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Fabricating multicolored electrochromic devices using conducting copolymers

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Abstract

A centrosymmetric polymer precursor, 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)butan-1-amine (TPBA), was synthesized via a Knorr–Paal reaction and its copolymer with EDOT was electrochemically synthesized and characterized. While P(TPBA) has only two colors in its oxidized and neutral states, its copolymer with EDOT has eight different colors. Electrochromic devices based on P(TPBA)/PEDOT and P(TPBA-*co*-EDOT)/PEDOT were constructed and characterized. The oxidized state of the device shows blue color whereas it shows purple for the reduced state. At moderate potentials the device has good transparency with green and gray colors. The maximum contrast and switching time of the multielectrochromic copolymer device were measured as 25% and 0.8 s at 575 nm. Copolymerization not only increases the polymer's color scheme, but also improves its properties, such as redox stability and switching time.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Conducting polymers (CPs) have been proposed for use in a wide variety of next generation technologies including organic photovoltaic devices [1], non-linear optical devices [2], polymer light emitting diodes [3], gas sensors [4, 5], fuel cells [6], organic transistors [7] and electrochromic devices [8, 9]. More recently, research on CPs has mostly focused on their optical properties in the visible [10] and near infra-red (NIR) [11] spectral regions. Polythiophene (PTh) derivatives have been the most studied materials since they exhibit fast switching times, high conductivity, outstanding stability and high contrast ratios in the visible and NIR regions [12].

PThs can be synthesized either chemically or electrochemically. Similarly to polypyrrole, the mechanism of polymerization involves the formation of radical cations that react with each other to develop the polymeric structure. However, the potential required to oxidize the thiophene monomer also leads to over oxidation of the polymer itself. This is known as the 'polythiophene paradox' [13]. In order to lower the potential, an approach that uses thiophene oligomers instead of thiophene monomers or chemical generation of dimers or trimers having two or more heteroaromatic rings derived from thiophene, furan and pyrrole has been suggested since oligomers can be polymerized at a considerably lower potential [14].

In common with several other research groups, this route is convenient for the preparation of 'trimeric' thiophene–pyrrole–thiophene derivatives substituted at the N atom of the pyrrole ring [15–18]. This strategy yields centrosymmetric polymer precursors and seeks to minimize the steric influence of the central substituent through the addition of the thiophene spacers. In this way, we synthesized 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)butan-1-amine (TPBA) via a Knorr–Paal reaction using 1,4-di(2-thienyl)-1,4-butanedione and 1,4-butane diamine.

Electrochromism involves electroactive materials that show a reversible color change when a small DC voltage is applied. Early studies on electrochromic materials were mainly focused on inorganic and organic small molecules. In recent years, electrochromic conducting polymers have received much attention due to several advantages such