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## ***Abstract***

This *Communication* reports for the first time on the clear evidence about laser oscillation in monolithic molecular single crystals of an oligothiophene derivative (P6T). The laser oscillations are characterized by naturally formed crystal facet cavities with molecular-scale flatness. The multi-mode laser oscillation in a Fabry-Pérot resonator is characterized by sharply resolved spectral lines with their full width at half maximum (FWHM) down to only 38 pm, close to our experimental limit of 35 pm. The laser oscillation is characterized by the presence of a well-defined threshold. The participation of the vibronic levels is briefly discussed.

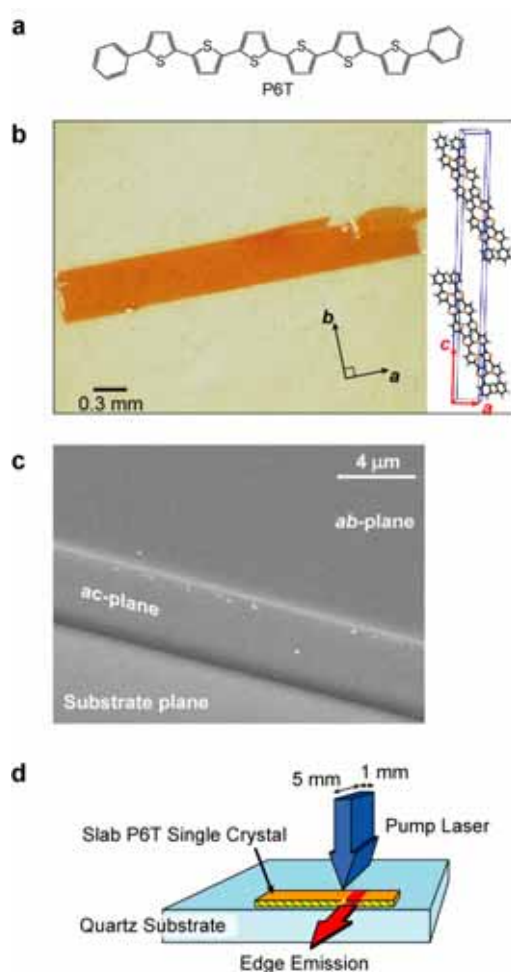
The achievement of long-lasting, bright electroluminescence with high efficiency in both polymeric<sup>1</sup> and low-molecular-weight organic materials<sup>2</sup> has strongly motivated the development of a new class of laser diodes (LDs). Within this framework, optically induced solid-state organic lasers have been proposed and fabricated in the form of thin films by methods such as solution casting and vacuum deposition with a wide class of related organic semiconductors.<sup>3-7</sup> Prior to this recently developed research stream, laser oscillation in organic molecular single crystals was conceptually postulated by Karl<sup>8</sup> in the early 1970s. Although this led to the first demonstration of optically pumped lasing in “doped” molecular crystals,<sup>8</sup> to date, laser oscillation in a “monolithic” (undoped) single crystal has not yet been demonstrated. At the moment, however, there are several examples of stimulated emission including amplified spontaneous emission<sup>9-14</sup> (ASE) from molecular single crystals. Here we show the first demonstration of optically induced laser oscillation in single crystals.

Laser emission from monolithic organic single crystals has proven highly problematic since Karl first suggested the possibility.<sup>8</sup> His reasoning was as follows. (i) As optical pumping usually creates mobile excitons in molecular crystals, these excitons may well collide with each other and dissipate their energy non-radiatively.<sup>15</sup> (ii) Because nearly all molecules within a certain volume in a crystal have to be pumped to produce population inversion, this will result in high energy densities, producing serious thermal strain. Nonetheless, molecular single crystals of  $\pi$ -conjugated oligomers have raised great interest in recent literature for their excellent, unique photonic properties, such as ASE<sup>9-14</sup> and stimulated Raman scattering<sup>16,17</sup>, based on cooperative interaction among the aligned molecules. Furthermore, monolithic organic molecular single crystals have the advantage of exhibiting superior charge-carrier transport properties as compared with amorphous and polymeric organic semiconductors.<sup>18</sup> This advantage results from the long-range structural ordering that these single crystals inherently possess. These excellent photonic and electronic features lead to the expectation that current-injection lasing will be achieved. Thus, demonstration of laser oscillation in a

single crystal is a top priority.

In this article, we describe how we have solved the historic open question raised by Karl in regard to monolithic molecular crystals. We have definitively observed laser oscillation by optically pumping a thin-plate single crystal with parallel crystal faces on either end, which together function as a Fabry-Pérot cavity. The key point is that we have carefully fabricated the single crystals by using a new method of crystal growth.<sup>19</sup> Most importantly, this method produces crystal faces, and thus, Fabry-Pérot cavities, of optically high flatness. This ensures strong self-cavity optical confinement in these crystals. We emphasize here that, unlike thin films, monolithic single crystals are hard to equip with a resonator without hampering its operation. Another key point lies in selecting a molecular semiconductor in which thiophenes and phenylenes are suitably hybridized at the molecular level.<sup>20</sup> Since the crystallographic structure of the single crystals that we used has been fully determined,<sup>21</sup> the relationship between that structure and the photo-pumping geometry can be uniquely defined.

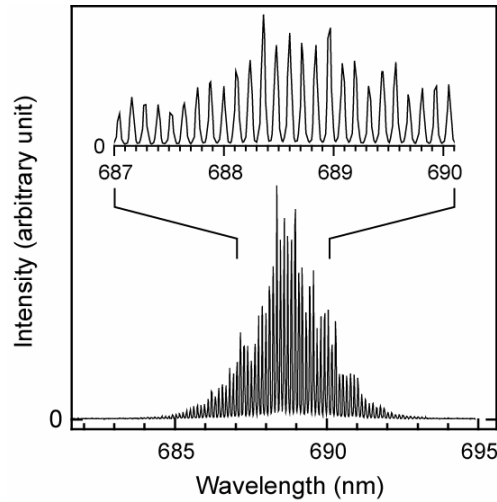
We used crystals of a thiophene/phenylene co-oligomer, P6T<sup>20</sup> (see Fig. 1a for the structural formula). The crystals were fabricated as thin rectangle plates (typically around 3-10 mm long, 0.5-1 mm wide, and 1-3  $\mu\text{m}$  thick). Figures 1b and 1c show micrographs of an as-grown single crystal of P6T at different magnifications. The thin crystals function as slab waveguides, ensuring that photons are confined and propagate within the slabs. The slab planes exhibit molecular-scale flatness (around a few nanometers within an area of 5  $\mu\text{m}$  x 5  $\mu\text{m}$ ) with steps of about 3 nm (approximately 1 step per 1-5  $\mu\text{m}$ ), as confirmed by atomic force microscope (AFM) observations. This step size is equivalent to half the lattice constant of 6.188 nm for the *c*-axis of a P6T crystal (i.e., the length of a single molecule).<sup>21</sup>



**Figure 1** Details of the P6T crystal lasers. **a**, Chemical structure of P6T. **b**, Global image of a P6T single crystal. The right inset shows the crystallographic structure of P6T. **c**, Scanning electron microscope image of a P6T crystal. The crystal face corresponding to the *ac*-plane is represented as a vertical “cliff”. The *ab*-plane parallels the substrate plane. **d**, Schematic of the laser structure with the P6T crystal and our experimental setup. The crystal face shown in black-hatched yellow corresponds to the cliff face shown in **c**, and together with the face on the opposite side, it constitutes a Fabry-Pérot cavity.

The features present in the scanning electron microscope (SEM) photograph in Fig. 1c are fully consistent with the crystallographic data for P6T.<sup>21</sup> Note that the pair of crystal faces paralleling the *ac*-plane constitutes an optical resonator with its length defined as the separation between the two ends (measured along the *b*-axis). In the case

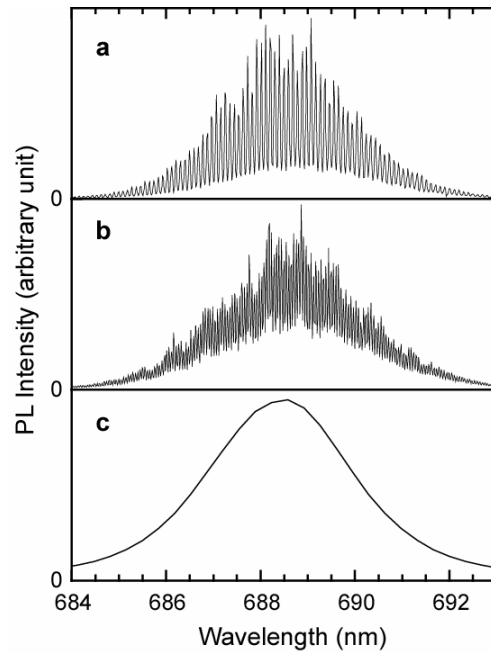
of the sample shown in Fig. 1b and designated as Sample A, for instance, the resonator length is 0.462 mm. These crystal end faces cross the other pair of crystal faces (i.e., the *ab*-plane) at right angles. Thus, these two pairs of crystal faces with the molecular-scale flatness can provide strong, two-dimensional self-cavity optical confinement. From the single crystals that we grew, we carefully selected two more samples with different resonator lengths (Sample B: 0.560 mm; Sample C: 1.02 mm). The part of each crystal surrounded by the two pairs of faces was entirely photo-pumped to detect the photoemission and record its spectrum (see Fig. 1d for the experimental setup).



**Figure 2** Laser-induced light emission spectrum of a P6T crystal (Sample A) at an incident laser fluence of  $1 \text{ mJ/cm}^2$ . The resonator length, defined as the separation between the two end faces (corresponding to the crystallographic *ac*-plane), is 0.462 mm. The inset shows an enlarged profile from the same spectrum.

Figure 2 shows the laser-induced emission spectrum of Sample A at the excitation (incident) laser fluence of  $1 \text{ mJ/cm}^2$ . The photoemission was highly directional and exhibited superior output stability after thousands of shots with the excitation pulse laser. As seen in the figure, a progression of extremely narrow emission lines clearly appears around 689 nm. The full width at half maximum (FWHM) of the individual sharp lines is limited to only 38 pm (as shown in the inset of Fig. 2), close to our experimental limit of 35 pm. The narrow bandwidth confirms the efficient optical

confinement in the crystals. In fact, a Q factor of the crystals of about 20,000 is reached on the basis of the well-known equation of  $Q = \nu_{LASER}/\Delta\nu$  ( $\nu_{LASER}$  and  $\Delta\nu$  are the laser oscillation frequency and the frequency full width at half maximum of the individual sharp spectra, respectively).<sup>22</sup> These narrow lines arise regularly at an interval of 121 pm. As depicted in Figs. 3a and 3b, the spectra of Samples B and C also show the same features as that of Sample A except for the difference in mode intervals. The mode intervals of Samples B and C are 96 and 52 pm, respectively.



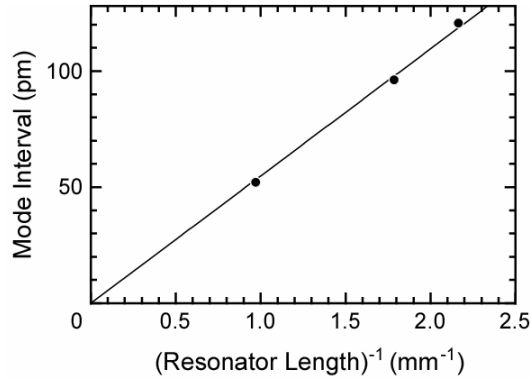
**Figure 3** Laser-induced light emission spectra of three P6T crystals at an incident laser fluence of 1 mJ/cm<sup>2</sup>. The resonator lengths of the crystals are **a**: 0.560 mm (Sample B) and **b**: 1.03 mm (Sample C). **c**: No cavity (Sample D, the pertinent end faces of this crystal have insufficient quality).

Figure 4 shows the resonator-length dependence of the mode interval for Samples A, B, and C. The diagram obviously indicates that the interval of the progressively structured emissions (see Figs 2, 3a, and 3b) is inversely proportional to the resonator length. This is in good accordance with the well-known relationship between the mode intervals ( $\Delta\lambda$ ) and resonator lengths ( $L$ ) as approximated below<sup>23</sup>

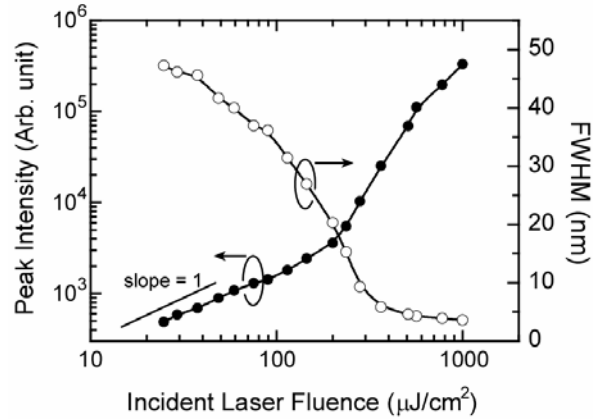


$$\Delta\lambda \propto \lambda^2/2L, \quad (1)$$

where  $\lambda$  is the center wavelength of the laser oscillation ( $\approx 689$  nm). The set of data in Fig. 4 is therefore a direct consequence of the presence of longitudinal cavity multi-modes confined in the resonator.



**Figure 4** Resonator-length dependence of the mode interval for Samples A, B, and C. The solid line was obtained by least mean square fitting with a constraint of the origin (0, 0).



**Figure 5** Photopumping intensity dependence of peak intensities (●) and FWHMs (○) of PL spectra from the P6T crystal (Sample D).

In Figure 3c we depict for comparison the photoluminescence (PL) spectrum from a crystal in which the pertinent crystal faces are of lower quality (Sample D). This spectrum was otherwise taken under the same experimental conditions as the above three samples. It is relatively broad (FWHM: 3.7 nm) and featureless and constitutes an

envelope of the sharply resolved progressions of lines demonstrated in Figs. 2, 3a, and 3b. Figure 5 shows photopumping intensity dependence of peak intensities and FWHMs of PL spectra from Sample D (no cavity). While the peak intensities increase nearly linearly with the incident laser fluence below the threshold of  $\sim 200 \mu\text{J}/\text{cm}^2$ , the peak intensities nonlinearly and abruptly increase with a slope of 3 or more above this threshold. Concomitantly, the FWHMs rapidly decrease around it. We judge this spectral narrowing results from the same mechanism that has been observed before (i.e., ASE).<sup>14,19</sup> The ASE wavelength and the center wavelength of the laser oscillation of 689 nm agree with that of the second vibronic peak of PL spectrum from P6T crystal under a weak excitation. Spontaneous emissions (i.e. PL in the weak excitation regime) from conjugated materials are usually accompanied by vibronic peaks where the emission intensities are maximal, producing the largest gain.<sup>5</sup> The relevant vibronic levels are thus expected to take part in the population inversion in stimulated emission. In addition, the extremely sharp emission depicted in Figs. 2 and 3 also ensures that there is a coherent photoemission process in P6T crystal, which causes ASE. This is because spontaneous emission from an optical resonator also shows the corresponding interference spectral structure but cannot lead to such a sharp structure.

It is worth mentioning the polarization characteristics of these emissions in association with the crystal structure. The P6T molecules are aligned with the molecular long axis, tilted by  $21^\circ$  from the normal to the *ab*-plane (the horizontal faces), and the direction of the transition dipole moment of these molecules is pretty close to that of the molecular long axis.<sup>21</sup> Therefore, we anticipate that the output beam is preferentially polarized along this normal direction. Defining the index of the polarization as the intensity ratio of the light polarized parallel to the normal to that polarized perpendicular to it, we obtained a value of about 4. This seems consistent with our expectation.

In conclusion, we have demonstrated, for the first time, multi-mode laser oscillation in self-cavity single crystals of P6T. The essential point is that in a slab

crystal of P6T, a pair of crystal faces corresponding to the *ac*-plane constitutes a perfect optical resonator (a Fabry-Pérot resonator), with its length defined as the separation between the two faces. The vibronic levels play a role in the laser oscillation through its large optical gain. The lasing occurs at the wavelength of the second vibronic peak of spontaneous emission from the P6T crystals.

### ***Methods***

The synthesis and purification methods for P6T can be found elsewhere.<sup>20</sup> The crystal growth procedure is described in our previous report.<sup>19</sup> The SEM photograph was taken with a Hitachi S-5000 field emission scanning electron microscope at a tilt angle of 40° against the normal of the slab crystal plane. The AFM observations were carried out in the dynamic mode using a Shimadzu SPM-9500J3 scanning probe microscope. An N<sub>2</sub>-gas laser, generating a light pulse of 500-ps duration at 337.1 nm with a repetition rate of 10 Hz, was used as the excitation light source. The rectangular-focused (1 mm x 5 mm) excitation laser light was normally incident to a horizontal crystal face that adhered closely to a quartz substrate. The light emitted from the end face was detected through a UV-cut filter.

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