

# Origin of the amplified spontaneous emission from thiophene/phenylene co-oligomer single crystals: Towards co-oligomer lasers

Kazuki Bando,<sup>a)</sup> Toshiteru Nakamura, and Yasuaki Masumoto  
*Institute of Physics, University of Tsukuba, Tsukuba 305-8571, Japan*

Fumio Sasaki and Shunsuke Kobayashi  
*Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST),  
 Tsukuba 305-8568, Japan*

Shu Hotta  
*Department of Polymer Science and Engineering, Faculty of Textile Science, Kyoto Institute of Technology,  
 Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan*

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Photoluminescence (PL) and optical gain measurements have been performed for single crystals of thiophene/phenylene co-oligomer at room and low temperatures. Broad PL bands are transformed to be an ensemble of several spectrally narrower vibronic peaks with decreasing temperature. Very sharp lines as narrow as  $\sim 3$  meV are observed at 10 K under weak excitation. Intensities of sharp emission lines superlinearly increased at 10 K under intense excitation, showing the amplified spontaneous emission (ASE). The ASE bands were clearly identified to the sidebands of  $B_1$  and  $A_1+B_1$  vibronic modes. The ASE is also observed at room temperature under the intense excitation. Spectroscopic investigation at varied temperatures enabled us to identify the origin of the ASE band to the vibronic sidebands of the electronic transition of the thiophene/phenylene co-oligomer crystals. In addition, highly polarized optical gains  $\sim 50$  cm<sup>-1</sup> were obtained for the two ASE bands at room temperature. © 2006 American Institute of Physics. [DOI: 10.1063/1.2159083]

## I. INTRODUCTION

Conjugated semiconducting polymers and oligomers are paid much attention as materials for optical and electronic devices in recent years. In particular, they are potentially useful for the development of laser devices, because spectrally narrowed emission (SNE) has been observed in them.<sup>1,2</sup> The SNE due to amplified spontaneous emission (ASE) has been demonstrated from single crystals of thiophene and phenylene oligomers,<sup>3-5</sup> and single crystals of thiophene/phenylene co-oligomers.<sup>6-8</sup> In addition to the ASE, stimulated resonance Raman scattering has been also observed from the co-oligomer crystals.<sup>9-12</sup> The single crystals of the co-oligomers in high quality and uniformity allow light propagation in the crystals working as a self-waveguide such as a polariton. The light propagation in the crystal waveguide is very important for efficient light amplification.

Nevertheless, fundamental optical properties and the origin of the ASE have not been known yet for 2,5-bis(4-biphenyl)thiophene (BP1T) crystals<sup>13,14</sup> from which the ASE has been demonstrated only at room temperature so far.<sup>6-8,12</sup> In order to elucidate those, we have investigated the photoluminescence (PL) properties of the BP1T crystal at low temperature and elevated temperatures under both weak and intense excitations. At low temperature, we have observed several equidistantly separated sharp PL lines from the BP1T crystal and identified them to vibronic sidebands of the molecules. With the increase of temperature, the PL bands broadened but their origins are clearly identified.

Moreover, superlinear increases of these vibronic sidebands are clearly observed. In addition, optical gain coefficients of the ASE are also obtained by using a variable-stripe-length (VSL) excitation method at room temperature.

## II. EXPERIMENT

First, PL measurements were performed at temperature ranging from 10 to 300 K. A He–Cd continuous-wave (cw) laser (325 nm) and a pulsed dye laser (400 nm, 30 ns) pumped by a XeCl excimer laser were used as excitation sources for weak and intense excitation, respectively. The BP1T plateletlike crystals whose dimensions are ranging from a few hundred micrometers to a few millimeters were used. The *ab* planes of the crystalline faces were in close contact with copper substrates. The crystals were cooled in a cryostat from room temperature to 10 K. The emission was detected by using a monochromator and a charge-coupled device. The laser beam excited the crystal and the PL including the ASE was detected along the normal direction of the substrate in the usual PL measurements. However, for the optical gain measurements, the ASE was detected from the in-plane direction and the gain coefficients of the ASE were obtained by using the VSL excitation method.<sup>15,16</sup> In the measurements, the stripe length of a rectangular excitation beam focused through cylindrical lenses and an aperture was varied from 0 to 0.15 mm, and the emitted light passing through the stripe region was detected.

<sup>a)</sup>Electronic mail: bando@sakura.cc.tsukuba.ac.jp

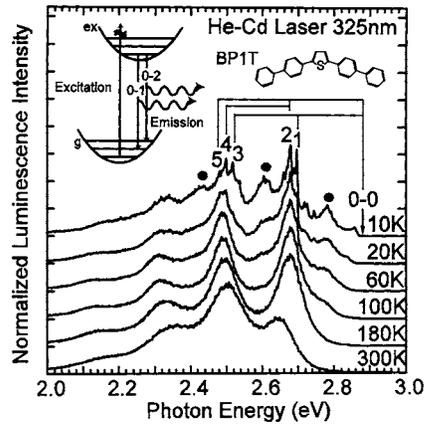


FIG. 1. Temperature dependence of PL spectra in the weak excitation condition. The PL bands appearing at low temperature are indicated by closed circles, which are due to extrinsic origins of the crystal. The sharp peaks indicated by 1–5 are due to vibronic sidebands of the 0–0 transition in the molecules. The right and left insets show the chemical structure of the BP1T molecule and excitation and emission processes of the BP1T crystals in the configuration coordinate, respectively.

### III. RESULTS AND DISCUSSION

Figure 1 shows PL spectra of the BP1T crystal under the weak excitation by a He–Cd laser as a function of temperature. The right inset of Fig. 1 shows the chemical structure of the BP1T molecule. Broad PL bands appear at room temperature, which are due to the vibronic modes of the oligomers.<sup>9</sup> The left inset shows excitation and emission processes of the BP1T crystals in the configuration coordinate.<sup>17</sup> The highest and second highest-energy bands in the PL spectrum at room temperature originate from 0–1 and 0–2 vibronic sidebands, respectively. The broadbands are changed to be an ensemble of several sharp peaks with decreasing temperature, and PL bands shown by closed circles appear, as is shown in Fig. 1. The PL bands are considered to be due to extrinsic origins in the crystal, such as aggregates of the molecules or defects of the crystal, because they appear only at low temperature.<sup>18</sup> The sharp peaks numbered by 1–5 can be interpreted as vibronic sidebands by using combinations of two vibronic modes. Two Raman modes in BP1T crystals have been reported to be  $\sim 1450$  ( $E_{A_1}$ ) and  $\sim 1600$  ( $E_{B_1}$ )  $\text{cm}^{-1}$  modes of  $A_1$  and  $B_1$  symmetries of the BP1T molecules, respectively.<sup>9,11</sup> A difference between the two modes is  $\sim 150$   $\text{cm}^{-1}$ , which is consistent with 150  $\text{cm}^{-1}$  (18.6 meV) of an energy difference between two remarkable peaks, 1 and 2, observed in the PL spectra. This indicates that peaks 1 and 2 are due to the 0–1 vibronic transitions of the  $A_1$  and  $B_1$  modes, respectively. Therefore, it is deduced that the 0–0 transition should be located at 2.877 eV, as is shown by an arrow in Fig. 1. In addition, subtraction of energies of two combinational modes,  $2E_{A_1}$ ,  $E_{A_1} + E_{B_1}$ , and  $2E_{B_1}$ , from the energy of the assumed 0–0 transition (2.877 eV), respectively, exactly coincide with those of peaks 3, 4, and 5. This again indicates that the 0–0 transition should be located at 2.877 eV. In consequence, the peaks 1 and 2 were assigned to the 0–1 vibronic transitions of the  $A_1$  and  $B_1$  modes, respectively. A reason why the 0–0 transition was not observed in PL spectra is considered as follows. The

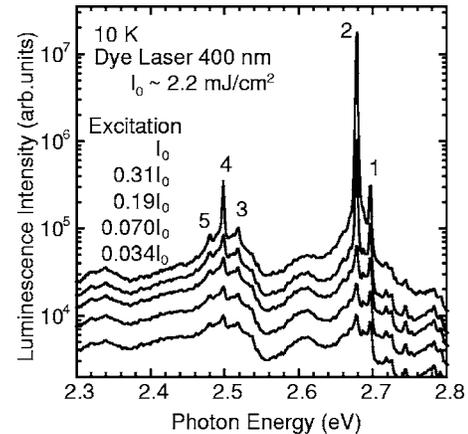


FIG. 2. Excitation density dependence of PL spectra under intense excitation at 10 K. The PL spectra are plotted on a logarithmic scale.

transition dipole moments are parallel to the long molecular axes for the BP1T molecules with  $C_{2v}$  symmetry, and the BP1T molecules are aggregated as crystals with a herringbone fashion on the  $ab$  plane of the crystalline face.<sup>14</sup> Therefore, the crystals are indicated as  $H$  aggregates which lead to the nonemissive 0–0 transition at the band edge. This feature for the optical transitions is also seen in odd-numbered oligothiophenes.<sup>19</sup>

Figure 2 shows PL spectra of the BP1T crystal at 10 K under pulsed excitation as a function of the excitation density. The PL spectra are drawn on a logarithmic scale. The PL measurements were performed under the excitation of a dye laser operated at 400 nm. A PL spectrum under the lowest excitation density shown by the undermost curve in Fig. 2 corresponds to that under the cw excitation at 10 K shown in Fig. 1. However, a line shape of the PL spectrum drastically changes under the intense excitation. The intensities of the three peaks indicated by 1, 2, and 4 superlinearly increase with increasing excitation density, as seen in Fig. 2. Spectral narrowing of the whole PL bands and superlinear increases of their intensities have been reported under intense excitation at room temperature.<sup>6–8,12</sup> The drastic behavior observed at 10 K is analogous to that of the SNE at room temperature. Therefore, the superlinear increases in the line intensities are considered to be the origin of the SNE and due to the ASE. In addition, it can be slightly observed that the peaks 3 and 5 also show superlinear increases in their intensities as well as the peaks 1, 2, and 4 (Fig. 2). These observations support that the vibronic modes of the BP1T molecules are responsible for the ASE at both room temperature and low temperatures. We also collected the ASE from the crystal edges along the direction parallel to the crystal plane, and confirmed that line shapes and the excitation density dependence of the obtained spectra were almost the same as that detected from the normal direction of the crystal. It is therefore considered that the ASE is observable from any directions because of the scattering of the ASE at the crystal edges.

The most intense ASE peak indicated by 2 is shown in Fig. 3 as a function of the excitation density with increasing temperature. The peak intensity linearly increases under the excitation density lower than  $\sim 400$   $\mu\text{J}/\text{cm}^2$  at any temperatures. However, the peak intensity superlinearly increases

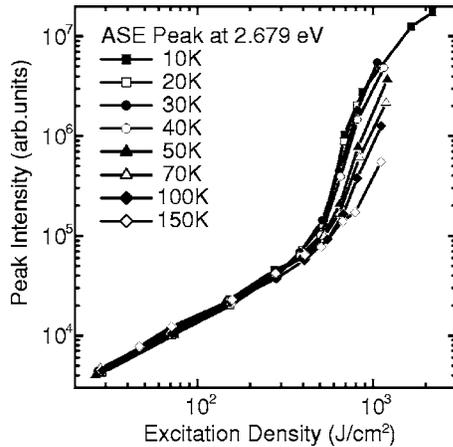


FIG. 3. Excitation density dependence of the PL intensity at 2.679 eV where the ASE appears.

with increasing excitation density above  $\sim 400 \mu\text{J}/\text{cm}^2$ , which reflects the appearance of the ASE. The thresholds of the ASE are almost independent of temperature, as seen in Fig. 3. The observed threshold almost agrees with that observed at room temperature in the previous report.<sup>6</sup> This means that the excited states are not activated to the nonradiative centers with increasing temperature at least up to 150 K. Weak temperature dependence of the threshold reflects that the BP1T single crystal is in high quality. The BP1T crystals are expected to generate the stable ASE output independent of temperature.

In order to examine the difference between the ASE spectra at low and room temperatures in detail, PL spectra under the intense excitation were measured at varied temperatures. Normalized PL spectra around the 0–1 and 0–2 bands at elevated temperatures are shown in Fig. 4. The excitation density was fixed to  $\sim 1 \text{ mJ}/\text{cm}^2$  which is 2.5 times higher than the threshold density. With increasing temperature, the intensity of the peak 1 at 2.70 eV decreases and immediately disappears in the spontaneous emission band of the background. With increasing temperature, the full width at half maximum (FWHM) of the peak 2 at 2.68 eV gradually increases, accompanied by a gradual shift in its peak

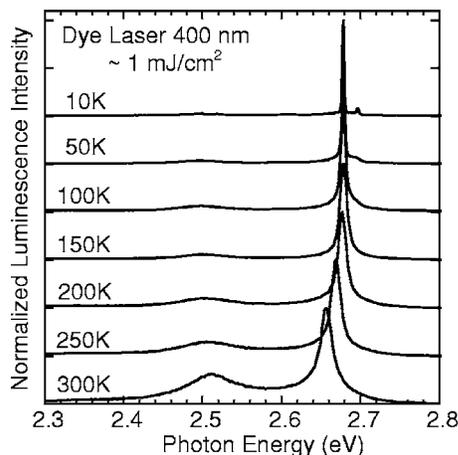


FIG. 4. Temperature dependence of PL spectra around the 0–1 and 0–2 transition energies during the appearance of the ASE. Each PL spectrum was normalized by the 0–1 peak intensity.

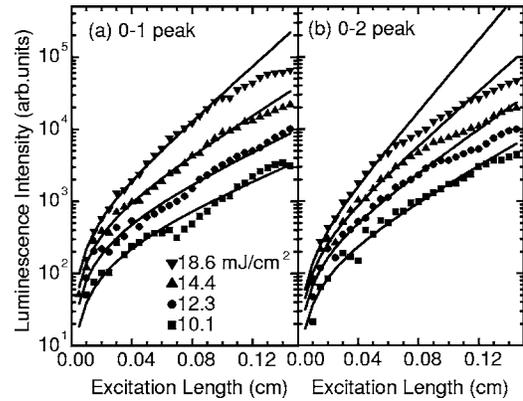


FIG. 5. Excitation length dependence of the luminescence intensity at the peaks of ASE spectra at 300 K. (a) and (b) show the output intensities at the 0–1 (2.66 eV) and 0–2 (2.51 eV) ASE peaks, respectively. The solid curves are fits to the data using Eq. (1).

position to the low-energy side. The similar temperature-dependent energy shift for the 0–1 band is also observed under the weak excitation, as shown in Fig. 1. Nevertheless, Fig. 4 shows that the peak 4 hardly shifts with increasing temperature. Similarly, the 0–2 band under the weak excitation does not shift with the increase in temperature (Fig. 1). We consider the different temperature-dependent energy shift of the peak 2 and the peak 4 comes from the reabsorption solely working for the peak 2. In other words, the high-energy side of the PL band around 2.70 eV is reabsorbed because the absorption band edge spreads out into the low-energy side with increasing temperature. The ASE peak appears always at the maximum of the spontaneous PL band, which is shifted by the reabsorption.

Figure 5 shows the luminescence intensity at the peaks of ASE spectra as a function of excitation stripe length under varied excitation densities at room temperature. Figures 5(a) and 5(b) show the output intensities at the 0–1 (2.66 eV) and 0–2 (2.51 eV) ASE peaks, respectively. The solid curves are fits to the data using the following equation:

$$I(\lambda) = \frac{AP_0}{g(\lambda)} [e^{g(\lambda)l} - 1], \quad (1)$$

where  $A$  is a parameter proportional to the PL quantum yield,  $P_0$  is the excitation density,  $g$  is the net gain coefficient, and  $l$  is the excitation stripe length.<sup>16</sup> The experimental results shown in Fig. 5 show good agreement with the curves expected from the Eq. (1) for shorter excitation lengths, but the gain saturation occurs for longer excitation lengths. The net gain coefficients obtained by fitting are plotted in Fig. 6(a) as a function of excitation density. The gain coefficients of the 0–1 and 0–2 ASE peaks are 43.4 and 57.1  $\text{cm}^{-1}$  under excitation density of 18.6  $\text{mJ}/\text{cm}^2$ , respectively. The net gain increases with increasing excitation density, and the gain of the 0–2 peak is larger than that of the 0–1 peak. It is considered that the net gain of the 0–1 peak is smaller because of the larger waveguide loss of the 0–1 peak than that of the 0–2 peak. The lower-energy tail of the absorption edge should remarkably contribute to the waveguide loss of the higher-energy lying 0–1 peak than that of the 0–2 peak. In fact, the loss coefficient was measured at the 0–1 peak en-

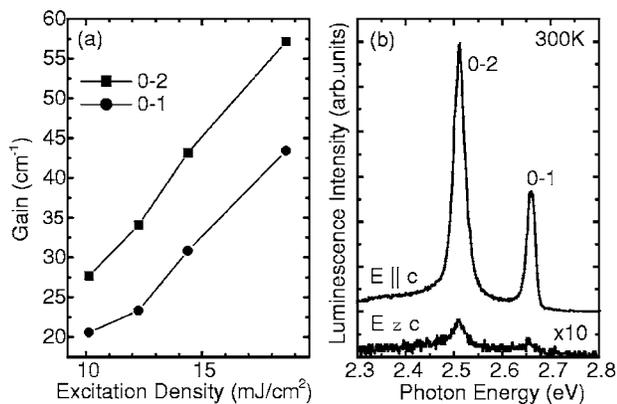


FIG. 6. (a) Excitation density dependence of the net gain coefficients obtained by fitting at 300 K. (b) ASE spectra observed for two polarizations  $E//c$  and  $E\perp c$  at 300 K.

ergy and it was estimated at up to  $\sim 30 \text{ cm}^{-1}$ . In the loss measurement, the excitation stripe length was kept constant and the ASE intensity was measured as a function of the length between the stripe and the edge of the sample. Although the waveguide loss is not negligible for the BPIT crystals, the net gain is relatively large in conjugated materials.

It can be considered that the aligned optical transition moments of the crystal contribute to such high-optical gain. The orientation of the optical dipole moments is not in the  $ab$  plane, as described previously, but along the  $c$  axis of the crystal. The PL from the crystal is exactly polarized to the  $c$  axis of the plateletlike crystals. Figure 6(b) shows the polarized components of the ASE spectra for  $E//c$  and  $E\perp c$ . In fact, the PL is highly polarized to the  $c$  axis, corresponding to the transverse-magnetic (TM) polarization, as is seen in Fig. 6(b). Therefore, the emission should propagate virtually solely as TM modes in the crystals and is efficiently amplified. Such the polarized optical transition is advantageous for lasing action.

#### IV. SUMMARY

In summary, we have performed PL measurements of the BPIT single crystal at low temperature and room temperatures. Several sharp peaks due to vibronic modes of the

BPIT molecules were remarkably observed in the PL spectrum at 10 K. Several fine peaks were assigned to the vibronic sidebands of the 0-0 transition shifted by the energies of vibronic modes in the  $A_1$  and  $B_1$  symmetry of the BPIT molecules and their combinations. Thus the 0-0 transition energy was definitely determined. Under the intense excitation, the sharp peaks due to the vibronic modes extremely grew, which indicates that the ASE noticeably appeared at 10 K. It has been demonstrated that the ASE observed at both room temperature and low temperatures takes place in the vibronic sidebands. In addition, highly polarized optical gain  $\sim 50 \text{ cm}^{-1}$  was obtained by using the VSL method at room temperature.

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