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# 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  $2.65 \pm 0.05$  V at a current density of 100 mA/cm<sup>2</sup>; (2) the onset voltage of EL ( $\approx 2.4$  V) corresponds to the photon energy of emitting molecules ( $\approx 2.5$  eV), while the onset voltage of currents is  $\approx 1.8$  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. [DOI: 10.1063/1.2844891]

Organic light-emitting diodes (OLEDs) doped with phosphorescent iridium complexes have been shown to achieve an internal electroluminescence (EL) efficiency of nearly 100%.<sup>1,2</sup> 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<sup>2,3</sup> and lifetimes.<sup>4</sup> In most OLEDs, carrier mobilities of organic layers are much lower than those of inorganic semiconductors<sup>5,6</sup> and carrier injection barriers are present at metal/organic and organic/organic interfaces,<sup>7–9</sup> 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<sup>2–4,10–13</sup> and softening energy barriers at the heterojunction interfaces<sup>7–9</sup> 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-7,7,8,8-tetracyanoquinodimethane (F<sub>4</sub>-TCNQ)-doped  $\alpha$ -6 T HTL (30 nm)/4,4',4''-tris(*N*-3-methylphenyl-*N*-phenyl-amino)triphenylamine (*m*-MTDATA) HTL (10 nm)/3 mol % - $\alpha$ -6 T-doped *m*-MTDATA emitting layer (EML) (10 nm)/3 mol % - $\alpha$ -6 T-doped phenyldipyrrenylphosphine oxide (POPy<sub>2</sub>) EML (10 nm)/POPy<sub>2</sub> ETL (10 nm)/30 mol % -Cs-doped POPy<sub>2</sub> ETL (30 nm)/Al cathode (100 nm). The schematic structure and energy-level diagram of this OLED are shown in Figs. 1(a) and 1(b). The  $\alpha$ -6 T HTL,<sup>3,8</sup> the *m*-MTDATA HTL,<sup>14</sup> and the POPy<sub>2</sub> ETL<sup>3,15</sup> 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 F<sub>4</sub>-TCNQ in the  $\alpha$ -6 T HTL and *n*-type Cs in the POPy<sub>2</sub> ETL and matched the energy levels among the neighboring organic layers and the  $\alpha$ -6 T emitting molecules, which resulted in an extremely low driving voltage of  $2.65 \pm 0.05$  V for the current density of 100 mA/cm<sup>2</sup>.

In most OLEDs, EL efficiencies markedly decrease at high current densities.<sup>16</sup> 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,<sup>17</sup> singlet-singlet exciton annihilation,<sup>16,18</sup> and singlet-polaron exciton annihilation.<sup>18,19</sup> Recently, Luo

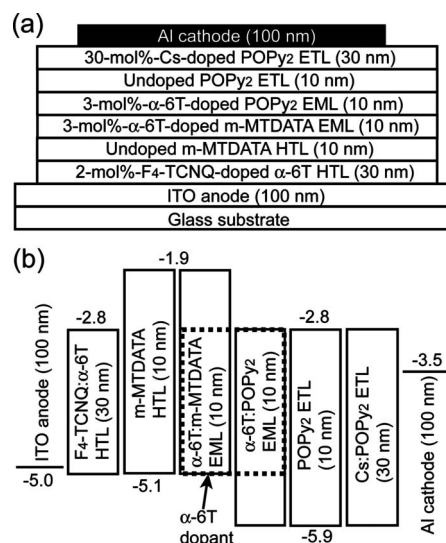


FIG. 1. (a) Schematic structure and (b) energy-level diagram of doped OLED. In (b), ionization potential energies of organic layers and work functions of metal layers were measured using AC-1 ultraviolet photoelectron spectrometer (Riken Keiki). Electron affinities of organic layers were calculated by subtracting optical absorption onset energies from ionization potential energies.

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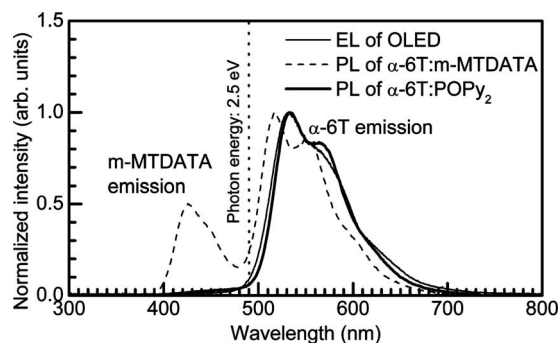


FIG. 2. EL spectrum of doped OLED (solid line) and PL spectra of 3-mol %- $\alpha$ -6T-doped *m*-MTDATA (broken line) and 3-mol %- $\alpha$ -6T-doped POPy<sub>2</sub> films (bold line).

*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.<sup>19</sup> 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  $\Omega/\text{sq}$  (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 F<sub>4</sub>-TCNQ: $\alpha$ -6 T ETL, 3 mol % for the  $\alpha$ -6 T-doped EMLs, and 30 mol % for the Cs:POPy<sub>2</sub> ETL using two quartz crystal microbalances. The active area of the device was 0.785 mm<sup>2</sup>. The EL spectrum of the device was measured with a spectrometer (SD-2000, Ocean Optics) at a constant current density of 100 mA/cm<sup>2</sup>. The current density-voltage-external quantum efficiency ( $J$ - $V$ - $\eta_{\text{ext}}$ ) characteristics of the device were measured using a semiconductor parameter analyzer (E5250A, Agilent Technology) and a calibrated silicon photodiode (1930-C, Newport). The luminance ( $L$ ) was calculated from  $\eta_{\text{ext}}$  assuming a Lambertian emission pattern.

The EL spectrum of the doped OLED and the photoluminescence (PL) spectra of 3 mol %- $\alpha$ -6 T-doped *m*-MTDATA and 3 mol %- $\alpha$ -6 T-doped POPy<sub>2</sub> films (100 nm) on quartz substrates are shown in Fig. 2. The excitation light wavelength for PL was 350 nm, where the absorption of POPy<sub>2</sub> and *m*-MTDATA is large while the absorption of  $\alpha$ -6 T is relatively small. We only observed the emissions arising from  $\alpha$ -6 T in the EL spectrum and the PL spectrum of the  $\alpha$ -6 T:POPy<sub>2</sub> film. However, there were two emission peaks arising from both  $\alpha$ -6 T and *m*-MTDATA in the PL spectrum of the  $\alpha$ -6 T:*m*-MTDATA film. Moreover, the EL spectrum better corresponded to the PL spectrum of the  $\alpha$ -6 T:POPy<sub>2</sub> film than that of the  $\alpha$ -6 T:*m*-MTDATA.

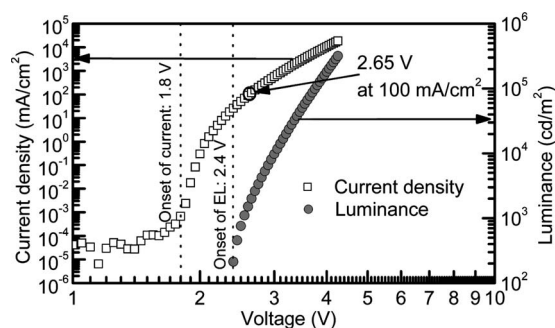


FIG. 3. Current density-voltage and luminance-voltage characteristics of doped OLED. Dotted lines highlight onset voltages of current and EL.

film. From these observations, we speculate that carrier recombination of electrons and holes mainly occur in the  $\alpha$ -6 T:POPy<sub>2</sub> EML. We calculated the photon energy of electrically excited  $\alpha$ -6 T molecules to be  $\approx 2.5$  eV from the high-energy edge of the EL spectrum.

The  $J$ - $V$  and  $L$ - $V$  characteristics of the OLED are shown in Fig. 3. We achieved an extremely low driving voltage of  $2.65 \pm 0.05$  V at 100 mA/cm<sup>2</sup> in the OLED. We can attribute this low voltage to the following factors. (1) We doped F<sub>4</sub>-TCNQ and Cs in the  $\alpha$ -6 T HTL and the POPy<sub>2</sub> 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<sup>20</sup> and induces the formation of nearly Ohmic contacts at the metal/organic interfaces.<sup>21</sup> (2) We used  $\alpha$ -6 T,<sup>3,8</sup> *m*-MTDATA,<sup>14</sup> and POPy<sub>2</sub> (Refs. 3 and 15) materials, which have high carrier mobilities. (3) We matched the energy levels among the neighboring organic layers and the  $\alpha$ -6 T emitting molecules, as shown in Fig. 1(b). 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 EL 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 ( $\approx 1.8$  V) and corresponded to the photon energy of emitting  $\alpha$ -6 T molecules ( $\approx 2.5$  eV).

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

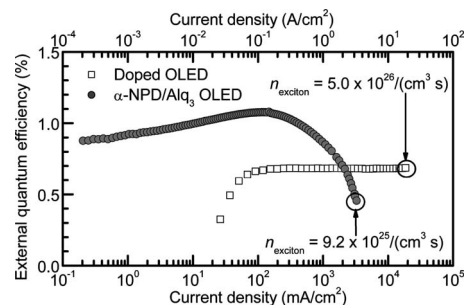


FIG. 4. External quantum efficiency-current density characteristics of doped OLED and Alq<sub>3</sub> OLED.

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 ( $\alpha$ -NPD) HTL (50 nm)/tris(8-hydroxy-quinoline) aluminum (Alq<sub>3</sub>) emitting ETL (50 nm)/MgAg cathode (100 nm) structure and measured its  $J$ - $\eta_{\text{ext}}$  characteristics, which are also shown in Fig. 4. Although the  $\eta_{\text{ext}}$  markedly decreased at high current densities in the Alq<sub>3</sub> OLED, we observed no decrease in  $\eta_{\text{ext}}$  of the doped OLED in the high current region of over two orders of magnitude. We attribute the unchanged  $\eta_{\text{ext}}$  to the energy-level alignments among the neighboring organic layers and the  $\alpha$ -6 T emitting molecules, which can prevent the accumulation of carriers at the heterojunction interfaces and carrier trapping on the  $\alpha$ -6 T molecules. In contrast, since there is a hole injection barrier of 0.2 eV at the  $\alpha$ -NPD/Alq<sub>3</sub> interface in the Alq<sub>3</sub> OLED,<sup>8</sup> 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  $\eta_{\text{ext}}$ .

We calculate the generation rates of singlet excitons ( $n_{\text{exciton}}$ ) in a carrier recombination zone of the OLEDs. The  $n_{\text{exciton}}$  can be estimated using

$$n_{\text{exciton}} = \frac{J}{e} \times \eta_{\text{ext}} \times \frac{1}{\eta_{\text{out}}} \times \frac{1}{\eta_{\text{PL}}} \times \frac{1}{L_{\text{exciton}}}, \quad (1)$$

where  $e$  is the electronic charge,  $\eta_{\text{out}}$  is the light out-coupling efficiency,<sup>17,22</sup>  $\eta_{\text{PL}}$  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  $5.0 \times 10^{26}/\text{cm}^2 \text{ s}$  using Eq. (1) with  $J = 18.5 \text{ A/cm}^2$ ,  $\eta_{\text{ext}} = 0.69$ ,  $\eta_{\text{out}} = 0.2$ ,<sup>17,22</sup>  $\eta_{\text{PL}} = 0.4$  (for the  $\alpha$ -6 T:POPy<sub>2</sub> EML),<sup>23</sup> and  $L_{\text{exciton}} = 20 \text{ nm}$  (the sum of the thickness of the  $\alpha$ -6 T:POPy<sub>2</sub> and  $\alpha$ -6 T:*m*-MTDATA EMLs). On the other hand, the  $n_{\text{exciton}}$  of the Alq<sub>3</sub> OLED at the maximum current can be calculated at  $9.2 \times 10^{25}/\text{cm}^2 \text{ s}$  using Eq. (1) with  $J = 3.3 \text{ A/cm}^2$ ,  $\eta_{\text{ext}} = 0.46$ ,  $\eta_{\text{out}} = 0.2$ ,<sup>17,22</sup>  $\eta_{\text{PL}} = 0.2$ ,<sup>23</sup> and  $L_{\text{exciton}} = 26 \text{ nm}$ .<sup>24</sup> To calculate this  $n_{\text{exciton}}$ , we assumed that the exciton diffusion length of 26 nm in Alq<sub>3</sub> films<sup>24</sup> corresponds to  $L_{\text{exciton}}$ . Although the  $n_{\text{exciton}}$  of the doped OLED was about five times higher than that of the Alq<sub>3</sub> OLED, we observed no decrease in  $\eta_{\text{ext}}$  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  $\alpha$ -6 T HTL and a POPy<sub>2</sub> ETL with F<sub>4</sub>-TCNQ and Cs and matched energy levels among neighboring carrier transport layers and  $\alpha$ -6 T emitting molecules. We achieved an extremely low driving voltage of  $2.65 \pm 0.05 \text{ V}$  at a current density of  $100 \text{ mA/cm}^2$  in the OLED. We found that the onset voltage of EL ( $\approx 2.4 \text{ V}$ ) corresponds to the photon energy of  $\alpha$ -6 T ( $\approx 2.5 \text{ eV}$ ) and a decrease in  $\eta_{\text{ext}}$  at high current densities is

suppressed by matching the energy levels. Our OLED with a low driving voltage and unchanged  $\eta_{\text{ext}}$  will lead to the development of higher performance passive matrix OLED displays and electrically pumped OLEDs as well as a better understanding of exciton quenching mechanisms.

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<sup>23</sup>We measured the  $\eta_{\text{PL}}$  of the organic films to be  $2\% \pm 2\%$  for  $\alpha$ -6T,  $35\% \pm 2\%$  for POPy<sub>2</sub>,  $4\% \pm 2\%$  for *m*-MTDATA,  $10\% \pm 2\%$  for 3 mol %- $\alpha$ -6T-doped *m*-MTDATA,  $40\% \pm 1\%$  for 3-mol %- $\alpha$ -6T-doped POPy<sub>2</sub>, and  $20\% \pm 2\%$  for Alq<sub>3</sub> using an integrating sphere system (Ref. 22).

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