Optically pumped lasing from single-crystal cavity of \( p \)-phenylene oligomer

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Abstract

Single-crystal cavities of \( p \)-sexiphenyl (\( p \)-6P) are prepared by precipitation from a solution phase. A typical \( p \)-6P crystal has a thin quasi-lozenge shape with a size of several hundreds of \( \mu \text{m} \) and a thickness of a few \( \mu \text{m} \). Under optical pumping with a pulsed laser, blue fluorescence is gain-narrowed to amplified spontaneous emission (ASE) due to light confinement inside the slab-type crystal cavity. With increasing excitation fluence, the time profiles of photoluminescence change from an exponential decay of spontaneous regime to a pulsed one typical for stimulated emission. Furthermore, multimode laser oscillations are obtained when a pair of parallel facets of the crystal cavity function as feedback mirrors.

Keywords: \( p \)-sexiphenyl, single-crystal cavity, amplified spontaneous emission, organic laser

Mathematics Subject Classification: 2.02, 4.05, 4.13

1. Introduction

\( \pi \)-conjugated oligomers are widely studied for organic optoelectronic devices such as field-effect transistors and photovoltaic cells. Since the successful development of organic light-emitting diodes (OLEDs), those \( \pi \)-conjugated materials have been further studied as a candidate for realizing organic lasers [1, 2]. A variety of \( \pi \)-conjugated oligomers, \( p \)-phenylenes (\( p \)-nP) are highly blue-fluorescent and very stable molecules. In \( p \)-nP, phenylene rings are linearly chained and the molecules from trimer to seximer (\( n=3\)–6) are commercially available. The \( \pi-\pi^* \) transition dipole moment between the highest occupied molecular orbital (HOMO) and the lowest unoccupied one (LUMO) is parallel to the oligomer axis [3]. Since the oscillation strength of the HOMO/LUMO transition becomes large with increasing phenylene rings, \( p \)-6P has been extensively studied as an excellent blue emitter in OLEDs [4–6].

In the previous studies, \( p \)-6P was crystallized in needle-like morphology by epitaxial growth on a cleaved surface of KCl substrate [7]. In the needle-like crystals, the \( p \)-6P molecules lying on the substrate surface orient perpendicular to the needle axis. Due to this epitaxial orientation in one-dimensional structure, the fluorescence light is polarized in the transverse electric (TE) mode and propagates along the needle cavity. Under optical pumping, the emitted light is gain-narrowed by the stimulated process; consequently, so-called amplified spontaneous emission (ASE) is radiated from the needle tips [8]. In contrast to this light amplification in the one-dimensional \( p \)-6P needles, two-dimensional crystals of \( \pi \)-conjugated oligomers are also capable of ASE. Representative, thiophene/phenylene co-oligomers (TPCOs) are crystallized in a thin platelet morphology in which the molecular axis is standing upright to the crystal plane [9]. This standing orientation effectively confines the fluorescence light polarized in the transverse magnetic (TM) mode resulting in ASE from crystal edges of the platelet [10]. Moreover, when a parallel pair of side facets of the platelet crystal acts as Fabry–Pérot (F–P) mirrors, laser oscillations have been obtained under optical excitation. This platelet crystal cavity is very useful for edge-emitting lasers since the standing molecular orientation minimizes an optical loss from the crystal surface and optimizes the stimulated emission condition. From these previous findings, a platelet crystal of \( p \)-6P is a promising candidate for blue-lasing organic media.
2. Experimental

Platelet crystals of p-6P were prepared by precipitation from a solution phase. 10 mg p-6P powder (Tokyo Chemical Industry) was dispersed in 15 ml 1,2,4-trichlorobenzene, and was heated at 170 °C to be dissolved. Then the solution was slowly cooled down to 43 °C at a rate of 10 °C h⁻¹, and the obtained suspension was poured onto a filter paper. After dryness, a selected single crystal was transferred onto a glass substrate using a tungsten tip.

Morphology of single crystals was observed with a fluorescence microscope (Olympus BX-51) under ultraviolet excitation (λex = 365 nm). Photoluminescence (PL) measurements were carried out with a Ti:S femtosecond pulsed laser (λ2ω = 397 nm, 1 kHz, 200–300 fs duration) as an excitation source. The emitted light was collected in the direction parallel to the crystal plane with a CCD spectrometer (Roper Scientific ST-133 series). Time-resolved PL spectroscopy was performed by introducing the emitted light to a synchro-scan streak camera (Hamamatsu photonics C5680) with a time resolution of 5 ps.

3. Results and discussion

Figure 1 shows a molecular structure of p-6P and a fluorescence micrograph of an obtained single crystal. The crystal is shaped in a thin quasi-lozenge morphology typically with a size of several hundreds of μm and a thickness of 2–3 μm. Under UV excitation, blue fluorescence is observed in particular at the crystal edges and little light is emitted from the crystal surface besides scattering from the defects. It is reported that the p-6P molecules crystallize in a monoclinic form (P2₁/c, a = 2.624, b = 0.557, c = 0.809 nm, β = 98.17°) [11–14]. The linear molecular axis is obliquely standing against the lozenge surface (ac-plane) so that the large component of the HOMO/LUMO transition dipole moment contributes to the standing polarization of fluorescence. Therefore, the emitted light is mainly propagated by the TM mode and is effectively confined inside the platelet crystal cavity.

Figure 2 shows excitation-density dependence of optically pumped PL spectra taken from the platelet crystal shown in figure 1(b). A stripe-shaped excitation beam was irradiated onto the crystal surface with an incident angle of 20° in the manner that the stripe axis was perpendicularly across the parallel side facets. The light emitted from one of the side facets was collected in the direction parallel to the crystal plane. Under weak excitation density at 56.5–112 μJ cm⁻², spontaneous fluorescence band with vibronic progressions appear in a wavelength range of 400–500 nm. Three peaks around λ = 425, 448 and 478 nm are assigned to the 0–1, 0–2 and 0–3 transitions, respectively. The 0–0 transition is extinct since the lowest π–π* transition is prohibited due to antiparallel interaction of excitons between the adjacent molecules. With increasing excitation density to 225 μJ cm⁻², the 0–1 and 0–2 intensities increase as compared to that of the 0–3 band. At excitation density of 283 μJ cm⁻², the spectral width of the 0–1 band starts to be narrowed. Finally, the 0–1 band is gain-narrowed into ASE at excitation density of 357 μJ cm⁻². In figure 3, the integrated 0–1 band intensities are plotted as a function of excitation density. It clearly indicates that the 0–1 band intensity is nonlinearly increased above an ASE threshold density estimated to be 283 μJ cm⁻². We have measured these ASE behaviors from several single crystals. When a defect-less single crystal was used, the ASE emerged at the 0–2 band. This suggests that the emitted light propagating in a long defect-less distance suffers from self-absorption at the short wavelength side of the PL spectrum so
that the 0–1 band is hardly amplified. On the other hand, the defects in the platelet crystal shown in figure 1(b) cause short-traveled light scattering which suppresses the self-absorption effect.

Figure 4 shows time-decay profiles of the 0–1 band intensity measured as a function of excitation density for the platelet crystal shown in figure 1(b). Under weak excitation at $56.5 \mu J/cm^2$, the 0–1 band intensity is exponentially decayed with a typical fluorescence lifetime of $\sim 1$ ns. With increasing excitation density, the lifetime is shortened and the decay profiles change to a pulsed shape above the ASE threshold. This pulse-shaped time profile is a clear indication of light amplification by the stimulated process.

As mentioned in the introduction, multimode laser oscillations can occur when the parallel side facets of the platelet crystal cavity function as an F–P resonator. However, we could not observe such F–P lasing from the platelet crystal shown in figure 1(b) probably due to its imperfect cavity structure with remarkable defects. Even if this crystal is feasible for lasing, multimode oscillations might not be observable since the resolution of used spectrometer is lower than a mode interval expected for the large cavity length of the platelet crystal. Therefore, we chose a single crystal with a smaller size and measured the 0–1 band emission with a high-resolution grating (1800 mm$^{-1}$). Figure 5 shows a representative lasing spectrum obtained from a single-crystal platelet with a cavity length smaller than 100 nm. According to the relation, $n_g = 1/2\Delta \nu$ ($n_g$: group index, $L$: cavity length, $\Delta \nu$: mode interval), $n_g \sim 6$ is obtained at the 0–1 ASE peak wavelength. This high refractive index supports effective light confinement in the platelet crystal cavity resulting in observed ASE and lasing.

4. Conclusions

Single-crystal platelet cavities were fabricated by solution growth of blue-emitting $\pi$-conjugated oligomer, $p$-6P. The thin slab morphology with standing molecular orientation facilitates light confinement and waveguiding of fluorescence with the TE-polarization. Under optical pumping, the 0–1 vibronic band is gain-narrowed showing a clear ASE threshold and lifetime shortening. The platelet crystal is also capable of optically pumped lasing owing to the F–P effect of the crystal cavity. Since the ASE and lasing are stably observed at room temperature in air, the $p$-6P crystal is a promising candidate of organic blue laser.

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