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Selective F or Br functionalization of dibenzofuran for application as host materials of phosphorescent organic light-emitting diodes

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Abstract

Four dibenzofuran type host materials substituted with a carbazolylcarbazole moiety were synthesized to investigate the effect of substitution position on the material parameters and device performances of host materials. The carbazolylcarbazole moiety was substituted at 1-, 2-, 3-, and 4- positions of dibenzofuran by F or Br functionalization approach for comprehensive study of positional effect of dibenzofuran derived host materials. Systematic synthesis and comparison of the four host materials revealed that 1-, 2-, and 4- position modification is better than 3- position modification for high triplet energy and high external quantum efficiency.

Key words : dibenzofuran, carbazolylcarbazole, efficiency, substitution position

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Introduction

High triplet energy host materials are essential in the development of high efficiency blue phosphorescent organic light-emitting diodes (PHOLEDs) because their major role is to harvest triplet excitons of phosphorescent emitters and to manage the triplet exciton formation in the emitting layer¹⁻⁵. High triplet energy is needed for triplet exciton harvesting and carrier control is necessary for the triplet exciton formation. One of candidates of the triplet exciton harvesting and managing hosts is a carbazole modified dibenzofuran compound⁶⁻¹⁰. Although only a few host materials sharing the dibenzofuran and carbazole platform are present, they already proved potential as the high triplet energy host materials. Both dibenzofuran and carbazole are high triplet energy moieties for triplet exciton harvesting and they can carry electrons and holes by electron poor and electron rich character of the dibenzofuran and carbazole, respectively. Therefore, the molecular design merging the dibenzofuran and carbazole moieties can be considered as a candidate of host materials for blue PHOLEDs. The dibenzofuran moiety has four different positions for functionalization and functionalization position may have great impact on the photophysical characteristics and device properties of the dibenzofuran derived host materials¹¹. Although a few papers examined the effect of functionalization position of the dibenzofuran derivatives¹¹⁻¹³, comprehensive study covering the host materials functionalized at all positions of dibenzofuran was not reported. In this work, four hosts derived from carbazolylcarbazole, 9-(dibenzo[*b*,*d*]furan-1-yl)-9H-3,9'-bicarbazole dibenzofuran and (1DBFCz), 9-(dibenzo[b,d]furan-2-yl)-9H-3,9'-bicarbazole (2DBFCz), 9-(dibenzo[b,d]furan-3-yl)-9H-3,9'-bicarbazole (3DBFCz), and 9-(dibenzo[b,d]furan-4-yl)-9H-3,9'-bicarbazole (4DBFCz), were synthesized by functionalizing all positions of dibenzofuran using either Br or F functional groups for carbazolycarbazole substitution. It was demonstrated that 1-, 2-, and 4- position substitution is better than 3- position substitution for high triplet energy and high

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external quantum efficiency (EQE). A high EQE over 25% was demonstrated using the dibenzofuran type hosts.

Results and discussion

1-, 2-, 3-, and 4- positions of dibenzofuran were functionalized with either F or Br to introduce carbazolylcarbazole in the molecular structure. The 2- and 4- positions were modified with Br according to well-known synthetic methods¹⁴⁻¹⁷ and the 1- and 3- positions were functionalized with F by ring closing reaction of F containing intermediates¹⁸. In general, the 1, and 3positions of dibenzofuran cannot be functionalized with halogen units because those positions are not activated for direct electrophilic halogen substitution. Therefore, we utilized one Br and two F substituted benzenes as starting materials to prepare the 1- and 3- position functionalized dibenzofuran units. 2-Bromo-1,3-difluorobenzene and (2-methoxyphenyl)boronic acid were starting materials for the 1- position functionalized dibenzofuran and 2-bromo-1,4difluorobenzene and (2-methoxyphenyl)boronic acid were starting materials for the 3- position functionalized dibenzofuran. Pd assisted Suzuki coupling reaction followed by BBr₃ aided deprotection K₂CO₃ mediated closing reaction produced and ring the 1fluorodibenzo [b,d] furan and 3-fluorodibenzo [b,d] furan intermediates. The Br functionalized dibenzofuran intermediates were coupled with carbazolylcarbazole by Pd catalyzed reaction and the F functionalized intermediates were jointed with carbazolylcarbazole by NaH initiated reaction. Preparation scheme of 1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz is shown in Scheme 1.



Scheme 1. Synthetic scheme of 1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz.

Overall material parameters of the four dibenzofuran derivatives were firstly estimated by examining electronic molecular orbital calculated using Gaussian 09 program based on B3LYP 6-31G basis set. **Figure 1** shows the molecular orbital distribution represented by the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The substitution position of dibenzofuran had little effect on the HOMO and LUMO dispersion of the dibenzofuran derivatives. In all compounds, the HOMO was dominantly dispersed over the carbazolylcarbazole unit and the LUMO was scattered over the dibenzofuran unit. Although the substitution position of dibenzofuran was different, the molecular orbital distribution was of little difference because both electron rich carbazolylcarbazole and electron poor dibenzofuran were included in the molecular structure. Electron donating and accepting nature of the building moieties synchronized the HOMO and LUMO distribution.



Figure 1. HOMO and LUMO distribution of 1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz by Gaussian molecular simulation.

The calculated HOMO and LUMO values were verified by experimental measurement using cyclic voltammetry (CV) which electrochemically analyzes the oxidation and reduction. The CV scan data in **Figure 2** provided the HOMO/LUMO of -5.99/-2.58, -5.96/-2.56, -5.99/-2.63, and -5.99/-2.62 eV in 1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz, respectively. The HOMO was quite similar in the four compounds because it is governed by the same carbazolylcarbazole unit. The HOMO of the four compounds was shifted by about 0.10 eV from that of common carbazole host because of electron richness of carbazolylcarbazole.



Figure 2. Oxidation and reduction scan data of 1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz using cyclic voltammetry.

In addition to the HOMO and LUMO levels governing the device performances, singlet energy and triplet energy of the hosts were analyzed by photophysical characterization. Photophysical data of the hosts are presented in **Figure 3(a) and (b)**. Room temperature fluorescence and low temperature phosphorescence of the hosts were characterized by photoluminescence (PL) measurement using a dilute toluene solution $(1.0 \times 10^{-5} \text{ M})$. The low temperature phosphorescence measurement delivered triplet energies of 2.97, 2.98, 2.86, and 3.00 eV in the 1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz, respectively. Except for the 3DBFCz host, all hosts showed very high triplet energy over 2.90 eV. The direct connection of dibenzofuran with

carbazolylcarbazole through 1-, 2-, and 4- position did not degrade the triplet energy of the hosts, but the connection through 3- position decreased the triplet energy because of paraorientation of aromatic units. The triplet energy of all compounds was higher than that of a common mCBP. The fluorescence emission energy was also high in the 1DBFCz, 2DBFCz and 4DBFCz as compared in the fluorescent emission spectra. Ultraviolet-visible (UV-vis) absorption data are presented in **Figure 4** and little change of the UV-vis absorption according to the substitution position was observed. All material analysis data are summarized in **Table**

1.



Figure 3. Room temperature PL (a) and low temperature PL (b) spectra of 1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz.



Figure 4. UV-vis absorption spectra of 1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz.

	1DBFCz	2DBFCz	3DBFCz	4DBFCz	mCBP
HOMO (eV)	-5.99	-5.99	-5.99	-5.99	-6.00
LUMO (eV)	-2.58	-2.56	-2.63	-2.62	-2.40
Singlet energy (eV)	3.38	3.31	3.37	3.40	3.42
Triplet energy (eV)	2.97	2.98	2.86	3.00	2.80

Table 1. Summary of analysis data of 1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz.

The high triplet energy of the hosts allowed application of 1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz as hosts of blue PhOLEDs with a tris[1-(2,4-diisoproplydibnezo[b,d]furan-3-yl)-2-

phenyl-1H-imidazole]-iridium(III) complex [Ir(dbi)₃] phosphorescent emitter. The Ir(dbi)₃ emitter was doped at a doping concentration of 5% in the four hosts to assess the performance of the hosts. A reference device with mCBP as the host was also studied. A device structure fully confining carriers and excitons was built to evaluate the hosts as explained in the experimental part. The device behavior of the four PhOLEDs was examined and the voltage sweep measurement of the blue PhOLEDs generated the current density (J) - voltage (V) and luminance (L) – voltage (V) plots (Figure 5). The J-V and L-V data of the blue PhOLEDs established that 2DBFCz is a high J provider and 3DBFCz is a low J supplier. 1DBFCz and 4DBFCz were in between 2DBFCz and 3DBFCz in terms of J and L values of the blue PhOLEDs. The J and L dependence of the blue PhOLEDs on the four hosts can be appreciated by studying the hole and electron transport performance of the hosts evaluated by hole and electron current densities of single carrier devices in **Figure 6** and **7**. The hole current density of the hole only devices was relatively high in the 2DBFCz and 3DBFCz hosts compared to 1DBFCz and 4DBFCZ hosts. On the other hand, the electron current density of the electron only devices was in the order of $2DBFCz > 1DBFCz \approx 4DBFCz > 3DBFCz$. In spite of high hole current density, the electron current density was very low in the 3DBFCz, which reduced the overall current density of the 3DBFCz blue PhOLEDs. In the case of the mCBP host, the hole current density was high, but the electron current density was very low relative to that of other hosts.



Figure 5. Current density and luminance against voltage plots of the1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz devices.



Figure 6. Current density against voltage plots of hole only devices of the1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz devices.



Figure 7. Current density against voltage plots of electron only devices of the1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz devices.

External quantum efficiency (EQE) of blue PhOLEDs obtained from the electrical and photometric measurements is plotted in **Figure 8**. The EQE of the 1DBFCz, 2DBFCz, and 4DBFCz devices was over 25%, but the EQE of the 3DBFCz device was 22.2%. There was only marginal difference of EQE in the 1DBFCz, 2DBFCz, and 4DBFCz devices. The high EQE of the three blue PhOLEDs demonstrates the superiority of the dibenzofuran type hosts due to high triplet energy and efficient carrier recombination. The rather low EQE of the 3DBFCz device is caused by the low electron density disrupting the carrier balance which is critical to the EQE. Analogously, the EQE of mCBP device was also lower than that of the blue PhOLEDs with the dibenzofuran derived hosts. The electroluminescence (EL) spectra of the blue PhOLEDs were pure Ir(dbi)₃ emission spectra because of high triplet energy of the

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dibenzofuran type hosts inhibiting reverse triplet energy transfer (**Figure 9**). All devices showed the same EL spectra irrespective of the hosts, demonstrating energy transfer from all hosts to Ir(dbi)₃. All device performances are summarized in **Table 2**.

Devices	Voltage (V)	Color coordinate (x, y)	Q. E (%)	C. E (cd/A)	P. E (lm/W)
1DBFCz	6.9	(0.18, 0.40)	26.4	61.0	38.3
2DBFCz	6.6	(0.17, 0.40)	25.7	59.0	40.7
3DBFCz	7.7	(0.18, 0.40)	22.2	51.6	35.7
4DBFCz	7.1	(0.18, 0.40)	26.2	61.4	38.6
mCBP	8.1	(0.19, 0.40)	14.8	34.4	17.1





Figure 8. External quantum efficiency against current density plots of the1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz devices.



Figure 9. Normalized electroluminescence spectra of the 1DBFCz, 2DBFCz, 3DBFCz and 4DBFCz devices at 1,000 cd/m²

Conclusions

Four dibenzofuran type hosts, 1DBFCz, 2DBFCz, 3DBFCz, and 4DBFCz, were synthesized by selective F- or Br- functionalization of dibenzofuran and clarified the effect of substitution position of carbazole type hole transport unit to the dibenzofuran unit. In material and device aspects, 1- and 4- position substitution was equivalent, but the 3- position substitution was inferior to other substitution by providing relatively low triplet energy and EQE. The 2position substitution was better than other position substitution in terms of carrier transport, but triplet energy and EQE were similar to those of 1- and 4- position substitution. 1DBFCz, 2DBFCz and 4DBFCz exhibited high triplet energy over 2.90 eV and EQE over 25% in the

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blue PhOLEDs. Therefore, this work can guide the selection of substitution position in the design of high triplet energy hosts.

Experimental

General information

(2-Methoxyphenyl)boronic acid and 1-bromo-2,4-difluorobenzene were purchased from Alfa Aesar Co. copper(I) Iodide(CuI), 1,10-phenanthroline and boron tribromide(BBr₃) were purchased from Sigma-Aldrich. Co. 2-bromo-1,3-difluorobenzene was purchased from Combi-Blocks Inc. 2-bromodibenzo[b,d]furan was purchased from INCO. 4-bromodibenzo[b,d]furan and tetrakis(triphenylphosphine)palladium(0)(Pd(pph₃)₄). 9*H*-3,9'bicarbazole was purchased from Sunfine global Co. Ltd. Dichloromethane(MC) for high performance liquid chromatography and Potassium carbanate(K₂CO₃) were purchased from Duksan Sci. Co. Tetr ahydrofuran (THF) was purchased from Samchun pure chemical Co. Ltd and distilled with sodium and calcium hydride.

The ultraviolet- visible (UV-Vis) spectra were measured to analyze absorption of compounds using a sample dissolved in refined THF. The photoluminescence (PL) were measured to analyze PL spectra of compounds dissolved in refined tetrahydrofuran. Low temperature PL measurement was carried out at 77k to measure triplet energy of compounds. The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded to identify the compounds. Samples were dissolved in deuterated dimethyl sulfoxide(DMSO) for ¹H and ¹³C NMR measurement. The mass were recorded by liquid chromatography-mass spectrometer (LC-MS) to measure the molecular weight of compounds. Detailed method is described in the literature¹⁹.

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Synthesis

2,6-Difluoro-2'-methoxy-1,1'-biphenyl (1)

(2-Methoxyphenyl)boronic acid (5.0 g, 32.9 mmol), 2-bromo-1,3-difluorobenzene (7.6 g, 39.5 mmol), potassium carbonate (13.6 g, 98.7 mmol) and tetrakis(triphenylphosphine)palladium(0) (1.9 g, 1.65 mmol) were stirred in a round-bottomed flask filled with tetrahydrofuran (100 ml) and distilled water (50 ml) under a nitrogen atmosphere at 260 °C overnight. After reaction, the mixture was cooled to room temperature and extracted with dichloromethane and distilled water. The dichloromethane layer was separated and the dichloromethane was evaporated. Purification by column chromatography (dichloromethane : n-hexane (20:80)) and drying afforded a white powder as a product (4.5 g, 62.7 % yield). ¹H NMR (500 MHz, dimethylsulfoxide-d6): δ 3.72 (s, 3H), 7.01-7.04 (t, 1H, J=7.5Hz), 7.11-7.15 (t, 3H, J=10.0Hz), 7.21-7.23 (d, 1H, J=10.0Hz), 7.41-7.47 (m, 2H), MS (API-) m/z: 221.2 [(M + H)-].

2',6'-Difluoro-[1,1'-biphenyl]-2-ol (2)

Compound **1** (4.5 g, 20.4 mmol) was stirred in dichloromethane (30 ml) under a nitrogen atmosphere at -78 °C for 20 min followed by injection of boron tribromide (13.9 ml, 81.6 mmol). After 2 h, the mixture was heated to room temperature and was stirred for additional 1 h. The reaction mixture was quenched carefully with sodium hydroxide (2.4 g, 2 M) aqueous solution (30 ml) followed by extraction with dichloromethane and distilled water. The dichloromethane layer was separated, dried and evaporated to provide a light yellow product (3.5 g, 83.2% yield). ¹H NMR (500 MHz, dimethylsulfoxide-d6): δ 6.85-6.88 (t, 1H, J=7.5Hz), 6.94-6.96 (d, 1H, J=10.0Hz), 7.08-7.14 (m, 3H), 7.22-7.26 (t, 1H, J=10.0Hz), 7.38-7.44 (m, 1H), 9.63 (s, 1H), MS (API-) m/z: 207.2 [(M + H)-].

1-Fluorodibenzo[*b*,*d*]furan (3)

Compound **2** (3.5 g, 17.0 mmol) and potassium carbonate (4.7g, 34 mmol) were stirred in a two-neck round-bottomed flask filled with dimethylformamide (DMF, 40 ml) under a nitrogen atmosphere at 160 °C overnight. After cooling to room temperature, the reaction mixture was extracted with dichloromethane and distilled water. The dichloromethane layer was separated and evaporated. Crude product was purified by column chromatography (dichloromethane:n-haxane (10:90)). After column chromatography, vacuum sublimation afforded a white product (2.8 g, 88.6% yield). ¹H NMR (300 MHz, dimethylsulfoxide-d₆): δ 8.07-7.31 (m, 7H), MS (API-) m/z: 187.5 [(M + H)⁻].

2,4-Difluoro-2'-methoxy-1,1'-biphenyl (4)

2,4-Difluoro-2'-methoxy-1,1'-biphenyl was synthesized according to the synthetic method of 2,6-difluoro-2'-methoxy-1,1'-biphenyl using 1-bromo-2,4-difluorobenzene (6.05 g, 31.38 mmol) as a starting material instead of 2-bromo-1,3-difluorobenzene. A white powder was obtained as a final product (5.2 g, 75.2% yield). ¹1H NMR (500 MHz, dimethylsulfoxide-d6): δ 3.72 (s, 3H), 7.00-7.03 (t, 1H, J=7.5Hz), 7.08-7.13 (t, 2H, J=10.0Hz), 7.19-7.26 (m, 2H), 7.34-7.41 (m, 2H), MS (API-) m/z: 221.3 [(M + H)-].

2',4'-Difluoro-[1,1'-biphenyl]-2-ol (5)

2',4'-Difluoro-[1,1'-biphenyl]-2-ol was synthesized according to the synthetic method of 2',6'difluoro-[1,1'-biphenyl]-2-ol using 2,4-difluoro-2'-methoxy-1,1'-biphenyl(5.72g,26.0 mmol) instead of 2,6-difluoro-2'-methoxy-1,1'-biphenyl. A light yellow powder was obtained as a product (4.5 g, 84% yield). ¹H NMR (500 MHz, dimethylsulfoxide-d6): δ 6.84-6.87 (t, 1H, J=7.5Hz), 6.90-6.92 (d, 1H, J=10.0Hz), 7.08-7.13 (m, 2H), 7.18-7.24 (m, 2H), 7.35-7.40 (m, 1H), 9.54 (s, 1H), MS (API-) m/z: 207.1 [(M + H)-].

3-Fluorodibenzo[*b*,*d*]furan (6)

3-Fluorodibenzo[b,d]furan was synthesized according to the synthetic method of 1fluorodibenzo[b,d]furan using 2',4'-difluoro-[1,1'-biphenyl]-2-ol (3.83 g, 18.6 mmol) instead of 2',6'-difluoro-[1,1'-biphenyl]-2-ol. A white powder was obtained as a product (3.2 g, 92.3% yield)

¹H NMR (300 MHz, dimethylsulfoxide-d₆): δ 8.20 (s, 1H), 7.73-7.13 (m, 6H), MS (API-) m/z: 187.2 [(M + H)⁻].

9-(Dibenzo[*b*,*d*]furan-1-yl)-9*H*-3,9'-bicarbazole (1DBFCz)

9H-3,9'-bicarbazole (2.0 g, 6.0 mmol) and sodium hydride (0.14 g, 6.0 mmol) were stirred in DMF (10 ml) under a nitrogen atmosphere. After 40 min, compound **3** (2 g, 4.0 mmol) in DMF (10 ml) was injected slowly and the mixture was stirred at 60 °C for 3 h. The reaction mixture was cooled to room temperature and quenched with distilled water. Extraction of the reaction mixture using dichloromethane and distilled water, separation of the dichloromethane layer and evaporation of dichloromethane produced a crude product. Purification of the crude product by column chromatography (dichloromethane : n-hexane (10:90)) followed by vacuum train sublimation afforded a pure white powder as a final product (1.35 g, 45% yield).

¹H NMR (500 MHz, dimethylsulfoxide-d₆): δ 8.65 (s, 1H), 8.45 (d, 1H, J=8.0Hz), 8.27 (d, 2H, J=8.0Hz), 8.03 (d, 1H, J=7.5Hz), 7.89 (t, 1H, J=8.0Hz), 7.80-7.77 (m, 2H), 7.54 (d, 1H, J=8.5Hz), 7.48-7.40 (m, 4H), 7.38-7.33 (m, 4H), 7.30 (t, 2H, J=8.0Hz), 7.15 (d, 1H, J=8.0Hz),

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7. 07 (t, 1H, J=8.0Hz), 6.33 (d, 1H, J=8.5Hz). ¹³C NMR (125 MHz, dimethylsulfoxide-d₆):
δ156.7, 155.6, 141.0, 140.7, 140.0, 139.1, 130.3, 129.4, 128.7, 128.1, 127.0, 126.1, 125.4, 123.9, 123.2, 123.1, 122.5, 122.4, 122.4, 122.0, 121.9, 121.4, 121.3, 121.0, 120.5, 120.4, 119.8, 119.8, 119.7, 119.7, 119.6, 112.2, 111.8, 111.2, 110.2, 109.6, MS (API-) m/z: 499.5 [(M + H)⁻].

9-(Dibenzo[*b*,*d*]furan-2-yl)-9*H*-3,9'-bicarbazole (2DBFCz)

2-Bromodibenzofuran (2.0 g, 8.0 mmol), 9*H*-3,9'-bicarbazole (3.2 g, 9.6 mmol), copper(I) iodide (0.76 g, 4.0 mmol), and potassium carbonate (3.3 g, 24.0 mmol) were put into a round-bottomed flask filled with DMF (50ml) under a nitrogen atmosphere. And 1 10-phenanthroline (0.72 g, 4.0 mmol) in DMF (10 ml) was added to the mixture. The reaction mixture was stirred at 100 °C for overnight and then the reaction was quenched with distilled water. After quenching, the reaction mixture was extracted with dichloromethane and distilled water. Crude product obtained from dichloromethane layer was purified by column chromatography (dichloromethane : n-hexane (10:90)) followed by vacuum train sublimation afforded a pure white powder as a final product (3.35g ,84% yield)

¹H NMR (500 MHz, dimethylsulfoxide-d₆): δ 8.55 (s, 1H), 8.47 (d, 1H, J=8.0Hz), 8.36 (d, 1H, J=8.0Hz), 8.29 (t, 3H, J=8.0Hz), 8.15 (s, 1H), 7.79 (d, 1H, J=8.0Hz), 7.75 (d, 1H, J=10.0Hz) 7.71 (d, 1H, J=8.5Hz) 7.6 (t, 2H, J=9.0Hz), 7.54-7.47 (m, 3H), 7.44 (t, 2H, J=8.0Hz), 7.37-7.31 (m, 3H), 7.30 (t, 2H, J=7.5Hz). ¹³C NMR (125 MHz, dimethylsulfoxide-d₆): δ156.2, 156.0, 141.1, 139.4, 135.7, 129.3, 127.9, 127.0, 126.1, 126.1, 125.5, 125.4, 123.9, 123.5, 123.4, 123.2, 123.0, 122.5, 122.4, 122.3, 122.0, 121.4, 121.1, 120.4, 120.3, 120.3, 119.7, 119.7, 119.6, 119.6, 119.5, 111.8, 111.1, 111.1, 110.6, 110.0, 109.6, MS (API-) m/z: 499.4 [(M + H)⁻].

9-(Dibenzo[*b*,*d*]furan-3-yl)-9*H*-3,9'-bicarbazole (3DBFCz)

3DBFCz was synthesized according to the synthetic method of 1DBFCz using 3-Fluorodibenzo[b,d]furan (0.7g, 3.5 mmol) instead of 1-Fluorodibenzo[b,d]furan. A white powder was obtained as a final product (0.9 g, 51% yield).

¹H NMR (500 MHz, dimethylsulfoxide-d₆): δ 8.60 (s, 1H), 8.42 (d, 1H, J=8.5Hz), 8.40 (d, 1H, J=8.0Hz), 8.31 (d, 1H, J=9.0Hz), 8.27 (d, 1H, J=8.0Hz), 7.90 (d, 1H, J=7.5Hz), 7.73 (t, 1H, J=7.8Hz) 7.64 (d, 1H, J=8.0Hz), 7.58 (d, 1H, J=9.5Hz), 7.55 (t, 1H, J=8.3Hz), 7.49-7.32 (m, 8H), 7.30-7.25 (m, 3H). ¹³C NMR (125 MHz, dimethylsulfoxide-d₆): δ155.5, 150.6, 141.1, 141.0, 141.0, 139.4, 129.4, 128.2, 127.0, 126.6, 126.2, 126.1, 125.4, 124.4, 124.0, 123.7, 123.4, 122.6, 122.4, 121.5, 121.2, 120.7, 120.5, 120.4, 119.7, 119.6, 119.6, 119.6, 119.6, 119.5, 112.0, 112.0, 112.0, 111.3, 110.3, 109.6, MS (API-) m/z: 499.6 [(M + H)⁻].

9-(Dibenzo[*b*,*d*]furan-4-yl)-9*H*-3,9'-bicarbazole (4DBFCz)

4DBFCz was synthesized according to the synthetic method of 2DBFCz using 4bromodibenzo[b,d]furan (1.0 g, 4.0 mmol) instead of 2-bromodibenzo[b,d]furan. A white product was obtained (1.2 g, 60% yield).

¹H NMR (500 MHz, dimethylsulfoxide-d₆): δ 8.57 (d, 2H, J=10.0Hz), 8.37 (d, 1H, J=7.5Hz), 8.27 (d, 3H, J=8.0Hz), 8.03 (d, 1H, J=8.5Hz), 7.84-7.79 (m, 2H), 7.63-7.58 (m, 3H), 7.52 (t, 1H, J=8.0Hz), 7.46-7.41 (m, 4H), 7.37-7.27 (m, 5H). ¹³C NMR (125 MHz, dimethylsulfoxided₆): δ156.2, 154.5, 141.6, 141.1, 140.0, 131.8, 129.1, 129.1, 128.3, 126.9, 126.7, 126.2, 126.1, 125.3, 125.3, 123.6, 123.4, 123.4, 123.3, 123.2, 122.4, 122.3, 121.8, 121.2, 120.5, 120.4, 120.4, 120.2, 119.7, 119.6, 119.5, 113.2, 111.8, 110.1, 109.9, 109.6, MS (API-) m/z: 499.5 [(M + H)⁻].

Device fabrication and characterization

The device structure of blue PhOLEDs was PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/1DBFCz, 2DBFCz, 3DBFCz or 4DBFCz:Ir(dbi)₃ (25 nm, 5 wt%)/TSPO1 (5 nm)/TPBi (20)nm)/LiF (1.5)nm)/Al (200)nm). where PEDOT:PSS is poly(3,4ethylenedioxythiophene):poly(styrenesulfonate), TAPC is 4,4'-cyclohexylidenebis[N,N-bis(4methylphenyl)benzenamine], mCP is 1,3-bis(N-carbazolyl)benzene, TSPO1 is diphenylphosphine oxide-4-(triphenylsilyl)phenyl, and TPBi is 2,2',2"-(1,3,5-benzinetriyl)tris(1-phenyl-1-H-benzimidazole). Devices were fabricated by thermal evaporation in vacuum under a pressure of 5×10^{-7} torr. J-V-L characteristics of 1DBFCz, 2DBFCz, 3DBFCz or 4DBFCz devices were analyzed by a Keithley 2400 programmable source meter and a PR650 (Photo Research) spectrometer according to the method in the literature 20 .

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