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Naphthalenediimide bridged D-A polymers: Design, synthesis and electrochromic properties☆

Emre Sefer[a,b], Fatma Baycan Koyuncu[a,b,*]

[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

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ABSTRACT

We have synthesized two new D-A electrochromic polymers; poly(*N,N'*-bis(2-hexyl)-2,6-dithiophene-1,4,5,8-naphthalenediimide) (PTNDI) and poly(*N,N'*-bis(2-hexyl)-2,6-(3,4-ethylenedioxythiophene)-1,4,5,8-naphthalenedimiide) (PENDI) bearing a naphthalenedimiide chromophore in the backbone. Structural characterization of initial compounds and products were carried out by using FT-IR and ^{1}H-NMR spectroscopies. The optical and electrochemical properties of these polymers were investigated by UV-Vis absorption spectroscopy and cyclic voltammetry, respectively. The results of spectroelectrochemical studies indicate that both polymers reveal various colors due to ambipolar redox behavior at cathodic and anodic regime. Both polymer films have reasonable redox stability (in the range of 75-80% after 1000 cycles), coloration efficiency (in the range of 80-100 cm^2 C^{-1}), and response time (approx. 1s). Moreover, it is clearly seen that replacing donor unit from thiophene to EDOT results in change only in neutral state color.

1. Introduction

Electrochromism is defined as a reversible and visible color change in a material upon applied voltage. Initially, inorganic semiconductors such as tungsten trioxide (WO_3) and iridium oxide (IrO_2) are widely used in the electrochromic technology [1], then organic small molecules such as metallophthalocyanines and viologens [2], and finally conducting polymers have received great attention for electrochromic applications [3]. Among the electrochromics, the conducting polymers have a great potential due to their structurally controllable HOMO–LUMO band gap that provides easy tunability of colors, solution processability, high contrast ratio, and fast response time [4]. These valuable properties render conducting polymers promising candidates to be used in smart windows [5,6], mirrors [7,8], displays [9], electrochromic devices [10–12], and camouflage materials [13–15].

Polythiophene derivatives [16] have gained a considerable interest in electrochromic technology over inorganic materials and other conductive polymers owing to some useful properties such as their good film forming characteristics, multicolor changes in the same structure, high switching stability as well as fast response time, and low operation voltage. On the other hand, five membered imide substituents have been used to impart n-type characteristics to small-molecule organic semiconductors because of their strong electron-withdrawing character. There are tremendous studies about imide-functionalized small molecules for n-type organic materials based on the arylene such as naphthalenediimide (NDI) and perylenediimide (PDI) [17–19]. The arylene imides are attractive candidates as the electron-accepting co-monomers in low band gap D–A polymers by virtue of their extremely facile synthesis and variable substitution at the nitrogen which allows a better manipulation of polymer solubility, packing and morphology. Moreover, the insertion of strong electron-withdrawing imide groups into polymer backbones can effectively change energy levels resulting in even n-type and p-type behavior [20–24]. Nevertheless, there are only a few reports about conjugated polymers containing imide-functionalized p-systems such as thiopheneimides [25], bithiopheneimide [26], iso-thianaphtheneimide [27], phthalimide [28] and aryleneimide [17–22].

Herein, we have designed, synthesized and investigated the electrochromic features of two new D–A type polymers with NDI as the acceptor unit along the backbone of polymers containing thiophene (**TNDI**) and 3,4-ethylenedioxythiophene (EDOT) (**ENDI**) as the donor moiety. Besides, effects of the donor moiety on the electronic and optical properties of monomers and their resulting polymers were investigated and compared in detail. Upon applied potentials on the polymer films resulted in numerous colors as

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* Corresponding author. Tel.: +90 286 2180018; fax: +90 286 2180533.
E-mail address: fatmabaycan@hotmail.com (F. Baycan Koyuncu).

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a result of multistep redox behavior at both anodic and cathodic regime.

2. Experimental

2.1. Materials

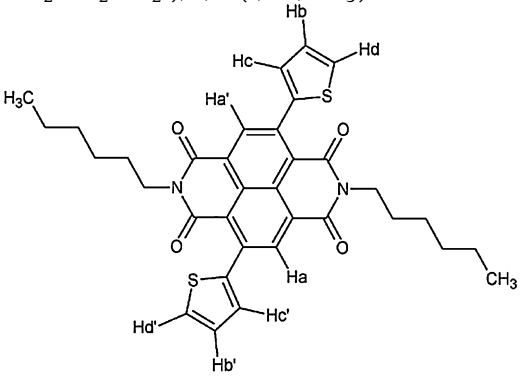
All chemicals were purchased from Aldrich Chemical and used without further purification.

N,N'-bis(2-hexyl)-2,6-dibromo-1,4,5,8-naphthalenediimide was prepared using a previously reported method [29].

2.2. Synthesis of *N,N'-bis(2-hexyl)-2,6-dithiophene-1,4,5,8-naphthalene diimide (TNDI)*

N,N'-bis(2-hexyl)-2,6-dibromo-1,4,5,8-naphthalenediimide (0.25 g, 0.42 mmol) and 30 mL THF were stirred in a 100 mL flask under Ar atmosphere. Then, 2-thiophene boronic acid (0.14 g, 1.1 mmol), 2.5 M Na_2CO_3 aqueous solution and $Pd(PPh_3)_4$ (5 mol %) were added to solution mixture. The mixture was refluxed at 80 °C for 24 h under Ar. At the end of the reaction, the reaction mixture was cooled to room temperature, poured into a large amount of methanol, and filtered. The precipitate was collected and purified with column chromatography ($CHCl_3$) to give N,N'-bis(2-hexyl)-(2,6-dithiophene)-1,4,5,8-naphthalenediimide **(TNDI)** as a red solid with a yield of 78%.

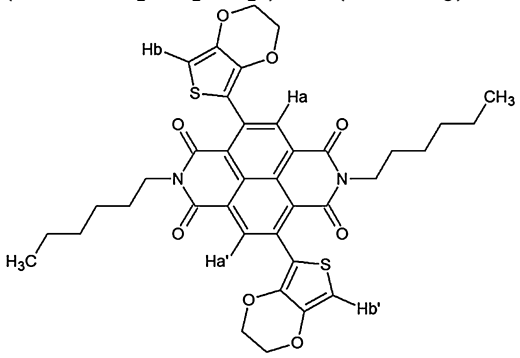
UV-Vis (λ_{max}, nm, DCM): 359, 379, 469; FT-IR (cm^{-1}): 3094 (C–H aromatic); 2957, 2931, 2856 (C-H aliphatic); 1701(C=O); 1578 (C=C aromatic); 1441 (C-N); ^{1}H-NMR ($CHCl_3$-d, ppm): δ 8,55 (s, 2H, Ar-$H_{aa'}$); 6,94 (d, 2H, Ar-$H_{cc'}$); 6,55 (d, 2H, Ar-$H_{dd'}$); 6,31 (t, 2H, Ar-$H_{bb'}$); 3,71(t, 4H, N-CH_2); 1,56 (m, 4H, -CH_2-); 1,46 (m, 12H, -CH_2- CH_2- CH_2-); 0,88 (t, 6H, -CH_3).



2.3. Synthesis of *N,N'-bis(2-hexyl)-2,6-(3,4-ethylenedioxythiophene)-1,4,5,8-naphthalenediimide (ENDI)*

N,N'-bis(2-hexyl)-2,6-dibromo-1,4,5,8-naphthalenediimide (0.25 g, 0.42 mmol) and 30 mL toluene were stirred in a 100 mL flask under Ar atmosphere. 2-(tributyl)stannyl-EDOT (0.47 g, 1.1 mmol) and $Pd(PPh_3)_4$ (5 mol %) were added. The reaction mixture was refluxed at 110 °C under Ar atmosphere for 24 h. At the end of the reaction, the reaction mixture was cooled to room temperature, poured into a large amount of ethanol, and filtered. The product was purified by column chromatography (silica gel, $CHCl_3$). The purple product was dried at 60 °C in vacuum oven. 73% yield

UV-Vis (λmax, nm, DCM): 318, 362, 381,525; FT-IR (cm^{-1}): 3183 (C–H aromatic); 2957, 2921, 2857 (C-H aliphatic); 1707(C=O); 1577 (C=C aromatic); 1494 (C-S aromatic); 1433 (C-N); ^{1}H-NMR ($CHCl_3$-d, ppm): δ 8,78 (s, 2H, Ar-$H_{aa'}$); 6,97 (s, 2H, Ar-$H_{bb'}$); 4,25 (t, 8H, EDOT-CH_2-); 4,12 (t, 4H, N-CH_2); 1,76 (m, 4H, -CH_2-); 1,37 (m, 12H, -CH_2- CH_2- CH_2-); 0,97 (t, 6H, -CH_3).



2.4. Electrochemical polymerization of monomers

Electrochemical polymerization was carried out in CH_3CN-CH_2Cl_2 solution (1/5; v/v) of 2.0×10^{-3} M monomer and 0.1 M $LiClO_4$ by repetitive cycling at a scan rate of 100 mV/s. The polymer was deposited onto platinum (0.02 cm^2) or indium–tin oxide/glass (ITO/glass, 8–12 Ω, 0.8 cm × 5 cm). A platinum wire was used as a counter electrode while Ag wire served as a reference electrode. The film was rinsed with CH_3CN to remove electrolyte salt.

2.5. Instrumentation

FT-IR spectra were recorded by a Perkin Elmer FT-IR Spectrum One by using an ATR system (4000–650 cm^{-1}). ^{1}H-NMR spectra were recorded on a Bruker Avance DPX-400 at 25 °C in deuterated chloroform solutions with TMS as internal standard.

Electrochemical measurements were carried out using a Biologic SP-50 electrochemical workstation. All measurements were carried out under argon atmosphere., Oxidation and reduction potential onsets of **TNDI** and **ENDI** monomers and corresponding polymers were used to calculate the HOMO-LUMO energy levels. The experiments were calibrated with the standard ferrocene/ferrocenium redox system ($E^{\circ}(Fc/Fc^+) = +0.48$ V) [30]. UV-Vis absorption spectra were measured using an Analytic Jena Speedcord S-600 diode-array spectrophotometer. The optical band gaps (E_g) of products were calculated from their absorption edges [31].

Spectroelectrochemical measurements were carried out using absorption spectra of the polymer films under applied potential. The spectroelectrochemical cell includes a quartz cuvette, an Ag wire (RE), Pt wire counter electrode (CE), and ITO/glass as the transparent working electrode (WE). 0.1 M $TBAPF_6$ in CH_3CN was used as the supporting electrolyte.

Colorimetric measurements were performed using an Analytic Jena Specord S600 UV-Vis spectrophotometer which consists of a chromometer module in reflection mode (standard illuminator D65, field of with 10° observer) with the viewing geometry as recommended by CIE. According to the CIE system, the color is made up of three attributes; luminance (L), hue (a), and saturation (b) [32]. Platinum cobalt DIN ISO 621, iodine DIN EN 1557, and Gardner DIN ISO 6430 are the references that are used for colorimetric measurements. These parameters were applied for the neutral and oxidized states of the polymers deposited onto ITO/glass surface.

AFM measurements were carried out at room temperature and ambient conditions using an Ambios QScope 250 instrument. The non-contact mode (wave mode) was used to take topographic images. A 20 μm scanner equipped with silicon tips having 10 nm tip-curvature and an ITO/glass substrate were used for measurements. The system is covered with an acoustic chamber to prevent electromagnetic noises which may affect the measurements.