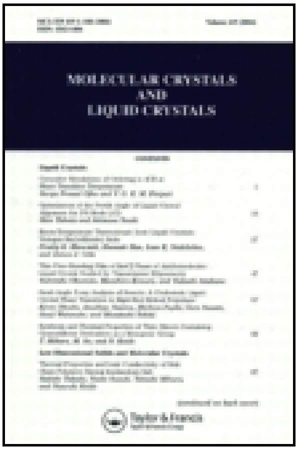

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Significantly Improved Power Efficiency of Organic Light-Emitting Diodes with Surface Dipole on Anode and Ohmic Cathode Contact

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Dramatically improved power efficiency and stability of organic light-emitting diodes (OLEDs) were achieved by using buckminsterfullerene (C_{60}) as an interlayer between indium tin oxide (ITO) anode and hole transporting layer of N, N′-diphenyl-N, N′-bis(1,1′-biphenyl)-4,4′-diamine (NPB) and electron transporting layer (ETL) at the same time. The results are ascribed to the interfacial-dipole formation of C_{60} on the surface of ITO anode and Ohmic cathode contact of C_{60}. The surface dipole of C_{60} on the ITO anode helps to lower the hole injection energy barrier from ITO to NPB. C_{60} also has an Ohmic cathode contact with high electron mobility in the typical structure of C_{60}/LiF/Al. These properties of C_{60} make it possible to simultaneously enhance the electron and hole injection from both cathode and anode. Lowered operating voltage by surface dipole and Ohmic cathode contact of C_{60} can eliminate Joule heating at both organic/cathode and organic/anode interfaces and as a result, provides the improved stability of OLEDs.

Keywords: buckminsterfullerene; charge injection; energy barrier for charge injection; hole injection; ohmic contact; surface dipole

1. INTRODUCTION

Organic light-emitting diodes (OLEDs) have been considered one of the most promising displays due to their technological potentials for multicolor flat panel displays since Tang and VanSlyke demonstrated the stable and efficient bilayer of OLEDs [1]. Many efforts to improve

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the performances of OLEDs have been done and many significant progresses have been accomplished in the research of highly efficient electroluminescence materials [2–4]. However, despite extensive studies on these devices, the power consumption and operating stability have been remained as critical issues for real applications. The power efficiency is particularly important for real applications because the operating voltage confines the capacity of drive integrated circuit (IC) that is directly related with the power consumption of OLEDs. It is well known that the metal-organic molecule interface determines the driving voltage and operating stability [5,6]. Therefore, It is crucial to build efficient and robust interface with the effective charge injection from electrode to organic layer. One of the most effective approaches to improve the charge injection is to lower the energy barriers for the charge injection from both anode and cathode to organic layers. The insertion of alkali (or alkaline earth) metal at an ETL/cathode interface and the modification of ITO workfunction have been used to lower the energy barriers for better electron and hole injection [7,8]. Recently, particular attention has been given to the energy barrier modulation of charge injection by grafting molecules having a specific functional group to induce the surface dipole on various metal substrates [9]. C_{60} itself does not have an intrinsic dipole moment but surface dipole due to the strong electron accepting nature can be formed when it is deposited on the metal surface [10]. In our previous publication, we demonstrated that the dramatically improved hole injection from ITO anode to hole transporting layer (HTL) could be achieved by forming surface dipole with a thin layer of C_{60} between ITO anode and NPB layer [11]. The surface dipole can lower the Schottky energy barrier for hole injection and to enhance the hole injection efficiency. Another effective method for enhancing the charge injection is the formation of Ohmic contact between metal electrode and organic layer. Very recently, it was reported by Feng *et al*. that C_{60} has an Ohmic contact in the structure of C_{60}/LiF/Al which can be found in a typical OLED cathode structure [12]. Moreover, C_{60} has high electron mobility that is an extremely important parameter for ETL. C_{60} can be a good candidate for an effective ETL since typical ETL of tris (8-hydroxyquinolinato) aluminum (Alq3) has comparatively low electron mobility with energy barrier for electron injection. Considering the fact that the hole mobility of NPB is a few orders of magnitude higher than the electron mobility of Alq_3, the major current must be hole current in the typical structure of ITO/NPB/Alq3/LiF/Al [13]. Therefore, C_{60} can be an excellent substitution of Alq3 to lower the operating voltage and to keep better hole-electron charge balance by introducing Ohmic cathode contact with a high electron mobility. These properties of C_{60} make it possible to simultaneously enhance the electron and hole injection from both cathode and anode. Low operating voltage of OLEDs can eliminate Joule heating at the cathode and anode interfaces and can provide the longer operating stability of OLEDs.

In the present work, we report the significantly improved power efficiency and stability of OLEDs by using C_{60}, at the same time, as an interlayer at the ITO/NPB interface and as ETL with Ohmic cathode contact.

2. EXPERIMENTAL

For the study of power efficiency improvement by C_{60}, we fabricated four different devices of A: ITO/NPB(600 Å)/Alq_3 (550 Å)/LiF(10 Å)/Al, B: ITO/C_{60}(25 Å)/NPB(600 Å)/Alq_3(550 Å)/LiF(10 Å)/Al, C: ITO/NPB (600 Å)/Alq_3(350 Å)/C_{60}(200 Å)/LiF(10 Å)/Al and D: ITO/C_{60}(25 Å)/NPB(600 Å)/Alq_3(350 Å)/C_{60}(200 Å)/LiF(10 Å)/Al. Device A, B, C, and D were used for the purpose of control device, surface dipole effect only device, Ohmic contact effect only device, and surface dipole and Ohmic contact effects device, respectively. Device fabrication process was described in a previous publication [11]. Briefly, the devices were fabricated on ITO coated-glass with a sheet resistance of $15\Omega/\square$. Active area of devices was $4\,\mathrm{mm}^2$. After routine cleaning process of the ITO substrate by mechanical scrubbing, then it was cleaned sequentially with the detergent, isopropanol and deionized water. The substrate was baked in an oven for 2 hours at 200°C and loaded to a deposition chamber. Oxygen plasma treatment was employed to remove excess moisture on the substrate. C_{60} interlayer, NPB and ETL (C_{60}, Alq_3) were subsequently deposited by conventional vapor deposition at the rate of 2 Å/sec. After the deposition of ETL (C_{60}, Alq_3), LiF and Al were deposited at another chamber without breaking the vacuum. The deposition rates were monitored independently with a thickness/rate monitor. During device fabrication, the pressure of the vacuum chamber was kept at $\sim 2 \times 10^{-6}$ torr. All devices were encapsulated with BaO in a dry nitrogen glove box to protect them from moisture in ambient atmosphere. The lifetime measurements were performed at the current density of $50\,\mathrm{mA/cm}^2$.

3. RESULTS AND DISCUSSION

For the studies of effective hole injection from the ITO anode to NPB layer we tested two different hole predominate devices of ITO/NPB(700 Å)/Al and ITO/C_{60} (25 Å)/NPB(700 Å)/Al. When a thin layer of C_{60} was introduced between ITO anode and NPB the hole injection from ITO anode to NPB was dramatically improved as shown at the top of Figure 1. The enhanced hole injection efficiency was ascribed to the formation of an interfacial dipole on the ITO anode that contributes to lower the energy barrier for hole injection from the ITO anode to NPB [11]. For an effective electron injection from cathode to ETL, we utilized the results in the literature [12]. Feng *et al*. recently

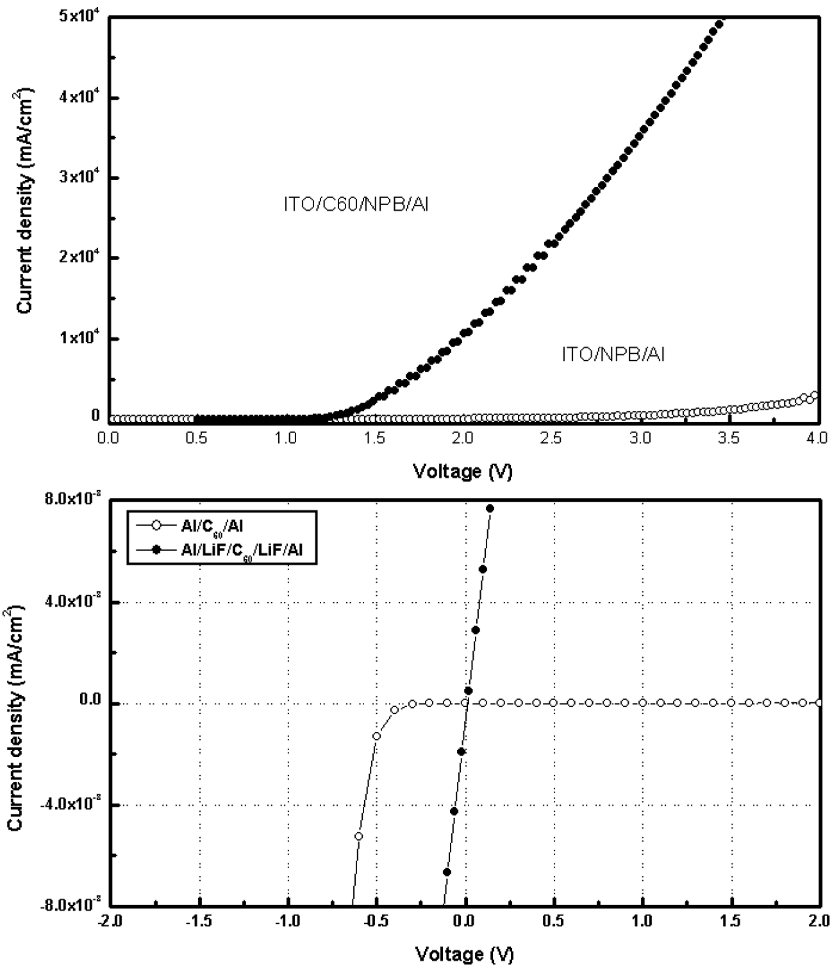


FIGURE 1 V-I characteristics (top) of ITO/C_{60} (25 Å)/NPB(700 Å)/Al and ITO/NPB(700 Å)/Al. Ohmic contact (bottom) of Al/LiF(50 Å)/C_{60} (1800 Å)/LiF(50 Å)/Al.

reported excellent works for the evidence of Ohmic cathode contact with the structures of Al/C_{60} (1000 Å)/Al and Al/LiF(50 Å)/C_{60} (1800 Å)/LiF(50 Å)/Al [12]. The result is extremely meaningful for effective electron injection from cathode to ETL in a conventional device. We have observed the same result of Ohmic contact with the same structure as shown at the bottom of Figure 1. While a strong rectifying I-V characteristic was observed on the Al/C_{60}/Al device a perfect linear I-V characteristic, as a result of Ohmic contact, was observed on Al/LiF/C_{60}/LiF/Al device. Feng *et al*. ascribed the results to the possible n-type doping near the interface by $F^{-}(-Li^{+})$ anion species and the reduced energy gap, which leads to a metallic-like interface, by LiF-C_{60} interaction [12].

The motivation of the present work is to lower the operating voltage of typical bilayer structure of ITO/HTL/ETL/LiF/Al by introducing both an interfacial dipole on anode and Ohmic contact to cathode. The I-V characteristics of Device A, B, C, and D are shown in Figure 2. While the operating voltage of the control device is 8.2 V at 100 mA/cm^2 the operating voltages of device B, C, and D are 5.8, 6.2, and 4.3 V, respectively. When we applied either surface dipole on anode (device B) or Ohmic contact to cathode (device C), the voltage decreased by $\sim$2 V

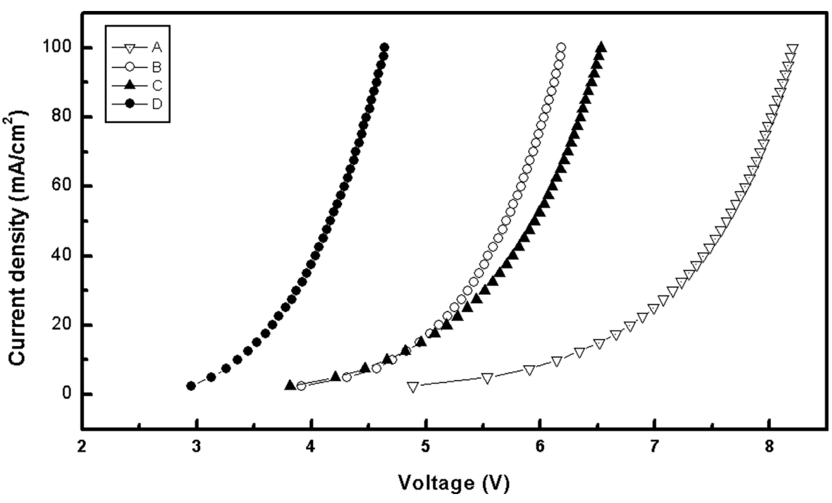


FIGURE 2 V-I characteristics of device A, B, C, and D; Device A: ITO/NPB(600 Å)/Alq_3(550 Å)/LiF(10 Å)/Al, Device B: ITO/C_{60}(25 Å)/NPB (600 Å)/Alq_3(550 Å)/LiF(10 Å)/Al, Device C: ITO/NPB(600 Å)/Alq_3(350 Å)/C_{60}(200 Å)/LiF(10 Å)/Al and Device D: ITO/C_{60}(25 Å)/NPB(600 Å)/Alq_3 (350 Å)/C_{60}(200 Å)/LiF(10 Å)/Al.

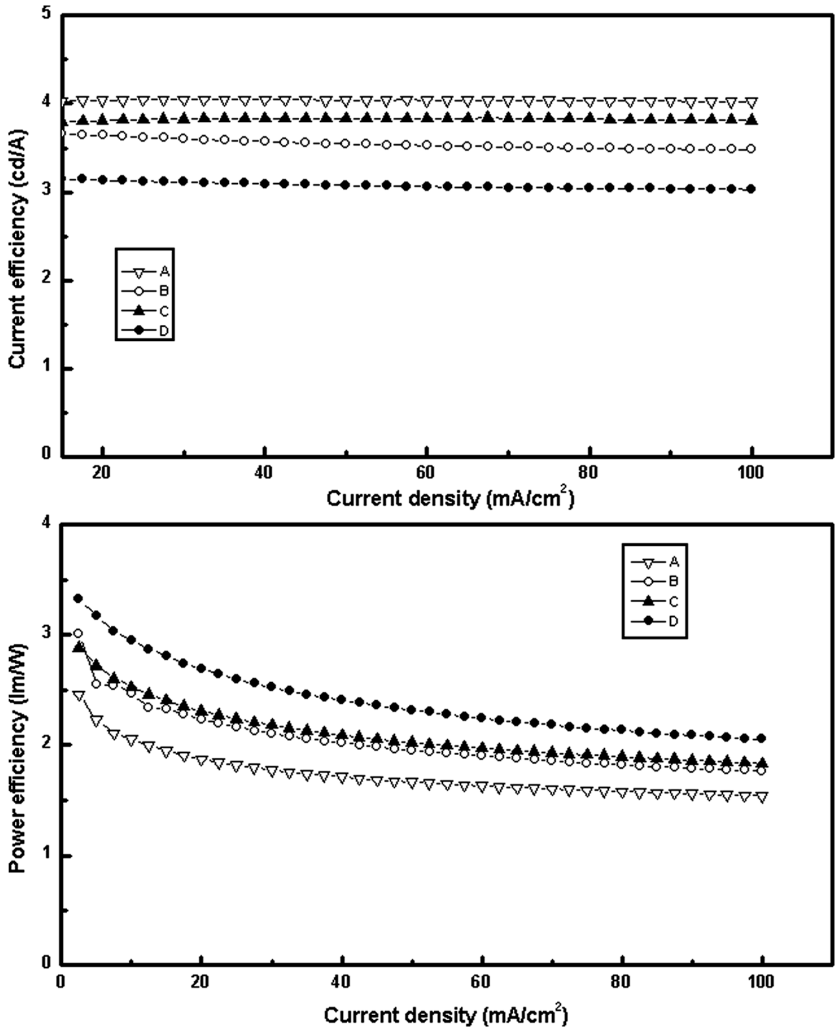
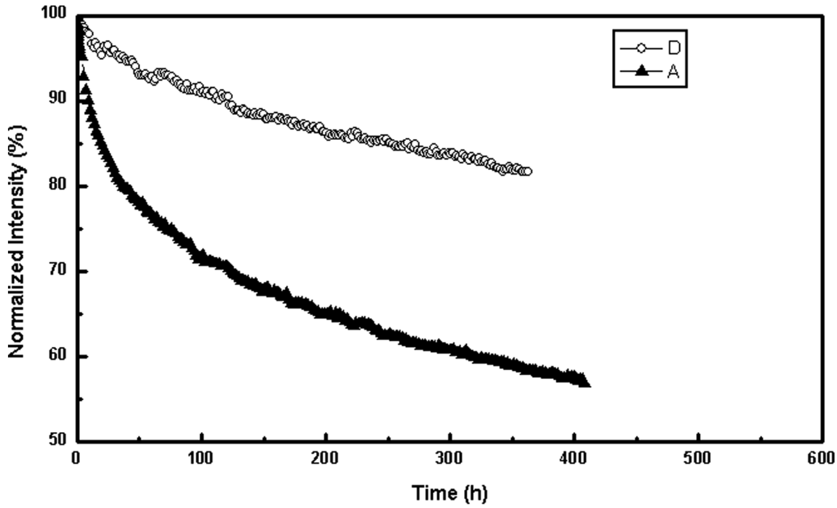


FIGURE 3 Current efficiency (top) and power efficiency (bottom) of device A, B, C,and D. Device A: ITO/NPB(600 Å)/Alq_3(550 Å)/LiF(10 Å)/Al, Device B: ITO/C_{60}(25 Å)/NPB(600 Å)/Alq_3(550 Å)/LiF(10 Å)/Al, Device C: ITO/NPB(600 Å)/Alq_3(350 Å)/C_{60}(200 Å)/LiF(10 Å)/Al and Device D: ITO/C_{60}(25 Å)/NPB(600 Å)/Alq_3(350 Å)/C_{60}(200 Å)/LiF(10 Å)/Al.

relative to the control device (device A), respectively. When we applied both parameters, surface dipole and Ohmic contact, at the same time additional voltage drop of 2 V was observed. The total voltage drop of device D was by ~4 V relative to the control device (device A). The current efficiency and power efficiency are shown at the top and bottom in Figure 3. The voltage of device D drops to the half of the control device and results in significantly improved the power efficiency. The current efficiencies of device A and C are ~4 cd/A. This is unexpected result because the improved current efficiency with device C was not observed. Considering the hole mobility of NPB is a few orders of magnitude higher than the electron mobility of Alq_3 and the major current is hole current in the typical structure of ITO/NPB/Alq3/LiF/Al. Therefore, the substitution of Alq3 with C_{60} can be expected to have better electron and hole balance since C_{60} helps to inject more electron into the recombination zone. However we could not observe the expectation. This can be explained by the fact that the emission zone in both device A and C is highly localized at the NPB/Alq3 interface and Alq3 has very low electron mobility [12]. C_{60} cannot contribute to improve the current efficiency because an emitting layer of Alq3 determines the current efficiencies of device A and C. On the other hand, device B shows a little lowered current efficiency of ~3.5 cd/A. This can be ascribed to the extra amount of hole, which can interact with Alq3 to produce none emissive Alq3 cationic species [13]. In the case of device D, relatively low current efficiency of ~3 cd/A was measured. This result could be explained by the formation of Alq3 cationic species and the mobility changes caused by significantly lowered operating voltage of device D. It cannot be neglected that C_{60} can act as a quencher of the excitons that are highly localized at NPB/Alq3 but partially distributed to the Alq3/C_{60} interface. It should be also emphasized that matching the mobility with the injection rates should be required for optimum efficiency. The reason why we could not observe the best current efficiency with device D might be ascribed to the mismatching of charge balance. Although the current efficiency of device D is not as high as we expected, the power efficiency of device D is the best due to its low operating voltage. The power efficiency of 2.4 lm/W is for device D while the power efficiency of 1.5 lm/W is for the control device (device A). We could also improve the stability by introducing C_{60}—modified ITO anode and ETL of C_{60} at the same time. Figure 4 shows the normalized operating lifetime and the operating voltage changes as a function of time. The measurements have been done at the constant current density of 50 mA/cm^2. They have not been completed but we can roughly estimate the operating lifetime by extrapolation. The estimated operating lifetimes of device A and D are ~700 and ~1500 hours, respectively. Clear mechanisms for the improved operating lifetime of device D are not available yet but the results could be ascribed to the elimination of Joule heating due to the low operating voltage of device.



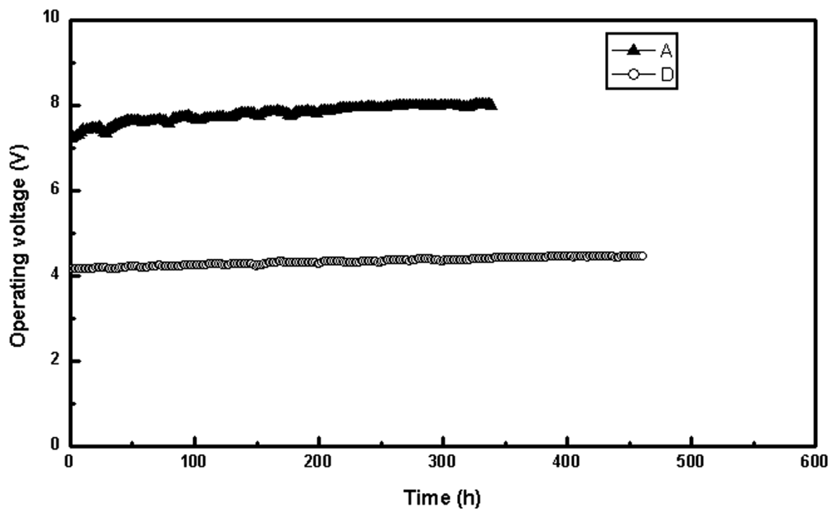


FIGURE 4 Normalized intensity change (top) and the operating voltage change (bottom) of device A and D in the function of time. Device A: ITO/NPB(600 Å)/Alq_3(550 Å)/LiF(10 Å)/Al, Device D: ITO/C_{60}(25 Å)/NPB(600 Å)/Alq_3(350 Å)/C_{60}(200 Å)/LiF(10 Å)/Al.

Another possible mechanism could be the improved thermal stability of NPB on the ITO substrate due to the template of C_{60} like the role of CuPc in the literature [14]. The clear mechanisms of improved stability have been investigated and will be published elsewhere.

4. CONCLUSIONS

In summary, significantly lowered operating voltage and improved stability of OLEDs were achieved by using C_{60} as an interlayer between ITO anode and Ohmic cathode contact. The results are ascribed to the formation of an interfacial dipole of C_{60} on the surface of ITO anode and Ohmic cathode contact of C_{60}. The surface dipole of C_{60} on the ITO anode helps to lower the hole injection energy barrier from ITO to NPB layer. C_{60} also has an Ohmic cathode contact with high electron mobility in the typical structure of C_{60}/LiF/Al. These properties of C_{60} make it possible to simultaneously enhance the electron and hole injection from both cathode and anode. Lowered operating voltage can eliminate Joule heating at the cathode and anode interfaces and provides improved stability of OLEDs.

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