enormous amount of work towards the description of the electronic properties of conjugated organic polymers.[6,7,8,9,10] Further studies figure out that they have appreciably fast charge-discharge kinetics, suitable morphology and fast doping-undoping processes. Especially thiophene-based organic conducting polymers continue to fascinate many scientists due to their potential applications in the development and construction of new advanced materials such as sensors, photovoltaic devices, rechargeable batteries, supercapacitors, artificial muscles and electrochromic devices.[11,12,13,14,15,16,17] It is important to point out that in designing and producing these devices, maintaining the structural regularity and stability are crucial. For instance, polythiophene (PTh) shows good conductivity and high stability in its oxidized form but suffers from structural defects arising from β-couplings, resulting in conjugation breaks. Blocking of the 3- and 4- positions, forces polymerization through the 2- and 5- positions, leading a linear polymer chain with no α-β coupling with fewer structural defects than most heterocyclics. The result yields in changes in the polymer's absorption characteristics and ultimately its color in its neutral form. During the oxidation process to form charge carriers, new electronic states are introduced into the polymers which exhibit absorptions at lower energies with a concomitant loss of absorption due to the neutral polymer. As such, these materials exhibit electrochromism during redox switching. Among these thiophene-based compounds; 3,4-ethylenedioxythiophene (EDOT) has accepted as one of the most successful materials from both fundamental and practical perspective. It possesses several advantageous properties when compared to other polythiophene derivates: it combines a low oxidation potential and moderate band gap with good stability in its oxidized state. Since the discovery of high conductivity in iodine-doped polyacetylene, many interesting conducting polymers have been developed. Of these, polythiophenes have been most studied as electronic materials, with poly(3,4-ethylenedioxythiophene) (PEDOT) being the most successful commercially used conducting polymer.[18]

In the term of conducting polymers estimated to be used as electrochromic materials; importance of long term stability, switching times, contrast ratios, coloration efficiency, electrochromic memory are obvious. Hence, it is pivotal to improve new electrochromic materials possessing the capability of derivatization, in addition to the ascendant properties of EDOT. For this purpose, synthesis and characterization of 5,10-dihydrobenzo[f]thieno[3,4-b][1,4]dioxocine (DTD) were rendered adequately. Electrochemical polymerization of the synthesized DTD was also carried out. In order to substantiate the copolymer studies; electrochemical studies with 4-(2,5-di(thiophen-2-yl)-1*H*-pyrrole-1-yl)butane-1-amine (TPA) were performed in detail. Since there are substantial numbers of studies on copolymerization of EDOT and thienyl pyrrole derivatives, we choose TPA as comonomer for a proper comparison. Besides these studies, by using TPA, we configured out a high quality device in ITO|P(DTD)||Gel Electrolyte||P(TPA)|ITO configuration and we investigated the properties of this device.

2. Experimental

2.1 Materials

Quinoline (*Merck*) was dried over anhydrous Na_2SO_4, filtered and subsequently distilled under reduced pressure from zinc dust. Flask containing distilled quinoline was covered by aluminium foil to protect the solvent from light and stored in refrigerator at about 5°C. N,N-Dimethylformamide (DMF) (*Sigma-Aldrich*) was dried over 4A molecular sieves and freshly distilled under vacuum prior to use. Anhydrous potassium carbonate was pre-dried in an oven at 150°C for 3 to 4 hours. Other dry solvents were stored over a suitable drying agent (usually 4A molecular sieves) under oxygen-free nitrogen. All of the other solvents, reagents and catalyzers used in this study; acetone (ACS reagent, ≥ 99.5%,*Sigma-Aldrich*), acetonitrile (*Sigma-Aldrich*), aluminium chloride (*Merck*), benzoyl peroxide (*Sigma-Aldrich*), N-bromosuccinimide (*Sigma-Aldrich*), 1,4-diaminobutane (*Sigma-Aldrich*), carbon tetrachloride (*Fluka*), copper chromite (*Sigma-Aldrich*), dichloromethane (DCM) (*Sigma-Aldrich*), diethyl ether (*Sigma-Aldrich*), diethyl oxalate (*Sigma-Aldrich*), ethyl chloroacetate (*Sigma-Aldrich*), ethanol (absolute, *Sigma-Aldrich*), hydrochloric acid (ACS reagent, 37%, *Sigma-Aldrich*), lithium perchlorate (*Sigma-Aldrich*), methanol (ACS reagent, ≥ 99.8%, *Sigma-Aldrich*), potassium carbonate (anhydrous, *Fluka*), potassium hydroxide (ACS reagent, 85%, *Sigma-Aldrich*), propionic acid (*Sigma-Aldrich*), sodium (*Sigma-Aldrich*), propylene carbonate (PC) (*Sigma-Aldrich*), poly(methylmetacrylate) (PMMA) (*Sigma-Aldrich*), sodium bicarbonate (*Sigma-Aldrich*), sodium sulfate (*Sigma-Aldrich*), sodium sulfide nonahydrate (ACS reagent, ≥ 99.5%, *Sigma-Aldrich*), succinyl chloride (*Sigma-Aldrich*), tetrabutylammonium hexafluorophosphate ($TBPF_6$) (*Sigma Aldrich*), thiophene (*Sigma-Aldrich*), toluene (*Sigma-Aldrich*), o-xylene (*Sigma-Aldrich*) were used as received from their *indicated* commercial suppliers without any further purification.

2.2 Equipment

The FT-IR spectra were acquired on a Perkin-Elmer Spectrum 100 Series FT-IR spectrometer. Measurements were collected in KBr pellets or in ATR mode using the average of 15 scans. The mass spectral analysis were performed with an Agilent Technologies 6890N Network GC System and Agilent Technologies 5975B VL MSD Mass Spectrometer operating at an ionization potential (EI) of 70 eV. 1H-NMR and 13C-NMR spectra were recorded at room temperature on a Varian-Mercury 400MHz high performance digital Fourier Transform (FT)-NMR Spectrometer (Mercury-400BB) and CDCl3 was used as solvent. The 1H-NMR chemical shifts were reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS, δ: 0) as internal standard. The 13C-NMR chemical shifts were also reported as δ values in ppm downfield from TMS. Melting points (up to 350°C, uncorrected) were obtained on an Electrothermal Programmable Melting Point Apparatus (IA9300). Thin layer chromatography (TLC) was used to track the progress of the experiments steadily. For this purpose, aluminum sheets (Merck, 20x20, Silica Gel 60 F254) were utilized. Purification of the desired products from common impurities -including byproducts, unreacted starting materials-was performed by column chromatography technique. Hence silica gel (SiO_2) (Merck, Silica Gel 60, 0.063-0.200 mm, 70-230 mesh ASTM) was selected as the column stationary phase.

In order to pursue electrochemical synthesis and performing cyclic voltammetry studies, an Ivium potentiostat/galvanostat was used in all electrochemical measurements. The spectra were collected with a Diode Array UV-vis spectrophotometer (Agilent 8453) with a PC interface. Spectrophotometer was used to conduct the spectroelectrochemical experiments of both polymer and electrochromic device. The indium tin oxide (ITO) coated glass plates of thickness of 0.7 mm with resistance of 8–12 $\Omega.sq^{-1}$ were purchased from Delta Technologies Limited, USA, and used as such for spectroelectrochemical studies. All electrochemical experiments were carried out in a one-component cell. The polymer films were deposited on ITO plates electrochemically using ITO-coated plate as working electrode, a Pt counter electrode and pseudo reference electrodes (calibrated against Fc/Fc^+ (0.3 V)).

2.3 Synthesis of 5,10-Dihydrobenzo[f]thieno[3,4-b][1,4]dioxocine (DTD)

The target monomer DTD was prepared through the synthetic route shown in Scheme 1. The detailed synthetic procedures and related spectral data are reported below:

Diethyl 2,2'-thiodiacetate (1): This compound was synthesized according to a similar procedure developed by

Kumar [13]. For this purpose, into a 250 mL round-bottomed flask containing a stirring bar and fitted with a reflux condenser, ethyl chloroacetate (36.60 g, 31.96 mL, d:1.15 g/mL, 300 mmol) was dissolved in anhydrous acetone (100 mL) and the solution was stirred at room temperature for a period of time (~15 minutes). Crystalline sodium sulphide ($Na_2S.9H_2O$) was added (36.00 g, 150 mmol) slowly and the mixture was stirred at 55-60°C using an oil bath. The heating process was terminated after the observation of the NaCl precipitation on the wall of the reaction flask. Then, the heterogeneous mixture was stirred at 25°C for 24 hours. The progress of the reaction was monitored by TLC (hexane/ethyl acetate, 2:1, v/v). After completion of the reaction, NaCl was filtered off under suction using a fritted glass funnel and washed thoroughly with cold acetone. After the removal of the solvent, the crude product was purified by vacuum distillation to yield 24.75g (80%) of diethyl 2,2'-thiodiacetate as slightly yellow liquid (observed b.p.: 140-145°C / 10-15 mmHg, lit b.p.: 150°C/18 mmHg).

^{1}H-NMR (400MHz, $CDCl_3$) δH/ppm:1.20 (t, J=8.8 Hz, 6H, ester -C*H₃*), 3.30 (s, 4H, S-C*H₂*), 4.15 (q, J=8.8 Hz, 4H, ester -C*H₂*).

MS (EI) m/z (%) calcd. for $C_8H_{14}O_4S$: 206.1; found: 206.1 (M+, 33), 160 (100), 133 (53), 115 (7), 105 (54), 88 (15), 77 (49), 60 (21), 45 (14), 29 (25).

IR (KBr), ν_{max}/cm^{-1}: 2984, 2939, 2909 (w, aliphatic C-H), 1732 (s, ester C=O stretching), 1447, 1367, 1276 (ester, C-O-C asymmetric stretching), 1154-1029 (ester, C-O-C symmetric stretching).

Diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (2): To a round-bottomed flask containing a stirring bar and connected to a reflux condenser and a pressure-equalizing dropping funnel, clean sodium metal (0.57 g, 24.7 mmol) and 20 mL of absolute ethanol were added attentively. The whole reaction steps were performed under nitrogen atmosphere. After the evolution of hydrogen gas was observed to decrease, the reaction mixture was hold in an ice-water bath and a mixture of 2,2'-thiodiacetate (1) (2.00 g, 9.7 mmol) and diethyl oxalate (1.42 g, 1.32 mL, d: 1.08 g/mL, 9.9 mmol) were added dropwise over 1 hour. Presently, color of the mixture became yellow-green and then stirred for an additional 24 hours at room temperature. Formation of a solid yellow chunk was observed. The mixture was poured in an ice-water mixture bath and the solution was acidified to pH:2 by adding hydrochloric acid solution. Primarily, the solution became like a milky liquid and then the formation of the crude product has occurred. The solids were separated from the solution by filtration and purified by recrystallization from methanol to yield 1.94 g (77%) of diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate as yellow solid (observed m.p: 132-134°C, lit m.p: 134.5°C).

^{1}H-NMR (400MHz, $CDCl_3$) δH/ppm: 1.20 (t, J=7.3 Hz, 6H, ester -CH_3), 4.30 (q, J=7.4 Hz, 4H, ester -CH_2), 9.40 (s, 2H, -OH).

MS (EI) m/z (%) calcd. for $C_{10}H_{12}O_6S$: 260.0; found: 260.0 (M+, 38), 214 (100), 187 (14), 168 (61), 146 (9), 118 (7), 100 (35), 85 (7), 69 (8), 57 (2), 45 (9), 29 (8.5).

IR (ATR), ν_{max}/cm^{-1}: 3324 (s, O-H stretching), 2982-2874 (w, aliphatic C-H stretching), 1670 (s, ester C=O stretching), 1405, 1373 (m, aliphatic C-H bending), 1309 (m, ester C-O-C asymmetric stretching), 1170, 1150 (s, ester C-O-C symmetric stretching), 1082, 1015, 885, 767, 683.

Elemental analysis: anal. calcd. for $C_{10}H_{12}O_6S$ (260.0): C 46.15 H 4.65 S 12.32; found: C 45.80 H 4.26 S 12.03.

1,2-Bis(bromomethyl)benzene (3): This procedure was developed according to a previously described pathway.[19] For this purpose, into a round-bottomed flask, *o*-xylene (5.80 g, 54.0 mmol) and N-bromosuccinimide (NBS) (20.00 g, 112.3 mmol) were dissolved in 25 mL of carbon tetrachloride. A half amount of benzoyl peroxide (0.01 g, 0.04 mmol) used as free radical initiator was added to the reaction medium and started to reflux under moderate stirring. After 20 minutes, the other half of benzoyl peroxide (0.01 g, 0.04 mmol) was added and the mixture was refluxed for an additional 6 hours. The reaction was monitored via TLC analysis (DCM). The flask content allowed cooling down to room temperature. Thereafter, succinimide solids precipitated during the reaction was separated from the solution under suction by using a Buchner funnel. The excess of carbon tetrachloride was removed by distillation. The crude mixture was chilled in the refrigerator overnight, and the precipitate product was filtered out. A white solid was obtained after recrystallization of the crude product from diethyl ether to yield 9.26 g (65%) of 1,2-bis(bromomethyl)benzene (observed m.p: 97°C, lit m.p: 99°C).

MS (EI) m/z (%) calcd. for $C_8H_8Br_2$: 264.0; found: 264.0 (M+, 11), 183.1 (97), 104.2 (100), 78.2 (19).

IR (ATR), ν_{max}/cm^{-1}: 3052-3021 (w, aromatic, C-H stretching), 2965 (w, aliphatic C-H stretching), 1489 (m, aliphatic C-H bending), 768 (s, aromatic C-H bending).

Diethyl 5,10-dihydrobenzo[f]thieno[3,4-b][1,4]dioxocine-1,3-dicarboxylate (4): In a 100-mL round-bottomed flask, diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (**2**) (0.75 g, 2.9 mmol) was dissolved in 15 mL anhydrous DMF under inert (nitrogen) atmosphere. Dry K_2CO_3 (1.38 g, 10.0 mmol) and 1,2-bis(bromomethyl)benzene (0.76 g, 2.9 mmol) were added to the solution and the mixture was heated at 100°C for 7 hours. After completion of the reaction, the mixture was poured into 100 mL ice-water. The precipitated crude product was filtered off, washed with 25 mL water once, and with 25 mL 0.1 N potassium hydroxide solution twice. Recrystallization was performed from dichloromethane to yield 0.94 g (87%) of diethyl 5,10-dihydrobenzo[f]thieno[3,4-b][1,4]dioxocine-1,3-dicarboxylate as yellow solid (observed m.p: 146-148°C, lit m.p: 147-148°C).

^{1}H-NMR (400MHz, $CDCl_3$) δH/ppm: 1.35 (t, 6H, J=6.8 Hz), 4.30 (q, 4H, J=7.2 Hz), 5.60 (s, 4H), 7.30 (m, 4H).

MS (EI) m/z (%) calcd. for $C_{18}H_{18}O_6S$: 362.0; found: 362.0 (M+, 75), 317 (23), 248 (28), 217 (20), 189 (29), 175 (21), 161 (13), 135 (18), 118 (7), 104 (100), 78 (36), 29 (13).

IR (ATR), ν_{max}/cm^{-1}: 2981-2909 (w, aliphatic C-H stretching), 1725, 1709 (s, ester C=O stretching), 1557, 1487 (s, aliphatic C-H bending), 1372-1242 (s, ester C-O-C asymmetric and symmetric stretching), 1059 (s, ether C-O symmetric stretching), 846, 765.

Elemental analysis: anal. calcd. For$C_{18}H_{18}O_6S$ (362.0): C 59.66 H 5.01 S 8.85; found: C 58.81 H 4.76 S 8.12.

5,10-Dihydrobenzo[f]thieno[3,4-b][1,4]dioxocine-1,3-dicarboxylic acid (5): Diethyl 5,10-dihydrobenzo[f]thieno[3,4-b][1,4]dioxocine-1,3-dicarboxylate (4) (1.00 g, 2.8 mmol) and 15 mL ethanol were put into a round bottomed flask fitted with a reflux condenser. After the addition of KOH (85%, 0.54 g, 9.9 mmol) and 1 mL distilled water, the mixture was refluxed in hot water bath for 6 hours. After termination of the reaction, the excess of ethanol was removed by distillation. Unreacted ester was removed by extraction with ether and then the residue was mixed with crushed ice. The cooled water phase was acidified with concentrated HCl (pH:2). The resulting crude product was separated by filtration to yield 0.79 g (92%) of 5,10-Dihydrobenzo[f]thieno[3,4-b][1,4]dioxocine-1,3-dicarboxylic acid as slightly yellow powder (observed m.p: 250°C).

IR (ATR), ν_{max}/cm^{-1}: 3400-2500 (O-H stretching), 2976-2918 (w, aliphatic C-H stretching), 1672 (s, carboxylic acid C=O stretching), 1489 (m, aliphatic C-H asymmetric bending), 1453 (m, aliphatic C-H symmetric bending), 1279 (s, C-O asymmetric stretching), 1039 (m, C-O symmetric stretching).

5,10-Dihydrobenzo[f]thieno[3,4-b][1,4]dioxocine (6): The dicarboxylic acid derivative; 5,10-Dihydrobenzo[f]thieno[3,4-b][1,4]dioxocine-1,3-dicarboxylic acid (5) (0.35 g, 1.6 mmol) was dissolved in 5 mL freshly distilled quinoline and catalytic amount of copper chromite (0.10 g, 0.32 mmol) was added to the reaction medium. The homogeneous dark brown solution was stirred under a nitrogen flow in a preheated oil bath at 180°C for 8 hours. The flask content allowed to cool down to room temperature, and mixed with ice-water and concentrated hydrochloric acid solution. This process was repeated several times in order to remove excess quinoline completely. Organic phase was extracted then with ethyl acetate, washed with brine and water. Solvent was removed under reduced pressure after drying the organic layer over anhydrous sodium sulfate. The crude product was purified by column chromatography (SiO_2, hexane/ethyl acetate, 3:1, v/v) to give 5,10-dihydrobenzo[f]thieno[3,4-b][1,4]dioxocine as light yellow solid (0.175 g) in 50% yield (observed m.p: 81°C, lit m.p: 80-83°C). At the end of the reaction and structure of DTD was characterized.

^1H-NMR (400MHz, $CDCl_3$) δH/ppm: 5.35 (s, 4H), 6.50 (s, 2H), 7.19-7.30 (m, 4H, aromatic).

MS (EI) m/z (%) calcd. for $C_{12}H_{10}O_2S$: 218.0; found: 218.0 (M+, 80), 173 (24), 162 (17), 145 (17), 129 (21), 117 (89), 104 (100), 91 (11), 78 (42) (Figure 1).

IR (ATR), ν_{max}/cm^{-1}: 3057-3032 (w, aromatic C-H stretching), 2934-2878 (w, aliphatic C-H stretching), 1373 (s, C-H symmetric bending), 1180, 1170, 1136 (w, C-O symmetric stretching).

Elemental analysis: anal. calcd. for $C_{12}H_{10}O_2S$ (218.0): C 66.03 H 4.62 S 14.69; found: C 65.40 H 4.03 S 13.96.

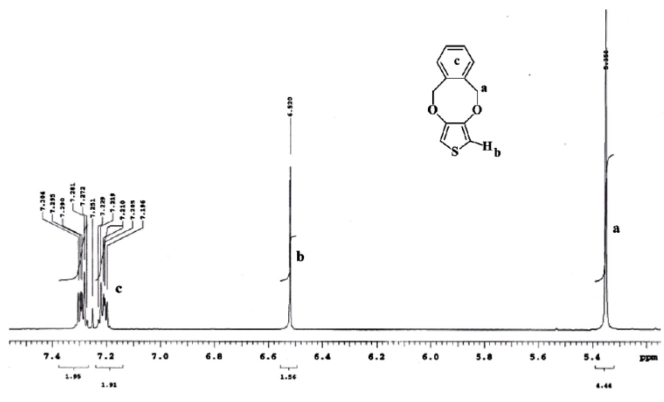
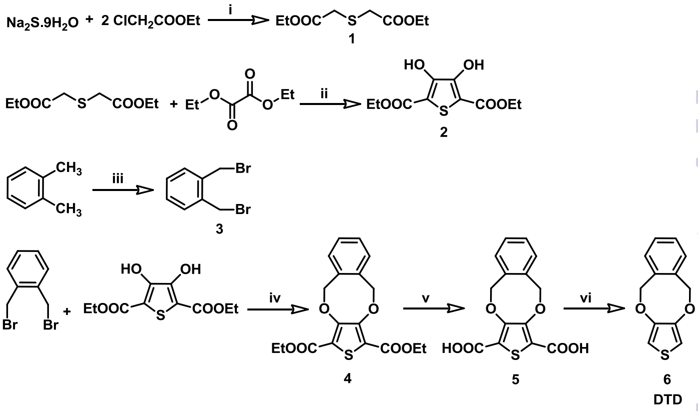


Figure 1. ^1H-NMR spectrum of DTD.



Scheme 1. Synthetic route to the monomer DTD, conditions: (i) $Na_2S.9H_2O$, acetone, rt, 24 h, 80%; (ii) **1**, NaOEt (freshly prepared from Na(s) and EtOH (abs.) under N_2 atmosphere), EtOH, 0°C, diethyl oxalate, 24 h, then treated with HCl (pH:2), 77%; (iii) NBS, CCl_4, reflux, 6 h, 65% (iv) K_2CO_3, DMF, reflux, 7 h, 87%; (vi) KOH, EtOH, 6 h, 92%; (vii) quinoline, $Cu_2Cr_2O_5$ (cat.), 180°C, 8 h, 50%.

2.4 Synthesis of 4-(2,5-Di(thiophen-2-yl)-1H-pyrrol-1-yl)butane-1-amine (TPA):

The TPA monomer; 4-(2,5-di(thiophen-2-yl)-1*H*-pyrrole-1-yl)butane-1-amine was synthesized from the reaction of 1,4-di(2-thienyl)-1,4-butanedione and butane-1,4-diamine in the presence of catalytic amounts of propionic acid according to the reported procedure.[20]

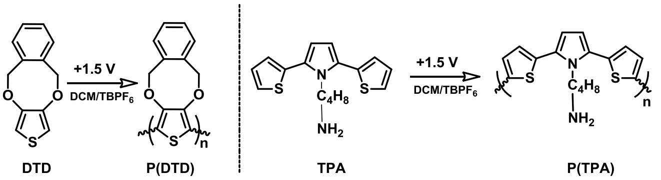
^1H-NMR (400MHz, $CDCl_3$) δH/ppm: 7.2 (d; 2H), 6.95 (dd; 2H), 6.9(dd; 2H), 6.25 (s, 2H), 3.95 (t; 2H), 1.5 (m; 4H), 1.30 (m; 4H).

2.5 Cyclic voltammetry (CV)

In order to assay the electroactivity of the polymers and to accomplish the oxidation/reduction behaviors of DTD, TPA and DTD-*co*-TPA; voltammetric measurements were carried out using the potentiostat with a conventional three electrode cell made from a quartz cuvette cell. An Ivium potentiostat/galvanostat interfaced with a personal computer was used in all electrochemical measurements. Additionally, a blanket of nitrogen was maintained above the solution during the experiment and a background voltammogram was run to ensure that no impurity was present before the addition of substrate. Spectroelectrochemical measurements were carried out in a three-electrode quartz cell. The spectra were collected with a Diode Array UV-vis spectrophotometer (Agilent 8453) with a PC interface. Solvent (DCM) and supporting electrolyte ($TBPF_6$) couples were used during the electrochemical studies.

2.6 Electrochemical polymerization of DTD and DTD-*co*-TPA

Electrochemical polymerization of DTD, TPA and DTD-*co*-TPA were performed by sweeping the potential between -0.5 to 1.5 V, -0.5 to 1.5 V and -0.3 to 1.5 V, respectively, with scan rate of 250 mV/s in a 0.05 M $TBPF_6$/DCM electrolyte-solvent couple system. The working and counter electrodes were ITO and Pt wire, respectively, and the reference electrode was Ag/Ag^+. P(DTD), P(TPA) and P(DTD-*co*-TPA) films were washed with DCM in order to remove excess of $TBPF_6$ and unreacted monomer after the potentiodynamic electrochemical polymerization. Similar method was used to synthesize the polymer on an ITO coated glass plate.



Scheme 2. Electrochemical synthesis route for P(DTD) and P(TPA).

2.7 Spectroelectrochemistry

Spectroelectrochemical analyses of the polymers were carried out to understand the band structure of the product. For spectroelectrochemical studies, the DTD, TPA and DTD-*co*-TPA film were deposited potentiostatically at 1.5 V in (0.05 M) $TBPF_6$/DCM solvent–electrolyte couple on indium tin oxide-coated glass slide (ITO). UV-vis spectra of the film were recorded at various potentials in (0.05 M) $TBPF_6$/DCM.

2.8 Switching

A square wave potential step method coupled with optical spectroscopy was used to investigate the switching times and contrast of the polymers. In this double potential step experiment, the potential was set to an initial potential (where the conducting polymer was in one of its extreme states) for 5 s and stepped to a second potential for another 5 s, before being switched back to the initial potential. During the experiment the percent transmittance (%T) and switching times at λ_{max} of the polymer were measured using a UV–Vis spectrophotometer.

2.9 Preparation of the gel electrolyte

The gel electrolyte was prepared by using $TBPF_6$:ACN:PMMA:PC in the ratio of 3:70:7:20 by weight. After dissolving $TBPF_6$ in ACN, PMMA was added into the solution. In order to dissolve PMMA, vigorous stirring and heating are required. Propylene carbonate (PC), as a plasticizer, was added to the reaction medium when all of the PMMA was completely dissolved. The mixture was stirred and heated until the highly conducting transparent gel was obtained.

2.10 Construction of electrochromic device

In this research, copolymer of DTD was utilized as the cathodically and TPA as the anodically coloring electrochromic materials. DTD copolymer was deposited on ITO-coated glass substrate via constant potential electrolysis in 0.05 M $TBPF_6$/DCM supporting electrolyte-solvent couple at +1.5 V. The TPA coated electrode was prepared at +1.5 V in 0.05 M $TBPF_6$/DCM the same electrolyte-solvent couple.
Chronocoulometry was employed to match the redox charges of the two complimentary polymer films to maintain a balanced number of redox sites for switching. Electrochromic devices (ECDs) were prepared by arranging two electrochromic polymer films -one film is in oxidized, the other is in neutral state-by facing each other in sandwich form and gel electrolyte was spread on the polymer-coated sides of the electrodes under atmospheric conditions.

3. Results and discussion

3.1 Electrochemical Properties of Polymers

3.1.1 Cyclic voltammetry studies of DTD and DTD-*co*-TPA

Cyclic voltammograms of the monomers were gathered in a solvent-supporting electrolyte system (DCM/$TBPF_6$) at room temperature and 0.01 M solution of DTD and TPA were polymerized by repeated potential scanning (250 mV/s) between -0.5 and +1.5 V. In order to get information about the electroactivity of the copolymer, we arranged CV studies in the medium of TPA. For this purpose, 1.25 mL DTD (0.001M) and 1.25 mL TPA (0.001 M) were introduced into the single compartment standard electrolysis cell. TBPF6 was utilized as the supporting electrolyte. The cyclic voltammetry study of copolymer was carried out between -0.3 V and 1.5 V. In all CV records, an increase in the peak intensities was observed upon sequential cycles which imply the formation of an electroactive polymer film on the working electrode surface. As we compared the voltammograms of homopolymer and copolymer; the reduction and oxidation potentials of DTD, TPA and DTD-*co*-TPA were determined as 0.01 - 0.45 V; 0.17 - 1.2 V; and 0.43 - 1.25 V, respectively. The observation of reduction and oxidation potentials with different values proved us the formation of copolymer. At the same time, observation of DTD-*co*-TPA's onset potential value at a different region showed occurrence of the copolymer as well. However, images of cyclic voltammograms and redox potential values of

P(DTD), P(TPA) and P(DTD-*co*-TPA) which were taken in the same solvent environments were different from each other as depicted in Figure 2. In order to determine the spectroelectrochemical and optical properties of the P(DTD), P(TPA) and P(DTD-*co*-TPA) with the evaluation of cyclic voltammograms; we decided to continue our studies by using DCM as solvent and $TBPF_6$ as supporting electrolyte.

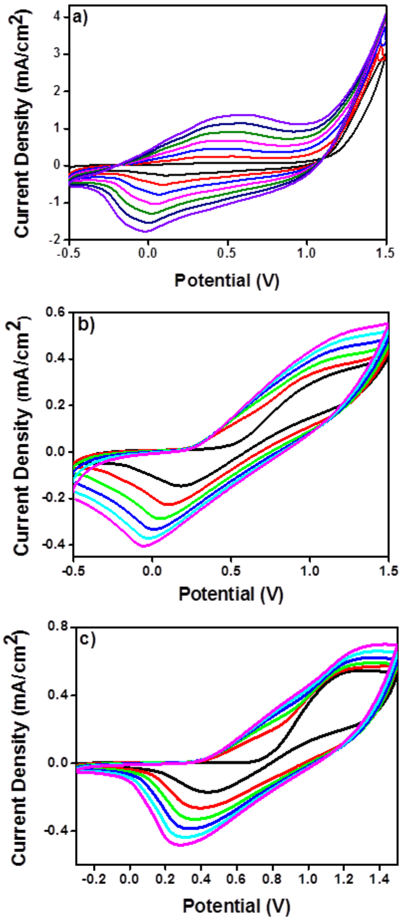


Figure 2. Cyclic Voltammograms of a) P(DTD), b) P(TPA) and c) P(DTD-*co*-TPA)in DCM containing 0.05 M $TBPF_6$ at 250 mV/s scan rate.

3.1.2 Scan rate dependence of the peak currents

P(DTD) and P(DTD-*co*-TPA) films were prepared using constant potential electrolysis. Cyclic voltammograms of prepared homopolymer and copolymer films with different scanning rates were taken and anodic/cathodic changes of the peak heights were also examined. Figure 3 shows cyclic voltammograms of P(DTD) and P(DTD-*co*-TPA) at different scan rates in DCM. With the increase of scan speed it was determined that anodic and cathodic current peak values were changed linearly. The scan rates for the anodic and cathodic peak currents show a linear dependence (anodic and cathodic least squares fit of R=0.999, R=0.998; R=0.999, R=0.999, respectively) as a function of the scan rate as illustrated in Figure 3 for P(DTD) and P(DTD-*co*-TPA). This demonstrates that the electrochemical processes are not diffusion controlled.

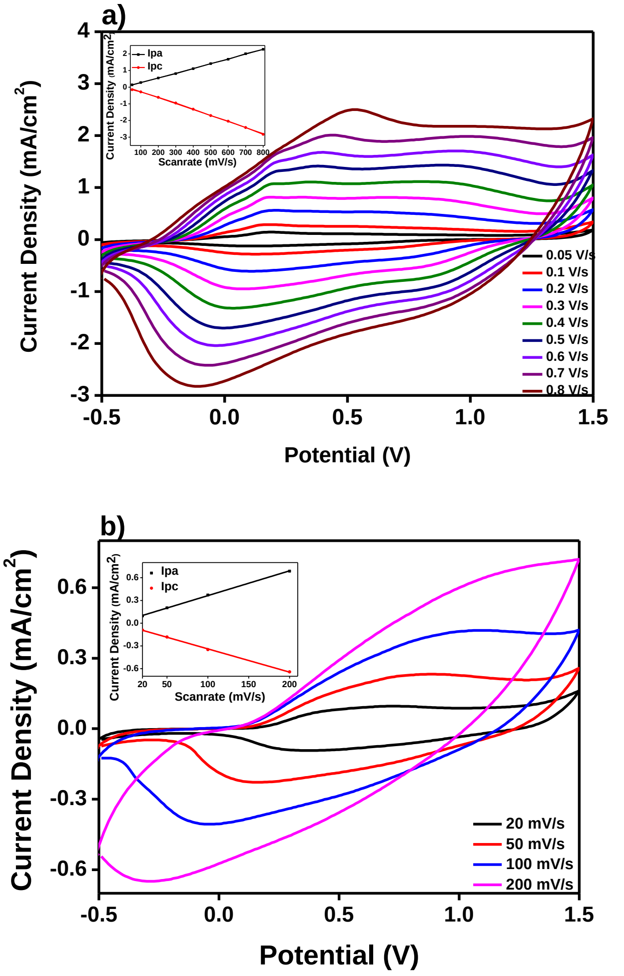


Figure 3. Redox behaviors of a) P(DTD) and b) P(DTD-*co*-TPA) at different scan rates in 0.05 M TBPF$_6$/DCM.

3.1.3 Stability

Electrochromic stability is frequently related with electrochemical stability since the degradation of the active redox couple results in the loss of electrochromic contrast and therefore the achievement of the electrochromic material. Cyclic voltammetry technique was functioning as an important appliance to inspect the long term stability of the conducting polymers. To interpret the stability of the polymers, the potential was swept repeatedly between -0.5 and +1.5 V for P(DTD) and between -0.5 and 1.5 V for P(DTD-*co*-TPA) with a scan rate of 250 mVs^{-1}. As shown in Figure 4, after 1000 cycles a decrement about 24.6% and 9.2% for P(DTD) and P(DTD-*co*-TPA) was detected, respectively. In the proportion of this result, the stability of the formed copolymer was detected to be much higher than the homopolymer.

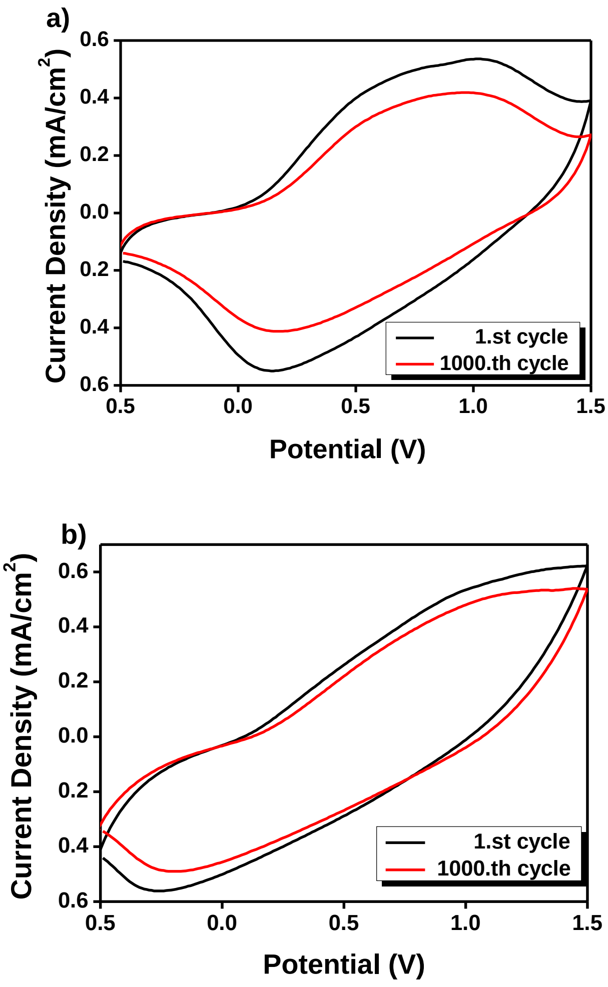


Figure 4. Stability tests of a) P(DTD) and b) P(DTD-*co*-TPA) via cyclic voltammetry with a scan rate of 250 mV/s 0.05 M TBPF$_6$/DCM.

3.2 Electrochromic properties of the P(DTD) and P(DTD-*co*-TPA)

3.2.1. In-situ polymerization of P(DTD)

Electropolymerization is a standard oxidative method for preparing electrically conducting conjugated polymers. Smooth, polymeric films can be efficiently electrosynthesized onto conducting substrates where their resultant electrical and optical properties can be probed easily by several electrochemical and coupled in situ techniques.

We investigated the in situ electrochemical polymerization by UV-vis spectrophotometer under 1.5 V at TBPF$_6$/DCM at every 10 s time interval (Figure 5).

It can be concluded from Figure 6 that there is a linear increase in absorbance with time until a certain time (0–40 s). After this time, linearity continues with the square root of the time due to polymerization rate becomes controlled by diffusion because of the consumption of monomer at the electrode double layer (Figure 6).

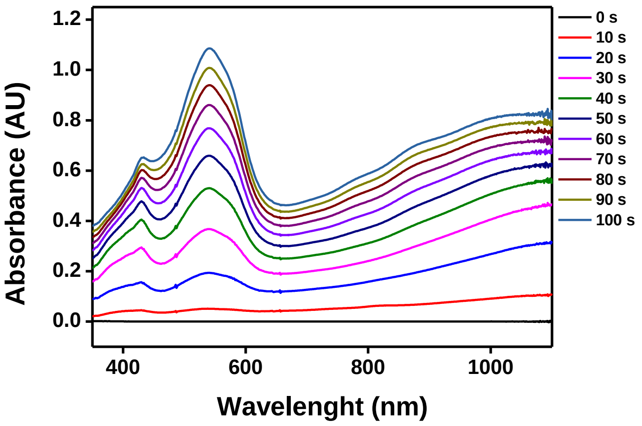


Figure 5. In situ electrochemical polymerization of DTD.

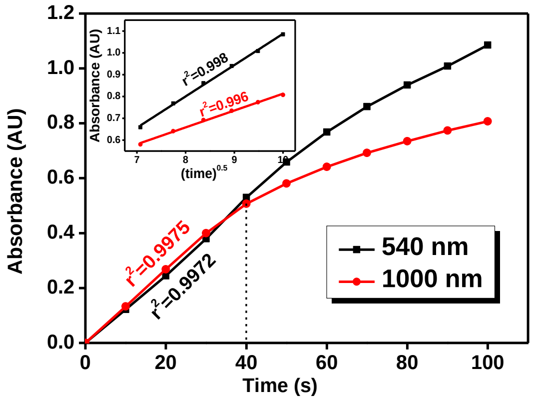


Figure 6. Absorbance recorded at different wavelengths during the polymerization. Inserted figure represents absorbance changes recorded with the square root of the time at different wavelengths (between 40 and 100 s.).

3.2.2 Spectroelectrochemistry of the P(DTD) and P(DTD-*co*-TPA)

Spectroelectrochemistry is a technique that examines the changes in optical properties of conducting polymers upon voltage change. It also provides useful data about the electronic structure of the polymer such as band gap (E_g) and the intergap states that appear upon doping. In order to detect the spectroelectrochemical and optical properties of the P(DTD) and P(DTD-*co*-TPA) with the appraisal of the cyclic voltammograms; we used DCM as solvent and $TBPF_6$ as supporting electrolyte. P(DTD) was coated on ITO and spectral changes were explored by UV-vis spectrometer in a monomer-free 0.05M $TBPF_6$ in DCM via incrementally increasing applied potential between -0.7 V and +0.7 V. While between -0.7 V and 0.0 V; P(DTD) film was dark blue, with a higher potential (0.0 V and +0.7 V interval) appliance it became transparent (Figure 7.a). Following to the applied voltage, decrease in the intensity of the π–π* transition wavelength (λ_{max}) and formation of charge carrier bands were determined. As seen in Fig. 7.a π–π* transition wavelengths (λ_{max}) of P(DTD) were determined as 585 nm. The onset energy for the π– π * transition (electronic band gap) was found to be 1.69 eV.

In order to interpret the spectroelectrochemical properties of the copolymer P(DTD-*co*-TPA), films were deposited onto ITO-coated glass plates in same solvent medium between -0.5 and 0.9 V via potentiodynamic method. The λ_{max} value for the π-π* transitions in the neutral state of copolymer was found to be 485 nm, revealing light orange color which was all significantly different than pure P(TPA) and P(DTD). The electronic band gap defined as the onset energy for the π-π* transition was found to be 1.78 eV. Upon increase in the applied voltage, the formation of a new absorption band at 900 nm was observed due to the evolution of charge carriers (Figure 7.b).

At the eventual state of this study, the color change of the homopolymer was observed in two different colors between dark blue and transparent. On the other hand, we detected 4 different colors of copolymer and with this outcome, a multichromic conducting polymer has been prepared.

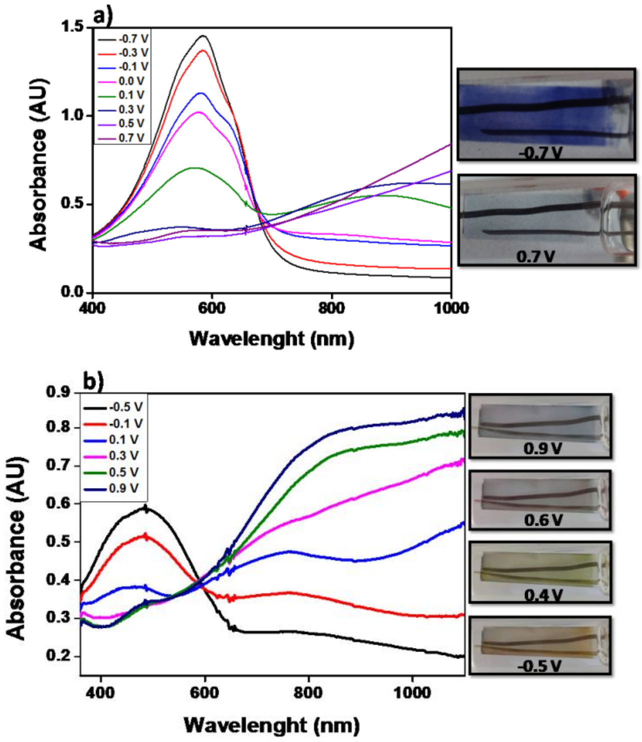
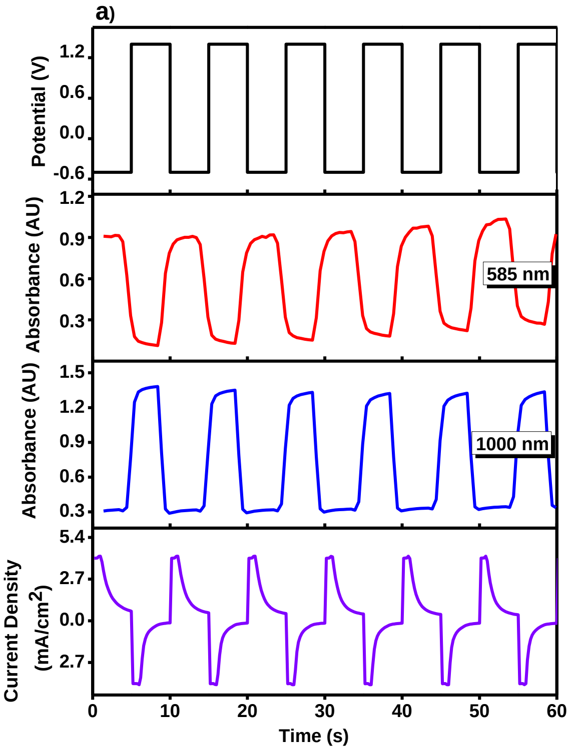


Figure 7. Spectroelectrochemical graphics of a) P(DTD) and b) P(DTD-*co*-TPA) 0.1 M $TBPF_6$ in DCM.

3.2.3 Electrochromic Switching

Electrochromic switching studies were performed to test the ability of a polymer to switch rapidly and the ability to exhibit striking color change. The experiments which were carried out by spectroelectrochemistry showed the ability of P(DTD) and P(DTD-*co*-TPA) to switch between its neutral and doped states with a change in transmittance at a fixed wavelength. Throughout the experiments, the percent transmittance (%ΔT) at the wavelength of maximum contrast was measured by utilizing UV-vis spectrophotometer.

For P(DTD) maximum contrast (%ΔT) and switching time were measured from Figure 8. as 43.4% and 2.5 s for 585 nm and 1.5 s and 62.5% for 1000 nm in DCM by adjusting the potential between -0.7 V and 0.7 V with a residence time of 5 s. The switching studies were executed for the gathered copolymer. For this execution, -0.5 V to 0.9 V were applied to P(DTD-*co*-TPA) film with 5 seconds intervals in order to calculate the maximum contrast and switching time values for copolymer. The maximum optical contrasts (ΔT%) and switching time for P(DTD-*co*-TPA) film were measured as 12% and 3s for 480nm and 29% and 3.5 s for 900 nm by step the potential between -0.5 V and 0.9 V (Figure 8.b).



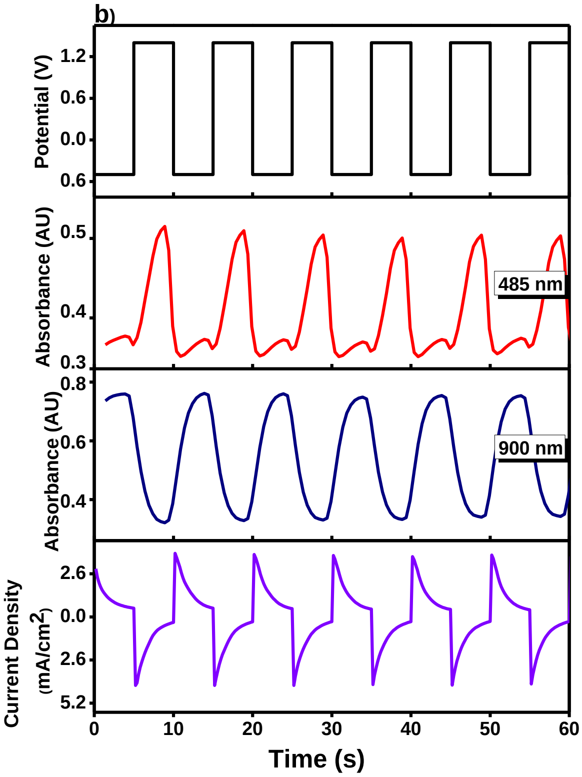


Figure 8. Potential-Time, Absorbance-Time, Current Density-Time graphics for a) P(DTD) and b) P(DTD-*co*-TPA) in DCM/TBPF$_6$.

3.2.4 Spectroelectrochemistry of Electrochromic Device (ECD)

While constructing the electrochromic device, the anodically coloring polymer film P(TPA) was fully reduced and the cathodically coloring polymer P(DTD) was fully oxidized. Upon application of a voltage, one of the polymer films is oxidized, whereas the other is neutralized, resulting in a color change. Spectroelectrochemistry experiments were performed to investigate the changes of the electronic transitions of the ECD, with the increase of the applied potential. Figure 9 represents the absorption spectrum of the ECD, recorded by application of different voltages between -0.5 V and 1.5 V. At -0.5 V the polymer layer was in its neutral state, where the absorption at 385 nm was due to π–π* transition of the polymer. At this potential, DTD was in oxidized state showing no pronounced absorption at the UV–Vis region of the spectrum, thus the color of the device was yellow. As the applied potential was increased the polymer layer started to get oxidized and a decrease in the intensity of the absorption was observed. Meanwhile, DTD layer was in its reduced state, which was followed by the appearance of the new absorption at 585 nm and dominated the color of the device was blue. A comparison of the optical properties of P(DTD)/P(TPA) device with other PEDOT/thienylpyrrole devices in literature are given in Table 1.

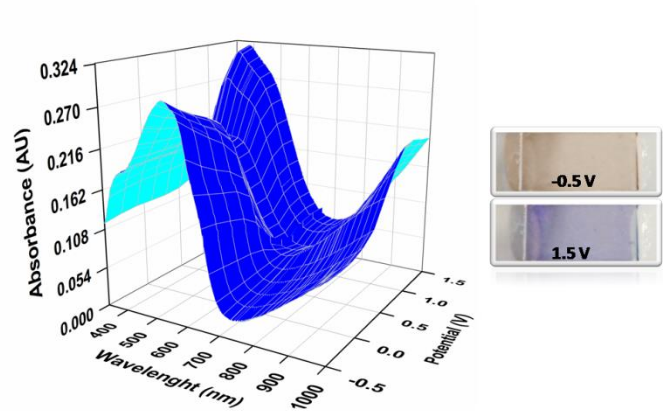


Figure 9. Spectroelectrochemical spectrum of the device as applied potentials between -0.5 and +1.5 V.

Table 1. Optical properties of PEDOT/Thienyl pyrrole devices in the literature

Structure	λ_{max} (nm)	% ΔT	Switcing Time (s)	References
P(SNSNO$_2$)/PEDOT device	400	6	-	21
	600	30	-	
P(PTP)/PEDOT device	386	13	2.1	22
	606	-	-	
P(DTTP)/PEDOT device	431	-	-	23
	617	29	1.5	
P(TPBA)/PEDOT device	575	25	1.3	20
	615	20	0.8	
P(FPTP)/PEDOT device	445	-	-	24
	615	19.4	1.4	
P(DTD)/P(TPA) device	385	25.5	0.5	This work
	550	21	1.0	

2.5 Switching of ECDs

To investigate switching characteristics of the ECD's the transmission and the response time at the maximum contrast wavelength was monitored during repeated redox stepping experiments. For the device, maximum contrast (%ΔT) and switching time were measured from Figure 10 as 25.5% and 0.5 s for 385 nm and 21% and 1.0 s for 550 nm by stepping potential between -0.5 V and +1.5 V with a residence time of 5 s.

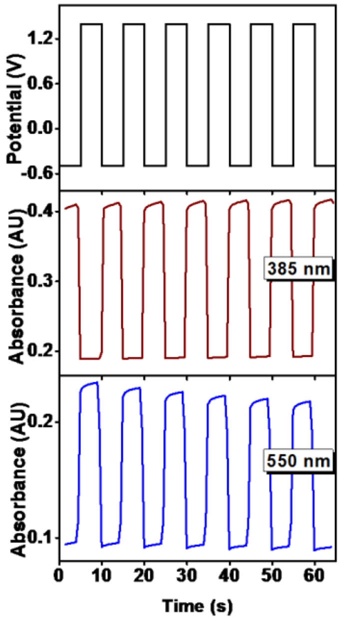


Figure 10. Potential-Time and Absorbance-Time at 385 and 550 nm for P(DTD-*co*-TPA) between -0.5 V and 1.5 V.

3.2.6 Stability of ECDs

Cyclic voltammetry is employed by monitoring current changes to figure out the long-term stability for devices. Cyclic voltammetry studies showed that the electrochromic devices operated stably with applied voltage of -0.3 V and 2.2 V with 250 mV/s scanrate under atmospheric conditions. P(DTD-*co*-TPA) device could be repeatedly switched up to 500 cycles. We determined that the device had good redox stability (Figure 11).

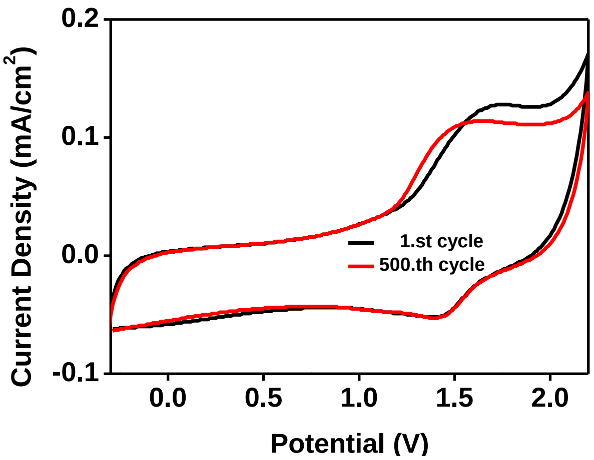


Figure 11. Cyclic Voltammograms of the device as a function of repeated scans at 250 mV/s: after 1st cycle, after 500 cycles.

Conclusions

Within the scope of these studies; synthesis, characterization, electropolymerization and polymer properties of two different types of thiophene-based monomers; 5,10-dihydrobenzo[f]thieno[3,4-b][1,4]dioxocine (DTD) and 4-(2,5-di(thiophen-2-yl)-1H-pyrrole-1-yl)butane-1-amine (TPA) have been investigated. Regarding to the condensation reaction of 2,3-bis(bromomethyl)quinoxaline and diethyl 5,10-dihydrobenzo[f]thieno[3,4-b][1,4]dioxocine-1,3-dicarboxylate with concomitant hydrolysis and decarboxylation steps gave the desired monomer DTD. When optical and electrochemical properties of electrochemically synthesized DTD were investigated, it was found that it possesses similar characteristics of EDOT. The incorporation of TPA into the conjugated DTD backbone unit via copolymerization results in different emission colors. Optical and electrochemical properties of the copolymer were investigated. We also successfully established the utilization of dual-type complementary colored polymer electrochromic devices using P(DTD)/P(TPA) in sandwich configuration. The switching ability and spectroelectrochemical properties of the electrochromic device were investigated by UV-vis spectrophotometry and cyclic voltammetry. This device exhibits moderate switching voltages (1.5 to 2.3 V) and low switching times (1.7 s) with a good switching stability.

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