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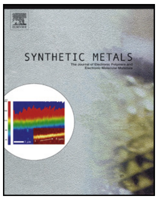

Synthesis and characterization of a dansyl-based fluorescent conjugated polymer

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ABSTRACT

A fluorescent polythiophene derivative bearing a donor–acceptor dansyl substituent was prepared by a simple synthetic route. Poly[2-(3′-thienyl)ethyl dansylglycinate] (PTEDG) is soluble in common organic solvents which allow the drop cast of films onto ITO electrodes. The electrochromic properties of these films were investigated and it was observed color variation from yellow, in the neutral state, to bluish-gray, in the oxidized state. Both the monomer 2-(3′-thienyl)ethyl dansylglycinate (TEDG) and its polymer PTEDG are, respectively, green and yellow light emitter materials.

1. Introduction

Conjugated polymers have attracted the attention of various researchers mainly because of their electrical, magnetic, and optical properties, which make them useful for applications in modern organic optoelectronic devices [1,2]. Nowadays, the majority of these devices are assembled by using inorganic semiconductors materials. However, significant research efforts have been devoted to the development of new organic materials, in order to obtain devices that are competitive with their conventional inorganic counterparts.

Compared with inorganic materials, conjugated polymers present the following advantages: they are light-weight and enable the fabrication of flexible appliances. It is foreseeable that when the large-scale industrial manufacture of devices based on organic conjugated polymers becomes feasible, the resulting appliances will be much cheaper and will have a larger number of functions [3]. Recently, the interest in conjugated polymers has rapidly increased due to the growing number of processable materials that is available and the improvement conferred to the electrical and physical properties of the final device [4].

New structural designs of conjugated polymers have afforded materials with excellent characteristics for application in such fields as organic light emitting diodes (OLEDs) [5], organic field effect transistors (OFETs) [6], organic solar cells [7], and electrochromic devices (ECDs) [8–10]. Polymers applicable to many areas are regarded as multipurpose materials that can potentially lower the cost of active layer production in the organic electronics industry [11,12].

The attractive properties of conjugated polymers mostly lie on their ability to alter the electronic and spectral features of a compound upon modifications of the chemical structure. This is because tailoring of the band gap (Eg) of these polymers allows for variation in the absorption or emission wavelength [4], or even in the electrochemical response [13].

Rational design and synthesis indeed play an important role in the tailoring of the performance of devices consisting of conjugated polymers. The properties of conducting polymers; *i.e.*, their electronic features, optical characteristics, and conductivity, among others, depend mainly on the electronic nature of the starting monomer. These properties can be adjusted by modification of the monomer through attachment to the system of different functional groups, such as electrondonating and/or electronwithdrawing, n-dopable, or fluorescent substituents [13–16]. For example, the appendage of appropriate fluorescent and anchoring groups to the structure of the monomer would make the resulting polymers amenable for use in OLEDs, ECDs, and analytical sensors [13,16–18].

Fluorescent conjugated polymers have been synthesized and characterized with a view to attaining new materials suitable for application in optoelectronic devices. Cihaner and Algi [15] have reported on the synthesis and characterization of a series of novel fluorescent polymers based on *N*-substituted thienylpyrrole bearing naphthalene and fluorene moyeties. A thiophene derivative functionalized with benzotriazole has been shown

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to be both p and n-dopable, fluorescent, soluble in common organic solvents, and processable [4]. In another paper, Lei and co-workers have described the preparation of a high-quality poly(*N*-phenyl-2-naphthylamine) film with excellent fluorescence by an electrochemical method [19].

Our group has synthesized and characterized a series of polypyrrole and polythiophene derivatives bearing dinitroaromatic (n-dopable), alkyl(methoxyphenoxy), or carboxylic acid substituents aiming at their application in ECDs [20–23] or as material for use in capacitors [24]. Recently, we have prepared fluorescent films based on chemically or electrochemically modified 1-(dimethylamino)-naphthalene-5-sulfonyl, also known as dansyl, derivatives [25,26]. Previous studies on the electrochemical properties of dansyl have aroused considerable interest in the attachment of the dansyl group to the thiophene ring, so as to achieve new fluorescent conjugated polymers.

The dansyl fluorophore contains both electrondonating and electronwithdrawing substituents in its molecular structure. The dimethylamino moiety functions as the electron donor, whereas the naphthalene sulfonyl group acts as an acceptor. Furthermore, 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 [27]. These characteristics, together with the synthetic flexibility of the sulfonyl group, have led the dansyl fluorophore to be a core-structure that is present in many fluorescent sensors and labels for the detection of both metal cations [28,29] and anions [30] as well as in larger supramolecular structures such as dendrimers [31,32].

Based on these considerations, in the present communication we report on a new synthetic route for the preparation of the monomer 2-(3′-thienyl)ethyl dansylglycinate (TEDG), its polymerization in chloroform with $FeCl_3$ as the oxidizing agent, and the characterization of the resulting product. The fluorescence and spectroelectrochemical properties of this polymer have also been investigated.

2. Experimental

2.1. Chemicals

Unless otherwise stated, all the chemical reagents were purchased from Sigma–Aldrich, Vetec, or Acros and used as received. The solvents, of analytical grade, were dried by conventional procedures and distilled prior to use. All the new compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, FTIR and elemental analysis.

2.2. Instrumentation

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometer operating at a frequency of 400 MHz. The FTIR spectra were acquired on a Bruker IFS66 spectrophotometer using KBr pellets. The elemental analysis determinations were performed on a Carlo Erba equipment. Melting points were determined on a Micro Química MQAPF 301 melting point apparatus and are uncorrected. Fluorescence spectra were registered at room temperature using a Fluorolog Horiba Jobin Yvon fluorometer.

Number- and weight-average molecular weights (Mn, Mw) were measured by size exclusion chromatography (SEC) against polystyrene (PS) standards, using two Polymer Laboratories PLGel 5 mm Mixed-C columns, a Shodex RI-71RI detector, and a Shimadzu LC-10 AD pump, in THF, at a1.0 mL min^{-1} flow rate.

UV-vis-NIR spectroelectrochemistry was carried out on a Hewlett-Packard 8453A diode array spectrometer. Cyclic voltammograms were registered on an Autolab PGSTAT30 galvanostat/potentiostat by using a three-electrode cell. The CIE chromaticity diagram and color coordinates of the polymer film were obtained using a Spectra Lux® Software v.2.0 Beta [33].

2.3. Synthesis

3-(2-Bromoethyl)thiophene was synthesized according to the procedure described in the literature [34] and was obtained in 67% yield (lit. 70%). 3-(2-Iodoethyl)thiophene was prepared by using a literature procedure, with slight modifications [35]. Briefly, 40 mL KI solution (6.46 g, 37.41 mmol) in acetone were added to the crude 3-(2-bromoethyl)thiophene (6.57 g, 34.42 mmol). The reaction mixture was stirred and refluxed for 4 h. Next, the mixture was filtered, and the resulting solution was distilled under reduced pressure, which furnished 6.47 g 3-(2-iodoethyl)thiophene (79% yield). ^{1}H NMR, FTIR and elemental analysis results matched the data shown in Refs. [34,35] for both thiophene derivatives.

2-(3′-Thienyl)ethyl-dansylglycinate (TEDG): 3-(2-iodoethyl) thiophene (0.77 g, 3.24 mmol) and 1,8-bis(dimethylamino) naphthalene (proton-sponge®, 0.69 g, 3.23 mmol) were added to a solution of dansylglycine (0.99 g, 3.23 mmol) in 15 mL dry CH_3CN. The reaction mixture was stirred at 50 °C for 1.5 h, and the white precipitate was removed by filtration. CH_3CN (15 mL) was added to the crude product, which was followed by stirring, and the precipitate was removed again by filtration. The filtration step was repeated until no more precipitate was formed. An orange ochre solid was obtained (0.34 g, 25% yield). m.p 132–134 °C; ^{1}H NMR (400 MHz, methanol-d$_4$, δ): 8.56 (d, J = 8.6 Hz, 1H, ArH), 8.37 (d, J = 8.6 Hz, 1H, ArH), 8.19 (dd, J = 7.3 and 1.2 Hz, 1H, ArH), 7.51 (m, 2H, ArH), 7.30–7.26 (m, 2H, ArH and ThH), 6.98 (dd, 1H, ThH), 6.86 (dd, 1H, ThH), 3.89 (t, J = 7.1 and 7.8 Hz, 2H, CH_2Th), 3.75 (t, 2H, SO_2NHCH_2), 2.86 (s, 6H, $N(CH_3)_2$), 2.56 (t, J = 7.0 and 7.9 Hz, 2H, $COOCH_2$). ^{13}C NMR (400 MHz, methanol-d$_4$, δ): 167.55, 150.21, 135.98, 134.20, 128.32, 128.16, 127.13, 126.22, 126.13, 123.55, 121.33, 119.62, 117.86, 113.48, 62.10, 42.82, 42.14, 26.98. FTIR (KBr): ν = 3276 (m, ν (N—H)), 3108 (w, ν (C—H$_\alpha$ thiophene)), 3053 (w, ν (C—H$_\beta$ thiophene)), 2940 (w, ν_{as} (C—H)), 2864 (w, ν_{as} (C—H)), 1741 (s, ν (C=O)), 1575 (w, δ (N—H)), 1452 (w, ν_{as} (C=C)), 1380 (w, ν_s (C=C)), 1348 (m, δ (C—H, CH_2)), 1238 (m, δ (C—H, naphthalene)), 1203 (m, ν (C—N)), 1160 (m, ν (C—O)), 881 (w, $\delta_{\text{out-of-plane}}$ (C—H, naphthalene), 831 (w, $\delta_{\text{out-of-plane}}$ (C—H)), 790 (s, $\delta_{\text{out-of-plane}}$ C—H)) cm^{-1}; 686 (w, $\delta_{\text{out-of-plane}}$ C—H$_\alpha$ thiophene)) cm^{-1}. Anal. calcd for $C_{20}H_{22}N_2O_4S_2$: C 57.39, H 5.30, N 6.69, O 15.29, S 15.32; found: C 57.25, H 5.48, N 6.09, O 15.99, S 15.19.

Poly[2-(3′-thienyl)ethyl-dansylglycinate, PTEDG: TEDG (88.0 mg; 0.21 mmol) dissolved in 20 mL dry $CHCl_3$ was by added dropwise to a $FeCl_3$ suspension (100 mg; 0.63 mmol) in 20 mL dry $CHCl_3$, under N_2. The mixture was stirred for 48 h at room temperature. The polymer was precipitated by addition of CH_3OH, filtered, and purified by Soxhlet extraction with CH_3OH. The purified polymer was dried under vacuum for 6 h. A reddish brown solid (0.457 g) was obtained. After grinding the dried polymer to a fine powder with a mortar and pestle, it was reduced by addition of aqueous hydrazine (2.0%) and chloroform extraction at reflux for 3 h. The organic layer was separated and solvent removal resulted in the reduced polymer [36]. ^{1}H NMR (400 MHz, dimethyl sulfoxide-d$_6$, δ): 8.53, 8.35, 8.27, 8.02, 7.50, 7.16, 4.20, 3.99, 3.68, 2.71, 2.50. ^{13}C NMR (400 MHz, dimethyl sulfoxide-d$_6$, δ): 170.53, 153.16, 137.12, 131.29, 130.10, 129.19, 129.11, 126.52, 124.31, 122.59, 120.81, 116.45, 66.08, 45.79, 45.11, 29.93. FTIR (KBr): ν = 3293 (m, ν (N—H)), 3079 (w, ν (C—H$_\beta$ thiophene)), 2929 (w, ν_{as} (C—H)), 2863 (w, ν_{as} (C—H)), 1735 (s, ν (C=O)), 1571 (w, δ (N—H)), 14502 (w, ν_{as} (C=C)), 1392 (w, ν_s (C=C)), 1315 (m, δ (C—H, CH_2)), 1228 (m, δ (C—H, naphthalene)), 1197 (m, ν (C—N)), 1139 (m, ν (C—O)), 941 (w, $\delta_{\text{out-of-plane}}$ (C—H, naphthalene), 829 (w, $\delta_{\text{out-of-plane}}$ (C—H)), 786 (s, $\delta_{\text{out-of-plane}}$ C—H)) cm^{-1}.