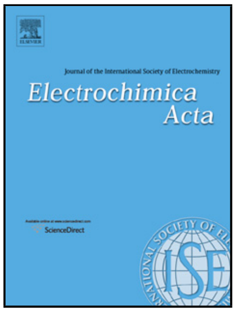

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Synthesis and spectroelectrochemical characterization of multi-colored novel poly(3,6-dithienylcarbazole) derivatives containing azobenzene and coumarin chromophore units

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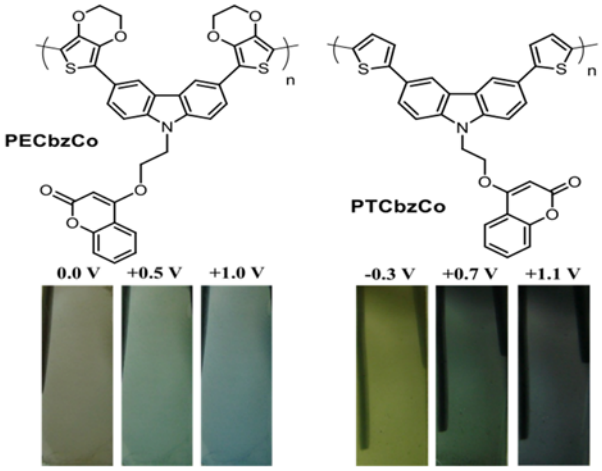
GRAPHICAL ABSTRACT



HIGHLIGHTS

- Poly(3,6-dithienylcarbazole) homopolymers containing strong chromophore units were electrochemically synthesized.
- Electrochemical and spectroelectrochemical behaviors of novel poly(3,6-dithienylcarbazole) modified with azobenzene and coumarin were evaluated.
- Poly(3,6-dithienylcarbazole) films exhibited multi-colored electrochromic characteristics.

Abstract

Azobenzene and coumarin units bearing four novel 3,6-linked thiophene-carbazole-thiophene type electroactive monomers were synthesized in order to observe the effects of strong chromophore units on the electrochemical and spectroelectrochemical behaviors of resulting π-conjugated conducting polymers (PTCbzAz, PECbzAz, PTCbzCo and PECbzCo). Electronic and optoelectronic properties of all polymers were investigated by cyclic voltammetry and *in situ* spectroelectrochemical studies, and their oxidation potentials, HOMO/LUMO energy levels, band gaps (E_g^{op}), optical contrasts ($\Delta T\%$) and switching times were reported in detail. It was observed that incorporation of strong chromophore units in polymer backbones resulted in poly(3,6-dithienylcarbazole) derivatives with different optical band gap values and different number of colored states. The optical band gap values for PECbzAz, PECbzCo, PTCbzAz, PTCbzCo and were calculated as 1.71 eV, 1.75 eV, 1.93 eV and 2.07 eV, respectively, from the onset of π-π* transition in polymer films' neutral state absorptions. All polymers exhibited multicolored electrochromic behavior upon extarnally applied potential. Reported electrochemical and optical features of PECbzAz, PECbzCo, PTCbzAz, PTCbzCo suggest that these poly(3,6-dithienylcarbazole) derivatives are promising candidates for multicolored electrochromic device applications.

1. Introduction

π-Conjugated conducting polymers (CPs) are extremely organic electroactive materials for commercial electronic devices due to their advantages of relatively low cost synthesis, easy structural modification and perfect integration into many electronic devices. CPs have been used in wide range of technological areas including electrochromic devices (ECDs) [1,2], organic light emitting diodes (OLEDs) [3,4], field effect transistors (FETs) [5,6], sensors [7,8], organic photovoltaics (OPVs) [9-11] and supercapacitors (SCs) [12-14], over the last two decades. Especially, the use of CPs as electrochromic materials has been attracting great deal of interest over inorganic counterparts since they exhibit excellent electronic and electrochromic properties such as reversible and steady color changes applying low potentials, high optical contrast in visible and near infra-red (NIR) regions, high coloration efficiency and fast switching times [15-19].

Electrochromic conducting polymers are mostly colored in their neutral states and they possess the ability to change color reversibly upon appropriate external bias. The apparent change in spectral properties of conjugated conducting polymers is related to doping-undoping processes on electroactive polymer chain [20,21]. Upon oxidation, new energy states arise in between HOMO and LUMO energy levels (band gap, Eg) of conducting polymers owing to formation of polarons and bipolarons termed as charge carriers. As a result of the structural modification on polymer backbone, a second colored or transmissive state emerges [22,23]. The value of the band gap of a neutral state conducting polymer is most important factor for manipulating electrochemical and spectroelectrochemical behaviors of the π-conjugated polymers, as well as optical properties. In the context of controlling electronic and optoelectronic features of conducting polymers, different directions including polymer backbone and bond length alternation, planarity, interchain alternation, resonance effect, diverse pendant groups and donor-acceptor concept have been developed until now [24-28]. Polymer backbone alternation, different pendant substituents and donor-acceptor theory among other approaches can be considered as the most convenient ones to obtain unique conducting polymers with better electrochemical and spectroelectrochemical properties.

The great majority of interest in electrochromic materials mainly focused on polythiophene, polypyrrole and their derivatives owing to their low band gap, low oxidation potential, good conductivity, high optical contrast and good environmental stability [29,30]. Furthermore, polythiophene and polypyrrole derivatives exhibit high stability in their oxidized form and multicolor electrochromism [31,32]. Because of their excellent electrochemical and spectroelectrochemical features, they have been most commonly utilized as electroactive layers in electrochromic device applications so far [33,34]. In addition to polythiophene and polypyrrole derivatives, recently, carbazole containing conducting polymers have become promising candidates for electrochromic materials because of various advantages such as high charge carrier mobilities, easy formation of stable radicals, strong electron-donating chromophore properties, high thermal and photochemical stabilities [35-37]. Carbazole-based conducting polymers (Cbz) can be also easily functionalized at their (3,6-), (2,7-) and N-positions. Moreover, conducting polymers based on 3,6-linked carbazole unit have interesting multicolored electrochromic properties due to broken conjugation at their 3,6-positions. The radical cations formed on the polymer chain via alternation of the applied potential do not incorporate with one another due to the effective conjugation break [38-40]. Thus, 3,6-linked Cbz-based electrochromic conducting polymers distinctively exhibit multiple colors in their neutral, oxidized and further oxidized states. According to above considerations, the design and synthesis of new precursor monomers containing 3,6-linked carbazole moetiy is believed to contribute diversity of electrochromic materials with superior electrochemical and spectroelectrochemical properties in terms of enlarging π-conjugated conducting polymers.

Herein, we report the synthesis, electropolymerization and electrochromic properties of four novel 3,6-dithienylcarbazole type monomers bearing highly optically potent chromophore groups in the UV-visible region (azobenzene and coumarin) as a pendant group. Conducting polymers of these compounds were produced by electropolymerization and named as poly[9-(2-4-(phenyldiazenyl)phenoxy)ethyl)-3,6-di(thiophen-2-yl)-9*H*-carbazole] **(PTCbzAz)**, poly[3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9-(2-(4-(phenyldiazenyl)phenoxy) ethyl)-9*H*-carbazole] **(PECbzAz),** poly[4-(2-(3,6-di(thiophen-2-yl)-9*H*-carbazol-9-yl)ethoxy)-2*H*-chromen-2-one] **(PTCbzCo)** and poly[3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9*H*-(carbazol-9-yl)ethoxy)-2*H*-chromen-2-one] **(PECbzCo)**. As reported in our previous publications, incorporation of a strong chromophore group (azobenzene, coumarin and fluorescein) with the monomer skeleton showed interesting electrochemical and spectroelectrochemical properties, as observed for terthienyl and 2,5-dithienylpyrrole (SNS) derivatives [41-43]. In this work, the same strategy was used for modification of carbazole units with azobenzene and coumarin groups *via* an ethylene bridge. It is anticipated that better electrochemical and optical properties for resulting π-conjugated conducting polymers can be obtained through the combination of carbazole ring and strong chromophore compounds since carbazole itself is also highly effective electroactive and photoactive material. Poly(carbazole) derivatives, however, have usually wider band gap energies. To the best of our knowledge, the most commonly used method is functionalization of carbazole unit with various functional electron-donating compounds via its 2,7- or 3,6-position in order to decrease their band gap values. For this purpose, 3,6-(dithiophenyl) and 3,6-[di(3,4-ethylenedioxythiophenyl)]carbazole derivatives containing strong chromophore groups have been prepared by Stille cross-coupling reaction. It is also expected that these 3,6-linked carbazole conducting polymers will exhibit multi colors for their neutral, polaronic and bipolaronic species at various oxidation states due to the presence of conjugation-breaking at 3- and 6- position. The electronic and optical properties of homopolymers electrochemically prepared on transparent ITO glass electrode surfaces, **PTCbzAz**, **PECbzAz**, **PTCbzCo** and

PECbzCo, were studied by using cyclic voltammetry and spectroelectrochemical techniques. Besides, both the effects of the type of chromophore groups and 3,6-linked electron-donating thiophene and 3,4-(ethylenedioxythiophene) units on electrochromic and electrochemical behaviors of resulting conducting polymers were investigated in detail.

2. Experimental

2.1. Materials

Carbazole, 4-hydroxyazobenzene, 4-hydroxy-2H-chromen-2-one, 1,2-dichloroethane (anhydrous, 99.8%), n-butyllithium solution (n-BuLi, 2.5 M in hexane), tributyltin chloride (Bu_3SnCl, 96%), 3,4-ethylenedioxythiophene (EDOT, 97%), 2-(tributylstannyl)thiophene (reagent grade, 97%), bis(triphenylphosphine)palladium (II) chloride (≥99%), lithium perchlorate ($LiClO_4$, 99.999%), sodium perchlorate ($NaClO_4$, ≥ 98.0%), N-bromosuccinimide (NBS, 99%), N,N-dimethylformamide (DMF, anhydrous 99.8%), cesium carbonate (Cs_2CO_3, 99%), potassium hydroxide (KOH, ACS reagent, ≥ 85%, pellets), dichloromethane (DCM, anhydrous, ≥ 99.8%) silica gel (SiO_2, high-purity grade, pore size 60Å, 200-425 mesh particle size), a platinum wire (Pt, 0.25 mm diameter, 99.999%), a silver wire (Ag, 0.05 mm diamater, 99.9%) and an indium tin oxide doped glass slide (ITO, slide resistance 8-12 Ω sq^{-1}) were purchased from Sigma Aldrich and used without any further purification. Prior to electrochemical measurements, acetonitrile (ACN, HPLC grade) was refluxed with P_2O_5 for 8 h, distilled fractionally, finally stored over activated 4A molecular sieves under a nitrogen atmosphere. 3,6-Dibromocarbazole [44] and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) stannane [45] were synthesized according to previously described methods in the litrature.

2.2. Instrumentation

Microwave-assisted reactions were carried out using a CEM Discover S-Class single-mode microwave synthesis instrument. Electrochemical data were collected using a Radiometer

VoltaLab PST 050 potentiastat/galvanostat in three-electrode cell configuration. An indium tin oxide doped glass slide, a platinum wire and a silver wire served as the working electrode, counter electrode and pseudo-reference electrode, respectively, in both electrochemical and spectroelectrochemical studies. The silver wire pseudo-reference electrode was calibrated to the ferrocene couple (+0.3 V vs Fc/Fc^+). The homopolymers of carbazole derivatives were electrochemically generated by the cyclic voltammetry technique (CV) in the presence of a 0.05 M monomer in 0.1 M solution of the $NaClO_4$-$LiClO_4$/ACN/DCM (95:5, v/v) supporting electrolyte under a nitrogen atmosphere at 100 mV s^{-1} scan rate for 10 cycles. UV-Vis-NIR spectra of the resulting conducting polymers were recorded on a Varian Cary 5000 spectrophotometer at a scan rate of 2000 nm min^{-1}. The potentials in spectroelectrochemical measurements were controlled by using a Solatron 1285 potentiastat/galvanostat. A Konica Minalto CS-100 colorimeter in a Pantone Colorviewing Light PJC/CV L3 Light Box 3 was used in order to perform color analysis of conducting polymer layer on ITO surfaces. FTIR spectra of monomers were recorded on a Perkin-Elmer Spectrum 100 spectrometer. Ambient temperature ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varion-Mercury 400 MHz (FT)-NMR spectrometer. All chemical shifts were given in ppm downfield from tetramethylsilane (Me_4Si). Mass spectra were recorded using a DI-2010 direct inlet probe on a Shimadzu GC-MS QP2010 mass spectrometer operating at an ionization potential (EI) of 70 eV. Elemental analyses of the novel monomers were performed with a Leco CHNS-932 elemental analyzer.

2.3. Syntheses of monomers

The 3,6-dithienylcarbazole derivatives containing strong chromophore groups were successfully synthesized via nucleophilic substitution reactions and Stille cross-coupling reactions as represented in Scheme 1.

2.3.1. Synthesis of 3,6-dibromo-9-(2-chloroethyl)-9*H*-carbazole (3)

In a dry 100 mL one-necked round-bottomed flask, 3,6-dibromo-9*H*-carbazole (2) (1.81 g, 5.58 mmol) and grinded potassium hydroxide (KOH, 1.28 g, 23 mmol) was suspended in dry 1,2-dichloroethane (80 mL). 1,2-Dichloroethane was used as both reactive and solvent for this reaction. The reaction mixture was refluxed at 85ºC overnight under nitrogen atmosphere. The reaction suspension was poured into ice-water (200 mL) and extracted with dichloromethane (3 x 30 mL). The organic phases were combined, washed with water and brine and dried over anhydrous Na_2SO_4. Dichloromethane was removed on a rotary evaporator under reduced pressure. The crude product was purified by column chromotography using hexane/ethyl acetate (95:5, v/v) as eluent (R_f, 0.70) afforded (3) (1.7 g, 4.4 mmol, 79%, mp.: 152-154˚C) as a white powder. FTIR v/ cm^{-1} 3079, 2953, 2921, 1741, 1623, 1568, 1471, 1352. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ_H 4.03 (t, J = 5.2 Hz, 2H), 4.41 (t, J = 5.2 Hz, 2H), 7.32-7.34 (d, J = 8.8 Hz, 2H), 7.54-7.56 (dd, J = 2Hz and J = 8.4 Hz, 2H), 8.13 (d, J = 2 Hz, 2H). MS (EI) calculated for $C_{14}H_{10}Br_2ClN$ m/z: 387.5, found m/z: 387 (M^+, 50), 338 (100), 324 (5), 271 (5), 257 (22), 243 (4), 191.1 (10), 178.1 (15), 164.1 (25), 151.1 (20), 89.1 (5), 62 (3).

2.3.2. General procedure for microwave-assisted nucleophilic substitution reaction

3,6-Dibromo-9-(2-chloroethyl)-9*H*-carbazole (3) (1.06 g, 2.76 mmol), a chromophore compound (3.31 mmol, hydroxyazobenzene or hydroxycoumarin derivative) and cesium carbonate (Cs_2CO_3, 2.69 g, 8.28 mmol) were thoroughly mixtured and placed in a microwave reaction vessel (30 mL). After adding dry ACN (3 mL), the eventual slurry reaction mixture was heated at 100˚C under microwave irradiation (150 W single-mode power) for 15 min. Then, the mixture was cooled to room temperature, poured into ice-water (150 mL) and vigorously stirred for 30 min. The solid crude product was filtered under reduced pressure, rinsed with alkaline solution and dried at room temperature. 3,6-Dibromocarbazole derivatives containing chromophore groups were purified by colomn chromatography to obtain pure target precursor compounds. The pure compounds were characterized by FTIR and ^{1}H NMR techniques and found to be satisfactory.

3,6-Dibromo-9-(2-4-(phenyldiazenyl)phenoxy)ethyl)-9*H*-carbazole (4a)

This carbazole derivative was prepared with the same procedure described above using 3,6-dibromo-9-(2-chloroethyl)-9*H*-carbazole (3) and 4-hydroxyazobenzene. The residue was subjected to column chromatography on silica gel eluting with hexane/ethyl acetate (80:20, v/v) (R_f, 0.65) to obtain **4a** as orange solid (1.22 g, 2.23 mmol, 81.5%, mp.: 168-169°C). FTIR v/ cm-^{1} 3064, 3043, 2939, 2875, 1600, 1581, 1473, 1359, 1246. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ_H 4.38 (t, J = 7.6 Hz, 2H), 4.66 (t, J = 7.5 Hz, 2H), 6.86-6.87 (dd, J = 8.7 Hz and J = 2.4 Hz, 2H), 7.37-7.39 (d, J = 8.8 Hz, 2H), 7.42-7.5 (m, 3H), 7.57-7.59 (dd, J = 8.4 Hz and J = 2 Hz, 2H), 7.82-7.86 (m, 4H), 8.12 (d, J = 2 Hz, 2H).

4-(2-(3,6-Dibromo-9*H*-carbazole-9-yl)ethoxy)-2H-chromen-2-one (4b)

This derivative was also prepared with the same procedure described for **4a** using 3,6-dibromo-9-(2-chloroethyl)-9*H*-carbazole (3) and 4-hydroxy-2H-chromen-2-one. The crude product was subjected to column chromatography on silica gel eluting with hexane/ethyl acetate (70:30, v/v) (R_f, 0.50) to obtain **4b** as orange solid (1.11 g, 2.18 mmol, 79.5%, mp.: 147-150°C). FTIR v/ cm-^{1} 3080, 2952, 2890, 1666, 1604, 1509, 1463, 1352, 1241. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ_H 4.57 (t, J = 7.5 Hz, 2H), 4.98 (t, J = 7.6 Hz, 2H), 5.82 (s, 1H), 7.15-7.25 (m, 1H), 7.55-7.59 (m, 1H), 7.29-7.31 (d, J = 8.7 Hz, 2H), 7.66-7.69 (dd, J = 8.4 Hz and J = 2 Hz, 2H), 7.79-7.81 (d, J = 8.8 Hz, 2H), 8.48 (d, J = 2 Hz, 2H).

2.3.3. General procedure for Stille cross-coupling reactions of 3,6-dibromocarbazole derivatives

In a dry 100 mL three-necked round-bottomed flask fitted with a condenser and argon inlet, 3,6-dibromocarbazole derivative (**4a** or **4b**, 0.45 mmol) and 2-(tributylstannyl)thiophene (0.5g, 1.35 mmol) or tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) stannane (0.58 g, 1.35 mmol) were dissolved in dry DMF (25 mL). The solution was intensely purged with argon at room temperature for 20 min and tetrakis(triphenylphosphine)palladium (0) ($Pd(PPh_3)_4$, 0,0289 g, 0.025 mmol) was added. The reaction suspension was heated at 110 ºC for 24 h under inert atmosphere. Then, the reaction mixture was cooled to room temperature and poured into ice-water (200 mL). The aqueous layer was washed with saturated KF solution (3 x 80 mL) to destroy the residual catalyst and tributylstannyl compounds, and extracted with chloroform (3 x 40 mL). The organic phases were combined, washed with water and brine and dried over anhydrous Na_2SO_4. After removal of solvent by evaporation under reduced pressure, the residue was subjected to column chromatography using SiO_2 as solid phase and hexane/dichloromethane mixture as eluent to afford a pure 3,6-linked carbazole-thiophene monomer. The chemical structure of monomer was characterized by FTIR, ^1H NMR, ^{13}C NMR, mass spectrometry techniques and elemental analysis.

9-(2-(4-(Phenyldiazenyl)phenoxy)ethyl)-3,6-di(thiophen-2-yl)-9*H*-carbazole (TCbzAz)

This monomer was synthesized via Stille cross-coupling reaction of 3,6-dibromo-9-(2-4-(phenyldiazenyl)phenoxy)ethyl)-9*H*-carbazole **(4a)** and 2-(tributylstannyl)thiophene. The crude product was purified by column chromatography using hexane/dichloromethane (90:10, v/v) as eluent (R_f, 0.65) to afford a bright orange solid (0,19 g, 0.35 mmol, 78%, mp.: 138-140˚C). FTIR *ν*/ cm-^{1} 3068, 3039, 2934, 2864, 1599, 1580, 1483, 1360, 1241. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ_H 4.37 (t, J = 7.6 Hz, 2H, ethylene bridge-CH_2-), 4.66 (t, J = 7.5 Hz, 2H, ethylene bridge-CH_2-), 6.86 (dd, J = 8.7 Hz and J = 2.4 Hz, 2H, Ar-H), 7.09-7.49 (m, 9H, Th-H, Ar-H), 7.37-7.75 (dd, J = 9.8 Hz and J = 2 Hz, 2H, Cbz-H), 7.81-7.85 (m, 4H, Ar-H), 8.32 (d, *J* = 2 Hz, 2H, Cbz-H). ^{13}C NMR (400 MHz, $CDCl_3$, Me_4Si) δ_C 42.6, 66.2, 109, 114.6, 117.9, 122.2, 122.5, 123.4, 123.8, 124.7, 126.4, 128, 129, 130, 140.4, 145.4, 147.2, 160. MS (EI) calculated for $C_{34}H_{25}N_3OS_2$ m/z: 555.7, found m/z: 555 (M^+, 5), 519 (2), 473 (30), 422 (15), 357 (10), 317 (5), 262 (55), 183 (10), 139 (5), 77 (100). Anal. Calcd. for ($C_{34}H_{25}N_3OS_2$): C, 73.48%; H, 4.53%; N, 7.56%. Found: C, 73.65%; H, 4.12%; N, 7.31%.

3,6-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9-(2-(4-phenyldiazenyl)phenoxy)ethyl)-9*H*- carbazole (ECbzAz)

This monomer was synthesized with the same procedure explained for **TCbzAz** using 3,6-dibromo-9-(2-4-(phenyldiazenyl)phenoxy)ethyl)-9*H*-carbazole **(4a)** and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) stannane. The residue was subjected to column chromatography using hexane/dichloromethane (95:5, v/v) as eluent (R_f, 0.50) to afford a pale orange solid (0,25 g, 0.38 mmol, 82%, mp.: 150-151˚C). FTIR *v*/ cm-^{1} 3100, 3063, 2921, 2871, 1598, 1582, 1473, 1362, 1245. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ_H 4.24-4.7 (m, 12H, EDOT-CH_2- and ethylene bridge –CH_2-), 6.27 (s, 1H, Th-H), 6.86-6.9 (t, *J* = 6.8 Hz, 2H, Ar-H), 7.35-7.51 (m, 7H, Ar-H and Cbz-H), 7.83-7.86 (m, 4H, Ar-H), 8.14 (d, *J* = 2 Hz, 2H, Cbz-H). ^{13}C NMR (400 MHz, $CDCl_3$, Me_4Si) δ_C 29.7, 42.6, 64.5, 64.8 64.9, 66.2, 96.6, 109, 110, 112.5, 114.5, 118, 122, 123, 124, 125, 128, 129, 130, 130.5, 139, 152.6, 160.4. MS (EI) calculated for $C_{38}H_{29}N_3O_5S_2$ m/z: 617.7, found m/z: 611 (2), 549 (25), 471 (10), 444 (5), 422 (5), 338 (25), 273 (5), 259 (10), 164 (12), 105 (8), 77 (100). Anal. Calcd. for ($C_{38}H_{29}N_3O_5S_2$): C, 67.94%; H, 4.35%; N, 6.26%. Found: C, 67.65%; H, 4.02%; N, 6.61%.

4-(2-(2-(3,6-Dithiophen-2-yl)-9H-carbazole-9-yl)ethoxy)-2H-chromen-2-one (TCbzCo)

This monomer was prepared by following general procedure using 4-(2-(3,6-dibromo-9*H*-carbazole-9-yl)ethoxy)-2*H*-chromen-2-one **(4b)** and 2-(tributylstannyl)thiophene. The crude product was purified by column chromatography using hexane/dichloromethane (70:30, v/v) as eluent (R_f, 0.65) to afford a bright yellow solid (0,15 g, 0.29 mmol, 65%, mp.: 165-168°C). FTIR *v*/ cm-^{1} 3102, 3053, 2956, 2850, 1713, 1700, 1608, 1566, 1438, 1355, 1234. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ_H 4.61 (t, *J* = 7.5 Hz, 2H, ethylene bridge-CH_2-), 4.99 (t, *J* = 7.6 Hz, 2H, ethylene bridge-CH_2-), 5.85 (s, 1H, Coumarine –C=CH), 7.09-7.32 (m, 4H, Th-H and Ar-H), 7.5-7.82 (m, 8H, Cbz-H, Th-H and Ar-H), 7.83 (d, *J* = 4.8 Hz, 2H, Cbz-H), 8.59 (d, *J* = 2 Hz, 2H, Cbz-H). ^{13}C NMR (400 MHz, $CDCl_3$, Me_4Si) δ_C 42.1, 68.8, 91.5, 111.2, 115.4, 117, 118.4, 123.2, 123.5, 126.3, 129.1, 129.4, 129.5, 132.1, 132.7, 133.4, 140.9, 145.3, 153.3, 162, 165.2. MS (EI) calculated for $C_{31}H_{21}NO_3S_2$ m/z: 519.6, found m/z: 519 (M^+, 25), 475 (3), 437 (65), 375 (35), 344 (75), 310 (5), 275 (15), 262 (100), 228 (5), 165 (5), 137 (3), 121 (12). Anal. Calcd. for ($C_{31}H_{21}NO_3S_2$): C, 71.65%; H, 4.07%; N, 2.70%. Found: C, 71.28%; H, 3.97%; N, 2.66%.

4-(2-(3,6-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9*H*-carbazole-9-yl)ethoxy)-2*H*-chromen-2-one (ECbzCo)

This monomer was synthesized via Stille cross-coupling reaction of 4-(2-(3,6-dibromo-9*H*-carbazole-9-yl)ethoxy)-2*H*-chromen-2-one **(4b)** and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) stannane. The residue was subjected to column chromatography using hexane/dichloromethane (60:40, v/v) as eluent (R_f, 0.45) to afford a pale yellow solid (0,23 g, 0.36 mmol, 81.5%, mp.: 154-156°C). FTIR *v*/ cm-^{1} 3103, 3065, 2955, 2872, 1706, 1685, 1621, 1505, 1473, 1362, 1235. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ_H 4.18-4.34 (m, 8H, EDOT -CH_2-), 4.56 (t, *J* = 7.5 Hz, 2H, ethylene bridge –CH_2-), 4.94 (t, *J* = 7.4 Hz, 2H, ethylene bridge –CH_2-), 5.8 (s, 1H, Coumarine –C=CH-), 6.55 (s, 2H, Th-H), 7.09-7.27 (m, 4H, Cbz-H and Ar-H), 7.51-7.84 (m, 4H, Cbz-H and Ar-H), 8.45 (d, *J* = 2 Hz, 2H, Cbz-H). ^{13}C NMR (400 MHz, $CDCl_3$, Me_4Si) δ_C 41.9, 64.4, 64.6, 65.1, 65.4, 68.5, 91.3, 97.3, 98, 110.8, 112.1, 112.5, 115.2, 116.8, 118.3, 122, 123.1, 124.2, 125.1, 129.3, 133.1, 139, 153, 161.7. MS (EI) calculated for $C_{35}H_{25}NO_7S_2$ m/z: 635.7, found m/z: 601 (5), 513 (60), 437 (10), 387 (5), 338 (100), 273 (15), 260 (40), 191 (50), 164 (60), 121 (65), 89 (35), 77 (48). Anal. Calcd. for ($C_{35}H_{25}NO_7S_2$): C, 66.13%; H, 3.96%; N, 2.20%. Found: C, 65.93%; H, 3.45%; N, 2.14%.

3. Results and discussion

3.1. Synthesis

Controlling the spectroelectrochemical properties and tuning the band gaps (Eg) of π-conjugated conducting polymers are crucial and possible by the design and synthesis of novel electroactive monomers. In this context, combination of strong chromophore compounds such as azobenzene, coumarin and fluorescein with different monomer units has been explored. This incorporation approach resulted with conjugated polymers having low band gaps, multicolor electrochromism, fast switching times and high optical contrast, as observed for poly(terthienyl) and poly(2,5-dithienylpyrrole) (PSNS) derivatives in our previous studies. In the present paper, a new kind of 3,6-thiophene-linked carbazole monomers containing azobenzene and coumarin chromophore units were designed for electrochromic applications and their electrochemical and spectroelectrochemical behaviors were investigated in detail for the first time. It is well known that carbazole structure has ability to form stable radicals and hence, conducting polymers containing carbazole moiety create stable polarons or dipolarons more effectively on the polymer backbones. Regarding their prominent features, carbazole based monomers were especially preferred for this study in order to increase the doping/undoping efficiency and stability of novel conducting polymer derivatives during oxidation/reduction processes. New 3,6-linked carbazole monomers were synthesized *via* a two-step synthetic strategy, as illustrated in Scheme 1. The first step of reaction pathway involves the microwave-assisted nucleophilic substitution reactions of 3,6-dibromo-9-(2-

chloroethyl)-9*H*-carbazole **(3)** with 4-hydroxyazobenzene or 4-hydroxy-2H-chromen-2-one in order to bring together carbazole moiety and a chromophore unit through an alkyl bridge. Then, Stille cross-coupling reactions were successfully carried out by using 2-(tributylstannyl)thiophene or tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) stannane in the presence of $Pd(PPh_3)_4$ to obtain desired 3,6-thiophene-linked carbazole monomers, 9-(2-4-(phenyldiazenyl)phenoxy)ethyl)-3,6-di(thiophen-2-yl)-9*H*-carbazole] **(TCbzAz)**, 3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9-(2-(4-(phenyldiazenyl)phenoxy)ethyl)-9*H*-carbazole **(ECbzAz),** 4-(2-(3,6-di(thiophen-2-yl)-9*H*-carbazol-9-yl)ethoxy)-2*H*-chromen-2-one **(TCbzCo)** and 3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9*H*-(carbazol-9-yl)ethoxy)-2*H*-chromen-2-one **(ECbzCo)**. The chemical structures of novel 3,6-thiophene-linked carbazole derivatives were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR, mass spectrometry techniques and elemental analysis.

3.2. Electrochemistry

In order to study electrochemical redox behavior of novel monomers and produce their corresponding conducting polymers, **TCbzAz**, **ECbzAz**, **TCbzCo** and **ECbzCo** were initially subjected to cyclic voltammetry (CV) in 0.1 M supporting electrolyte solution containing equimolar amounts of a sodium perchlorate ($NaOCl_4$) and lithium perchlorate ($LiOCl_4$) in acetonitrile/dichloromethane (ACN/DCM) (95:5, v:v) on indium tin oxide (ITO) coated glass slides. The cyclic voltammograms were recorded by scanning potential in between 0.0 V and 1.2 V for **TCbzAz** and **ECbzAz**, between 0.0 V and 1.3 V potential range for **TCbzCo** and **ECbzCo** at a scan rate of 100 mV s^{-1} under nitrogen atmosphere. During repeated potential scanning, all monomers exhibited typical irreversible oxidation behavior versus Ag wire pseudo-reference electrode as represented in **Fig.1**. In the first cycle of oxidative electrochemical polymerizations, irreversible monomer oxidation peaks of **TCbzCo**, **TCbzAz**, **ECbzCo** and **ECbzAz** were centered at +0.96 V, +0.98 V, +0.76 V and +0.77 V, respectively.

After the monomer oxidations, reversible redox waves appeared with an increase in the current density after each succussive oxidation/reduction cycle and the resulting conducting polymers were regularly grown on ITO electrode surfaces. As seen from cyclic voltammograms in **Fig.1a** and **Fig.1c**, coumarin moiety containing monomers **TCbzCo** and **ECbzCo** revealed slightly lower oxidation potentials than those of their azobenzene included analogues; **TCbzAz** and **ECbzAz**. This trend can be explained by weak inductive effect of adjacent chromophore units over monomer chains. The carbonyl (-C=O) and etheric (-C-O-C-) functional groups in the structure of coumarin more increase resonance stabilization of the chromophore unit more by distributing electron density in the hetereoaromatic system compared to azobenzene moiety. This effect relatively decreases the electron withdrawing property of coumarin unit as a pendant group and increases electron densities on the monomer skeletons of coumarin containing monomers. Therefore, **TCbzCo** and **ECbzCo** were slightly easily oxidized than **TCbzAz** and **ECbzAz**. In addition, 3,4-ethylenedioxythiophene (EDOT) bearing 3,6-linked carbazole monomers (+0.76 V for **ECbzCo** and +0.77 V for **ECbzAz**) distinctly exhibited lower monomer oxidation potentials than those for thiophene bearing ones (+0.96 V for **TCbzCo** and +0.98 V for **TCbzAz**) as expected owing to EDOT's better electron donating character. The thicknesses of the electrochemically deposited conducting polymer films on ITO surfaces were calculated as 0.80 μm for **PTCbzAz** 0.55 μm for **PTCbzCo**, 0.15 μm for **PECbzCo** and 0.05 μm for **PECbzAz**. The corresponding deposition charges for each polymer film were also calculated from the last cycle of the cyclic voltammograms as; 37.75 mC (**PTCbzAz**), 24.57 mC (**PTCbzCo**), 6.5 mC (**PECbzCo**) and 2.34 mC (**PECbzAz**).

In order to investigate doping/dedoping properties of resulting electroactive polymers, single scan cyclic voltammograms of **PTCbzCo**, **PTCbzAz**, **PECbzCo** and **PECbzAz** were recorded in a monomer free 0.1 M $NaClO_4$-$LiClO_4$/ACN solution. All polymers have a tendency to be p-doped when the polymer layers were cycled between different positive potentials, as illustrated in **Fig.2**. The reversible redox couples were determined at +1.0 V/+0.61 V for **PTCbzCo,** at +0.58 V/+0.37 V for **PTCbzAz,** at +0.51 V/+0.33 V and +0.82 V/+0.64 V for **PECbzCo** and at +0.48 V/+0.36 V and +0.80 V/+0.70 V for **PECbzAz**.

The cyclic voltammograms of **PTCbzCo**, **PTCbzAz**, **PECbzCo** and **PECbzAz** were also recorded at different scan rates (between 50 and 300 mV s^{-1}) in a monomer free medium in order to examine the scan rate dependence of doping/dedoping peak currents of the conducting polymer films. A linear relationship between the peak currents and scan rates proves that electroactive polymer films were well adhered and the doping/dedoping processes were non-diffusion controlled (**Fig. 3**). HOMO energy levels of novel conducting polymers were calculated from oxidation onset values in cyclic voltammograms as -5.40 eV (**PTCbzCo**), -5.35 eV (**PTCbzAz**), -4.85 eV (**PECbzCo**) and -5.21 eV (**PECbzAz**). The onset values are generally determined by taking the interaction between the baseline and tangent line drawn to the increasing part of current. On the other hand, LUMO energy levels were calculated from HOMO energy levels and optical band gaps (E_g^{op}) which are calculated from π-π* transition onset in UV-Vis spectrum since all polymer films revealed only p-doping property. LUMO energies were calculated as -3.33 eV for **PTCbzCo,** -3.42 eV for **PTCbzAz,** -3.50 eV for **PECbzCo** and -3.10 eV for **PECbzAz**, as summarized in Table 1. The reference electrodes were calibrated to Fc/Fc^+ (+0.30 V) and HOMO-LUMO energies were calculated relative to the vacuum level (NHE is -4.75 eV versus vacuum).

To evaluate the long-term redox stabilities of conducting polymers films, single scan cyclic voltammograms of **PTCbzCo**, **PTCbzAz**, **PECbzCo** and **PECbzAz** were recorded in a monomer free 0.1 M NaClO4-LiClO4/ACN electrolyte/solvent couple for 500 cycles. As seen in **Fig. 4**, especially PTCbzAz and PECbzCo exhibited good stability and redox activity after 500 cycles.

3.3. Spectroelectrochemistry

UV-vis-NIR absorption spectra of **PTCbzCo**, **PTCbzAz**, **PECbzCo** and **PECbzAz** were recorded in a monomer free 0.1 M $NaClO_4$-$LiClO_4$/ACN solution upon gradually increasing external bias in order to evaluate the optical behaviors and spectral responses of corresponding conducting polymers. Prior to spectroelectrochemical analysis, all polymer films coated electrochemically on ITO surfaces were subjected to -0.3 V to reduce them into their neutral states and remove any trapped charge or dopant ions on the polymer chains during electrochemical polymerization processes. The *in situ* spectroelectrochemical studies were performed between -0.3 V and +1.1 V for **PTCbzCo**, -0.3 V and +1.2 V for **PTCbzAz**, 0.0 V and +1.0 V for **PECbzCo** and -0.2 V and +1.0 V for **PECbzAz** using a UV-vis-NIR spectrophotometer coupled to cyclic voltammetry. As can be seen in **Fig.5a and Fig.5b**, **PTCbzCo** exhibited a sharper absorption maximum in the visible region centered at 410 nm whereas **PTCbzAz** revealed broad absorption maxima at 370 nm with a shoulder at 415 nm in the neutral state. Substitution of 3,4-ethylenedioxythiophene (EDOT) units on the conjugated main chain instead of thiophene also resulted in relatively bathochromically shifted absorption maxima for **PECbzCo** (λ_{max}= 470 nm) and **PECbzAz** (λ_{max}= 437 nm) compared to **PTCbzCo** and **PTCbzAz**. The maximum absorption peaks (λ_{max}) are due to the conducting polymers' high energy π-π* transition. Hence, the bathochromic (red) shift for **PECbzCo** (λ_{max}= 470 nm) and **PECbzAz** (λ_{max}= 437 nm) can be attributed to intramolecular π-interaction (π-orbital overlap) between coumarin chromophore unit and 3,6-linked EDOT-carbazole-EDOT polymer backbone is more effective than those of 3,6-linked thiophene-carbazole-thiophene in **PTCbzCo** and **PTCbzAz**.

Upon stepwise oxidation, new absorption bands in NIR region appeared at around 630/1010 nm for **PTCbzCo** and 640/1100 nm for **PTCbzAz** as intensity of absorption bands in the visible region diminished. These new electronic transitions with lower energies at longer wavelengths prove the formation of polarons (radical cations) and bipolarons (dications) on the polymer films. On the other hand, it was observed that there was no decrease in the neutral state absorption intensities of **PECbzCo** and **PECbzAz** during the formation of polaronic absorption bands at 850 nm and 590 nm/950 nm were determined for **PECbzCo** and **PECbzAz,** respectively (**Fig. 5c** and **Fig. 5d**). This tendency is probably a result of intersection of the polaron bands of **PECbzCo** and **PECbzAz** with those of the neutral absoprtion peaks. Spectroelectrochemical studies also showed that the incorporation of strong chrmophore units (azobenzene and coumarin) in thiophene-carbazole-thiophene polymer backbone resulted in multicolored property. Colorimetry studies were also performed in order to identify conducting polymer films' colors and *L*, a, b coordinates for their different states. The *L*, a, b coordainates and colors of **PECbzCo**, **PECbzAz**, **PTCbzCo** and **PTCbzAz** films upon different potentials are given in **Fig. 6**.

The optical band gaps (E_g^{op}) for **PECbzCo**, **PECbzAz**, **PTCbzCo** and **PTCbzAz** were calculated by utilizing the onsets of the lowest energy π-π* transitions on the neutral state absorption spectra ($E_g^{op} = 1241/\lambda_{max}$) as 1.75 eV, 1.71 eV, 2.07 eV and 1.93 eV, respectively (Table 1). Low optical band gap values for **PECbzCo** and **PECbzAz** can be explained by planar conformity. The 3,6-linked EDOT-carbazole-EDOT polymer backbone in **PECbzCo** and **PECbzAz** is more planar and rigid conjugated chain owing to the fact that the presence of EDOT units provides extra planarity, compared to thiophene-carbazole-thiophene skeleton. Hence, π-orbital overlapping between polymer chains and chromophore units in **PECbzCo** and **PECbzAz** are more effective than those of **PTCbzCo** and **PTCbzAz**. The enhaced possibility of π-orbital interactions gave rise to a distinctive decrease in band gap values of **PECbzCo** and **PECbzAz**. These results observed for novel poly(3,6-dithienylcarbazole) type conducting polymer derivatives (**PECbzCo**, **PECbzAz**, **PTCbzCo** and **PTCbzAz**) were compared with poly(2,5-dithienylpyrrole) (PSNS) (**PTPTCo** and **PTPTAz**) derivatives, containing the same chromophore units in order to have a better understanding of the influence of the type of monomer backbone on electronic and optical properties of corresponding polymers [43]. It was seen that the poly(3,6-dithienylcarbazole) derivatives have conspicuously lower band gap values (1.75 eV, 1.71 eV, 2.07 eV and 1.93 eV) than those for poly(2,5-dithienylpyrrole) derivatives (2.44 eV and 2.88 eV). Also, **PECbzCo**, **PECbzAz**, **PTCbzCo** and **PTCbzAz** revealed intermediate colored states with a wide color scale different from their poly(2,5-dithienylpyrrole) analogues. These results proved that structural designs for the 3,6-linked carbazole derivatives were accomplished in terms of improving electronic and spectral features of conducting polymers.

3.4. Kinetic Studies

Kinetic measurements together with spectroelectrochemical experiments were performed in order to observe percent transmittance changes (ΔT%) and to calculate switching times required for the transition period between neutral and oxidized states. The novel π-conjugated conducting polymer films were initially subjected to chronoabsorptometry studies in a monomer free solution containing 0.1 M $NaClO_4$-$LiClO_4$/ACN and the percentage transmittances of **PECbzCo**, **PECbzAz**, **PTCbzCo** and **PTCbzAz** were recorded for their dominant wavelenghts in visible and NIR regions as a function of time upon applied external bias within 5 s time intervals. As depicted in **Fig.7a** and **Fig.7c**, **PTCbzCo** films revealed optical contrast values (ΔT%) of 44% at 1010 nm, 11% at 630 nm and 18% at 410 nm while the transmittance changes (ΔT%) for **PECbzCo** were calculated as 31% at 850 nm and 14% at 470 nm. As seen, **PTCbzCo** and **PECbzCo** exhibited the superior optical contrast characteristics in NIR region due to multicolor formation between their doped/states in the UV-Vis region. On the other hand, **PTCbzAz** (22% at 1100 nm, 11% at 640 nm and 6% at 415 nm) and **PECbzAz** (10% at 950 nm and 7% 590 nm) showed lower optical contrast values than **PTCbzCo** and **PECbzCo** in both UV-Vis and NIR regions (**Fig.7b** and **Fig.7d**).

The significant differences in optical contrast values are due to the difficulty in charge injection/ejection processes for **PTCbzAz** and **PECbzAz** compared to those of **PTCbzCo** and **PECbzCo**. In other words, **PTCbzAz** and **PECbzAz** can switch rather slowly between their extreme states.

The switching times for **PECbzCo**, **PECbzAz**, **PTCbzCo** and **PTCbzAz** were calculated by utilizing kinetic studies for both visible and NIR regions. The switching times were determined as 0.7 s at 850 nm and 470 nm for **PECbzCo** while **PECbzAz** revealed switching times of 2.4 s (950 nm) and 3.3 s (590 nm). **PTCbzCo** has switching times of 1.3 s, 1.9 s and 2.1 s at 1010 nm, 630 nm and 410 nm, respectively. Similary, the switching times for **PTCbzAz** at 1100 nm, 640 nm and 415 nm were found to be 3.0 s, 2.4 s and 2.8 s. When strong chromophore units containing multicolored conducting polymer films are compared in terms of their switching abilities, **PECbzCo** and **PTCbzCo** functionalized with coumarin unit switch faster than **PECbzAz** and **PTCbzAz** derivatives bearing an azobenzene unit.

4. Conclusions

Four novel 3,6-linked thiophene-carbazole-thiophene type monomers bearing azobenzene and coumarin units as the pendant groups were designed and synthesized successfully in order to have a better comparison and understanding the effect of chromophore units on electrochromic properties of conjugated conducting polymers. **PECbzCo**, **PECbzAz**, **PTCbzCo** and **PTCbzAz** polymers were electrochemically synthesized on ITO coated glass slides and characterized in terms of their electrochemical and optical behaviors. The oxidation potentials, HOMO/LUMO energy levels, optical band gap values (E_g^{op}), optical contrast ($\Delta T\%$) and switching times of the novel π-conjugated conducting polymers were evaluated by utilizing cyclic voltammetry and *in situ* spectroelectrochemical studies. The results revealed that electronic and optical properties of conducting polymers were remarkably affected by the type of strong chromophore group. The coumarin unit containing polymers **PECbzCo** and **PTCbzCo** exhibited better electrochemical and optical characteristics in terms of band gaps, optical contrast and switching times than their analogues bearing an azobenzene unit as the pendant group; **PECbzAz** and **PTCbzAz**. All electrochemical and spectroelectrochemical studies also proved that the incorporation of strong chromophore units with 3,6-linked thiophene-carbazole-thiophene polymer backbone resulted in lower band gaps and multichromic properties with a wide color scale compared to poly(2,5-dithienylpyrrole) (PSNS), poly(2,5-di-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-ylthienyl) and poly(2,2′:5′,2″-terthien-3′-yl) derivatives functionalized with the same chromophore units in our previous published papers [41-43]. In the lights of results in hand, it may be inferred that the novel 3,6-linked thiophene-carbazole-thiophene type conducting polymers are good candidates and have the potential to be used in different electrochromic applications.

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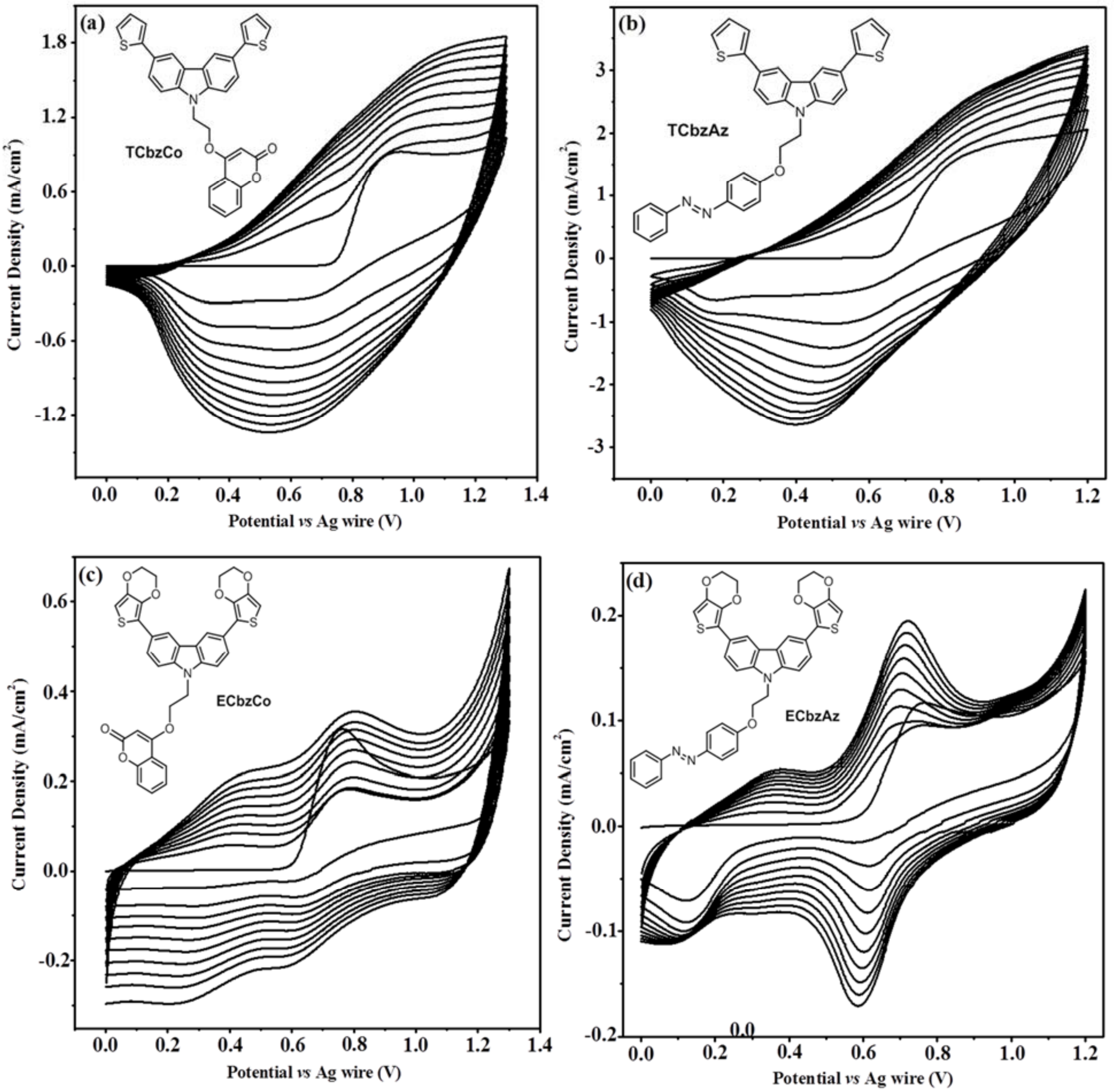


Fig.1. Repetitive cyclic voltammograms of (a) TCbzCo, (b) TCbzAz, (c) ECbzCo and (d) ECbzAz in 0.1 M $NaClO_4$/$LiClO_4$/ACN/DCM on an ITO electrode

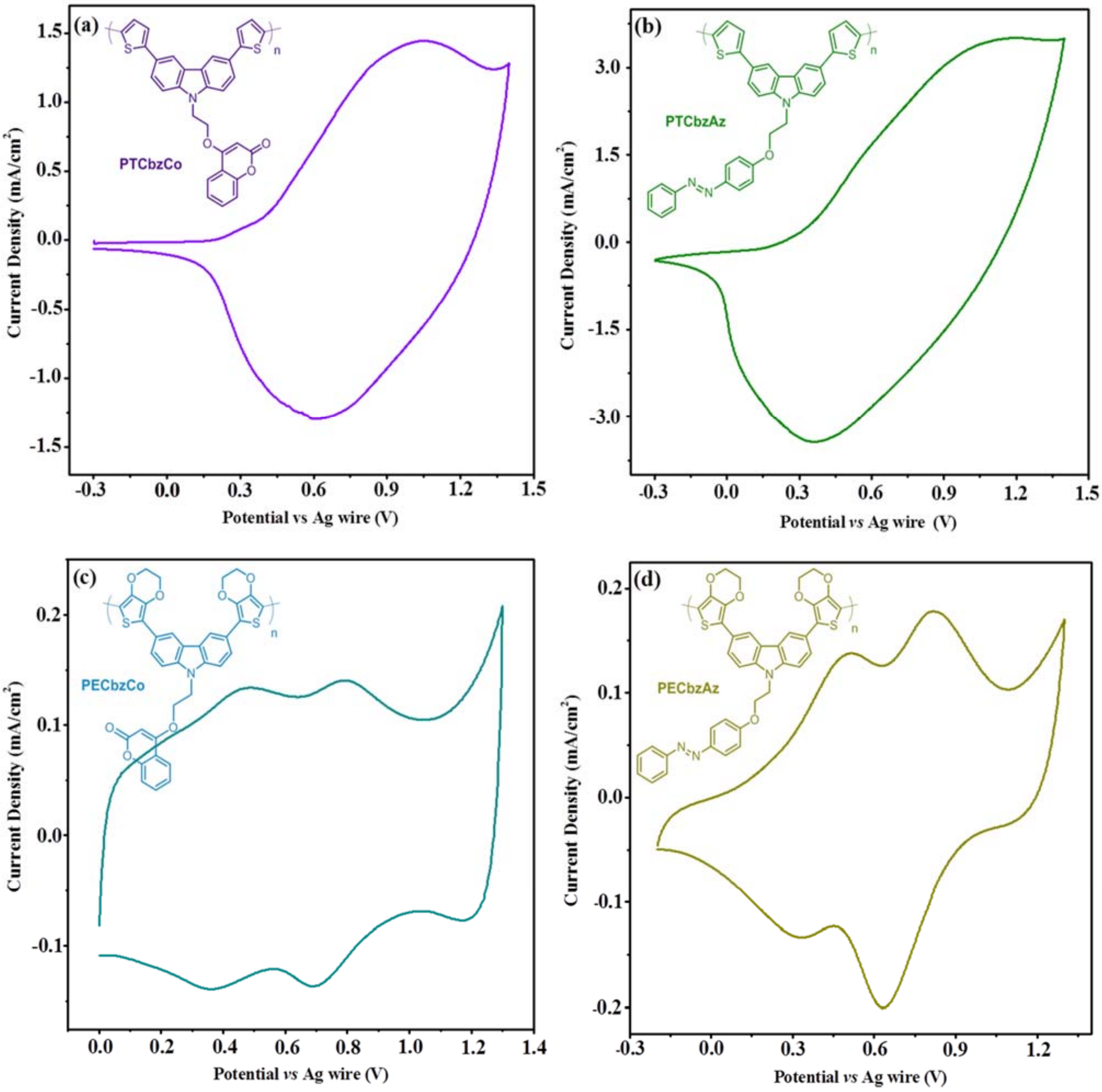


Fig.2. Single scan cyclic voltammograms of (a) PTCbzCo, (b) PTCbzAz, (c) PECbzCo and (d) PECbzAz in 0.1 M $NaClO_4$/$LiClO_4$/ACN/DCM monomer free solution

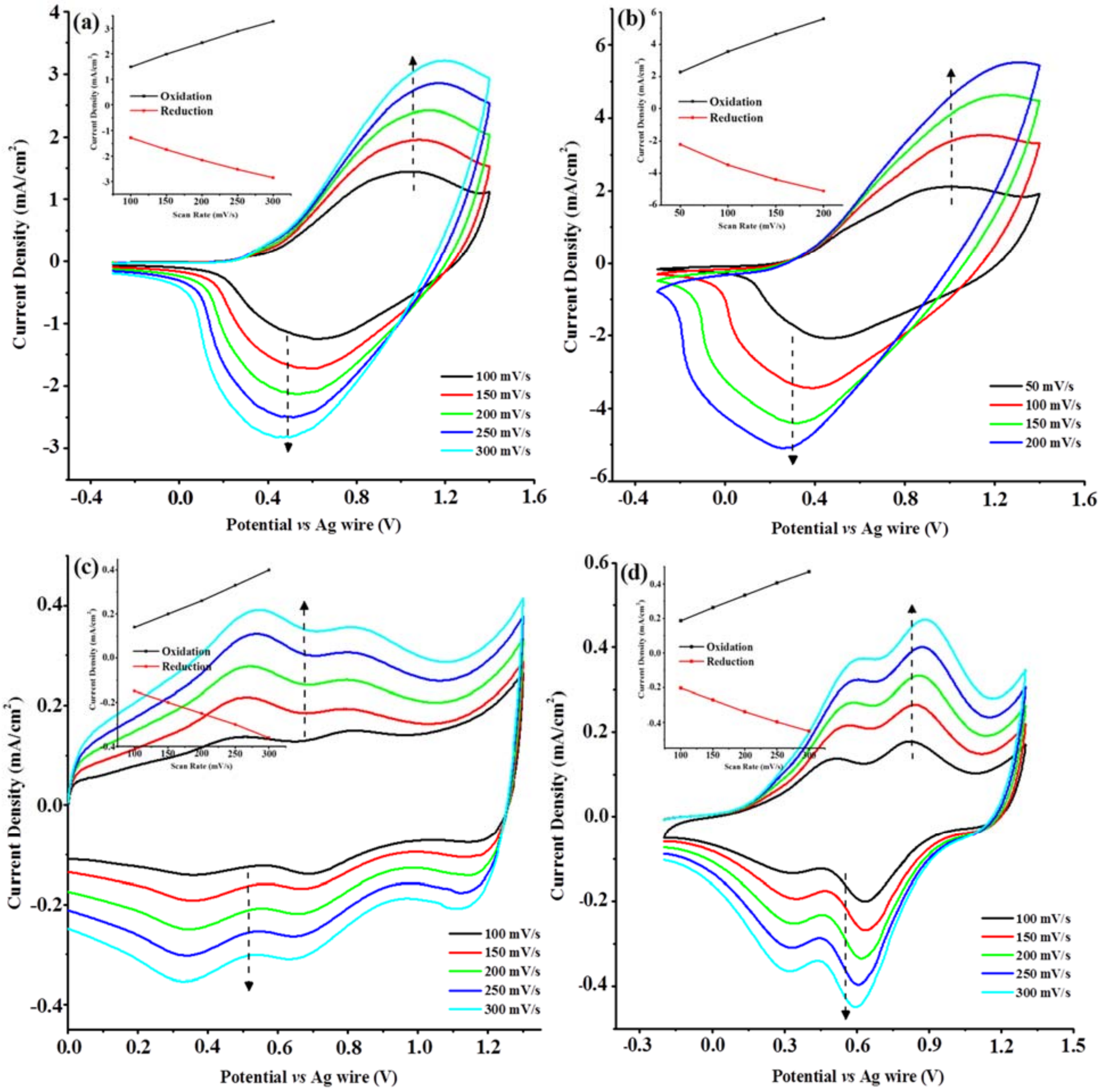


Fig.3. Scan rate dependence of (a) PTCbzCo, (b) PTCbzAz, (c) PECbzCo and (d) PECbzAz conducting polymer films

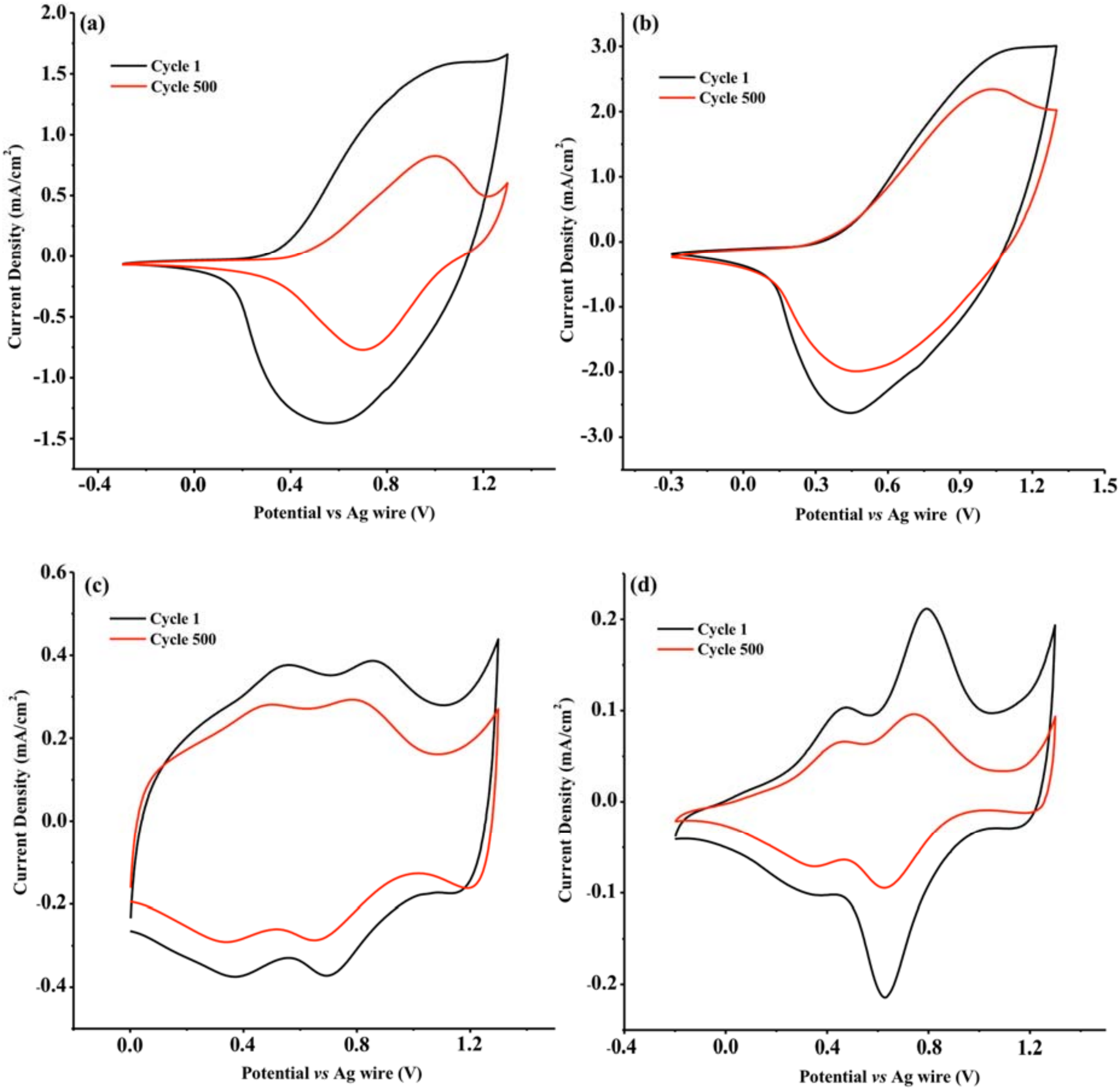


Fig.4. The stability of the electrochemically synthesized conducting polymer films (a) PTCbzCo, (b) PTCbzAz, (c) PECbzCo and (d) PECbzAz

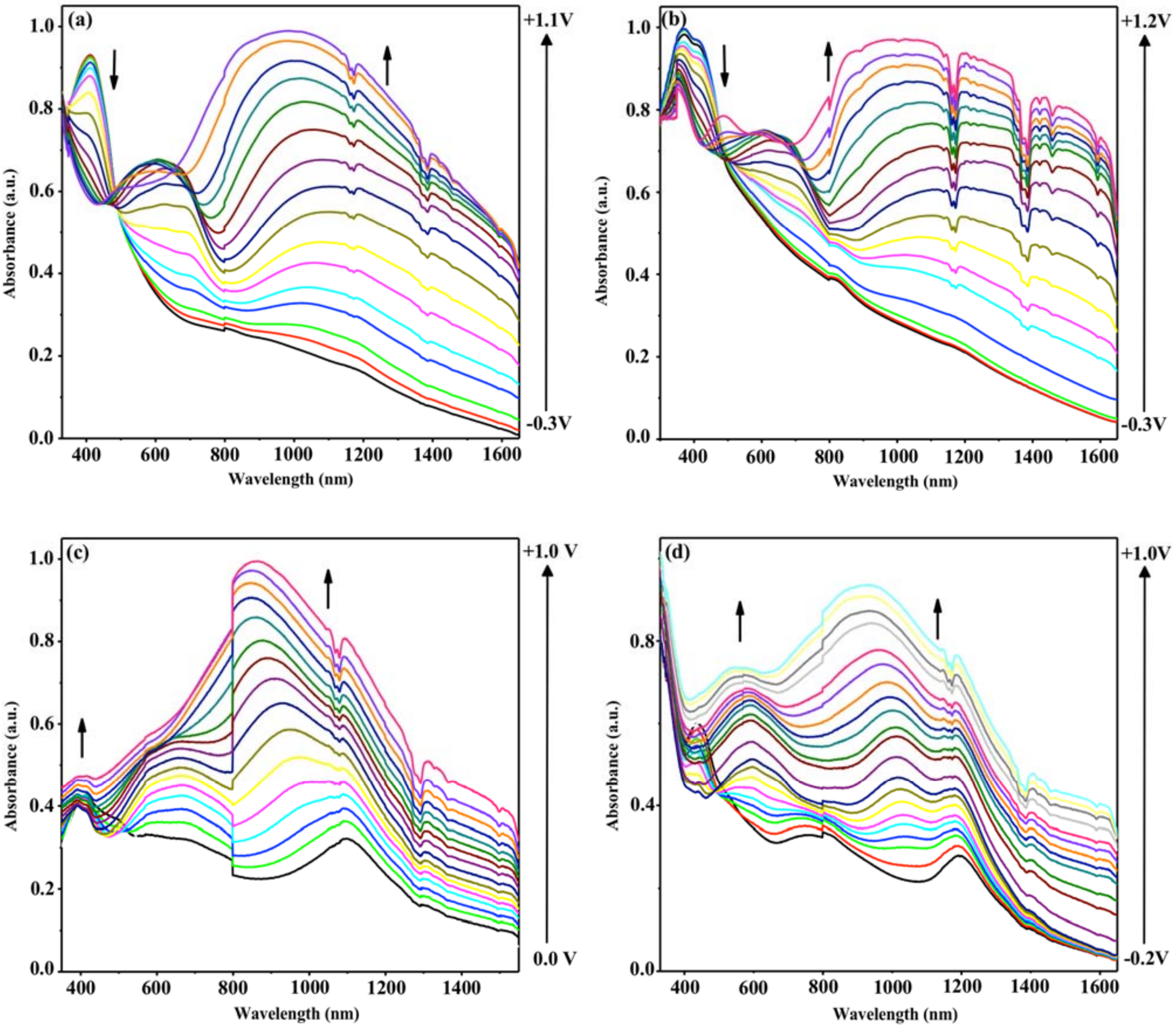
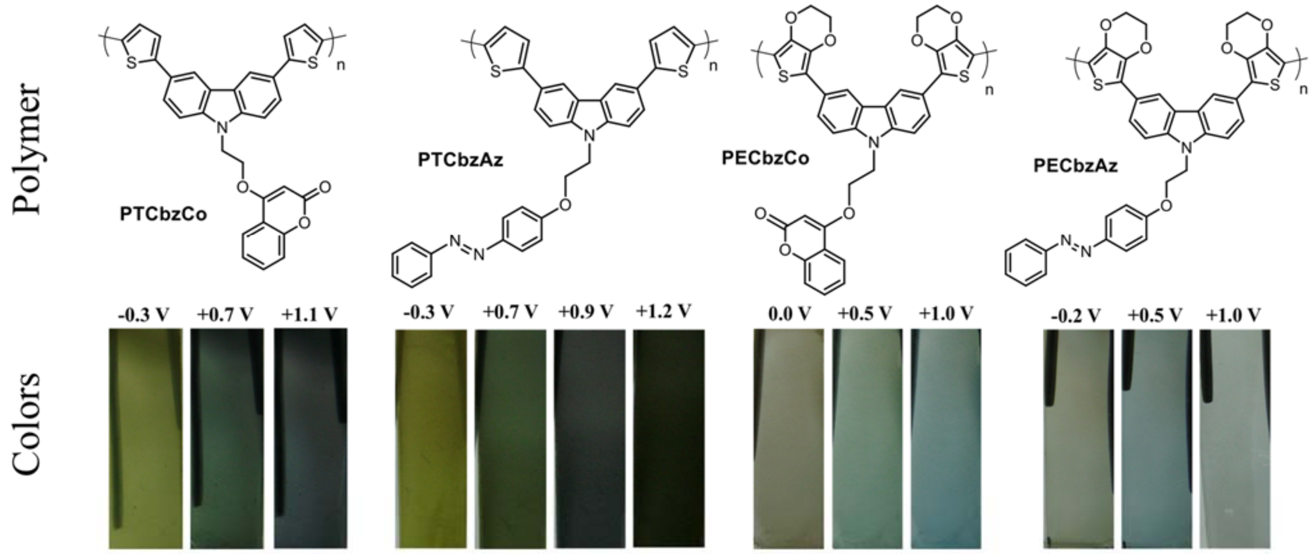


Fig.5. Electronic absorption spectra of (a) PTCbzCo film between -0.3 V and +1.1 V, (b) PTCbzAz film between -0.3 V and +1.2 V, (c) PECbzCo film between 0.0 V and +1.0 V and (d) PECbzAz film between -0.2 V and +1.0 V on an ITO coated slide in a momomer-free in 0.1 M $NaClO_4$/$LiClO_4$/ACN/DCM electrolyte-solvent couple



L	68.926	40.567	22.438	67.900	33.049	14.595	2.468	54.338	58.809	58.897	78.407	55.636	70.306
a	-14.570	-20.583	0.773	-23.670	-17.893	-0.800	-1.480	-10.060	-16.073	-13.784	-8.753	-8.637	-3.185
b	38.428	17.613	-11.131	67.600	9.007	-12.344	1.616	20.607	10.850	-3.306	13.883	-3.503	10.410

Fig.6. The colors and chromaticity coordinates of PTCbzCo, PTCbzAz, PECbzCo and PECbzAz films at their neutral and various oxidized states

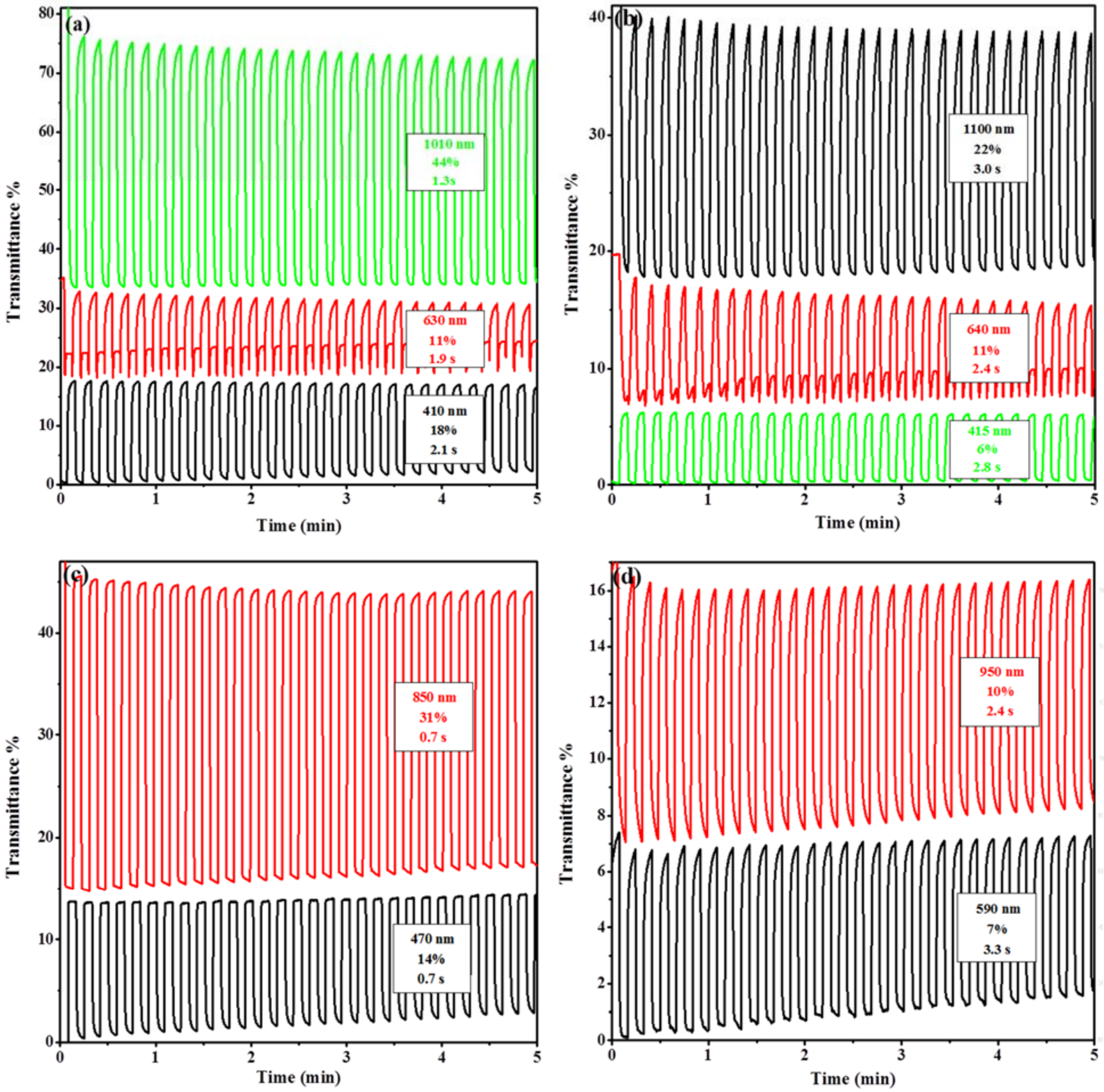
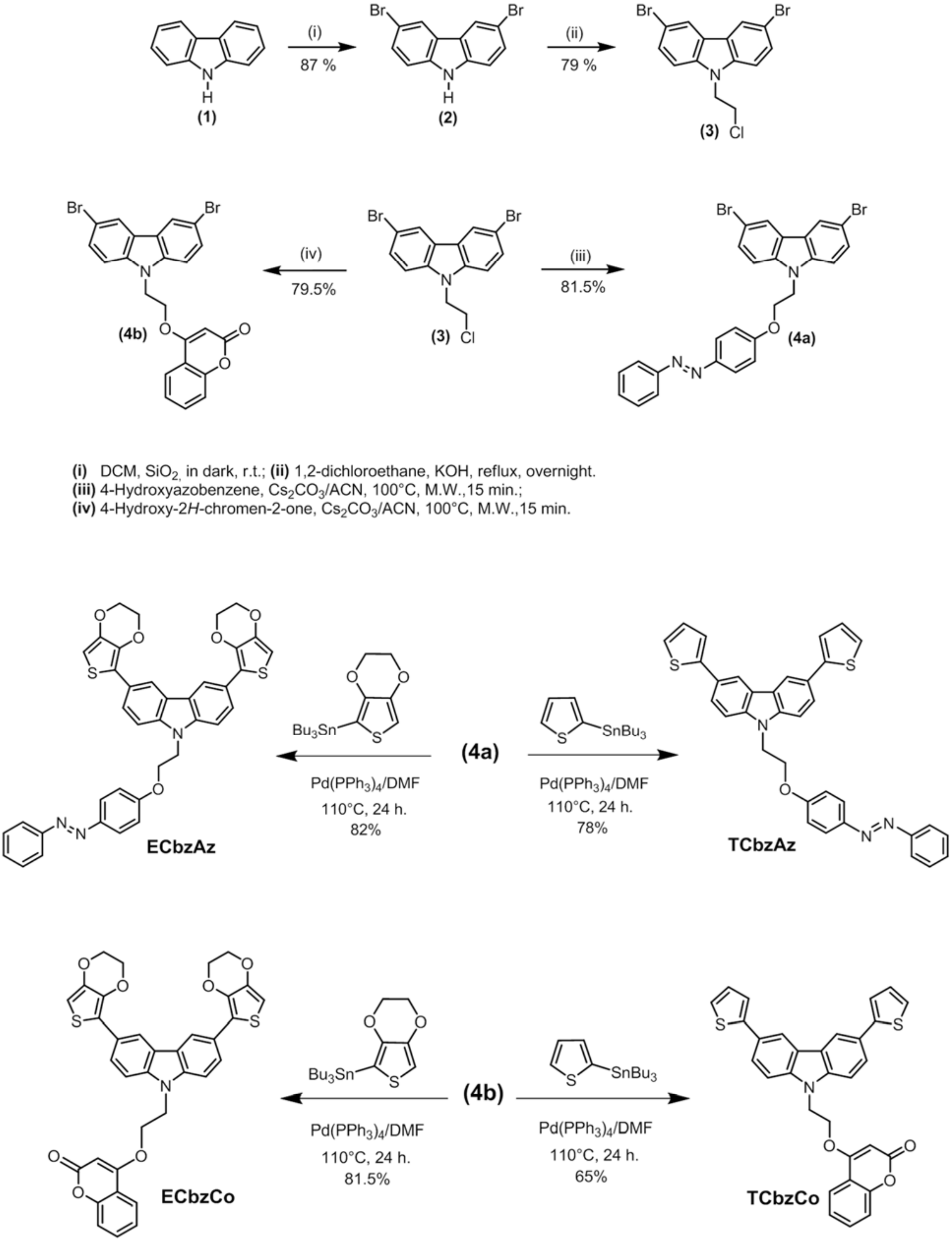


Fig.7. Percent transmittance changes as a function of time for (a) PTCbzCo, (b) PTCbzAz, (c) PECbzCo and (d) PECbzAz films at their maximum absorption wavelenghts in visible and NIR regions



(i) DCM, SiO_2, in dark, r.t.; **(ii)** 1,2-dichloroethane, KOH, reflux, overnight.
(iii) 4-Hydroxyazobenzene, Cs_2CO_3/ACN, 100°C, M.W.,15 min.;
(iv) 4-Hydroxy-2*H*-chromen-2-one, Cs_2CO_3/ACN, 100°C, M.W.,15 min.

Scheme 1. Synthetic pathway for TCbzAz, ECbzAz, TCbzCo and ECbzCo

Table 1. Electrochemical and optical results for PTCbzCo, PTCbzAz, PECbzCo and PECbzAz

Polymer Film	E^{ox}_{mon} (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)
PTCbzCo	0.96	1.0	0.61	-5.40	-3.33	410	2.07	630/1010
PTCbzAz	0.98	0.58	0.37	-5.35	-3.42	370/415	1.93	640/1100
PECbzCo	0.76	0.48/0.80	0.36/0.70	-4.85	-3.10	470	1.75	850
PECbzAz	0.77	0.51/0.82	0.33/0.64	-5.21	-3.50	437	1.71	590/950