Journal of The Electrochemical Society, **164** (13) H925-H930 (2017)
0013-4651/2017/164(13)/H925/6/$37.00 © The Electrochemical Society

A Fluorescence and Electroactive Surface Design: Electropolymerization of Dansyl Fluorophore Functionalized PEDOT

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Fluorescent conducting polymers are gaining increasing popularity in actual applications such as electrochromic device, cell detection and fluorescence sensor. This paper describes the synthesis of new both fluorescent and electrochromic polymer. A new bifunctional material 2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methyl 5-(dimethylamino)naphthalene-1-sulfonate (ED) has been synthesized, characterized and electropolimerized. The polymer film which obtained as a highly stable conducting polymer on ITO glass was characterized by cyclic voltammetry (CV), colorimetry, UV–Vis spectroscopy, fluorescence spectroscopy, fluorescence microscopy and scanning electron microscopy (SEM). The PED film demonstrated light blue, gray and purplish blue colors as well as turquoise blue fluorescence color. Both CV and spectroelectrochemical studies proved that the PED film has exhibited high stable electro activity (98%). Further kinetic studies presented that the PED revealed high optic contrast (36%) and relatively low electrochromic response time (2.0 s). The results prevailed that the PED film is promising candidates for fluorescent detection and device applications.

Manuscript submitted September 14, 2017; revised manuscript received October 16, 2017. Published October 27, 2017.

As a recent class of polymers, in spite of their short history, conjugated polymers have been of tremendous significance.[1–4] Conjugated polymers have attracted a remarkable interest from research areas and industry due to potential application of functional materials. Because of their superior electrical and optical properties, conducting polymers have also been widely used in technological applications such as smart windows[5–11] organic light emitting diodes (OLEDs)[12] and sensors.[10,13–15] Furthermore, depend on the recent advances in the technology it is required that the novel multifunctional conducting polymers are designed and synthesized. For this purpose, different functional groups can be attached to the monomer chain for multiple purposes such as n-dopable, solvable, electron donating or fluorescent group.[16,17] If an appropriate fluorescent group is attached to structure, the resulting polymer would be demonstrated both fluorescence and electrochemical properties including multifunctional response.

Synthesis of new fluorescent conjugated polymers has attracted considerable interest for application in optoelectronic devices, chemo sensors or fluorescent sensing platforms. For example, Almeida et al.[18] have reported on the synthesis of a fluorescent pyrrole derivative bearing a dansyl substituent. They investigated fluorescence and electrochromic properties. Ayranci et al. synthesized a pyrene-substituted fluorescent poly-thienylpyrrole by electrochemical polymerization and interaction of fluorescent monomer between metal ions was investigated as a sign of the chemical sensor.[19] Besides, novel rhodamine based fluorescent polymer film was synthesized as good candidate for fluorescent sensing platform as well as other optoelectronic applications.[20–22]

Thiophene derivatives are preferred in the synthesis of electrochromic polymers since they demonstrate superior advantages such as high coloration efficiency, tunable colors and short response time.[23–25] As functional fluorescent group dansyl chloride presents intense absorption bands in the near UV region as well as strong fluorescence in the visible region with high emission quantum yields.[26]

In this study, in order to design the fluorescent conducting polymer, dansyl chloride, excellent fluorescent functional molecule, was introduced in thiophene derivate. Monomer characterization was investigated with ^{1}H-NMR and FTIR. After then, this molecule electropolimerized on ITO glass to act as fluorescent polymer thin film. The optical absorption, electrochemical, electrochromic and fluorescent properties of the polymer materials were characterized. Owing to this study, candidate for new sensor platform which can achieve bifunctional of electrochromic and fluorescent were designed.

Experimental

Materials.—In order to synthesis of monomer, 5- (Dimethylamino) naphthalene-1-sulfonyl chloride (dansyl chloride), triethylamine, chloroform (anhydrous, ≥99%), dichloromethane (anhydrous, ≥99.8%), sodium carbonate (anhydrous), magnesium sulfate (anhydrous, ≥99.5%) and (2,3-Dihydrothieno[3,4-b][1,4]dioxin-2-yl)methanol, EDT-methanol, Thieno[3,4-b]-1,4-dioxin-2-methanol (hydroxyl methyl edot), ethyl acetate (anhydrous, 99.8%), n-hexane (anhydrous, 95%) were purchased from Sigma-Aldrich. For investigation of electrochemical performance of polymer, supporting electrolyte lithium perchlorate (≥95.0%) and acetonitrile (anhydrous, 99.8%) were purchased from Sigma-Aldrich.

Instruments.—^{1}H-NMR spectrum was measured by 400 MHz/54 mm Ultra Shield. An FTIR spectrum was measured using Perkin-Elmer 2000 FTIR spectrophotometer with its Universal ATR Polarization. Carl Zeiss (Supra 40 VP) model Scanning Electron Microscopy (SEM) was used to characterization of polymer film surface. The absorption spectra of monomer and thin films were measured with an Agilent 8453 UV-vis spectrophotometer. Colors of thin films were determined by Minolta CS-100 spectrophotometer. Electrochemical performance measurements were performed using Ivium potentiostat/galvanostat in three-electrode cell. Working electrode is indium tin oxide coated glass called as ITO. (Thickness: 7 × 50 × 0.5 mm, surface resistivity: 8–12 Ω sq^{-1}). The Ag wire uses as pseudo-reference electrode and is calibrated presence of ferrocene Fc/Fc$^+$ redox couple. The platinum wire uses as counter electrode in electropolymerization cell. The fluorescent behavior of monomer and corresponding polymer film were characterized by Varian Cary Eclipse Fluorescence Spectrophotometer. An Olympus CKX41 model inverted microscope equipped with a DC30 camera was carried out to examine fluorescence image of polymer.

Synthesis of ED.—Under inert atmosphere, hydroxy methyl edot (0.361 g, 2.1 mmol) and triethylamine (0.273 g, 2.7 mmol) were dissolved in dry chloroform (15 mL). Then, dansyl chloride (0.67 g, 2.5 mmol) dissolved in chloroform (10 mL) was added to mixture of hydroxy methyl edot and triethylamine drop by drop. The reaction mixture was refluxed for 10 h. At the end of the reflux, the solvent removed from the reaction medium. The obtained product was washed with water and sodium carbonate. Anhydrous magnesium sulfate was added to the organic part for drying. Finally, purification was accomplished by using ethyl acetate/hexane (1:9, v/v) solvent mixture with column chromatography. The bright green product 2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methyl 5-(dimethylamino)naphthalene-1-sulfonate (ED) was

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