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# A new multi-electrochromic 2,7 linked polycarbazole derivative: Effect of the nitro subunit

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#### ABSTRACT

A new poly-2,7-di-2-thienyl-9*H*-carbazole derivative (poly(TCT-N)) bearing nitro (-NO<sub>2</sub>) subunit has been reported. The electrochemical and optical properties of TCT-N monomer and its polymer have been compared to the 9-phenyl-2,7-di-2-thienyl-9*H*-carbazole (TCT) standard molecule. Cyclic voltammetry revealed that TCT-N and TCT have excellent polymerization activity; due to extended conjugation with the attached thiophene unit and also their low oxidation potentials. The oxidation potential of TCT-N is higher than that of TCT, because of electro-withdrawing effect of -NO<sub>2</sub> moiety. Besides, the TCT-N polymeric film prepared via electrochemical process exhibits a multi-electrochromic behavior compared with TCT standard molecule. The electrocactive orange color of poly-TCT-N film converted respectively to green, turquoise and dark blue upon applied positive potentials. Consequently, the polymeric electrochrome exhibits multi-electrochromic behavior, high redox stability, high coloration efficiency and reasonable response time for electrochromic applications.

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# 1. Introduction

After polyacetylene as first conducting polymer which has gained conductivity by using dopant ion was prepared by Shirakawa et al. they have begun to attract interest in this type of polymeric material rather have the space and now widely used for industrial applications [1]. The potential applications include their use as molecular electronics [2], nonlinear optical devices [3], organic light emitting diodes (OLEDs) [4], organic solar cells (OSCs) [5], organic field effect transistors (OFETs) [6], memories [7] and energy storage [8]. A large number of applications exist based on electrochromism, which relies on the reproducible switching characteristics of conjugated polymers [9]. All these applications usually require the modification of the monomer structure to tune the properties of the polymers (electronic, optical, conductivity, etc.) with respect to desired applications. In addition, the physical and chemical properties of the conjugated polymers can efficiently be controlled by some basic factors such as bond length alternation, aromaticity, planarity, substitution and intermolecular interaction [10]. For this purpose, functionalization of the electroactive monomer structure before polymerization and association of the conducting polymer with other materials are widely used [11]. Besides, the attachment of electro-withdrawing and/or electron-donating moieties onto conjugated system is the most promising way to control the properties of the electroactive polymers [12]. For instance, in spite of the rich chemistry of thiophene, only a few polythiophene systems with electro-withdrawing moieties such as nitro, carboxy or cyano on the thiophene ring exist in the literature; however, a number of polythiophene with alkyl and/or electron-donating substituents

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have been reported [13]. These attachments, based on the electronic properties of the neutral semiconducting form of conjugated systems, have had a great effect on the chemistry of these systems. This new formation has created a strong change in point of view regarding the molecular engineering of the electronic properties of materials derived from conjugated systems and hence on the structural control of their band gap [10].

In particular, thiophene and carbazole containing polymers have been of recent attraction due to their interesting electrochemical and optical behavior, and electrochromic properties [14]. Using these materials in electrochromic applications that possess the ability to reversibly color change by altering redox state has emerged [15]. Besides, polycarbazole is well-known as a good hole transport and photonic material for optoelectronic devices [16]. Polycarbazoles are known as not only an efficient short wavelength emitter but also as a strong electro-donating (p-type) chromophore [17]. Another advantage of carbazole is that it can be easily functionalized at its (3,6-) [18], (2,7-) [19] or Npositions [20] and then covalently linked into polymeric systems, both in the main chain [21] as building blocks and in a side chain as pendant unit [22]. Furthermore, poly(3,6-carbazole)s show interesting electrochromic properties because of the conjugation breaks that are present due to the inclusion of a 3,6-linkage. These broken conjugation lengths generate radical cations, which are separated from one another and do not combine. Therefore, the ability of poly(3,6-carbazole) derivatives to form two distinct oxidation states further ability to exhibit many colors on the ITO/glass surface upon applied positive potentials [15a,23].

Since 2,7-carbazoles were theoretically found to have smaller energy gaps than the 3,6-carbazoles, the small energy gaps of these monomers are expected to contribute to a lowering of the band gaps in the resulting polymers [17b–e]. Due to easily synthesized, there are many reports about poly(3,6-carbazole)s [24]. For instance, direct oxidative polymerization or electropolymerization of carbazoles resulted in just oligomeric materials linked at the 3,6- positions [23,25]. On the other hand, the synthesis of poly(2,7carbazole)s was not straightforward due to unreactive the 2 and 7 positions of carbazole. Several approaches have been developed to overcome the barrier to obtaining various poly(2,7-carbazole) derivatives [19].

Herein, we synthesized a new poly(2,7-carbazole) derivative bearing electro-withdrawing  $-NO_2$  substituent that could easily be polymerized electrochemically to give stable, electroactive and electrochromic materials (Scheme 1). When compared to the poly-9-phenyl-2,7-di-2-thienyl-9H-carbazole (poly(TCT)) standard molecule, as a result of the attachment of  $-NO_2$  moiety to the structure, it gain many useful properties such as multi-electrochromic behavior, high redox stability, and high coloration efficiency.

#### 2. Experimental

#### 2.1. Materials

All chemicals purchased from Aldrich, Merck and Fluka and used without further purification. 2-Azido-4,4'-dinitrobiphenyl (1), 2,7-dinitro-9*H*-carbazole (2), 2,7-diamino-9*H*-carbazole (3), 2,7-diiodo-9*H*-carbazole (4) were prepared from previously published procedures [19].

#### 2.2. Synthesis of 2,7-di-2-thienyl-9H-carbazole (5)

Compound 4 (0.5 g, 0.95 mmol) was dissolved in acetic anhydride (20 mL) and added boron trifluoride diethyl etherate (0.15 mL) with refluxing for 1 h to yield 9-acetyl-2,7-diiodocarbazole as a residue. A mixture of 9-acetyl-2,7-diiodocarbazole (0.44 g, 1 mmol) 2-thiopheneboronicacid (0.27 g, 2 mmol), 20 mL THF and 3 M 5 mL of Na<sub>2</sub>CO<sub>3</sub> solution was stirred at room temperature for 2 h under argon atmosphere. Then  $Pd(PPh_3)_4$  (0.02 g) was added to this solution as catalyst and the reaction was refluxed for 24 h. The mixture was cooled to room temperature and then poured into a large amount of methanol (500 mL), and the mixture of 9-acetyl-2,7-di-2-thienylcarbazole was obtained by filtration. Finally the residue was dissolved in THF (50 mL), DMSO (10 mL), H<sub>2</sub>O (5 mL), and then KOH (9.72 g, 0.173 mol) was added, and the mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature, neutralized by HCl, and then poured into water to give the final product. Remaining solid was crystallized in methanol two times. The solid was dried at 50 °C under vacuum. Yield: 0.34 g, 87%, brown color product.

FT-IR (cm<sup>-1</sup>): 3397 (–NH); 3063, (C–H aromatic); 1605, (C=C aromatic), 685 (thienyl C–H) (<sup>1</sup>H NMR, CHCl<sub>3</sub>-d, ppm):  $\delta$ , 11.96, (s, 1H, N–H); 7.94 (d, 2H, Ar-H<sub>ff</sub>); 7.62 (d, 2H, Ar-H<sub>cc'</sub>); 7.55, (s, 2H, Ar-H<sub>dd'</sub>); 7.39, (d, 2H, Ar-H<sub>aa'</sub>); 7.14, (m, 4H, Ar-H<sub>ff</sub>, Ar-H<sub>bb'</sub>).



2.3. Synthesis of 9-(4-nitrophenyl)-2,7-di-2-thienyl -9H-carbazole (TCT-N)

Compound **5** (0.18 g, 0.54 mmol),  $K_2CO_3$  (0.15 g, 1.0 mmol), Cu powder (0.05 g) and 1-iodo-4-nitrobenzene (0.135 g, 0.54 mmol) were added to 30 mL nitrobenzene and heated to reflux temperature for 48 h under argon atmosphere. Then the reaction mixture was cooled, filtered through a pad of celite and nitrobenzene was removed under vacuum. Remaining solid was dissolved in DMF and poured into cold water. The precipitated product was filtered, recrystallized from a mixture of chloroform/hexane (1/3; v/v) dried at 60 °C under vacuum. *Yield: 0.1 g, 41%, yellow color product.* 

FT-IR (cm<sup>-1</sup>): 3093, 3068, (C–H aromatic); 1594 (C=C aromatic); 1522, 1340 (–NO<sub>2</sub>), (<sup>1</sup>H NMR, CHCl<sub>3</sub>-d, ppm): δ, 8.18, (d, 2H, H<sub>hh</sub>'); 7.89 (d, 2H, Ar-H<sub>ee</sub>'); 7.57 (d, 2H, Ar-

H<sub>cc'</sub>); 7.37, (d, 2H, Ar-H<sub>gg'</sub>); 7.35, (d, 2H, Ar-H<sub>aa'</sub>); 7.28, (d, 2H, Ar-H<sub>ff</sub>); 7.22, (s, 2H, Ar-H<sub>dd'</sub>); 7.13, (dd, 2H, Ar-H<sub>bb'</sub>).



2.4. Synthesis of 9-phenyl-2,7-di-2-thienyl -9H-carbazole standard molecule (TCT)

2,7-Di-2-thienyl-9*H*-carbazole (0.09 g, 0.27 mmol),  $K_2CO_3$  (0.075 g, 0.05 mmol), Cu powder (0.05 g) and iodobenzene (0.2 g, 0.49 mmol) were added to 20 mL nitrobenzene and heated to reflux temperature for 48 h under argon atmosphere. Then the reaction mixture was cooled, filtered through a pad of celite and nitrobenzene was removed under vacuum. Remaining solid was dissolved in DMF and poured into cold water. The precipitated product was filtered, recrystallized from a mixture of chloroform/ hexane (1/2; v/v) dried at 60 °C under vacuum. Yield: 0.08 g, 70%, light yellow color product.

FT-IR (cm<sup>-1</sup>): 3088, 3045, (C–H aromatic); 1592, 1450 (C=C aromatic); (<sup>1</sup>H NMR, DMSO-d<sub>6</sub>, ppm):  $\delta$ , 7.98, (d, 2H, H<sub>ff</sub>); 7.52 (d, 2H, Ar-H<sub>aa'</sub>); 7.41 (t, 2H, Ar-H<sub>hh'</sub>); 7.37, (d, 2H, Ar-H<sub>gg'</sub>); 7.24, (d, 2H, Ar-H<sub>cc'</sub>); 7.16, (d, 2H, Ar-H<sub>lif</sub>); 7.13, (s, 2H, Ar-H<sub>dd'</sub>); 6.97, (d, 2H, Ar-H<sub>bb'</sub>); 6.77, (d, 2H, Ar-H<sub>bb'</sub>).



#### 2.5. Electrochemical polymerization

Electrochemical polymerization of TCT-N and TCT were carried out in a dichloromethane solution of  $2.0 \times 10^{-3}$  M monomers and 0.1 M TBAPF<sub>6</sub> by repetitive cycling at a scan rate of 100 mV/s. A platinum wire was used as a counter electrode and Ag wire as a pseudo reference. The polymer

was directly coated onto platinum disk  $(0.02 \text{ cm}^2)$  or indium-tin oxide (ITO, 8-12  $\Omega$ , 0.8 cm  $\times$  5 cm) and then the film was rinsed with acetonitrile to remove from electrolyte salt.

#### 2.6. Instrumentation

FT-IR spectra were recorded by a Perkin Elmer FT-IR Spectrum One by using ATR system (4000–650 cm<sup>-1</sup>). <sup>1</sup>H NMR (Bruker Avance DPX-400) spectra were recorded at 25 °C in deuterated chloroform and TMS as internal standard.

Cyclic voltammetry (CV) technique used for electrochemical measurements was performed using Biologic SP50 potentiostat–galvanostat system. The electrochemical cell includes an Ag/AgCl as reference electrode (RE), Pt wire as counter electrode (CE) and glassy carbon as working electrode (WE) immersed in 0.1 M TBAPF<sub>6</sub>/acetonitrile as the supporting electrolyte. CV measurements were carried under argon atmosphere. HOMO and LUMO energy levels of polymer were calculated according to the inner reference ferrocene redox couple E (Fc/Fc+) = +0.41 V (vs. Ag/AgCl) in acetonitrile by using the formula EHOMO =  $-e(E_{ox}-E_{Fc})$  + (-4.8 eV) [26]. Onset values of oxidation potentials were taken into account while calculating HOMO energy levels. LUMO energy levels of TCT and poly-TCT were calculated by subtracting the optical band gap from HOMO level.

UV–Vis spectra were recorded by Analytic Jena-Speedcord S600 spectrophotometer. The absorption spectra of monomer and polymer were recorded in dichloromethane. The optical band gap ( $E_g$ ) of products were calculated from their low energy absorption edges ( $\lambda_{onset}$ ) ( $E_g = 1241/\lambda_{onset}$ ) [27].

Spectro-electrochemical measurements were carried out to consider absorption spectra of this polymer film under applied potential [28]. The spectroelectrochemical cell consisted of a quartz cell, an Ag wire (RE), Pt wire counter electrode (CE) and ITO/glass as transparent working electrode (WE). Measurements were carried out in the 0.1 M TBAPF<sub>6</sub> as supporting electrolyte in acetonitrile.

Colorimetric measurements were performed by using Konica Minolta CS-200 chromameter with viewing geometry as recommended by CIE. According the CIE system, the color is made up of three attributes; luminance (L), hue (a), and saturation (b) [29]. These parameters were measured at neural and oxidized state of the poly-TCT-N and poly-TCT on the ITO/glass surface.

## 3. Results and discussion

#### 3.1. Synthesis and characterization

The new 2,7-carbazole derivative bearing –NO<sub>2</sub> pendant was synthesized in six steps. Starting from 2-amino-4,4'- dinitrobiphenyl, 2,7-dinitro functionalized carbazoles typically obtained from the Cadogan ring-closure reactions were firstly synthesized by Morin and Leclerc [19]. Reduction of nitro group of this intermediate product was performed by using Pd/C and hydrazine monohydrate, a different reducing conditions used by Morin and Leclerc



Scheme 1. (a) (i) NaNO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, AcOH 0 °C, 2 h, (ii) NaN<sub>3</sub>, r.t., 18 h; (b) Kerosene, 250 °C, 6 h; (c) Pd/C, N<sub>2</sub>H<sub>5</sub>OH, EtOH, reflux, 24 h; (d) (i) NaNO<sub>2</sub>, AcOH, 0 °C, 2 h, (ii) KI, r.t., 18 h; (e) (i) Acetic anhydride, BF<sub>3</sub>-Et<sub>2</sub>O, reflux, 1 h, (ii) 2-thiopheneboronic acid, Pd(Ph<sub>3</sub>P)<sub>4</sub>, THF-Water (4:1), Na<sub>2</sub>CO<sub>3</sub>, reflux 24 h, (iii) KOH, THF-DMSO-Water (10:2:1), reflux, 24 h; (f) Cu powder, 18-Crown-6, K<sub>2</sub>CO<sub>3</sub>, 1-iodo-4-nitrobenzene, nitrobenzene, reflux, 24 h; (g) Cu powder, 18-Crown-6, K<sub>2</sub>CO<sub>3</sub>, iodobenzene, nitrobenzene, reflux, 24 h.

[19]. 2,7-Diiodo-9*H*-carbazole (**4**) was synthesized in two steps. In the first step, 2,7-diamino-9*H*-carbazole (**3**) was converted to diaazonium salt and then to give **4** adding KI to this solution [19]. After that, the diiodo compound coupled with thiophene was carried out by using Suzuki type coupling reaction to get 2,7-dithienyl-9*H*-carbazole (**5**). Consequently, the electroactive monomers (TCT-N and TCT) were synthesized by Ullman type condensation of 5 and iodophenyl derivatives in nitrobenzene in the presence of Cul as catalyst and K<sub>2</sub>CO<sub>3</sub>. The reaction yields of TCT-N and TCT were found to be 41% and 70%, respectively.

After completion of the synthetic works, chemical structure of TCT-N was identified by FT-IR, and <sup>1</sup>H NMR. Significant changes were observed in the spectral properties of the initial compounds and the products. In FT-IR spectrum of **1**, characteristic triple bond vibration exerted by azide  $(-N_3)$  groups was observed at 2123 cm<sup>-1</sup> and also characteristic  $-NH_2$  vibrations at about 3200–3400 cm<sup>-1</sup> were disappeared. In the next step, as a result of the ring closure reaction, characteristic N–H vibration band for secondary amines of obtained carbazole derivative was observed at 3339 cm<sup>-1</sup>. Then, **3** obtained from reduction of **2** was identified from its characteristic  $-NH_2$  bond vibration at 3306 and 3205 cm<sup>-1</sup>. In the FT-IR spectra of

**4** characteristic  $-NH_2$  vibration attributed to **3** disappeared. The FT-IR spectrum of 5 obtained with the attached thienyl moiety on the structure exhibits characteristic strong peak at 685 cm<sup>-1</sup> (for  $\alpha$ -hydrogens of thiophene rings). Finally, TCT-N synthesized from Ullmann condensation of **F10** with 1-iodo-4-nitrobenzene, their characteristic unsymmetric and symmetric  $-NO_2$  vibrations were observed at 1522 and 1340 cm<sup>-1</sup>, respectively. Also characteristic –NH vibration for secondary amines was removed in this spectrum (see Electronic Supplementary information).

In the <sup>1</sup>H NMR spectrum of TCT-N monomer, the phenylene proton signals neighboring  $-NO_2$  moiety were observed at higher ppm (8.09 ppm) than that of other proton signals due to electro-withdrawing effect of  $-NO_2$ substituent. Besides characteristic thienyl  $\beta$ -H doublet signal was observed at 7.12 ppm. Furthermore, other signals attributed to thiophene and carbazole moieties were observed as expected. Finally, FT-IR and <sup>1</sup>H NMR spectroscopy results proved that all chemical reactions were completed successfully (Fig. 1).

Electrochemical polymerization was carried out in a reaction medium containing  $2.0 \times 10^{-3}$  M TCT-N or TCT monomer and 0.1 M TBAPF6/dichloromethane via repetitive cycling at a scan rate of 100 mV s<sup>-1</sup>. The electroactive



Fig. 1. <sup>1</sup>H NMR spectrum of TCT-N.



Fig. 2. Repeated potential scan of TCT-N between 0 and 1.45 V (a) TCT (b) between 0 and 1.45 V in 0.1 M TBAPF<sub>6</sub>/dichloromethane, scan rate 100 mV/s, vs. Ag/AgCl.



Fig. 3. UV-Vis absorbtion spectra of TCT-N (a) and TCT (b) inset: poly-TCT-N (a) and poly-TCT (b) in dichloromethane.

polymers were directly coated onto the working electrode (platinum disk or ITO/glass surface). Potentiodynamic electrochemical polymerization of TCT-N was carried out repetitive cycling at a potential between 0 and 1.45 V exhibited a new redox couple at 0.89–1.31 V ( $E_{p,1/2}^{ox}$  = 1.12) (Fig. 2a). Due to presence of –NO<sub>2</sub> moiety, electrochemical polymerization of TCT-N requires to reach higher potentials compared with TCT standard molecule. Because of this reason. the electrochemical polymerization of TCT was carried out by repetitive cycling at a potential between 0 and 1.40 V exhibited two new redox couples at 0.85-0.95 V  $(E_{p,1/2}^{ox1} = 0.90 \text{ V})$ , and 1.08–1.22 V  $(E_{p,1/2}^{ox2} = 1.15 \text{ V})$  (Fig. 2b). These two redox couple may be attributed to polaronic and bipolaronic formation of the occurred polymer chain by the electrochemical process [30]. Due to electro-withdrawing effect of the -NO<sub>2</sub> substituent on the poly(TCT-N), the two redox states could not be observed at this potential of 1.40 V. In addition, all peaks were increased current density after each successive cycle clearly indicated the formation of poly(TCT-N) and/or poly(TCT) deposited onto the surface of the working electrode. Prepared polymer films on ITO/glass surface was dedoped electrochemically in monomer free-electrolyte solution to equilibrate the redox behavior after washing with an acetonitrile to remove the unreacted monomers and/or oligomeric species. Then, the polymers on ITO/glass surface partly dissolved in dichloromethane by using ultrasonic bath for UV-Vis absorption measurements.

#### 3.2. Optical and electrochemical properties

The UV–Vis absorption spectra of TCT-N and TCT monomers and polymers were recorded in dichloromethane (Fig. 3). The lowest energy bands of TCT-N and TCT standard molecule at about  $\lambda_{max} = 350$  nm attributed to thiophene-carbazole-thiophene (TCT)  $\pi$ -conjugated system. Although  $\lambda_{max}$  of TCT-N and TCT are the same, the absorption band of TCT-N is broadened than that of TCT. Thus, TCT-N has an onset value of 472 nm corresponding to a 76 nm red shift with respect to that of the TCT. This significant bathochromic shift is attributed to the -NO2 electrowithdrawing effect. According to these results, the optical band gap values of TCT and TCT-N were found to be 3.13 and 2.63 eV. On the other hand, the lowest energy transition band  $(\lambda_{max})$  of poly(TCT-N) was observed at about 415 nm. This significant bathochromic shift is attributed to resulting the polymer with extended  $\pi$ -system. Due to TCT-N consist of -NO<sub>2</sub> moiety, the molecule require for higher potential than that of TCT and thus reduced both the length of chain and degree of conjugation with respect to that of the TCT. Because of this effect, 20 nm red shift of  $\lambda_{max}$  was observed in the  $\lambda_{max}$  of TCT. Finally, for poly(TCT-N), the onset absorption is 580 nm corresponding to an energy band gap of 2.13 eV. Besides, the poly-TCT has an onset value of 615 nm (equal to a band gap of 2.01 eV) corresponding to a 35 nm red shift with respect to that of the poly(TCT-N).

The electrochemical properties of TCT-N and TCT monomer and their polymers were investigated by cyclic voltammetry (CV). An explicit difference in redox behavior of the TCT-N and TCT can be deduced from the CV which was depicted in Fig. 4. During CV scan in the anodic regime of TCT-N and TCT monomer, TCT-N exhibited an irreversible oxidation peak at  $E_{m,a}^{ox}$  = 1.46 V vs. Ag/AgCl during an anodic scan, and this oxidation potential is higher than that of TCT (semi reversible;  $E_{m,a}^{ox} = 1.25$  and  $E_{m,c}^{ox} = 1.11$  V;  $E_{m,1/2}^{ox} =$ 1.19 V vs. Ag/AgCl). As expected, this result indicated that TCT has a more electron rich nature than TCT-N when attaching the -NO<sub>2</sub> moiety in a similar system. On the other hand, to record the cyclic voltammogram of poly(TCT-N) and poly(TCT), the polymer films prepared by repetitive potential cycling were rinsed in a monomer-free-electrolyte solution. Due to the extended conjugation in the polymers backbone, the oxidation potentials were observed as reversible and at lower potential with compared to corresponding monomers. On the other hand, in the cathodic regime, cyclic voltammogram of TCT-N exhibits characteristic reversible reduction couple with potentials of  $E_{m,c}^{red} = -0.93 \text{ V} - E_{m,a}^{red} = -0.85 \text{ V}$  and  $E_{m,1/2}^{red} = -0.85 \text{ V}$ -0.89 V which reflects the reduction process of  $-NO_2$ 



Fig. 4. Cyclic voltammogram of TCT-N (a) TCT (b) in the 0.1 M  $TBAPF_{6/}$  dichloromethane, scan rate 100 mV/s, vs. Ag/AgCl.

moiety. In comparison to the monomer, the reduction couple of poly(TCT-N) broadened and slightly shifted positively ( $E_{p,c}^{red} = -0.91 \text{ V} - E_{p,d}^{red} = -0.77 \text{ V}$  and  $E_{m,1/2}^{red} = -0.84 \text{ V}$ ) and the conjugated backbone is still sufficiently conducting to allow electron transfer at potentials. Besides, HOMO–LUMO energy levels of TCT-N and poly(TCT-N) were calculated according to the onset values of their oxidation and reduction potentials. The LUMO energy levels of TCT and poly(TCT) were calculated by adding the optical band gap from their HOMO levels (Table 1). As a result of the data in Table 1, optical and electrochemical properties of the molecules were greatly influenced by the addition of electro-withdrawing  $-NO_2$  as subunit in the structure.

The spectro-electrochemical properties of the poly(TCT-N) film were determined upon doping process (Fig. 5) and compared to poly-TCT (Fig. 6) in order to get further support for the effect of -NO<sub>2</sub> electro-withdrawing moiety. In the neutral state, the poly(TCT-N) had one maximum absorption at 418 nm ( $\lambda_{max}$ ,  $\pi$ - $\pi^*$  transition). The optical band gap  $(E_{\sigma})$  of poly(TCT-N) was found to be 2.18 eV from the onset of absorption, which is somewhat higher than the Eg of poly-TCT (2.06 eV). Upon oxidation, the intensity of the  $\lambda_{max}$  was simultaneously decreased up to a certain first and second broad bands intensified at about 762 (0-1.0 V) and 1000 nm (1.0–1.6 V) indicated the formation of polarons and bipolarons on poly(TCT-N) film, respectively (Fig. 5). Thus, NIR region, above 700 nm, was strongly absorbed at the fully oxidized state. Based on foregoing results, the orange color of the film with Commision Internationale de l'Eclairage (CIE) color parameters (Luminance L = 60, hue a = 7, and saturation b = 57) turned into green (L: 54; a: -20; b: 43), turquoise (L: 42; a: -16; b: 2), and dark blue (L: 38; a: -2; b: -10), respectively, upon oxidation (Fig. 5). On the other hand, when the intensity of the  $\pi$ - $\pi$ \* transition band of poly(TCT) film ( $\lambda_{max}$  = 422 nm) decreased, a new broad absorption band at about 790 nm started to intensify due to the polaron formation (0-0.8 V). Upon further oxidation, a broad band between 400 and 1000 nm also intensified (1-1.4 V). Thus all visible and near-IR regions were absorbed by the poly(TCT) film at fully oxidized state. The yellow color of the film with CIE color parameters (L: 75; a: -11; b: 64) turned into dark gray (L: 39; a: -6; b: 13), upon oxidation (Fig. 6).

Double step chronoamperometry technique was used to monitor the changes in the electro-optical responses during switching. Electrochromic parameters of the polymer

Table 1

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HOMO and LUMO energy levels, electrochemical (E'_{e}) and optical band gaps (E_{g}) values of TCT-N and TCT standard molecules.
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Molecules	Reduced group and its peak potential (V)	Oxidized group and its peak potential (V)	HOMO (eV)	LUMO (eV)	E <sub>g'</sub> , Electrochemical band gap (eV)	<i>E</i> <sub>g</sub> , Optical band gap (eV)
	$-NO_2$	TCT (Ring)				
TCT-N	$E_{m,c}^{red} = -0.93$ $E_{m,c}^{red} = -0.85$ reversible $E_{m,c}^{red} = -0.76$	$E_{m,a}^{ox} = 1.46$ Irreversible $E_{m,on}^{ox} = 1.25$	-5.64	-3.63	2.01	2.63
TCT		$\begin{array}{l} E^{ox}_{m,a}=1.25\\ E^{ox}_{m,c}=1.11\\ Semi-reversible\\ E^{ox}_{m,on}=1.04 \end{array}$	-5.43	-2.30ª	-	3.13
Poly-TCT-N	$E^{red}_{p,c}=-0.91$ $E^{red}_{p,a}=-0.77$ reversible $E^{red}_{m,on}=-0.71$	$E_{p,a}^{ox} = 1.31$ $E_{p,c}^{ox} = 0.89$ reversible $E_{m,on}^{ox} = 0.91$	-5.30	-3.68	1.62	2.18
Poly-TCT	_ <sup>^</sup>	$E_{p,a}^{ox1} = 0.95$ $E_{p,c}^{ox1} = 0.85$ reversible $E_{p,a}^{ox2} = 1.22$ $E_{p,c}^{ox2} = 1.08$ reversible $E_{m,on}^{ox2} = 0.73$	-5.12	-3.06 <sup>a</sup>	-	2.06

<sup>a</sup> Calculated by the addition of the optical band gap to the HOMO level.



Fig. 5. Spectro-electrochemical behavior of poly-TCT-N film on the ITO/glass surface.



Fig. 6. Spectro-electrochemical behavior of poly-TCT film on the ITO/glass surface.

films were analyzed by changes that occurred in the transmittance (increments and decrements of the absorption band at 420 and 1000 nm with respect to time) while switching the potential step wisely between neutral and oxidized states with a residence time of 10 s [28a]. The percentage transmittance changes ( $\%\Delta T$ ) of poly(TCT-N) between the neutral (at 0 V) and oxidized states (at 1.6 V) were found to be 22% for 420 nm and 57% for 1000 nm (Fig. 5). For poly(TCT), these values were found as 8% for 420 nm and 55% for 1000 nm (Fig. 6). Besides, the oxidation and reduction response times were measured to be 4.3 and 1.3 s for poly(TCT-N) and 0.8 and 1.8 s for poly(TCT) (Fig. 7). Optical activities of the poly(TCT-N) and poly(TCT) polymer film were retained by 92% and 77% even after 1000 cycles of operation, respectively (Fig. 7). Although the response times were relatively slow, the polymer film of TCT-N was more stable than that of TCT upon repetitive cycles.

On the other hand, the coloration efficiency (CE) was calculated by using CE =  $\Delta$ OD/ $Q_d$  and  $\Delta$ OD = log ( $T_{colored}/T_{bleached}$ ), where  $Q_d$  is the injected/ejected charge between neutral and oxidized states,  $T_{colored}$  and  $T_{bleached}$  are the

transmittance in the oxidized and neutral states, respectively. Using this equation, CE of poly(TCT-N) and poly(TCT) was measured to be 264 and 126 cm<sup>2</sup> C<sup>-1</sup> by chronoamperometry, while switching the polymer films between oxidized and reduced states. The results clearly show that the coloration efficiency of poly(TCT-N) is two times greater than that of poly(TCT). Toppare et al. reported the multi-electrochromic polymer of thiophenepyrrole-thiophene (SNS) analogue containing electro-withdrawing  $-NO_2$  substituent [31]. Based on previous results, it can be easily seen that the prepared polymer film of TCT-N has much better electrochromic performance than that of its SNS analogue and poly(TCT) standard.

# 4. Conclusion

Herein, we have reported the synthesis of a new multielectrochromic 2,7 linked thiophene-carbazole-thiophene (TCT) derivative containing an electro-withdrawing  $-NO_2$ substituent. It has been determined that the optical and the electrochemical properties of the monomer were



Fig. 7. Electrochemical switching, optical absorbance monitored at 1000 nm for poly-TCT-N (a) and poly-TCT (b) film between 0 and 1.6 V.

greatly influenced the presence of the electro-withdrawing  $-NO_2$  as subunit in the structure. TCT-N monomer was electrochemically polymerized onto transparent ITO/glass surface to give a quite stable multi-electrochromic polymer with a high contrast ratio in the NIR region ( $\Delta T = 57\%$  at 1000 nm). In comparison to TCT standard reference, polymer film of TCT-N has much better electrochromic performance in terms of multielectrochromic behavior, high resistance to over oxidation and high contrast ratio an impressive electrochemical stability, TCT-N is a possible good candidate for electrochromic applications.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.orgel.2011. 06.023.

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