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ARTICLE TYPE

Novel poly(2,5-dithienylpyrrole) (PSNS) derivatives functionalized with azobenzene, coumarine and fluorescein chromphore units: Spectroelectrochemical properties and electrochromic device applications

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Three novel 2,5-dithienylpyrrole (SNS) derivatives containing strong chromophore units such as azobenzene, coumarine and fluorescein were synthesized to investigate the effects of chromophore substituents on the electrochemical and spectroelectrochemical properties of resulting polymers. Electrochemical and optoelectronic characteristics of the homopolymers, poly(1-(2-(4-(phenyldiazenyl)phenoxy)ethyl)-2,5-di(thiophen-2-yl)-1*H*-pyrrole) (PTPTAz), poly(4-(2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethoxy)-2*H*-chromen-2-one) (PTPTCo) and poly(methyl 2-(6-(2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethoxy)-3-oxo-3*H*-xanthen-9-yl)benzoate) (PTPTFlo), were investigated in detail. The combination of a strong chromophore pendant group with poly(2,5-dithienylpyrrole) (PSNS) backbone significantly influences electronic and optoelectronics behaviors of conducting polymers. PTPTAz and PTPTCo exhibited different colors in their neutral and oxidized states while PTPTFlo showed yellow color in all states. The optical band gap (E_g) values of PTPTAz, PTPTCo and PTPTFlo films were calculated as 2.81 eV, 2.44 eV and 2.31 eV respectively. Moreover, a PTPTFlo/PEDOT based dual type solid state electrochromic device (ECD) was constructed. The ECD exhibited quite well long-term stability with reasonable optical memory performance under ambient conditions.

Introduction

Due to such advantages of low cost synthesis, easy derivatization and impeccable integration into many electronic devices, π-conjugated conducting polymers (CPs) have attracted great attention over the last decade. CPs have been extremely used in a wide field of industrial applications including organic light emitting diodes (OLEDs),[1,2] field effect transistors (FETs),[3,4] electrochromic devices,[5-7] sensors,[8,9] organic photovoltaics (OPVs),[10-12] and supercapacitors (SCs).[13-16] Particularly, the use of CPs as electrochromic materials has been widely investigated since π-conjugated conducting polymers exhibit reversible and steady color changes with low potentials, high optical contrast in visible and near infra-red (NIR) region and have high coloriation efficiency and fast switching times.[17-22]

The electrochromism phenomenon in conducting polymers is related to doping-undoping processes of electroactive polymers. The great majority of electrochromic polymers are colored in their neutral states (π-π* transition) since their band gap (E_g) lies within the visible region of electromagnetic spectrum.[23,24] Upon oxidation or reduction, new low-energy transitions emerge in the band gap (E_g) of conducting polymer on account of formation of charge carriers (polarons and bipolarons) and incorporation of counter ions into polymer backbones (doping process). The structural modification on polymer chain results in a second colored or transmissive state.[25,26] The color and other spectroelectrochemical behaviors of a conducting polymer mostly depend on the band gap (E_g). Hence, in the context of the band gap tuning, the design and synthesis of monomer is a crucial tool to control electrochromic properties of a conducting polymer and obtain unique electrochromic materials. Till now, various directions have been developed for structural modification of conducting polymers however, polymer backbone alteration and diverse pendant group or substituent approaches can be considered as the most effective ones among different concepts.[27-32]

Polythiophene, polypyrrole and their derivatives have been most commonly utilized as active layers in electrochromic device applications owing to their low band gap, good conductivity, low oxidation potential, high optical contrast, high stability in their oxidized form and multicolor electrochromism.[33-39] In addition to polythiophene and polypyrrole derivatives, recently, poly(2,5-dithienylpyrrole) derivatives (PSNS) have become promising π-conjugated conducting polymers for electrochromic applications

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due to their relatively lower oxidation potential, multichromic properties, high chemical and electrochemical stability, effortless synthesis methods. 2,5-Dithienylpyrrole type monomers (SNS) can be also easily modified with multifarious electron-donating and electron-withdrawing functional groups through the nitrogen atom in pyrrole ring of SNS unit.[45-48] Even though many researchers reported on the synthesis and electrochromic properties of PSNS derivatives in the literature, the majority of these PSNS derivatives have been functionalized using similar substituted aryl and alkyl amine compounds.[45-48] Hence, design and synthesis of novel SNS derivatives containing different pendant substituents is quite necessary in terms of obtaining excellent precursor compounds for producing SNS type π-conjugated conducting polymers with better electrochemical and spectroelectrochemical properties.

In the context, we report herein the synthesis and electrochromic properties of three novel 2,5-dithienylpyrrole (SNS) type π-conjugated conducting polymers, namely poly(1-(2-(4-(phenyldiazenyl)phenoxy)ethyl)-2,5-di(thiophen-2-yl)-1*H*-pyrrole) (PTPTAz), poly(4-(2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethoxy)-2*H*-chromen-2-one) (PTPTCo) and poly(methyl 2-(6-(2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethoxy)-3-oxo-3*H*-xanthen-9-yl)benzoate) (PTPTFlo), functionalized with strong chromophore units such as azobenzene, coumarine and fluorescein which are highly optically potent in the UV-Vis region. The new approach based on the combination of chromophore groups with monomer chains was reported previously by our group and interesting electrochemical and spectroelectrochemical behaviors were observed for terthienyl derivatives containing the same chromophore units.[49,50] In the light of our preliminary results, it is expected that similar electrochromic behaviors can be obtained through the incorporation of the strong chromophore groups and 2,5-dithienylpyrrole (SNS) monomer chain. For this purpose, the electroactive SNS type monomers bearing an azobenzene, a coumarine or a fluorescein unit attached to 2,5-dithienylpyrrole monomer chain via an ethylene bridge, respectively TPTAz, TPTCo and TPTFlo, were firstly synthesized and their homopolymers, PTPTAz, PTPTCo and PTPTFlo, were electrochemically prepared on ITO glass slide electrodes. The electronic and optical properties of homopolymers were investigated by cyclic voltammetry and spectroelectrochemical techniques. The effects of type of chromophore units as a pendant substituent on electrochemical and spectroelectrochemical behaviors of SNS type π-conjugated conducting polymers were also evaluated and compared in detail. Besides, a dual type electrochromic device (ECD) based on poly(3,4-ethylenedioxythiophene) (PEDOT) / PTPTFlo was constructed and its electrochromic performance was characterized.

Experimental section

Materials and instrumentation

All chemicals, including thiophene (≥ 99.0%), succinyl dichloride (95%), aluminium (III) chloride ($AlCl_3$, anhydrous, 99.999%), ethanolamine (≥ 99%), p-toluenesulfonic acid (PTSA, ≥ 99.5%), toluene (anhydrous, 99.8%), p-toluenesulfonyl chloride (≥ 99.0%), triethylamine (Et_3N, ≥ 99%), lithium perchlorate ($LiClO_4$, 99.999%), sodium perchlorate ($NaClO_4$, ≥ 98%), cesium carbonate (Cs_2CO_3, 99%), acetonitrile (ACN, HPLC grade), N,N-dimethylformamide (DMF, anhydrous, 99.8%), dichloromethane (DCM, anhydrous, ≥ 99.8%), 4-hydroxyazobenzene, 4-hydroxy-2*H*-chromen-2-one, 3,4-ethylenedioxythiophene (EDOT), platinum wire (Pt, 0.25 mm diameter, 99.999%) and silver wire (Ag, 0.05 mm diameter, 99.9%) were purchased from Sigma Aldrich and used without any further purification. Methyl 2-(6-hydroxy-3-oxo-3H-xanthen-9-yl)benzoate,[51] 1,4-di(thiophen-2-yl)butane-1,4-dione **(1)**[41] and 2-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)ethanol **(2)**[41] were synthesized according to previously described methods. Microwave-assisted nucleophilic substitution reactions were performed using a CEM Discover S-Class single-mode microwave synthesis instrument. Electrochemical studies were carried out with a Radiometer VoltaLab PST 050 potentiostat/galvanostat in a three-electrode cell configuration consisting an indium tin oxide doped glass slide (ITO, 12 Ω sq^{-1}), a platinum wire and a silver wire as the working, counter and pseudo-reference (+0.3 V *vs* Fc/Fc^+) electrodes, respectively. The homopolymers were electrochemically deposited with cyclic voltammetry technique (CV) in the presence of 0.05 M monomer in 0.1 M solution of $NaClO_4$-$LiClO_4$/ACN/DCM (95:5, v/v) supporting electrolyte under nitrogen atmosphere at a scan rate of 100 mV s^{-1} for 10 cycles. The spectroelectrochemical studies of the homopolymers films on ITO surfaces were done via a Varian Carry 5000 spectrophotometer at a scan rate of 2000 nm min^{-1}. The potentials were controlled by using a Solartron 1285 potentiostat/galvanostat. Konica Minalto CS-100 colorimeter in a Pantone Colorviewing Light PJC/CV L3 Light Box 3 was used to perform color analysis of the polymers. FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at room temperature on a Varian-Mercury 400 MHz (FT)-NMR spectrometer. All chemical shifts were given in ppm downfield from tetramethylsilane (TMS). Mass spectra were recorded using a DI-2010 direct inlet probe on a Shimadzu GC-MS QP2010 mass spectrometer operating at ionization potential (EI) of 70 eV. Elemental analyses were conducted by Eurovector CHNS Elemental Analyzer.

Syntheses

The SNS type novel monomers (**TPTAz**, **TPTCo** and **TPTFlo**) containing strong chromophore groups were synthesized in three steps as explained below.

Synthesis of 2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethyl 4-methylbenzenesulfonate (3)

2-(2,5-Di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethanol **(2)** was firstly prepared according to an earlier reported work.[41] In a 100 mL two-necked round-bottomed flask, 2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethanol **(2)** (10 mmol) and p-toluenesulfonyl chloride (10.54 mmol) were dissolved in THF (30 mL). Aqueous solution of NaOH (30 mmol) /10 mL H_2O was added dropwise to the solution at 0˚C and then, the suspension was stirred at room temperature overnight. The solvent was removed on a rotary

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evaporator under reduced pressure. The oily residue was extracted with chloroform (3 x 25 mL), the combined organic phase was washed with water and brine, then dried over anhydrous Na_2SO_4. After removal of the chloroform by evaporation, the crude product was purified by column chromatography using dichloromethane as eluent (R_f, 0.6). 2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethyl 4-methylbenzene sulfonate **(3)** was obtained as a light brown solid (3.98 g, 9.3 mmol, 93%, mp 68-70°C). FTIR ν_{max}/cm^{-1} 3090, 2930, 1729, 1593, 1492, 1415, 1385, 1365, 1295, 1187, 1169. ^1H NMR δ_H (400 MHz, $CDCl_3$, Me_4Si) 2.45 (s, 3H, CH_3), 3.92 (t, *J*= 6 Hz, 2H, CH_2-), 4.39 (t, *J*= 6 Hz, 2H, CH_2-), 6.2 (s, 2H, ArH), 6.96-7.06 (m, 4H, ArH), 7.25-7.31 (m, 4H, ArH), 7.53 (d, *J*= 8.4 Hz, 2H, ArH). MS (EI): *m/z* 429.1 (M^+, 100%), 339 (2), 274.1 (10), 258 (12), 244.1 (20), 230.1 (30), 199.1 (15), 155.1 (10), 121.1 (10), 91.1 (35).

General procedure for microwave-assisted nucleophilic substitution reactions

A mixture of 2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethyl 4-methylbenzene sulfonate **(3)** (1.0 mmol), chromophore compound (1.0 mmol) and Cs_2CO_3 (2 mmol) were placed in a microwave reaction vessel (30 mL) and DMF (5 mL) was added. The slurry reaction mixture was heated at 85°C under microwave irradiation (110 W single-mode power) for 8 min. Then, the mixture was cooled to room temperature, poured into ice-water (100 mL) and vigorously stirred for 1 h. The solid crude product was filtered under reduced pressure, dried and purified by column chromatography to afford pure target SNS type monomer. The monomer was characterized by FTIR, ^1H NMR, ^{13}C NMR, mass spectrometer techniques and elemental analysis.

1-(2-(4-(Phenyldiazenyl)phenoxy)ethyl)-2,5-di(thiophen-2-yl)-1*H*-pyrrole (TPTAz)

This monomer was synthesized via nucleophilic substitution reaction between 2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethyl 4-methylbenzene sulfonate **(3)** and 4-hydroxyazobenzene. The crude product was subjected to column chromatography using hexane/CH_2Cl_2 (10:1, v/v) as the eluent (R_f, 0.55). **TPTAz** was obtained as a bright orange solid (0.42 g, 0.92 mmol, 92%, mp 132-140°C). FTIR ν_{max}/cm^{-1} 3094, 3064, 2953, 2919, 2873, 1603, 1501, 1456, 1406, 1330, 1308, 1239, 1142, 1076. ^1H NMR δ_H (400 MHz, $CDCl_3$, Me_4Si) 4.06 (t, *J* = 6 Hz, 2H, CH_2), 4.61 (t, *J* = 6 Hz, 2H, CH_2), 6.39 (s, 2H, Ar H), 6.75 (d, *J* = 8.8 Hz, 2H, Ar H), 7.11-7.17 (m, 4H, Ar H), 7.36-7.38 (dd, *J* = 6.4 Hz and *J* = 1.2 Hz, 2H, Ar H), 7.44-7.52 (m, 3H, Ar H), 7.81-7.88 (m, 4H, Ar H). ^{13}C NMR δ_C (400 MHz, $CDCl_3$) 43.7, 66.8, 111.5, 114.6, 122.5, 124.6, 125.8, 126.7, 127.4, 128.5, 129, 130.4, 134.3, 147.1, 152.7, 160.5. MS (EI): *m/z* 455 (M^+, 100%) 429 (4), 350 (4), 317 (20), 258 (30), 225 (10), 186 (8), 147 (10), 97 (5), 77 (28). Anal. Calcd. for ($C_{26}H_{21}N_3OS_2$): C, 68.54%; H, 4.65%; N, 9.22%. Found: C, 68.77%; H, 4.18%; N, 8.89%.

4-(2-(2,5-Di(thiophen-2-yl)-1H-pyrrol-1-yl)ethoxy)-2*H*-chromen-2-one (TPTCo)

This monomer was synthesized via nucleophilic substitution reaction between 2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethyl 4-methylbenzene sulfonate **(3)** and 4-hydroxy-2*H*-chromen-2-one. The crude product was subjected to column chromatography using hexane/CH_2Cl_2 (5:1, v/v) as the eluent (R_f, 0.35). **TPTCo** was obtained as a dark yellow solid (0.36 g, 0.87 mmol, 87%, mp 148-151°C). FTIR ν_{max}/cm^{-1} 3109, 3083, 2980, 2959, 1710, 1653, 1620, 1610, 1500, 1491, 1455, 1351, 1317, 1236, 1181, 1109, 1039. ^1H NMR δ_H (400 MHz, $CDCl_3$, Me_4Si) 4.08 (t, *J* = 6 Hz, 2H, CH_2), 4.77 (t, J = 6 Hz, 2H, CH_2), 5.36 (s, 1H, -C=C$\underline{H}$-), 6.38 (s, 2H, Ar H), 7.08-7.18 (m, 4H, Ar H), 7.34-7.35 (dd, *J* = 6.5 Hz and *J* = 1.2 Hz, 2H, Ar H), 7.4 (dd, *J* = 5.0 Hz and *J* = 1.2 Hz, 1H, Ar H), 7.47-7.51 (m, 1H, Ar H), 7.64 (dd, *J* = 5.2 Hz and *J* = 1.2 Hz, 1H, Ar H), 7.81 (dd, *J* = 5.2 Hz and *J* = 1.2 Hz, 1H, Ar H); ^{13}C NMR δ_C (400 MHz, $CDCl_3$) 43.3, 67.7, 90.6, 111.8, 115.3, 116.5, 123.3, 123.7, 125.9, 126.5, 127.6, 128.8, 132.1, 132.3, 133.6, 134.1, 153.1 (-$\underline{C}$-O-), 162.5 (-$\underline{C}$=O), 165.9 (O-$\underline{C}$=CH-). MS (EI): *m/z* 419 (M^+, 100%), 385 (2), 335 (3), 310 (2), 258 (12), 244 (20), 230 (18), 199 (10), 155 (43), 139 (10), 111 (80), 91 (50). Anal. Calcd. for $C_{23}H_{17}NO_2S_2$: C, 65.85%; H, 4.08%; N, 3.34%. Found: C, 65.63%; H, 3.87%; N, 3.11%.

Methyl 2-(6-(2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethoxy)-3-oxo-3H-xanthen-9-yl) benzoate (TPTFlo)

This monomer was synthesized via nucleophilic substitution reaction between 2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethyl 4-methylbenzene sulfonate **(3)** and methyl 2-(6-hydroxy-3-oxo-3H-xanthen-9-yl)benzoate. The crude product was subjected to column chromatography using hexane/ethyl acetate (1:3, v/v) as the eluent (R_f, 0.40). **TPTFlo** was obtained as a dark red solid (0.47 g, 0.78 mmol, 78%, mp 167-171°C). FTIR ν_{max}/cm^{-1} 3094, 3047, 2949, 2935, 1729, 1642, 1591, 1509, 1455, 1439, 1414, 1276, 1257, 1213, 1151, 1105, 1081. ^1H NMR δ_H (400 MHz, $CDCl_3$, Me_4Si) 3.62 (s, 3H, CH_3), 4.04 (t, *J* = 6 Hz, 2H, CH_2), 4.62 (t, *J* = 6 Hz, 2H, CH_2), 6.43-6.62 (m, 4H, C$\underline{H}$=C$\underline{H}$-, and Ar H), 7.09-7.13 (m, 4H, Ar H), 7.25-7.27 (m, 1H, Ar H), 7.35-7.36 (dd, *J* = 6 Hz and *J* = 1 Hz, 2H, Ar H), 7.63-7.73 (m, 2H, Ar H), 8.21-8.23 (d, J = 6.8 Hz, 1H, Ar H). ^{13}C NMR δ_C (400 MHz, $CDCl_3$) 43.4, 52.4, 67.2, 100.6, 105.7, 111.7, 113.5, 115, 117.6, 125.9, 126.7, 128.5, 128.7, 129.6, 129.9, 130.1, 130.5, 131.1, 132.6, 134.2, 134.5, 150, 154, 158.8, 162.4, 165.5 (ester C=O), 185.6 (quinoid C=O). MS (EI): *m/z* 603 (M^+, 30%), 529 (3), 454 (2), 440 (3), 389 (12), 364 (45), 288 (15), 258 (50), 202 (20), 150 (5), 111 (100). Anal. Calcd. for $C_{35}H_{25}NO_5S_2$: C, 69.63%; H, 4.17%; N, 2.32%. Found: C, 70.08%; H, 3.92%; N, 2.11%.

The construction of electrochromic device (ECD)

Both polymers (PTPTFlo and PEDOT) were electrochemically coated onto the ITO-coated glass and ECD was constructed by arranging two electrochromic polymers (with two different states, doped and neutral) facing each other separated by gel electrolyte.[45,48] The gel electrolyte was prepared according to literature.[52] Schematic representation of the electrochromic device based on PTPTFlo/PEDOT is shown in Fig. 1.

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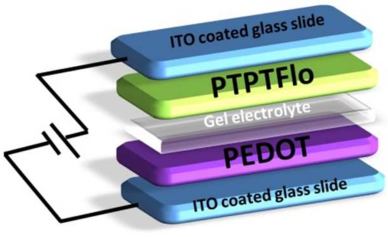


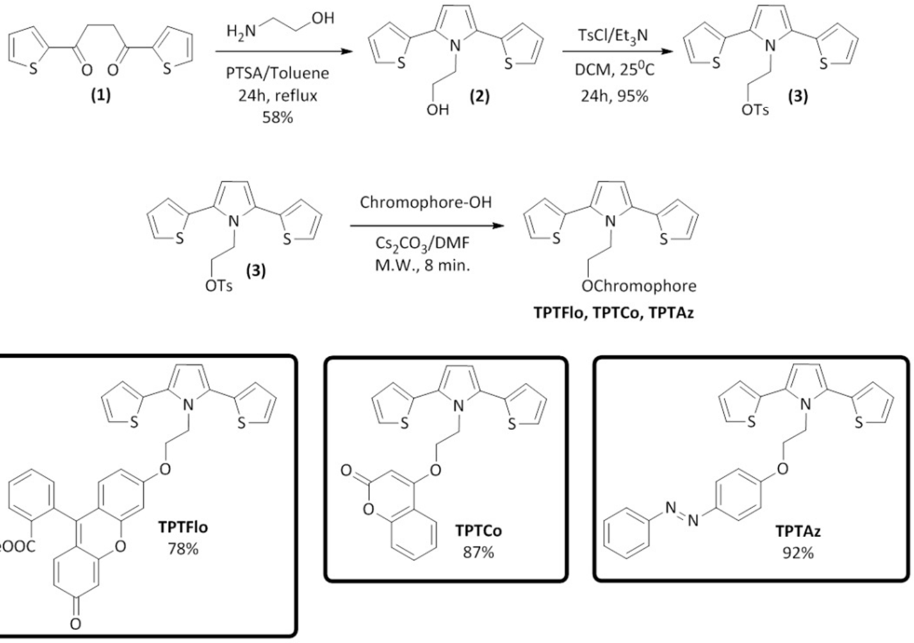
Fig.2 Schematic representation of the PTPTFlo/PEDOT ECD

Results and discussions

Synthesis

The design and synthesis of novel precursor molecules are one of the most effective tools in order to control electrochemical and optical properties of π-conjugated conducting polymers. In this context, the novel conducting polymer derivatives bearing azobenzene, coumarine and fluorescein dyes have been synthesized in our previous study and their electrochemical and spectroelectrochemical properties have been investigated in detail.[49,50] The new approach based on the incorporation of chromophore units with thiophene polymer backbones significantly enhanced electronic and optoelectronic behaviors of conducting polymers.

This favorable effect of chromophore groups on electrochemical and spectroelectrochemical properties resulted in low band gaps, multicolored characteristics, high optical contrasts and fast switching times for terthienyl-based π-conjugated conducting polymers. In the present study, the new kind of 2,5-dithienylpyrrole (SNS) type monomers containing an azobenzene, a coumarine and a fluorescein were synthesized for the first time according to a three-step synthetic methodology, as briefly illustrated in Scheme 1. Initially, synthesis of 2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl) ethanol **(2)** was performed with a Paal-Knorr condensation reaction between 1,4-di(2-thiophenyl)-1,4-butanedione **(1)** and ethanolamine in the presence of catalytical amount p-toluenesulfonic acid. The second step involves treatment of 2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethanol **(2)** with p-toluenesunfonyl chloride to obtain 2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethyl 4-methylbenzenesulfonate **(3)**. Microwave-assisted nucleophilic substitution reaction of toluene-4-sulfonic acid 2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)ethyl ester with the chromophore compound (4-hydroxybenzene, 4-hydroxy-2*H*-chromen-2-one and methyl 2-(6-hydroxy-3-oxo-3*H*-xanthen-9-yl)benzoate) was finally carried out in order to connect a SNS unit and a chromophore dye through a ethylene bridge. The chemical structures of SNS type monomers,1-(2-(4-(phenyldiazenyl)phenoxy) ethyl)-2,5-di(thiophen-2-yl)-1*H*-pyrrole (TPTAz), 4-(2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl) ethoxy)-2*H*-chromen-2-one (TPTCo) and methyl 2-(6-(2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl) ethoxy)-3-oxo-3*H*-xanthen-9-yl)benzoate (TPTFlo), were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR, mass spectroscopy and elemental analysis techniques.



Scheme 1 Synthetic route to SNS type monomers **TPTFlo**, **TPTCo** and **TPTAz**

Cyclic voltammetry studies

Cyclic voltammetry is a useful technique that can be used for both electrochemical polymerization and to investigate redox properties of polymers. In this study after polymerization via electrochemically, electroactivity and HOMO and LUMO energy levels of resulting polymers (PTPTCo, PTPTFlo and PTPTAz) were determined by cyclic voltammetry (CV) to get a deeper insight on redox behaviors. **TPTFlo**, **TPTCo** and **TPTAz** were polymerized electrochemically on ITO coated glass slides in a mixture of dichloromethane (DCM) and acetonitrile (ACN) (5:95, v:v) in the presence of 0.1 M supporting electrolyte formed of equimolar amounts of sodium perchlorate ($NaClO_4$) and lithium perchlorate ($LiClO_4$) mixture with repeated scan intervals between 0 V and +1.2 V for **TPTFlo**, 0 V and +1.5 V for **TPTCo** and 0 V and +1.5 V for **TPTAz**. Fig. 2 represents the cyclic voltammograms (CV) of all monomers at 100 mV s^{-1} scan rate. During electropolymerization, irreversible monomer oxidation peaks at +0.82 V (TPTFlo), +0.96 V (TPTCo) and +1.05 V (TPTAz) were observed in the first cycle of voltammograms (Fig. 2). After observing monomer oxidations in the first cycle, oligomers and polymers were electrodeposited on the ITO surfaces which can be proved with increasing current intensity of each successive cycle.

Resulting polymers (PTPTFlo, PTPTCo and PTPTAz) were subjected to CV in a monomer free 0.1 M $NaClO_4$-$LiClO_4$/CAN solution in order to explore the doping property of resulting electroactive polymers as illustrated in Fig. 3. As depicted in Fig. 3, all polymers have p-type doping property with a reversible redox couple centered at +0.74 V/ +0.63 V for **PTPTFlo**, at +1.01 V/ +0.63 V for **PTPTCo** and at +0.87 V/ +0.62 V for **PTPTAz**. HOMO-LUMO energy levels of conducting polymers are very important for the application fields and could be tailored via changing the donor and acceptor units in the donor-acceptor-donor systems. Oxidation and reduction onset values were used to calculate the HOMO energy levels for all polymers as -5.08 eV, -4.93 eV and -5.07 eV, respectively. Since all polymers have only p-type doping character, LUMO energies were calculated from HOMO energy levels and optical band gaps (E_g^{op}) were calculated as -2.62 eV (PTPTFlo), -2.64 eV (PTPTCo) and -2.26 eV (PTPTAz). For these calculations, the reference electrode was calibrated with respect to Fc/Fc^+ (+0.30 V) and the HOMO-LUMO energies were calculated relative to the vacuum level taking the SHE value as -4.75 eV vs. vacuum.

When **TPTFlo**, **TPTCo** and **PTPAz** were compared in terms of their monomer oxidations and polymer oxidations of corresponding polymers, it can be easily seen that **TPTFlo** has the lowest value. Low oxidation potential **TPTFlo** can be attributed to the electronic nature of chromophore groups.

Ethylene bridges between SNS monomer chains and chromophore units hinder the steric and mesomeric effects of these strong chromophore groups on electronic nature of electroactive polymers which make inductive effect dominant over the others. The carbonyl groups in the structure of fluorescein group decrease the electron withdrawing capability of chromophore unit which increase the electron density on the main polymer chain and makes it more ready for redox reactions with lower oxidation potential.

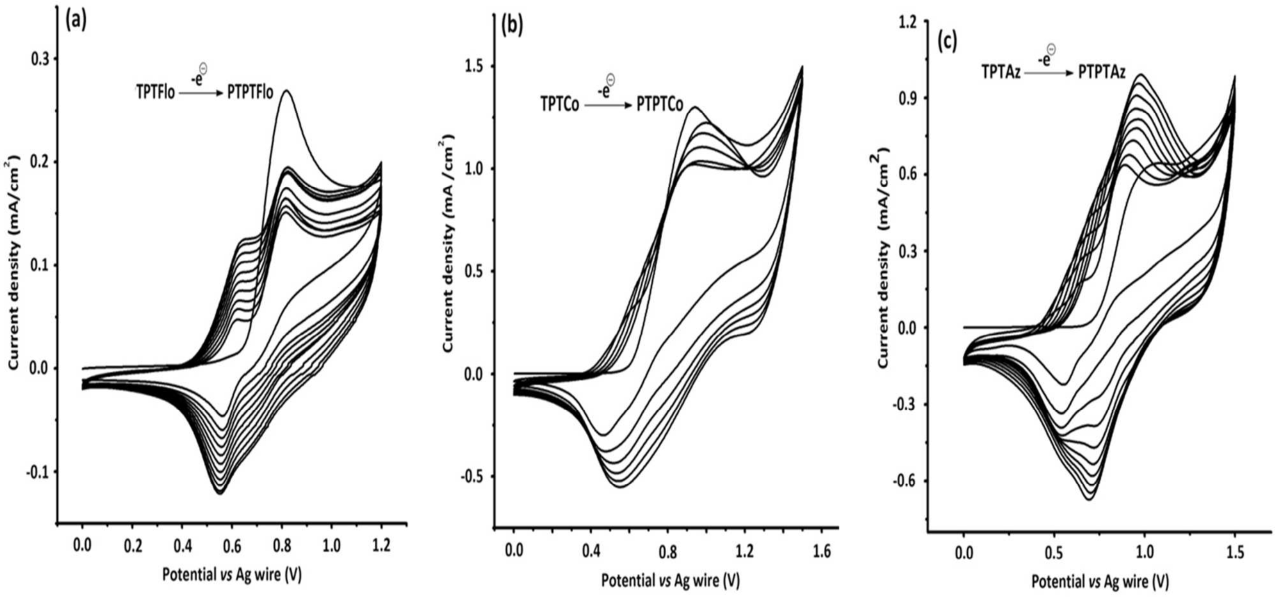


Fig.2 Repeated potential scan polymerization of (a) **TPTFlo** (b) **TPTCo** and (c) **TPTAz** in 0.1 M $LiClO_4$/ $NaOCl_4$/DCM/ACN (5:95,v:v) solution at 100 mV s^{-1} scan rate

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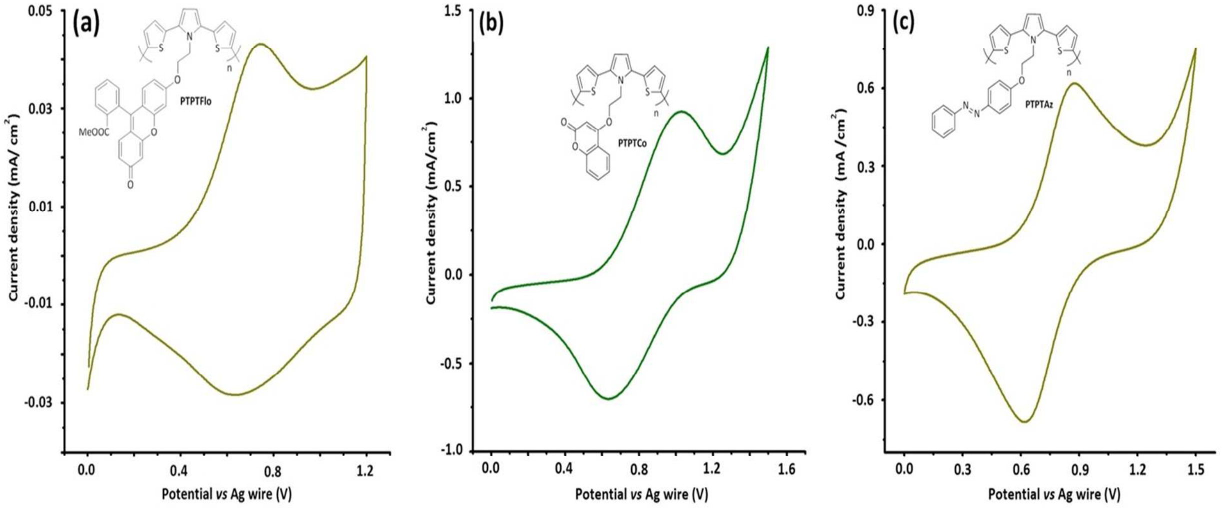

Fig.3 Single scan cyclic voltammograms for (a) **PTPTFlo** (b) **PTPTCo** and (c) **PTPTAz** in a monomer free, 0.1 M $NaClO_4/LiClO_4/ACN$ solution

Spectroelectrochemistry

Spectroelectrochemical studies were performed in order to investigate the optical and electrochromic properties of conjugated polymers upon doping process. **PTPTFlo**, **PTPTCo** and **PTPTAz** were electrochemically coated on ITO surface and spectral changes were recorded by UV-vis-NIR spectrophotometer. Similar to the single scan cyclic voltammograms, a monomer-free 0.1 M $NaClO_4$-$LiClO_4$/ACN solution was used for recording the electronic absorption spectra. During the spectral studies, recording neutral state absorption is very crucial for comparison with other states. For this purpose, polymer films were subjected to 0 V to reduce and to remove any trapped charge and dopant ion arising from electrochemical polymerization. Then stepwise oxidation was performed via incrementally increasing applied potential between +0.3 V and +1.4 V for **PTPTFlo**, +0.5 V and +1.1 V for **PTPTCo** and 0.0 V and +1.0 V for **PTPTAz**. The normalized electronic absorption spectra of all polymers were depicted in Fig. 4.

Maximum wavelength (λ_{max}) can be defined as the wavelength at which a polymer shows π-π^*transition. In this study, they are at 459 nm/490 nm for **PTPTFlo**, 370 nm for **PTPTCo** and 347 nm for **PTPTAz**. Via oxidation, while the absorption in the visible region decreasing for **PTPTCo** and **PTPTAz**, new absorption bands called as polaron bands (radical cations), bipolaron bands (bications) appeared at 620 nm/920 nm for **PTPTCo** and 610 nm/ 970 nm for **PTPTAz**. As illustrated in Fig. 4a PTPTFlo has two absorption maxima in the visible region centered at 459 nm/ 490 nm. Although formation of new bands (polaron and bipolaron) at 610 nm/1120 nm were observed it has a yellow color at both states (neutral and oxidized), since there was no decrease in the neutral absorption during stepwise oxidation. This may be due to the fact that the tail of the polaron band intersects with that of the neutral band absorption peak. The optical band gaps (E_g^{op}) of **PTPTFlo**, **PTPTCo** and **PTPTAz** were also calculated from the onsets of the lowest energy π-π^* transitions on the neutral state absorption spectra (Fig. 4). They were calculated as 2.31 eV, 2.44 eV and 2.81 eV respectively. Summary of all electrochemical and spectroelectrochemical data were depicted in Table 1.

The structures and colors of **PTPTFlo**, **PTPTCo** and **PTPTAz** at neutral and oxidized states were illustrated in Fig. 4. Spectroelectrochemical studies were also consistent with recorded colors. While all polymers have yellow color in the neutral state, **PTPTCo** reveals gray and **PTPTAz** has blue color in the fully oxidized states. On the other hand, **PTPTFlo** shows all states yellow character and as a result of this unique property we constructed a PTPTFlo/PEDOT based electrochromic device (ECD). Characterization of PTPTFlo/PEDOT ECD will be discussed in the next section with some important properties such as; stability, open circuit memory and spectral response.

Electrochromic device (ECD) application and characterization

As mentioned before because of the all state yellow character of **PTPTFlo**, we constructed a prototype electrochromic device based on **PTPTFlo** and PEDOT in order to investigate the electrochromic performance of ECD in ITO/PTPTFlo/ITO configuration.

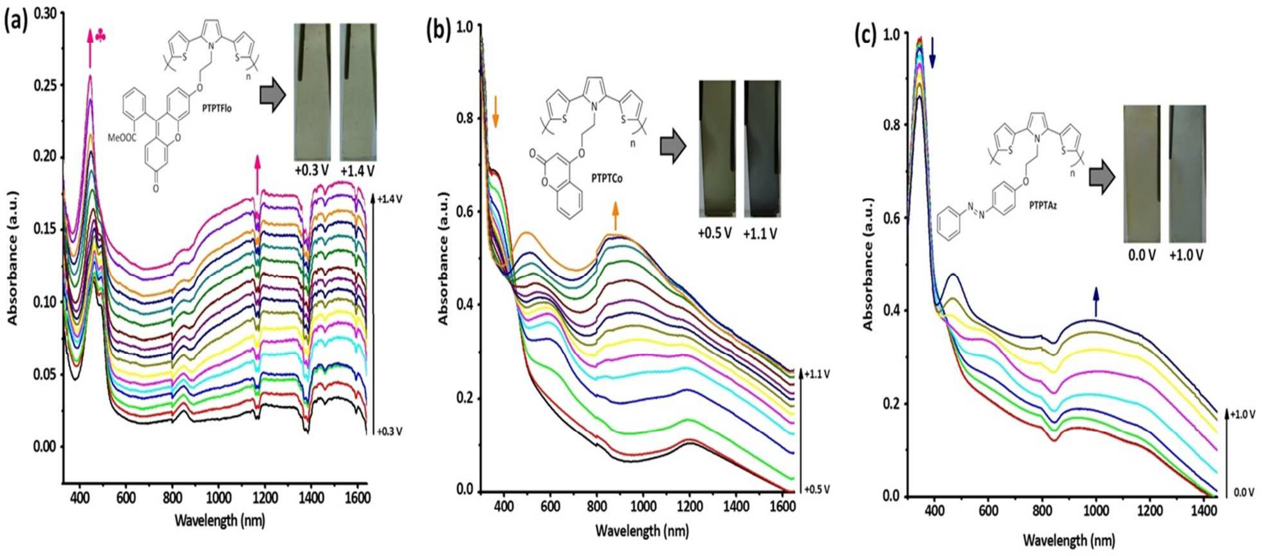

Fig.4 Electronic absorption spectra of (a) **PTPTFlo** (b) **PTPTCo** (c) **PTPTAz** in 0.1 M $NaClO_4$-$LiClO_4$/ACN electrolyte solution between +0.3 V and +1.4 V for **PTPTFlo,** +0.5 V and +1.1 V for **PTPTCo** and 0.0 V and +1.0 V for **PTPTAz**

Table 1 Summary of electrochemical and optical properties of **PTPTFlo**, **PTPTCo** and **PTPTAz**

Polymer Film	E_{mon}^{ox} (V)	$E_{p\text{-}doping}$ (V)	$E_{p\text{-}dedoping}$ (V)	HOMO (eV)	*LUMO (eV)	λ_{max} (nm)	E_g^{op} (eV)	Polaron/Bipolaron (nm)
PTPTFlo	0.82	0.74	0.63	-4.93	-2.62	459/ 490	2.31	610/ 1120
PTPTCo	0.96	1.01	0.63	-5.08	-2.64	370	2.44	620/ 920
PTPTAz	1.05	0.87	0.62	-5.07	-2.26	347	2.81	610/ 970

After construction of the ECD, working range was determined from cyclic voltammogram of PTPTFlo/PEDOT device at 100 mV s^{-1}. As illustrated in Fig. 5a, single scan cyclic voltammogram bears characteristic redox couples for both **PTPTFlo** and PEDOT.

The long-term switching stability of the PTPTFlo/PEDOT ECD were investigated by chronoamperometry technique while switching the device between two extreme states (-1.8 V and +2.0 V) at every 5 seconds. In Fig. 5b the stability of the device initially and after 1500 seconds (300th cycles) were reported and it can be clearly stated that after 300 cycles PTPTFlo/PEDOT ECD retain its electrochromic performance without any significant electroactivity loss.

The optoelectronic properties of the PTPTFlo/PEDOT ECD were investigated via UV-vis spectrophotometer while incrementally increasing the applied potential between -1.8 V and +1.8 V. The spectroelectrochemistry study of the device was shown in Fig. 6. At -1.8 V PTPTFlo/PEDOT ECD has two absorption maxima centered at 458 nm and 490 nm as a result of the neutral state yellow color of the PTPTFlo, at that time PEDOT is expected to have transmissive color due to oxidized state. When the applied potential was changed to +1.8 V, the yellow color of the device changed to blue with an absorption maximum at 580 nm. The color change was caused by the oxidation of **PTPTFlo** layer whereas PEDOT layer started to get neutralized (Fig. 6).

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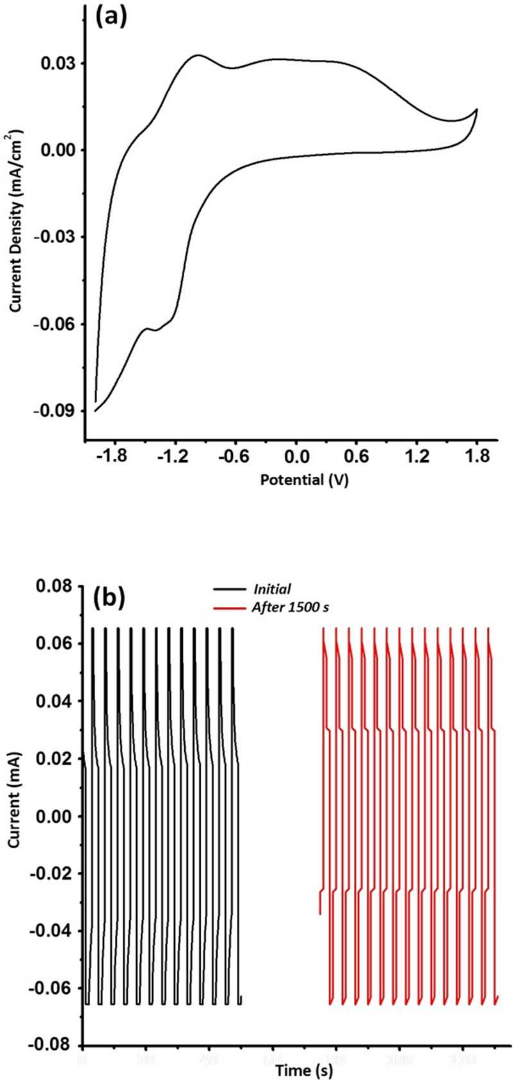

Fig.5 (a) Cyclic voltammogram (b) stability after 1st and 300th cycles of PTPTFlo/PEDOT ECD

The open circuit memory (optical memory) is another parameter for electrochromic device characterization. This can be defined as the time which the device maintains its color under open circuit conditions.[45,48] For open-circuit stability experiment, 1 s pulse of +2.0 V or 1.8 V was applied to PTPTFlo/PEDOT ECD at 580 nm and then for the next 200 s the device was kept under open-circuit condition while simultaneously probing the percent transmittance for 20 min. As summarized in Fig. 7, the optical properties of the device remained almost the same after applying 1 s pulse during the period.

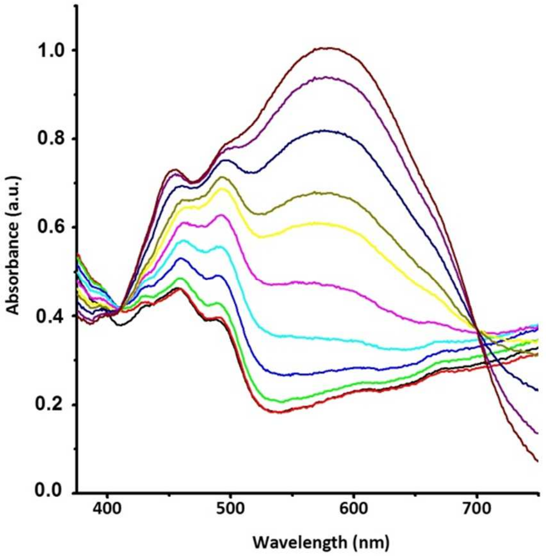

Fig.6 Electronic absorption spectra of PTPTFlo/PEDOT ECD at various applied potentials (between -1.8 V and +1.8 V)

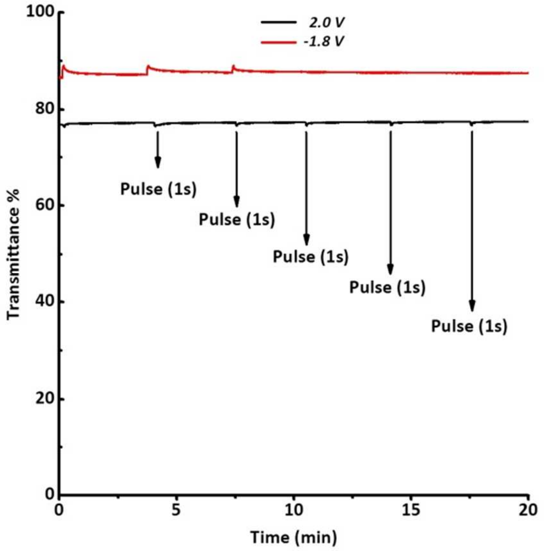

Fig.7 Open circuit memory of PTPTFlo/PEDOT ECD recorded at 580 nm, +2.0 V and -1.8 V pulse were applied for 1 s every 200 s

Conclusions

To conclude, three novel 2,5-dithienylpyrrole (SNS) derivatives containing strong chromophore substituents such as azobenzene, coumarine and fluorescein were designed, synthesized and characterized successfully. The corresponding conducting polymer films of SNS type monomers, **PTPTAz**, **PTPTCo** and **PTPTFlo**, were electrochemically synthesized on ITO coated glass slide electrodes and then, their electrochemical and spectroelectrochemical properties were investigated in detail.

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Redox potentials and HOMO/LUMO energy levels of all π-conjugated conducting polymers were characterized by means of cyclic voltammetry and *in-situ* spectroelectrochemical studies. The optical band gap values of homopolymer films were also calculated by utilizing the onset of π-π* transition in their neutral states. The values were found to be 2.31 eV, 2.44 eV and 2.81 eV for **PTPTFlo**, **PTPTCo** and **PTPTAz** respectively. **PTPTAz** and **PTPTCo** exhibited different colors in their neutral and fully oxidized states whereas **PTPTFlo** showed all states yellow character. A PTPTFlo/PEDOT based dual type electrochromic device (ECD) was constructed by taking advantage of **PTPTFlo** polymer film and its electrochromic performance was investigated by cyclic voltammetry, chronoamperometry and UV-vis spectrophotometer techniques. ECD exhibited quite well long-term stability with reasonable optical memory under atmospheric conditions. To summarize, our results showed that the combination of a strong chromophore group with polymer backbone significantly affect electronic and optoelectronic behaviors of resulting conducting polymers. Besides, electrochemical and spectroelectrochemical properties of novel poly (2,5-dithienylpyrrole) (PSNS) derivatives functionalized with strong chromophore units revealed that they are promising candidates as electrochromic materials for many different electrochromic applications.

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