

## Photoluminescence Efficiency of Substituted Quaterthiophene Crystals

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The photoluminescence (PL) efficiency of substituted  $\alpha$ -conjugated quaterthiophene crystals shows marked differences depending on crystal packing and molecular geometry. This effect is studied by evaluating the role of the intermolecular interactions and the effects of the single molecule conformation on the intersystem crossing (ISC) rate. The comparison of these calculations with absolute quantum efficiency measurements and with the experimental temperature dependence of the PL decay time, indicates that the differences in PL efficiency are not inherent to crystal packing effects but they are determined by the ISC rate.

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The interest in conjugated polymers and oligomers is due to the application of these materials to optoelectronic devices such as light emitting diodes (LEDs) [1], lasers [2], and photovoltaic cells [3]. The possibility of realizing low cost, large area, and eventually flexible devices makes organic compounds excellent materials for a large extent of applications for which inorganic semiconductors are not suitable. However, problems such as device lifetime, electron-hole injection in the active material [4], and photoluminescence (PL) quenching [5] have to be faced before a real competitiveness with the inorganic counterpart can be envisaged.

A key issue for the improvements of the LEDs and laser performances is the PL quantum yield. In isolated oligomers and polymers, neutral excited states produced by photoexcitation can decay radiatively or through non-radiative processes such as internal conversion (IC) and intersystem crossing (ISC) [6]. In the solid state, intermolecular interactions can increase the probability of nonradiative decay of excitons due to the formation of  $H$  aggregates characterized by lower-energy optically forbidden states [7] or the formation of charge-transfer excitons [8]. In addition, extrinsic processes, such as exciton migration to structural defects and impurities [9], can influence the PL efficiency in a substantial way, so that great care has to be taken in selecting high quality crystals for the optical experiments.

In this Letter we present a study of the correlation between luminescence and structural properties in a relevant class of materials, namely, high-purity differently substituted  $\alpha$ -conjugated quaterthiophene crystals, in which different substitution patterns determine a different degree of molecular distortion and a different crystalline supramolecular organization.

Accurate measurements of the PL efficiency and of the temperature dependence of the PL decay time, together with the calculation of the electronic energy levels and of

the intermolecular interactions, have been carried out. We show that the luminescence is mainly affected by the conformational structure of the single molecule constituting the crystal rather than by the long range symmetry of the crystal itself. The main nonradiative decay process has been found to be the intersystem crossing of the excitation from singlet to triplet molecular states.

The compounds examined are microcrystals of low-temperature unsubstituted quaterthiophene (No. 1), two different tetramethyl quaterthiophenes (Nos. 3 and 5), a dimethyl quaterthiophene (No. 4), and two different polymorphic tetrakis methylsulphonyl quaterthiophenes (Nos. 2 and 6).

In Fig. 1 we display the molecules constituting the crystals. The samples are ordered for increasing average inter-ring dihedral angle [10], a simple geometrical parameter for estimating the molecular distortion. Details on sample preparation, x-ray characterization and room-temperature optical characterization of these compounds are reported elsewhere [10–13].

PL efficiency measurements were carried out by using a nitrogen purged integrating sphere, at room temperature, by exciting the samples with an Ar-ion laser

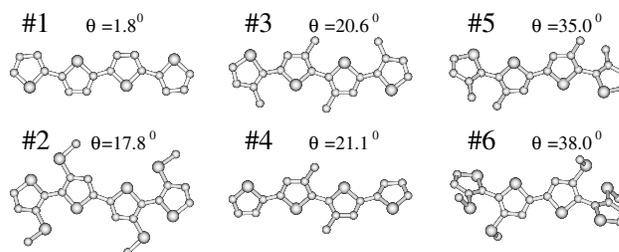


FIG. 1. Schematic view of the considered compounds, in their crystalline conformation:  $\theta$  is the average inter-ring dihedral angle.

( $\lambda_{\text{ex}} = 364 \text{ nm}$ ) and collecting the photoluminescence with a charge-coupled device (CCD) matrix spectrograph.

Lifetime measurements were made by using a Ti-sapphire mode-locked laser delivering 2 ps pulses at 82 MHz repetition rate. The luminescence was dispersed by a 0.24 m single monochromator coupled with a streak camera equipped with a two-dimensional CCD. The overall time resolution was about 8 ps. The samples were mounted in a closed cycle Helium cryostat operating between 20 K and 300 K.

The measured PL efficiencies are quoted in Table I. Crystal No. 1, constituted by planar nonsubstituted quaterthiophene molecules arranged in a strongly packed herringbone (HRB) structure, shows a high PL efficiency of 12%. A comparable quantum yield was recently reported in crystalline thin film [14]. Crystal Nos. 3, 4, and 5, where the functionalization with methyl groups distorts the molecules in a less-compressed quasi-HRB structure, exhibit a PL efficiency reduced to 1%–2%. Compound No. 2 which is characterized by a slipped  $\pi$ - $\pi$  stacking structure shows PL efficiency of 14%. Finally, compound No. 6 presents a packing structure similar to compound No. 5 and low PL efficiency.

We note that the present data cannot be directly compared to the efficiency measured in solution, frozen solution, or inclusion compound due to the different conformation taken by the single molecule in these environments. In fact the molecular distortion in our samples is not only an intrinsic molecular property (induced by substituents) but it is strongly affected by the crystal packing. This is clearly evident in the two polymorphic crystals. We note also that, in solution, the luminescence is expected to come from a more planarized conformation [15], whereas the occurrence of a geometrical relaxation is much more difficult in the crystalline form.

In order to elucidate whether the intermolecular interactions can be responsible for the strong PL efficiency variations, we have first taken into account the exciton resonance interaction [16] and then the role of charge-transfer excitons [17].

The exciton resonance interaction ( $\gamma$ ) is proportional to the rate of excitation transfer between molecules: thus the optical properties of single molecules are fully retained in a

crystal with small  $\gamma$ , whereas for high values of  $\gamma$  the crystalline supramolecular structure should play an important role. We have calculated the exciton resonance interaction [18] for each couple of molecules ( $A, B$ ), along all of the directions, using the x-ray structural data [12]:

$$\gamma_{AB} = \iint dr_1 dr_2 P_A(r_1) \frac{1}{r_1 - r_2} P_B(r_2). \quad (1)$$

The transition density  $P(r_i)$  and the two-electron integrals have been calculated within the intermediate neglect of differential overlap/single configuration interaction (INDO/SCI) scheme [19]. The evaluation of the exact resonance interaction overcomes all of the limitations of the dipole-dipole approximations [18] and, even though the absolute values may be improved [20], the method well reproduces the relative values of the different compounds. We also want to point out that the molecular distortion and the presence of substituents have only a minor effect on the transition density, i.e., the intermolecular resonance interaction depends mainly on the relative distance and position of the molecules in the crystal.

In Table I the values of  $\gamma$  are reported for the first couple of neighbor molecules along three almost orthogonal directions. In all of our crystals along two of these directions, the molecules form a closely packed  $H$  aggregate ( $\gamma > 0$ ) [7], whereas along the third direction a  $J$ -aggregate-type interaction ( $\gamma < 0$ ) [21] is present. The resonance interaction is, however, always maximum along the  $H$  aggregates, indicating a clear predominance of these structures.

We found that  $\gamma$  is very high for compound Nos. 1 and 4, but sample No. 1 shows high PL efficiency. This is clearly in contrast with the general argument that the PL efficiency must be strongly reduced in  $H$  aggregates, whose lowest exciton state is optically forbidden [7,22–24]. Furthermore, we note that compound No. 2, having different crystalline structure and lower  $\gamma$  compared to compound No. 1, has instead a comparable PL efficiency.

Thus, in our samples, no direct correlation can be found between resonance interactions and measured values of PL efficiency. Even if the description of the absorption spectra in terms of excitonic band structure is well established [16], the photoluminescence process cannot be directly explained by the exciton relaxation to low-energy optically forbidden states.

The role of charge-transfer excitons in PL quenching has been evaluated considering the interchain transfer integrals [17]. The interchain hopping process is in fact proportional to the transfer integrals [17]: these transfer integrals also describe the coupling between Frenkel excitons and charge-transfer excitons [25]. We have calculated the electron- and the hole-transfer integrals [25] by using the INDO/SCI wave functions, for each couple of molecules in their crystalline positions. The maximum values obtained (see Table I) are quite small, due to the absence of a complete  $\pi$ - $\pi$  stacking in all of our samples. We found that

TABLE I. Measured PL efficiency ( $\eta$ ), intermolecular resonance interaction for the two  $H$ -aggregate directions ( $\gamma_{H1}$ ,  $\gamma_{H2}$ ) and for the  $J$ -aggregate direction ( $\gamma_J$ ), hole transfer ( $t_h$ ), and electron transfer ( $t_e$ ). All of the calculated values are in meV.

Sample No.	$\eta$ (%)	$\gamma_{H1}$	$\gamma_{H2}$	$\gamma_J$	$ t_h $	$ t_e $
1	12	115	103	-47	42	40
2	14	59	58	-59	24	7
3	1.5	90	74	-47	43	26
4	1.6	119	61	-47	45	13
5	1.8	60	25	-38	17	3
6	1.1	52	51	-25	8	1

the charge-transfer contribution is strongly suppressed in Nos. 6 and 5, but again we do not find any direct correlation to the PL efficiency.

Assuming that extrinsic processes are not dominant in our crystals due to the comparable and high degree of purity [26], the variations in the PL efficiency of our compounds must therefore be caused by intramolecular processes.

A nonradiative channel which deserves special attention is the crossing of the excitations from the singlet to the triplet manifold (ISC), which decay nonradiatively. Actually, ISC is known to be the main cause of PL quenching in oligothiophenes [27–29] compared to other nonradiative processes, such as IC.

Using the theory of the radiationless transitions [30], the ISC rate from the first singlet excited state  $S_{1i}$  to the triplet manifolds  $T_{nj}$  ( $i$  and  $j$  are vibrational quantum numbers) can be written as

$$k_{\text{ISC}} = \frac{2\pi}{\hbar} \sum_n |C_{1n}^{\text{ISC}}|^2 \sum_{ji} p_{1i} |S_{1i,nj}|^2 \delta(E_{S_{1i}} - E_{T_{nj}}), \quad (2)$$

where  $C_{1n}^{\text{ISC}}$  contains the spin-orbit coupling matrix element,  $p_{1i}$  is the occupancy probability, and  $S_{1i,nj}$  is the Franck-Condon overlap factor.

For large organic molecules it can be theoretically shown [31] that a good approximation to Eq. (2) is the phenomenological *energy-gap law*:

$$k_{\text{ISC}} \approx A e^{-|\Delta E|/\hbar\Omega}, \quad (3)$$

where  $\Delta E = E_{S_1} - E_{T_n}$  is the singlet-triplet energy splitting for the most coupled triplet  $T_n$ ,  $A$  is the *pre-exponential factor* (proportional to  $|C^{\text{ISC}}|^2$ ), and  $\hbar\Omega$  is related to the highest vibrational frequency.

According to the principle of detailed balance, if  $\Delta E < 0$  a Boltzmann factor  $\exp(-|\Delta E|/k_B T)$  must be inserted into Eq. (3) [32].

In Fig. 2 we report the energy position, calculated with the INDO/SCI [19] method, of the first singlet excited ( $S_1$ ) state and of triplet state ( $T_4$ ) closest in energy to the singlet state. The state  $T_4$  has already been identified [27] as the state mainly responsible for the ISC in oligothiophenes.

It is worth noting that the energy splitting  $\Delta E = S_1 - T_4$  increases with increasing molecular distortion, and that for compound Nos. 1 and 2 it takes a negative value which involves a thermal activation of the ISC process. The simple exponential law in Eq. (3) cannot, however, account for significant differences in the ISC rate because  $\hbar\Omega$  can be quite large [32]. A dominant role is instead played by the pre-exponential factor  $A$  in Eq. (3). We have calculated the spin-orbit matrix elements [33] and we have found that in the more planar compounds the spin-orbit coupling is very low, whereas in the distorted compounds it increases by several orders of magnitude. Thus the ISC rate is higher in the distorted compound mainly due to the

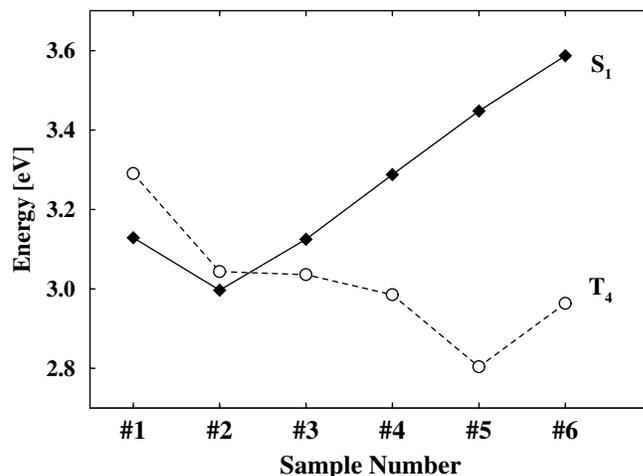


FIG. 2. INDO/SCI energies of the first singlet excited state ( $S_1$ ) and the fourth triplet state ( $T_4$ ) for all of the samples, using x-ray geometry. Other triplets are well separated in energy.

higher spin-orbit coupling. Even if a more complete treatment is needed, including, for instance, vibrational coupling [30] to all triplets, the differences of the experimental PL efficiency between sample Nos. 1 and 2 and the others can be well explained by the different ISC rate. Our findings are also in agreement with the recent studies on bridged quaterthiophenes in solution [34], where higher quantum yields have been obtained for the more planarized compounds.

We have also estimated the PL efficiency at 20 K by normalizing the room-temperature values to the quenching factor of the PL and absorption intensity with temperature. The efficiencies estimated for compound Nos. 1 and 2 are 22% and 17% respectively, consistent with the idea that, in the more planar compound No. 1, the spin-orbit coupling is smaller and  $|\Delta E|$  is larger.

In order to further support this interpretation and to clarify the origin of the nonradiative process, a temperature dependent study of the PL decay times has been carried out. Assuming that the radiative decay time is temperature independent, these measurements provide directly the temperature dependence of the nonradiative decay. The nonradiative decay rate  $k_{\text{NR}}$  can be generally expressed as [35]

$$k_{\text{NR}}(T) = k_1 + k_2(T) = k_1 + k_2 \exp\left(-\frac{E_a}{k_B T}\right), \quad (4)$$

where  $k_1$  accounts for the temperature independent process decay rate [27], and  $k_2(T)$  accounts for temperature dependent decay processes, characterized by the activation energy  $E_a$ .

The main result of this experiment is that the measured activation energies  $E_a$  are in agreement with the calculated singlet-triplet energy splitting, showing that the measured  $k_2(T)$  directly reflects the temperature activated ISC rate. In fact sample Nos. 3–6 do not show any measurable temperature dependence of the decay times, whereas

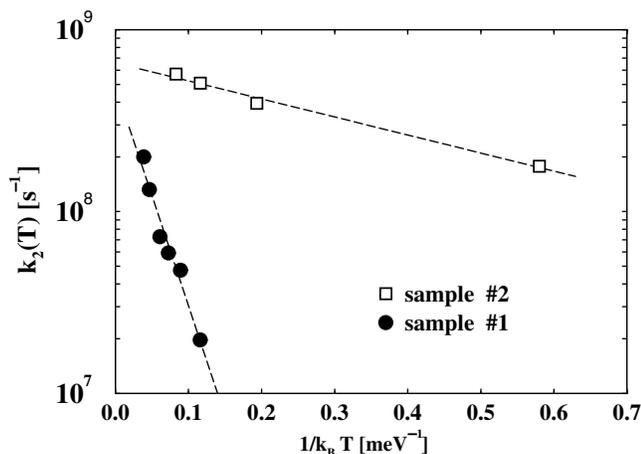


FIG. 3. Temperature dependence of PL decay rate.  $k_2(T)$  is null for sample Nos. 3–6.

sample Nos. 1 and 2, with  $\Delta E < 0$ , show the temperature dependence reported in Fig. 3.

From these data, we estimate (dashed lines in Fig. 3) activation energies of 27 and 3 meV for compound Nos. 1 and 2, respectively. We note also that the extrapolated value of  $k_2$  is  $6 \times 10^8 \text{ s}^{-1}$ . This value is comparable to the one measured in solution [35], confirming the ISC origin of the nonradiative decay. For sample No. 2 the measured  $E_a$  is very low also in agreement with the small calculated  $\Delta E$ . We should mention that though the qualitative agreement between the data is very good, exact quantitative agreement cannot be obtained due to the inherent accuracy of the INDO/SCI scheme and to the neglect of the effects of the surface potential.

In summary, for Nos. 1 and 2 the main nonradiative channel has been found to be an activated ISC process, whereas for the other compounds the nonradiative decay is a balance of nonactivated ISC and an exciton-phonon scattering process which increases with increasing the molecular distortion induced by the intermolecular interactions [16]. Thus, the luminescence of our quaterthiophene crystals is more correlated to the single molecule conformation than to crystal packing.

In conclusion, we have shown that the distortion of a quaterthiophene molecule can strongly affect the alignment of singlet and triplet states and the intensity of the spin-orbit coupling. This modifies the ISC rate and in turn the PL efficiency. The main effect of the intermolecular interactions is to determine the conformational structure of the molecules constituting the crystals. Obviously, the general validity of our results might be influenced by the possible occurrence of defects and impurity which might contribute in a substantial way to the nonradiative processes, depending on sample quality.

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