

# Amplified spontaneous emission in the cyano-substituted oligo(p-phenylenevinylene) organic crystals: Effect of excitation wavelength

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We report an unusual phenomenon in amplified spontaneous emission (ASE) from cyano-substituted oligo(p-phenylenevinylene) (CNDPASDB) single crystals, i.e., the ASE peak wavelength, exhibits varied dependence on the pumping wavelength  $\lambda_{\text{ex}}$ . The former is basically kept a constant when  $\lambda_{\text{ex}} < 505$  nm, while a rapid redshift from 560 to 572 nm occurs when  $\lambda_{\text{ex}} > 505$  nm. The observation is different from stimulated Raman resonant scattering (SRRS) in two following aspects: the nonconstant Stokes shift and a much broader emission linewidth. A model describing competition between the stimulated emission and vibration relaxations has been proposed to interpret the underlying mechanism. © 2010 American Institute of Physics.

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Organic crystals are currently attracting keen attention as the active media for optoelectronic devices such as photovoltaic cells,<sup>1</sup> field-effect transistor,<sup>2,3</sup> and solid-state lasers.<sup>4,5</sup> Beside their intrinsically excellent charge-carrier transport capability compared with amorphous materials, they exhibit a remarkable optical gain.<sup>6</sup> A deep insight into the optical gain behaviors of the crystals is needed in order to realize organic crystal-based laser devices. Amplified spontaneous emission (ASE) is a useful technical route to explore effective lasing conditions. In the early 1970s, stimulated emission (SE) was demonstrated in pure and doped crystals of organic semiconductors.<sup>7,8</sup> In 1997, Fichou *et al.*<sup>9</sup> reported SE from a monolithic organic single crystal. Since then, an increasing number of ASE have been obtained from several classes of molecular crystals such as thiophene derivatives,<sup>10,11</sup> p-sexiphenyl,<sup>12</sup> fluorene/phenylene cooigimer.<sup>13,14</sup> However, most of the reported ASEs are pumped at a fixed wavelength in the violet or the blue part of the visible spectrum. Few researches deal with excitation wavelength effect. Yanagi *et al.*<sup>15,16</sup> studied narrow emissions [full width at half-maximum (FWHM)  $< 0.5$  nm] based on stimulated resonance Raman scattering (SRRS) by changing the excitation wavelength near the absorption edge, and found that the excitation wavelength played an extremely important role on the spectral position of emission. The emission peak was moved when the excitation wavelength varied, but with a constant Stokes shift, corresponding to a certain molecular vibration mode. Inspired by this work, we investigated excitation wavelength dependent ASE. Surprisingly, similar spectrally narrowed emissions (SNEs) from cyano-substituted oligo(p-phenylenevinylene) (CNDPASDB) single crystals under different pump wavelengths were found. A redshift as large as

12 nm of ASE line was attained when the pump-wavelength exceeded 505 nm. However, a pronounced difference with SRRS is, here the Stokes shift is not fixed, but decreased as the excitation wavelength increase and the FWHM is much broader. A different carrier relaxation scenario has been presented in this letter to clarify the underlying physics.

The inset of Fig. 1(a) shows the chemical structure of CNDPASDB. Single crystals ( $P\bar{1}$  space group with a

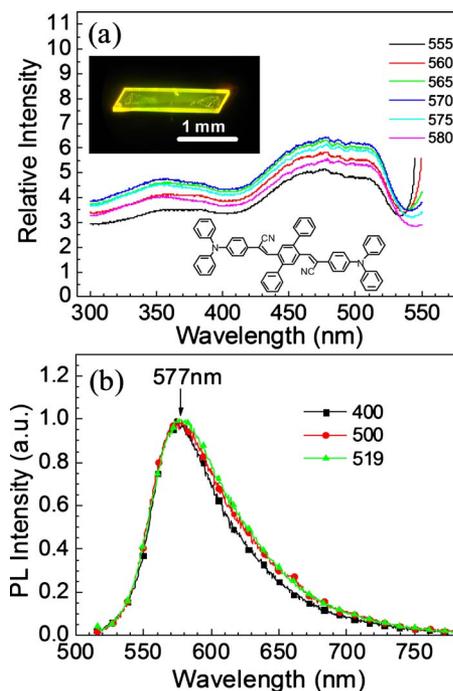


FIG. 1. (Color online) (a) Excitation spectra of a CNDPASDB single crystal (monitored at different wavelength). Inset: the photograph of the crystal under fluorescence microscope and the chemical structure of CNDPASDB. (b) PL spectra acquired at variable excitation wavelength.

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$=6.6429 \text{ \AA}$ ,  $b=10.541 \text{ \AA}$ ,  $c=16.573 \text{ \AA}$ ,  $\alpha=83.88^\circ$ ,  $\beta=86.20^\circ$ ,  $\gamma=84.05^\circ$ , and  $Z=1$ ) were prepared by solvent-exchange process at room temperature under rigorous exclusion of light according to the described procedure.<sup>17</sup> The excitation spectra of crystals at room temperature are shown in Fig. 1(a). Owing to the interactions between the molecules, the excitation spectroscopy in the crystals is different from their monomer counterpart in solution.<sup>15</sup> Photoluminescence (PL) and ASE were recorded using AS5216 AvaSpec spectrometers. Optical pumping by the femtosecond (fs) laser pulses ( $<130$  fs) was performed using a kilohertz ultrafast optical parametric amplifier (OPA) that is tunable from 235 nm to 3  $\mu\text{m}$ . An amplified Ti:sapphire laser (Spitfire Pro) emitting pulses at 800 nm with a duration of 120 fs was used to pump the OPA, from which the fourth harmonic of the idler beam was used in the region from 450 to 525 nm. The 400 nm wavelength was directly produced from the amplifier by a nonlinear optical crystal of  $\beta$ -barium borate (BBO). Pump pulses illuminated the sample at normal incidence and they were focused to an elliptical spot using a cylindrical lens. The pump energy was varied using a neutral density filter and monitored with a joule meter. The crystal was glued on a quartz substrate. In both PL and ASE experiments, light emitted from the crystals was collected from the edge using a lens with focus length=50 mm to couple the light into the input fiber of a spectrometer. All measurements were conducted in air at room temperature.

The steady-state fluorescence spectra pumped at different wavelengths [Fig. 1(b)] ( $\lambda_{\text{ex}}=400, 500$ , and 519 nm) are almost identical, suggesting that the emission is consistent with Kasha's rule.<sup>18</sup> At low pump energy, the spectrum consists of a broad fluorescence band (FWHM $>60$  nm). While the PL intensity abruptly increases upon the pump rising above the ASE threshold, and the PL spectrum is narrowed to FWHM $\sim 15$  nm. In the steady state, the PL spectra are independent of the excitation wavelength. However, the situation is changed when the excitation is high enough. For example, the emission is centered at about 560 nm for  $\lambda_{\text{ex}}=495$  nm, where there is a relative blueshift with spontaneous emission. The peak position alters when  $\lambda_{\text{ex}}$  exceeds 505 nm. Figure 2(a) shows the PL spectra taken at  $\lambda_{\text{ex}}=495, 509, 517$ , and 523 nm. In order to investigate the excitation-wavelength effect in a wider region, the pump was extended from 400 to 523 nm. Figure 2(b) shows the ASE wavelength as a function of  $\lambda_{\text{ex}}$ . The ASE peak position did not change when  $\lambda_{\text{ex}}<505$  nm. However, it is very interesting when the pump wavelength further increases. The ASE line became redshifted with the increase in pump wavelength. The shift is as large as 12 nm, when the pumping changes from 505 to 523 nm. No gain narrowed was observed when the  $\lambda_{\text{ex}}$  was raised to beyond 523 nm.

The redshift behavior is very similar to the stimulation of resonance Raman scattering (SRRS),<sup>16</sup> which is assisted by molecular vibrations. To determine the physical origin of the shift, off-resonant Raman spectroscopy was performed under excitation with 785 nm laser, as is shown in inset of Fig. 3(a). The prominent peak is at  $1580 \text{ cm}^{-1}$  for the CNDPASDB crystals. The dependence of the ASE shift on the excitation wavelength was also plotted (Fig. 3) for comparison. As we can see, the wavenumber of the ASE shift is slight higher than  $1580 \text{ cm}^{-1}$  suggesting the vibration of the molecule did not contribute to the shift, and it also shows

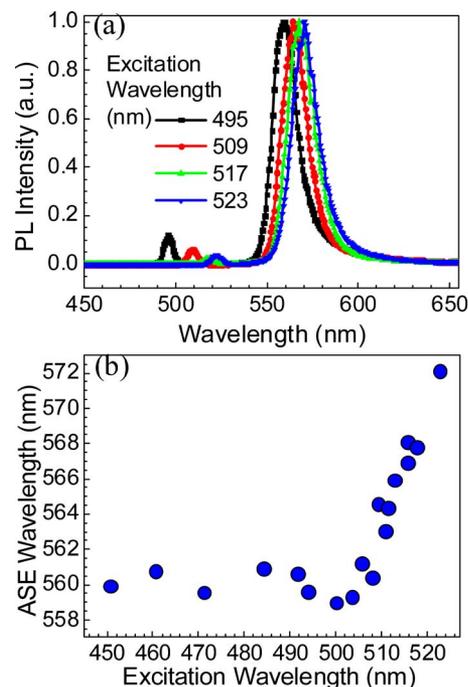


FIG. 2. (Color online) (a) Normalized light emission spectra of CNDPASDB crystals above the ASE threshold at varied excitation wavelength. (b) Relationship between the ASE emission wavelength and excitation wavelength in CNDPASDB organic crystal.

minute change when the excitation wavelength increase, differing from the constant Stokes shift characteristic of SRRS. All these evidences rule out the possibility of SRRS, and the light (from 505 to 523 nm) is ordinary amplified by SE, i.e., ASE.

A simple model [Fig. 3(b)], i.e., SE process compete with vibration relaxation (VR) in the crystals, was proposed for this wavelength shift. It is reasonable to assume that there is a "induction time"<sup>19-21</sup> a time lag in the appearance of SNE after an instantaneous the building up of a normal emis-

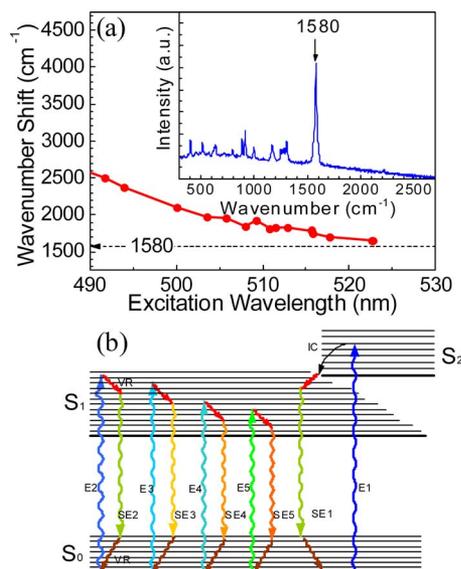


FIG. 3. (Color online) (a) ASE emission shift with varied excitation wavelength. Inset: off-resonant Raman spectrum of CNDPASDB crystals. (b) Proposed ASE and vibration relaxation competition model to explain the ASE line shift. VR: vibrational relaxation; IC: internal conversion; E: excitation; and SE: stimulated emission.

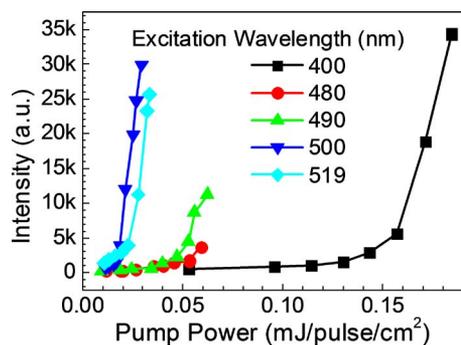


FIG. 4. (Color online) PL peak intensity of light emission as a function of the incident laser energy intensity at different wavelengths.

sion, for the ASE in the first picoseconds. The lag is comparable with the time of “slow” VR in this region. Then the ASE and the relaxation will complete with each other. A blueshift of the ASE peak maximum is evident as mentioned above by comparing the ASE spectroscopy and spontaneous emission, indicating that the ASE process occurs on a time scale faster than the spectral diffusion.<sup>22</sup> For the higher energy excitation, it will need longer time to relax for the electrons, and the SE begins to start at high vibration level, corresponding to short wavelength. For the low energy excitation, the SE occurs at low vibration level, corresponding to long wavelength, and the ASE peak will relatively red shift.

Furthermore, the wavelength-dependent ASE threshold were also evaluated for the same crystal. Note in Fig. 4 that the threshold at 400 nm is almost one order of magnitude different from the case of 500 nm pump, 0.152 mJ/pulse/cm<sup>2</sup> and 0.017 mJ/pulse/cm<sup>2</sup>, respectively. The loss coefficient decreases rapidly when the wavelength increases because of residual absorption. This should be a part reason for the high threshold of pumping at 400 nm. Another reason may arise from the less effective excitation (see the excitation spectrum, where the 400 line is in the valley). Therefore, it is important to choose suitable pump wavelength to lower the threshold.

In conclusion, we investigated ASE properties of cyano-substituted oligo(p-phenyl enevinylene) (CNDPASDB) single crystals with different pump wavelengths ranging from 400 to 523 nm. The excitation wavelength tuning resulted in the following unique spectral features: a wavelength shift of ASE was observed as large as 12 nm when the excitation exceeds certain wavelength, as is very similar with

SRRS. The unusual observation is explained with a model involving the competition between the SE and VR. The mechanism is promisingly useful for realizing effective lasing and amplification devices from organic crystalline materials. This work was supported by NSFC (Grant Nos. 60525412 and 90923037).

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