Role of intermolecular coupling and electron-nuclear coupling in the photophysics of oligothiophenes

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The role of intermolecular coupling and coherent electron-nuclear coupling in the photophysics of the conjugated compound α-quaterthiophene (α-4T) has been investigated. For this purpose, we have measured the photoluminescence (PL) spectra from α-4T as a thin film (80 nm) and a single crystal. Singlet and triplet excitons were brought into play using different excitation energies. By means of Franck-Condon (FC) analysis, we show that for the film, the PL is due to a single intrachain FC progression coupled to a single phonon mode (the C=C mode; $\hbar\omega_{C=C} = 0.18$ eV). For the single crystal the PL profile is adequately reproduced by taking into account a pair of modes (C=C and C–C modes; $\hbar\omega_{C=C} = 0.18$ eV, $\hbar\omega_{C-C} = 0.15$ eV). Moreover, the exciton band edge of the film exhibits a redshift ($\sim$100 meV) as compared to that of the single crystal. This redshift has been attributed to an enhanced conjugation length due to an enhanced chain-chain contact. In the case of the single crystal, the latter effect cannot take place, yet the involvement of the second mode leads to an effective conjugation length. The direct targeting of the first triplet level of the single crystal induces an interchain intermolecular coupling, which in turn induces a coherent electron-nuclear coupling. This latter appears in the delayed fluorescence spectrum as shifted bands ($\sim$100 meV) with respect to the bands observed in the prompt fluorescence.

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I. INTRODUCTION

Oligothiophenes have been the subject of much interest. Their well-defined conjugation length and chemical structure provide a better understanding of the excited-state photophysics.[1,2] So far, temperature-dependent and time-dependent measurements have been the main tools in investigating the optical properties of oligothiophenes and polythiophenes. Sassella *et al.* proposed two temperature- and time-dependent emissive states in α-quaterthiophene (α-4T), one with a slow decay time and one with a fast decay time due to a modification of the molecular electronic levels upon aggregation. The typical times of the processes involved in the emission have been estimated to be below the instrumental resolution.[3] Later on, Kobayshi *et al.* proposed that two intrachain states contribute to the emission spectra of a polythiophene derivative, a fast one with allowed transition to the ground state, and a slow one allowed due to vibronic coupling despite being forbidden according to selection rules. In this case, the improved instrumental resolution allowed measuring the exciton lifetime, which went down to several tens of femtoseconds.[4]

On the other hand, the presence of the sulfur atoms in oligothiophenes gives rise to an enhancement of the intersystem crossing rate, which leads in turn to a triplet population enhancement.[5,6] The triplet transfer occurs via a multiphonon hopping process, down to a transition temperature below which an adiabatic tunneling process prevails.[7–9] Thus, when changing the temperature we intentionally change the triplet exciton transfer type. Therefore, we can, neither rule out nor confirm the role of triplets in the apparent temperature-dependent features of the photoluminescence (PL) spectra. We have recently shown that when the first triplet excited state of an α-quaterthiophene single crystal is

targeted, the fluorescence spectrum exhibits the same features as a fluorescence spectrum recorded at low temperature and obtained through the excitation of the first excited singlet state.[10] Thus, the study of different PL spectra, obtained by exciting singlet or triplet excitons, using different excitation energies at room temperature, would clarify the origin of the mentioned features.

In organic semiconductors, molecular vibrations are expected to play an important role in exciton migration.[11] A Franck-Condon (FC) analysis is thus crucial to understanding the exciton-phonon coupling since this latter occurs as a result of the FC principle, for which the Born-Oppenheimer approximation holds. However, the absorption and emission spectra of polythiophenes and oligothiophenes exhibit *apparent* non-Condon emission, which led to more complicated models.[4,12,13] Moreover Repp *et al.* have recently unmasked a coherent electron-nuclear coupling in an oligothiophene, indicating a complete breakdown of the Born-Oppenheimer approximation.[14]

In the present work, we particularly focus on the optical properties of α-4T as a prototype for systems of linear oligothiophenes with a limited number of double bonds. In such systems, the promotion of an electron from the ground state to the first excited state has a large effect on the local bond order; thus we expect to see a large exciton-phonon coupling. In addition, calculations[2] and experimental verifications[10] show the presence of an electronic level spacing of the order of the vibrational energies in these systems, which makes them fulfill the prerequisite for the coherent electron-nuclear coupling mentioned above.[14]

We suggest here a simple approach that permits incorporation of the latter effect into a FC progression, and we show that it permits adequate modeling, without the need to invoke more

complicated models,[4,12,13] of the fluorescence profile from an α-4T single crystal, obtained at room temperature by exciting triplet excitons, and exhibiting temperature-dependent-like features. PL measurements, for different excitation energies, on highly ordered thin-film and single-crystal α-4T, are also compared by means of a FC analysis, revealing the role of morphology in the intermolecular coupling and in determining the nature of the primary neutral excitation.

II. EXPERIMENTS

A single crystal of α-4T in its low-temperature polymorphic structure was grown and purified as described elsewhere.[15] Thin films of α-4T were evaporated at 6×10^{-7} Torr pressure at a rate of 6 Å/min on a quartz substrate. Such a relatively low evaporation rate results in crystallites with the long axis perpendicular to the substrate.[16] PL measurements from single crystal and film of α-4T were performed using the different wavelengths of an Ar$^+$ laser as exciting source with a power of 20 (40) mW for the single crystal (film). The excitation light was then focused onto a 0.2 (0.5) mm spot on the sample for an exposure time of 1 s. The spectral response was collected and relayed to a Ramanor Jobin-Yvon spectrometer (3 cm^{-1} spectral resolution) equipped with a photomultiplier. The signal was then diffused and processed on a computer after being treated with synchronous detection. The recorded PL intensities were multiplied by the used scales and are measured in units of millivolts; thus they are directly comparable. We have also used a Kr$^+$ laser (647 nm, 20 mW) to populate the first triplet level of the α-4T single-crystal sample, but the measured spectrum is in arbitrary units in this case. We have also performed a UV excitation of both thin-film and single-crystal samples of α-4T using a nitrogen pulsed laser (337 nm) with a duration pulse of 1 ns, The response was guided through an optical fiber toward a CCD camera connected to a computer, where the PL spectrum is directly exhibited in arbitrary units.

III. RESULTS AND DISCUSSION

PL spectra from an evaporated α-4T film, for different excitation energies, are shown in Fig. 1. They exhibit well-resolved bands, near 2.07, 2.25, and 2.43 eV, with an almost constant spacing between each neighbor peak of about 0.18 eV.

Figure 2 shows PL spectra from an α-4T single crystal. They exhibit also three bands with an almost constant spacing between each neighbor peak.

A. FC analysis of the PL spectra

In the case of an undistorted lattice, the normal-mode vibrational wave functions $\chi(\nu_i)$ form an orthonormal set. As a result, transitions between different vibrational states are prohibited:

$$\langle \chi(\nu_i) | \chi(\nu'_j) \rangle = \delta_{ij} \delta_{\nu\nu'}. \quad (1)$$

This strict orthogonality is removed through an exciton-phonon coupling, which leads to a change in the equilibrium positions of the lattice ions in the excited state relative to that
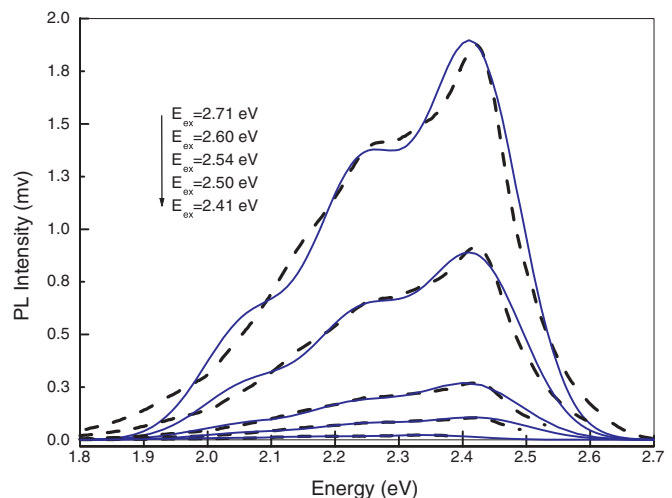

FIG. 1. (Color online) PL spectra of an α-4T thin film recorded at room temperature and obtained using different excitation energies. The solid curves through experimental data are FC fits. The PL intensity is in units of millivolts.

of the ground state. Hence, it is appropriate to model this structural relaxation by a set of orthonormal coordinates Q_i. Within the harmonic approximation, the shift of the excited-state vibronic potential surface with respect to that of the ground state is commonly characterized by the dimensionless Huang-Rhys factor, which corresponds to the average number of phonons involved in the emission process:[17,18]

$$S_i = \frac{1}{2} \frac{M_i \omega_i^2}{\hbar \omega_i} (\Delta Q_i)^2, \quad (2)$$

where $\hbar \omega_i$ is the vibronic level spacing, ΔQ_i is the normal coordinate displacement, and M_i is the reduced ionic mass for the mode Q_i.[17,18] In the film PL spectra, the intensities of the peaks (Fig. 1) decrease on going from the highest-energy band down to the lower-energy bands. This suggests that the PL spectra can be modeled by a single intrachain FC progression coupled to a single phonon mode. We have
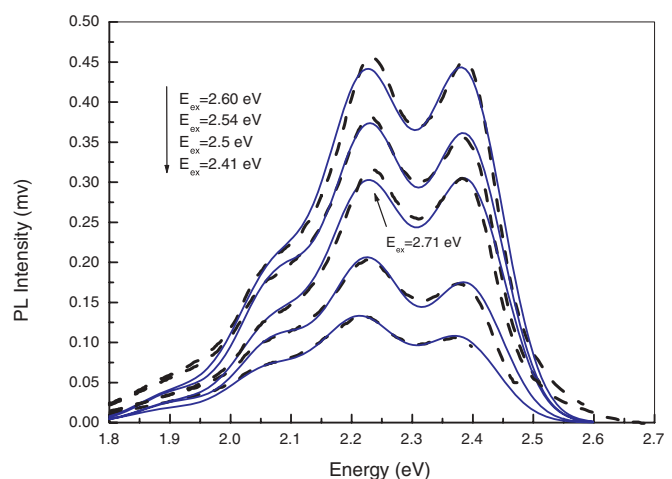

FIG. 2. (Color online) PL spectra of an α-4T single crystal recorded at room temperature and obtained using different excitation energies. The solid curves through experimental data are FC fits. The PL intensity is in units of millivolts.

considered a single progression originating from the coupling with the C=C stretching mode; thus we assume that the FC factors can be written as[17,18]

$$|\langle \chi(\nu_i)|\chi(0)\rangle|^2 = \frac{e^{-S_i} S_i^{\nu_i}}{\nu_i!}, \tag{3}$$

where S_i is the number of phonons in the excited-state vibronic potential. These factors account for the 0-ν_i vibrational transition, and according to Eq. (3) they map a Poisson probability distribution with the Huang-Rhys parameter as mean and variance. Accordingly, the PL spectra can be modeled as a FC progression:[17,19]

$$I(\hbar\omega) \propto (\hbar\omega)^3 e^{-S_i} \sum_{\nu_i} \frac{S_i^{\nu_i}}{\nu_i!} \Gamma(\hbar\omega - E_0 + \nu_i \hbar\omega_i) \tag{4}$$

with E_0 the 0-0 transition energy and Γ the line shape function which we assume (for simplicity) to be Gaussian with constant width. Fits to Eq. (4) are shown along with the experimental data in Fig. 1. Furthermore, the total relaxation energy associated with the geometrical rearrangement after an excitation or deexcitation process is related to the Huang-Rhys factors:[11,19]

$$E_{\rm rel} = \sum_i S_i \hbar\omega_i. \tag{5}$$

From this analysis we have also obtained the 0-0 transition energy (E_0) and the mean phonon energy ($\hbar\omega_i$). The derived parameters for the film are summarized in Table I.

The derived mean Huang-Rhys factor is in good agreement with the work of Kanemoto *et al.*[19] Indeed, the proposed empirical rule giving the Huang-Rhys factor as a function of the thiophene's monomer number yields a Huang-Rhys factor as large as 1.8 for 4T. PL spectra from the α-4T single crystal (Fig. 2) show that the band intensity does not fall according to a simple FC progression. This suggest the presence of two, or more, vibronic oscillators or the contribution of more than one emissive state.[3,4,12,13] The stretching vibrational mode of the simple C–C bond bridging the thiophene units has been detected in α-4T single crystal.[20] The PL spectra can be modeled then, taking the latter mode into account according to the following expression:[17–19]

$$I(\hbar\omega) \propto (\hbar\omega)^3 \sum_{\{\nu_i\}} \left(\prod_i e^{-S_i} \frac{S_i^{\nu_i}}{\nu_i!} \right) \Gamma(\hbar\omega - E_0 + \nu_i \hbar\omega_i). \tag{6}$$

TABLE I. The parameters determined from nonlinear least-squares fit of PL profiles to Eq. (4) (5% uncertainty); the Huang-Rhys factor (S), the PL 0-0 transition energy (E_0), the mean phonon energy of the C=C mode ($\hbar\omega_1$), and the relaxation energy ($E_{\rm rel}$).

$\hbar\omega_{ex}$ (eV)	S	$E_{\rm rel}$ (meV)	E_0 (eV)	$\hbar\omega_1$ (eV)
2.41	1.79	311.51	2.517	0.177
2.50	1.77	318.60	2.599	0.180
2.54	1.79	291.60	2.587	0.180
2.60	1.70	300.90	2.589	0.177
2.71	1.70	300.90	2.588	0.177

TABLE II. The parameters determined from nonlinear least-squares fit of PL profiles to Eq. (6) (5% uncertainty); the Huang-Rhys factors (S_1 and S_2), the PL 0-0 transition energy (E_0), the mean phonon energies of the two involved modes ($\hbar\omega_1$ and $\hbar\omega_2$) for the C=C and the C–C modes, respectively, and the relaxation energy ($E_{\rm rel}$).

$\hbar\omega_{ex}$ (eV)	S_1	S_2	$E_{\rm rel}$ (meV)	E_0 (eV)	$\hbar\omega_1$ (eV)	$\hbar\omega_2$ (eV)
2.41	1.63	1.51	519.9	2.704	0.18	0.15
2.50	1.50	1.50	420.0	2.716	0.18	0.15
2.54	1.24	1.26	412.2	2.716	0.18	0.15
2.60	1.20	1.30	411.0	2.713	0.18	0.15
2.71	1.11	1.50	424.8	2.716	0.18	0.15

All the symbols are defined as before. Fits of experimental data with Eq. (5) are shown in Fig. 2. The derived parameters for the single crystal are summarized in Table II.

B. Role of intermolecular coupling

The findings reveal that the onset of the emission profile is redshifted (100 meV) in the film as compared to the single crystal. The molecule in the crystal is always in anticonformation.[21] Thus the mentioned redshift could be attributed to the more rigid planar molecular structure in the film, which could be accompanied by a longer effective conjugation length due to a decrease of the rotational energy barrier of the simple C–C bond bridging the thiophene units. Consistently, the relaxation energy in the film is lower than that in the single crystal, which reveals that the diffusion rate of excitations is also higher in the film. The redshifted transition energies in conjugated systems are believed to arise from specific morphological features, like chain-chain contacts.[22–24] Thus, the redshift of the exciton band edge in the film with respect to that of the single crystal could be attributed to an enhancement of the intrachain intermolecular interaction in the film due to the formation of rodlike chains of coupled molecules. Indeed, it has been shown that it is possible, in some cases, to observe an anomalous stacking, where the periodicity along the [001] direction can reach 54 nm,[25] instead of the correct unit-cell periodicity ($\sim$3.048 nm) required by the symmetric extinction rules of the single-crystal space group.[26] On the other hand, we have chosen a range of excitation energies for which the sample exhibits decreasing absorption coefficients with decrease of the excitation energy. Thus, with this latter decrease, by virtue of the Beer-Lambert rule, the excitation wave penetrates deeply in the crystal before being absorbed. When the excitation energy decrease and the PL spectra become dominated by emission from the closest molecules to the substrate, the PL profile redshifts as shown in Fig. 3; this suggests that the enhancement of the intrachain intermolecular coupling discussed above is due to a strong coupling to the substrate.

C. Role of electon-phonon coupling

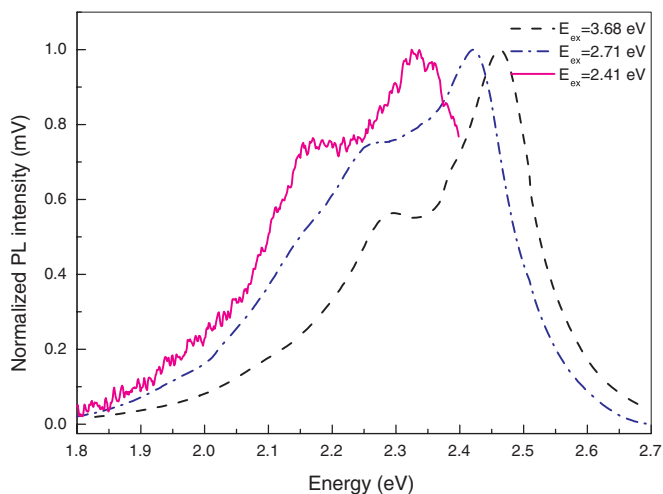The involvement of the stretching vibrational mode of the inter-ring bond between the thiophene units in the FC

FIG. 3. (Color online) Normalized PL spectra of an α-4T thin film, recorded at room temperature, and obtained using different excitation energies.

FIG. 4. (Color online) Normalized PL spectra of an α-4T single crystal, recorded at room temperature, and obtained using different excitation energies.

analysis of the PL spectra from an α-4T single crystal can be interpreted within the effective conjugation coordinate theory. In the framework of this theory, developed by Zerbi *et al.*, the oscillation of the alternating C=C and C–C bonds of the π-conjugated backbone is defined by a specific vibrational coordinate in order to account for the effective electron-phonon coupling in the π-conjugated materials.[20,27] The coordinate mentioned above describes a state in which all the C=C bonds extend, while all the C-C bonds contract. This gives rise to an effective conjugation length, which counters the poor π-orbital overlap along the [001] direction of the single crystal, along which the intrachain intermolecular contact ($\sim$3.2–3.9 Å) is the shortest and prevails in the whole crystal.[26] Thus, we consider that the coordinate mentioned above mimics the major geometrical changes occurring in the π-conjugated skeleton during the π-π* transition. Hence, along this coordinate the electron-phonon interaction, is expected to be the largest. This is supported by the relatively high Huang-Rhys factors inferred from Frank-Condon analysis of the PL spectra of the single crystal compared to those obtained for the film. In the case of aromatic and heteroaromatic systems, such as quaterthiophene, this coordinate describes the evolution of the π-conjugated backbone from the aromatic structure of the ground electronic state to the quinoid structure which characterizes the first excited electronic state.[27] Moreover, the PL intensity decreases with decrease of the excitation energy for the film as well as for the single crystal. This decrease is accompanied, in both cases, by an increase in the relaxation energy, which suggests that the major part of the excitation energy is consumed in vibration through electron-phonon coupling. The only exception for this trend in the PL spectra is the single-crystal PL spectrum obtained under resonant excitation (2.71 eV). The FC analysis of this spectrum reveals that the shift (ΔQ_i)(C=C) of the potential energy curves along the C=C coordinate due to resonant excitation is the smallest. In contrast, the displacement from the ground-state equilibrium upon the coupling to the C–C phonon mode is relatively strong, consistent with the decrease of the PL intensity. This suggests that the decrease of the PL intensity arises essentially from
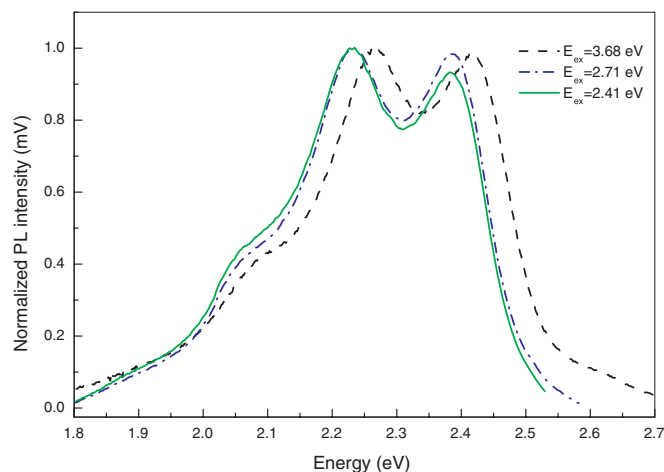
the coupling of the electronic transition to the C-C phonon mode.

Furthermore, the PL spectra from the film are more intense than those from the single crystal, in spite of the more important absorption in the crystal and consistent with the higher relaxation energy in the latter; which points out that the electron-phonon coupling effect prevails over the absorption effect in the PL quantum yield. Unlike the PL profile of the film, that of the α-4T single crystal does not exhibit a redshift (Fig. 4), which is consistent with the fact that in the single-crystal phase, a fixed intermolecular distance prevails in the whole crystal as discussed above. It is worth mentioning here that the spectra obtained upon UV excitation in both cases display a blueshift, due to emission from the less strongly bound molecules of the surface. Further explanations on this issue are available elsewhere.[10]

IV. DELAYED FLUORESCENCE SPECTRUM OF α-4T SINGLE CRYSTAL

We turn now to the emission spectrum of α-4T single crystal obtained by a selective targeting of the first triplet excited state. This spectrum has been attributed to delayed fluorescence due to triplet-triplet bimolecular annihilation; see Fig. 5.

Clear evidence has been found supporting the interchain nature of the triplet migration in π-conjugated molecules.[28] In addition, it has been shown that in organic one-dimensional semiconductors, like quaterthiophene, the molecules involved in the annihilation process, could be the two inequivelent molecules per unit cell.[29,30] The spectrum of delayed fluorescence (DF) is due to triplet-triplet annihilation;[29–32] this latter affects the interaction of the two molecules giving rise to the two electronic Davydov components.[17,29,30] Among the nine spin states of the triplet pair, a singlet character is equally distributed between three states; this singlet character is oscillating and is the main source of the interaction of the pair of excited molecules in the triplet state, leading to the DF. Hence, the interaction of the two molecules giving rise to the two Davydov components will be affected by the
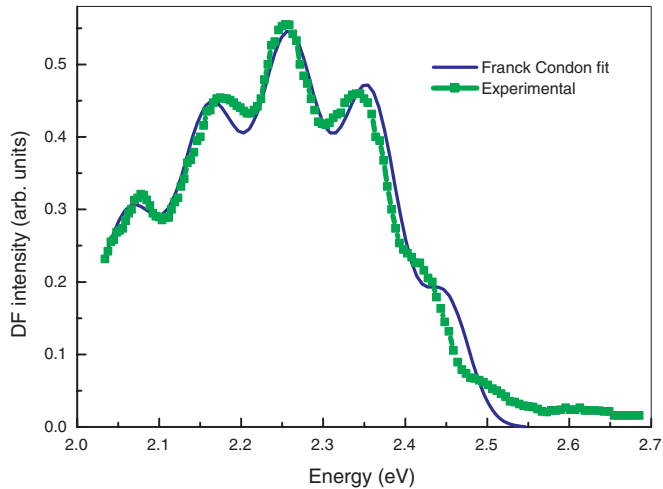
FIG. 5. (Color online) Delayed fluorescence spectrum from an α-4T single crystal, obtained at room temperature by a selective targeting of triplet levels ($\hbar\omega_{ex} = 1.91$ eV). The solid curve through the experimental data is a FC fit.

TABLE III. The parameters determined from nonlinear least-squares fit of DF profiles to Eq. (6) (5% uncertainty): the PL 0-0 transition energy (E_0), the relaxation energy (E_{rel}), and the Huang-Rhys factors (S_1 and S_1) of the two involved modes, the C=C mode and the effective mode which couples the two inequivalent molecules in the unit cell.

$\hbar\omega_{ex}$ (eV)	S_1	S_2	E_{rel} (meV)	E_0 (eV)	$\hbar\omega_1$ (eV)	$\hbar\omega_2$ (eV)
1.91	0.51	2.92	394	2.713	0.18	0.1

and an effective mode with an energy ($\sim$0.1 eV), which is the spacing energy between the two Davydov components. This implicitly suggests that the upper Davydov component exhibits vibronic-level-like features in these conditions. The delayed fluorescence profile has been adequately modeled using the expression of Eq. (6). Table III summarizes the parameters derived from a nonlinear least-squares fit to Eq. (6).

oscillatory singlet character. This could result in a molecular vibration with the same energy as the spacing between the two electronic Davydov components. And thus we may assume that they can become coupled by a molecular vibration when the first vibronic level of the lower Davydov component matches the electronic upper Davydov component. Moreover, we have shown through FC analysis that there is strong exciton-phonon coupling in α-4T single crystal. Thus the prerequisite for coherent electron-nuclear coupling is fulfilled;[14] this coupling describes a situation in which electrons and phonons do not evolve independently after a vibronic excitation. The emergence of such coupling indicates a complete breakdown of the Born-Oppenheimer approximation. Our simple approach to incorporate the latter effect into a FC progression is to consider a single intrachain FC progression coupled to two modes: the C=C bond stretching mode ($\sim$0.18 eV)

V. CONCLUSION

In summary we have shown that our findings permit attribution of the PL spectra to intrachain singlet excitons in both the film and single crystal. Compared to the single crystal, the film exhibits enhanced intrachain intermolecular coupling due to an enhanced chain-chain contact. This reveals a higher conjugation length in the film, which results in lower relaxation energy and higher diffusion rate of excitations as well. In the single crystal, where the electron-phonon coupling is relatively strong, the selective targeting of the first triplet level gives rise to triplet-triplet annihilation. This latter involves an oscillating interchain intermolecular coupling and fulfills the prerequisite for a coherent electron-nuclear coupling, which is monitored in the DF spectrum as bands shifted by $\sim$0.1 eV with respect to the bands observed in the prompt fluorescence spectrum. Apart from being of fundamental interest, these findings reveal that the thin film has a better potential for optoelectronic application than the single-crystal phase.

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