



Synthesis and electropolymerization of 3,4-substituted quinoxaline functionalized pyrrole monomer and optoelectronic properties of its polymer



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ABSTRACT

We synthesized a new electroactive pyrrole functionalized monomer; 2-butyl-5,12-dihydro-2H-pyrrolo[3',4':2,3][1,4]dioxocino[6,7-b]quinoxaline (BuDQP) where β -positions of the pyrrole ring are blocked. With the help of this strategy, formation of α - β linkages during polymerization was prevented, resulting in a more regiochemically defined material. Characterization of newly synthesized compounds was performed by FTIR, GC-MS, ¹H NMR, ¹³C NMR techniques and elemental analysis. Polymerization and copolymerization of BuDQP and characterization of the resulting polymers were also performed. Spectroelectrochemical investigations, switching abilities, colorimetry studies and stability experiments were performed on both for polymer and copolymer. Spectroelectrochemical analysis of P(BuDQP) reflected electronic transitions at 328 nm (π - π^* transition) and 500 nm (polaron bands) with an electronic band gap of 2.30 eV, while copolymer (P(BuDQP-co-Py)) revealed electronic transitions at 346 nm (π - π^* transition) and 518 nm (polaron bands) with an electronic band gap of 2.24 eV. Colorimetry studies revealed that P(BuDQP) has only two colors (blue and yellow) whereas copolymer film has six different colors in its oxidized and neutral states.

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1. Introduction

Electrochromism arises from the generation of different electronic absorption bands in the visible region, which corresponds to the changes between at least two redox states [1]. Conducting polymers (CPs) have attracted considerable interest as electrochromic materials since ingenious modifications on the monomer can significantly alter the spectral properties of the polymer. Such modifications may also alter the switching ability of the material between its oxidized and neutral states over many redox cycles [2–6]. They are usually colored in their reduced states due to the energy difference between π -bonding orbitals and the π^* -antibonding orbitals in the visible region. When a polymer is oxidized, the lower energy transitions become dominant and another color is formed.

Polypyrrole can easily be synthesized chemically or electrochemically and has a wide range of optoelectronic properties

available through alkyl and alkoxy substitution which gives it an extensive value as an electrochromic material. The pristine polypyrrole however, has low quality electrochromic properties. It switches between gray and turquoise color which makes it unusable in electrochromic devices since it switches between two dark colors with a low optical contrast and moderate switching time in the visible region [7–9]. The material is also highly susceptible to degradation upon color switching. Compared to the immense literature on functionalized conducting polymers such as polythiophenes [10,11], the number of functionalized polypyrrole derivatives is quite low [12–16], though numerous studies have been conducted on pristine polypyrrole [17]. Polypyrrole is promising for several applications such as batteries, supercapacitors, electrochemical biosensors, conductive textiles and fabrics, mechanical actuators, electromagnetic interference shielding, anti-static coating, electrochromic devices and drug delivery systems [18–20]. Polypyrrole films with better chemical and physical properties can be produced by gaining better control on the structure [20–24].

Electrochemically prepared polypyrroles and other CPs suffer from undesired α - β and β - β couplings during polymerization [25].

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Such defects not only deteriorate the conductive properties of the materials but also cause cross-linking which is particularly efficient in decreasing the solubility of the polymers [26]. The presence of β -capping moieties is thus the best solution. Also since the oxidized form of polypyrrole may be deprotonated by basic anions [27] and since the NH group may not favor solubility, a protection of the N-position may be desirable. Thus, a complete 1,3,4-substitution is the optimal achievement and this strategy may introduce novel features in its conductive properties [28].

In order to improve vital properties of pyrrole, we synthesized and characterized a new electroactive 3,4-substituted quinoxaline functionalized pyrrole monomer; 2-butyl-5,12-dihydro-2H-pyrrolo[3',4':2,3][1,4]dioxocino[6,7-b]quinoxaline where β -positions of the pyrrole ring are blocked. With this strategy formation of α - β or β - β linkages during polymerization is prevented, resulting in a more regiochemically defined material. Polymerization and copolymerization of BuDQP and characterization of the resulting polymers were performed. Spectroelectrochemical investigations, switching abilities, colorimetry studies and stability experiments were performed on both for polymer and copolymer.

2. Experimental

2.1. Materials

N,N-Dimethylformamide (DMF) (*Sigma-Aldrich*) was dried over 4A molecular sieves and freshly distilled under reduced pressure prior to use. Doubly distilled water was used in the experiments. Dry solvents were stored over molecular sieves under nitrogen. The other reagents and chemicals; n-Butylamine (*Merck*), dichloromethane (DCM) (*Sigma-Aldrich*), chloroform (*Sigma-Aldrich*), diethyl ether (*Sigma-Aldrich*), acetonitrile (ACN) (*Merck*), ethyl chloroacetate (*Sigma-Aldrich*), o-phenylenediamine (*Sigma-Aldrich*), diethyl oxalate (*Sigma-Aldrich*), 2,3-butanedione (*Sigma-Aldrich*), bromine (reagent grade, *Sigma-Aldrich*), acetic acid (*Merck*), ethanol (absolute, *Sigma-Aldrich*), potassium carbonate (anhydrous, *Fluka*), potassium hydroxide (ACS reagent, %85, *Sigma-Aldrich*), triethanolamine (*Sigma-Aldrich*), hydrochloric acid (ACS reagent, %37, *Sigma-Aldrich*), propylene carbonate (*Sigma-Aldrich*), tetrabutyl ammonium hexafluorophosphate (TBAFP) (*Sigma-Aldrich*) were purchased from the indicated commercial sources and used as received without any further purification.

2.2. Equipment

A Gamry Reference 600 potentiostat was used for the cyclic voltammetry studies and electrochemical syntheses. ^1H NMR and ^{13}C NMR spectra of the synthesized compounds were recorded at room temperature on a Varian-Mercury 400 MHz high performance digital Fourier Transform (FT)-NMR Spectrometer (Mercury-400BB) using CDCl_3 as the solvent and tetramethylsilane as the internal standard (0.00 ppm) relative to which the chemical shifts (δ) were given. The FT-IR spectra were recorded on a Perkin-Elmer spectrometer (Spectrum 100). IR measurements for characterization of molecules were carried out with KBr pellets and/or ATR. Mass spectra were recorded with an Agilent Technologies 6890N Network GC system and Agilent Technologies 5975B VL MSD Mass Spectrometer operating at an ionization potential (EI) of 70 eV. Elemental analysis for C, H and N were performed with an Eurovector CHNS Elemental Analyser. Melting points (up to 350 °C, uncorrected) were determined on an Electrothermal Programmable Melting Point Apparatus (IA9300). During the experiments, thin layer chromatography (TLC) was used to

monitor the progress of reactions. To separate the desired product from unreacted starting materials, byproducts and/or other impurities, column chromatography technique was performed. Therefore, TLC aluminum sheets (Merck, 20 × 20, Silica Gel 60 F₂₅₄) and silica gel (SiO_2) (Merck, Silica Gel 60, 0.063–0.200 mm, 70–230 mesh ASTM) were used, respectively.

UV–vis–NIR spectra were recorded on a Varian Cary 5000 spectrophotometer at a scan rate of 2000 nm/min. Spectrophotometer was used to conduct the spectroelectrochemical experiments of polymer and copolymer. The indium tin oxide (ITO) coated glass plates of thickness of 0.7 mm with resistance of 8–12 Ωsq^{-1} were purchased from Delta Technologies Limited, USA, and used as such for spectroelectrochemical studies. The polymer films were deposited on ITO plates electrochemically using ITO coated plate as working electrode, a Pt counter electrode and silver wire (Fc/Fc^+ (0.3 V)) pseudo reference electrode in Gamry Reference 600 potentiostat.

Conductivity measurements were carried out on the pressed compact disk pellets of polymers having 12.7 mm of diameter and 0.5 mm of thickness using a four-point probe connected to a home-made conductivity meter. Conductivities were calculated based on the average of at least ten pairs of consistent readings taken at different points on the pressed polymer pellets.

2.3. Synthesis of 2-butyl-5,12-dihydro-2H-pyrrolo[3',4':2,3][1,4]dioxocino [6,7-b]quinoxaline (BuDQP)

Synthesis of the monomer was carried out following the route as shown in Scheme 1. The detailed synthetic procedures are as follows:

2.3.1. Diethyl N-butyl-iminodiacetate (1)

To a 200-mL round bottomed flask containing a stirring bar; n-butylamine (4.24 g, 5.75 mL, 58 mmol, d: 0.74 g/mL) and dry K_2CO_3 (24.9 g, 180 mmol) in 50 mL of anhydrous acetonitrile were added and the mixture was stirred at room temperature, under nitrogen atmosphere for a period of time (~10 min) in order to provide a homogeneous reaction environment. Ethyl chloroacetate (13.4 g, 11.7 mL, 110 mmol, d: 1.145 g/mL) was added drop-wise to the stirred reaction mixture over a period of 1 h, after which the mixture was allowed to reflux for 9 h. The reaction was monitored by TLC analysis. After completion of the reaction, K_2CO_3 was filtered off and the acetonitrile solution was evaporated. The remaining crude product was purified by distillation under reduced pressure to yield 12.9 g (85%) of diethyl N-butyl iminodiacetate as slightly yellow liquid (bp: 230–235 °C/100–150 mmHg).

^1H NMR (400 MHz, CDCl_3) δ_{H} /ppm: 0.85 (t, J = 8.1 Hz, 3H, butyl $-\text{CH}_3$), 1.2 (t, J = 7.1 Hz, 3H, ester $-\text{CH}_3$), 1.25 (sextet, J = 7.3 Hz, 2H, butyl $-\text{CH}_2$), 1.4 (p, J = 6.2 Hz, 2H, butyl $-\text{CH}_2$), 2.65 (t, J = 8.0 Hz, CH_2 , N- CH_2), 3.5 (t, 2H), 4.1 (q, J = 6.1 Hz, 2H, ester $-\text{CH}_2$).

MS (EI) m/z (%) calcd. for $\text{C}_{12}\text{H}_{23}\text{NO}_4$: 245.3; found: 245.2 (M^+ , 6), 202 (6.3), 172 (100), 154 (2), 144 (3), 130 (30), 116 (6), 98 (5), 88 (3.5), 59 (7), 42 (15), 29 (5.4).

IR (KBr), ν_{max} / cm^{-1} : 2982–2874 (aliphatic C–H), 1747 (ester, C=O), 1467, 1376, 1190 (ester, C–O–C stretching), 1031 (C–N–C stretching), 976, 917.

2.3.2. Diethyl 1-butyl-3,4-dihydroxyppyrrrole-2,5-dicarboxylate (2)

To a 200-mL round bottomed flask containing a stirring bar and connected with a reflux condenser and a dropping funnel, clean sodium metal (1.61 g, 70 mmol) and 30 mL of absolute ethanol were added carefully under nitrogen atmosphere. When the evolution of hydrogen gas was observed to diminish, the reaction mixture was heated in a hot water bath at 75–80 °C and a mixture of

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