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Citation: AIP Advances **2**, 012192 (2012); doi: 10.1063/1.3701685
View online: http://dx.doi.org/10.1063/1.3701685
View Table of Contents: http://scitation.aip.org/content/aip/journal/adva/2/1?ver=pdfcov
Published by the AIP Publishing

AIP ADVANCES **2**, 012192 (2012)

Graded-host phosphorescent light-emitting diodes with high efficiency and reduced roll-off

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(Received 4 October 2011; accepted 9 March 2012; published online 29 March 2012)

We demonstrated graded-host phosphorescent organic light-emitting diodes with high efficiency and reduced efficiency roll-off. The emissive layer of the graded host device consists of both electron and hole transport type hosts, 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBI) and 4,4′,4″-tris(N-carbazolyl)triphenylamine, respectively, with graded composition, and the phosphorescent red emitter bis(2-phenylquinoline) (acetylacetonate) iridium(III), which was uniformly doped into the graded host matrix. The graded host device shows improved quantum efficiency and power efficiency with significantly reduced efficiency roll-off as compared to the unipolar-host and double layer heterojunction host devices. *Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License*. [http://dx.doi.org/10.1063/1.3701685]

Organic light-emitting diodes (OLEDs) are regarded as one of the most promising technology platforms for next generation flat panel displays and solid state lighting owing to their potential for low power consumption, large area fabrication, low manufacturing cost, ease of processing and compatibility with flexible substrates.[1,2] Since the demonstration of nearly unity internal quantum efficiency (IQE) using phosphorescent materials,[3] phosphorescent organic light-emitting diodes (PHOLEDs) have attracted great attention thanks to their capability to harvest both singlet and triplet excitons. However, the efficiency of the PHOLED at high current density tends to decrease because of the triplet-triplet annihilation (TTA) originating from the long triplet excited state lifetime and narrow recombination zone.[4]

There are many reports of previous studies that investigated the origin of efficiency roll-off and recombination zone distribution within the emission layer (EML),[4–6] and corresponding strategies to broaden the recombination zone and reduce the TTA at high luminance.[6–13] Recently, Padmaperuma *et al.* have shifted the location of the recombination zone from the hole transport layer interface to the electron transport layer interface within the EML by chemical modification of the phosphine oxide-based host molecules, such that the transport property of the matrix material was changed.[6] Other than the approach of chemically modifying the materials, Lee *et al.* doped the charge transport material into the host-dopant matrix.[11] By using the composite emitter approach, Lee *et al.* tuned the charge transport properties of the host matrix and achieved a significantly higher current efficiency (2.5 times larger than conventional devices) at a current density of 20 mA/cm^2, Lee *et al.* proposed

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that good charge injection and transport of both electrons and holes within the EML were the reasons for the better performance. Also, Chu *et al.* reported a high efficiency and reduced efficiency roll-off in blue and white PHOLEDs based on a mixed host structure using one electron transport type host and one hole transport type host.[12,13] By carefully controling the mixed host concentration, Chu *et al.* achieved a peak external quantum efficiency (EQE) of 21.6% and a power efficiency of 44.9 lm/W for the blue device, while a power efficiency of 37 lm/W was realized for the white PHOLED at a luminance level of 1000 cd/m^2. Here the much higher efficiency and reduced efficiency roll-off were attributed to increased charge injection and reduced TTA because of effective distribution of recombination zone. Despite the large performance improvement of the mixed host device as compared to a single host device, however, a significant charge leakage may occur if a proper charge confinement layer is not used, since a steady charge transport path exists within the EML.[14]

In this letter, we present the utilization of a graded-host (G-host) structure to achieve high efficiency red PHOLEDs while enabling a decreased operating voltage, improved efficiency and reduced efficiency roll-off. The EML of the G-host was fabricated in such a way that the concentration of the hole transport type host was uniformly decreased towards the electron transport layer (ETL) side, whereas the concentration of the electron transport type host was decreased uniformly towards the hole transport layer (HTL) side. The improved charge transport and self-confinement characteristics within the G-host structures allow for an effective distribution of the recombination zone and efficient charge confinement within the EML.

The device configuration used in this study was ITO substrate/molybdenum trioxide (MoO_3) (5 nm)/4,4′,4″-tris(N-carbazolyl)triphenylamine (TCTA) : molybdenum trioxide (40 nm)/4,4′,4″-tris(N-carbazolyl)triphenylamine (TCTA) (10 nm)/Host : bis(2-phenylquinoline) (acetylacetonate) iridium(III) (Ir(2-phq)$_2$(acac)) (5%, 30 nm)/1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBI) (10 nm)/1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBI) : Cs (40 nm)/Al (100nm), where MoO_3 was used as the hole injection layer (HIL), MoO_3 doped TCTA was used as the hole transport layer (HTL), the host doped with 5% Ir(2-phq)$_2$(acac) was the EML, Cs doped TPBI was used as the electron transport layer (ETL), the intrinsic TCTA and TPBI layers were used as the spacer to avoid the diffusion of dopants from the transport layers into the EML. The corresponding device structure, graded host composition and proposed energy diagram are shown in Fig. 1, using the values of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) from literature.[15,16] The conventional single host devices in this work utilized TCTA for the hole transport type host or TPBI for the electron transport type host, both doped with 5% Ir(2-phq)$_2$(acac). On the other hand, the G-host device utilized both TCTA and TPBI hosts, with the TCTA concentration decreasing uniformly from 100% at the TCTA spacer/host interface to 0% at the host/TPBI spacer interface, and the concentration of TPBI decreasing uniformly from 100% at the host/TPBI spacer interface to 0% at the TCTA spacer/host interface in a complimentary fasion.

The OLEDs were fabricated on glass substrates with an ITO film thickness of 120 nm and a sheet resistance of 10 Ω/square. The substrates were firstly cleaned using detergent (Decon 90), rinsed in DI water and subsequently ultrasonicated in acetone and IPA for 30 min, respectively. After drying in oven, the substrates were treated by O_2 plasma for 2.5 min, and then loaded into the deposition chamber (with base pressure $< 7\times10^{-7}$ torr) for material deposition. The electroluminescence (EL) spectra of the fabricated devices were measured using a PR650 Spectra Scan spectrometer, while the luminance-current density-voltage (L-J-V) characteristics were obtained from the spectrometer and the Yogakawa source measurement unit. All measurements were carried out at room temperature under ambient conditions without encapsulation.

To have a better understanding of the G-host device, we first compare it with the single host devices. The normalized electroluminescence (EL) spectra of the devices with TCTA host, TPBI host, and G-host at a current density of 0.07 mA/cm^2 are shown in Fig. 2(a). The emission spectra all show a peak emission wavelength at 600 nm, which is the characteristic emission peak for Ir(2-phq)$_2$(acac). There is no difference among the three emission spectra, which implies that there is no emission contributed from the host material (i.e., no host emission). The current density-voltage-luminance (L-I-V) characteristics of the G-host and single host devices are shown in Fig. 2(b). Compared to the single host device, the G-host device shows the largest current density. This is understandable since TCTA is a good hole transport material and TPBI is a good electron

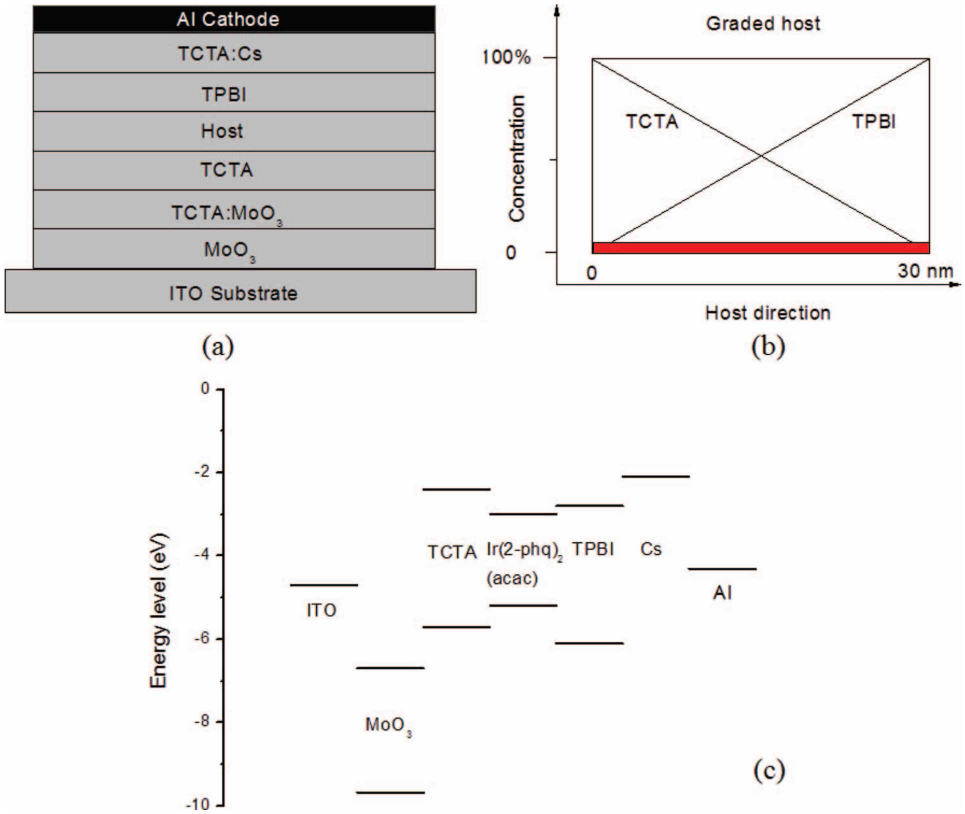

FIG. 1. (a) Device structure with layer compositions, (b) illustration of graded hosts with uniformly varying host concentration, and (c) proposed energy diagram with HOMO-LUMO values available in the literature.

transport material. The electron and hole injection and transport in the G-host are, therefore, very efficient and, as a result, both electrons and holes contribute to the total current density in the G-host device.[16] Furthermore, the elimination of energy barriers at the transport layer/EML interfaces helps to further reduce the applied voltage. The device with the TCTA host yields a higher current density compared to the TPBI host device, which indicates a better hole transport ability of the TCTA (hole mobility approximately 10^{-4} cm^2/Vs) than the electron transport ability of the TPBI (electron mobility approximately 10^{-5} cm^2/Vs).[17] Because of efficient injection of both electrons and holes within the EML of the G-host device, the luminance of the G-host device is the largest. We also observe that the TCTA host device shows a smaller luminance level compared to the TPBI device. For the TCTA host device, because of the hole transport nature of the host, the recombination zone is located at the TCTA/TPBI interface, although both carriers face similar barriers of 0.4 eV (Fig. 1), the hole mobility of TCTA is larger than the electron mobility of TPBI. Therefore, some hole carriers may overcome the barrier more easily and recombine with electrons in the TPBI spacer region, where they are likely to be quenched by the doped ETL,[5] resulting in lower luminance level.

As compared to the single host devices, we observe a large increase in the device efficiency in the G-host device (Fig. 3). The improved efficiency and reduced efficiency roll-off (which can be observed by the normalized luminance efficiency and power efficiency in the inset of Fig. 3(a) and 3(b), respectively) indicate the charges in the G-host device are more balanced and exciton formation region is more widely distributed. Because of the unipolar charge transport nature of the TCTA and TPBI materials, the exciton formation zone of the single host devices will be located at the EML and transport layer interface. Thus, very high exciton density exists in a narrow zone at the interface, which may induce significant quenching of the triplet excitons, resulting in larger efficiency roll-off.[18,19] Furthermore, the HOMO and LUMO levels of the host matrix material are very important parameters for the charge balance, since electron and hole injections from the neighbouring charge

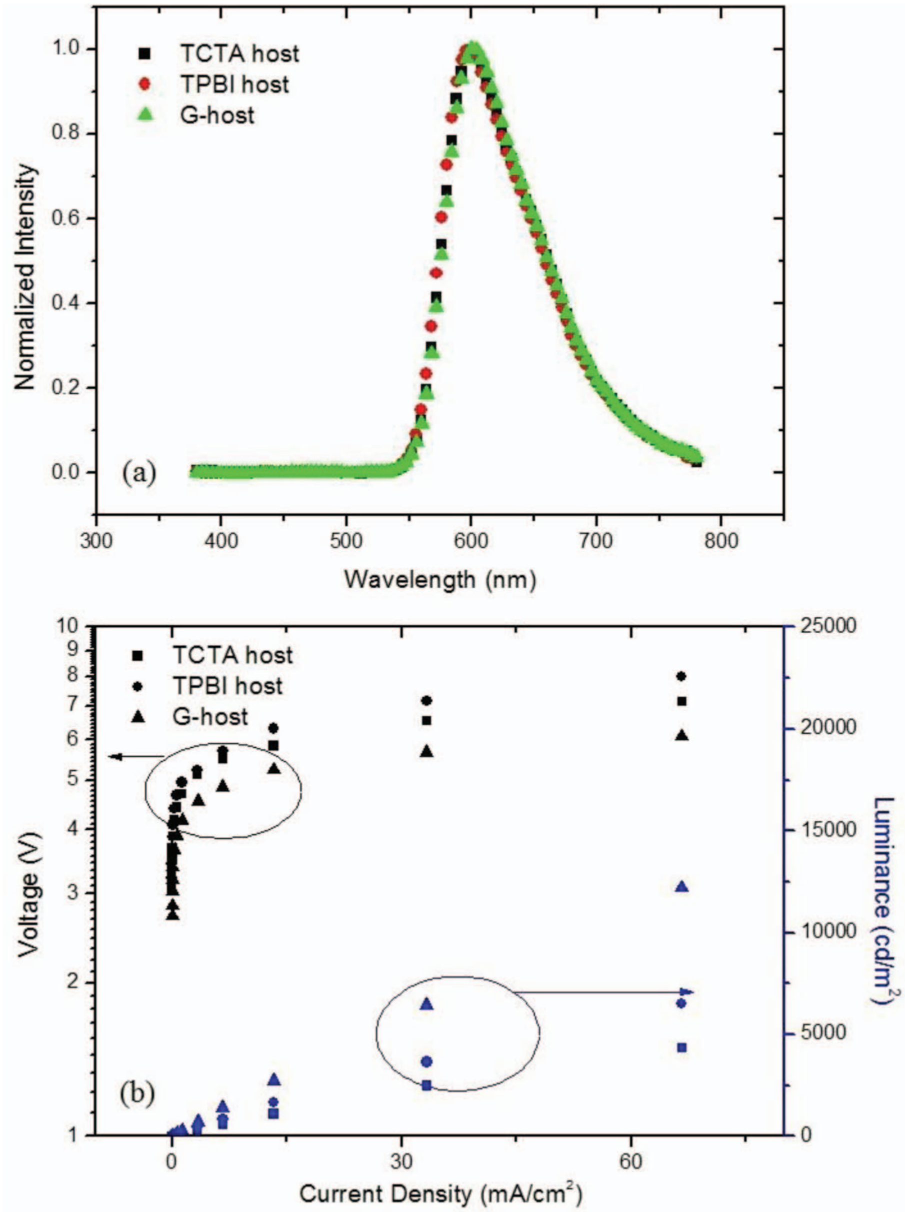

FIG. 2. (a) Electroluminescence spectra for the devices with TCTA hole transport material host, TPBI electron transport material host and graded mixed hosts of TCTA and TPBI (G-host) and (b) current density-voltage-luminance (LIV) characteristics of the three devices.

transport layer are determined by the interfacial energy barrier.[20] For the G-host device, however, the TCTA concentration at the EML/TCTA interface is 100%, and there is no energy barrier to impede hole injection. After holes are injected into the EML, the steady decreasing concentration of hole transport molecules and increasing content of electron transport molecules slow holes down, since the intermolecular distance of the TCTA material is increased and there are fewer hopping sites for holes as they penetrate further towards the ETL side. At the EML/ETL interface, there is no TCTA content and the TPBI concentration is 100%, which implies that hole transport will be minimized at this interface. At the TPBI/EML interface, since TPBI concentration is 100%, the electron injection is very efficient and electrons are steadily slowed down when they hop towards the HTL with decreasing TPBI concentration and the electron transport is minimized at the TCTA/EML interface, where TPBI concentration is 0%. Therefore, somewhere close to the center of the EML,

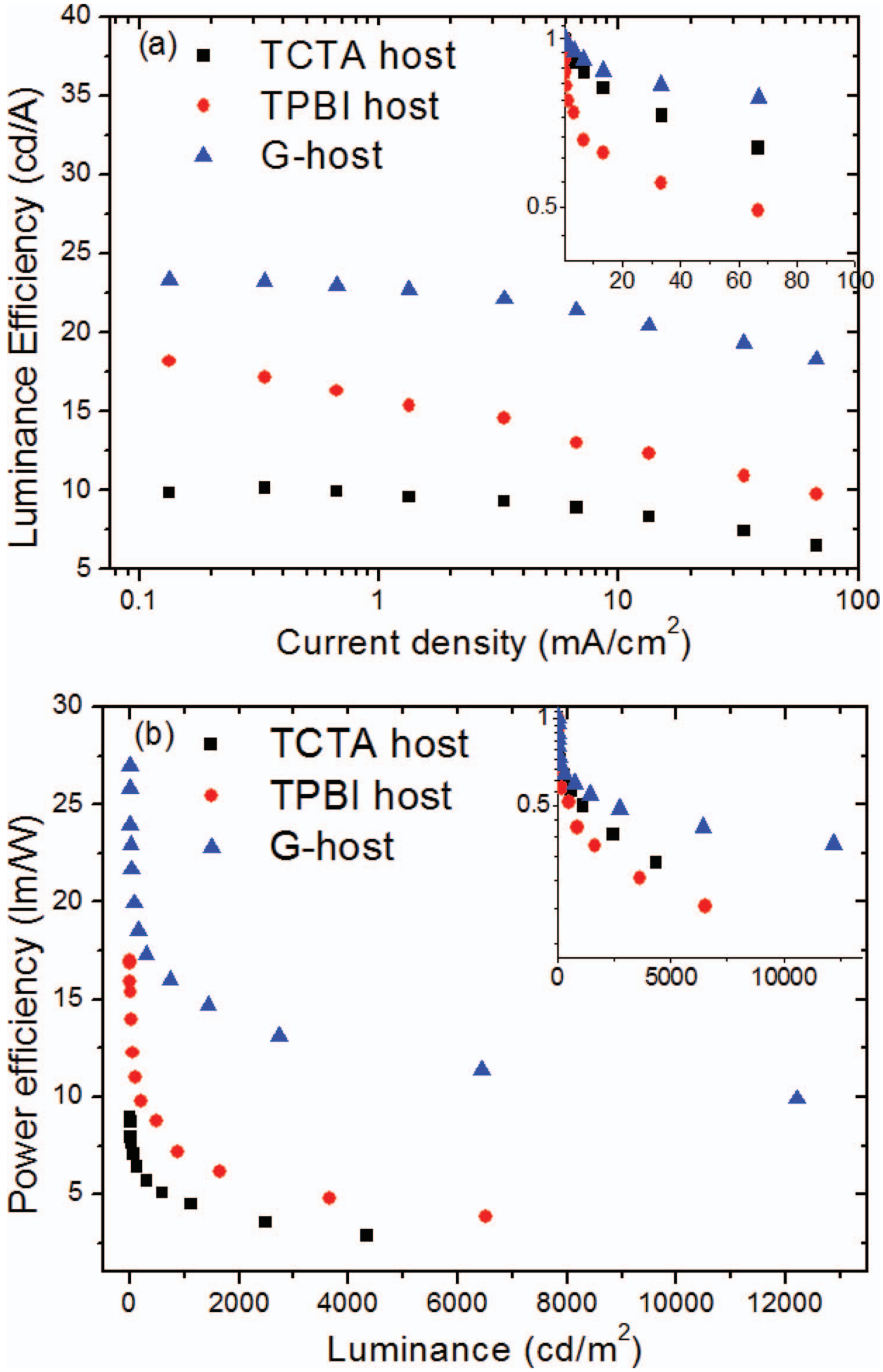

FIG. 3. (a) Luminance efficiency *vs.* current density and (b) power efficiency *vs.* luminance of the devices with TCTA hole transport material host, TPBI electron transport material host and the graded mixed hosts of TCTA and TPBI (G-host). Inset of (a) Normalized luminance efficiency *vs.* current density, inset of (b) Normalized power efficiency *vs.* luminance.

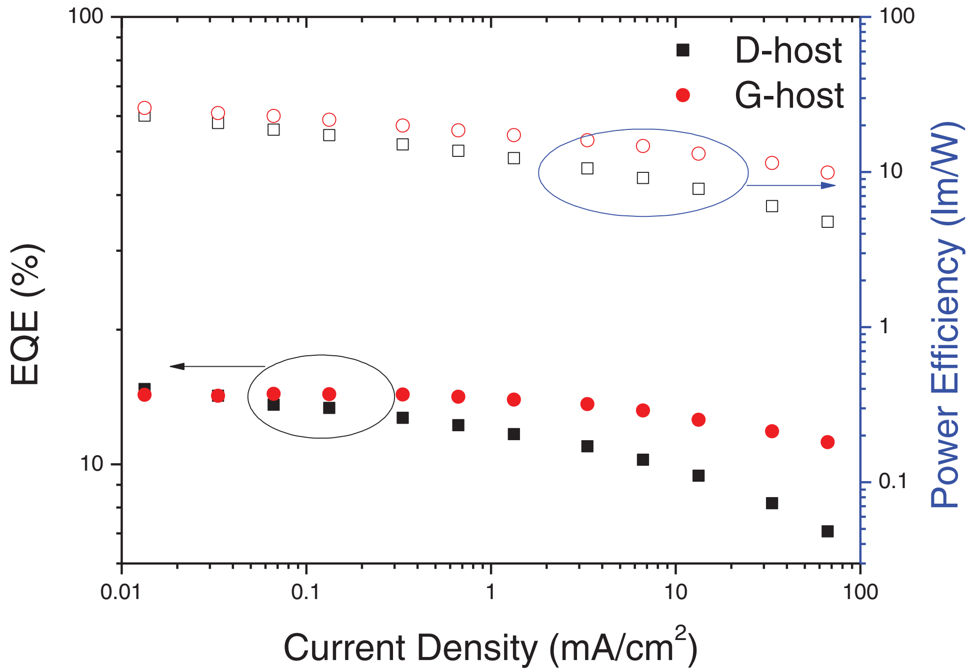

FIG. 4. Comparison of power efficiency and external quantum efficiency (EQE) *vs.* current density between the D-host and G-host devices.

electron and hole concentration will be automatically balanced, and the recombination zone will thus be shifted from the EML/transport layer interface towards the center of the EML. The absence of the sharp interfaces and self-confinement nature of the G-host device enable better charge injection and transport, which effectively broadens the recombination zone. This results in an increased efficiency with reduced efficiency roll-off.

To confirm the effects of the G-host structure on the device performance, we constructed a double layer heterojunction host (D-host) device with a similar structure: ITO/MoO_3 (5 nm)/TCTA:MoO_3 (40 nm)/TCTA (10 nm)/TCTA : Ir(2-phq)$_2$(acac) (5%, 15 nm)/TPBI: Ir(2-phq)$_2$(acac) (5%, 15 nm)/TPBI (10 nm)/TPBI: Cs (40 nm)/Al (100 nm), where TCTA and TPBI both doped with Ir(2-phq)2(acac) are the two host layers and form a sharp interface. The D-host of the device consists of 15 nm TCTA and 15 nm TPBI with uniformly doped Ir(2-phq)$_2$(acac). A comparison of the power efficiency and quantum efficiency of the D-host device with that of the G-host device is shown in Fig. 4, from which we can see that the D-host device has smaller power efficiency and larger efficiency roll-off. The external quantum efficiency of the D-host device decreased from 14.2% at the current density of 0.03 mA/cm^2 to 8% at 30 mA/cm^2, and the efficiency roll-off is more than 40%. For the G-host device, however, the efficiency decreased from 14.2% at the current density of 0.03 mA/cm^2 to 11.8% at 30 mA/cm^2, and the efficiency roll-off is only 16%. The inferior performance of the D-host device is likely due to the narrow recombination zone and poor charge balance. The delocalization of the recombination zone from the interface and self-confining effect allows the G-host device to outperform the D-host device. Although charge trapping may occur in both the G-host device and the D-host device as indicated by the energy level diagram shown in Fig. 1(c), it is not significant as shown by previous studies.[21,22] And our conclusion that the G-host device enhances device performance with reduced efficiencies roll-off is still valid.

In summary, we have fabricated a graded-host device with its EML layer constructed in such a way that the concentration of the hole transport type host was uniformly decreased from the HTL side (100% in concentration) towards the ETL side (0% in concentration), while the concentration of the electron transport type host was decreased uniformly from the ETL side (100% in concentration) towards the HTL side (0% in concentration). The G-host device showed improved device efficiency with reduced efficiency roll-off compared to the unipolar host and double layer heterojunction host devices. The superior performance was attributed to the better charge injection and balance, and widened recombination zone.

This work is supported by Science and Engineering Research Council, Agency for Science, Technology and Research (A-STAR) of Singapore (Project No. 092 101 0057), and National Research Foundation of Singapore under Grant No. NRF-CRP-6-2010-2 and NRF-RF-2009-09.

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