Organic Electronics 14 (2013) 1094–1102

Contents lists available at SciVerse ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

A new electrochromic copolymer based on dithienylpyrrole and EDOT

Melek Pamuk Algi [a], Zahide Öztaş [a], Seha Tirkes [b,*], Atilla Cihaner [b], Fatih Algi [a,*]

[a] Laboratory of Organic Materials (LOM), Çanakkale Onsekiz Mart University, TR-17100 Çanakkale, Turkey
[b] Chemical Engineering and Applied Chemistry, Atilim Optoelectronic Materials and Solar Energy Laboratory (ATOMSEL), Atilim University, TR-06836 Ankara, Turkey

ARTICLE INFO

Article history:
Received 9 December 2012
Received in revised form 29 January 2013
Accepted 30 January 2013
Available online 18 February 2013

Keywords:
Multicolor electrochromism
Camouflage
Dithienylpyrrole
EDOT

ABSTRACT

A new compound, namely diethyl 2,5-di(thiophen-2-yl)-1H-pyrrole-3,4-dicarboxylate (**1**), was copolymerized with 3,4-ethylenedioxythiophene (EDOT) via electrochemical method. The copolymer exhibits multicolor electrochromic property: It is found that the copolymer, poly(**1**-co-EDOT), has a specific optical band gap (1.71 eV) to reflect and/or transmit reddish brown color in the neutral state, and it can be switched to reddish orange, orange, yellowish green and blue colors upon oxidation in a low switching time (1.0 s). Importantly, these colors are essential for camouflage and/or full color electrochromic device/display applications. In addition to these, the obtained copolymer has a coloration efficiency of 173 cm^2/C at 500 nm.

1. Introduction

Functional conjugated polymers have attracted considerable attention since they are promising candidates to be amenable for use in a variety of advanced technological applications such as sensors [1–3], light emitting diodes [4,5], photovoltaic cells [6–8], transistors [9,10], electrochromic devices [11–13], and optical displays [14]. Especially, conjugated polymers have been envisaged as one of the most useful electrochromic materials due to their multicolors with the same material under externally applied potentials. Also, they have high optical contrast ratio between various redox states with a short response time, high redox stability and long cycle life under ambient conditions. Furthermore, they can be coated onto large area surfaces by spin and spray coating [15] or roll-to-roll technique [16]. More importantly, all of these properties can be adjusted by structural design of the starting materials [17–22].

Recently, significant effort has been devoted to design and syntheses of novel, simple and effective functional and solution-processable polymeric materials [17,23–25]. Among these materials, dithienylpyrrole (SNS) is one of the most useful core units in order to obtain materials with distinct properties [19,26–37]. For instance, the flavin functionalized polydithienylpyrrole (PSNS) fabricated by electrochemical methods could be used for the detection of 2,6-diamidopyridine, which is a biologically important redox-active molecule [33]. Furthermore, it was recently shown that a chemiluminescent PSNS functionalized with luminol appendages could be used for the detection of reactive oxygen species [34]. In addition, by the help of fluorescent substituents like naphthalene and fluorene, PSNS based polymers could exhibit both fluorescent and electrochromic properties [38–40]. It was also shown that the intrinsic properties could easily be controlled through rational design of the backbone structures. Nonetheless, examples of processable fluorescent and electrochromic polymeric materials based on SNS unit have still been rare

---

* Corresponding authors. Tel.: +90 3125868390x8528; fax: +90 3125868091 (S. Tirkes), tel.: +90 2862180018x2415; fax: +90 2862180536 (F. Algi).

E-mail addresses: stirkes@atilim.edu.tr (S. Tirkes), falgi@comu.edu.tr (F. Algi).

1566-1199/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.orgel.2013.01.036

and newer ones are welcome. Moreover, SNS based materials can be amplified to create viable materials.

In this context, SNS based polymeric systems with electron-withdrawing units such as ester groups have not been investigated so far probably due to the difficulties in the synthesis. Herein we wish to report the synthesis and properties of a novel polymeric material, which is based on a novel SNS bearing strong electron-withdrawing substituents (**1**). In addition, electrochemical copolymerization of **1** and 3,4-ethylenedioxythiophene (EDOT) were investigated for electrochromic applications. It was noted that the copolymer, P(**1**-co-EDOT), had a specific optical band gap (1.71 eV) to reflect and/or transmit reddish brown color in the neutral state, and it could be switched to reddish orange, orange, yellowish green and blue colors upon oxidation. Importantly, these colors are essential for camouflage and/or full color electrochromic device/display applications.

2. Experimental

All chemicals were purchased from Sigma Aldrich Chemicals or Merck Company and used as received unless otherwise noted. FTIR spectra were recorded on Perkin Elmer Spectrum 100 model FTIR with an attenuated total reflectance (ATR). ^{1}H (400 or 300 MHz) and ^{13}C (100 or 75 MHz) NMR spectra were recorded on a Bruker DPX-400 or Ultrashield 300 NMR Spectrometers. Combustion analysis was carried out by using a LECO CHNS-932 analyzer. High resolution mass spectra (HRMS) were recorded on Waters SYNAPT MS system. UV–Vis and fluorescence measurements were recorded on Varian Cary 50 and Varian Cary Eclipse spectrophotometers, respectively. Melting points were determined on a Schorrp MPM-H2 model apparatus and are uncorrected. Column chromatography was performed on silica gel (60–200 mesh) from Merck Company. TLC was carried out on Merck 0.2 mm silica gel 60 F254 analytical aluminum plates. The syntheses of **3** [41] and **4** [42] were carried out according to published procedures.

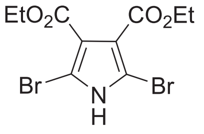
0.1 M $TBAClO_4$ dissolved in acetonitrile (ACN) was used as electrolyte solution. A platinum disk (0.02 cm^2) and a platinum wire were used as working and counter electrodes, respectively, as well as a Ag/AgCl reference and a Ag wire pseudo-reference electrodes (calibrated externally using 10 mM solution of ferrocene/ferrocenium couple which is an internal standard calibrated to be 0.44 V in ACN solution both vs. Ag/AgCl and vs. Ag wire). Repetitive cycling was used to obtain the polymer films. Electro-optical properties were investigated by using an indium tin oxide (ITO, Delta Tech. 8–12 ohm, 0.7×5 cm) electrode as well as a platinum wire as counter electrode and a Ag wire as a pseudoreference electrode. For the spectroelectrochemical measurements, the polymer film was coated on ITO electrode via cyclic voltammetry or constant potential electrolysis in 0.1 M ACN/$TBAClO_4$. In order to break in the polymer film, it was switched between 0.0 and 1.25 V in a monomer-free electrolytic solution. Electroanalytical measurements were performed using a Gamry PCI4/300 potentiostat–galvanostat. The electro-optical spectra were monitored on a Specord S600 spectrometer.

2.1. Synthesis of diethyl 2,5-dibromo-1H-pyrrole-3,4-dicarboxylate (*3*)

Br_2 (0.11 mL, 2.1 mmol) was dropwise added to a magnetically stirred solution/suspension of diethyl-1H-pyrrole-3,4-dicarboxylate (**2**) (211.2 mg, 1 mmol) and $NaHCO_3$ (252 mg, 3 mmol) in CH_2Cl_2 (20 mL) at 0 °C. After the addition was completed, the mixture was stirred at room temperature until **2** was totally consumed (TLC, overnight). The mixture was filtered to remove the solid part, washed with water (100 mL) and dried over $MgSO_4$. The solvent was evaporated and the residue was subjected to column chromatography on silica gel eluting with 5% $CH_3OH–CHCl_3$ (v/v) to give **2**: $R_f = 0.56$; 347 mg; 94% yield; white solid; m.p. 102 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 9.50 (bs, 1H, –NH), 4.33 (q, $J = 7.1$ Hz, 4H, $–CH_2$), 1.35 (t, $J = 7.1$ Hz, 6H, $–CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 162.7, 117.5, 104.2, 61.2, 14.1; FTIR (ATR, cm^{-1}): 3106, 3059, 3006, 2973, 2934, 2870, 2639, 1714, 1677, 1492, 1460, 1446, 1375, 1291, 1214, 1191, 1068, 1024, 862, 800, 783, 765, 678; Anal Calcd. for $C_{10}H_{11}Br_2NO_4$: C, 32.55; H, 3.00; N, 3.80; Found: C, 32.53; H, 3.05; N, 3.82. HRMS Calcd. for $NaC_{10}H_{11}Br_2NO_4$: 389.8952; Found: 389.8951.

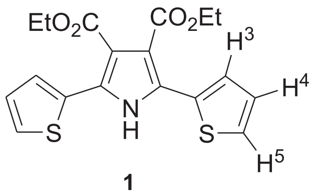
2.2. Synthesis of diethyl 2,5-di(thiophen-2-yl)-1H-pyrrole-3,4-dicarboxylate (*1*)

To an argon degassed solution of compound **3** (185 mg, 0.5 mmol) and **4** (400 mg, 1.1 mmol) in dry toluene (25 mL) was added $Pd(PPh_3)_4$ (20 mg) as catalyst and the solution was heated under reflux until all the starting materials were consumed (TLC, 5 h). The flask was cooled and the solvent was removed under reduced pressure. The residue was filtered through a short pad of silica gel by eluting with CH_2Cl_2 to give **4**: $R_f = 0.70$; 168 mg; 90% yield; m.p. 129–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.70 (s, 1H, –NH), 7.40 (dd, $J = 4–2$ Hz, 2H, H^3),



3

Scheme 1. Diethyl 2,5-dibromo-1H-pyrrole-3,4-dicarboxylate.



1

Scheme 2. Diethyl 2,5-di(thiophen-2-yl)-1H-pyrrole-3,4-dicarboxylate.