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Journal Name

ARTICLE

A soluble and fluorescent new type thienylpyrrole based conjugated polymer: Optical, electrical and electrochemical properties

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Recently, increased attention has been focused on synthesis of soluble and processable conducting polymers due to interests in their potential application. For this purpose new type electroactive 2,5-di(2-thienyl)pyrrole derivative was synthesized and its novel solution-processable and fluorescent polymer namely, poly(N-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-3,4,5-tris(dodecyloxy) benzamide) (P(TPDOB)) was electrochemically synthesized. Characterization of monomer and polymer were performed by ¹H-NMR, ¹³C-NMR, cyclic voltammetry, UV-vis and fluorescence spectroscopy. This soluble polymer has very well-defined and reversible redox processes in acetonitrile-lithium perchlorate (ACN/LiClO₄) couple. Moreover, P(TPDOB) illustrate multielectrochromic behavior: blue in the oxidized state, caesious in the intermediate state and greenish in the neutral state. Also the copolymer consists of EDOT and TPDOB was synthesized by cyclic voltammetry. Copolymer film has superior electrochromic and electrical properties when compared with homopolymer. Furthermore, fluorescence features of the monomer and polymer were investigated. Although monomer is violet light emitter, its polymer is a yellow light emitter. Synthesis of this new type solution-processable and fluorescent conducting polymer is an alternative to conventional synthesis of soluble conducting polymers which allow direct application of conductive polymer to any desired surface for potential technological application.

Introduction

There has been great interest in the area of conjugated polymers (CPs) which display a wide range of applications during the last three decades. Among these, polythiophenes, a versatile class of CPs, are still of growing interest due to their potential applications in the development of new materials such as light emitting diodes (LEDs)^{1,2}, photovoltaics³ and transistors⁴. In particular, they have been envisioned as one of the most useful electrochromes for high performance innovative devices⁵, sensors⁶, electrochromic device⁷⁻⁹, smart windows¹⁰, mirrors¹¹ and camouflage materials¹². Although conducting polymers have various potential applications, lack of solubility is an impediment in their direct application^{13,14}. So, their insolubility and infusibility restricted their use. This essential problem has been overcome by preparing hybrid materials in which the properties of different compounds could be combined¹³. With the discovery of soluble derivatives, conjugated polymers have become one of the major research topics. For instance, Ferraris et al. was

obtained soluble and conducting polymers via various techniques of α -linked thienylpyrrole ring systems with alkyl substituents on the position of the central pyrrole ring¹⁵. The following studies of Ferraris et al. and Toppare et al. mainly focused on the elucidation of both electrochemical and optical properties of *N*-substituted polythienylpyrroles¹⁶⁻¹⁸. Electropolymerizations of monomers derived from 2,5-di(2-thienyl)pyrroles are also frequently reported by others authors^{19,20}. The corresponding conducting polymers containing aromatic tailoring groups at *N*-pyrrole position presented interesting electrochromic and fluorescent properties. Some important applications can be derived from materials that combine these properties.

Herein we reported the fluorescent and electrochromic properties of a new soluble and fluorescent polymer (P(TPDOB)), which is based on SNS with a hydrazide appendage; namely, N-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-3,4,5-tris(dodecyloxy) benzamide (TPDOB). In this unique combination, while SNS unit provides low oxidation potential as well as electrochromic features; long alkyl chains contribute to polymer's solubility. More importantly, the polymer, P(TPDOB), had a specific optical band gap (2.01 eV) to reflect the greenish color in the neutral state and blue colors upon oxidation. Besides, a new multicolored electrochromic copolymer based upon TPDOB and EDOT was carried out by electrochemical copolymerization. The obtained copolymer

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film showed four different colors with the different applied potential. Besides that, fluorescence measurement showed that the soluble polymer is good yellowish light emitter. Finally, there are only a very limited number of examples of processable neutral state green electrochromic material in the literature²¹. We believe that this highly soluble conducting polymer is promising candidates for a wide range of applications.

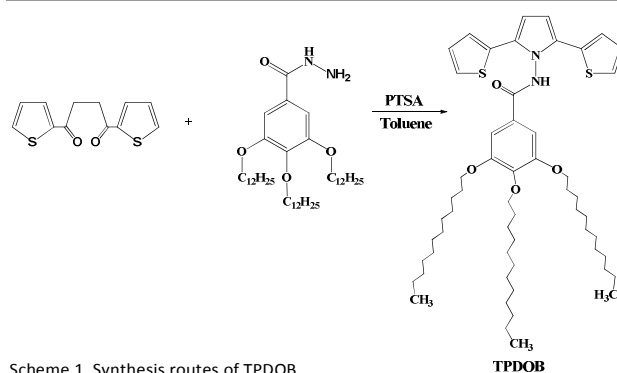
Experimental

2.1. Equipments

NMR spectrum of the monomer was recorded on a Bruker-Instruments-NMR Spectrometer (DPX-400) using CDCl_3 as the solvent. The FTIR spectra were recorded on a Varian 1000 spectrometer. Ivium Compactstat potentiostat/galvanostat was used to supply a constant potential during the electrochemical synthesis and cyclic voltammetry experiments. An Agilent 8453 UV-vis spectrophotometer was used in order to conduct the spectroelectrochemical studies of the conducting polymers. Colorimetry measurements were made with a Minolta CS-100 Spectrophotometer. Elemental analysis of the monomer was performed on LECO-CHNS-932.

2.2. General synthesis of monomer

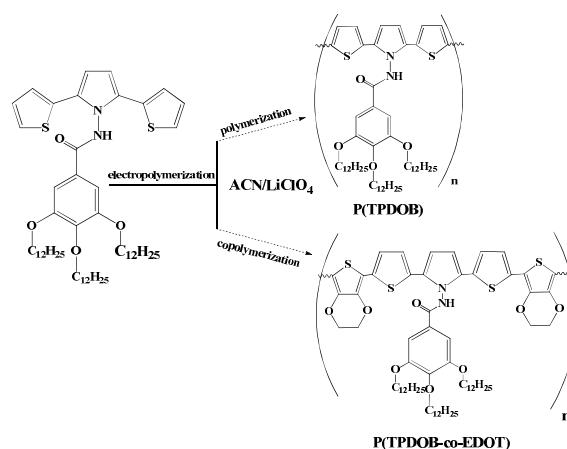
3,4,5-tris(dodecyloxy)benzohydrazide was synthesized using a method similar in the literature²². The monomer (TPDOB) was prepared from reaction of 1,4-di(2-thienyl)-1,4-butanedione and 3,4,5-tris(dodecyloxy)benzohydrazide²³ in toluene. All experiments were performed under dry, oxygen-free argon by using Standard Schlenk techniques. Solvents were dried with a convenient drying method and distilled before use. A small amount p-toluenesulphonic acid (PTSA) is used as catalysts in this reaction. A round bottomed three-necked flask equipped with a reflux condenser, was charged with 1 g (4 mmol) 1,4-di(2-thienyl)-1,4-butanedione, 2.75 g (4 mmol) 3,4,5-tris(dodecyloxy) benzohydrazide, 35 mg (0.2 mmol) PTSA, 0.2 mL DMSO and 50 mL toluene. The mixture was stirred and refluxed for 18 h under argon atmosphere. Dark-green oily product was dissolved 30 mL methanol and the precipitated solid was filtered and air dried, yield 2.168 g %60.05 (mp 126°C). The synthetic route of the monomer is shown in Scheme 1. The structure of the monomer was confirmed by ^1H NMR and ^{13}C NMR spectral analyses (Fig. 1a and b). Elemental analysis: C, 73.01; H, 9.43; N, 3.02; S, 7.05.



Scheme 1. Synthesis routes of TPDOB

2.3 Electropolymerization and characterization of P(TPDOB) and P(TPDOB-co-EDOT)

A three-electrode cell assembly was used where the working electrode was an ITO-coated glass, the counter electrode was a platinum wire and an Ag wire (0.35 V vs. SCE) was used as the pseudo reference electrode. An Ivium potentiostat/galvanostat interfaced with a personal computer was used in all electrochemical measurements. Cyclic Voltammetry technique was employed to investigate electrical activity of the compounds and determine their oxidation-reduction peak potentials. All of the electrochemical experiments were carried out using a $\text{LiClO}_4/\text{ACN}$ supporting electrolyte-solvent couple at room temperature. The homopolymer films of P(TPDOB) was carried out potentiostatic method at 1.3 V in (0.05 M) $\text{LiClO}_4/\text{ACN}$ (Scheme 2). Additionally, the conducting copolymers P(TPDOB-co-EDOT) was obtained in the presence of 10^{-2} M of TPDOB and 10^{-2} M EDOT (Scheme 2). 10^{-2} M of TPDOB and 10^{-2} M of EDOT was dissolved in 0.1 M LiClO_4 in ACN. The copolymer was potentiostatically (at 1.5 V) deposited on ITO.



Scheme 2. Synthesis routes of P(TPDOB) and P(TPDOB-co-EDOT)

3. Results and discussion

3.1. Synthesis and structural characterization

The monomer, N-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-3,4,5-tris(dodecyloxy)benzamide (TPDOB) has been synthesized via reaction of 1,4-di(2-thienyl)-1,4-butanedione and 3,4,5-tris(dodecyloxy)benzohydrazide. The structure of the monomer was approved by ^1H -NMR and ^{13}C -NMR spectral analyses (Figure 1a and Figure 1b). According to ^1H -NMR and ^{13}C -NMR spectra, the monomer have the characteristic peaks of the structure.

^1H NMR (400 MHz, CHCl_3) δ 8.65 (s; 1H^f , -NH-), 7.08 (m; 8H^e), 6.48 (s; 2H^d), 3.97(m; 6H^c), 1.26 (m; 60H^b), 0.89 (s; 9H^a).

^{13}C NMR (101 MHz, CHCl_3) δ 167.09, 152.95, 142.17, 135.47, 132.42, 129.36, 127.35, 126.32, 124.67, 107.87, 106.18, 91.35, 82.94, 73.49, 69.11, 29.36, 22.69, 14.19.

On the other hand, the structure of the polymer was confirmed by ^1H -NMR spectral analyses (Figure 1c). The ^1H -NMR spectra of the polymer have the characteristic peaks of the structure.

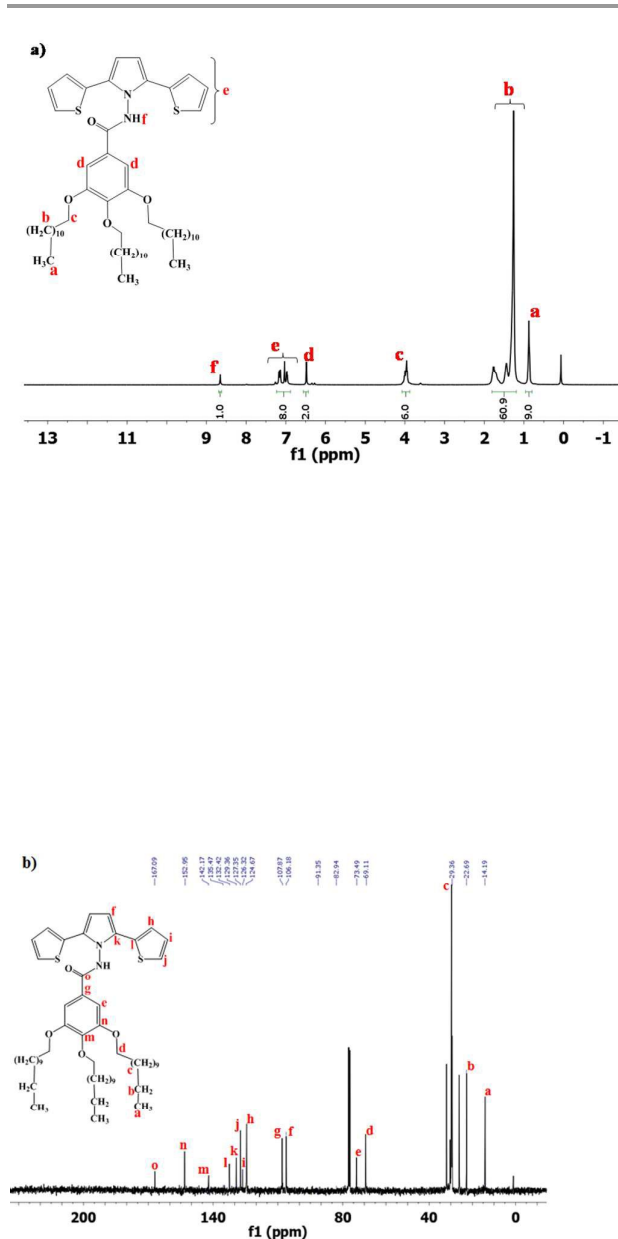
^1H -NMR (400 MHz, CHCl_3) δ 7.26 (s, 10H), 3.99 (s, 6H), 2.04 – 0.28 (m, 70H).

3.2. Electrochemical polymerization and electrochromic properties

3.2.1 Electrochemical polymerization and characterization of P(TPDOB) and P(TPDOB-co-EDOT)

Typical successive CV's of the P(TPDOB) and P(TPDOB-co-EDOT) during the process of electrochemical polymerization are shown in Fig. 2a and Fig. 2b. The cyclic voltammetric data prove that the electrochemical formation of the polymer film on the surface of the working electrode and the increase in the redox cycle current demonstrated that increased the amount of polymer on the electrode. Such behavior is consistent with other studies in the literature based on SNS-based derivatives²⁴. During potential scanning, the formation of the polymer film has been observed even with the naked eye.

Fig. 2b presents the CV of (TPDOB-co-EDOT). As shown in the figure, the oxidation peak of the homopolymer is different from the oxidation peak of the copolymer. Copolymerization has been evidenced that successfully. As the CV scan continued, a polymer film was formed onto the surface of the ITO electrode. It is apparent that the CV process of the comonomer is different from that of the parent monomers, indicating the formation of the copolymer.



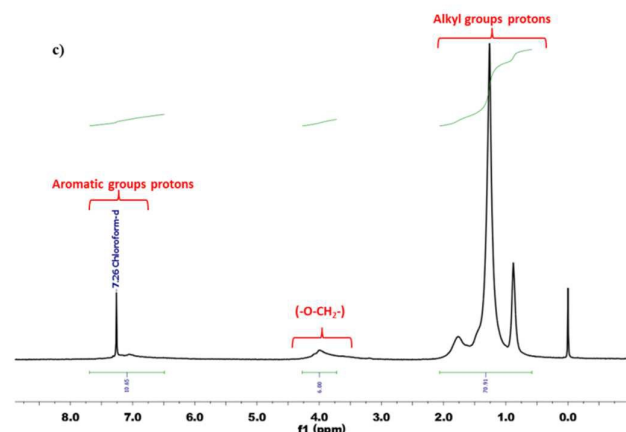


Figure 1. a) ^1H -NMR spectrum of the TPDOB b) ^{13}C -NMR spectrum of the TPDOB and c) ^1H -NMR spectrum of the P(TPDOB).

The electro activity of the P(TPDOB) and P(TPDOB-co-EDOT) were studied in $\text{LiClO}_4/\text{ACN}$ couple. In Fig. 2c and Fig. 2d cyclic voltammograms and plots of current density vs potential scan rate has been represented. Besides, anodic and cathodic current densities concerning with homopolymer and copolymer shows a linear dependence in parallel with the scan rate, having an anodic and cathodic regression fit of $R = 0.999$; $R = 0.994$ and $R = 1.00$; $R = 1.00$ respectively. Linearity of the peak current values indicated that the polymer growth rate was not diffusion-controlled and polymer films could be reversibly oxidized or reduced.

Besides, the HOMO and LUMO energy levels of TPDOB and TPDOB-co-EDOT molecules can be calculated from the onset oxidation potential ($E_{\text{ox}}(\text{onset})$) and optical band gap as in literature²⁵. HOMO and LUMO energy levels were calculated -4.32, -2.31 eV, and -4.42, -2.76 eV, respectively.

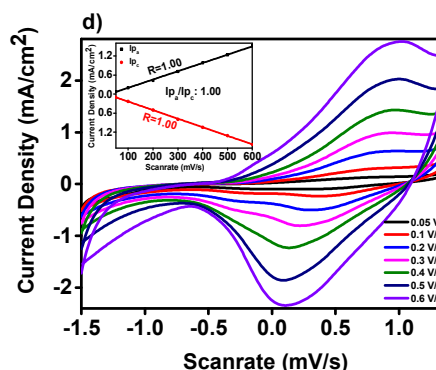
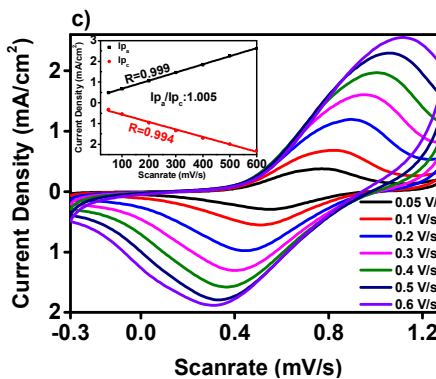
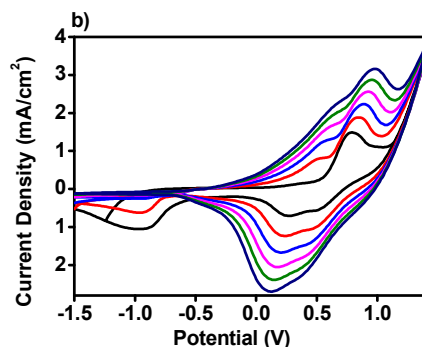
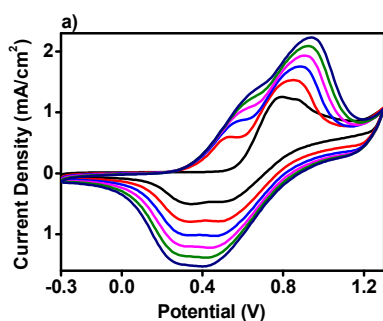


Figure 2. Cyclic voltammograms of a) P(TPDOB) and b) P(TPDOB-co-EDOT), and redox behaviors of c) P(TPDOB) and d) P(TPDOB-co-EDOT) at different scan rates in 0.05 M $\text{LiClO}_4/\text{ACN}$

3.2.2. Stability of P(TPDOB) and P(TPDOB-co-EDOT)

Redox stability is a notable characteristic of conducting polymer with long lifetimes. The main causes of conducting polymer failure are different applied voltages and environmental conditions. The electrochemical stability of P(TPDOB) and P(TPDOB-co-EDOT) films are also investigated by non-stop cycling of the applied potential between -0.3 and 1.3 V, -1.5 and 1.4 V, respectively, with a potential scanning rate of 500 mV/s and presented in Figure 3. As seen in Figure 3a, after 200 cycles, the P(TPDOB) film retains 99% of its original electro activity. For P(TPDOB-co-EDOT), between the 1st and 200th cycles decrease (50%) in the current response was observed

(Figure 3b), which shows that the P(TPDOB) have good environmental and redox stability than P(TPDOB-co-EDOT).

voltammetry with a scan rate of 500 mVs^{-1} $0.05 \text{ M LiClO}_4/\text{ACN}$.

3.2.3. Electrochromic properties of P(TPDOB) and P(TPDOB-co-EDOT)

Spectroelectrochemistry is a useful method for studying the changes in the absorption spectra and obtaining information about the electronic structures of conjugated polymers as a function of the applied potential difference. Figure 4 shows the spectroelectrochemical properties studied by applying potentials ranging between -0.3 and 1.4 V and -1.5 and 1.4 V of P(TPDOB) and P(TPDOB-co-EDOT) film in the monomer-free solution. As seen from Fig. 4a and Fig. 4b, the peak at 455 and 520 nm is assigned to the π - π^* transition of P(TPDOB) and P(TPDOB-co-EDOT), respectively. P(TPDOB) and P(TPDOB-co-EDOT) films has distinct electrochromic properties. Optical band gaps, $\Delta T\%$ and switching time of P(TPDOB) and P(TPDOB-co-EDOT) were calculated as in Table 1.

Table 1. Electrochemical and optical properties of P(TPDOB) and P(TPDOB-co-EDOT).

* LUMO energy levels calculated using optical band-gap values and HOMO energy levels

While P(TPDOB) film has only three colours at different potentials, its copolymer with EDOT has four different colours. Furthermore, copolymerization not only increases the polymer's colour, but also improves its properties, such as optic contrast. However, when the compare stability of P(TPDOB) and P(TPDOB-co-EDOT), copolymerization is caused to fall of stability.

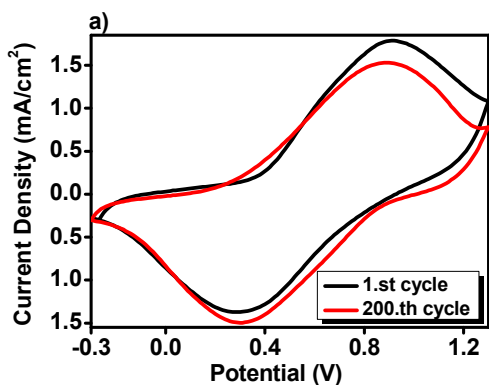
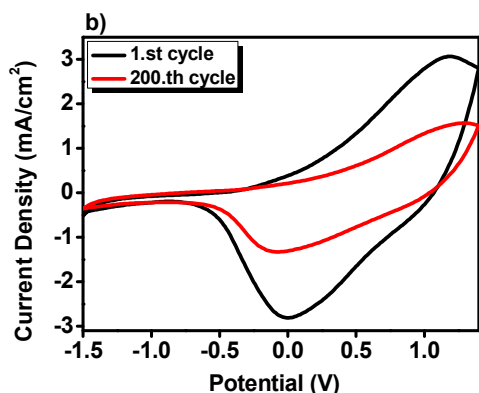
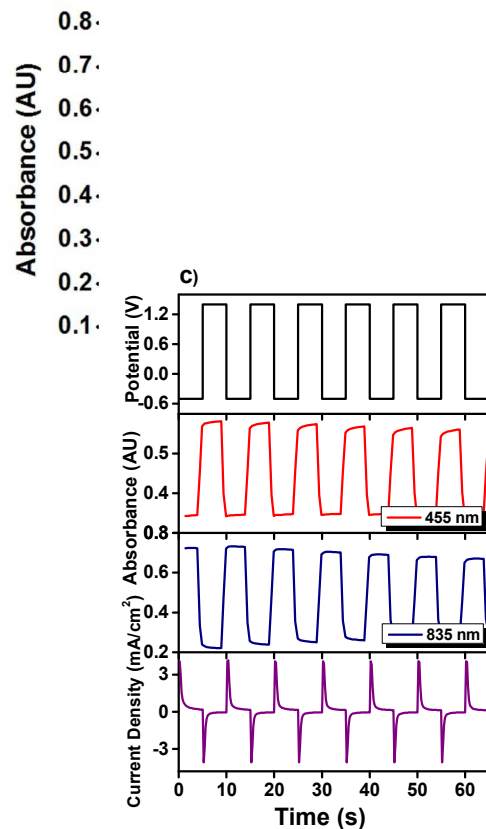
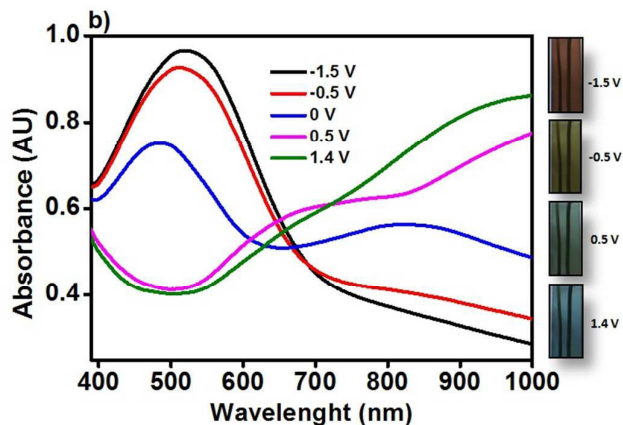


Figure 3. Stability tests of a) P(TPDOB) and b) P(TPDOB-co-EDOT) via cyclic



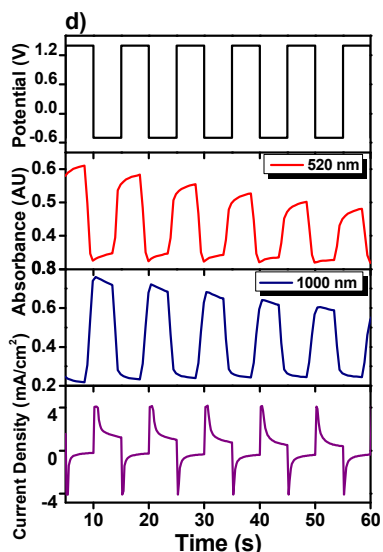


Figure 4. Spectroelectrochemical properties of the a) P(TPDOB) and b) P(TPDOB-co-EDOT), Electrochromic switching, optical absorbance change monitored for c) P(TPDOB) between -0.3 and $+1.4$ V, and d) P(TPDOB-co-EDOT) between -1.5 and $+1.4$ V.

Besides that the colors of the electrochromic polymers were characterized certainly by performing colorimetry measurements. CIE system was used as a quantitative scale to describe and compare colors. Three features of color; luminance (L), hue (a), saturation (b) were measured and represented in Table 2.

Table 2. P(TPDOB) and P(TPDOB-co-EDOT) in accordance with CIE standards.

Polymer	Potential (V)	Luminance (L)	Hue (a)	Saturation (b)
P(TPDOB)	-0.3	66	-18	43
	0.4	53	-6	15
	1.4	58	-11	-14

	-1.5	39	14	17
P(TPDOB-co-EDOT)	-0.5	44	-4	29
	0.5	45	-14	5
	1.4	38	-10	-13

3.3. Fluorescence study

Fluorescence properties of both monomer and polymer were investigated. Since the electrochemically obtained TPDOB and P(TPDOB) were found to be soluble in CHCl_3 , its fluorescence property was investigated in this solvent. The monomer exhibits a three different emission at 395 nm when excited at 312 nm, corresponding to violet color (Fig. 5). Besides that, its polymer has a relatively intense emission at about 511 nm when excited at 426 nm, corresponding to yellow color (Fig. 6). These results indicate that the polymer is a yellowish emitter and may find applications in various fields, such as light emitting diode, organic lasers and electroluminescent materials. Fluorescence properties of the P(TPDOB-co-EDOT) was not examined because of solubility problem.

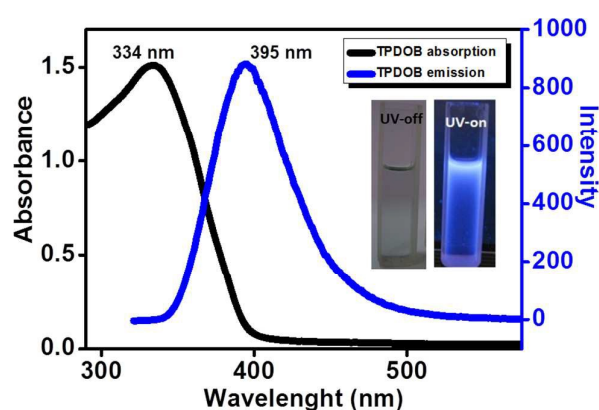


Figure 5. Absorbance and emission spectra of TPDOB in CHCl_3 .

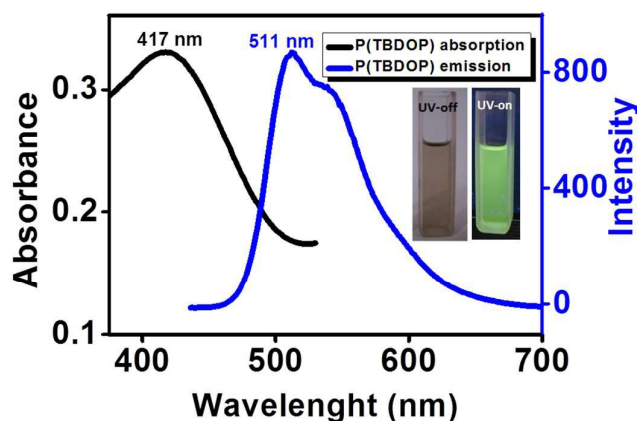


Figure 6. Emission spectra of P(TPDOB) excited at 426 nm in CHCl_3 . Inset Absorbance and emission spectra of P(TPDOB) in CHCl_3 .

Conclusion

A fluorescent and electrochromic properties of a new soluble conducting polymer (P(TPDOB)), which is based on SNS with long alkyl groups functioned hydrazide appendage was investigated. In this unique combination, while SNS unit provides low oxidation potential as well as electrochromic features; long alkyl chains contribute to polymer's solubility. This combination ensured a new electrochrome which had a reversible redox switching and also exhibited multi electrochromic behavior. This wide color range makes the copolymer an excellent candidate for electrochromic device, display or camouflage applications. Additionally, fluorescence studies showed that the new polymer a good yellowish light emitter which may useful in many applications such as LED or organic laser. More importantly, the polymer, P(TPDOB), had a specific optical band gap (2.01 eV) to reflect the green color in the neutral state and blue colors upon oxidation. Besides, a new multicolored electrochromic copolymer based upon TPDOB and EDOT was carried out by electrochemical copolymerization. The obtained copolymer film showed four different colors with the different applied potential. Finally, there are only a very limited number of examples of processable neutral state green colored electrochromic material in the literature. We believe that this highly soluble conducting polymer is promising candidates for a wide range of applications.

Acknowledgements

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