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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, ^{1}H NMR, ^{13}C 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.

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, antistatic 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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