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Lasing in low-dimensional single crystals of hexyl-substituted thiophene/phenylene co-oligomer

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We report on the fabrication and characterization of low-dimensional single crystals of hexyl-substituted thiophene/phenylene co-oligomer, 5,5’-Bis(4’-n-hexyl-4-biphenylyl)-2,2’-bithiophene (BP2T-Hx). X-ray diffraction measurements of the single crystals reveal that BP2T-Hx molecules crystallize in a monoclinic form. Temperature dependence of photoluminescence (PL) decay profiles of the BP2T-Hx crystal results in a PL quantum yield of 39%. Above an excitation threshold of 262 μJ/cm², amplified spontaneous emission is obtained in a disk-shaped crystal of BP2T-Hx based on the self-waveguiding effect of fluorescence light. Owing to two-dimensional light confinement supported by high group refractive index of 3.4 and high quality factor of 3800, the one-dimensional needle crystal with a cavity length of 70 μm realizes a Fabry-Pérot lasing at a threshold of 186 μJ/cm² which is 29% lower than that of the disk-shaped crystal.
1. Introduction

Organic lasers having characteristics of ultracompact physical sizes with microresonators formed by self-assembled processes are promising building blocks for integrated photonic and optoelectronic devices.1-11) Organic crystals with the unique molecular packing mode and the minimized defects are suitable for bottom-up approach to fabricate optical gain media. In the fabrication of organic crystals, a great deal of efforts has been focused on the shape control of crystals because the properties of organic nano- and micro-structures depend not only on the molecular packing in crystals but also on the crystal dimensions.12, 13) So far, lasing1, 5, 7-25) from organic materials has extensively been reported for anthracene,14,15) conjugated polymers,16,17) distyrylbenzene derivatives,23-25) thiophene/phenylene co-oligomers (TPCOs),5, 18-22, 26-31) etc. Lasing and amplified spontaneous emission (ASE) have mostly been achieved in self-assembled TPCO crystals with a pair of well-defined parallel facets acting as Fabry-Pérot (F-P) resonators.5, 19, 21, 22) In order to construct such self-assembled structures, molecular orientation control is of pivotal importance for providing self-waveguiding and light confinement effects. For example, in-plane orientation of transition dipole moments is necessary in an active layer of vertical-cavity surface-emitting laser (VCSEL)9, 18, 20) to enhance the stimulated emission process. In cyano-substituted TPCO, 2,5-bis(4'-cyanobiphenyl-4-yl)thiophene (BP1T-CN),18-20) surface-emitting lasing has been demonstrated owing to the lying molecular orientation against the basal face of the crystal. The introduction of different substituents at the molecular terminal leads to different molecular alignment due to the change in intermolecular interactions.19, 21, 32) Moreover, since the introduction of terminal groups change the molecular packing, their crystal structures are different from that in the unsubstituted TPCO crystals.30, 33) In the present study, to investigate the effect of molecular orientation and crystal structures on amplified light emission properties, we prepared single crystals of hexyl-substituted TPCO, 5,5'-Bis(4'-n-hexyl-4-biphenyl)-2,2'-bithiophene (BP2T-Hx).

2. Experimental methods

BP2T-Hx was purchased from Sumitomo Seika Chemicals Co., Ltd. Two crystallization processes were carried out as follows.33) First, 8 mg of BP2T-Hx powder was dissolved in 8 mL of 1,2,4-trichlorobenzene (Nakarai Tesque) by heating at 180 °C, then crystals were precipitated by slowly cooling to 40 °C in 16 h. After filtrating the resulting solution and drying in air, this process resulted in disk-shaped platelet crystals. In the second process, 5
mg of BP2T-Hx powder was dissolved in 10 mL of a solvent mixture of 1,2,4-trichlorobenzene (Nakarai Tesque) and dimethyl sulfoxide (DMSO) (Wako) (3:1 volume ratio) by heating at 180 °C. Then, needle-like crystals were precipitated by slowly cooling to 40 °C in 16 h.

Fluorescence images of the BP2T-Hx crystals were taken under ultraviolet excitation (photon energy of 3.397 eV) using a fluorescence microscope (Olympus BX-51) with a 20× objective lens and a digital camera (Olympus DP21). X-ray diffraction (XRD) measurements of the BP2T-Hx single crystals were performed on a X-ray diffractometer (Rigaku R-AXIS RAPID) using filtered Mo-Kα radiation (λ = 0.71075 Å). We employed a Ti:sapphire pulsed laser with 100-150 fs duration and repetition of 76 MHz for time-resolved spectroscopy. The second harmonic light pulse at a photon energy of 3.10 eV was used for sample excitation. To perform the time-resolved photoluminescence (PL) measurements, the fluorescence from the BP2T-Hx crystal was collected and focused on an entrance slit of an imaging polychromator (Hamamatsu, C5094). The spectrally dispersed fluorescence was detected by a streak camera (Hamamatsu, C4334) with time resolution of 15 ps. Optical absorption spectra of the BP2T-Hx crystal were measured using an ultraviolet-visible (UV-Vis) spectrophotometer (JASCO V-530, Japan). For PL measurements, an excitation light of 3.493 eV from a neodymium (Nd):YAG laser (repetition rate of 1.2 kHz, pulse duration of <1.1 ns) was used. A stripe-shaped excitation beam (p-polarization) was focused on the BP2T-Hx crystal with an incident angle of approximately 45° against the substrate, and light emitted from the crystal edges was detected using a CCD spectrometer (Hamamatsu PMA-50).

3. Results and discussion

Molecular structure of BP2T-Hx and fluorescence micrograph of an obtained disk-shaped crystal are shown in Figs. 1(a) and 1(b), respectively. Bright emission radiated from the crystal edge is seen, and this indicates that the crystal itself functions as a thin-film waveguide. Absorption (blue) and PL (red) spectra are shown in Fig. 1(c). The absorption peaks at 2.638 eV and 2.796 eV can be assigned to the 0-1 and 0-2 transitions, respectively. The PL bands at 2.362 eV, 2.204 eV, and 2.046 eV are assigned to the 0-1, 0-2, and 0-3 transitions, respectively.

XRD measurements were performed to determine the crystal structure of BP2T-Hx. Figures 2(a)-2(c) show the determined structure indicating unit-cell projections on the ac-, bc-, and ab-planes, respectively. The enlarged structure of hexyl-substituents in neighboring
molecules is shown in Fig. 2(d). This XRD analysis revealed that the BP2T-Hx molecules were packed in a monoclinic form with the lattice parameters of \(a = 5.61\, \text{Å}, b = 7.50\, \text{Å}, c = 42.15\, \text{Å},\) and \(\beta = 93.37^\circ\) (space group: \(P2_1\), \(Z\) value: 2, cell volume \(V\): 1771 Å\(^3\)). This monoclinic structure of the BP2T-Hx crystal is similar to that of unsubstituted 5,5′-di(4-biphenylyl)-2,2′-bithiophene (BP2T) (monoclinic, space group: \(P2_1/c\), \(Z\) value: 4, cell volume \(V\): 2276.8 Å\(^3\), lattice parameters: \(a = 5.708\, \text{Å}, b = 7.604\, \text{Å}, c = 52.869\, \text{Å} \) and \(\beta = 97.15^\circ\)).\(^{30}\) In both crystals, the molecules stand almost upright against the \(ab\)-plane of the crystal. Although alkyl chains at the molecular terminal of BP2T-Hx hinder dense molecular packing, the XRD analysis showed no different impact on the molecular orientation and crystal structure by the introduction of substituents. In these crystals, the transition dipole moments which are parallel to the molecular axis align in a parallel configuration like \(H\)-aggregates. In the lowest excited state, since the dipole moments of nonequivalent molecules are almost antiparallel to each other and cancel out, 0-0 transition is forbidden in analogy with other TPCS crystals.\(^{21, 22}\) Accordingly, the 0-0 band has not been observed in the optical spectra shown in Fig. 1(c). Moreover, the XRD measurements reveal that the surface of the disk-shaped crystal of BP2T-Hx corresponds to the (001) plane indicating standing molecular orientation against the crystal \(ab\)-plane (see Fig. 2(c)).

A PL decay profile of the 0-1 band emission in the disk-shaped crystal of BP2T-Hx measured at 300 K is shown in Fig. 3(a). The decay exhibits a simple single-exponential profile with a time constant of 1.53 ns. Figure 3(b) shows the temperature dependence of the PL lifetime of the 0-1 band. The decay curves measured at each temperature showed a single-exponential decay, and the PL lifetime of 2.16 ns at 10 K was shortened as the temperature increased up to 300 K. The temperature dependence of this spontaneous 0-1 band emission lifetime was analyzed using the equation: \(\tau(T) = 1 / (k_t + k_{nr} \exp(-E_a / (k_B T)))\), where \(\tau, k_t, k_{nr}, E_a, k_B,\) and \(T\) are the spontaneous emission lifetime, radiative transition rate constant, non-radiative transition rate constant, activation energy of non-radiative transition, Boltzman constant, and temperature, respectively.\(^{27}\) The temperature dependence of the PL lifetimes was fitted by a dotted line shown in Fig. 3(b). The parameters at the best fitting were: \(k_t = 4.7 \times 10^8\, \text{s}^{-1}, k_{nr} = 7.3 \times 10^8\, \text{s}^{-1}, E_a = 40\, \text{meV}\). We estimated a PL quantum yield \(\Phi\) by using the equation: \(\Phi = k_t / (k_t + k_{nr})\) and a value of 0.39 by using the above parameters.

To demonstrate amplified light emission properties of the BP2T-Hx crystals, we next investigated the excitation fluence dependence of PL spectra. Figures 4(a) and 4(b) show the excitation density dependence of PL spectra and integrated intensity of 0-1 band (2.318-
2.455 eV) taken from the disk-shaped crystal. At low excitation density of 35 μJ/cm², a broad spontaneous emission spectrum was observed. With increasing excitation density, amplified spontaneous emission (ASE) was observed at the 0-1 band. In Fig. 4(b), integrated 0-1 band intensity $I$ increased linearly in the low excitation range, and it increased superlinearly ($\propto I^{1.9}$) above a threshold of 262 μJ/cm².

By using a mixture solvent of 1,2,4-trichlorobenzene:DMSO (3:1) for the crystal growth procedure of BP2T-Hx, we obtained needle-like crystals as shown in fluorescence micrographs in Figs. 5(a) and 5(b). The addition of polar solvent DMSO into 1,2,4-trichlorobenzene caused the BP2T-Hx molecules to crystallize into needles. XRD measurement confirmed that the surface of BP2T-Hx needle crystal corresponded to the (001) plane as schematically shown in Fig. 5(c) as similar to that in the disk-shaped crystal. The images of Figs. 5(a) and 5(b) were taken with and without using a variable aperture to select the excitation area. The difference in two images indicates that the emitted light is confined in the crystal and propagates along the needle axis. The brighter PL spots at both ends of the crystal in Fig. 5(b) demonstrates that the needle crystal functions as an optical waveguide. The emission from the directly excited crystal surface is non-propagated fluorescence due to slightly oblique standing of the transition dipoles. A bright light emitted from both ends of the needle indicates that as-grown BP2T-Hx crystal may simultaneously serve as an active medium and an optical resonator. Figures 5(d) and 5(e) show excitation density dependences of PL spectra and integrated intensity of the 0-1 band (2.211-2.296 eV) taken from the needle crystal shown in Figs. 5(a) and 5(b). In contrast to the case of disk-shaped crystal (see Fig. 4(a)), the 0-2 band emission at 2.261 eV was prominently amplified for the needle crystal, probably due to less self-absorption effect by the reduced cavity length of the needle crystal. Above a threshold excitation density of 186 μJ/cm², a superlinear increase in the emission intensity ($\propto I^{1.8}$) of the 0-2 band was observed as shown in Fig. 5(e).

Figure 5(f) indicates a high-resolution PL spectrum of the 0-2 band showing lasing measured at 552 μJ/cm². Taking into account of a cavity length $L$ (length between both ends of the needle) of 70 μm, the mode interval $\Delta\lambda^{-1}$ of 21 cm⁻¹ corresponds to the group refractive index $n_g$ of 3.4 from the relation of F-P mode lasing: $n_g = 1 / (2\Delta\lambda^{-1}L).^{19,21}$ The quality ($Q$) factor estimated from the lasing spectrum measured at 552 μJ/cm² is approximately 3800. The lower lasing threshold for the needle crystal that was approximately 29% reduced compared to that in the disk-shaped crystal is attributed to two-dimensional light confinement in the needle crystal F-P resonator supported by its high $n_g$ and high $Q$ factor.
4. Conclusions

We have fabricated low-dimensional single crystals of BP2T-Hx and determined the crystal structure. The XRD measurements indicated that alkyl chains at the molecular terminal of BP2T-Hx have no significant impact on the molecular orientation and crystal structure. The BP2T-Hx molecules have been controllably self-assembled into one-dimensional needle- and two-dimensional disk-shaped crystals by changing solvents in the solution growth processes. A PL quantum yield of 39% was determined from the temperature dependence of time decay profiles for the BP2T-Hx crystals. Moreover, owing to two-dimensional light confinement in the needle crystal with high $n_g$ and high $Q$ factor, optically pumped lasing was observed above an excitation threshold density of 186 μJ/cm² that was 29% lower than that of the disk-shaped crystal.

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Figure Captions

Fig. 1. (a) Molecular structure of BP2T-Hx. Fluorescence micrograph (b) and normalized absorption/PL spectra (c) of disk-shaped single crystal.

Fig. 2. Crystal structure of BP2T-Hx with projections on the ac-plane (a), bc-plane (b), and ab-plane (c). (d) Enlarged image showing hexyl-substituents in neighboring molecules.

Fig. 3. (a) Photoluminescence (PL) decay curve of 0-1 band emission taken from disk-shaped crystal of BP2T-Hx at 300 K. (b) Temperature dependence of PL lifetimes of the 0-1 band.

Fig. 4. (a) Excitation density dependence of PL spectra taken from disk-shaped crystal of BP2T-Hx excited at a photon energy of 3.493 eV. (b) Integrated PL intensity of the 0-1 band as a function of excitation density.

Fig. 5. Fluorescence micrographs of needle-like BP2T-Hx crystal taken with (a) and without (b) using a variable aperture to select excitation area. (c) Schematic diagram of the BP2T-Hx needle crystal. Excitation density dependences of PL spectra (d) and integrated PL intensity of 0-1 band (e) taken from the needle crystal. (f) High-resolution PL spectrum showing lasing modes at excitation density of 552 μJ/cm².
Fig.1.
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