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Conjugated and fluorescent polymer based on dansyl-substituted pyrrole prepared by electrochemical polymerization in acetonitrile containing boron trifluoride diethyl etherate

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ABSTRACT

A fluorescent pyrrole derivative bearing a dansyl substituent was prepared by a simple synthetic route and electropolymerized onto Indium Tin Oxide (ITO) electrodes. The presence of the dansyl group in the monomer precursor prevents the electropolymerization in usual systems, such as $(C_4H_9)_4NBF_4$ in acetonitrile (CH_3CN). For this reason, it was added 20% boron trifluoride diethyl etherate (BFEE) to this system, to achieve electropolymerization. The resulting poly[3-(*N*-pyrrolyl)propyl dansylglycinate] (PPyPDG) films displayed electrochromic behavior. Their color varied from greenish-yellow, in the neutral state, to greyish-green, in the oxidized state; moreover PPyPDG is a good green light emitter material. Therefore, PPyPDG films might be potentially applicable in displays and optoelectronic devices.

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1. Introduction

In recent years, a great deal of interest has been focused on the synthesis of novel π-conjugated polymers, because they display intriguing features such as electrical conductivity, electroluminescence, third-order non-linear optical properties and chemical sensing [1]. Their potential applications include their use as materials for electrochromic devices [2,3], organic light emitting diodes (OLEDs) [4], organic solar cells (OSCs) [5], organic field effect transistors (OFETs) [6], and energy storage [7,8]. All these applications usually require the modification of the monomer structure, to tune the properties of the polymers with respect to desired applications [9]. Hence, creating new design and strategies to synthesize new conjugated polymers constitutes a rapidly expanding area: it provides a wealth of possibilities, leading to interesting materials and electro-optical devices with enhanced performance. Furthermore, this approach has created a strong change in point of view regarding the molecular engineering of the electronic properties of materials derived from conjugated systems and hence on the structural control of their band gap [9,10].

Among conjugated polymers, polythiophenes and polypyrroles are particularly important, because they exhibit good electric conductivity and chemical stability in ambient atmosphere, besides their structural versatility, which allows tailoring of their electronic and electrochemical properties by the manipulation of the monomer structure [11–13]. These modifications in the main chain of the conjugated polymer generally occurs by the changing of the appending moiety [14,15], or by preparation of fused rings [16–18] or either by copolymerization [19,20]. Different functional groups, such as electron donating and/or electron withdrawing, n-dopable, or fluorescent substituents [21–24], can be attached to the system. However, substitution of the electron withdrawing groups on the precursor usually lead to a monomer with higher oxidation potential, culminating in poor film quality [25].

One way to prepare good-quality conjugated polymer films bearing electron withdrawing substituents involves replacement of common organic media with a strong Lewis acid, such as boron trifluoride diethyl etherate (BFEE) [13,25]. BFEE solution has been widely used as catalyst to electrochemically polymerize aromatic monomers, such as polythiophene and its derivatives, polyselenophene, oligopyrene, and so on [13,26,27], however the mechanism of interaction between BFEE and the aromatic ring and/or the effects of different substituents present in the monomer precursor are still poorly discussed in the literature.

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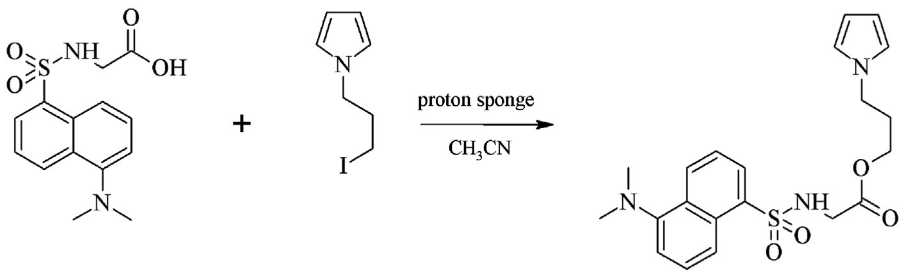

Scheme 1. Synthetic route to obtain PyPDG.

Our group has synthesized and characterized a series of fluorescent materials based on 1-(dimethylamino)-naphthalene-5-sulfonyl, also known as dansyl, derivatives [28–30]. The dansyl fluorophore contains both electron donating and electron withdrawing substituents in its molecular structure: the dimethylamino moiety acts as an electron donor, whereas the naphthalene sulfonyl group acts as an acceptor. This fluorophore exhibits intense absorption bands in the near UV region as well as strong fluorescence in the visible region with high emission quantum yields [31]. These characteristics, together with the synthetic versatility of the sulfonyl group, aroused considerable interest in attaching the dansyl group to the pyrrole ring, to obtain a new fluorescent conjugated polymer.

Based on these considerations, in this paper, a dansyl-based pyrrole precursor was synthesized and electrochemically polymerized using a mixed electrolyte containing $(C_4H_9)_4NBF_4/CH_3CN$ and 20% BFEE (by volume). New insights about energetically favorable interactions between the active sites of this pyrrole derivative and BFEE during electropolymerization process were presented and discussed with basis in theoretical calculations and electrochemical results. Also, the electrochemical, morphological, UV–vis-NIR spectroscopy and fluorescence properties of the as-prepared polymer films deposited onto ITO electrodes were investigated.

2. Experimental

2.1. Materials and instrumentation

All the chemical reagents for synthesis were purchased from Sigma-Aldrich or Acros and used as received. Anhydrous acetonitrile 99.8% (CH_3CN <0.001% water, Sigma-Aldrich), tetrabutylammonium tetrafluoroborate ($(C_4H_9)_4NBF_4$, Aldrich) and lithium perchlorate ($LiClO_4$, Aldrich) were used as received, boron trifluoride diethyl etherate (BFEE, Sigma-Aldrich) was freshly distilled before use.

The ^{1}H NMR spectrum of 3-(*N*-pyrrolyl)propyl dansylglycinate (PyPDG) was recorded on a Bruker spectrometer operating at a frequency of 400 MHz. The FTIR spectrum was acquired on a Bruker IFS66 spectrophotometer using KBr pellets. The elemental analysis determinations were performed on a Carlo Erba EA 1110 CHNS equipment. Melting points were determined on a Micro Química MQAPF 301 melting point apparatus and are uncorrected. Scanning Electron Microscopy (SEM) analysis was conducted on a JEOL JSM 6340F microscope using secondary electrons (SE) mode. UV–vis-NIR spectroelectrochemistry was carried out on a Hewlett-Packard 8453A diode array spectrometer. The CIE (Commission Internationale de l'Eclairage) chromaticity diagram and color coordinates [32] of the polymer films were obtained using a Spectraluxs Software v.2.0 Beta [33]. Fluorescence spectra were registered at room temperature using a Fluorolog Horiba Jobin Yvon fluorometer.

2.2. Synthesis

Scheme 1 illustrates the synthetic route used to obtain 3-(*N*-pyrrolyl)propyl dansylglycinate (PyPDG). 1-(3-Iodopropyl)pyrrole (0.66 g, 2.82 mmol) and 1,8-bis(dimethylamino)naphthalene (proton-sponge®, 0.44 g, 2.09 mmol) were added to a solution of dansylglycine (0.63 g, 2.05 mmol) in 15 mL of dry CH_3CN. The reaction mixture was stirred at 50 °C for 1.5 h; a white precipitate was generated and removed by filtration. CH_3CN (15 mL) was added to the solution, which was then stirred; the precipitate was formed again and removed by filtration. The filtration step was repeated until no more precipitate was detected. The solvent present in the remaining solution was evaporated in a rotatory evaporator; the crude product was chromatographed on silica using CH_2Cl_2 as eluent, to give 0.50 g (59% yield) of the compound as a pale yellow solid. *M.p.* 84.9–85.5; ^{1}H NMR (400 MHz, methanol-d$_4$, δ): 8.56 (d, J = 8.6 Hz, 1*H*), 8.37 (d, J = 8.6 Hz, 1*H*), 8.18 (dd, J = 7.3 and 1.2 Hz, 1*H*), 7.62–7.54 (m, 2*H*), 7.27 (dd, J = 7.5 and 1.2 Hz, 1*H*), 6.57 (m, 2*H*), 5.99 (m, 2*H*), 3.80–3.70 (m, 6*H*), 2.87 (s, 6*H*), 1.92–1.78 (m, 2*H*); FTIR (KBr): 3287 (s, ν (N–H)), 3098 (w, ν (C–H$_\alpha$ pyrrole)), 2928 (m, ν_{as} (C–H)), 2776 (m, ν_{as} (C–H)), 1752 (s, ν (C=O)), 1576 (w, ν_{as} (C=C)), 1325 (w, δ (N–H)), 1227 (m, δ (C–H, naphthalene)), 1160 (m, ν (C–O)), 789 (m, $\delta_{\text{out-of-plane}}$ (C–H, naphthalene), 721 (s, $\delta_{\text{out-of-plane}}$ (C–H$_\alpha$ pyrrole)) cm^{-1}. Anal. calcd for $C_{21}H_{25}N_3O_4S$: C 60.70, H 6.06, N 10.11, O 15.42, S 7.72; found: C 63.05, H 6.27, N 9.09, O 14.05, S 7.54.

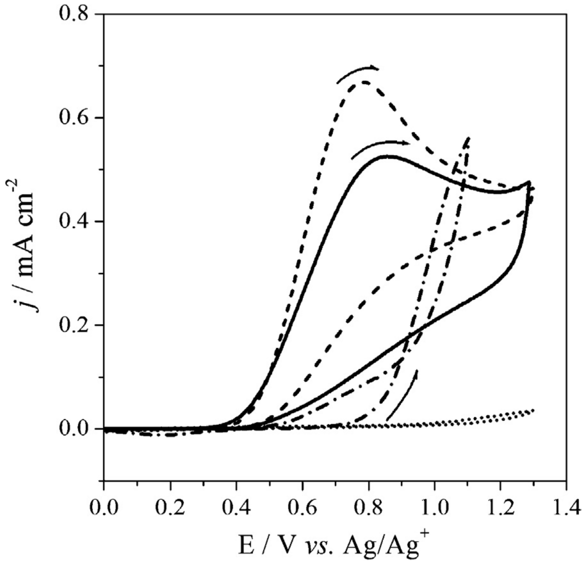

Fig. 1. Cyclic voltammograms on ITO registered during the attempts to electrochemically polymerize PyPDG using $(C_4H_9)_4NBF_4/CH_3CN$ solution (—); dansylglycine solution in the same electrolyte (----) and PyPDG (-·-·-) or dansylglycine (····) in 0.1 mol L^{-1} $(C_4H_9)_4NBF_4/CH_3CN$ with 20% BFEE (by volume), ν = 0.02 V s^{-1}.

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