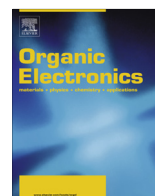




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# A new multicolored and near-infrared electrochromic material based on triphenylamine-containing poly(3,4-dithienylpyrrole)

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## ABSTRACT

A new compound containing both 3,4-dithienylpyrrole (DTP) and triphenylamine (TPA) groups, namely, 4'-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-N,N-diphenylbiphenyl-4-amine (**DTP-Ph-TPA**), was designed and synthesized. The polymer poly-**DTP-Ph-TPA** (**PDTP-Ph-TPA**) was prepared by electropolymerization from **DTP-Ph-TPA**. When the applied potential circulates from 0.0 V to 1.4 V, the polymer not only exhibits reversible multicolor in the visible region (yellow, light green, magenta and blue), but also shows excellent electrochromic properties in the NIR region with high contrast ratio ( $\Delta T = 70.5\%$  in 1550 nm,  $\Delta T = 67.9\%$  in 1310 nm) and a very short response time (about 1.4 s for 1550 nm, 0.9 s for 1310 nm). A single layer electrochromic device (ECD) based on polymer **PDTP-Ph-TPA** was constructed and characterized.

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## 1. Introduction

Electrochromic materials, which exhibit reversible absorption spectral changes by changing the applied potentials, have attracted much attention in recent years [1–8]. Originally, the research of electrochromic materials was mainly focused on the optical changes in the visible region (e.g., 350–750 nm), which had variable applications such as smart windows, E-paper, optical switching devices, variable reflectance mirrors, and camouflage materials. Later, efforts has also been made on near-infrared region (NIR; e.g., 750–2000 nm), which are useful in optical fiber-based telecommunication (specifically, 850 nm, 1310 nm and 1550 nm), optical attenuator, data storage, thermal control and aerospace and military camouflage [9–16]. Reynolds demonstrated color-to-transmissive NIR electrochromic conjugated polymers poly(3,4-propylenedioxythiophene)

(PProDOTs) which showed essentially no color change in the visible region [9]. Wang and Wan reported a quinone-containing electrochromic materials, which showed high absorption in the NIR region in the range of 700–1100 nm by electrochemical reduction [10]. Liou made efforts on the triarylamine-containing electroactive aramids, which revealed highly stable electrochromism and high contrast ratio between NIR and visible light region [11–14]. However, so far there is less work on electrochromic materials that can function in both the UV–Vis and near-IR region [4], which makes it possible to monitor the near-IR electrochromic process through naked eye. Actually, it is a challenge to obtain a material that can be switched from highly transmissive state to highly absorbed state in a wide range from UV–Vis to near-IR region.

Typical electrochromic materials are coordination complexes, transition-metal oxides, organic molecules and conjugated polymers [4–6]. Among these different types of electrochromic materials, conjugated polymers have several advantages, such as multiple hues within the same material, absorption spectral tunability through structural

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modification, flexibility, easy processability, fast switching, high optical contrast ratio and coloration efficiency [2]. Polythiophene, polypyrrole, polyaniline, poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3,4-dithienylpyrrole) (PDTP), and their derivatives are the typical electrochromic conjugated polymers reported in literature [4,7]. Particularly, PDTP and its derivatives have become one of the most important electrochromic materials during the past 20 years [17–21]. They have many advantages over other conjugated polymers such as lower oxidation potentials (about 0.7 V vs SCE), sufficient electron density and good hole-transporting ability, and better film-forming properties. If the substituent group on the N-position were modified, they can show more electrochromic hues ranging from yellow [21,22], green [23], magenta [24], and cyan [25], to blue [23]. So far, most of the PDTP derivatives can show electrochromism only in the UV–Vis region, electrochromic PDTP polymers which can exhibit reversible absorption changes in both the near-IR region and UV–Vis region are scarce [4].

In the literature, two groups were typically introduced to induce near-IR electrochromic properties. One is triphenylamine (TPA) and its derivatives, which are well-known electron-rich compounds and have been widely used as electron-donating and hole-transporting materials in the fields of photovoltaics [26] and electrochromism [27]. Because triphenylamines can easily be oxidized to form TPA cationic radicals with an obvious change of absorption spectrum in the NIR region, it has been reported that TPA can be used to improve the electrochromic performance in the NIR regions [28]. The other one is *p*-diphenylenediamine-containing molecules, which are also excellent anodic electrochromic systems for NIR applications because of its particular low energy intramolecular charge transfer under the oxidized states. Moreover, the *p*-diphenylenediamine cation radical has been reported as a symmetrical delocalized class III structure with a strong electronic coupling, leading to an intervalence charge transfer absorption band in the NIR region [29–31].

In this work, we designed and synthesized a new electrochromic material by substitution of N-position of DTP unit with Ph-TPA group. The novel TPA-containing DTP derives monomer, 4'-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-N,N-diphenylbiphenyl-4-amine (**DTP-Ph-TPA**; see Scheme 1), was synthesized by Knorr–Paal reaction and SUZUKI coupling reaction, and the corresponding polymer was obtained by electrochemical polymerization. The polymer **PDTP-Ph-TPA** is expected to have excellent electrochromic properties in the visible and NIR region because the DTP section has the variable hues while the TPA section can enhance the NIR electrochromic performance due to its electron sufficiency and hole-transporting properties. Moreover, the two nitrogen atoms in the DTP and TPA groups are connected by diphenylene moiety thus forming a *p*-diphenylenediamine unit, which could further strengthen the absorption spectral in NIR region. Here we demonstrate that the polymer **PDTP-Ph-TPA** exhibits reversible multicolor in the visible region (yellow, light green, magenta and blue) when the applied potential circulates from 0.0 V to 1.4 V. Furthermore, it also shows excellent electrochromic properties in the NIR region with high contrast ratio ( $\Delta T = 70.5\%$  in 1550 nm,  $\Delta T = 67.9\%$

in 1310 nm) and a very short response time (about 1.4 s for 1550 nm, 0.9 s for 1310 nm). Such features are very intriguing in electrochromic materials for wide applications like data storage, optical attenuators, and thermal control (heat gain or loss) in buildings and spacecrafts [32,33].

## 2. Experiments

### 2.1. Materials and instrumentation

All reagents and solvents were purchased from commercial sources and used as received without further purification. The solvent used for the electrochemical measurements were purchased from Sigma Aldrich with the purity of HPLC, which include dichloromethane (DCM) and acetonitrile (ACN). The ITO substrates as the working electrode were purchased from Kaivo with the resistance ( $\Omega$ ) below 10  $\Omega$ /sq. Mass spectra were acquired on a time of flight mass spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker spectrometer at 500 MHz using TMS as an internal standard. Elemental analyses of the compounds were performed on a Perkin-Elmer 240 analyzer. UV–Vis–NIR spectra were measured on a UV-3600 spectrophotometer. The absorption to the monomer was recorded in DCM with the concentration of  $10^{-5}$  M, and the optical band gap ( $E_g$ ) of the monomer and polymer was calculated from their low-energy absorption edge ( $\lambda_{\text{onset}}$ ) ( $E_g = 1241/\lambda_{\text{onset}}$ ). The cyclic voltammetry (CV) measurement was performed by CHI-660D electrochemical workstation. The measurements were carried out under an argon atmosphere, and the electrochemical three-electrode cell includes a Pt disk ( $d = 0.2$  cm) or ITO (Kaivo,  $<10$   $\Omega$ /sq, 9 mm  $\times$  50 mm) as the working electrode, Pt wire as counter electrode and the Ag wire as the quasi-reference electrode which was calibrated vs  $\text{Fc}/\text{Fc}^+$  to be 0.62 V in DCM solution. 0.1 M  $\text{Bu}_4\text{NClO}_4$  dissolved in DCM was used as electrolyte solution. HOMO and LUMO energy levels of the polymer were calculated according to the Ferrocene/Ferrocenium standard redox couple  $E(\text{Fc}/\text{Fc}^+) = 0.62$  V (vs Ag wire) in DCM by using the formula  $E_{\text{HOMO}} = -e(E^{\text{OX1}} - E_{\text{Fc}}) + (-0.62 \text{ eV})$  [23], and  $\text{LUMO} = \text{HOMO} - E_g$ .

To perform the spectroelectrochemical measurements and electrochromic switching studies, the polymer films were deposited on the ITO by electrochemical polymerization. The measurements were carried out by a spectroelectrochemical cell which consists of a quartz cell with an Ag wire, a Pt wire, and an ITO as the transparent working electrode. 0.1 M  $\text{Bu}_4\text{NClO}_4$  dissolved in DCM was used as electrolyte solution during all the measurement.

### 2.2. Synthetic procedure

The synthesis of the monomer **DTP-Ph-TPA** and corresponding polymer **P-DTP-Ph-TPA** is outlined in Scheme 1. The monomer **DTP-Ph-TPA** was prepared from Paal–Knorr reaction [34,35] and subsequent Suzuki coupling reaction. Succinyl chloride, 4-bromoaniline,  $\text{Pd}(\text{PPh}_3)_4$ , 4-(diphenylamino) phenylboronic acid was purchased from Alfa-Aesar, and used as received. Polymer **PDTP-Ph-TPA** was prepared by electrochemical polymerization.

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