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**Description**

The article discusses the suppression of exciton annihilation at high current densities in organic light-emitting diodes (OLEDs) due to energy-level alignments of carrier transport layers. The authors, Matsushima, Toshinori, and Adachi, Chihaya, present their findings in Applied Physics Letters, Volume 92, Issue 6, Pages 063306-1 to 063306-3. The research was published on February 14, 2008, and is classified as a journal article. The text version of the article can be accessed through the publisher's website or via the handle provided. The copyright is reserved by the American Institute of Physics, and permission is required for any other use besides personal download. The original article was published in Applied Physics Letters, Volume 92, Issue 6, and can be found at the provided URL.
Suppression of exciton annihilation at high current densities in organic light-emitting diode resulting from energy-level alignments of carrier transport layers

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We manufactured an organic light-emitting diode (OLED) in which the hole and electron transport layers are chemically doped with p- and n-type dopants and energy levels in between neighboring carrier transport layers and emitting molecules are aligned. From the results of the electroluminescence (EL) characteristics of the OLED, we found that (1) the OLED has an extremely low driving voltage of 2.65 ± 0.05 0.05 V at a current density of 100 mA/cm²; (2) the onset voltage of EL (≈ 2.4 V) corresponds to the photon energy of emitting molecules (≈ 2.5 eV), while the onset voltage of currents is ≈ 1.8 V; and (3) a decrease in EL efficiency at high current densities can be suppressed by matching the energy levels. © 2008 American Institute of Physics.

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Organic light-emitting diodes (OLEDs) doped with phosphorescent iridium complexes have been shown to achieve an internal electroluminescence (EL) efficiency of nearly 100%. Researchers are now interested in reducing driving voltages and improving durability for practical display and lighting applications. In particular, reducing the driving voltage is required for improving power conversion efficiencies and lifetimes. In most OLEDs, carrier mobilities of organic layers are much lower than those of inorganic semiconductors, and carrier injection barriers are present at metal/organic and organic/organic interfaces, resulting in much higher driving voltages of OLEDs than those of inorganic LEDs. Doping organic hole transport layers (HTLs) and electron transport layers (ETLs) with p- and n-type dopants and softening energy barriers at the hetero-junction interfaces have been frequently used to reduce driving voltages. However, the voltage levels reported thus far are still higher than the corresponding photon energy levels of emitting molecules. We have now reduced the voltages to a level equivalent to that of the photon energies using the above-mentioned techniques.

We manufactured an OLED with a device structure of glass substrate/indium tin oxide (ITO) anode (100 nm)/2 mol %-2,3,5,6-tetrafluoro-7,7,8-tetracyanoquinodimethane (F₄TCNQ)-doped alpha-sexithiophene (α-6 T) HTL (30 nm)/4,4′,4″-tris(N-3-methylphenyl-N-phenyl-amino)triphenylamine (m-MTDATA) HTL (10 nm)/3 mol %-α-6 T-doped m-MTDATA emitting layer (EML) (10 nm)/3 mol %-α-6 T-doped phenyldipyreneylphosphine oxide (POPy₂) EML (10 nm)/POPy₂ ETL (10 nm)/30 mol %–Cs-doped POPy₂ ETL (30 nm)/Al cathode (100 nm). The energy-level diagram of this OLED is shown in Figs. 1(a) and 1(b). The α-6 T HTL, the m-MTDATA HTL, and the POPy₂ ETL have been previously used to reduce driving voltages because these layers have relatively high carrier mobilities among organic materials. In our OLED, we doped p-type F₄TCNQ in the α-6 T HTL and n-type Cs in the POPy₂ ETL and matched the energy levels among the neighboring organic layers and the α-6 T emitting molecules, which resulted in an extremely low driving voltage of 2.65 ± 0.05 V for the current density of 100 mA/cm².

In most OLEDs, EL efficiencies markedly decrease at high current densities. This decrease makes fabricating electrically pumped organic laser diodes (OLDs) difficult and, thus, the decrease must be completely eliminated in order to develop OLEDs and OLDs. The causes of this decrease have been ascribed to the lowered carrier balance of electrons and holes, singlet-singlet exciton annihilation, and singlet-polaron exciton annihilation. Recently, Luo
et al. reported that charge carriers, which are built up at heterojunction interfaces and are trapped on small-energy-gap dopant molecules, cause a strong quenching of excitons in EMLs. From results of our study of OLED characteristics, we found that the decrease in \( \eta_{\text{ext}} \) at high current densities is suppressed due to the energy-level alignments among the organic layers and the emitting molecules, as shown in Fig. 1(b).

We manufactured the OLED using the following steps. Glass substrates coated with a 100-nm-thick ITO layer with a sheet resistance of 25 \( \Omega \)/sq (Sanyo Vacuum Industries) were ultrasonically cleaned in a mixture of detergent (Cica clean LX-II, Kanto Chemicals) and pure water (1/10 by volume). This was followed by ultrasonication in pure water, acetone, and isopropanol. The substrates were soaked in boiling isopropanol and then placed in an UV-ozone treatment chamber. In a vacuum evaporator, which was evacuated to \( \approx 10^{-4} \) Pa, organic and Al layers were vacuum deposited on the ITO surfaces at deposition rates of 0.3 nm/s for the organic layers and 0.1 nm/s for the Al layer. The doping concentrations of the guest-to-host molecules were controlled at 2 mol % for the F4-TCNQ: \( \alpha \)-6T ETL, 3 mol % for the \( \alpha \)-6T-doped EMLs, and 30 mol % for the Cs:POPy2 ETL, which resulted in a charge transfer between the host and guest molecules and an increase in free carrier concentration. We used a 6T-doped POPy2 films. Moreover, \( \eta_{\text{ext}} \) increases due to the formation of nearly Ohmic contacts at the metal/organic interfaces and induces the formation of nearly Ohmic contacts at the metal/organic interfaces. We achieved an extremely low driving voltage of 2.65 \( \pm \) 0.05 V at 100 mA/cm\(^2\) in the OLED. We can attribute this low voltage to the following factors. (1) We doped F4-TCNQ and Cs in the \( \alpha \)-6T ETL and the POPy2 ETL, which resulted in a charge transfer between the host and guest molecules and an increase in free carrier concentration. This concentration increase enhances electrical conductivities in the doped layers and the \( \alpha \)-6T emitting molecules, as shown in Fig. 1(b). (2) We matched the energy levels among the neighboring organic layers and the \( \alpha \)-6T emitting molecules, as shown in Fig. 3. (3) Matching the energy levels leads to efficient carrier injection at the heterojunction interfaces and prevents carrier accumulation at the interfaces, resulting in a reduction in the driving voltage of the OLED.

Since our OLED had much lower voltages than those of conventional OLEDs, we were able to investigate detailed \( J-V \) and \( L-V \) characteristics at low voltages. When the device was biased beyond the flatband condition to cause current flow, the currents abruptly increased at \( \approx 1.8 \) V (Fig. 3). However, we observed no EL from the device at this voltage. The onset voltage of EL was \( \approx 2.4 \) V, which was higher than the onset voltage of the currents \( (=1.8 \) V) and corresponded to the photon energy of emitting \( \alpha \)-6T molecules \( (=2.5 \) eV).

The \( J-\eta_{\text{ext}} \) characteristics of the doped OLED are shown in Fig. 4. To compare these characteristics, we manu-

![](image1.png)

**Fig. 2.** EL spectrum of doped OLED (solid line) and PL spectra of 3 mol %-\( \alpha \)-6T-doped m-MTDATA (broken line) and 3 mol %-\( \alpha \)-6T-doped POPy2 films (bold line).

![](image2.png)

**Fig. 3.** Current density-voltage and luminance-voltage characteristics of doped OLED. Dotted lines highlight onset voltages of current and EL.

![](image3.png)

**Fig. 4.** External quantum efficiency-current density characteristics of doped OLED and Alq3 OLED.
factured a conventional OLED with a glass substrate/ITO anode (100 nm)/N,N'-diphenyl-N,N'-bis(1-naphthyl)-
1,1'-biphenyl-4,4'-diamine (α-NPD) HTL (50 nm)/tris(8-
hydroxyquinoline) aluminum (Alq3) emitting ETL
(50 nm)/MgAg cathode (100 nm) structure and measured its
J-ηext characteristics, which are also shown in Fig. 4. Al-
though the ηext markedly decreased at high current densities
in the Alq3 OLED, we observed no decrease in ηext of the
doped OLED in the high current region of over two orders of
magnitude. We attribute the unchanged ηext to the energy-
level alignments among the neighboring organic layers and
the α-6 T emitting molecules, which can prevent the accu-
cumulation of carriers at the heterojunction interfaces and car-
rier trapping on the α-6 T molecules. In contrast, since there
is a hole injection barrier of 0.2 eV at the α-NPD/Alq3 in-
terface in the Alq3 OLED, a number of holes injected from
the ITO contact are built up at this interface, resulting in
exciton quenching by the accumulated holes and the marked
decrease in ηext.

We calculate the generation rates of singlet excitons (nexciton)
in a carrier recombination zone of the OLEDs. The
nexciton can be estimated using

\[
n_{\text{exciton}} = \frac{J}{e} \times \eta_{\text{ext}} \times \frac{1}{\eta_{\text{out}}} \times \frac{1}{\eta_{\text{PL}}} \times \frac{1}{L_{\text{exciton}}},
\]

where \(e\) is the electronic charge, \(\eta_{\text{out}}\) is the light out-coupling efficiency, \(\eta_{\text{PL}}\) is the PL quantum efficiency, and \(L_{\text{exciton}}\) is the width of a carrier recombination zone. The \(n_{\text{exciton}}\) of the doped OLED at the maximum current can be calculated at 5.0 \(\times\) \(10^{25}\) cm\(^{-2}\) s using Eq. (1) with \(J = 185\) A/cm\(^2\), \(\eta_{\text{ext}} = 0.69\), \(\eta_{\text{out}} = 0.2\), \(\eta_{\text{PL}} = 0.4\) (for the α-6 T:POPy2 EML), and \(L_{\text{exciton}} = 20\) nm (the sum of the thickness of the α-6 T:POPy2 and α-6 T:m-MTDATA EMLs). On the other hand, the \(n_{\text{exciton}}\) of the Alq3 OLED at the maximum current can be calculated at 9.2 \(\times\) \(10^{25}\) cm\(^{-2}\) s using Eq. (1) with \(J = 3.3\) A/cm\(^2\), \(\eta_{\text{ext}} = 0.46\), \(\eta_{\text{out}} = 0.2\), \(\eta_{\text{PL}} = 0.2\), and \(L_{\text{exciton}} = 26\) nm. To calculate this \(n_{\text{exciton}}\), we assumed that the exciton diffusion length of 26 nm in Alq3 films corresponds to \(L_{\text{exciton}}\). Although the \(n_{\text{exciton}}\) of the doped OLED was about five times higher than that of the Alq3 OLED, we observed no decrease in ηext at the maximum current in the doped OLED, which is caused by the energy-level alignments among the organic molecules.

In an OLED, we chemically doped an α-6 T HTL and a PO Py2 ETL with F\(_6\)-TCNQ and Cs and matched energy lev-
els among neighboring carrier transport layers and α-6 T emitting molecules. We achieved an extremely low driving
voltage of 2.65 ± 0.05 V at a current density of 100 mA/cm\(^2\) in the OLED. We found that the onset voltage of EL
(≈2.4 V) corresponds to the photon energy of α-6 T
(≈2.5 eV) and a decrease in ηext at high current densities is
suppressed by matching the energy levels. Our OLED with a
low driving voltage and unchanged ηext will lead to the de-
velopment of higher performance passive matrix OLED dis-
plays and electrically pumped OLEDs as well as a better un-
derstanding of exciton quenching mechanisms.

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23. We measured the \(\eta_{\text{e}}\) of the organic films to be 2% ± 2% for α-6T,
35% ± 2% for PO Py2, 4% ± 2% for m-MTDATA, 10% ± 2% for
3 mol %-α-6T-doped m-MTDATA, 40% ± 1% for 3 mol %-α-6T-
doped PO Py2, and 20% ± 2% for Alq3 using an integrating sphere system
(Ref. 22).