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# Synthesis and electrochromic properties of 3,5-diphenyl-2,6-dithiophene-2-yldithieno[3,2-*b*;2',3'-*d*]thiophene

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ABSTRACT

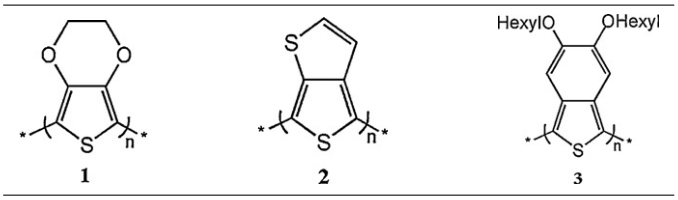
A conducting polymer of 3,5-diphenyl-2,6-dithiophene-2-yl-dithieno[3,2-*b*;2',3'-*d*]thiophene ($Thy_2Ph_2DTT$) was synthesized by potentiodynamic method in dichloromethane (DCM)/acetonitrile (AN) (1/1)-$NaClO_4$/$LiClO_4$ (0.1:0.1 M) solvent-electrolyte mixture. The resulting polymer was characterized *via* cyclic voltammetry (CV), Fourier transform infrared (FTIR) and UV-Vis spectroscopy. Its dual type electrochromic device (ECD) with PEDOT was constructed. Spectroelectrochemical and electrochromic properties of the polymer film and the device were investigated in detail. A potential range of 0.0–2.0 V was found to be suitable for operating the P($Thy_2Ph_2DTT$)/PEDOT device between red and blue colors. The device displayed good open circuit memory and stability. Properties of $Thy_2Ph_2DTT$ and P($Thy_2Ph_2DTT$) were compared with 3,5-diphenyldithieno[3,2-*b*;2',3'-*d*]thiophene ($Ph_2DTT$) and its polymer P($Ph_2DTT$), reported previously, which revealed that introduction of thiophenes to the peripherals of $Ph_2DTT$ improved the properties of the corresponding polymer.



## 1. Introduction

Electrochromism is a reversible and visible change in transmittance and/or reflectance that is associated with an electrochemically induced redox reactions [1–4]. All conducting polymers such as polythiophenes, polypyrroles and polidithienothiophenes are potentially electrochromic in thin-film form [5–7]. The requirements for high performance electrochromic devices (ECD) are high electrochromic efficiency, short response time, good stability, optical memory, which is defined as color stability under open circuit conditions, optical contrast and color uniformity [8].

Electrochemically polymerized polythiophene (PT) was reported to display a red to blue and a red to black-green switches on p- and n-dopings, respectively [9,10], and the energy gaps falls into 2.0–2.2 eV, depending on the molecular weights of the polymers [3]. Various efforts have been devoted to modify thiophene to obtain electrochromically superior materials, such as poly(ethylenedioxy)thiophene (PEDOT) [3] **1** (deep blue in neutral state and sky blue on oxidation oxidation), polybenzothiophene (PBT) [11] **2** (blue-black in neutral state and light yellow on oxidation) and polythienothiophene (PTT) [12,13] **3** (deep blue in natural state and transmissive tan on oxidation), having lover band gaps of 1.6–1.7, 0.92 and 0.85 eV, respectively.




**1** **2** **3**

Dithienothiophene (DTT) **4** based compounds are rich in electrons, having three sulfur atoms, as they possess three fused thiophene rings, which make them good electron donors. Upon polymerization, due to their extended conjugate π-bonds, they can be used in different areas such as electroluminescence, fluorescence, photochromism, optical chromophors, thin-film transistors etc. [14]. First electropolymerization of DTT was reported in 1985 [15,16], which was explained to be cathode active and had a high charge storage capacity with a fast discharge rate. As polydithienothophene (PDTT) electrodes could recover their original voltage and cycling capabilities through recharging, fast discharging was not considered to be the result of polymer degradation.

PDTT was reported to be an important candidate for electrochromic applications, which displayed reversible electrochromic properties with a high contrast in color between red neutral and blue-black oxidized states [17,18]. Moreover, it had a switching time of less than 1 s, a good stability of repeated

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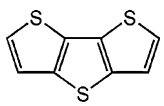
switching and an optical memory up to 11,000 cycles. On the other hand, to our best knowledge, investigations on electrochromic properties of DTTs still remain scarce, only few examples are available in the literature [17–19].

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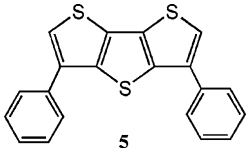


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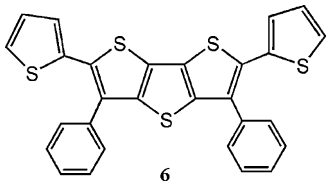


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Recently, we reported the synthesis and electrochromic properties of 3,5-diphenyldithieno[3,2-*b*;2',3'-*d*]thiophene ($Ph_2DTT$) **5** [20]. As a continuation of this study, we disclose herein the preparation and electrochromic properties of dithienyl analogue of $Ph_2DTT$, 3,5-diphenyl-2,6-dithiophene-2-yldithieno[3,2-*b*;2',3'-*d*]thiophene ($Thy_2Ph_2DTT$) **6** and its poymer P($Thy_2Ph_2DTT$), which revealed that introduction of two thienyl groups to the peripherals of the core DTT moiety improved the electrochromic properties of the material.

$Ph_2DTT$ **5** was synthesized through 1,8-diketone ring closure reaction, using $P_4S_{10}$ [21], which is the reaction developed by our group [20,22]. After bromination of **5**, the obtained $Br_2Ph_2DTT$ **7** was coupled with 2-pinacolborylthiophene **8** by Suzuki coupling reaction to obtain 3,5-diphenyl-2,6-dithiophene-2-yl-dithieno[3,2-*b*;2',3'-*d*]thiophene ($Thy_2Ph_2DTT$) **6**, possessing two thiophene groups at 2- and 6- carbons of $Ph_2DTT$.

## 2. Experimental

### 2.1. Materials and reagents

Thiophene (Across), EDOT (Aldrich), phosphorusdecasulfide ($P_4S_{10}$) (Merck), and 2–bromo acetophenone (Aldrich) were used without further purification. Bromine, diethylether ($Et_2O$), acetic acid (AcOH), tetrahydrofuran (THF), tetrakis [$Pd(PPh_3)_4$], toluene, potassium carbonate ($K_2CO_3$) and *N*-bromosucsinimide (NBS) were purchased from Merck. Dichloromethane (DCM), acetonitrile (AN) were received from Aldrich. Calcium hydride, tertiarybutyllithium (*t*-BuLi), *n*-butyllithium (*n*-BuLi), lithium perchlorate ($LiClO_4$), sodium perchlorate ($NaClO_4$) were purchased from Across. Propylene carbonate (PC) and polymethylmetacrylate (PMMA) were received from Alfa Aesar. $Et_2O$ and THF were dried over sodium and 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 FT–IR spectrometer. UV and colorimetry measurements were studied on Bio Photometer U–0080D and Conica Minolta CS–100 chromometer, respectively. $^1H$ and $^{13}C$ NMR spectra were recorded on Varian model NMR. Proton and carbon chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). Mass spectra were recorded on Bruker MICROTOFQ and Thermo LCQ-Deca ion trap mass instruments.

### 2.3. Synthesis of 2,6-dibromo-3,5-diphenyldithieno[3,2-b;2',3'-d]thiophene ($Br_2Ph_2DTT$) **4**

To the solution of 3,5-diphenyldithieno[3,2-*b*:2',3'-*d*]thiophene **5** [20,22] (0.5 g, 1.43 mmol) dissolved in DCM/AcOH (1:1) and cooled to −15 °C was added NBS (0.58 g, 3.2 mmol) in dark. The mixture was left stirring for 2 h. It was extracted with KOH (2 M), $NaHCO_3$ (2 M) and water. 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 hexane to obtain the title compound **7** (white needle, 0.65 g, 90%), 238 °C. $^1H$-NMR (600 MHz, $CDCl_3$) δ 7.60 (dd, $J$ = 16.45 Hz, $J$ = 7.6 Hz, 4 H), 7.42 (m, 4 H), 7.35 (td, $J$ = 7.6 Hz, $J$ = 1.2 Hz, 2 H), $^{13}C$-NMR (150 MHz,$CDCl_3$) δ 139.0, 132.5, 132.4, 128.9, 128.6, 128.4, 124.5, 116.5; EIMS (*m/z*) 506 ($M^+$)

### 2.4. Synthesis of 3,5-diphenyl-2,6-dithiophene-2-yldithieno [3,2-b;2',3'-d]thiophene ($Thy_2Ph_2DTT$) **6**

Compounds **7** (0.21 g, 0.415 mmol) and **8** [23] (0.35 g, 1.67 mmol) were dissolved in THF (30 ml) and then $K_2CO_3$ (2 M, 1.05 mL) and the catalysis, [$Pd(PPh_3)_4$] (24 mg, 20 mmol) were added. The mixture was degassed *via* inert nitrogen atmosphere and heated for 36 h at 80 °C. It was extracted with DCM and water. Organic layer was dried over $Na_2SO_4$, and filtered. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, eluting with hexane to obtain the title compound **6** (yellow powder, 0.12 g, 58%), 255 °C. $^1H$-NMR (600 MHz, $CDCl_3$) δ 7.48 (dd, $J$ = 8.2 Hz, $J$ = 1.1 Hz, 4 H), 7.39 (m, 6 H), 7.20 (bs, 2 H), 7.05 (bs, 2 H), 6.95 (dd, $J$ = 5.0 Hz, $J$ = 3.6 Hz, 2 H); $^{13}C$-NMR (150 MHz,$CDCl_3$) δ 143.4, 136.2, 134.4, 132.3, 132.1, 129.3, 128.9, 128.4, 128.2, 127.3, 126.6, 126.2; EIMS (*m/z*) 513 ($M^+1$)

### 2.5. Cyclic voltammetry (CV)

CV was used to investigate the electroactivity of the monomer and the polymer. A CV compartment having Pt-working, Pt-counter and Ag-wire reference electrodes was employed. $NaClO_4$-$LiClO_4$ as a supporting electrolyte and AN/DCM (1:1) solvent mixture were used. All the measurements were conducted at room temperature.

### 2.6. Electropolymerization of $Thy_2Ph_2DTT$ and Spectroelectrochemical Measurements

Polymerization of $Thy_2Ph_2DTT$ was accomplished *via* constant potential electrolysis in a single compartment cell at 1.3 V. The concentrations of the monomer ($Thy_2Ph_2DTT$) and the electrolyte ($NaClO_4$/$LiClO_4$) were kept as $10^{-3}$ M and 0.1/0.1 M (1/1), respectively, in DCM/AN (1:1) solvent mixture. The freestanding polymer film was washed with AN in order to remove unreacted monomers.

Spectroelectrochemical studies of the polymer 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 + 1.5 V. Spectroelectrochemistry and switching measurements of the polymer film deposited on ITO were carried out in the same media in the absence of the monomer.

### 2.7. Preparation Gel electrolyte for the device

PMMA, $NaClO_4$, $LiClO_4$ were dissolved in AN. While the homogenous mixture was prepared by stirring and heating, the solution