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Simplified Organic Light-Emitting Devices Utilizing Ultrathin Electron Transport Layers and New Insights on Their Roles

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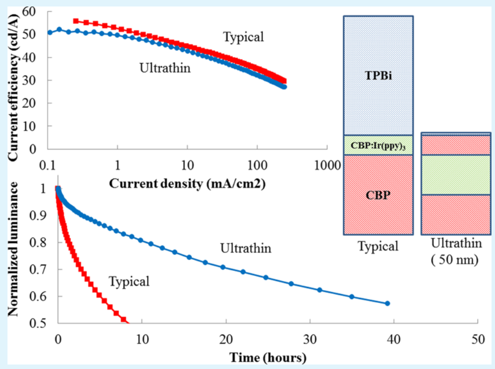
ABSTRACT: The lifetime of organic light-emitting devices (OLEDs) can be limited by exciton−polaron interactions at the organic/organic interfaces. In this work, we show that simplified phosphorescent OLEDs (PHOLEDs) are subjected to this phenomenon. By reducing the exciton concentration at the emission layer (EML)/electron transport layer (ETL) interface by means of increasing the EML thickness, hence broadening the recombination zone, the device lifetime can indeed be improved. Moreover, we report a device that displays the same extended lifetime, but with only 1 nm thin ETL. Studying the roles of this ultrathin ETL in increasing device efficiency reveals that electron injection, hole blocking, and triplet exciton blocking are all important factors. Hole blocking of the ETL can be achieved by highest occupied molecular orbitals level mismatch, where a layer thickness as low as 1 nm is sufficient, or by low hole mobility of the ETL, where a much thicker layer is required (> 5 nm). This ultrathin ETL also enables devices with only 50 nm total organic stacks, which is more than 50% thinner than the typical. This structure opens up opportunities for much shorter processing time and lower fabrication costs in the OLED industry.



KEYWORDS: *PHOLEDs, lifetime, exciton−polaron interactions, ultrathin ETL, BmPyPhB*

1. INTRODUCTION

Having the potential to exhibit 100% internal quantum efficiency,[1] phosphorescent organic light-emitting devices (PHOLEDs) have been attracting much attention in the fields of flat panel displays and general lighting.[2,3] Recently, Helander et al. showed that by using 4,40-bis(carbazol-9-yl)biphenyl (CBP) as both the hole transport layer (HTL) and the host, simplified PHOLEDs with high efficiencies can be realized.[4] Despite the high efficiencies of these devices, simplified PHOLEDs tend to have shorter lifetimes than their conventional counterparts.[5] Our recent work has shown that one reason for the shorter lifetime is the exciton-induced degradation of the indium tin oxide (ITO)/organic interface.[6] This degradation mechanism can be mostly avoided by using an electron-blocking HTL, for example, 2,6-bis[3-(carbazol-9-yl)phenyl] pyridine (26DCzPPy) or molybdenum oxide (MoO_x), at the ITO/organic interface.[6,7] In this work, we show that the lifetime of the simplified PHOLEDs can be further extended by reducing the exciton density at the emission layer (EML)/electron transport layer (ETL) interface. These results are consistent with our recent findings on degradation of the organic/organic interface due to exciton−polaron interactions.[8]

In addition, we show that the thickness of the organic stack in the devices can be substantially reduced from the typical 100 nm to only 50 nm, by utilizing an ultrathin ETL (~ 1 nm), without a significant loss in efficiency. The much thinner organic stack opens up opportunities in reducing device fabrication time and costs. Our study also sheds new light on the roles of ETLs in these devices.

2. EXPERIMENTAL SECTION

In this work, CBP is used as both hole transport and host material. Tris(2-phenylpyridine)iridium(III) ($Ir(ppy)_3$) is used as the green emitter. The compounds 1,3,5-tris(2-*N*-phenylbenzimidazolyl) benzene (TPBi), 1,3-bis[3,5-di(pyridin-3-yl)phenyl]benzene (BmPyPhB), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), bis(2-methyl-8-quinolinolate)-4-(phenylphenolato)aluminium (BAlq), and tris(8-hydroxy-quinolinato)aluminium (Alq3) are used as electron transport materials. All organic materials are obtained from Luminescence Technology Corp. and used as received without further sublimation. All devices are fabricated on 150 nm thick ITO patterned glass substrates with 15 Ω/□ sheet resistance. Prior to device fabrication, the ITO substrate was sonicated in acetone and isoproponal for 5 min each in respective order. Devices are fabricated in an Angstrom's EVOVAC system. All materials are thermally evaporated at a rate of 0.1−2 Å/s at a base pressure of 5×10^{-6} Torr. Devices are kept in a N_2 environment during measurements. All electrical stress tests use a constant 20 mA/cm^2 current density.

3. RESULTS AND DISCUSSION

We recently found that organic/organic interfaces degrade as a result of exciton−polaron interactions, a phenomenon that likely contributes significantly to the degradation in device

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performance.[8] Therefore, by reducing the exciton concentration at the interface, the device lifetime can be expected to be increased. In order to investigate the role of this phenomenon in the stability behavior of simplified PHOLEDs, we study the effect of increasing the thickness of the EML. A thicker EML can be expected to lead to a wider and less confined electron-hole (e−h) recombination zone and thus a lower exciton concentration at the EML/ETL interface. Therefore, we study devices of the structure, ITO/MoO_3 (5 nm)/CBP (30 nm)/CBP:Ir(ppy)$_3$ (5%) (x nm)/TPBi (40 nm)/LiF (0.8 nm)/Al (80 nm), where x = 10, 20, and 30, as shown in the Figure 1 inset. Figure 1 shows the changes in electroluminescence (EL) with respect to time under electrical bias to maintain constant current flows of 20 mA/cm^2 for devices with 10, 20, and 30 nm EML. In this figure, the change in EL is represented in the form of normalized luminance (i.e., luminance/initial luminance) where the initial luminance for these devices with 10, 20, and 30 nm EML are 6720, 6840, and 5640 cd/m^2, respectively. It clearly shows that increasing the thickness of the EML leads to a longer device lifetime. To verify if a thicker EML indeed leads to a broader recombination zone, hence a lower exciton concentration at the organic/organic interface, we study devices in which a neat layer of the host material−CBP is inserted between the EML and the ETL, to be employed as a marking layer. The Figure 2 inset (a) shows the EL spectra for devices with and without the neat CBP layer. The device structures for these devices are ITO/MoO3 (5 nm)/CBP (20 nm)/CBP:Ir(ppy)3 (5%) (15 nm)/CBP (10 nm)/TPBi (1 nm)/LiF/Al and ITO/MoO3 (5 nm)/CBP (25 nm)/CBP:Ir(ppy)3 (5%) (15 nm)/TPBi (40 nm)/LiF/Al, respectively. Since only the device with the neat CBP marking layer shows emission from CBP, it is clear that significant electron-hole recombination occurs in the neat CBP layer, suggesting that charge transport in it is primarily bipolar, and is therefore not limited to electron transport. The intensity of the CBP emission is used to probe the exciton concentration at the CBP/TPBi interface. Figure 2 shows the EL spectra of the devices with the neat CBP marking layer and with different CBP:Ir(ppy)$_3$ layer thickness x (where, x = 10, 15, 20, 25, and 30), normalized to the Ir(ppy)$_3$ intensity. The EL spectra of these devices without normalization are provided in inset (b). As the thickness x increases, the emission from CBP is seen to decrease, indicating a decrease in exciton density. This observation verifies that increasing the thickness of the EML indeed leads to a lower exciton density in the vicinity of the CBP/TPBi interface.

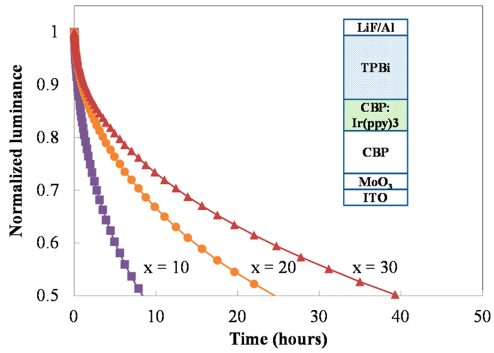

Figure 1. Changes in EL with time under 20 mA/cm^2 current density for devices with 10, 20, and 30 nm EML, all utilizing 30 nm CBP HTL and 40 nm TPBi ETL. (Inset) The structures of these devices.

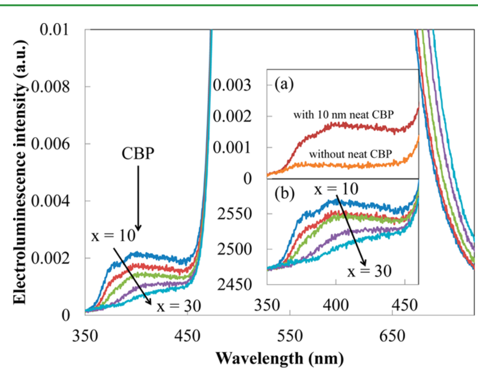

Figure 2. Inset (a) EL spectra for devices with and without the 10 nm neat CBP layer. EL spectra for devices with 10, 15, 20, 25, and 30 nm EML and with 10 nm neat CBP marking layer, normalized to Ir(ppy)$_3$ emission. Inset (b) EL spectra of these devices without normalization.

Although the lifetime of a simplified PHOLED can be increased by increasing the thickness of the EML, the charge balance and hence the device efficiency is also altered. Figure 3 shows the current efficiency versus current density of devices with various organic layer structures. The current density versus voltage (J−V) characteristics of these devices are also shown in the inset. It can be seen that the current efficiency of a device with 30 nm EML is significantly lower than that of a device with 10 nm EML (denoted as device A), both utilizing a 30 nm CBP HTL and a 40 nm TPBi ETL. Changing the ETL thickness from 40 nm to 2 nm in this device (i.e., with 30 nm EML) results in a significant efficiency improvement (denoted as device B). Further improvement can be achieved by removing the Ir(ppy)$_3$ dopant for the 10 nm of the EML adjacent to the EML/ETL interface, thereby having only a neat CBP layer. Using 1 nm of BmPyPhB[9] instead of 2 nm of TPBi is found to benefit the efficiency even further (denoted as device C). It is important to point out that although device C has relatively high efficiency, it is still slightly less efficient than device A. This may be due to the smaller distance between the EML and the reflective cathode, which can lead to less optimal optical interference. Optical modeling of OLEDs with the ultrathin ETLs can provide invaluable guidance in this regard and will therefore be pursued in the future. Despite less optimal optical interference, it is still quite surprising that a device with an ETL as thin as only 1 nm can have such comparable efficiency.

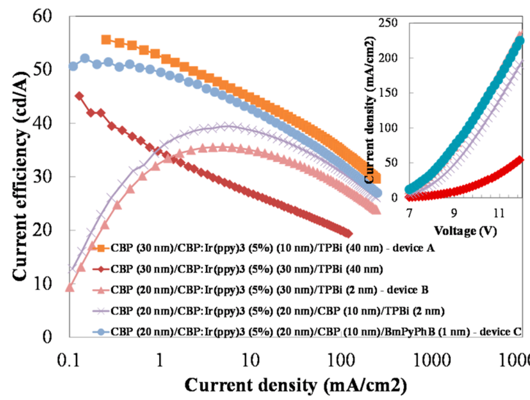

Figure 3. Current efficiency vs current density characteristics of selected devices. (Inset) Current density vs voltage characteristics of these devices.

Figure 4 shows the changes in EL over time under constant 20 mA/cm^2 current density for devices A, B, and C. The device

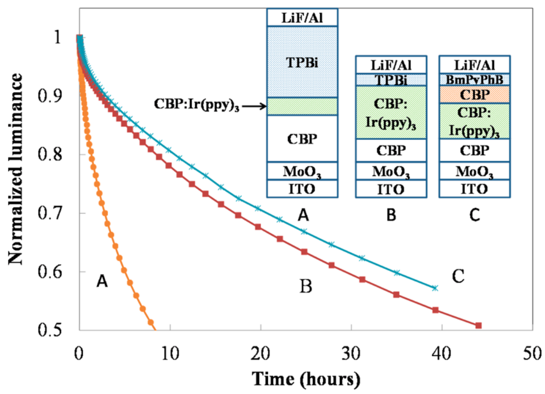

Figure 4. Changes in EL with time of devices A, B, and C. (Inset) The structures of these devices.

structures are also shown in the Figure 4 inset. The initial brightness for device A, B, and C are 5640, 6960, and 7870 cd/m^2, respectively. It can be seen that the device with 1 nm BmPyPhB (device C) has roughly the same lifetime (i.e., the extended lifetime) as the device with 30 nm EML (device B). Therefore, by using this structure with only 1 nm BmPyPhB ETL, higher efficiency and stability can be simultaneously achieved. Another benefit is the significant reduction in device thickness. The structure with the ultrathin ETL has around 50 nm thick organic materials in total (i.e., only half the thickness of typical PHOLEDs). This thinner structure can be expected to offer advantages in lowering fabrication cost by reducing material consumption and processing time.

It is noteworthy to point out that in our tests on various ETL/EIL configurations, we found that only a few electron transport materials can be used in this ultrathin structure to obtain high device efficiencies. Figure 5 shows the current

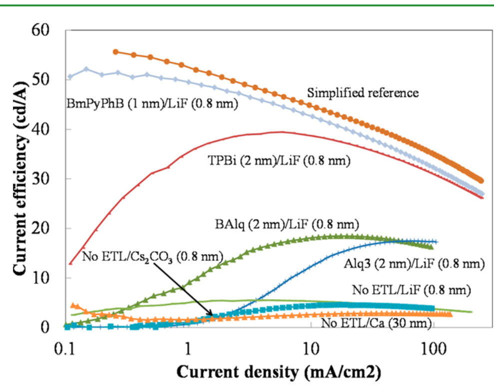

Figure 5. Current efficiency vs current density characteristics of selected devices with different ETL/EIL configurations.

efficiency versus current density of devices with selected ETL/EIL configurations. The "simplified reference" device refers to the device with the CBP (30 nm)/CBP:Ir(ppy)$_3$ (5%) (10 nm)/TPBi (40 nm)/LiF (0.8 nm) structure. All other devices use the common CBP (20 nm)/CBP:Ir(ppy)$_3$ (5%) (20 nm)/CBP (10 nm) stack, followed by an ultrathin ETL and/or EIL. All devices with only an EIL (but no ETL) have poor efficiencies, regardless of the EIL material (LiF, Cs_2CO_3, or Ca). Surprisingly, despite being very thin, different ETLs (i.e. TPBi, BmPyPhB, BAlq, and Alq_3) can lead to vastly different efficiencies, with only TPBi and BmPyPhB giving the highest efficiencies. Considering an ETL as thin as 1 nm can have such a major impact on device current efficiency, what roles this ETL plays in the device becomes an interesting question.

In addressing the roles of these ETLs, it is important to first examine layer coverage and whether continuous layers of these materials at these thicknesses (~1 nm) are formed. For this purpose, we study devices with the common CBP (20 nm)/CBP:Ir(ppy)$_3$ (5%) (20 nm)/CBP (10 nm) structure followed by the specific ETL listed. An EIL consisting 0.8 nm LiF and a cathode of 80 nm Al is used in all devices. Figure 6a shows the

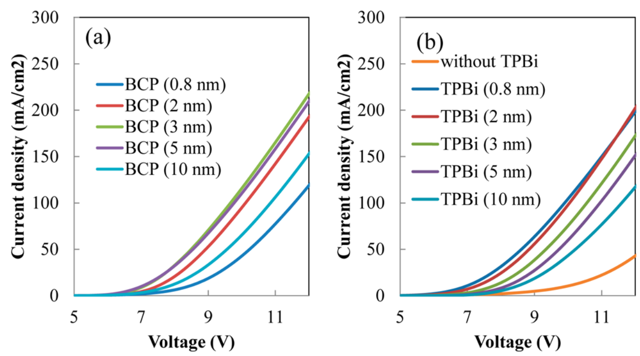

Figure 6. Current density vs voltage characteristics of devices with various (a) BCP and (b) TPBi ETL thicknesses.

J−V characteristics of devices in which BCP is used as the ETL, of various thicknesses. It is important to note that the driving voltage first decreased as the thickness of the BCP layer is increased from 0.8 nm to 3 nm, and then the voltage is increased on further increasing the thickness to 10 nm. This trend suggests that a complete coverage of the CBP layer by the BCP layer is achieved at a minimum BCP thickness of 3 nm, below which the coverage is only partial and leads to non-efficient electron injection. Thus, as the BCP thickness is increased to 3 nm, the driving voltage gradually decreases. On the other hand, an increase in film thickness beyond 3 nm results in a longer electron transport pathway, hence the increase in driving voltage. Therefore, the coverage of the ETL appears to play an important role in the J−V characteristics behavior of the device.

We then examine the roles of the ultrathin ETL in increasing device efficiency. In general, ETLs increase device efficiency by the following means: facilitating electron injection/transport, blocking holes, and blocking excitons.[10] In the context of devices with ETLs as thin as 1 nm, electron mobility of the ETL cannot play an important role. Moreover, since the cathode is at ~1 nm distance of the interface where excitons are created (i.e., the EML/ETL interface), the role of the ETL in blocking singlet excitons must be insignificant since quenching by long-range Förster transfer to the metal can occur. As a result, only triplet exciton blocking can have an effect on device efficiency. Therefore, the three possible roles of the ultrathin ETL on increasing efficiency are (1) electron injection, (2) hole blocking, and (3) triplet exciton blocking.

In order to examine the role of the ultrathin ETL in facilitating electron injection, we study the driving voltage of the device with and without the ultrathin ETL. Figure 6b shows that the driving voltage of the device without a TPBi ETL is significantly higher than that of the device with a 2 nm TPBi

ETL, beyond which the coverage of the TPBi film becomes complete, as indicated in the figure. It is clear that the electron injection is facilitated when the ultrathin ETL is present. Since electron injection significantly affects charge balance, it is natural that electron injection plays an important role in increasing device efficiency.

We then examine the hole blocking role of the ETL by studying OLEDs utilizing various ETL materials (BAlq, BmPyPhB, and Alq_3) in different thicknesses. At first glance, it seems that the highest occupied molecular orbitals (HOMO) level of the ETL has an effect on device efficiency, as shown in Figure 5. When the HOMO level of the ETL is shallower than that of the CBP (e.g., 5.9 eV for BAlq and 5.7 eV for Alq_3 versus 6.1 eV for CBP), holes can leak to the ETL, and the devices have low efficiencies. On the other hand, when the HOMO level of the ETL is deeper than that of CBP (e.g., 6.2 eV for TPBi and 6.67 eV for BmPyPhB versus 6.1 eV for CBP), which leads to an injection barrier for holes, the devices exhibit high efficiencies. Considering that BAlq is widely used as an ETL for $Ir(ppy)_3$-based highly efficient PHOLEDs,[11,12] this finding is very surprising. A closer look at the effect of the ETL thickness on device efficiency, however, reveals that high efficiency can still be achieved in the device with ~10 nm BAlq ETL, as shown in Figure 7a. This result suggests that hole

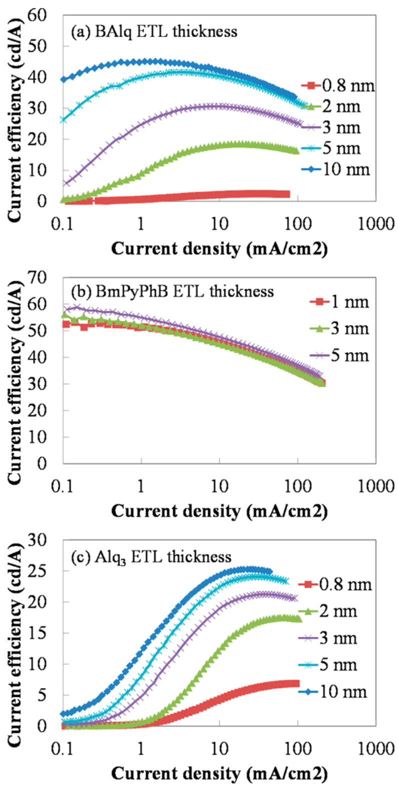

Figure 7. Current efficiency vs current density characteristics of devices with various (a) BAlq, (b) BmPyPhB, and (c) Alq_3 ETL thicknesses.

blockage by BAlq is achieved by the low hole mobility of the material,[13] hence a relatively thicker ETL is required. On the other hand, hole blocking by TPBi and BmPyPhB is obtained by deeper HOMO levels, thus only a thinner ETL is sufficient in these cases, as indicated in Figure 7b that a thicker BmPyPhB does not improve efficiency much. When Alq_3 is used as the ETL in this study, the efficiency of the device increases as the ETL thickness increases but saturates at ~25 cd/A (shown in Figure 7c). Since hole mobility in Alq_3 is comparable to that in BAlq,[13,14] it is expected that the capacity of hole blocking in both thick films are similar. However, since the triplet energy of Alq_3 is lower than that of BAlq,[15,16] better triplet exciton blocking and hence higher efficiency is expected in BAlq devices. This is in line with the common understanding that triplet exciton blocking is important in achieving high efficiency in PHOLEDs.

4. CONCLUSION

In conclusion, the high exciton density at the EML/ETL interface is found to play a major role in limiting lifetime of simplified PHOLEDs, likely due to exciton−polaron interactions. Reducing the exciton density near the interface by means of increasing the EML thickness can lead to increased device lifetime. Moreover, we have shown that devices incorporating a BmPyPhB ETL as thin as 1 nm can have both high efficiency and this extended lifetime. The roles of this ultrathin ETL include facilitating electron injection and blocking holes and triplet excitons. In order to utilize this structure with an ultrathin ETL, this layer should satisfy the following requirements: (1) the layer should have complete coverage; (2) it should help lower the electron injection barrier; (3) the HOMO level of the material should be deeper than that of the host to ensure good hole blocking; and (4) the triplet energy of the material should be comparable to or preferably wider than that of the host to have good blocking on triplet excitons. Another benefit of this structure is that the organic stack used is only 50 nm thick, which is more than 50% thinner than the typical PHOLEDs. This opens up opportunities for much shorter processing time and lower fabrication costs in PHOLEDs industry.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *J. Appl. Phys.* **2001**, *90*, 5048.
(2) Reineke, S.; Lindner, F.; Schwartz, G.; Seidler, N.; Walzer, K.; Lüssem, B.; Leo, K. *Nature* **2009**, *459*, 234−238.
(3) Su, S.-J.; Sasabe, H.; Takeda, T.; Kido, J. *Chem. Mater.* **2008**, *20*, 1691−1693.
(4) Helander, M. G.; Wang, Z. B.; Qiu, J.; Greiner, M. T.; Puzzo, D. P.; Liu, Z. W.; Lu, Z. H. *Science* **2011**, *332*, 944−947.
(5) Gao, C.-H.; Cai, S.-D.; Gu, W.; Zhou, D.-Y.; Wang, Z.-K.; Liao, L.-S. *ACS Appl. Mater. Interfaces* **2012**, *4*, 5211−5216.
(6) Zhang, Y.; Abdelmalek, M. M. A.; Wang, Q.; Aziz, H. *Appl. Phys. Lett.* **2013**, *103*, 063307.
(7) Wang, Q.; Williams, G.; Aziz, H. *Org. Electron.* **2012**, *13*, 2075−2082.
(8) Wang, Q.; Aziz, H. *ACS Appl. Mater. Interfaces* **2013**, *5*, 8733−8739.

(9) Sasabe, H.; Takamatsu, J.; Motoyama, T.; Watanabe, S.; Wagenblast, G.; Langer, N.; Molt, O.; Fuchs, E.; Lennartz, C.; Kido, J. *Adv. Mater.* **2010**, *22*, 5003−5007.
(10) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556−4573.
(11) Kwong, R. C.; Nugent, M. R.; Michalski, L.; Ngo, T.; Rajan, K.; Tung, Y.-J.; Weaver, M. S.; Zhou, T. X.; Hack, M.; Thompson, M. E.; Forrest, S. R.; Brown, J. J. *Appl. Phys. Lett.* **2002**, *81*, 162.
(12) D'Andrade, B. W.; Forrest, S. R.; Chwang, A. B. *Appl. Phys. Lett.* **2003**, *83*, 3858.
(13) Schwartz, G.; Ke, T.-H.; Wu, C.-C.; Walzer, K.; Leo, K. *Appl. Phys. Lett.* **2008**, *93*, 073304.
(14) Naka, S.; Okada, H.; Onnagawa, H.; Yamaguchi, Y.; Tsutsui, T. *Synth. Met.* **2000**, *111*−*112*, 331−333.
(15) Chu, T.-Y.; Wu, Y.-S.; Chen, J.-F.; Chen, C. H. *Chem. Phys. Lett.* **2005**, *404*, 121−125.
(16) Tanaka, I.; Tabata, Y.; Tokito, S. *J. Appl. Phys.* **2006**, *99*, 073501.

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