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# Synthesis and spectroscopic characterization of a fluorescent pyrrole derivative containing electron acceptor and donor groups



SPECTROCHIMICA ACTA

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# HIGHLIGHTS

# GRAPHICAL ABSTRACT

- The synthesis of a new pyrrole derivative containing the dansyl group is reported.
- The emission of PyPDG is high sensitive to the temperature and polarity environment.
- The emission intensity of PyPDG enhances as the solvent temperature is increased.
- The fluorescence of PyPDG is analyzed in light of a thermally activated mechanism.
- We characterize the electrochemical and emission properties of the polymerized material.

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# Introduction

The synthesis of new organic  $\pi$ -conjugated compounds has attracted remarkable interest over the past decade due to the

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# ABSTRACT

The synthesis and fluorescence characterization of a new pyrrole derivative (PyPDG) containing the electron donor–acceptor dansyl substituent is reported. The effects of temperature and solvent polarity on the steady-state fluorescence of this compound are investigated. Our results show that PyPDG exhibits desirable fluorescent properties which makes it a promising candidate to be used as the photoactive material in optical thermometry and thermography applications. Further, the electrochemical and emission properties of polymeric films obtained from the oxidation polymerization of PyPDG are also analyzed. © 2014 Elsevier B.V. All rights reserved.

> possibility of exploring such materials in the design of new electro-optical devices [1–3]. In fact, highly conjugated compounds have been reported as an excellent alternative to sensing and imaging applications which require an active matrix with luminescent properties that are sensitive to the external conditions, such as the medium polarity [4,5] and the environment temperature [6,7]. In this context, the class of organic molecules containing

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electron donor and acceptor groups has played an important role once they present a rich phenomenology related to the mechanism of intramolecular charge transfer (ICT) [8]. In particular, dimethylamino-substituted aromatic compounds may exhibit a dual fluorescence upon a single excitation which is directly associated with a large charge separation and the emergence of highly polar excited states from the process of the Twisted Intramolecular Charge Transfer (TICT) [8]. Indeed, the TICT state corresponds to a rotational isomer stabilized by a polar medium in which a complete charge transfer has occurred [8,9]. In addition to the short wavelength emission arising from the locally excited (LE) state [10], the deexcitation from the TICT state takes place at a lower energy level, thus leading to a red-shifted second emission which is sensitive to the temperature, the polarity, and the viscosity of the solvent environment [8,10,11]. As a consequence. compounds presenting the TICT mechanism have been successfully used in distinct timely applications, such as in real-time microviscosity probes [12], molecular recognition [13], as well as in the imaging of living cells [14].

Since the prominent work reporting the assembly of a lightemitting diode based on a polymeric material [15], several studies have been devoted to the design of new  $\pi$ -conjugated polymers containing fluorescent groups in their architectures [16-18]. In particular, such systems exhibit optical and electronic properties similar to inorganic semiconductor materials, giving rise to a new generation of organic semiconductors with useful characteristics, such as mechanical flexibility, thermal stability, and low cost of production. In fact, a large variety of optoelectronic devices based on conjugated polymers has been demonstrated from the electronic transport and/or the light emission in these systems, including organic light emitting diodes (OLED) [19], organic fieldeffect transistors (OFET) [20,21], and photovoltaic devices [22,23]. Although many conjugated polymers have been explored in the development of optoelectronic devices, polypyrrole and its derivatives constitute an important class of polymeric compounds due to their low oxidation potential, high stability, and the good capability of being chemically modified without the loss of the conductive properties [24,25]. As a result, properly functionalized pyrrole derivatives have been identified as ideal photoactive materials for a large variety of chemosensing applications, such as DNA recognition [26], diagnosis of hepatitis C virus [27], electronic tongue [28], and gases detection [29].

An attractive feature of polymeric materials is the possibility to alter their electronic and spectral properties through the attachment of different functional groups in their polymeric backbone [30–32]. Such a desirable characteristic has been widely used in the fluorescent label technique, which explores the side attachment of fluorophore groups in the polymeric chain [33]. Among the large variety of fluorophore groups, dansyl probes have played an important role due to their high sensitivity to the environmental conditions which is associated with the formation of TICT states [18,4,34,35]. As a consequence, several practical applications have been realized from the covalent linkage of dansyl groups in a polymer backbone [18,36,37]. By using blends of electroluminescent polymers and polysilanes functionalized with dansyl moieties, it was demonstrated that blend-based OLEDs present an improved performance as compared with OLEDs based on single electroluminescent polymer [37]. Recently, the synthesis was reported of a fluorescent polythiophene derivative bearing a donor-acceptor dansyl substituent that exhibits fluorescent and electrochromic properties [17].

In the present work, we report the synthesis and spectroscopic characterization of a new pyrrole derivative containing the electron donor–acceptor dansyl substituent. 3-(N-pyrrolyl)propyl dansylglycinate (PyPDG) was prepared by simple route using dansylglycine as a precursor [38]. The effects of solvation and

temperature on the steady-state fluorescence of PyPDG are investigated. We show that the resultant compound preserves the fluorescent properties of the dansylglycine and presents an electrochemical response inherent to polypyrrole.

# Experimental

#### Materials

Unless otherwise stated, all 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. The compounds were characterized by <sup>1</sup>H NMR spectroscopy, FTIR and elemental analysis.

#### Instrumentation

The <sup>1</sup>H NMR spectra were recorded using a Bruker spectrometer operating at a frequency of 400 MHz. The FTIR spectra were acquired with a Bruker IFS66 spectrophotometer using KBr pellets. The elemental analysis determinations were performed using a Carlo Erba equipment. Melting points were determined on a Micro Química MQAPF 301 melting point apparatus and are uncorrected.

Number- and weight-average molecular weights ( $M_n$ ,  $M_w$ ) were measured by size exclusion chromatography (SEC) against polystyrene (PS) standards, using a Polymer Laboratory PLGel 10 mm Mixed-C column, a Shodex RI-71RI detector, and a Shimadzu LC-10 AD pump, in THF, at a 1.0 mL min<sup>-1</sup> flow rate. Cyclic voltammograms were recorded on an Autolab PGSTAT30 galvanostat/ potentiostat by using a three-electrode cell.

#### Steady-state fluorescence and absorption

In order to investigate the solvation and thermal effects, the steady-state fluorescence of PyPDG was probed by exciting the sample with the Innova 90 CW Argon laser (Coherent) tuned at 457 nm. The excitation power was fixed at  $P_0 = 5.2$  mW in all measurements to allow a comparative analysis of the emission intensity. The emission was collected by an optical fiber connected to a monochromator Sciencetech, model 9057. The signal was detected by a photomultiplier tube model S-20 and it was amplified with a lock-in amplifier SR530 (Stanford Research Systems). By using a homemade electric oven with a precision of 0.1 K, the sample temperature was varied from 295 K up to 316 K, in steps of 3 K. The solutions of PyPDG presented a concentration of 1.0 mg/mL and all emission measurements were carried out at the same experimental conditions. Absorption spectra were obtained using a spectrophotometer Perkin Elmer LAMBDA 1050.

### Synthesis

1-(3-Bromopropyl)pyrrole and 1-(3-iodopropyl)pyrrole were synthesized according to the procedure described in previous literature [38] and were obtained in 64% and 57% yield, respectively. The data of <sup>1</sup>H NMR, FTIR and elemental analysis are in agreement with those previous reported for both pyrrole derivatives [38].

#### 3-(N-pyrrolyl)propyl dansylglycinate (PyPDG)

1-(3-lodopropyl)pyrrole (0.66 g, 2.82 mmol) and 1,8-bis(dimethylamino)naphthalene (proton-sponge<sup>®</sup>, 0.44 g, 2.09 mmol) were added to a solution of dansylglycine (0.63 g, 2.05 mmol) in 15 mL dry CH<sub>3</sub>CN. The reaction mixture was stirred at 50 °C for 1.5 h, and the white precipitate was removed by filtration. CH<sub>3</sub>CN (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. The crude product was chromatographed on silica using CH<sub>2</sub>Cl<sub>2</sub> as eluent to give 0.50 g (59% yield) of the compound as a pale yellow solid. M.p. 84.9–85.5 °C; <sup>1</sup>H NMR (400 MHz, methanol-d<sub>4</sub>,  $\delta$ ): 8.56 (d, *J* = 8.6 Hz, 1H), 8.37 (d, *J* = 8.6 Hz, 1H), 8.18 (dd, *J* = 7.3 and 1.2 Hz, 1H), 7.62–7.54 (m, 2H), 7.27 (dd, *J* = 7.5 and 1.2 Hz, 1H), 6.57 (m, 2H), 5.99 (m, 2H), 3.80–3.70 (m, 6H), 2.87 (s, 6H), 1.92–1.78 (m, 2H); FTIR (KBr): 3287 (s, v (N–H)), 3098 (w, v (C–H<sub>α</sub>) pyrrole)), 2928 (m, v<sub>as</sub> (C–H)), 2776 (m, v<sub>as</sub> (C–H)), 1752 (s, v (C=O)), 1576 (w, v<sub>as</sub> (C=C)), 1325 (w,  $\delta$  (N–H)), 1227 (m,  $\delta$  (C–H, naphthalene)), 1160 (m, v (C–O)), 789 (m,  $\delta_{out-of-plane}$  (C–H, naphthalene)), 721 (s,  $\delta_{out-of-plane}$  (C–H<sub>α</sub> pyrrole)) cm<sup>-1</sup>. Anal. calcd for C<sub>21</sub>H<sub>25</sub>N<sub>3</sub>O<sub>4</sub>S: 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.

# Poly[3-(N-pyrrolyl)propyl dansylglycinate] (PPyPDG)

PyPDG (0.40 g; 1.01 mmol) dissolved in 100 mL dry CHCl<sub>3</sub> was added by dropwise to a FeCl<sub>3</sub> suspension (0.80 g; 5.04 mmol) in 20 mL dry CHCl<sub>3</sub>, under N<sub>2</sub>. The mixture was stirred for 48 h at room temperature. The polymer was precipitated by addition of CH<sub>3</sub>OH, filtered, and purified by Soxhlet extraction with CH<sub>3</sub>OH. The purified polymer was dried under vacuum at 50 °C for 6 h. A black solid (0.16 g) was obtained. <sup>1</sup>H NMR (400 MHz, dimethyl sulfoxide-d<sub>6</sub>,  $\delta$ ): 8.53, 8.35, 8.22, 8.12–7.97, 7.52, 7.37, 7.29, 2.83, 3.80–3.65, 1.78–1.90. FTIR (KBr): 3460 (s, v (N–H)), 2928 (m, v<sub>as</sub> (C–H)), 2779 (m, v<sub>as</sub> (C–H)), 1752 (s, v (C=O)), 1560 (w, v<sub>as</sub> (C=C)), 1322 (s,  $\delta$  (N–H)), 1203 (m,  $\delta$  (C–H, naphthalene)), 1143 (m, v (C–O)), 791 (m,  $\delta_{out-of-plane}$  (C–H, naphthalene)) cm<sup>-1</sup>.  $M_w = 2.67 \times 10^4$ ,  $M_n = 1.93 \times 10^4$  and polydispersity index ( $M_w/M_n$ ) of 1.38.

# Film deposition

The polymer films were prepared by dissolving 1.0 mg PyPDG in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL), followed by their coating onto ITO/glass (Delta Technologies, 8–12  $\Omega$ , coated area = 1.0 cm<sup>2</sup>) electrodes via casting of the polymer solution onto the electrode (100  $\mu$ L cm<sup>-2</sup>). The films were then dried at room temperature. The polymer films had been rinsed with CH<sub>3</sub>CN prior to the electrochemical analysis.

# Electrochemistry

The polymer films deposited onto ITO/glass were characterized by cyclic voltammetry in 0.1 mol L<sup>-1</sup> LiClO<sub>4</sub>/CH<sub>3</sub>CN solution as supporting electrolyte, using a Pt wire as the counter electrode and an Ag/Ag<sup>+</sup> (0.1 mol L<sup>-1</sup>, CH<sub>3</sub>CN) electrode as reference, at a scan rate of 20 mV s<sup>-1</sup>. Cyclic voltammograms were acquired within the potential scan range of  $-1.8 \le E \le 0.85$  V vs. Ag/Ag<sup>+</sup> (0.1 mol L<sup>-1</sup>, LiClO<sub>4</sub>/CH<sub>3</sub>CN).

# **Results and discussion**

#### Synthesis

The synthetic route to obtain PyPDG and its polymer was divided into three steps: the first one involved preparation of pyrrole derivatives, the second was the esterification step and the third was the polymerization of the monomer using FeCl<sub>3</sub> (Fig. 1). Pyrrole derivative was prepared by condensation of the primary amines with 2,5-dimethoxytetrahydrofuran, in glacial acetic acid, to give in one step N-substituted pyrrole. This method is applicable to a large variety of substituted aliphatic and aromatic amines and it has the advantages of simplicity, mild conditions and good yields from readily available starting

materials. 1-(3-Iodopropyl)-pyrrole was prepared by nucleophilic substitution of the brominated precursor. The esterification of the 1-(3-Iodopropyl)-pyrrole with dansylglycine using proton-sponge<sup>®</sup> as a selective proton abstractor affords PyPDG with good yield. Finally, the oxidative polymerization of PyPDG with FeCl<sub>3</sub> in CHCl<sub>3</sub> generates a black polymer (PPyPDG).

# Fluorescence of PyPDG

In Fig. 2, we exhibit the absorption and emission spectra of PyPDG in toluene. In both cases, the sample temperature was kept at 295 K. From the absorption spectrum, we observe that the PyPDG presents two absorption bands at  $\lambda_a = 260.5 \text{ nm}$  and  $\lambda_{\rm h} = 338.4 \, \rm nm$ , corresponding to the lowest  $\pi \to \pi^*$  transitions which are typical of the aminonaphthalene derivatives [39]. In particular, the absorption band centered at  $\lambda_a = 260.5$  nm corresponds to the  $\pi \to \pi^*$  transition from the fundamental state,  $S_0$ , to the short-axis polarized state,  ${}^{1}L_{a}$ , while the absorption band centered at  $\lambda_a = 338.4$  nm is associated with the transition from  $S_0$  to the long-axis polarized state  ${}^{1}L_{b}$ . It is important to stress that the lowest absorption bands of the aminonaphthalene derivatives are associated with the formation of locally excited states (LE), which tend to be insensitive to the solvent polarity. In fact, we have not observed any effect associated with the solvent polarity on the absorption spectrum of PyPDG. Concerning with the fluorescence, we observe that PyPDG presents a broad emission spectrum ranging from 420 nm to 650 nm, with a maximum intensity at  $\lambda_f = 501.9$  nm. The fluorescence spectrum of PyPDG is quite similar to the emission spectrum of dansylglycine (not shown), indicating a minor contribution of the pyrrole group to the emission state of PyPDG. The broad emission of PyPDG can be directly attributed to the radiative relaxation from the LE and TICT states, with the later being very sensitive to the polarity of the solvent. Indeed, it was previously reported that dansyl moieties exhibit a dual fluorescence which is characterized by a double exponential decay of the transient fluorescence intensity [40,41]. More specifically, the mixing of  ${}^{1}L_{a}$  and  ${}^{1}L_{b}$  polarized states of the aminonaphthalene group constitute the emitting state of PyPDG, with the emergence of a charge-transfer state from the promotion of a lone-pair electron of the amino group into a  $\pi^*$ -antibonding orbitals of the naphthalene ring [39.41]. As consequence, we observe a noticeable red shift in the emission of PyPDG as the polarity of the solvent is increased. Although the red shift in the fluorescence spectrum is typical of  $\pi \to \pi^*$  electronic transition, several works have reported a red shift on the fluorescence phenomenon involving a TICT state [8]. The data of absorption and fluorescence from PyPDG are summarized in Table 1.

The Stokes shift  $v_a - v_f$  can be used to estimate the variation in the dipole moment of the PyPDG molecule upon excitation [6]. In particular, we use the empirical polarity parameter  $E_T^N$  introduced by Reichardt and Welton [5,42], which reduces the effects associated with the error estimative of the Onsager cavity radius of the molecule of interest. Further, the  $E_T^N$  parameter provides a better description of the microscopic environment of molecular dipoles in solution rather than the other bulk polarity functions based on the permittivities and the refractive indices of the solvents, by including the formation of hydrogen bonding and the distinct mechanisms of the intramolecular charge transfer [42,43]. More specifically, the variation of molecular dipole moment can be obtained from:

$$v_a - v_f = 11307.6 \left[ \left( \frac{\delta \mu}{\delta \mu_B} \right)^2 \left( \frac{a_B}{a} \right)^3 \right] E_T^N + constant.$$
(1)

Here,  $v_a$  and  $v_f$  are respectively the absorption and fluorescence maximum wavenumbers in cm<sup>-1</sup>.  $\delta \mu_B = 9 \text{ D}$  and  $a_B = 6.2 \text{ Å}$  are



Fig. 1. Synthetic route for the preparation of 3-(N-pyrrolyl)propyl dansylglycinate (PyPDG) and polymerization of PyPDG, to obtain PPyPDG.



**Fig. 2.** Absorption (solid black line) and fluorescence (solid red line) of PyPDG in toluene. The dashed lines correspond to the Gaussian deconvolution of the fluorescence spectrum of PyPDG. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

respectively the dipole moment change upon excitation and the Onsager cavity radius of the betaine dye [5].  $\delta\mu$  and *a* corresponds to the variation of the dipole moment and the Onsager cavity radius of the molecule of interest. In Fig. 3, we present the Stokes shift of PyPDG as a function of the solvent polarity parameter  $E_T^N$ . By determining the slope *m* from linear regression of the data (dashed line), we can evaluate the dipole moment variation for PyPDG by using the following relation:

$$\delta\mu = \sqrt{\frac{\delta\mu_B^2 \times m \times a^3}{11307.6 \times a_B}}.$$
(2)

From the molar mass and the density of PyPDG,  $M_P = 415.50 \text{ g/mol}$  and  $\rho_P = 1.21 \text{ g/cm}^3$ , we estimate the Onsager cavity radius a = 5.14 Å and the variation of the dipole moment  $\delta \mu = 3.48 \text{ D}$  for PyPDG molecule. This value is in good agreement with previous results reported for other dansyl derivatives [4,39,49]. However, the small variation of dipole moment indicates that the radiative decay from locally excited state corresponds to the main mechanism for the fluorescence spectrum of the dansyl

Table 1

Solvatochromic data and solvents parameters:  $\lambda_a$  ( $\nu_a$ ) and  $\lambda_f$  ( $\nu_f$ ) are the absorption and fluorescence peak wavelengths (wavenumbers), respectively. ( $\nu_a - \nu_f$ ) is the Stokes shift.  $\epsilon$  is the solvent dielectric constant and  $E_T^N$  is the Reichardt solvent parameter [5].

Solvent	$\epsilon$	$\lambda_a$ (nm)	$\lambda_f$ (nm)	$(v_a - v_f)$ (cm <sup>-1</sup> )	$E_T^N$
Toluene	2.36	338.4	501.9	9626.5	0.099
Chloroform	4.81	338.9	512.0	9975.9	0.259
Dichloromethane	8.93	338.5	515.0	10124.6	0.309
Acetone	21.01	338.1	525.6	10551.1	0.355
Acetonitrile	36.64	338.4	528.2	10618.6	0.460



**Fig. 3.** Stokes shift as a function of the solvent polarity parameter  $E_T^N$ . The dashed line represents the linear regression of the data.

moiety. In this case, the deactivation of the TICT state is expected to occur through a non-radiative decay which tend to be more pronounced as the solvent temperature is enhanced.

In order to investigate the thermal effects on the fluorescence properties of the system, we show in Fig. 4 the emission spectra of the PyPDG dissolved in acetonitrile for different temperatures. For all measurements, the excitation laser power was fixed at  $P_0 = 5.2 \text{ mW}$  and it was rigorously monitored in order to allow a comparative analysis of the measured spectra. As one can note, the emission intensity of PyPDG increases as the solvent temperature is raised, indicating that the reduction of the solvent viscosity does not play a major role in the fluorescence of this compound. Such a result contrasts with the typical behavior reported for molecular rotors based on the TICT phenomenon. Indeed, the emission intensity of molecular rotors decreases as the solvent viscosity diminishes due to the enhancement of the molecular torsional relaxation that induces the radiationless decay [12,44,45]. This is not the case of PyPDG, although it presents the pyrrolyl propyl as a very flexible group. In fact, the enhancement of emission intensity with the solvent temperature shows that the fluorescence of PyPDG takes place through a thermally activated mechanism. Further, we observe that the fluorescence peak wavelength is not shifted as the solvent temperature is raised and thus the thermochromic effect on this system can be disregarded.



**Fig. 4.** Emission spectra of PyPDG in acetonitrile for different temperatures. Notice the increase of the emission intensity as the solvent temperature is raised.

The maximum of the emission intensity  $I_{max}(T)$  can be directly related with fluorescence quantum yield  $\Phi_F$  by [12]:

$$I_{max}(T) = \gamma \cdot \mathbf{c} \cdot I_{exc} \cdot \Phi_F(T), \tag{3}$$

where  $\gamma$  represents the gain of the detection apparatus, *c* is the fluorophore concentration, and  $I_{exc}$  is excitation intensity. If a reference temperature  $T_0$  is defined, we can compute

$$\frac{I_{max}(T)}{I_{max}(T_0)} = \frac{\Phi_F(T)}{\Phi_F(T_0)}.$$
(4)

By considering that the fluorescence of PyPDG is governed by a thermally activated mechanism, we can write the effective emission rate as [8]

$$k_f = k_0 + k_1 e^{-\frac{\omega_a}{k_B T}},\tag{5}$$

where  $\varepsilon_a$  is the activation energy.  $k_0$  is the residual emission rate at low temperature, while  $k_1$  is the amplitude of the thermally activated contribution. Disregarding the thermal effects on the non-radiative decay from the excited state, it is straightforward to show that the quantum yield satisfies an Arrhenius relation which is given by:

$$\ln\left[\frac{\Phi(T)}{\Phi(T_0)}\right] = \frac{\varepsilon_a}{k_B} \left(\frac{1}{T_0} - \frac{1}{T}\right). \tag{6}$$

In Fig. 5 we exhibit the Arrhenius plot for the quantum yields of the PyPDG as a function of temperature, in solvents with distinct polarities. As one can observe, the quantum yield increases in both solvents as the sample temperature is raised. By using Eq. (6), we can estimate the activation energy from the angular or linear coefficients of the linear regression (dashed lines). Here, we notice that the activation energy is very sensitive to the solvent polarity, presenting a higher value in acetonitrile ( $\varepsilon_a = 0.13 \text{ eV}$ ) than that obtained in toluene ( $\varepsilon_a = 0.08 \text{ eV}$ ). Such a result shows that the radiative decay process of PyPDG is favored in a non-polar environment, in agreement with previous solvatochromic analysis that revealed that the fluorescence phenomenon in PyPDG is governed by the radiative decay from the locally excited state. The enhancement of the fluorescence intensity of PyPDG as the environment temperature is increased opens the possibility of using such compound as the photoactive material in optical thermometry and thermography applications.



**Fig. 5.** Thermal dependence of the quantum yields of PyPDG in solvents with distinct polarities: toluene (circle) and acetonitrile (square). Dashed lines represent the linear regression by using Eq. (6).

#### Electrochemistry and fluorescence of PPyPDG

As we have presented above, PyPDG presents a broad fluorescence spectrum which is sensitive to the polarity and temperature of the environment. The presence of pyrrole moiety on its molecular structure provides the possibility of producing polymeric films with interesting conductive and fluorescent properties. In order to characterize the conductive properties of PPyPDG, we present in Fig. 6 the cyclic voltammogram of the PPyPDG films deposited by casting onto ITO/glass electrodes. It was observed that PPyPDG films display an irreversible anodic wave with anodic peak potential ( $E_{pa}$ ) at 0.52 V vs. Ag/Ag<sup>+</sup> and a poorly defined redox pair in the cathodic region. Such a result is associated with *n*-doping of the polymer, a process in which the cation enters in the polymeric structure and neutralizes the negative charge formed during the reduction process.

The cyclic voltammetry can be used to estimate the relative position of HOMO and LUMO energy levels of the conjugated polymer,  $E^{HOMO}$  and  $E^{LUMO}$ , respectively. According to empirical relationship proposed in previous works [46,47], HOMO and LUMO energy levels can be obtained from the onset oxidation potential,  $E_{ox}^{onset}$ , and the onset reduction potential,  $E_{red}^{onset}$ , as follows:

$$E^{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.40)\text{eV}$$
<sup>(7)</sup>

 $E^{LUMO} = -(E_{red}^{onset} + 4.40) eV$ (8)

$$E_{\sigma}^{ec} = (E^{LUMO} - E^{HOMO}) eV, \tag{9}$$

where  $E_g^{ec}$  represents the electrochemical band gap energy. Here, the energy value of -4.40 eV corresponds to the HOMO/LUMO energy levels of the reference ferrocene/ferricenium redox pair [48]. Thus, the HOMO and LUMO energy levels as well as the electrochemical band gap energy of the PPyPDG films are respectively  $E^{HOMO} = -4.72 \text{ eV}$ ,  $E^{LUMO} = -3.84 \text{ eV}$ , and  $E_g^{ec} = 0.92 \text{ eV}$ . The data obtained from the PPyPDG cyclic voltammetry show that the electrochemical oxidation process involves the electron withdrawing from the HOMO of the polypyrrole moiety, while the reduction process involves the electron addition to the LUMO of the dansyl moiety. Therefore, a possible electronic transition between polypyrrole and dansyl groups ( $E_g^{ec} = 0.92 \text{ eV}$ ) could be expected for an absorption band at  $\lambda_{onset} = 1347 \text{ nm}$ . Although, this electronic transition was not observed.

Optical band gap energy  $E_g^{opt}$  of PPyPDG was empirically calculated from the respective onset absorption wavelength  $\lambda_{onset}$ , determined from UV–Vis spectrum in CH<sub>2</sub>Cl<sub>2</sub>. PPyPDG shows an absorption band at  $\lambda_{max} = 338$  nm (not shown), similar to the



**Fig. 6.** Cyclic voltammogram of the PPyPDG film deposited onto ITO by casting, recorded in 0.1 mol  $L^{-1}$  LiClO<sub>4</sub>/CH<sub>3</sub>CN, with  $\nu = 0.02$  V s<sup>-1</sup>.

PyPDG. The corresponding band gap energy was determined from  $\lambda_{onset}$  of PPyPDG as being  $E_g^{opt} = 2.72$  eV. The electrochemical band gap,  $E_g^{ec}$  of the polymer is clearly lower than the optical gap. This discrepancy shows that the process of absorption and emission associated to the band at 338 nm must occur in strictly related electronic transitions by molecular orbitals HOMO/LUMO of the dansyl chromophore. The pyrrol group (PyPDG) or polymer chain (PPyPDG) is not associated with the fluorescence process. The Stokes shift observed between monomer and polymer emissions occurs due to the change in the molecular dipole moment of these molecules.

In Fig. 7a, we present the emission spectra of the PPyPDG and PyPDG dissolved in dichloromethane, at a temperature of T = 23 °C. As one can note, PPyPDG presents a broad emission band that almost covers the entire range of the visible spectrum, with a maximum intensity taking place at  $\lambda_f = 562$  nm. Further, a large red shift is observed as compared to the fluorescence of PyPDG, which presents a maximum intensity at 512 nm. Such a red shift of the polymer emission is associated with the enhancement of conjugation length in the polymeric backbone. Due to the broad emission band of PPyPDG, it is interesting to characterize the chromatic sensation of human eyes to this specific fluorescence spectrum from the chromaticity diagram. In what follows, we use the CIE 1931 representation which is based on the tristimulus values of a color, representing the intensity combination of primary colors basis [50]. The chromaticity is represented by a point coordinate (x,y), which is obtained from the color match functions [51]. In



**Fig. 7.** (a) Emission spectra of PyPDG (black line) and PPyPDG (red line) in  $CH_2CI_2$ , under a 457 nm laser excitation. (b) CIE 1931 chromaticity diagram for the emission of PyPDG and PPyPDG in  $CH_2CI_2$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 7b, we show the CIE 1931 chromaticity diagram for the emission of PyPDG and PPyPDG in CH<sub>2</sub>Cl<sub>2</sub>. The chromatic point coordinates are: (x = 0.413, y = 0.484) for the PPyPDG and (x = 0.209, y = 0.537) for the PyPDG. We observe that the fluorescence of PyPDG is located in the green region of the chromatic diagram, while the emission of PPyPDG is close to the yellow region.

# Summary and conclusion

In summary, we have synthesized a new fluorescent pyrrole derivative (PvPDG) containing the electron donor-acceptor dansyl substituent from a simple route. The thermal and solvatochromic effects on the fluorescence spectra of PyPDG were investigated. We showed that the emission intensity of the PyPDG presents a pronounced enhancement as the solvent temperature is increased, indicating that the fluorescence of this compound consists of a thermally activated process. The variation in the dipole moment of PyPDG molecules upon a photoexcitation was also estimated from the Stokes shift of PyPDG fluorescence in different solvents. The dependence of emission spectra on the temperature and solvent polarity provides a clear evidence that the radiative relaxation from a locally excited state constitutes the major contribution to the fluorescence phenomenon of this compound. Our results show that PyPDG is a promising candidate to be used as a photoactive material in sensor applications, due to the high sensitivity of its fluorescent properties on the temperature and polarity of the environment. Further, we performed the electrochemical and emission characterization of the polymeric material (PPyPDG) obtained from the oxidative polymerization of PyPDG. A broadening and a shift in the emission band of PPyPDG was observed when compared to the original emission band of PyPDG. The resulting polymer is therefore a robust platform to produce light-emitting devices based on electronic properties of pyrrole group and the fluorescence of the dansyl moiety.

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#### References

- [1] S. Günes, H. Neugebauer, N.S. Sariciftci, Chem. Rev. 107 (2007) 1324–1338.
- [2] Y. Shirota, J. Mater. Chem. 10 (2000) 1–25.
- [3] U. Mitschke, P. Bäuerle, J. Mater. Chem. 10 (2000) 1471-1507.
- [4] B. Ren, F. Gao, Z. Tong, Y. Yan, Chem. Rev. Lett. 307 (1999) 55-61.
- [5] C. Reichardt, T. Welton, Solvents and Solvent Effects in Organic Chemistry, fourth ed., Wiley-VCH, Weinheim, 2011.
- [6] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, second ed., Kluwer Academic/Plenum Publishers, New York, 1999.
- [7] P.F. Aramendía, R.M. Negri, R.S. Román, J. Phys. Chem. 98 (1994) 3165-3173.
- [8] Z.R. Grabowski, K. Rotkiewicz, W. Rettig, Chem. Rev. 103 (2003) 3899–4031.
- [9] J. Santos-Pérez, C.E. Crespo-Hernández, C. Reichardt, C.R. Cabrera, I. Feliciano-Ramos, L. Arroyo-Ramírez, M.A. Meador, J. Phys. Chem. A 115 (2011) 4157– 4168.

- [10] M.V. der Auweraer, Z.R. Grabowski, W. Rettig, J. Phys. Chem. 95 (1991) 2083– 2092.
- [11] M.A. Haidekker, T.P. Brady, D. Lichlyter, E.A. Theodorakis, Biorg. Chem. 33 (2005) 415–425.
- [12] S. Howell, M. Dakanali, E.A. Theodorakis, M.A. Haidekker, J. Fluoresc. 22 (2012) 457–465.
- [13] A. Ito, S. Ishizaka, N. Kitamura, Phys. Chem. Chem. Phys. 12 (2010) 6641–6649.
   [14] X. Qian, Y. Xiao, Y. Xu, X. Guo, J. Qiana, W. Zhu, Chem. Commun. 46 (2010)
- 6418-6436. [15] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, ;K. Mackay, R.H.
- Friend, P.L. Burn, A.B. Holmes, Nature 347 (1990) 539–541. [16] S.J. Evenson, M.J. Mumm, K.I. Pokhodnya, S.C. Rasmussen, Macromolecules 44
- (2011) 835–841. [17] A.K.A. Almeida, J.M.M. Dias, A.J.C. Silva, M. Navarro, J. Tonholo, A.S. Ribeiro,
- Syn. Met. 171 (2013) 45–50.
  [18] E.C. Buruiana, A.L. Chibac, T. Buruiana, V. Musteata, J. Lumin. 131 (2011) 1492–1501.
- [19] S.R. Forrest, Nature 428 (2004) 911–918.
- [20] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A. Dos Santos, J.L. Brédas, M. Lögdlund, W.R. Salaneck, Nature 397 (1999) 121–128.
- [21] H. Sirringhaus, N. Tessler, R.H. Friend, Science 280 (1999) 1741–1744.
- [22] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science 270 (1995) 1789– 1791.
- [23] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, Nat. Mater. 4 (2005) 864–868.
- [24] J.R. Reynolds, A.R. Katritzky, J. Soloducho, S. Belyakov, G.A. Sotzing, M. Pyo, Macromolecules 27 (1994) 7225–7227.
- [25] S.-N. Ding, S. Cosnier, M. Holzinger, X. Wang, Electrochem. Commun. 10 (2008) 1423–1426.
- [26] J. Travas-Sejdic, H. Penga, P.A. Kilmartin, M.B. Cannell, G.A. Bowmaker, R.P. Cooney, C. Soeller, Syn. Met. 152 (2005) 37–40.
- [27] T. Konry, A. Novoa, Y. Shemer-Avni, N. Hanuka, S. Cosnier, A. Lepellec, R.S. Marks, Anal. Chem. 77 (2005) 1771–1779.
- [28] A. Riul Jr., A.M. Gallardo Soto, S.V. Mello, S. Bone, D.M. Taylorb, L.H.C. Mattoso, Syn. Met. 132 (2003) 109–116.
- [29] J. Jatana, M. Josowicz, Nat. Mater. 2 (2003) 19-24.
- [30] M. Gerard, A. Chaubey, B.D. Malhotra, Biosens. Bioelectron. 17 (2002) 345-359.
- [31] M. Asano, F.M. Winnik, T. Yamashita, K. Horie, Macromolecules 28 (1996) 5861–5866
- [32] M.D. Disney, J. Zheng, T.M. Swager, P.H. Seeberger, J. Am. Chem. Soc. 126 (2004) 13343–13346.
- [33] I. Grabchev, X. Qian, Y. Xiao, R. Zhang, New J. Chem. 26 (2002) 920-925.
- [34] A.J.C. da Silva, J.G. Silva Jr., S. Alves Jr., J. Tonholo, A.S. Ribeiro, J. Braz. Chem. Soc. 22 (2011) 1808–1815.
- [35] A.P.P. Praxedes, A.J.C. da Silva, R.C. da Silva, R.P.A. Lima, J. Tonholo, A.S. Ribeiro, I.N. de Oliveira, J. Colloid Interface Sci. 376 (2012) 255–261.
- [36] N. San-José, A. Gómez-Valdemoro, P. Estevez, F.C. García, F. Serna, J.M. García, Eur. Polym. J. 44 (2008) 3578–3587.
- [37] V. Cimrová, D. Výprachtický, H.-H. Hörhold, J. Polym. Sci. A 49 (2011) 2233– 2244.
- [38] A.S. Ribeiro, A. Kanazawa, N.M.A.F. Navarro, J.C. Moutet, M. Navarro, Tetrahedron: Asymmetry 10 (1999) 3735–3745.
- [39] Y.-H. Li, L.-M. Chan, L. Tyer, R.T. Moody, C.M. Himel, D.M. Hercules, J. Am. Chem. Soc. 97 (1975) 3118–3126.
- [40] B. Bednář, J. Trněná, P. Svoboda, Š. Vajda, V. Fidler, K. Procházka, Macromolecules 24 (1991) 2054–2059.
- [41] R. Métivier, I. Leray, B. Valeur, Chem. Eur. J. 10 (2004) 4480-4490.
- [42] M. Ravi, A. Samanta, T.P. Radhakrishnan, J. Phys. Chem. 98 (1994) 9133–9136.
  [43] M. Ravi, A. Samanta, T.P. Radhakrishnan, J. Chem. Soc. Faraday Trans. 91 (1995) 2739–2742.
- [44] N. Dash, G. Krishnamoorthy, Spectrochim. Acta A 95 (2012) 540-546.
- [45] S.K. Saha, P. a Purkayastha, A.B. Das, S. Dhara, J. Photochem. Photobiol. A: Chem. 199 (2008) 179–187.
- [46] J.L. Bredas, R. Silbey, D.X. Boudreux, R.R. Chance, J. Am. Chem. Soc. 105 (1983) 6555–6559.
- [47] D.M. deLeeuw, M.M.J. Simenon, A.R. Brown, R.E.F. Einerhand, Syn. Met. 87 (1997) 53–59.
- [48] A. Misra, P. Kumar, R. Srivastava, S.K. Dhawan, M.N. Kamalasanan, S. Chadra, Indian J. Pure Appl. Phys. 43 (2005) 921–925.
- [49] N. Tewari, N.K. Joshi, R. Rautela, R. Gahlaut, H.C. Joshi, S. Pant, J. Mol. Liq. 160 (2011) 150–153.
- [50] H.R. Kang, Computational Color Technology, SPIE Press, Washington, 1993.
- [51] E.M. Nascimento, F.M. Zanetti, M.L. Lyra, I.N. de Oliveira, Phys. Rev. E 81 (2010) 031713.