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Organic Light-Emitting Diodes with F_{16}CuPC as an Efficient Hole-Injection Layer

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We report a new hole-injection material, copper hexadecafluorophthalocyanine (F_{16}CuPC) for organic light-emitting diodes (OLEDs) consisting of N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (α-NPD) as a hole-transport layer and 8-tris-hydroxyquinoline aluminum (Alq_3) as a light-emitting and electron-transport layer. The insertion of the F_{16}CuPC between indium-tin oxide (ITO) and α-NPD reduces the operating voltage significantly and thereby increases the luminous efficiency. By measuring the device characteristics for various F_{16}CuPC thicknesses, we find that an optimum F_{16}CuPC thickness is about 15 nm. At a luminance of 1000 cd/m^2, the device with 15-nm-thick F_{16}CuPC shows a luminous efficiency of 1.5 lm/W and a device operating voltage of 7.2 V while the device without the F_{16}CuPC layer shows 1.1 lm/W and 10.4 V. The significant decrease in a driving voltage and increase in the luminous efficiency can be attributed to the high hole-injection efficiency when F_{16}CuPC is inserted between ITO and α-NPD.

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I. INTRODUCTION

Since the first report of efficient organic light-emitting diodes (OLEDs) by Tang and VanSlyke [1], intensive research has been carried out to improve the devices' performance characteristics, such as the luminous efficiency, the driving voltage, and the lifetime [2]. Since light-emission in OLEDs depends on the injection and recombination of electrons and holes, it is very important to enhance the carrier injection efficiency and the electron-hole balance to obtain a low operating voltage and high efficiency [3–5]. However, the work function difference between the electrode and the organic materials results in a potential energy barrier that limits the carrier injection at organic/electrode interfaces [6–8]. One way to improve the carrier injection is to insert an appropriate carrier injection layer, which effectively lowers the potential barrier. At the interface of an electron-transport layer (ETL) and the cathode, the insertion of a very thin layer of LiF [9,10], CsF [11], MgF_2 [12], *etc.* has been proven to be very efficient for electron injection. At the transparent anode [typically, an indium tin oxide (ITO)] interface, poly(ethylene-dioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) [4,13] is most widely used as a hole-injection layer (HIL) in polymer light-emitting diodes. In small molecule OLEDs, various buffer materials, such as 4,4', 4''-trisN,(3-methylphenyl)-N-phenylamino-triphenylamine) (m-MTDATA) [14], copper phthalocyanine (CuPC) [15,16], or conducting fluorocarbon coatings (CF_x) [17], are often used at the interface between ITO and the hole-transport layer (HTL) and have been found to enhance the quantum efficiency and the durability of the OLEDs.

Since CuPC has merits, such as high thermal and chemical stability and the capability of forming a good-quality film between ITO and the HTL, the device stability can be significantly enhanced by inserting CuPC between the ITO anode and N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (α-NPD) [15]. However, CuPC is believed to decrease hole injection into the HTL, thus leading to an undesirable increase in the device's operating voltage [16]. Therefore, it is necessary to modify CuPC to enhance hole injection and decrease the operating voltage. It is well-known that the ionization potential (IP) of CuPC can be changed significantly by the degree of fluorination [18]. In this paper, we will show that fluorinated CuPC, especially, copper hexadecafluorophthalocyanine (F_{16}CuPC), which is well known for high mobility and stability in air for n-channel operation in TFTs [19], leads to a marked reduction of the operational voltage and an enhanced luminous efficiency when the F_{16}CuPC with thicknesses up to about 15 nm is inserted between ITO and α-NPD. At a luminance of 1000 cd/m^2, the

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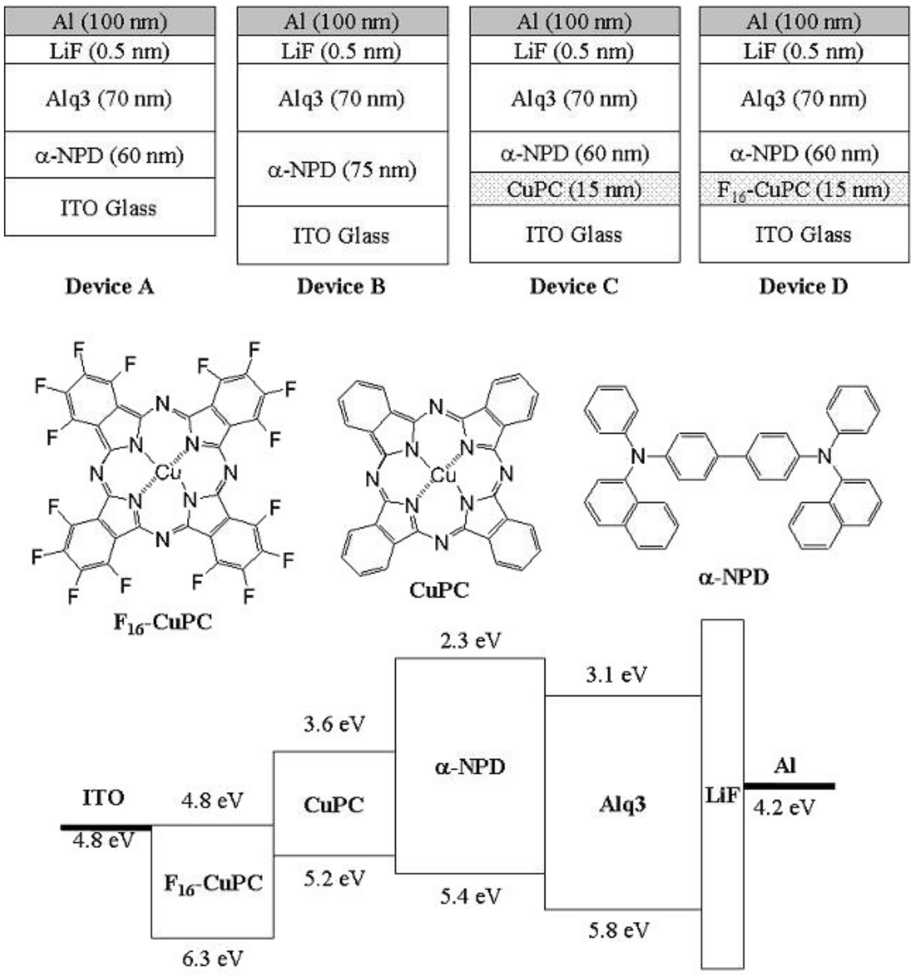

Fig. 1. Device structures and the schematic energy level diagram of the devices, along with the molecular structures of CuPC, F_{16}CuPC, and α-NPD.

device with 15-nm-thick F_{16}CuPC shows a luminous efficiency of 1.5 lm/W and a driving voltage of 7.2 V while the device without the F_{16}-CuPC layer shows 1.1 lm/W and 10.4 V.

II. EXPERIMENT

The OLEDs with various thicknesses of F_{16}CuPC or CuPC as the HIL layer, α-NPD as the HTL layer, and Alq_3 as the ETL layer, and with a cathode of LiF/Al were fabricated on precleaned ITO glass substrates (sheet resistance of about 10 $\Omega/\square$). Fig. 1 shows the configuration of four types of devices, the molecular structures of F_{16}CuPC, CuPC, and α-NPD, and a schematic diagram of energy levels [18,20–22]. In order to confirm the effect of the F_{16}CuPC on lowering the operation voltage, we compared the devices with 15-nm-thick CuPC (Device C) or F_{16}CuPC (Device D) as a buffer layer and those without the buffer layer [α-NPD thickness of 60 nm (Device A) and 75 nm (Device B)].

The ITO substrate (10 $\Omega/\square$, 150-nm thick) was cleaned ultrasonically in organic solvents (isopropyl alcohol, acetone, and methanol), rinsed in de-ionized (DI) water, and dried in an oven at 100 °C for more than 30 minutes. The device was fabricated with successive vacuum depositions of F_{16}CuPC with various thicknesses (1 nm, 5 nm, 15 nm, and 25 nm), α-NPD with a thickness of 60 or 75 nm, Alq_3 with a thickness of 70 nm, LiF with a thickness of 0.5 nm, and aluminum with a thickness of 100 nm, without breaking vacuum. The active area of the OLED, defined by the overlap of the ITO and the Al cathode, was 1.96 mm^2. The deposition of the materials was executed under a vacuum ($<3 \times 10^{-6}$ Torr) without breaking vacuum. The deposition rates for the organic layers were about 0.2 nm/sec, and that for Al was about 0.3 nm/sec.

The current-voltage-luminance (I-V-L) characteristics were measured with a Keithley 236 source-measure unit and a Keithley 2000 multimeter equipped with a photomultiplier tube (PMT) through an ARC 275 monochromator. The external quantum efficiency (QE) of the elec-

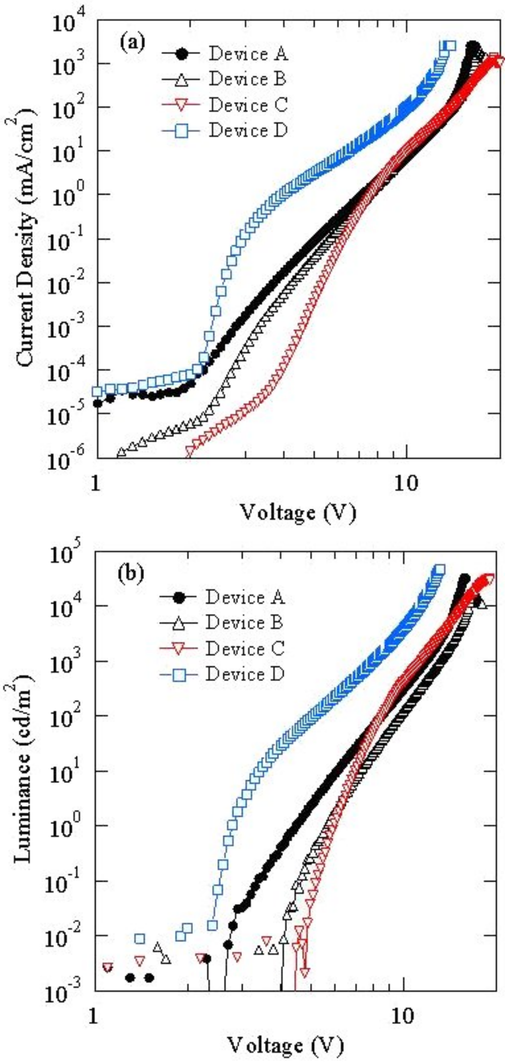

Fig. 2. (a) Current density-voltage and (b) luminance-voltage characteristics of the devices with 15-nm-thick CuPC and $F_{16}CuPC$ as hole-injection layers, compared with the reference devices with the α-NPD thicknesses of 60 and 75 nm.

troluminescence (EL), defined as the ratio of the emitted photons to the injected electric charges, was calculated from the EL intensity measured by using a calibrated Si photodiode placed at an angle normal to the device's surface, assuming that the device was a Lambertian source.

III. RESULTS AND DISCUSSION

Fig. 2 show the (a) current density - voltage (J-V) characteristics and the (b) luminance - voltage (L-V) characteristics of four types of devices: devices without the buffer layer [α-NPD thickness of 60 nm (Device A) and 75 nm (Device B)] and devices with 15-nm-thick CuPC (Device C) or $F_{16}CuPC$ (Device D) as a buffer

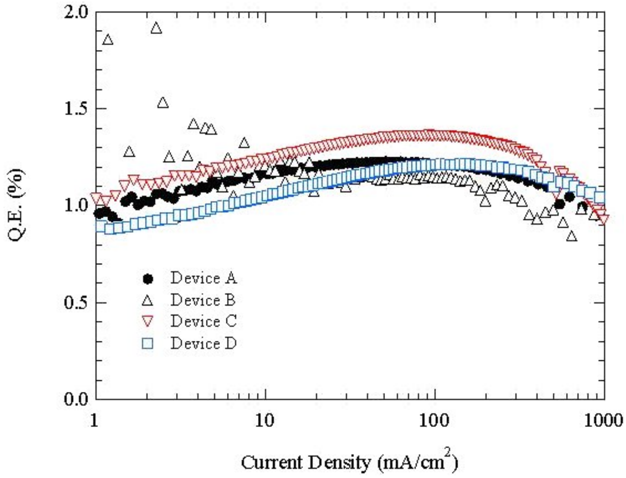

Fig. 3. Comparison of the external quantum efficiency (QE) of devices A, B, C, and D as functions of the current density.

layer. All devices exhibit rectifying I-V characteristics and emit a bright green light when a positive voltage is applied to the ITO electrode. The EL spectra of all devices are identical with the photoluminescence of the Alq_3 thin film [23], showing that the emission of light originates from the Alq_3 layer.

The device with the $F_{16}CuPC$ buffer layer (Device D) exhibits a much higher current density and luminance at any forward bias voltage than the other three devices. The device with the CuPC buffer layer (Device C) shows the lowest current density, even less than those of the devices without the buffer layer (Devices A and B), which is consistent with previous reports [15,16]. This behavior is more pronounced at a low bias voltage where the hole-injection process is the dominant limiting mechanism for current flow. Fig. 2(b) shows that the L-V characteristics follow a tendency similar to that of the J-V characteristics. The device with the $F_{16}CuPC$ buffer layer exhibits the lowest EL onset voltage V_{on} of 2.4 V, much less than $V_{on} \sim 4.8$ V for the device with CuPC. Since the total thickness of the organic layers is the same (d = 145 nm) for Devices B, C, and D and the only difference between them is the 15-nm-thick buffer layer interposed between ITO and α-NPD, the much enhanced current density for the device with $F_{16}CuPC$ implies that, compared to α-NPD and CuPC, $F_{16}CuPC$ may effectively increase the hole-injection efficiency or that it may have a higher hole mobility. However, the current density is increased only slightly by reducing the α-NPD thickness from 75 nm (Device B) to 60 nm (Device A), but it increase more than an order of magnitude when 15-nm-thick $F_{16}CuPC$ is inserted between ITO and α-NPD (Device D). Therefore, this result implies that the much higher current density for the device with the additional 15-nm-thick $F_{16}CuPC$ can be mainly attributed to the enhanced hole-injection efficiency.

Table 1. Device characteristics measured at a luminance of 1000 cd/m^2.

F_{16}-CuPC Thickness (nm)	Current Density (mA/cm^2)	Voltage (V)	Quantum Efficiency (%)	Luminous Efficiency (lm/W)
0	11.8	10.4	1.2	1.1
1	16.9	8.7	0.9	1.2
5	18.2	7.6	1.0	1.3
15	16.7	7.2	1.1	1.5
25	18.9	10.5	0.9	0.85

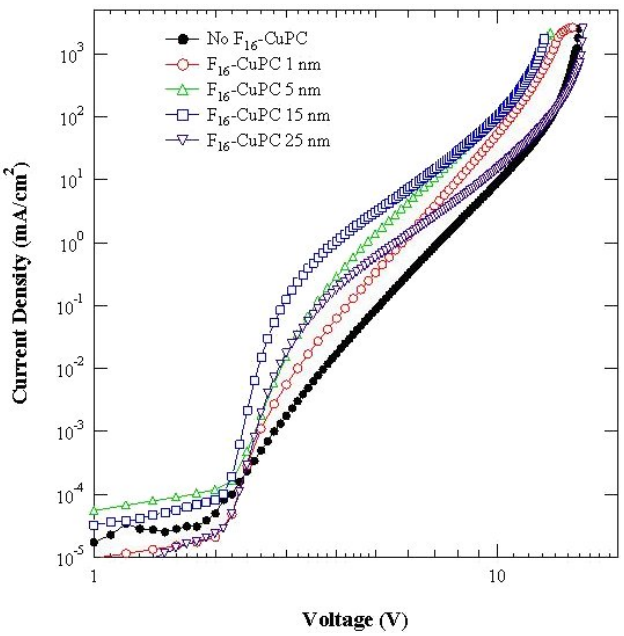

Fig. 4. Current density-voltage characteristics of devices with various thicknesses of a F_{16}CuPC layer between ITO and α-NPD.

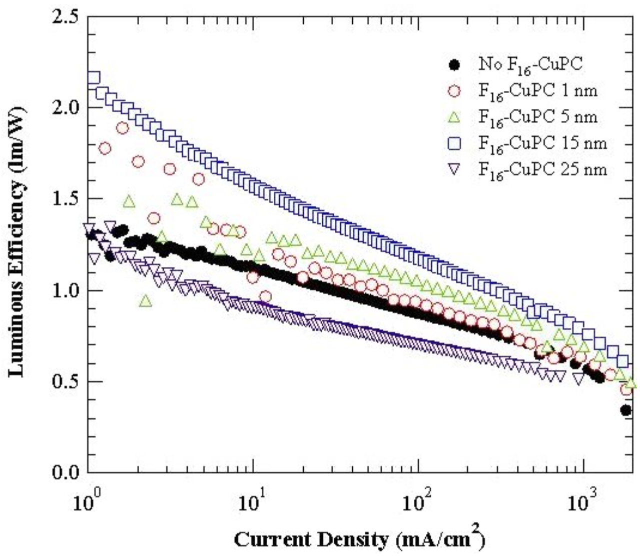

Fig. 5. Luminous efficiency as a function of the current density for devices with various thicknesses of a F_{16}CuPC layer between ITO and α-NPD.

Fig. 3 shows the external quantum efficiency (QE) of the four devices as functions of the current density. The device with the CuPC buffer layer shows the highest efficiency among them. The maximum external QE is about 1.4 %, which is larger than the QE $\sim$ 1.2 % for the device with F_{16}CuPC and the QE $\sim$ 1.2 % for the device without the buffer layer. This result is consistent with a previous report by Forsythe *et al.* [16]. The CuPC reduces the hole injection and, thus, improves the electron-hole balance in the recombination zone. For the device with F_{16}CuPC, the higher hole injection efficiency leads to a slight imbalance of charges, thus resulting in a slightly lower QE. However, the insertion of F_{16}CuPC as a buffer layer reduces the operational voltage significantly, thereby resulting in a much enhanced luminous power efficiency. At a luminance of 1000 cd/m^2, the device with 15-nm-thick F_{16}CuPC shows a luminous efficiency of 1.5 lm/W while the devices with 15-nm-thick CuPC and without the buffer layer shows 1.2 and 1.1 lm/W, respectively.

In order to find the optimal thickness of F_{16}CuPC for the best device performance, we investigated the current-voltage-luminance characteristics for varying thicknesses of the F_{16}CuPC layer between ITO and α-NPD. Fig. 4 shows the current density - voltage characteristics for the devices with F_{16}CuPC thicknesses of 1 nm, 5 nm, 15 nm, and 25 nm compared with the device without the F_{16}CuPC layer. As the F_{16}CuPC thickness increases up to a thickness of about 15 nm, the current density increases. It then decreases at higher F_{16}CuPC thicknesses. The luminance-voltage characteristics also show the same thickness dependence as the current density-voltage characteristics. At a luminance of 1000 cd/m^2, the operating voltage for the device without the F_{16}CuPC layer is 10.4 V. It continuously decreases down to 7.2 V up to a F_{16}CuPC thickness of 15 nm. Then, it increases to 10.5 V at a F_{16}CuPC thickness of 25 nm. Since the operating voltage decreases significantly with the F_{16}CuPC thickness up to 15 nm, the luminous power efficiency increases significantly as shown in Fig. 5. The luminous efficiency is about 1.5 lm/W at a luminance of

1000 cd/m^2 for the device with 15-nm-thick F_{16}CuPC while it is about 1.1 lm/W for the device without the F_{16}CuPC layer. Table 1 summarizes the device characteristics measured at a luminance of 1000 cd/m^2.

The results in Figs. 2-5 unambiguously demonstrate that the F_{16}CuPC layer inserted between ITO and α-NPD can effectively enhance the injection and the transport of charge carriers. However, the ionization potential of F_{16}CuPC, reported as 6.1 eV [18] $\sim$ 6.3 eV [20], is much higher than the work function of ITO ($\sim$4.8 eV [21]) and the IP of α-NPD ($\sim$5.4 eV [22]). Therefore, the potential barrier for hole injection appears to be higher when the F_{16}CuPC layer is inserted between ITO and α-NPD. Although the tunneling mechanism can enhance hole injection for a thin buffer layer of a few nanometers [24], it is quite difficult to account for the higher hole injection for F_{16}CuPC thicknesses up to 15 nm. Thus, the mechanism of F_{16}CuPC for enhancing hole injection is not clear yet, and further study is necessary.

IV. CONCLUSION

We have shown that the insertion of F_{16}CuPC between ITO and α-NPD reduces the operating voltage significantly and increases the luminous efficiency. By measuring the device characteristics with various F_{16}-CuPC thicknesses, we found the optimum F_{16}CuPC thickness to be about 15 nm. The markedly reduced operating voltage and enhanced luminous efficiency when F_{16}CuPC with thicknesses up to about 15 nm is inserted between ITO and α-NPD can be attributed to the high hole-injection efficiency. At a luminance of 1000 cd/m^2, the device with 15-nm-thick F_{16}CuPC shows a luminous efficiency of 1.5 lm/W and an operating voltage of 7.2 V while the device without the F_{16}CuPC layer shows a luminous efficiency of 1.1 lm/W and an operating voltage of 10.4 V. Therefore, F_{16}CuPC appears to be a better hole injection material than conventional CuPC, which has an undesirable increase in the device's operating voltage.

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