

Investigation of electrochromic properties of poly(3,5-bis(4-methoxyphenyl)dithieno[3,2-*b*;2',3'-*d*]thiophene)

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ABSTRACT

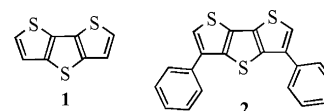
Electropolymerization of 3,5-bis(4-methoxyphenyl)dithieno[3,2-*b*;2',3'-*d*]thiophene BMPHDTT, having strong electron-donating methoxy groups, was performed, utilizing potentiodynamic method. The homopolymer was characterized by cyclic voltammetry (CV), Fourier transform infrared (FTIR) and UV–vis spectroscopy. Spectroelectrochemical and electrochromic properties of the homopolymer film were investigated and a PBMPHDTT/PEDOT device was constructed to understand its characteristics in detail. It was revealed that the potential range of 0.0–2.0V is suitable for operating the device between yellow and blue colors. It indicated a good open circuit memory and stability.

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1. Introduction

As electron rich species, dithienothiophenes (DTT) possess three fused thiophene rings, which make them good electron donors. Such a property brings them to the forefront of organic material chemistry as they find electronic and optoelectronic applications [1,2]. Although DTTs have six isomers, depending on the location of the sulfur atoms in the peripheral thiophene rings, the most elaborated one is dithieno[3,2-*b*;2',3'-*d*]thiophene **1**. This is due to its structure which enables the most suitable conjugation among DTT family, particularly when polymerized. Although the first report on the synthesis of **1**, containing proper spectroscopic data appeared in 1971 [3], its first electrochemical polymerization was reported in 1985 [4,5]. The polymer was explained to be cathode active and had a high charge storage capacity with a fast discharge rate, which was not connected to the polymer degradation since PDTT electrodes could recover their original voltage and cycling capabilities through recharging. PDTT was disclosed to have an excellent cycling ability, high doping level and high coulombic ability for battery applications [6]. For a supercapacitor application, n- and p-dopings of PDTT were reported [7] and in a separate study a detailed spectroelectrochemical property of DTT was disclosed [8]. Moreover, the copolymers of DTT with its oxidized form of DTT-S-S-dioxide were investigated for photovoltaic applications, which revealed

that they could become possible candidates as transporters in organic donor–acceptor photoactive layer [9].



PDTT was disclosed to be an important candidate for electrochromic devices. Its electrochromic studies showed reversible electrochromic properties, which displayed a high contrast in color between red neutral and blue-black oxidized states [10,11]. It displayed a switching time less than 1 s, a good stability to repeated switching and an optical memory up to 11,000 tested cycles.

In continuation of our studies on the synthesis and electrochromic properties of PDTT derivatives [12–14], 3,5-bis(4-methoxyphenyl)dithieno[3,2-*b*;2',3'-*d*]thiophene BMPHDTT **6**, having strong electron-donating methoxy groups, was synthesized and its homopolymer PBMPHDTT was prepared electrochemically. The polymer was characterized by FTIR and UV–vis spectroscopy. Electroactivities of the monomer and the polymer were investigated using cyclic voltammetry (CV). Spectroelectrochemistry of the deposited polymer was studied by CV–UV in situ technique. The second part of the study included the device preparation with PEDOT and investigation of the properties of the electrochromic device (ECD). Although the presence of strong electron-donating groups on BMPHDTT did not make considerable difference compared with the PPh₂DTT **2** [13], which has no electron-donating or withdrawing groups, it displayed comparable properties.

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2. Experimental

2.1. Materials and reagents

Thiophene (Acros), EDOT (Aldrich), phosphorus decasulfide (P_4S_{10}) and 2-bromo-4'-methoxyacetophenone (Aldrich) were used without further purification. Bromine, diethylether (Et_2O), toluene, sodium bicarbonate ($NaHCO_3$) and tetrabutylammonium tetrafluoroborate ($TBABF_4$) were obtained from Merck. Tertiary-butyllithium (*t*-BuLi), dichloromethane (DCM) and acetonitrile (AN) were received from Aldrich. Calcium hydride, lithium perchlorate ($LiClO_4$) and sodium perchlorate ($NaClO_4$) were purchased from Acros. Propylene carbonate (PC) and polymethylmethacrylate (PMMA) were received from Alfa Aesar. Et_2O was dried over sodium. DCM, AN, and toluene were dried over CaH_2 . All the solvents were distilled prior to use.

2.2. Equipment

CH-Instruments Model 400A was used as a potentiostat for the CV studies. FTIR spectrum was recorded on a Thermo Nicolet 6700 FTIR spectrometer. UV and colorimetry measurements were studied on Bio HITACHI U-0080D and Conica Minolta CS-100 chromometer, respectively. Mass spectra were recorded on Bruker MICROTOFQ and Thermo LCQ-Deca ion trap mass instruments.

2.3. Synthesis of 1,8-diketone **5**

To the solution of 3,4-dibromothiophene (2 g, 8.26 mmol) **3** dissolved in dry diethylether (50 ml) and cooled down to $-78^\circ C$ was added dropwise *t*-BuLi (5.6 ml, 9.09 mmol, 15% in pentane) under inert atmosphere. It was left stirring for 45 min, after which S_8 (0.27 g, 8.26 mmol) was added portionwise. Addition of *ter*-BuLi and S_8 was repeated with 45 min interval. After stirring the mixture for 2 h at $-78^\circ C$, it was allowed to warm up to room temperature and then cooled $0^\circ C$ at which temperature 2-bromo-4'-methoxyacetophenone (4.17 g, 18.17 mmol) **4** was added. The mixture was left stirring overnight at room temperature. It was extracted with dichloromethane and the organic layer was dried over Na_2SO_4 , filtered and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography eluting with the mixture of dichloromethane:hexane (6:1) to obtain the title compound **5** (white powder, 2.32 g, 63%), mp $92^\circ C$. 1H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, $J=8.8$ Hz, 4H), 7.28 (s, 2H), 6.9 (d, $J=8.8$ Hz, 4H), 4.2 (s, 4H), 3.86 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.7 (C=O), 163.7, 132, 131.7, 128, 127.3, 113.8, 55.4 (CH_3O), 40.9 (CH_2S), EIMS (m/z) $M^+ + 1$ 445; HRESIMS m/z $M^+ + Na$ calculated for $C_{22}H_{20}O_4S_3Na$ m/z 467.0421, found 467.0429

2.4. Synthesis of

3,5-bis(4-methoxyphenyl)dithieno[3,2-b;2',3'-d]thiophene **6**

To the mixture of P_4S_{10} (0.55 g, 1.24 mmol) and *p*-toluenesulfonic acid (0.856 g, 4.52 mmol) dissolved in dry toluene (50 ml) and stirred for 1 h, at $45^\circ C$ was added the 1,8-diketone **5** (0.500 g, 1.13 mmol). The mixture was left refluxing for 2 h. It was then cooled to room temperature and extracted with dichloromethane and washed with $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 , filtered and the solvent was evaporated under reduced pressure. The product was purified by column chromatography, eluting with hexane:dichloromethane (3:1) to obtain the title compound **6** (white powder, 0.3 g, 65%), mp $181^\circ C$. 1H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, $J=8.8$ Hz, 4H), 7.37 (s, 2H), 7.03 (d, $J=8.8$ Hz, 4H), 3.88 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 139.9, 132.5, 131, 128, 127.5, 120, 114, 54.5 (CH_3O) EIMS

(m/z) $M^+ + 1$ 409; HRESIMS m/z $M^+ + 1$ calculated for $C_{22}H_{17}O_2S_3$ m/z 409.0391, found 409.0395

2.5. Cyclic voltammetry (CV)

To investigate the electroactivity of the monomer and polymer, cyclic voltammetry was utilized. A CV compartment having Pt-working, Pt-counter and Ag-wire reference electrode was employed. $NaClO_4/LiClO_4$ (0.1:0.1 M) as a supporting electrolyte and AN/DCM (9:1) solvent mixture were used. All the measurements were recorded at room temperature under nitrogen atmosphere.

2.6. Electrochemical polymerization of *BMPPhDTT* and spectroelectrochemical measurements

Polymerization was carried out in a single compartment cell under constant potential. The concentrations of the monomer and the electrolyte were kept as 1×10^{-3} M and 0.1 M, respectively, in AN/DCM (9:1) solvent mixture. A constant potential of +1.3 V was applied at room temperature under inert atmosphere, after which free standing film was vigorously washed with AN/DCM (9:1) to remove unreacted monomers.

Spectroelectrochemical studies of the homopolymer were conducted in a UV cuvette employing ITO coated glass as a working, Pt-wire as a counter and Ag-wire as a reference electrodes. Potential was switched between 0.0 and +1.4 V. Spectroelectrochemistry and switching measurements of the polymer film deposited on ITO were carried out in monomer free conditions.

2.7. Gel electrolyte preparation for the devices

PMMA and tetrabutylammonium tetrafluoroborate were dissolved in AN. As the mixture was heated and stirred, PC was added into the medium. Stirring and heating was maintained until the mixture was turned into viscous gel. The ratio of the AN:PC:PMMA: $TBABF_4$ was 70:20:7:3, respectively, by weight.

2.8. Construction of electrochromic devices (ECDs)

The gel electrolyte was sandwiched between anodically coloring *PBMPPhDTT* and cathodically coloring *PEDOT* layers for the preparation of ECD. The electrodeposition of *PBMPPhDTT* on to ITO was carried out in $NaClO_4/LiClO_4$ (0.1:0.1 M) in AN/DCM solution under the constant potential of +1.3 V, and EDOT (0.01 M in AN) was electrodeposited in 0.1 M $NaClO_4$ in AN under the constant potential of +1.3 V. In order to have a balanced number of redox sites for switching, Chronocoulometry was employed to match the redox charges of the two complementary polymer films. The device was built as one of the polymer film is in the oxidized and the other film is in the neutral states. The gel electrolyte was spread on the electroactive polymer coated sides and sandwiched.

3. Result and discussion

3.1. Synthesis of

3,5-bis(4-methoxyphenyl)dithieno[3,2-b;2',3'-d]thiophene (*BMPPhDTT*) **6**

The monomer, 3,5-bis(4-methoxyphenyl)dithieno[3,2-b;2',3'-d]thiophene **6** was synthesized, employing 1,8-diketone ring closure reaction (Scheme 1) [12,14]. The synthesis of the monomer required two steps starting with 3,4-dibromothiophene **3**, to which α -thioketones at the 3 and 4 positions were introduced via a one-pot, three-step reaction: (i) lithiation with *t*-BuLi at $-78^\circ C$, (ii) addition of elemental sulfur and (iii) introduction of α -thioketone

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