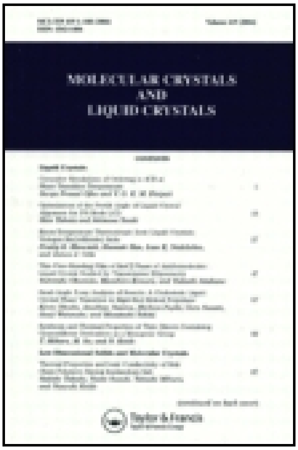

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Light Emitting Properties of Molecular Thin Films with Epitaxially Oriented and Confined Structures

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Light Emitting Properties of Molecular Thin Films with Epitaxially Oriented and Confined Structures

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Abstract One-dimensional needlelike crystals of energy-band-tuned thiophene/*p*-phenylene co-oligomers were epitaxially grown by vapor-deposition onto the KCl (001) surface. Fluorescence spectroscopy and microscopy elucidated various emission color depending on their frontier orbital energies which were changed by the coplanar or twisted molecular structures. The emitted light was confined within the co-oligomer crystals and self-waveguided along the needle axis, then radiated from the tips of the needles. When the co-oligomer needles were confined in a heterostructure within a thin film of a wide-bandgap *p*-sexiphenyl oligomer, the self-waveguided emission from the co-oligomer was also observed due to the confinement of excitons and emitted light in the crystal.

Keywords epitaxial crystals; vapor-deposition; thiophene/*p*-phenylene co-oligomers; organic confinement structure; self-waveguided emission

INTRODUCTION

Extensive researches are now approaching to realize lasing with organic materials

[1] and organic laser diodes (OLD) by extending organic electroluminescence devices (OLED) [2]. Among different classes of light-emissive molecules, π-conjugating materials such as polythiophene, poly-*p*-phenylene and their oligomer species [3-10] have attracted interests from their practical stability and linearly polarized emission. In the active layers of OLEDs, generally amorphous thin films have preferably been used for reducing intermolecular quenching and thermal deactivation. However, such amorphous structures spoil one-dimensional anisotropic properties of these linear π-conjugaiting molecules. By aligning their molecular axes in specific directions, therefore, polarized and directed luminescence can be obtained towards enhancement of light emission [11]. π-Conjugating oligomers are more favorable to be crystallized in an ordered alignment due to their definite molecular lengths. The previous study [12] reported that *p*-sexiplenyl (*p*-6P) was grown in epitaxially oriented films when vapor-deposited on the (001) surface of KCl, and its OLED showed anisotropic, blue electroluminescence depending on the molecular orientation. Furthermore, one-dimensional *p*-6P crystals of submillimeter scale in length grown by mask-shadowing vapor-deposition on the KCl (001) surface exhibited the self-waveguided emission where perfectly polarized emission was confined inside the crystals and propagated along the needle axis of the crystal [13]. In view of structures of semiconductor LDs precisely designed for confinement of carriers and emitted light, such low-dimensional molecular crystals of the π-conjugating oligomers are promising candidates to realize solid state organic lasing.

Towards electrically pumped light amplification, carrier trapping, exciton accumulation and light confinement in the active molecular crystals are considered by employing energy-band-tuned carrier injection and transport layers. In this work, we used *p*-phenylene/thiophene co-oligomers [14-16], the frontier molecular orbital energies of which can be controlled by different sequences, block length and alternateness of the thiophene and *p*-phenylene units in the linear chain. Epitaxially ordered low-dimensional crystals and heterostructures were prepared by vapor-deposition of various co-oligomers onto the KCl (001) surface. Their self-waveguided and confined light-emission were investigated by fluorescence spectroscopy and microscopy.

EXPERIMENTAL

Molecular structures and frontier orbital configurations of *p*-phenylene/thiophene co-oligomers used were estimated by molecular orbital calculations using ZINDO parameters. Epitaxial crystals and thin films of π-conjugating oligomers were grown by vapor-deposition onto a freshly cleaved (001) surface of a KCl single-crystal under a vacuum of 5×10^{-4} Pa. Powder sample loaded on a quartz crucible was resistively heated with a coiled tungsten. Substrate temperature was kept constant at 25-150°C during deposition. After cooled at room temperature, thin specimens grown on the KCl substrate were provided for further characterization under an ambient atmosphere. Fluorescence microscopy and spectroscopy were carried out using an inverse microscope equipped with a CCD multichannel spectrometer under ultraviolet excitation at λ_{ex}=365 nm with a high-pressure Hg lamp. Morphology of the deposited crystals on the KCl surface was observed by atomic force microscopy (AFM) by the contact mode with a Si_3N_4 cantilever.

RESULTS AND DISCUSSION

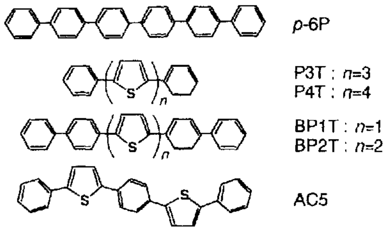

FIGURE 1 Chemical structures of *p*-6P and *p*-phenylene/thiophene co-oligomers.

Chemical structures of *p*-6P and *p*-phenylene/thiophene co-oligomers used are shown in Fig. 1. Their symmetry classification and energies of the highest occupied orbital (HOMO) and lowest unoccupied one (LUMO) optimized by the ZINDO calculations are summarized in Table I. The π-conjugation in *p*-6P is limited due to its alternately twisted structure of the six phenyl rings so that the HOMO-LUMO gap is the highest, resulting in a blue light-emission as shown in the fluorescence spectrum of the vapor-deposited film in Fig. 2. On the other hand, P3T, P4T and AC5 are planar giving rise to the red shift of their fluorescence bands while BP1 and BP2 have intermediate HOMO-LUMO gaps due to their planar thiophene blocks and twisted biphenyl ones. The transition dipoles between their HOMO and LUMO are all directed along their molecular chain axes.

Figure 3 shows representative fluorescence micrographs of BP1T and AC5 vapor-deposited on the KCl (001) surface kept at 150°C. Both crystals epitaxially grow in long needles aligning along the KCl [110] directions. Polarization of the emitted light and their electron diffraction indicate that their molecular chains orient parallel

TABLE I Symmetry and frontier orbital energies of the oligomers calculated by ZINDO.

Molecule	Point group	Symmetry species and energy (eV) HOMO	LUMO	$\Delta E_{HOMO-LUMO}$ (eV)
p-6P	D_2	b_2 -7.494	b_3 0.063	7.557
P3T	C_{2v}	a_2 -7.148	b_2 -1.114	6.034
P4T	C_{2h}	b_g -7.118	a_u -1.183	5.935
BP1T	C_1	a -7.033	b -0.695	6.338
BP2T	C_2	b -6.849	a -0.948	5.901
AC5	C_{2h}	b_g -7.184	a_u -0.891	6.293

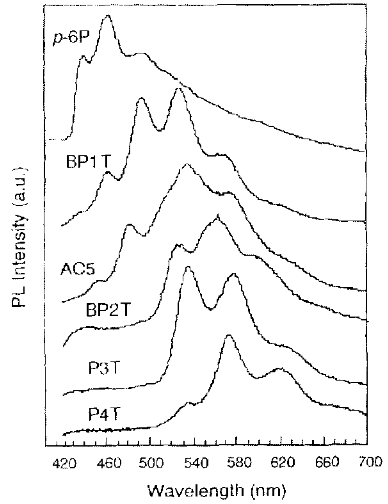

FIGURE 2 Fluorescence spectra of vapor-deposited thin films of the oligomers.

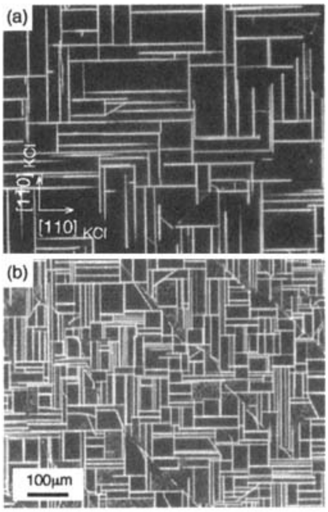

FIGURE 3 Fluorescence micrographs of BP1T (a) and AC5 (b) vapor-deposited on KCl kept at 150°C.

to the KCl surface but perpendicular to the long axis of the needle crystal as similar as those of *p*-phenylene oligomers on KCl [17]. Figure 4 shows a topographic image and a height profile of the BP2T crystal on KCl observed by AFM. The needles extending up to the submillimeter length have the width of 400-600 nm and the height of 200-300 nm. Such crystal dimensions comparable to the wavelength of light enable the epitaxial needles to act as a self-waveguide for the emitted light

Figure 5 (a) shows a fluorescence micrograph of the BP2T crystals indicating that a spotty emission appears at the terminal ends of the orthogonally crossing needles. When the excitation was focused on a center region with a round aperture, such a spotty emission still occurs at the both ends of the needlelike crystals extending out-

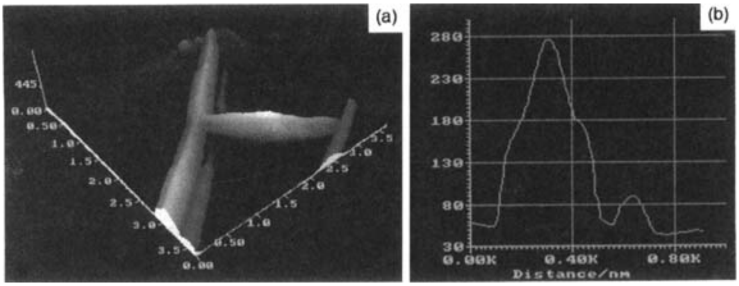

FIGURE 4 AFM image (a) and height profile (b) of BP2T needlelike crystal vapor-deposited on KCl kept at 150°C.

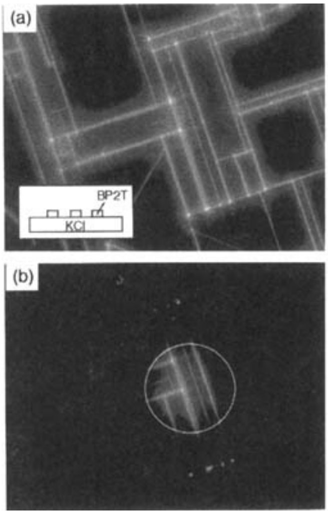

FIGURE 5 Fluorescence images of BP2T crystals. Only the center round region was UV-excited in (b).

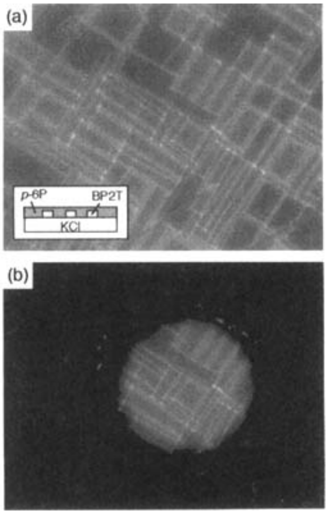

FIGURE 6 Fluorescence images of BP2T crystals covered with *p*-6P film. Only the center round region was UV-excited in (b).

side the excited region, as shown in Fig. 5 (b). It demonstrates that the emitted light is confined in the crystals and propagated along the needle axis by the self-waveguiding effect as similar as reported for the *p*-6P crystals [13]. This self-waveguided emission was also observed when the BP2T crystals were confined within *p*-6P as shown in Fig. 6, where a polycrystalline film of *p*-6P was vapor-deposited on top of the BP2T crystals grown on the KCl substrate kept at 25°C. The whole area covered with the *p*-6P film gives blue fluorescence while the greenish yellow emission of BP2T appears at the tips of the needlelike crystals. Only this spotty emission of the BP2T crystals appears even outside the excited region in Fig. 6 (b). It suggests that the emitted light of BP2T is confined inside the crystal and propagated along the needle axis based on its higher refractive index that is expected from the smaller HOMO-LUMO gap of BP2T as compared to that of *p*-6P (Table I).

In conclusion, the *p*-phenylene/thiophene co-oligomers exhibit stable light-emission even in epitaxial crystals with tunable wavelengths controlled by molecular design. Their highly polarized self-waveguided emission confined in the low-dimensional epitaxial crystals is one possible candidate for solid-state organic lasing.

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