Strong Exciton-photon Coupling in Organic Microcavity Electroluminescence Devices with Thiophene/Phenylene Co-oligomer Derivatives

Shohei Dokiya¹*, Hideyuki Mizuno¹, Hitoshi Mizuno², Hiroyuki Katsuki², Kenichi Yamashita³, Fumio Sasaki⁴, and Hisao Yanagi²*

¹Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, Japan
²Graduate School of Science and Technology, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, Japan
³Faculty of Electrical Engineering and Electronics, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan
⁴Electronics and Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

E-mail: yanagi@ms.naist.jp

Abstract

Organic electroluminesence (EL) devices with surface-emitting microcavity structure were fabricated using vapor-deposited films of thiophene/phenylene co-oligomer (TPCO) derivatives, aiming at polariton formation under electrical excitation. Owing to strong coupling between excitons and photons in the device, we demonstrated the formation of cavity polaritons with a large Rabi-splitting energy ($2\hbar\Omega = 250$ meV). Furthermore, efficient relaxation into the bottom of lower polariton branch (LPB) was confirmed from angle-resolved EL spectra. In excitation-density dependence, the luminance of microcavity EL devices showed a superlinear increase with an elevation of current density indicating a contribution of triplet excitons.
An organic semiconductor laser is expected to be one of future research targets toward flexible and tunable photonic devices. The realization of electrically pumped organic lasers requires high-density carrier injection, reduced waveguiding loss, and the avoidance of non-radiative triplet excitons and polarons. An alternative way to overcome these issues is polariton lasing that is coherent radiation from exciton-polaritons created by strong coupling between emissive excitons and photons typically confined in a microcavity.\(^2\)\(^-\)\(^7\) A low threshold polariton lasing is possible due to the strong coupling regime in semiconductor microcavities without formation of the conventional population inversion scheme.\(^8\)\(^,\)\(^9\) Owing to the large oscillator strength and high exciton binding energy in Frenkel excitons, polariton formation and lasing from its Bose-Einstein condensate have been reported for microcavities filled with molecule-based materials under optical excitation at room temperature.\(^10\)\(^-\)\(^14\) Moreover, some extensive studies have achieved strong exciton-photon coupling in microcavity EL devices\(^15\)\(^-\)\(^19\) and light-emitting field-effect transistors (LEFETs),\(^20\)\(^,\)\(^21\) although electrically injected polariton lasing is still challenging.

As an advanced functional material for organic lasers, here we chose thiophene/phenylene co-oligomers (TPCOs)\(^22\)\(^-\)\(^24\) which has a high fluorescence quantum yield with excellent charge transport characteristics, and their emission color is easily tuned by modification of molecular structures. So far, optically pumped lasing with TPCO single crystals has been established at room temperature owing to their efficient light confinement in the crystal cavity with high group refractive index \(n_g \sim 5.0\) and high quality factor \(Q \sim 5000\).\(^25\)\(^-\)\(^29\) In addition, spectrally narrowed EL \(^30\) has been recently obtained in LEFET devices using TPCO crystals. Our previous studies have reported the formation of exciton-polaritons in cyano-substituted TPCO crystals under optical excitation using vertical-cavity surface emitting laser (VCSEL) structure.\(^31\)\(^-\)\(^35\) The cyano-substituted TPCO molecules orient lying in their platelet-shaped crystals that is suitable for the VCSEL structure since the transition dipole moments being parallel to the linear molecular axis enhance the strong coupling between the cavity photons and the confined excitons.\(^29\)\(^,\)\(^34\)\(^,\)\(^35\) These studies using single-crystal TPCO microcavities have reported a high exciton-photon coupling strength (Rabi splitting energy) of \(~100~\text{meV}\), demonstrating stable formation of exciton polaritons at room temperature. Since TPCO crystals typically grown with a thickness of 1-2 \(\mu\text{m}\) give rise to multiple photon modes, it could be further improved by thinning the crystal thickness to confine a single cavity photon mode. However, their precise thickness control is difficult, and such thin crystals are not easily handled to construct electrically driven VCSELs.
In this study, therefore, we try to fabricate microcavity EL devices by using conventional vapor deposition of thickness-controlled films with TPCO derivatives. While these films are inferior to single crystal media, we have previously found that the cyano-substituted TPCO molecules tend to orient lying on the substrate also in vapor-deposited thin films.\textsuperscript{36,37} To fabricate p/n-junction devices, we used 5,5’-bis(4-biphenyl)-2,2’-bithiophene (BP2T) and 5,5’-bis-(4’-cyanobiphenyl-4-yl)-2,2’-bithiophene (BP2T-CN) in a microcavity EL structure (Fig. 1(a)). The device was constructed by vapor-depositing BP2T-CN (125-170 nm thick), BP2T (90 nm thick), MoO\textsubscript{3} and Au onto an indium-tin-oxide (ITO) coated distributed Bragg reflector (DBR) mirror (Fig. 1(b)). The highest occupied and lowest unoccupied molecular orbital (HOMO/LUMO) energies of BP2T (-4.86/-2.71 eV) and BP2T-CN (-5.25/-3.21 eV) were estimated by density functional theory (DFT) calculations (Fig. 1(c)). Our previous study indicated that the EL spectrum from this device was dominantly attributed to the BP2T-CN layer in which injected electrons were accumulated there due to the energy barrier of LUMO at the BP2T/BP2T-CN interface.\textsuperscript{36} Moreover, the deposition order of the BP2T and BP2T-CN layers affected their molecular orientation. When the BP2T layer was first deposited on ITO, and then the BP2T-CN layer was deposited (BP2T-CN/BP2T/ITO), both BP2T and BP2T-CN molecules dominantly orient standing. When the deposition order was reversed as in the present device (BP2T/BP2T-CN/ITO), its EL performance was significantly improved since both molecules tend to orient lying.\textsuperscript{37} Therefore, this inverted structure is here adopted to construct the microcavity EL device.

Figure 1(d) displays photoluminescence (PL) and optical absorption spectra of the vapor-deposited BP2T-CN film with 125 nm thickness on a glass substrate together with a transmission spectrum of the DBR mirror. Vibronic progressions of the 0-1 and 0-2 absorption bands appear at around 2.61 and 2.78 eV, and the 0-1, 0-2 PL bands appear at around 2.22 and 2.09 eV, respectively. The 0-0 transition is estimated at 2.42 eV under the harmonic oscillation approximation. Thus, we determined the 0-0 and 0-1 exciton energies at $E_{\text{ex0-0}} = 2.42$ eV and $E_{\text{ex0-1}} = 2.61$ eV, respectively. The DBR mirror consisting of SiO\textsubscript{2}/Ta\textsubscript{2}O\textsubscript{5} multilayers has a high reflectivity of ~99% at energies from 2.0 to 2.7 eV which covers the emission band of the BP2T-CN layer. The DBR was coated with 64-nm-thick ITO to give a quarter wavelength layer at its central reflection energy ($E_0 = 2.3$ eV).

For the observation of exciton-polariton formation, angle-resolved reflectance spectroscopy was first performed with s-polarized white light from a deuterium tungsten lamp. Figure 2(a) shows reflection spectra as a function of reflectance angle $\theta = 26-60^\circ$ taken from the top Au surface. As marked in the spectra, three series of reflection dispersions are
observed and their negative peak positions shift to the higher energy with increasing $\theta$. The lowest energy dispersion appears below $E_{ex0-0}$ while the middle one emerges between $E_{ex0-0}$ and $E_{ex0-1}$. Although the highest energy peaks are weak, their magnified spectra show the dispersion above $E_{ex0-1}$. These anticrossing behaviors are a strong indication of exciton-photon coupling. The observed spectra were analyzed using a phenomenological 3 x 3 Hamiltonian, which describes interactions between one cavity photon mode and two exciton modes:

$$H = \begin{pmatrix} E_{ph}(\theta) & \hbar \Omega_0 & \hbar \Omega_1 \\ \hbar \Omega_0 & E_{ex0-0} & 0 \\ \hbar \Omega_1 & 0 & E_{ex0-1} \end{pmatrix},$$  \hspace{1cm} (1)

where $\hbar \Omega_0$ and $\hbar \Omega_1$ are the exciton-photon interaction terms with respect to the $E_{ex0-0}$ and $E_{ex0-1}$ excitons, respectively. The cavity photon $E_{ph}(\theta)$ is given by

$$E_{ph}(\theta) = E_{ph}(0) \left(1 - \frac{\sin^2 \theta}{n^2_{eff}}\right)^{1/2}.$$  \hspace{1cm} (2)

As shown in Figure 2(b), the three dispersions are characterized as the lower, middle and upper polariton branches (LPB, MPB, and UPB). The fitting parameters are $E_{ph}(0) = 2.35$ eV, $n_{eff} = 1.68$, $2\hbar \Omega_0 = 250$ meV, and $2\hbar \Omega_1 = 244$ meV. Mixing coefficients of photonic and excitonic fractions are estimated for the LPB, MPB, and UPB as shown in Fig. S1 (supplementary data).

The obtained strong coupling regime is discussed with the cavity quality ($Q$) factor of the microcavity evaluated by

$$Q = \frac{2\pi n_{eff}}{\lambda} \left[\alpha - \frac{1}{L_{cav}} \ln\left(\sqrt{R_{top} R_{bot}}\right)\right],$$  \hspace{1cm} (3)

where $\lambda$ is the resonance wavelength, $R_{top}$ (~0.75) and $R_{bot}$ (~0.99) are the reflectance of the top Au and bottom DBR mirrors, respectively. $L_{cav}$ is the cavity length including a mirror penetration depth in the DBR. The cavity loss $\alpha$ was ignored. From Eq. (3), a $Q$ factor value of ~147 was obtained for the present device. For strong exciton-photon coupling, the following inequality should be satisfied:

$$Q >> \hbar \omega / 2 \hbar \Omega.$$  \hspace{1cm} (4)

where $\hbar \omega$ is exciton transition energy. The estimated values of $\hbar \omega_0 / 2 \hbar \Omega_0 = 9.68$ and $\hbar \omega_1 / 2 \hbar \Omega_1 = 10.7$ confirm to satisfy this condition. The Rabi-splitting energy ($2\hbar \Omega$) is described as

$$2\hbar \Omega \propto \left(\frac{FV}{V}\right)^{1/2},$$  \hspace{1cm} (5)
where \( f, N, \) and \( V \) are the magnitude of transition dipole moment, the number of dipoles coupled in the cavity, and the photonic volume of the cavity, respectively. As compared to the single-crystal microcavity, the present vapor-deposited film results in lower \( N \), however, its thinner thickness contributes to reduce \( V \) to give the large Rabi splitting. The normalized coupling factor \( (g = 2h\Omega/h\omega) \) of the present device is about 10\%. Further improvement in the molecular orientation and crystallinity in the vapor-deposited films is required to increase the \( Q \) factor and achieve an ultrastrong coupling regime \( (g > 20\%) \). For this purpose, we have been developing an improved method called vaporized film deposition which can produce polycrystalline BP2T-CN films with highly ordered orientation.\(^{38}\)

Next, we performed angle-resolved PL measurements under ns-pulsed excitation \( (\lambda_{\text{ex}} = 355 \text{ nm}, 1.4 \text{ ns}, 1 \text{ kHz}) \) at power density of \( 5\text{mW/cm}^2 \). The excitation beam was incident normal to the bottom surface of the DBR/glass substrate, and the far-field emission from the top Au surface was collected as a function of emission angle \( \theta \). Figure 3(a) shows PL spectra taken at \( 0 < \theta < 60^\circ \) with \( s \)-polarized excitation. The emission peak at \( \theta = 0^\circ \) appears at 2.26 eV. This peak position is blue-shifted approaching to the 0-0 exciton energy \( (E_{\text{ex}0-0} = 2.42 \text{ eV}) \) with increasing \( \theta \). In analogy to the angle-resolved reflection spectra (Fig. 2(a)), this PL dispersion is assigned to the LPB emission. In addition, a weak emission dispersion corresponding to the MPB is faintly observed in the energy range between \( E_{\text{ex}0-0} \) and \( E_{\text{ex}0-1} \). However, no UPB emission is visible, probably due to the fast energy relaxation to the lower polariton states. As shown in Fig. 3(b), the emission is mostly converged within the angle range of \( \theta < 30^\circ \) indicating that the created polaritons are efficiently relaxed into the lowest LPB state \( (k = 0) \). We have also confirmed that the exciton-photon interaction can be controlled by changing the BP2T-CN layer thickness (see Figs. S2 and S3, supplementary data, available online at ).

We examined such polariton formation in the microcavity device also under electrical excitation. Figure 4(a) displays the angle-resolved EL spectra taken from the microcavity EL device \( (\text{Au/MoO}_3/\text{BP2T}/\text{BP2T-CN}/\text{ITO}/\text{DBR}) \) with 125-nm-thick BP2T-CN layer at a constant voltage of 12 V at room temperature. As similar to the PL measurements (Figure 3(a)), the emission peak at 2.26 eV at \( \theta = 0^\circ \) corresponding to the LPB emission shifts to the higher energy approaching to \( E_{\text{ex}0-0} \) with increasing \( \theta \). Weak emissions assigned to the MPB are also visible in the energy range between \( E_{\text{ex}0-0} \) and \( E_{\text{ex}0-1} \). Another peak at around 1.86 eV comes from the uncoupled mode at a lower order. The same measurement using a non-cavity EL device without the DBR mirror \( (\text{Au/MoO}_3/\text{BP2T}/\text{BP2T-CN}/\text{ITO}) \) indicates no such angular dispersion as shown in Fig. 4(b), and its EL spectrum is consistent with the PL
spectrum of the BP2T-CN film. These results demonstrate that cavity-polaritons are formed in the microcavity device under electrical excitation. It is also noted that the EL intensity of the LPB emission in the microcavity device remarkably increases as the $\theta$ approaches to $0^\circ$ (Fig. 4(a)) while that in the non-cavity EL device changes a little. Figure 4(c) shows spatial distribution of angle dependent emission intensity around 2.2-2.4 eV for both devices. The non-cavity device indicates a Lambertian-like spatial distribution typical for surface-emitting organic EL devices. By contrast, the EL intensity of the microcavity device is concentrated within smaller angles from the normal direction. This narrow convergence of the microcavity EL again suggests effective relaxation of cavity polaritons into the lowest LPB state. The cavity-length dependence of polariton formation was also confirmed under electrical excitation (see Fig. S4, supplementary data).

Figures 5(a) and 5(b) display current density-voltage and luminance-current density characteristics, respectively, taken for the microcavity and non-cavity EL devices. Electrical properties for both devices are similar since their carrier injection, transport and recombination properties are independent on the existence of the bottom DBR mirror. Contr astingly, the luminance is remarkably higher for the microcavity device than the non-cavity one. Some previous studies in organic microcavities$^{17,39,40}$ have reported that their output intensities are reduced compared to non-cavity EL devices since most excitons remain in the reservoir rather than being relaxed into the emissive polariton branches due to the slow scattering of excitons into the polariton state. By contrast, our present device can avoid these relaxation bottleneck effects probably owing to better molecular orientation and device geometry for longer polariton lifetime and efficient condensation into $k = 0$.

It is noted that both the microcavity and non-cavity EL devices show superlinear increase of luminance with increasing current density up to $\sim$300 mA/cm$^2$ (Fig. 5(b)). As well-known, triplet-triplet annihilation (TTA) is involved in electrically injected the emission process where the fusion of two excited triplet excitons ($T_1 + T_1$) gives a upconverted singlet exciton ($S_1$) and a ground state ($S_0$) so that the $S_1$ exciton is generated in proportion to the square of $T_1$ density.$^{41}$ This TTA contribution in electrical excitation is also confirmed from the nonlinear increase of integrated EL intensity of the microcavity device (Fig. S5(b), supplementary data) while the excitation density dependence of PL intensity shows a linear increase (Fig. S5(a)) since triplet excitons are not significant in TPCO materials under optical excitation. However, the superlinear inclination of EL is considerably higher for the microcavity device than for the non-cavity device. This difference might suggest that the efficient relaxation of polaritons into the LPB would involve other contribution of electrically injected excitons more than expected
from the TTA process. In the study for a GaAs polariton-LED, both polariton intensity in the PL and EL spectra shows a superlinear increase with increasing excited density,\textsuperscript{42) which is ascribed to polaritonic interaction even below the excitation threshold of polariton lasing. Therefore, the enhanced superlinear behavior observed in our microcavity EL device could be another proof of polariton formation under electrical excitation.

Further increase of current density in our microcavity EL device results in a roll-off of the EL intensity (Fig. 5(b)) indicating that the generated excitons are quenched by injected carriers even though the excited density is still 2-3 orders of magnitude lower than that to reach polariton lasing. In the present vapor-deposited BP2T-CN layer, the suitable lying molecular orientation probably contributes to strong coupling between the oligomer excitons with large transition dipoles and favorably polarized photons. However, such oriented molecular domains are limited within a microcrystalline grain in the film. Further improvement to realize polariton lasing demands the development of film growth techniques enabling large-domain crystallization with favorable orientation as well as the optimization of OLED structures to reduce exciton quenching.

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References


**Figure Captions**

**Fig. 1.** (a) Molecular structures of BP2T and BP2T-CN. (b) Schematic diagram of fabricated microcavity EL device. (c) Energy diagram for multilayered components in the device. The HOMO/LUMO energies of BP2T and BP2T-CN were determined by DFT calculation. (d) PL and absorption spectra of BP2T-CN film vapor-deposited on glass substrate and transmission spectrum of bottom DBR mirror used in the device.

**Fig. 2.** (a) Angle-resolved reflectance spectra taken from microcavity EL device with 125-nm-thick BP2T-CN layer showing LPB (closed triangle), MPB (open triangle) and UPB (arrow). (b) Dispersion relations of LPB, MPB and UPB plotted from angle-resolved reflectance spectra in (a). The solid blue lines show a fitting result obtained from calculation with phenomenological Hamiltonian. Dashed black and red lines indicate uncoupled cavity photon and exciton modes, respectively.

**Fig. 3.** (a) Angle-resolved PL spectra taken from microcavity EL device with 125-nm-thick BP2T-CN layer under ns-pulsed excitation at power density of 5mW/cm². Closed triangles correspond to energy dispersion of LPB. (b) Contour map of PL spectra taken at 1° increments. Open circles show LPB peaks plotted from EL spectra in Fig. 4(a).

**Fig. 4.** Angle-resolved EL spectra for microcavity EL device with 125-nm-thick BP2T-CN layer (a) and non-cavity EL device (b) taken at current density of ~80 and ~40 mA/cm², respectively, at constant bias voltage of 12 V. Closed triangles in (a) correspond to energy dispersion of LPB. (c) Spatial distribution of angle-dependent emission intensity for microcavity EL device with 125-nm-thick BP2T-CN layer (blue dots) and non-cavity EL device (red dots). The black solid line shows a curve of Lambertian distribution.

**Fig. 5.** Current density-voltage (a) and luminance-current density (b) characteristics for microcavity EL device with 125-nm-thick BP2T-CN layer (blue dots) and non-cavity EL device (red dots). The black solid line in (b) is eye guide for linear dependence.
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