Air-Stable Inverted Blue OLEDs Without Encapsulation

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Abstract
We demonstrated low-driving voltage and air-stable inverted blue fluorescent OLEDs using a novel phosphine based electron injection material. The optimized inverted OLED had excellent air stability with an operational lifetime of over 1,400 h at 5 mA/cm² without any protection.

Author Keywords
Electron injection; Air stability; Coordination reaction; Cathode; Organic light-emitting diodes; Flexible electronics

1. Introduction

Although flexible OLED devices have demonstrated significant advantages in terms of high affinity to various flexible environments such as curved or deformed surfaces, their widespread use remains a challenge due to issues with their long-term operational stability and sensitivity to moisture and oxygen in the air environment. In the event of ambient oxygen and moisture penetrating the OLED layer, this can lead to the degradation of the organic materials and metal electrodes, resulting in a reduction in the light-emitting area from the edge. In order to protect OLEDs strictly from ambient air, various encapsulants have been developed to form high-performance barrier layers [1-2]. However, this strict encapsulation requirement not only reduces yield rates and throughput, but also limits the flexibility and may hider their widespread use. An alternative approach to improve the air stability of OLEDs is the careful design of the chemical structure of organic materials. In this approach, by optimizing the device structure and materials, it is possible to achieve thin, flexible and air-stable OLEDs without the need for strict encapsulation [3]. As the display industry rapidly evolves towards flexible technologies such as bending, folding, and stretching, air-stable OLEDs are becoming even more important.

To achieve long-lasting flexible OLEDs without strict encapsulation requirements, we previously developed inverted OLEDs using low work-function (WF) electrodes and electron injection materials (EIM) to reduce the electron injection barrier near the cathode [4-5]. Eliminating chemically reactive alkali elements from the electron injection layer (EIL) led to these inverted OLEDs exhibiting high stability and low-voltage operation capability in air environments. The key factor in this development is a coordination reaction between metals or metal oxides and EIMs, such as phenanthroline derivatives [5-7]. Recently, a research group from Tsinghua University and our group reported a phenanthroline derivative *p*-Pyrrd-Phen that can reduce the WF of electrodes to below 3.0 eV by utilizing the coordination reaction from N atoms of phenanthroline ligand with metals or metal oxides (5, 8). We have also demonstrated that the superbase EIM of Py-hpp$_2$ reduced the WF near an Al cathode to about 2.0 eV through both the coordination reaction and the formation of hydrogen bonds (7).

In this study, we demonstrated inverted blue fluorescent OLEDs using a novel EIL in two device types: an encapsulated device with high efficiency and long-operational lifetime, and a non-encapsulated device that can be driven stably in air without any protection. The structure of the inverted OLEDs and the chemical structure of the materials used in the EIL and the emitting layer (EML) are shown in Fig. 1. To improve the electron injection property and air stability, we developed a novel phosphine based EIM (PD-1) with high coordination ability with metals such as Ag, Cu, and Pd, which are highly stable in the atmosphere. As references of EIM, we used the phenanthroline derivative *p*-Pyrrd-Phen, which showed excellent electron injection and air stability in our previous research [6], and BPhen. The encapsulated inverted blue OLED exhibited an extremely low driving voltage of 3.42 V @ 10,000 cd/m² and a half-lifetime (LT50) of over 10,000 h from an initial luminance of 1,000 cd/m². The origin of the reduced driving voltage with phosphine was revealed by ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). The non-encapsulated OLED had an operating lifetime of over 1,400 hours before the emitting area decreased by 1% in a non-encapsulated environment at room temperature and humidity.

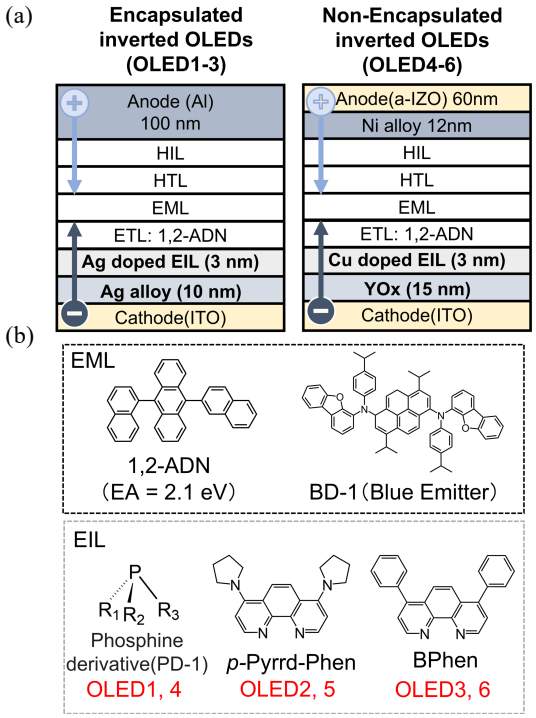

Fig. 1. (a) Multilayer structure of inverted OLEDs and (b)chemical structure of the materials used in the EIL and the emitting layer.

2. Evaluation of the electron injection property and stability of phosphine based EIL

The electron injection property and stability of the PD-1 were clarified by investigating the EIL-dependent characteristics of encapsulated inverted OLEDs 1-3. The anthracene derivative 9-

ISSN 0097-996X/25/5603-2205-$1.00 © 2025

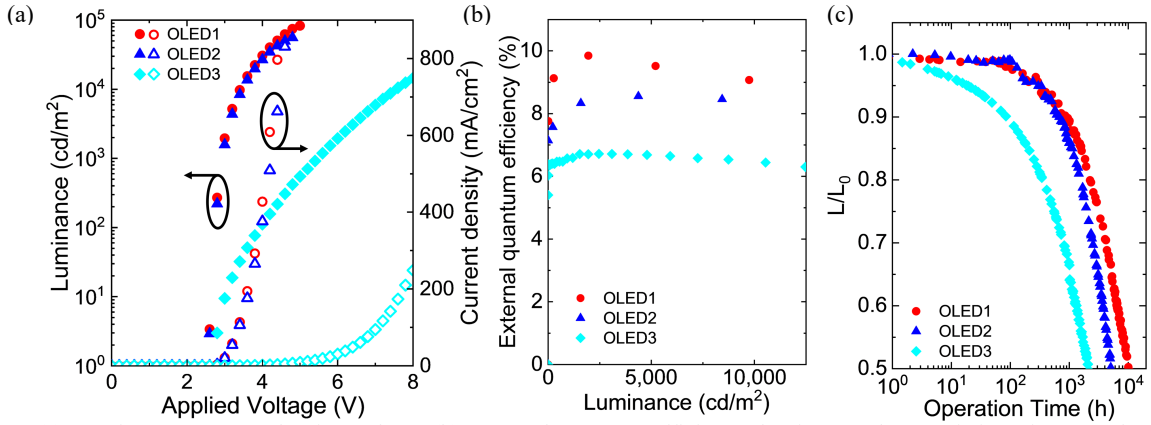

Fig. 2. (a) Luminance, current density–voltage (b) External quantum efficiency–luminance characteristics of encapsulated inverted OLEDs 1-3. (c) Luminance–time characteristics of inverted OLEDs 1-3 under constant dc with initial luminance L_0 of 1,000 cd m^{-2}.

(1-naphthyl)-10-(2-naphthyl)anthracene (1,2-ADN) was used as the emitting host and N1,N6-bis(dibenzo[b,d]furan-4-yl)-3,8-diisopropyl-N1,N6-bis(4-isopropylphenyl)-3a1,5-dihydropyrene-1,6-diamine (BD-1) was used as the emitter [10]. Inverted OLEDs 1-3 were encapsulated using a UV-epoxy resin and glass cover in an N_2 atmosphere.

Fig. 2(a) and 2(b) show the luminance–voltage, current density–voltage, and external quantum efficiency–luminance characteristics of inverted OLEDs 1-3. The operational stability is shown in Fig. 1(c). The device performance with Ag-doped PD-1 was significantly improved compared with that of Ag-doped BPhen. The results for inverted OLED 1 with a doped layer were comparable to those of inverted OLED 2 with Ag-doped *p*-Pyrrd-Phen, which is considered to be one of the most promising materials for electron injection utilizing coordination reactions between stable metals.

The UPS spectrum of the secondary cut-off region shown in Fig. 3 (a) indicates that Ag-doped PD-1 could significantly reduce the WF near the Ag cathode to 2.45 eV through the coordination reaction. This low WF is equivalent to that of Ag-doped *p*-Pyrrd-Phen, confirming efficient charge transfer between PD-1 and Ag atoms. Next, the binding energies of specific elements were analyzed by X-ray photoelectron spectroscopy (XPS). Fig. 3(b) - 3(c) shows that the XPS main peaks for C 1s and P 1s shifted toward higher binding energies (0.7 and 0.8 eV, respectively). In contrast, the Ag 3d peak in Fig. 3(d) shifted by 0.6 eV toward a lower binding energy, suggesting that the chemical environments of the C and P atoms on the ligand were changed This phenomenon confirms that free electrons from Ag dopants are indeed donated to PD-1 ligands, thereby inducing a distinct n-doping effect. In Ag-PD-1 complexes, the metal and organic ligands were identified as electron donors and electron acceptors, respectively.

3. Development of air-stable inverted OLEDs

The stability of the PD-1 based OLED in an air environment was examined by measuring the light-emitting areas of inverted OLEDs 4-6, as shown in Fig. 1 (a), which were operated continuously under atmospheric conditions without encapsulation. The pixels are separated by the pixel definition layer PDL made of curable resin. Fig. 4(a) and 4(b) show the Luminance–operation time and emitting area–operation time characteristics of non-encapsulated OLEDs.

By using YOx as the cathode interlayer and Ni alloy as the anode interlayer, metal diffusion caused by driving under atmospheric conditions was suppressed, as was the degradation in carrier injection caused by the formation of insulating metal oxide. On the other hand, the water vapor transmission rate of the top IZO anode and PDL were ~1.2 x 10^{-1} and ~1.0 x 10^{0} g/ m^2/ day at 40°C and 90% RH, respectively, which are far below the performance required for encapsulation of OLEDs. At a current density of 5 mA/cm^2, the driving voltage for the non-encapsulated inverted OLED 4 was low, 3.2 V, and close to the 2.8 V for the encapsulated OLED 1. Inverted OLED 4 also showed extremely high atmospheric and operational stability: the air stability was more than ten times that of the OLED 6 that used Cu-doped-BPhen. These results indicate that the combination of the low WF metal oxide and the EIL utilizing the coordination reaction between the metal oxide and Cu is extremely effective for improving the air stability of OLEDs.

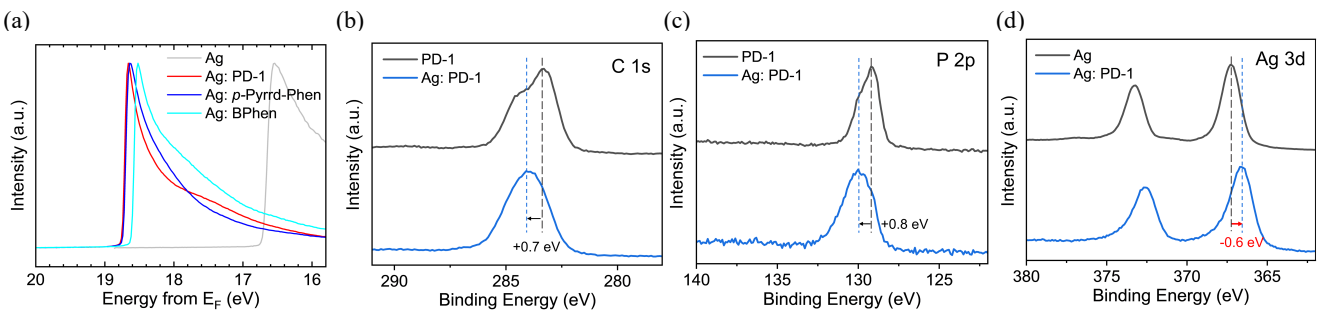

Fig. 3. (a) UPS spectra of EILs on Ag in secondary-cutoff region. (b-d) XPS spectrum of PD-1 and Ag-doped PD-1.

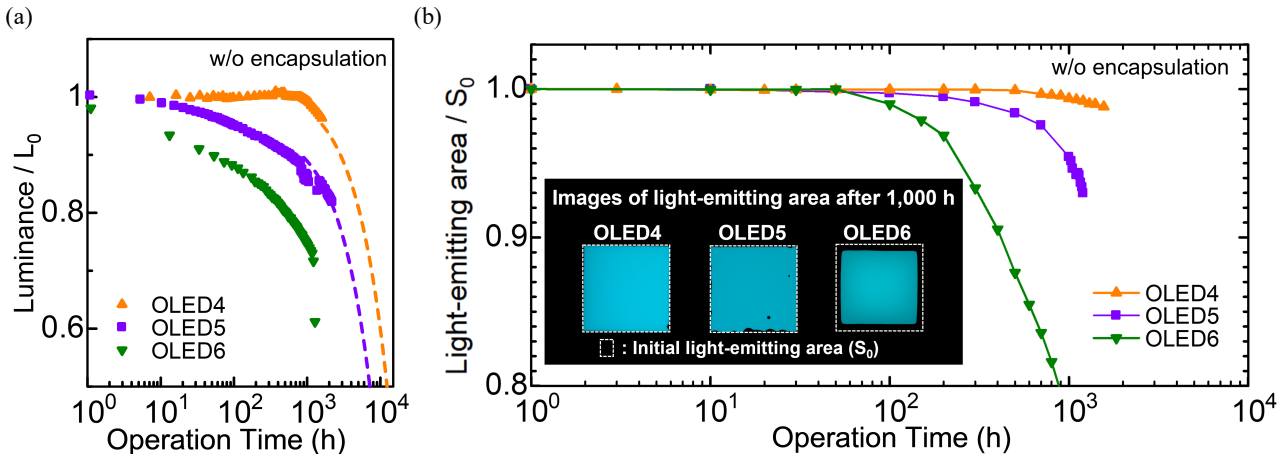

Fig. 4. (a) Luminance–time characteristics of inverted OLEDs 4-6 under constant dc with initial current density of 5 mA/ cm^2. (b) Light-emitting area–time characteristics of inverted OLEDs 4-6 under constant dc with initial current density of 5 mA/ cm^2. Inset: Images of the light-emitting area after 1,000 h.

4. Conclusion and impact

We demonstrated the inverted blue fluorescent OLED using the phosphine based EIM in the non-encapsulated device that can be driven stably in air without any protection. Although there have been many reports on air-stable OLEDs, a highly operational and air-stable OLED without encapsulation has not been demonstrated. To the best of our knowledge, this is the first report on using phosphine derivatives as an EIL of highly efficient blue OLEDs. Although the surface WF of the fabricated electron injection layer was significantly improved, the air stability of this layer was demonstrated to be very high. Our results suggest that further development of high-performance EIMs based on coordination reaction strategies will pave the way to achieving air-stable OLEDs without encapsulation.

5. Acknowledgements

We would like to extend our gratitude to NIPPON SHOKUBAI, Co., LTD. for their collaboration and support in designing the materials in this research.

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