Diarylmethylene-bridged 4,4′-(bis(9-carbazolyl))biphenyl: morphological stable host material for highly efficient electrophosphorescence†

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A novel compound (BCBP) based on the modification of a well-known host material 4,4′-(bis(9-carbazolyl))biphenyl (CBP) through arylmethylene bridge linkage was synthesized, and fully characterized. Its thermal, electrochemical, electronic absorption and photoluminescent properties were studied. A high glass transition temperature (T_g) of 173 °C is observed for BCBP due to the introduction of the bridged structure, remarkably contrasting with a low T_g of 62 °C for CBP. Furthermore, the bridged structure enhances the conjugation and raises the HOMO energy, thus facilitating hole-injection and leading to a low turn-on voltage in an electroluminescent device. With the device structure of ITO/MoO_3/NPB/Ir complex: BCBP/BCP/Alq_3/LiF/Al, maximum power efficiencies of 41.3 lm/W and 6.3 lm/W for green- and blue-emitting OLED were achieved, respectively.

Introduction

During the past decade, phosphorescent organic light-emitting diodes (PHOLEDs) have attracted much attention from both academic and industrial communities.[1] PHOLEDs are able to fully utilize both singlet and triplet exciton emission, and therefore realize nearly 100% internal quantum efficiencies in theory.[2] For PHOLEDs, the appropriate host material is of equal importance to the triplet guest to achieve high device efficiency.[3] The development of an effective host material for a triplet emitter imposes some challenges to molecular design. The triplet energy of the host must be higher than that of the guest to prevent energy transfer from the guest back to the host and confine triplet excitons on guest molecules.[4] To this goal, the extent of conjugation and molecular size of the host must be constrained. This requirement makes it difficult for the molecules to acquire the morphological stability that is necessary for forming stable and uniform amorphous thin films.[5] Furthermore, decreasing the π-aromatic conjugation system may adversely affect the charge transport properties.[6]

As we know, carbazole derivatives can usually be used as host materials due to their high triplet energy and good hole-transporting ability.[7] For example, 4,4′-(bis(9-carbazolyl))biphenyl (CBP) is a prominent host for triplet emitters. PHOLEDs using CBP as a host material with a peak efficiency as high as 28 cd/A for green $Ir(ppy)_3$ have been reported.[1b] Unfortunately, the CBP host is prone to crystallize, especially when the dopant concentration is too low.[8] Moreover, the CBP host shows poor morphological stabililty with a low T_g of 62 °C,[9] which could be the result of its low molecular weight, non-rigid and symmetric molecular architecture. It is of important significance to develop morphologically stable CBP derivatives as host materials. Up to now, to improve morphological stability of carbazole-based host materials, molecular modifications mainly involved the introduction of nonconjugated moieties (such as sp^3-hybridized C-9 of fluorene or a Si atom of triphenylsilyl group) to the *para* position of the nitrogen atom,[10,4c] In this paper, we report a new solution to achieve a thermally and morphologically stable CBP derivative by diarylmethylene-bridged 9-phenyl-9*H*-carbazole. The bridged group could serve as not only the nonconjugated group to the CBP, but also as a rigid and steric group, therefore fulfilling the trade off between the increasing molecular size and constraint of molecular conjugation.

Experimental

General information

^1H NMR and ^{13}C NMR spectra were measured on a Varian Mercury 300 spectrometer in $CDCl_3$. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a PE-2400C micro-analyzer. Mass spectra were measured on a VJ-ZAB-3F-Mass spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit. The samples were heated at a heating rate of 10 °C min^{-1} from 30 to 220 °C under argon, then cooled quickly to room temperature, and then heated again from 30 to 220 °C. The glass transition temperature (T_g) was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. 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 25 to 600 °C. Cyclic

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voltammetry (CV) was carried out in nitrogen-purged dichloromethane at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and a Ag wire pseudo-reference electrode with ferrocenium–ferrocene (Fc^+/Fc) as the internal standard. Cyclic voltammograms were obtained at a scan rate of 100 mV s^{-1}. Formal potentials are calculated as the average of cyclic voltammetric anodic and cathodic peaks.

X-Ray structural analysis

Single crystal X-ray diffraction data were obtained from a Bruker AXS Smart CCD diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073Å) radiation. The data were collected using the $\omega/2\theta$ scan mode and corrected for Lorentz and polarization effects as well as the absorption during data reduction suing Shelxtl 97 software. Crystal data for BCBP: $(C_{51}H_{36}N_2)_2$.EtOH.CH_2Cl_2, triclinic, P-1, cell parameters a = 10.1508(11) Å, b = 12.2571(13) Å, c = 16.6606(18) Å, α = 79.161(2), β = 77.551(2), γ = 88.507(2), V = 1987.8(4) $Å^3$, z = 1, M_r = 1484.69, D_c = 1.240 g/cm^3, F(000) = 780, μ = 0.137 mm^{-1}, 10 775 reflections were collected yielding 6918 independent data (R_{int} = 0.0156).

Device fabrication and performance measurements

The hole-injection material MoO_3, hole-transporting material NPB (1,4-bis(1-naphthylphenylamino)-biphenyl), hole-blocking material BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) and electron-transporting materials Alq_3 (tris(8-hydroxyquinoline)aluminium) were commercially available. Commercial indium tin oxide (ITO) coated glass with a sheet resistance of 10Ω/□ was used as the starting substrates. Before device fabrication, the ITO glass substrates were pre-cleaned carefully and treated by UV/O_3 for 2 min. Then the sample was transferred to the deposition system. 10 nm of MoO_3 was firstly deposited to ITO substrate, followed by 40 nm NPB, 30 nm emissive layer, 10 nm BCP, and 30 nm Alq_3. Finally, a cathode composed of 1 nm of lithium fluoride and 100 nm of aluminium were sequentially deposited onto the substrate in the vacuum of 10^{-6} Torr to construct the device. The I–V–B of EL devices was measured with a Keithey 2400 Source meter and a Keithey 2000 Source multimeter equipped with a calibrated silicon photodiode. The EL spectra were measured by a JY SPEX CCD3000 spectrometer. All measurements were carried out at room temperature under ambient conditions.

Materials

Synthesis of methyl 5-bromo-2-(9*H*-carbazol-9-yl)benzoate (1). A 100 ml of round bottom flask equipped with a magnetic stirrer bar and reflux condenser was charged with carbazole (1.67 g, 10 mmol), methyl 4-bromo-2-iodobenzoate (3.41 g, 10 mmol), K_2CO_3 (5 g, 36.2 mmol), activated copper bronze (0.1 g, 1.6 mmol), and 18-crown-6 (0.10 g, 0.4 mmol), and then 20 ml of *o*-dichlorobenzene was added. The reaction mixture was refluxed under argon for 24 h. After it was cooled to room temperature, the mixture was filtered through celite and the solvent was distilled under reduced pressure. The crude product was purified by column chromatography on silica gel using 10:1 petroleum/ethyl acetate as the eluent. Yield: 1.71 g, 45%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.22 (s, 1H), 8.11 (d, J = 7.8 Hz, 2H), 7.85 (d, J = 8.7 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.35 (t, J = 7.8 Hz, 2H), 7.25 (t, J = 7.2 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 3.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 164.95, 141.30, 136.43, 135.96, 134.93, 131.69, 131.49, 126.12, 123.40, 121.80, 120.41, 120.15, 109.16, 52.38. Anal. Calcd. for $C_{20}H_{14}BrNO_2$ (%): C, 63.18; H, 3.71; N, 3.68. Found: C, 63.33; H, 3.28; N, 3.54. GC-MS m/z 379 [M^+].

Synthesis of 10-bromo-8,8-di-*p*-tolyl-8*H*-indolo[3,2,1-*de*]acridine (2). A solution of **1** (3.81 g, 10 mmol) in dry THF (100 ml) was added slowly a 0.6 M 4-methylphenylmagnesium bromide (36.7 ml, 22 mmol), then the reaction mixture was stirred overnight at 80 °C. After that, the reaction mixture was quenched with a dilute solution of ammonium chloride, extracted with ether, and the organic layers were washed with brine, dried over anhydrous sodium sulfate, and evaporated to get a yellow solid (used for the next step without further purification). The yellow solid was dissolved in the boiling acetic acid (38 ml), and concentrated HCl(aq.) (4 ml) was added dropwise. After reflux for 3 h, the mixture was poured into ice water (300 ml). The precipitate was collected and washed twice with ethanol, then purified by column chromatography on silica gel using 3:1 petroleum/chloroform as the eluent to afford a white solid. Yield: 2.4 g, 47%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.12 (d, J = 7.5 Hz, 1H), 8.00 (t, J = 6.6 Hz, 2H), 7.93 (d, J = 8.1 Hz, 1H), 7.55–7.45 (m, 2H), 7.36–7.29 (m, 2H), 7.22 (d, J = 1.5 Hz, 1H), 7.05–6.9 (m, J = 8.1 Hz, 5H), 6.91 (d, J = 8.1 Hz, 4H), 2.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 143.16, 138.95, 137.80, 136.86, 136.57, 135.28, 134.77, 130.84, 130.50, 129.19, 128.31, 127.41, 126.93, 126.85, 123.23, 122.53, 122.03, 121.79, 118.77, 115.93, 115.34, 114.87, 57.08, 21.53. Anal. Calcd. for $C_{33}H_{24}BrN$ (%): C, 77.04; H, 4.70; N, 2.72. Found: C, 76.71; H, 4.88; N, 2.99. MS (EI) m/z 513.0 [M^+].

Synthesis of 10-(4-(9*H*-carbazol-9-yl)phenyl)-8,8-di-*p*-tolyl-8*H*-indolo[3,2,1-*de*]acridine (BCBP, 3). A mixture of 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole (0.37 g, 1 mmol), **2** (0.51 g, 1 mmol), $Pd(PPh_3)_4$ (60 mg, 4.5% mmol) and potassium carbonate (1.38 g, 11.4 mmol) in 18 ml of THF and 5.8 ml of distilled water in a 100 ml round bottom flask was stirred at 90 °C for 36 h under argon. The mixture was extracted with chloroform, and the organic layers were washed with brine and dried over anhydrous sodium sulfate. The crude product was purified by column chromatography on silica gel using 3:1 petroleum/chloroform as the eluent to afford a white solid. Yield: 0.45 g, 67%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.09–7.01 (m, 6H), 6.92–6.89 (m, 12H), 6.91 (s, 6H), 6.72–6.68 (m, 6H), 2.37 (s, 6H), 2.22 (s, 6H), 1.09 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 149.50, 141.03, 139.80, 138.81, 137.63, 136.79, 136.67, 136.36, 134.43, 133.35, 130.55, 130.32, 128.79, 128.40, 128.16, 127.54, 127.12, 126.59, 126.24, 126.17, 123.60, 122.60, 122.21, 121.57, 121.46, 120.55, 120.17, 118.35, 114.68, 114.18, 110.07, 56.89, 21.22. Anal. Calcd. for $C_{51}H_{36}N_2$ (%): C, 90.50; H, 5.36; N, 4.14. Found: C, 90.05; H, 5.76; N, 4.39. MS (EI) m/z 676.4 [M^+].

Results and discussion

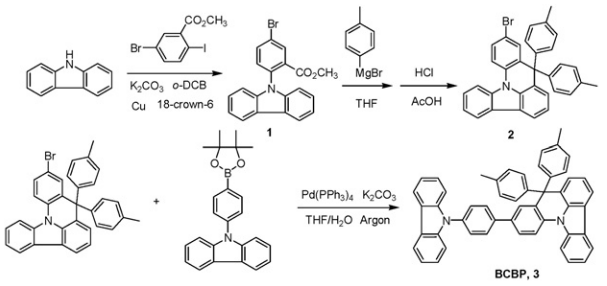
Synthesis and characterization

The synthesis of BCBP is outlined in Scheme 1. The intermediate methyl 5-bromo-2-(9*H*-carbazol-9-yl)benzoate was prepared by a classic Ullmann reaction, and treated with *p*-tolylmagnesium bromide followed by subsequent ring closure through a Friedel–Crafts reaction to construct the bridged structure **2**. BCBP was afforded by the Suzuki-coupling reaction of **2** with 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole. These compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis.

Colorless crystals of BCBP suitable for X-ray crystallographic analysis were grown by carefully layering a dichloromethane solution of BCBP with ethanol. The molecular structure by ORTEP drawing is shown in Fig. 1. The geometry of BCBP reveal a torsion angle of 20.8° between the carbazole and phenyl ring on the briged moiety, which is much smaller than 56.3° between the carbazole and phenyl ring on the non-bridged moiety. The value of 56.3° is close to the torsion angle 49.5° in CBP.[11]

Thermal analysis

The bridge linkage of 9-phenyl-9*H*-carbazole is strongly beneficial to the thermal stability of the new compound,[12] as indicated by the high decomposition temperature (T_d, corresponding to 5% weight loss) of 412 °C in the thermogravimetric analysis (Fig. 2). Noticeably, the BCBP shows a glass-transition temperature (T_g) of 173 °C, which is much higher than those of carbazole analogues,[7b] such as CBP (62 °C) and *m*CP (60 °C).[9] In addition, the asymmetric molecular design may decrease the crystallization tendency. As a consequence, the novel compound can form morphologically stable and uniform amorphous films, an essential property for OLEDs upon thermal evaporation.



Scheme 1 Synthesis of BCBP.

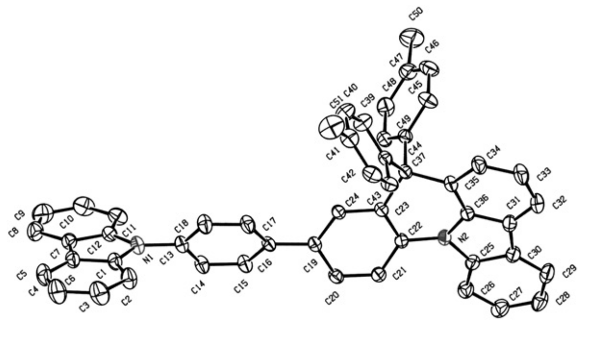


Fig. 1 ORTEP diagram of BCBP. (For clarity, atoms are shown with 30% thermal ellipsoids probability; hydrogen atoms and disordered solvent molecules of EtOH and CH_2Cl_2 in BCBP are omitted).

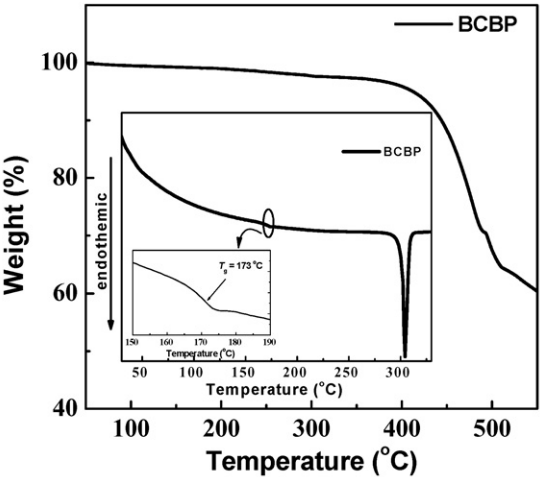


Fig. 2 TGA thermogram of BCBP at a heating rate of 10 °C min^{-1}. Inset: DSC traces of BCBP recorded at a heating rate of 10 °C min^{-1}.

Electrochemical analysis

The electrochemical property of BCBP was studied by cyclic voltammetry (CV), and the compound shows two irreversible oxidation potentials in CH_2Cl_2 solution at 0.81 and 1.02 V, respectively (Fig. 3, CV of CBP was also measured under identical conditions for comparison). The HOMO energy level determined from the onset of the oxidation is −5.45 eV (relative to vacuum energy level). This value is significantly higher than that of CBP (−5.7 eV), indicating that the bridge linkage could raise the HOMO energy level, and thus lead to a lower barrier of hole-injection. The LUMO energy level is estimated to be −2.13 eV from the difference between the HOMO level and the optical band gap.

Photophysical properties

Fig. 4 shows the absorption (in CH_2Cl_2), fluorescence (in toluene), and phosphorescence (in a frozen toluene matrix

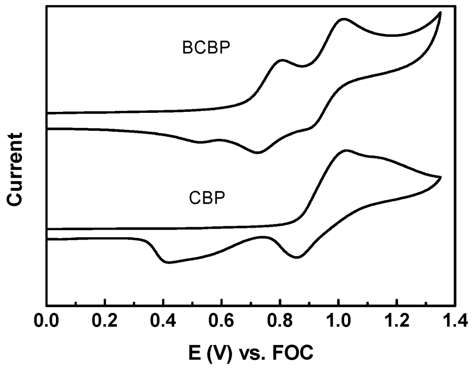


Fig. 3 Cyclic voltammograms of BCBP and CBP.

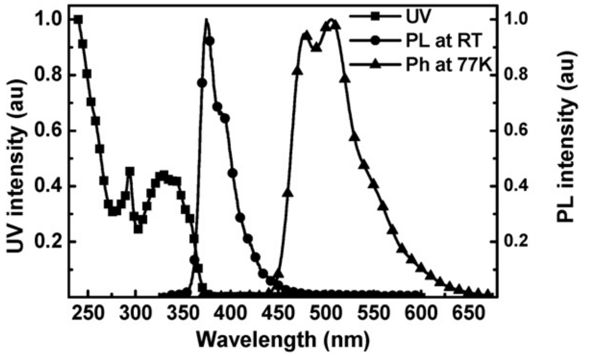


Fig. 4 Absorption and emission spectra of BCBP at room temperature, and phosphorescence spectrum of BCBP in toluene at 77 K.

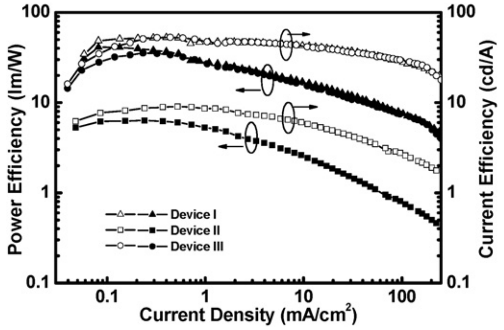


Fig. 6 Power efficiency and current efficiency *versus* current density curves of device I to device III.

Table 1 EL data of the devices with BCBP as host

Device	Host/guest	V_{on} [V]	L_{max}[a] [cd/m^2]	$\eta_{c.max}$[b] [cd/A)]	$\eta_{p.max}$[c] [lm/W]	$\eta_{ext.max}$[d] [%]
I [e]	BCBP/Ir(ppy)$_3$	2.9	48 420	52.7	41.1	13.7
II	BCBP/FIrpic	3.5	4613	9.0	6.3	4.0
III	CBP/Ir(ppy)$_3$	3.3	44 733	52.8	35.5	13.6

[a] Maximum luminance. [b] Maximum current efficiency. [c] Maximum power efficiency. [d] Maximum external quantum efficiency.

at 77 K) spectra of BCBP. The absorptions at 293 and around 329 nm can be attributed to π–π* transitions of carbazole and bridged-carbazole subunits, respectively. BCBP exhibits ultraviolet fluorescence emission at 374 nm at room temperature. The triplet energy (E_T) is determined to be *ca.* 2.60 eV by the highest-energy vibronic sub-band of the phosphorescence spectrum. This value is close to that of CBP (2.56 eV).[9] The photophysical results indicate evidently that there is little effect on the triplet energy from the partial planarization.

Electroluminescence properties

We investigated the utility of BCBP as the host material for blue and green phosphorescent devices with the following configurations: ITO/MoO$_3$ (8 nm)/1,4-bis[(1-naphthylphenyl)- amino]-biphenyl (NPB, 40 nm)/9% Ir(ppy)$_3$:BCBP (25 nm) (device I) or 7% FIrpic:BCBP (25 nm) (device II) or 9% Ir(ppy)$_3$: CBP (25 nm) (device III)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 10 nm)/tris(8-hydroxyquinoline)aluminium (Alq$_3$, 30 nm)/LiF (1 nm)/Al (100 nm). Device III is constructed for comparison. NPB and Alq$_3$ are used as the hole- and electron-transporting materials, respectively; Ir(ppy)$_3$ ($E_T = 2.42$ eV) or FIrpic ($E_T = 2.62$ eV) doped in host BCBP is used as the emitting layer, with optimized doping levels of Ir(ppy)$_3$ at 9 wt% and FIrpic at 7 wt%; BCP is used as hole and exciton blocking layer; MoO$_3$ and LiF serve as hole- and electron-injecting layer, respectively. The luminance–voltage–current density (L–V–J) characteristics, and current efficiency and power efficiency *versus* current density curves of the devices are shown in Fig. 5 and Fig. 6, respectively. The device data are summarized in Table 1. The devices show typical emissions from the Ir complexes with CIE coordinates of (0.26, 0.65) for device I and (0.11, 0.34) for device II.

Device I with Ir(ppy)$_3$ as the dopant exhibits a maximum current efficiency of 52.7 cd/A at 0.40 mA/cm^2, equivalent to an external quantum efficiency (EQE) of 13.7%, and a maximum luminance of 48 420 cd/m^2. The device turns on at a rather low voltage of 2.9 V, which may be attributed to the low hole-injection barrier of BCBP (HOMO = −5.45 eV) as indicated by the energy level diagram (Fig. 7).[13] High quantum efficiency along with low voltage gives a maximum power efficiency of 41.1 lm/W. At the practical brightness of 100 cd/m^2 and 1000 cd/m^2, the power efficiencies are still as high as 39.6 lm/W and 23.7 lm/W,

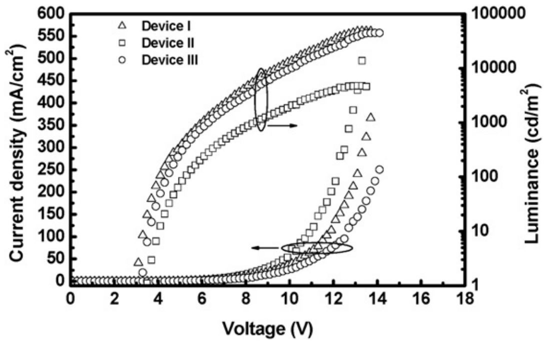


Fig. 5 Luminance–voltage–current density (L–V–J) curves of device I to device III.

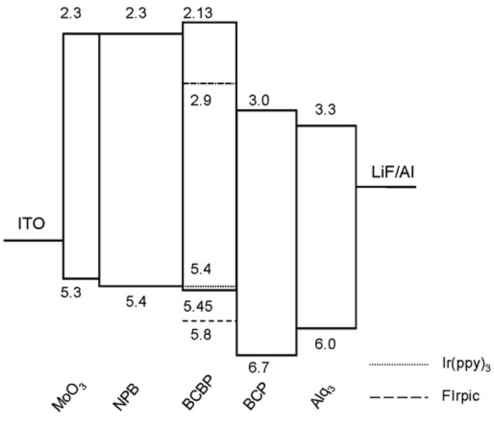


Fig. 7 Proposed energy level diagram showing HOMO and LUMO levels for the materials used in devices.

respectively. We note that the power efficiency of the BCBP-hosted device I is enhanced as compared with CBP-hosted device III. Device II with FIrpic as the dopant shows a maximum current efficiency of 9.0 cd/A at 0.52 mA/cm^2 (EQE of 4.0%), a maximum power efficiency of 6.3 lm/W, and a maximum luminance of 4613 cd/m^2. The device data are comparable with those using CBP/Firpic as the host/guest system under the configuration of ITO/CuPc/NPB/CBP:6%FIrpic/BAlq/LiF/Al reported by Forrest and coworkers.[4a]

Conclusions

In summary, we have designed and synthesized a novel CBP derivative (BCBP) through diarylmethylene-bridged 9-phenyl-9*H*-carbazole. The asymmetric BCBP with confined carbazole shows a remarkably enhanced glass transition temperature (173 °C) as compared to a low T_g of 62 °C for CBP. Moreover the increased molecular size does not decrease its triplet energy in comparison with CBP. Utilizing the new compound as host material, green phosphorescent OLEDs with Ir(ppy)$_3$ as emitter exhibit a low turn-on voltage of 2.9 V and a high power efficiency of 41.1 lm/W; blue phosphorescent OLEDs with FIrpic as a dopant show a maximum current efficiency of 9.0 cd/A, and a maximum power efficiency of 6.3 lm/W. This work reveals that aryl bridge linkages could be a good approach to fulfil the trade off between the increasing molecular size and constraint of molecular conjugation.

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