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To cite this article: Zhengyang Bin et al 2016 Nanotechnology 27 174001

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Using an organic radical precursor as an electron injection material for efficient and stable organic light-emitting diodes

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Received 16 January 2016, revised 13 February 2016
Accepted for publication 29 February 2016
Published 18 March 2016

Abstract
Materials with strong reducibility have been used as electron injection layers (EILs) to lower the work function of cathodes and reduce the driving voltage of organic light-emitting diodes (OLEDs). However, the most prominent electron injection materials presented so far are high-temperature-evaporable inorganic salts based on alkaline metals, which suffer from a high tendency of metal diffusion throughout the organic layer and thus reduce the device efficiency and stability. Here, we introduce a new kind of EIL based on a stable precursor of a strongly reducing organic radical. By using an organic precursor, we are able to take the advantage of the low-evaporation-temperature and avoid the problem of metal diffusion, thus improving the device efficiency and stability. Ultraviolet photoelectron spectroscopy (UPS) study indicates that inserting a thin layer of organic radical between the electron transport layer and cathode could greatly reduce the electron injection barrier due to the strong interaction of radical with cathode and the electron transporting material. As a result, OLEDs with an organic radical as the EIL showed a 25.2% higher efficiency and 2.2 times longer lifetime than the control device with conventional LiF as the EIL.

Keywords: electron injection, precursor, organic radical, organic light-emitting diodes, efficiency and stability

(Some figures may appear in colour only in the online journal)

1. Introduction
Organic light-emitting diodes (OLEDs) are regarded as the most promising candidate for next generation displays and lighting owing to their low cost and high quantum efficiency [1–5]. Although significant progress has been made in vacuum-deposited OLEDs, low driving voltage remains a crucial requirement to improve the power efficiency and reduce the power consumption of OLEDs [6]. For low power consuming devices, low work function metals are needed for cathodes, like calcium and magnesium. However, these cathodes are highly reactive and easily oxidized in air, leading to fast deterioration of device performance [7]. Thus, the air-stable metal of aluminum (Al) is widely used as a cathode in OLEDs. Although Al is relatively stable in air, its high work function (WF) leads to a large injection barrier with the unoccupied molecular orbital (LUMO) level of electron transport material, which hampers the electron injection [8]. Surface modification by an electron injection layer (EIL) can be used to lower the WF of a cathode and reduce the energy barrier. Therefore, a great deal of research on efficient electron injection materials (EIMs) has been carried out.

Strongly reducing molecules are one type of efficient EIM to lower cathode WF. The electron transfer from reducing molecules to the cathode results in a layer of corresponding cations on the negatively charged surface and consequently in a surface dipole. Furthermore, stronger reductants are expected to lead to a greater extent of electron transfer, and therefore potentially larger WF modification [9]. The most prominent materials presented so far as EILs are
inorganic salts based on alkaline metals, such as alkaline fluorides (LiF [10–12], CsF [13]), alkaline quinolone (Liq [14]) and alkaline salt (Cs₂CO₃ [15]). Among these, LiF is the most widely used in high-efficiency OLED devices [10–12, 16]. But the drawback of using an EIL based on alkaline metal is the high tendency of metal diffusion throughout the organic layer, which behaves as an exciton-quenching center to reduce device efficiency and stability [17–19]. The relatively high deposition temperature is another shortcoming of those alkaline metal containing devices. Here, we introduce the precursor of a strongly reducing organic radical as a new kind of EIL for efficient and stable OLEDs. Using a precursor of an organic radical as an EIL possesses several advantages: first, the precursor is stable in air, while the decomposition product is a strongly reducing organic radical, which behaves as an efficient EIM. Second, the organic precursor decomposes only at a low temperature, thus it could be handled in organic chamber and simplifies the fabricating process. Third, no alkaline metal means no exciton-quenching by migrated metals, thus improving the device efficiency and stability.

In this work, 2-(2-methoxyphenyl)-1,3-dimethyl-1H-benzimidazol-3-ium iodide (o-MeO-DMBI-I) [19–21], the precursor of a strongly reducing organic radical 2-(2-methoxyphenyl)-1,3-dimethyl-1H-benzimidazol-3-ium (o-MeO-DMBI), was used as an EIL to fabricate efficient and stable OLEDs. The molecular structure of o-MeO-DMBI and its precursor o-MeO-DMBI-I are shown in figure 1. o-MeO-DMBI has great potential to improve electron injection; the current density of electron-only device showed increase of 4 orders of magnitude at a 12 V bias, which is surprising as it is even higher than that of a device using o-MeO-DMBI as an n-dopant. Ultraviolet photoelectron spectroscopy (UPS) analysis indicates that using 4.5 nm o-MeO-DMBI film as an EIL could reduce the interfacial energy barrier from 0.8 eV to 0.3 eV between Bphen/Al interface, which is nearly an ohmic contact. Compared with OLED devices using LiF as an EIL, the device using an organic radical injection layer shows a low driving voltage from 3.5 V to 3.2 V, and the device efficiency is improved by 25.2% while lifetime is 2.2 times longer.

2. Materials and methods

2.1. Device fabrication

o-MeO-DMBI-I was synthesized as reported previously [20], and Bphen was purchased from Jilin Optical and Electronic Materials Company, which had been purified by repeated temperature-gradient vacuum sublimation and received with a purity of more than 99.5%. Thus, it was used directly without further purification. All the films were prepared by conventional thermal deposition inside a high vacuum chamber at 10⁻⁶ Pa. A quartz crystal sensor monitored the thickness of organic layers in situ. All devices were fabricated on ITO substrates with sheet resistances of about 15 Ω/□ after UV-ozone treatments. After vacuum deposition, the devices were transferred to a glovebox filled with nitrogen without being exposed to air and then encapsulated with glass plates.

2.2. Measurements

Absorption spectra were recorded with an UV–vis spectrophotometer (Jobin Yvon, FluoroMax-3). The current density–luminance–voltage characteristics were measured by a Keithley 4200 semiconductor characterization system. The photoluminescence spectra and luminance of the devices were obtained on a PR650 spectrometer. The ultraviolet photoelectron spectroscopy (UPS) characterizations were carried out with monochromatized HeI radiation at 21.2 eV. The work functions of samples were determined according to $WF = hv - Be_{\text{He}}$, where $Be_{\text{He}}$ is the binding energy relative to the Fermi level of the calibrated spectrometer that corresponds to the secondary electron cutoff, and $hv$ is the HeI photon energy [9].

3. Results and discussion

3.1. Current density of electron-only devices

The current–voltage characteristics of the electron-only devices were used to evaluate the injection properties of o-MeO-DMBI. The structures of electron-only devices were ITO/BCP (10 nm)/Bphen (100 nm)/o-MeO-DMBI (x nm)/Al and performances are summarized in figure 2. In these devices, BCP stands for 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline and was used as a blocking layer.
As can be seen from figure 2, the energy barrier between Bphen and Al is rather high, thus few electrons could be injected, resulting in a rather low current density. Using the organic radical of o-MeO-DMBI as an EIL, devices showed a great increase in the current density, attributed to an efficient electron transfer from the highly reducing organic radical to cathode. Thus, the current density of the electron-only device showed an increase by about 4 orders of magnitude at a 12 V bias. On the other hand, the current density only changed a little with different thicknesses of EIL, which indicates that electron injection ability is not very sensitive to EIL thickness and it is good for mass production.

According to our previous study \[19\], we showed that o-MeO-DMBI is an efficient n-type dopant in Bphen to improve the electron injection. Here, it is promising that using o-MeO-DMBI as an EIL between Bphen and Al is more effective in improving the electron injection and increase the current density of electron-only devices, as can be seen in figure 3.

### 3.2. Energy level alignment of Bphen and Al interfaces

To further investigate the electron injection property of o-MeO-DMBI, the energy level alignment at interfaces between Al/Bphen and Al/o-MeO-DMBI/Bphen was measured using UPS.

Figure 4 shows the UPS-derived valence band spectra of 5 nm Bphen on Al and 5 nm Bphen on o-MeO-DMBI/Al. The WF of Al is 4.3 eV, and is reduced to 3.2 eV when a 5 nm Bphen is directly deposited on Al. The 1.1 eV interfacial dipole at the Bphen/Al interface is mainly attributed to the 'push back effect' at the cathode surface, which decreases the effective WF \[22\]. But when 4.5 nm o-MeO-DMBI is deposited on Al to behave as an EIL between Bphen/Al, the WF is changed to 2.9 eV. Moreover, compared with the Bphen/Al interlayer, the three typical electronic features of Bphen/o-MeO-DMBI/Al are shifted by 0.2–0.4 eV uniformly toward a higher binding energy. The energy shift is mainly attributed to the charge transfer from o-MeO-DMBI to Bphen at the interface \[23, 24\].

Utilizing 4.5 nm o-MeO-DMBI as an EIL gives rise to a Fermi level shift away from the HOMO and towards the LUMO of Bphen, leading to a reduced electron injection barrier and an improved current density. From UPS analysis, the energy barrier between HOMO of Bphen and Fermi energy of Al could be drawn. However, electrons are injected to the LUMO of Bphen from the Fermi energy of Al, thus to calculate the electron injection barrier, the energy gap of Bphen should be measured.

A UV–vis absorption spectrum is used to measure the energy gap of Bphen, which is estimated to be 3.6 eV, as shown in figure 5. Thus with the energy of interfaces and energy gap of Bphen, the energy level alignment diagrams for Bphen/Al and Bphen/o-MeO-DMBI/Al interfaces could be drawn, as depicted in figure 6.

The WF of the Bphen/Al cathode is 3.1 eV, and electron injection barrier between Bphen and Al is 0.8 eV, which
is rather deep and hampers the electron injection. But after inserting a 4.5 nm $\alpha$-MeO-DMBI layer between Bphen/Al, the interfacial dipole shifts down to a WF about 2.9 eV, and a vacuum level shift of 1.4 eV is formed for the Bphen/$\alpha$-MeO-DMBI/Al contact. Thus, the electron injection barrier between Bphen and Al is deduced as 0.3 eV, 0.5 eV lower than that for Bphen/Al contact without a $\alpha$-MeO-DMBI injection layer. Thus, as for the findings in electron-only devices, using a 4.5 nm $\alpha$-MeO-DMBI film as an EIL could both greatly reduce the interfacial energy barrier between Al and Bphen, and lead to an incredible boom in current density.

3.3. Film morphology of EIL

The film morphology is another crucial parameter that has to be accounted for when introducing an interfacial layer, and it could greatly affect the injection behavior [25]. Figure 7 shows atomic force microscopy (AFM) images of the surface morphologies of 4.5 nm $\alpha$-MeO-DMBI.

As can be inferred from figure 7, the surface of the $\alpha$-MeO-DMBI film is relatively smooth, with a root-mean-square (rms) roughness of 3.44 nm, which is good for electron injection.

Thus, viewing the two analyses above, the organic radical of $\alpha$-MeO-DMBI is a new kind of EIM, which could not only form an ordered structure and a smooth surface, but also has a strong reducibility to go through electron transfer with the cathode and reduce the electron injection barrier.

3.4. Performances of OLEDs

In OLED devices, the most-reported EIL has been LiF, which can reduce the energy barrier and help electron injection. Compared with other highly reactive EILs such as

![Image of energy level alignment diagrams and AFM images]
alkali metals, LiF has an outstanding property of air stability, but it still suffers from a high evaporation temperature and strong diffusion tendency of Li, which behaves as an exciton-quenching center to reduce device efficiency [17–19]. Thus, strongly reducing the organic radical o-MeO-DMBI, decomposed from the stable precursor o-MeO-DMBI-I, is promising for use as a new kind of EIL in phosphorescent OLEDs to improve device efficiency and enhance operation stability.

The device structures are ITO/HAT-CN (5 nm)/NPB (40 nm)/Ir(ppy)3:CBP (10%, 30 nm)/Bphen (40 nm)/LiF (0.5 nm) or o-MeO-DMBI (4.5 nm)/Al, where HAT-CN stands for 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile, NPB stands for N,N′-di(naphthalene-1-yl)-N,N′-diphenylbenzidine, Ir(ppy), stands for tris(2-phenylpyridine) iridium, and CBP stands for 4,4-N,N-dicarbazolylbiphenyl. Figure 8 compares the device performances of the three devices and the data are summarized in Table 1.

**Table 1. Performance of OLED devices with different injection layers.**

<table>
<thead>
<tr>
<th>Devices</th>
<th>$V_{on}$ [V]</th>
<th>$\eta_c$, max [cd A$^{-1}$]</th>
<th>$\eta_p$, max [lm W$^{-1}$]</th>
<th>Lifetime [h]</th>
<th>CIE (x, y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bphen/Al</td>
<td>4.8</td>
<td>24.6</td>
<td>8.3</td>
<td>57.3</td>
<td>(0.32, 0.62)</td>
</tr>
<tr>
<td>Bphen/LiF/Al</td>
<td>3.5</td>
<td>29.4</td>
<td>15.3</td>
<td>40.0</td>
<td>(0.32, 0.62)</td>
</tr>
<tr>
<td>Bphen/o-MeO-DMBI/Al</td>
<td>3.2</td>
<td>36.8</td>
<td>19.4</td>
<td>87.4</td>
<td>(0.32, 0.62)</td>
</tr>
</tbody>
</table>

Figure 8. (a) The energy level diagram of devices. (b) current density–voltage, (c) luminance–voltage, (d) current efficiency–luminance, (e) power efficiency–luminance characteristics and (f) the normalized EL spectra of devices utilizing Al, LiF/Al, and o-MeO-DMBI/Al as cathodes, separately.

Figure 9. Luminance deterioration curves of devices utilizing Al, LiF/Al, and o-MeO-DMBI/Al as cathodes, separately.

![Figure 9](image-url)
All the three devices give the typical green emission at 516 nm from Ir(ppy)$_3$, corresponding to Commission Internationale de L’Eclairage (CIE) 1931 chromaticity coordinates of (0.32, 0.62). When $\alpha$-MeO-DMBI was inserted between Bphen and Al, a remarkable increase in current density and luminance was achieved. The turn on voltage ($V_{on}$) decreased from 4.8 V to 3.2 V, and a low driving voltage could lead to improved power efficiency ($\eta_{p,\max}$) and reduced power consumption of OLEDs. Thus a highly efficient OLED is fabricated using $\alpha$-MeO-DMBI as an EIL, which shows an improvement in current efficiency ($\eta_{c,\max}$) from 29.4 cd A$^{-1}$ to 36.8 cd A$^{-1}$.

Besides the improvement in device efficiency, using an organic radical as an EIL instead of alkali metal could also enhance the device operation stability. Lifetime ($T_{50\%}$), defined as the time when the actual luminance decays to 50% of the initial luminance of 1000 cd m$^{-2}$ at a room temperature, was measured to compare the device stability. As can be seen from figure 9, the lifetime of device using a LiF EIL is only 40.0 h, which is even shorter than the lifetime of a control device (57.3 h). However, using an organic radical $\alpha$-MeO-DMBI as an EIL instead of LiF greatly improved the device stability, prolonging the lifetime to 87.4 h, 2.2 times longer than a LiF-containing device.

4. Conclusions

In summary, we have demonstrated the use of a stable pre-cursor of an organic radical as an EIL in OLEDs to reduce the driving voltage, improve the device efficiency and enhance the operation stability. $\alpha$-MeO-DMBI, formed during vacuum decomposition from $\alpha$-MeO-DMBI-I, is promising for use as an EIL due to its strong reducibility, ordered arrangement in a smooth film and lack of atom diffusion. Utilizing a 4.5 nm $\alpha$-MeO-DMBI film as an EIL will reduce the interfacial energy barrier from 0.8 eV to 0.3 eV between Bphen/Al interface, and lead to an incredible boom in current density. As a result, an OLED with $\alpha$-MeO-DMBI as the EIL showed 25.2% higher efficiency and 2.2 times longer lifetime than the control device with conventional LiF as the EIL.

Acknowledgments

We would like to thank the National Science Fund for Distinguished Young Scholars of China (Grant No. 51525304) and the National Key Basic Research and Development Program of China (Grant No. 2015CB655002) for financial support.

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