ADVANCED FUNCTIONAL MATERIALS

Designing a Stable Cathode with Multiple Layers to Improve the Operational Lifetime of Polymer Light-Emitting Diodes

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The short device lifetime of blue polymer light-emitting diodes (PLEDs) is still a bottleneck for commercialization of self-emissive full-color displays. Since the cathode in the device has a dominant influence on the device lifetime, a systematic design of the cathode structure is necessary. The operational lifetime of blue PLEDs can be greatly improved by introducing a three-layer (BaF_2/Ca/Al) cathode compared with conventional two-layer cathodes (BaF_2/Al and Ba/Al). Therefore, the roles of the BaF_2 and Ca layers in terms of electron injection, luminous efficiency, and device lifetime are here investigated. For efficient electron injection, the BaF_2 layer should be deposited to the thickness of at least one monolayer ($\sim$3 nm). However, it is found that the device lifetime does not show a strong relation with the electron injection or luminous efficiency. In order to prolong the device lifetime, sufficient reaction between BaF_2 and the overlying Ca layer should take place during the deposition where the thickness of each layer is around that of a monolayer.

1. Introduction

Although a great deal of research has been undertaken to improve the device efficiency and lifetime of polymer light-emitting diodes (PLEDs), the device performance still needs improvement to meet the requirements for full-color panel displays.[1,2] In particular, the lifetime of blue PLEDs is still much shorter than that of green and red color devices.[1] When extrinsic factors such as moisture and oxygen are under good control, device degradation takes place during its operation according to several degradation modes related to the emitting or transporting materials,[3,4] electron–hole balance,[5] organic–organic or metal–organic interfaces,[3,6,7] and electrodes.[8] Although the stability of the emitting material itself is dominant on the device lifetime, the charge injection or transport for balanced recombination in PLEDs should be controlled by introducing a hole injection layer (HIL) on top of the anode,[5] an electron injection layer underneath the cathode,[9] or a hole transporting interlayer between the HIL and the emitting layer.[10,11] In addition, anode surface modification has proven effective in enhancing the device lifetime.[12] Designing cathode structures is also a very important issue that determines the device lifetime as well as the device efficiency. Engineering of a cathode to optimize the device performance is necessary before we perform other research on the charge injection/transport and emitting materials to find the major degradation modes in device lifetime. In this respect, it is still a challenge to provide reliable electron injection contacts in organic/PLEDs.

To provide an efficient electron injection contact, metals with a low work function, such as Li, Ca, or Mg, have often been used for organic/PLEDs.[13] Since these metals are highly reactive to oxygen and moisture, and thus tend to give unstable electrodes, a thin metal fluoride layer combined with a pure metal layer, such as LiF/Al and BaF_2/Al, has been alternatively used for cathodes.[14–18] These metal fluoride layers provide an efficient and stable electron injection contact even though the metal fluorides themselves are insulators.[14–18] Since Al and metal fluorides are easier to handle compared with the low work function metals, the metal fluoride/Al cathodes are generally used for fabrication of organic light-emitting diodes (OLEDs).[14–18] The underlying mechanisms to elucidate the role of metal fluorides for efficient electron injection are still under investigation. There have been three major models to explain efficient electron injection: a reaction model,[15,16] a dipole-moment

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model,[17] and a tunneling model.[18] In the reaction model, free metal atoms are released from the metal fluoride to the interface upon evaporation of hot reactive metals, which results in lowering of the work function of the cathode. As for the dipole-moment model, since LiF and BaF_2 have high dielectric constants (9.1 and 7.33 at 1 MHz, respectively), it has been suggested that the large dipole moment in the thin fluoride layer (e.g., 6.33 D for LiF) decreases the surface potential of the aluminum cathode and thus the effective work function, which results in favorable electron injection.[17] Finally, in the tunneling model, the thin metal fluoride layer can also enhance the electron injection by lowering the effective energy barrier within a tunneling range as the metal fluoride layer reduces the effective electric field in the emitting layer and thus reduced banding of the emitting layer occurs.[18] The exact mechanism for efficient electron injection in this system is still under debate but nowadays much evidence suggests that the reaction model is prevailing.[15,16] For example, a LiF/Ca/Al cathode shows more efficient electron injection than a LiF/Al cathode because of a reduction of the injection barrier height.[19]

In this article, we basically report three-layer cathode engineering for lifetime improvement in PLEDs where the cathode is composed of a metal fluoride layer, a reactive metal, and a capping metal layer in sequence. The use of the three-layer cathode of BaF_2/Ca/Al results in a more balanced recombination and longer device lifetime compared with PLED devices with two-layer cathodes such as BaF_2/Al and Ba/Al. In addition, we attempt to clarify the underlying electron injection enhancement mechanism and lifetime enhancement mechanism by using a combinatorial method for the thickness of each layer. The roles of the metal fluoride and the overlying metal layer in the three-layer cathode are suggested. It is found that although the efficient electron injection of the cathode can be well understood by the reaction model, a sufficient reaction between the metal fluoride and the reactive metal is crucial to achieve reliable devices with a prolonged device lifetime.

2. Results and Discussion

Blue-emitting PLED devices with varying cathode structures, such as BaF_2/Ca/Al, BaF_2/Al, Ba/Al, and BaF_2/Ba/Al, have been fabricated (see Experimental for details).

Figure 1 shows the current–voltage–luminance (*I–V–L*) characteristics of the PLED devices with varying cathode structures (BaF_2/Ca/Al, BaF_2/Al, Ba/Al, and BaF_2/Ba/Al; 6 nm BaF_2, Ca 5 nm, and 5 nm Ba). Figure 1a shows that the BaF_2/Ca/Al cathode improves the electron injection compared with the BaF_2/Al cathodes because of a greater release of Ba atoms from the reaction between BaF_2 and Ca. Ca is much more reactive with BaF_2 than Al such that Ba can be effectively released from the BaF_2 upon evaporation of hot Ca metal. As a result, CaF_2 can be generated. Based on a bulk chemical reaction of $M_1 + M_2F \rightarrow M_1F + M_2$ (M is the metal and F is fluoride; here M_1 is Ca or Al and M_2 is Ba), the free energy to form M_2 can be estimated. The overall heat of formation for the chemical reaction of $Ca + BaF_2 \rightarrow CaF_2 + Ba$ and of $Al + BaF_2 \rightarrow 2AlF_3 + 3Ba$ was -17.15 and 605.44 kJ mol^{-1}, respectively.[20] The reaction between BaF_2 and Ca is exothermic, which implies that upon deposition of a reactive metal, BaF_2 dissociates spontaneously to liberate Ba metal with a low work function ($\Phi = 2.7$ eV).[21] On the other hand, since the reaction between BaF_2 and Al is endothermic, the dissociation reaction requires additional thermal energy. The Al metal arrives at the surface of BaF_2 as a hot metal so that the thermal energy can activate the reaction.

We estimated the work function of BaF_2/Ca/Al and BaF_2/Al by photocurrent measurement to investigate their electron injection.[22] The estimated work function for BaF_2/Ca/Al and BaF_2/Al cathodes were ~2.6 and ~2.9 eV, respectively. Therefore, the electron injection of the device with a BaF_2/Ca/Al cathode is more favorable as shown in Figure 1a. It is notable that the device with BaF_2/Al (Φ ~2.9 eV) showed an increase in both current and luminance with respect to the device with Ba/Al (Φ 2.7 eV). This implies that the residual BaF_2 insulating dipole layer can induce additional electron injection from the cathode in accordance with the dipole moment model or the tunneling model. Although we understand the roles of the BaF_2 layer predominantly based on the reaction model, the dipole layer model and the insulating model should also be considered when the unreacted BaF_2 layer remains. However, based on our device results, the tunneling model seems to be the least plausible because the luminous efficiency was almost maintained even at a thickness above 10 nm. When Ba was deposited instead of Ca on top of BaF_2, the

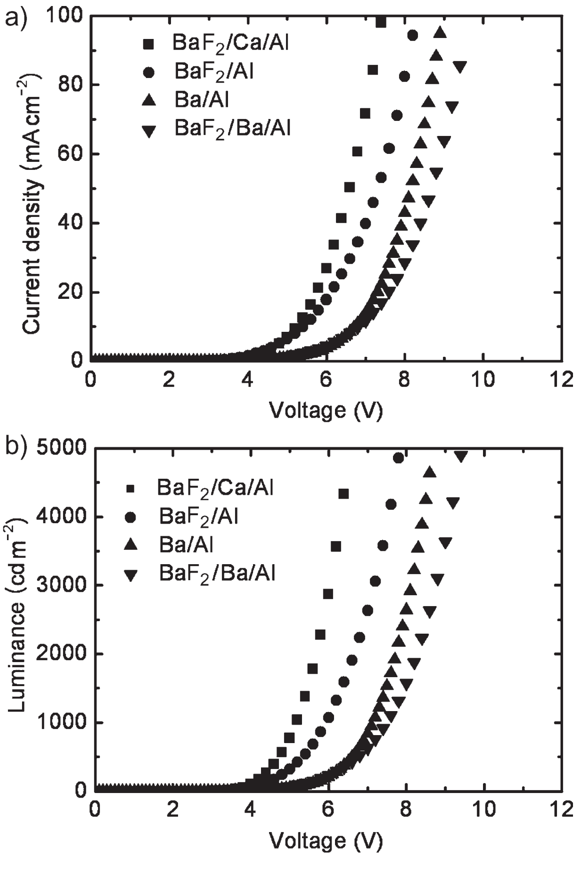


Figure 1. Current–voltage–luminance characteristics of the blue emitting devices with BaF_2/Ca/Al, BaF_2/Al, Ba/Al, and BaF_2/Ba/Al cathodes. a) Current density versus voltage. b) Luminance versus voltage.

device performance became poorer (Figs. 1 and 2). Although a metal-exchange reaction can occur between the BaF_2 and overlying metal (Ba), there is apparently no significant chemical change in the multilayer cathode, and the unreacted BaF_2 acts only as a separate dipole layer. When a metal-exchange reaction between the metal fluoride and the overlying metal takes places, the released metal atoms can reside closer to the emitting layer and thus the reaction model seems to be dominant lowering the work function of the cathode. However, when the BaF_2 thickness becomes thicker than a monolayer thickness, the released metal atoms can be located inside the mixed layer, which consists of BaF_2, CaF_2, and Ca apart from the emitting layer. In this case, the dipole moment effect of the unreacted BaF_2 layer will be helpful to inject electrons. BaF_2/Ca/Al and BaF_2/Al can form a new composite layer of BaF_2–CaF_2 and BaF_2–AlF_3, respectively, while the BaF_2/Ba/Al can not. This might be the reason for the lower electron injection from the BaF_2/Ba/Al cathode as the inorganic metal fluoride compounds in a binary mixture system may have a different structure and conductivity.[23]

Figure 1b shows that the luminance versus voltage characteristics also have the same trend as the current density versus voltage characteristics. The device lifetime was observed at the initial luminance of 800 cd m^{-2} for the four different devices with varying cathodes. Figure 2 shows that the stability of the BaF_2/Ca/Al device is better than the BaF_2/Al and BaF_2/Ba/Al devices, which implies that the reaction between BaF_2 and the overlying metal atoms is also important for the device stability as well as the electron injection. In addition, the result that the BaF_2/Ca/Al and the BaF_2/Al devices are better than the Ba/Al device implies that the BaF_2 layer plays an important role as a buffer to reduce cathode quenching, chemical interaction with the emitting layer, and cathode migration into the emitting layer.[8,24,25]

As a result of the random conformations of the spin-cast amorphous emitting polymer film, its free volume is larger than vacuum deposited amorphous small-molecule films. Since free volume plays a very important role in diffusion in amorphous polymers,[25] the cathode diffusion can take place more easily in PLEDs than the small molecule (SM)-based OLEDs. Although the emitting layer in SM OLEDs is sandwiched between a hole transporting layer and an electron transporting layer, the polymeric emitting layer in PLEDs usually makes direct contact with either the metal cathode (e.g., Ca/Al or Ba/Al) or a thin interlayer (e.g., metal fluorides)/metal cathode. In these regards, metal diffusion into the polymeric emitting layer in PLEDs should be considered more seriously than in SM OLEDs. Researchers at Uniax Coporation (currently Dupont Displays) reported that the ionic radius of the cathode metal with alkali and alkaline earth metals is a much more important factor than their work functions in the luminance decay process during operation.[26] They report that among the alkali and alkaline earth metals, the device with a larger ionic radius metal resulted in a longer device lifetime and, in particular, a Ba cathode (ionic radius:1.42 Å) gave the best lifetime in PLEDs, which could be attributed to the reduced mobility of the larger metal atoms into the emitting layer film. This is also the reason why BaF_2 was chosen here instead of LiF or CaF_2 (the ionic radii of Li and Ca are 0.76 and 1.00 Å, respectively). Therefore, the diffusion of the Ba metal released from BaF_2 into the emitting polymer layer during device operation should be minimized especially in PLEDs. The diffused metal atoms can act as luminescence quenching centers.[24] This is one of the critical factors that affect the luminance drop during operation. Indeed, a previous report showed that a PLED with a BaF_2/Al cathode had a much longer operational lifetime than the device with a LiF/Al cathode at an elevated temperature (85 °C).[14] Since the BaF_2 acts as a buffer layer to protect the emitting layer, it is important to have a BaF_2 layer thicker than one monolayer. Otherwise, the emitting layer will have an exposed area with which the evaporated Ca has direct contact, which results in lower electron injection and luminescence quenching by non-radiative energy transfer to the metal.

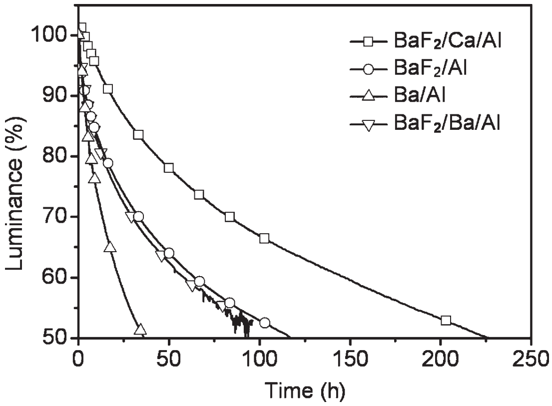
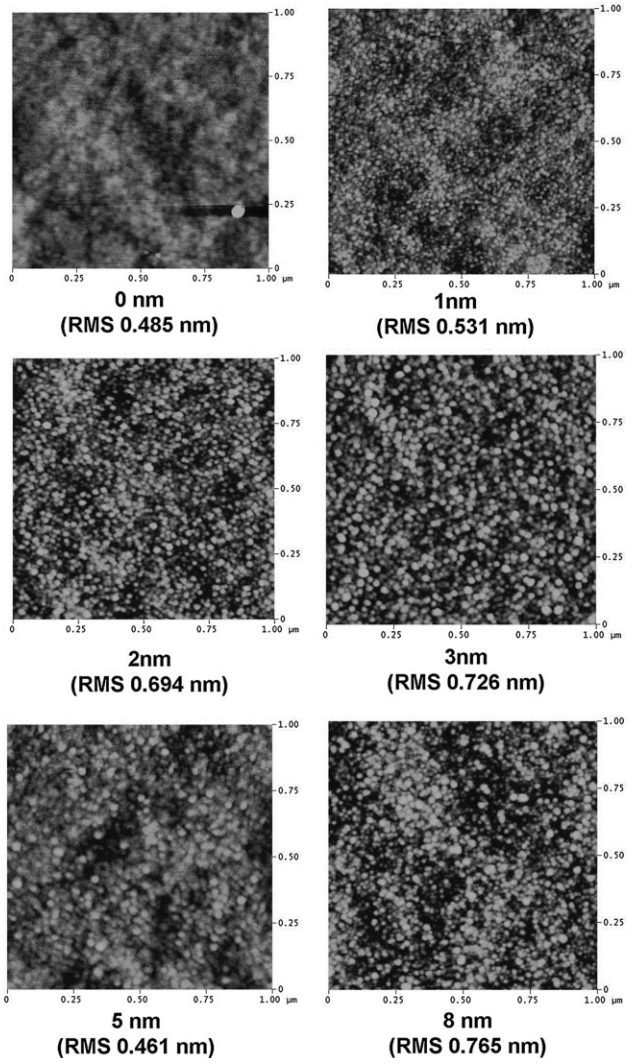


Figure 2. a) Current density versus voltage of bipolar devices, b) luminance versus voltage of bipolar devices, and c) current efficiency versus voltage of bipolar devices. Luminance decay under continuous direct current operation at a constant current starting at an initial brightness of 800 cd m^{-2} for the blue emitting devices with BaF_2/Ca/Al, BaF_2/Al, Ba/Al, and BaF_2/Ba/Al cathodes.

Figure 3 shows the atomic force microscope images of the BaF_2 films deposited on the emitting layer with varying thickness monitored with a quartz crystal microbalance sensor. The grain size of BaF_2 tends to increase as the deposited thickness increases. The BaF_2 shows an island growth on the polymer surface, which is similar to the growth of LiF as observed previously.[15] Accordingly, the root-mean-square (RMS) roughness increased from 0.531 (1 nm thickness) to 0.726 (3 nm thickness). However, for a 5 nm thick film, the RMS roughness decreased to 0.461 nm, which implies that small grains start to grow between the large grains after formation of one monolayer, which results in the free space being filled between the large grains. Again, the RMS roughness increased to 0.765 nm for an 8 nm thick film. From these AFM results, we can conclude that BaF_2 forms one monolayer at around 3 nm thickness. Additional AFM studies also revealed that the Ca layer becomes one monolayer at around 3 nm.

We fabricated the PLEDs with varying BaF_2 thickness to check whether the morphological trend of the grown BaF_2 films is consistent with the current–voltage characteristics of the devices. Figures 4a and 4b show the operating voltages and current densities that correspond to 800 cd m^{-2} as a function of BaF_2 thickness. Figure 4 clearly shows that the operating voltage and current densities at 800 cd m^{-2} drastically decrease as the BaF_2 thickness increases up to around 3 nm and is then maintained above 3 nm. This supports that the BaF_2 film becomes a



0 nm
(RMS 0.485 nm)

1nm
(RMS 0.531 nm)

2nm
(RMS 0.694 nm)

3nm
(RMS 0.726 nm)

5 nm
(RMS 0.461 nm)

8 nm
(RMS 0.765 nm)

Figure 3. Atomic force microscope images of thermally evaporated BaF_2 on the blue emitting polymer film with varying thickness. Root-mean-square (RMS) roughness values are indicated.

monolayer at 3 nm thickness. On the other hand, the device efficiency was a maximum at 5 nm thickness. The efficiency tends to decrease gradually as the thickness increases above 8 nm. Therefore, the optimal thickness of the BaF_2 film for the device efficiency is around 3–8 nm. A similar trend with the LiF layer thickness was found for LiF in the work by Brown et al.[27]

The role of BaF_2 and Ca layers for device performance is depicted in Figure 5. When the BaF_2 thickness is below 3 nm, the Ca layer makes direct contact with the emitting layer, which results in luminescent quenching by the Ca metal. In addition, BaF_2 with these thicknesses can not prevent Ca and Al diffusion into the emitting layer, which leads to a lower device lifetime. In contrast, with a thicker BaF_2 layer, direct contact of Ca with the emitting polymer is avoided and a sufficient reaction between BaF_2 and Ca can take place to produce a CaF_2 layer or a mixed layer of BaF_2 and CaF_2. As a result, the electron injection can be facilitated. The exact picture of the mixed layer after dissociation may be a topic of research for further investigation.

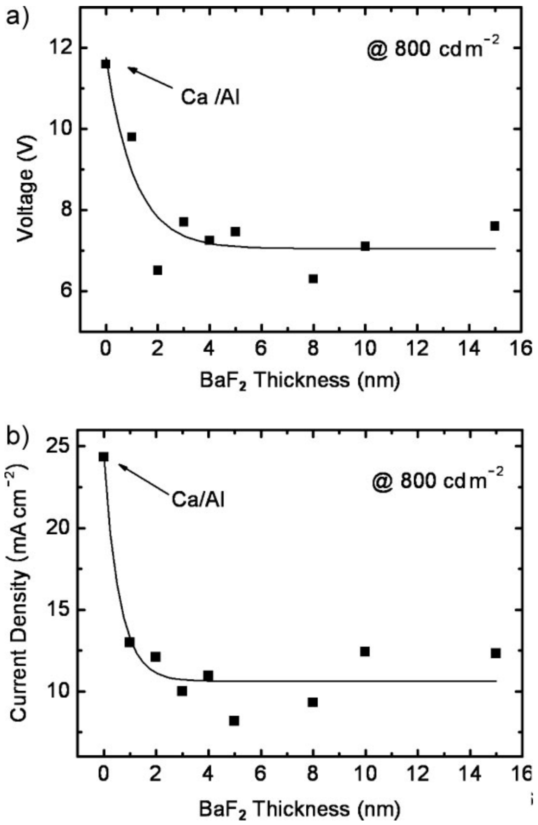


Figure 4. The operating voltages and the current densities of the blue-emitting devices at 800 cd m^{-2} with varying BaF_2 thickness and a fixed Ca thickness of 5 nm.

Since the BaF_2 thickness can have a crucial effect on both the device efficiency and the lifetime in PLEDs, the optimum thickness should be determined in combination with Ca thickness in this three-layer cathode structure. Therefore, we tried to optimize the BaF_2/Ca/Al cathode to improve the device efficiency and lifetime by a combinatorial change of BaF_2 and Ca thicknesses. The roles of each layer in the three-layer cathode can be summarized as such: First of all, the BaF_2 acts as an electron injection layer. In respect of device lifetime, BaF_2 can be a buffer layer to reduce the adverse effect by the cathode as described above. As far as the reaction of BaF_2 with overlying metal (the second cathode layer; Ca) is involved, it should be very reactive to provide a large amount of dissociated metal close to the emitting layer surface. The third cathode layer (Al) is deposited as a capping layer. Figure 6 shows the contour plot of the device efficiency and the lifetime in blue PLEDs as a function of the BaF_2 and the Ca layer thickness. We increased the BaF_2 thickness starting from 3 nm, i.e., one monolayer thickness. The optimum device luminous efficiencies were found in the region of 4.5–7 nm BaF_2 thickness and 4.5–6.5 nm Ca thickness (Fig. 6a), at which thicknesses a sufficient amount of released Ba for electron injection was generated by the exchange reaction. When a thin layer of BaF_2 (below 4 nm) and a Ca layer thinner than 2.5 nm were used, the efficiency dropped because of insufficient release of Ba. On the other hand, when the BaF_2 layer was thicker than 10.5 nm with a thin Ca layer below 2.5 nm, the efficiency was also

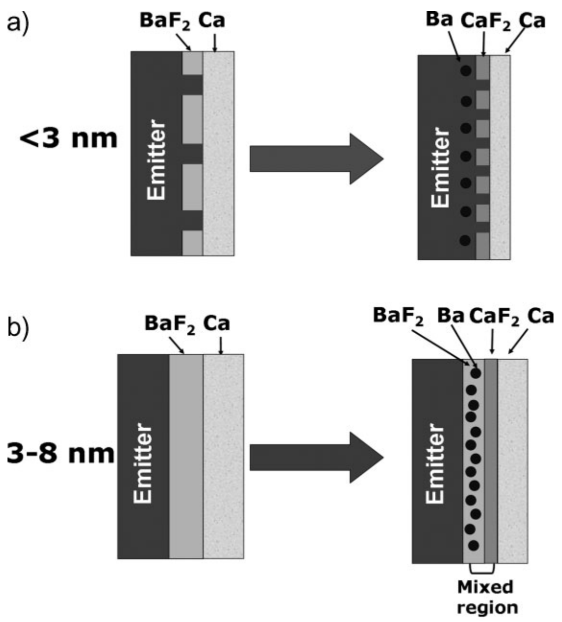


Figure 5. Schematic illustration of the triple-layer cathode in contact with the emitting layer depending on the BaF_2 thickness. The BaF_2 layer can react with Ca layer, which results in the release Ba and thus CaF_2 forms immediately. a) When the BaF_2 thickness is below 3 nm, the BaF_2 layer can not cover the emitting layer completely. Direct contact of Ca with the emitting polymer results in a formation of bipolarons, which leads to non-radiative decay of the excitons. As a result, the luminous efficiency can be low. Ca can easily migrate into the polymer layer, which has an adverse effect on the device lifetime. b) When the BaF_2 thickness is above 3 nm, the BaF_2 layer can sufficiently react with the Ca layer, which results in efficient electron injection contact. In addition, the thick BaF_2 layer can play an important role in preventing the migration of Ca into the polymer.

lowered owing to an insufficient exchange reaction and too thick a BaF_2 layer for the electron injection. However, the device lifetime showed a different trend from the device efficiency as Figure 6b shows. The optimum device lifetime was obtained over the thickness range of 3–4 nm for BaF_2 and 2–3.8 nm for Ca, which is around the monolayer thickness of each layer. It has been previously reported that the optimum thickness of reactive metal cathodes (Ca and Ba) for device lifetime is around 3 nm.[14] When a BaF_2 interlayer is not used, low work function metals dope the conjugated polymers even at room temperature and the formation of bipolarons thereby occurs.[22] A thicker metal layer can extend the doped region deeper into the polymer by diffusion during electrical stress, which can be a reason for luminescence decay. Therefore, the BaF_2 layer should be at least one monolayer for the full coverage of the emitting layer in terms of device stability. However, for the device with a thick BaF_2 layer above 10.5 nm and a thin Ca layer below 4 nm, the device lifetime was extremely poor even though the efficiency drop was not so large. Even if BaF_2 can prevent the diffusion of the Ca layer into the emitting layer, a BaF_2 layer thicker than one monolayer (~3 nm) can have unreacted BaF_2 without sufficient reaction with Ca, which results in a much shorter device lifetime. This implies that the dissociation of BaF_2 by an exchange reaction plays an important role in improving the lifetime. After dissociation of BaF_2, there will be a mixed region of Ba, BaF_2, and CaF_2 (Fig. 5).

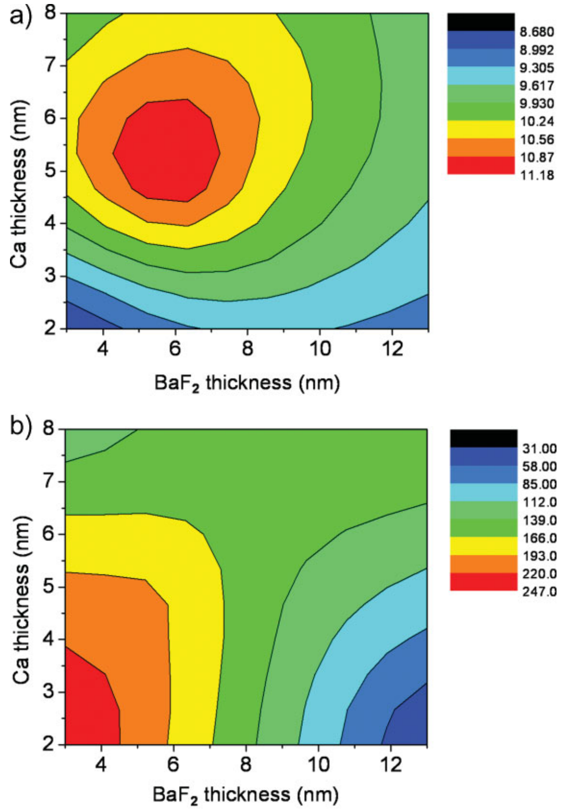


Figure 6. The contour plots of a) the device luminous efficiency (cd A^{-1}) and b) the half-lifetime (h) at an initial brightness of 800 cd m^{-2} with a combined thickness variation of the BaF_2 and Ca layers.

At this stage of our research, we do not fully understand the role of the mixed layer. However, our results suggest that efficient and stable PLEDs with a three-layer cathode require sufficient reaction between BaF_2 and Ca, which is also supported by Figures 1 and 2. When the BaF_2 thickness is fixed around 3 nm but the Ca thickness is much higher than 3 nm, the device lifetime tends to decrease as the Ca thickness increases, even if the BaF_2 layer can effectively react with the sufficient Ca layer. This implies that the extra calcium layer thickness can be another factor to accelerate the device failure in the same way that the thick reactive metal layer in Ca/Al or Ba/Al devices results in a shortened device life, as reported previously.[14] The migration of the extra Ca layer by diffusion into the emitting layer, and the high reactivity of the Ca layer with oxygen and moisture, can deteriorate the device stability. The contour patterns of Figure 6b suggest that the optimum thickness ratio of the BaF_2 to Ca layer is around 1: 1.

3. Conclusion

In conclusion, the device efficiency and lifetime in PLEDs can be improved using a multi-layer cathode of a BaF_2/Ca/Al structure where a metal exchange reaction between the metal fluoride and the overlying metal plays a key role. The electron injection by the cathode can be limited when the BaF_2 thickness is below one monolayer (~3 nm) because of incomplete coverage of the BaF_2

on the emitting polymer film. As a result, the maximum luminous efficiency was determined at thicknesses of $\sim$6 nm of BaF_2 and $\sim$5.5 nm of Ca. The device lifetime tended to decrease as the BaF_2 thickness increased above one monolayer, which was also amplified by insufficient reaction between BaF_2 and Ca (i.e., thick $BaF_2 > 10.5$ nm and thin Ca < 4 nm). Our results demonstrate that efficient and stable PLEDs require sufficient reaction between BaF_2 and Ca, which basically supports that the reaction model is the major underlying mechanism to form an efficient and stable multi-layer cathode. Since electrodes for efficient charge injection and stable device operation are also required in other organic electronics such as organic thin-film transistors, organic photovoltaic cells, and organic memories, our results can give insights to design electrodes to achieve high device performance.

4. Experimental

PLED devices were fabricated by varying the cathode structures such as BaF_2/Ca/Al, BaF_2/Al, Ba/Al, and BaF_2/Ba/Al. A hole injection layer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin coated on indium tin oxide (ITO)/glass to achieve a 50 nm thickness and then the film was baked at 200 °C for 5 min in a N_2 glove box after drying the film at 110 °C for 5 min on a hot plate in air. A hole-transporting material, poly(9,9-dioctylfluorene-*co*-bis-*N,N*′-(4-butylphenyl)-bis-*N,N*′-phenyl-1,4-phenylenediamine) (PFB) dissolved in *m*-xylene, was spin-coated on top of the PEDOT:PSS layer to achieve a 25 nm thickness, which was reduced by intermixing upon spin-casting the emitting-layer solution. The thermal annealing was performed at 180 °C for 1 h on a hot plate in a N_2 glove box. A proprietary blue emitting material (a polyspirofluorene derivative) dissolved in *m*-xylene was then spin-coated to give $\sim$70 nm thickness. The Commission Internationale de l'Eclairage (CIE) 1931 coordinate of the device was (0.15, 0.30). Three-layer cathodes (BaF_2/Ca/Al, BaF_2/Ba/Al) and two-layer cathodes (BaF_2/Al, Ba/Al) were employed for device optimization while fixing the Al electrode thickness at 150 nm. BaF_2, Ba, and Ca were thermally deposited at 0.1 Å s^{-1}. Devices were encapsulated using a UV curable resin and a glass lid. The current–voltage–luminescence characteristics were measured using a Keithley 238 source-measure unit and SpectraScan PR650 spectroradiometer. The device lifetime was recorded starting at an initial luminance 800 cd m^{-2} at room temperature by using a McScience Polaronix OLED Lifetime Test System. The contour plots were generated by using OriginPro 7.5 (OriginLab Corporation).

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