Laser oscillation from hexagonal crystals of a thiophene/phenylene co-oligomer

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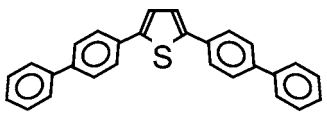
The characteristics of the unusually narrowed emission from hexagon BP1T crystals were investigated by photopumping them with a line laser beam. The wavelengths and strengths of the emission lines sensitively depended on the position and the angle of the crystal. The threshold of the excitation fluence decreases inversely proportional to the crystal length. We have concluded that the unusually narrowed emission is the laser oscillation by laser cavity resonance within a waveguide. The shape and size of the excitation laser beam play an important role in the laser oscillation. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2181278]

I. INTRODUCTION

Organic semiconductors have attracted growing interest over the past decade due to their excellent optoelectronic properties. Especially conjugated semiconducting molecules and polymers have great potentials as useful materials for photonic devices, because spectrally narrowed emissions (SNEs) were observed in these materials through photoexcitation.[1,2] Fichou *et al.*[3] and Horowitz *et al.*[4] first demonstrated the SNE from the thiophene-based conjugated molecules in the form of single crystals. Yanagi *et al.*[5] also observed the SNE from epitaxially oriented *p*-sexiphenyl crystals. Nagawa *et al.*,[6] Hibino *et al.*,[7] and Ichikawa *et al.*[8] also observed the SNE using a variety of thiophene/phenylene co-oligomers. They attributed the relevant SNE to the amplified spontaneous emission (ASE). The linewidths of these SNEs were usually level with several nanometers. However, we observed the unusually narrowed emission with the linewidth of 0.07 nm under an absence of an active oscillation resonator from hexagonal organic crystals by photopumping them with a line laser beam.[9]

The SNEs may be connected with, e.g., ASE, mirrorless ASE lasing, and laser cavity resonance. The ASE is related with any situation in which the spontaneous emission coming from population-inverted atoms is linearly amplified by the same group of atoms with an optical gain.[10] As mentioned above, in fact, the ASE has definitively been observed with crystals of various thiophene/phenylene co-oligomers.[6–8] The origin of such ASE is likely to be sought from the following possibilities.[9] (i) Some laser systems have such extremely high gain that they need no mirrors. They can emit very bright and more or less quasicoherent beams from either end of the laser medium simply as a result of very high-gain amplification of their own internal spontaneous emission traveling along the length of the laser-gain medium.[10] (ii) Alternatively, crystal edges may well function as an optical resonator; for instance, a couple of crystal edge planes paralleling each other can be a Fabry-Pérot cavity whose length is defined as a separation between the two planes.

With these possibilities in mind we have further pursued the unusually narrowed emissions from long hexagonal crystals of 2,5-bis(4-biphenylyl)thiophene[11,12] (BP1T; see Fig. 1 for its structural formula). In other words, we chose different crystals in size and determined the excitation fluence threshold for the spectral narrowing as a function of crystal lengths. We also varied the excitation geometry within the crystal. This was done either by changing the excitation position or by rotating the crystal around the normal to the hexagonal crystal face. Most importantly, the excitation beam shape and size significantly influence the emission characteristics. When the excitation beam of 12–20 μm in width is used, the unusually narrowed emissions [full width at half maximum (FWHM) typically 0.1 nm or less than that] can reproducibly be observed. As a result, we found out the following important results. (i) The wavelengths and strengths of the unusually narrowed emission lines sensi-



2,5-Bis(4-biphenylyl)thiophene

FIG. 1. Molecular structure of BP1T.

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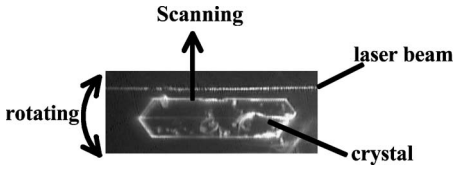

FIG. 2. Scanning and rotating of the BP1T crystal.

tively depended on the excitation geometry. (ii) The threshold for the spectral narrowing has decreased inversely proportional to the crystal lengths. On the basis of these observations we conclude that the unusually narrowed emissions result from the laser oscillation within a Fabry-Pérot cavity formed with the crystal edges on either side.

II. EXPERIMENTAL SETUP AND EMISSION MEASUREMENTS

A schematic representation of the experimental apparatus and their setup can be seen elsewhere.[9] The crystal was photopumped by a *Q*-switched Nd:YAG (yttrium aluminum garnet) laser with a pulse width of 1.8 ns and a wavelength of 355 nm. The laser beam was expanded with a spherical planoconcave lens with a focal length of −25 mm and a spherical planoconvex lens with a focal length of 100 mm. An iris diaphragm and cylindrical lens (100 mm focal length) were used to focus the laser beam upon a $0.012-0.073(\text{width})\times 6.0(\text{length})\ \text{mm}^2$ line-shaped rectangle that crossed the whole crystal along the crystal long axis. The beam width on the crystal was changed by shifting the position of the focusing cylindrical lens. The crystal was fixed on a quartz glass slide substrate with its crystal face in close contact with the substrate plane. We carefully chose different hexagon BP1T crystals of 0.56–1.06 mm in length and ~0.15 mm in width (and the thickness of ~10 μm).

The line-shaped rectangular beam was incident vertical to the crystal face with the beam long axis parallel to the direction of the crystal long axis (see Fig. 2). The laser beam was linearly polarized by using a half wave plate in the direction either perpendicular or parallel to the crystal long axis. The emission from the edge of the crystal long axis was introduced via an optical fiber to a spectrometer with a focal length of 0.75 m and a 300 or 1200 line/mm grating. The resolutions of the spectrometer were 0.2 and 0.05 nm using the 300 and 1200 line/mm gratings, respectively. A thermoelectrically cooled image-intensified charge-coupled-device (ICCD) camera was used to measure the emission spectra. An ultraviolet cut filter was inserted between the crystal and the fiber to avoid the damage of the ICCD camera caused by the laser beam. A polarizer for visible light was used to measure the polarization of the emission. The space distribution of emission spectrum was measured continuously, moving the crystal that was mounted on a motorized stage. The laser beam was scanned from the top to the bottom of the crystal. In turn, the crystal was continually rotated around the normal to the hexagonal crystal face. The rotation angles were set at 0–36 mrad by a 3 mrad step. Figure 2 shows the image of scanning and rotating of the BP1T crystal. The space resolution of the emission measurement was 1 μm (from the laser repetition rate of 50 Hz, the stage traveling speed of 2 μm/s, and integration of 25 times). Spectra at various rotation angles of the crystal were measured.

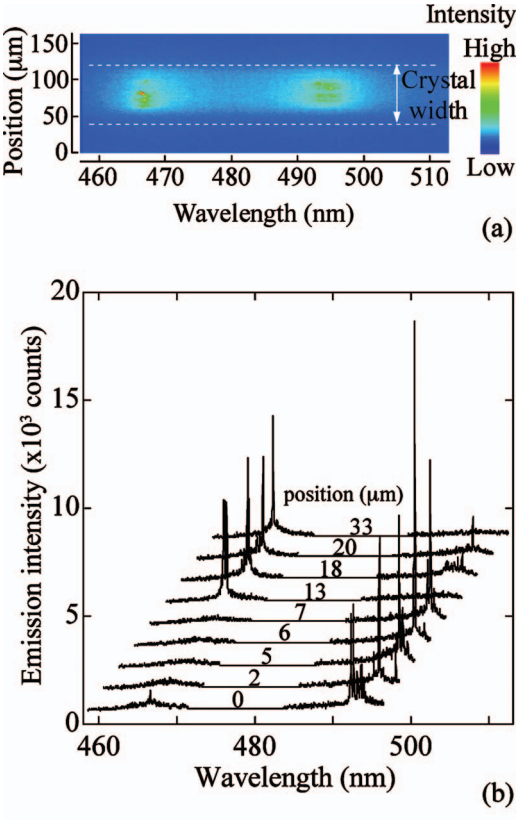

FIG. 3. (Color) Space distribution of the emission. The beam width was 20 μm.

III. RESULTS

The results relevant to all the spectral data were obtained with the excitation beam of 12–20 μm in width except for those in Fig. 6.

The wavelengths and strengths of the emission lines sensitively depended on the specific excitation geometry of the crystal. When the crystal was scanned to obtain the spectrum space distribution, the unusually narrowed emission lines were observed at some specific locations of the crystal. Figure 3 shows the space distribution of the emission. In Fig. 3(a), the red points show the unusually narrowed emission and other colors are photoluminescence or ordinary ASE. These spectra were taken with the lower line-density grating (300 lines/mm). In Fig. 3(b), from the zero position arbitrarily chosen to 7 μm an unusually narrowed emission line at 493 nm dominates, while from the irradiated location of 13–33 μm an emission line changes to around 466 nm. These spectra were taken with the higher line-density grating (1200 lines/mm). The emission spectrum changes greatly by the difference in the position of several micrometers.

Figure 4 shows spectra at various rotation angles of the crystal. The unusually narrowed emissions were observed at angles 9–24 mrad. Thus, the occurrence of the unusually narrowed emission is again sensitive to the excitation geometry of the crystal.

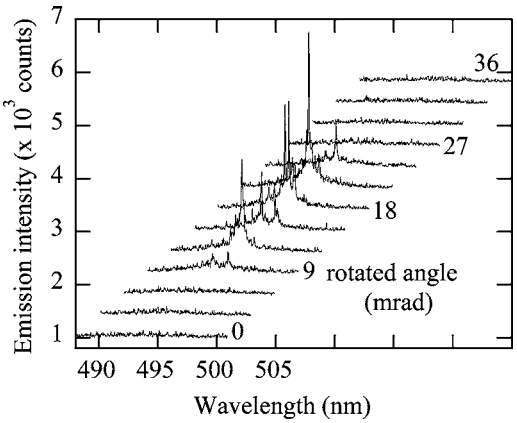

FIG. 4. Spectra at various rotation angles of the crystal. The rotation angles were set at 0–36 mrad by a 3 mrad step. The beam width was 12 μm.

Figure 5 depicts as a function of reverse crystal lengths the threshold of the excitation fluence, at which the narrowing of spectrum starts. The threshold of the excitation fluence increases lineally proportional to the reverse excitation length. Figure 6 shows the spectral width for various beam width as a function of the excitation fluence. When the beam width was 43 or 73 μm, the spectral width gradually decreased beyond the definitive threshold with increasing the excitation fluence and became constant (~5 nm). Note that the threshold in the beam widths of 43 and 73 μm is slightly different. This could be attributed to the difference of the absorption loss in nonexcitation region. On the other hand, when the beam width was 12 μm, the emission width suddenly decreased to ~0.1 nm around the fluence of 8 mJ/cm^2.

Figure 7 shows the dependence of the emission spectrum on the rotated angle of a half wave plate, which changes the polarization of the excitation laser beam. The rotated wave plate angles of 0° (90°) and 45° correspond to the polarization in the direction perpendicular and parallel to the crystal long axis, respectively. The data were collected using a crystal with 0.72 mm in length. The emission intensity of parallel polarization is 3.8 times as large as the perpendicular polarization.

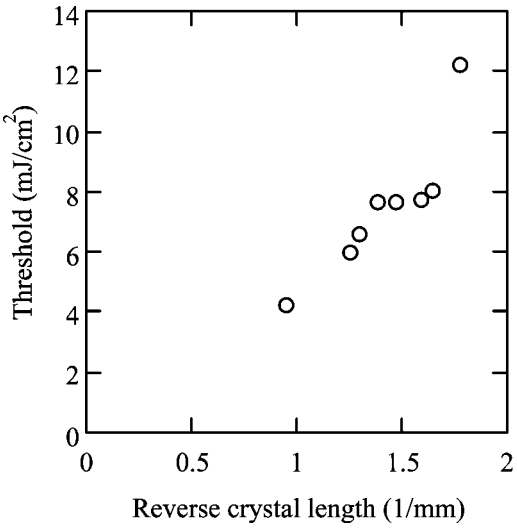

FIG. 5. The threshold of the excitation fluence, at which the narrowing of spectrum starts, for various crystal lengths. The beam width was 12 μm.

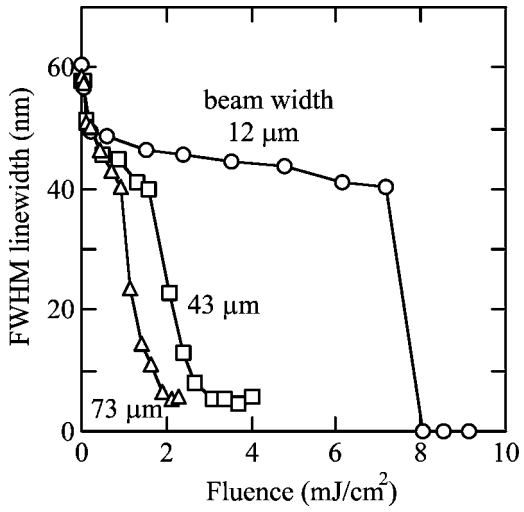

FIG. 6. The spectral width for various beam widths as a function of the excitation fluence.

Figure 8 shows the polarization of the emission, which was measured by rotating the polarizer in front of the optical fiber. The rotated polarizer angles of 0° and 90° correspond to the transverse electric (TE) and transverse magnetic (TM) modes, which are polarized parallel and perpendicular to the hexagonal face of the crystal, respectively. The emission intensity of the TM mode is larger than the TE mode and the polarization ratio defined as the TM/TE intensities is 5.6. This large ratio obviously reflects the upright disposition of the transition dipole moments against the hexagonal face.

IV. DISCUSSION

The occurrence of the unusually narrowed emissions depends strongly upon the excitation geometry of the crystal. This is clearly indicated in Figs. 3 and 4 and most likely related to the fact that the mode stability should rigorously

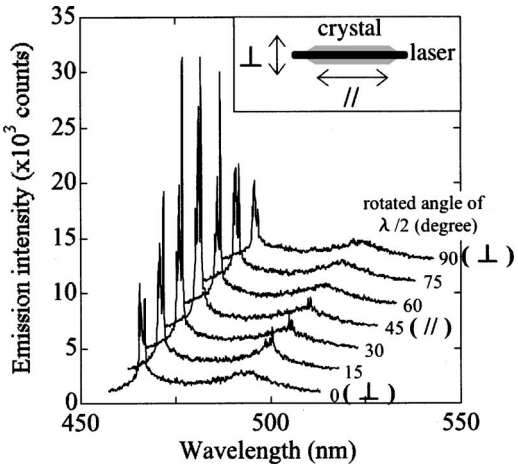

FIG. 7. The dependence of the emission spectrum on the polarization of the excitation laser beam. The inset represents the perpendicular ($\perp$) and parallel ($\parallel$) polarizations of the excitation laser beam. The beam width was 20 μm.

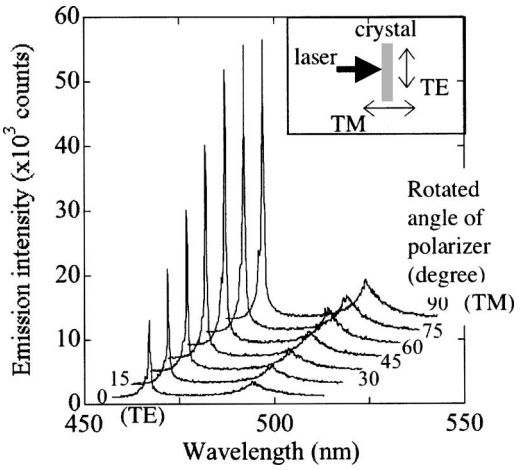

FIG. 8. The polarization of the emission. The inset shows the cross section of a crystal. TE and TM denote the transverse electric and transverse magnetic, respectively. The beam width was 20 μm.

be maintained for the laser oscillation. Note that in this respect the laser oscillation differs from the ASE. The excitation beam shape and size also play a crucial role. We emphasize that only when the excitation beam width is as narrow as 10 μm in width, the unusually narrowed emissions can reproducibly be observed. We refer this to the decrease in the number of transverse electromagnetic modes. The anisotropic emission from organic molecules might be responsible as well.

The amplification of the ordinary ASE can be written as

$$I_{\text{out}} = I_{\text{in}} \exp[(\gamma - \alpha)L], \tag{1}$$

where I_{out} and I_{in} are, respectively, the output and input intensities of light, γ is an amplification gain per length, α is a loss per length, and L is a gain length. The amplification of the light occurs when $\gamma > \alpha$ and the spectrum width of the ASE becomes narrow with increasing gain length. However, because in the case of the ASE the loss (α) does not depend on the gain length, the threshold of the excitation fluence should not depend on the gain (crystal) length either. On the other hand, in a Fabry-Pérot resonator with reflectivity R and the distributed absorption coefficient of the crystal β, the laser oscillation sets in when the amplification gain per length (γ) is equal to the total loss (α) including that arising from the reflection at both sides of the cavity,[13]

$$\alpha = \beta - (1/L)\ln(R). \tag{2}$$

Since the gain is proportional to the excitation fluence at and below the oscillation threshold,[13] Eq. (2) implies that the threshold fluence in laser oscillation changes inversely proportional to the excitation length. This is indeed the case with our results (see Fig. 5). Therefore the data of Fig. 5 rule out the possibility of ASE and indicate that the unusually narrowed emission results from the laser oscillation by cavity resonance. Both the crystal edges comprise the cavity (Fig. 2).

Figure 7 demonstrates the presence of a set of sharply resolved split lines. The average number of intervals of those lines is estimated to be ~0.63 nm. This number is consistent with that (0.47–0.65 nm) calculated for a Fabry-Pérot resonator with its length of 0.72 mm (i.e., an actual size of the crystal). The calculation was made on the assumption that a refractive index of the crystal falls within 2–1.47. Notice that 1.47 is the refractive index of the quartz glass substrate and that of crystal should be no smaller than this. Thus the laser oscillation is characterized by the presence of a Fabry-Pérot cavity formed with the crystal edges on either side.

V. CONCLUSION

The characteristics of the unusually narrowed emission from a hexagon BP1T crystal were investigated by photopumping with a line laser beam. The wavelengths and strengths of the emission lines sensitively depended on the excitation geometry. In particular, the width of the excitation beam plays a crucial role. Only when the excitation beam is as narrow as 10 μm in width, the unusually narrowed emissions can reproducibly be observed. The threshold of the excitation fluence for the spectral narrowing decreases inversely proportional to the crystal length. This obviously indicates that the unusually narrowed emission is the laser oscillation by laser cavity resonance within a waveguide. The numerical calculation of intervals of the lasing lines implies that the laser oscillation is characterized by the presence of a Fabry-Pérot cavity formed with the crystal edges on either side.

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