High Current Density in Light-Emitting Transistors of Organic Single Crystals

Taishi Takenobu,[1,2,*] Satria Zulkarnaen Bisri,[1] Tetsuo Takahashi,[1] Masayuki Yahiro,[3]
Chihaya Adachi,[3] and Yoshihiro Iwasa[1,2]
[1]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[2]*CREST, Japan Science and Technology Corporation, Kawaguchi 332-0012, Japan*
[3]*Center for Future Chemistry, Kyushu University, Nishi, Fukuoka 819-0395, Japan*

(Received 3 August 2007; published 13 February 2008)

We measured the external electroluminescence quantum efficiency (η_{ext}) in light-emitting field-effect transistors (LETs) made of organic single crystals and found that, in the ambipolar transport region, η_{ext} is not degraded up to several hundreds $\mathrm{A/cm^2}$ current-density range, which is 2 orders of magnitude larger than that achieved in conventional organic light-emitting diodes. The present result indicates the single-crystal organic LET is a promising device structure that is free from various kinds of nonradiative losses such as exciton dissociation near electrodes and exciton annihilations.

DOI: 10.1103/PhysRevLett.100.066601 PACS numbers: 72.80.Le, 71.35.−y, 73.40.−c, 73.61.Ph

The great advances achieved in organic materials science have accelerated the development of devices such as organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs) [1–3]. In spite of rapid progress, several important and open questions still remain regarding the underlying transport, recombination, and emission physics. For example, despite the achievement of amplified spontaneous emission (ASE) using optically pumped organic thin films and single crystals, electrically driven organic lasers have not yet been realized [4–6]. OLEDs have demonstrated a maximum internal efficiency approaching 100% [7]. Also, extremely high current densities, which may produce sufficient exciton density for population inversion, have been reported in thin films of copper phthalocyanine [8]. However, the highest electroluminescence (EL) efficiencies have been typically realized at low current densities (less than 1–10 $\mathrm{A/cm^2}$), because nonradiative losses increase at higher biases [4,5]. This would seriously limit the realization of organic laser devices. One possible source of the nonradiative losses is the quenching of singlet excitons due to high density of excitons and carriers. Optical excitation mainly leads to the formation of singlet excitons, which are the excited states required for radiative relaxation. On the other hand, electrical excitation involves charge injection followed by capture of charges to form an exciton, which can be either a singlet or a triplet. Triplet excitons could quench singlet excitons [9,10]. Similarly, singlet excitons could also be quenched by the other singlet excitons and charge carriers, for example, polarons [11]. These annihilation processes greatly affect the density of the singlet and triplet excitons, resulting in roll-off of the external EL quantum efficiency (η_{ext}). Another possible source of the nonradiative losses is the metal electrodes. In the diode configuration, the resonator is in the plane of the film allowing long interaction lengths with the electrodes, which absorb light. Indeed, the threshold pump energy density is greatly increased when a metal electrode is present [12].

Besides a conventional LED device, a novel class of organic devices has been demonstrated—namely, organic light-emitting FETs (OLETs) [13,14]. In particular, OLETs with ambipolar charge transport are suitable for laser devices, since they offer an attractive geometry in which the contacts could be substantially separated from the optical mode in the gain medium [15–18]. Indeed, the maximum current density of ambipolar polymer LETs can reach 50 $\mathrm{A/cm^2}$ without degradation of η_{ext} [17]. This value is much higher than the typical limitation of OLEDs (1–10 $\mathrm{A/cm^2}$). However, the intrinsically low mobility of organic polymers [typically less than 10^{-3} $\mathrm{cm^2/(V\,s)}$] makes it difficult to reach current density to the $\mathrm{kA/cm^2}$ range, which is comparable to the expected threshold current density for electrically driven ASE [4,5,11]. Since higher mobility helps to solve both issues, a recent report of ambipolar LETs based on single crystals is encouraging [18].

In this Letter, we present an experiment to investigate current-density dependence of η_{ext} in single-crystal OLETs. Tetracene and rubrene were chosen as active materials because of their high FET mobility and reasonable fluorescence quantum yield [3,14,18–20]. By preparing nearly best performing single-crystal OLETs, we found an absence of roll-off behavior in η_{ext} up to the current density of several hundreds (or thousands) $\mathrm{A/cm^2}$ range, which is 2 orders of magnitude larger than the maximum current density in conventional OLED devices. The present result indicates that ambipolar light-emitting FETs using single crystals provide a novel opportunity in investigating recombination physics in organic semiconductors as well as a novel route to current driven organic lasers.

Device fabrication procedures have been described in detail elsewhere [18,21,22]. A highly doped silicon wafer with a 400 nm thermally oxidized SiO_2 layer was spin coated with poly(methyl methacrylate) from a toluene solution (4–10 nm). Single crystals, typically less than 1 μm in thickness, were grown by physical vapor transport. Since electron transport in organic crystals is extremely sensitive to air, we transferred single crystals grown in a quartz tube into a glove box without exposing them to air and then laminated the crystals onto a substrate [23]. The top-contact asymmetric electrodes were fabricated by thermally evaporating gold and calcium through a shadow mask on top of the single crystals in an evaporation chamber, which was directly connected to the glove box. Electrical and optical characterizations were performed in the dark inside the glove box using a semiconductor parameter analyzer (Agilent Technology E5270), a spectrometer (ORIEL FICS$^{\mathrm{TM}}$ imaging spectrograph, model 77440), and an optical power meter (Newport model 1930).

Figure 1 shows the transfer characteristics of the tetracene and rubrene single-crystal FETs. We observed ambipolar transport in both devices. In the tetracene single crystal, the mobilities for hole and electron, obtained from Fig. 1(a), are 2.3 and 0.12 $\mathrm{cm^2/(V\,s)}$, where the channel width and length were 30 and 50 μm, respectively. These are the highest mobilities ever observed until now for tetracene FETs [14,18]. Meanwhile, the estimated hole and electron mobilities in the rubrene single crystal from Fig. 1(b) are 0.82 and 0.27 $\mathrm{cm^2/(V\,s)}$, respectively. The channel width and length of this device were 400 and 220 μm. Though the hole mobility is smaller than the maximum values reported for similar single-crystal rubrene FETs, the electron mobility is comparable with the best mobilities reported thus far [3,21,22].

It is commonly known that the ambipolar FETs emit light when the gate voltage is nearly half of the source-drain voltage [15–18]. We observed visible light emission from the ambipolar FETs based on tetracene and rubrene single crystals under appropriate bias conditions. Figure 2 shows the EL and photoluminescence (PL) spectra of the tetracene and rubrene single-crystal devices. The EL and PL spectra display reasonable agreement, particularly in terms of peak positions, indicating that the emission characteristics are not notably affected by the peculiar properties of single-crystal LETs, such as high electric fields and high current densities [14,19]. The rubrene spectra in Fig. 2(b) suggest the presence of the oxygen impurity, although we took all necessary precautions to avoid an air-induced contamination of the single-crystal surface [20]. Figure 3 shows output characteristics for the tetracene single-crystal LET together with the drain bias dependence of the light-emission intensity. The observed output characteristics in Fig. 3(a) are almost identical to that in our previous paper [18]. The constant drain current corresponds to a hole saturation current, and the steep current increase at a high drain bias indicates the onset of electron transport. Below a certain drain voltage, no ambipolar transport was observed, as hole transport dominated the channel, and the electrons were injected only at the metal-organic interface, as has been reported in unipolar LETs [14,24]. Thus, a weak light is emitted along the edge of the

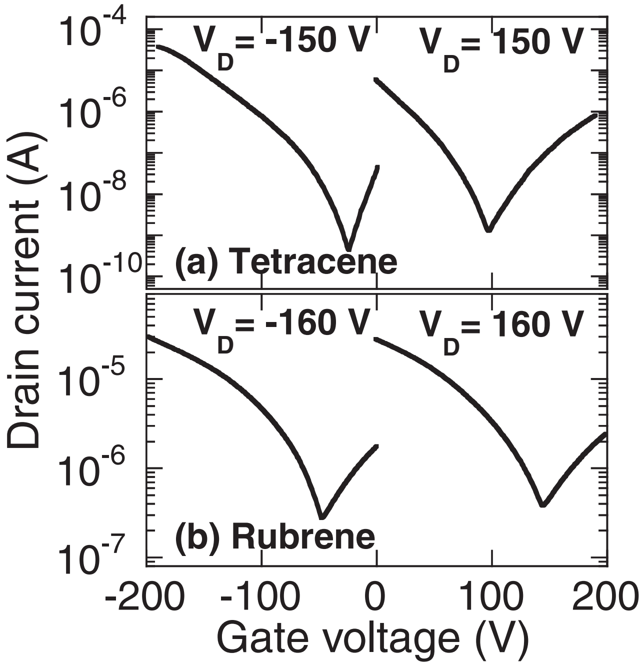

FIG. 1. (a) Transfer characteristics of the ambipolar tetracene single-crystal field-effect transistor at negative and positive drain voltages (150 V), V_D. The channel width and length are 30 and 50 μm, respectively. (b) Transfer characteristics of the ambipolar rubrene single-crystal field-effect transistor at negative and positive drain voltages (160 V), V_D. The channel width and length are 400 and 220 μm, respectively.

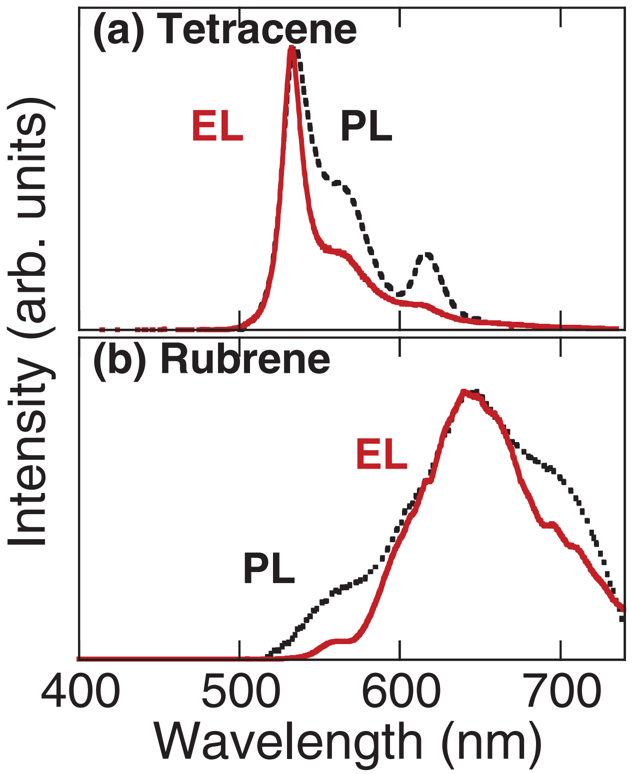

FIG. 2 (color). Electroluminescence (solid red line) and photoluminescence (dashed black line) spectra of (a) tetracene and (b) rubrene single-crystal devices.

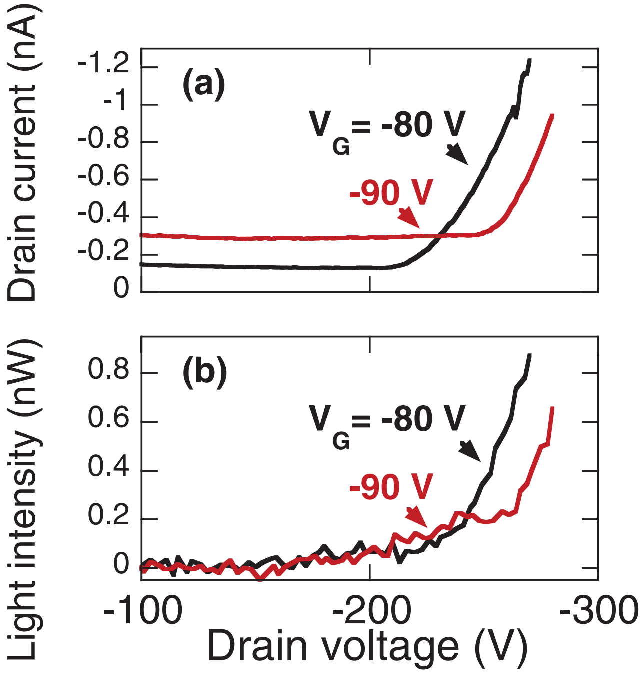

FIG. 3 (color). (a) Output characteristics and (b) corresponding light output of the tetracene single-crystal LET at different gate voltages, V_G.

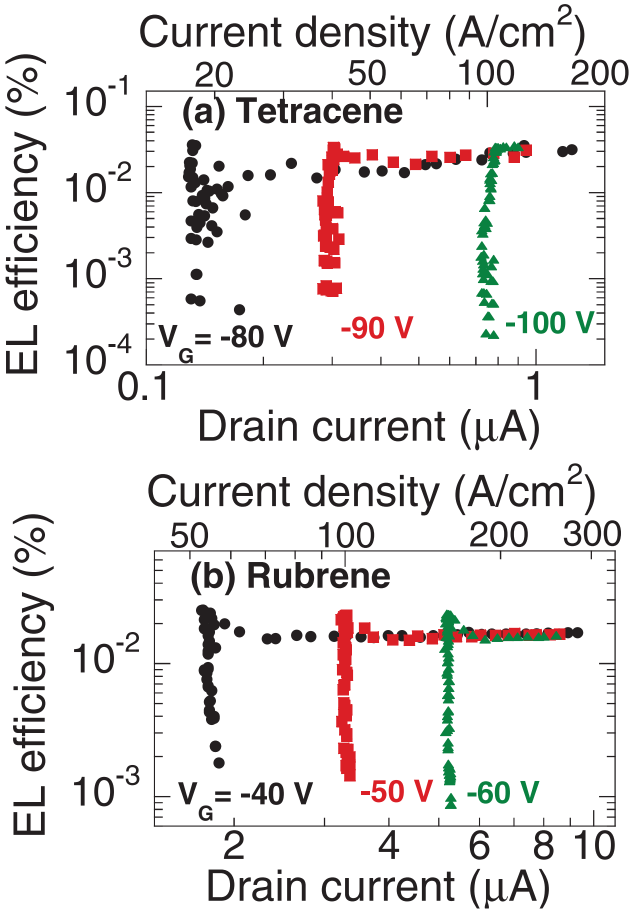

FIG. 4 (color). External electroluminescence quantum efficiency (η_{ext}) vs drain current characteristics of (a) tetracene and (b) rubrene single-crystal LETs at different gate voltages. The upper horizontal axis corresponds to the estimated current density, when we assume the current flow to be confined to a 15 nm, which corresponds to approximately 10 monolayers of the organic molecules [25]. If we take a value of 1 nm as a thickness of accumulation layer, as reported in Refs. [16,17], the estimated maximum current density reaches more than 2 $\mathrm{kA/cm^2}$ and 4 $\mathrm{kA/cm^2}$ for tetracene and rubrene LETs, respectively.

electron-injecting calcium electrode (unipolar region). When drain voltage increased, the relative bias between the drain and gate exceeded the threshold voltage for the formation of an electron accumulation layer, and, accordingly, the emission zone moved through the channel toward the gold electrodes as the electron accumulation region was extended further into the channel. As the drain voltage and current increased, the light became brighter (ambipolar region). This behavior agrees with the data for other LETs [13,15–18]. Moreover, we also observed similar results in the rubrene single-crystal LETs.

In Fig. 4, we plot η_{ext} vs drain current, which is derived from the current-voltage and output light-intensity characteristics. For a given gate voltage, η_{ext} first increases with constant drain current (unipolar region) and then reaches a maximum plateau (ambipolar region). In the unipolar region, the major accumulated carriers are holes, and the minority-carrier injection of electrons is enhanced with increasing drain voltage. The drain current, however, is constant due to the saturation behavior of unipolar FETs. The increase in η_{ext} corresponds to initial light emission from the edge of the calcium electrode, as has been reported in unipolar organic LETs [24]. In sharp contrast to the unipolar region, both hole and electron channels are present in the ambipolar region, and the electron and hole currents are perfectly balanced [9,13,15–18]. All injected holes and electrons have to recombine as it is unlikely that they would be able to cross tens of micrometers of an oppositely charged accumulation layer without recombining. The maximum η_{ext} is 0.03% and 0.015% for the tetracene and rubrene single crystals, respectively. These EL quantum efficiencies are very reasonable if we consider the PL quantum efficiency of these materials (less than 1% for both tetracene and rubrene).

Since we are interested in the current-density dependence of η_{ext}, we attempted to convert the drain current into current density. The current density in FETs is, however, based on an assumption about the thickness of the transport layer, which is still an open question. Since we need to perform numerical simulations to clarify the spatial distribution of the current flow, in this study we assumed that the thickness of the transport layer is mainly equal to the thickness of the accumulation layer. Direct measurements of the accumulation layer thickness are very difficult, and the reported values vary among research groups from 10 monolayers to 1 nm [16,17,25]. In Fig. 4, we assumed the current flow to be confined to a 15 nm thick accumulation layer (see the upper horizontal axis in Fig. 4), which corresponds to approximately 10 monolayers of the organic molecule [25]. Typical OLEDs operate at much lower current densities (typically 10^{-2} A/cm^2), and mostly, a roll-off in $\eta_{\rm ext}$ at higher current densities (typically 1–10 A/cm^2) is observed [4,5,11]. Hence, the flat behavior in Fig. 4 is particularly surprising, if taking into account the high current density of several hundreds A/cm^2. We insist that several hundreds A/cm^2 is the lowest limit. If we take a value of 1 nm as an accumulation layer thickness, as reported in Refs. [16,17], the estimated maximum current density reaches more than 2 kA/cm^2 and 4 kA/cm^2 for tetracene and rubrene LETs, respectively. This current density is much higher than that in polymer OLETs [17], and, more interestingly, it is comparable to the expected threshold current density for electrically driven ASE, indicating the possibility of realizing an electrically driven organic laser by using ambipolar single-crystal OLETs [4,5,11].

It is emphasized that the present experiment is the first unambiguous report that a high current density without degradation of $\eta_{\rm ext}$ can be realized in single-crystal OLETs. The achievement of lossless radiation is due to the near total absence of exciton quenching at the electrodes and annihilation processes caused by high carrier densities. Basically, it is understood by the device configuration of ambipolar LETs, in which the metal electrodes could be substantially separated from the exciton-recombination zone, and the low concentration of carriers because of high carrier mobility in single crystals. We note that the situation is in sharp contrast to the configuration of LEDs, wherein $\eta_{\rm ext}$ decreases at higher current densities. Since it was commonly believed that nonradiative losses are inevitable in organic light-emitting devices, successful lossless radiation up to several hundreds (or thousands) A/cm^2 is significant experimental progress for designing organic laser devices, as well as to present the underlying recombination and emission physics. Another possible mechanism for lossless radiation is an impurity-terminated electron-hole recombination. Figure 3(b) suggests the presence of the oxygen impurity at least in rubrene LETs, and such impurities might possibly bypass a formation of exciton. A detailed analysis of exciton-recombination dynamics is still under investigation.

In conclusion, we have investigated the current-density dependence of $\eta_{\rm ext}$ in single-crystal OLETs. High current and exciton densities were realized in the ambipolar region without any decrease in $\eta_{\rm ext}$, taking the advantage of high mobility in organic single crystals. Interestingly, the above processes are applicable to highly photoluminescent materials [26] and promising to push the performance limit of organic light-emitting devices to an electrically driven organic laser.

This study was partly supported by Grant-in-Aid for Scientific Research (No. 17069003, No. 17204022, and No. 18710091) from MEXT, Japan.

---

*takenobu@imr.tohoku.ac.jp

[1] R.H. Friend, R.W. Gymer, A.B. Holmes, and J.H. Burroughes, Nature (London) **397**, 121 (1999).

[2] C. D. Dimitrakopoulos and P. R. L. Malenfant, Adv. Mater. **14**, 99 (2002).

[3] R.W.I. De Boer, M.E. Gershenson, A.F. Morpurgo, and V. Podzorov, Phys. Status Solidi A **201**, 1302 (2004).

[4] I. D.W. Samuel and G. A. Turnbull, Chem. Rev. **107**, 1272 (2007).

[5] H. Yamamoto, T. Oyamada, H. Sasabe, and C. Adachi, Appl. Phys. Lett. **84**, 1401 (2004).

[6] M. Ichikawa, R. Hibino, M. Inoue, T. Haritani, S. Hotta, T. Koyama, and Y. Taniguchi, Adv. Mater. **15**, 213 (2003).

[7] C. Adachi, M.A. Baldo, M.E. Thompson, and S.R. Forrest, J. Appl. Phys. **90**, 5048 (2001).

[8] T. Matsushima, H. Sasabe, and C. Adachi, Appl. Phys. Lett. **88**, 033508 (2006).

[9] S. Verlaak, D. Cheyns, M. Debucquoy, V. Arkhipov, and P. Heremans, Appl. Phys. Lett. **85**, 2405 (2004).

[10] C. Gärtner, C. Karnutsch, U. Lemmer, and C. Pflumm, J. Appl. Phys. **101**, 023107 (2007).

[11] M. A. Baldo, R. J. Holmes, and S. R. Forrest, Phys. Rev. B **66**, 035321 (2002).

[12] P. Andrew, G.A. Turnbull, I.D.W. Samuel, and W.L. Barnes, Appl. Phys. Lett. **81**, 954 (2002).

[13] M. Muccini, Nat. Mater. **5**, 605 (2006).

[14] A. Hepp, H. Heil, W. Weise, M. Ahles, R. Schmechel, and H. von Seggern, Phys. Rev. Lett. **91**, 157406 (2003).

[15] J. S. Swensen, C. Soci, and A. J. Heeger, Appl. Phys. Lett. **87**, 253511 (2005).

[16] J. Zaumseil, R. H. Friend, and H. Sirringhaus, Nat. Mater. **5**, 69 (2006).

[17] J. Zaumseil, C.L. Donley, J.-S. Kim, R.H. Friend, and H. Sirringhaus, Adv. Mater. **18**, 2708 (2006).

[18] T. Takahashi, T. Takenobu, J. Takeya, and Y. Iwasa, Adv. Funct. Mater. **17**, 1623 (2007).

[19] H. Najafov, I. Biaggio, V. Podzorov, M.F. Calhoun, and M. E. Gershenson, Phys. Rev. Lett. **96**, 056604 (2006).

[20] O. Mitrofanov, D.V. Lang, Ch. Kloc, J.M. Wikberg, T. Siegrist, W.-Y. So, M.A. Sergent, and Arthur P. Ramirez, Phys. Rev. Lett. **97**, 166601 (2006).

[21] T. Takahashi, T. Takenobu, J. Takeya, and Y. Iwasa, Appl. Phys. Lett. **88**, 033505 (2006).

[22] T. Takenobu, T. Takahashi, J. Takeya, and Y. Iwasa, Appl. Phys. Lett. **90**, 013507 (2007).

[23] J. Takeya, C. Goldmann, S. Haas, K.P. Pernstich, B. Ketterer, and B. Batlogg, J. Appl. Phys. **94**, 5800 (2003).

[24] T. Oyamada, H. Uchiuzou, S. Akiyama, Y. Oku, N. Shimoji, K. Matsushige, H. Sasabe, and C. Adachi, J. Appl. Phys. **98**, 074506 (2005).

[25] R. Ruiz, A. Papadimitratos, A.C. Mayer, and G.G. Malliaras, Adv. Mater. **17**, 1795 (2005).

[26] S.Z. Bisri, T. Takahashi, T. Takenobu, M. Yahiro, C. Adachi, and Y. Iwasa, Jpn. J. Appl. Phys. **46**, L596 (2007).