ZnO/Polyethyleneimine Ethoxylated/Lithium Bis(trifluoromethanesulfonyl)imide for Solution-Processed Electron Injection Layers in Organic Light-Emitting Devices

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We applied lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) salt for electron injection layers (EILs) in solution-processed organic light-emitting devices (OLEDs). The application result indicates that the alone Li-TFSI EIL was insufficient. Meanwhile, zinc oxide (ZnO) nanoparticle (NP)/polyethyleneimine ethoxylated (PEIE)/Li-TFSI trilayer was a highly efficient EIL compared with conventional lithium (Li) 8-quinolate and ZnO NPs/PEIE EILs and we realized a low-driving voltage OLED. Possibly, Li cations were reduced to Li atoms by the thermally evaporated aluminum (Al) atoms with adjacent Al cathode, and Li atoms reduced the work function of the cathode, resulting in the driving voltage reduction of the OLED. In the triple EIL structures, Li-TFSI was changed to magnesium and silver salts. Among the three types of TFSI salts, Li-TFSI exhibited the most efficient electron injection property.

Keywords: Electron injection layers, Solution-processed OLEDs, Metal-TFSI salts

1. Introduction

Organic light-emitting devices (OLEDs) have elicited remarkable attention as high-quality displays and lightings [1]. Currently, OLEDs have been extensively used as smartphone and TV displays, and the market of OLEDs is rapidly growing at present. Nevertheless, the price of OLEDs is still high for general consumers. One of the solutions for the price problem is the reduction of manufacturing costs using high-speed solution processing [2-6]. However, device performances of solution-processed OLEDs are lower than conventional evaporation-processed OLEDs. To obtain highly efficient OLEDs, efficient electron injection from a cathode to organic functional materials is a key technique; hence, electron injection layers (EILs) are often inserted between the cathode and organic functional materials [7-14]. Presently, various types of solution-processed EILs have been reported [15-25]. Generally, these EILs are stacked onto the light-emitting layers (EMLs) in

completely solution-processed OLEDs. In this study, EMLs are easily dissolved in solvents, such as ester, ketone, and aromatic ones. Meanwhile, properly designed EMLs cannot be dissolved in alcohol solvents, such as methanol and ethanol; thus, alcohol-soluble EILs can be stacked onto the EMLs [15-20,22-24]. Since the report of Zhou et al., alcohol-soluble polyethyleneimine derivatives, among the various types of reported EILs, have elicited remarkable attention owing to their high electron injection capability, achieving low-driving voltages [26]. These derivatives are often used with metal oxide semiconductors. For example, we realized low-driving voltage OLEDs using the zinc oxide (ZnO) nanoparticle (NP)/polyethyleneimine ethoxylated (PEIE) double EILs [24,27,28]. However, the efficiency of electron injection still has room for improvement. One of the methods to realize additional low-driving voltage is the utilization of low-work-function (WF) metal cathodes, such as lithium (Li) [7]. Smaller electron

injection barriers between the cathodes and organic functional layers may lead to effortless electron injection. However, these low-WF metal cathodes are sensitive to air, and handling of these cathodes is challenging. Li complexes are known to be alcohol-soluble EILs, and they are thermally reduced to Li metal by the thermally evaporated aluminum (Al) atoms constituting the adjacent Al cathode [12]. Hence, if the Li complexes are stacked onto the ZnO NPs/PEIE, then additional low-driving voltages can be realized. However, the alcohol solvents of Li complexes easily dissolve the alcohol-soluble PEIE underlayer. Meanwhile, bis(trifluoromethanesulfonyl)imide (TFSI) salts, which include Li-TFSI, are known to dissolve in acetonitrile. The relatively weak electrostatic forces between the cations and TFSI anions, whose negative charges are delocalized over their molecular frameworks, lead to the high solubility of the salts in acetonitrile [25,29,30]. In this work, acetonitrile cannot dissolve the ZnO NPs/PEIE layers; hence, stacking them into the ZnO NP/PEIE layers is possible. The OLEDs with the ZnO NP/PEIE/TFSI salt EILs are expected to achieve lower driving voltages than the conventional ZnO NP/PEIE EILs.

In this work, we applied ZnO NP/PEIE/TFSI salts, including Li, magnesium (Mg), and silver (Ag) cations, as the triple EILs for the completely solution-processed regular structure OLEDs. The device with Li-TFSI exhibited the lowest driving voltage among them and attained lower driving voltage than that with the conventional ZnO NP/PEIE double EIL. Furthermore, we investigated the electron injection mechanism of the Li-TFSI by fabricating three types of devices, including Li-TFSI.

2. Experimental

2.1. Materials

Poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) (Clevios P VP CH 8000) was purchased from Heraeus Materials Technology. Poly(9,9-dioctylfluorene-*alt*-N-(4-butylphenyl)-diphenylamine) (TFB) was purchased from American Dye Source, Inc. The host material ICTRZ-1 (Fig. 1) was synthesized in accordance with the reported scheme [31]. Tris[2-(4-n-hexylphenyl)quinoline]iridium(III) (Hex-Ir(phq)₃) was purchased from Luminescence Technology Corp. Methanol dispersible ZnO NPs were synthesized in accordance with the reported procedure [31,32]. The ZnO NPs have a diameter of

6–8 nm. PEIE was purchased from Sigma-Aldrich Co. LLC. Li-TFSI, Mg-TFSI, and Ag-TFSI were purchased from Tokyo Chemical Industry Co., Ltd. Li 8-quinolate (Liq) was purchased from e-Ray Optoelectronics Technology Co., Ltd. Finally, the glass substrates with indium tin oxide (ITO) electrodes were purchased from Asahi Glass Co., Ltd., and these electrodes were patterned via photolithography.

2.2. Devices and characterizations.

The ITO substrates were cleaned using an ultrasonic sonicator and a UV-ozone cleaner. First, Devices A with a structure of [ITO (130 nm)/PEDOT:PSS (30 nm)/TFB (20 nm)/ICTRZ-1:12 wt% Hex-Ir(phq)₃ (70 nm)/EILs/Al(100 nm)] were fabricated. In this work, the EILs used were Liq (A-1), Li-TFSI (A-2), and ZnO NPs/Li-TFSI (A-3). Second, Devices B were fabricated, in which the EILs were changed to ZnO NPs/PEIE (B-1), ZnO NPs/PEIE/Li-TFSI (B-2), and ZnO NPs/PEIE:10 wt% Li-TFSI (B-3), respectively. Finally, Devices C were also fabricated, in which the EILs were changed to ZnO/PEIE/Mg-TFSI (C-1) or Ag-TFSI (C-2). The device emitting area was 2 mm × 2 mm. The PEDOT:PSS solution was spin coated onto the ITO substrates and baked in air at 200 °C for 10 min. The substrates were then transferred into a nitrogen-filled glove box. TFB was spin coated onto the PEDOT:PSS layer from the p-xylene solution and baked at 180 °C for 60 min. ICTRZ-1:12 wt% Hex-Ir(phq)₃ was spin coated onto the TFB layer from the tetrahydrofuran solution and baked at 100 °C for 10 min. The ZnO NP dispersion solution was spin coated onto the ICTRZ-1:12 wt% Hex-Ir(phq)₃ layer and baked at 100 °C for 10 min. PEIE and PEIE:Li-TFSI were spin coated onto the ZnO NP layer from the 2-propanol solution and baked at 100 °C for 10 min. The TFSI salts at a concentration of 0.5 mg/mL were spin coated onto the ICTRZ-1:12 wt% Hex-Ir(phq)₃ or ZnO NP/PEIE layer from the 2-propanol or acetonitrile solution and baked at 100 °C for 10 min. In addition, a 1.0 mg/mL Liq was spin coated onto the ZnO NP layer from the methanol solution. Al cathodes were thermally evaporated onto the EILs in a vacuum. The current density–voltage (J–V) characteristics of the OLEDs were measured using the current source meter Keithley 2400. Meanwhile, the luminance–voltage (L–V) characteristics of the OLEDs were measured using the luminance meter Konica Minolta CS-200. The electroluminescence (EL) spectra were measured using the photonic multichannel analyzer

Fig. 1. Utilized chemical compounds in OLEDs.

Hamamatsu PMA-11. Moreover, external quantum efficiencies (EQEs) were regulated using angular dependent light emission intensities.

3. Results and discussion

Figure 1 shows the utilized compounds in the fabricated OLEDs and their optoelectronic properties [5,26,28,32–35]. Figure 2 shows the architectures of the fabricated device. The EML host material ICTRZ-1 has a molecular weight of 970 [31]. Generally, carbazole-based host materials with molecular weight of more than 800 do not dissolve in alcohols, such as methanol and 2-propanol [5,36, 37]. Hence, the ZnO NP layers can be successfully stacked into ICTRZ-1:12 wt% Hex-Ir(phq)₃ from the methanol solutions. In addition, the hydrophilic PEIE layer can be uniformly formed onto the hydrophilic ZnO NP layer [27].

Figures 3(a)–(d) show the EL spectra and the J–V–L and J–EQE characteristics of Devices A. At 5 mA/cm² in the J–V characteristics, the driving voltages were 8.70 V for Liq (A-1), 11.9 V for Li–TFSI (A-2), and 11.0 V for ZnO NPs/Li–TFSI (A-3). The driving voltage of Devices A-2 (11.9 V) was remarkably higher than Device A-1 (8.70 V), indicating that the alone Li–TFSI EIL is insufficient when compared with Liq. According to previous research [38], a combination of ZnO NPs and Liq can relatively reduce the driving voltages compared with Liq only. Hence, Device A-3 with ZnO NP/Li–

Al (–)	EILs: Devices A Liq (A-1) LiTFSI (A-2) ZnO NPs/LiTFSI (A-3)
EILs	
ICTRZ-1: 12wt% Hex-Ir(phq) ₃ (70 nm)	
TFB (20 nm)	Devices B ZnO NPs/PEIE (B-1) ZnO NPs/PEIE/LiTFSI (B-2) ZnO NPs/PEIE:10wt% LiTFSI (B-3)
PEDOT:PSS (30 nm)	
ITO (+)	

Fig. 2. Structure of the fabricated device.

TFSI, which is a combination of ZnO NPs and Li–TFSI, was fabricated to reduce the driving voltage. Device A-3 exhibited lower driving voltage (i.e., 11.0 V) than Device A-2 (i.e., 11.9 V), which was still higher than that of Device A-1 with Liq (i.e., 8.70 V). In the L–V and J–EQE characteristics, the driving voltage and EQE value of Device A-1 at 100 cd/m² were 6.20 V and 5.57%, respectively. Meanwhile, the maximum luminance of Devices A-2 and A-3 did not reach 100 cd/m². Thus, Li–TFSI and ZnO NP/Li–TFSI EILs were inferior to the conventional Liq EIL. Possibly, the aromatic ligand of Liq significantly contributed to the reduction of the driving voltage.

Fig. 3. (a) Current density–voltage, (b) luminance–voltage, (c) EQE–current density characteristics, and (d) EL spectra of Devices A-1, A-2, and A-3.

Figures 4(a)–(d) show the EL spectra and the J–V–L and J–EQE characteristics of Devices B. At 5 mA/cm² in the J–V characteristics, the driving voltages were 5.74 V for ZnO NPs/PEIE (B-1), 4.93 V for ZnO NPs/PEIE/Li–TFSI (B-2), and 6.34 V for ZnO NPs/PEIE:10 wt% Li–TFSI (B-3), respectively. Device B-1 generated a significantly lower driving voltage (i.e., 5.74 V) than Device A-1 (i.e., 8.70 V), indicating that only the ZnO NP/PEIE EIL is superior to the Liq EIL as shown in Fig. 3. Then, ZnO NP/PEIE/Li–TFSI was applied to Device B-2. Here, Li–TFSI can be stacked onto the PEIE layer because the material can be dissolved in acetonitrile, which is a poor solvent for PEIE. Device B-2 exhibited lower driving voltage (i.e., 4.93 V) than Device B-1 (5.74 V), indicating that the trilayered ZnO NP/PEIE/Li–TFSI has superior electron injection efficiency than the bilayered ZnO NP/PEIE. ZnO NP/PEIE:10 wt% Li–TFSI was also applied to Device B-3, which shows higher driving voltage (i.e., 6.34 V) than Device B-1 (i.e., 5.74 V). Therefore, doping of Li–TFSI to PEIE is not efficient to reduce the driving voltages. Li–TFSI in Device B-2 existed at the electrode interface, whereas Li–TFSI in Device B-3 mainly existed in the PEIE layer. Considering these results, Li–TFSI

in Device B-2 efficiently worked at the electrode interface for the reduction of driving voltages. Possibly, Li cations of Li–TFSI were reduced to Li atoms by the thermal evaporated Al atoms at the interface, and the Li atoms reduced the WF value of the Al cathode, resulting in the reduction of the driving voltages [12]. These results seem to conflict with the result of Devices A-2 and A-3, where Li–TFSI existed at the electrode interfaces. The difference between Devices A-3 and B-2 was whether PEIE was contained in the device. Thus, PEIE played a significant role for the driving voltage reduction. Possibly, there was specific interaction between PEIE and Li–TFSI, contributing to the driving voltage reduction. Based on the L–V and J–EQE characteristics, the driving voltages and EQE values at 100 cd/m² were 4.64 V and 11.8% for Device B-1, 4.46 V and 5.10% for Device B-2, and 5.07 V and 11.7% for Device B-3, respectively. Unfortunately, based on these characteristics, Device B-2 showed lower performance than Device B-1, which possibly resulted from the deteriorated charge carrier balance in Device B-2.

Figures 5(a)–(d) show the EL spectra and the J–V–L and J–EQE characteristics of Devices C. At 5

Fig. 4. (a) Current density–voltage, (b) luminance–voltage, (c) EQE–current density characteristics, and (d) EL spectra of Devices B-1, B-2, and B-3.

Fig. 5. (a) Current density–voltage, (b) luminance–voltage, (c) EQE–current density characteristics, and (d) EL spectra of Devices C-1, and C-2.

mA/cm², based on the J–V characteristics, the driving voltages were 6.08 V for ZnO NPs/PEIE/Mg–TFSI (C-1) and 6.45 V for ZnO NPs/PEIE/Ag–TFSI (C-2). These driving voltages were higher than that of Devices B-2 with ZnO NPs/PEIE/Li–TFSI. Among the three types of TFSI salts, Li–TFSI achieved the highest driving voltage reduction. The WFs of metals are known to be ca. 2.9 eV for Li, ca. 3.7 eV for Mg, and ca. 4.7 eV for Ag atoms [39]. The order of the driving voltages accorded with the order of the WFs of the metal cations. Low-WF metal cation contributed to the driving voltage reduction. Based on the L–V and J–EQE characteristics, the driving voltages and EQE values at 100 cd/m² were 5.02 V and 9.10% for Device C-1 and 6.42 V and 1.30% for Device C-2, respectively. Device C-1 with ZnO NPs/PEIE/Mg–TFSI demonstrated the highest EQE value, which resulted from the improved charge carrier balance compared with ZnO NPs/PEIE/Li–TFSI. In this system, unfortunately, ZnO NPs/PEIE/Li–TFSI caused too large driving voltage reduction and deteriorated charge carrier balance, resulting in low EQE value. However, in terms of electron injection efficiency, we believe that ZnO NPs/PEIE/Li–TFSI is the best EIL structure in this work.

4. Conclusion

We were successful in the development of a low-driving voltage OLED using the ZnO NP/PEIE/Li–TFSI triple EILs. The fabricated device demonstrated a lower driving voltage than the conventional ZnO NP/PEIE double EILs based on the J–V characteristics. Hence, the developed ZnO NPs/PEIE/Li–TFSI can be used for the realization of highly efficient OLEDs although the EQE value of the device with ZnO NPs/PEIE/Li–TFSI was lower than that of the device with ZnO NPs/PEIE owing to the changes of the charge carrier balance in the device system. We hope that the newly developed ZnO NP/PEIE/Li–TFSI is applied to highly efficient OLEDs in the near future.

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