

A novel terthienyl based polymer electrochrome with peripheral BODIPY

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ABSTRACT

Design, synthesis and electropolymerization of a new hybrid material based on terthienyl system bearing BODIPY appendage are reported. This electrochemically polymerized unique combination readily gives an electrochromic polymer with a narrow optical band gap (1.71 eV). The electrochrome exhibits purple color when neutralized and sky blue color when oxidized in a monomer-free electrolyte solution containing 0.1 M tetrabutylammonium tetrafluoroborate dissolved in acetonitrile. Spectroscopic and electrochemical features of the electroactive polymer electrochrome indicate that it is a promising candidate for electrochromic device and display applications.

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1. Introduction

The design and synthesis of novel organic materials, specifically the conjugated polymers based on heteroaromatic systems like thiophene and pyrrole, are of considerable interest since they hold great promise for advanced technological applications in the fields of light emitting diodes (LEDs) [1,2], solar energy materials [3,4], transistors [5,6] and electrochromic devices [7–13]. In particular, dialkoxy-substituted thiophenes (EDOT, ProDOT, etc.) have recently held the attention of synthetic chemists due to the fact that the electron-donating effect of the disubstitution of two oxygen atoms directly to the thiophene ring dramatically changes the optical and electronic properties of the system when compared to that of thiophene. For example, the oxidation potential of the system can be decreased by this way, which allows deposition of highly homogeneous films by electrochemical polymerization with almost no degradation. Therefore, significant effort has been devoted to design, synthesis and applications of novel dioxythiophene based systems [14–21]. In this context, we recently reported a series of novel donor-acceptor type polymeric systems and their electrochromic features in order to reveal the structure-property relationship [22–24].

On the other hand, 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene and its derivatives (BODIPYs) are an important class of fluorescent

dyes due to their unique photophysical characteristics such as high molar absorption coefficients, high fluorescence quantum yields, good chemical, thermal and photo stability, and narrow emission band widths. The fact that BODIPYs are lack of net ionic charge, their fluorescence is highly insensitive to solvent and/or pH. An additional advantage of this class of compounds is that their visible excitation and emission can be tuned by structural modification of the pyrrole core through its rich chemistry [25–29]. Consequently, these features have made BODIPYs to be excellent candidates for biological labeling [30], artificial light harvesters [31–35], fluorescent switches [36–39], chemosensors [40–44], self-assembling systems [45] and electron-transfer agents [46] during the last decade. In spite of these numerous applications in different fields, conducting BODIPY polymers have remained elusive for a long time [29]. A few years ago, we have speculated that polymeric systems with BODIPY scaffold in the main chain, where photo and electroactive multiple fluorogenic units were concentrated in a single macromolecule, might hold promise for new applications in material sciences [47]. To this purpose, we have reported the design and synthesis of hitherto unexplored BODIPY-based macromolecular architectures (Chart 1) [47–49], and we have been able to show that switchable multielectrochromic materials, which were highly stable and giving fast responses to external stimulus, could be obtained from these materials. Additionally, polymeric BODIPYs [29,50–62], which have only begun to appear as relatively new comers to the repertoire of macromolecular systems, are now finding an increasing number of applications in both the materials and optical imaging fields.

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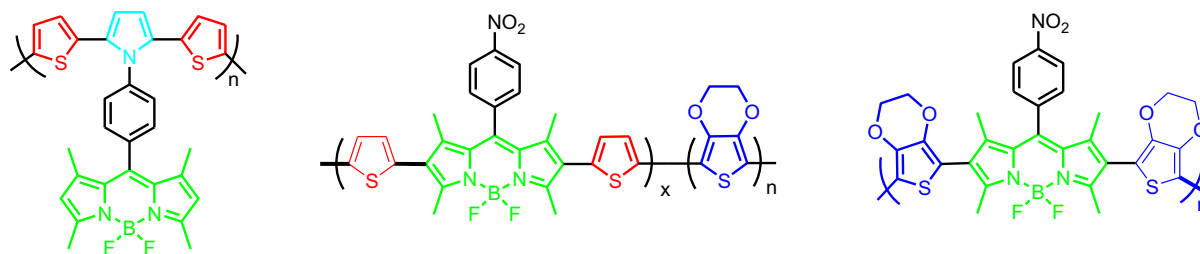


Chart 1. BODIPY-based macromolecular architectures.

In the present work, we wish to report the synthesis and properties of a novel electroactive polymer **P1**, which is based on a terthienyl system (3,4-ethylenedioxythiophene (**E**) and thiophene (**T**)), and peripheral BODIPY (**B**) units. This novel system was designed considering the facts that: i) first of all, previous studies of our group have shown that electrochemical polymerization of the monomers containing BODIPY unit as a part of polymer backbone is rather difficult when compared to the monomers containing BODIPY unit in the periphery, ii) it would be possible to incorporate the intriguing properties of the BODIPY unit even when used as a side group in the electroactive polymer film. Furthermore, it was assumed that the color of the polymer electrochrome in the neutral state might be adjusted. Therefore, in this unique combination, **E** units provide both low oxidation potential for facile electropolymerization and electrochromic features. It is noteworthy that this novel polymer has a narrow optical band gap (1.71 eV) to reflect or transmit the purple color in the neutral state, which can be switched to a sky blue upon doping. Furthermore, significant changes in transmittance were observed when the polymer was switched between -0.5 V and 1.6 V. Spectroscopic and electrochemical features of the polymer PETEB were investigated in comparison with the previous analogs.

2. Experimental details

All chemicals were purchased from Aldrich Chemical and used as received unless otherwise noted. Air- and moisture-sensitive reactions were carried out in oven-dried glassware under an inert atmosphere of dry nitrogen and argon. 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄) dissolved in acetonitrile (ACN) was used as electrolyte solution. A platinum button (0.02 cm²) and

a platinum wire were used as working and counter electrodes, respectively, as well as Ag/AgCl reference electrode (calibrated externally using 10 mM solution of ferrocene/ferrocenium couple which is an internal standard calibrated to be 0.44 V in ACN solution vs. Ag/AgCl). Repetitive cycling or constant potential electrolysis was used to obtain the polymer films. Electro-optical properties were investigated by using an indium tin oxide (ITO, Delta Tech. 8–12 Ω, 0.7 cm × 5 cm) electrode as well as a platinum wire as counter electrode and an Ag wire as a pseudo-reference electrode. For the spectroelectrochemical measurements, **P1** polymer film was coated on ITO electrode via cyclic voltammetry from a solution of **1** (5×10^{-3} M) in 0.1 M TBABF₄/ACN. In order to break in the polymer film, it was switched between 0.0 and 1.1 V in a monomer-free electrolytic solution. Electroanalytical measurements were performed using a Gamry PCI4/300 potentiostat-galvanostat. The electro-optical spectra were monitored on a Spedcor S 600 spectrometer. FTIR spectra were recorded on Nicolet 510 FTIR with an attenuated total reflectance (ATR). ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Bruker DPX-400 NMR Spectrometer. Combustion analysis was carried out by using a LECO CHNS-932 analyzer. Melting points were determined on a Büchi model 530 apparatus and are uncorrected. Column chromatography was performed on silica gel (60–200 mesh) from Merck Company. Thin layer chromatography (TLC) was carried out on Merck 0.2 mm silica gel 60 F254 analytical aluminum plates. The synthesis of **3** [63] and **7** [64] were carried out according to previously reported procedures.

2.1. 2,5-Dibromothiophene-3-carbaldehyde (**3**)

A mixture of **2** (1.00 mL, 1.28 g, 11.4 mmol), 48% aqueous hydrobromic acid (3.4 mL), and ether (3 mL) cooled at 0 °C was stirred vigorously while a mixture of bromine (1.18 mL, 3.68 g, 23.0 mmol) and 48% aqueous hydrobromic acid (3.4 mL) was added dropwise. The reaction mixture was then heated at 50 °C and monitored by TLC. After 3 h the mixture was diluted with water (50 mL) and extracted with ether (2 × 50 mL). The organic layers were combined, washed with 10% sodium thiosulfate solution (2 × 15 mL) and water (30 mL), and dried (MgSO₄). The solvent was removed under reduced pressure, diluted with dichloromethane/hexane (1:2), and passed through a column of silica to give the product as white solid (2.26 g, 73%): mp 45 °C (lit. mp 46–47 °C); ¹H NMR (400 MHz, CDCl₃) δ/ppm: 9.80 (s, 1H, –CHO), 7.34 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 183.1, 139.10, 128.6, 124.1, 113.4.

2.2. Synthesis of **5**

To a 250 mL round-bottomed flask containing 150 mL argon-degassed CH₂Cl₂ were added 3-ethyl-2,5-dimethyl-pyrrole (**4**, 2 mmol, 246 mg) and **3** (1 mmol, 269 mg). One drop of trifluoroacetic acid (TFA) was added and the solution was stirred overnight under N₂ at room temperature. After addition of

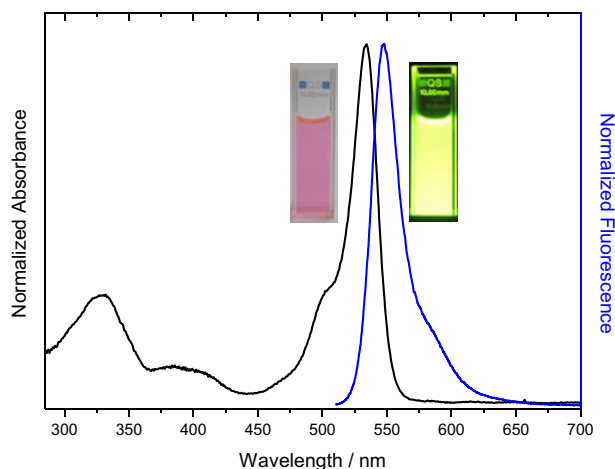


Fig. 1. UV-Vis absorption and emission spectra ($\lambda_{\text{exc}} = 510$ nm) of **1** (1.05×10^{-2} M) in toluene. Inset: photographs of **1** under day light (left) and UV light (365 nm, right).

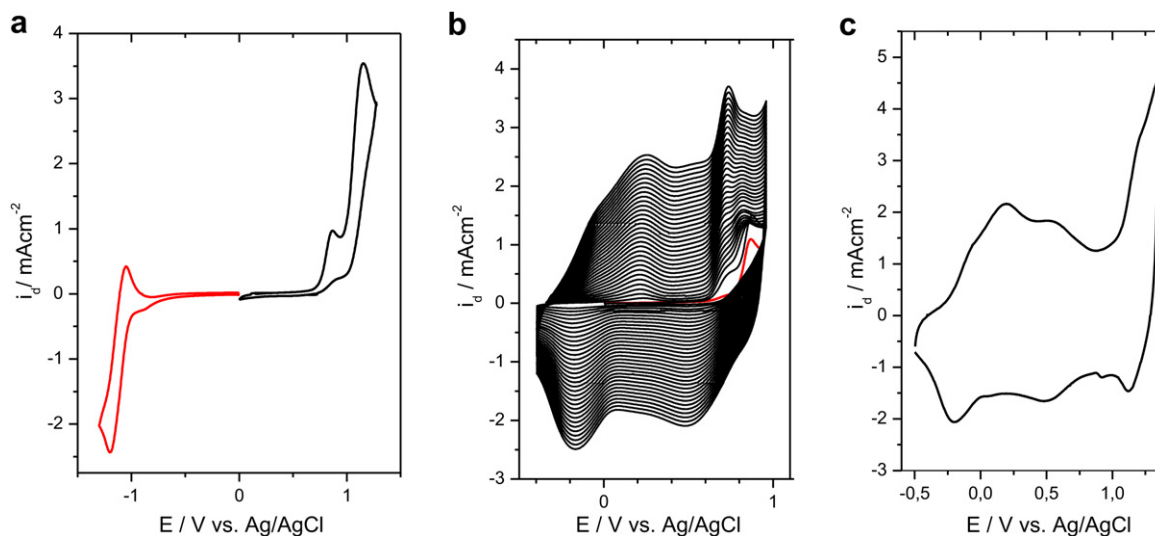


Fig. 2. (a) Cyclic voltammogram of **1** (1.05×10^{-2} M), (b) electropolymerization of **1** (1.05×10^{-2} M) by potential scanning to give polymer **P1** and (c) redox behavior of **P1** film in an electrolyte solution consisting of 0.1 M TBABF₄ dissolved in ACN at a scan rate of 100 mV/s.

a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1 mmol, 227 mg) in 30 mL of CH₂Cl₂ to the reaction mixture, stirring was continued for 30 min. Triethylamine (NET₃) (2 mL) and BF₃·OEt₂ (3 mL) were successively added and after 30 min, the reaction mixture was washed with water (3 × 100 mL) and dried over anhydrous Na₂SO₄. The solvent was evaporated and the residue was subjected to silica gel column chromatography using chloroform-hexane (1:1, v/v) as the eluent to give the product as orange solid (200 mg, 36%): mp 220 °C (decomp.); ¹H NMR (400 MHz, CDCl₃) δ/ppm: 6.85 (s, 1H), 2.53 (s, 6H, -CH₃), 2.34 (q, *J* = 7.8 Hz, 4H, -CH₂), 1.59 (s, 6H, -CH₃), 1.02 (t, *J* = 7.8 Hz, 6H, -CH₃); ¹³C NMR (75 MHz, CDCl₃) δ/ppm: 154.9, 137.6, 136.8, 133.1, 130.9, 130.6, 130.3, 113.0, 111.6, 17.1, 14.6, 12.6, 10.6; FTIR (ATR, cm⁻¹): 3105, 2957, 2922, 1544, 1477, 1461, 1316, 1183, 966, 757;

Elemental Anal. Calcd. for C₂₁H₂₃BBR₂F₂N₂S: C, 46.36; H, 4.26; N, 5.15; S, 5.89. Found: C, 46.32; H, 4.29; N, 5.18; S, 5.81.

2.3. 2-(Tributylstannyl)-3,4-ethylenedioxythiophene (**7**)

A 1.0 g (7 mmol) sample of 3,4-ethylenedioxythiophene (**6**) in 100 mL of dry tetrahydrofuran was treated dropwise with 3.3 mL (8.1 mmol) of 2.5 M *n*-butyllithium at -78 °C under argon. After the solution was stirred for 0.5 h and warmed to -40 °C, 3 g (9.4 mmol) of tributylstannyl chloride (Bu₃SnCl) was added to the solution, and the new solution was warmed to room temperature. The solvent was removed by rotary evaporation after the solution was stirred for 8 h. The residue was dissolved in hexane and filtered. The filtrate was dried in vacuum to afford the product (2.59 g, 6 mmol, 86%

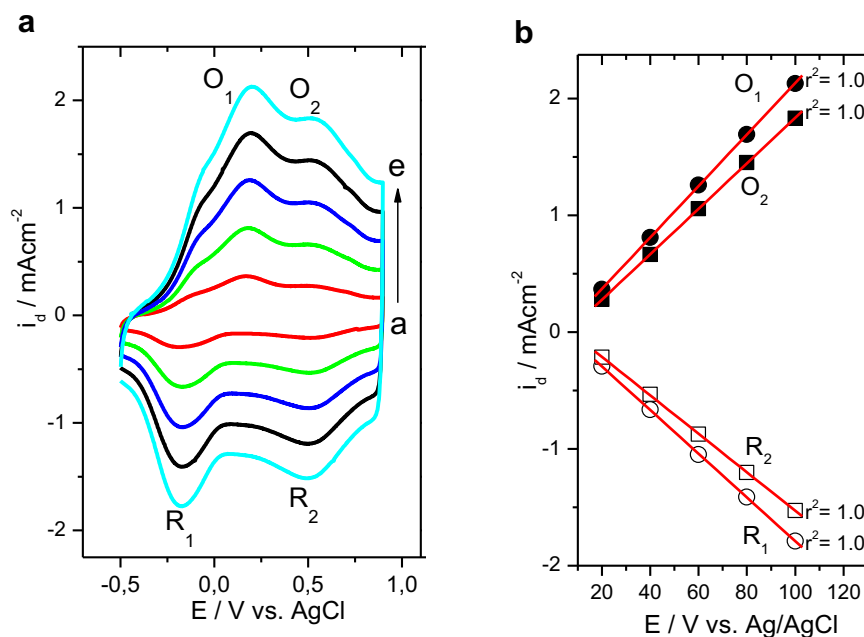


Fig. 3. (a) Scan rate dependence of **P1** film on a Pt disk electrode in 0.1 M TBABF₄/ACN at different scan rates, a: 20 mV/s, b: 40 mV/s, c: 60 mV/s, d: 80 mV/s, and e: 100 mV/s. (b) Relationship of anodic and cathodic current peaks as a function of scan rate between neutral and oxidized states of **P1** film in 0.1 M TBABF₄/ACN. O₁/R₁ and O₂/R₂ are quasi-reversible redox couples.

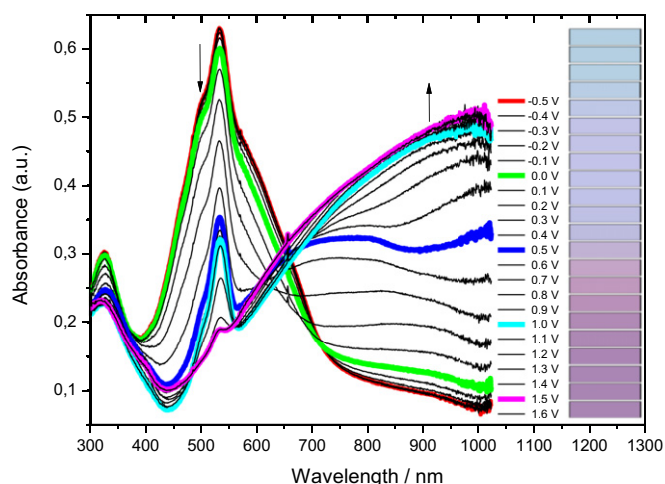


Fig. 4. Electronic absorption spectra and colors of **P1** on ITO in 0.1 M TBABF₄/ACN at various applied potentials between -0.5 V and 1.6 V vs Ag wire.

yield) as yellow liquid. The compound was used for the next reaction as obtained, with no further purifications. ¹H NMR (400 MHz, CDCl₃) δ /ppm: 6.58 (s, 1H), 4.15 (s, 4H), 1.64–1.60 (m, 6H), 1.39–1.28 (m, 6H), 1.10 (t, 9H), 0.92 (q, 6H).

2.4. Synthesis of **1**

To argon-degassed solution of **5** (0.2 g, 0.36 mmol) and **7** (0.32 g, 0.75 mmol) in dry toluene (40 mL) was added Pd(PPh₃)₄ (0.02 g, 2% mmol) and the mixture was heated under reflux until all the starting materials were consumed (TLC). The flask was cooled and the solvent was removed under reduced pressure. The residue was filtered through a short pad of silica gel by eluting with hexane–CH₂Cl₂ (1:1, v/v) to give red solid (0.204 g, 0.30 mmol, 80% yield): mp: 178–180 °C (decomp.); ¹H NMR (400 MHz, CDCl₃) δ /ppm: 7.03 (s, 1H), 6.25 (s, 1H), 6.16 (s, 1H), 4.37–4.32 (m, 4H), 4.26–4.20 (m, 4H), 2.54 (s, 6H), 2.31 (q, $J = 8$ Hz, 4H), 1.59 (s, 6H), 0.98 (t, $J = 8$ Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ /ppm: 153.8, 152.5, 141.9, 138.4, 138.1, 136.8, 135.3, 135.1, 132.7, 131.0, 128.8, 123.0, 121.4, 111.4, 97.3, 96.7, 96.0, 68.1, 65.0, 64.6, 61.8, 16.6, 13.8, 12.7, 10.5; FTIR (ATR, cm⁻¹): 3105, 2960, 2925, 1544, 1475, 1441, 1320, 1191, 1068, 977; Elemental Anal. Calcd. for C₃₃H₃₃BF₂N₂O₄S₃: C, 59.46; H, 4.99; N, 4.20; S, 14.43. Found: C, 59.43; H, 5.01; N, 4.23; S, 14.39.

3. Results and discussion

For the synthesis of compound **1**, initially, thiophene-3-carbaldehyde (**2**) was treated with HBr and Br₂ according to

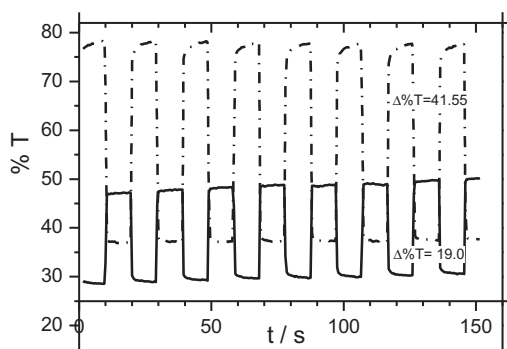


Fig. 5. Chronoabsorptometry experiments for **P1** on ITO in 0.1 M TBABF₄/ACN while the polymer was switched between -0.5 V and 1.1 V at 533 nm (solid line) and at 900 nm (dashed line) vs Ag wire.

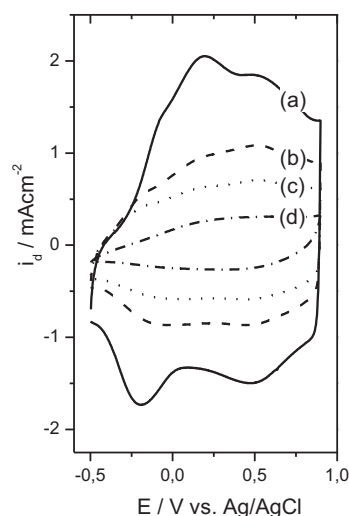


Fig. 6. Cyclic voltammograms of **P1**, switched for electrochemical stability by a square wave potential method with a 2 s interval at -0.5 V and 0.90 V, after (a) 1. switch, (b) 500. switch, (c) 1000. switch and (d) 5000. switch.

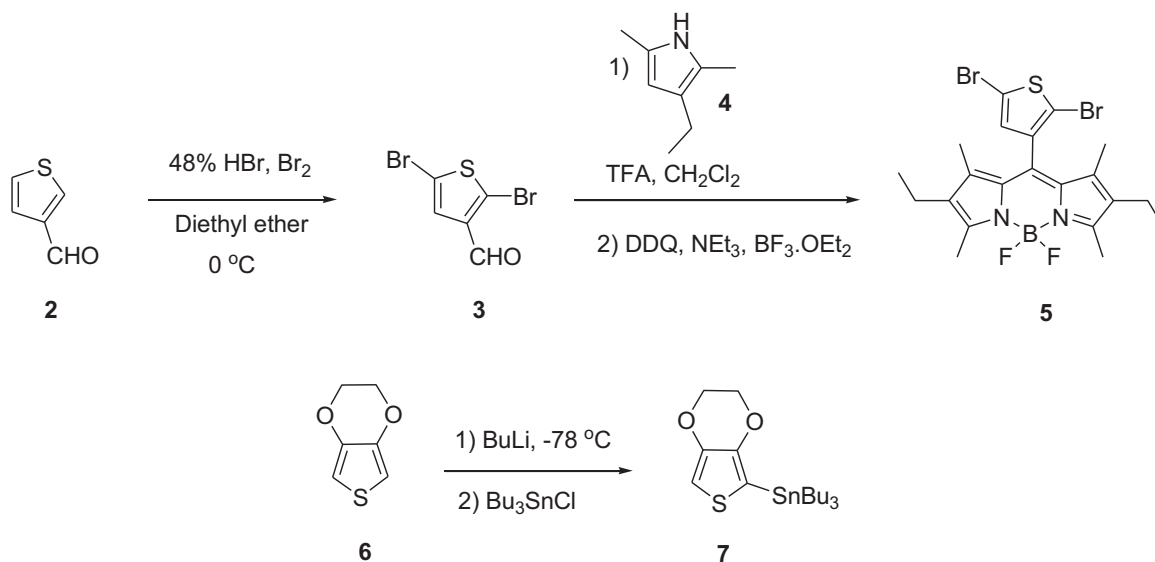
a published procedure to give **3** [63] as outlined in Scheme 1. Next, condensation of **3** with **4** in the presence of catalytic amount of TFA resulted in the formation of dipyrromethane, which was then oxidized by DDQ to generate dipyrromethene followed by complexation with BF₃·OEt₂ to provide BODIPY **5**. In ¹H NMR spectrum of **5**, aromatic proton of thiophene ring and methyl protons of BODIPY unit peaked as singlets at 6.85, 2.53 and 1.59 ppm, respectively, and ethyl substituents of BODIPY unit gave two sets of signals at 2.34 (q, $J = 7.8$ Hz, 4H, $-\text{CH}_2$) and 1.02 (t, $J = 7.8$ Hz, 6H, $-\text{CH}_3$) ppm. A thirteen-line ¹³C NMR spectrum was consistent with the structure.

In order to insert the dioxythiophene units to the structure of BODIPY **5**, compound **7** was prepared from the reaction of **6** with BuLi followed by the addition of Bu₃SnCl [64]. Finally, Stille coupling reaction of compounds **5** and **7** in the presence of Pd (0) catalyst provided the BODIPY **1** in 80% yield (Scheme 2). Compound **1** was initially characterized by spectral data (¹H, ¹³C NMR, FTIR), which was in well agreement with the structure.

UV–Vis absorption and emission spectra of **1** were depicted in Fig. 1. It was found that **1** emits greenish yellow light (547 nm) in toluene.

The electrochemical behavior of **1** (1.05×10^{-2} M) was investigated by cyclic voltammetry in an electrolyte solution consisting of 0.1 M TBABF₄ dissolved in ACN. Upon anodic scans, two oxidation peaks were observed at 0.87 V and 1.15 V, which were attributed to dioxythiophene and BODIPY units, respectively (Fig. 2(a)), since the first oxidation peak was very close to 2,5-bis(2-(3,4-ethylenedioxy)thienyl)-thiophene (ETE) monomer without BODIPY unit [65]. On the other hand, during cathodic scan, **1** exhibited a reversible redox couple, attributed to the BODIPY unit, with a half peak potential of -1.12 V on the negative side of the voltammogram. The data was in well agreement with the literature [47–49,66,67]. For example, this value is somewhat smaller than dithienylpyrrole (SNS) based analog (-1.16 V vs Ag/AgCl) [47]. Also, the optical band gap of the ETE monomer was calculated as 1.72 eV from the onset potentials of oxidation and reduction peaks. Based on foregoing result, it can be concluded that the electronic nature of the BODIPY unit was not affected considerably.

Repetitive anodic scans were carried out between -0.40 V and 0.96 V in order to get an electroactive polymer film. During this process, new reversible redox couples were observed with half-wave potentials of 0.04 V and 0.61 V. The increase in the current



Scheme 1. Syntheses of 5 and 7.

intensities of this redox couple clearly indicated that the polymer film **P1** was formed on the electrode surface (Fig. 2(b), Scheme 3).

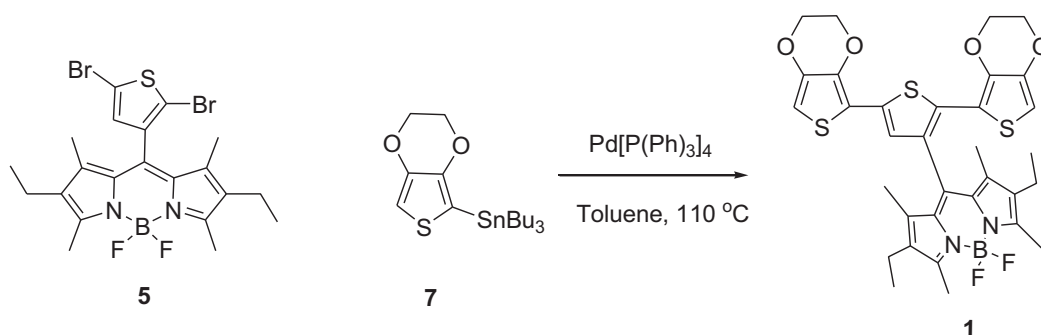
When the as-prepared **P1** film was anodically scanned in a monomer-free electrolyte solution of 0.1 M TBABF₄/ACN (Fig. 2(c)), three reversible redox couples were observed with half-wave potentials at 0.0 V, 0.50 V due to the formation of charge carriers, and 1.18 V, which was ascribed to the BODIPY units since the polymer of ETE (PETE film) without BODIPY unit exhibits one reversible oxidation peak [65]. The oxidation peak potentials of this novel system, 0.20 V and 0.51 V, were lower when compared to its polydithienylpyrrole (PSNS) analog (0.79 V and 0.93 V) [47].

As shown in Fig. 3, a linear increase in the peak currents as a function of the scan rates confirmed that the polymer film **P1** was tightly bounded to the electrode surface and the redox process was non-diffusional.

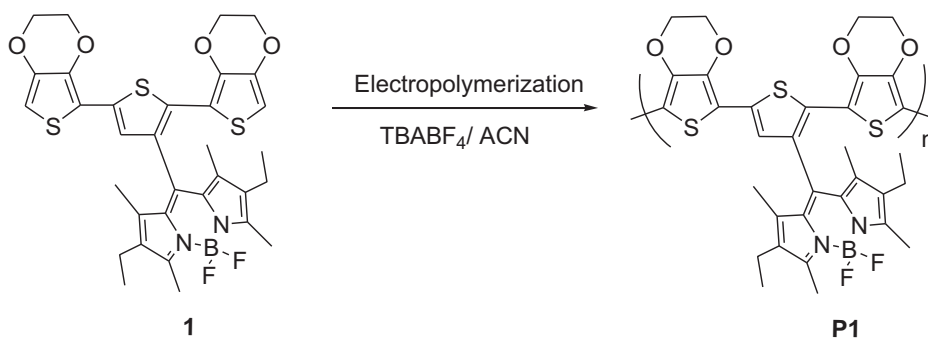
In order to elucidate the electrochromic features of **P1**, a simple electrochromic device was constructed and the spectroelectrochemical behavior of the polymer film coated on ITO electrode was examined under a variety of voltage pulses between -0.50 V and 1.60 V. During p-doping, the higher energy absorbances at wavelengths shorter than 600 nm ($\pi-\pi^*$ transition at 533 nm) started to decrease with an apparent new absorption band at around 750 nm, which was attributed to the formation of polaron charge (Fig. 4). Upon further oxidation, the polaron charge carriers turned into the bipolaron charge carriers above 900 nm. In this process, it was assumed that charge carriers (polarons and

bipolarons) were delocalized as the conformation of the polymer was planarized to some extent. As a result of these variations in the conformation and the absorption spectrum of **P1**, the color of the polymer changed from purple in the neutral state to sky blue state upon doping (Fig. 4). Also, the absorption band at 533 nm confirms the presence of BODIPY units in the polymer chain. As a result, when compared to PETE analog, the effect of the presence of BODIPY unit on polymer backbone can be seen readily in the color of the polymer electrochromism since PETE film exhibits deep blue when reduced and blue when oxidized [65]. Also, the presence of BODIPY results in a bathochromic shift of the maximum wavelength of $\pi-\pi^*$ transition from 590.5 nm (2.1 eV) to 533 nm (2.3 eV) when compared to PETE.

On that basis, the band gap (E_g) of polymer **P1** was calculated from the onset of $\pi-\pi^*$ transition at 533 nm, and it was found to be 1.71 eV, which was very close to its PETE analog (1.70 eV) [65] and lower than its PSNS analog (2.90 eV) [47]. It can be easily concluded that the presence of BODIPY unit on PETE polymer backbone was hardly effective on the band gap of the material. The percentage transmittance change ($\Delta\%T$) and coloration efficiency (CE at 95% of the full optical switch, after which point the naked eyes couldn't sense the changes in the color) of the polymer film were also calculated to be 19.0% and 91 cm²/C at 533 nm during p-doping, respectively (Fig. 5). In addition, the CE value was also found as 91 cm²/C for 100% of full optical switch. The response time of the polymer film was found to be 0.9 s for 95% of full optical switch.



Scheme 2. Synthesis of 1.



Scheme 3. Electrochemical polymerization of **1** to give **P1**.

Stability of the material is a key parameter for any potential application of the polymers. For that reason, the electrochemical stability of the polymer was examined under ambient conditions without purging with an inert gas (in the presence of air). First of all, the electrochemical stability of **P1** was tested by switching between neutral (-0.50 V) and oxidized (0.90 V) states vs. Ag/AgCl. It was found that **P1** retained 56.5% of its electroactivity even after five hundreds of cycles (Fig. 6).

4. Conclusion

In conclusion, the design, synthesis and electrochromic features of a novel regioregular electroactive BODIPY polymer (**P1**) were described. It is noteworthy that this unique combination has an optical band gap (1.71 eV) to reflect or transmit the purple color in the neutral state, which can be switched to a sky blue state upon doping. Furthermore, significant changes in transmittance were observed when the polymer was switched between -0.5 V and 1.6 V. Although, the presence of BODIPY unit at the periphery of the terthienyl system was hardly effective on both the oxidation potential and the band gap of the system, the results of the present work have clearly indicated that the obtained polymer PETEB film exhibited quite different electrochromic behaviors when compared to the precedent terthienyl system. Spectroscopic and electrochemical features of the polymer indicated that **P1** is a promising candidate for electrochromic applications. Work in this line is currently underway in our laboratories.

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