

Emission gain narrowing from single crystals of a thiophene/phenylene co-oligomer

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Emission gain narrowing has been observed for single crystals of a thiophene/phenylene co-oligomer. The hexagon flake crystals were placed on a quartz substrate with the crystals' face in close contact with the substrate plane. These crystals were irradiated with a N₂ laser with a 337.1 nm wavelength at a repetition rate 10 Hz that tuned its intensity to 100–1150 μJ/cm². The emission gain narrowing takes place at 21490 (465.4 nm) and 20220 cm⁻¹ (494.5 nm) with increased intensities, with their half width at half maxima reaching ~50 cm⁻¹. On the basis of the nonlinear relationship between the emission peak intensities and the laser light intensity, the gain narrowing has been attributed to the amplified spontaneous emission. © 2002 American Institute of Physics. [DOI: 10.1063/1.1435797]

Conjugated semiconducting polymers and oligomers are currently attracting great attention as potentially useful materials for optoelectronic devices such as thin-film transistors and light-emitting diodes.¹ Solid-state lasing and amplified spontaneous emission (ASE) have been observed in these materials.² Since excitation through photopumping is a facile way to attain lasing and ASE, this method has long been used.^{3–5} The earliest examples can be found for anthracene molecules embedded in host matrices of, e.g., fluorene.⁶ Later this approach was more widely applied to dye-doped systems and polymer thin films.⁷

Very recently solid-state injection lasing was achieved using a tetracene single crystal, vouching for the high practicality of organic semiconductors.⁸ In view of current injection, crystals of high quality are more advantageous than any other systems that involve defects which may well act as carrier traps. Reported observation of lasing or ASE of the crystals, however, remains scarce even in the case of photopumping. This is partly because the photoluminescent efficiency of chromophores is decreased by higher concentrations,⁹ even though their efficiency is high at dilution. Yet a typical examples for the ASE have been verified by Fichou *et al.*¹⁰ and by Horowitz *et al.*¹¹ using single crystals of octithiophene and sextithiophene, respectively.

Yanagi and Morikawa¹² showed that self-waveguided emission takes place along the crystals' long axis of needle-shaped crystals of *p*-sexiphenyl that are epitaxially grown on

top of a single crystal substrate of potassium chloride. The molecular axes of *p*-sexiphenyl align perpendicular to the crystals' needle axis so that the propagation of the polarized emission can be enhanced with the transverse electric mode along that needle. The uniaxially aligned transition dipoles in the *p*-sexiphenyl crystals are responsible for the self-waveguided emission. Recent progress demonstrated that this is analogous to the case of a newly emerging class of semiconducting molecular crystals, thiophene/phenylene co-oligomers.¹³ These materials were developed by Hotta and co-workers¹⁴ and are characterized by a variety of extensions of π conjugation along the backbone. The conjugation extension can be tuned by changing the total number of thiophenes and phenylenes and their arrangement in the molecules. Since self-waveguided propagation of the emission is a prerequisite for lasing or ASE, the thiophene/phenylene co-oligomers are expected to be good candidates for organic laser materials. In this letter we report initial results of the ASE, which has been observed for a co-oligomer BPIT [see its structural formula in Fig. 1(a)].

The experimental setup for the optical measurements is schematically represented in Fig. 2. In Fig. 2 the crystals were irradiated with a N₂ laser with a 337.1 nm wavelength at a repetition rate 10 Hz. Laser light of 1 mm×5 mm was perpendicularly incident on a quartz substrate. The hexagon crystals of typically ~100 μm and thickness of ~5 μm [see Fig. 1(b)] were dispersed in water and this dispersion was drop cast onto the substrate and subsequently dried. These flake crystals showed good adhesion to the substrate with the crystals' face in close contact with the substrate plane. Thus

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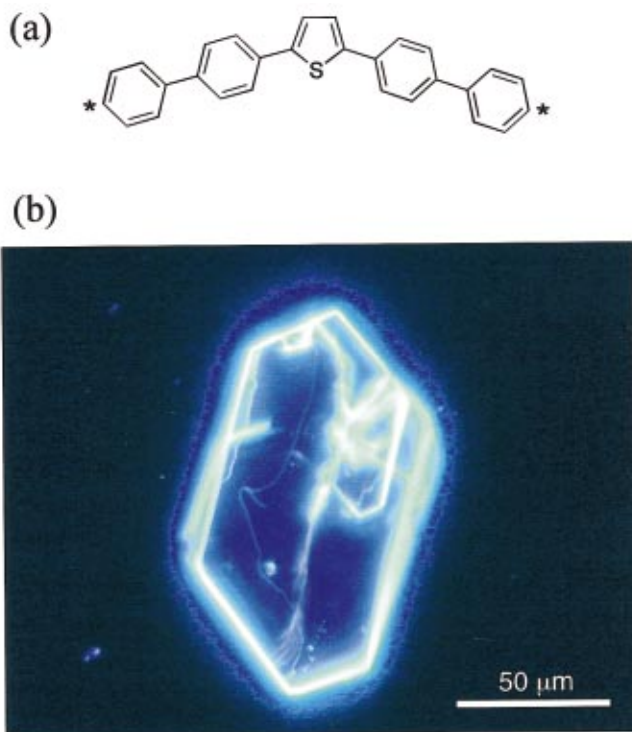


FIG. 1. (Color) (a) Structural formula of BPIT. The four carbons located on the terminal phenyls are indicated by asterisks. (b) Micrograph of a BPIT crystal.

several crystallites were irradiated at once with the rectangular laser beam. The intensity of the excitation beam was regulated from 100 to 1150 $\mu\text{J}/\text{cm}^2$ using a ND filter. The light emitted from the crystal edges was collected along the direction parallel to the substrate plane. That emitted light was detected through a UV cut filter with an Oriel MS-127I spectrometer connected to an Andor ICCD V charge-coupled imaging device. Standard x-ray diffraction (XRD) measurements ($\theta-2\theta$) were carried out using Cu $K\alpha$ radiation.

The XRD measurements of the “on-substrate” crystals

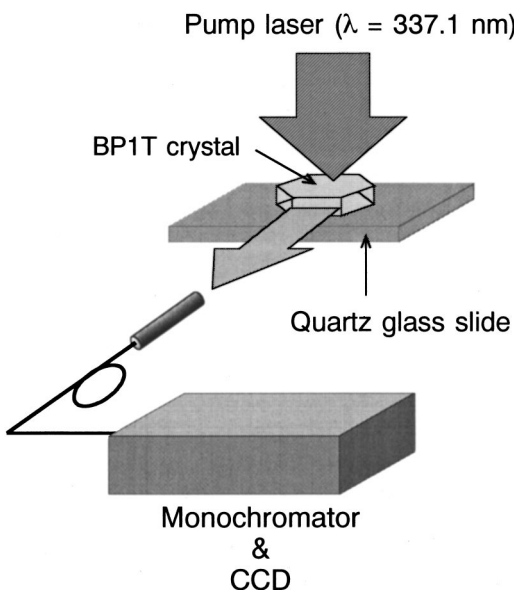


FIG. 2. Schematic of the experimental setup for optical measurements.

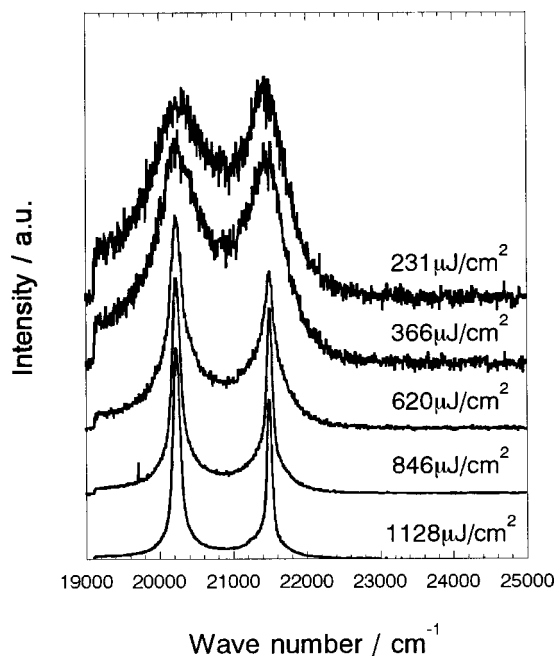


FIG. 3. Emission spectra of BPIT crystals as a function of the intensity of the incident laser light.

indicate that the diffractions comprise primary diffraction spacing of ~ 2.2 nm and its higher order reflections.¹⁵ This means that the crystals consist of a molecular layered structure with the “molecular long axis” exhibiting vertical alignment against the substrate plane.¹⁵ (*vide infra*).

Under weaker incident intensities the emission spectra exhibit a broad feature with relatively fine modes superimposed on it. These fine modes can be assigned to the vibronic structures that are frequently observed in solid-phase molecules with well-defined molecular symmetry.¹⁶ Of these vibronic modes, only a few specific modes are strongly narrowed by an increase in incident intensities. Figure 3 shows emission spectra from the BPIT crystals as a function of the intensity of the incident laser light. In Fig. 3 two lines are clearly narrowe at 21490 (465.4 nm) and 20220 cm^{-1} (494.5 nm). At intensity of 366 $\mu\text{J}/\text{cm}^2$ the half widths at half maximum (HWHMs) of the former and latter lines were 276 and 381 cm^{-1} , respectively. With an increase in intensity the HWHMs rapidly became narrowe so that they were 51 and 46 cm^{-1} for the 21 490 and 20 220 cm^{-1} lines, respectively. At the same time, the peak intensities rapidly increased as well. Figure 4 presents the HWHMs and photoluminescence (PL) peak intensities as a function of the incident laser light intensity. When the incident laser intensity is increased, the PL peak intensities grow nonlinearly, accompanied by the narrowing shown in Fig. 4. Therefore, we conclude that the narrowing is caused by gain narrowing, namely, ASE.⁹⁻¹¹ We present the extent of the gain narrowing in terms of the HWHM, because the positions of the gain-narrowed lines are not fully resolved at weaker excitation intensities (see Fig. 3). The HWHM approaches half of the full width at half maximum (FWHM) with stronger excitation intensities. The linewidths are usually measured with the FWHM. Compare the above-mentioned HWHMs (~ 50 cm^{-1}) with the FWHM (~ 170 cm^{-1}) determined by Fichou *et al.* for oc-tithiophene crystals.¹⁰ Note here that the linewidth of gain-

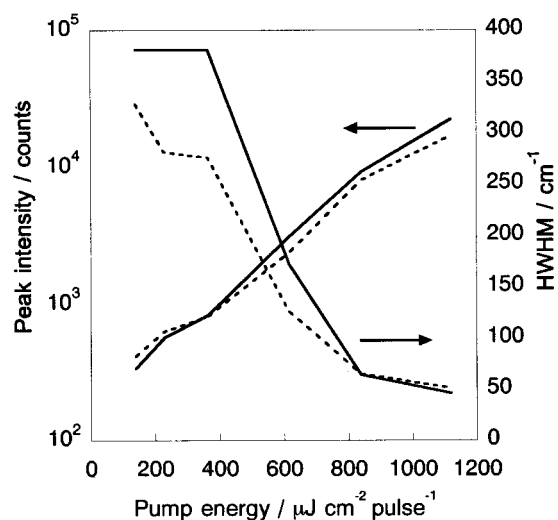


FIG. 4. HWHMs and PL peak intensities as a function of the incident laser light intensity. Solid and dashed lines represent 20 220 and 21 490 cm^{-1} lines, respectively.

narrowed emissions by ASE is governed by many factors, for example, the linewidth of spontaneous emission.¹⁷

The relevance of the crystal and molecular structures of BP1T to the ASE observed is worth briefly mentioning. In the crystals the deviation from C_{2v} symmetry is relatively small,¹⁸ so the transition dipoles are likely to be parallel to the line connecting the four carbons located on the terminal phenyls [see Fig. 1(a)].¹⁹ This line represents the molecular long axis. The angle between said line and the normal of the ab plane of the crystals (that parallels to the crystal faces) is roughly 1° .¹⁸ Since the ab plane parallels the crystals' faces, the transition dipoles are nearly upright against them (and the substrate plane also). In this vertical dipole configuration, the light emissivity from the molecules is maximum in the direction parallel to the crystals' faces and amplification of self-waveguided light propagating in this direction can readily be attained.

With Regard to the excitation experiments the two lines were narrowed to a similar extent at once in some cases, as can be seen in Fig. 3. In other cases, on the other hand, either the longer wavelength line or the shorter wavelength one was preferentially gain narrowed according to the individual measurements. In this context, Fichou *et al.*¹⁰ observed related narrowing trends for α -octithiophene crystals and pointed out that those trends are associated with the sample size and irradiated location of the crystals. In other words, they carried out the experiments such that a crystal 1–3 mm long was irradiated with a focused beam of diameter of ~ 0.3 mm and its position was scanned along the crystals' length. What was observed was that the 700 nm line was gain narrowed over most of the crystals' surface while the 640 nm line was almost inactive with gain narrowing except near the crystals' edge or on a second single crystal stacked

on top of the main one. Note that here the experimental conditions in our studies are totally different from those of Fichou *et al.*¹⁰ As mentioned earlier, we used conditions in which several small crystallites were irradiated at once. Since the individual crystallites contained further smaller ones on their surface [Fig. 1(b)], the main crystals and secondary smaller ones were irradiated all together. Consequently, it follows that we have observed collective PL from crystals of different size. The question of how the relevant lines are gain-narrowed under each specific condition, however, needs thorough investigating by accumulating more data using more materials.

In conclusion, we have investigated the emission gain narrowing of BP1T single crystals. The gain-narrowed emissions take place as a consequence of waveguided propagation of the light emitted and are associated with ASE. The disposition of the transition dipoles optimizes this self-waveguided ASE that occurs as edge emission. This is expected to lead to lasing under suitable conditions.

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