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Organic light-emitting diodes based on a cohost electron transporting composite

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The efficiency of green organic electroluminescent devices have been improved by cohosting the electron dominant complex, 4,7-diphenyl-1,10-phenanthroline into the traditional electron transporting layer of *tris* (8-hydroxyquinoline) aluminum. In this cohost strategy, we demonstrate that the luminous efficiency is enhanced by >20% while the driving voltage can be reduced by ∼30% in a uniformly mixed composition as compared to the traditional device configuration. The corresponding device lifetime under atmospheric condition is extended by a factor of ∼1.8, attributed to the reduction of the accumulated positive charges near the electron-hole recombination regime. Results indicate that the knowledge of bulk conductivity engineering of organic *n*-type transporters is essential in enhancing organic light-emitting devices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2178409]

Tris (8-hydroxyquinoline) aluminum (Alq_3), possessing superior film stability and thermal endurance, is one of the reliable hosts for both achieving different colors and enhancing luminous efficiency by means of dye doping since the demonstration of organic light-emitting diode (OLEDs) by Tang *et al.*[1] However, due to its low electron mobility of 10^{-6} cm^2 V^{-1} s^{-1} and intrinsic degradation,[2,3] Alq_3 is responsible for the undesirable voltage drop appearing in Alq_3-based devices. Consequently, the device operating lifetime of Alq_3-based devices is usually affected by unbalance charges originated from the substantial difference between hole mobility in hole transporting layer (HTL) and electron mobility in the Alq_3 electron transporting layer (ETL).[4] Experimental evidence strongly suggested that the excess amount of holes generate nonemissive cationic species and fluorescence quenchers in the Alq_3.[4,5]

Inserting a buffer layer such as copper phthalocyanine (CuPc) between indium tin oxide (ITO) and HTL, doping the HTL by rubrene, and introducing a cohost hole transporting composite improves device efficiency by impeding the hole injection/transport and stability.[6–9] Alternatively, increasing the electron conduction in the ETL sounds like a more promising approach to achieve a charge balance compared to reducing the amount of holes by doping the HTL since the ETL usually exhibit poor electron conductivity, limiting the power efficiency. Although some electron transporting materials such as phenanthroline and oxadiazole compounds have been suggested for replacing Alq_3 as the ETL due to their improved drift mobilities, the device reliability such as film stability and thermal endurance is insufficient for commercial display purpose.[10,11] Highly reactive metal (e.g., Li) doping reported by Kido *et al.*[12] is an alternative means to enhance the device electron conduction. However, the photoluminescence quenching occurs if the doped region locates too close to the emitting zone.

Here, we establish a cohost electron transporting composite (c-ETL) to replace the traditional single host ETL. The mobility measurement shows that 4,7-diphenyl-1,10-phenanthroline (BPhen) possesses a considerable high electron mobility of 5×10^{-4} cm^2 V^{-1} s^{-1}.[10] The electron mobility of 10 wt % BPhen-doped Alq_3 can be improved for five times as compared to that of the pristine Alq_3 ETL.[13] It is thus suggested that BPhen is presumably suitable for cohosting.

Device fabrication followed the standard procedures, as described elsewhere.[14] Alq_3, purchased from Tokyo Kasei Kogyo Co. Ltd., was used as an ETL and light-emitting layer/host and its electron mobility was verified.[15,16] NPD acted as a HTL. Coumarin 540 (C540) was used as a green fluorescent dye for doping the light-emitting layer (EML). All materials were purified once by zone sublimation prior to thin-film coating, except C540. Three devices containing different configurations of ETL have been prepared: (i) device A—Alq_3; (ii) device B—BPhen; and (iii) device C—*n* wt % BPhen-mixed Alq_3, i.e., a cohost ETL (henceforth, *c*-ETL). The basic device structure: ITO/CuPc (15 nm)/NPD (45 nm)/EML (20 nm)/ETL (60 nm) (A: Alq_3; B: BPhen; C ≔ *n* wt % BPhen-doped Alq_3.)/LiF (0.5 nm)/Al (150 nm). The coating rates of two ET hosts, Alq_3 and BPhen were ∼1 Å/s. The 20 nm of Alq_3 adjacent to the NPD layer is suitable to be defined as the EML, where excitons are mostly confined for both undoped and C540-doped EML devices,[3,17,18] for impeding holes to enter the ETL which can thus be viewed as an electron-only transporting region. For doped EML devices, the doping concentration of C540 remained 2 wt %. C540 was deposited at 0.02 Å/s. Device thicknesses were not attempted to be optimized to the maximal luminous efficiency here.

In the typical device using Alq_3 as the ETL (device A), the efficiency is ∼3 cd/A at 20 mA/cm^2, which is similar to the reported values.[19] Replacing ETL by BPhen (device B), the efficiency is significantly enhanced by ∼50%, to 4.4 cd/A. Previous time-of-flight results indicate that under electric field of ∼1 MV/cm, Alq_3 electron mobility is ∼10^{-6} cm^2 V^{-1} s^{-1} while that of BPhen is ∼5

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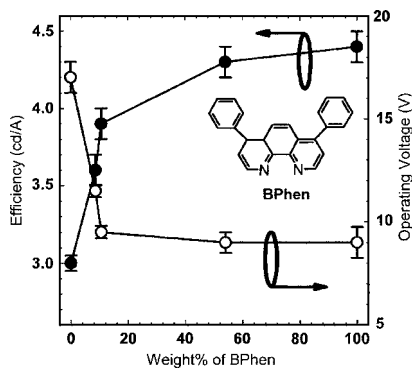[b] Author to whom correspondence should be addressed; electronic mail: chchoy@eee.hku.hk

FIG. 1. Comparison of luminous efficiency and driving voltage of undoped devices driven at 20 mA/cm^2. The ETL consists of a composite layer of BPhen and Alq$_3$. Inset: Molecular structure of BPhen.

FIG. 3. Luminous efficiency of undoped EML devices—(a), (b), and C540-doped EML devices—(c), (d). The ETLs of (a), (c) and (b), (d) consist of a pristine Alq$_3$ layer and a 50 wt % BPhen:Alq$_3$ cohost layer, respectively. Inset: Molecular structure of C540.

$\times 10^{-4}$ cm^2 V^{-1} s^{-1}.[2,3,10] The electron drift mobility difference between BPhen and Alq$_3$ is thus responsible for the luminous gain. When only 10 wt % of BPhen is doped into the ETL, the luminous efficiency increases about 20% compared to device A. The efficiency increases monotonically with the BPhen doping concentration which implies that more electrons are supplied into the EML as the BPhen concentration increases in the BPhen:Alq$_3$ cohost ETL. Figure 1 also shows the corresponding driving voltage for the whole series of devices operated at a current of 20 mA/cm^2. The turn-on voltage drops rapidly from 17 to 9 V when 10 wt % of BPhen is participated in the ETL, and reduces gradually to ~8 V at a higher doping ratio. Figure 1 reveals that BPhen does not behave as an electron trap in the Alq$_3$ at a doping ratio as low as 10 wt %. The thick-film transient electroluminescence method and device studies also confirm the increasing of electron mobility of Alq$_3$ after 10 wt % of BPhen doping.[13,20] The overall device performance approaches to a maximum efficiency when the BPhen composition is beyond 50 wt %. Practically, the ETL containing a pristine or heavily doped BPhen would encounter recrystallization that is unfavorable.[21] Thus, we will further focus on comparison between a pristine Alq$_3$ and a 50 wt % BPhen:Alq$_3$ cohost ETL.

The current-voltage-luminance characteristics among different ETLs are compared as follows: device A—a single Alq$_3$ host, and device C—a 50 wt % BPhen:Alq$_3$ c-ETL. Their device performances are shown in Figs. 2(a) and 2(b),
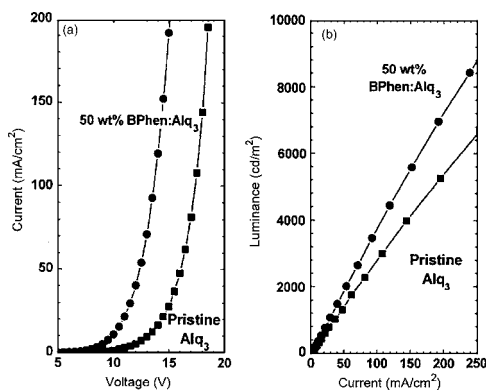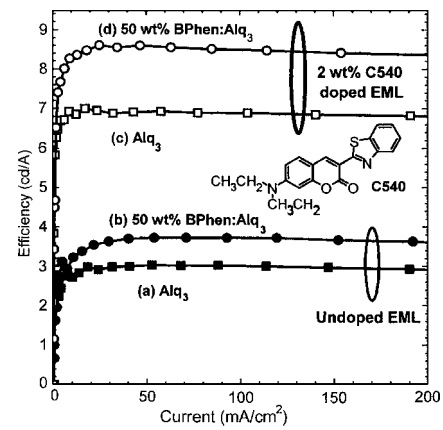

FIG. 2. Plots of (a) current-voltage and (b) luminance-current of devices without doping the EML: Device A (squares) contains a single ETL (Pristine Alq$_3$). Device C (circles) contains a cohost ET composite (50 wt % BPhen mixed Alq$_3$).

respectively. As shown in Fig. 2(a), the driving voltage required for the device operating at a current of 20 mA/cm^2 is lowered from 14.3 to 10.8 V after introducing a BPhen:Alq$_3$ c-ETL. The corresponding luminance increases from ~580 to 760 cd/m^2, (see in Fig. 2(b)). Without thickness optimization, the maximum luminance of the c-ETL device is over 16 000 cd/m^2 under a current of 475 mA/cm^2 (at 18 V) which is ~73% higher than that of the single Alq$_3$ host device. The CIE coordinates of the C540-doped devices generally retain (0.29, 0.63) that is consistent to emission of C540-doped Alq$_3$ device.

The advantage of using BPhen:Alq$_3$ cohost can be explained by *electron hopping exchange* along their lowest unoccupied molecular orbitals (LUMOs). In a single host device, electrons hop along the LUMO in Alq$_3$. The LUMO-LUMO difference between BPhen and Alq$_3$ is neglectable, subject to their similar LUMOs, i.e., −3 eV.[22] Transport manifolds along their LUMOs is expected to exhibit a certain extent of overlap after a mixing ratio goes beyond 10 wt %. Driving voltage monotonically decreases as BPhen composition increases, implying that Alq$_3$ does ignorably participate as an electron trap in BPhen-rich samples. On the contrary, it is likely that a large energetic disorder of Alq$_3$ contributes to electron hopping from Alq$_3$ to BPhen when BPhen dominates the cohost.[2] The electric field dependence on the drift mobility can be phenomenologically described by the Poole-Frenkel (PF)-like slope, β. Both pristine (BPhen or Alq$_3$) films and a 10 wt % BPhen:Alq$_3$ film show similar PF dependence, $\beta = 6-7 \times 10^{-3}$ (cm V^{-1})$^{0.5}$, implying that electron hopping among BPhen and Alq$_3$ sites is favorable in the cohost.[2,3,16]

To examine the device applicability employing the concept of electron transporting cohost, devices A (single host) and C with equally weighted BPhen:Alq$_3$ cohost are compared systematically in Fig. 3. The typical Alq$_3$ devices exhibit a luminous efficiency of 3 cd/A (undoped) and 7 cd/A (2 wt % C540-doped), as depicted in Fig. 3(a) and 3(c), respectively, similar to the reported value.[19] Replacing the ETL by 50 wt % BPhen:Alq$_3$, the efficiency is then drifted up to 3.7 cd/A [Fig. 3(b)] and 8.6 cd/A [Fig. 3(d)] which is more than 20% higher than the single ET host device. The maximum luminance of 60 000 cd/m^2 can be achieved in 2 wt % C540-doped device with a 50 wt % BPhen:Alq$_3$ ETL, without further optimizations in doping and layers' thicknesses.
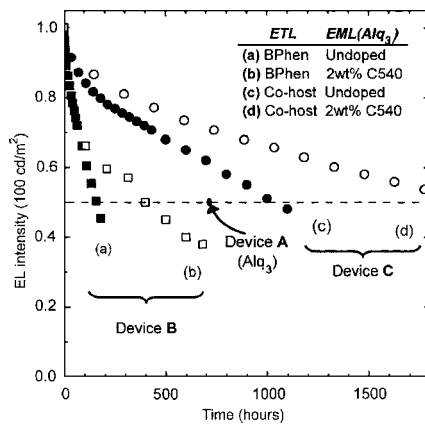
FIG. 4. Device lifetime measured under air (relative humidity 50%). ITO/CuPc (15 nm)/NPD (45 nm)/EML (20 nm)/ETL (60 nm)/LiF (0.5 nm)/Al. ETL=BPhen in devices (a), (b) and equally mixed BPhen:Alq₃ ET composite in devices (c) and (d). EML is undoped Alq₃ in devices (a) and (c), and is 2 wt % C540-doped Alq₃ in devices (b) and (d).

Moreover, these *c*-ETL devices [Figs. 3(b) and 3(d)] are practically robust which exhibit a flat "cd/A" response of efficiency under a wide range of operating currents. One of the best commercial green dopant reported by Chen and Tang is 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-benzo[l] pyrano[6,7,8-ij quinolizin-11-one (C545T) which is often used to replace the C540.[19,23] Since C545T is more resistant to concentration quenching than C540, the 2 wt % C545T-doped Alq₃ device generally gives better efficiency than the C540-doped device for ~20%. In our doped device demonstrated in Fig. 3(d), we eventually achieve 8.6 cd/A driven at 20 mA/cm² by introducing BPhen:Alq₃ *c*-ETL. This luminous performance is comparable to the traditional Alq₃ device doped with a more efficient dye C545T (~8.5 cd/A) in the EML.

We can conclude that improving the bulk ETL conductivity in the bilayer OLED device by selective cohost composite benefits to both the luminous efficiency and the turn-on voltage. Generally, our devices based on Alq₃ as the emitter host demonstrates ~20% enhancement in luminous efficiencies, independent of the EML composition. In other words, either a pristine or cohost ETL, doping of C540 almost identically increases the luminous efficiency to a factor of 2.2, indicating that only the bulk transport is engineered but not the recombination dynamics. In addition, electron conduction in our devices is not limited by the injection since LiF drastically improves the electron injection, realizing the observation of space charge limited current in Alq₃.[24] Therefore, we demonstrate that engineering the bulk mobility of the ETL can enhance the electron conduction in the Alq₃ based bilayer devices.

The device lifetime tests were performed for single and cohost devices. Devices were driven by a constant current of 80 mA/cm² under a rigorous environment (relative humidity ~50%). Assuming the scalable Coulombic degradation,[6] the half-life of devices A–C can be extracted for the driving luminance at 100 cd/m², (see in Fig. 4). A reference undoped Alq₃ device (device A) gives a mean half-life of ~800 h. Devices B with an undoped and a C540-doped EML have the half-life of 150 and 450 h respectively, as shown in Figs. 4(a) and 4(b). The shorter lifetime of devices

B is due to recrystallization.[21] The corresponding cohost BPhen:Alq₃ devices (device C) are also shown in Figs. 4(c) and 4(d), respectively. Without C540, the cohost device exhibits a half-life of 1100 h while the C540-doped one approaches 1800 h. One of the reasons for lengthening the lifetime can be attributed to the reduction of accumulated positive charge near the NPD/Alq₃-based EML interface. Previous current-voltage modeling on the TPD/Alq₃ bilayer device predicts that the amount of accumulated positive charges along the TPD/Alq₃ interface can be minimized by either reducing the electron injection barrier or increasing the electron mobility of the ETL.[25] As a result, a better charge balance can be achieved in the device, leading to an extended lifetime.

In summary, we demonstrated that engineering the bulk mobility of the electron transporting layer is essential to enhance the device luminous efficiency and lifetime in addition to engineering the charge injection. By a proper selection of electron transporting cohost system, electron trapping can be minimized, establishing mixed/exchange transport manifolds.

[1]C. W. Tang and S. A. Van Slyke, Appl. Phys. Lett. **51**, 913 (1987).
[2]H. H. Fong, K. C. Lun, and S. K. So, Jpn. J. Appl. Phys., Part 2 **41**, L1122 (2002).
[3]S. C. Tse, H. H. Fong, and S. K. So, J. Appl. Phys. **94**, 2033 (2003).
[4]H. Aziz, Z. D. Popovic, N. X. Hu, A. M. Hor, and G. Xu, Science **283**, 1900 (1999).
[5]Z. D. Popovic, H. Aziz, N. X. Hu, A. Ioannidis, and P. N. M. dos Anjos, J. Appl. Phys. **89**, 4673 (2001).
[6]S. A. Van Slyke, C. H. Chen, and C. W. Tang, Appl. Phys. Lett. **69**, 2160 (1996).
[7]H. Aziz and Z. D. Popovic, Appl. Phys. Lett. **80**, 2180 (2002).
[8]H. H. Fong, K. C. Lun, and S. K. So, Chem. Phys. Lett. **353**, 407 (2002).
[9]C. H. Liao, M.-T. Lee, C.-H. Tsai, and C. H. Chen, Appl. Phys. Lett. **86**, 203507 (2005).
[10]S. Naka, H. Okada, H. Onnagawa, and T. Tsutsui, Appl. Phys. Lett. **76**, 197 (2000).
[11]H. Tokuhisa, M. Era, T. Tsutsui, and S. Saito, Appl. Phys. Lett. **66**, 3433 (1995).
[12]J. Kido and T. Matsumoto, Appl. Phys. Lett. **73**, 2866 (1998).
[13]H. H. Fong, S. C. Tse, and S. K. So, We-03–05, Conference Proceedings for International Display Manufacturing Conference 2003 (IDMC 2003).
[14]W. C. H. Choy, H. H. Fong, K. N. Hui, and Y. J. Liang, SPIE's Proceedings, San Diego, CA, **5937**, 593721 (2005).
[15]W. Brütting, S. Berleb, and A. G. Mückl, Org. Electron. **2**, 1 (2001).
[16]H. H. Fong, Ph.D. thesis, Hong Kong Baptist University, 2004.
[17]C. W. Tang, S. A. VanSlyke, and C. H. Chen, J. Appl. Phys. **65**, 3610 (1989).
[18]K. Yamashita, J. Futenma, T. Mori, and T. Mizutani, Synth. Met. **111**, 87 (2000).
[19]C. H. Chen and C. W. Tang, Appl. Phys. Lett. **79**, 3711 (2001).
[20]W. C. H. Choy, H. H. Fong, K. N. Hui, Y. J. Liang, and P. C. Chui, Thin Solid Films (to be published).
[21]K. Naito and A. Miura, J. Phys. Chem. **97**, 6240 (1993).
[22]G. He, M. Pfeiifer, K. Leo, M. Hofmann, J. Birnstock, R. Pudzich, and J. Salbeck, Appl. Phys. Lett. **85**, 3911 (2004).
[23]M.-T. Lee, C.-K. Yen, W.-P Yang, H.-H. Chen, C.-H. Liao, C.-H. Tsai, and C. H. Chen, Org. Lett. **6**, 1241 (2004).
[24]M. Stößel, J. Staudigel, F. Steuber, J. Blässing, J. Simmerer, and A. Winnacker, Appl. Phys. Lett. **76**, 115 (2000).
[25]M. Matsumura, A. Ito, and Y. Miyamae, Appl. Phys. Lett. **75**, 1042 (1999).