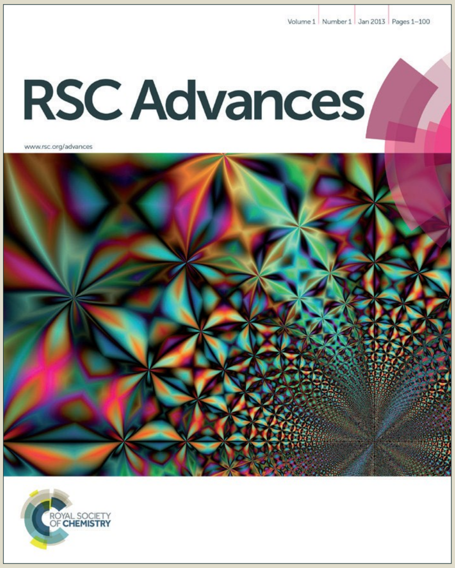
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Smart Window Application of Hydrazide Type New SNS Derivative

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In this article smart window application of the new type thienylpyrrole derivative was presented. For this purpose, new type 2,5-di(2-thienyl)pyrrole derivative which is named N-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-4-(vinyloxy)benzamide (TPVB) has been prepared by the reaction of 1,4-di(2-thienyl)-1,4-butanedione and 4-(vinyloxy)benzohydrazide. Usage of hydrazine instead of amine in synthesis process has been perfectly improved the related polymers' optical properties. Spectroelectrochemical investigations revealed that P(TPVB) is more durable and it has better long-term stability and the lowest band gap compared with the other SNS derivatives. Chronoamperometry experiment showed that P(TPVB) polymer film has excellent redox stability, moderate switching time and it has high optical contrast. So it is possible to use this polymer with superior optical properties in the smart window applications. Smart window based on P(TPVB) and poly(3,4-ethylenedioxythiophene) (P(EDOT)) was set up in a sandwich configuration. Optoelectrochemical investigations displayed that the reduced state of the device displays an orange color whereas it shows blue for the oxidized state. Switching time and optical contrast (Δ%T) of the device for 625 nm have resulted as 1.0 s and 43% respectively.

Introduction

A major amount of interest has been consumed on conducting polymers (CPs) due to usage of the wide field of applications [1]such as solar cell devices [2], light emitting devices [3], electrochromic devices [4] and diverse types of biosensors [5,6,7].
Studies on new functional conductive polymers have attracted great interest of the researchers. Especially, conducting polymers exhibiting electrochromism [8], photochromism [9] due to their optical response property which are particularly desired for the usage in data storage or display technology.
Designing monomer having superior properties is important for technological applications. Currently a rising class of CP, poly(2,5-dithienylpyrrole) derivatives (SNS) have been searched for their electro-optical properties by a number of research groups. There are a lot of manuscripts in literature in which different dithienylpyrrole derivatives containing alkyl derivates [10], aryl derivatives [11,12], substituted phenyl derivatives [13,14,] hyrazide derivates [7], BODIPY [15], anthraquinone [16]. Between them, specially substituted hyrazide derivatives showed higher quality CP films upon electrochemical synthesis. Their electrochemical polymerization of this type of thienylpyrrole derivative was easily obtained due to its low oxidation potential of the monomer and optical, electrical property of the obtained conductive polymer. On the other hand, to our best knowledge, in literature there is only a single study [7] involving an hydrazide functionalized dithienylpyrrole derivative. In this study we have investigated electrochromic and electrochemical properties of new hyrazide functionalized dithienylpyrrole derivative and its usage in smart window application.
According to above considerations a new monomer, N-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-4-(vinyloxy)benzamide (TPVB) is obtained by Paal-Knoor pyrrole synthesis [17,18] and its homopolymer (P(TPVB)) was obtained by electrochemical method. Moreover, we constructed a high quality absorption/transmission type smart window in ITO|P(TPVB)||Gel Electrolyte||P(EDOT)|ITO configuration.

Experimental

Equipments

NMR spectrum of TPVB was recorded on a Bruker-Instruments-NMR Spectrometer (DPX-400) using $CDCl_3$ as the solvent. The FTIR spectra were recorded on a Perkin Elmer FT-IR spectrometer. Ivium Compactstat was used to cyclic voltammetry experiments and to supply a constant potential during the electrochemical synthesis and. Agilent 8453 UV-vis spectrophotometer was used in order to perform spectro-

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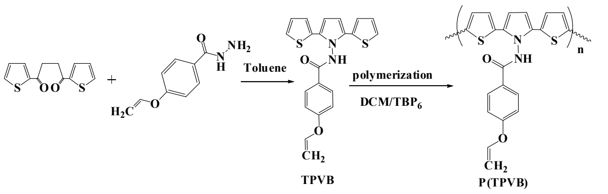
electrochemical studies of the CP. Elemental analysis of the monomer was performed on LECO-CHNS-932.

Monomer synthesis

The reagents 1,4-di(2-thienyl)-1,4-butanedione and 4-(vinyloxy)benzohydrazide were synthesized in accordance with the method found in the literature [19]. All experimental studies were performed under inert atmosphere. All solvents were distilled, dried and saturated with argon. (TPVB) was obtained from condensation of 1,4-di(2-thienyl)-1,4-butanedione and 4-(vinyloxy)benzohydrazide in the existence of catalytic amount of p-toluenesulphonic acid (PTSA). A round bottomed flask was charged with 1 g (4 mmol) 1,4-di(2-thienyl)-1,4-butanedione, 0,72g (4 mmol) 4-(vinyloxy)benzohydrazide, 35 mg (0.2 mmol) PTSA, 0.2 mL DMSO and 50 mL toluene. The reaction mixture was refluxed for 24 h under argon atmosphere. In order to eliminate oily by-products, darkened solution was filtered. After the mixture was cooled to ambient condition, title compound was filtered off and washed with pentane (3x15 mL) to give a green powder, yield 1.5 g %96 (mp 195 °C). The synthetic route of the monomer is shown in Scheme 1. The structure of the monomer was confirmed by 1H NMR and 13C NMR spectral analyses (Fig. 1a and b). Elemental analysis: C, 64.19; H, 4.13; N, 7.62; S, 16.24.

Electrochemical polymerization of P(TPVB)

Cyclic voltammetry (CV) experiments were performed using a potentiostat (Ivium potentiostat/galvanostat) with common three electrode cell. This electrochemical cell contains a working electrode (ITO-coated glass), a counter electrode (platinum wire) and a Ag wire (0.35 V vs. SCE) used as the pseudo reference electrode. Cyclic voltammetry technique (CV) was used to analysis the electrochemical behaviour of the materials and identifies their redox peak potentials. All electrochemical experiments were carried out in tetra butyl ammonium hexafluoro phosphate (TBP$_6$) / dichloromethane (DCM) solvent-electrolyte couple at room temperature. Electropolymerization of TPVB was carried out via potentiostatic method in (0.05 M) TBP$_6$/DCM at 1.2 V (Scheme 1).



Scheme 1. Synthesis route of TPVB and P(TPVB)

Results and discussion

Structural characterization

^{1}H-NMR and ^{13}C-NMR Spectra

The monomer, N-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-4-(vinyloxy) benzamide (TPVB) has been obtained via condensation reaction of 1,4-di(2-thienyl)-1,4-butanedione and 4-(vinyloxy) benzohydrazide. Structural analysis of the TPVB was performed by ^{1}H-NMR and ^{13}C-NMR spectral analyses. The ^{1}H-NMR and ^{13}C-NMR spectra of the TPVB have characteristic peaks of the structure.

^{1}H-NMR (400 MHz, 25 °C, in DMSO-d^6) 11.82 δ (s; 1H^{e,} -NH-), 7.96δ (d; 2H^d), 7.37δ (d; 2H^f), 7.26δ (d; 2Hh), 7.12δ (t; 2H^g), 7.01δ (d; 2H^c), 6.57δ (s; 2H^k), 6.05δ (br s; 1H^b), 5.35δ (2H^a).

^{13}C-NMR (101 MHz, DMSO) δ 165.91 (s), 161.98 (s), 133.68 (s), 132.82 (d, J = 3.0 Hz), 130.17 (s), 129.37 (s), 127.76 (s), 124.94 (s), 123.71 (d, J = 3.1 Hz), 118.38 (s), 115.21 (s), 107.25 (s), 68.89 (s).

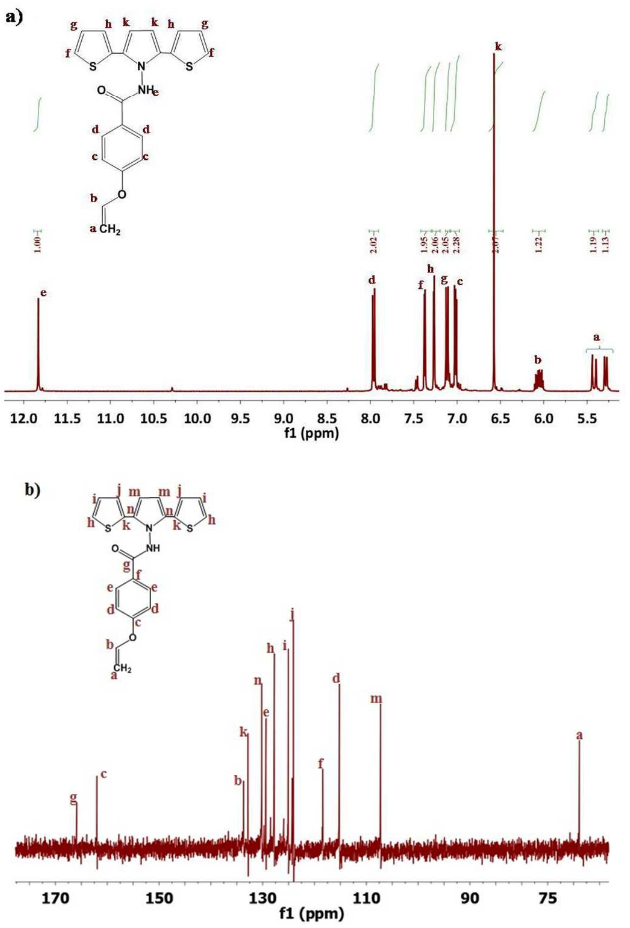


Figure 1. a) ^{1}H-NMR spectrum of TPVB, b) ^{13}C-NMR spectrum of the TPVB

FT-IR Spectra

FTIR spectra of TPVB and P(TPVB) are given in Figure 2. The monomer (TPVB) revealed the following absorption peaks: 3219 cm^{-1} (N–H stretching), 3111 cm^{-1} (CH$_2$=CH- stretching), 2991 cm^{-1} (C–Hα stretching of thiophene), 1659 cm^{-1} (-C=O stretching). Predictable peaks of the TPVB remained unperturbed upon electrochemical polymerization. FTIR spectrum of the P(TPVB) displays a strong peak at 1049 cm^{-1} which belongs to the dopant ions. Because of more conjugated structure of P(TPVB), a new band appears at 1680 cm^{-1}. On the other hand, C–Hα stretching absorption bands of thiophene moiety in the monomer at 2991 cm^{-1} disappeared completely for the P(TPVB) [20]. This shows that polymerization take place from 2,5 positions of thiophene moiety of the TPVB.

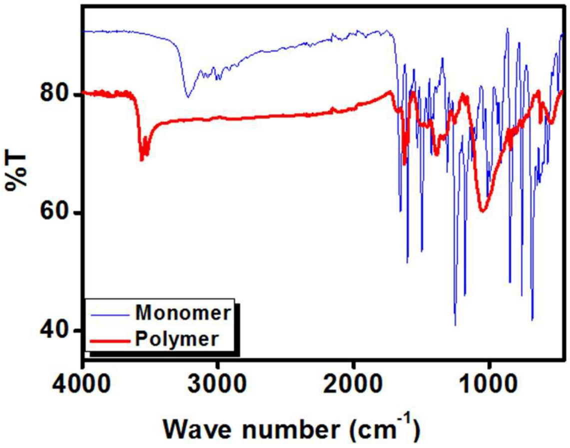


Figure 2. FT-IR spectra of monomer and polymer

Electrochemical polymerization and electrochromic properties

Electrochemical polymerization and characterization of P(TPVB)

Typical consecutive CV of the TPVB in the course of electrochemical polymerization is displayed in Fig. 3a. TPVB showed an irreversible broad oxidation peak at about 0.9 V, indicating the emergence of radical cation of the TPVB through its dithienylpyrrole moiety in the potential scale of -0.1/+1.2 V. Also increasing in the redox wave currents imply that the quantity of the P(TPVB) on the electrode was increased [21]. Adherent and homogeneous thin film deposition on the electrode was observed in the course of potential scanning.

Electroactivity of the P(TPVB) was investigated in monomer free TBP_6/DCM system. CVs and plots of potential scan rate vs wave current density are displayed in Fig. 3b. As observed both the cathodic and anodic current densities of the P(TPVB) reveal a linear dependence with the scan rate, having an cathodic and anodic regration fit of R = 0.9875; R = 0.9825, respectively. The wave currents have linear relationships with potential scan rates, which are the characteristics of mass transfer in the electroactive film on the electrode. This consideration demonstrates that migration of the electroactive species is not diffusion controlled and conducting polymer film is well adhered the electrode. Besides, the HOMO and LUMO energy levels of TPVB molecule can be calculated from the onset oxidation potential (E_{Ox}(onset)) and optical band gap as in literature [22]. HOMO and LUMO energy levels were calculated as -4.54, -2.55 eV, respectively.

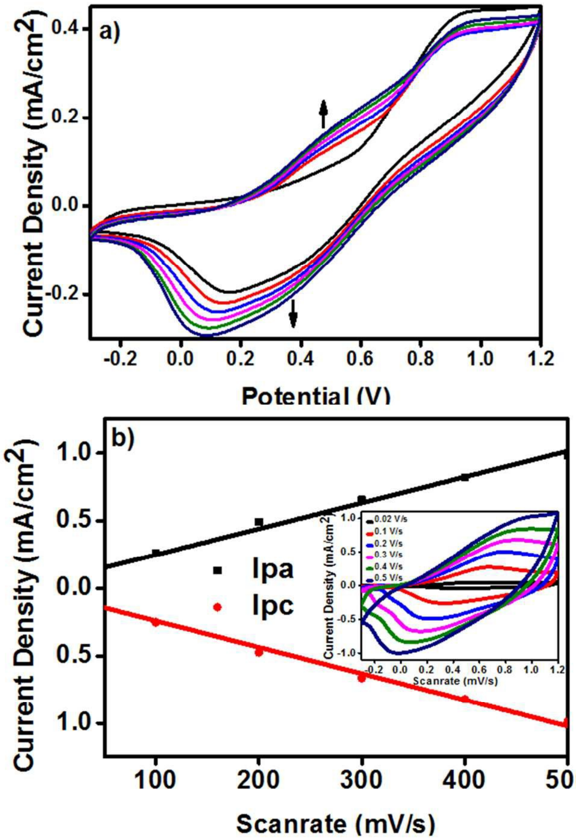


Figure 3. Potentiodynamic electropolymerization of P(TPVB) (a), Cyclic voltammograms of the P(TPVB) on ITO electrode in 0.05 M TBP6/DCM at various scanrate (b).

Electrochromic properties of P(TPVB)

Spectroelectrochemistry has been broadly used to evaluate the electronic structure and the character of electrochromism in CPs. Figure 4a and b show the spectroelectrochemical properties of P(TPVB) film investigated by applying potentials ranging between -0.2 and 1.0 V in the monomer free solution. It can be concluded from Fig. 4a, the peak at 430 nm at neutral state is appointed to the π-π* transition of P(TPVB). ΔT% and switching time found to be 23% and 2.5 s for 430 nm, respectively and ΔT% and switching time for 875 nm is found to be 42% 2.5 s. Besides, optical band gap (Eg) was calculated as 1.99 eV.

P(TPVB) film has distinct electrochromic properties. The colors of P(TPVB) film at different applied potentials were revealed three different hues: blue (1.0 V), greenish (0.4 V), and reddish orange (-0.2 V), which is different from the electrochromic properties of the other SNS derivatives. Comparative literature survey on SNS derivatives are given in Table 1.

Table 1. Spectroelectochemical data for SNS derivates.

Structure	λ_{max}(nm)	Eg (eV)	%ΔT	Reference
	430	**1.99**	**23 (430 nm)** **42 (830 nm)**	**This work**
	411	2.13	16.5 (780 nm)	16
	338	2.96	33 (437 nm)	23
	430	2.34	-	24
	334	3.36	20 (860 nm)	25

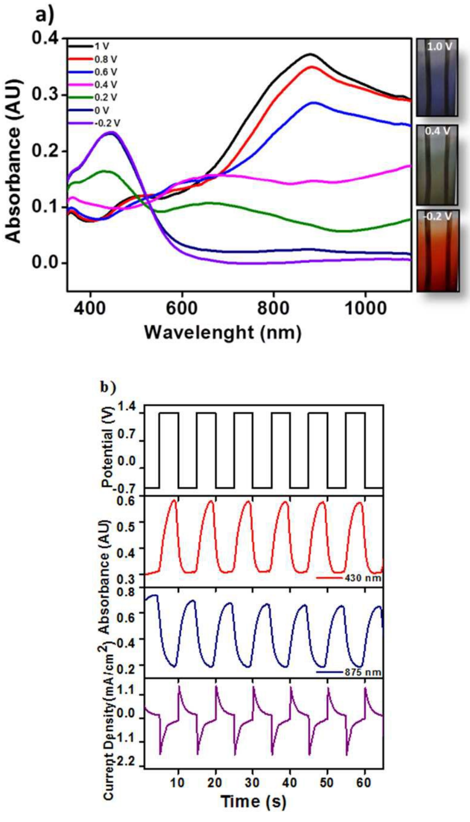


Figure 4. UV-vis spectroelectrochemical spectra at different potentials (a),Potential–time, absorbance–time, current density–time graphics(b), of P(TPVB) film on te ITO glass in 0.05 M TBP$_6$/DCM solution.

In-situ polymerization of P(TPVB)

Oxidative electropolymerization is a classical process for synthesis electrically CPs. Polymeric films can be effectively deposited on the conducting electrodes where their resultant optical and electrical properties can be easily modified by several electrochemical and coupled in situ techniques.

In-situ electrochemical synthesis of TPVB was analyzed at 1.4 V in TBP$_6$/DCM by UV-vis spectrophotometer at every 10 s time interval (Figure 5a).

As it can be shown in Figure 5, absorbance values increase linearly until a certain time.

After this certain time absorbance linearity continues with the square root of the time due to polymerization rate becomes diffusion controlled (Figure 5.b).

This fact can be explained by consumption of monomer due to polymerization in the diffusion layer and after this certain time polymerization rate becomes diffusion controlled.

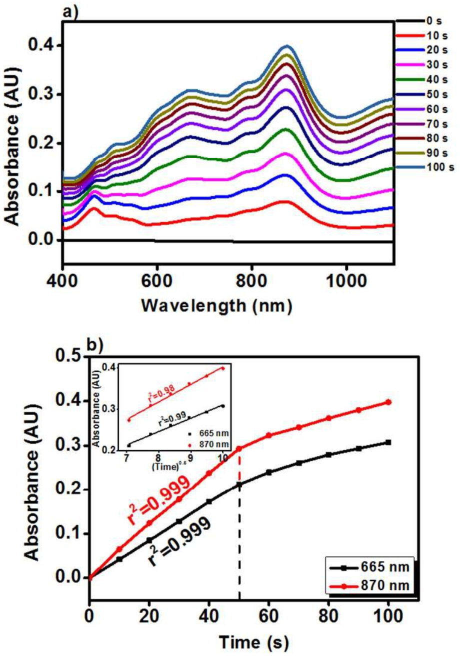


Figure 5. Absorbance recorded at different wavelengths during the polymerization. Inserted figure represents absorbance changes recorded with the square root of the time at different wavelenght (between 50 and 100 s).

Thermal Analysis

Thermal analyses of TPVB and P(TPVB) were carry out in the range 30^{0}C to 1000^{0}C at a heating rate of 10^{0}C/min under nitrogen atmosphere. Because influences of intermolecular forces due to secondary valance bonds as a result of induction, dipole-dipole interaction, and hydrogen bonding are crucial for functional polymers, the thermal stability of polymer film (P(TPVB)) is much higher than its monomer. The weight loss were found 92% and 17% for TPVB and P(TPVB), respectively (Fig 6a and Fig.6b).

DTA thermogram of the TPVB reveals a melting point at 195 ^{o}C. It is durable up to 220 ^{o}C and it begins to degrade at this temperature. In the DTA thermogram of the homopolymer, there is a exothermic peak at transitions at 56.8 ^{0}C due to removal of the solvent (Fig 6d).

It was found that TPVB melts at 195.8 ^{0}C from Fig 6c. The melting of TPVB is an exothermic process due to it melts with decomposition.

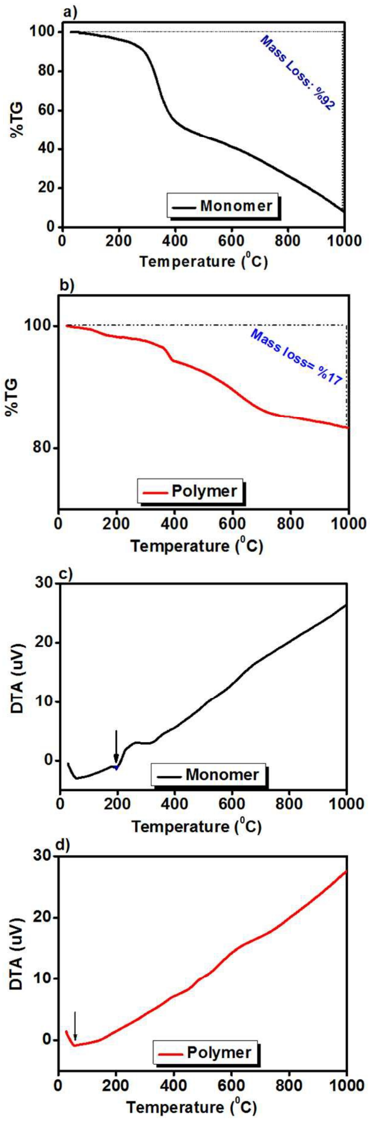


Figure 6. TG curves of a) TPVB, b) P(TPVB) and DTA curves of c) TPVB, d) P(TPVB) at 10 ^{0}C/min

Spectroelectrochemistry of ECD

In this research, the gel electrolyte which is used provide to passage of electrone, was prepared according to the reported procedure [26]. EDOT was used as the cathodically and TPVB as the anodically coloring electrochromic materials. EDOT was electrosynthesized on ITO-coated glass electrode at +1.5 V in 0.1 M TBP_6/DCM supporting electrolyte/solvent couple. Whereas TPVB electrosynthesized at +1.0 V in the same electrolyte–solvent couple. With changing potential, one of the polymer films is oxidized, whereas the other is neutralized, resulting in a color change. Schematic representation of electrochromic device is shown in Fig.7.

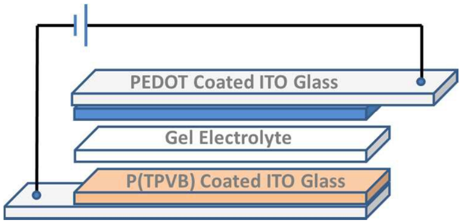


Figure 7. Schematic representation of electrochromic device.

Spectroelectrochemical investigations were fulfilled to search the changes of the electronic transitions of the smart window, with the application of different voltages. Figure 8 represents the UV-vis spectrum of the electrochromic device, recorded by increase of the applied potential between -1.5 and 1.5 V. Due to π-π* transition of the PEDOT (625 nm), PEDOT layer was in its neutral state (blue) at -1.5 V. At this potential smart window has blue colour, because of oxidized state color of P(TPVB) layer is also blue. As the applied potential was increased the polymer layer started to get neutralized, where the absorption at 460 nm was due to π-π* transition of the polymer. Simultaneously, PEDOT layer was in its oxidized state revealing no absorption at the UV-vis region of the spectrum, thus the color of the device was orange.

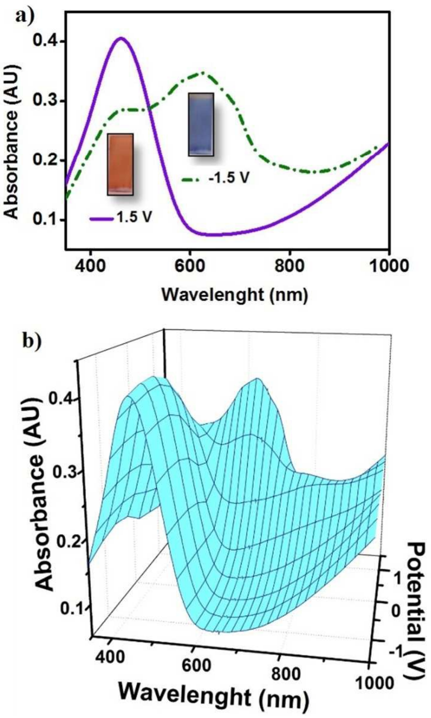


Figure 8. Spectroelectrochemical spectra of device at applied potentials between at -1.5 and 1.5 V a) 2D, b) 3D.

Switching of the ECD

Time elapsed between the lowest and highest optical transmittance values which were calculated from time-absorbance change graph were defined as switching time.

P(TPVB) has complementary visible region absorption to the PEDOT layer. So PEDOT and P(TPVB) could give an optimized contrast ratio in a electrochromic device. P(EDOT) is used as the cathodically coloring and P(TPVB) used as anodically coloring polymer due to theirs outstanding contrast in the visible region. Figure 9 reveals the time-absorbance graph of the electrochromic device in its two extreme states. The device has a Δ%T of 13% at 460 nm (λmax for the device), Δ%T of 43% at 620 nm and switches between states in 1.0 s, respectively under a bias voltage of ±1.5. In this way, high contrast electrochromic device based on conducting polymers can be reproducibly constructed.

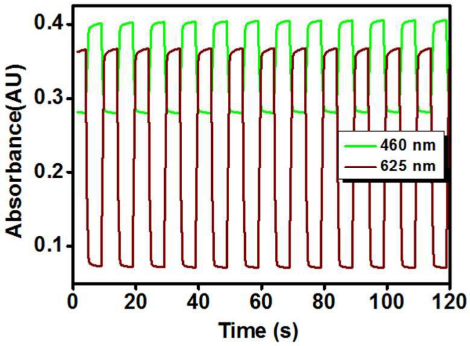


Figure 9. Electrochromic switching, absorbance-time monitored for device at 460 and 625 nm.

Conclusion

As a conclusion, we have presented the synthesis of a novel N-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-4-(vinyloxy)benzamide (TPVB) monomer. TPVB was polymerized electrochemically in order to give thin film electrochromic conducting polymer which have resulted change from reddish orange to blue upon oxidative doping. Furthermore, we successfully set P(TPVB)||P(EDOT) dual type ECD. The ECD showed high optical contrast (ΔT%) and short switching time under atmospheric conditions. Finally, we have shown that TPVB based conducting polymers can be used as electrochromic materials without any doubts.

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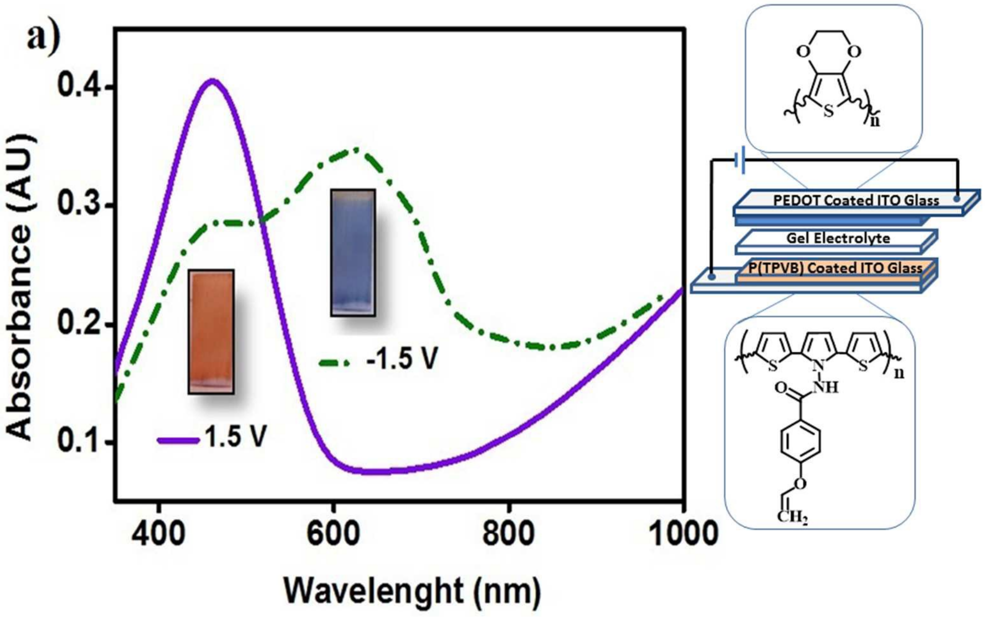

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