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Ultrafast studies of laser-action in poly(*p*-phenylene vinylene) films

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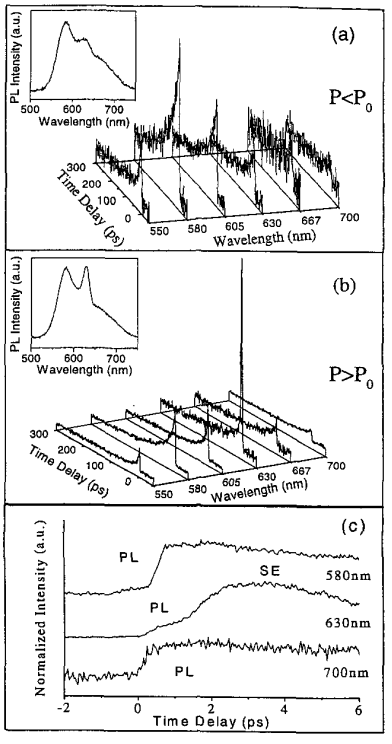
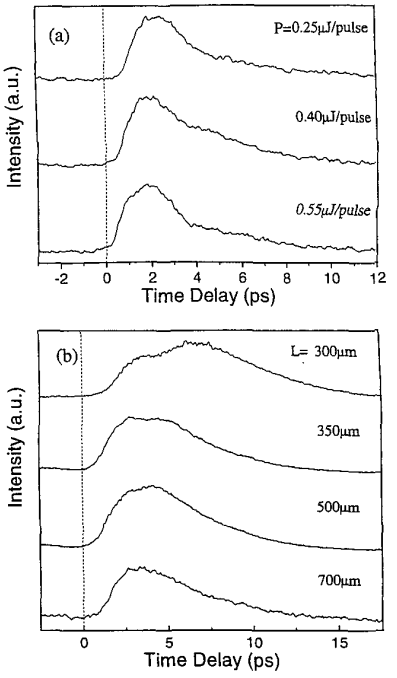
The recent demonstration of emission spectral narrowing in π-conjugated polymer films,[1-8] has stirred widespread interest to the phenomenon of laser-action in these materials. It is now generally believed that spectral narrowing in superior polymer films is caused by amplified spontaneous emission (i.e. single pass stimulated emission (SE)) enhanced by the optical waveguiding in the film.[2,8] However, the femtosecond exciton dynamics under SE conditions, and the effects of exciton inhomogeneity in the films on the properties of the SE and its dynamics have not been investigated.



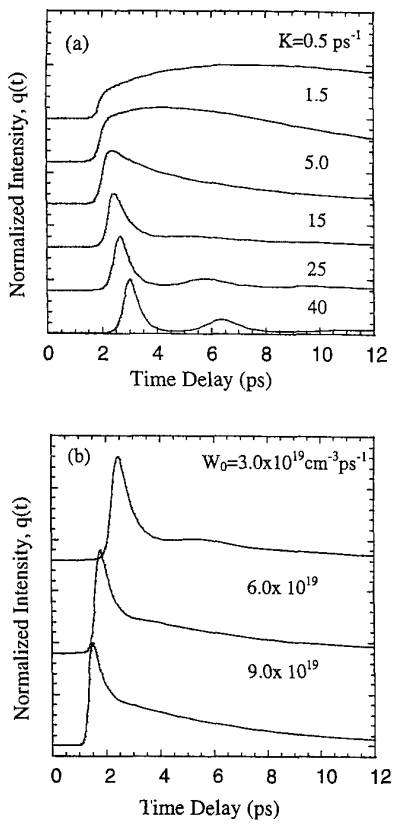
QThF4 Fig. 1. Transient emission at different λ across the PL band of DOO-PPV film at 300 K, measured with a round spot geometry. (a) P = 0.1 μJ/pulse ($P < P_o$) and (b) P = 0.25 μJ/pulse ($P > P_o$), where P_o is the SE threshold (P_o = 0.2 μJ/pulse). The insets show the time-integrated PL spectra for each case. (c) Normalized emission decay of (b) up to 6 ps, for three different λ; λ = 580 and 700 nm represent regular PL, whereas λ = 630 nm is the SE peak.



QThF4 Fig. 2. Picosecond SE dynamics of DOO-PPV at 630 nm (a) constant L (=600 μm) for various P. (b) At constant intensity (=300 μJ/cm^2 per pulse) for various L.

In this study we have used the gated frequency up-conversion technique with 300 fs time resolution to fully resolve the emission dynamics in thin films of 2,5-dioctyloxy poly(*p*-phenylene vinylene) (DOO-PPV) at excitation power, P below and above the threshold power, P_o for spectral narrowing. Figures 1(a) and 1(b) shows the emission dynamics using front emission geometry for $P < P_o$ and $P > P_o$ respectively. A narrow SE band is formed at the 0–1 transition at ~630 nm for $P > P_o$. Furthermore, the SE dynamics is much faster than that of the photoluminescence (PL) when $P < P_o$. This indicates that exciton thermalization dynamics within the DOS distribution in the film is much faster at higher P. The faster thermalization rate may be caused by the SE process which rapidly depopulates the most strongly coupled excitons. We estimate from Fig. 1(b) that this exciton thermalization time τ_{th}, is of the order of 5 ps. This relatively long energy relaxation process indicates that the most strongly coupled excitons are generated for a much longer time than the actual excitation pulse duration. One immediate consequence of this prolonged generation process for the most strongly coupled exciton is a delay emission, in respect to the spontaneous emission, or PL, as shown in Fig. 1(c) for 630 nm. It is seen that whereas the PL onset is at t = 0 (λ = 580 nm and 700 nm), the SE at λ = 630 nm reaches its maximum at a time delay τ_D = 2 ps.

More detailed insight into the SE dynamics



QThF4 Fig. 3. Theoretical simulations of the SE dynamics using Eqs. (1) and (2) with parameters $B = 2 \times 10^{-17}$ cm^3 ps^{-1}, $\tau = 250$ ps and $\tau_R = 1$ ns, (a) constant W_0 ($=3 \times 10^{19}$ cm^{-3} ps^{-1}) for various K and (b) constant K($=12$ ps^{-1}) for various W_0. The variation in K is analogy to changing L, since K increases with increasing L. These simulations reproduce the experimental observation of the changes in τ_D and T for different values of K and P.

can be obtained for various excitation stripe length L and excitation power using edge emission geometry, as shown in Fig. 2. In Fig. 2(a) we show the SE decay at 630 nm for a fixed stripe length L = 600 μm and various P ($>P_o$). It is seen that the SE delay time, τ_D decreases with P and at the same time the SE decay acquires a second "bump" at about 5 ps. But the clearer indication of a series of "relaxation bumps" in the SE decay can be seen in Fig. 2(b) measured at various L for constant excitation intensity. The first SE maximum at this intensity occurs for L = 300 μm at $\tau_D \approx 4$ ps, whereas the second maximum occurs now at 7.5 ps. At longer L, both the "relaxation" period T in the SE decay and τ_D dramatically decreased.

We were able to simulate the observed SE dynamics by the following coupled exciton-photon SE rate equations,[5] with a time dependent exciton generation rate $W(t) = W_0[1 - \exp(-t/\tau_h)]\exp(-t/\tau_{th})$, where W_0 is a constant, τ_h is the exciton intrachain thermalization time ($\tau_h \approx 0.5$ ps) and τ_{th} is the exciton interchain thermalization time:

$$dN/dt = W(t) - BqN - N/\tau\,, \quad (1)$$

$$dq/dt = BqN - Kq + pN/\tau_R. \quad (2)$$

In Eqs. (1) and (2), N(t) and q(t) are the transient exciton and photon density, respectively, B is the coupling constant ($B = \sigma c/n$, where σ is optical cross-section), τ is the exciton lifetime, τ_R is the exciton radiative time and p is the fraction of spontaneous emission photons which are directed along L for optimum coupling. In Eq. (2) K is the film effective optical loss which strongly increases with L. Eqs. (1) and (2) were solved numerically to give q(t) as shown in Fig. 3(a) and 3(b). The numerical simulations in Fig. 3(a) well reproduce the SE delay time and relaxation oscillation in Fig. 2 and their dependence on L.

In summary, we found that the inhomogeneity in the exciton ensemble causes dramatic effects in the emission dynamics, both for $P < P_o$ and $P > P_o$. Detail of these unusual dynamics, which are caused by the interplay between the film optical gain and loss, and the prolonged exciton generation process, will be discussed.

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