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Benzimidazole–carbazole-based bipolar hosts for high efficiency blue and white electrophosphorescence applications

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Received 21st March 2012, Accepted 24th April 2012 DOI: 10.1039/c2jm31765f

A series of novel bipolar blue phosphorescent host materials **mBICP**, **mBINCP** and **mBIPhCP** have been designed and synthesized, which comprehensively outperform the widely used phosphorescent host, 1,3-di(9*H*-carbazol-9-yl)benzene (**mCP**). The thermal, photophysical and electrochemical properties of these host materials were finely tuned through linking different carbazole moieties to the benzimidazole. **mBICP** ($T_g = 84 \,^{\circ}$ C) and **mBIPhCP** ($T_g = 103 \,^{\circ}$ C) exhibit high morphological stabilities in comparison with **mCP**. Theoretical calculations show that the HOMO/LUMO orbitals of these materials are mainly dispersed on the electron donating and electron accepting groups, respectively. A blue PhOLED device fabricated using **mBICP** as the host exhibits a maximum external quantum efficiency ($\eta_{EQE,max}$) of 18.7% and a maximum power efficiency ($\eta_{P,max}$) of 33.6 lm W⁻¹. Interestingly, the external quantum efficiencies (η_{EQE}) are still as high as 17.1% at a high luminance of 1000 cd m⁻². Furthermore, the two-color, all-phosphor and single-emitting-layer white device hosted by **mBICP** achieved a maximum external quantum efficiency ($\eta_{EQE,max}$) of 20.5% corresponding to a maximum power efficiency ($\eta_{P,max}$) of 53.3 lm W⁻¹.

1. Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs) have attracted much attention because they can approach 100% internal quantum efficiency by utilizing both singlet and triplet excitons when they incorporate organometallic complexes as triplet emitters.¹⁻⁴ To date, red and green phosphorescent electroluminescent devices with high efficiencies, long lifetimes, and proper CIE coordinates have been well developed.⁵⁻⁷ However, highly stable and efficient blue PhOLEDs are still rare. As the host for blue OLED devices, the following aspects need to be considered: (i) higher triplet energy than photon energies of blue light ($\geq 2.7 \text{ eV}$), preventing a reverse energy transfer, (ii) HOMO/LUMO levels match with the neighboring functional layers, reducing charge carriers injection barrier into the emitting layer and (iii) bipolar transporting characteristics, to increase the electron and hole recombination ratio in the emitting layer.

Based on these issues, a few of bipolar hosts⁸⁻¹¹ capable of hosting phosphors have been developed. For example, Lee

et al.¹² synthesized carbazole-diphenylphosphine hybrids (mCPPO1), in which the introduction of PO and carbazole units simultaneously endowed the material with bipolar charge transport properties, and the external quantum efficiency of bis((3,5-difluoro-4-cyanophenyl)pyridine) iridium picolinate (FCNIrpic)-doped blue PhOLEDs was enhanced to 25.4%. Cheng reported another carbazole-phosphine oxide hybrid (BCPO) with a high T_g of 137 °C and high E_T of 3.01 eV.¹³ BCPO was applied as a host for FIrpic, which exhibited a low turn-on voltage of 2.8 V and a maximum external quantum efficiency of 23.5%. Recently, Gong et al.13 introduced a benzimidazole and diphenylamine into a tetraphenylsilicon skeleton to form a bipolar host, a device with p-BISiTPA as a host shows excellent performance, with external quantum efficiency as high as 16.1% for blue, and 19.1% for WOLED. All of these efficient blue bipolar hosts have great potential application in practical PhO-LEDs. Nevertheless, efficient PhOLED host materials still require further developments.

Generally, there are two methods for designing high triplet energy bipolar hosts for blue PhOLEDs, one approach is to apply extremely high triplet energy units to constitute the molecules.¹⁴⁻¹⁶ The other way is to limit the extent of conjugation between groups.¹⁷⁻¹⁹ Groups with high triplet energies usually possess small steric volumes and the bipolar hosts built with them often exhibit low thermal and bad morphological stabilities.²⁰ Thus, in this study, the compromises between the two methods were adopted to design blue bipolar host materials. Hole-transporting carbazole groups²¹⁻²³ and electron-transporting

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benzimidazole groups,^{9,23–25} which all possess relatively high triplet energies, were selected for the construction of the novel bipolar compounds. As the carbazole units are linked to the benzimidazole segment *via* the *meta*-position of the C2-phenyl, the target molecules are highly nonplanar and have minimal donor–acceptor interactions. As a result, all the new blue hosts keep high triplet energies in a range of 2.7–3.0 eV, which enable their applications as hosts for blue phosphorescent dopants. Blue PhOLED hosts doped with iridium(III) bis[2-(4',6'-diffuorophenyl)-pyridinato-*N*,*C*(2')]-picolinate (FIrpic) were fabricated and these showed excellent performances. Meanwhile, the twocolor, all-phosphor and single-emitting-layer white device hosted by these new materials were also fabricated, and achieved a maximum external quantum efficiency ($\eta_{EQE,max}$) of 20.5% and a maximum power efficiency ($\eta_{P,max}$) of 53.3 lm W⁻¹.

2. Experimental section

2.1. General information

All solvents and materials were used as received from commercial suppliers without further purification. ¹H NMR and ¹³C NMR spectra were measured on a Bruker-AF301 AT 400 MHz spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on an Elementar (Vario Micro cube) analyzer. Mass spectra were carried out on an Agilent (1100 LC/MSD Trap) using ACPI ionization. UV-Vis absorption spectra were recorded on a Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600). PL spectra were recorded on Edinburgh instruments (FLSP920 spectrometers). Differential scanning calorimetry (DSC) was performed on a PE Instruments DSC 2920 unit at a heating rate of 10 °C min⁻¹ from 30 to 250 °C under nitrogen. The glass transition temperature (T_g) was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken with a PerkinElmer Instrument (Pyris1 TGA). The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 °C min⁻¹ from 30 to 700 °C. Cyclic voltammetry measurements were carried out in a conventional three-electrode cell using a Pt button working electrode of 2 mm in diameter, a platinum wire counter electrode, and an Ag/AgNO₃ (0.1 M) reference electrode on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature. Reductions CV of all compounds were performed in dichloromethane containing 0.1 M tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram.

2.2. Computational details

The geometrical and electronic properties were performed with the Amsterdam Density Functional (ADF) 2009.01 program package. The calculation was optimized by means of the B3LYP (Becke three parameters hybrid functional with Lee–Yang–Perdew correlation functionals)^{26,27} with the 6-31G(d) atomic basis set. Then the electronic structures were calculated at the τ -HCTHhyb/6–311++G(d, p) level.²⁸ Molecular orbitals were visualized using ADF view.

2.3. Device fabrication and measurement

The EL devices were fabricated by vacuum deposition of the materials at a base pressure of 5×10^{-6} Torr onto glass precoated with a layer of indium tin oxide (ITO) with a sheet resistance of 20 Ω per square and transmissivity of 80% in blue light. Before deposition of an organic layer, the clear ITO substrates were treated with oxygen plasma for 5 min. The deposition rate of organic compounds was 0.9–1.1 Å s⁻¹. Finally, a cathode composed of LiF (1 nm) and aluminium (100 nm) was sequentially deposited onto the substrate in the vacuum of 10^{-5} Torr. The *L*–*V*–*J* of the devices was measured with a Keithley 2400 Source meter and PR655. All measurements were carried out at room temperature under ambient conditions.

2.4. Synthesis

9-(3-(1-Phenyl-1H-benzold)imidazol-2-yl)phenyl)-9H-carbazole (mBICP). A mixture of 2-(3-bromophenyl)-1-phenyl-1H-benzo [d]imidazole (1.39 g, 4.00 mmol), carbazole (0.75 g, 4.50 mmol), CuI (23 mg, 0.12 mmol), 18-crown-6 (32 mg, 0.12 mmol), K₂CO₃ (2.76 g, 20 mmol), and DMPU (2.0 mL) was refluxed under nitrogen for 48 h. After cooling, the mixture was extracted with CH₂Cl₂ and washed with the dilute HCl solution, and then the organic layer was dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel using CH₂Cl₂ as the eluent to give a white powder. Yield: 88%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.09– 8.07 (m, 2H), 7.92-7.90 (m, 2H), 7.65-7.57 (m, 6H), 7.41-7.23 (m, 9H), 7.01–6.99 (d, J = 8.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ [ppm]: 151.55, 142.93, 140.48, 137.61, 137.31, 136.81, 131.98, 130.30, 128.77, 128.55, 127.95, 127.54, 125.98, 123.73, 123.37, 123.27, 120.20, 120.05, 110.58, 109.55. MS (APCI): m/z 436.1 $[M + H]^+$. Anal. calcd for $C_{31}H_{21}N_3$ (%): C 85.34, H 4.93, N 9.73; found: C 85.36, H 4.94, N 9.70.

5-(3-(1-Phenyl-1*H***-benzo[***d***]imidazol-2-yl)phenyl)-5***H***-pyrido [4,3-***b***]indole (mBINCP). The compound 2** was prepared according to the same procedure as the compound **1** but using 5*H*-pyrido[4,3-*b*]indole instead of carbazole. Yield: 85%. ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 9.33 (s, 1H), 8.43–8.41 (d, *J* = 6.0 Hz, 1H), 8.17–8.15 (m, 1H), 7.96–7.90 (m, 2H), 7.68–7.56 (m, 6H), 7.42–7.26 (m, 7H), 7.10–7.08 (d, *J* = 7.6 Hz, 1H), 6.85–6.84 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 151.11, 145.43, 144.57, 142.96, 142.92, 140.50, 137.38, 136.83, 136.35, 132.34, 130.49, 130.37, 129.24, 128.89, 127.58, 127.51, 127.07, 123.86, 123.34, 121.73, 121.53, 120.64, 120.09, 110.59, 110.06, 104.79. MS (APCI): *m/z* 437.1 [M + H]⁺. Anal. calcd for C₃₀H₂₀N₄ (%): C 82.55, H 4.62, N 12.84; found: C 82.52, H 4.63, N 12.85.

9-Phenyl-3-(3-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)-9*H*-carbazole (mBIPhCP). A mixture of 2-(3-bromophenyl)-1-phenyl-1*H*-benzo[*d*]imidazole (1.04 g, 3.00 mmol), 9-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (1.29 g, 3.50 mmol), Pd(PPh₃)₄ (173 mg, 0.15 mmol), 2 M aqueous sodium carbonate solution (10 mL), and toluene (50 mL) and ethanol (25 mL) was stirred under reflux for 24 h. The mixture was cooled to room temperature and saturated (sat.) ammonium chloride solution (50 mL) was added, the mixture

was extracted with CH₂Cl₂, after removal of the solvent, the residue was purified by column chromatography on silica gel using CH₂Cl₂ as the eluent to give a white powder. Yield: 92%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.17–8.15 (d, J = 7.6 Hz, 1H), 8.06 (s, 1H), 7.96–7.94 (d, J = 7.6 Hz, 1H), 7.86 (s, 1H), 7.71–7.69 (d, J = 7.6 Hz, 1H), 7.66–7.56 (m, 8H), 7.50–7.29 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ [ppm]: 152.47, 143.06, 141.84, 141.36, 140.48, 137.59, 137.36, 137.29, 132.52, 130.25, 130.05, 129.96, 128.90, 128.63, 128.39, 128.31, 127.72, 127.68, 127.59, 127.09, 126.21, 125.33, 123.85, 123.43, 123.08, 120.36, 120.15, 119.93, 118.85, 110.50, 109.99, 109.97. MS (APCI): *m/z* 512.3 [M + H]⁺. Anal. calcd for C₃₇H₂₅N₃ (%): C 86.83, H 4.94, N 8.23; found: C 86.85, H 4.90, N 8.25.

3. Results and discussion

3.1. Synthesis and characterization

The bipolar molecules were synthesized by the Ullman & Suzuki Coupling reaction in one step. The synthetic routes and chemical structures of compounds, **mBICP**, **mBINCP** and **mBIPhCP** are depicted in Scheme 1.

The intermediate 2-(3-bromophenyl)-1-phenyl-1*H*-benzo[*d*] imidazole, 5*H*-pyrido[4,3-*b*]indole and 9-phenyl-3-(4,4,5,5-tetra-methyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole were synthesized according to the literature.^{29,30} For the compounds **mBICP** and **mBINCP**, the electron-donating carbazole moiety was introduced into the withdrawing benzimidazole segment through the



Scheme 1 Synthesis routes of the compounds mBICP, mBINCP and mBIPhCP.

copper(1)-catalyzed C–N coupling at *meta*-position in good yields (88% and 85%, respectively), and for the compound **mBIPhCP**, the carbazole moiety was linked by the Pd-catalyzed Suzuki coupling reaction in a very good yield (92%). All the target materials were further purified by repeated temperaturegradient vacuum sublimation. The chemical structures of the compounds **mBICP**, **mBINCP** and **mBIPhCP** were fully characterized by ¹H NMR and ¹³C NMR spectroscopies, mass spectrometry and elemental analysis.

3.2. Thermal properties

The thermal properties of compounds mBICP, mBINCP and **mBIPhCP** were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. 1). Key thermal data of these compounds are listed in Table 1. The compounds mBICP and mBIPhCP exhibit relatively high glass transition temperatures (T_{o}) at 84 °C and 103 °C in the DSC heating cycle, respectively, which are significantly higher than the T_{\circ} of widely used 4,4'-N,N'-carbazole-biphenyl (CBP: 62 °C) and 1,3-bis(9-carbazolyl)benzene (mCP: 60 °C).31 The compound **mBINCP** exhibits no discernible T_g in the heating cycle even after rapid cooling. Compounds mBICP, mBINCP and mBIPhCP exhibit good thermal stability with decomposition temperatures $(T_d, 5\%$ weight loss) at 359, 337, and 395 °C, respectively. All of these indicate that the introduction of the benzimidazole moiety improves the morphological stability of host materials. The relatively high T_g and T_d values make these compounds avoid phase separation upon heating and have the potential to be fabricated into high performance devices by vacuum thermal evaporation technology.

3.3. Photophysical properties

Fig. 2 presents the absorption spectra and photoluminescence (PL) spectra of compounds **mBICP**, **mBINCP** and **mBIPhCP** in toluene (*ca.* 2×10^{-5} M) and as the vacuum-evaporated film on a quartz substrate. The related photophysical properties are summarized in Table 1. The absorption maxima of compounds **mBICP**, **mBINCP** and **mBIPhCP** in dilute toluene solution were observed at 292, 282 and 295 nm, respectively, which are assigned to the carbazole-centered n– π^* transition. For the compounds **mBICP** and **mBIPhCP**, the absorption peak in the thin film is similar to that in dilute solution, which means that no significant intermolecular interactions occur in the ground state. But for



Fig. 1 (a) DSC traces of the compounds **mBICP**, **mBINCP** and **mBIPhCP** recorded at a heating rate of 10 °C min⁻¹. (b) TGA thermo-grams of the compounds **mBICP**, **mBINCP** and **mBIPhCP** recorded at a heating rate of 10 °C min⁻¹.

Table 1 Physical data of compounds mBICP, mBINCP and mBIPhCP

Compound	λ_{abs} (nm)		$\lambda_{em,max}$ (nm)						
	Solution ^a	Film	Solution ^a	Film	$T_{\rm g}^{\ b} (^{\circ}{\rm C})$	$T_{\rm d}^{\ c} (^{\circ}{\rm C})$	HOMO/LUMO $_{\exp}^{d}$ (eV)	HOMO/LUMO _{cal} ^{e} (eV)	$E_{\mathrm{T}}^{f}(\mathrm{eV})$
mBICP mBINCP mBIPhCP	292 282 295	290 288 295	346, 363 337, 351 364, 380	389 378 390	84 No 103	359 337 395	-5.7/-2.3 -5.8/-2.4 -5.6/-2.4	-5.2/-2.1 -5.5/-2.1 -5.3/-2.0	3.0 2.8 2.7

^{*a*} Measured in toluene. ^{*b*} Obtained from DSC measurements. ^{*c*} Obtained from TGA measurements. ^{*d*} Determined from the onset of oxidation potentials and the $E_g = HOMO - LUMO$. ^{*e*} Values from DFT calculation. ^{*f*} Measured in 2-methyltetrahydrofuran at 77 K.



Fig. 2 (a) Absorption and PL-emission spectra of **mBICP**, **mBINCP** and **mBIPhCP** in toluene; (b) absorption and PL-emission spectra of **mBICP**, **mBINCP** and **mBIPhCP** in thermally evaporated film (*ca.* 40 nm).

compound **mBINCP**, the maximum absorption is red shifted by 6 nm in the thin film, which may be caused by the strong electron affinity of pyrido[4,3-b]indole. mBICP, mBINCP and mBIPhCP show the main emission peaks at 363, 351, and 380 nm in toluene solution, respectively. In the solid state, the main emission peaks of them shifted to 389, 378, 390 nm, respectively. The optical energy bandgaps of mBICP, mBINCP and mBIPhCP are 3.4, 3.4, and 3.2 eV, respectively, which are calculated from the threshold of the absorption spectra in toluene solution. The phosphorescence spectra were measured in a frozen 2-methyltetrahydrofuran matrix at 77 K (Fig. 3), and the triplet energy levels were estimated from the highest-energy vibronic sub-band of the phosphorescence spectra. These novel compounds show higher triplet energy levels (3.0 eV for mBICP, 2.8 eV for **mBINCP** and 2.7 eV for **mBIPhCP**) than that of blue phosphor iridium(III) bis[2-(4',6'-diffuorophenyl)-pyridinato-N, C(2')]picolinate (FIrpic, 2.65 eV), which implies that they could serve as host materials for blue triplet emitters.

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Fig. 3 The phosphorescence spectra of **mBICP**, **mBINCP** and **mBIPhCP** in a frozen 2-methyltetrahydrofuran matrix at 77 K.

3.4. Electrochemical properties

The electrochemical properties of these compounds were probed by cyclic voltammetry (CV) (Fig. 4). The compounds exhibit reversible oxidation behaviors, which can be assigned to the oxidation of the carbazole moiety. The energy of the highest occupied molecular orbital (HOMO) determined from the onset of the oxidation potentials is -5.6 to -5.8 eV. And the lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the HOMO values and the energy gaps (E_g), which are about -2.3 to -2.4 eV. The HOMO level of these compounds is adjacent to that of the widely used hole transport material NPB (-5.4 eV),³¹ which means the hole-injection barriers from NPB to the compounds are small. The LUMO level of **mBICP** (-2.3 eV) is slightly higher than that of **mBIPhCP** (-2.4 eV), which could be attributed to the different linking modes.



Fig. 4 CV curves of **mBICP**, **mBINCP** and **mBIPhCP**. Working electrode: Pt button; reference electrode: Ag/Ag⁺. Oxidation CV was performed in dichloromethane containing 0.1 M n-Bu₄NPF₆ as the supporting electrolyte at a scan rate of 100 mV s⁻¹.



Fig. 5 The molecular-orbital surfaces of HOMO and LUMO of the compounds **mBICP**, **mBINCP** and **mBIPhCP** calculated at the DFT// B3LYP/6-31G level.

3.5. Quantum chemical calculations

Theoretical calculations on the electronic states of these compounds were carried out at the DFT//B3LYP/6-31G level in the Amsterdam Density Functional (ADF) 2009.01 program to acquire a better understanding of the bipolar properties. As shown in Fig. 5, the HOMO orbitals are mainly located on the electron-donating carbazole moiety or 5H-pyrido[4,3-b]indole moiety, while the LUMO orbitals are mainly dispersed in the electron-accepting benzimidazole moiety. These new compounds have almost complete separation of the HOMO and LUMO orbitals at the hole- and electron-transporting moieties, which

can be rationalized by the disruption of the π -conjugation between the electron-donating and electron-accepting moieties. The complete separation is preferable for efficient hole- and electron-transporting properties and the prevention of reverse energy transfer.³² The calculated HOMO/LUMO values are in the range of -5.5 to -5.2/-2.1 to -2.0 eV, which correlates well with the experimental data.

3.6. Carrier-transport properties

To evaluate the bipolar characters of the compounds mBICP, **mBINCP** and **mBIPhCP**, hole-only devices with configuration: ITO/MoO₃ (10 nm)/NPB (80 nm)/mBICP or mBINCP or mBIPhCP (20 nm)/MoO₃ (10 nm)/Al (100 nm) and an electrononly device having the configuration: Al (100 nm)/mBICP or mBINCP or mBIPhCP (20 nm)/Alq₃ (80 nm)/LiF (1 nm)/Al (100 nm) were fabricated, respectively. MoO₃ and Alq₃ layers were used to prevent hole- and electron-injection from the cathode and anode, respectively. For the hole-only devices, most of the electrons can be impeded and only holes can be injected from the anode to the organic layer, which could be assigned to the large energy injection barrier between the MoO₃ (LUMO = -2.3 eV) and Al (-4.3 eV) layers. In the case of the electron-only devices, the Alq₃ layer, which has a low-lying HOMO level of -5.8 eV, was used to prevent hole-injection from the Al anode (-4.3 eV)to the organic layers. As shown in Fig. 6, all of these compounds exhibit higher hole mobility than the electron mobility. Especially, the hole mobility of the compounds mBICP and **mBIPhCP** are much higher than the electron mobility, which could be attributed to the hole mobility of the carbazole that is much greater than the electron mobility of the benzimidazole. The difference between the compounds mBICP and mBIPhCP could be determined by the different linking modes. For the



Fig. 6 The current density versus voltage curves of the hole-only and electron-only devices for the compounds mBICP, mBINCP and mBIPhCP.

compound **mBINCP**, the hole mobility is close to the electron mobility, which indicates that the 5*H*-pyrido[4,3-*b*]indole possesses both high hole mobility and high electron mobility. This indicates that these new compounds are capable of transporting both electrons and holes, and exhibit bipolar transporting properties.

3.7. Electroluminescent devices

To evaluate these new compounds as potential host materials for a triplet dopant, devices A-C with typical device architectures of ITO/MoO₃ (10 nm)/NPB (40 nm)/mCP (5 nm)/mBICP or mBINCP or mBIPhCP: FIrpic (6 wt%, 20 nm)/TmPyPB (40 nm)/ LiF (1 nm)/Al (100 nm) were initially examined. NPB and TmPvPB were used as the hole- and electron-transporting layers, respectively; mCP as a hole-transporting material and also as an exciton blocker ($E_{\rm T}$, 2.9 eV) to prevent diffusion of exciton to the NPB layer; MoO₃ and LiF served as hole- and electron-injecting layers, respectively. FIrpic doped in mBICP or mBINCP or mBIPhCP was used as the emitting layer. Fig. 7 depicts the relative energy levels of the materials employed in the devices. Fig. 8 shows the current density-voltage-brightness (J-V-L)characteristics and efficiency versus current density curves for the devices and all of the EL spectra of the devices. The EL data of the devices are summarized in Table 2.



Fig. 7 Energy level diagram of HOMO and LUMO levels (relative to vacuum level) for materials investigated in this work.

Device A hosted by the compound mBICP exhibits a maximum current efficiency ($\eta_{c,max}$) of 36.4 cd A⁻¹, a maximum power efficiency ($\eta_{p,max}$) of 33.6 lm W⁻¹ and a maximum external quantum efficiency ($\eta_{EQE,max}$) of 18.7%, and device B using pyridine-carbazole **mBINCP** as the host exhibits a performance with $\eta_{c,max}$ of 29.0 cd A⁻¹, $\eta_{p,max}$ of 21.0 lm W⁻¹, and $\eta_{EQE,max}$ of 13.8%. In comparison, device C with the FIrpic doped into the host **mBIPhCP** as the emitting layer shows high performance with $\eta_{c,max}$ of 33.5 cd A⁻¹, $\eta_{p,max}$ of 30.3 lm W⁻¹, and $\eta_{EQE,max}$ of 17.0%. Especially, these devices show a low external quantum efficiency roll-off (Fig. 8b). For example, when the brightness reached 1000 cd m⁻², the $\eta_{\rm EOE}$ was still as high as 17.0% for device A. The low efficiency roll-off can be attributed to the bipolar transporting properties of the compounds, and the fieldassisted dissociation of Coulombically correlated electron hole (e-h) pairs^{32,33} was blocked effectively. The Commission International de l'Eclairage (CIE) coordinates vary very little for the devices based on the compounds mBICP, mBINCP and mBIPhCP, and are the same as the emission of the phosphorescent emitter FIrpic, suggesting that the triplet energy completely transfers from the hosts to the guest (Fig. 8c). The EL performances of the devices A-C coincide with the difference in the hole- and electron-injection barriers and the $E_{\rm T}$ of the hosts.³

In terms of the applicability of the host materials for allphosphor WOLEDs (devices D–F) with the configuration of ITO/MoO₃ (10 nm)/NPB (70 nm)/mCP (5 nm)/**mBICP** or **mBINCP** or **mBIPhCP**: 5 wt% FIrpic: 0.5 wt% (fbi)₂Ir(acac) (20 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (100 nm) were fabricated. FIrpic and (fbi)₂Ir(acac) were co-doped into the bipolar host **mBICP** or **mBINCP** or **mBIPhCP** as the single-emitting layer. Fig. 9 shows the *J*–*V*–*L* characteristics and curves of external quantum efficiency and power efficiency *versus* current density. Device D with the compound **mBICP** as the host achieves a maximum brightness of 48 473 cd m⁻² at 13.7 V, $\eta_{c,max}$ of 55.2 cd A⁻¹, $\eta_{p,max}$ of 53.8 lm W⁻¹, and $\eta_{EQE,max}$ of 20.5%; these values are 23 030 cd m⁻² at 13.8 V, 36.7 cd A⁻¹,



Fig. 8 (a) Current density-voltage-brightness (J-V-L) characteristics for devices A–C; (b) external quantum efficiency and power efficiency versus current density curves for devices A–C and (c) the EL spectra of the devices A–C.

 Table 2
 Electroluminescence properties of the devices^a

Device	Host/guest	$V_{\rm on}\left({\rm v}\right)$	$\begin{array}{c} L_{\max} \ [cd \ m^{-2}] \\ (V \ at \ L_{\max}, \ V) \end{array}$	$\eta_{c}^{b} [cd A^{-1}]$	$\eta_{ m p}^{\ b} [{ m lm} { m W}^{\scriptscriptstyle -1}]$	$\eta_{\mathrm{EQE}}{}^{b}$	CIE $(x, y)^c$
А	mBICP/Ir-B	3.2	21 550 (10.8)	36.4, 35.1, 32.7	33.6, 24.0, 17.0	18.7, 18.2, 17.1	(0.14, 0.32)
В	mBINCP/Ir-B	3.7	9279 (11.2)	29.4, 28.3, 26.7	21.0, 16.9, 11.6	13.8, 13.4, 12.6	(0.14, 0.32)
С	mBIPhCP/Ir-B	3.3	18 170 (11.2)	33.5, 31.6, 28.7	30.3, 20.5, 13.5	17.0, 16.0, 14.6	(0.14, 0.32)
D	mBICP /Ir–B + Ir–O	3.1	48 473 (13.7)	55.2, 44.7, 39.4	53.3, 27.2, 16.7	20.5, 14.3, 12.8	(0.34, 0.45)
Е	mBINCP/Ir-B + Ir-O	3.7	23 030 (13.8)	36.7, 34.1, 31.5	31.7, 19.9, 12.7	12.7, 11.8, 11.0	(0.42, 0.48)
F	mBIPhCP/Ir-B + Ir-O	3.4	31 920 (13.8)	45.4, 39.7, 35.3	39.4, 19.8, 12.3	16.6, 13.9, 12.5	(0.38, 0.47)

^{*a*} Abbreviations: V_{on} : turn-on voltage; L_{max} : maximum luminance; V: voltage; η_c : current efficiency; η_p : power efficiency; CIE [x, y]: Commission International de l'Eclairage coordinates. ^{*b*} Order of measured value: maximum, then values at 100 and 1000 cd m⁻². ^{*c*} Measured at 8 V.

31.7 lm W⁻¹, and 12.7% for device E with the compound **mBINCP** as the host, and for device F with the compound **mBIPhCP** as the host, the maximum brightness is 31 920 cd m⁻² at 13.8 V, 45.4 cd A⁻¹, 39.4 lm W⁻¹, and 16.6%. The efficiencies of devices D and F are remarkably higher than those of the comparable white device using the conventional host *m*CP ($\eta_{c,max}$ of 42.6 cd A⁻¹, $\eta_{p,max}$ of 24.3 lm W⁻¹, and $\eta_{EQE,max}$ of 14.7%),³⁴ and among the highest for single-emitting layer WOLEDs reported till now.³⁴ Device D based on **mBICP** has the lowest turn-on voltage and the highest power efficiency among

all the three WOLED devices, which could be attributed to the well-matched energy levels of the host **mBICP** compared to the dopants FIrpic and (fbi)₂Ir(acac). Additionally, the performance of devices D–F exhibits a significant enhancement in comparison with the previously reported results under the similar device structures using the conventional host material of *m*CP,³⁵ in which the η_{EQE} of the device based on *m*CP drops to only 6.3% at the luminance of 10 000 cd m⁻². In this work, η_{EQE} of devices D–F at the luminance of 10 000 cd m⁻² is still as high as 10.2%, 9.3% and 10.5%, respectively. The high efficiencies at high luminance



Fig. 9 (a) Current density–voltage–brightness characteristics for devices D–F. (b) Current efficiency and power efficiency *versus* current density curves for devices D–F. (c) The normalized EL spectra of device D at various voltages. (d) The normalized EL spectra of device E at various voltages. (e) The normalized EL spectra of device F at various voltages.

for devices D–F can be attributed to the use of the bipolar hosts, which may result in balanced charge fluxes and a broad distribution of recombination regions within the emitting layer. In addition, devices D–F show good color stability (Fig. 9c–e). When the voltage increases from 8 to 12 V, the CIE coordinates vary only slightly from (0.34, 0.45) to (0.34, 0.44) for device D, from (0.42, 0.48) to (0.41, 0.48) for device E, and from (0.38, 0.47) to (0.37, 0.47) for device F. At the driving voltage of 8 V, devices D, E and F exhibit color rendering indexes (CRI) of 60, 52.0 and 53.8, respectively. The relative low value may be induced by the absence of red light.

4. Conclusion

In conclusion, a series of bipolar hosts based on benzimidazolecarbazole aromatic cores were designed and synthesized. Highly efficient blue and single-emitting layer white devices were successfully fabricated by using the bipolar compounds as host materials. The devices hosted by mBICP, mBINCP and mBIPhCP obtain maximum external quantum efficiencies of 18.7%, 13.8% and 17.0% for blue electrophosphorescence, respectively. The two-color, all-phosphor single-emitting layer white devices hosted by mBICP acquire a maximum external quantum efficiency of 20.5% corresponding to a maximum power efficiency of 53.3 lm W⁻¹, which are among the highest for single-emitting layer white PhOLEDs reported. Also, for the devices hosted by the compounds **mBINCP** and **mBIPhCP**, the single-emitting layer all-phosphor white devices exhibit a maximum external quantum efficiency of 12.7% and 16.6%, and a maximum power efficiency of 31.7 lm W⁻¹ and 39.4 lm W^{-1} , respectively. All of these qualities can be attributed to the usage of the bipolar compounds as hosts.

Acknowledgements

This research work was supported by the central allocation grant from NSFC/China (21161160442) and Wuhan Science and Technology Bureau (no. 01010621227) and the Analytical and Testing Centre at Huazhong University of Science and Technology.

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