



Synthesis of a dipyrromethane functionalized monomer and optoelectrochromic properties of its polymer

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ABSTRACT

A dipyrromethane functionalized monomer; 5-(4-*tert*-butylphenyl)dipyrromethane (BPDP) was synthesized. The structure of the monomer was characterized by nuclear magnetic resonance (¹H NMR and ¹³C NMR) and Fourier transform infrared (FTIR) spectroscopies. Electrochemical polymerization of BPDP was performed in acetonitrile (AN)/LiClO₄. The resulting conducting polymer was characterized by FTIR spectroscopy and electrical conductivity measurements. Spectroelectrochemical behavior and switching ability of P(BPDP) film were investigated by UV–Vis spectroscopy. P(BPDP) revealed color changes between yellow and blue in the reduced and oxidized states, respectively. In order to investigate electrochromic properties and stability of the P(BPDP) in electrochromic device (ECDs) application, dual type polymer ECD based on P(BPDP) and poly(ethylene dioxythiophene) (PEDOT) were constructed. Spectroelectrochemistry, switching ability and stability of the devices were investigated by UV–Vis spectroscopy and cyclic voltammetry.

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1. Introduction

Conducting polymers have received considerable attention in recent years due to their attracting practical applications. Among these polymers, a great deal of work was devoted to polyheterocycles such as polypyrrole and polythiophene.

Electrochemistry has played a significant role in the preparation and characterization of electronically conducting polymers. Electrochemical techniques for the synthesis of conjugated conducting polymers have been considered for a number of optoelectronic and redox properties, such as electrochromism, which is defined as the reversible absorbance/transmittance change in response to an externally applied potential [1]. Conjugated polyheterocyclic polymers, such as polypyrroles, polythiophenes and poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives have been studied as electrochromic materials [1–4].

These materials provide color changes within the visible spectrum, and some exhibit electrochromicity changing color between transparent doped and colored neutral states. The definition has been extended to a multi-spectral energy modulation that might cover ultraviolet (UV), near infrared (NIR), mid infrared (mid-IR) and microwave regions, with “color” corresponding to the response of detectors [5]. Electrochromic techniques are readily employed in a multitude of applications such as display panels, camouflage materials, variable transmittance windows and variable reflectance mirrors [6].

5-Substituted dipyrromethanes are important precursors for the synthesis of meso-substituted porphyrins, corroles, expanded and reduced porphyrins and related compounds such as dipyrrens, calixpyrroles and chlorins [7,8]. Although a number of methods have then been developed for the synthesis and purification of dipyrromethanes in the past decade, there is no report on their electrochromic properties in literature. Design and synthesis of new conjugated polymers are significant as a part of the conducting polymer research. In this study, we synthesized

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dipyromethane functionalized monomer namely 5-(4-*tert*-butylphenyl)dipyromethane (BPDP). Electrochemical polymerization of BPDP was achieved in acetonitrile (AN) using LiClO_4 as the supporting electrolyte. The resultant polymer was characterized by cyclic voltammetry, FTIR spectroscopy and conductivity measurements. The second part of the study was devoted to investigate an interesting property of conducting polymers, the ability to switch reversibly between the two states of different optical properties, “electrochromism”. Finally, we utilized dual type ECDs where P(BPDP) was used as the anodically coloring and PEDOT as the cathodically coloring electrochromic materials.

2. Experimental

2.1. Materials

Trifluoroacetic acid (TFA), 4-*tert*-butylbenzaldehyde, 3,4-ethylenedioxythiophene (EDOT), poly(methyl methacrylate) (PMMA), LiClO_4 were purchased from Aldrich and used without further purification. Acetonitrile (AN) (Merck) and pyrrole (Py) (Aldrich) were distilled prior to use.

2.2. Instrumentation

A three-electrode cell containing an ITO coated glass slide as the working electrode, a platinum foil as the counter electrode and a silver wire as the pseudo-reference electrode were used for electrodeposition of polymer films via potentiostatic or potentiodynamic methods. N_2 gas was passed through the solution to provide an inert atmosphere. All electrochemistry experiments were carried out using a Voltalab PST 50 model potentiostat/galvanostat. NMR spectrum of the monomer was recorded on a Bruker-Instrument-NMR Spectrometer (DPX-400) using CDCl_3 as the solvent and tetramethylsilane as the internal standard relative to which the chemical shifts (δ) are given. The FTIR spectrum was recorded on a Nicolet 510 FTIR spectrometer. Agilent 8453 spectrophotometer was used in order to perform the spectroelectrochemical studies of the copolymer and the characterization of the devices. Colorimetry measurements were performed via Minolta CS-100 spectrophotometer. Conductivity measurements were done with standard four-probe technique via passing a current through the outer probes and measuring the voltage drop across the inner two.

2.3. Synthesis of 5-(4-*tert*-butylphenyl)dipyromethane (BPDP)

5-(4-*tert*-Butylphenyl)dipyromethane was synthesized according to literature [9,10]. A 100 ml dry round-bottomed flask was charged with 4-*tert*-butylbenzaldehyde (15.7 mmol) and 64.2 mmol pyrrole. The mixture was degassed with N_2 for 15 min. Then TFA (84 μL) was then added and the solution was stirred under N_2 at room temperature for 30 min before quenching with triethylamine (1 mL). Ethyl acetate was then added to the reaction mix-

ture. The organic phase was washed with brine and dried over MgSO_4 , and the solvent was removed under vacuum. Recrystallization (ethanol/water (20:1)) afforded a light gray crystalline solid (1.66 g, 33%, mp 160–163 °C) (see Scheme 1).

2.4. Cyclic voltammetry

The oxidation/reduction behaviors of monomer and polymer were investigated by cyclic voltammetry (CV) in 0.1 M LiClO_4/AN . Experiments were carried out in an electrolysis cell equipped with ITO coated glass plate Pt wire and Ag wire as the working, the counter and the pseudo-reference electrodes (0.3 V negative with respect to ferrocene/ferrocene+), respectively.

2.5. Electrochemical synthesis of P(BPDP)

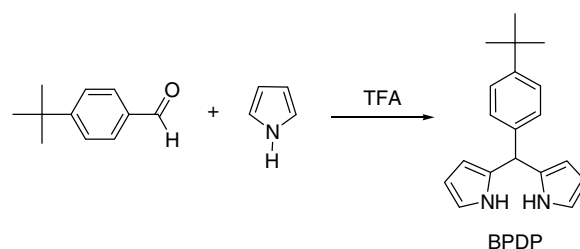
For the synthesis of P(BPDP), 14.4 mmol BPDP were dissolved in 15 mL AN and 0.1 M LiClO_4 were introduced into a single compartment electrolysis cell. Electrolysis was run for 30 min at 1.0 V at room temperature under inert atmosphere. Resulting conducting polymer film was washed with AN after the electrolysis. Similar method was used to synthesize the polymer on an ITO coated glass plate.

2.6. Preparation of the gel electrolyte

The gel electrolyte was prepared by using $\text{LiClO}_4:\text{AN}:\text{PMMA}:\text{PC}$ in the ratio of 3:70:7:20 by weight. After LiClO_4 was dissolved in AN, PMMA was added into the solution. To dissolve PMMA vigorous stirring and heating were required. Propylene carbonate (PC), as the plasticizer, was introduced to the reaction medium when all of the PMMA was completely dissolved. The mixture was stirred and heated until the highly conducting transparent gel was produced [1].

2.7. Construction of electrochromic devices

In this study, P(BPDP) were utilized as the anodically, and PEDOT as the cathodically coloring electrochromic materials. BPDP was deposited on ITO via constant potential electrolysis in 0.1 M LiClO_4/AN supporting electrolyte-solvent couple at +1.0 V. The PEDOT coated electrode was prepared at +1.5 V in the same electrolyte-solvent couple. Chronocoulometry was employed to match the redox charges of the two complimentary polymer films to main-



Scheme 1. Synthesis route of BPDP.

tain a balanced number of redox sites for switching. The redox sites of these polymer films were matched by stepping the potentials between -0.6 and $+0.8$ V for P(BPDP), and -1.0 and $+1.5$ V for PEDOT. ECDs were built by arranging two electrochromic polymer films (one oxidized, the other neutral) facing each other separated by a gel electrolyte.

3. Results and discussion

3.1. FTIR spectra of BPDP and P(BPDP)

The identification of BPDP was carried out by FTIR spectroscopy. Fig. 1a shows the FTIR spectrum of BPDP in the range of 4000 – 500 cm^{-1} and peaks at 3348 cm^{-1} (N–H stretching), 3105 cm^{-1} (aromatic C–H stretching), 2962 – 2870 cm^{-1} (aliphatic C–H stretching), 1558 cm^{-1} , 1462 cm^{-1} (aromatic C=C stretching), 1400 cm^{-1} (symmetric bending vibrational modes of CH_3) 1111 cm^{-1} ,

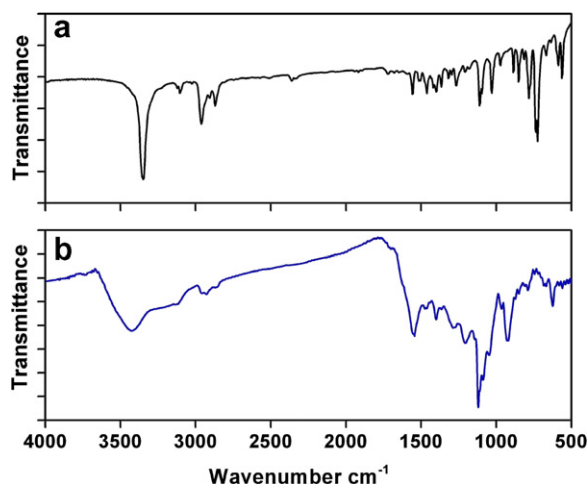


Fig. 1. FTIR spectra of (a) BPDP and (b) P(BPDP).

1096 cm^{-1} and 887 cm^{-1} (N–H and C–H deformation vibrations of 2-subst. Pyrroles) 725 cm^{-1} (sym. skeletal vibration of *tert*-butyl) 563 cm^{-1} (out-of-plane ring deformation vibrations of benzene) were identified.

As seen in Fig. 1b, along with the characteristic monomer peaks, FTIR spectra of P(BPDP) also contain a new shoulder at 1637 cm^{-1} indicating the polyconjugation upon polymerization and the strong absorption peak at 1118 cm^{-1} , 1087 cm^{-1} and 628 cm^{-1} were attributed to the incorporation of ClO_4^- ions into the polymer film as a result of the doping process taking place during the electrochemical synthesis.

3.2. ^1H NMR and ^{13}C NMR spectra of the BPDP

The ^1H NMR spectrum of the monomer (Fig. 2) shows resonance signals of pyrrole, phenyl and tributyl protons of relative intensities corresponding to the number and type of protons.

^1H NMR (400 MHz, 25°C , in CDCl_3) δ ppm: 1.24 (s, 9H), 5.32 (s, 1H), 5.82 (m, 2H), 6.05 (m, 2H), 6.54 (m, 2H), 7.03 (d, $J = 7.8$ Hz, 2H), 7.24 (d, $J = 7.8$ Hz, 2H), 7.72 (br s, 2H).

The ^{13}C NMR spectrum of the monomer is shown in Fig. 3. ^{13}C NMR (400 MHz, 25°C , in CDCl_3) δ ppm: 149.8, 139.1, 132.8, 128.1, 125.6, 117.1, 108.4, 107.2, 43.6, 34.5, 31.4.

3.3. Cyclic voltammetry

Redox behavior of the monomer (BPDP) was investigated by cyclic voltammetry (CV). CV of the BPDP showed an oxidation between -0.2 and $+0.7$ V and a reduction with a peak at $+0.1$ V. An increase in the peak intensities was observed upon sequential cycles which implies the formation of a polymer on the electrode surface (Fig. 4).

3.4. Conductivity measurements

Electrical conductivity measurement was carried out by using four-point probe technique. The conductivity of P(BPDP) was measured as 6×10^{-4} S cm^{-1} .

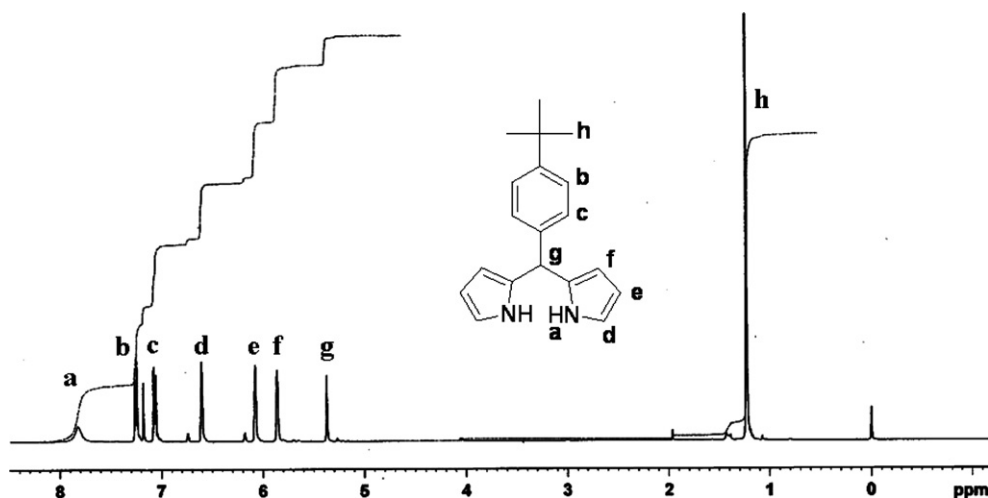


Fig. 2. ^1H NMR spectrum of the monomer.

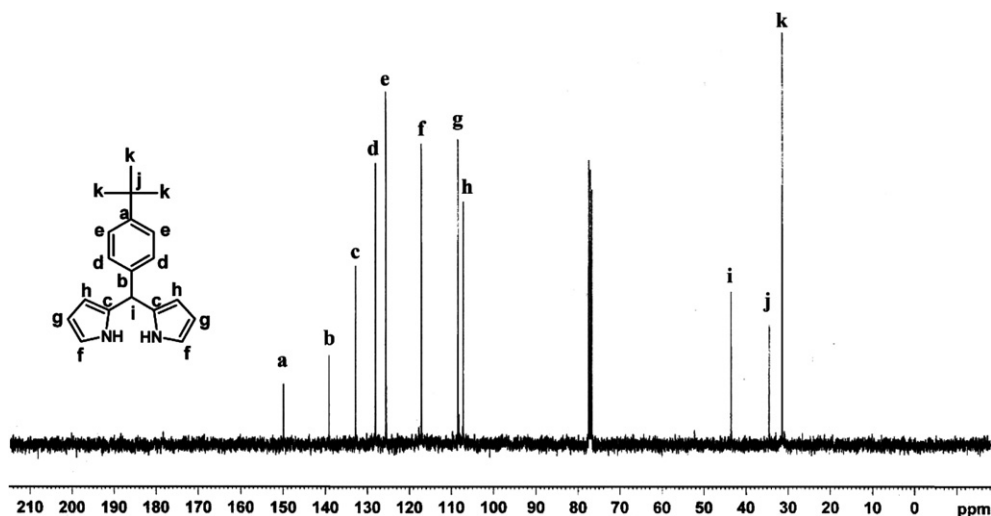


Fig. 3. ^{13}C NMR spectrum of the monomer.

3.5. Spectroelectrochemistry of the P(BPDP)

The film was deposited on ITO via potentiostatic electrochemical polymerization of BPDP in the presence of LiClO_4/AN at +1.0 V. P(BPDP) coated ITO was investigated by UV-Vis spectroscopy in the monomer free electrolytic system by switching between -0.6 V and $+0.8$ V (Fig. 5). The onset energy for the π - π^* transition (electronic band gap) was 2.39 eV and λ_{max} was found to be 364 nm. There was a gradual decrease in the peak intensity at 354 nm

upon increase in the applied potential, which was accompanied by an increase in the intensity of peaks at 523 nm due to the formation of charge carrier bands (Fig. 5). The appearance of the peak at 523 nm is attributed to the evolution of a polaron band. Colors and corresponding L , a and

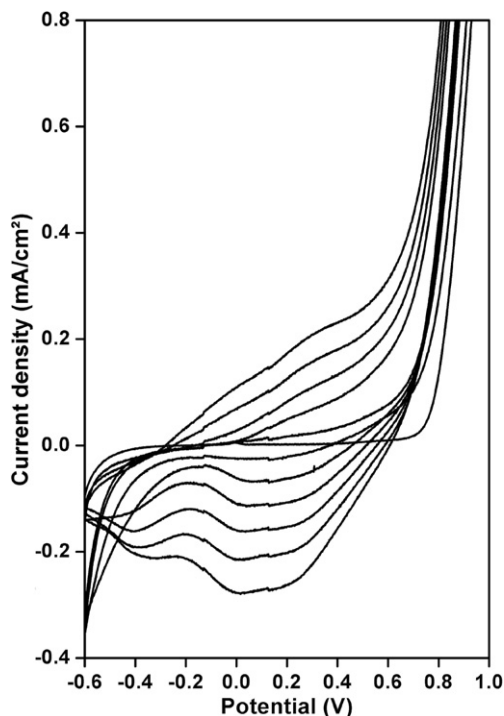


Fig. 4. Cyclic voltammogram of BPDP.

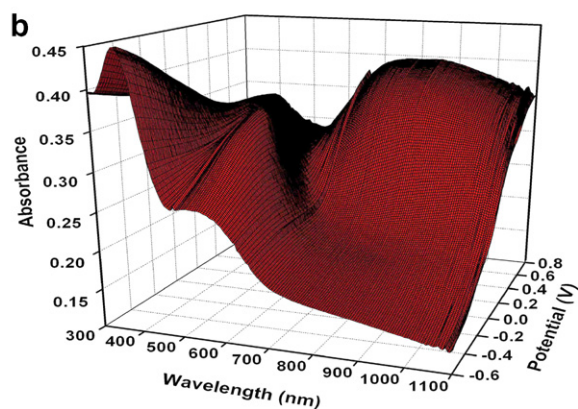
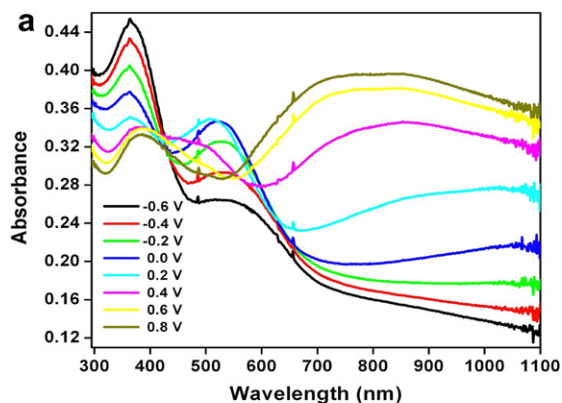


Fig. 5. Optoelectrochemical spectrum of P(BPDP) film at applied potentials between -0.6 and $+0.8$ V (a) (2D) and (b) (3D).

Table 1
Electronic and electrochromic properties of the P(BPDP) and its device

| | λ_{\max} (nm) | Redox state | L | a | b | Color | E_g (eV) |
|-----------------------------|--------------------------|---------------------|----------|------------|-----------|----------------|---------------|
| P(BPDP) | 364 | Oxidized Neutral | 65 90 | 3 –8 | 0 46 | Blue Yellow | 2.39 |
| P(BPDP)/ PEDOT Device | 368 585 | Oxidized Neutral | 81 66 | –12 –10 | 41 –19 | Yellow Blue | – |

b values of P(BPDP) film, where L corresponds to luminance and a , b values to color coordinates, are given in Table 1.

3.6. Electrochromic switching

The ability of a polymer to switch without delay and exhibit a sharp color change are very significant. Double potential step chronoamperometry was carried out to estimate the response time. The potential was stepped between -0.6 and 0.8 V with a residence time of 5 s. in a monomer free solution where the polymer coated ITO electrode was used as the working electrode. During the experiment, the % transmittance at the wavelength of maximum contrast was measured by an UV–Vis spectrophotometer. The optical contrast was monitored by switching the polymer film between -0.6 and 0.8 V at 850 nm. Fig. 6 shows the potential-time (a), current-time (b) and transmittance-time (c) profiles of the P(BPDP) film recorded during double step spectrochronoamperometry. As seen in Fig. 6, P(BPDP) has a fast switching time (1.2 s) and a reasonable optical contrast (35%). These values are comparable with some other anodically coloring polymers [2,5].

3.7. In situ electrochemical polymerization of BPDP

In situ electropolymerization of BPDP was carried out in a solution containing 0.01 M BPDP in LiClO_4 (0.1 M)/AN solvent–electrolyte couple by constant potential of 1.0 V. During the electrolysis, UV–Vis spectra were taken for every 10 s time interval (Fig. 7). It can be concluded from inserted graph in Fig. 7 that there is a linear increase in absorbance with time.

3.8. Scan rate dependence of the peak currents

P(BPDP) film prepared via constant potential electrolysis (1.0 V) was switched in a monomer free electrolyte to yield a single, well-defined redox process (Fig. 8a). The current response was directly proportional to the scan rate indicating that the polymer film was electroactive and adhered well to the electrode. Anodic and cathodic peak currents shows a linear dependence as a function of the scan rate as illustrated in Fig. 8b. This demonstrates that the electrochemical processes are not diffusion limited and reversible up to a scan rate of 400 mV s^{-1} .

3.9. Spectroelectrochemistry of electrochromic device (ECD)

A dual type ECD consists of two electrochromic materials (one anodically coloring, the other cathodically color-

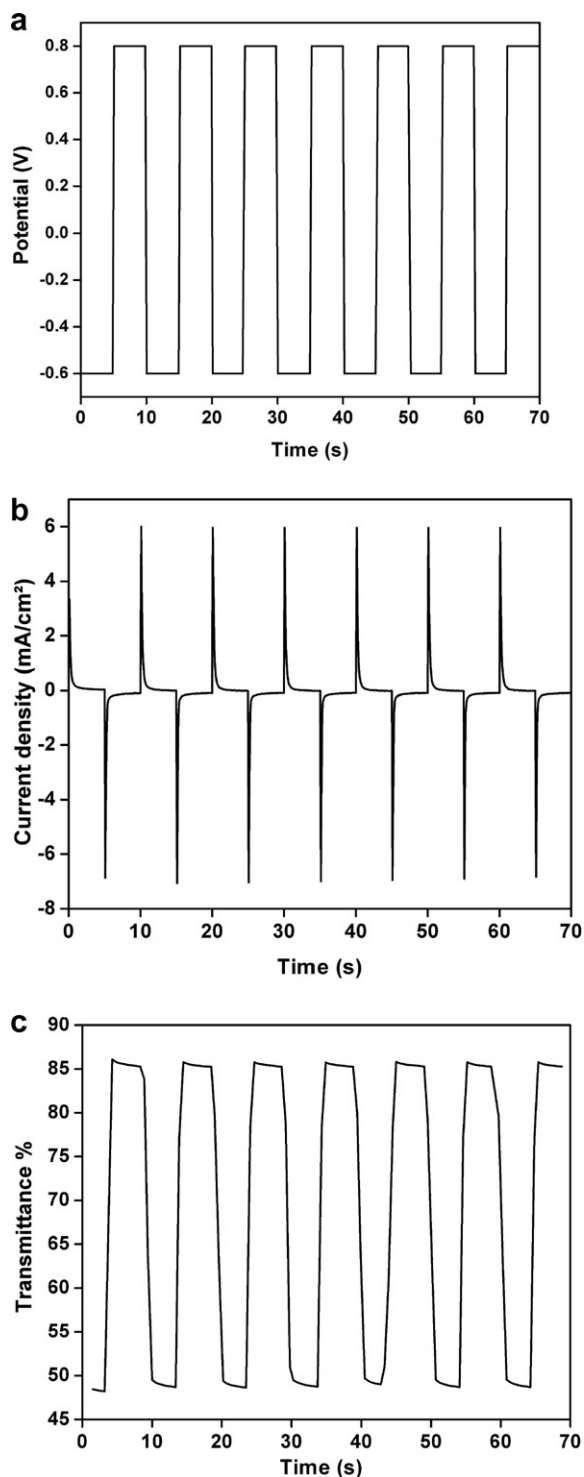


Fig. 6. Potential-time (a), current-time (b) and transmittance-time (c) profiles of the P(BPDP) film recorded during double step spectrochronoamperometry.

ing) deposited on transparent ITO, placed in a position to face each other and a gel electrolyte in between. The anodically coloring polymer film (P(BPDP)) was fully reduced

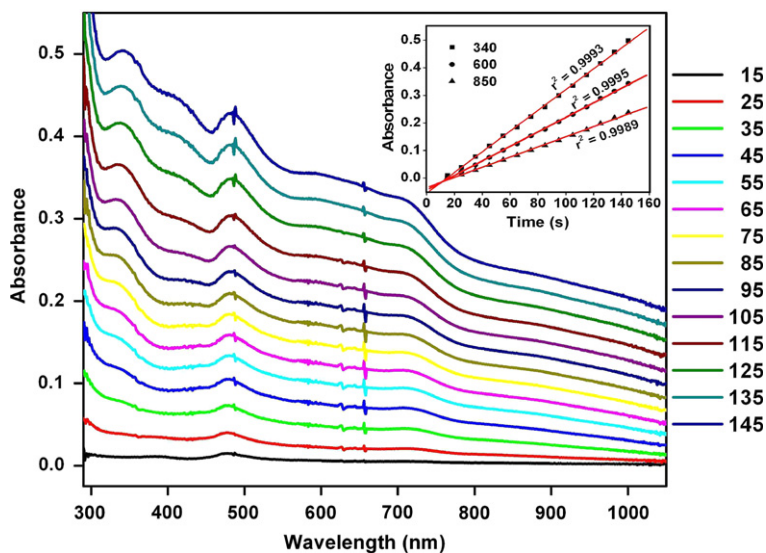


Fig. 7. In situ electrochemical polymerization of BPDP. Inserted figure represents absorbance changes recorded at different wavelengths during the polymerization.

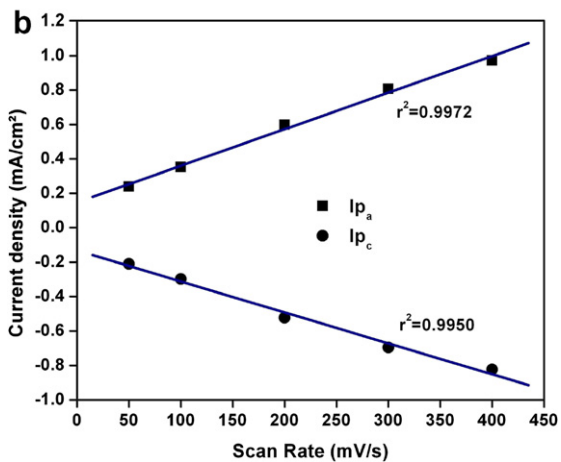
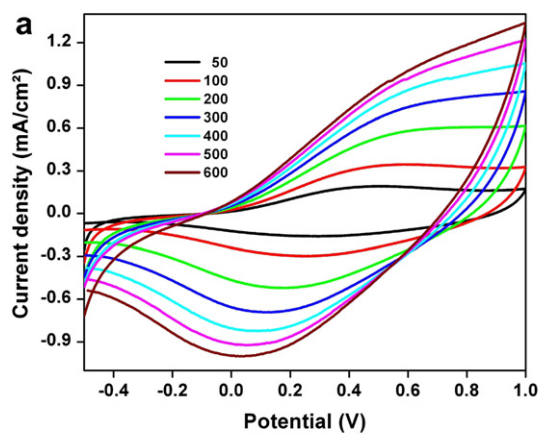


Fig. 8. (a) Cyclic voltammograms of P(BPDP) in monomer free ACN/LiClO₄ solvent/electrolyte. (b) Peak current vs scan rate for P(BPDP).

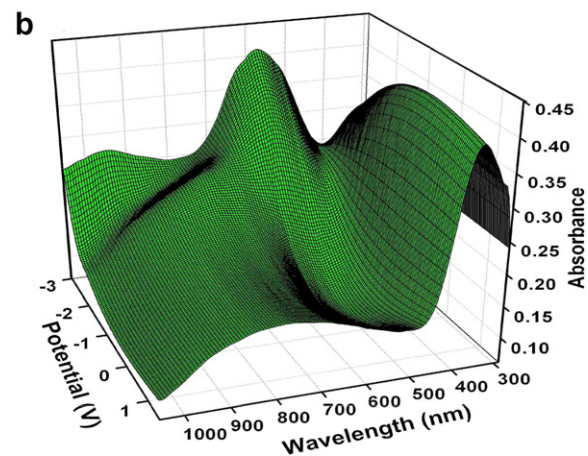
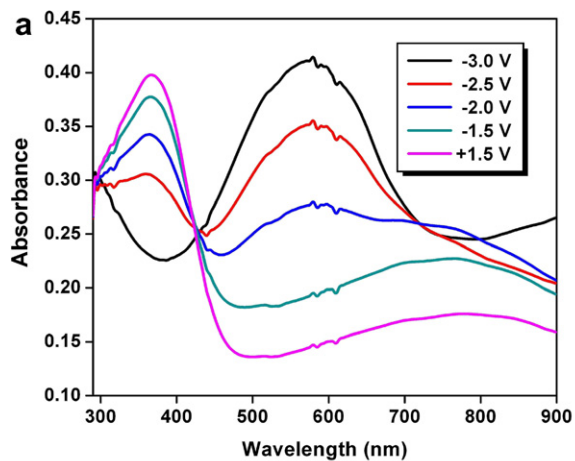


Fig. 9. Optoelectrochemical spectrum of the device at applied potentials between -3.0 and $+1.5$ V (a) (2D) and (b) (3D).

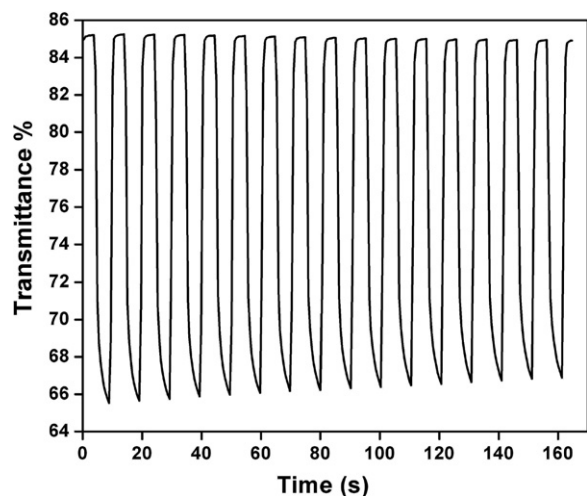


Fig. 10. Electrochromic switching, optical absorbance change monitored for ECD between -3.0 and $+1.5$ V at 585 nm.

and the cathodically coloring polymer (PEDOT) was fully oxidized prior to the construction of electrochromic devices (ECD). Optoelectrochemical spectra of the dual type ECD as a function of applied potential is given in Fig. 9. For the P(BPDP)/PEDOT device, a maximum absorption at 368 nm revealing yellow color was observed due to $\pi-\pi^*$ transition upon application of positive voltages. At that state, PEDOT did not reveal discernible absorption in the UV-Vis region of the spectrum and the device revealed yellow color. When the applied potential was negative bias, due to the reduction of PEDOT layer, blue color became dominant and a new absorption was observed at 585 nm (Fig. 9).¹ Colors and corresponding L , a and b values of the device are given in Table 1.

3.10. Switching of ECDs

One of the most important characteristics of ECDs is the response time. It is the time required to perform switching between the two colored states. For this purpose chrono-absorptometry was employed by stepping the potential with a residence time of 5 s. During the experiment, the % transmittance ($T\%$) at the wavelength of maximum contrast was measured by an UV-Vis spectrophotometer. For the P(BPDP)/PEDOT device, maximum contrast ($\Delta T\%$) and switching time were measured as 20% and 1.7 s at 585 nm (Fig. 10).

3.11. Colorimetry

L , a and b values of the P(BPDP) and its device where L corresponds to luminance and a , b values to color coordinates were measured at the fully oxidized and fully

reduced states of the polymer films and the data are given in Table 1.

4. Conclusion

A dipyrromethane functionalized monomer; 5-(4-*tert*-butylphenyl)dipyrromethane was successfully synthesized, and characterized via NMR and FTIR. The conducting polymer of BPDP was synthesized potentiostatically in AN using TBAFB (0.1 M) as the supporting electrolyte. Spectroelectrochemical analyses revealed that the homopolymer of BPDP has an electronic band gap of 2.39 eV. The contrast was measured as the difference between $T\%$ in the reduced and oxidized forms. P(BPDP) has good optical contrast (35%) and switching time (1.2 s).

Dual type polymer electrochromic device (ECD) based on P(BPDP) was constructed with poly(ethylene dioxythiophene) (PEDOT). Spectroelectrochemistry and switching ability of the device was investigated by UV-Vis spectroscopy and cyclic voltammetry. Maximum contrast ($\Delta T\%$) and switching time was measured as 20% and 1.7 s.

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¹ For interpretation of the references to color in this figure, the reader is referred to the web version of this article.