Intrinsic Excitonic Luminescence in Odd and Even Numbered Oligothiophenes

F. Meinardi,[1,*] M. Cerminara,[1] A. Sassella,[1] A. Borghesi,[1] P. Spearman,[2] G. Bongiovanni,[3] A. Mura,[3] and R. Tubino[1]
[1]*INFM and Department of Material Science, University of Milano-Bicocca, via Cozzi 53, I-20125 Milano, Italy*
[2]*School of Chemical and Pharmaceutical Sciences, Penrhyn Road, Kingston upon Thames, Surrey KT1 2EE, United Kingdom*
[3]*INFM and Department of Physics, University of Cagliari, I-09042 Monserrato, Cagliari, Italy*
(Received 25 February 2002; published 24 September 2002)

The emission properties of crystalline oligothiophenes (OTs) are investigated and related to the different selection rules arising from the number of rings. In odd OT crystals the purely electronic emission is absent since the molecular A_1-$1B_1$ transition dipoles cancel at the bottom of the excitonic band. On the contrary, in crystals of even OTs this transition is allowed due to the constructive interference of the off-axis components of the molecular transition dipole. It possesses a polarization in the herringbone plane and exhibits superradiant behavior.

DOI: 10.1103/PhysRevLett.89.157403 PACS numbers: 78.55.Kz, 63.20.Kr, 77.84.Jd

Despite their good emission properties in solution, oligothiophenes (OT) are usually considered weakly emissive in the solid state because of their supramolecular organization. In vacuum grown thin films and free-standing single crystals aggregation leads to crystallites with a herringbone fashion [1]. These structures, in which the long molecular axes are parallel, are usually indicated as H aggregates. In perfect H aggregates the molecular transition dipole moments cancel at the exciton band edge from which, according to Kasha's rule, emission takes place [2]. The photoluminescence (PL) spectra of solid state OTs, in particular, of quater- and sexithiophene (4T and 6T, respectively), has been reported and discussed by various authors [3–8] in view of the fundamental and applied interest of this important class of polyconjugated materials, which have been successfully employed in devices ranging from high mobility thin film transistors [9] to light emitting diodes [10] and electrically pumped laser [11]. However, despite the large amount of optical data and of interpretative models, the nature of the intrinsic emission in OTs is still debated. Furthermore, the analysis of the emission spectra is often complicated by the presence of chemical impurities and/or by the presence of defect states [5,12]. While these chemical and structural imperfections do not affect the absorption spectrum, they are often strongly emissive, lying just below the bottom of the exciton band and receiving excited state population funneled by hopping and resonant transfer processes such as Förster energy transfer.

In this Letter we examine the emission properties of high quality crystalline samples of unsubstituted OTs in order to clarify the origin of the intrinsic emission. The data are well interpreted in the framework of the theory recently developed by Spano [13,14] for pinwheel aggregates, which are precursors of the herringbone lattice. In this model there is a strong correlation with the orientational order within the aggregate dictated by the off-molecular axis transition dipole moment. Hence, emission from solid state OTs is expected to differ for odd and even numbered rings. Indeed we observe that: (i) in odd numbered OTs the emission corresponding to the purely electronic transition (0-0 line) is absent while vibronic replicas involving a finite number of phonons with proper symmetry are allowed. (ii) In even numbered OTs the 0-0 line is allowed, is polarized in the herringbone plane, and can become superradiant in the sense that its intensity increases with the number of molecules emitting in phase.

These results suggest a new way to enhance the PL quantum yield of OT-based devices that does not involve an alteration of the molecular packing via molecular engineering [15], but rather the realization of superradiant aggregates.

Ultrathin films of 4T were grown by organic molecular beam deposition on potassium acid phtalate (KAP), and highly oriented pyrolitic graphite (HOPG) as described in [16]. Free-standing quinqe- (5T) and sexithiopene (6T) crystals were prepared as reported elsewhere [17,18]. Steady-state PL spectra were obtained by exciting the samples within the respective exciton bands with a monochromated Xe lamp and collecting the signal with a CCD camera coupled with a polychromator. The spectral resolution was better than 0.3 nm. Time resolved PL measurements were performed using the second harmonic of a Ti:sapphire laser. Temporal dispersion of the PL signal was achieved with a Hamamatsu C5680 streak camera with overall time resolution better than 4 ps. In order to maintain well-polarized exciting and signal beams, and to prevent the system collecting unpolarized luminescence from sample borders and crystal imperfections, polarized PL spectra were recorded (i) by exciting the sample with a laser spot of about 50 μm diameter, (ii) by reducing the numerical aperture of the optics down to $f/22$, and (iii) by inserting a spatial filter in the collection path. A He continuous flow cryostat was used to cool the samples down to 5 K.

All OT crystals studied possess the low temperature polymorphic structure with four molecules per unit cell. The molecules in the cell are planar with C_{2h} and C_{2v}

symmetry depending on the number of conjugated rings (even or odd, respectively), and are arranged in a herringbone fashion in two molecular layers. The space group is $P2_1/a$ for short OTs (4T and 5T) and $P2_1/n$ for intermediate ones (6T). Henceforth, we indicate as bc the plane of the herringbone, and as ac the plane containing the long molecular axis.

The crystal field splits each nondegenerate molecular level into as many components as there are molecules in the unit cell. For OTs this implies that the lowest unoccupied molecular orbital gives rise to four exciton bands with symmetry, at the center of the Brillouin zone, a_u, a_g, b_u, and b_g of which only a_u and b_u are accessible by one photon spectroscopy. In particular, the a_u component arises from an antisymmetric combination of interaction integrals between molecules in the crystal. It has been calculated and experimentally verified to lie at the lowest energy and is therefore the level from which the PL is expected to originate [5].

Figure 1 shows a comparison of the emission spectrum of samples of 5T and 4T grown on HOPG collected at 5 K in the region around the pure electronic transition (about 2.61 eV for 4T and 2.41 eV for 5T [19]. The spectra are obtained using the same experimental conditions and are normalized to the intensity of the more intense peak which corresponds to the first vibronic replica due to a 0.182 eV phonon as discussed below. The difference between the two spectra is quite striking. In 4T a strong emission is detectable at 2.608 eV, which is resonant with the lowest absorption peak within 1–2 meV [19]. Moreover a complex vibrational structure involving five different intramolecular phonons and their combination is also observed. The position of these peaks, indicated as $\nu_1 - \nu_5$, matches well the energy of all vibrational modes found in matrix-isolated 4T [20], indicating their intramolecular character. The origin of the vibronic progression at 2.608 eV is usually ascribed to the free exciton recombination [4,6]. However, because in a perfect H-type aggregate the bottom of the exciton band would be nonemissive, some authors state that, in 6T, the corresponding peak comes from shallow traps with the same symmetry properties as the free exciton [5].

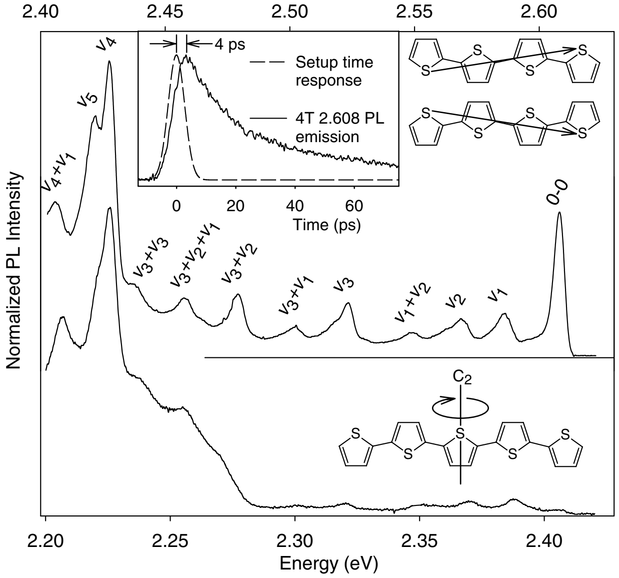

FIG. 1. Comparison between the PL spectra of a 5T crystal (lower part and lower energy scale) and a 4T film grown on HOPG (upper part and upper energy scale) collected at 5 K in the region around the pure electronic transition (2.41 and 2.61 eV, respectively). In the inset the time resolved PL measurement of the 4T 0-0 peak shows a rise time of less 4 ps for this emission.

In order to clarify the origin of this emission in even OTs, we have measured its time evolution (inset of Fig. 1). By assuming exciton diffusion within the herringbone plane the trap-related PL rise time (τ_r) is proportional to the square of the defect-free crystalline domain size (L). In broad terms $\tau_r = L^2/D$ where D is the exciton diffusion constant, which is of the order of 6×10^{-3} cm^2/s in unsubstituted OTs [21]. In our measurements τ_r is shorter than the instrumentation time resolution of 4 ps. With these values we obtain an upper limit for L of 1.5 nm which would imply an unrealistic trap density of the same order as the crystal molecular density [18] and thus ruling out attribution of this emission to defects.

In an odd numbered OT (5T) the PL spectrum is completely different: the emission resonant with the bottom of the absorption band (0-0 line at 2.407 eV) is strongly suppressed as expected for an H aggregate as are vibronic replica built on this origin with low energy phonon modes $\nu_1 - \nu_3$. Rather, the intense ν_4/ν_5 phonon replicas dominate the spectrum.

For the interpretation of the intrinsic emission spectra of OTs, we turn to the model developed by Spano for PPV oligomers [13,14]. This model is essentially based on the presence of a small misalignment, for molecules possessing proper symmetry, between the transition moment of the lowest electronic transition and the long molecular axis. In this context, OTs represent an interesting case since even and odd numbered oligomers (sketched in Fig. 1) possess different point groups, C_{2h} and C_{2v}, respectively. The main difference between these two symmetry groups is the presence of an inversion center (C_{2h}) or of a C_2 axis in the molecular plane and perpendicular to the long molecular axis (C_{2v}). This implies that for odd numbered OTs the transition moment of the lowest electronic transition ($A_1 \rightarrow B_1$) is perfectly aligned with the long molecular axis ($\mu_\parallel$), while for even oligomers the symmetry requires only that the corresponding transition ($A_g \rightarrow B_u$) lie in the molecular plane, thus allowing for a component $\mu_\perp$ of the transition dipole perpendicular to the molecular axis. Such misalignment has been confirmed by quantum mechanical calculations on OTs carried out by Kouki *et al.* [19], which predict a small but not vanishing component $\mu_\perp$ of the transition dipole in 2T

(1.7 D), 4T (0.5 D), and 6T (0.3 D). Thus, the absence of a perpendicular transition dipole moment for odd numbered OTs gives rise to purely H-type electronic interactions between the molecules and therefore the bottom of the exciton band is strictly nonemissive. On the contrary, even numbered OTs possess a transition dipole moment $\mu_\perp$ at each molecular site. In perfect herringbone crystals the presence of a long-range orientational order produces a constructive interference of this off-axis component, giving rise to arrays of head to tail transition dipoles (J aggregates) in the ab plane with an allowed low energy a_u transition polarized along the b axis (symmetry arguments imply that, in the OT herringbone structure, this transition is polarized not simply in the bc plane but entirely along the b axis [8]).

In order to more fully describe the emission spectra one must include exciton coupling to intramolecular vibrations since vibronic replica appear in both OT series. Following Spano [13,14], we write the intensity of the p_{th} vibronic replica:

$$I_p = \delta_{p0} N_c F(\mu_\perp^2/2\mu^2)\cos^2(\Phi) + (1-\delta_{p0})K_p, \qquad (1)$$

where N_c is the number of molecules composing the aggregate and emitting in phase, F is the generalized Franck-Condon factor (FC), which ranges from e^{-S} in the weak coupling regime to unity in the strong coupling regime (S the Huang-Rhys factor), and $\cos(\Phi)$ is a geometrical factor (about 0.8–0.9 for all studied OTs). K_p contains generalized FC factors for emission to the ground state with p phonons with appropriate wave vectors and the square of the total dipole moment $\mu^2 = \mu_\perp^2 + \mu_\parallel^2$ (see Ref. [14] for the exact expression of K_p and F).

The above equation shows that the purely electronic 0-0 transition is allowed only when $\mu_\perp \neq 0$ and therefore polarized along the b direction. This is the case for the even OTs. On the contrary, when $\mu_\perp = 0$ (as in 5T) only vibronic progressions with $p > 0$ appear if $S \neq 0$, and they are polarized primarily in the ac plane assuming $\mu_\perp < \mu_\parallel$. Such existence of an allowed excitonic state with perpendicular polarization in the even numbered OTs has some implication also in the low energy tail of the absorption spectrum. Indeed a sharp, b-polarized state at 2.613 eV has been observed in the absorption spectrum of a 4T single crystal, while the spectrum of 5T contains only a weak shoulder in the corresponding region [19].

To explain the different efficiency of the various vibrational modes in enhancing the PL intensity of the corresponding phonon replicas in 4T and 5T spectra, it is necessary to recognize the nature of these vibrations. The vibrations $\nu_1 - \nu_3$ are similar ring deformations, the ν_4 is assigned as a ring breathing and the ν_5 is a symmetric ring stretch primarily involving the C=C double bonds [22,23]. All these internal modes give rise to dispersionless phonons in a molecular crystal, but only the latter two are capable of modulating the effective OTs conjugation length and consequently modify the p electronic charge distribution along the long molecular axis. For this reason $\nu 1 - \nu 3$ modes are barely efficient to produce vibronic progressions arising from the parallel component of the molecular transition dipole moment, but they are observed (Fig. 1) as standard Franck-Condon progressions of the 0-0 transition when $\mu_\perp \neq 0$. On the contrary, the ν_4 and ν_5 modes affect the charge distribution in the direction of $\mu_\parallel$ and generate vibronic replicas in both T4 and T5 when adjacent molecules vibrate in and out of phase, respectively.

Measuring the polarization properties of an even numbered OT can further assess the validity of the model proposed. Low temperature measurements on a 6T single crystal [8] have indeed shown that the 0-0 emission is polarized along the b axis, while the polarization of the vibronic replicas is somewhat unclear. Figure 2 depicts the polarized emission in the 0-0 region from a 6T single crystal for light propagating along the a axis and polarization parallel to the b and c axes. The measurements were performed at room temperature because the sample stress due to the cooling process strongly increases the scattered light. The spectra show that, while the 0-0 purely electronic transition is completely polarized parallel to the b axis, its main vibronic replicas are predominantly polarized along the c axis, as indeed predicted by the model.

Another interesting implication of this model is that the intensity of the 0-0 emission (when present) scales with N_c, the number of molecules emitting in phase, leading to a form of superradiance. Strictly speaking this occurs when I_0 exceeds the single molecule emission intensity, i.e., when $N_c > 2\mu_\parallel^2/\mu_\perp^2$. Even though $\mu_\perp \ll \mu_\parallel$, the 0-0 emission can become observable and, in principle, even dominant for a sufficiently large number of perpendicular transition dipoles constructively interfering. N_c is of course not exactly the number of

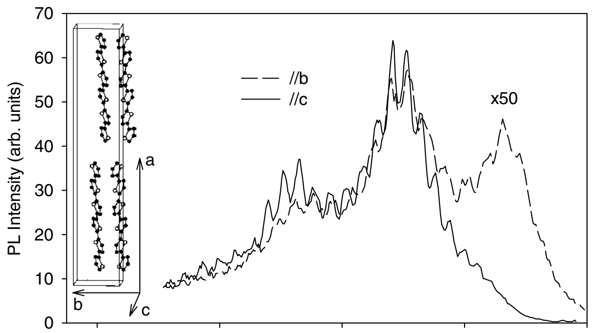

FIG. 2. Polarized PL spectra of 6T crystal excited in the excitonic absorption band at 300 K. Fringes arise from the interference between sample surfaces. In the inset the crystal cell with the crystallographic axes is sketched.

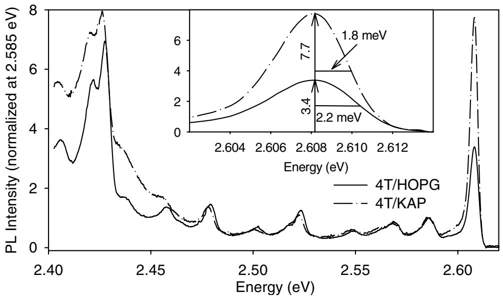

FIG. 3. Comparison between the PL spectra of 4T films grown on different substrates (KAP and HOPG) collected at 5 K. In the inset the enlarged plot of the 0-0 region is reported. The true HWHM of the 0-0 transitions, calculated by deconvolving the high energy peak wings with the setup spectral response (measured HWHM = 0.97 meV at 2.6 eV) are, respectively, 1.58 and 2.04 meV for the 4T on KAP and on HOPG.

molecules in the crystal, but is limited by thermal fluctuations and defects that break the coherence among the molecules. By contrast, the remaining vibronic progression intensities cannot exceed that for a single molecule; they depend only on the Huang-Rhys factor and the strength of the exciton coupling.

Superradiance is disrupted by both phonon and impurity scattering. Indeed in J aggregates, in which the molecules are arranged in a head to tail fashion the intensity of the 0-0 emission increases by decreasing the temperature because the reduction of the thermal disorder increases the coherence domain size. However in all even OTs we studied, both the purely electronic transition and its replicas strongly increase at low T, simply indicating the quenching of nonradiative decay channels.

We have found evidence for superradiant behavior, namely, of the relative intensity enhancement of the 0-0 emission scaling with the number N_c of molecules which coherently emit, in comparison to the intensity of the vibronic replicas, by comparing the emission from ultrathin films of 4T grown on different substrates, HOPG and KAP (see Fig. 3). These films have the same crystallographic structure but a completely different morphology, with grain size larger on KAP that on graphite as shown by the AFM analysis [4,24,25] which leads to a different degree of order in the crystalline domains constituting the two films. At very low temperature (usually below 20 K in J aggregates), the exciton delocalization domain is no longer limited by phonons but by the lattice disorder and the corresponding emission peak becomes inhomogeneously broadened (i.e., depends on the crystal quality). It is well known that, in this case, the linewidth is proportional to the square root of the number of molecules over which the exciton is delocalized. Furthermore, the delocalization usually extends over a region which is much smaller than the crystalline domains [26]. Therefore the square of the ratio of the linewidth of the 0-0 emission collected from 4T grown on KAP and HOPG gives the ratio $N_{c(\mathrm{KAP})}/N_{c(\mathrm{HOPG})}$. By deconvolving the high energy wings of these emissions with the bandwidth of our experimental setup, we obtain $N_{c(\mathrm{KAP})}/N_{c(\mathrm{HOPG})} = 1.7 \pm 0.1$ (see Fig. 3 inset). Because the intensity of the 0-0 transition of even OTs scales linearly with the number of molecules emitting in phase, also the intensity ratio $I_{(\mathrm{KAP})}/I_{(\mathrm{HOPG})}$ is expected to be 1.7 ± 0.1, in close agreement with the observed experimental value 1.9 ± 0.1.

In summary we have interpreted the intrinsic emission properties of crystalline OTs in the solid state on the basis of the different point group properties to which odd and even numbered oligomers belong and applying a model developed by Spano [13,14]. Even OTs contain an off-axis transition dipole moment that gives rise to a resonant 0-0 peak in emission and absorption that exhibits superradiant behavior as the coherence length is increased.

---

*Electronic address: meinardi@mater.unimib.it

[1] L. Antolini, G. Horowitz, F. Kouki, and F. Garnier, Adv. Mater. **10**, 382 (1998).
[2] M. Pope, *Electronic Processes in Organic Crystals* (Oxford University Press, New York, 1982).
[3] W. Gebauer and C. Taliani, *Handbook of Polythiophenes* (Wiley-VCH, Weinheim, 1998), and references therein.
[4] W. Gebauer, M. Sokolowski, and E. Umbach, Chem. Phys. **227**, 33 (1998).
[5] M. Muccini *et al.*, J. Chem. Phys. **108**, 7327 (1998).
[6] M. Hopmeier *et al.*, Chem. Phys. Lett. **314**, 9 (1999).
[7] M. A. Loi *et al.*, Phys. Rev. Lett. **86**, 732 (2001).
[8] R. N. Merks *et al.*, Chem. Phys. **227**, 49 (1998).
[9] J. H. Schön, A. Dodabalapur, C. Kloch, and B. Batlogg, Science **290**, 963 (2000).
[10] G. Gigli *et al.*, Appl. Phys. Lett. **75**, 439 (1999).
[11] J. H. Schön, C. Kloch, A. Dodabalapur, and B. Batlogg, Science **289**, 599 (2000).
[12] P. Mei *et al.*, J. Appl. Phys. **88**, 5158 (2000).
[13] F. C. Spano, Chem. Phys. Lett. **331**, 7 (2000).
[14] F. C. Spano, J. Chem. Phys. **116**, 5877 (2002).
[15] G. Gigli *et al.*, Phys. Rev. Lett. **86**, 167 (2001).
[16] A. Sassella *et al.*, Synth. Met. **121**, 1421 (2001).
[17] G. Horowitz *et al.*, Phys. Rev. B **59**, 10 656 (1999).
[18] G. Horowitz *et al.*, Chem. Mater. **7**, 1337 (1995).
[19] F. Kouki *et al.*, J. Chem. Phys. **113**, 385 (2000).
[20] D. Birnbaum, D. Fichou, and B. Kohler, J. Chem. Phys. **96**, 165 (1992).
[21] G. Lanzani, R. Danieli, M. Muccini, and C. Taliani, Phys. Rev. B **48**, 15 326 (1993).
[22] E. Faulques, W. Wallnofer, and H. Kuzmany, J. Chem. Phys. **90**, 7585 (1989).
[23] G. Zerbi, B. Chierichetti, and O. Inganas, J. Chem. Phys. **94**, 4637 (1991), and references therein.
[24] A. Sassella *et al.* (to be published).
[25] S. Tavazzi *et al.*, Phys. Rev. B **65**, 205403 (2002).
[26] E. W. Knapp, Chem. Phys. **85**, 73 (1984).