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Journal of Photochemistry and Photobiology A: Chemistry 144 (2001) 3–12

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Luminescence quenching by inter-chain aggregates in substituted polythiophenes

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Received 27 March 2001; received in revised form 1 April 2001; accepted 5 April 2001

Abstract

Time-resolved photoluminescence spectra measured in solid films of two polythiophene derivatives with different chain packing allow to distinguish emission of intra-chain excitations from the luminescence of inter-chain aggregates. Aggregate luminescence is red shifted by about 0.1 eV relative to intra-chain emission and shows vibronic coupling to the C=C bond stretch with the Huang–Rhys factor of $S \approx 1.5$, which is twice bigger than that of the intra-chain emission. Combining time resolved luminescence data with femtosecond transient absorption, we show that the dynamic quenching of the luminescence in films with dense chain packing is mainly due to excitation energy transfer to aggregates. The radiative lifetime of the lowest excited state of the aggregate with the optical gap of 1.84–1.9 eV is estimated to be about 20 ns. The aggregate contribution to the total luminescence in the polythiophene films with dense chain packing is about 50% and does not change significantly with temperature. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Conjugated polymers; Luminescence; Excitation energy transfer; Physical dimers

1. Introduction

Conjugated polymers are promising materials for light-emitting diodes, organic lasers, photosensors, solar cells, etc. In most of these applications the properties of electronic excited states play a crucial role, and the photophysics of these materials has been studied extensively during the last decade. There are abundant evidences that in the isolated polymer chains with aromatic repeat units, such as benzene, thiophene, fluorine, etc. the lowest singlet excited state has high oscillator strength, resulting in efficient luminescence. It was also observed that these single-chain excitations can migrate along the polymer chain and between chains [1], thus they are often called intra-chain excitons. However, when conjugated chains are closely packed in a thin polymer film, the luminescence quantum yield decreases. The signatures of several non-emissive or less emissive states, such as polarons (photogenerated charge carriers) [2–8], inter-chain aggregates [9–13] and excimers [14,15], have been reported, but quantitative determination of each relaxation channel is complicated due to many competing processes and also due to the spectral overlap of excited states of different nature.

Here we present systematic studies of time resolved photoluminescence (PL) and transient absorption in polythiophene derivatives with different side-chain substituents, which change the inter-chain distances by about a factor of two. We show that exciton trapping at aggregate sites is dominating the photoexcitation dynamics in polythiophene films with dense chain packing. The radiative lifetimes of intra-chain excitons and inter-chain aggregates are estimated.

2. Materials and methods

Different side groups of polythiophenes cause different chain packing and distance between the conjugated backbones (Fig. 1). The two octyl side groups in poly[3-(2,5-dioctyl-phenyl)thiophene] (PDOPT) are expected to force the phenyl ring to be out of the plane of the conjugated backbone, which explains the large inter-chain distance of 10 Å determined in films of this polymer by

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PII: S1010-6030(01)00517-2

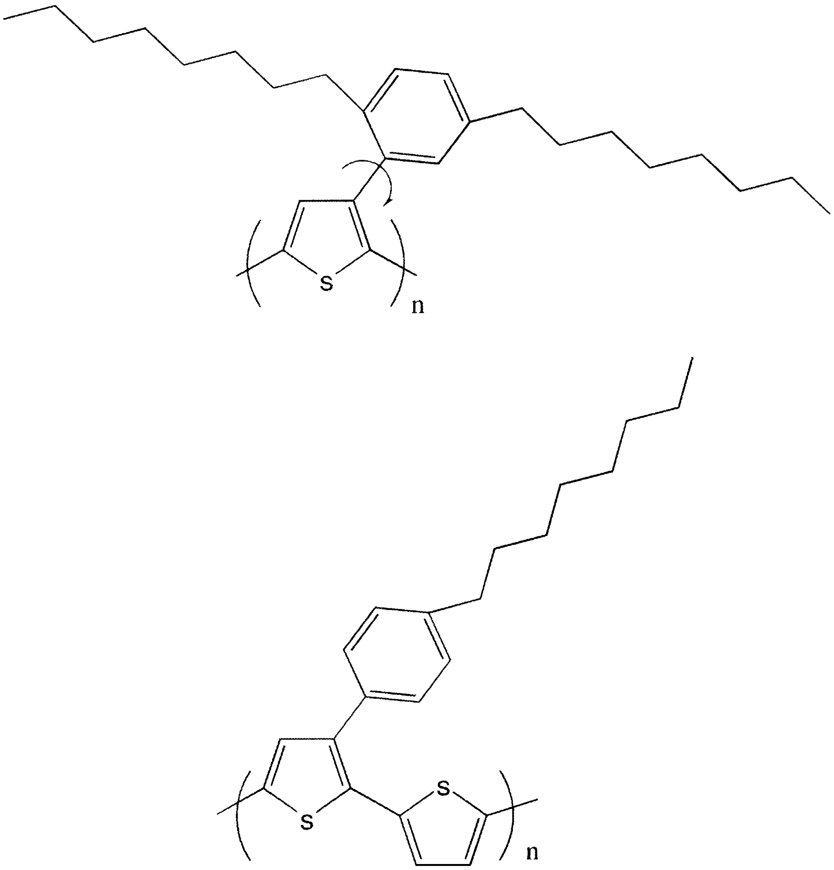

Fig. 1. Chemical structures of the polymers used in this work.

X-ray diffraction [16]. Poly[3-(4-octyl-phenyl)-2,2′-bithiophene] (PTOPT) contains small side groups, which in principle allow face-to-face packing of conjugated backbones. PTOPT films are amorphous, and the inter-chain distance at the sites of face-to-face packing we expect to be in the range from 4 to 5 Å, as it has been estimated for solid films of regioregular polythiophenes with a similar chemical structure [9,17]. Synthesis of the polymers is described in [18]. Solid films were prepared from concentrated chloroform solutions (~5 mg/ml) by spin-coating at 1000 rpm on glass or fused silica substrates in ambient atmosphere and dried in nitrogen atmosphere. A double-layer film was assembled of two spin-coated films by joining them after heating to the glass transition temperature (~160°C for PTOPT) for 1 min in ambient atmosphere and pressing against each other under the load of about 10 kg. Measurements on the single-layer films were performed at a dynamical vacuum of less than 0.1 mbar to avoid photo-oxidation. The time evolution of the PL in the double-layer films did not differ when performing experiments in vacuum or ambient atmosphere and no sample degradation was observed, which indicates prevention of the lateral diffusion of the oxygen into the polymer sandwiched between glass plates.

The time evolution of the luminescence was measured with a Hamamatsu streak camera using the second harmonic of a Ti:sapphire laser at 3.1 eV (~100 fs pulses) for excitation at a pulse repetition rate of 82 MHz. Luminescence was collected at ~180° to the incident beam and the apparatus response function was ~2 ps. Transient absorption was measured with a spectrometer based on an amplified Ti:sapphire laser system with a 5 kHz pulse repetition rate. Using light pulses of ~80 fs duration (FWHM) from an optical parametric amplifier for excitation and white light continuum for probe, the apparatus response was ~120 fs. Signal and reference beams were spectrally filtered by a monochromator placed after the sample and detected using photodiodes. The excitation light was polarized at the magic angle (54.7°) relative to the probe light. The excitation density when measuring kinetics was kept below 10^{17} cm^{-3} to avoid intensity dependence.

3. Results and discussion

3.1. Time-resolved photoluminescence

Fig. 2 shows the time-resolved PL spectra of polymer films at 77 K. The PL spectrum of PDOPT (Fig. 2a) shows a pronounced structure with 3 equally spaced peaks at 2.01, 1.84 and 1.66 eV. Gradual decay of PL but no dramatic change of its spectral shape is observed. Since the conju-

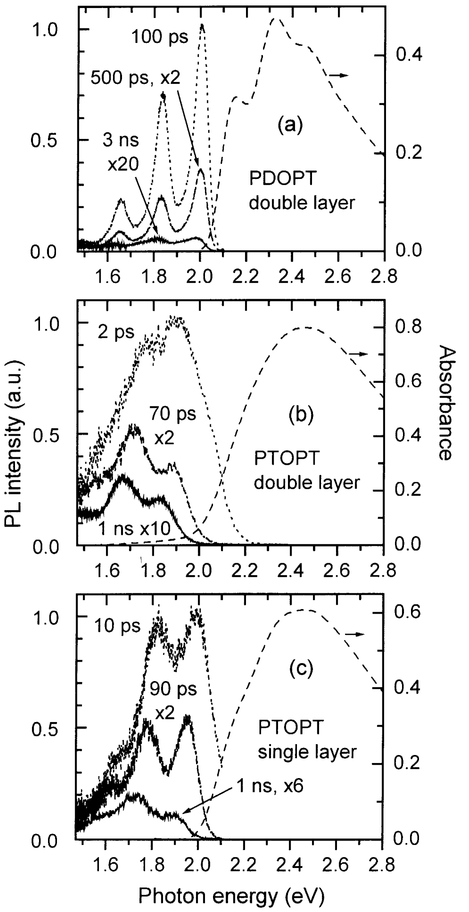

Fig. 2. PL spectra of polymer films at 77 K at various delay times after excitation at 3.2 eV. Ground state absorbance spectra at 293 K are shown by dashed lines.

gated backbones are well separated in PDOPT film by at least 10 Å, we attribute this emission to intra-chain singlet excitons, with the three equally spaced peaks corresponding to the 0–0, 0–1 and 0–2 vibronic progression. The energy position is very similar to the PL observed in films of α-oligothiophene with 11 thiophene units [19], implying that the size of the intra-chain exciton in PDOPT film is about 11 repeating thiophene units. The spacing between vibronic peaks is ∼0.17 eV (∼1400 cm^{-1}) and it corresponds to the frequency of the C=C bond stretch. The intensity of the ith vibronic transition relative to that of the 0–0 transition is defined by the expression

$$\frac{I_i}{I_0} = \frac{S^i}{i!} \tag{1}$$

where S is the Huang–Rhys factor of vibronic coupling. Using this expression, we obtain $S = 0.7$ for the coupling of the intra-chain emission to the high-frequency vibration. The ratio of vibronic peaks changes slightly with time and indicates $S \approx 1$ at time delay of 3 ns.

Meanwhile, the PL spectrum of PTOPT films (Fig. 2b and c) changes dramatically from a broad spectrum at early time (2 ps) with a spectral position and overall shape resembling that of the intra-chain luminescence, to a red-shifted PL at time delays >70 ps. The long-lived PL in a double-layer PTOPT film exhibits a pronounced structure with the peaks at 1.84, 1.67 and ∼1.5 eV. The spacing between those peaks is again 0.17 eV, i.e. the same as for the intra-chain emission. Since the spectral shape of the long-lived PL does not change further on a nanosecond time scale, it is obvious that these peaks correspond to the vibronic progression of an electronic transition. The estimated Huang–Rhys factor of this long-lived luminescence in PTOPT is $S \approx 1.5$, i.e. twice higher than that of the intra-chain excitation. The long-lived luminescence in the double-layer PTOPT film is significantly red-shifted (by 0.17 eV) relative to the intra-chain luminescence of PDOPT. A similar evolution of PL spectra is observed for the single-layer PTOPT film (Fig. 2c): at long delay time (1 ns) the red-shifted PL occurs, which shows three vibronic peaks at 1.9, 1.73 and ∼1.55 eV and their relative intensities indicate $S \approx 1.5$. Absorption spectra of both polymers (dashed lines in Fig. 2) have a red edge at about 2 eV, but in PTOPT double-layer film a weak absorption tail extending down to ∼1.8 eV is observed. The absorption spectrum of the single-layer PTOPT film is similar

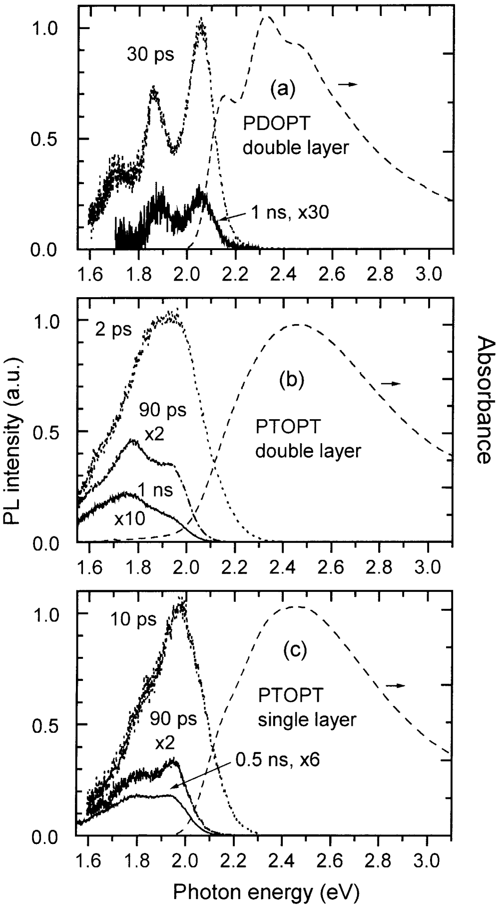

Fig. 3. Same as in Fig. 2 but all spectra recorded at 293 K.

to that of double-layer film, except that the low energy tail in single-layer extends only down to ∼1.9 eV.

At room temperature (293 K) the PL spectra of PDOPT film (Fig. 3a) are a bit blue shifted as compared to 77 K, maximum of the 0–0 band is at 2.06 eV and the vibronic bands are broader. As at low temperature, there is very little change of the PDOPT PL spectral shape. The long-time PL in double-layer PTOPT (Fig. 3b) exhibits a similar spectral shape as at 77 K, only the vibronic structure is blurred due to spectral broadening of individual bands. Since the 0–1 vibronic peak is clearly apparent at 1.76 eV, and assuming the same distance of 0.17 eV between vibronic peaks, the 0–0 and 0–2 transitions are expected to be at ∼1.93 and 1.59 eV, respectively and their intensities are consistent with $S \approx 1.5$. The temporal evolution of PL spectra in single-layer film at 293 K (Fig. 3c) is also similar to that at 77 K: the spectra at longer delay time (100–500 ps) are again red-shifted and have a similar spectral shape.

Fig. 4 shows the PL kinetics at 1.8 eV for different films and temperatures. In PDOPT film, the PL decay (Fig. 4a) is close to mono-exponential with a dominating component of ∼300 ps. The entire kinetics at both temperatures can be fitted to a three-exponential decay and fitting parameters are given in Table 1. In PTOPT films the initial decay of the PL (Fig. 4b) is much faster than in PDOPT and does not show pronounced dependence on temperature, while the decay of the longer-lived PL is significantly slower at lower temperature. We have fitted the kinetics to a three-exponential decay model and fitting parameters are given in Table 1. A closer look at the PL kinetics in PTOPT films on a short time scale (Fig. 5), shows that the initial decay is slightly slower at lower temperature and also it is slower in single-layer film.

Additional information about the nature of the long-lived red-shifted PL is obtained from the dependence of the time-integrated PL on excitation photon energy (Fig. 6).

Table 1
Time constants and relative amplitudes of the three-exponential decay fitted to the PL kinetics at 1.8 eV

Sample, temperature	τ_1 (ps) (a_1)	τ_2 (ps) (a_2)	τ_3 (ps) (a_3)
PDOPT			
293 K	30 (0.05)	300 (0.93)	500 (0.02)
77 K	30 (0.14)	300 (0.82)	600 (0.04)
PTOPT double-layer			
293 K	8 (0.60)	160 (0.30)	550 (0.10)
77 K	11 (0.54)	200 (0.36)	1100 (0.10)
PTOPT single-layer			
77 K	25 (0.60)	160 (0.34)	1000 (0.06)

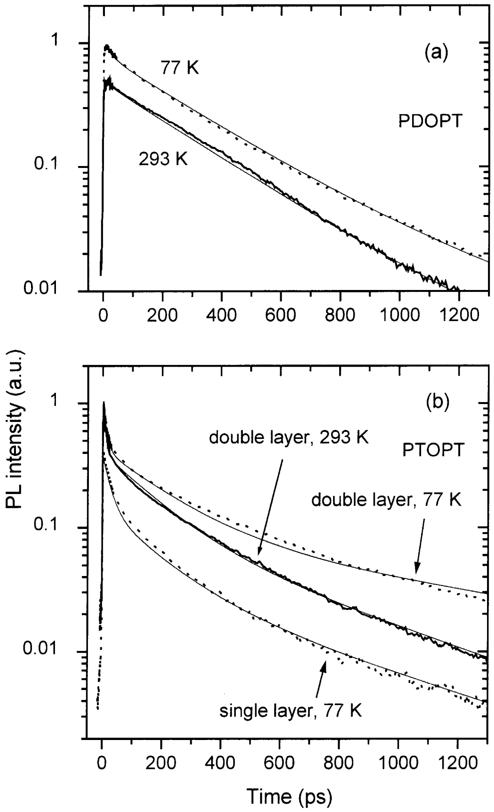

Fig. 4. PL kinetics at 1.8 eV in PDOPT (a) and PTOPT (b) films at different temperature. The PL trace in PDOPT at 293 K (a) is normalized to 0.5, the trace in the single-layer PTOPT at 77 K (b) is normalized to 0.4, all other traces are normalized to unity. Thin solid lines are fits to a three-exponential decay with the parameters presented in Table 1.

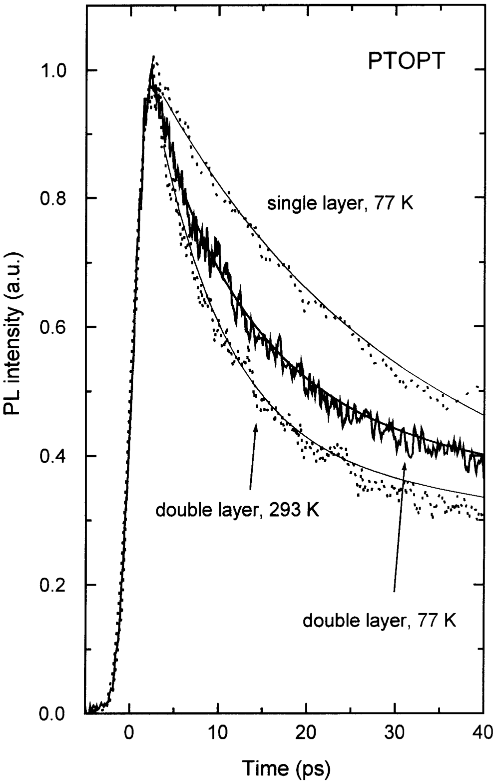

Fig. 5. PL kinetics in PTOPT films at 1.8 eV in a short time range. Thin solid lines are fits to a three-exponential decay with the parameters in Table 1.

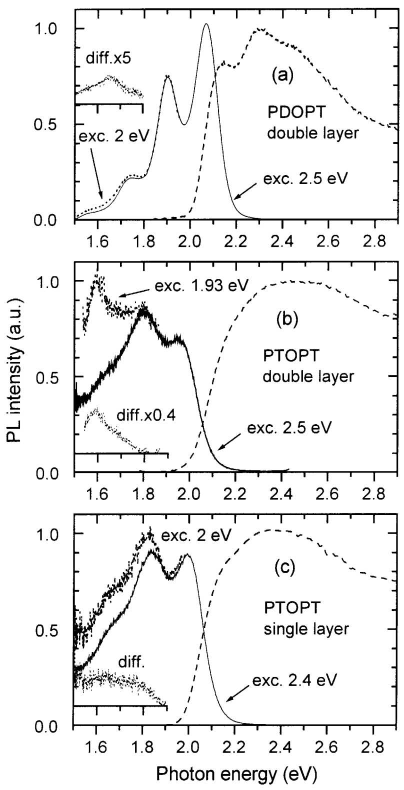

Fig. 6. Time-integrated PL spectra for polymer films recorded at different excitation photon energies and normalized at the PL maximum. In the inset of each panel the difference spectrum is shown, which is obtained by subtracting a PL spectrum at high excitation energy from the normalized PL spectrum, which was measured exciting at the red absorption tail. Dashed lines represent PL excitation spectra when detecting PL at 1.7 eV.

The PL spectrum of PDOPT film (Fig. 6a) is basically independent of the excitation photon energy, only when exciting at 2 eV or lower in energy the red shoulder in PL at 1.7 eV is somewhat more pronounced. The inset in Fig. 6a shows the difference between the two displayed PL spectra scaled by a factor of five. The PL spectra of PTOPT films are independent of the excitation photon energy in the range of 2.1–3.3 eV (represented by the solid line in Fig. 6b and c). However, when exciting at the red tail of the absorption spectrum (below 2.1 eV), the spectral shape of the emission changes so that the relative intensity of the low energy emission (lower than 1.9 eV) grows, though the total PL intensity drops by an order of magnitude as indicated by the PL excitation spectra, which are plotted as dashed lines in Fig. 6. The effect is about the same in single- and double-layer films. By subtracting a high-excitation energy PL spectrum from the normalized PL spectrum measured with excitation at the red absorption tail, we obtain a difference spectrum, which resembles the shape of the long-lived emission, only the difference spectrum is a bit red-shifted in both single- and double-layer films.

It is obvious that the red-shifted emission observed at longer times (>70 ps) in single- and double-layer PTOPT films is from some inter-chain excited states, because no such emission is observed in the PDOPT with chains further apart. Impurities can be ruled out because their emission would not differ in the single- and double-layer films and they also would be seen in PDOPT film due to efficient excitation transfer [20]. The inter-chain excitations responsible for the long-lived emission in PTOPT films could be physical dimers and higher aggregates, excimers or inter-chain charge pairs. The vibronic structure of the PL spectrum is in favor of inter-chain dimers or higher aggregates. Excimer emission would be structureless due to the dissociative nature of the ground state potential energy surface. Recombination of photogenerated inter-chain charge pairs can give vibronically-structured emission, only in the case when they form a ground state charge transfer (CT) complex. Luminescence of CT complexes usually shows little vibronic structure, because of the inhomogeneous broadening of the CT transition and coupling to low energy inter-molecular vibrations, which would obscure the vibronic structure. For these reasons, we assign the long-lived red-shifted luminescence in PTOPT to "sandwich-type" inter-chain aggregates formed in the ground state, consistent with the observation that these inter-chain species can be selectively excited at the red edge of the absorption spectrum (Fig. 6). The red-shift of the PTOPT PL difference spectra in Fig. 6b and c relative to the long-lived PL (Fig. 3b and c) can be explained presuming that the migrating excitons are trapped efficiently by aggregates with various site energies, and that only a small part of excitons reach the aggregates with the lowest-energy emission. These aggregates, however, can be selectively excited at the red tail of the absorption. The spectral position of the 0–0 peak of the aggregate emission at ∼1.84 eV (Fig. 2b) agrees well with the calculated energy gap between the lowest excited state and ground state of the physical dimer consisting of two parallel oligomers with eight thiophene units each, placed at the distance of ∼4 Å [21]. All aggregates most likely are physical dimers, because higher aggregates would require face-to-face packing of more than two adjacent chains, which is unlikely in essentially amorphous films. Aggregate emission in double-layer films is red-shifted by ∼0.05 eV with respect to that in single-layer films implying stronger inter-chain interaction in double-layer films. A faster decay of the PL observed in double-layer film as compared to single-layer film (Fig. 5) implies that the aggregate concentration is higher in double-layer film, resulting in a shorter time needed for excitation to be trapped by aggregates. This difference most likely is due to increase of the co-planarity of neighboring chains when heating the spin-coated films to the glass transition temperature, which allows a shorter inter-chain distance and parallel orientation favorable for the formation of inter-chain dimers. The absorption spectra of single- and double-layer films are very similar (Fig. 2b and c), indicating that the average conjugation length does not differ significantly in contrast to the annealed films of regioregular polythiophenes, which showed significantly red-shifted and less broadened absorption manifesting longer conjugation [22–24]. Thus, annealing seems to have small but non-negligible effect on the photophysics of PTOPT films, similar to that observed in poly(2-methoxy-5-ethylhexyloxy-phenylene-vinylene) (MEH-PPV) [13].

3.2. Transient absorption

Additional information on the excited state dynamics in these films is obtained from femtosecond transient absorption measurements. Fig. 7 shows the transient absorption spectra in double-layer PDOPT (a) and PTOPT (b) films at 293 K. The decrease of sample absorbance ($-\Delta A$) in the visible spectral range is due to photo-induced bleaching of the ground state absorption (above 2 eV) and amplification of the probe light due to stimulated emission (SE). The spectral shape of the latter closely resembles the shape of the PL spectrum. The intensities of vibronic peaks in the SE spectra are different from the corresponding peaks in PL spectra, but they are consistent with the ratio of Einstein coefficients for spontaneous and stimulated emission $A_{fi}/B_{fi} \propto (h\nu)^3$, where $h\nu$ is the photon energy. The SE peak at $\sim$2.1 eV is blue-shifted relative to the corresponding PL peak and more intense due to overlap of the SE with the ground state bleaching. The photo-induced absorption with a maximum at 1 eV (PA_1) is observed in both polymers at early time delay (200 fs). PA_1 exhibits decay identical to that of the SE and is, therefore, safely assigned to the emissive intra-chain singlet excitations, which are created by photon absorption. At a time delay of 100 ps in PTOPT (Fig. 7b) only the broad absorption band (PA_2) with a maximum at $\sim$1.35 eV is observed, which does not change up to 500 ps, the longest time delay in this transient absorption experiment. We have previously assigned PA_2 to charge pairs generated on adjacent chains [8].

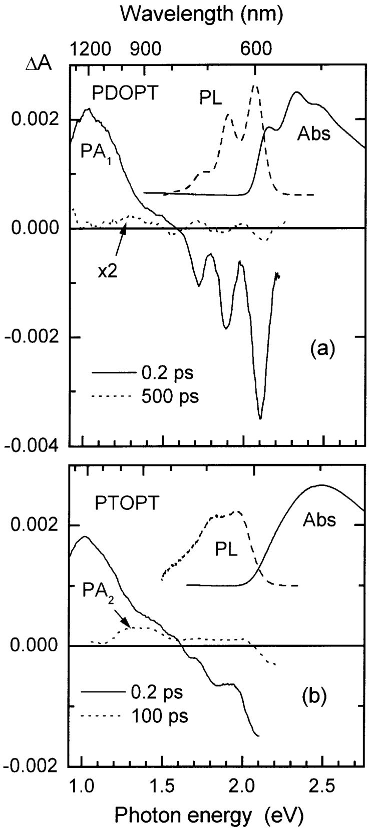

Fig. 7. Transient absorption spectra of double-layer PDOPT (a) and PTOPT (b) films at various delay times after excitation after photoexcitation at 2.3 eV with the excitation density of 5×10^{17} cm^{-3}. Ground state absorption and time-integrated PL spectra are given for reference.

3.3. Resolving the kinetics of different excitations

In Fig. 8a, the decay of the SE signal at 1.8 eV (solid line) is plotted for comparison with the PL kinetics at the same photon energy (dotted line) after adding a 10% offset to the SE signal to account for the long-lived PL. Both SE and PL kinetics match well as expected, except that the time resolution of the streak camera does not allow resolving of the

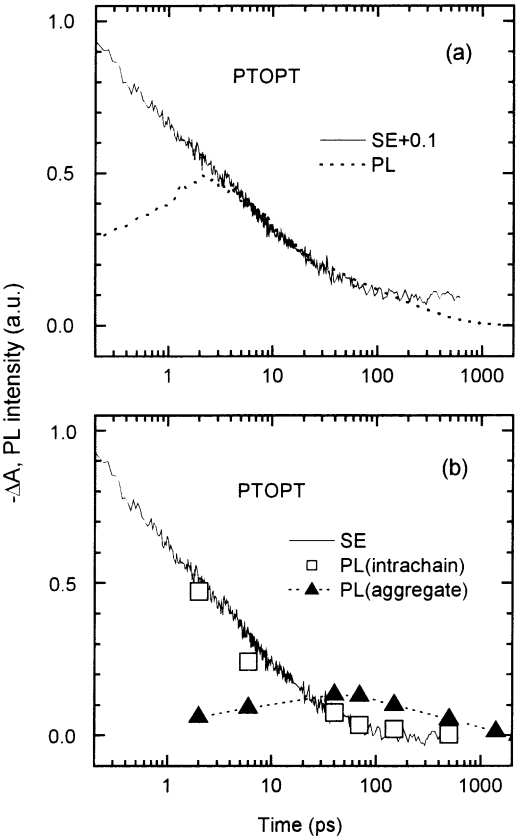

Fig. 8. (a) Kinetics of the SE signal in the double-layer PTOPT film at 1.8 eV plotted with a 10% offset (solid line) and PL kinetics at the same photon energy (dotted line). (b) Kinetics of the SE signal in PTOPT film at 1.8 eV as in (a) but without offset (solid line) and the time-dependence of the energy-integrated PL intensity from intra-chain excitons (open squares) and aggregates (filled triangles) obtained by fitting the time-resolved PL spectra.

initial PL decay within the first 2 ps after excitation. We have fitted the PL spectra recorded in the double-layer PTOPT film at different time delays at 77 K as a superposition of the intra-chain exciton emission with the vibronic progression characteristic of the intra-chain exciton in PDOPT and the aggregate emission with its PL spectrum matching the long-lived emission in the PTOPT film. The points in Fig. 8b represent the PL intensities, which were obtained by integrating the fitted PL spectra of both species over photon energy. We can clearly see that the decay of intra-chain excitons represented by SE (solid line) and by energy-integrated PL (open squares) matches the build-up of aggregate emission (filled triangles), indicating that excitation trapping by aggregates is the dominating process. To obtain good fits to the time-resolved PL spectra we needed to assume that the 0–0 PL band of intra-chain excitons is centered at ∼1.95 eV, i.e lower by ∼0.05 eV than the peak position of the 0–0 PL band in PDOPT film (Fig. 2a), implying very fast excitation transfer in PTOPT to the segments of longest conjugation, which are slightly longer than in PDOPT. The 0–0 peak of the fitted aggregate emission spectrum shows a dynamic red-shift from 1.88 to 1.84 eV in the time span from picoseconds to nanosecond, suggesting that at longer delay times trapping occurs to aggregates with a lower emission energy.

The position and spectral shape of the aggregate emission are very similar to the time-integrated PL spectrum observed in a regular conformation of poly(3-octylthiophene), which showed the 0–0 PL peak at 1.8 eV and $S \approx 2$ [24]. These authors assigned the PL to intra-chain excitons. However, our results show that such energy gap and the Huang–Rhys factor are characteristic for aggregate luminescence, not for single-chain excitations.

The fact that the dynamic quenching of intra-chain PL does not depend significantly on temperature (Fig. 5) indicates that no energy barrier exists for excitation trapping by aggregates on the short time scale. This behavior also proves that no detrapping (re-formation of intra-chain excitons) occurs at room temperature. Then, the depth (ΔE) of traps, which quench PL, should be $\Delta E > k_B T = 0.03$ eV, where k_B is the Boltzmann constant and $T = 293$ K. This observation is consistent with the fact that the PL from aggregates is red-shifted by at least 0.05 eV relative to the intra-chain exciton emission for all PTOPT samples at 77 and 293 K (Figs. 2 and 3).

Now we turn to the estimates of PL quantum yields of intra- and inter-chain excited states and their radiative lifetimes. The PL quantum yield, which is defined as the ratio of the number of photons emitted to the number of photons absorbed, is a sum of intra- and inter-chain contributions:

$$\Phi_{\mathrm{PL}} = G_{\mathrm{intra}} \left(\frac{\tau^{\mathrm{intra}}}{\tau_0^{\mathrm{intra}}} \right) + G_{\mathrm{aggr}} \left(\frac{\tau^{\mathrm{aggr}}}{\tau_0^{\mathrm{aggr}}} \right) \qquad (2)$$

where G_{intra} and G_{aggr} are generation efficiencies of intra-chain excitons and aggregates, respectively, τ^{intra} and τ^{aggr} are their PL lifetimes, while τ_0^{intra} and τ_0^{aggr} are natural radiative lifetimes. The natural radiative lifetime of the intra-chain exciton was estimated to $\tau_0^{\mathrm{intra}} = 1.28$ ns for a substituted polythiophene in solution [25]. For this polythiophene an intra-chain PL with a 0–0 peak at 2.02 eV was observed, decaying mono-exponentially with a time constant of 640 ps. In PDOPT film no significant change of the PL spectral shape is observed at least up to 500 ps (Fig. 2a), thus the decay components with $\tau_1 \approx 30$ ps and $\tau_2 \approx 300$ ps in Table 1 apparently correspond to the intra-chain excitons, which then yield the mean (weight-averaged) lifetime $\langle \tau^{\mathrm{intra}} \rangle \approx 286$ ps. The generation efficiency of intra-chain excitons on well-separated chains in PDOPT film is expected to be unity ($G_{\mathrm{intra}} = 1$). Then, the first term in Eq. (2) representing the PL quantum yield of intra-chain excitons is ∼0.22, which is very close to the typical measured value of $\Phi_{\mathrm{PL}} = 0.24$ [26]. The intra-chain PL lifetime in PDOPT film is shorter by a factor of two than in isolated polythiophene chains [25] indicating that intra-chain excitons are quenched in PDOPT film as well. Inter-chain aggregates could be responsible for this quenching even though their concentration is small due to large inter-chain separation. They can be associated with a long-lived, red-shifted PL having a higher Huang–Rhys factor of $S \approx 1$ (Fig. 2a). The long component ($\tau_3 \approx 500$ ps at 293 K) most likely contains contributions of both intra-chain and aggregate emission.

The SE kinetics in the double-layer PTOPT film shown in Fig. 8b can be fitted to a three-exponential decay with time constants $\tau_1 \approx 0.5$ ps (30% of the full amplitude), $\tau_2 \approx 6$ ps (40%) and $\tau_3 \approx 40$ ps (30%), corresponding to a weight-averaged lifetime $\langle \tau^{\mathrm{SE}} \rangle \approx 15$ ps. The initial decay of the SE with $\tau_1 \approx 0.5$ ps can be associated with exciton dissociation into inter-chain polaron pairs, which, according to recent results [8], are formed on the femtosecond time scale with a quantum yield of ∼20% in PTOPT film. The weight-averaged lifetime of the SE in double-layer PTOPT films, however, varied significantly in the range from $\langle \tau_{\mathrm{min}}^{\mathrm{SE}} \rangle \approx 12$ to 40 ps, depending on sample preparation (mainly on the temperature of the substrates when joining two single-layer films). The films, which showed the shortest lifetime of SE, also exhibited the most red-shifted PL spectrum. From measurements of five different samples, we obtain the statistical average lifetime of SE, which is also the mean lifetime of intra-chain excitons in PTOPT films at 293 K, as $\langle \tau^{\mathrm{intra}} \rangle \approx \langle \tau^{\mathrm{SE}} \rangle \approx 26 \pm 14$ ps, where the error bars represent the biggest deviation from the mean value. Assuming that nearly all the initial excitations are intra-chain excitons (i.e. $G_{\mathrm{intra}} \approx 1$), we estimate the first term in Eq. (2) (contribution of intra-chain emission to the PL quantum yield) to be 0.02 ± 0.01. Having in mind that ∼20% of the intra-chain excitons turn into polaron pairs [8] and that the rate of radiative and non-radiative decay is about the same [25] and assuming that all residual excitations can be trapped by aggregates, we estimate $G_{\mathrm{aggr}} \approx 0.8 \times 0.96 = 0.77$. The PL quantum yield in PTOPT films is typically $\Phi_{\mathrm{PL}} \approx 0.04$ at 293 K [26]. Since the PL decay kinetics and the mean PL lifetime does not differ significantly in single- and double-layer films (Fig. 4), the PL quantum yield is also expected to be about the same. It implies that the aggregate contribution to the PL quantum yield in PTOPT films is ~0.02 at 293 K. Taking the longest time constant fitted to the PL decay in PTOPT double-layer film as the aggregate PL lifetime ($\tau^{\rm aggr} = \tau_3 \approx 550$ ps at 293 K), we obtain the natural radiative lifetime of aggregates: $\tau_0{}^{\rm aggr} \approx 21 \pm 10$ ns. It is interesting to note that very similar value of $\tau_0{}^{\rm aggr} \approx 20$ ns was estimated for regioregular poly(3-dodecylthiophene) in a poor solvent [27]. In the deconvoluted PL intensities (Fig. 8b), we see that the intensity of the aggregate luminescence reaches to ~10% of the PL intensity from intra-chain excitons. This value is consistent with ~10 times weaker oscillator strength of the lowest excited state in aggregates, hence ~10 times longer radiative lifetime. The ratio of ~10 has also been determined for inter- and intra-chain radiative lifetimes in cyano-substituted poly(*p*-phenylene-vinylene) [28].

Fig. 9a shows the time-integrated PL spectra of the single-layer PTOPT film recorded at 77 K and at 293 K. The PL spectrum at 77 K is red-shifted relative to the spectrum at 293 K and shows higher intensity: the PL quantum yield, which is represented by the area under the corresponding PL spectrum (where PL intensity is plotted as the number of emitted photons), increases by a factor of two going from 293 to 77 K. The PL spectral shape and the ratio of the apparent peaks however does not change with temperature, suggesting that the relative contribution of intra-chain excitons and aggregates to the total PL remains about the same at both temperatures and is about 50% from each of these excited species. To check this, we assumed that aggregate emission is well represented by the time-resolved PL spectrum observed at the time delay of 1 ns (Fig. 2c). This spectrum is scaled to give a relative contribution of 50% to the total PL intensity integrated over photon energy (Fig. 9b) and subtracting this spectrum from the time-integrated PL spectrum at 77 K (Fig. 9a), we obtain the difference spectrum (Fig. 9c), which resembles the shape of the intra-chain exciton emission with a 0–0 peak at 1.95 eV. This similarity confirms our estimate from time-resolved data of approx. equal contributions from intra-chain excitations and aggregates to the time-integrated PL in PTOPT. The increase of the aggregate PL by a factor of two at 77 K as compared to 293 K correlates with the increase of PL lifetime of aggregates ($\tau^{\rm aggr}$), from ~550 to 1100 ps (Table 2). The quantum yield of intra-chain PL should then also increase by a factor of two when going to lower temperature. This behavior is verified by the increase of the intra-chain PL lifetime (Fig. 4). In Table 2, we summarize energetic and dynamic parameters of the PL from intra-chain excitons and inter-chain aggregates.

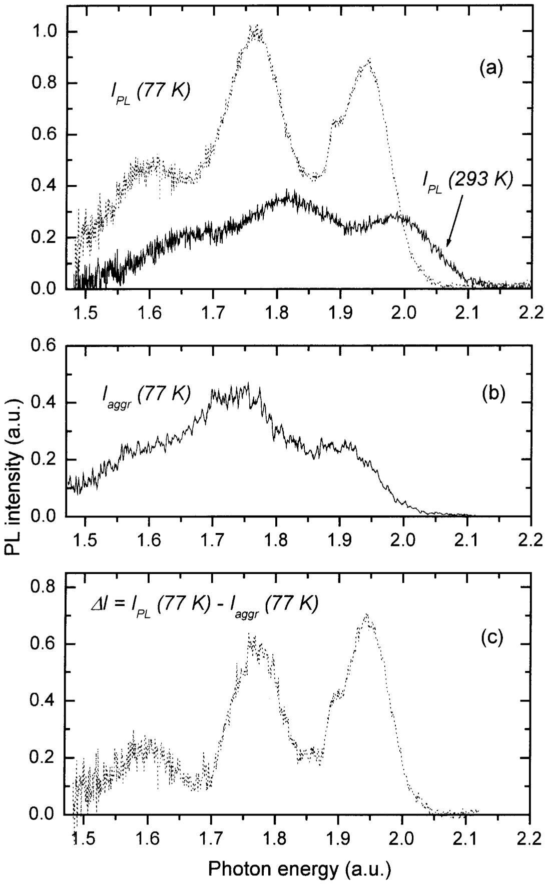

Fig. 9. (a) Time-integrated PL spectra in the single-layer PTOPT film recorded at different temperatures. (b) The aggregate emission spectrum observed at the time delay of 1 ns (from Fig. 2c), scaled to give the relative contribution of 50% to the total PL. (c) The intra-chain PL spectrum obtained by subtracting the aggregate emission spectrum (b) from the time-integrated PL spectrum at 77 K (a).

Our estimate of $\tau_0^{\rm aggr} \approx 20$ ns is smaller than the calculated radiative lifetime of the order of 30–70 ns for the lowest excited state of the physical dimer consisting of two parallel oligothiophenes (8T) with the calculated energy gap of 1.84–1.95 eV between ground state and the lowest excited state [21]. A long radiative lifetime is expected for parallel orientation of interacting segments since the transition between the lowest excited state and ground state is dipole-forbidden. In reality, some twisting of the interacting segments from a parallel configuration would break the symmetry and the transition would become partially allowed. This transition can also gain oscillator strength due to vibrational coupling to the higher energy state, which is expected to be higher in energy by the Davydov splitting. The Davydov splitting in the excited state and in ground state is expected to have similar values, since dipole moment of conjugated segments in different states is usually very similar. Then, the Davydov splitting should be equal to the red-shift of the aggregate luminescence relative the intra-chain emission, i.e. to ~0.1 eV (Figs. 2 and 3).

Luminescence spectra of intra-chain excitons at 293 K are blue shifted by ~0.05 eV with respect to the corresponding spectra at 77 K. This is a general phenomena in conjugated molecules comprised of aromatic rings, which are connected by single covalent bonds. The torsional

Table 2
Energy positions of the 0–0 emission peak, PL lifetimes, radiative lifetimes as well as PL quantum yields of intra-chain exciton and aggregate

Sample, temperature	Photon energy of 0–0 PL (eV)		PL lifetime, τ (ps)		Contribution to PL quantum yield		Radiative lifetime, τ_0 (ns)	
	Intra-chain	Aggregate	Intra-chain	Aggregate	Intra-chain	Aggregate	Intra-chain	Aggregate
PDOPT								
293 K	2.06	<2	$\sim$286	$\sim$500	>0.22		1.28	
77 K	2.01	<2	$\sim$280	$\sim$600				
PTOPT double-layer								
293 K	$\sim$2	1.93	$\sim$26	$\sim$550	$\sim$0.02	$\sim$0.02	1.28	$\sim$21
77 K	$\sim$1.95	1.84	$\sim$50	$\sim$1100	$\sim$0.04	$\sim$0.04	1.28	$\sim$21
PTOPT single-layer								
77 K	$\sim$1.95	1.9	$\sim$50	$\sim$1000	$\sim$0.04	$\sim$0.04	1.28	$\sim$20

motion of aromatic rings around these single bonds is likely to be the major factor decreasing the conjugation length in such the molecules. At low temperature, these torsional motions seem to be restricted due to energy barrier. The temperature effect on aggregate luminescence is even more pronounced: PL spectrum at 77 K is red-shifted by $\sim$0.1 eV as compared to that at 293 K, implying that the Davydov splitting is bigger at lower temperature. This points to the increase of the interaction strength at lower temperature, which can be simply due to the thermal shrinkage of the inter-chain distance. The torsional motion of aromatic rings introduces the dynamic disorder, which is also expected to decrease the interaction at higher temperature.

4. Conclusions

We have shown that excitation energy transfer to inter-chain aggregates (presumably physical dimers) is the dominating mechanism decreasing the PL quantum yield in polythiophene films with a short inter-chain distance. The natural radiative lifetime of the lowest excited state of the aggregate is estimated to be $\sim$20 ns. Aggregate luminescence as well as intra-chain emission show pronounced coupling to a vibration with a frequency $\nu_{\mathrm{vibr}} \approx 1400\,\mathrm{cm}^{-1}$ (0.17 eV energy), which is attributed to the C=C bond stretch. The Huang–Rhys factor is different for the two transitions: $S \approx 0.7$ for the intra-chain emission and $S \approx 1.5$ for aggregate luminescence. As judged from the shift of the aggregate luminescene spectrum relative to the intra-chain exciton emission, the Davydov splitting in the aggregate is $\sim$0.1 eV, which is substantially smaller than the nuclear relaxation energy estimated as $\delta E = Sh\nu_{\mathrm{vibr}} \approx 0.25\,\mathrm{eV}$. The aggregate contribution to the total luminescence is $\sim$50% in the temperature range 77–293 K.

Acknowledgements

Financial support is gratefully acknowledged from the Swedish Natural Science Research Council, the Royal Swedish Academy of Science, the Knut and Alice Wallenberg Fundation and the Trygger Fundation.

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