Cooperative Emission in π-Conjugated Polymer Thin Films

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Picosecond dynamics of exciton emission and absorption have been studied in neat thin films of a variety of poly (phenylene vinylene) derivatives. We found that the stimulated emission band of 120 nm width and ~ 1 ns duration, which is observed at low exciton density n, collapses at $n > 10^{17}$ cm^{-3} into a much narrower band of 7 nm width and lifetime $\tau \ll 10$ ps. Based on its excitation intensity dependence, polarization, lifetime, illuminated area, and film thickness dependencies, we assign this narrow band to superfluorescence rather than to amplified spontaneous emission. [S0031-9007(96)02274-0]

Cooperative emission from an ensemble of N_c correlated emitters is a many body phenomenon with a characteristic emission of a coherent radiation pulse with a peak intensity proportional to N_c^2 and duration proportional to N_c^{-1} [1]. The cooperative emission has been dubbed either superradiance (SR), if it originates from an ensemble of emitters which are initially excited into a correlated state with a macroscopic dipole moment; or superfluorescence (SF), if the emitters are initially uncorrelated, but spontaneously develop a cooperative macroscopic dipole moment [2]. Amplified spontaneous emission (ASE), on the other hand, is a *collective* rather than *cooperative* process, in which the spontaneous emission originating from an ensemble of emitters is linearly amplified by the same group of emitters with a large gain; but the more complex features of SF are not present [3,4]. In spite of the differences between these processes, it has been difficult to separate them experimentally [5].

In this Letter we report the first observation of excitonic cooperative emission in thin films of poly (*p*-phenylene vinylene) (PPV) derivatives [6]. The transient stimulated emission band of 120 nm width and 1 ns duration that is generated at low exciton density n, collapses at $n > 10^{17}$ cm^{-3} into a much narrower (FWHM ~ 7 nm) emission band with lifetime $\tau \ll 10$ ps. We show that the narrow emission band is in agreement with SF rather than ASE.

Photogenerated excitons at low densities ($n < 10^{17}$ cm^{-3}) were studied by the pump and probe correlation technique using two dye lasers synchronously pumped by a frequency-doubled mode-locked Nd:YAG laser [7]. These lasers produced ~ 5 ps pulses with ~ 1 nJ energy per pulse at 76 MHz repetition rate; their cross-correlation time was ~ 7 ps. The pump wavelength was fixed at 570 nm, whereas the time-delayed probe could be varied between 570 and 1000 nm to obtain the transient photomodulation (PM) spectrum $\Delta T/T$, where T is the probe transmission and $\Delta T(t)$ is its transient modulation. For higher exciton densities we employed a Nd:YAG regenerative laser amplifier at 532 nm, producing 1 KHz

pulses of 120 ps and 1 mJ per pulse, and a dye laser amplifier at 550 nm with 1 KHz pulses of 10 ps and 1 μJ per pulse. For the transient PM detection we used a high frequency modulation scheme described elsewhere [7]. For the transient emission measurements we used a streak camera (Hadland Photonics 500) of 10 ps time resolution. The emission spectrum was measured with 2 nm resolution using a $\frac{1}{4}$-meter JarrellAsh monochromator.

Neat thin films of PPV derivatives with various thicknesses d were fabricated on quartz substrates by spin coating from polymer solutions in chloroform with concentrations ranging from 5 to 50 mMol/liter. We studied PPV derivatives with side groups $R_{2,5}$, where $R = $ OC$_8$H$_{17}$ (DOO-PPV), $R = $ OC$_9$H$_{19}$ (NO-PPV), and $R = $ OC$_{15}$H$_{31}$ (PDO-PPV), all with very similar results. During the measurements the films were kept at room temperature in a dynamic vacuum of 10^{-4} torr, or under N_2 flow. Typical diameters of the films illuminated area were ~ 30 μm for excitation with the dye lasers and ~ 1 mm for excitation with the two laser amplifier systems.

Figure 1(a) shows the transient PM spectrum $(-\Delta T/T)$ of a DOO-PPV film with $d \sim 1000$ nm for $n \sim 10^{16}$ cm^{-3} at $t = 0$ ps. The gain spectrum $(\Delta T > 0)$, which is due to stimulated emission (SE) induced by the probe beam [8], is peaked at 1.98 eV and has two phonon replicas at 2.15 and 1.8 eV, respectively; it is very similar to the photoluminescence (PL) spectrum shown in Fig. 2. This indicates that there is little or no spectral overlap between the SE and the photoinduced absorption (PA) band $(\Delta T < 0)$, which unlike the SE is peaked at 1.5 eV. The SE decay shown in Fig. 1(b) can be fitted using a single exponential decay with a lifetime $\tau_{ex} = 240$ ps. The PA decay follows the SE decay in the first few hundred picoseconds and, therefore, is due to the same excitons in this time interval [6–9]. We conclude that the ps transient PM spectrum of Fig. 1(a), including both SE and PA bands, is due to a single excitation, namely a photogenerated intrachain singlet exciton [6–9]. The important energy levels and optical transitions associated with the exciton PM spectrum are
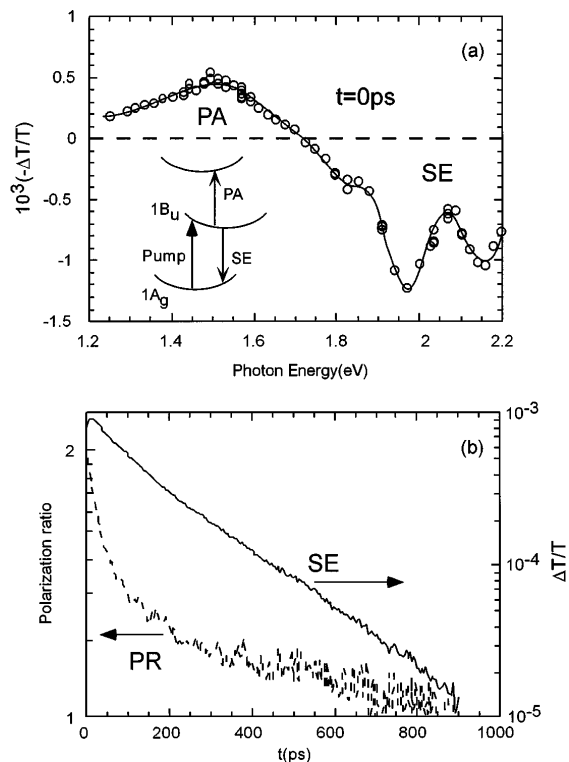
FIG. 1. (a) Ps transient PM spectrum of DOO-PPV film at $t = 0$ ps for $n \sim 10^{16}$ cm^{-3}. The SE and PA bands are assigned and their origin is shown schematically in the inset. (b) Ps transient decays of SE and polarization ratio at 2.0 eV.

shown schematically in Fig. 1(a) inset, where $1A_g$ is the polymer ground state and $1B_u$ is the first allowed exciton level [7]. This diagram shows that excitons in DOO-PPV form an ideal "four-level" medium for lasing, where the active optical transition is the Stokes-shifted $1B_u \rightarrow 1A_g$ transition. Using the quantum efficiency (Q_{PL}) relation for radiative transition [9,10], $Q_{PL} = \tau_{ex}/\tau_0$, where τ_0 is the radiative lifetime ($\tau_0 \sim 1$ ns in PPV's [10]) and
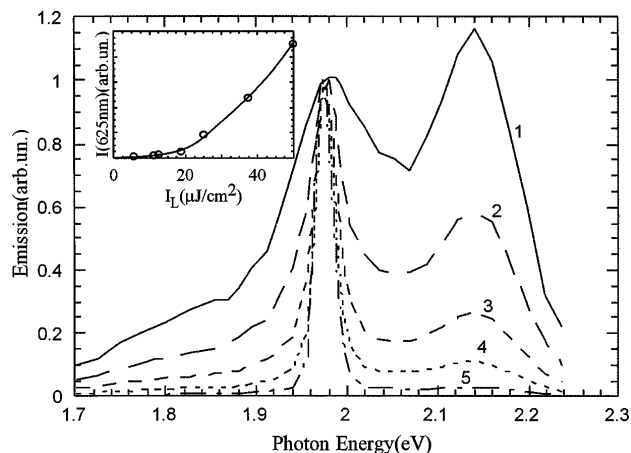

FIG. 2. Normalized emission spectra of DOO-PPV film at various pulsed excitation fluence ($\tau_p = 120$ ps): $I_1 = 10 \ \mu$J/cm^2, $I_2 = 2I_1 (\times 1/3)$, $I_3 = 3I_1 (\times 1/8)$, $I_4 = 5.4I_1$ ($\times 1/26$), $I_5 = 25I_1 (\times 1/200)$. The inset shows the amplification at 625 nm close to the threshold intensity $I_L = I_2$.

$\tau_{ex} = (\tau_0^{-1} + \tau_{NR}^{-1})^{-1}$, we find from the measured τ_{ex} of 240 ps that $Q_{PL} = 25\%$ for excitons in DOO-PPV films. We note that in dilute DOO-PPV solutions we measured [7] $\tau_{ex} = 440$ ps, showing that $Q_{PL} = 45\%$ can be reached in isolated DOO-PPV chains. From the PM relation $\Delta T/T = \gamma d$, where γ is the excitonic optical gain per unit length, we calculate $\gamma \approx 10$ cm^{-1} at 2.0 eV. Consequently, from $\gamma = n\sigma$, where σ is the optical gain cross section for the correspond excitonic transition, we calculate $\sigma \approx 10^{-15}$cm^2, which is one of the largest σ values known in solids. γ can be directly calculated using the following expression [11]:

$$\gamma = \frac{n\lambda^2}{8\pi\tau_0 n_f^2} g(\nu),\tag{1}$$

where $g(\nu)$ is the normalized gain spectrum and $n_f \approx 2$ is the refraction index of the polymer film. At the band center $g(\nu)$ is proportional to $(\Gamma)^{-1}$, where Γ is the SE bandwidth. For $\Gamma \sim 40$ THz from Fig. 1(a), we estimate $g(2 \text{ eV}) \sim 25$ fsec; using this g value and Eq. (1), we calculated γ in good agreement with our measurements. Neglecting losses, the condition for lasing (or ASE) can be defined as $\gamma L > 1$, where L is the effective length of the gain medium. Considering an ASE process perpendicular to the film surface where $L = d = 100$ nm, we calculate from Eq. (1) that in order to achieve lasing conditions (or ASE) in thin DOO-PPV films, $n > 10^{20}$ cm^{-3} must be generated.

To investigate the emission behavior at high n and find the proper lasing conditions, we have increased the excitation intensity I_L and measured the emission spectra, as shown in Fig. 2. It is seen that the broad PL spectrum (FWHM $\Gamma \sim 80$ nm) obtained at low intensities collapses at high intensities ($n > n_0 \sim 10^{17}$ cm^{-3}) into a much narrower and stronger emission band peaked at $\lambda_0 = 625$ nm (or 1.98 eV) with FWHM $\Gamma_0 = 7$ nm [12]. The spectral narrowing is accompanied by a nonlinear amplification (Fig. 2, inset). Its characteristic properties are summarized in Figs. 3(a) and 3(b), where the emission linewidth Γ and the peak intensity I (625 nm) are plotted vs the input intensity I_L. Γ abruptly decreases at a threshold intensity I_0 of 20 μJ/cm^2, where I (625 nm) changes its dependence on I_L from linear to superlinear. We also found that the emission intensity from the sides is higher than that from the front or backside of the film. This is due to light confinement (waveguiding) inside the polymer film caused by internal reflections at the polymer/substrate and polymer/air interfaces, respectively. We observed, however, that the emission from the front and backside of the film remains isotropic at all I_L.

The spectrally narrow emission band can be attributed to two different phenomena, namely SF and ASE. We argue below that the observed effect in films of PPV derivatives is most likely due to SF.

(i) The spectral narrowing occurs at $n_0 \sim 10^{17}$ cm^{-3}, not 10^{20} cm^{-3} as calculated before, based on the transient SE results [Fig. 1(a)]. It might be argued, however, that
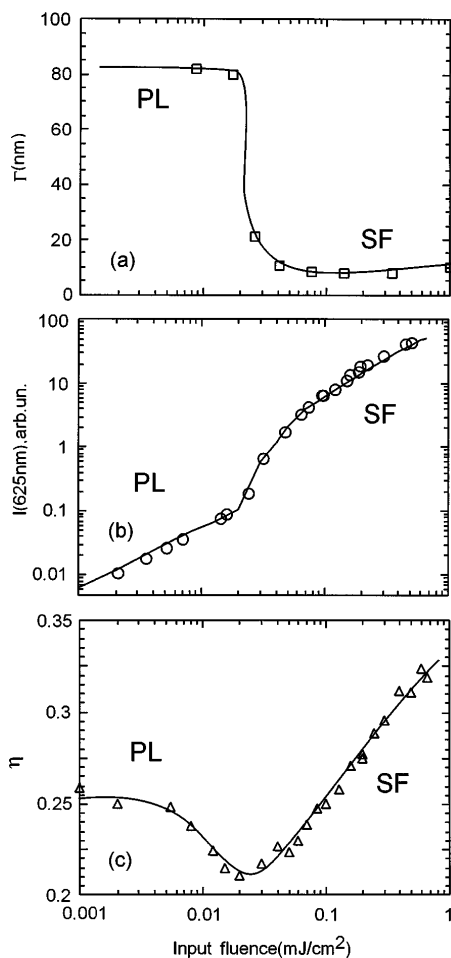
FIG. 3. The excitation intensity dependencies of (a) the emission linewidth, (b) the emission intensity at 625 nm, and (c) the emission yield η.

this discrepancy is due to lateral ASE, occurring parallel to the film surface and not in the direction perpendicular to the surface, on which our estimates were based. The effective gain length L in this case may be much larger than d, and it requires waveguiding. It is well known that the mode frequencies in planar waveguiding depend on d [13]. Therefore we can expect in case of ASE that the peak emission wavelength λ_0 would depend on d. We found, however, that λ_0 does not depend on d for $35\,\text{nm} < d < 2000\,\text{nm}$. Moreover, we varied the excitation area A from 0.01 to 3 mm^2 and measured the corresponding linewidth narrowing intensity dependencies [Fig. 3(a)]. In case of ASE, the linewidth narrowing is given by $\Gamma \sim (\gamma L)^{-1/2}$ [11], where γ is proportional (through n) to I_L, and therefore $\Gamma(I_L)$ should depend on $A \sim L^2$. We measured, however, a universal dependence for $\Gamma(I_L)$, which does not depend on A.

(ii) We measured the emission polarization ratio (PR) defined as PR $= I_{11}/I_{\perp}$, where I_{11} and $I_{\perp}$ are the emission intensities with polarizations parallel and perpendicular to the pump beam polarization, respectively. We found that whereas at low I_L PL is quite depolarized (PR $\sim$

1.3), the narrow band emission is polarized with PR = 2. From our transient PR measurements of the SE band [Fig. 1(b)] we found that PR decays within 40 ps from an initial value of PR(0 ps) = 2 to PR $\sim$ 1.3. Since PR = 2 for the narrow band emission, we conclude that it has to occur very fast within a radiation time $\tau_R \ll$ 40 ps. We have subsequently measured the transient emission decay at various excitation intensities, pumping with 10 ps pulses from the dye laser amplifier. We found (Fig. 4) that whereas PL decays exponentially with $\tau_{ex} \sim 240$ ps, as determined before from the SE decay in Fig. 1(b), the narrow emission band decays much faster. It simply follows the excitation pulse temporal profile, and therefore its characteristic emission time τ_R has to be even faster than the pulse duration $t_p = 10$ ps. Moreover, we found that τ_R does not change gradually with I_L, as appropriate for an ASE process [4]. On the contrary, it is seen (Fig. 4) that τ_R abruptly changes to $\tau_R \ll 10$ ps, whereas the rest of the PL emission still decays with $\tau_{ex} = 240$ ps. Such a behavior is in agreement with a cooperative emission process where τ_R for the SF excitons is determined intrinsically.

(iii) The spectral narrowing quickly saturates at $\Gamma_0 =$ 7 nm for $I_L > I_0$ [Fig. 3(a)]. In case of simple ASE Γ_0 is determined by the emission gain saturation intensity I_s [11]. From the measured gain coefficient $\gamma(\lambda)$ in Fig. 1 we estimate $I_s \sim 10^{25}$ photons/cm^2 sec, which is more than two orders of magnitude larger than the maximum emission intensity achieved in our measurements (10^{23} photons/cm^2 sec). The conditions for gain saturation are not satisfied in our measurements, and therefore Γ_0 is not determined by ASE. Such a behavior, again, is in agreement with a cooperative emission process, and we conclude that the spectral and temporal narrowing of the emission are indicative of SF. In this case Γ_0 is determined by inhomogeneous broadening, and from $\Gamma_0 = 7$ nm we estimate the dephasing time T_2^* of the SF state ($\Gamma_0 \sim 1/T_2^*$ [4]) to be $T_2^* \sim 200$ fsec.

In Fig. 3 we present further analysis of the spectra shown in Fig. 2. The SF threshold intensity I_0 separates two different emission regions: PL at low I_L and SF at
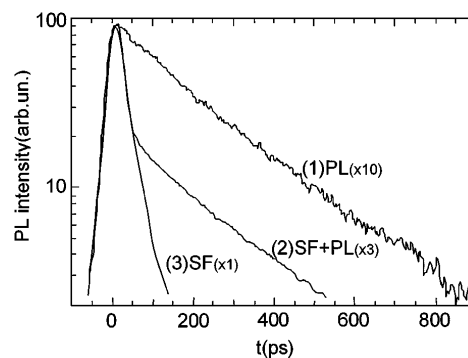

FIG. 4. Normalized decay dynamics of the emission band at various I_L: $I_1 = 10\ \mu\text{J/cm}^2$, $I_2 = 30\ \mu\text{J/cm}^2$, $I_3 = 54\ \mu\text{J/cm}^2$.

high I_L. In both regions the linewidths (3a) and peak emission intensities (3b) are characterized by different I_L dependencies. The emission yield η, defined as I_i/I_L, where I_i is the integrated emission measured with a Si detector through an optical transmission filter with a cutoff wavelength of 550 nm, is plotted in Fig. 3(c) vs I_L. At very low I_L, η is independent on I_L with an approximate value $\eta = Q_{PL} = 25\%$. However, at intensities $I_0/4 < I_L < I_0$ η decreases to about 20%. This effect can be assigned to a bimolecular exciton recombination kinetics [14]. At higher I_L, additional interactions occur among the excitons via the retarded transverse electric field due to radiation and this forms the SF correlated state [2]. Consequently, for $I_L > I_0$ η increases with I_L [Fig. 3(c)] and we attribute this effect to the SF state, because during its short lifetime $\tau_R \ll 10$ ps excitons have a lesser chance to recombine nonradiatively.

Several theoretical models have been developed for SF in extended gaseous media with pencillike excitation volumes [2,3]. The emissions in these media were characterized by narrow PL spectra even at low intensities (below the SF threshold) [2]. The SF process in thin conducting polymer films (disk-shaped volume) with strongly broadened emission is significantly different from a "usual" SF, and therefore, SF theories developed earlier do not directly apply to our case. However, there are some general conditions for SF which should hold in any case. These are given by the inequality [2,3]

$$\tau_c < \tau_R \leq T_2^*, \tag{2}$$

where τ_R is the SF radiation time and τ_c is the cooperation time [15], $\tau_c = (\tau_E \tau_R)^{1/2}$, where τ_E, in turn, is the light travel time inside the film (given by $n_f d/c$). Since τ_E is of order 1 fsec in such thin films as ours, $\tau_E < \tau_R$ for $n > 10^{16}$ cm^{-3} and the left-hand side of (3) is satisfied for all I_L used here. Examining now the right-hand side of (3), we can calculate τ_R using the relation $\tau_R = \tau_0/N_c$. There has been no estimate of N_c for our disk-shape geometry, but if we use N_c derived for a pencil-like geometry, $N_c = (8\pi)^{-1}\lambda_0^2 nL$ [2,3], and assume $L = d$, we calculate $\tau_R \sim 200$ fsec $\sim T_2^*$, and this fulfills condition (2).

The SF conditions (2) are easily satisfied for neat polymer thin films, where T_2^* is not very short, since $\tau_E < \tau_R \sim T_2^*$, and therefore the communication time τ_c needed to establish a coherent state is much shorter than the dephasing time T_2^*. Moreover, the threshold intensity for SF in such films is much smaller than the threshold intensity for ASE, or lasing. This can be easily seen from the gain coefficient γ, where at the threshold intensity $\gamma L > 1$. The SF effective gain coefficient γ_{SF} can be defined using Eq. (1) where $g(\nu)$ is replaced by T_2^* [16]. Then since Γ (PL) is much larger than Γ_0 (SF) in DOO-PPV films and $\gamma \sim \Gamma^{-1}$, we obtain $\gamma_{SF} > \gamma_{ASE}$. This relation, however, may be more general and hold for many π-conjugated polymer films [17], since their relatively strong electron-phonon interaction broadens the PL spectrum, resulting in large Γ. We note that the relation $\gamma_{SF} > \gamma_{ASE}$ drastically limits the threshold conditions for lasing in such films.

The best conditions for lasing can be achieved with films of minimum optical losses, e.g., due to impurities and defects with subgap absorption. But at the same time, the dephasing time in such films is also large and therefore the SF state is easier to obtain. In order to obtain a lasing threshold below that of SF, the relation $\gamma > \gamma_{SF}$ must be obtained, assuming that the effective length L is the same for both processes. Decreasing γ_{SF} using films with smaller T_2^* also increases the optical losses and, therefore, increasing γ is more attractive for reaching the condition $\gamma > \gamma_{SF}$. This can be achieved by decreasing the gain linewidth Γ, since $\gamma \sim \Gamma^{-1}$ [(Eq. (1)]; if $\Gamma < \Gamma_0$ (SF) then condition $\gamma > \gamma_{SF}$ is satisfied. This may happen in certain microcavities, where $\Gamma < 4$ nm $< \Gamma_0$ has been measured. Indeed, under these conditions laser action in PPV microcavities has been recently claimed [18].

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