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Light-emitting organic field-effect transistors based on highly luminescent single crystals of thiophene/phenylene co-oligomers†

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A series of thiophene/phenylene co-oligomers containing π-conjugated anthracene, naphthalene, and biphenyl central cores have been developed as new organic laser active materials. Light-emitting organic field-effect transistors (LE-OFETs) based on 2,6-bis(5-phenylthiophen-2-yl)anthracene (BPTA), 2,6-bis(5-phenylthiophen-2-yl)naphthalene (BPTN), and 2,6-bis(5-phenylthiophen-2-yl)-1,1′-biphenyl (BPTB) single crystals were fabricated. A clear laser oscillation was observed for BPTN and BPTB single crystals. Especially for BPTB, a low amplified spontaneous emission threshold of 1.8 ± 0.2 μJ cm^{-2} was achieved. In addition, all of the devices showed ambipolar transport characteristics, in which both electron and hole carriers are transported in a single FET device, and electroluminescence was clearly observed. An obvious difference in the light emission direction was observed for LE-OFET devices, which is attributed to the difference in transition dipole moment arrangement of individual molecules within the crystal.

Introduction

Organic semiconductors have shown great potential as laser active materials because of their attractive features, such as high optical gain, broad emission spectra, and good processability. The realization of organic injection laser is a challenging research subject in the field of organic semiconductor devices, and various approaches have been attempted.[1–4] In particular, light-emitting organic field-effect transistors (LE-OFETs) are suitable for laser devices in terms of their efficient electroluminescence (EL) properties and high current capabilities.[5] LE-OFETs have been extensively investigated to achieve superior transistor characteristics, and the basic properties for carrier transport and light emission have been clarified. High performance ambipolar LE-OFETs strongly require high carrier mobility and luminescence efficiency for their active materials. It has been reported that a rubrene single-crystal OFET shows excellent p-channel transistor characteristics with a hole mobility (μ) as high as 40 cm^2 V s^{-1} in the four-terminal measurement, and 18 cm^2 V s^{-1} in the two-terminal measurement.[6] Despite its high mobility, significant reduction in the photoluminescence (PL) quantum yield (Φ_{PL}) is generally seen in such p-type organic semiconductor systems, due to detrimental concentration quenching.

In this context, we focus on thiophene/phenylene co-oligomers (TPCOs) as a promising active material for LE-OFETs, which can offer both high luminescence and charge transport capability. With the recent seminal report by Hotta and coworkers,[7–9] TPCOs are of great interest as laser active materials. Stimulated emission behavior, including amplified spontaneous emission (ASE),[10–15] is observed in molecular single crystals. In particular, LE-OFETs based on a single crystal of 5,5′′-bis(1,1′-biphenyl-4-yl)-2,2′:5′,2′′-terthiophene (BP3T) have shown a high hole mobility of over 1.0 cm^2 V s^{-1} and an electron mobility of over 0.24 cm^2 V s^{-1} and a threshold for stimulated emission as low as 8.0 μJ cm^{-2}.[5,16] In addition to the high carrier transport ability, suitably well-aligned transition dipole moments in BP3T single crystals can promote a high optical gain. These excellent photonic and electronic functions prompted us to investigate the laser and LE-OFET properties of new TPCO derivatives (Fig. 1). In this study, we designed and synthesized a series of TPCOs incorporating π-conjugated anthracene, naphthalene, and biphenyl cores (BPTA, BPTN, and BPTB), and studied their ASE and LE-OFET properties.

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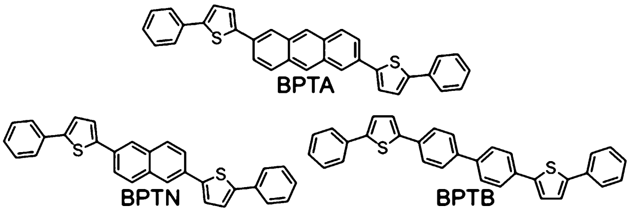


Fig. 1 Chemical structures of thiophene/phenylene co-oligomers.

Results and discussion

Single crystals of BPTA, BPTN, and BPTB were grown by means of physical vapor transport with a continuous flow of pure argon gas. The sizes of individual single crystals range from approximately 100 to 500 μm with the thickness of 200–300 nm. Fig. 2 shows the PL and ASE spectra of BPTA, BPTN, and BPTB single crystals. Table 1 summarizes the photophysical characteristics of each material. For the anthracene-based BPTA single crystals, yellow-green PL with a Φ_{PL} of 31% was observed. In the naphthalene-based BPTN single crystals, emerald-green PL with a Φ_{PL} of 56% was observed. For the biphenyl-based BPTB single crystals, a slight blue shift of the PL peaks was observed compared with that of BPTN, giving rise to a high Φ_{PL} of 87%. In addition, it is noteworthy that BPTN and BPTB display lasing activity in crystalline states. The ASE spectra of BPTN and BPTB appeared at 518 nm and 514 nm, respectively, suggesting that the 0–1 transition is the highest gain for ASE. Fig. 3 presents the pumping energy dependence of the peak full-width at half maximum (FWHM) of the ASE spectra for the BPTN and BPTB single crystals. The ASE threshold (E_{th}) for these single crystals was determined to be 9 ± 1 and 1.8 ± 0.2 μJ cm^{-2}, respectively. Upon UV irradiation, intense fluorescence emission was detected only from the crystal edges in the BPTN and BPTB single crystals, whereas in BPTA, both the crystal surface and edges were highly luminescent (Fig. 4). This result indicates that optical confinement inside the single crystals is attained for BPTN and BPTB, and this confined propagation propensity is similar to the case of a single crystal of 1,4-bis(5-phenylthiophene-2-yl)benzene (AC5) reported previously.[17]

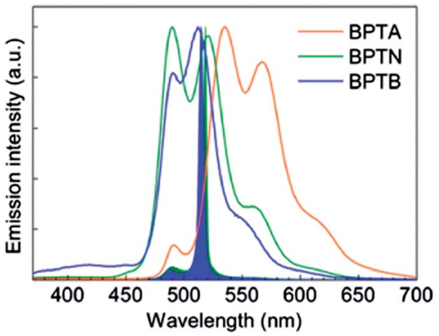


Fig. 2 Photoluminescence and amplified spontaneous emission spectra of BPTA, BPTN, and BPTB single crystals.

Table 1 Photophysical properties of BPTA, BPTN, and BPTB single crystals[a]

Compound	Φ_{PL} (%)	τ_{PL} (ns)	λ_{PL} (nm)	λ_{ASE} (nm)	E_{th} (μJ cm^{-2})
BPTA	31	2.28	567	—	—
BPTN	56	1.76	521	518	9 ± 1
BPTB	87	1.97	512	514	1.8 ± 0.2

[a] Abbreviations: Φ_{PL} = PL quantum yield; τ_{PL} = PL emission lifetime; λ_{PL} = PL emission peak at the 0–1 transition; E_{th} = ASE threshold.

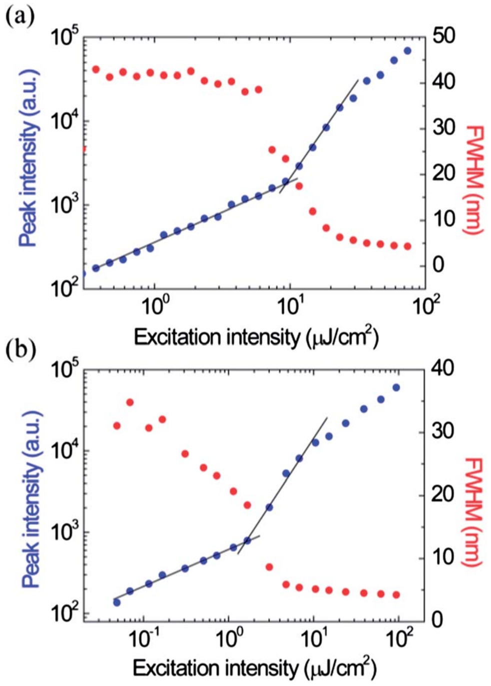


Fig. 3 Emission peak intensity and FWHM of PL spectra of (a) BPTN and (b) BPTB single crystals as a function of incident photon density (with 337 nm excitation).

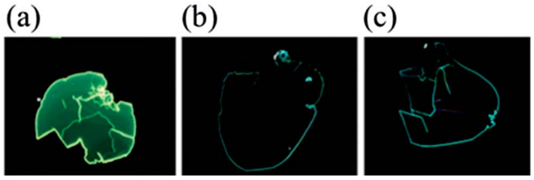


Fig. 4 Fluorescence micrographs of (a) BPTA, (b) BPTN, and (c) BPTB single crystals taken under UV irradiation (365 nm).

We also observed similar light propagation behavior in emission from LE-OFETs based on the BPTA, BPTN, and BPTB single crystals. The LE-OFETs were fabricated using the following procedures (Fig. 5). A highly doped silicon wafer with a 500 nm SiO$_2$ layer was coated with a 30 nm thick poly(methyl methacrylate) (PMMA; Sigma-Aldrich Co., average $M_w \sim 930\ 00$) layer to remove electron traps on the surface of an SiO$_2$ layer. The substrates were heated at 70 °C for 8 h, followed by

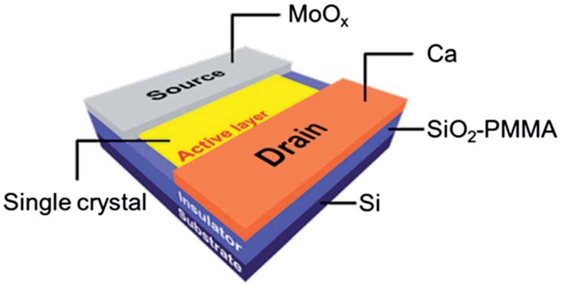


Fig. 5 Schematic representation of an LE-OFET based on an organic single crystal.

annealing at 110 °C for 1 h.[18] The BPTA, BPTN, and BPTB single crystals were laminated onto the PMMA-coated SiO_2–Si substrates in a globe box. Molybdenum oxide (MoO_x) and calcium were used as the source and drain electrodes, respectively, to reduce the injection barrier for both the hole and electron carriers.[19]

Electrical measurements of the devices were performed under vacuum ($<1.0 \times 10^{-3}$ Pa) in the dark using a semiconducting parameter analyzer (Agilent Co., E5273A). Fig. 6 shows the gate voltage (V_G) dependence of current (I_D) between the drain and source electrodes, and the photographs of light emission from each device. All of the LE-OFET devices showed ambipolar transport characteristics, in which electron and hole carriers are transported within the single device. The hole and electron mobilities were $\mu_h = 1.4 \times 10^{-1}$ cm^2 V s^{-1} and $\mu_e = 1.9 \times 10^{-1}$ cm^2 V s^{-1} for BPTA; $\mu_h = 2.6 \times 10^{-2}$ cm^2 V s^{-1} and $\mu_e = 4.6 \times 10^{-2}$ cm^2 V s^{-1} for BPTN; $\mu_h = 3.6 \times 10^{-3}$ cm^2 V s^{-1} and $\mu_e = 1.6 \times 10^{-2}$ cm^2 V s^{-1} for BPTB. Furthermore, bright EL was clearly observed from the single-crystal devices. Yellow emission was observed from both the top surface and side edges of the BPTA single crystal, whereas blue and green emissions were detected only from the side edges of the BPTN- and BPTB-based LE-OFETs, similar to the case of the ongoing optical excitation experiments (Fig. 2). It is thus inferred that the difference in light propagation and emission patterns of the devices should be attributed to the variation of molecular orientation in single crystals.

To clarify the molecular orientation in crystals, X-ray diffraction (XRD) measurements were performed.[20] Fig. 7 depicts the out-of-plane XRD patterns of BPTA, BPTN, and BPTB single crystals. Predominant peaks assignable to the (00*l*) reflections are obtained. For the BPTA single crystals, the first order diffraction peak with a *d*-spacing of 2.62 nm coincides well with the molecular length of BPTA (2.59 nm), indicating that the molecules are arranged with their long axis perpendicular to the substrate to form a lamellar structure. Likewise, the XRD patterns of BPTN and BPTB single crystals exhibit a set of (00*l*) reflections. The molecular lengths of these compounds also agree with the *d*-spacing of the respective (001) peak, indicative of perpendicular molecular orientation to the substrate surface in single crystals.

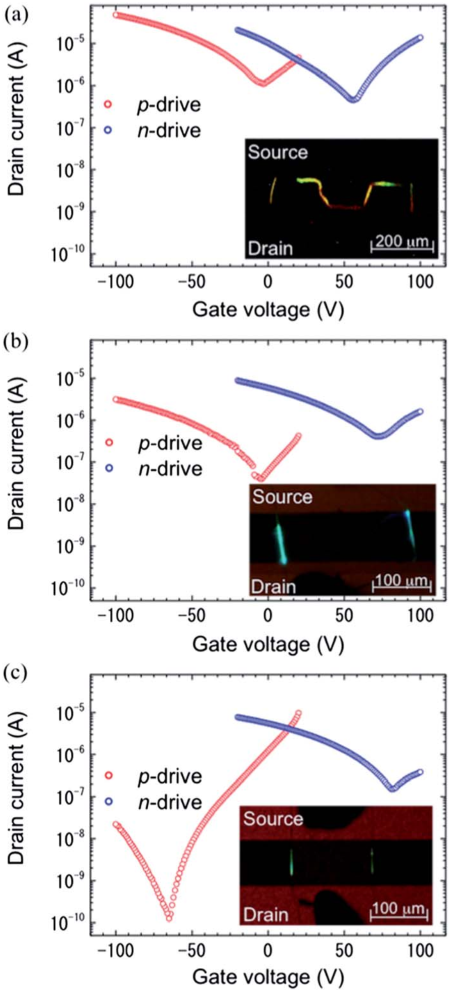
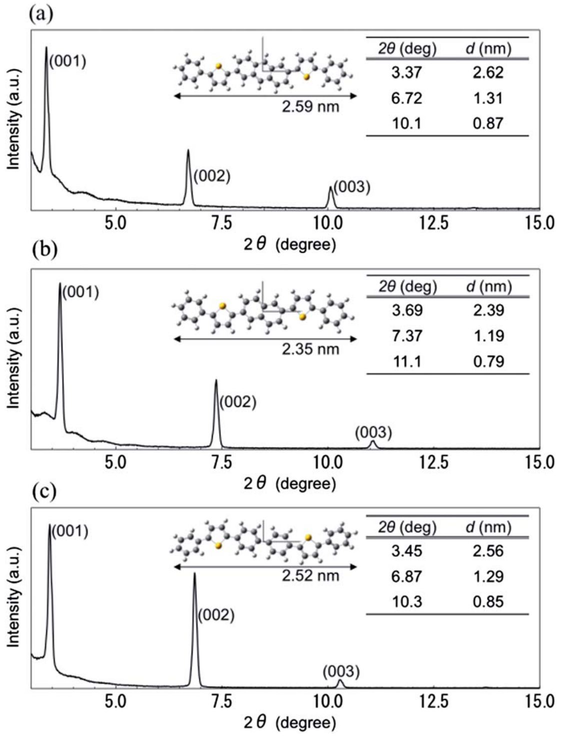


Fig. 6 Plots of I_D–V_G transfer characteristics of the devices based on (a) BPTA, (b) BPTN, and (c) BPTB single crystals during *n*-channel operation at $V_D = 100$ V (blue circles), and p-channel operation at $V_D = -100$ V (red circles). The insets represent optical photomicrographs demonstrating EL emission from the devices. The channel width (W) and length (L) are W/L = 459/87, 240/92, and 129/71 μm for BPTA-, BPTN-, and BPTB-based devices, respectively.

To assess the light emission direction, we calculated the transition dipole moment for individual molecules by time-dependent density functional theory (TD-DFT) computations (see ESI†). In general, light emission of organic molecules occurs along the direction perpendicular to the transition dipole moment. For instance, in an LE-OFET based on a tetracene single crystal the transition dipole moment is parallel to the substrate, and hence light emission from the crystal surface (*i.e.*, the direction perpendicular to the transition dipole moment) can be observed.[21] In our study, the calculated transition dipole moments for BPTN and BPTB are parallel to the longitudinal molecular axes. The angle between the dipole moment and the molecular long axis is 1.5° and 0.1° for BPTN and BPTB, respectively. Therefore, the EL emission from the BPTN- and BPTB-based LE-OFETs was detected predominantly from the crystal side edges, as a result of effectively waveguided emission parallel to the device substrate. In contrast, for BPTA the inclination angle of the transition dipole moment is calculated to be 11.5° with respect to the molecular long axis,



(a)

2θ (deg)	d (nm)
3.37	2.62
6.72	1.31
10.1	0.87

(b)

2θ (deg)	d (nm)
3.69	2.39
7.37	1.19
11.1	0.79

(c)

2θ (deg)	d (nm)
3.45	2.56
6.87	1.29
10.3	0.85

Fig. 7 XRD patterns of (a) BPTA, (b) BPTN, and (c) BPTB single crystals on a substrate. The molecular lengths of each compound are also indicated.

presumably because the local electric transition in the anthracene core is polarized perpendicular to the molecular long axis. Thus, the difference in light propagation and emission patterns should be ascribed to the inclination of the transition dipole moment to the longitudinal axis of the luminescent molecules, which can also influence their ASE activity in single crystals.

Conclusions

In this study, we have developed TPCO derivatives (BPTA, BPTN, and BPTB) by incorporating anthracene, naphthalene, and biphenyl cores as laser active materials, and fabricated LE-OFET devices based on the BPTA, BPTN, and BPTB single crystals. A clear laser oscillation is observed for BPTN and BPTB. A significantly low ASE threshold (1.8 ± 0.2 μJ cm^{-2}) is obtained for the BPTB single crystals. In addition, EL along with ambipolar transport can be induced in the LE-OFETs based on the BPTA, BPTN, and BPTB single crystals. It has been found that the direction of the transition dipole moment of the molecules significantly affects the light emission pattern as well as the ASE characteristics in single-crystalline states. To attain high optical gain and lower the ASE threshold, the control of molecular orientation and transition dipole moment arrangement should be crucial for single-crystal organic materials.

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