Development of Low-work-function Electrodes Using Strong Organic Bases and Their Application in Blue OLEDs

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ABSTRACT

The use of strong organic bases was found to decrease the work function of a cathode to a value in the range of 2 to 3 eV. Low-work-function electrodes are effective for not only simplifying the configuration of blue OLEDs but also decreasing their operating voltages.

1. Introduction

Organic electronics such as organic thin-film transistors (OTFTs), organic light-emitting diodes (OLEDs), organic solar cells (OSCs), and organic semiconductor laser diodes (OSLDs) have made significant progress in recent years. Since barrier-free contacts for holes and electrons are essential for efficient organic optoelectronic devices, an anode with a high work function (WF) and a cathode with a low WF are required [Fig. 1(a)]. The electron injection/collection efficiency at cathode/organic semiconductor interfaces has mainly been tuned by using reactive materials such as alkali metals that have a WF lower than 3 eV [1,2]. However, the applicability of alkali metals is proved to be limited by their high reactivity and diffusivity [3]. In addition, little has been known about the actual electron affinity (EA) of organic compounds with a low EA until recently. Yoshida clarified by low-energy inverse photoemission spectroscopy (LEIPS) that the actual EA is much lower than the EA estimated from an optical gap [4]. The EA of n-type organic semiconductors suitable for OSCs and OTFTs is about 4 eV, whereas that of organic semiconductors used as the emitting layer (EML) and the electron transporting layer (ETL) in OLEDs is lower than 2.5 eV [4,5]. Since the actual EA of materials used in OLEDs is much lower than the EA estimated from the optical gap, it is important for investigating the effect of the actual energy diagram in OLEDs on the characteristics of OLEDs.

Here, we report on the development of low-WF electrodes using strong organic bases and their application to blue OLEDs. An electrode with a WF equivalent to the actual EA of materials used in OLEDs is required to investigate the effect of the actual energy diagram in OLEDs on the characteristics of OLEDs. The method of fabricating a low-WF electrode without using reactive alkali elements, which are widely used for electron injection, from organic devices has been the subject of intensive studies in recent years [6–11]. We have reported on some phenanthroline derivatives that can reduce the WF of electrodes to lower than 3 eV via the coordination reaction [8,9]. We also demonstrated that the formation of hydrogen bonds (H-bonds) between nitrogen in bases and other organic semiconductors reduces the WF to about 3 eV [10,11]. The novel electron injection layer (EIL) found in this study is the superbase 2,6-bis(1,3,4,6,7,8-tetrahydro-2H-pyrimido[1,2-a]pyrimidin-1-yl)pyridine (Py-hpp$_2$) [12], which can reduce the WF near an Al cathode to about 2.0 eV through both the coordination reaction and the formation of H-bonds [13]. Since materials for blue OLEDs have a large band gap and a relatively low EA, the Py-hpp$_2$/Al cathode seems to be useful for evaluating the characteristics of blue OLEDs. It was found that employing Py-hpp$_2$ as the EIL is effective for not only simplifying the configuration of blue OLEDs but also decreasing their operating voltages.

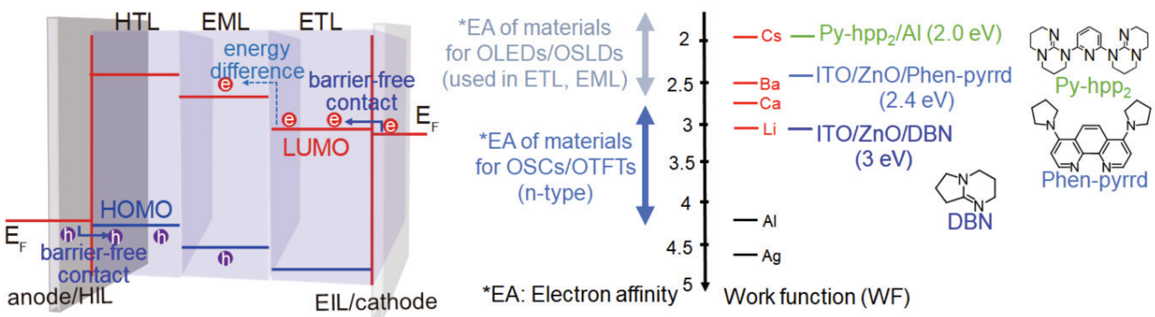

Figure 1: (a) Schematic illustration of chemical interactions related to WF tuning. (b) Summary of WFs tuned by chemical reactions.

2. Effect of EIL/ETL on the operating voltage of blue fluorescent OLEDs

The effect of the actual energy diagram in OLEDs on the characteristics of OLEDs was investigated by evaluating the EIL- and ETL-dependent characteristics of blue fluorescent OLEDs, as shown in Figs. 2(a) and 2(b). The emitting host 1,2-ADN is effective for improving the external quantum efficiency (EQE) by utilizing triplet–triplet annihilation, the fluorescent emitter BD-1 is a promising material for demonstrating long-lived OLEDs, and DBzA is reported to be useful for demonstrating fluorescent OLEDs with low operating voltage [14,15]. In previously reported blue OLEDs, compounds with nitrogen-containing heterocycles, such as pyridine, imidazole, and phenanthroline, have been typically used in the ETL, and Li compounds such as (8-quinolinolato)lithium (Liq) have been used in both the EIL and ETL [14,16]. Actually, the operating voltage of Devices 2 and 3 is lower than that of Device 4. In addition, Liq-doped ETL is effective for decreasing the operating voltage of blue fluorescent OLEDs since Device 2 exhibits lower operating voltage than OLED-3. However, the blue OLED consisting of 1,2-ADN and Py-hpp$_2$ (Device 1) exhibits a lower operating voltage than the OLEDs consisting of Liq-doped ETL. Thus, it was demonstrated that Liq-doped ETL is not essential for operating blue fluorescent OLEDs at low operating voltages.

The differences in the observed operating voltage are discussed on the basis of energy levels. The EA of 1,2-ADN measured using LEIPS was about 2.0 eV, which is equivalent to the WF of Py-hpp$_2$/Al cathode [13]. Since the material used as the ETL is the same as that used as the EML, there is no energy barrier in transporting electrons from the cathode to the EML. It is likely that the lack of energy difference enables the driving of the OLED at a lower operating voltage. On the other hand, in Devices 2 and 3 fabricated using Liq as the EIL, the WF near the cathode is about 3.0 eV [13,17]. In Device 2, the energy barrier between the cathode and the ETL is zero owing to the coordination reaction, whereas there is an energy barrier between the ETL and the EML as illustrated in Fig. 1a. In the case of Device-3, the energy barrier between the cathode and the ETL is significantly decreased by the coordination reaction between BPhen and Al; nevertheless, there is still an energy barrier for electron injection. There is a large energy barrier of 1.33 eV between the cathode and the ETL in Device-4 since there is no coordination reaction between 1,2-ADN and Al. The low-WF electrode realized by using Py-hpp$_2$ can eliminate the energy difference in the blue OLED, resulting in a lower voltage. The relatively low EQE of Device 1 in the low-current-density region may originate from the lack of holes rather than electrons.

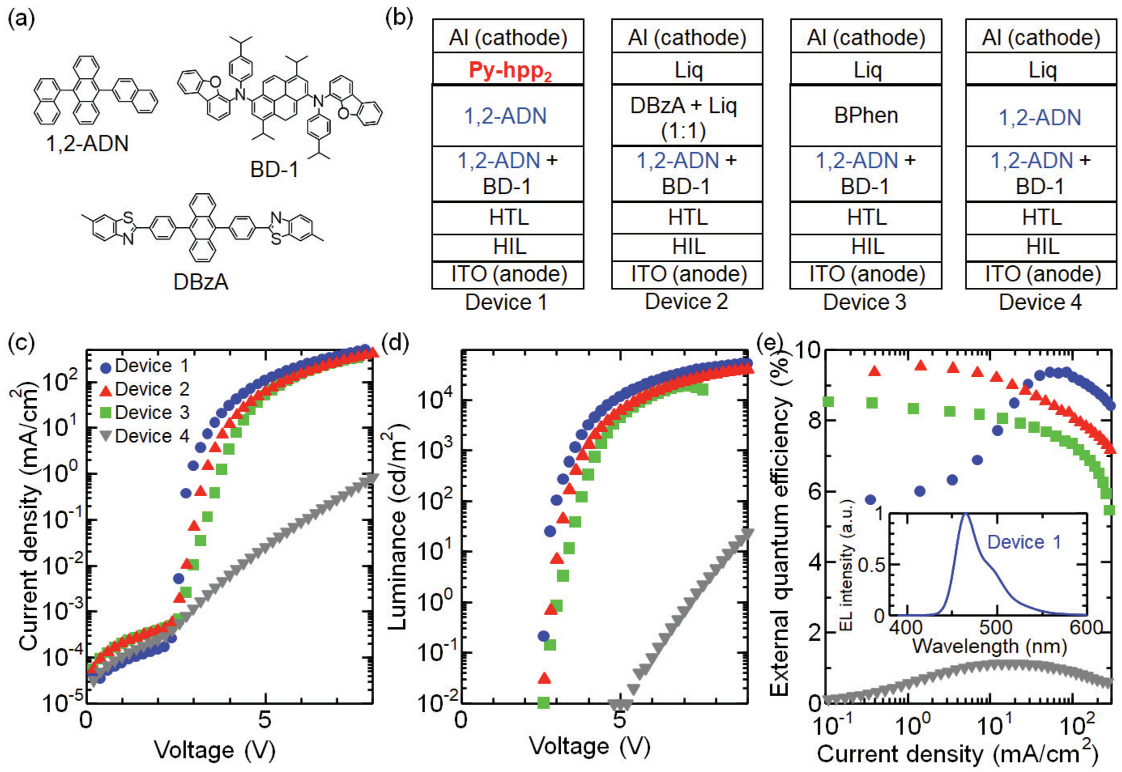

Figure 2: (a) Chemical structure of the material used in blue fluorescent OLEDs. (b) Multilayer structure of blue fluorescent OLEDs (c, d) Luminance–voltage and current density–voltage characteristics of blue fluorescent OLEDs prepared using various EIL/ETL combinations. (e) EQE traces of devices with different EIL/ETL combinations. Inset: Normalized EL spectra of Device 1.

3. Simply structured blue thermally activated delayed fluorescent (TADF) OLEDs

In recent years, blue TADF emitters with high color purity and high efficiency have been developed and vigorously studied [18–23]. To achieve a highly efficient TADF OLED, the excited state of the blue emitter must be confined in the surrounding layers around the EML. Therefore, many blue TADF OLEDs have complex layer structures and many energy differences within an OLED, as shown in Fig. 3(a) [20–23]. The energy difference in an OLED causes an increase in operating voltage. We have attempted to reduce the operating voltage of blue TADF OLEDs by taking advantage of the ability to inject electrons directly from the Py-hpp$_2$/Al cathode into various materials. As a result, we have found that by using an exciplex consisting of a donor and an acceptor as a host to eliminate the energy difference in the OLED, we can decrease the operating voltage of the blue TADF OLED [24,25].

Figure 3(b) shows the configuration and energy diagram of the fabricated blue TADF OLED. The material that has both high triplet energy level and a low IP of about 5.8 eV was used as the HTL and donor of the exciplex host, whereas the material that has both high triplet energy level and a relatively low EA of about 2.2 eV was used as the ETL and acceptor of the exciplex host. Since electrons can be injected directly from the Py-hpp$_2$/Al cathode to the acceptor, hole and electron transport without energy difference is possible, as shown in Fig. 3(b). t-DABNA, a blue TADF material with high color purity, was used as an emitter and doped in an exciplex host.

Figure 3(c) shows the luminance–voltage characteristics of the simply structured blue TADF OLED prepared using the exciplex host. Luminances of 50 and 1,000 cd/m^2 were observed at applied voltages of 3 and 4V, respectively. Considering the operating voltages for blue TADF OLEDs reported in recent years, the luminance is about 1 cd/m^2 at an applied voltage of 3 V, and a voltage of 4 V or higher is generally required to obtain 100 cd/m^2 in most previous reports [20-23]. Therefore, it was demonstrated that the simply structured OLED shown in Fig. 3(b) can emit light at a lower operating voltage than the conventional OLED shown in Fig. 3(a). We see from Fig. 3(e) that the blue OLED exhibits a high EQE of about 24%. This high EQE is attributed to the efficient energy transfer from the exciplex host to t-DABNA [24,25].

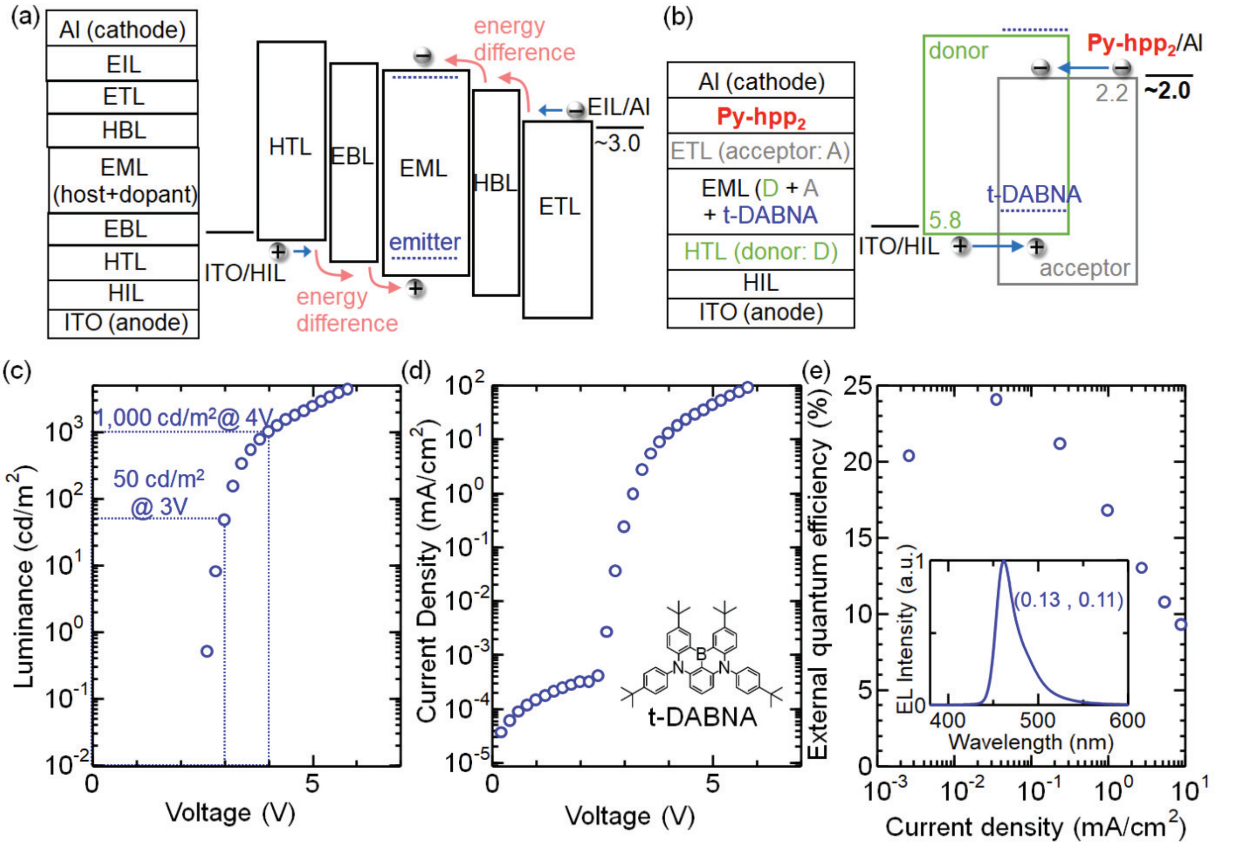

Figure 3. Schematic illustrations of (a) conventional blue TADF OLED and (b) simply structured blue TADF OLED prepared using exciplex. (c, d) Luminance–voltage and current density–voltage characteristics of blue TADF OLED prepared using exciplex. (e) EQE traces of devices with different EIL/ETL combinations. Inset: Normalized EL spectra of the blue TADF OLED.

4. Conclusion

We have fabricated low-WF electrodes using strong organic bases. The WF of a cathode was tuned to be about 2.0 eV, which is equivalent to the EA of organic semiconductors used in OLEDs. Since direct electron injection from the Py-hpp_2/Al cathode to the emitting host is possible, the operating voltage of the blue fluorescent OLED prepared using the Py-hpp_2/Al cathode is lower than that of the blue fluorescent OLED prepared using a Liq-doped ETL. The Py-hpp_2/Al cathode can also contribute to the simplification and decrease in the operating voltage for blue TADF OLEDs. The simply structured blue TADF OLED, consists of only the HIL, donor, acceptor, emitter, and Py-hhp_2, exhibits 50 cd/m^2 at an applied voltage of 3 V and a maximum EQE of about 24%. From the above results, it is expected that the use of a low-WF electrode will markedly reduce power consumption and further improve the performance of blue OLEDs in the future.

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