

Electrosynthesis of a new indole based donor-acceptor-donor type polymer and investigation of its electrochromic properties



Buket Bezgin Carbas^{a, b, *}, Arif Kivrak^{c, **,}, Emrah Kavak^c

^a Department of Energy Systems Engineering, Karamanoglu Mehmetbey University, 70100 Karaman, Turkey

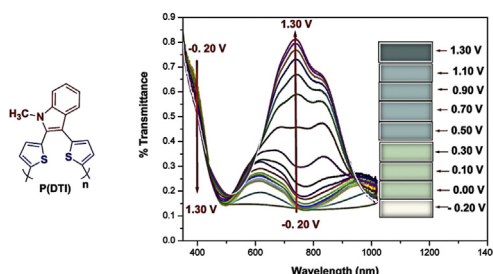
^b Conductive Polymers and Energy Applications Laboratory, Karamanoglu Mehmetbey University, 70100 Karaman, Turkey

^c Yüzüncü Yıl University, Department of Chemistry, Faculty of Sciences, 65080 Van, Turkey

HIGHLIGHTS

- A new thiophene donor groups involved indole derivative monomer (DTI) was synthesized.
- The polymer film, P(DTI) displayed pale green to dark green color when oxidized.
- It is the first electrochromic indole polymer based on thiophene donor groups.

GRAPHICAL ABSTRACT



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ABSTRACT

The purpose of this research is to synthesize a novel monomer, namely, 1-methyl-2,3-di(thiophen-2-yl)-1H-indole (DTI) and to present optical and electrochemical characterization of its corresponding polymer film, P(DTI). The donor thiophene unit was matched with acceptor indole unit in consideration of donor-acceptor-donor approach in order to achieve DTI monomer. This monomer was electropolymerized in the medium 0.1 M LiClO₄/Ethanol:ACN solution mixture and a conductive indole based polymer, P(DTI) was obtained. The spectroelectrochemical studies show that P(DTI) has a band gap of 2.45 eV and a color change from pale green to dark green with a switching time of 0.9 s during oxidation and a high coloration efficiency (286 cm²/C) at 830 nm. Furthermore, P(DTI) shows good environmental and redox stability with a retention of 85% after 1500th switching.

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1. Introduction

Conducting materials based on heteroaromatic systems have been regarded as promising materials for leading-edge technological

devices, such as light emitting diodes (LEDs) [1,2], solar energy materials [3,4], transistors [5,6], capacitors and electrochromic device [7–13]. Among them, electrochromic materials are attaining popularity because of their rapid response and high contrast. Based on this viewpoint, a wide variety of electrochromic conjugated polymers have been developed and improved with their derivatives such as polythiophene [14], poly(3,4-ethylenedioxythiophene) [15] and polypyrrole [16]. Lately, poly-indole and its derivatives get much interest due to their some advantages, especially higher thermal and redox stability, slower degradation rate than those of poly-aniline and poly-pyrrole conjugated polymers as well as air-stable electrical

* Corresponding author. Department of Energy Systems Engineering, Karamanoglu Mehmetbey University, 70100 Karaman, Turkey.

** Corresponding author.

E-mail addresses: bcarbas@kmu.edu.tr (B.B. Carbas), akivrak@yyu.edu.tr (A. Kivrak).

conductivity in the doped state for electrochromic applications [17–22]. In addition, it is also important to synthesize new poly-indole derivatives for various applications such as, electrocatalysis [23], active materials for batteries [24], electrochromic devices [17,25,26], nanofiber membranes [27], electrochemical biosensor [28] with a wide variety of substituent groups. Billaud et al. first succeeded in polymerization of indole electrochemically [17]. Recently; poly-indole derivatives, such as Poly (5-formyl indole) [26] and poly(-indole-6-carboxylic acid) [28], were prepared, and their electrochromic properties were reported by Nie et al. Moreover, Wang et al. synthesized another new polymer including indole structure, poly (1H-benzof[*g*]indole), and investigated fluorescence and electrochromic properties [29]. Although, there are some studies about poly-indoles in literature, it is necessary to expand the range of novel indole based polymers due to their unique electrochromic and electrochemical properties. It is also important to get high quality poly-indole films at low potential which prevents possible side reactions and activities of radical cation during the electropolymerization reactions [30]. For that reason, many researchers have focused on oxidation potential with a lower value for indole monomers in order to obtain high-grade poly-indole films. Among them, repeat unit modification of the indole type monomer or functional groups substitution onto polymer backbone seems the simplest strategy in order to get molecular level control of polymer properties [30]. Electrochemical and optical property improvements for a polymer also depend on structural modifications on its monomer. Based on this viewpoint, monomer groups could be modified with various donor groups (furan, thiophene, 3,4-ethylenedioxythiophene). Donor–acceptor–donor (D–A–D) system, which is related with the combination of two donor units to one acceptor unit, is an important approach to obtain polymers with small band gaps. There is an electronegativity difference between donor and acceptor units for these kinds of polymers in the main chain backbone, which leads to the lowest band gap. In comparison with homopolymers, D–A–D copolymers have different electron affinity because of alternating arrangement of units, which makes this polymer system efficient intermolecular charge carrier transport [31]. That kind of strategy opens up a new door to researchers to control the value of the band gap with superior optical properties [32–38].

In the present study, a novel donor acceptor type indole monomer, 1-methyl-2,3-di(thiophen-2-yl)-1H-indole (DTI) and its corresponding polymer, poly (1-methyl-2,3-di(thiophen-2-yl)-1H-indole) P(DTI) were synthesized. To the best our knowledge, there is not any report including donor-acceptor-donor typed indole based electrochromic polymer in the same polymer structure in literature. Hence, this study may provide an insight into the donor group effect on the poly-indole chain structure in terms of electrochemical and optical properties. Furthermore, it was found that P(DTI) polymer exhibited remarkable electrochromic features that could be switched from pale green in the neutral state to dark green under externally applied potentials.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma Aldrich, across and used as received unless otherwise noted. 1-methyl-2,3-di(thiophen-2-yl)-1H-indole, monomer was synthesized according to Scheme 1.

2.1.1. Synthesis of monomer, 1-methyl-2,3-di(thiophen-2-yl)-1H-indole

2.1.1.1. Synthesis of *N,N*-dimethyl-2-iodoaniline (I). 2-Iodoaniline (2.19 g, 10 mmol), K₂CO₃ (3.45 g, 25 mmol) and

iodomethane (1.87 mL, 30 mmol) in 10 mL CH₃CN were stirred under reflux for 12 h. When the reaction was done, the mixture was treated with water (50 mL), extracted with DCM (2 × 30 mL). The organic phase was dried over anhydrous magnesium sulfate and filtered. The solvents were evaporated and the residue purified by silica gel column chromatography eluting with Hexane/EtOAc (19:1) yielding *N,N*-dimethyl-2-iodoaniline (I) (2.37 g, 96%). ¹H NMR (400 MHz, CDCl₃) δ 7.85 (dd, *J* = 7.84, 1.48 Hz), 7.31 (m, 1H), 7.1 (dd, *J* = 8.04, 1.56 Hz 1H), 6.77 (m, 1H), 2.77 (s, 1H). ¹³C NMR (400 MHz, CDCl₃) δ 154.95, 140.19, 129.08, 125.01, 120.5, 97.21, 45.03. The spectral data were in agreement with those reported previously for this compound [39].

2.1.1.2. Synthesis of *N,N*-dimethyl-2-((trimethylsilyl)ethynyl)aniline (II). To a stirred solution of *N,N*-dimethyl-2-iodoaniline (2.47 g, 10 mmol) in 5 mL DMF were added triethylamine (1.4 mL, 10 mmol), bis(triphenylphosphine)palladium(II) dichloride (70.1 mg, 0.1 mmol), CuI (57 mg, 0.3 mmol), and (trimethylsilyl)acetylene (11–15 mmol), under argon atmosphere. When the reaction was done, the mixture treated with saturated aqueous ammonium chloride solution (50 mL) and extracted with diethyl ether (50 mL). The organic phase was dried over anhydrous magnesium sulfate and filtered. The solvents were evaporated and the residue purified by silica gel column chromatography eluting with Hexane/Diethyl ether (100:1) yielding *N,N*-dimethyl-2-((trimethylsilyl)ethynyl)aniline (II) (1.96 g, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.43 (dd, *J* = 7.6, 1.7 Hz 1H), 7.24 (m, 1H), 6.87 (m, 2H), 2.97 (s, 6H), 0.28 (s, 9H). The spectral data were in agreement with those reported previously for this compound [39].

2.1.1.3. Synthesis of *N,N*-dimethyl-2-ethynylaniline (III). To a stirred solution of *N,N*-dimethyl-2-((trimethylsilyl)ethynyl)aniline (1.99 g, 9.15 mmol) in 100 mL methanol was added potassium carbonate (3.79 g, 27.45 mmol) under argon atmosphere. When the reaction was done, the mixture was treated with brine and extracted with diethyl ether. The organic phase was dried over anhydrous magnesium sulfate and filtered. The solvents were evaporated and the residue purified by silica gel column chromatography eluting with Hexane/EtOAc (19:1) yielding *N,N*-dimethyl-2-ethynylaniline (1.18 g, 81%). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (dd, *J* = 7.6, 1.27 Hz, 1H), 7.27 (m, 1H), 6.90 (m, 2H), 3.43 (s, 1H), 2.93 (s, 6H). ¹³C NMR (400 MHz, CDCl₃) δ 155.59, 134.94, 129.73, 120.76, 117.16, 114.5, 82.97, 82.47, 43.68. The spectral data were in agreement with those reported previously for this compound [39].

2.1.1.4. Synthesis of 1-methyl-2,3-di(thiophen-2-yl)-1H-indole (DTI). To a stirred solution of *N,N*-dimethyl-2-ethynylaniline (50 mg, 0.35 mmol) in 5 mL DMF was added 2-iodothiophene (151.9 mg, 0.72 mmol), Pd(PPh₃)₂Cl₂ (12.1 mg, 0.0172 mmol), CuI (3.28 mg, 0.0172 mmol) Et₃N (0.071 mL, 0.5167 mmol) under argon atmosphere. After being stirred for 16 h at room temperature, the mixture was treated with saturated sodium bicarbonate solution (50 mL) and extracted DCM (3 × 50 mL). The organic phase was dried over anhydrous magnesium sulfate and filtered. The solvents were evaporated and the residue purified by silica gel column chromatography eluting with Hexane/EtOAc (50:1) yielding 1-methyl-2,3-di(thiophen-2-yl)-1H-indole (DTI) (83.6 mg, 81%). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (dt, *J* = 3.16, 1 Hz, 1H), 7.53 (t, *J* = 3.16, 1H), 7.37 (m, 2H), 7.24 (m, 4H), 7.06 (m, 2H), 3.7 (s, 3H) (Fig. S1.1). ¹³C NMR (400 MHz, CDCl₃) δ 137.2, 136.7, 131.8, 130.6, 130.3, 128.4, 127.33, 126.9, 126.4, 125.1, 123.8, 122.9, 120.9, 120.1, 110.9, 109.6, 30.8 (Fig. S1.2). HRMS (ESI) calculated for C₁₇H₁₃NS₂ 295.0489; found 295.0486. FTIR (ATR, cm⁻¹): 2957, 2922, 2851, 1540, 1492, 1460, 1393, 1346, 1312, 1265, 1185, 1174, 1121, 1084, 1060, 997, 917, 824, 794, 755, 695.

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