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Electrochemical polymerization of a new low-voltage oxidized thienylenepyrrole derivative and its electrochromic device application

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ABSTRACT

Synthesis of a new monomer, 2,5-bis-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-1-phenyl-1*H*-pyrrole (**ENE**), from pyrrole, iodobenzene and 3,4-ethylenedioxythiophene (**EDOT**), and its electropolymerization are reported. **ENE** was oxidized at a low oxidation potential (0.45 V vs. Ag/AgCl) and successfully electropolymerized in acetonitrile containing 0.1 M $NaClO_4$ and $LiClO_4$ electrolyte mixture. The resulting polymer, **P(ENE)**, revealed five distinctive colors upon doping, which indicated that the polymer is multichromic. **P(ENE)** has a coloration efficiency of 288 cm^2/C at 422 nm with a specific optical band gap of 2.0 eV. Furthermore, an electrochromic device (ECD) based on **P(ENE)** and poly(ethylene dioxythiophene) (PEDOT) was constructed and its switching was investigated by UV–vis spectroscopy.

1. Introduction

Functional conjugated polymers are still of great interest since they are promising candidates for a large number of advanced technological applications including solar cells [1,2], light emitting diodes [3–5], optical displays and sensors [6–8]. Although the first generation electrochromic materials have been mostly inorganic oxides due to their some advantages [9–12], functional conjugated polymers have also been widely employed as electrochromic materials in electrochromic devices [13–15]. These advantages include not only multicolors and high contrast ratio but also include fast switching capability and long cycle times. Furthermore, these properties can be tuned via structural tailoring of the starting materials. Thus, significant effort has been devoted to the design and synthesis of new polymeric electrochromics based on conjugated polymers [16]. Among various conjugated polymers, polythienylpyrroles, having 2,5-di(2-thienyl)pyrrole (SNS) repeating units, have been extensively investigated since functionalization of the monomer structure prior to polymerization is possible via *N*-substitution. This functionalization allows easy tuning of optoelectronic properties of the resulting conjugated polymer. Ferraris et al. reported the electrochemical and optical properties of various N-substituted polythienylpyrroles and obtained soluble polymers via alkyl group substitution on the central pyrrole unit [17–20]. Otero et al. investigated the electrochemical polymerization and electrodissolution process of SNS in acetonitrile using various electrolytes [21,22]. Synthesis of a large number of soluble conjugated polymers from substituted SNS derivatives and their device applications were also reported by Toppare et al. [23–26]. In addition, Cihaner et al. reported the formation of soluble polymers from several SNS derivatives, exhibiting electrochromic and fluorescence properties [27–30]. We have also investigated the electrochemical polymerization and optoelectronic properties of phthalonitrile, phthalocyanine and luminol substituted SNS derivatives [30–33].

After Otero et al. reported the electrochemical polymerization of SNS in acetonitrile [17,18], Ferraris et al. investigated the electrochemical and optical properties of various *N*-substituted polythienylpyrroles and obtained soluble polymers via alkyl group substitution on the central pyrrole unit [19–22]. Synthesis of a large number of soluble conjugated polymers from substituted SNS derivatives and their device applications were also reported by Toppare et al. [22–26]. In addition, Cihaner et al. reported the formation of soluble polymers from several SNS derivatives, exhibiting electrochromic and fluorescence properties [27–30]. We have also investigated the electrochemical polymerization and optoelectronic properties of phthalonitrile, phthalocyanine and luminol substituted SNS derivatives [30–33].

Herein, we report the electrochemical polymerization of a new monomer, 2,5-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-1-phenyl-1*H*-pyrrole **(ENE)** bearing 3,4-ethylenedioxythiophene (EDOT) side groups. EDOT is a widely used analog of thiophene

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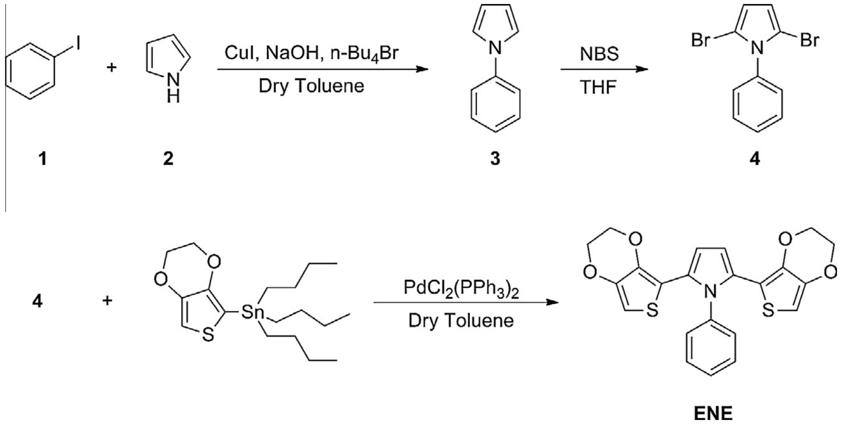

Scheme 1. Synthesis of 2,5-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-1-phenyl-1H-pyrrole (**ENE**).

and it is expected that the replacement of thiophene side groups in SNS scaffold will not only lower the oxidation potential of the corresponding monomer but also prevents the side reactions during the electrochemical polymerization, leading to formation of regioregular conjugated polymers [7,33–35]. The monomer, **ENE**, was polymerized via potential cycling and the electrochromic properties of the resulting polymer, **P(ENE)**, was investigated via *in situ* spectroelectrochemical techniques. An electrochromic device, switching from −1.0 V at neutral state to 1.8 V at oxidized state, was also prepared by utilizing **P(ENE)** and PEDOT as anodically and cathodically coloring electrochromic materials.

2. Experimental

2.1. Electropolymerization and characterization

All chemicals were purchased from Aldrich and Merck chemical companies and used without any further purification. Prior to electrochemical polymerization, redox behavior of the monomer, **ENE**, was investigated using cyclic voltammetry (CV) in acetonitrile (ACN) solution containing 0.1 M $LiClO_4$ and $NaClO_4$ in the ratio of 1:1 on platinum electrode. The monomer was successfully electropolymerized via potentiodynamic or potentiostatic methods using three-electrode system containing a platinum disc (0.02 cm^2) and a platinum wire as working and counter electrodes, respectively, as well as Ag/AgCl electrode (in 3 M NaCl (aq) solution) as a reference electrode. Prior to spectroelectrochemical investigations, the polymer film was switched between its neutral and doped state several times in order to equilibrate redox behavior in monomer-free electrolytic solution. For electro-optical studies, indium-tin oxide (ITO, Delta Tech. 8–12 Ω, 0.7 cm × 5 cm) electrodes were coated by the polymer film. The coated electrode was dipped into a rectangular UV quartz cuvette (light path length = 1.0 cm, purchased from Sigma–Aldrich) together with Pt wire and Ag wire as counter and reference electrodes, respectively.

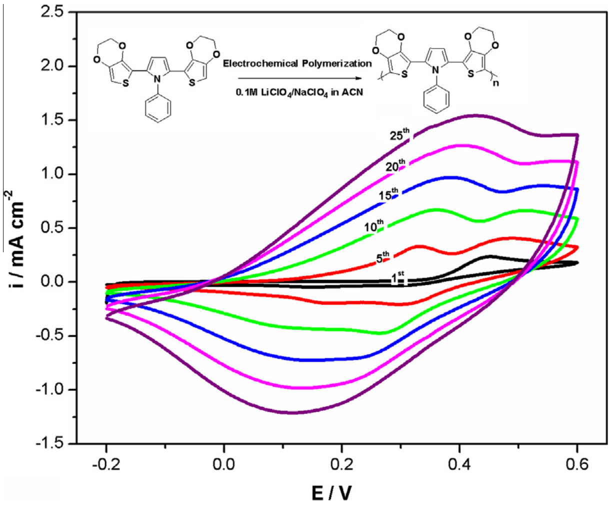

Fig. 1. Repetitive cyclic voltammograms of 2 mM **ENE** in 0.1 M $LiClO_4/NaClO_4$/ACN at a scan rate of 100 mV s^{-1} on Pt electrode.

In situ spectroelectrochemical studies were performed using Hewlett–Packard 8453A diode array spectrometer. A Pt wire was used as a counter electrode and an Ag wire as a pseudo-reference electrode which was calibrated externally using 5 mM solution of ferrocene/ferrocenium couple in the electrolytic solution. Electroanalytical measurements were performed using a Gamry PCI4/300 potentiostat–galvanostat. FTIR spectra were recorded on a Bruker Vertex 70 Spectrophotometer.

2.2. Fabrication of electrochromic device

For a dual type electrochromic device (ECD) fabrication, PEDOT as a cathodically coloring polymer was electropolymerized onto a 1.25 cm^2 ITO glass surface from an ACN solution containing 2×10^{-3} M EDOT and 0.1 M $TBAPF_6$ via constant potential electrolysis at 1.2 V. After coating PEDOT onto the ITO-glass surface, the film was rinsed with ACN to remove all the unreacted monomers on the electrode surface. **P(ENE)** was also electropolymerized using CV method in ACN solution containing 0.1 M $LiClO_4$ and $NaClO_4$ in the ratio of 1:1 on Pt electrode. The device was constructed using the electrochromic electrodes stacked face-to-face separated by gel electrolyte ($TBABF_4$; ACN; poly(methyl methacrylate); polycarbonate in the ratio of 3:70:7:20) [23,25]. The electrochromic device was allowed to dry for 48 h at room temperature under atmospheric pressure. The electro-optical properties of the device were recorded *in situ* under various applied potentials. Finally, square wave potential method was used to perform switching between the colored states.

2.3. Synthesis of 2,5-bis-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-1-phenyl-1H-pyrrole (*ENE*)

2.3.1. Synthesis of N-phenylpyrrole (*3*)

This compound was prepared from iodobenzene (**1**) according to a literature procedure [36]. To a stirred solution of iodobenzene (**1**) (2.850 g, 14 mmol), CuI (0.133 g, 0.7 mmol), *n*-Bu_4NBr (0.225 g, 0.7 mmol) and NaOH (1.120 g, 28 mmol) in dry toluene (15 mL)