Bottom Emission Organic Light-Emitting Diode with Asymmetric Host and Multiple Resonance Emitter Achieving Blue Index of 253

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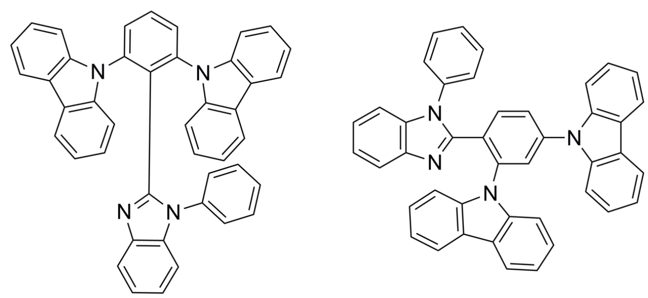
Abstract
We demonstrated a blue MR-OLED using an asymmetric host doped with ν-DABNA-O-Me as the emitting layer achieving maximum current efficiency, power efficiency, and external quantum efficiency of 19.0 cd/A, 20.0 lm/W, and 27.8%, respectively. CIE coordinates of the OLED was (0.130, 0.075) which resulted in blue index of achieving 253 in a conventional bottom emission device structure.

Keywords
blue OLED, bi-EML, high efficiency, asymmetric host

Introduction

For display and lighting applications of organic light-emitting diode (OLED), development of blue light emission is still a bottleneck among three primary colors [1]. Recently, blue multiple resonance (MR) emitters have attracted lots of attentions due to: (1) thermally activated delayed fluorescence (TADF) characteristics for efficient utilization of triplet exciton, (2) high ratio of horizontal-dipole for high light extraction efficiency, and (3) narrow full-width at half maximum (FWHM) for pure blue emission [2,3]. However, it is still challenging to find an appropriate host material, which requires a suitable emission wavelength for overlapping with the absorption spectrum of MR emitter. Besides, energy levels (including highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)) of host and dopant should be match for facilitating carrier transport. In previous reports, sym-DiCbzBz (as shown in **Fig. 1**) exhibited wide bandgap and can be used as the host for blue phosphorescent and TADF OLED, which consisted of two carbazole units at meta positions, and one benzimidazole unit at ortho position, resulting a symmetric configuration. It formed crystallized structure which helped molecular packing and improved light coupling [4,5,6,7]. In this paper, we used an asymmetric host, asym-DiCbzBz (also shown in **Fig. 1**), doped with blue MR emitter, ***ν***-DABNA-O-Me, as the emitting layer (EML) of the OLED, achieving maximum external quantum efficiency (EQE) of 27.8%, spectral peak at 464 nm, CIE of (0.13, 0.07), and blue index of 253 in a bottom-emission structure. In asym-DiCbzBz, two carbazole units were at meta positions, and one benzimidazole unit was at para position, resulting asymmetric configuration. Compared to the symmetric counterpart, sym-DiCbzBz, OLED with asym-DiCbzBz host reduced molecular packing and demonstrated amorphous morphology which inhibited the aggregation of emitters inside the host. Besides, smaller energy bandgap of asym-DiCbzBz improved spectral overlapping with dopant absorption, together with better carrier injection and transport characteristics for the superior device performances.



sym-DiCbzBz asym-DiCbzBz

Figure 1 Molecular structure of sym-DiCbzBz and asym-DiCbzBz.

Experiments
Conventional bottom emission OLED structure was employed in this study. Device was fabricated on a glass substrate with patterned indium-tin-oxide (ITO) as the transparent anode. Prior thin film deposition, ITO was treated with oxygen plasma to clean the surface and improve the workfunction of ITO for facilitating hole-injection. Organic and cathode layers were deposited in a vacuum chamber through thermal evaporation sequentially. Here, we used 4,4'-Cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine] (TAPC) as the hole transporting layer (HTL) material, N, N-dicarbazolyl-3, 5-benzene (mCP) as the exciton blocking layer (EBL) material, Diphenylbis(4-(pyridin-3-yl) phenyl)silane (DPPS) as the electron transporting layer (ETL) material, respectively. LiF and Al were electron injection layer (EIL) and cathode, respectively. The thicknesses of TAPC, mCP, DPPS, LiF, and Al were 50, 10, 40, 0.8, and 120 nm, respectively. 30-nm EML consists of asym-DiCbzBz and sym-DiCbzBz doped with 1% ***ν***-DABNA-O-Me. After thin film deposition, encapsulation process was performed in nitrogen glove box, followed by electrical and optical measurements. Current density vs voltage was recorded by

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source meter (Keithley 2400), while luminance and EL spectrum were obtained by spectrometer (Minolta CS-1000). Angle-dependent photoluminescence (ADPL) was used to understand the horizontal dipole ratio in the EML, and grazing-incident wide-angle x-ray scattering (GIWAXS) was employed to study the molecular packing of the host material.

Result

Fig. 2 and **Table 1** shows the photophysical properties of sym-DiCbzBz and asym-DiCbzBz in thin film form. Compared to sym-DiCbzBz, asym-DiCbzBz exhibited a redshifted absorption and fluorescence spectra which resulted in a smaller singlet excited state (S_1), and it also improved spectral overlapping between asym-DiCbzBz fluorescence and *ν*-DABNA-O-Me absorption. From Photo-electron spectroscopic measurement, HOMO level of asym-DiCbzBz was shallower compared to sym-DiCbzBz which was matched to the HOMO of MR-emitter, *ν*-DABNA-O-Me. Besides, hole and electron mobilities in asym-DiCbzBz were also higher which resulted in better carrier transport. Triplet energy of asym-DiCbzBz (2.9 eV) was not as high as sym-DiCbzBz (3.1 eV), but was still high enough when doping with *ν*-DABNA-O-Me.

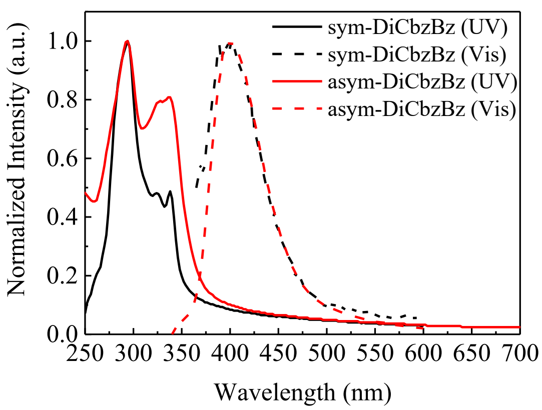

Figure 2 UV-vis spectra of sym-DiCbzBz and asym-DiCbzBz thin films.

Table 1 Photophysical properties of sym-DiCbzBz and asym-DiCbzBz thin films.

	λ_{onset}^{abs} [nm]	λ_{onset}^{FL} [nm]	S_1 [eV]	T_1 [eV]	HOMO [eV]	LUMO [eV]
sym-DiCbzBz	354	341	3.5	3.1	-5.8	-2.2
asym-DiCbzBz	369	359	3.4	2.9	-5.7	-2.3

Fig. 3 shows the electrical and optical characteristics of blue MR-OLED with two different hosts, and **Table 2** summary their device performances. From J-V characteristics in **Fig. 3 (a)**, OLED with asymmetric host (asym-DiCbzBz) showed lower driving voltage compared to symmetric counterpart (sym-DiCbzBz) due to smaller bandgap and higher carrier mobilities. **Fig. 3 (b), (c),** and **(d)** showed the current efficiency, power efficiency, and EQE versus the current density characteristics, and **Fig. 3 (e)** shows the EL spectra of two OLEDs. OLED with sym-DiCbzBz showed higher maximum current efficiency of 20.6 cd/A, and asym-DiCbzBz device showed higher maximum power efficiency and EQE of 20.0 lm/W and 27.8%, respectively. Blueshift of EL peak was observed in asym-DiCbzBz device (464 nm) compared to symmetric OLED (468 nm), which resulted in lower CIE-y value (0.075 vs 0.100). Hence, blue index of two MR-OLED were 206 and 253, respectively, as shown in **Table 2**.

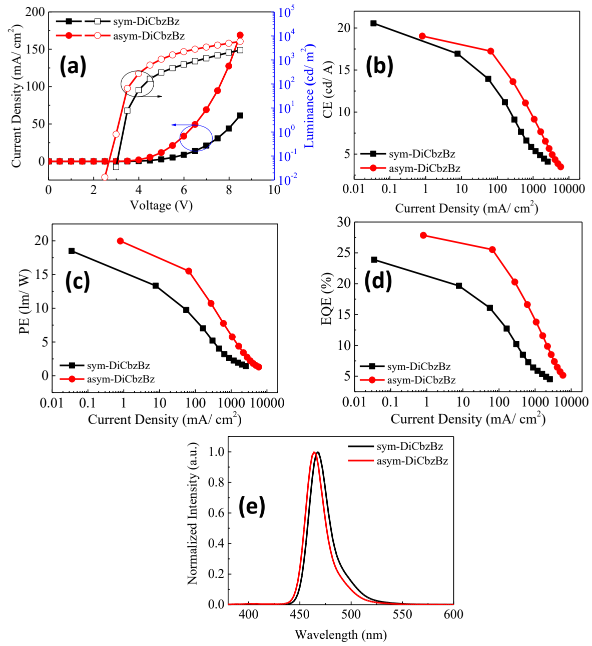

Figure 3 Device performances of blue MR-OLED with sym-DiCbzBz and asym-DiCbzBz hosts: **(a)** current density (J)-luminance (L)- voltage(V) curve, **(b)** CE, **(c)** PE, and **(d)** EQE (%)- versus different current density, and **(e)** normalized EL spectra.

Table 2 EL performance of blue MR-OLED with sym-DiCbzBz and asym-DiCbzBz hosts.

	Voltage@ 1 cd/m² [V]	CE_{max} (cd/A)	PE_{max} (lm/W)	EQE_{max} (%)	EL_{peak} (nm)	CIE	Blue index	Horizontal dipole ratio (%)
sym-DiCbzBz	3.3	20.6	18.5	23.9	468	(0.123, 0.100)	206	91
asym-DiCbzBz	3.0	19.0	20.0	27.8	464	(0.130, 0.075)	253	91

For understanding the horizontal dipole ratio in the EML, ADPL of the doped films (asym-DiCbzBz and sym-DiCbzBz doped with 1% *ν*-DABNA-O-Me) were performed as shown in Fig. 4 (a). 91% horizontal dipole ratio was achieved which improved the light extraction efficiency and EQE. However, interestingly, when measuring the molecular packing of the host-only thin films (asym-DiCbzBz and sym-DiCbzBz) with GIWAXS as shown in Fig. 4 (b), totally different situation was observed. Clear diffraction pattern was observed in sym-DiCbzBz, consistent with the previous report [6]. However, pure amorphous structure was observed in asym-DiCbzBz, which also explained the blue shift of EL spectrum due to suppression of inhomogeneous broadening. Fig. 4 (c) shows the thin films on the glass substrate after storage for 1 year. Clearly, sym-DiCbzBz was crystallized after long term storage, while asym-DiCbzBz thin film has kept amorphous phase which looks like transparent. It also affected the operation lifetime of blue MR-OLED. In our preliminary results, device with asym-DiCbzBz host exhibited 5-times longer lifetime, compared to sym-DiCbzBz counterpart.

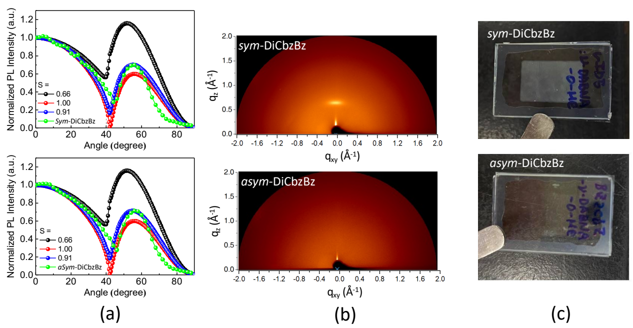

Figure 4 (a) ADPL of sym-DiCbzBz and asym-DiCbzBz thin film doped with *ν*-DABNA-O-Me, (b) GIWAXS sym-DiCbzBz and asym-DiCbzBz thin film, and (c) photos of sym-DiCbzBz and asym-DiCbzBz thin film after 1-year storage.

Impact

We have introduced an asymmetric material as the host of the blue MR-OLED which achieved EQE of 27.8%, together with blue index of 253. Thin film of this asymmetric host exhibited redshift spectra which improved energy transfer to MR emitter and reduced driving voltage. Amorphous morphology of the thin film suppressed inhomogeneous broadening which blueshifted the EL spectra and elongated the operation lifetime.

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