



## Full Length Article

# Molecular relaxation temperature of poly(9,9-dioctylfluorenyl-2,7-diyl) using the Franck-Condon emission analysis



R.H. Longaresi<sup>a,\*</sup>, A. Marletta<sup>b</sup>, G.C. Faria<sup>c</sup>, R.M. Faria<sup>c</sup>

<sup>a</sup> UFSCar – Universidade Federal de São Carlos, Campus Lagoa do Sino, C.P.094, 13290-000 Buri - SP, Brazil

<sup>b</sup> InFis - Universidade Federal de Uberlândia, C.P. 593, 38400-902 Uberlândia - MG, Brazil

<sup>c</sup> IFSC - Universidade de São Paulo, C.P. 369, 13660-970, São Carlos - SP, Brazil

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## ABSTRACT

We report on the Franck-Condon analysis of temperature dependence emission spectra (140–340 K) of spin-casted poly(9,9-dioctylfluorenyl-2,7-diyl)(PF8) thin films. The photoluminescence spectra were analyzed considering the contribution of two species: isolates and aggregates. Results obtained from photoluminescence excitation and confocal spectroscopy measurements corroborate the hypothesis of two emitting species. FT-IR and Raman spectroscopy were used to obtain the effective electron-vibrational modes for the isolate ( $700\text{ cm}^{-1}$ ) and aggregate ( $1250\text{ cm}^{-1}$  and  $1400\text{ cm}^{-1}$ ) species, providing values to be used in the Franck-Condon analysis. From the half maximum Gaussian bandwidth ( $\Delta\epsilon$ ), we calculated an activation energy of approximately 250 meV for the inter-chain interaction (aggregates species), which were associated with the onset of movement on the polymer's side chain ( $\beta$ -relaxation).

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## 1. Introduction

Organic semiconductors based on polyfluorenes (PFs) have received a great deal of attention due to their high-emission efficiency in the blue spectral region, good stability, solubility in a wide variety of organic solvents, as well as a processing dependent morphology [1–6]. Polyoctylfluorenes (PF8), for instance, exhibit a strong interchain interaction forming  $\beta$ -phase and also nematic-isotropic liquid-crystalline phase [7] that strongly influence its opto-electronic properties [8]. Film morphology is especially critical for PF8 emission due to the fact that the strong inter-chain interaction can ban emission in lower energy regions ( $\sim 2.5$ – $2.2\text{ eV}$ ) [9–11]. The high energy emission ( $2.8$ – $3.0\text{ eV}$ ) is normally attributed to the isolated PF8 species which normally presents rigid monomers [12]. In solid-state films, where morphology is processing dependent, both emission species are normally observed [9,13], which is not always the case for liquid samples. In addition, knowing that the side chain of PF8 is responsible for aggregate species formation (polymer-polymer interaction) [14], any type of molecular relaxation occurring in the side-chain, i.e.,  $\beta$ -relaxation, would affect the packing structure, thereby modifying

its opto-electronic properties [15]. As demonstrated by Marletta et al. and Atvars et al., the quantum emission efficiency depends on polymer molecular relaxation temperature due to internal conversion of excited intra-chain into inter-chain states [14,15,16]. Therefore the comprehension of molecular dynamics and its correlation with photophysics of those states are fundamental to achieve higher radiative efficiency.

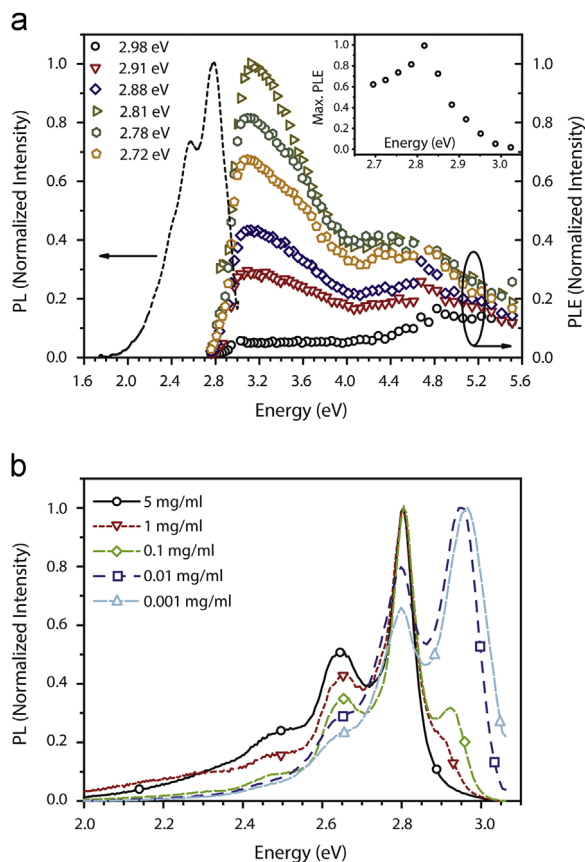
In this paper, we carried out an emission temperature dependence (140–340 K) investigation on poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) films, considering the contributions of both aggregate and isolate molecules. We used the Franck-Condon (FC) analysis of the emission line shape to calculate the electron-vibrational modes coupling (Huang-Rhys parameter) for radiative processes [3,17] considering the emission of both species. Photoluminescence excitation (PLE), infrared and confocal spectroscopy were performed to support our results. The FC analysis provides an alternative method to calculate the  $\beta$ -relaxation temperature ( $T_\beta$ ) which was confirmed by means of dielectric relaxation (DR).

## 2. Experimental and theoretical methods

Thin films of Poly(9,9-dioctylfluorenyl-2,7-diyl), purchased from American Dye Source under the name of 129BE, were obtained by spin-casting a 15 mg/ml stock solution in chloroform

\* Corresponding author.

E-mail address: [longaresi@gmail.com](mailto:longaresi@gmail.com) (R.H. Longaresi).



**Fig. 1.** Teflon/PFO spin-casting film (a) PL and photoluminescence excitation (PLE) detected at 2.69–5.2 eV and (b) photoluminescence spectra excited at 3.06 eV (405 nm) as a function of solution concentration (5–0.001 mg/ml). The inset in Fig. 1(a) shows the PLE curves maximum as a function of detected energy.

on a teflon tape substrate (PTFE from Dielectric). Infrared transmittance measurements were performed using a Thermo Nicolet Nexus spectrometer 479 FT-IR, in the 250–3800  $\text{cm}^{-1}$  range over NaCl solid substrate. Photoluminescence excitation (PLE) spectra were carried out at room temperature using a Shimadzu RF-5301 Fluorometer. Photoluminescence (PL) measurement were obtained by exciting the thin-films samples with linear polarization at 405 nm, using a 30  $\text{mW}/\text{mm}^2$  solid state laser LASERline iZi 405 and a USB2000 Ocean Optics spectrometer. PL Stationary temperature dependence was obtained from 140 K to 340 K, using a closed cycle Helium cryostat. PL measurements of PF8 solution in quartz cuvette (5–0.001 mg/ml) was carried out using the spectrofluorometer Shimadzu RF5301-PC. The confocal spectroscopy measurements were conducted at room temperature using the Zeiss LSM780 microscope.

PFO films emission spectra were simulated using the Frank-Condon analysis. Considering the Fermi's golden rule for electronic transition probability for non-entangled polymer chains and the electron-vibrational modes coupling (Huang-Rhys parameters ( $S$ )), the emission intensity can be calculated supposing the fundamental state for  $T=0$  K [18,19]:

$$I_{ab}(\epsilon) = \frac{8\pi^3 \epsilon^3}{3a_n h^2 c} |\vec{\mu}_{ab}|^2 \sum_{\nu} \frac{S^{\nu} \exp(-S)}{\nu!} D_I(\epsilon_{b0, a\nu} - \epsilon) \quad (1)$$

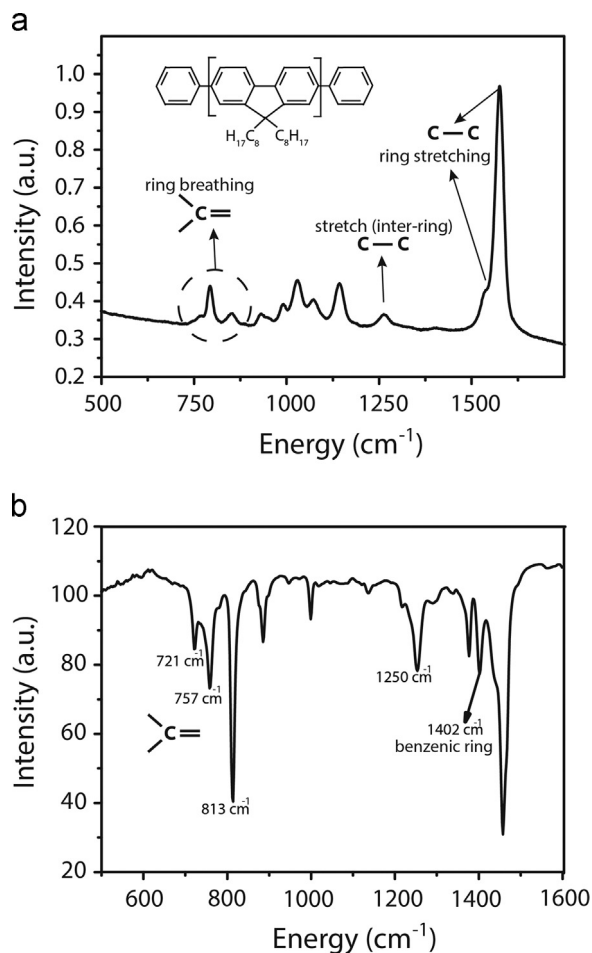
where  $\vec{\mu}_{ab}$  is the electronic transition moment,  $h$  is Planck's constant,  $c$  the speed of light,  $a_n$  describes the refraction index medium effect,  $\epsilon_{b0, a\nu}$  is the energy (zero-phonon) difference between the HOMO ( $b0$ ) and LUMO ( $a\nu$ ) states,  $\nu$  is the vibration mode label, and  $D_I$  is the electronic-vibrational state density approximated by a Gaussian function.

The limitations of our modeling rely on the assertion that typical phonon population energy related to the thermal energy ( $\sim 100$  meV) can be despised. However, the width of the zero phonon peak of about 100–150 meV cannot be evaluated due the poor peak resolution which limits the measurements of all optically active phonons. However, it has already been shown that it is sufficient to adjust the PF8 emission to consider just one effective optical active phonon [04,19].

### 3. Results and discussion

#### 3.1. Spectroscopy analysis

Fig. 1(a) shows the photoluminescence excitation (PLE) spectra in the range of 2.69–5.2 eV for the Teflon/PFO spin-casting film. The lower energy peak ( $\sim 3.01$  eV) corresponds to the absorption of the isolated species and the highest energy peak ( $\sim 4.7$  eV) to the aggregate ones (interchain interaction). By decreasing the detected energy, the PLE line shape changes significantly at  $\sim 3.1$  eV. The inset of Fig. 1(a) displays the maximum of PLE curves as a function of detected energy. It presents higher intensity at  $\sim 2.83$  eV, corresponding to the expected band gap value for PF8. Fig. 1(b) shows the photoluminescence spectra for PF8 solution (chloroform) at different dilutions (5–0.001 mg/ml) excited at 3.06 eV. For the most diluted solutions we observe a blue-shift of



**Fig. 2.** (a) Raman spectrum of PFO beta phase at room temperature and (b) FTIR transmittance spectra of cast poly(9,9-dioctylfluorenyl-2,7-diyl) film deposited on a NaCl solid state substrate. The main vibrational modes and chemical structure of PF8 are indicated.

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