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Self-Waveguided Gain Narrowing of Light Emission from Single Crystals of Hexyl-Substituted Thiophene/Phenylene Co-Oligomer

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Abstract

Single crystals of hexyl-substituted thiophene/phenylene co-oligomer (TPCO) are fabricated by a solution-grown method. Optical transitions are determined by ultraviolet-visible (UV-Vis) and photoluminescence (PL) spectroscopies. Owing to self-waveguiding and one-dimensional light confinement in the hexyl-substituted TPCO platelet crystal, emission gain narrowing is observed above an excitation density of 262 μJ/cm^2 under Nd:YAG nanosecond pulsed laser excitation at room temperature.

1. Introduction

Organic lasers owing to their ultracompact physical sizes, high optical gain coefficients and efficient waveguiding are promising building blocks for integrated photonic and optoelectronic devices [1-5]. Organic crystals with the unique molecular packing mode and the minimized defects are advantageous for bottom-up approach to fabricate optical gain media. So far, lasing from organic materials has extensively been reported for anthracene [4], conjugated polymers [3], thiophene/phenylene co-oligomers (TPCOs) [5-10], etc. Particularly, owing to self-waveguiding and light confinement effects, self-assembled TPCO crystals with a pair of well-defined parallel facets act as gain media with Fabry-Pérot (F-P) feedback mirrors [8, 9]. For the TPCO crystals, lasing and amplified spontaneous emission (ASE) have stably been observed even in air at room temperature [5, 8, 9]. The stable lasing performance in ambient atmosphere, along with high fluorescence quantum yield and crystal structure controlled by an introduction of a substituent at the molecular terminal, is of pivotal importance in realizing the organic lasers. In vertical cavity surface emitting laser (VCSEL), a molecular orientation should be necessarily controlled to optimize the refractive index anisotropy and polarization properties. In cyano-substituted TPCO, 2,5-bis(4′-cyanobiphenyl-4-yl)thiophene (BP1T-CN), surface emitting lasing has been demonstrated owing to the lying molecular orientation against the basal face of the crystal [5, 10]. The introduction of different substituents leads to different molecular alignment due to a change in the intermolecular interaction [5, 9, 10]. For example, since the introduction of alkyl chain at the molecular terminal hinders a dense molecular packing resulting in the improvement of solubility [11], it is expected that the molecular arrangement in single crystals is different from that in the conventional TPCO crystals [5, 9, 10]. In the present study, to investigate the effect of the substituent on the molecular orientation and amplified light emission properties, we prepared a single crystal of hexyl-substituted TPCO, 5,5'-Bis(4'-n-hexyl-4-biphenylyl)-2,2'-bithiophene (BP2T-Hx).

2. Experiment

The synthesis and purification of BP2T-Hx were carried out according to the literature procedures [6-8]. Crystallization of BP2T-Hx was carried out by the following method. After 8 mg of BP2T-Hx powder was dissolved in 8 mL of 1,2,4-trichlorobenzene (Nakarai Tesque) by heating at 150 °C, the crystals were precipitated by slowly cooling to 40 °C in 16 h. By filtrating the resulting solution, thin platelet crystals were obtained.

Fluorescence image of the BP2T-Hx crystal was taken under ultraviolet excitation (λ_{ex} =365 nm) using a fluorescence microscope (Olympus BX-51) with a 20× objective lens and an Olympus DP21 digital camera. An ultraviolet-visible (UV-Vis) spectrophotometer (JASCO V-530, Japan) was used to measure the absorption spectra. For the PL measurement, an excitation light of λ_{ex}=355 nm from Nd:YAG laser (repetition rate of 1 kHz, pulse width of <1.1 ns) was incident to the BP2T-Hx crystal. The PL spectra were detected from the crystal edges using a CCD spectrometer (Hamamatsu PMA-50).

3. Results and Discussion

Molecular structure of BP2T-Hx and fluorescence micrograph of the crystal are shown in Fig. 1. In Fig. 1(b), edge emission from a disk-shaped crystal is seen, and this indicates that the crystal itself functions as a thin-film waveguide. Optical absorption and photoluminescence (PL) spectra are shown in Fig. 2. The peaks at 470 nm, 440 nm, and 410 nm can be assigned to 0-1, 0-2, and 0-3 absorption bands, respectively. The PL bands at 530 nm, 560 nm, and 590 nm are assigned to 0-1, 0-2, and 0-3 transitions, respectively. From these spectra, it is expected that the lowest 0-0 transition is forbidden due to antiparallel exciton coupling in the excited state in analogy with other TPCO crystals [9, 10]. X-ray

diffraction analysis is undergoing to determine the crystal structure and molecular orientation.

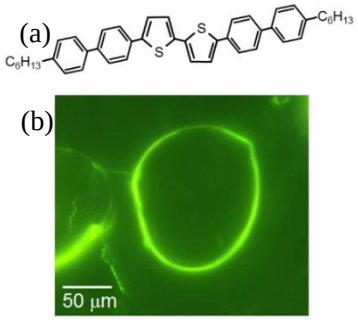

Fig. 1. Molecular structure of BP2T-Hx (a) and fluorescence micrograph of BP2T-Hx crystal (b).

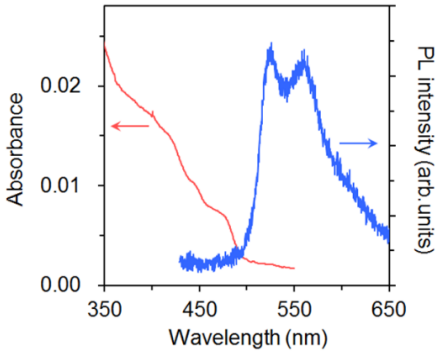

Fig. 2. Optical absorption and photoluminescence (PL) spectra of BP2T-Hx crystal.

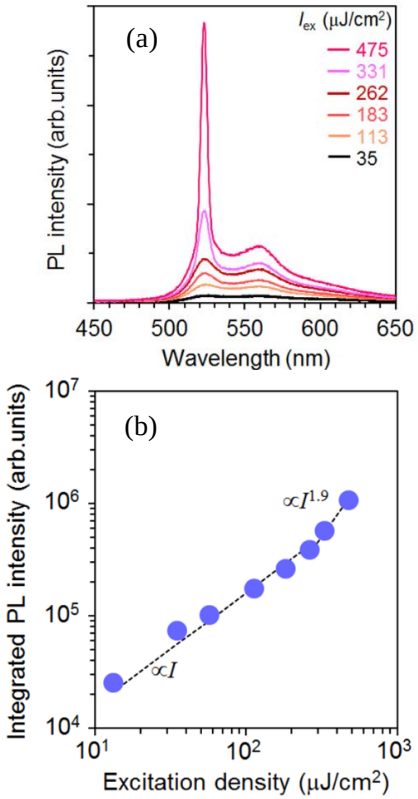

Fig. 3. (a) Excitation density dependence of PL spectra of the BP2T-Hx crystal. (b) Excitation density dependence of the integrated PL intensity of the 0-1 band.

Figure 3(a) shows the excitation density dependence of PL spectra of the BP2T-Hx crystal. At low excitation density of 35 μJ/cm^2, broad emission peaks are observed at the 0-1 and 0-2 bands. With increasing excitation density to 262 μJ/cm^2, the 0-1 emission is amplified by stimulated emission. At an excitation density of 475 μJ/cm^2, the 0-1 emission band with a full width of half maximum (FWHM) of ~5.8 nm was observed. Figure 3(b) shows the excitation density dependence of the integrated PL intensity of the 0-1 band in the BP2T-Hx crystal. The 0-1 emission intensity increases linearly with an increase in the excitation density ($\propto I^1$) under the low excitation density region, while the integrated intensity increases superlinearly ($\propto I^{1.9}$) when the excitation density is beyond a threshold of 262 μJ/cm^2. These results show clearly that the light emission from the BP2T-Hx crystal is gain-narrowed by self-waveguiding in the planar cavity.

4. Conclusions

We have fabricated the single crystals of BP2T-Hx which is a new derivative of TPCOs by using a solution-grown method. The BP2T-Hx platelet crystal with self-waveguiding and one-dimensional light confinement resulted in amplified light emission at excitation threshold of 262 μJ/cm^2 under Nd:YAG nanosecond pulsed laser excitation at room temperature.

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