



Conjugated and Fluorescent Polymer Based on Dansyl-Substituted Carbazole: Investigation of Electrochromic and Ion Sensitivity Performance

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Fluorescent conjugated polymers have been used as excellent optical sensing materials to develop high sensitive and selective sensors by using their large extinction coefficient and high fluorescence quantum yield. Thanks to these features, conjugated polymers are used in a wide range of applications, including metal ion sensing and detection. In this study, a dansyl-substituted fluorescent polycarbazole was synthesized by electrochemical polymerization of 9H-carbazol-2-yl 5-(dimethylamino)naphthalene-1-sulfonate (CZD). CZD was characterized by ¹H-NMR, FT-IR, UV-vis and fluorescence spectroscopy. Optical and electrochemical properties of polymer (PCZD) were investigated by voltammetric, spectroelectrochemical, kinetic studies and colorimetry measurements. Polymer showed a reversible electrochromic behavior from green to light yellow color. Moreover, the sensitivities of CZD toward metal cations were examined by observing the change in the fluorescence intensity. CZD was found to be selective toward Zn²⁺ with significant quenching emission intensity while the other metal ions did not show any interaction with CZD. This novel monomer CZD can be used as metal ion sensor, besides PCZD used in good electronic and optical applications.
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In recent years, a great deal of attention has been devoted on the synthesis of new organic π -conjugated compounds because of their superior properties such as electrical conductivity, optical behaviors etc. Thanks to these excellent properties, π -conjugated polymers have been used for application in such fields as electrochromic glasses,¹⁻⁷ organic solar cells,^{8,9} organic field effect transistors¹⁰ and sensor platform.¹¹⁻¹⁶ The appealing features of new organic π -conjugated polymers mainly depend on modifications of the chemical structure to interchange the electronic properties of materials. These modifications of the monomer consist through appending different functional moiety, such as fluorescent, electron donating and/or electron withdrawing, n-dopable substituents.^{17,18}

Fluorescent probe containing conducting polymers that indicate extensive p-electron delocalization and excellent fluorescent properties have proven to be efficient sensing materials for chemosensory systems.¹⁹⁻²² The design and synthesis of fluorescent chemo sensors for heavy and transition-metal ions is arising as a research topic of receiving attention for environmental or biological applications. One of the important requirements in designing fluorescent chemo sensor for metal ion detection is that the signaling unit must be capable of providing a spectral response. Many of the metal cations are known as fluorescent quenchers via enhancement of spin-orbit coupling like Hg²⁺ or energy/electron transfer like paramagnetic Cu²⁺.

Among the many various fluorophores, dansyl probes have attracted considerable attention since it contains both electron donor group and electron acceptor group in its molecular structure.²³ Furthermore, dansyl based molecules indicate fluorescence intensity in the visible region depend on high emission quantum yields.

In this study, we report the synthesis and characterization of novel monomer CZD which is based on dansyl group substituted carbazole. In this distinctive combination, carbazole group has electronic and optical properties due to its highly delocalized p-electrons. Besides, the dansyl moiety functions as a fluorescent reporter as a receptor to response to metal ions. Thus, when metal ion interaction with this monomer fluorescence enhancement or fluorescence quenching are expected to be observed depend on dansyl group. In addition to this features, electrochemical and electrochromic properties of the P(CZD) film deposited onto ITO electrodes were investigated using cyclic voltammetry and spectroelectrochemical techniques. Thanks to this study, a new strategy for designing and synthesizing the fluorescent conducting polymer of merged fluorescent sensitivity system and electrochemistry is proposed and achieved with a simple, low-cost procedure.

Experimental

Materials and instrumentation.—2-Hydroxycarbazole, 5-(Dimethylamino) naphthalene-1-sulfonyl chloride (dansyl chloride), triethylamine, chloroform (anhydrous, $\geq 99\%$) were used as synthesis of monomer. All chemicals were purchased from Sigma-Aldrich. For electrochemical experiments, lithium perchlorate ($>99\%$) was used as a supporting electrolyte. ACN (anhydrous, 99.8%), NMP (anhydrous, 99.5%) were used as solvent. All metal salts Cd(NO₃)₂·4H₂O, ZnN₂O₆, HgCl₂, FeCl₃, Cu(NO₃)₂·3H₂O were performed on the metal ion sensitivity experiments. FT-IR spectra were taken on a Perkin-Elmer 2000 FTIR spectrophotometer (4000–400 cm⁻¹) with Universal ATR Polarization Accessory. ¹H-NMR and ¹³C-NMR spectrum was taken on a 400 MHz/54 mm Ultra Shield plus with CDCl₃ as the solvent. Metal ion sensitivity experiments were carried on by successive additions of metal ions to the solution of CZD in ACN:H₂O (1:1) v/v. Electrochemical synthesis and characterization were performed on an Ivium potentiostat/galvanostat. Spectroelectrochemistry of the polymer film was determined on an Iviumstat potentiostat/galvanostat in combination with the Agilent 8453 UV-vis spectrophotometer. Fluorescence spectroscopic measurements were performed on Varian Cary Eclipse Fluorescence Spectrophotometer. Colorimetry measurements were carried on with a Minolta CS-100 spectrophotometer.

Synthesis of CZD.—2-Hydroxycarbazole as called CZ (0.385 g, 2.1 mmol) and triethylamine (0.273 g, 2.7 mmol) were dissolved in 15 ml of dry chloroform under argon atmosphere. A solution of dansyl chloride (0.67 g, 2.5 mmol) in 10 ml of chloroform was added dropwise to the refluxing mixture. Reaction mixture was refluxed for 10 h. The solvent was removed and the mixture was washed with water and Na₂CO₃. The organic phase was dried with anhydrous MgSO₄. Finally, purification was accomplished by column chromatography by using ethyl acetate/hexane (1:9, v/v) solvent mixture. The resulting yellow 9H-carbazol-2-yl 5-(dimethyl amino)naphthalene-1-sulfonate (CZ-dansyl = CZD) was obtained in % 68 yield. Monomers melting point was 157.0°C–158.0°C. Synthesis scheme of CZD was shown in Scheme 1.

The structure of the CZD was approved using FTIR, ¹H-NMR and ¹³C-NMR spectroscopy as shown in Fig. 1. In FTIR spectrum of the CZD monomer, absorption bands were observed at 3391 cm⁻¹ (N-H stretching), 1570 cm⁻¹ (aromatic C=C), 1448 cm⁻¹ (C-H stretching), 1171–1336 cm⁻¹ (C-N stretching), 1091 cm⁻¹ (C-O stretching) and 770–900 cm⁻¹ (C-H band) (Fig. 1a). In order to identify the new dansyl based structure of CZD, the ¹H-NMR and ¹³C-NMR spectra was used.

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