Spectrally narrowed emissions occurring near an interface between a single crystal thiophene/phenylene co-oligomer and a glass substrate

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Polarized emission microspectroscopy has been investigated on a single crystal of a thiophene/phenylene co-oligomer. We measured polarized emissions occurring from the thin cloven facets of the crystal mounted on a glass substrate. The polarized UV light from a mercury lamp was used for the excitation. The spectrally narrowed emissions have been observed with an unusually low excitation intensity (~ 90 mW/cm^2) at the parts of the substrate very close to the interface between the crystal and the substrate. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2815642]

Organic semiconducting molecules and polymers are currently attracting keen attention as potentially useful materials for photonic devices because partly of the spectrally narrowed emissions (SNEs) observed for those materials.[1,2] Of these, thiophene-based conjugated molecules have been widely investigated and the relevant spectroscopic data are well documented with their crystals.[3–7] The researchers attributed the SNE either to the stimulated emission or to the amplified spontaneous emission. Such SNE led to the laser oscillation in case a couple of parallel crystal edges formed a resonator. Ichikawa *et al.*[8] and Shimizu *et al.*[9] independently observed the laser oscillation using the crystals of thiophene/phenylene co-oligomers. Very recently, spin-cast conjugated polymer films were found to exhibit the SNE with a full width at half maximum (FWHM) down to several nanometers on the layered heterostructures comprising the said polymer and a dielectric.[10,11] Pauchard *et al.*[10] ascribed this SNE to the cutoff mode which propagates near the polymer/dielectric interface. Li *et al.*[11] concluded that the SNE was due to a cavity effect between the polymer/air and the polymer/glass interfaces. So far, the SNE has been observed only through photoexcitation with a high intensity pulsed laser.[1–11] An optical gain threshold intensity as low as 190 W/cm^2 was observed.[11]

In crystals of the thiophene/phenylene co-oligomers,[12] the molecular long axes are nearly upright against the wide crystal face (the *ab* plane) and parallel to the *c* axis.[13] It will therefore be of great interest with the emission measurements to excite molecules with a light polarized along the molecular long axes that parallel the transition dipoles with a large oscillator strength. In this context, the microspectroscopy gives a powerful tool. This method enables us to closely examine thin cloven facets (both the *bc* and *ca* planes that parallel the transition dipoles). In the present studies, we report characteristics of the SNE with unusually weak excitation intensities (~ 90 mW/cm^2) that takes place upon irradiation with a mercury lamp.

Figure 1 shows the experimental setup and the measuring configuration. The polarization measurements were performed using a polarizing microscope equipped with a mercury lamp. The microscope includes two polarizing plates; one polarizes excitation light incident to the crystal (polar-

izer), and another polarizes emission light occurring from the crystal (analyzer). The polarized excitation light was separated into the several lines in the UV region (330–380 nm) by an excitation filter and then made incident perpendicularly to the thin *bc* and *ca* facets. The polarized emission light was guided to a detector (photonic multichannel analyzer) with an optical fiber. The polarization directions of both the excitation and emission lights were set parallel to one of the crystallographic axes. The detected parts are schematically marked with circles in Fig. 1(b). Thus, we are able
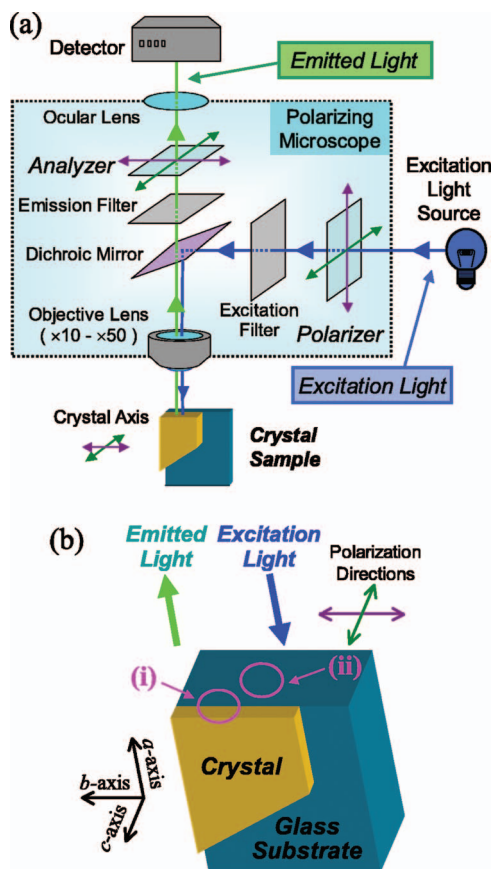

FIG. 1. (Color) (a) Experimental setup of the microspectroscopic measurements. (b) Enlarged drawing around the crystal/substrate interface. The depicted geometry is for the *b*- and *c*-polarized measurements. The detected parts are marked with circles: (i) the crystal/substrate interface and (ii) the glass substrate.
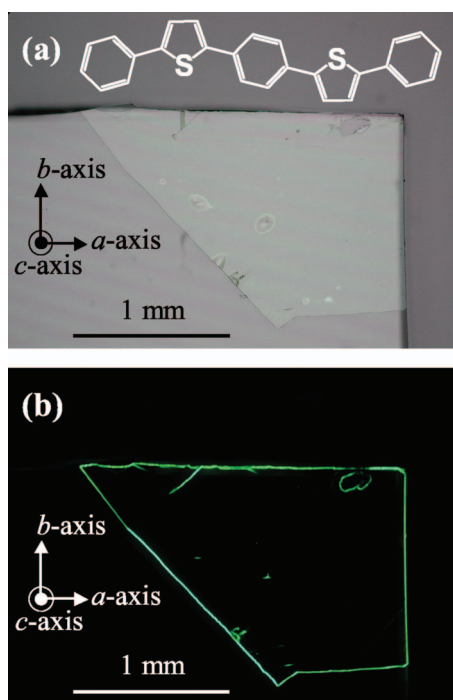
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FIG. 2. (Color) (a) Glass substrate laminated with an AC5 crystal. The substrate and the crystal were cloven together at the upper side and the right side. The inset shows the structural formula of AC5. (b) Luminescent micrograph of the AC5 crystal.
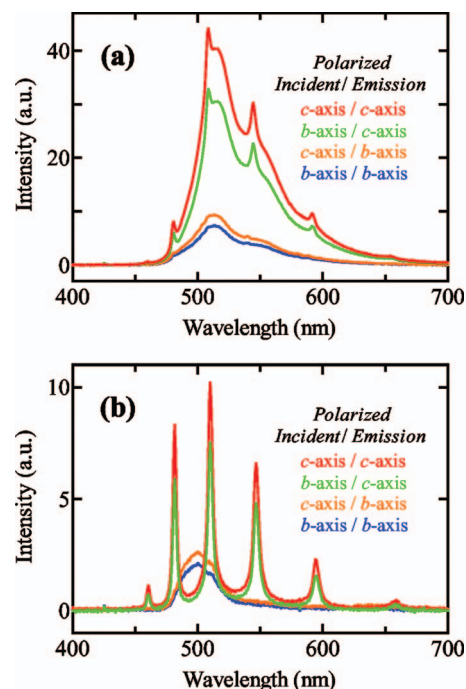

FIG. 3. (Color) (a) Polarized emission spectra of the AC5 crystal from the parts including the AC5/glass interface. (b) Polarized emission spectra of the AC5 crystal from the parts of the substrate just below the AC5/glass interface. To both the cases, the excitation intensity was 92 mW/cm^2 and the magnification was 10.

to observe polarized emission spectra on a part of $\sim$20–100 μm in size depending upon the magnifications of 10–50.

We grew in a vapor phase a flat crystal of 2.37 $\times$3.01 mm^2 in size and 1.72 μm in thickness of 1,4-bis(5-phenylthiophen-2-yl)benzene[12] [AC5; see Fig. 2(a) for its structural formula]. Note that the normal to the wide crystal face (the *ab* plane) is nearly parallel to the molecular long axis with an angle between them being 1.5°.[14] That crystal was mounted on a cleansed glass substrate ($\sim$0.32 mm thick) and cloven twice together with the substrate to make both the cloven *bc* and *ca* facets and the substrate edges align [see also Fig. 1(b)]. Here, we referred to the statement by Kozlov *et al.*[2] that before organic film deposition, the (100) InP substrate was cleaved and that the vacuum-deposited organic film conformed to the shape of the underlying substrate. Figure 2(b) depicts the luminescent micrograph of the crystal. Only the crystal edges are luminescent, apart from luminescent defects dilutely interspersed inside the crystal. This feature plays an important role in the weak-excitation SNE.

Figure 3 shows the polarized emission spectra related to the *bc* facet of the AC5 crystal. In Fig. 3(a), where the measurement includes the AC5/glass interface, a featureless broad and weak band is observed with the *b*-polarized emission (regardless of the excitation polarization). The *c*-polarized emission band, on the other hand, is strong with four well-resolved peaks superimposed at 481, 509, 544, and 591 nm. Figure 3(b) displays the polarized emission spectra from the glass substrate just below the AC5/glass interface. The featureless broad and weak band is again observed with the *b*-polarized emission. In contrast with Fig. 3(a), the *c*-polarized emissions are observed as isolated narrow lines with FWHM down to 4 nm. Five distinct lines arise at 461,

482, 510, 547, and 594 nm, and an additional peak is noticeable at 659 nm though less intense. Four peaks out of them are of the same origin as those observed in Fig. 3(a). More importantly, the SNE has taken place with a very low excitation intensity of 92 mW/cm^2. This is lower by several orders of magnitude than ever reported with the related materials (i.e., conjugated polymers and molecules). In particular, the three major lines occurring at $\sim$480–550 nm [see Fig. 3(b)] retain a narrowed feature even at excitation intensities down to $\sim$10 mW/cm^2. The threshold for the spectral narrowing was not observed within our measuring range. We confirm similar results with the *ca*-plane measurements; the *c*-polarized SNE lines are again clearly noted at the related locations and with similar FWHMs. The SNE, however, could not be detected remote from the interface.

There were many studies and reports on the SNE observations on the various configurations. The emission measurements were carried out using thin films (or crystals) that were cast (or mounted) on the substrate such as (quartz) glass and dielectrics such as silicon dioxide.[15] In most cases, the excitation light was incident perpendicular to the wide film (or crystal) plane and the emission occurring nearly vertical to the excitation light was detected. In this situation, it was easy to change the excitation length of the gain medium. In turn, there are two major difficulties with the optical measurements of the thin cloven facets: (i) The measurement itself is difficult; the edge of the material must be a vertical "cliff" of optically high quality. (ii) To change the excitation length is virtually impossible because the gain "length" is limited to the film (or crystal) thickness of at most $\sim$10 μm. Nonetheless, we had a unique opportunity to fabricate single crystals of a laser quality.[8,9] This means not only that the crystal edges function as a resonator but also that the other way around one can readily let the light in from the outside of the

crystal and excite it effectively. The measurement configuration is related to one studied by Li *et al.*[11] in that the conjugated material [AC5; refractive index $n \approx 1.62–1.87$ (Ref. 14)] is located between the glass substrate ($n \approx 1.52$) and air ($n \approx 1$). The SNE observed close to the AC5/glass interface is also related to their observation.[11]

The narrowed lines observed at 510 and 547 nm are positionally related to those causing the emission gain narrowing with a clear threshold excitation energy in the *same* AC5 (poly)crystalline material.[6,7] We therefore attribute the SNE in the present studies to the gain-narrowed emission as in many other cases of the related materials.[5–7] The argument is as follows: Let us assume in our measurement configuration that the light intensity I at the position x measured from the crystal edge in the direction of the incident light is described as[15]

$$I = I_0 \exp\{[g_i(x) - \alpha]x\}, \tag{1}$$

where I_0 is the initial light intensity (at the crystal edge), $g_i(x)$ is a gain coefficient related to the i polarization ($i = a, b, c$) as a function of x, and α is the loss coefficient. The $g_i(x)$ varies following x, since the magnitude of the population inversion changes depending on x. The implication of Eq. (1) is as follows: The excitation is effective only for the parts close to the crystal edge ($x = 0$), because the light is rapidly absorbed as x increases. Concomitantly, the amplification becomes ineffective deep inside the crystal. Consequently, α should be negligibly small so that the SNE can take place and be propagated within the whole crystal. Its optically high quality [Fig. 2(b)] ensures this. The small α, at the same time, probably explains the experimental result of the unnoticeable threshold for the spectral narrowing. The SNE may well be emitted after multiple reflections inside the crystal.[16]

In conclusion, we have measured polarized emissions occurring from the thin cloven facets of the crystal mounted on the glass substrate. The spectrally narrowed *c*-polarized emissions were observed with an unusually low excitation intensity (approximately 90 mW/cm^2) at the parts of the substrate very close to the interface between the crystal and the substrate.

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