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# Refractive Index along the Molecular Long Axis of an Orthorhombic Thiophene/Phenylene Co-Oligomer Crystal

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## 1. Introduction

Thiophene/phenylene co-oligomers (TPCOs) [1,2] are a novel class of organic semiconductors. The crystals of TPCOs are characterized by the regular layered structure of molecules [3–5], and have shown peculiar optoelectronic properties [6–8]. Recently, the refractive indices for thin single crystals of AC5, one of TPCOs, have been demonstrated. The indices along the crystal axes parallel to the flat crystal surface were determined to be ~1.6–1.9 from the interference of the polarized reflectance spectra [5], and the index along the direction perpendicular to the surface was estimated to be 4.0 from the mode interval of the multimode laser oscillation [9]. The experimental indices were compared with those computed semiempirically from the atomic coordinates of the crystallographic data [9]. The comparison demonstrated the crystal axes to be rotated by several degrees against the principal axes of the refractive indices around the unique axis of the AC5 crystal [9]. The monoclinic TPCO crystals [3–5] are regarded as the origin of this axis rotation.

Meanwhile, the crystal of BP1T-OMe [10], one of TPCO materials, is orthorhombic [11], and has shown strongly polarized spectrally-narrowed emission (SNE) [12]. This polarized SNE was attributed partly to the upright configuration of the molecular long axis exactly parallel to the crystal long axis. In such a crystal, the crystal axes are expected to be identical to the principal axes. In the present studies, we have investigated the refractive index along the molecular long axis of the orthorhombic BP1T-OMe crystal from the multi-mode laser oscillation. The experimental indices are compared with the computed ones as well.

## 2. Experimental

Figure 1(a) shows the structural formula of BP1T-OMe. Single crystals of BP1T-OMe were grown in a vapor phase [12,13]. The molecular long axis is parallel to the crystal $a$-axis [11]. We selected a crystal with its thickness of 1.0–1.8 μm. The crystal gives a pair of parallel $ac$-planes with a separation of 505.6 μm, which acts as a laser resonator. The crystal was mounted on a $SiO_2/Si$ substrate for the measurements.

Figure 1(b) schematically depicts the measurement geometry around the crystal. We used for the excitation light source an optical parametric oscillator pumped with a Nd:YAG laser. The excitation wavelength, pulse duration, and pulse repetition rate were 420 nm, 16 ns, and 10 Hz, respectively. The excitation light polarized along the $c$-axis
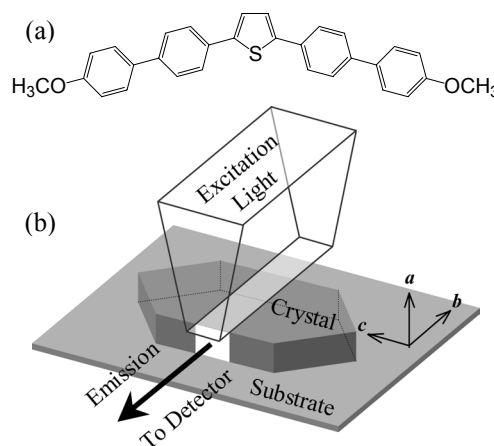


Fig. 1 (a) Structural formula of BP1T-OMe. (b) Schematic diagram of the measurement geometry around the crystal.

was incident perpendicular to the $bc$-plane. The light was focused with a cylindrical lens so as to be a line shape (~80 μm × 2 mm) in parallel with the $b$-axis. Emissions occurring from the $ac$-plane were polarized with a polarizer either along the $a$- or $c$-axis before being detected with a monochromator-spectrograph equipped with a charge-coupled device camera.

The quantum chemical calculations were carried out on a MOS-F program [14] at a semiempirical level to compute the dynamic polarizability tensor. The refractive indices can be estimated from this tensor [9]. For the calculations we have used the atomic coordinates from the crystallographic data for BP1T-OMe crystal [11].

## 3. Results and Discussion

Figure 2(a) shows the polarized emission spectra under the pulse excitation of 6.7 mJ/cm². For the $a$-axis polarized emission, equally spaced lines due to a multimode oscillation are well resolved in the wavenumber region of 19850–20050 cm⁻¹ while no lines are found in the $c$-axis polarized emission. The emission polarization ratio of the $a$-axis to $c$-axis was calculated to be ~20 from the integrated intensity between 19850 and 20050 cm⁻¹.

We carried out the line shape analysis on 53 lines for the $a$-axis polarized emission from 19865 to 20002 cm⁻¹ using the pseudo-Voigt function as a fitting function. Figure 2(b) shows example lines with fitted curves in the region of 19895–19945 cm⁻¹. The fitting functions for the above-mentioned 53 lines were found to well replicate the
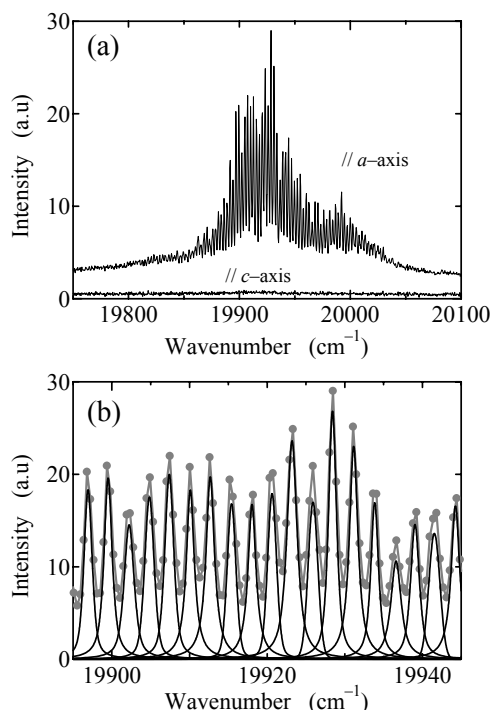
Fig. 2 (a) Polarized emission spectra of a BP1T-OMe crystal along the *a*- and *c*-axes. (b) The enlarged *a*-axis polarized spectrum around 19920 cm$^{-1}$. The gray line and dots indicate the experimental data. The black lines are fitted curves.

original emission spectrum. We calculated from these functions the averaged mode interval $\Delta\nu$ and the averaged full width at half maximum (FWHM) to be 2.64 cm$^{-1}$ and 1.60 cm$^{-1}$, respectively.

From the calculated $\Delta\nu$, we can determine the refractive index $n$ based on $n = 1/2L\Delta\nu$, where $L$ is the separation between a pair of parallel crystal faces. We estimated $n$ to be 3.75 on the basis of both the above-mentioned $\Delta\nu$ and the separation (505.6 μm). We also estimated the indices from the emission spectra under the excitations of 8.4 and 5.3 mJ/cm$^2$ to be 3.76 and 3.77, respectively. The averaged index is 3.76. This is pertinent to the *a*-axis due to the strong *a*-axis polarized emission from the crystal.

The refractive indices along the crystal axes of BP1T-OMe are summarized in Table I. The experimentally determined refractive indices associated with the *b*- and *c*-axis are the representative numbers [5]. The index pertinent to the *a*-axis is larger than the others. We calculated the refractive indices semiempirically from the polarizability tensor at 19921 cm$^{-1}$. Both the computational and experimental results qualitatively agree even though the computed results are systematically smaller than experi-

Table I Refractive indices determined by experiments and computations. Experimental results associated with the direction of the *b*- and *c*-axes are taken from Ref. [5].

| | Refractive index | | |
|---|---|---|---|
| | *a*-axis | *b*-axis | *c*-axis |
| Experimental | 3.76 | 1.50 | 1.66 |
| Computational | 3.13 | 1.22 | 1.49 |

mental ones as seen in the monoclinic AC5 crystal [9].

It is noted here that the polarizability tensor is diagonalized when three Cartesian axes agree with the crystal axes. This indicates that in the BP1T-OMe crystals the principal axes of the refractive indices are exactly identical to the crystal axes. This is due to both the orthorhombic BP1T-OMe crystal and the molecular long axis parallel to the crystal long axis [11].

## 4. Conclusions

The refractive index along the molecular long axis has been determined for the orthorhombic BP1T-OMe crystal from the well-resolved longitudinal multimode laser oscillations. Semiempirically calculated indices qualitatively agree with the experimental ones. The calculation reveals that the principal axes of the refractive indices are identical to the crystal axes. The present orthorhombic organic crystals and its large refractive indices perpendicular to the crystal face are useful for the laser device applications.

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