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Communication

A Streak Camera Study of Amplified Spontaneous Emission in Polyfluorene Thin Film

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ABSTRACT: We report on the photoluminescence (PL) properties of poly[2,7-(9-9-dioctylfluorene)] (PF) thin film under strong optical pumping using a streak camera system. When the excitation energy density increases above 72 μJ·cm^{-2}, the emission spectrum becomes narrower and PL decay curve comes to be faster simultaneously. These behaviors are clear evidence of Amplified Spontaneous Emission (ASE) due to a waveguided Stimulated Emission in slab structure of thin film. ASE threshold of 72 μJ·cm^{-2} is comparable with previous reports and PF is attractive as a gain medium for plastic lasers.

Since the first investigation on the electroluminescence (EL) of poly(p-phenylenevinylene),[1] semiconducting π-conjugated polymers have become more attractive materials for applications in optoelectronic devices such as light emitting diodes (LED), plastic lasers, and optical amplifiers.[2-5] Among the π-conjugated polymers, particularly a number of polyfluorene polymers and its copolymers could be promising candidates for realizing these devices due to the unique properties of good thermal and oxidative stability, good solubility in common organic solvents, excellent charge transport ability, and high photoluminescence (PL) quantum efficiency.[6-9] In addition to, they offer a wide range of available emission wavelength through chemical modification.[10]

In this letter, we studied the amplified spontaneous emission (ASE) in poly[2,7-(9-9-dioctylfluorene)] (PF) film with a planar structure by using a picosecond streak camera system. Because of the peculiar feature of streak camera, it provided two-dimensional (2-D) information about the changes of PL spectra and decay curves concurrently during the ASE process.

Up to now, it has been reported that polyfluorene derivatives showed low threshold of ASE, and a large net optical gain coupled with low loss in slab waveguide geometries.[11,12]

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However, there is a few studies on the PL lifetime of them although it is important parameter of pumping condition for lasing.[13] Especially, PL lifetime changes depending on ASE process has not been reported yet. Therefore, we have demonstrated the threshold behavior of ASE based on the spectral evolution as well as the change of PL lifetime.

The synthesis of PF and characterization has been described elsewhere.[14] The PF thin film with thickness of 100 nm was spin-coated on a quartz plate using chlorobenzene as a solvent. The thickness of PF film was determined by a TENCOR P-10 surface profiler.

The steady-state absorption and PL spectra were obtained through the use of Shimadzu UV-1800 and Hitachi F-4500, respectively. For the investigation on ASE behaviors of PF thin film, sample was excited by 315 nm pulses generated from a Raman shifter which was filled with 18-atm methane gas and pumped by the fourth harmonic (266 nm, FWHM 20 ps, 10 Hz) of a hybrid mode-locked Nd:YAG laser (Continuum, Leopard D-10). Excitation energy density was controlled by a set of neutral density filter and 200 shots of pulses were used for each acquisition. Emission from the PF thin film was obtained using a picosecond streak camera system which is consisted of main unit (Optronis, SCMU-ST-S20) combined with a spectrometer (CVI, DKSP240) and a CCD detector (Optronis, SCRU-SE-S).[15] After that, the time-resolved and time-integrated PL spectra and PL decay curves were extracted from the streak images obtained.

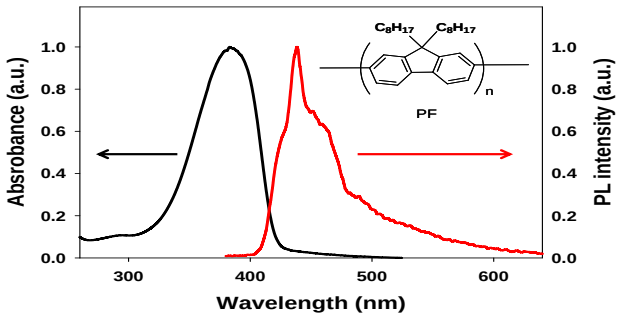

Figure 1. Steady-state UV-Vis absorption (black) and emission (red) spectra of PF thin film. Inset indicates chemical structure of PF.

Steady-state UV-Vis absorption and PL spectra of PF thin film are shown in Figure 1. Maximum absorption band is around 380 nm and PL spectrum shows vibronic structure with a maximum band of 440 nm, which are correspond to the previous result.[10]

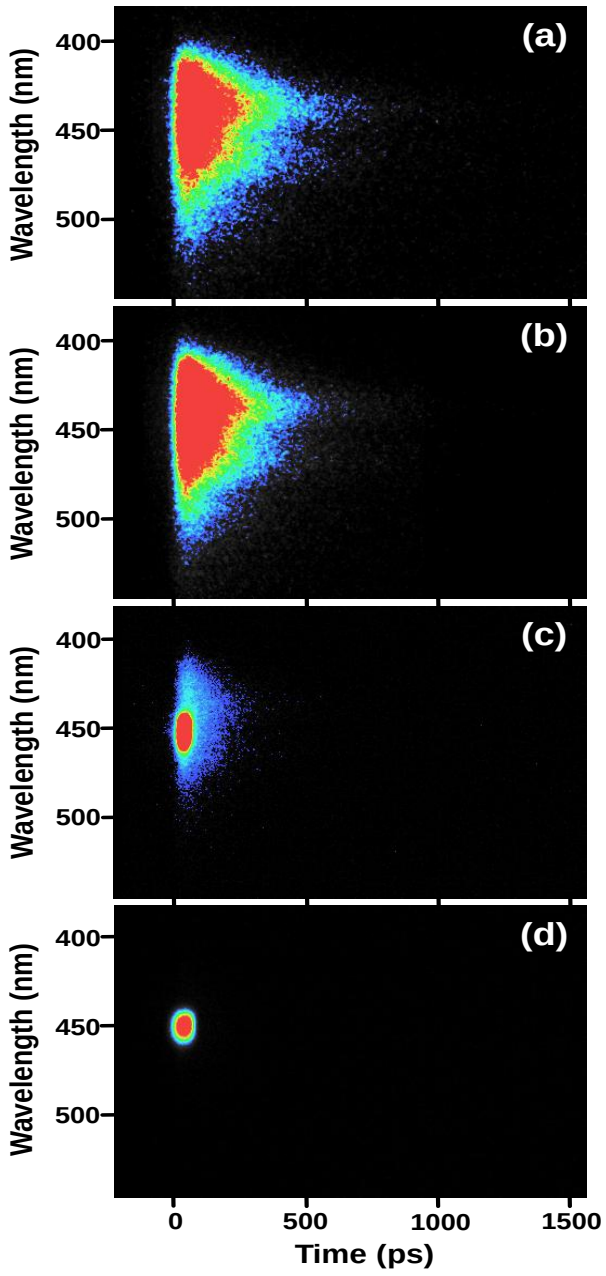

Figure 2. Two-dimensional images from streak camera of PF thin film with the excitation energy density of (a) 36, (b) 72, (c) 144, and (d) 360 μJ·cm^{-2}, respectively. Excitation wavelength is 315 nm and 200 shots of pulse are averaged.

Figure 2 shows the 2-D streak images of PF thin film measured under the excitation energy density of (a) 36, (b) 72, (c) 144, and (d) 360 μJ·cm^{-2}, respectively. As expected, when the excitation power increases gradually, the PL spectrum becomes narrower and PL decay curve gets to be faster at the same time. In particular, the PL feature at higher density of 360 μJ·cm^{-2}, it seems like a laser light (see Figure 2(d)). In order to easily understand the PL spectral evolution and change of PL decay curves as a function of excitation energy densities, the normalized PL spectra and decay curves were depicted in Figure 3.

In Figure 3(a), at low density of 36 μJ·cm^{-2}, the PL spectrum exhibits a broad spontaneous emission with the maximum at 440 nm and the full width at half maximum (FWHM) of 48 nm. Meanwhile, when excitation energy density increases to 144 μJ·cm^{-2}, a strong and narrow emission band emerges with a peak at 449 nm in the region that lies between two vibronic bands. As the excitation energy density increases above 360 μJ·cm^{-2}, the broad spontaneous emission rapidly collapses and only a narrowed PL band (FWHM of 12 nm) is observed.

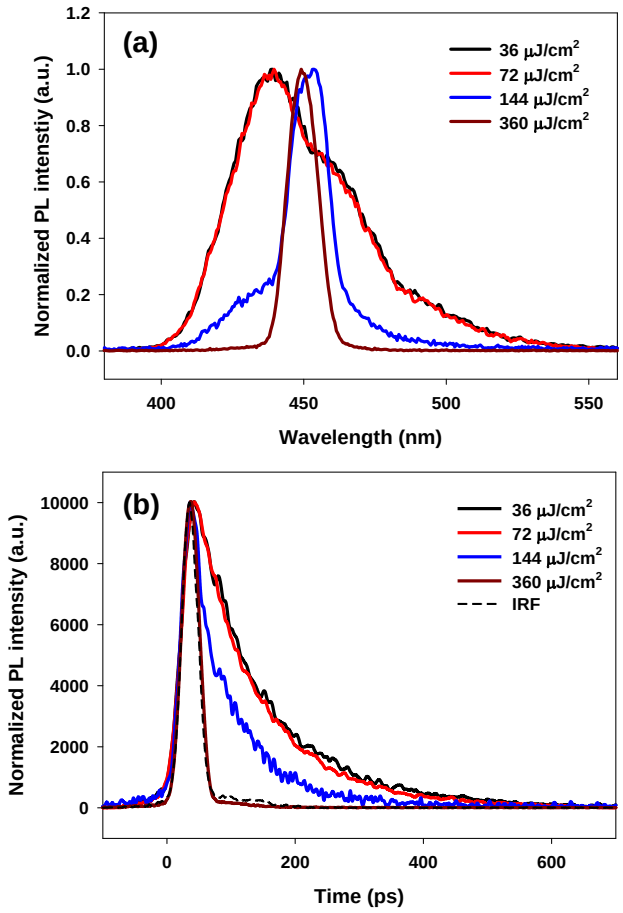

Figure 3. (a) PL spectral evolution and (b) change of PL decay curves which measured maximum intensity as a function of excitation energy densities. Each excitation energy density is denoted in figure. IRF indicates instrumental response function.

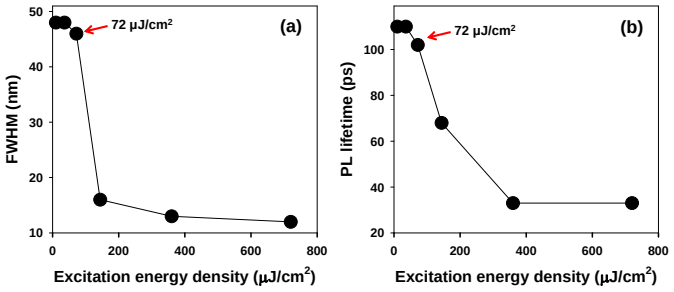

Figure 4. (a) Spectral bandwidths and (b) PL lifetimes of the PF thin film versus excitation energy densities.

Figure 3(b) presents the normalized PL decay curves which measured at maximum wavelength of each spectrum. At low density of 36 μJ·cm^{-2}, the emission follows a single exponential decay with a lifetime of 110 ps, while PL decay curve becomes faster with increasing of excitation energy density. Finally, PL lifetime of PF thin film reaches to 33 ps of instrument response function (IRF) at higher density of 360 μJ·cm^{-2}.

Appearance of a spectrally narrow band with suppression of the broad spontaneous emission and the shortening of PL lifetime are obviously ascribed to the stimulated emission process (ASE).[16] Figure 4 indicates a well-defined ASE threshold. Furthermore, there is good consistent threshold behavior which is based on either spectral narrowing or PL lifetime changes.

In summary, we have demonstrated the ASE in PF thin film by using a streak camera system. The estimated ASE threshold is 72 μJ·cm^{-2}, which is slightly higher than that of other PF film (29 μJ·cm^{-2})[17]. Above a threshold of ASE, it is observed the shortening of PL lifetime concomitant with the spectral narrowing.

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KEYWORDS: Amplified Spontaneous Emission (ASE), Polyfluorene thin film, Streak camera

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