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Femtosecond pump-probe investigation on relaxation of photoexcitations and spectral narrowing of photoluminescence for poly(para-phenylenevinylene)

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Photoinduced absorption spectra and their temporal profiles of poly(para-phenylenevinylene) thin film exhibit a strong correlation with an appearance of spectrally narrowed emission bands. The dependence of transient absorption signals on excitation and probe power denotes much lower saturation intensity in photoinduced absorption than that in stimulated emission arising from the identical photoexcitations, singlet excitons. We interpreted the peculiar emission bands in terms of superradiance or superfluorescence with a time constant of around 1 ps rather than amplification of spontaneous emission from uncorrelated emitters. © *1999 American Institute of Physics.* [S0003-6951(99)03802-4]

The efforts to develop lasing materials with conjugated polymeric systems have been focused on the investigation of lasing phenomena in solution and in dilute blends of polymer films.[1] The polymer in pure thin film was found to be difficult to be used as a lasing medium due to the internal loss of stimulated emission (SE) induced by the spectral coincidence between SE and photoinduced absorption (PA).[2] As for SE from poly(para-phenylenevinylene) (PPV) thin films, Yan *et al.* reported that the spectral feature of SE is strongly dependent upon the excitation wavelength,[3] and proposed that spatially indirect excitons rather than singlet excitons are primary photoexcitations. On the other hand, Friend *et al.* recently reported that the major primary photoexcitations might be singlet excitons rather than the proposed spatially indirect excitons by measuring emission quantum efficiency.[4]

The observation of the spectrally narrowed emission (SNE) bands from π-conjugated polymers has also attracted much attention because of the possibility that the narrowed emission bands may result from the lasing action in microcavity and/or SE.[5] Frolov *et al.* recently interpreted SNE from PPV derivatives in terms of excitonic cooperative superradiation rather than amplified spontaneous emission (ASE) or lasing by measuring the dependence of the threshold intensity for various film thickness.[2] Up to date, however, no systematic investigation has been reported to give a clear answer to the origin of SNE as well as the nature of the primary photoexcitations in detail.

In this work, we report the femtosecond pump-probe experimental results and emission spectral changes varying the excitation as well as the probe power density in order to have a deeper understanding on the primary photoexcitations and the nature of SNE.

The detailed description of the experimental setup for femtosecond transient absorption was given in Ref. 6. Probe beam with a diameter of 0.7 mm was spatially overlapped with pump beam ($d=1.5$ mm) on the thin film. The thickness and optical densities of PPV thin films were maintained around 70 nm and 1.5, respectively.[7] The samples were kept in vacuum in order to avoid any photodegradation due to the presence of oxygen.[4]

Figure 1 shows the time-integrated emission spectra with a change of excitation power density of the femtosecond laser pulses at 400 nm. With lower than 0.4 mW excitation, the emission spectral feature is almost identical to that observed upon photoexcitation at 442 nm from a cw HeCd laser. An increase in the excitation power density of the pulsed laser, however, changes the emission spectral feature abruptly to SNE peaking at 555 nm. We found that the observed emission spectra in the range of excitation power density investigated in this work are well separated into two parts; one is normal emission spectrum, which is defined as the spectral feature measured with lower than 0.2 mW excitation and the other one is SNE with the full width at half maximum (FWHM) of 10 nm. The total emission intensity monotonically increases with an excitation power density less than 0.9 mW, while both SNE and normal emission intensity exhibit a nonlinear behavior above 0.4 mW. From the slope of log–log plot, SNE intensity exhibits roughly sixth-order dependence on the excitation power density. Furthermore, it is also interesting to note that FWHM of SNE is nearly constant to be 10 nm within the pump power intensity range employed in this work.

Figures 2(a), 2(b), and 2(c) show the transient absorption
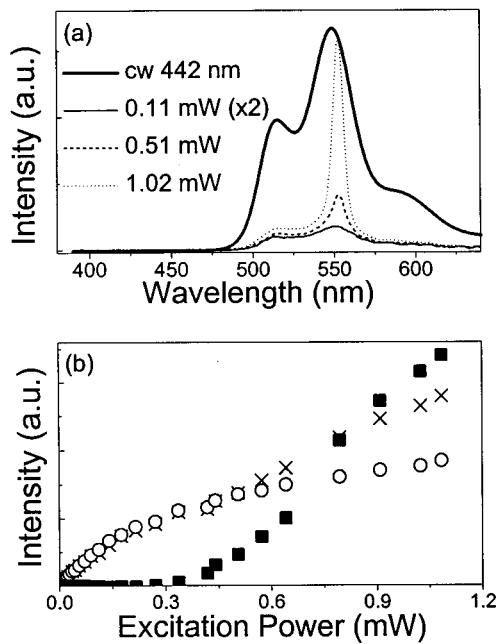
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FIG. 1. (a) Time-integrated emission spectra of PPV film upon photoexcitation at 400 nm with a pulse width and repetition rate of ~150 fs and 1 kHz, respectively. The pump powers are listed in the figure. The emission spectra upon cw 442 nm photoexcitation is also shown for a comparison. (b) Total (cross), normal (open circle), and spectrally narrowed (solid square) emission intensities a function of the pump power density.

FIG. 3. ΔOD vs pump intensity measured at 560 nm under two different probe intensities maintaining the same time delay of 0.5 ps. $I_{\text{probe},2}$ (open circles) is five times greater than $I_{\text{probe},1}$ (solid circles). Inset: Transient absorption spectra under pump power density of 0.1 mW. The probe power density was increased about five times as that in Fig. 2(a). The other conditions are the same as those in Fig. 2(a).

spectra at 0.5, 1.5, and 10 ps delay times for the three different excitation power densities under the same probe beam intensity. With excitation power density of 0.2 mW where
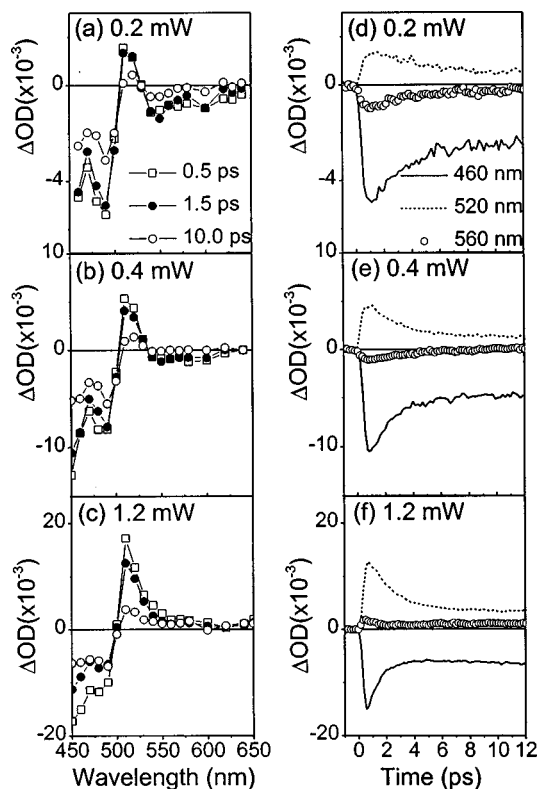

FIG. 2. (a)–(c) Transient absorption spectra measured at various time delays between pump and probe pulses and (d)–(f) their temporal profiles at three different probe wavelengths. The pump power is represented in each figure. The conditions of marks and lines in (b) and (c) and (e) and (f) are the same as those in (a) and (d), respectively. The solid line is used just for a guide.
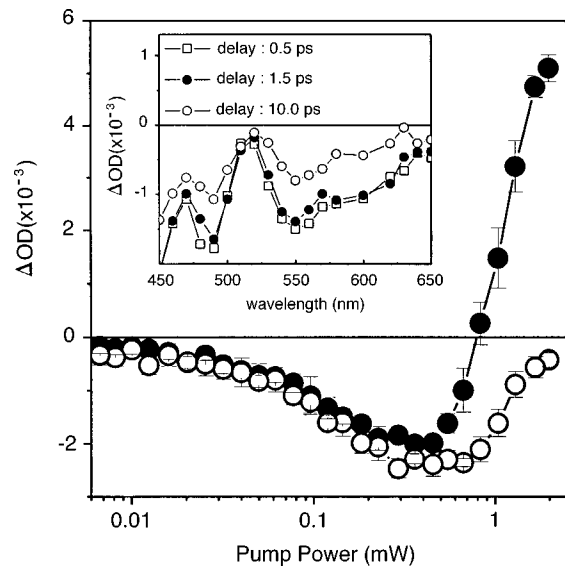
SNE is absent, SE becomes manifest to the red side of PA. However, a slight increase in the excitation power density (0.4 mW) results in a profound decrease in the relative SE intensity compared with PA. When the excitation power density is further increased to 1.2 mW, which gives rise to prominent SNE, PA rather than SE prevails longer than 500 nm. Especially, band-structured PA signal peaking at 510 nm at short delay times in addition to the PA tail around 650 nm becomes pronounced. After the ultrafast disappearance of that band in PA, the resultant PA spectrum exhibits a broad and structureless band and a much slower decay without any apparent spectral changes.

Figures 2(d), 2(e), and 2(f) show the temporal decay profiles measured at three different wavelengths corresponding to the ground state bleaching at 460 nm, PA at 520 nm, and SE at 550 nm. Photoexcitation with low power density induces a fast relaxation of which time constant is several picoseconds. This fast relaxation signal is superimposed upon a slowly decaying signal. The ultrafast relaxation time constant (~1 ps), which was observed in the previous pump-probe experiment, was not observed at low pump power density.[3,4] However, an increase in excitation power density results in an appearance of ultrafast decay component correlated with SNE shown in Fig. 1. With further increase in excitation power density, the overall temporal profiles remain almost unchanged. Meanwhile, it is interesting to note that the two temporal profiles corresponding to SE and PA upon photoexcitation with the pump power density less than 0.4 mW exhibit almost the same time constants as well as their relative amplitudes. These observations led us to suppose that the two transient species responsible for PA and SE are the same each other.

Figure 3 shows the pump power dependence of optical density changes at 560 nm under the two different probe power intensities. In the case of lower probe intensity ($I_{\text{probe},1}$), SE signals monotonically increase with the pump
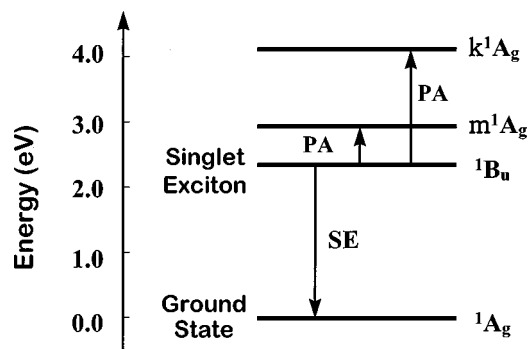
FIG. 4. Simplified energy levels and optical transitions in PPV thin film. The optical transitions related to the singlet exciton (^1B_u) are only shown. The excited states are located in energy according to Ref. 8.

power density in the range of 0.006–0.2 mW. Further increase of the pump power density, however, results in the decrease of SE signal and finally alters the sign of optical density change from SE to PA at the pump power density of ~0.85 mW. If the probe intensity is further increased ($I_{\text{probe},2}$), the SE signal is more pronounced under the pump power density lower than 0.85 mW. For pump power density higher than 0.85 mW, it is interesting to note that the increase in the probe intensity from $I_{\text{probe},1}$ to $I_{\text{probe},2}$ alters the sign of optical density changes from PA to SE. We have also investigated the changes in the transient absorption spectral feature with changing the probe power density and show the results in the inset of Fig. 3. In most of probe wavelength region, SE prevails PA spectral feature with increasing the probe intensity under the same pump power density.

As stated above, the observation that the signals due to SE and PA under low pump as well as probe power density exhibit the same temporal profile [see Fig. 2(d)] led us to propose that these two optical transitions are from the same transient species, singlet excitons. Furthermore, the recent theoretical and experimental works have also proposed that the presence of the two even parity states of mA_g and kA_g above the singlet excitons, ^1B_u, results in PA bands in near infrared and visible region, respectively.[8] Based on these considerations, we propose a simplified energy level diagram shown in Fig. 4. According to this scheme, the PA and SE observed in the current work could be explained in terms of optical transitions from ^1B_u to $k\,^1A_g$ and from ^1B_u to ^1A_g, respectively. If one concentrates on the transient absorption longer than 510 nm which is the absorption band edge of PPV, the spectrum contains only the sum of SE and PA because of the lack of ground state absorption. Assuming that both the Einstein coefficient and lifetime of the resultant state responsible for PA are larger than those for SE process, the saturation intensity of probe beam for PA is lower than that for SE. It is straightforward to explain the fact that a decrease in the probe intensity at a certain pump power density alters the sign of transient absorption signals from SE to PA because of the spectral coincidence between the two optical transitions. These interpretations again support the assumption that the Einstein coefficient responsible for SE is smaller than that for PA. Furthermore, all the transient absorption spectra at longer than the band edge wavelength exhibit a spectral feature of SE with an increase in the probe power density even though PA spectral feature remains still

the same (see the inset in Fig. 3).[9] For pump-power dependence at constant probe power, it could be understood as followings; the net absorption coefficient from singlet exciton ^1B_u to $k\,^1A_g$ is increased with the initial population of singlet excitons under constant probe power density. As a result, the used probe intensity is not strong enough to saturate the optical transition of PA from the singlet excitons to the proposed even parity excited states.

Finally, let us consider the origin of SNE based on our experimental observations. Previous reports on this peculiar phenomena proposed the two plausible mechanisms: one is the amplification of uncorrelated emitters, i.e., ASE, and the other is the amplification of correlated emission, i.e., superfluorescence or superradiance. The experimental observations that (1) the FWHM of SNE is independent of excitation power density, (2) the PA spectral feature and its decay time constant, which were found to be strongly correlated with the appearance of SNE, are quite different from those for SE, (3) the absence of any spectral feature of SE in the wavelength region of the peculiar strong emission under any experimental conditions employed in this work, led us to conclude that SE is an improper candidate to describe SNE. From our present understanding, we propose that SNE is most likely to occur from superfluorescence or superradiance. If our interpretation on SNE is correct, the duration of SNE should be limited by the dephasing time of materials, T_2. In fact, T_2 time constant for polymeric materials in thin films was reported to be around 1 ps, of which the value is surprisingly similar to that of the ultrafast decay component measured in this work.[10]

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