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Fabrication of Multifunctional 2,5-Di(2-Thienyl) Pyrrole Based Conducting Copolymer for Further Sensor and Optoelectronic Applications

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In this work a multifunctional amid substituted 2,5-di(2-thienyl)pyrrole derivative (BTP), has been synthesized. The synthesized monomer has unique properties for improving the optical and electrical properties of its conductive polymer. The amide substitution in the monomers provides an effective delocalization of the π-bonds by forcing the conjugated thienylpyrrole electroactive group into the more planar structure. This improves the optical and electrical properties of the conductive polymer. Moreover, electropolymerization has resulted in a cross-linked conductive polymer with three-dimensional conductivity as the monomer structure contains two electroactive groups. Finally, the amine group in the structure allows for further functionalization of the conducting polymer and its use in various sensor platforms. Furthermore, the synthesized monomer (BTP) has been copolymerized with EDOT using different monomer feed ratios and the properties of the copolymer have been investigated in comparison with the homopolymer. Electrochromic devices have constructed with the obtained polymer and it has been determined that constructed device has a high optical contrast and stability when compared with other 2,5-di(2-thienyl)pyrrole derivatives in the literature.
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Conducting polymers (CPs) generate a significant class of organic functional materials. Due to the their unique physical and electrical properties, conducting polymers have potential usage in a variety of practical applications such as electrochromic device,[1–7] solar cells,[8–11] sensors,[12–16] and biomedical applications.[15,17–19]

Morphology of conductive polymers plays an important role in their physical properties such as mechanical, electrical and optical properties. Monomer properties and polymerization environment are most crucial parameters that affect the morphology. For this reason, the design and synthesis of functional monomers are very important in order to form unique and potentially useful conducting polymers for a wide variety of applications. For advanced developments in conductive polymers, it is also important to better understand the relationships between the chemical structure of these polymers and their electronic and optical properties. Researchers have tried to obtain materials with superior optical and electrical properties by designing new monomers or by copolymerization with the help of structure-property relationships. Copolymerization, a process in which two or more monomers are incorporated as integral segments of a polymer, is used to produce copolymers with properties that are different from those of the homopolymers. The properties of the resulting copolymer are dependent on the concentration of the monomer units incorporated into the copolymer. Thus, the fact that tuning the copolymer properties by adjusting feed ratio of the monomers can provide the researcher with a unique and unlimited ability or opportunity to design and construct materials with specific optical and electronic properties.

Nowadays researchers are widely using the copolymerization process to improve the electrochromic properties of conducting polymers.[20–27]

Among the co-monomer derivatives used to obtain unique materials by the copolymerization process, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most favorable conductive polymers because of its superior electrochemical and optical properties.[28,29] Moreover, many studies in literature have demonstrated that electrochemically synthesized PEDOT is suitable for electrochromic devices owing to its high contrast value, stability and transmissivity in the oxidized state.[5,30,31]

Lately, the electrochemical copolymerization of 3,4-ethylenedioxythiophene (EDOT) with different monomers such as thiophene,[32–34] pyrrole,[35] dithienyl pyrrole (SNS)[6,36,37] and carbazole[38–43] derivatives has attracted considerable interest due to the improved electrochromic properties obtained from the resulting copolymer.

Optical properties of conducting polymers have been investigated in many papers. For example, Roncali[44] has investigated polythiophene derivatives and Mortimer et al.[45] have investigated polypyrrole and polyaniline derivatives. Polycarbazole and poly(2,5-di(2-thienyl)pyrrole derivatives have been investigated by Abashev[46] and Guzel et al.[47] et al. Reynolds[48] has explored color control in p-conjugated polymers. Based on these researches, there is a huge interest in these polymeric materials as a response to the development and demand of the new electrochromic materials.

In this work a multifunctional amid substituted 2,5-di(2-thienyl)pyrrole derivative, 5-amino-N,^{1}N^3-bis(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)isophthalamide (BTP), has been synthesized.

The synthesized monomer has unique properties for improving the optical and electrical properties of its conductive polymer. Amide substituted dithienyl pyrrole derivatives have been synthesized for the first time in literature by our research group.[6,7,31,36,37,49–51] Presence of the amide group in the monomer structure has been found to increase synthesis efficiency, but also improve the optical properties of the resulting polymer film. In addition, it has forced the conjugate system to be more planar structure, thereby providing the desired optical and electrical properties of the polymer.[52,53] The amide substitution in the monomers provides an effective delocalization of the π-bonds by forcing the conjugated thienylpyrrole electroactive group into the planar structure.[52,53] Moreover, as the monomer structure contains two electroactive groups, electropolymerization has resulted in a cross-linked conductive polymer with three-dimensional conductivity. Finally, the amine group in the structure allows for further functionalization of the conducting polymer and its use in various sensor platforms.

The synthesized monomer (BTP) has been copolymerized with EDOT using different monomer feed ratios and the properties of the copolymer have been investigated in comparison with the homopolymer. Electrochromic devices have constructed with the obtained polymers and it has been determined that constructed device has a high optical contrast and stability when compared with other SNS derivatives in the literature.

Besides being multifunctional, the conductive polymer investigated in this research has a satisfactory (61% at 900 nm) optical contrast when compared to similar derivatives in the literature. Tirkeş et al.[54] have used a 1-(pyren-3-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole (SNS-P) and it has been obtained that the optical contrast as 16.7%. Guzel et al.[47] have synthesized conducting polymer of the 2,4,6-tris((9H-carbazol-2-yl)oxy)-1,3,5-triazine (CTR) with 50% optical

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