PHYSICAL REVIEW B VOLUME 62, NUMBER 16 15 OCTOBER 2000-II

Optical properties of highly oriented quaterthiophene thin films grown by organic molecular-beam deposition

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(Received 30 December 1999; revised manuscript received 6 April 2000)

The molecular-beam deposition of quaterthiophene (4T) oligomer on potassium acid phtalate (001) single crystals yields thin films exhibiting a peculiar supramolecular organization induced by the interaction with the substrate. The 4T thin films, which exhibit an extremely large optical anisotropy arising from the alignment of the 4T molecular axis along the *b* crystallographic axis of the substrate, allow one to carry out polarized transmission measurements over the whole π-π^* absorption band. The observation of a strong polarized band, together with very weak unpolarized absorption peaks originating from isolated molecules, is consistent with the formation of a tilted H aggregate in which the molecular transition moments form a 38° angle with the substrate surface. The low luminescence quantum yield further supports the formation of this very ordered structure. Exciton migration and decay paths in the 4T films have been established by studying, with time-resolved photoluminescence spectroscopy, the emission originating from traps and imperfect aggregates.

I. INTRODUCTION

The well-defined conjugation length and chemical structure of oligothiophenes have allowed, in recent years, a better understanding of the parameters controlling a number of physical properties of interest for applications, such as charge transport, linear and nonlinear optical response, decay dynamics, etc. X-ray structural characterization of these oligomers has shown that the supramolecular organization attained in the solid state is a key parameter for controlling these properties.[1]

In molecular crystals van der Waals forces usually affect only weakly the ground-state properties of the constituent molecules, which retain their chemical individuality. However, certain conjugated molecules (notably carotenoids and oligothiophenes) exhibit the remarkable property that a strong perturbation of the excited-state levels occurs upon aggregation, because of the interaction between transition charge densities on neighboring molecules. This effect has been observed in carotenoids[2] which, in bad-solvent solutions, form high-molecular-weight aggregates, whose absorption spectrum exhibits significant bandwidth narrowing and blueshift of about 200 meV. A blueshift of the absorption spectrum upon aggregation has also been observed in oligothiophenes of various lengths, when the molecules are unsubstituted or end capped, since in these cases the distance between the conjugated backbones, on which the transition dipole resides, is small and exciton delocalization can take place.[3–6]

One way of carefully controlling the solid state structure of oligothiophenes is through organic molecular-beam deposition (OMBD) in ultrahigh vacuum.[7,8] With this technique, molecular thin films are fabricated through repeated stacking of monomolecular layers onto a properly selected substrate. The resulting supramolecular organization of the grown film, which is determined by the orientation of the first overgrown layer with respect to the substrate, originates from the balance between the molecule-molecule and molecule-substrate interactions. A proper choice of the substrate properties (chemical composition, surface structure, defects, temperature, etc.), as well as of the evaporation rate yields samples possessing a controlled and reproducible solid state organization.[7,9,10] For example, deposition of oligothiophenes on highly oriented pyrolitic graphite yields films with the molecular planes parallel to the substrate, while the use of fused silica as substrate yields films in which the molecular axis is almost orthogonal to the surface.[1]

In this paper, the optical and photophysical properties of unsubstituted quaterthiophene (4T) films grown on a single crystal of potassium acid phthalate (KAP) are discussed. This particular substrate has been selected because it is expected that the presence of phthalate conjugated rings surfacing at the cleavage plane can induce, through the π-π^* interaction, a specific orientation of the oligothiophene molecules with respect to the substrate. Moreover, it is ob-

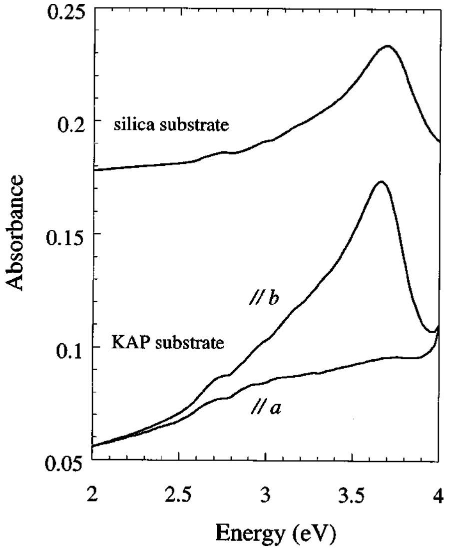

FIG. 1. Absorbance spectrum of a 10-nm-thick 4T film deposited on silica (upper curve, shifted upward by 0.1 absorbance units for clarity), taken with unpolarized light; absorbance spectra of a 10-nm-thick 4T film deposited on (001) single crystal of KAP (lower curves), taken with linearly polarized light along the directions of the *a* and *b* axes of the KAP crystal lattice.

tained by cleavage along the (001) or *ab* lattice plane,[11] which ensures good surface quality, with the additional advantage that it is a single crystal and is transparent up to 4 eV.

II. EXPERIMENT

4T oligomers have been synthesized according to a standard chemical procedure described elsewhere.[12] The compound was repeatedly purified by vacuum sublimation.

Thin films of 4T were grown by OMBD at 1×10^{-9} Torr pressure at a rate of 6 Å/min. After a slow heating ramp up to the deposition temperature of about 175 °C, the 4T source was kept within less than 1 °C around the evaporation temperature during the whole deposition process, while the effusion orifice of the cell was maintained 8 °C above that temperature to avoid condensation of the 4T molecule. Both fused silica and freshly cleaved (001) oriented KAP single crystals were used as substrates to demonstrate how they influence the structural and optical properties of the films. Both substrates are transparent slabs with optically polished surfaces, giving rise to negligible light scattering; deposition of ultrathin layers of 4T produces a pale yellow color when the films are thicker than 15 nm. The film thickness was monitored by a quartz oscillator mounted close to the substrate and several films from 10 to 30 nm thick were grown.

Absorption measurements at normal and oblique incidence were performed in the spectral range from 1.5 to 6.5 eV with resolution better than 10 meV using a Perkin-Elmer Lambda 900 spectrometer. Measurements were also performed with linearly polarized light using Glan-Taylor calcite polarizers. Low-temperature absorption measurements were performed down to 70 K using a continuous-flow static cryostat (Oxford Optistat).

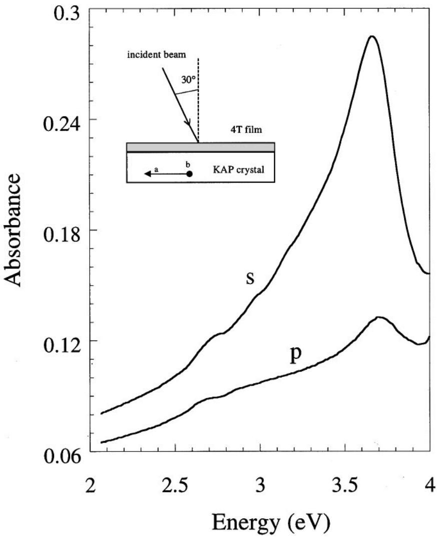

FIG. 2. Absorbance spectra of a 20-nm-thick 4T film deposited on a (001) single crystal of KAP, taken at 30° incidence with *s* and *p* polarized light. Inset: sketch of the experimental configuration, where the plane of incidence is perpendicular to the *b* direction.

Photoluminescence (PL) and PL excitation profiles were measured with a SPEX 270M monochromator equipped with a liquid-nitrogen-cooled charge-coupled device detector by exciting with an Ar^+ laser and a monochromated Xe lamp, respectively. Polarized PL measurements were performed in the backscattering configuration by exciting with the 363 nm line of an Ar^+ laser, using a polarizing prism and a sheet polarizer to change the incident and emitted light polarization.

Time-resolved PL measurements were realized by using a synchronously pumped Coherent 700 dye laser at 700 nm with 5 ps pulse duration and 76 MHz repetition rate. Second-harmonic generation in a barium borate (BBO) crystal produces the excitation beam at 350 nm with an averaged power of the order of 0.1 mW, which was focused onto 0.2 mm spot on the sample. The photoluminescence was dispersed by a SPEX 1680 double monochromator (1 nm spectral resolution was used) and detected by a Hamamatsu M 1955 streak camera apparatus with a time resolution of 30 ps and a time window of 1.5 ns. The sample was placed in a bath cryostat in order to vary and control the temperature down to 80 K. All the PL spectra were corrected for the optical response of the different equipments.

III. RESULTS

Typical absorption spectra of 4T films deposited on the two different substrates are shown in Fig. 1. The upper spectrum refers to a film deposited on amorphous silica and is taken with unpolarized light, while the lower two spectra refer to a film deposited on KAP and are taken with light linearly polarized along the *b* and *a* lattice axes of the substrate. To be able to deduce the orientation of the 4T molecular axis in the film, oblique-incidence measurements were also performed; in this way, possible absorption of light polarized perpendicularly to the substrate surface can be detected. Figure 2 reports two spectra, taken in *s* and *p* polarization with light impinging on the sample surface with 30° angle of incidence with the plane of incidence perpendicular

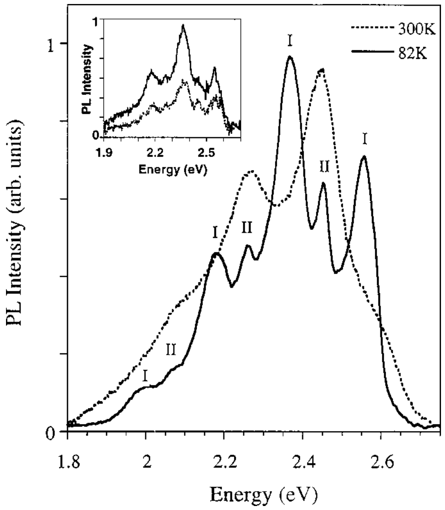

FIG. 3. Normalized cw PL spectra taken at two temperatures on a 20-nm-thick 4T film deposited on (001) single-crystal KAP. Inset: cw PL spectra taken at 82 K by exciting at 3.4 eV with the laser beam linearly polarized along the *b* axis of the KAP substrate and collecting the emission polarized parallel and perpendicular to the *b* axis (full and dotted lines, respectively).

to the *b* axis direction, as sketched in the inset. The spectra of the same samples taken at 70 K (not shown) with unpolarized and polarized light at normal incidence and with polarized light at oblique incidence do not show any differences from the corresponding spectra taken at room temperature and reported in Figs. 1 and 2.

In Fig. 3 the cw photoluminescence spectrum of a 4T film deposited on KAP is reported at two different temperatures for 3.42 eV excitation. The room-temperature spectrum shows three broad bands at 2.45, 2.27, and about 2.07 eV, with a shoulder at higher energy. At low temperature, four new bands peaked at 2.56, 2.37, 2.18, and 2.00 eV dominate the spectrum, and the bands observed at room temperature sharply narrow, displaying a behavior very similar to that observed in sexithiophene thin films.[13,14] Both the high-temperature and the additional low-temperature bands display a well-defined energy separation of 0.18 eV, suggesting that they are associated with two vibronic progressions with origin at 2.56 and 2.45 eV (states I and II, respectively). On decreasing the excitation energy down to 2.75 eV, no change in the spectral shape and position of the PL spectrum was observed.

Polarized cw PL measurements show an anisotropy of about 2 in the emission after exciting with polarization parallel to the *b* axis of the KAP substrate (see the inset in Fig. 3). A smaller anisotropy of about 1.2 is measured on exciting with the light polarized parallel to the *a* axis of KAP. The spectral shape is insensitive to the exciting and emission polarization directions.

In Fig. 4 the PL excitation profile of the 2.37 eV emission peak of a 30-nm-thick 4T film deposited on KAP measured at 13 K is reported together with the $1-T$ spectrum taken with unpolarized light, where the sharp absorption edge of KAP is visible above 4 eV; the excitation profiles of all other PL peaks show the same spectral shape. As for the sample reflectance, it is constant and less than 4% over the whole visible spectrum, originating mainly from the KAP substrate as expected, since the 4T film is very thin.

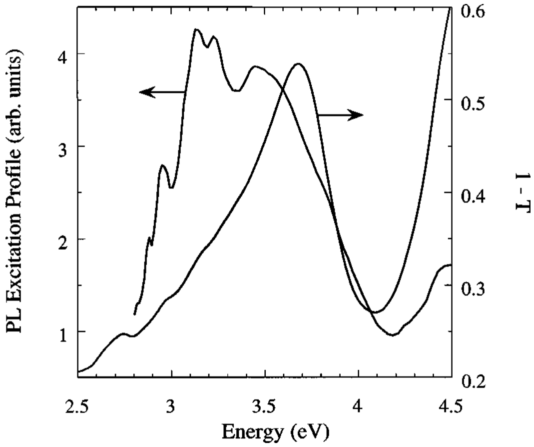

FIG. 4. Low-temperature (13 K) PL excitation profile of the 2.37 eV emission measured in the 2.8–5 eV range and $1-T$ spectrum measured with unpolarized light of a 30-nm-thick 4T film deposited on (001) single-crystal KAP.

The decay time of the PL has been measured in steps of 5 nm; typical PL decays at $T=85\,\mathrm{K}$ are reported in Fig. 5(a) for two different emission energies close to those of states I and II (2.34 and 2.43 eV, respectively). In fact, the PL emission of the phonon replica of both state I and state II shows a very similar time evolution with respect to the correspond-

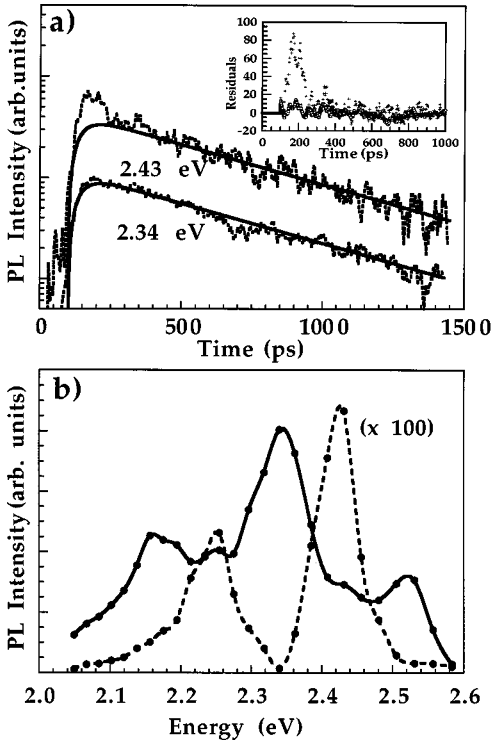

FIG. 5. (a) Time decay (dashed lines) of the 2.43 and 2.34 eV emission peaks of a 20-nm-thick 4T film deposited on (001) single-crystal KAP measured at 85 K; solid lines represent the exponential fit. The inset shows the residuals on a linear scale as dots and crosses for states I and II, respectively. (b) Spectral shape of the slow (solid line) and fast (dashed line) components of the PL spectrum. Dots are the experimental data, lines are drawn as a guide for the eye.

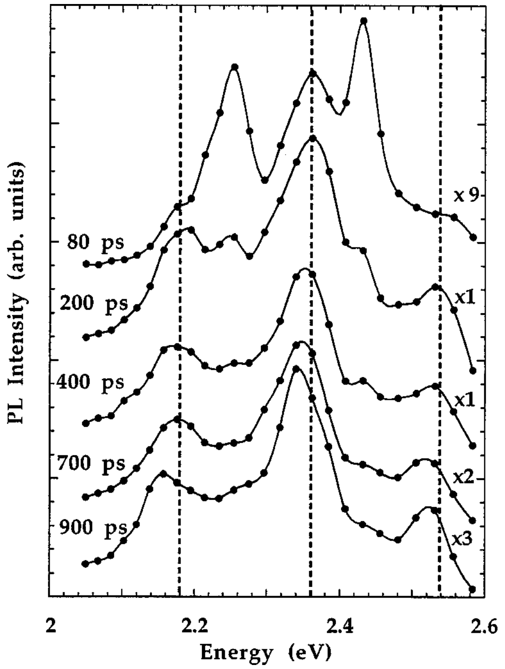

FIG. 6. Time evolution of the PL spectrum of a 4T film deposited on (001) single-crystal KAP, measured at 85 K in the first nanosecond after excitation. Dots are the experimental data, lines are drawn as a guide for the eye.

ing dominant line. The main contribution is a decay time of the order of 500 ps, which is present over the whole emission band [the exponential fits are reported as solid lines in Fig. 5(a)], while the rise time is below the instrumental resolution. The residuals from the fits (i.e., the difference between the signal and the fits, divided by the square root of the signal[15]) are reported in the inset of Fig. 5(a) as dots and crosses for states I and II, respectively. It turns out that a single exponential fit nicely agrees with the PL emission of state I, while a second fast contribution is clearly observed in the PL emission at 2.43 eV; in addition, such a fast component is also detected at energies shifted by a vibrational quantum. In order to evaluate the relative weights of the slow and fast contributions, we have first performed, for each emission wavelength, an exponential fit of the long exponential tails and extracted the integrated intensity of the slow component. Then the fits have been subtracted from the experimental data and the residuals integrated over a time interval of 100 ps around the PL maximum. The integrated intensity of the slow and fast components, reported in Fig. 5(b), clearly shows the different spectral compositions of the two contributions. The slow decay time is associated with the 2.56 eV emission from state I while the fast decay time is related to that at 2.45 eV from state II; as expected, the phonon replicas of these emissions show the same time evolution.

Similar information can be extracted directly from the analysis of time-resolved spectra, obtained by integrating the decay curve over a 60 ps time windows for each detected wavelength. The spectra at different delay times with respect to excitation are reported in Fig. 6, together with the relative scale factors. The 2.43 eV component and its replica at 2.25 eV are present only in the early-time emission and disappear for delay time longer than 200 ps. In fact, the long-time emission is dominated by the PL of the 2.53 eV component and its two phonon replicas. Note that the two emission components are overlapped due to their inhomogeneous broadening; however, the time-resolved measurements allow a clear discrimination due to the very different decay kinetics, which also point out the different physical natures of the two emitting states. Finally Fig. 6 shows the presence of a redshift of the high-energy progression for increasing delay after excitation; the dynamical Stokes shift is of the order of 30 meV after 1 ns delay.

IV. DISCUSSION

A. Supramolecular structure

Absorption measurements taken at normal incidence on the sample deposited on silica with light linearly polarized along different directions did not show any difference from the spectrum in Fig. 2, indicating that the film is isotropic on the substrate surface, while oblique-incidence measurements showed a slight increase in the peak intensity. Considering that the transition dipole moment of oligothiophenes is along the main molecular axis,[5] these findings suggest some preferential orientation of the 4T molecular axis perpendicular to the substrate surface, as also reported in the literature for other oligothiophene films deposited on silica.[1,16]

In the spectra of the sample deposited on KAP taken under normal-incidence conditions, the main peak at 3.67 eV is found only in the polarization labeled ''$\parallel b$,'' i.e., with the electric field parallel to the *b* axis of the KAP crystal lattice. This means that the transition dipole moments lie in a plane parallel to that crystal axis. Spectra taken at normal incidence with light polarized along different directions indicate that the absorption intensity decreases as a function of the polarization angle θ (measured with respect to the *b* axis direction) and scales as $\cos^2\theta$, as expected.

The angle formed by the molecular transition moments with the *ab* plane of KAP (substrate surface) can be inferred from the spectra taken at oblique incidence with polarized light after rotating the sample around the *b* axis (spectra taken at 30° incidence are reported in Fig. 2); in the oblique-incidence configuration the absorbance values scale very well with the optical path length in the film. The intensity ratio $r = I_p/I_s$ between the intensity of the peaks observed in the *s* and *p* polarizations at oblique incidence, corrected for the polarization-dependent contribution of reflectance, yields the tilt angle α between the 4T molecular axis and the substrate surface from

$$r = \sin^2\beta \tan^2\alpha, \tag{1}$$

where β is the incidence angle. The value of the tilt angle is estimated as $\alpha = 37°$ for the 30° incidence configuration and $\alpha = 39°$ for the 45° incidence configuration, this complete consistency indicating that the parameter α can be used with confidence in elaboration of the structural model for the 4T film deposited on KAP. In addition, it should be mentioned that the optical absorption spectra are independent of temperature down to 70 K, indicating that the order and orientation of the 4T film are already complete and stable at room temperature.

On the basis of the above analysis of optical absorption and by considering results of x-ray diffraction, measured in

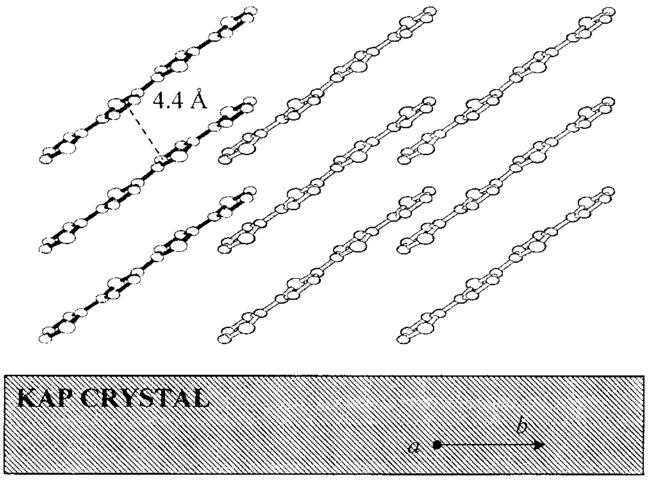

FIG. 7. Sketch of the structure of the 4T film deposited on (001) single-crystal KAP (*ab* lattice plane), where the molecules form tilted H aggregates along the growth direction; the three stacks are lying at different positions along the *a* axis of KAP, as illustrated by their different gray color.

the Bragg-Brentano geometry and with synchrotron radiation, a structural model was drawn,[17] which is in agreement with all experimental data and exhibits some similarity with the 4T phases observed on [111] Ag.[18] It consists of a triclinic crystal with lattice parameters $a = 7.21\,\text{Å}$, $b = 6.32\,\text{Å}$, $c = 9.56\,\text{Å}$, $\alpha = 90.5°$, $\beta = 91.0°$, and $\gamma = 90.5°$, with one molecule per unit cell, and with $1.26\ \text{g}\,\text{cm}^{-3}$ density. As for the molecular arrangement on the substrate, this structure results in a card-pack arrangement of the 4T molecules, which form an H aggregate along the growth direction with the molecules tilted by 38° as shown in Fig. 7 (where the three stacks lie on different planes along the *a* axis direction, displaced with respect to each other by more than 6 Å). The tilted H aggregate mentioned consists of one stack, where each 4T molecule faces the nearest-neighboring molecules with a distance between the mean molecular planes of 4.47 Å.

B. Energy levels and photoexcitation

The main peak detected in all the absorbance spectra of thin films is located at 3.67 eV (see Fig. 1). This corresponds to a large blueshift (about 1 eV) with respect to the spectrum of quasiplanar 4T molecules electronically decoupled through inclusion in a proper matrix (2.79 eV, as measured at 80 K on 4T included in perhydrotriphenylene[19]), or 4T molecules in frozen solution.[6,20]

A blueshift of the absorption of a thin film is predicted to occur by the Fresnel formulas when the dipoles are perpendicular to the film thickness with respect to the behavior of a film with the same dipole species aligned parallel to the film.[3,21,22] Thus, it has been argued[3] that the blueshift of the absorption maximum observed in thin films of oligothiophene evaporated on quartz substrates with respect to the absorption of films deposited on other substrates might be related to the molecular arrangement in which the molecular axis (and therefore the molecular dipoles) is perpendicular to the substrate surface. Since in the present case the 4T molecules deposited on KAP are inclined by more than 50° with respect to the direction normal to the substrate, this optical effect would produce a shift much lower than on silica, where oligothiophenes are known to stand almost perpendicular to the substrate,[1,16] while the experimental spectra show only a small difference. In addition, it is interesting to observe that the spectra reported in Fig. 2 show a slight blueshift of the main peak from 3.67 to 3.70 eV between the *s* and *p* polarized spectra, where the latter is the one corresponding to the component of the transition dipole moments perpendicular to the substrate. Only this small shift as a function of polarization can be related to the mentioned optical effect, the large blueshift detected with respect to the spectrum of isolated molecules (about 1 eV) being much more likely related to excited-state molecular interactions. Indeed, following the molecular exciton model,[23,24] the close packing of the H aggregates formed by the 4T molecules in films deposited by OMBD can lead to exciton formation, with a subsequent energy increase of the transition of the first allowed collective excited state.

On this basis we distinguish two different contributions in the optical absorption which differ in their polarization properties.

(a) The polarized main peak at 3.67 eV is assigned to a collective exciton $(k=0)$ state delocalized over the crystal. Its blueshift Δ, with respect to the position of the 0-0 transition of the isolated molecule, depends on the interaction between the transition densities ρ_A and ρ_B on neighboring molecules at *A* and *B*,

$$\Delta = \int \int \rho_A(\mathbf{r}_1)\rho_B(\mathbf{r}_2)(|\mathbf{r}_2 - \mathbf{r}_1|)^{-1} d\mathbf{r}_1 d\mathbf{r}_2, \tag{2}$$

and increases with reduction of the intermolecular distance. As a matter of fact Cornil and co-workers have performed a correlated quantum chemical calculation on close-packed supramolecular structures of thiophene-based oligomers showing a strong absorption peak at 3.61 eV as a result of the excited-state interactions between translationally equivalent transition dipoles.[25,26]

A strong blueshift of the absorption spectrum has been observed even in aggregates in solution[2] and the shift has been accounted for by strong excited-state interactions between neighboring molecules within the aggregate.[6] The lack of vibronic replicas also confirms this interpretation. As a matter of fact solid state theory[6,27] and physical intuition suggest that, when the excitation is delocalized over a region comparable in size with the wavelength of the light (i.e., an exciton state), interaction with intramolecular vibrations—peculiar to the isolated molecular states—is weak and no vibronic progression is observed. Of course, interaction with collective phonon states (such as low-frequency acoustic phonons) is likely and this accounts for some of the observed broadening of the 3.67 eV peak. Other sources of broadening include the activation of $k \neq 0$ exciton states due to selection rule relaxation. This band is also completely polarized along the orientation axis, indicating that it originates from a regular assembly of transition dipoles.

(b) The unpolarized structured low-energy bands (below 3.2 eV) originate from traps (isolated molecules, misaligned molecules at the grain boundaries) and/or imperfect aggregates and therefore, because the excitation is localized and

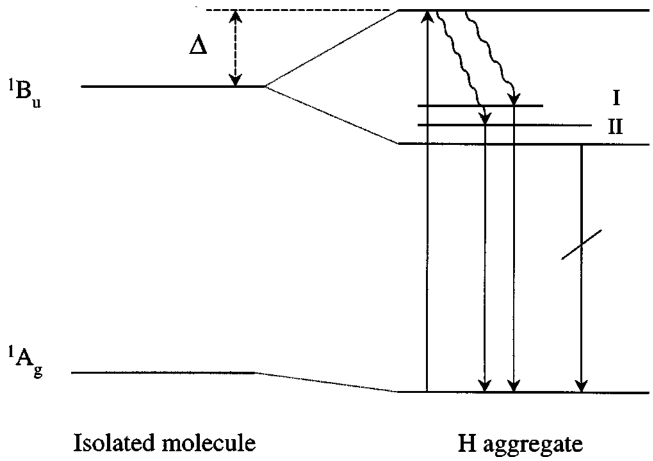

FIG. 8. Scheme of the molecular electronic states of the isolated 4T molecule and of the H aggregate, with excitation and decay transitions.

interacts with the local intra-ring vibrations, shows the standard vibronic progression. Indeed, many authors have demonstrated that the low-energy region is more prominent in samples obtained with less controlled evaporation techniques on nonorienting substrates. This is clearly shown in a recent paper on the optical and structural properties of oligothiophene crystalline films.[28]

It is interesting to notice that the emission excitation profile does not reproduce the absorption spectrum (Fig. 4). In particular, the PL excitation profile exhibits the most intense peaks in correspondence with the low-energy, weak, and unpolarized bands of the absorption spectrum, therefore suggesting them as responsible for radiative decay. Within the molecular exciton the energy absorbed by the collective $k = 0$ exciton states at 3.67 eV is quickly transferred to lower-lying band states and traps, on which radiative recombination appears to be more efficient. Figure 4 shows that, if these trap states are directly excited, quenching originating from the excitation migration is strongly reduced. The attribution of the low-energy peaks to isolated molecules is in agreement with the spectral position of the absorption and PL excitation profiles of 4T molecules in solid solutions[6,20] or inserted in channel-forming host compounds,[19] where the isolated molecule states are directly identified and their vibronic components well resolved.

The results reported above, compared to data on isolated molecules processing a conformation close to that of the film, can be used to propose the energy level scheme depicted in Fig. 8. As discussed above, the position of the isolated molecule levels is inferred from the absorption of 4T in solid solutions or in inclusion compounds,[6,19,20] where the molecules posses a quasiplanar conformation, very similar to that assumed in the film because of the π-π interaction.

Both cw and time-resolved photoluminescence data indicate the presence of two emitting states, one at 2.56 eV (I) and the other at 2.45 eV (II), accompanied by their low-energy vibronic progressions [see Figs. 3 and 5(b)]. A similar behavior of PL, where the contemporary presence of emission from two different states is observed, has been reported also for sexithiophene, 4T, and end-capped 4T thin films.[14,29–31] In particular, in the last case a large Stokes shift has been related to structural defects playing a significant role in the emission process; in addition, the intensity of one of the PL peaks with its vibronic replica changes strongly as a function of film thickness and experimental configuration, suggesting that it comes from radiative traps at the substrate/film interface. This is not the case for the 4T films on KAP, which show a large Stokes shift, but with fully reproducible, sample-independent PL spectra. Finally, the peak attributed to state I corresponds very well in both spectral position and line shape to the PL spectrum of 4T included in a matrix.[19] The energy position of the I PL component is higher than that obtained on polycrystalline films grown on glass,[30,32] but lower than that reported for films grown on pyrolytic graphite or single crystals.[31,32]

The two emitting states strongly differ in their decay kinetics and temperature dependence, but are coupled to the same vibration at 0.18 eV (1450 cm^{-1}), which corresponds to the intraring C═C stretching also observed in resonant Raman spectra. Such phonon coupling indicates that the states are not due to chemical defects or impurities, but rather they should be viewed as arising from molecules possessing a different organization and short-range order with respect to the bulk film. This is consistent with the PL excitation spectra, where the bands of isolated molecules are observed as the most intense ones (see Fig. 4). Similarly, phonon coupling has been observed also for 4T single crystals and films,[31,33,34] in good agreement with the behavior of matrix-isolated molecules, while it has been ruled out for single-crystal sexithiophene, due to the different temperature dependence observed for the different PL peaks.[35] The observations that excitations with energy below 2.7 eV do not produce any emission and that the shape of the emission spectrum is insensitive to excitation changes within the absorption band suggest that the two emitting states are not directly populated by photon absorption, but rather they trap the excitation during the process of spectral (and spatial) relaxation toward the nonradiative bottom of the exciton band. Excitation migration also accounts for the large Stokes shift and the reduced anisotropy of the emission with respect to that of absorption (see Figs. 1 and 3).

The higher-energy state (I), which has an energy very close to that of the isolated molecule, could be related to weakly interacting molecules, which do not permit the propagation of the excitation to neighboring sites. The fact that state I is localized is further supported by the slow, exponential decay of its radiative population and by the stronger exciton-phonon interaction, inferred by the observation of three vibronic replicas. The spectral redshift of 30 meV undergone by the slow component between 80 ps and 1 ns could be explained by assuming that state I consists of a ladder of closely spaced levels, among which the localized excitation undergoes spectral migration toward the lowest-energy level.

On the other hand, the state II at lower energy appears to be a collective state (possibly a somewhat disordered aggregate), on which the excitation is rapidly quenched by migration toward nonradiative sites, as detected from the faster decay. The temperature dependence of the emission indicates that at higher temperatures it predominantly arises from state II, probably populated by a thermally activated mechanism.

Both cw and time-resolved emissions from 4T thin films originating from different types of trap states and/or preaggregates have been reported by other authors who have studied polycrystalline films grown on highly oriented pyrolytic graphite and glass.[30,32] In the present case the supramolecular organization of the sample obtained by growing 4T on a highly orienting KAP substrate (shown in Fig. 1) is quite different, and relevant differences are also observed in both the absorption line shapes and emission positions. These considerations further support the crucial role of the structure (packing arrangement and structural defects) of 4T films in determining both their cw optical properties and the dynamics of their photoexcitations. Indeed, for molecules such as 4T, which can crystallize in different polymorphic structures,[36] any structural defect can easily act as an efficient trap for PL emission, since exciton mobility is extremely high within defect-free regions with a molecular close-packed arrangement.

V. CONCLUSIONS

Highly anisotropic thin films of oligothiophenes can be grown by vacuum deposition onto a single crystal of KAP and are found to possess a macroscopic orientation coming from a supramolecular architecture consisting of tilted H aggregates. Within such aggregates the strong intermolecular interactions resulting from the short interplanar distances (4.47 Å) lead to the formation of molecular excitons, whose migration and decay are investigated by analyzing the cw and time-resolved photoemission. Two emitting states with different decay rates and temperature dependence have been clearly identified. On this basis, a scheme of the modification of the molecular electronic levels upon aggregation in this unusual supramolecular arrangement is drawn.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Italian Consiglio Nazionale delle Ricerche and PFMSTAII (Demo) for financial support; work at LENS was supported by the EC through the TMR program, Contract No. ERBFMGECT950017.

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