



Franck-Condon analysis of the photoluminescence spectra of a triple-bond containing polymer as a solution and as a thin film



M.A. Saidani^{a,*}, A. Benfredj^a, Z. Ben Hamed^a, S. Romdhane^{a,b}, C. Ulbricht^c,
D.A.M. Egbe^c, H. Bouchriha^a

^a Laboratoire Matériaux Avancés et Phénomènes Quantiques, Faculté des Sciences de Tunis, Université Tunis El Manar, 2092 Campus Universitaire Tunis, Tunisia

^b Faculté des Sciences de Bizerte, Université de Carthage, 7021 Zarzouna, Bizerte, Tunisia

^c Linz Institute for Organic Solar Cells, Johannes Kepler University Linz, Altenbergerstr. 69, 4040 Linz, Austria

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ABSTRACT

The vibronic structures of the photoluminescence spectra of a triple-bond-containing polymer (AnE-PVstat) as a solution and as a thin film were investigated by means of Franck-Condon analysis. We have inferred the energetic disorder which led in turn to an estimation of the diffusion length of excitations. A good diffusion length of excitations (L_D) as large as (21 nm) has been estimated in both film and solution. Exciton migration was found to be morphology-independent thanks to the cylindrical symmetry of the triple bond which acts as a bridge between aromatic groups in case of poor π -overlapping.

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1. Introduction

In organic photovoltaics, the received energy from the sunlight, leads first to the formation of excitons in a conjugated polymer. Then, excitons diffuse to the interface between an acceptor donor hetero-junction where they can split into separate charges [1,2]. The diffusion length of excitons is thus of particular relevance to organic photovoltaics, since being the first parameter governing their internal quantum yield. Microwave conductivity, exciton–exciton annihilation and thickness dependent Photoluminescence (PL) quenching, are the main invoked experiments in the assessment of the diffusion length of excitations in organic semiconductors [3,4]. Yet, the complexity of these experimental methods and the involvement of some theoretical models requiring several fitting parameters, drastically alter their accuracy and lead to uncertain and overestimated exciton diffusion lengths values which led to the development of more accurate techniques [4]. The reported values span typically a range of 5–20 nm [3,4].

In the optoelectronic devices based on organic materials, the active layers are often easily prepared using spin coating or vapor phase deposition techniques. This reduces the cost of production but gives rise to disorder effects. In particular, the energetic disorder has been shown to play a prominent role in the flow of

excitations. Recently, Athanasopoulos et al. studied the relation between the energetic disorder and the diffusion length of excitations in a great detail and offered a direct link between them [3].

On the other hand, in organic semiconductors, the molecules are weakly bound through Van-der-Waals interactions [5]. Thus, the effect of molecular vibrations in the flow of excitations is expected to be strong. The study of such effect, usually involves a Franck-Condon (FC) analysis of absorption and/or emission spectra. This analysis permits to infer, among others, a PL spectrum broadness which monitors the energetic disorder [6–8]. Hence, a FC analysis of a steady state PL spectrum would permit at once, the determination of the diffusion length of excitations and the simulation of the real conditions in an organic solar cell where the active layer is under the continuous wave excitation of the sun light. This is expected to enhance the accuracy of the extracted parameters.

The positional disorder, the conjugation, and the hyperconjugation (due to the presence of the triple bond), as pointed out recently by Camaioni et al. [9] need also to be taken into account in order to build a clear picture about exciton migration.

In this paper, we provide a comparative analysis of the vibronic progressions exhibited in the emission spectra of a side chain based statistical copolymer named (AnE-PVstat) Fig. 1 as a solution and as a spun thin film by means of FC analysis. Through this analysis we have determined the energetic disorder present in the material and the amount of the molecular vibration associated with the exciton. We report also the good diffusion length of excitation in this

* Corresponding author. Tel.: +216 23109652.

E-mail address: saidani.amin@gmail.com (M.A. Saidani).

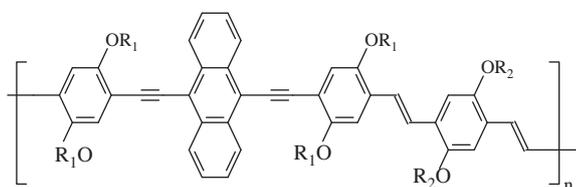


Fig. 1. AnE-PVstat: $R_1 = R_2 =$ octyl or 2-ethylhexyl (randomly) [10].

material, referring to the works of Athanasopoulos et al. mentioned above. The role of the triple bond in the diffusion of excitations is also unmasked.

2. Experiment

The material has been synthesized and purified as described elsewhere [10]. Optical measurements have been carried out at room temperature on solution and spin cast thin film on quartz substrate. In both cases, we have used a chloroform solution of concentration 10 mg/ml. The thickness of the spin cast film is estimated to be about 150 nm. A Perkin-Elmer fluorescence spectrometer has been used for PL measurements. Samples as a solution and as thin film were excited in their absorption bands using an excitation energy of about 3.6 eV [10].

3. Results and discussions

Due to the simple harmonic progressions exhibited in the emission spectra, we have considered a single progression coupled to a single mode thus we assume that FC factors which account for the $0-v$ vibrational transition can be written as [11,12]:

$$|\langle \chi(v_i) | \chi(0) \rangle|^2 = \frac{e^{-S_i} S_i^{v_i}}{v_i!} \quad (1)$$

where S is the Huang Rys factor which corresponds to the average number of phonons involved in the emission process and v_i is the number of phonons in the excited state vibronic potential. Accordingly, the PL spectrum can be modeled as a FC progression [11–13]:

$$I(\omega) = A \sum_{v_i} e^{-S_i} \frac{S_i^{v_i}}{v_i!} \Gamma(\hbar\omega - E_0 + v_i \hbar\omega_i) \quad (2)$$

with $\hbar\omega_i$ is the vibronic level spacing, E_0 is the $0-0$ transition energy, A is a constant and Γ is the line shape function which we assume (for simplicity) to be Gaussian with constant width. The disorder energy referred to as σ is simply the Gaussian variance [14]. The Huang-Rhys factor has also a relation with the total relaxation energy [11,13]:

$$E_{rel} = \sum_i S_i \hbar\omega_i \quad (3)$$

The excitation diffusion length referred to as L_D has been evaluated through the disorder energy σ according to the equilibrium hopping model including first and second nearest neighbours as presented in detail in reference [3].

The PL spectrum from the spin cast film, exhibits two well resolved bands spaced by about 0.18 eV, with a decrease of the band intensity ongoing from the high energy band down to the lower energy band. In the most of the π -conjugated systems such progressions originate from the coupling with the $-C=C$ stretching mode [11,13]. FC fits to Eq. (2) have been made assuming the contribution of the mentioned mode and are shown along with the experimental data in Fig. 2.

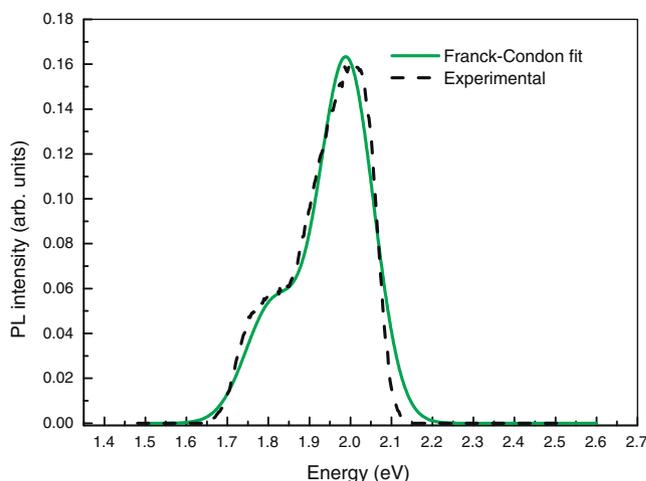


Fig. 2. Experimental emission band shape from a thin film of AnE-PVstat (dashed curve) and its best Franck-Condon fit (solid curve).

The emission spectrum from the solution exhibits a unique band. However, this band looks broader from low energy side, which suggests that it consists of two convoluted bands. Hence it is appropriate to model this spectrum with a single intrachain FC progression coupled to a single phonon mode. The nonlinear least square fit to Eq. (2) along with the experimental data are exhibited in Fig. 3. It worth mentioning that in a previous work we have recorded a PL spectrum from the solution which exhibits two bands, but unlike the present work, the used solvent was the Chlorobenzene. Hence we tentatively attribute the difference between the mentioned spectra to change of the solvent.

We empathize here that the positions of the bands, the $0-0$ transition energy and even the states involved in the emission process cannot be determined from the direct observation of the PL spectra, instead we have determined them from FC analysis.

The derived parameters for the thin film and the solution are displayed in Table 1. A part from the latter parameters, from FC analysis we have also determined the relevant transitions contributing to the PL spectra which are the $0-1$ transition at about 2.35 eV (2.335 eV) and the $0-2$ transition at about 2.53 eV (2.485 eV) for the film (the solution). Referring to the work presented in reference [3] the derived energetic disorder corresponds to a diffusion length of excitation as large as 21 nm.

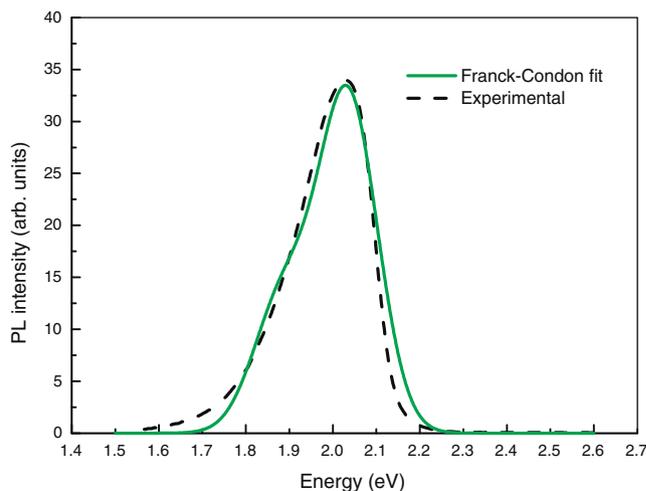


Fig. 3. Experimental emission band shape from a solution of AnE-PVstat (dashed curve) and its best Franck-Condon fit (solid curve).

Table 1

The parameters determined from nonlinear least square fit of PL profiles to Eq. (2) (5% uncertainty); the Huang Rhys factors (S), the relaxation energy (E_{rel}), the PL 0–0 transition energy (E_0), the mean phonon energy of the vibrational mode involved in the emission process ($\hbar\omega_i$) and the disorder parameter σ .

Sample	S	E_{rel} (meV)	E_0 (eV)	$\hbar\omega_i$ (eV)	σ (meV)
Thin film	0.69	124.2	2.17	0.18	67.8
Solution	0.79	118.5	2.185	0.15	67.8

The results reveal also that the good match of the FC fit with the experimental results confirms that the vibrational structure in the PL spectrum of the thin film corresponds to the C=C bond stretching mode. For the solution, the energy of the vibrational mode is of about 0.15 eV, this energy is in close proximity to that of the bending mode of the triple bond [15]. Moreover the PL spectrum in the thin film exhibits a slight redshift as compared to that of the solution. In conjugated polymers such redshift points out the formation of dimer or excimer [15–18]. We have recently shown, through studying the optical properties of quaterthiophene; which is a good prototype for conjugated systems; that such red shift may arise from a chain–chain contact enhancement due to the formation of rod-like chains of quasi coupled molecules [11]. The latter effect is expected to make the molecules more rigid and more planar; hence the diffusion of the excitations becomes more likely to take place through the π – π overlap, this assumption is supported by the involvement of the C=C bond stretching mode in the FC analysis of the PL spectrum from the thin film. Furthermore, in the case of the film where the energy of the phonon mode involved in the emission process is higher than that involved in the case of the solution the Huang Rhys factor; and hence the exciton phonon coupling; is smaller. Hence the displacement of the molecule ions in the excited state relative to that of the ground state is more important in the case of the solution, which points out a more rigid planar structure in the film and confirms our assumption linking the redshift in the film case to specific morphological features. For the solution, the emission spectrum, displays a single progression and according to FC analysis, this progression is coupled to the bending mode of the triple bond. The involvement of the latter mode in the case of the solution counters the poor π -overlapping resulting from the non-planar structure of the molecules. Indeed, it has been recently shown that the triple bond, thanks to its cylindrical symmetry, acts as a bridge between aromatic groups in case of rotation of the aromatic plane [9]. Therefore, we do not expect a difference between the solution and the film regarding the diffusion length of excitation and hence regarding the energetic disorder, though the more planar structure in the case of the film, which explains our findings exhibited in Table 1.

On the other hand, it has been shown that the exciton migration strongly depends upon the solid state packing and drastically decreases with the positional disorder in some organic semiconductors, which would wash out the advantage of the low cost

and the ease of processing qualifying this class of materials. Contrarily to this, our material meets the recent quantum chemical calculations pointing out that the interchain excitonic coupling features a decrease upon the increase of the number of monomers down to a complete vanishing in the case of ideal polymers [19] which clearly excludes the role of any positional order in the diffusion of excitations. This is consistent with the very good diffusion length of excitation in our material independently from morphology, which shows that it holds a significant promise for improved photovoltaics cells with reduced cost [20].

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