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Synthesis, characterization and electrochromic properties of a near infrared active conducting polymer of 1,4-di(selenophen-2-yl)-benzene

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ABSTRACT

A novel selenophene-based monomer, 1,4-di(selenophen-2-yl)-benzene (DSB), was synthesized via Stille coupling reaction of 1,4-dibromobenzene and tributyl(2-selenophenyl)stannane. Conducting polymer (PDSB) was prepared electrochemically in the presence of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte in dichloromethane (DCM). The resulting conducting polymer was characterized by Cyclic Voltammetry, Fourier Transform Infrared and Ultraviolet–visible spectroscopy. Spectroelectrochemistry analysis and kinetic studies of PDSB revealed a π–π^* transition at 340 nm with a striking and rapid (0.6 s) transmittance change (35%), at near infrared region (1250 nm), indicating that PDSB is a very suitable near infrared electrochromic material.

1. Introduction

Electrochromism is predominantly defined as the reversible optical change of a material observed upon alternation of the applied potential. Conducting organic polymers are one of the leading options in the field of electrochromism due to their fast switching times, high optical contrasts and ease of processability [1–3].

Electrochromic materials have been used in smart windows, displays, automotive industry and architecture [4]. Thiophene, pyrrole and their derivatives are widely studied [5] for electrochromic applications since the discovery of organic conducting polymers. However, exiguous attention was given to polymers of selenophene and its derivatives [6–9] even though selenophene has lower oxidation potential in compare to its sulfur or oxygen analogs. The reason is the higher electron donating character of selenium atom [10]. Lower oxidation potential engenders high quality polymer films during electropolymerization since harmful effects of high potential were minimized (such as degradation of the polymer through overoxidation) [11].

Recently near infrared active electrochromic materials found important applications in telecommunication windows where electro-optic switching in response to applied potential changes modulation of light transmission at near infrared region. Near infrared active devices, namely variable optical attenuators (VOA) have been employed to vary power [12,13]. Moreover, near infrared active materials can be exploited for environmental control (heat gain or loss) in buildings. Recently, there have been an interest in the near infrared electrochromic properties of transition metal oxides such as WO_3 and organic metal complex such as ruthenium dendrimer in the near infrared region [14–16]. Organic polymer based materials are also utilized as NIR active materials for electrochromic device applications [17,18].

There are limited number of selenophene-bis-substituted monomers that are polymerized to give luminescent materials which are used as active layers in LEDs and solar cell applications [19].

Poly(1,2-di(2-selinyl)ethene) [20] and poly(biselenophene) [7] were previously reported and limited data were supplied on their electrochromic properties. These preliminary results encouraged us to synthesize selenophene-bis-substituted monomers with different acceptor units on the center. Herein, we report the synthesis and electrochromic properties of poly(1,4-di(selenophen-2-yl)-benzene). The polymer has a very low optical contrast in the visible region with a satisfactory optical contrast of 35% in NIR region indicating that polymers synthesized from selenophene-bis-substituted monomers are promising materials for NIR active electrochromic materials.

Compound **1** was synthesized utilizing 1,4-dibromobenzene and tributyl(2-selenophenyl)stannane (**2**) via Stille coupling reaction as shown in Scheme 1. Benzene moiety was inserted in the middle of two selenophene groups with the aim of decreasing the oxidation potential of the polymer. 1,4-di(selenophene-2-yl)-benzene (DSB) monomer was electrochemically polymerized using $TBAPF_6$ as the supporting electrolyte. Cyclic Voltammetry, Fourier Transform Infrared, Nuclear Magnetic Resonance, Mass Analysis and

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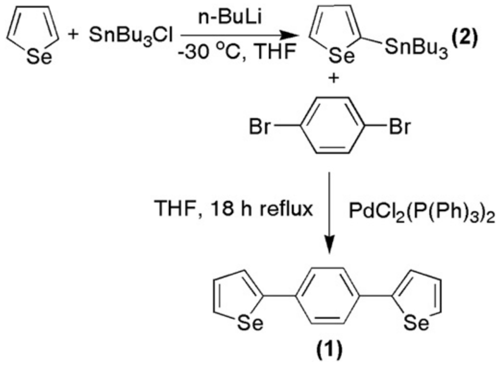

Scheme 1. Synthetic route of 1,4-di(selenophene-2-yl)-benzene.

Ultraviolet–visible spectra were employed for the characterization of the polymer.

2. Experimental

2.1. Materials

1,4-Dibromobutane (Aldrich), selenophene (Aldrich), tributyltin chloride (Aldrich), *n*-butyllithium (Aldrich), dichlorobis(triphenyl phosphine)-palladium(II) (Aldrich) were used as received. The electrolysis solvents; dichloromethane (DCM) (Merck) and acetonitrile (ACN) (Merck) were used without further purification. The supporting electrolyte $TBAPF_6$ (Aldrich) was used as received. Tetrahydrofuran (THF) (Merck) was distilled prior to use.

2.2. Instrumentation

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer at 400 MHz and chemical shifts (δ) were given relative to tetramethylsilane as the internal standard. FTIR spectrum of the polymer was recorded on Varian 1000 FTIR spectrometry, where samples were dispersed in KBr. Spectroelectrochemical and kinetic studies were carried out on Voltalab PST 50 potentiostat and Varian Cary 5000 UV–vis–NIR spectrophotometer at a scan rate of 2000 nm/min. Colorimetry results were acquired by a Minolta CS-100A Chromameter with a 0/0 (normal/normal) viewing geometry as recommended by CIE. A 5973 HP quadruple mass spectrometer coupled to a JHP SIS direct insertion probe pyrolysis system was used. The 70 eV EI mass spectra were recorded at a scan rate of 2 scans/s.

2.3. Synthesis of tributyl(2-selenophenyl)stannane (**2**)

Tributyl(2-selenophenyl)stannane was synthesized following the published procedures with some modifications [19,21]. Selenophene (1 g, 7.64 mmol) was dissolved in anhydrous THF (10 ml) in argon atmosphere. Solution was cooled to −30 °C in *ortho*-xylene – dry ice bath and subsequently *n*-butyllithium (1.76 ml of 2.0 M solution in hexane, 3.52 mmol) was added dropwise. Mixture was stirred at this temperature for 3.5 h. Tributyltin chloride (1.3 g, 4 mmol) was added dropwise and stirred for another hour at this temperature. Dichloromethane (20 ml) was added and the solution was extracted three times with saturated aqueous sodium carbonate. Organic phase was extracted two times with brine solution, dried over sodium sulfate and solvent was evaporated under vacuum. The residue was further purified by neutral alumina with petroleum ether as the eluent to yield a colorless oil (0.72 g, 45%).

^1H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, 1H), 7.4 (m, 2H), 1.5 (m, 6H), 1.27 (m, 6H), 1.02 (t, 6H), 0.81(t, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.19, 13.68, 27.32, 29.13, 130.55, 135.29, 137.81, 143.57.

2.4. Synthesis of 1,4-di(selenophene-2-yl)-benzene (DSB) (**1**)

1,4-Dibromobenzene (236 mg, 1 mmol), tributyl(2-selenophenyl)stannane (1.68 g, 4 mmol) and dichlorobis(triphenyl phosphine)-palladium(II) (50 mg, 0.045 mmol) were dissolved in anhydrous THF and refluxed for 18 h under argon atmosphere. Solvent was evaporated under vacuum and the residue was purified by column chromatography (5:1 hexane:DCM as eluent) to yield yellow solid product (202 mg, 60%).

^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.25 (t, $J = 3.9$ Hz, 2H, selenophene), 7.42 (d, $J = 3.5$ Hz, 2H, selenophene), 7.48 (s, 4H), δ 7.88 (d, $J = 5.4$ Hz, 2H, selenophene). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 125.29, 126.79, 129.70, 130.12, 130.24, 130.73. MS: m/e 338 [M^+].

2.5. Cyclic Voltammetry (CV)

CV system consists of a potentiostat, an XY recorder and a CV cell. A platinum bead was used as the working electrode, a platinum wire as counter electrode and a Ag wire as a pseudo reference electrode. The experiments were done at room temperature and under nitrogen atmosphere in DCM/$TBAPF_6$. CV was employed to determine electroactivities, oxidation and reduction potentials of the monomer and the polymer.

2.6. Electrochemical polymerization of the monomer

PDSB was achieved potentiodynamically in the potential range between −300 mV and 1300 mV at a scan rate of 100 mV/s in the presence of 50 mg of (**2**), $TBAPF_6$/DCM supporting electrolyte–solvent couple where indium tinoxide (ITO) coated glass was used as the working electrode. PDSB film was washed with DCM to remove unreacted monomer and excess $TBAPF_6$.

3. Results and discussion

3.1. Cyclic Voltammetry

Cyclic Voltammetry was employed to demonstrate redox behavior of the monomer. Fig. 1 reveals electrochromic behavior between orange-yellow and green colors. Oxidation potential of the monomer appeared at 1.1 V and the polymer revealed two oxidation peaks at +0.95 V, +0.25 V and two reduction peaks at +0.7 V, +0.05 V, respectively.

3.2. FTIR spectra

FTIR spectrum of DSB monomer showed the following absorption bands: 3051 cm^{-1} (aromatic C–H), 1635 cm^{-1}, 1496 cm^{-1} (aromatic C=C stretching), 933 cm^{-1}, 817 cm^{-1}, 690 cm^{-1} (C–H in plane bending of benzene and thiophene), 1112 cm^{-1} (C=Se stretching).

In the FTIR spectrum of PDSB in addition to the characteristic peaks of the monomer, the bands at 933 cm^{-1}, 817 cm^{-1} and 690 cm^{-1} corresponding to the out of plain C–H vibration of the monomer were almost disappeared. The wide band at 1644 cm^{-1} proves the formation of polyconjugation. The peaks at 1081 cm^{-1} and 795 cm^{-1} showed incorporation of the PF_6^- ions (dopant ion) into the polymer film during doping process. Hence, the results depict successful polymerization of the monomer.

3.3. Spectroelectrochemistry of the polymer

Spectroelectrochemical analyses highlight optical changes and electronic transitions by applying different potentials to an ITO glass slide previously coated with polymer film. Key electronic properties of the polymer such as the band gap (E_g) and intergap

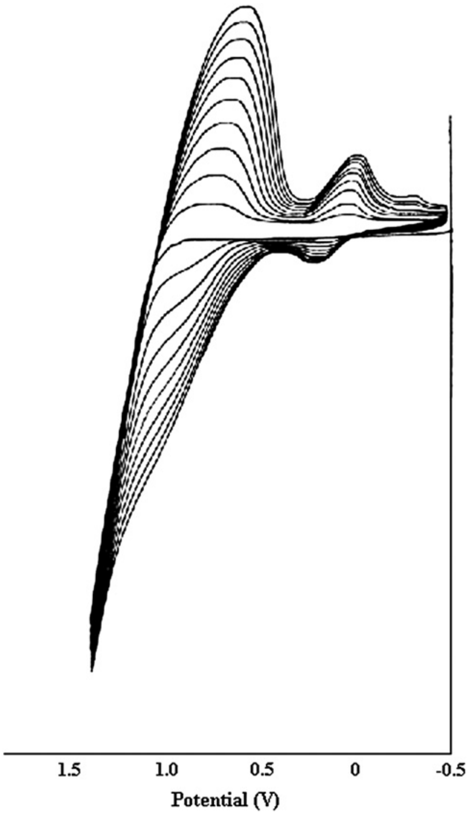

Fig. 1. Cyclic voltammogram of DSB at a scan rate of 100 mV/s.

states that appear on doping were demonstrated. PDSB film was potentiodynamically synthesized on ITO electrode in the presence of 0.01 M DSB, while the potential was swept between −0.5 V and 1.3 V in TBAPF$_6$/DCM. The electrochemical and electrochromic properties of the polymer film were studied with a monomer-free medium. A π–π^* transition was revealed at 340 nm and the band gap (E_g) was calculated as 1.85 eV (Fig. 2). As applied potential was incrementally increased between −0.3 V and 1.0 V, the absorption at near infrared region drastically increased. The polaron band (radical cation) and the bipolaron band (dication) were observed at 608 nm and 1250 nm, respectively.

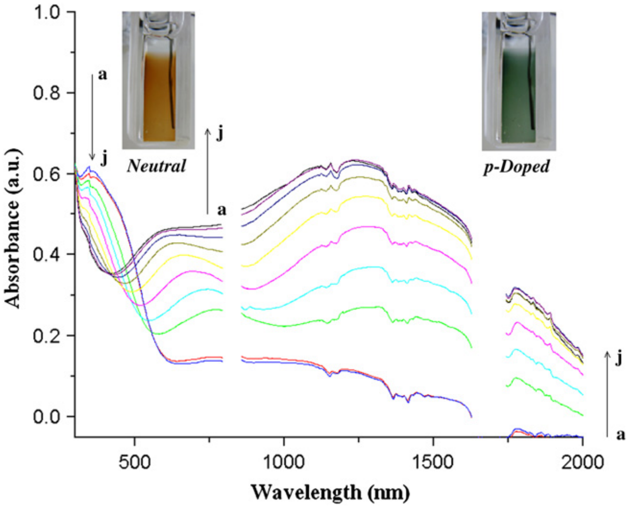

Fig. 2. Spectroelectrochemistry of PDSB film on an ITO-coated glass slide in monomer-free 0.1 M TBAPF$_6$/DCM solution where (a) −0.3, (b) 0.0, (c) 0.3, (d) 0.4, (e) 0.5, (f) 0.6, (g) 0.7, (h) 0.8, (i) 0.9, and (j) 1.0 V vs Ag/Ag$^+$.

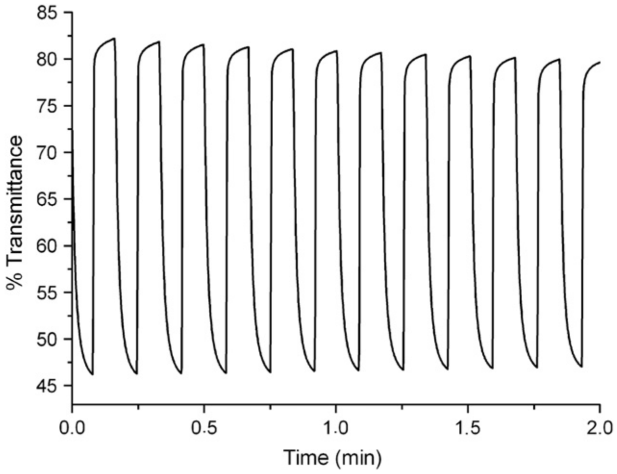

Fig. 3. Electrochromic switching and optical absorbance change monitored at 1250 nm for PDSB in 0.1 M TBAPF$_6$/ACN.

3.4. Electrochromic switching of the polymer

Electrochromic switching studies are employed to determine the ability of the polymer to switch rapidly and exhibit striking color change. Chronoabsorptometry is a square-wave potential step method coupled with UV–vis spectroscopy. It is used to investigate switching time and contrast of the polymer. The polymer films synthesized on ITO-coated glass as described previously were switched while the potential was stepped between −0.3 V and 1.0 V with a switching time of 5 s (Fig. 3). From these experiments the contrast value was measured as the difference between the transmittance in the reduced and oxidized forms (% ΔT) and found to be 0.2% at 340 nm. At 1250 nm a percent transmittance of 35% with a switching time of 0.6 s was observed. A very low contrast in the visible region with a satisfactory contrast in the NIR region indicates its potential application as a near infrared active electrochromic material. Many polymers have shown to have NIR activity but polymers with such a small contrast in the visible region are limited in literature [22].

3.5. Scan rate dependence of the polymer

Investigation of peak current intensity with respect to scan rate indicates whether the process is controlled by diffusion or not [14,15]. The current response was directly proportional to the scan rate with a potential range between 0.3 V and 1.4 V, indicating the non-diffusion controlled character of the polymerization (Fig. 4).

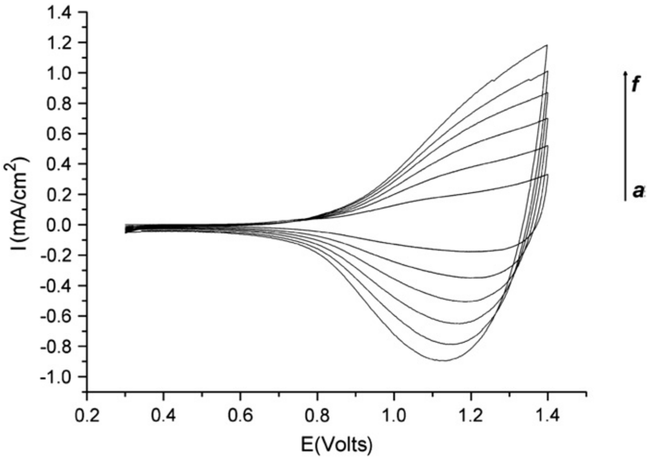

Fig. 4. Scan rate dependence of PDSB in TBAPF$_6$/DCM (a) 50, (b) 100, (c) 150, (d) 200, (e) 250, and (f) 300 mV/s.

3.6. Colorimetry

CIE system is used in quantitative scale to report colors in a scientific way. CIE system consists of three attributes: luminance (L), hue (a), and saturation (b). These values are obtained using a Minolta spectrophotometer. PDSB displays orange-yellow color (Y: 526, x: 0.410, y: 0.413) in the neutral form and green color (Y: 428, x: 0.300, y: 0.361) in the oxidized state.

4. Conclusions

1,4-di(selenophene-2-yl)-benzene was synthesized in high purity and characterized by spectral methods (^{1}H NMR, ^{13}C NMR and FTIR). Characterization of the electrochemically synthesized polymer was performed by FTIR, spectroelectrochemical analysis, electrochromic switching and colorimetry studies. Spectroelectrochemistry experiments demonstrated π–π^* transition, polaron and bipolaron band formations at 340 nm, 608 nm and 1250 nm, respectively. Band gap was calculated as 1.85 eV. Furthermore, the % ΔT at 340 nm was found as 0.2% and 35% at 1240 nm with a switching time of 0.6 s. Considering these results, we can conclude that polymer of DSB is a promising candidate for near infrared applications.

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