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Tetra-methyl substituted copper (II) phthalocyanine as a hole injection enhancer in organic light-emitting diodes

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We have enhanced hole injection and lifetime in organic light-emitting diodes (OLEDs) by incorporating the isomeric metal phthalocyanine, CuMePc, as a hole injection enhancer. The OLED devices containing CuMePc as a hole injection layer (HIL) exhibited higher luminous efficiency and operational lifetime than those using a CuPc layer and without a HIL. The effect of CuMePc thickness on device performance was investigated. Atomic force microscope (AFM) studies revealed that the thin films were smooth and uniform because the mixture of CuMePc isomers depressed crystallization within the layer. This may have caused the observed enhanced hole injection, indicating that CuMePc is a promising HIL material for highly efficient OLEDs.

Over the last two decades, organic light-emitting diodes (OLEDs) have attracted increasing attention and considerable research effort because they show potential for use in flat/flexible displays, and large area solid-state lighting.1–6 To achieve the required device performance, it is crucial to optimize charge injection and transportation.7,8 The Schottky barrier and contact resistance present at the electrode/organic interface,9–11 means charge injection depends significantly on this interface, and therefore interface modification is usually required to enhance power conversion efficiency and operational lifetime.8,12–17 Recently, a series of phthalocyanines (CuPc, 17 AlPc, 8 and MnPc11) were employed as an anodic buffer layer to facilitate hole injection from the ITO anode within OLEDs. These materials have been found to effectively modulate the work function of the electrodes, and substantially change the contact between the electrode and the semiconducting layer, resulting in improved performance.

CuPc is an efficient hole injection enhancer in organic devices. It contains a low-lying highest occupied molecular orbital (HOMO) that induces a small hole injection barrier between itself and the anode in an OLED.18 However, hole injection is not only determined by the HOMO level of the materials, but is affected significantly by the morphology of the CuPc layer, such that a dopant is usually necessary to obtain a uniform conducting path between the indium tin oxide (ITO) anode and hole injection layer (HIL).17

We have reported the use of tetra-methyl substituted copper (II) phthalocyanine (CuMePc) in solar cells to promote charge mobility and photon harvesting (Fig. 1(a)).19 As the HOMO level of CuMePc (5.1 eV) is comparable to that of CuPc (5.2 eV), the energy barrier of hole injection could be lowered by inserting a CuMePc buffer layer between the ITO anode and the HTL. Additionally, the carrier mobility of CuMePc is approximately three times that of CuPc, which makes it more favorable for hole transport. The fact that CuMePc consists of a mixture of isomer is expected to

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FIG. 1. (a) Chemical structures of the materials used in this work. (b) Device structure and energy level diagram of the diodes fabricated.

depress the crystallization of the HIL, and promote device stability and durability compared with devices using a CuPc buffer layer. Herein, we report the use of CuMePc as a HIL to modify the ITO/HTL interface in OLEDs, which led to enhanced luminous efficiency and durability of devices.

Three types of diodes were fabricated in this work. The influence of the thickness of CuMePc layer was examined in diode type 1 [structure: ITO/CuMePc (2.5 nm, 5 nm, 7.5 nm or 10 nm)/NPB (50 nm)/Alq3 (50 nm)/LiF (0.5 nm)/Al (100 nm)] To understand the enhanced hole injection observed, a single HTL device, diode type 2 was fabricated [ITO/NPB (50 nm)/Alq3 (50 nm)/LiF (0.5 nm)/Al (100 nm)]. To compare the device with alternative anode modifying layers, diode type 3 was fabricated using CuPc as the HILs [ITO/CuPc (2.5 nm, 5 nm, 7.5 nm or 10 nm)/NPB (50 nm)/Alq3 (50 nm)/LiF (0.5 nm)/Al (100 nm)]. The OLEDs were fabricated on patterned ITO glass with a sheet resistance of 20 Ω/□. All layers were grown by thermal evaporation under a vacuum of ∼1 × 10^{-6} Torr (Mbraun MB200), and the layer thickness was monitored in-situ using quartz crystal monitors during deposition. After fabrication, all OLEDs were encapsulated using UV adhesive under a nitrogen atmosphere. The emissive area of the devices was 10 mm².

The luminance-voltage (L-V), luminance-current density (L-J) and radiance of all devices were recorded using an automatic system containing a source-measure unit (Keithley 2400) and a calibrated spectrometer (Photo Research PR680). The surface morphologies of the ITO, CuPc modified ITO and CuMePc modified ITO surfaces were examined using atomic force microscopy (AFM, VEECO Multimode V, tapping mode). The crystallinity of CuMePc and CuPc layer deposited on ITO glass was studied using Grazing Incidence X-Ray Diffraction (GIXRD, Bruker D8 Advanced). All measurements were carried out under ambient condition after device fabrication and encapsulation.
FIG. 2. AFM images of (a) pristine ITO glass, (b) CuMePc (7.5 nm), (c) CuMePc (10 nm), (d) CuPc (7.5 nm) and (e) CuPc (10 nm) thin films deposited on top of ITO anode (Scale bar of 500 nm).

FIG. 3. GIXRD patterns of 50 nm thin films of (a) CuMePc and (b) CuPc deposited on ITO glass.
CuMePc was synthesized according to reported literature, and purified by vacuum sublimation before use. All other materials were used as purchased from Sigma-Aldrich. The energy levels of CuMePc were determined using cyclic voltammetry combined with UV-Vis absorption spectroscopy using methods described in the literature. The energy levels of ITO, CuPc, NPB, Alq3, and LiF/Al were obtained from the literature. The device structure and energy level band of the OLEDs are shown in Fig. 1(b).

Prior to OLEDs fabrication, the morphology of the ITO glass and the CuMePc and CuPc thin films deposited onto ITO at various thicknesses were characterized using AFM (Fig. 2). The device structure and energy level band of the OLEDs are shown in Fig. 1(b).

Prior to OLEDs fabrication, the morphology of the ITO glass and the CuMePc and CuPc thin films deposited onto ITO at various thicknesses were characterized using AFM (Fig. 2).

The pristine ITO glass had a rough surface with a surface root-mean-square (RMS) roughness of 6.65 nm (Fig. 2(a)). The CuMePc film significantly reduced the crystallization, and therefore produced a flat and uniform anode modified film. Lower average surface RMS roughness values were found for the 7.5 nm (Fig. 2(b)) and 10 nm (Fig. 2(c)) CuMePc layers, respectively. This indicated that the use of CuMePc formed ideal film morphologies for OLED anodic buffer layers. CuPc formed a crystalline structure during the vacuum deposition, as evidenced by the higher RMS values of 2.61 and 3.49 nm for the 7.5 nm (Fig. 2(d)) and 10 nm (Fig. 2(e)) CuPc thin films, respectively. The decreased crystallinity of CuMePc is also confirmed by Grazing Incidence X-Ray Diffraction (GIXRD) study. Figure 3 depicts GIXRD measurement of CuMePc and CuPc thin film deposited on ITO glass with the same thickness of 50 nm. The diffraction peak intensity of CuMePc (2 theta of 6.07) was found to be less than 100 arb. Units, it revealed an almost amorphous thin film structure. While that of CuPc (2 theta of 6.9) is 1300 arb. Units, which suggests a high crystalline structure for CuPc. With the same thickness, higher diffraction intensity suggests higher crystallinity.

Diodes types 1-3 were fabricated and the device performances compared. Electroluminescent spectra of the three different diodes are shown in Fig. 4. All have an emission maximum around

![Image](image_url)
512 nm, exhibiting electroluminescent characteristics of Alq₃-based OLEDs. This result shows that the HILs do not cause any significant change to the emission spectrum.

The L-V and L-J characteristics of OLEDs were shown in Fig. 5(a) and 5(b). For comparison, a device without an HIL was also characterized. The luminance of an OLED can be significantly improved by inclusion of an HIL insertion layer between the ITO anode and the NPB layer. Luminance maxima of 20040 and 13680 cd/m² were found for devices containing CuPc and CuMePc, respectively, showing remarkable enhancement of hole injection by balancing and optimizing charge carrier flow into the Alq₃ emissive confinement zone.

Similar results can be found for devices containing HILs with other thicknesses, as summarized in Table I. The luminance as a function of current density is shown in Fig. 5(b). The luminance increased linearly with increasing current density for the devices containing HILs, which suggested increased charge balance in the device. This was similar to literature reports, in which phthalocyanines were employed as a hole injection enhancer. A substantial roll-off effect was observed at high luminance for the single HTL device type 2, which might have been caused by exciton-exciton interactions, exciton-charge carrier interactions, and exciton dissociation. The introduction of HILs into the OLEDs generally led to an enhancement of the L-J performance when compared with devices without HILs (Fig. 5(b)). Moreover, the insertion of a CuMePc HIL resulted in superior L-J behavior compared with that of the device using a CuPc layer, showing a higher maximum luminous efficiency of 4.08 cd/A compared with 3.13 cd/A for the CuPc containing device. Similarly, OLEDs containing 5 and 10 nm CuMePc layers exhibited enhanced L-J characteristics (3.83 and 3.56 cd/A, respectively) than those of devices containing a CuPc layer (3.57 and 3.04 cd/A for 5 and 10 nm HILs, respectively), illustrated in Table I. Notably, the HIL morphology plays an important role in allowing holes to cross from ITO to the HIL. The enhancement observed in the OLEDs containing CuMePc can be attributed to the flat and uniform anodic buffer film formed. The film exhibited reduced crystallization because of the presence of a mixture of CuPc isomers.
TABLE I. Comparison of device performances of three types of diodes.

<table>
<thead>
<tr>
<th>Hole injection layer</th>
<th>$\lambda_{EL,max}^{a}$ (nm)</th>
<th>CIE$^{b}$ (x, y)</th>
<th>$V_{turn-on}^{c}$ (V)</th>
<th>$LE_{max}^{d}$ (cd/A)</th>
<th>$PE_{max}^{e}$ (lm/W)</th>
<th>$I_{max}^{f}$ (cd/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o hole injection layer</td>
<td>508</td>
<td>0.360, 0.540</td>
<td>3.6</td>
<td>3.30</td>
<td>1.13</td>
<td>6600</td>
</tr>
<tr>
<td>CuPc</td>
<td>2.5 nm</td>
<td>514</td>
<td>0.357, 0.535</td>
<td>4.0</td>
<td>3.80</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>5 nm</td>
<td>512</td>
<td>0.358, 0.538</td>
<td>3.5</td>
<td>3.57</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>7.5 nm</td>
<td>512</td>
<td>0.356, 0.533</td>
<td>3.4</td>
<td>3.13</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>10 nm</td>
<td>514</td>
<td>0.362, 0.543</td>
<td>3.5</td>
<td>3.04</td>
<td>1.28</td>
</tr>
<tr>
<td>CuMePc</td>
<td>2.5 nm</td>
<td>514</td>
<td>0.358, 0.538</td>
<td>4.0</td>
<td>3.15</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>5 nm</td>
<td>512</td>
<td>0.357, 0.535</td>
<td>4.5</td>
<td>3.83</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>7.5 nm</td>
<td>512</td>
<td>0.359, 0.539</td>
<td>4.6</td>
<td>4.08</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>10 nm</td>
<td>512</td>
<td>0.361, 0.541</td>
<td>4.8</td>
<td>3.56</td>
<td>1.12</td>
</tr>
</tbody>
</table>

$^{a}$Maximum peak of EL spectra.
$^{b}$Measured at maximum luminance.
$^{c}$Turn-on voltage obtained at the luminance of 1 cd m$^{-2}$.
$^{d}$Maximum luminous efficiency.
$^{e}$Maximum power efficiency.
$^{f}$Maximum luminance.

Additionally, as the CuMePc thin film had been a smooth surface morphology (Fig. 2), the contact at the CuMePc/NPB junction was increased, leading to more effective hole transportation from the CuMePc layer into the HTL.

To investigate the influence of the HIL quality on device performance, the OLED lifetimes were examined. The measurement was performed under a constant driving current density of 100 mA/cm$^2$ at which roughly the same initial brightness of ~2000 cd/m$^2$ was obtained in each diode. The luminance of the device without an HIL decayed rapidly, with a poor half-lifetime of 18 min (Fig. 6). The OLEDs that contained CuMePc/CuPc HILs exhibited a remarkable improvement in operational stability compared with the single HTL device. A half-lifetime of 1314 min was observed for the OLED containing CuMePc, while than that of the device that contained CuPc was 1074 min. During the lifetime measurements, dark spots were observed in both the single HTL device and the device containing a CuPc layer, leading to the decreased device lifetimes, while the OLED containing a CuMePc layer exhibited homogenous emission with no obvious dark spots. This fact indicated that surface morphology of the anode is important for the operational stability of devices. The CuMePc modified anode possessed a relatively fine and smooth surface (e.g. $RMS = 0.75$ nm for 7.5 nm CuMePc layer) compared with that of the untreated ITO ($RMS = 6.65$ nm) and the CuPc layer (e.g. $RMS = 2.61$ nm for 7.5 nm CuPc layer), as shown in Fig. 2. The increased smoothness improved hole injection from the anode and lowered the pin-hole

FIG. 6. Normalized luminance under constant current density of 100 mA/cm$^2$ of OLEDs.
effect at the ITO/HIL interface, leading to the lack of dark spots and improved device stability and durability.

In summary, we have used a mixture of isomers of the phthalocyanine, CuMePc as a hole injection enhancer for Alq3-based OLEDs. AFM studies revealed that the presence of CuMePc depressed the crystallization of the HILs, and effectively reduced the surface roughness of the thin films, leading to fine and uniform surface morphologies when compared with CuPc layers. Superior \( L\text{-}J \) luminance performance and operational durability was achieved when compared with devices that contained a CuPc layer. This was caused by the superior quality of the CuMePc HIL. The optimum thickness of the CuMePc layer was found to be 7.5 nm, which led to a luminous efficiency maximum of 4.08 cm/A and a half-lifetime as high as 1314 min. This study shows that isomeric phthalocyanines have great potential to enhance hole injection and device stability in OLEDs. Further work is necessary to find other metal phthalocyanine derivatives with potentially higher hole injection properties and an improved interface with the various layers used in OLED.

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