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Novel ferrocene derivatized poly(2,5-dithienylpyrrole)s: Optoelectronic properties, electrochemical copolymerization

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ABSTRACT

In this study a novel ferrocene-substituted electrochromic polymer, poly(4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-N-(ferrocenyl methyl)-phenylamine), poly(SNS-An-Fc), was electrochemically synthesized and its electrochromic properties were investigated in detail. The cyclic voltammogram of SNS-An-Fc involves a reversible $Fe^{II/III}$ wave and an irreversible SNS based oxidation wave at higher potentials. Contrary to some of the previous thiophene based systems, the homopolymer was successfully synthesized and the redox activity of the homopolymer film virtually did not change upon repeated cycling between 0.0 and 1.1 V while showing the characteristic of a surface–confined redox couple. The homopolymer has a band gap of 2.02 eV and it displays yellow to blue coloration upon doping. Copolymerization, which is known as an effective method to tune the electrochromic properties of the material, was also realized in the presence of 3,4-ethylenedioxythiophene (EDOT). The copolymer revealed multichromic behavior displaying four different colors. Our studies have shown that SNS-An-Fc based polymers are promising candidates for electrochromic applications.

1. Introduction

Since 1977 [1] conducting polymers continue to fascinate many scientists and it has become the center of attraction of many technological and academic researches. Great efforts have been devoted especially for the design and synthesis of novel polymers in order to achieve desirable properties for commercial applications. Adjustment of optoelectronic properties of a conjugated polymer could be achieved by specific structural changes within the polymer backbone or by the use of distinct functional groups [2–4]. Other than laborious chemical approach, electrochemical copolymerization also provides an effective method for controlling the properties of conducting polymers. Contrary to synthetic approach, especially electrochemical copolymerization is an easy, facile method to unite the electrochromic properties of the parent polymers [5].

The incorporation of organometallic units into conjugated polymers have been particularly investigated owing to their potential application in areas such as electrocatalysis [6], biosensors [7,8], gas sensors [9], photovoltaic devices [10,11], reference electrodes [12]. Among various metallocenes, ferrocene is known for its high stability against humidity and air, therefore it is especially preferred and utilized in most of the pioneer studies. Recently, an interest in ferrocene functionalized conducting polymers has aroused since these materials reveal low redox potential, high electron-donor ability and they generally show the redox properties of both ferrocene and the conducting polymer [13].

It is often the case that the ferrocene groups which are covalently tethered to the monomers cause an interference during electrochemical polymerization and some problems in the deposition of films on electrodes [14,15]. The underlying reason for this circumstance was considered to be due to the large potential difference that the aromatic cation radical produced at the electrode solution interface were scavenged by the neutral ferrocene groups present in the bulk of solution. Hence in most of the previous studies polymerization ferrocene-derivatized pyrrole and EDOT could only be achieved through co-electropolymerization with similar heterocyclic units without ferrocene unit [8,16,17].

Materials based on poly(2,5-dithienylpyrrole) derivatives (polySNS) have developed into one of the most promising electrochromic materials, owing to their low oxidation potential and facile electrochemical polymerization. In order to explore the effect of substitution through pyrrole unit, a number of SNS derivatives have been synthesized with substituted phenyl derivatives [18–25], aryl derivatives [26–29], BODIPY [30], 1,10-phenanthrolinyl [31], anthraquinone [32]. These polymers are reported to have satisfying electrochromic ability. Introduction of a redox group into a conducting polymer could be used to control the electrochromic properties of the polymer and to achieve an additional electrochemical activity. Up to date, utilization of a redox active group such as ferrocene and investigation of its effects on

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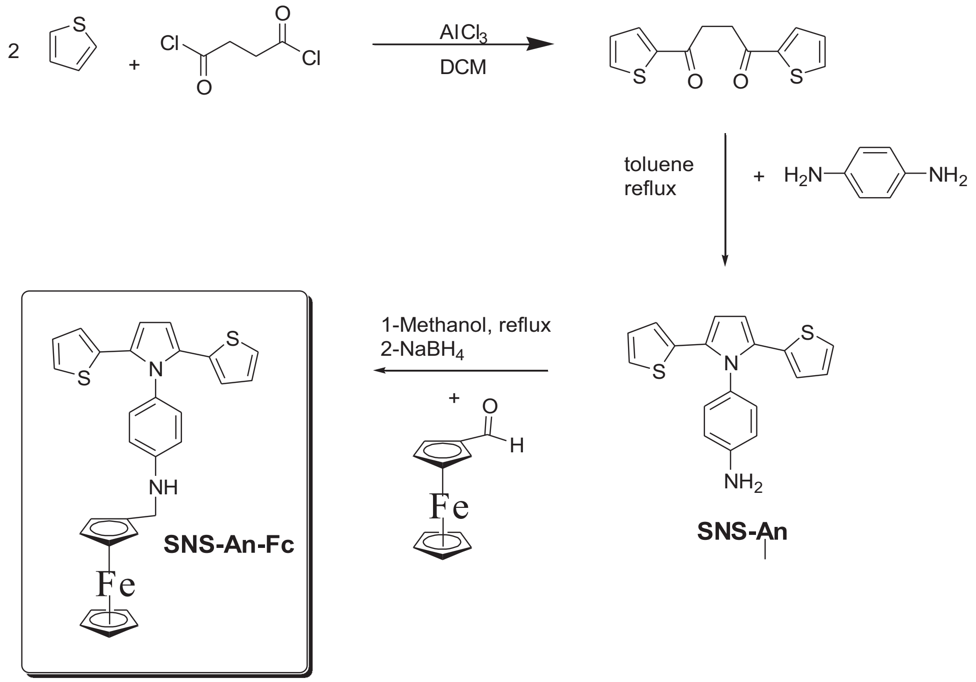

Scheme 1. The synthetic route of SNS-An-Fc.

electrochromic and electrochemical properties on polySNS derivatives were not reported.

Hence, in this study we disclose the synthesis and characterization of optoelectronic properties of a novel ferrocene-functionalized conducting polymer based on 4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-N-(ferrocenyl methyl)-phenylamine (SNS-An-Fc) in detail (Scheme 1). Additionally, novel multi-colored electrochromic copolymer based on SNS-An-Fc and 3,4-ethylenedioxythiophene (EDOT) was achieved by electrochemical copolymerization. Electrochromic properties of all polymers were investigated by spectroelectrochemistry, switching studies and colorimetry measurements.

2. Experimental

2.1. General

All chemicals were purchased from Aldrich, Merck Chemical as analytical grade. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was electroanalytical grade and thiophene, succinyl chloride, *p*-diaminophenylene, EDOT were used as received. Acetonitrile (ACN) was distilled over calcium hydride and kept on 4 Å molecular sieves. 1,4-di(2-thienyl)-1,4-butanedione [33,34] and 4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenylamine [24] were synthesized according to literature.

2.2. Equipments

NMR spectra were recorded with a Bruker Spectrospin Avance DPX-400 spectrometer at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Chemical shifts (δ) were given relative to tetramethylsilane (TMS) as the internal standard. Mass spectroscopy (MS) was performed on DP-MS 5973 HP quadruple MS. The FTIR spectra were recorded on a Brucker Tensor 27 spectrometer. Ivium stat potentiostat/galvanostat was used to supply a constant potential during electrochemical synthesis and cyclic voltammetry. Spectroelectrochemical and kinetic studies of the polymers were performed on Varian Cary 100 UV–vis spectrophotometer. Colorimetry measurements were recorded on a Minolta CS-100A Chroma meter in a proper box having D-50 illumination. Measurements were performed with a 0/0 (normal/normal) viewing geometry as recommended by CIE.

2.3. Synthesis of 4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-N-(ferrocenyl methyl)-phenylamine (SNS-An-Fc)

0.326 g (1 mmol) 4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenylamine and 0.214 g (1 mmol) ferrocene carbaldehyde and ethanol (20 ml) was charged in round-bottomed flask and refluxed for 24 h under nitrogen. Later on 0.0378 g (1 mmol) $NaBH_4$ was added and stirred for another 2 h. Evaporation of the ethanol, followed by column chromatography made it affordable for the title compound to yield in 40%. ^{1}H NMR (in $CDCl_3$) (δ/ppm): 7.14 (d), 7.04 (dd), 6.85 (dd), 6.67 (d), 6.66 (d), 6.54 (s), 4.29 (t), 4.21 (s), 4.19 (t), 4.02 (s). ^{13}C NMR (in $CDCl_3$) (δ/ppm): 148.80, 135.40, 130.89, 130.56, 126.83, 123.70, 123.61, 112.80, 109.03, 68.57, 68.29, 68.08, 43.40. FT-IR (KBr, cm^{-1}): 3407, 3100, 3080, 2820, 1611, 1521, 1461, 1409, 1310, 1254, 1197, 1174, 1104, 1040, 924, 821,757, 692 cm^{-1}. MS· $C_{29}H_{23}FeN_2S_2$ (*m*/*z*) calculated: 521.12 found: 521.

2.4. Synthesis of homopolymer (poly(SNS-An-Fc))

Poly(SNS-An-Fc) films were prepared potentiodynamically on ITO electrodes, using 0.01 M monomer in a solution containing $TBAPF_6$ in dichloromethane (DCM). A platinum wire was used as the counter electrode and Ag/Ag^+ electrode calibrated against ferrocene was used as the reference electrode. During the electrochemical process, the color of the solution in the vicinity of working the electrode darkened progressively. However, as the polymerization proceeded, part soluble oligomers became insoluble and deposited on the working electrode.

2.5. Synthesis of copolymers (poly(SNS-An-Fc-co-EDOT))

SNS-An-Fc (50 mg) was dissolved in 5 ml of DCM and 5 μl of EDOT was introduced into the electrolysis cell containing TBAPF$_6$. The films were either prepared potentiodynamically scanning the potential between 0.0 and 1.1 V or potentiostatically at 1.1 V on ITO glass electrodes. Electrochromic measurements; spectroelectrochemistry, and switching studies of the polymer film deposited on ITO coated glass slide were performed using a UV–cuvette with three-electrodes placed in the sample compartment of a spectrophotometer. In these studies platinum and Ag wires were used as the counter and reference electrodes respectively due to geometrical restrictions [35].

3. Results and discussion

3.1. Synthesis of SNS-An-Fc

4-(2,5-di-Thiophen-2-yl-pyrrol-1-yl)-N-(ferrocenyl methyl)-phenylamine (SNS-An-Fc) was synthesized by four-step synthetic route, as shown in Scheme 1. The first step involves synthesis of 1,4-di(2-thienly)-1,4-butanedione through thiophene and 1,4-dichlorobutanedione and the second step includes a Paal–Knorr reaction between 1,4-di(2-thienly)-1,4-butanedione and *p*-phenylenediamine in the presence of catalytical amount of propionic acid. Finally ferrocene carbaldehyde condenses with SNS-An to form a Schiff base which is subsequently reduced by NaBH$_4$ to yield SNS-An-Fc as an orange powder. Formation of the Schiff base and reduction were carried out in a one-pot without isolation of the Schiff base. Structural investigation of monomer was performed via ^{1}H, ^{13}C NMR, FTIR and MS analyses.

3.2. Redox properties of SNS-An-Fc

The cyclic voltammogram (CV) of SNS-An-Fc in DCM shows a reversible redox process at $E_{\mathrm{p}½} = 0.57$ V which is followed by an irreversible oxidation peak at 0.88 V (Fig. 1a). In order to evaluate the true nature of these redox processes, cyclic voltammogram of the SNS-An (a monomer having the very similar structure, except the ferrocene unit) was also recorded under same conditions. When we compare CV of both monomers it is evident that the reversible redox wave observed in case of SNS-An-Fc is due to presence of electroactive ferrocene moiety. As we could see both monomers revealed an irreversible oxidation processes taking place within the same potential window. Similarity of this oxidation wave in both monomers confirms the absence of direct electronic effect of the ferrocene group on the electron density of the SNS moiety [36,37]. Upon successive cycling homogeneous, adherent thin film coating on the electrode was observed and the color of the solution close to the working electrode changed probably due to some dissolved oligomers.

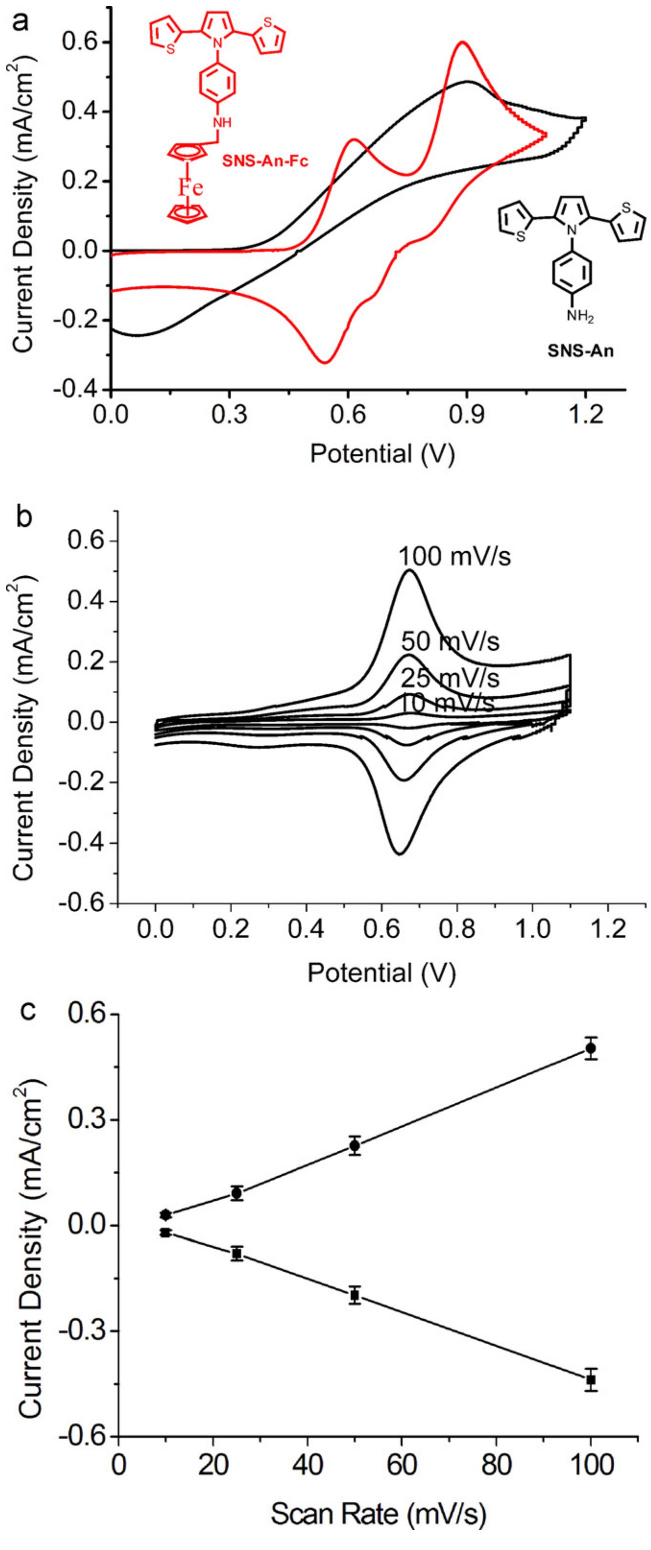

Fig. 1. (a) Cyclic voltammogram of SNS-An-Fc and SNS-An at a scan rate of 100 mV/s, (b) cyclic voltammogram of the homopolymer at various scan rates, (c) plot of anodic and cathodic peak current density vs. scan rate in 0.1 M· TBAPF$_6$/DCM.

Cyclic voltammetry studies, which are given in Fig. 1b, were conducted on the polymer coated electrodes in the same supporting electrolyte system. Similar to the monomer itself a symmetric oxidation wave at around $E_{\mathrm{p,a}} = 0.67$ V which we attribute to Fc/Fc$^+$ oxidation was observed along with the associated reduction wave with approximately equal area to the oxidation wave at around $E_{\mathrm{p,c}} = 0.65$ V at a scan rate of 100 mV/s. Moreover the redox behavior of the ferrocene group (both the peak maximum and the peak width) did not alter upon variation of potential scan range. However, as in the case of other studies [14] a well defined redox couple related to the poly(2,5-dithienylpyrrole) backbone was not observed. The redox activity of the homopolymer film virtually did not change upon repeated cycling between 0.0 and 1.1 V. Conversely, if the applied potential were to be increased furthermore; reduction of the peak was observed. As seen in Fig. 1c the redox wave showed the characteristic of a surface–confined redox couple, with the expected linear relationship of peak current with the potential scan rate having an anodic and cathodic least squares fit of $R = 0.999$; $R = 0.999$, respectively [38]. However, as expected, increase of scan rate beyond 100 mV/s resulted in a shift of peak

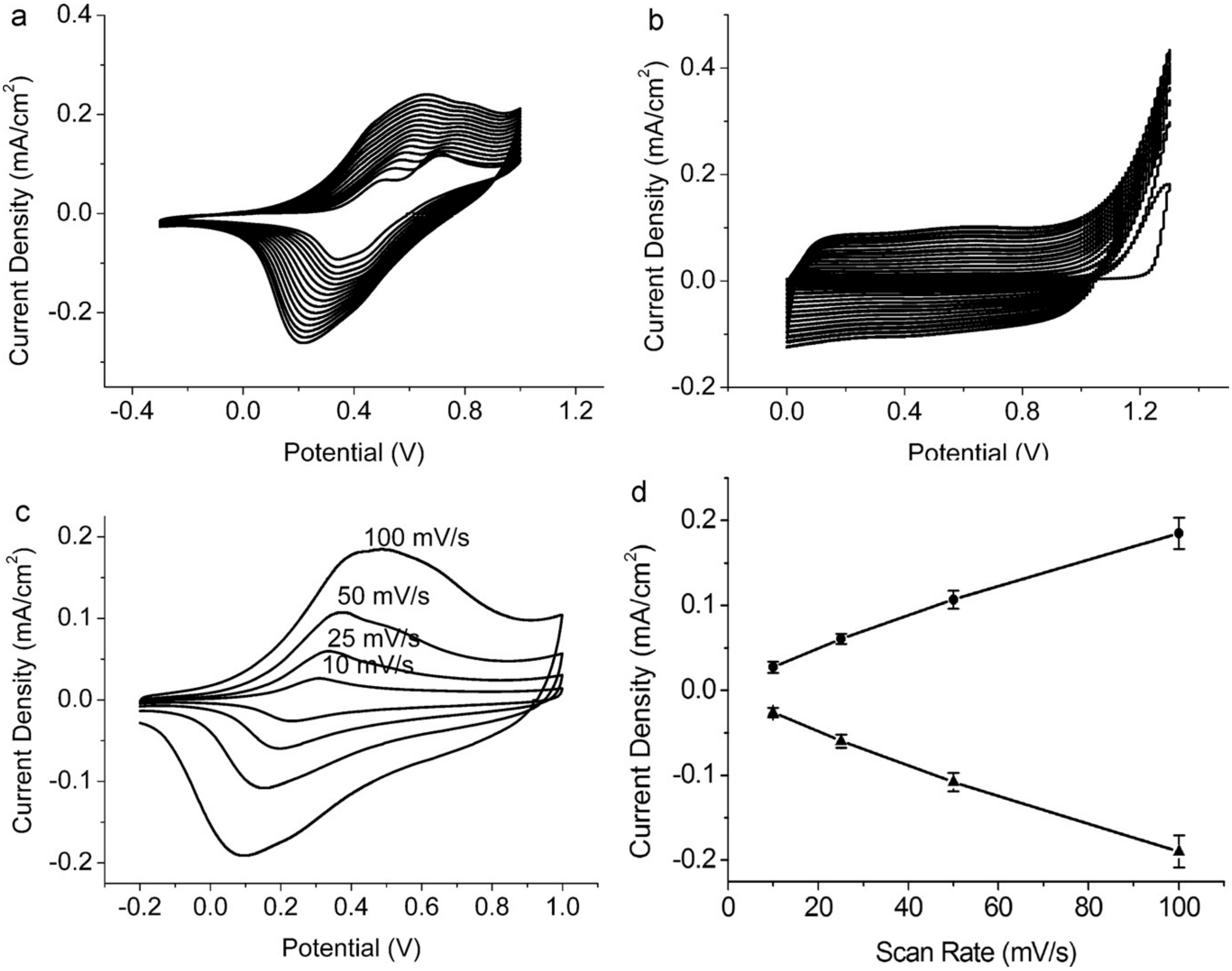

Fig. 2. Cyclic voltammogram of (a) SNS-An-Fc and EDOT, (b) EDOT at a scan rate of 100 mV/s, (c) the copolymer at various scan rates, (d) plot of anodic and cathodic peak current density vs. scan rate of the copolymer in 0.1 M· $TBAPF_6$/DCM.

maximum and deviation from the linear dependence between the current and the scan rate. All these voltammetric studies clearly indicate the success in the synthesis of ferrocene containing electroactive poly(2,5-dithienylpyrrole) and its the surface confined nature.

3.3. Electrochemical copolymerization of SNS-An-Fc with EDOT

Electrochemical copolymerization is an effective, robust approach to attain pristine polymers having sophisticated properties compared to the homopolymers. Fig. 2a and b displays potentiodynamic scans of the monomer in the presence of EDOT and pure EDOT in $TBAPF_6$/DCM system with ITO working electrode at a scan rate of 100 mV/s, respectively. During potentiodynamic scan the anodic peaks of the copolymer appeared at 0.50 and 0.71 V. As seen redox potentials of copolymer is noticeably different from PEDOT and poly(SNS-An-Fc) which could be interpreted as a proof for the formation of a true copolymer [24,39,40]. The redox activity of the copolymer was investigated in monomer free 0.1 M· $TBAPF_6$/DCM and the related cyclic voltammograms, plots of wave current density versus potential scan rate are illustrated in Fig. 2c and d. Contrary to the homopolymer, the copolymer film revealed a broad, quasi-reversible redox behavior. The discrete redox peaks of the conjugated copolymer backbone and ferrocene were not observed, it was considered that the peaks of the copolymer backbone may be overlapped by that of ferrocene. As seen both the anodic and cathodic current densities of the copolymer shows a linear dependence with the scan rate, having an anodic and cathodic least squares fit of $R = 0.997$; $R = 0.997$, respectively. Such observation indicates that migration of the electroactive species is not diffusion controlled, the electroactive polymer is well adhered and electrode supported.

3.4. Electrochromic properties

The optoelectronic behavior (Fig. 3) of the poly(SNS-An-Fc) was investigated by UV–vis spectrophotometer in a monomer-free electrolyte system while incrementally increasing the applied potential between −0.2 and 1.1 V. In the neutral state, poly(SNS-An-Fc) showed a single broad absorption peak at 440 nm, which corresponded to the $\pi-\pi^*$ transition (E_g = 2.02 eV) and the polymer appeared yellow in color. On the other hand, poly(SNS-An) synthesized and characterized under same conditions revealed single broad transition at 425 nm, which could be considered an effect of ferrocene substitution. Upon increase of the applied potential, the peak height of the interband transition was suppressed and simultaneously a new absorption peak appeared due to charge carrier band formations. At 1.1 V the homopolymer appeared in blue color revealing a transition 661 nm. Absence of isosbestic point during electrochemical oxidation might indicate the occurrence of more

Table 1
Electrochromic properties of the polymers.

Material	λ_{max} (nm)	E_g[b] (eV)	Switching time (s)[c] t_{100}, t_{95}, t_{90}	Optical contrast (%T)	L, a, b[d]
Poly(SNS-An-Fc)	440[a]	2.02	0.78, 0.50, 0.45	13.7	86, 6, 28 (n) 82, −4, 5 (i) 76, −5, 2 (o)
Poly(SNS-An-Fc-EDOT)	524[a]	1.72	0.87, 0.59, 0.50	43.0	47, 13, −3 (n) 68, −5, −2 (i) 66, −9, −2 (o)

[a] For the neutral polymer films.

[b] Band gap, estimated from the optical absorption band edge of the films.

[c] The switching time of the copolymers at t_{100}: 100%, t_{95}: 95%, t_{90}: 90% of ultimate contrast.

[d] Colorimetry study results at n: neutral, i: intermediate, o: oxidized states.

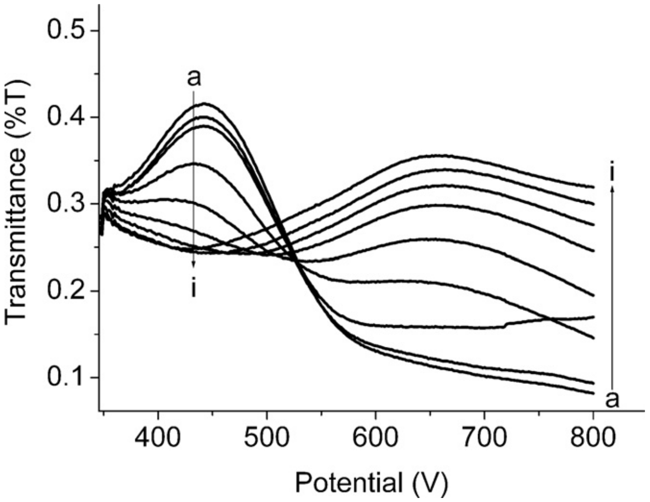

Fig. 3. Spectroelectrochemistry of poly(SNS-An-Fc) film on an ITO coated glass slide in monomer-free 0.1 M· TBAPF$_6$/ACN electrolyte solution at applied potentials: (a) −0.2 V, (b) 0.0 V, (c) 0.2 V, (d) 0.4 V, (e) 0.6 V, (f) 0.8 V, (g) 0.9 V, (h) 1.9 V, and (i) 1.1 V.

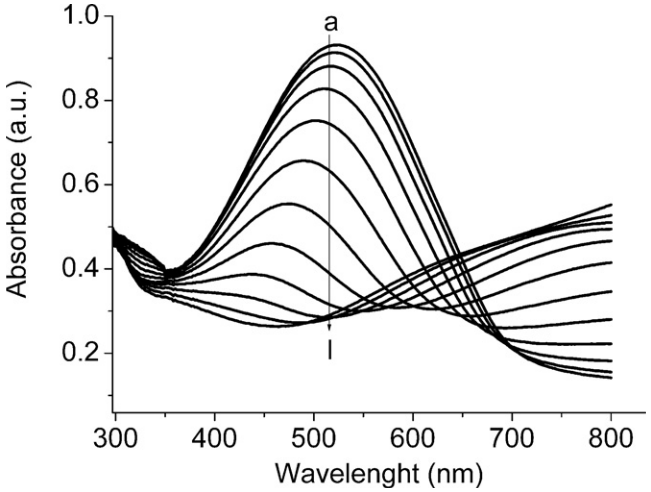

Fig. 4. Spectroelectrochemistry of poly(SNS-An-Fc-co-EDOT) film on an ITO coated glass slide in monomer-free 0.1 M· TBAPF$_6$/ACN electrolyte solution at applied potentials: (a) −0.2 V, (b) 0.0 V, (c) 0.1 V, (d) 0.2 V, (e) 0.3 V, (f) 0.4 V, (g) 0.5 V, (h) 0.6 V, (i) 0.7 V, (j) 0.8 V, (k) 0.9 V and (l) 1.0 V.

than two spectroscopically distinct charge carriers or the dielectric effect in condensed phases which also leads to the disappearance of the isosbestic point in two-component systems [41] Contrary to the most of the ferrocene containing polymers poly(SNS-An-Fc) did not rapidly lose its electroactivity. The switching ability of the polymer was evaluated by monitoring the changes in the percent transmittance (at 440 nm) of the polymer while applying potential in square wave form between −0.5 and 0.8 V. The polymer's switching time and optical contrast were calculated to be 0.78 s and 13.7%, respectively.

On the other hand, poly(SNS-An-Fc-co-EDOT), synthesized at 1.1 V, revealed maximum absorption at 524 nm (Fig. 4). Upon increase of the applied potential, the peak height of the interband transition was suppressed and simultaneously a new absorption peak appeared at around 760 nm due to charge carrier band formations. Fig. 5 represents the normalized spectra and colors of the copolymer and the parent homopolymers in their neutral state. The copolymer's band gap was calculated as 1.72 eV and it was in between the two parent polymers (PEDOT: 1.6 eV and poly(SNS-An-Fc): 2.02 eV). The optoelectronic properties of the copolymer confirmed that the copolymer has intermediate characteristics between the homopolymers, implying that polymer backbone may accordingly be composed of SNS-An-Fc and EDOT units. The copolymer displayed distinct multichromism, revealing maroon, cupper rose, gray, blue colors in neutral, mid and highly oxidized state. In order to measure these colors in an accurate-quantitative manner and represent the track of doping induced state, we performed colorimetry analysis and provided the relevant data in Table 1.

Kinetic studies were performed in order to evaluate the switching ability of the copolymer synthesized at 1.1 V. Fig. 6a, b and c represent the percent transmittance change (at 524 nm), applied potential profile and the current density of the copolymer as a function of time. As seen the copolymer is persistent and uniform transmittance and current change upon alternation of applied potential. The switching time of the copolymer was measured at 90% of ultimate contrast and it was found to be 0.5 s and the optical

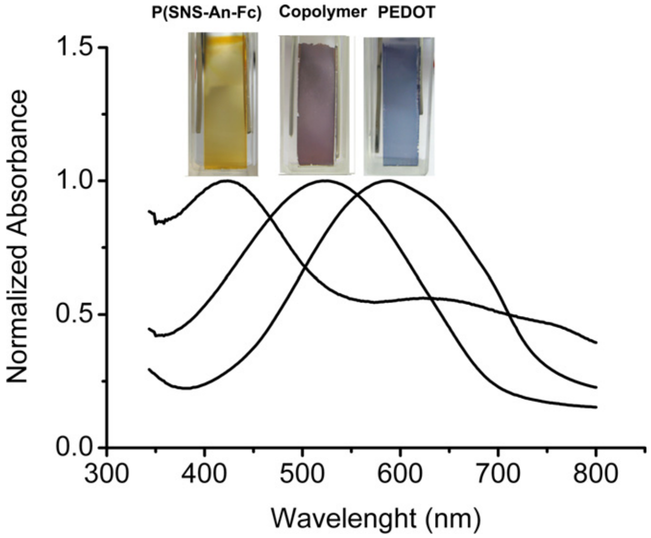

Fig. 5. Normalized UV–vis spectrum of homopolymer, copolymer and PEDOT in neutral state.

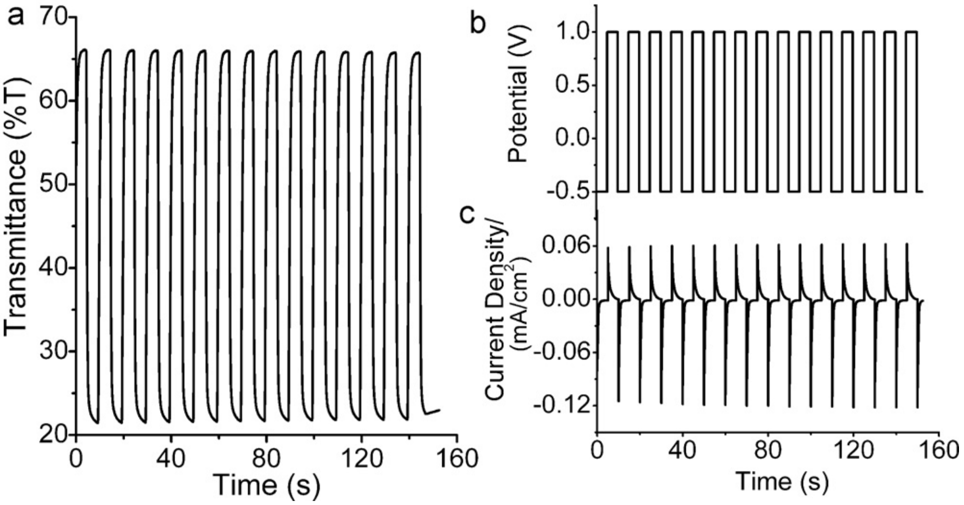

Fig. 6. (a) *T*%, (b) applied potential, (c) current density, during repetitive electrochromic switching of the copolymer deposited at 1.1 V on ITO electrode, monitored at 555 nm in 0.1 M· $TBAPF_6$/ACN.

contrast was calculated to be 43.0%. Such definition was proposed [42,43] due to limitation of human eye to perceive any variations beyond this limit.

4. Conclusions

In this study, we disclosed synthesis and characterization of a novel ferrocene containing poly(2,5-dithienylpyrrole) which formed stable films on the electrode surfaces during electrochemical polymerization. Contrary to most of the literature studies based on pyrrole and EDOT derivatives, SNS-An-Fc revealed facile, rapid homopolymerization, electrochemical stability and yellow to blue coloration upon doping. Additionally, electrochemical copolymerization of SNS-An-Fc and EDOT was achieved and investigation of electrochromic properties of both the homopolymer and the copolymers were performed via spectroelectrochemistry, kinetic and colorimetry studies. Our studies have shown that SNS-An-Fc based polymers are promising candidates as electrochromic device applications. Owing to superior properties of these polymers we are now focused on detailed studies on both electrochromic devices and biosensors.

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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.electacta.2011.12.097.

References

[1] H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang, A.J. Heeger, Chem. Commun. 578 (1977).
[2] J. Roncali, Macromol. Rapid Commun. 28 (2007) 1761.
[3] A. Balan, D. Baran, L. Toppare, Polym. Chem. 2 (2011) 1029.
[4] M.P. Beaujuge, R.J. Reynolds, Chem. Rev. 110 (2010) 268.
[5] C.L. Gaupp, J.R. Reynolds, Macromolecules 36 (2003) 6305.
[6] T.K. Maishal, B. Mondal, V.G. Puranik, P.P. Wadgaonkar, G.K. Lahiri, A. Sarkar, J. Organomet. Chem. 690 (2005) 1018.
[7] N.C. Foulds, C.R. Lowe, Anal. Chem. 60 (1988) 2473.
[8] J. Chen, C.O. Too, G.G. Wallace, G.F. Swiegers, B.W. Skelton, A.H. White, Electrochim. Acta 47 (2002) 4227.
[9] S. Radhakrishnan, S. Paul, Sens. Actuators B 125 (2007) 60.
[10] E. Ramasamy, J. Lee, Carbon 48 (2010) 3715.
[11] R.A. Afre, Y. Hayashi, T. Soga, Synth. Met. 160 (2010) 779.
[12] T. Inagaki, M. Hunter, X.Q. Yang, T.A. Skotheim, Y. Okamoto, J. Chem. Soc. Chem. Commun. (1988) 126.
[13] C. Peng, X. Zhou, G.Z. Chen, F. Moggia, F. Fages, H. Brisset, J. Roncali, Chem. Commun. 48 (2008) 6606.
[14] A. Iraqi, D.F. Pickup, Polym. Int. 55 (2006) 780.
[15] G. Zotti, S. Zecchin, G. Schiavon, A. Berlin, G. Pagani, A. Canavesi, Chem. Mater. 7 (1995) 2309.
[16] H. Brisset, A.E. Navarro, C. Moustrou, I.F. Perepichka, J. Roncali, Electrochem. Commun. 6 (2004) 249.
[17] J. Chen, C.O. Too, G.G. Wallace, G.F. Swiegers, Electrochim. Acta 49 (2004) 691.
[18] S. Tarkuc, E. Sahmetlioglu, C. Tanyeli, I.M. Akhmedov, L. Toppare, Sens. Actuators B 121 (2007) 622.
[19] B. Yigitsoy, S. Varis, C. Tanyeli, I.M. Akhmedov, L. Toppare, Thin Solid Films 515 (2007) 3898.
[20] S. Tarkuc, E. Sahmetlioglu, C. Tanyeli, I.M. Akhmedov, L. Toppare, Electrochim. Acta 51 (2006) 5412.
[21] A. Arslan, O. Turkarslan, C. Tanyeli, I.M. Akhmedov, L. Toppare, Mater. Chem. Phys. 104 (2007) 410.
[22] E. Sahin, E. Sahmetlioglu, I.M. Akhmedov, C. Tanyeli, L. Toppare, Org. Electron. 7 (2006) 351.
[23] S. Varis, M. Ak, C. Tanyeli, I.M. Akhmedov, L. Toppare, Eur. Polym. J. 42 (2006) 2352.
[24] E. Yildiz, P. Camurlu, C. Tanyeli, I.M. Akhmedov, L. Toppare, J. Electroanal. Chem. 612 (2008) 247.
[25] N.A. Lengkeek, J.M. Harrowfield, G.A. Koutsantonis, Synth. Met. 160 (2010) 72.
[26] A. Cihaner, F. Algı, Electrochim. Acta 53 (2008) 2574.
[27] A. Cihaner, F. Algı, J. Electroanal. Chem. 614 (2008) 101.
[28] S. Koyuncu, C. Zafer, E. Sefer, F.B. Koyuncu, S. Demic, I. Kaya, E. Ozdemir, S. Icli, Synth. Met. 159 (2009) 2013.
[29] A. Cihaner, F. Algı, Electrochim. Acta 54 (2008) 665.
[30] A. Cihaner, F. Algı, Electrochim. Acta 54 (2008) 786.
[31] J. Hwang, J.I. Son, Y. BoShim, Solar Energy Mater. Solar Cells 94 (2010) 1286.
[32] G. Wang, X. Fu, J. Huang, L. Wu, Q. Du, Electrochim. Acta 55 (2010) 6933.
[33] P. Camurlu, A. Cirpan, L. Toppare, Synth. Met. 146 (2004) 91.
[34] P.E. Just, K.I.C. Ching, P.C. Lacaze, Tetrahedron 58 (2002) 3467.
[35] E. Sahin, P. Camurlu, L. Toppare, Synth. Met. 156 (2006) 1073.
[36] B. Jousselme, P. Blanchard, E. Levillain, R.D. Bettignies, J. Roncali, Macromolecules 36 (2003) 3020.
[37] H. Brisset, A.E. Navarro, F. Moggia, B. Jousselme, P. Blanchard, J. Roncali, J. Electroanal. Chem. 603 (2007) 149.
[38] P. Chandrasekhar, Conducting Polymers, Fundamentals And Applications: A Practical Approach, Spring, 1999, p. 83.
[39] P. Camurlu, S. Tarkuc, E. Şahmetlioglu, İ.M. Akhmedov, C. Tanyeli, L. Toppare, Solar Energy Mater. Solar Cells 92 (2008) 154.
[40] P. Camurlu, E. Şahmetlioğlu, E. Şahin, İ.M. Akhmedov, C. Tanyeli, L. Toppare, Thin Solid Films 516 (2008) 4139.
[41] I.A. Vinokurov, J. Kankare, J. Phys. Chem. B 102 (1998) 1136.
[42] D.M. DeLongchamp, M. Kastantin, P.T. Hammond, Chem. Mater. 15 (2003) 1575.
[43] Y. Coskun, A. Cirpan, L. Toppare, Polymer 45 (2004) 4989.