



A regiosymmetric blue-to-transmissive electrochromic polymer based on 3,4-ethylenedioxythiophene with bromomethyl pendant groups

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ABSTRACT

The synthesis and electrochromic properties of a novel regiosymmetric polymer based on 3,4-ethylenedioxythiophene, poly(2,3-bis(bromomethyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine) (PEDOT(MeBr)₂) were highlighted. The monomer was electrochemically polymerized via repetitive cycling between 0 and 1.8 V in lithium perchlorate (LiClO₄)-acetonitrile (ACN) electrolytic medium. The corresponding polymer was characterized by FTIR spectra, scanning electron microscopy, cyclic voltammetry, UV-Vis-NIR spectroscopy and colorimetry. It features a reversible redox process and demonstrates a stable blue-to-transmissive electrochromic behavior with very low driving potentials (−0.1 and 0.65 V). Additionally the polymer film exhibits enhanced optical contrast (60% at 669 nm) and improved coloration efficiency (183.1 cm²/C at 100% full contrast during bleaching process) which are higher than those of PEDOT, a relatively longer response time compared with PEDOT and reasonable redox stability.

1. Introduction

Electrochromes exhibit repeated and reversible changes in optical properties through electrochemical oxidation or reduction reactions induced by external driving potentials [1–4]. A large number of electrochromic materials are well documented, including transition metal oxides [5], mixed-valence metal complexes [6], organic small molecules [7] and conjugated polymers [8–10]. In general most of conjugated polymers feature absorption bands in the visible region (a color neutral state) because of the extended delocalization of π electrons along the backbones [11]. Through electrochemical oxidation or reduction charge carriers (polarons and bipolarons) form, and it is accompanied by a change of the aromatic structural form of the polymer chain toward a quinoid-like structure, therefore, new electronic states with lower energies of the polymer are introduced which exhibit absorption bands at longer wavelength with an accompanying decrease of absorption belong to the neutral polymer. As a result, conjugated polymers demonstrate attracting electrochromic phenomena during the redox cycles [12].

Moreover conjugated polymers have attracted much attention as electrochromes in smart windows and displays because of their excellent electrochromic properties such as tunability of the color via structure modification [13–18], multiple colors achievement in one material (multichromism) [19], high optical contrast ratio, short response time, superior coloration efficiency, thin film flexibility [8–10]

and ease of processing [20,21]. The most important among them is that, creative structure modifications of the monomer can noticeably adjust the optical properties of its corresponding polymer. Specific differences in the monomer structure may also alter the electrochromic switching performance of the polymer during redox processes [22].

Therefore the synthesis of new conjugated polymers by functionalizing monomers is an appealing way to adjust their optical and electronic characteristics. That will be achieved by altering the nature of the repeating unit through attachment of electron withdrawing/donating pendant substituents or backbone building blocks [23]. It has been well noted that the pendant groups markedly impact the optoelectronic properties of the polymer, and the position of substitution also plays an important role [24–26].

Compared with the other conjugated polymers, polythiophenes have attained appreciable research interest in electrochromic field on account of various benefits including ease of synthesis and modification, low driving potentials, high conductivity, high transmittance changes, short response times and high stability in the oxidized states [27]. Poly(3,4-ethylenedioxythiophene), also known as PEDOT, is a gold standard as an electrochromic material by virtue of its high conductivity and high transparency in the oxidized state [28,29].

Development of new PEDOT derivatives with enhanced electrochromic properties is one of the most important topics of scientific research in electrochromic research field [30]. Although based on the rich chemistry of thiophene, various polythiophenes with electron-donating

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pendant groups such as alkyl or alkoxy groups have been developed, only a few polythiophenes with electron-withdrawing moieties such as $-F$, $-Br$, $-NO_2$, $-COOH$ or $-CN$ have been synthesized and characterized [31]. However the presence of heteroatoms in the π -conjugated monomers may play a significant role in tailoring the optoelectronic properties of the polymers by reason of their intrinsic electron-donating or electron-withdrawing characteristic, hydrogen bonding and polarizability [32].

Our research group has devoted ourselves to the research of new electrochromic materials, particularly electrochromic polymers in the last years [33,34]. Compared with chemical polymerization, the easily performed electrochemical polymerization has been well noted as one of the most convenient methods to obtain electrochromic polymer films because it accomplishes polymerization and film deposition in one step and avoids the isolation and purification of the polymer [35]. As a continuation of our interests in synthesizing novel electrochromic materials, in this study we disclose the electrochemical synthesis and characterization of a novel regiosymmetric double bromomethyl functionalized conjugated polymer based on PEDOT, namely PEDOT(MeBr)₂ in detail. The use of symmetric substitution on the ethylenedioxy bridge is because the asymmetric substitution pattern may result in a steric hindrance for counter-ion injection/ejection during the redox processes, therefore, induce a lower optical contrast [36]. We hope that derivatization of ethylenedioxythiophene (EDOT) with symmetric bromomethyl pendant groups will improve the optoelectronic properties of the polymer. The experimental results show that as a blue-to-transmissive electrochromic material PEDOT(MeBr)₂ has an improved optical contrast and coloration efficiency, but a relatively longer response time compared with the parent PEDOT.

2. Experimental

2.1. Materials

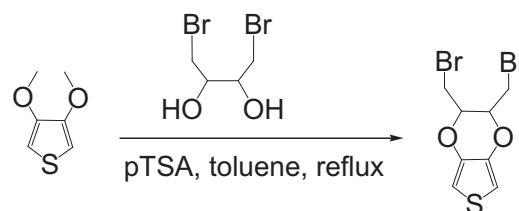
3,4-Di(methoxy)thiophene (DMOT) and lithium perchlorate (LiClO₄, 99%, anhydrous) were purchased from Aladdin Industrial Inc., 1,4-dibromo-2,3-butanediol was obtained from Sigma-Aldrich Co. LLC. The other chemicals were bought from Sinopharm Chemical Reagent Co. Ltd. All reagents were used as received.

2.2. Instruments

NMR spectra were collected on a 400 MHz Bruker Avance 400 spectrometer in deuteriochloroform (CDCl₃). IR spectra were determined using NICOLET 6700 FTIR spectrometer (Thermo Scientific). High resolution mass spectrum was obtained on a LTQ ORBITRAP XL mass spectrometer (Thermo Scientific). SEM images were collected on a JSM-7500F field emission scanning electron microscope (JEOL). Cyclic voltammetry, spectroelectrochemistry and colorimetry studies were performed using a CHI600E electrochemical analyzer (CH Instruments Ins.) and T6 New Happy UV-Vis-NIR spectrometer (Beijing Persee General).

2.3. Synthesis of 2,3-bis(bromomethyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (EDOT(MeBr)₂)

3,4-Di(methoxy)thiophene (14 mmol, 2.02 g), *p*-toluenesulfonic acid monohydrate (1.4 mmol, 0.266 g), 1,4-dibromo-2,3-butanediol (20 mmol, 4.96 g) and 250 mL toluene were loaded in a 500 mL round bottom flask with a Soxhlet extractor with type 4 Å molecular sieves. The reaction mixture was refluxed for 24 h, then cooled and washed with deionized water for three times. The toluene was removed by rotary evaporation under vacuum. The residue was subjected to column chromatography (petroleum ether/ethyl acetate = 30:1, v/v) to give the final product as a white solid 1.3 g (28% yield). ¹H NMR (400 MHz, CDCl₃, δ): 6.41 (s, 2H), 4.47 (m, 2H), 3.61 (m, 4H). ¹³C NMR (100 MHz,



Scheme 1. The synthesis of EDOT(MeBr)₂.

CDCl₃, δ): 139.5, 100.9, 73.1, 29.6. HRMS m/z = 328.8662 [M+H]⁺, calc. for C₈H₈Br₂O₂S = 328.87. The synthetic route of EDOT(MeBr)₂ is shown in Scheme 1.

2.4. Synthesis of PEDOT(MeBr)₂

The electrochemical polymerization was carried out in a one-compartment cell (Pt wire as the counter electrode, Ag wire as the pseudo-reference electrode and an ITO-coated glass slide as the working electrode) which has a solution consisting of 0.01 M EDOT(MeBr)₂ and 0.1 M LiClO₄/ACN electrolyte-solvent couple. Ag wire pseudo reference electrode was calibrated externally using 5 mM solution of ferrocene (Fc/Fc⁺) in the same electrolyte ($E_{1/2}(Fc/Fc^+) = 0.36$ V versus Ag wire in 0.1 M LiClO₄/PC). The potentials are reported versus Ag wire. The solution was deaerated by dry nitrogen gas and maintained under a small overpressure during the polymerization to circumvent the effect of oxygen. The polymer was directly deposited on ITO/glass potential-dynamically through cyclic voltammetry scan between 0 V and 1.8 V for 5 cycles. After polymerization, the polymer film was electrochemically reduced to its neutral form in monomer-free electrolytic medium and repeatedly washed with ACN to remove the electrolyte, monomers and oligomers. The synthetic route is depicted in Scheme 2.

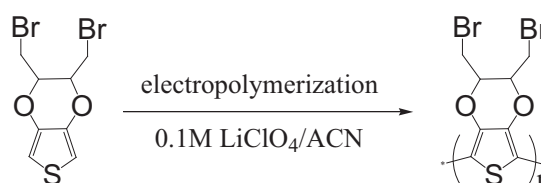
2.5. Electrochemical and spectroelectrochemical experiments

The electrochemical and spectroelectrochemical characterizations were performed in a quartz cuvette consisting of an ITO/glass (4 cm × 0.7 cm) as the working electrode, a Pt wire as the counter electrode and an Ag wire as the pseudo-reference electrode. All measurements were carried out in monomer-free lithium perchlorate (LiClO₄)-propylene carbonate (PC) electrolytic medium as PC is a good solvent to dissolve and dissociate lithium salts [37]. Following the suggestion of Silva and Ribeiro et al. [38], CIE (Commission Internationale de l'Eclairage) 1976 color coordinates (L^* , a^* , b^*) and relative luminance were calculated from UV-Vis-NIR spectroscopy using a Spectra Lux Software [39] and a spreadsheet developed by Mortimer and Varley [40].

3. Results and discussion

3.1. Electrochemical polymerization

The monomer EDOT(MeBr)₂ (0.01 M) in 0.1 M LiClO₄ solution in ACN was initially subjected to repetitive cyclic voltammetry (CV) between 0 and 1.8 V at a potential scan rate of 100 mV/s for 5 cycles as



Scheme 2. The synthesis of PEDOT(MeBr)₂.

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