

Luminescence of pure and iodine doped PPV: internal energetic structure revealed through spectral signatures

L. Bakueva^{*}, D. Matheson, S. Musikhin, E.H. Sargent

Department of Electrical & Computer Engineering, University of Toronto, Toronto, Canada, M5S 3G4

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Abstract

Stationary and time-resolved luminescent characteristics were investigated in a large number of poly(*p*-phenylene vinylene) (PPV) samples including as-grown films on different substrates, those subjected to thermal curing and vapor-phase iodine doping. The thermal treatment changes the intensity and characteristic time of photoluminescence in different manner for different luminescence lines. The iodine doping causes an additional luminescence peak at the photon energy 2.61 eV with simultaneous suppression of the basic emission band. Photoluminescence also depend on the energy of excitation quanta $\hbar\omega_{\text{ex}}$, and for $\hbar\omega_{\text{ex}} = 4.12$ eV, becomes sensitive to the incidence angle of exciting light. The established correlations between technological parameters and emission spectra can be used for controlled modification of the latter. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymer-based structures are the focus of intensive investigations as mechanically and physically flexible, processible materials for large-area photoemitting and photosensitive devices. Their wide practical applications is inhibited by present-day limitations in control over luminescent spectra, sensitivity and efficiency. The development of a toolkit of methods for the modification of the luminescent characteristics of conducting polymers and polymer-based devices is, therefore, of great practical importance.

We report herein results of our investigations into the use of thermal treatment and vapor-phase iodine impurity doping of poly(*p*-phenylene vinylene) (PPV) light-emitting films grown on a variety of substrates.

2. Description of experiment

PPV samples were fabricated by spin coating from PPV pre-polymer solution manufactured by Lark Enterprises. Both pure PPV and PPV doped with tris(8-hydroxyquinoline) aluminium (Alq₃) were subjected to vapor-phase iodine

doping. The doping was performed using the procedure reported in [1] for p-doping of conducting polymers.

Polymer thin films were spun onto transparent substrates consisting variously of glass, mylar and quartz. Two types of the post-deposition treatment were used: one group of samples was dried at room temperature, whereas, the other group was cured by annealing it for 3 h at 170 °C in a gas mixture consisting of 95% Ar and 5% H₂.

Photoluminescence measurements were made using the Photon Technology International spectrofluorometer C-60. Spectra were acquired from 300 to 900 nm for optical excitation ranging in wavelength from 220 to 400 nm. Any luminescence observed from substrates (in particular mylar and ITO-covered glass) was measured and subtracted from thin film luminescence spectra reported herein. The same spectrofluorometer was used for the measurement of time-resolved luminescence spectra, as well as decay characteristics of the principal luminescence peaks.

3. Influence of annealing

The luminescence spectra of undoped PPV films are well known (see, e.g. [2]) to contain well-developed peaks at 2.38 eV (520 nm) and 2.25 eV (550 nm). All of our samples, independent of the substrate type, demonstrate similar spectra with the additional smaller maximum represented by a

^{*} Corresponding author. Tel.: +1-416-978-8935; fax: +1-416-971-3020.
E-mail address: luda.bakoueva@utoronto.ca (L. Bakueva).

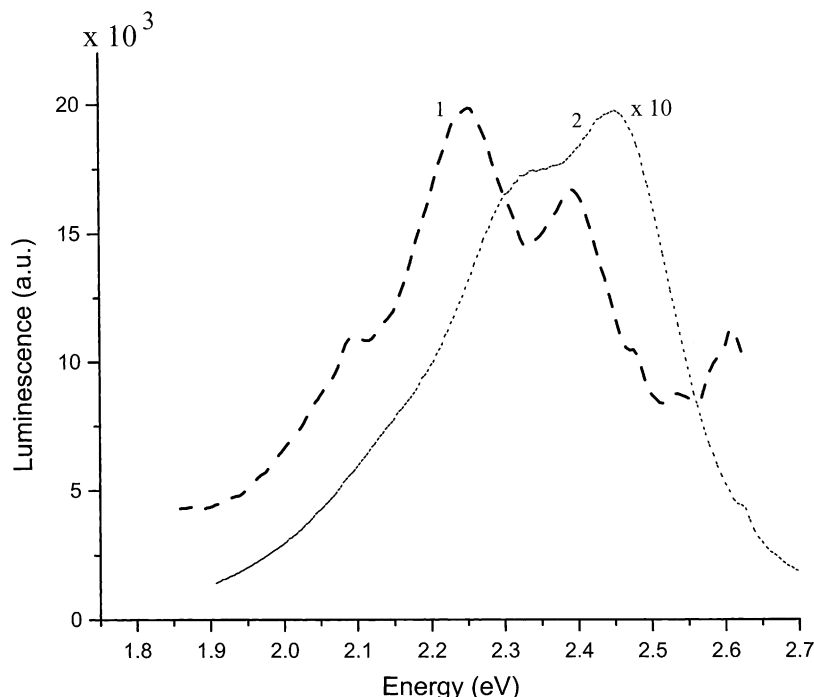


Fig. 1. Luminescence spectra of annealed (1) and non-annealed (2) PPV films.

shoulder at the long-wavelength wing (curve 1 in Fig. 1). All three peaks are associated with vibronic transitions $0 \rightarrow 0$, $0 \rightarrow 1$, $0 \rightarrow 2$ (transitions a, b, c in Fig. 2) [3]. The addition of Alq_3 results in a strong increase of luminescence in the vicinity of 2.35 eV (527 nm). The result was observed for all substrates and post-deposition treatment conditions presented herein.

The annealing or curing of PPV films is a standard procedure widely used for improving their electroluminescent properties [4,5]. We carried out a systematic comparison of the properties of cured and uncured samples. This

confirmed a noticeable difference in their electrical conductivity and electroluminescence [6]. Fig. 1 demonstrates the difference in the photoluminescence spectra of these two groups of samples. Annealing results in a red shift in the peaks attributable to an increased polymer chain length: the energy of LUMO–HOMO energy gap, as well as its vibronic replicas, decreases as the chain length increases [7]. The effect is accompanied by a decrease in luminescence intensity attributable to increased ordering, delocalization and decay of excitons, which in the case presented herein possess properties intermediate between the Frenkel and Wannier–Mott excitons [3].

As-grown and annealed polymer films are also characterized by different transient characteristics. Excitation and recombination in as-grown samples are slower (characteristic time: ≈ 0.7 ns) than in annealed samples (characteristic time: ≈ 0.4 ns) and the corresponding spectra exhibit a different time-evolution. In as-grown material the spectrum decays uniformly (Fig. 3), whereas, in annealed samples the $0 \rightarrow 0$ transitions are initially faster than $0 \rightarrow 1$ and $0 \rightarrow 2$ and only after 1.2 ns the luminescence decay become spectrally uniform (Fig. 4).

This character of luminescence is attributed to a higher degree of disorder and, hence, of carrier localization, in non-annealed films. Recombination occurs as a result in the same chains as excitation, whereas in annealed samples the additional exciton decay may be due to electron and hole separation and escape into neighbouring chains [8,9].

The relative intensity of $0 \rightarrow 0$ and $0 \rightarrow 1$ transitions also depends on the degree of annealing which in turn influences electron–phonon coupling, resulting in enhanced intensity

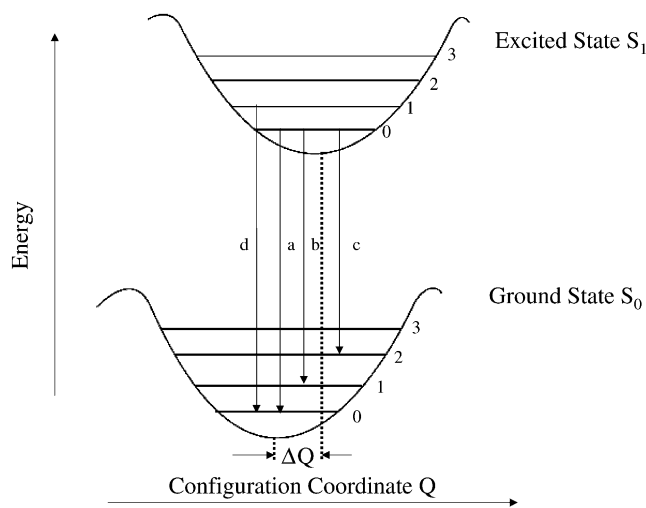


Fig. 2. Configurational coordinate diagram for transitions between different PPV states (a: $0 \rightarrow 0$; b: $0 \rightarrow 1$; c: $0 \rightarrow 2$; d: $1 \rightarrow 0$).

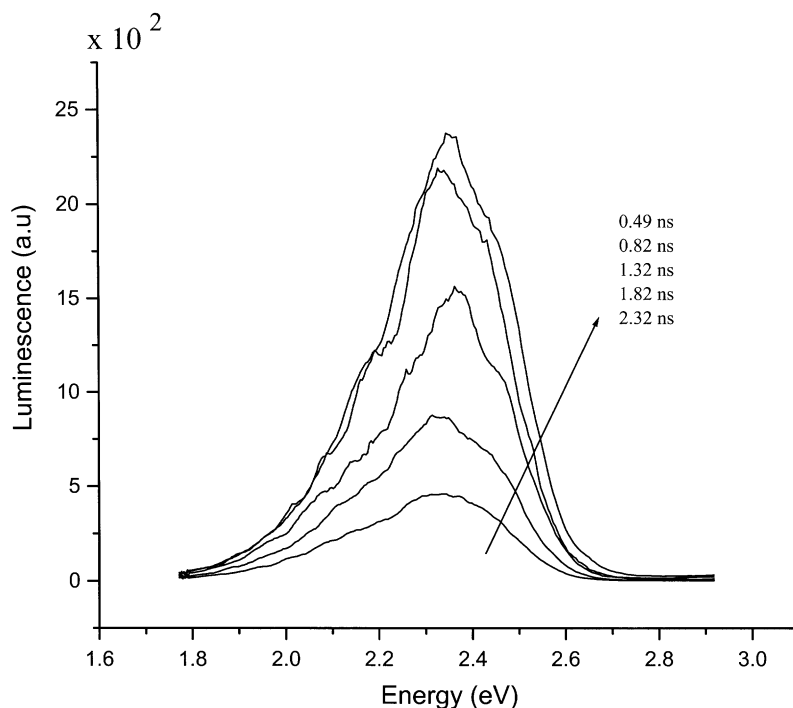


Fig. 3. Time-resolved luminescence spectra in non-annealed PPV films. The indicated time of measurement is counted from the laser pulse maximum.

of the $0 \rightarrow 1$ transition compared with the $0 \rightarrow 0$ transition [10]. Annealed samples are characterized by an additional luminescence peak at 2.61 eV (see curve 1 in Fig. 1).

The intensity of photoluminescence was higher in the samples fabricated at room temperature, contrary to the case of electroluminescence. The benefits of annealing on

electroluminescence thus, arise not from improved luminescent properties, but as a result of improved electron and hole transport, which influences electroluminescence but not photoluminescence. This is consistent with the view that annealing enhances packing of polymer chains in materials with some free volume or pores following deposition [5].

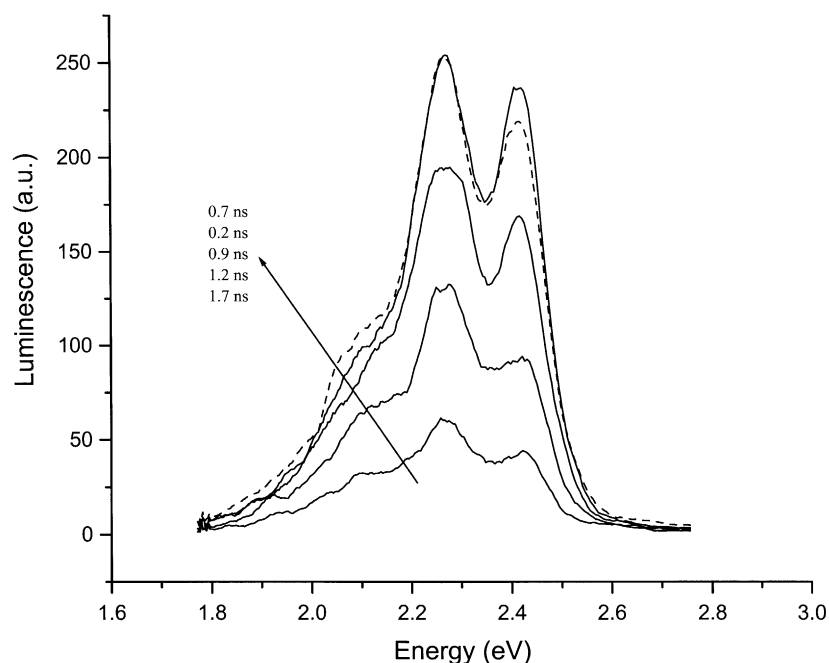


Fig. 4. Time-resolved luminescence spectra in annealed PPV films. The indicated time of measurement is counted from the laser pulse maximum.

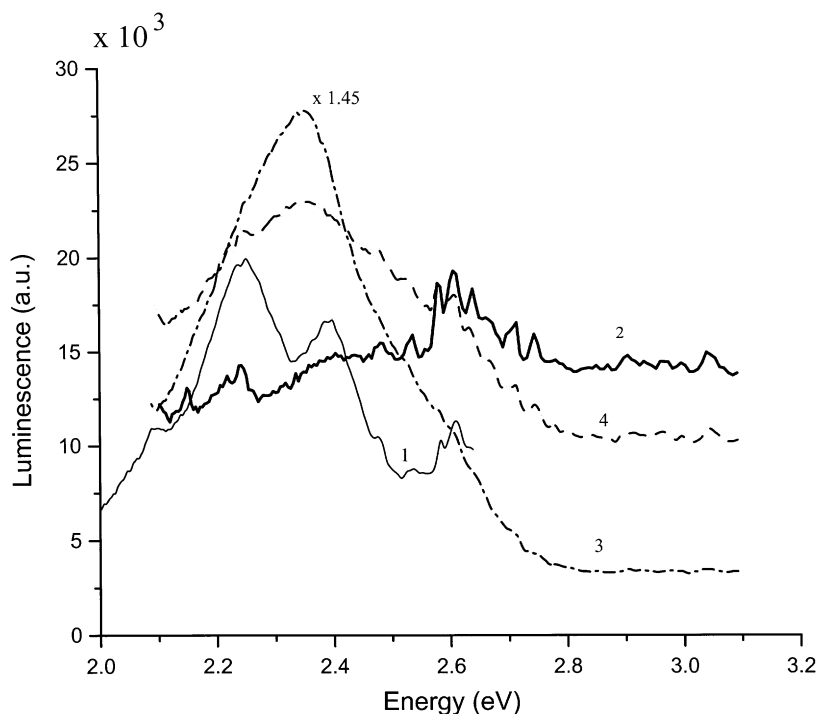


Fig. 5. Luminescence spectra of undoped PPV films (1), films doped by iodine (2), Alq₃ (3), and iodine and Alq₃, simultaneously.

4. Influence of doping

Doping with iodine is often used to increase the electrical conductivity of some conducting polymers, such as polyaniline [11], PBMPV [12], PFS [1] and PPV [13]. Previous studies have reported negligible influence of iodine doping on PPV material conductivity [14]. We have found that while conductivity does indeed see little influence, the photoluminescence of PPV is noticeably modified by iodine doping. Fig. 5 reveals a two-fold influence of iodine on photoluminescence. The existing luminescent peak of pure PPV is suppressed in doped materials, attributable to non-radiative recombination of excitons at the iodine centers or to more intensive transitions from singlet to the optically inactive triplet state in samples in which the hydrogen atoms are replaced by the much heavier iodine [3]. Luminescence of pure PPV (curve 1 in Fig. 5) becomes strongly suppressed as a result of iodine doping (curve 2). Luminescence suppression in PPV films after iodine implantation has been already observed [16] and explained in terms of implantation-induced radiation defects serving as quenching centers. In the present work, radiation centers are absent, a consequence of the method of iodine doping. Luminescence quenching can be also due to charged centers caused by chemical doping [17], which may occur in the present work in combination with the inter-system crossing.

The hypothesis of transition into a triplet state is confirmed by the presence of a 1.5 eV luminescence maximum in iodine-doped and undoped samples. The energy at which the maximum is reached is associated with the transition from the triplet state T₁ to the ground state S₀. In the samples

with Alq₃ doping, the Alq₃-related peak at 2.35 eV is also suppressed by iodine, though to a lesser degree than the main peak at 2.38 eV (curve 3 versus 4 in Fig. 5).

Iodine doping creates a strong new luminescence band at 2.61 eV. This not only suppresses the characteristic luminescence of the host material; it also results in a considerable short-wavelength shift in the total luminescence spectrum (Fig. 5).

Luminescence at 2.61 eV occurs in annealed films (curve 1 in Fig. 1) with an intensity much less than that of the main peaks. The iodine doping suppresses transitions from the singlet excited state S₁ in the lowest vibrational mode “0” to the ground state S₀ with different excitation level of the vibrational states (transition d in Fig. 2). The energy of this luminescence quantum indicates the transition from the first excited vibrational state “1” of the electron singlet S₁ to the ground electron state S₀ with lowest vibrational state “0”. Such transitions have previously been reported in several organic materials [3]. The inter-system crossing from S₁ in the lowest vibrational mode “0” is stronger than for the excited state “1”. Moreover, the intensity of such transitions increases in the presence of iodine (curve 2 in Fig. 5 in comparison with curve 1). Fig. 5 demonstrates that d-transitions are accompanied by the excitation of rotational vibrations [18] with the energies of some tens of meV evidenced by replicas in the vicinity of 2.6 eV peak.

Transition d in Fig. 2 from S₁ in the first excited vibrational state can be also observed in pure, annealed PPV if luminescence is excited using high-energy photons. Fig. 6 shows the luminescence spectra of PPV for the exciting photon energies equal to 3.1 eV (curve 2) and to 4.12 eV

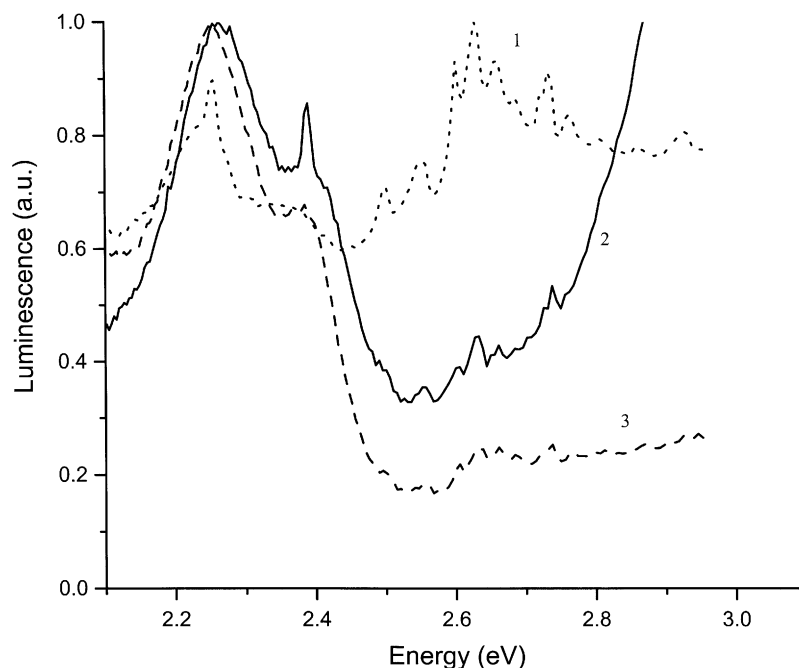


Fig. 6. Photoluminescence spectra of PPV for the exciting photon energy 4.12 eV (curves 1 and 3) and 3.1 eV (curve 2). Curves 1 and 2 correspond to the incidence angle $\theta \simeq 45^\circ$ and curve 3, $\theta \simeq 55^\circ$.

(curves 1 and 3). The intensity of transitions d from S_1 in the first excited vibrational state at the quantum energy 4.12 eV is higher than in the main region of transitions, whereas for excitation at 3.1 eV this relationship is inverted. The luminescence spectrum for excitation at 4.12 eV depends on the incidence angle (θ) of exciting light. The maximum luminescence intensity in the vicinity of 2.6 eV is observed for angles close to 45° (curve 1 in Fig. 6). For $\theta \simeq 55^\circ$ (curve 3) the character of luminescence changes. The emission spectrum for excitation at 3.1 eV is independent of θ .

The character of the spectra may be a result of preferential orientation of polymer chains in the film plane. In this case, even for non-polarized excitation, changes in angle of incidence would result in a dependence of absorption on the orientational relationship between the polymer chain and the plane of incidence of the incident electromagnetic field [15].

5. Conclusions

We summarize our findings as follows: (i) Annealing of PPV films causes ordering of polymer chains and, as a result, change in the luminescence intensity and spectra. (ii) Iodine doping of PPV films creates additional luminescence peak at 2.61 eV with simultaneous quenching in the main spectral band. (iii) The presence of a 1.5 eV luminescence maximum is associated with the transition from the triplet state T_1 to the ground state S_0 . (iv) Luminescence spectra of annealed films at the excitation photon energy 4.12 eV are sensitive to the average light polarization and, hence, to the angle of incidence for exciting light.

Acknowledgements

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