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<td>Fong Wallace, HH; Choy, CH; Hui, KN; Liang, YJ</td>
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Organic light-emitting diodes based on a cohost electron transporting composite
H. H. Fong,a) Wallace C. H. Choy,b) K. N. Hui, and Y. J. Liang
Department of Electrical and Electronic Engineering, The University of Hong Kong, Pokfulam Road,
Hong Kong, China
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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
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Tris (8-hydroxyquinoline) aluminum (Alq3), 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 diodes (OLEDs) by Tang et al.1 However, due to its low electron mobility of
10−6 cm2 V−1 s−1 and intrinsic degradation,2,3 Alq3 is responsible for the undesirable voltage drop appearing in
Alq3-based devices. Consequently, the device operating lifet ime of Alq3-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 Alq3 electron transporting layer (ETL).4 Experimental evidence strongly suggested that the excess
amount of holes generate nonemissive cationic species and fluorescence quenchers in the Alq3.4,5

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.5–9 Alternatively, increasing the electron conduction in the ETL sounds like a more prom-
ising 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 materi-
als such as phanthenaline and oxadiazole compounds have been suggested for replacing Alq3 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 en-
hance 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 cm2 V−1 s−1.10 The electron mobility of 10 wt % BPhen-doped Alq3 can be improved for five
times as compared to that of the pristine Alq3 ETL.13 It is thus suggested that BPhen is presumably suitable for
cohosting.

Device fabrication followed the standard procedures, as described elsewhere.14 Alq3, purchased from Tokyo Kasei
Kogyo Co. Ltd., was used as an ETL and light-emitting layer/host and its electron mobility was verified15,16 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 dif-
ferent configurations of ETL have been prepared: (i) device A—Alq3; (ii) device B—BPhen; and (iii) device C—n wt %
BPhen-mixed Alq3, 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: Alq3; B: BPhen; C: n wt % BPhen-doped Alq3)/LiF (0.5 nm)/Al (150 nm).
The coating rates of two ET hosts, Alq3 and BPhen were ~1 Å/s. The 20 nm of Alq3 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 Alq3 as the ETL (device A), the efficiency is ~3 cd/A at 20 mA/cm2, 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, Alq3 electron mobility is
~10−6 cm2 V−1 s−1 while that of BPhen is ~5

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a)Present address: Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853-1501; electronic mail: hhf4@cornell.edu
b)Author to whom correspondence should be addressed; electronic mail: chchy@eee.hku.hk

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The electron drift mobility difference between BPhen and Alq₃ 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:Alq₃ cohost ETL. Figure 1 also shows the corresponding driving voltage for the whole series of devices operated at a current of 20 mA/cm². 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 Alq₃ 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 Alq₃ after 10 wt % of BPhen doping. The overall device performance approaches to a maximum efficiency when the Alq₃ layer is beyond 50 wt %. Practically, the ETL containing a pristine or heavily doped BPhen would encounter recrystallization that is unfavorable. Thus, we will further focus on comparison between a pristine Alq₃ and a 50 wt % BPhen: Alq₃ cohost ETL.

The current-voltage-luminance characteristics among different ETLs are compared as follows: device A—a single Alq₃ host, and device C—a 50 wt % BPhen: Alq₃ c-ETL. Their device performances are shown in Figs. 2(a) and 2(b), respectively. As shown in Fig. 2(a), the driving voltage required for the device operating at a current of 20 mA/cm² is lowered from 14.3 to 10.8 V after introducing a BPhen: Alq₃ c-ETL. The corresponding luminance increases from ~580 to 760 cd/m², (see in Fig. 2(b)). Without thickness optimization, the maximum luminance of the c-ETL device is over 16 000 cd/m² under a current of 475 mA/cm² (at 18 V) which is ~73% higher than that of the single Alq₃ host device. The CIE coordinates of the C540-doped devices generally retain (0.29, 0.63) that is consistent to emission of C540-doped Alq₃ device.

The advantage of using BPhen: Alq₃ 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 Alq₃. The LUMO-LUMO difference between BPhen and Alq₃ is negligible, subject to their similar LUMOs, i.e., ~3 eV. 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 Alq₃ does ignorably participate as an electron trap in BPhen-rich samples. On the contrary, it is likely that a large energetic disorder of Alq₃ contributes to electron hopping from Alq₃ to BPhen when BPhen dominates the cohost. The electric field dependence on the drift mobility can be phenomenologically described by the Poole-Frenkel (PF)-like slope, β. Both pristine (BPhen or Alq₃) films and a 10 wt % BPhen: Alq₃ film show similar PF dependence, β = 6−7 × 10⁻⁴ (cm V⁻¹ s⁻¹), implying that electron hopping among BPhen and Alq₃ sites is favorable in the cohost.

To examine the device applicability employing the concept of electron transporting cohost, devices A (single host) and C with equally weighted BPhen: Alq₃ cohost are compared systematically in Fig. 3. The typical Alq₃ 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. Replacing the ETL by 50 wt % BPhen: Alq₃, the efficiency is then shifted 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/m² can be achieved in 2 wt % C540-doped device with a 50 wt % BPhen: Alq₃ ETL, without further optimizations in doping and layers’ thicknesses.
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[1]pyrano[6,7,8-ij] quinolizin-11-one (C545T) which is often used to replace the C540. 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. 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, 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. 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 ETL 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. 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.

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