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Optical pumping and time-resolved photoluminescence studies of phenyl-substituted-PPV derivatives

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Abstract
We present the results of optical pumping (spectral narrowing), absorption, steady state and time-resolved photoluminescence (PL) measurements of two phenyl-substituted PPV derivatives. Simulated emission (SE) was observed from one derivative film having weak interchain interactions, while no SE was observed from the other derivative film showing strong interchain interactions. The nature and effects of interchain species on spontaneous and SE are investigated.

1. Introduction
There is much interest recently in the stimulated emission (SE) and lasing action in optically pumped conjugated polymers [1-5] due to the potential applications of conjugated polymers as novel laser materials for solid-state lasers. Organic solid-state lasers are naturally attractive because of their wide wavelength tunability and processing flexibility. Recently, an electrically driven organic diode laser that incorporates high-quality tetracene single crystal was reported [6]. Although optical pumped SE and lasing action have been demonstrated in a wide variety of conjugated polymers and laser structures consisting of conjugated polymers as active medias, no electrically driven polymer diode laser has been achieved so far. Besides the low charge injection efficiency and charge-induced absorption, interchain interactions in neat films might be another detrimental factor in realizing polymer diode laser. It has been proposed that the interchain interactions lead to reduced photoluminescence (PL) efficiency in conjugated polymers [7-10]. While it is generally agreed that the intrinsic photophysics of luminescent conjugated polymers is exciton, the nature and role of interchain interactions is a topic of widespread debate [7-11]. Therefore, a complete understanding of the nature of interchain interactions in conjugated polymers, their role in determining emission efficiency, and means of avoiding their detrimental effects is importance. In this work, using the optical pumping (spectral narrowing), absorption, steady state and time-resolved PL measurements, we study the effects of interchain interactions on spontaneous and stimulated emission.

2. Experiment
Two phenyl-substituted poly(p-phenylene vinylene) (PPV) derivatives, abbreviated as 2P-PPV and 4P-PPV, are used in this study. Their chemical structures are shown in figure 1. The polymers were prepared through Gilch route by dehalogenation of their corresponding monomers at room temperature using potassium tert-butoxide (tert-BuOK) as the base and tetrahydrofuran (THF) as the solvent. After precipitated the reaction mixture in methanol and purified through Soxhlet extraction, orange-yellow polymer powders were obtained. The polymer solution samples were prepared by dissolving 2P-PPV and 4P-PPV in THF, while the films samples were prepared by drop- or spin-casting their corresponding concentrated solutions onto glass substrates.

All the measurements were preformed at room temperature. The absorption measurements were performed with a Shimadzu UV-VIS-NIR 3100 spectrophotometer. The steady state PL measurements were performed using a Perkin Elmer LS 50B luminescence spectrometer. For the time-resolved PL measurements, the samples were excited using the frequency-doubled output of a mode-locked Ti:sapphire femtosecond laser from Spectra-Physics, operating at 800 nm with a pulse width of 100 fs at a 82 MHz repetition rate. The time-evolution of luminescence was recorded using a streakscope from Hamamatsu with a time resolution of 15 ps. For optical pumping (spectral narrowing) measurements, the frequency tripled output (355 nm) of a 10 Hz, mode-locked Nd:YAG (yttrium aluminum garnet) laser served as the excitation source. The pulse width was 35 ps. The pump power was adjusted by using a combination of a λ/2 plate and a linear polarizer. Two cylindrical lenses were used to generate a rectangular pumping stripe. Adjustable slits were used to change the dimension of the pumping strip. Emission was dispersed in a 0.25 m monochromator and detected by a gated CCD array.

3. Results and discussion

In figure 2, the narrow spectrum of SE of 2P-PPV film, with a pump energy of 130 µJ per pulse and a pump stripe of 300 × 500 µm, is shown together with steady state PL spectrum of the same film sample. The SE occurs at 2.35 eV (528 nm), close to the 0-1 vibronic peak of PL spectrum and not close the 0-0 peak. The reason is probably with the large self-absorption at 0-0 peak and less self-absorption at 0-1 peak, thus enhancing the net gain. The mechanism of the spectrally narrowed SE was a subject of intense debate, but most researchers now agree that it is waveguided amplified spontaneous emission (ASE) [12,13].

However, no spectral narrowing was observed from 4P-PPV film, even with the excitation of highest laser pulse energy of 196 µJ, suggesting that the PL efficiency of 4P-PPV film is lower than that of 2P-PPV film. The lower PL efficiency is due to the stronger interchain interactions in the 4P-PPV film than that in the 2P-PPV film. It has been proposed that the interchain interactions lead to reduced photoluminescence (PL) efficiency in conjugated polymers [7-10]. Although 2P-PPV and 4P-PPV have same conjugated main chain, their side chain configurations are different. In the case of 2P-PPV, the aliphatic side chains at the ortho-position on the side phenyl ring can effectively isolate the polymer backbone thus prevent interchain interactions in films. However, in the case of 4P-PPV, the aliphatic side chains are less effective in isolating the polymer backbone thus interchain interactions in films are much stronger.
The nature and effects of interchain species become apparent when the steady state spectroscopic properties of the film samples are compared with those of the solution. Figure 3 shows the absorption and PL spectra of film samples of 2P- and 4P-PPV, together with those of the corresponding solutions. The film absorption and PL spectra of 2P-PPV show a small redshift of 44 meV, as compared with those of the corresponding solution, indicating interchain interactions in 2P-PPV film are weak. In the case of 4P-PPV, the film absorption spectrum shows a redshift of 45 meV, while the redshift of film PL spectrum is 145 meV, when compared with those of the 4P-PPV solution. The much stronger redshift of film PL spectrum than the film absorption spectrum indicates that the interaction species is mainly with excited states, other than with ground states, suggesting the excimer nature of interchain species in 4P-PPV films [8,14]. The excimer is an emissive excited state complex delocalized over two molecular units [15]. Furthermore, the excimer cannot be directly excited optically, this explains why the significant redshift is observed in film PL spectrum of 4P-PPV only, not in film absorption spectrum. Excimer formation is accompanied by a strong geometric distortion along the intermolecular axis that leads to featureless, strongly Stokes-shifted emission in comparison to dilute solution. This is right what we observed in the 4P-PPV film sample.

Time-resolved PL measurements supply further information on the interchain interactions. Figure 4 shows the time-resolved PL decays of the 2P- and 4P-PPV films and the corresponding solutions. The time-resolved PL decay of dilute solutions of 2P- and 4P-PPV exhibit a single exponential decay, indicating a single fluorescent species and the interchain interactions are negligible. The measured decay times are 630 ps for 2P-PPV solution and 660 ps for 4P-PPV solution. The PL decay of 2P-PPV film can also be fitted by a single exponential function with a lifetime of 250 ps. The faster decay of the 2P-PPV film in comparison with its corresponding solution is due to the impurity-related nonradiative recombination processes. However, the decay of 4P-PPV film is nonexponential, and can be well fitted with a biexponential function with lifetimes of 510 ps and 1480 ns. The biexponential decay dynamics of 4P-PPV film may be a result of complex kinetics that includes excitons and excimers. The long-lived component of 1480 ps, does not appear in decay dynamics of the 4P-PPV solution, suggests it is associated with excimer recombinations, while the component of 510 ps associated with exciton recombinations.

4. Conclusions

In summary, we present the results of optical pumping (spectral narrowing), absorption, steady state and time-resolved PL measurements on two phenyl-substituted PPV derivatives. ASE was observed from the 2P-PPV film showing weak interchain interactions, while no ASE was observed from the 4P-PPV films having strong interchain interactions. The strong interchain interactions of 4P-PPV film induce the formation of excimers, thus leads to the reduced PL efficiency and prevent the ASE. Our experiments illustrate the polymer side chains can be used to modify the polymer chain packing morphology thus to affect the optical properties of conjugated polymers.

References
Figure captions

Figure 1. Chemical structures of the two phenyl-substituted-PPV derivatives used in this study.
Figure 2. The stimulated emission spectrum (solid line) and the steady state PL spectrum (dotted line) of the 2P-PPV film sample.
Figure 3. The absorption and PL spectra of film samples of 2P- and 4P-PPV, together with those of the corresponding solutions.
Figure 4. PL decays of the 2P- and 4P-PPV films and the corresponding solutions.