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New Bipolar Green Host Materials Containing Benzimidazole-Carbazole Moiety in Phosphorescent OLEDs

Jung Hwan Park,[*] Eun Kyung Kim, Ibrahim M. El-Deeb,[‡] Su Jin Jung,[†] Dae Hyuk Choi, Dong-Ha Kim, Kyung Ho Yoo,[†] Jang Hyuk Kwon,[§] and So Ha Lee[†,*]

DUKSAN Hi-METAL Co., Ltd. 404-1, Kyunggi Province 463-420, EL Material Dept., Korea. [*]E-mail: jhpark@dshm.co.kr
[†]Life/Health Division, Korea Institute of Science and Technology, Seoul 130-650, Korea. [*]E-mail: LSH6211@kist.re.kr
[‡]Department of Biomolecular Science, University of Science and Technology, Daejeon 305-333, Korea
[§]Department of Information Display, Kyung Hee University, Seoul 130-701, Korea
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New green host materials, 9-phenyl-3-(4-(1-phenyl-1*H*-benzo[*d*] imidazol-2-yl)phenyl)-9*H*-carbazole (**3a**) and 9-(naphthyl-2-yl)-3-(4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)-9*H*-carbazole (**3b**), have been designed and synthesized by attaching the electron transporting benzimidazole moiety to the hole transporting carbazole unit. These compounds have similar HOMO, LUMO levels and band-gap characteristics compared with CBP (4,4'-di(*N*-carbazolyl)biphenyl). The fabricated green phosphorescent OLED with this **3a** host shows much better device performances compared to CBP-based one. The current and power efficiency is enhanced at least by 60 percent at a given constant luminance of 1000 cd/m^2.

Key Words : Benzimidazole, Carbazole, Phosphorescent green host, OLED

Introduction

The field of organic light emitting diodes (OLEDs) has grown rapidly since the development of the first electro-luminescent device by Ching Tang and Stephen VanSlyke in 1987.[1] The recent developments of both organic light emitting diodes (OLEDs)[2] and polymer light emitting diodes (PLEDs)[3] have lead to a new promising generation of flat panel displays, due to their low cost, compact size, low operating voltage, wide viewing angel, high contrast, and mechanical flexibility.[4]

Recently, a great interest has been given to phosphorescent OLEDs (PhOLEDs) employing phosphorescent emitter, since in these devices both electro-generated singlet and triplet excitons contribute to the light emission, leading to internal quantum efficiency of almost 100%.[5] In PhOLEDs, the phosphorescent emitter is normally used as an emitting guest doped into a host material in order to reduce quenching associated with relatively long excited state lifetime of triplet emitters such as triplet-triplet annihilation.[5b]

In the phosphorescent process, energy is transferred from both singlet and triplet excited states of the host to the triplet excited state of the phosphorescent guest. In addition, direct excitation of guest may also occur by charge trapping.[6] Accordingly, the development of both efficient emitters and host materials are of equal importance for the formation of highly efficient PhOLEDs. However, the development of efficient host materials for triplet emitters is not an easy process since a group of features related to host materials should be controlled. These features include optical and semi-conducting characteristics, HOMO-LUMO levels, film forming behavior, thermal stability and photoluminescent wavelength.[5b] The triplet energy of host material is another critical feature since to prevent reverse energy transfer from guest emitter back to the host, the triplet energy of host material must be higher than that of the guest emitter.[6b,7]

Accordingly, it is important for the host material to have a large energy gap, and to do so, the extent of conjugation in the molecule must be confined, which in turn imposes limitations on the molecular size. On the other hand, for the host material to be able to form a stable and uniform amorphous thin film, it is usually important for the molecule to be bulky and steric.[8] The balance between these two groups of features is a critical issue in the design of an efficient host material.

4,4'-Di(*N*-carbazolyl)biphenyl (CBP) is a popular green host material for triplet emitters in PhOLEDs.[9] The efficiency of CBP as a host material is limited by its liability for crystallization, especially when the dopant concentration is too low.[10] It has a very good hole transporting capability, but unfortunately poor electron transporting ability because of the carbazole chemical unit.[10b] In fact, most of the host materials available so far are capable of transporting either holes[11] or electrons.[12] Furthermore, most of hole-transporters display electron blocking properties, and most of electron-transporters display hole blocking properties. To overcome this common problem in host materials, exciton blocking layer (EBL) is used to increase the efficiency, which adds more cost and increase the complexity of the resulted device.[13] For this reason, there is a high demand for the development of bipolar hosts that can provide more balance in hole and electron fluxes and accordingly simplify the device structure.

Examples for efficient hole transporting host materials are triarylamines and carbazoles,[14] while for electron transporting host materials, more diverse structures are available,

including metal complexes, such as tris(8-hydroxyquinolinato)aluminum (Alq_3),[1] and organic molecules, such as oxadiazole, triazole derivatives[15] and the benzimidazole derivative, 1,3,5-tris(*N*-phenylbenzimidazole-2-yl)benzene (TPBI).[16] TPBI is used as both electron transporter and host material for fluorescent and phosphorescent dopants because of its large HOMO-LUMO energy gap.

Results and Discussion

The combination of electron transport and hole transport materials in a single structure is a good and efficient approach to achieve a bipolar host material, that is capable of transferring both holes and electrons.[8,10c,17] However, the link between these two moieties is highly critical, since the extension of conjugation between the two groups may result in decreasing the HOMO-LUMO energy gap, and consequently decreases the efficiency of the material as a host, by minimizing the triplet energy gradient between the host and the triplet emitter, giving a chance for back energy flow to occur. In order to overcome this problem during the design of new host materials, the conjugation between the two moieties must be interrupted, either by the insertion of a sp^3 hybridized junction,[8] or by high steric design of the molecule that makes a large torsional angle between the planes of the two moieties.[17a] In this study, two green host materials **3a** and **3b** were designed and synthesized by combining both of the hole-transporting carbazole moiety and electron-transporting benzimidazole moiety in one structure (Figure 1).

The synthesis of the target compounds is illustrated in Scheme 1. 9-Phenyl-9*H*-carbazole (**1a**) and 9-(naphth-2-yl)-9*H*-carbazole (**1b**) were synthesized by refluxing a mixture of carbazole, copper powder, K_2CO_3 and crown ether with iodobenzene (for **1a**) or 2-bromo-naphthalene (for **1b**) in anhydrous DMF for 24 h.[18] Bromination of the resulted products was carried out by stirring of compounds **1a** and **1b** with *N*-bromosuccinimide in the presence of benzoyl peroxide in dichloromethane for 12 h at room temperature.[19] The final products **3a** and **3b** were obtained by Suzuki coupling of the 3-bromocarbazoles (**2a** and **2b**) with 4-(1-phenyl-1*H*-benz[*d*]imidazol-2-yl)phenylboronic acid, in the presence of $Pd(PPh_3)_4$ and K_2CO_3 (2M solution). The reaction was carried out in THF under reflux for 48 h.[20]

Although the two moieties were linked directly without sp^3 interruption of conjugation, we believe that the conjugation was not extended between the two moieties for the following reasons; First of all, the force field energy-minimized structures of the two compounds (**3a** & **3b**) have showed a large dihedral angel of 77.7° between the two planes of the carbazole and benzimidazole moieties. This significant deviation between the two planes prevents the extension of conjugation between the two moieties. Another evidence was given by comparing the HOMO-LUMO energy levels and energy gaps in our new compounds **3a** and **3b** with those of the reference compounds CBP[21] and TPBI (Table 1).[16a]

The energy gaps of compounds **3a** and **3b** were found to be 3.24 and 3.16 eV from edge of UV-vis absorption spectra, respectively, which are closer to that of CBP (3.1 eV) rather than that of TPBI (3.93 eV). HOMO level of **3a** and **3b** were measured from cyclic voltammetry (CV) and the oxidation-reduction reaction as potential variation was shown in Figure 2. The HOMO level can be calculated from first oxidation peak and electron energy level of reference electrode.[22] The band gap (E_g) was measured from

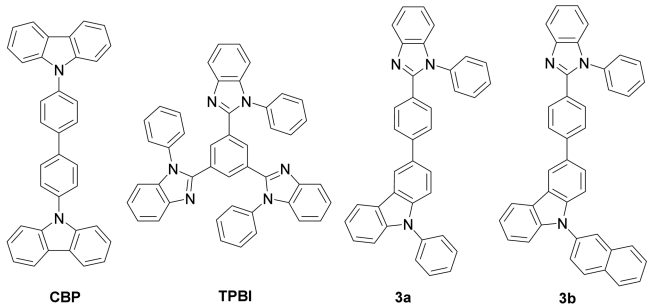
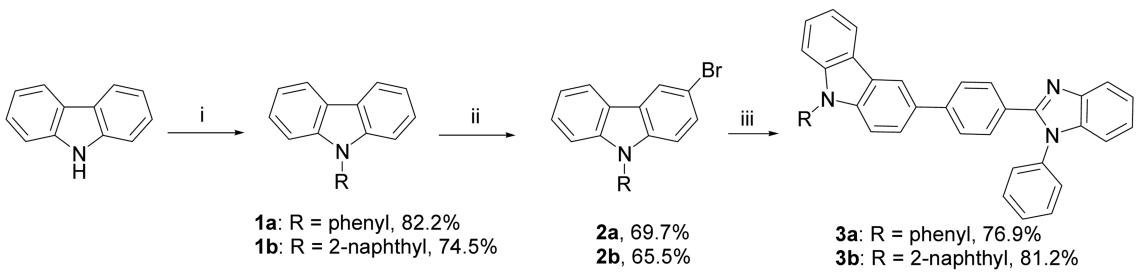


Figure 1. Structure of CBP and TPBI, and new hosts **3a** and **3b**.

Table 1. The experimental data of HOMO, LUMO and energy gaps for host materials

Hosts	HOMO (eV)	LUMO (eV)	E_{gap} (eV)
3a	6.10	2.86	3.24
3b	5.93	2.77	3.16
CBP	6.00	2.90	3.10
TPBI	6.03	2.10	3.93



Scheme 1. Synthesis of compound **3a** and **3b**.
Reaction conditions: (i) R-X, Cu, 18-crown-6, K_2CO_3, DMF, reflux, 24 h, (ii) NBS, BPO, CH_2Cl_2, rt, 12 h, (iii) 4-(1-phenyl-1*H*-benzo[*d*]-imidazol-2yl)phenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3 (2M), THF, reflux, 48 h

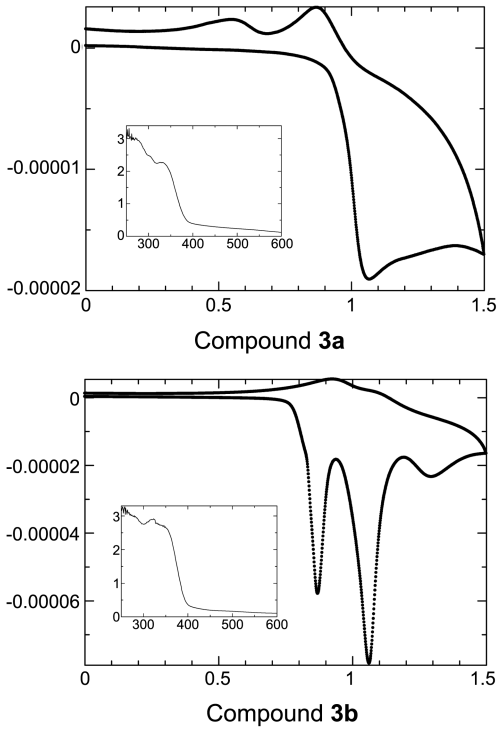


Figure 2. Cyclic voltammograms (inset; UV/vis. spectrum) of compound **3a** and **3b**.

absorption edge of UV/vis. spectrum shown in inset of Figure 2.

These energy gap values prove that the conjugation in the new compounds is not extended between the carbazole and the benzimidazole moities, and accordingly, energy gaps were not reduced (relative to that of CBP) by the conjugation effect. The larger energy gaps of our compounds relative to that of CBP suggest a higher efficiency, caused by the higher energy gradient, as green host materials in comparison to CBP. The HOMO levels of the four compounds are somewhat close to each other, while the LUMO levels of our compounds are closer to that of CBP rather than that of TPBI. The band gap of **3b** is smaller than that of **3a**, and this could be attributed to the extension of conjugation over the *N*-naphthylcarbazole moiety.

In order to demonstrate the efficiency of **3a** and **3b** as green host materials, the following green emitting devices have been fabricated: indium tin oxide (ITO)/4,4′,4″-tris(*N*-(2-naphthyl)-*N*-phenyl-amino)triphenylamine (2-TNATA) (60 nm)/*N,N*′-bis(1-naphthyl)-*N,N*′-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) (30 nm)/10% fac-tris(2-phenylpyridine) iridium(III) ($Ir(ppy)_3$) doped in green host material (**3a** in device A), (**3b** in device B) and (CBP in device C) (45 nm)/ tris(8-quinolinato)aluminum (Alq_3) (25 nm)/LiF/Al. 2-TNATA, NPB, Alq_3 and LiF were used as hole injection material, hole transport material, electron transport material, and electron injection material, respectively. The electroluminescent (EL) spectra with these three hosts (**3a**, **3b** and CBP) were recorded from devices A, B and C, respectively (Figure 3). The three devices emit green light having maximum luminescent intensity within the range of 500-530 nm, which indicates that **3a** and **3b** have similar optical properties with CBP. The L-V characteristics of these devices are shown in Figure 3. The turn-on voltage of device A and B is lower than that of control device C. Furthermore, the resistance to current conduction in device A and B is significantly reduced. The turn-on voltage is 3.55 V for device A and 4.13 V for device B, respectively, while device C has about 5.27 V. Also, the driving voltage to reach 1000 cd/m^2 is 7.74, 8.93, and 9.82 V for devices A, B and C, respectively.

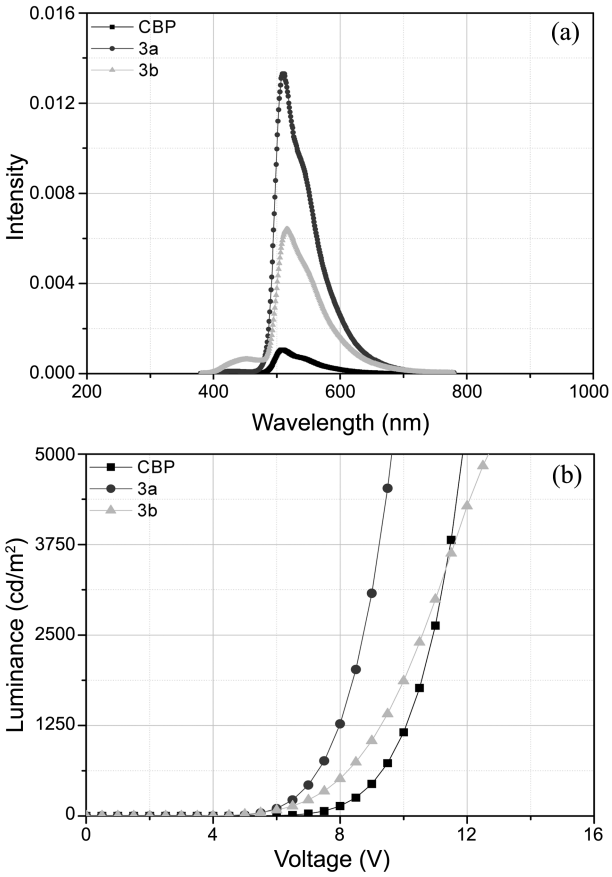


Figure 3. (a) EL spectra and (b) L-V for devices A (**3a** as green host), B (**3b** as green host) and C (CBP as green host).

The current flow through **3a** and **3b** was significantly improved as indicated by the higher current densities relative to that of CBP at the same operating voltage (Figure 4). At a driving voltage of 10 V, the current densities in devices A, B and C were 73.1, 22.6 and 5.1 $mAcm^{-2}$, respectively. This improvement in current flow is probably due to the lower electron injection barrier and the reduction of carrier trapping by the dopant material. The highest current and power efficiencies are expressed by device A, followed by device C, then B. At a given constant luminance of 1000 cd/m^2, the current efficiencies are 37.5 cd/A, 2.5 cd/A, and 23.5 cd/A for device A, B. and C, respectively.

The current and power efficiencies of device A are enhanced by factors of 1.6 and 2.0 times, respectively, compared with those of device C. The maximum current

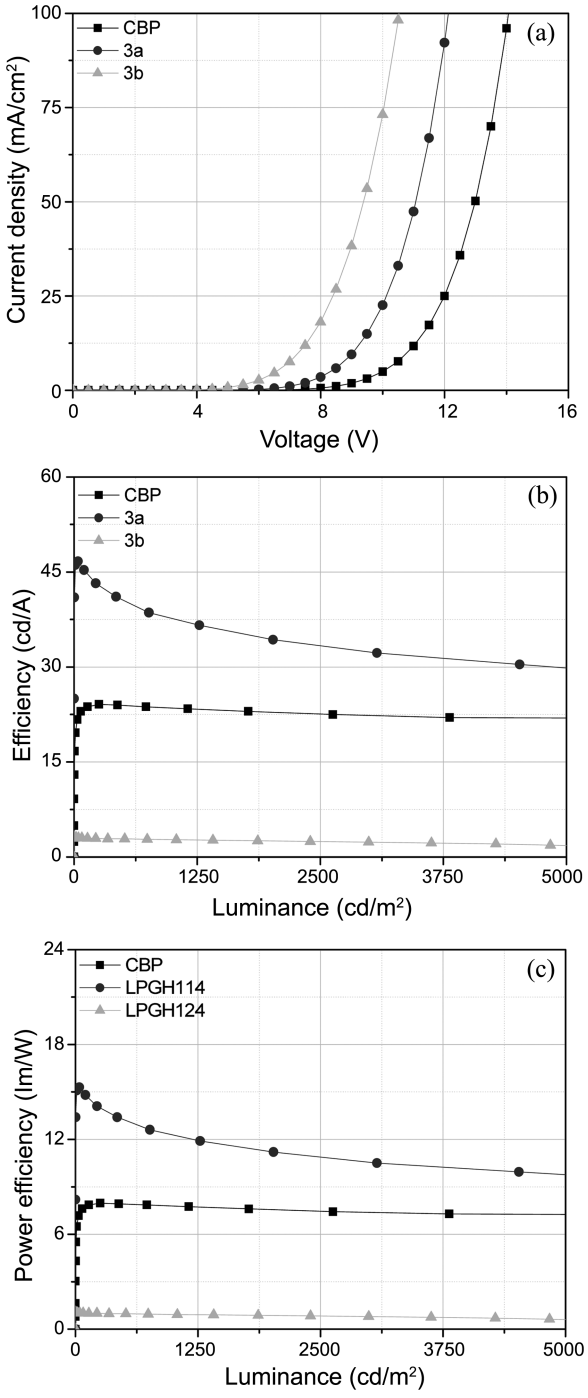


Figure 4. (a) I-V, (b) Current efficiency-brightness, and (c) Power efficiency-brightness for devices A, B and C.

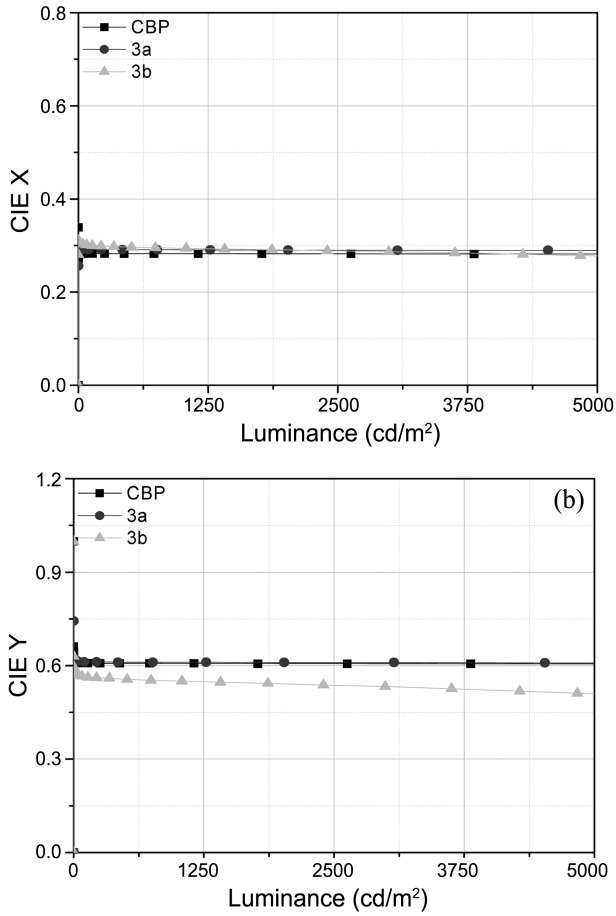


Figure 5. CIE values for devices A, B and C. (a) X values and (b) Y values.

efficiencies are 46.7 cd/A for device A, 3.2 cd/A for device B, and 24.1 cd/A, respectively.

As shown in Figure 5, device A was found to emit green light with CIE (Commission Internationale del'Eclairage) values of (0.29, 0.61), while the values for devices B and C were (0.28, 0,52) and (0.28, 0.61), respectively. Device A and C emit clean green light at a wavelength of between 509-510 nm, indicating that there is almost complete energy transfer from hosts to dopants. While Device B shows some y value changes with increasing luminescence and some NPB emissions. This indicates that energy transfer from **3b** host to $Ir(ppy)_3$ dopant is incomplete.

In order to have a better insight on host performances in the device, the molecular simulation was employed to

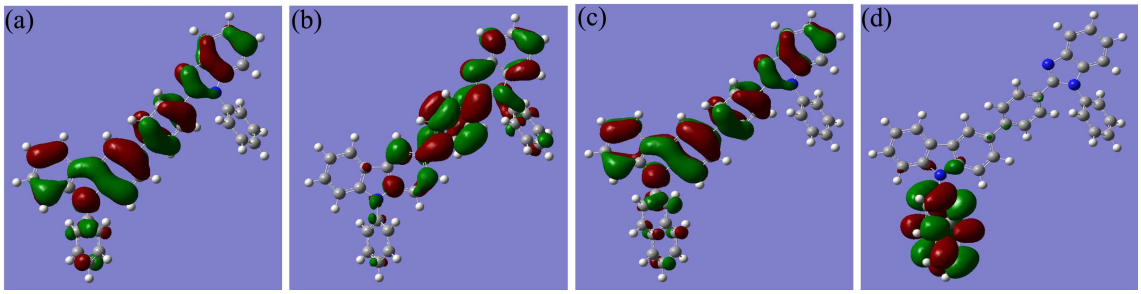


Figure 6. Compound **3a**; (a) HOMO and (b) LUMO levels and Compound **3b**; (c) HOMO and (d) LUMO levels.

deduce the triplet energy of these materials. The triplet energies of **3a**, **3b**, and CBP were estimated from DFT (density function theory) molecular modeling using the DMoL3 program. The estimated triplet energies of **3a**, **3b** and CBP are 2.6, 2.5, and 2.7 eV, respectively. Our calculation data of CBP is well matched with previous reported one.[23] The triplet energy of $Ir(ppy)_3$ phosphorescent dopants is about 2.4 eV. The **3b** host has a little higher triplet energy than $Ir(ppy)_3$, indicating that back energy transfer from the dopant to the host may occur in this host guest system. In additon, as shown in Figure 6. the electron clouds in compound **3a** were entirely delocalized in both of the HOMO and LUMO levels, which suggests smooth energy transfer in compound **3a**, while in compound **3b**, LUMO levels were localized at the naphthyl group, which means that smooth energy transfer would be difficult.

Conclusions

New green host materials of **3a** and **3b** have been designed and synthesized by attaching the electron transporting benzimidazole moiety to the hole transporting carbazole unit. The **3a** host exhibits very good device performances in the green PhOLED. The current and power efficiency is enhanced by 1.6 and 2.0 times at a given constant luminance of 1000 cd/m^2 compared with a CBP host device. The moderate efficiency of compound **3b** relative to that of **3a** is probably due to low triplet energy with the extension of conjugation at the *N*-naphthylcarbazole moiety and the localization of LUMO levels at the naphthyl group.

Experimental Section

Materials. ^{1}H-NMR (300 MHz) were recorded on a Bruker Avance 300 spectrometer with TMS as an internal reference. The IR spectra were recorded on Perkin Elmer Spectrum GX spectrometer. Melting points were taken on a Thomas-Hoover capillary melting apparatus and were uncorrected. Column chromatography was performed on Merck silica gel 60 (230-400 mesh). TLC was carried out using glass sheets precoated with silica gel 60 F_{254} prepared by E. Merck. Many commercially available reagents were obtained from Aldrich and Tokyo Kasei Chemical and generally used without further purification. 4-(1-Phenyl-1*H*-benzo[d]imidazol-2-yl)phenylboronic acid was bought in Suzhou Rovathin Foreign Trade Product List.

9-Phenyl-9*H*-carbazole (1a): A mixture of carbazole (10.0 g, 60.0 mmol), iodobenzene (13.4 g, 65.8 mmol), copper powder (5.7 g, 89.7 mmol), potassium carbonate (12.4 g, 89.7 mmol) and 18-crown-6 (0.8 g, 3.0 mmol) was added to anhydrous DMF (150 mL) at room temperature. The mixture was stirred at reflux for 24 h under N_2 atmosphere. The reaction mixture was poured into water (500 mL) and extracted with diethyl ether. The combined organics were washed with 5% aqueous HCl solution and brine, dried over anhydrous $MgSO_4$ and filtered. After evaporation of organic solvent under reduced pressure, the residue was purified by column chromatography (silica gel, ethyl acetate : hexane) to give pure **1a** (12.0 g, 82.2%). mp 85-87 °C (lit.,[18] 88-90 °C).

9-(Naphth-2-yl)-9*H*-carbazole (1b): A mixture of carbazole (10.0 g, 60 mmol), 2-bromonaphthalene (13.62 g, 65.8 mmol), copper powder (5.7 g, 89.7 mmol), potassium carbonate (12.4 g, 89.7 mmol) and 18-crown-6 (0.8 g, 3.0 mmol) was added to anhydrous DMF (150 mL) at room temperature. The mixture was stirred at reflux for 24 h under N_2 atmosphere. The reaction mixture was poured into water (500 mL) and extracted with diethyl ether. The combined organics were washed with 5% aqueous HCl solution and brine, dried over anhydrous $MgSO_4$ and filtered. After evaporation of organic solvent under vacuum, the residue was purified by column chromatography (silica gel, ethyl acetate:hexane) to give pure **1b** (13.1 g, 74.5%). mp 125-127 °C; IR (KBr, cm^{-1}) 3054, 1596, 1452, 1232, 818, 750; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.70-7.26 (m, 9H), 8.09-7.89 (m, 4H), 8.20 (d, J = 7.7 Hz, 2H).

3-Bromo-9-phenyl-9*H*-carbazole (2a): A mixture of compound **1a** (10.0 g, 41.1 mmol), *N*-bromosuccinimide (NBS, 7.3 g, 41.1 mmol) and benzoyl peroxide (BPO, 0.5 g, 2.1 mmol) in CH_2Cl_2 (100 mL) was stirred at room temperature for 12 h under N_2 atmosphere. The reaction mixture was washed with water, and extracted with CH_2Cl_2. The combined organics were dried over anhydrous $MgSO_4$ and filtered. After evaporation of organic solvent under reduced pressure, the residue was purified by column chromatography (silica gel, ethyl acetate:hexane) to give pure **2a** (9.2 g, 69.7%). mp 97-98 °C (lit.,[19] 98 °C).

3-Bromo-9-(naphth-2-yl)-9*H*-carbazole (2b): A mixture of compound **1b** (12.1 g, 41.1 mmol), *N*-bromosuccinimide (NBS, 7.3 g, 41.1 mmol) and benzoyl peroxide (BPO, 0.5 g, 2.1 mmol) in CH_2Cl_2 (100 mL) was stirred at room temperature for 12 h under N_2 atmosphere. The reaction mixture was washed with water, and extracted with CH_2Cl_2. The combined organics were dried over anhydrous $MgSO_4$ and filtered. After evaporation of organic solvent under reduced pressure, the residue was purified by column chromatography (silica gel, ethyl acetate:hexane) to give pure **2b** (10.0 g, 65.5%). mp 124-126 °C; IR (KBr, cm^{-1}) 3053, 1599, 1443, 1230, 1058, 746; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64-7.26 (m, 8H), 8.20-7.88 (m, 5H), 8.28 (d, J = 1.91 Hz, 1H).

9-Phenyl-3-(4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)-9*H*-carbazole (3a)[20]: A mixture of compound **2a** (8.99 g, 27.9 mmol), 4-(1-phenyl-1*H*-benzo[d]imidazol-2-yl)-phenylboronic acid (13.2 g, 41.9 mmol), $Pd(PPh_3)_4$ (1.6 g, 1.4 mmol) and K_2CO_3 (2 M, 40 mL) was added to THF (120 mL) and stirred under reflux for 48 h under N_2 atmosphere. The reaction mixture was cooled to room temperature and added to 2 N aqueous HCl solution. The mixture was then extracted with CH_2Cl_2 and washed with water. The combined organic solution was dried over anhydrous $MgSO_4$ and filtered. After evaporation of organic solvent under reduced pressure, the residue was purified by column chromatography (silica gel, ethyl acetate:hexane) to give pure **3a** (11.0 g, 76.9%). mp > 250 °C; IR (KBr, cm^{-1}) 3052, 1599, 1450, 1380, 1265, 750; ^{1}H NMR (DMSO-d_6, 300

MHz) δ 7.94-7.18 (m, 23H), 8.66 (d, J = 5.77 Hz, 2H), 8.72 (d, J = 1.2 Hz, 1H); HOMO (eV) 6.10, LUMO (eV) 2.86.

9-(Naphthyl-2-yl)-3-(4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)-9*H* carbazole(3b): A mixture of compound **2b** (10.4 g, 27.9 mmol), 4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl) phenylboronic acid (13.2 g, 41.9 mmol), $Pd(PPh_3)_4$ (1.6 g, 1.4 mmol) and K_2CO_3 (2 M, 40 mL) was added to THF (120 mL) and stirred under reflux for 48 h under N_2 atmosphere. The reaction mixture was cooled to room temperature and added to 2 N aqueous HCl solution. The mixture was then extracted with CH_2Cl_2 and washed with water. The combined organic solution was dried over anhydrous $MgSO_4$ and filtered. After evaporation of organic solvent under reduced pressure, the residue was purified by column chromatography (silica gel, ethyl acetate:hexane) to give pure **3b** (12.7 g, 81.2%). mp 185-187 °C; IR (KBr, cm^{-1}) 3050, 1599, 1471, 1379, 1281, 808, 744; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.83-7.17 (m, 25H), 8.07-8.04 (m, 1H), 8.20 (s, 1H), 8.88 (s, 1H); HOMO (eV) 5.93, LUMO (eV) 2.77.

Fabrication of OLED with 3a, 3b, CBP and Measurement of their Electrolumincesce Properties. The PHOLEDs were fabricated by vapor depositing organic layers onto a glass substrate precoated with indium-tin oxide (ITO) with a sheet resistance of 15 Ω/cm. The substrate was washed, dried, and then immediately loaded into the evaporation system. The organic and metal cathode layers were grown in the chamber at 1×10^{-7} and 6×10^{-7} torr without breaking vacuum, respectively. The deposition process started with a 30 nm thick hole-transporting layer of NPB, followed by a 45 nm-thick layer of $Ir(ppy)_3$-3%: **3a** or **3b** (dopant:host), a 25 nm thick electron-transporting layer of tris(8-hydroxyl quinolinato)aluminum(III) (Alq_3), and finally a metallic LiF/Al. After deposition, the device was measured immediately without encapsulation. Electroluminence (EL) spectra were recorded using Minolta CS-1000. Current-voltage (I-V) and luminance-voltage characteristics of the device were simultaneously measured with a Keithley 2400 source measuring unit and a Minolta LS-100. Cyclic voltammetry (CV) was performed on CHI660B for HOMO and LUMO values. The HOMO energy levels were inferred from their on-set voltage of oxidation potentials measured by CV and the LUMO energy levels were estimated based on the HOMO energy levels and the band gaps obtained from the λ edge of absorption spectra. All device testing was carried out at room temperature under ambient atmosphere, and testing results from the three devices were obtained on the same testing day. UV spectra were determined by Perkin Elmer Lambda 35 UV/VIS Spectrometer and photoluminescent spectra were recorded on Perkin Elmer LS55 Luminescence Spectrometer.

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