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Experimental and Theoretical Investigations of an Electrochromic Azobenzene and 3,4-Ethylenedioxythiophene-based Electrochemically Formed Polymeric Semiconductor

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An electrochromic material based on azobenzene and 3,4-ethylenedioxythiophene (EDOT) semiconducting layer was electrochemically deposited on an indium tin oxide coated glass electrode. Chemical synthesis of the azobenzene and EDOT-based chromophore (DAE) and electrochemical formation of its corresponding polymer (pDAE) are reported. The electrochromic properties of the synthesized polymer pDAE were investigated by electrochemical and spectroelectrochemical methods. pDAE exhibited an optical bandgap of 1.82 eV and three distinct colored states in its reduced, neutral, and oxidized forms. The pDAE polymer showed 44% optical contrast at 710 nm between its reduced and oxidized states and a fast electrochromic switching time of 1.0 s. The frontier molecular orbitals, Raman shifts, and semiconducting properties of this electrochromic polymer were evaluated by density functional theory calculations. The optical absorption bands of the polymer charged states were assigned and investigated.

1. Introduction

Organic electrochromic semiconducting polymers, which are capable of changing their colour upon applied electrochemical potential, in the design are revolutionary multifunctional materials, which already are being successfully applied in smart windows,[1–3] switchable mirrors[4] and displays.[5] Moreover, a development of smart windows which can regulate transmission of visible and near-infrared light, thereby reducing the energy costs for building air conditioning, is important for the nowadays technology.[6,7] Extensive engineering efforts are being made to develop the materials capable of colour change at low electric potential in a wide spectral range and excellent electrochromic properties such as switching speed, lifetime, colour control and cost.[8–10] To extend the field of possible applications for electrochromic materials, new classes of the materials need to be explored and examined. Organic polymeric semiconductors possess wavelength-specific light transparency and excellent charge carrier mobility. In turn, azobenzenes belong to a group of widely studied and applied organic compounds containing aryl and azo moieties. The azobenzene compounds possess vibrant and eye-catching colours, which paves the way for a broad application in dyes,[11] pigments[12] and colorimetric pH indicators.[13] Due to these properties, the azobenzene compounds hold promising prospects for application in polymer chemistry in pursuit of creating polymeric coatings with valuable optical characteristics. Early attempts to obtain polymeric azobenzenes in the main polymer chain resulted in black or brown products of low molecular weight and poor solubility.[14] Later approaches involved synthesis of polymeric materials in which azobenzenes were included as side-chain[15,16] or pendant[17] groups or served as counterions.[18] A successful approach to include azobenzene unit into conjugated polymer main chain was demonstrated by Zaytungul et al. by coupling azobenzene with thiophene and obtaining a polymer which exhibited chromic response to organic acids.[19] The following successful attempt to obtain electrochromic conjugated azobenzene polymers was performed investigated by Apaydin et al.[20] They reported electrochemical polymerization of donor-acceptor-donor type polymers containing azobenzene group in polymer main chains, which exhibited multi-coloured electrochromism. On the other hand, conjugated polymers based on thiophene have attracted great interest towards their application in various semiconducting

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