



A new processable donor–acceptor polymer displaying neutral state yellow electrochromism



Eda Oguzhan^{a,b}, Hakan Bilgili^c, Fatma Baycan Koyuncu^{a,b}, Eyup Ozdemir^{a,b}, Sermet Koyuncu^{b,d,*}

^a Department of Chemistry, Faculty of Sciences and Arts, Çanakkale Onsekiz Mart University, 17020 Çanakkale, Turkey

^b Polymeric Materials Research Laboratory, Çanakkale Onsekiz Mart University, 17020 Çanakkale, Turkey

^c Solar Energy Institute, Ege University, 35100 Bornova, Izmir, Turkey

^d Çan Vocational School, Çanakkale Onsekiz Mart University, 17400 Çanakkale, Turkey

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ABSTRACT

We report here the synthesis of a new solution processable neutral state yellow polymeric electrochromic material containing 2,5-bis-dithienyl-1H-pyrrole (SNS)-donor and 1,8 naphthalimide-acceptor (SNS-NI) as a subunit. The electrochemical and optical properties were investigated via cyclic voltammetry (CV), UV–Vis absorption and fluorescence emission measurements, respectively. Besides, electrochromic performance of poly(SNS-NI) has been compared to the both the film preparation method and poly(1-phenyl-2,5-dithiophen-2-ylpyrrole) [poly(SNS-P)] as a standard polymer. In the poly(SNS-NI), yellow color of the polymer film at neutral state converted to green and then dark blue upon the polymer film fully oxidized in the positive regime. SNS-NI polymer film prepared via spin casting process exhibits a high contrast ratio in the near-IR region ($\Delta T\% = 56\%$ at 890 nm), a response time of about 1 s, high coloration efficiency ($299 \text{ cm}^2 \text{ C}^{-1}$) and retained its performance by 98.6% even after 5000 cycles. Finally, the results clearly indicate that both electronic nature of the molecule and film preparation method have a major impact on electrochromic performance of these polymers.

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1. Introduction

Especially in the last quarter century, the field of conducting polymers has grown enormously in both scientific and commercial areas because of their promising electronic, optoelectronic and electrochemical properties [1,2]. Conducting polymers can be obtained from suitable oxidizable monomers chemically or electrochemically [3]. These polymers have various application areas such as photovoltaic devices, electroluminescent displays, emissive layers in full-color video matrix displays, superadsorbents, ion sensors, field-effect transistors, active thin layers of various sensing devices, supercapacitors and electrolytic-type capacitors, corrosion

inhibitors, and “smart windows” that absorb sunlight [4–14]. For device applications, it is especially important to control the electronic band structure of the polymer to achieve a band gap of the desired magnitude and frontier orbitals, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) (or band edges), of the proper energies [15]. As a result, among the conducting polymers, low band gap polymers are very important [16].

Electrochromism is defined as a reversible optical change in a material under external applied potentials [17,18]. Polymeric electrochromic materials show different redox states that derive distinct absorption bands at different wavelengths [19]. If more than two redox states are present in the visible region, this type of materials exhibit multielectrochromic behavior. Although the first studies concerning electrochromic materials involved inorganic semiconductors [20,21] and organic small molecules [22], conducting polymers received increasing attention in the course of time, due to their superior features such as their ability to

* Corresponding author. Çan Vocational School, Çanakkale Onsekiz Mart University, 17400 Çanakkale, Turkey. Tel.: +90 286 4167705; fax: +90 286 4167706.

E-mail address: skoyuncu@comu.edu.tr (S. Koyuncu).

form durable films and also the tunable nature of their HOMO–LUMO band gap, resulting from changes in molecular architecture [19].

Recently, 2,5-bis-dithienyl-1H-pyrrole (SNS) containing electroactive polymers have been found to be very important for electrochromic applications [23–25]. Along the SNS backbone, electroactive or photoactive moieties are placed to tune the band gap and thus to gain useful properties. On the other hand, 1,8-naphthalimide (NI) derivatives are n-type materials and have a relatively high electron affinity and excellent transport properties. Owing to these properties, they are used as n-type semiconductors in various fields such as laser active media [26–28], coloration of polymers [29], photo-induced electron transfer sensors [30], electroluminescent materials [31], liquid crystal displays [32], light emitting diodes [33–35], and ion probes [36]. Moreover, they are also used as potential photosensitive biological units [37], anticancer agents [38,39] and analgesics [40] in medicine.

In this work, we synthesized a new SNS type donor–acceptor monomer [6-(dihexylamine)-2-[4-(2,5-di-2-thienyl-1H-pyrrole-1-yl)phenyl]-1H-benzo[de]isoquinoline-1,3(2H)-dione] (SNS–NI) containing a 1,8-naphthalimide electron–acceptor with a branched alkyl chain as a subunit. The polymer prepared via an electrochemical process can be soluble in the chloroform and then recoloring to ITO/glass surface via a spin casting process to give a multi-electrochromic polymer film having high redox stability, a high coloration efficiency and a fast response time. Further, intramolecular electronic interactions in the donor acceptor SNS–NI monomer and its polymer have been investigated by using cyclic voltammetry (CV), UV–Vis absorption and fluorescence spectroscopy. Finally, there are only a very limited number of examples of processable neutral state yellow electrochromic material in the literature [41,42], we believe the highly soluble synthesized material may be very important for electrochromic applications.

2. Experimental

2.1. Materials

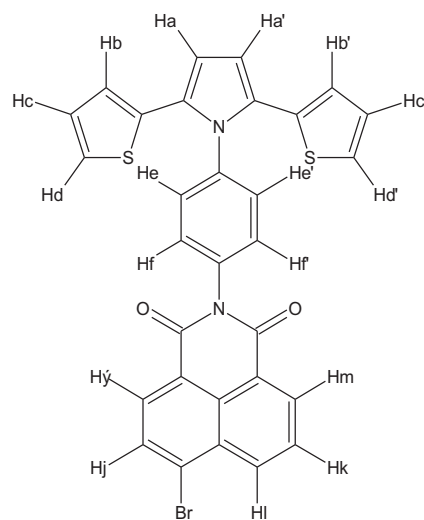
Thiophene (Aldrich), 4-bromo-1,8-naphthalicanhydride (Aldrich), hidrazinium hydroxide (Merck), Cu (Merck), K_2CO_3 (Merck), ethanol (Merck), pyridine (Merck), $AlCl_3$ (Merck), $NaHCO_3$ (Merck), 4-nitroaniline (Aldrich), 18-Crown-6 (Fluka), succinyl dichloride (Aldrich) and palladium on activated carbon (10%, w/w) (Fluka) were supplied from Aldrich, Merck and Fluka, and were used without further purification. The syntheses and characterizations of 1,4-bis(2-thienyl)butan-1,4-dione (**1**) [43], 1-(4-nitrophenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole (**2**) [44] and 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)aniline (**3**) [45], 1-phenyl-2,5-dithiophen-2-ylpyrrole (SNS–P) as a standard molecule 1-(4-nitrophenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole [46] were previously described in the literature.

2.2. Synthesis of 6-bromo-2-[4-(2,5-di-2-thienyl-1H-pyrrole-1-yl)phenyl]-5,6-dihydro-1H-benzo[de]isoquinoline-1,3(2H)-dione

4-Bromo-1,8-naphthalicanhydride (0.533 g, 1.92 mmol), was added into 40 ml dry pyridine and refluxed under argon atmosphere for 30 min. After 30 min, [4-(2,5-di-2-thienyl-1H-pyrrole-1-yl)phenyl]amine (0.155 g, 0.481 mmol) was added by small portions and this mixture was stirred at 120 °C for 8 h. After that the reaction mixture was cooled to room temperature and poured into HCl aqueous solution (3 M, 500 ml). The resulting precipitate (1.11 g) was collected by filtration, washed with $NaHCO_3$ solution

(2 M, 100 ml) and then water (50 ml), and finally the product was purified by column chromatography (silica gel, 3/1; chloroform/hexane). The purified product was dried at 60 °C in vacuum oven. Yield: 89%; 0.25 g.

FT-IR (cm^{-1}): 3059 (C–H, aromatic); 1704, 1666; (C=O imide); 1552, 1487 (C=C aromatic). 1H NMR ($CHCl_3$ -d): δ ppm, 8.66 (d, 1H, Ar-H_i); 8.48 (d, 1H, Ar-H_m); 8.06 (d, 1H, Ar-H_j); 7.69 (d, 1H, Ar-H_l); 7.62 (m, 1H, Ar-H_k); 7.58 (d, 2H, Ar–H'_{dd}); 7.36 (t, 2H, *currhskip0ptAcurrhskip0ptr* – H'_{ee}); 7.45 (t, 2H, Ar – H'_{ff}); 6.63 (d, 2H, *currhskip0ptAcurrhskip0ptr* – H'_{cc}); 6.80 (d, 2H, Ar – H'_{bb}); 6.41 (s, 2H, Ar – H'_{aa}); MALDI-ToF (m/z): [M^+] calcd. for $C_8H_{17}BrN_2O_2S_2$, 581.50; found, 581.44.



2.3. Synthesis of 6-(dihexylamine)-2-[4-(2,5-di-2-thienyl-1H-pyrrole-1-yl)phenyl]-1H-benzo[de]isoquinoline-1,3(2H)-dione (SNS–NI)

6-Bromo-2-[4-(2,5-di-2-thienyl-1H-pyrrole-1-yl)phenyl]-5,6-dihydro-1H-benzo[de]isoquinoline-1,3(2H)-dione (**4**) (0.095 g, 0.163 mmol), dihexylamine (0.302 g 1.63 mmol) and 30 ml DMA stirred in a 100 ml flask and then CuI, (0.9 g) K_2CO_3 (1.55 g, 11.2 mmol) and 18-Crown-6 (0.02 g) were added. The reaction mixture was refluxed under argon atmosphere for 48 h. Then this mixture was filtered through cellulite to remove the copper impurities. After that, the solution was poured into cold water and the precipitate was collected by filtration. The product was purified by column chromatography (silica gel, 2/1; chloroform/hexane) and finally was dried at 60 °C in vacuum oven. Yield: 80%, 0.09 g.

FT-IR (cm^{-1}): 3093 (C–H aromatic); 2916 (C–H aliphatic); 1702, 1660 (C=O imide); 1508, 1387, (C=C aromatic); 1H NMR ($CHCl_3$ -d, ppm): δ 8.78, (d, 1H, Ar-H_g); 8.43, (d, 1H, Ar-H_i); 8.23, (t, 1H, Ar-H_j); 7.88, (d, 2H, Ar – H'_{ff}); 7.61, (d, 1H, Ar-H_m); 7.45, (d, 2H, Ar – H'_{ee}); 7.39, (d, 2H, Ar – H'_{hh}); 7.32, (d, 2H, Ar – H'_{aa}); 7.04, (d, 2H, Ar – H'_{cc}); 6.93, (d, 2H, Ar – H'_{bb}); 6.61, (d, 2H, Ar – H'_{dd}); 3.46, (m, 4H, N–CH₂); 2.24–1.22, (m 16H, –CH₂–); 0.86, (t, 6H, –CH₃); ^{13}C NMR ($CHCl_3$ -d, ppm): 157.77, 157.01, 144.85, 136.92, 134.25, 134.07, 132.78, 132.01, 130.91, 128.44, 127.36, 123.66, 121.81, 119.08, 118.88, 116.76, 115.44, 109.22, 103.77, 51.34, 31.77, 29.55, 27.71, 22.55, 13.96; MALDI-ToF (m/z): [M^+] calcd. for $C_{42}H_{43}N_3O_2S_2$, 685.94; found, 685.83.

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