



Efficient blue-to-transmissive electrochromic transitions of alkylated quinoxaline-thiophene based donor-acceptor type conjugated polymers

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HIGHLIGHTS

- We prepare alkylated quinoxaline-thiophene based donor-acceptor type conjugated polymers.
- The prepared polymers exhibit reversible blue-to-transmissive switching at a low voltage of 1.2 V.
- The alkyl side-chains on the acceptor unit significantly influenced the electrochromic behaviors of the polymers.
- The polymer **P1** showed superior electrochromic performances and operating stability.

ARTICLE INFO

Keywords:

Alkylated quinoxaline
Donor-acceptor-type electrochromic polymer
Thiophene
Coloration efficiency

ABSTRACT

Two electrochromic copolymers, **P1** and **P2**, were synthesized from Stille coupling reactions of dibrominated phenazine having branched and linear alkyl side-chains, respectively, with distannyl thiophene. The prepared donor-acceptor type electrochromic polymers showed good solution processability, superior switching characteristics, and high redox stability. In electrochromic measurements, the polymers exhibited reversible blue-to-transmissive switching at an applied voltage of 0.9 V and 1.2 V, respectively, with transmittance changes of 18.1% at 597 nm and 25.3% at 653 nm for **P1** and **P2**, respectively. They showed high coloration efficiencies of 232.5 and 132.6 cm²/C, respectively, in the visible region and long-term stability for more than a hundred cycles. Furthermore, the polymers were completely transparent in the bleached state, accompanied by high NIR absorption, upon oxidation. These results manifest that the alkyl side-chains on the quinoxaline acceptor unit could dictate the intermolecular interactions of polymer chains affecting the electrochromic performances. The findings of this study suggest the strategy of designing and preparing efficient electrochromic polymers with selective absorption in long visible and NIR regions for smart windows and displays.

1. Introduction

Electrochromic devices (ECDs) have found numerous applications, including smart windows, reflective displays, anti-glare sunglasses, and fabric electrochromics [1–6]. Recently, donor-acceptor (D-A) alternating conjugated polymers have been often employed in electrochromic devices as electroactive materials due to fast switching speed, easy solution processability, facile color-tuning, and high optical contrasts [7–9]. These attractive performances were attributed to the ability to lower the band gap energies and control inter-chain charge transfers by adjusting the HOMO and LUMO levels and rendering the intermolecular packing and backbone conformation. In this regard, the side-chain engineering is as important as the conjugated backbones in designing D-A type polymer structures. The flexible side-chains

provides the necessary solubility of rigid π -conjugated backbones in organic solvents, which makes it possible for solution-based processings [10–12]. While extensive researches have been carried out concerning the effect of π -conjugated backbones on the electrical and electrochemical properties of polymers, the study about the side-chains has been scarce. Only recently several researches concerning side-chain engineering of D-A type conjugated polymers have been reported, in which enhanced electrical, optical and electrochemical properties were examined [13–17]. It is noteworthy to mention that, in most cases, the flexible side-chains were attached to the donor unit, such as thiophene and ethylenedioxythiophene, of the conjugated polymer [18–21].

Quinoxaline derivatives, an important heterocyclic molecule, have been widely used for metal corrosion inhibition, pharmacology against bacteria, and active layers in organic light-emitting diodes [22–25].

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Two nitrogen atoms at 1- and 4-positions make the quinoxaline highly electron-deficient. Interestingly, quinoxaline-based organic semiconductors have been suggested for photonic devices [26–28] and photovoltaic cells [29,30].

Recently, our group reported the benzotriazole-based D-A type low-bandgap polymers having a siloxane-terminated side-chain in electrochromic devices [31]. Gunbas and coworkers reported the ethylenedioxythiophene and benzotriazole based D-A type conjugated polymers containing alkylated side-chains [32]. Inspired by these previous results, herein, we present quinoxaline-thiophene based D-A type electrochromic polymers, which can exhibit complete transparency, but with high NIR absorption. We have specifically interested in the design of new electron-accepting moieties containing flexible side-chains, as a measure to examine the effect of branched and linear alkyl side-chains on the electrochromic transitions of the polymers. Two acceptor compounds, 7,8-bis(2-ethylhexyloxy)-1,4-dibromophenazine (**M1**) and 1,4-dibromo-7,8-bis(dodecyloxy)phenazine (**M2**), were synthesized and employed for the preparation of the electrochromic copolymers **P1** and **P2**, respectively, using Stille coupling reactions with distannyl thiophene. The introduction of the alkylated side-chains into acceptor units would allow the ease of processing and alter the intermolecular interactions of polymer backbones. Consequently, it was expected to affect the morphological and electrochromic properties of the resulting polymers. The side-chain modification of 1,4-dibromophenazine acceptor unit has not been reported elsewhere. Optical and morphological properties of the prepared polymers were examined by various characterization techniques, including UV–vis absorption, photoluminescence, cyclic voltammetry (CV), and atomic force microscope (AFM) measurements. The electrochromic properties of glass cells were investigated in terms of spectroelectrochemistry and cyclic switching stability.

2. Experiments

2.1. Materials

The materials, such as 2,1,3-benzothiadiazole, 2,5-dihydroxy-1,4-benzoquinone, 2-ethylhexyl bromide, 1-bromododecane, and 2,5-bis(trimethylstannyl)thiophene, were purchased. Dry solvents, such as toluene, dimethyl formamide (DMF), and chloroform (CHCl₃), were obtained from Sigma Aldrich (Korea). These materials and solvents were used as received. Indium tin oxide (ITO) coated glass slides were used as substrates for electrochemical measurements.

2.2. Synthesis

2.2.1. General procedure for the synthesis of **M1** and **M2**

A mixture of 6,9-dibromophenazine-2,3-diol (1 mmol) and K₂CO₃ (4 mmol) in DMF (5 mL) was stirred for 1 h under a nitrogen atmosphere. 1-Bromoalkyl (3 mmol) dissolved in DMF (2 mL) was added to the mixture. The mixed solution was heated at 100 °C for 24 h. Then, it was cooled to ambient temperature and poured into deionized water (200 mL). The precipitate was isolated by filtration and washed with water. Further purification was carried out by chromatography on silica gel using dichloromethane as the eluent. A light yellow powder was collected and dried (75% yield).

7,8-bis(2-ethylhexyloxy)-1,4-dibromophenazine (**M1**): ¹H NMR (500 MHz, CDCl₃): δ 7.92 (s, 2H), 7.53 (s, 2H), 4.18–4.11 (m, 4H), 1.90–1.88 (m, 2H), 1.55–1.40 (m, 8H), 1.37–1.34 (m, 8H), 1.00–0.91 (m, 12H). ¹³C NMR (500 MHz, CDCl₃): δ 155.98, 142.81, 139.43, 131.50, 131.37, 123.19, 105.28, 105.07, 71.83, 39.28, 30.63, 29.07, 24.01, 23.02, 14.12, 13.99, 11.26, 11.17 ppm.

1,4-dibromo-7,8-bis(dodecyloxy)phenazine (**M2**): ¹H NMR (500 MHz, CDCl₃): δ 7.91 (s, 2H), 7.47 (s, 2H), 4.26–4.24 (t, *J* = 10 Hz, 4H), 1.98–1.94 (m, 4H), 1.58–1.52 (m, 2H), 1.42–1.39 (m, 4H), 1.34–1.27 (m, 30H), 0.89–0.87 (t, *J* = 10 Hz, 6H). ¹³C NMR (500 MHz, CDCl₃): δ 155.83, 142.95, 139.70, 131.78, 131.54, 123.40, 105.75, 105.54, 68.81, 32.12, 29.89, 29.86, 29.80, 29.57, 28.94, 28.88, 26.20, 22.88, 14.39, 14.22 ppm.

2.2.2. General procedure for the polymerization of **P1** and **P2**

Dibrominated phenazine (0.1 mmol), distannyl thiophene (0.1 mmol), tris(dibenzylideneacetone)dipalladium (2 mol%), and tri (*o*-tolyl)phosphine (4 mol%) were placed in a pressure vial, followed by the addition of anhydrous toluene (8 mL). The reaction mixture was purged with argon for 1 h and then heated at 95 °C for 48 h under vigorous stirring. After cooling to room temperature, the mixture was poured into methanol (250 mL). The solid was filtered and dissolved in chloroform. The residual palladium particles were removed by flash column chromatography on silica. After the chloroform was concentrated, methanol was added to re-precipitate the polymers. The dark blue and purple-colored product were obtained and dried in vacuum.

Polymer 1 (**P1**): ¹H NMR (500 MHz, CDCl₃): δ 8.12 (br), 7.45 (br), 4.14–4.07 (br), 3.76–3.73 (br), 1.86–1.84 (br), 1.52 (br), 1.27–0.81 (br). Gel permeation chromatography (GPC) analysis (PS standard in THF): Mn 14070, Mw 18780, PDI 1.33.

Polymer 2 (**P2**): ¹H NMR (500 MHz, CDCl₃): δ 8.21–7.99 (br), 4.35–3.75 (br), 1.70–0.75 (br). GPC analysis (polystyrene standard in THF): Mn 35900, Mw 49820, PDI 1.39.

2.3. Characterization

The molecular weight of the polymers was measured by GPC using an YL9100 HPLC system (Young-Lin, polystyrene standards), with THF as the eluent. The UV–Vis spectra were measured using a UV-1800 UV spectrophotometer (Shimadzu). The emission of the polymers was measured with a LS-45 fluorescence spectrometer (Perkin-Elmer). The polymer films were prepared by spin-coating the corresponding polymer solutions (1 mL of 20 mg/mL THF solution) on the ITO glass (2.5 × 5.5 cm², 1000 rpm × 60 s). The electrochemical and spectroelectrochemical properties were measured in a three-electrode cell consisting of a polymer-coated ITO glass slide, a Pt wire, and a Ag wire as the working, counter, and reference electrodes, respectively. A 0.1 M tetrabutyl ammonium hexafluorophosphate (TBAPF₆) in acetonitrile was used as the supporting electrolyte solution for all measurements. The electrochromic glass cells were prepared by spin-coating the **P1** and **P2** (15 mg/mL) chloroform solutions on ITO-coated glass.

The change in optical density (ΔOD) and coloration efficiency (*CE*) were calculated by the following relation,

$$CE = \frac{\Delta OD}{Q_d} = \frac{\log(T_{ox}/T_{red})}{Q_d}$$

, where *T_{ox}* and *T_{red}* denote the percent transmittance of the bleached and colored states, respectively, and *Q_d* is the injected/ejected charge per unit area (C/cm²) [33].

3. Results and discussion

Scheme 1 presents the synthetic schemes of alkylated quinoxaline-thiophene based D-A type electrochromic polymers. Intermediates **2**, **3**, and **4** were synthesized using the procedures described above and their spectroscopic data were well matched with previous results [34]. Dihydroxy quinoxaline was alkylated with 1-bromo-2-ethylhexane and 1-bromododecane, respectively, in the presence of K₂CO₃ in DMF. Two quinoxalines having branched and linear alkyl side-chains, **M1** and **M2**, were obtained and isolated by column chromatography. Furthermore, alkylated dibromo-quinoxalines and distannylated thiophenes were reacted in toluene via Stille coupling in the presence of Pd₂(dba)₃ and P (*o*-tolyl), to give the corresponding electrochromic copolymers, **P1** and **P2**, respectively. The structures of the monomers and copolymers were characterized by ¹H NMR spectroscopy and GPC.

The UV–Vis absorption spectra of **P1** and **P2** were measured in the solution and the film state (**Fig. 1a**). In THF solution, **P1** showed two absorption maxima at 390 and 585 nm, corresponding to π–π* transition and intramolecular charge transfer (ICT) and a, respectively [29,30]. Two absorption peaks appeared at 390 and 597 nm, in case of

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