Supplementary Information

Enhancing Electroluminescence Performance of Ultra-Deep-Blue Through-Space Charge Transfer Emitters with CIEy ≈ 0.05 Via Methyl-modification

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Experimental Procedures

1.1 General Information. Materials were purchased from Bide Pharmatech, Energy Chemical, Heowns, and other commercial suppliers, and were used without further purification, unless otherwise noted. Tetrahydrofuran was purchased from Beijing Tong Guang Fine Chemicals Company, and the moisture was removed with sodium reflux for 4 hours. All reactions were carried out using Schlenk techniques under an argon atmosphere. The NMR spectra were performed using a Bruker AVANCE III 400 MHz spectrometer with the internal standard of tetramethylsilane (TMS). High resolution mass spectra (HRMS) were determined on Thermo Fisher-Orbitrap Exploris 120 mass spectrometer. Elemental analysis (EA) was determined on the Vairo EL CUBE-CHNS model.

1.2 Thermal Stability Measurement. Thermogravimetric analysis (TGA) was performed with a TA TGA55 instrument. The thermal stability of the samples was obtained by measuring their 5% weight loss while heating at a rate of 10 °C min⁻¹ from 25 to 800 °C under a nitrogen atmosphere.

1.3 Electrochemical measurement. Cyclic voltammetry (CV) was performed in nitrogen-bubbled acetonitrile using CHI660E voltammetric analyzer at room temperature. Tetrabutylammonium hexafluorophosphate (TBAPF₆ 0.1 M) was adopted as the electrolyte, and a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgNO₃ pseudo-reference electrode were used in the conventional three-electrode system. Cyclic voltammograms were performed at a scan rate of 100 mV s⁻¹. Then the HOMO and LUMO energy levels could be calculated by using the following formulas:

$$E_{HOMO} = -(E_{(onset, ox vs Fc^+/Fc)} + 4.8)$$
(1)

$$E_{LUMO} = -(E_{(onset, red vs Fc^+/Fc)} + 4.8)$$
(2)

1.4 Single-Crystal Structure. The single-crystal X-ray diffraction data were collected on a Rigaku XtaLAB synergy R/S diffractometer with graphite monochromated Mo K_{α} radiation. All calculations were performed using the SHELXL and the CrystalStructure crystallographic software package. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 2402467 (1MeCz-BO), 2402468 (2MeCz-BO) and 2402469 (3MeCz-BO).

1.5 Photophysical characterization. UV-Vis absorption spectra were recorded on a Hitachi U-2910 spectrophotometer. The photoluminescence spectra, including fluorescence and phosphorescence at 77 K, were recorded on a Hitachi F-7000 fluorescence spectrophotometer, and the energy gap (ΔE_{ST}) between lowest singlet (S₁) and triplet excited states (T₁) were determined from the difference values of the onset positions of fluorescent and phosphorescent spectra. The fluorescence spectra at 298 K were obtained with FS-5 spectrometer from Edinburgh Instruments Limited with an Xe lamp source. The transient PL decay curves were determined using nanosecond gated luminescence and lifetimes measurements with a high-energy pulsed Nd: YAG laser emitting at 340 nm. The photoluminance quantum yields (PLQY) of the doped films were measured on FLS-1000 with an integrating sphere.

1.6 Device Fabrication and Characterization. Solution-processed device: Commercially purchased indium tin oxide (ITO) glass was subjected to ultrasonic cleaning with isopropanol, rinsed with deionized water, and dried in an oven at 100 °C. Afterward, the glass underwent a hydrophilic treatment using UV ozone for 6 minutes. PEDOT: PSS aqueous solution was then spin-coated onto the ITO substrates at a speed of 3000 rpm. The substrates were transferred to a glovebox and heat-treated at 110 °C to eliminate residual water. Next, the electron-blocking and emissive layers were applied by spin-coating, respectively. After each time of spin coating, the substrates underwent a heat treatment for 15 minutes at 70 °C. When these procedures have been done, the substrates are moved to the deposition system. Under a pressure of less than 10⁻⁵ Pa, the evaporations of TmPyPB, LiF, and Al were carried out. The electroluminescence properties of the OLEDs were characterized by a PR670 spectrometer, connected to a Keithley 2400 source meter.

Thermal evaporation device: The cleaning of ITO glass substrates and the evaporation of organic materials are similar to the fabrication process of solution-processed devices. The deposition rates of all organic materials and aluminum were 1-2 Å s⁻¹, while that of the LiF layer was 0.1 Å s⁻¹. The electrical characteristics of the devices were measured using a Keithley 2400 source meter. The electroluminescence spectra and luminance of the devices were obtained using a Hamamatsu external quantum efficiency measurement system.

1.7 Theoretical calculations. The calculations were performed with the Gaussian 09 package using the density functional theory (DFT) and time-dependent density functional theory (TDDFT) method based on the B3LYP-D3/6-31G(d) functional.^[1] All calculations were performed in the gas phase. The reduced density gradient (RDG) utilized to evaluate non-covalent interactions was calculated by the Multiwfn program^[2] and plotted by VMD^[3]. The charge transfer (CT) proportions of excited states

were evaluated by hole-electron analysis and the interfragment charge transfer (IFCT) method with the Multiwfn program^[2].

Synthetic Procedures



Scheme S1. The synthesis routes of 1MeCz-BO, 2MeCz-BO, and 3MeCz-BO.

Synthesis of 9-(2-bromo-4-methylphenyl)-9H-carbazole (1): Under argon atmosphere, carbazole (20.00 g, 119.6 mmol), 2-bromo-1-fluoro-4-methylbenzene (45.22 g, 239.2 mmol), cesium carbonate (Cs₂CO₃) (77.95 g, 239.2 mmol), were dissolved by 150 mL N, N-Dimethylformamide (DMF) in a two necked round bottom flask equipped with a reflux condenser. The mixture was stirred at 150 °C for 10 hours. Afterwards, pour the reaction solution into water (400 mL) to precipitate the product. The crude product was obtained by filtration under reduced pressure. The product was purified by silica-gel column chromatography (Petroleum ether: $CH_2Cl_2 = 19:1$). Compound **1** (33.18 g, yield of 82.5%) was obtained as a white solid. ¹H NMR (400 MHz, Acetone-*d*₆) δ 8.24 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.83 (d, *J* = 1.7 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.44 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 2H), 7.30 (td, *J* = 7.5, 1.0 Hz, 2H), 7.06 (dt, *J* = 8.1, 0.9 Hz, 2H), 2.55 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 141.08, 140.71, 134.61, 134.01, 130.71, 129.68, 125.99, 123.51, 123.28, 120.42, 119.98, 110.13, 21.06. HRMS (APCI) *m/z* calcd. for $C_{19}H_{14}BrIN [M+H]^+$: 336.0382, found: 336.0376. Elemental

analysis: calcd. for C₁₉H₁₄BrIN: C, 67.87%; H, 4.20%; N, 4.17%, found: C, 67.93%; H, 4.16%; N, 4.14%.

Synthesis of 9-(2-bromophenyl)-3,6-dimethyl-9H-carbazole (2): Under argon atmosphere, 3,6dimethyl-9H-carbazole (23.35 g, 119.6 mmol), 1-bromo-2-fluorobenzene (41.86 g, 239.2 mmol), cesium carbonate (Cs₂CO₃) (77.95 g, 239.2 mmol), were dissolved by 150 mL N, N-Dimethylformamide (DMF) in a two necked round bottom flask equipped with a reflux condenser. The mixture was stirred at 150 °C for 10 hours. Afterwards, pour the reaction solution into water (400 mL) to precipitate the product. The crude product was obtained by filtration under reduced pressure. The product was purified by silica-gel column chromatography (Petroleum ether: CH₂Cl₂ = 19:1). Compound **2** (30.12 g, yield of 71.9%) was obtained as a white solid. ¹H NMR (400 MHz, Acetone-*d*₆) δ 8.09 – 7.86 (m, 3H), 7.70 (td, *J* = 7.5, 1.5 Hz, 1H), 7.64 – 7.51 (m, 2H), 7.23 (dd, *J* = 8.3, 1.7 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 2.52 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 139.44, 137.18, 134.20, 131.12, 129.93, 129.14, 128.77, 127.11, 123.88, 123.30, 120.31, 109.69, 21.48. HRMS (APCI) *m/z* calcd. for C₂₀H₁₆BrIN [M+H]⁺: 350.0539, found: 350.0535. Elemental analysis: calcd. for C₂₀H₁₆BrIN: C, 68.58%; H, 4.60%; N, 4.00%, found: C, 68.51%; H, 4.68%; N, 4.05%.

Synthesis of 9-(2-bromo-4-methylphenyl)-3,6-dimethyl-9H-carbazole (3): Under argon atmosphere, 3,6-dimethyl-9H-carbazole (23.35 g, 119.6 mmol), 2-bromo-1-fluoro-4-methylbenzene (45.22 g, 239.2 mmol), cesium carbonate (Cs₂CO₃) (77.95 g, 239.2 mmol), were dissolved by 150 mL N, N-Dimethylformamide (DMF) in a two necked round bottom flask equipped with a reflux condenser. The mixture was stirred at 150 °C for 10 hours. Afterwards, pour the reaction solution into water (400 mL) to precipitate the product. The crude product was obtained by filtration under reduced pressure. The product was purified by silica-gel column chromatography (Petroleum ether: CH₂Cl₂ = 19:1). Compound **3** (32.33 g, yield of 74.2%) was obtained as a white solid. ¹H NMR (400 MHz, Acetone-*d*₆) δ 8.08 – 7.85 (m, 2H), 7.78 (d, *J* = 1.8 Hz, 1H), 7.49 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.21 (dd, *J* = 8.3, 1.7 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 2.51 (d, *J* = 2.0 Hz, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 140.43, 139.63, 134.55, 134.40, 130.67, 129.60, 129.02, 127.12, 123.53, 123.28, 120.33, 109.74, 21.54, 21.04. HRMS (APCI) *m/z* calcd. for C₂₁H₁₈BrIN [M+H]⁺: 364.0695, found: 364.0692. Elemental analysis: calcd. for C₂₁H₁₈BrIN: C, 69.24%; H, 4.98%; N, 3.85%, found: C, 69.16%; H, 5.03%; N, 3.89%.

Compound 4 was synthesized following the references.^[4] After the solvent was removed from the

reaction solution, the solid residue was washed with water, methanol, and CH_2Cl_2 . Then the crude product (4) (yield of 68.6%) was used directly without further purification due to its poor solubility. HRMS (APCI) *m/z* calcd. for $C_{33}H_{21}BO_3$ [M+H]⁺: 477.1657, found: 477.1654.

Synthesis of 1MeCz-BO: In a two-neck flask, compound 1 (1.01 g, 3.0 mmol) was dissolved in 30 mL dehydrated THF under argon atmosphere. The mixture was cooled to -78 °C for 10 minutes. Then 2.4 M n-BuLi (1.5 mL, 3.6 mmol) was added drop by drop, and the mixture was stirred at -78 °C for 0.5 h. After that, the compound 4 (1.43 g, 3.0 mmol) was added and stirred at room temperature for 2 hours. Then 10 mL distilled water was added to quench the reaction. The mixture was dried under reduced pressure to get the intermediate, and then the intermediate was purified by silica-gel column chromatography (Petroleum ether: $CH_2Cl_2 = 2:1$). The product was dissolved in 40 mL AcOH and then 10 mL HCl was added. The mixture was stirred under 120 °C for 2 h. After cooling to room temperature, the mixture was filtered to get crude product. Afterward, the product was purified by silica-gel column chromatography (Petroleum ether: CH₂Cl₂ =4:1), and 1MeCz-BO (1.13 g, yield of 52.7%) was obtained as a white solid. ¹H NMR (400 MHz, THF-*d*₈) δ 8.39 – 8.28 (m, 2H), 8.05 – 7.95 (m, 2H), 7.67 (d, J = 7.5 Hz, 1H), 7.58 – 7.44 (m, 4H), 7.43 – 7.39 (m, 1H), 7.37 – 7.33 (m, 1H), 7.27 -7.21 (m, 2H), 7.21 - 7.12 (m, 2H), 7.07 - 7.00 (m, 2H), 6.98 (t, J = 7.5 Hz, 2H), 6.66 - 6.60 (m, 1H), 6.49 (t, J = 7.4 Hz, 1H), 6.42 – 6.33 (m, 2H), 5.76 (s, 2H), 2.55 (s, 6H), 2.09 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 158.34, 155.19, 145.17, 140.44, 139.91, 139.04, 134.00, 133.97, 131.90, 131.13, 130.21, 128.80, 128.49, 128.25, 127.71, 127.56, 126.44, 125.93, 124.47, 123.48, 123.17, 122.15, 121.91, 121.72, 119.93, 119.75, 119.53, 119.50, 117.83, 117.45, 113.87, 111.95, 108.44, 56.22, 21.22, 20.73. HRMS (APCI) *m/z* calcd. for C₅₂H₃₄BNO₂ [M+H]⁺: 716.2756, found: 716.2754. Elemental analysis: calcd. for C₅₂H₃₄BNO₂: C, 87.27%; H, 4.79%; N, 1.96%, found: C, 87.20%; H, 4.83%; N, 2.01%.

Synthesis of 2MeCz-BO: In a two-neck flask, compound 2 (1.05 g, 3.0 mmol) was dissolved in 30 mL dehydrated THF under argon atmosphere. The mixture was cooled to -78 °C for 10 minutes. Then 2.4 M n-BuLi (1.5 mL, 3.6 mmol) was added drop by drop, and the mixture was stirred at -78 °C for 0.5 h. After that, the compound 4 (1.43 g, 3.0 mmol) was added and stirred at room temperature for 2 hours. Then 10 mL distilled water was added to quench the reaction. The mixture was dried under reduced pressure to get the intermediate, and then the intermediate was purified by silica-gel column chromatography (Petroleum ether: $CH_2Cl_2 = 2:1$). The product was dissolved in 40 mL AcOH and then

10 mL HCl was added. The mixture was stirred under 120 °C for 2 h. After cooling to room temperature, the mixture was filtered to get crude product. Afterward, the product was purified by silica-gel column chromatography (Petroleum ether: $CH_2Cl_2 = 4:1$), and 2MeCz-BO (1.10 g, yield of 50.3%) was obtained as a white solid. ¹H NMR (400 MHz, THF- d_8) δ 8.36 (s, 2H), 8.06 – 7.92 (m, 2H), 7.58 – 7.35 (m, 6H), 7.34 – 7.05 (m, 5H), 7.03 – 6.96 (m, 3H), 6.83 – 6.62 (m, 1H), 6.51 – 6.33 (m, 2H), 6.30 – 6.22 (m, 1H), 5.74 (s, 2H), 2.56 (s, 6H), 2.30 (s, 3H), 2.04 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 158.45, 158.00, 155.31, 145.32, 140.60, 140.08, 139.12, 137.52, 135.93, 135.15, 134.07, 134.01, 131.19, 130.11, 129.04, 128.93, 128.52, 127.83, 127.68, 127.54, 127.07, 126.63, 124.89, 124.43, 122.71, 122.30, 120.50, 119.85, 119.63, 118.05, 117.93, 113.74, 111.90, 108.60, 21.77, 21.38, 21.05. HRMS (APCI) *m/z* calcd. for C₅₃H₃₆BNO₂ [M+H]⁺: 730.2912, found: 730.2909. Elemental analysis: calcd. for C₅₃H₃₆BNO₂: C, 87.24%; H, 4.97%; N, 1.92%, found: C, 87.18%; H, 4.94%; N, 2.00%.

Synthesis of 3MeCz-BO: In a two-neck flask, compound 3 (1.09 g, 3.0 mmol) was dissolved in 30 mL dehydrated THF under argon atmosphere. The mixture was cooled to -78 °C for 10 minutes. Then 2.4 M n-BuLi (1.5 mL, 3.6 mmol) was added drop by drop, and the mixture was stirred at -78 °C for 0.5 h. After that, the compound 4 (1.43 g, 3.0 mmol) was added and stirred at room temperature for 2 hours. Then 10 mL distilled water was added to quench the reaction. The mixture was dried under reduced pressure to get the intermediate, and then the intermediate was purified by silica-gel column chromatography (Petroleum ether: $CH_2Cl_2 = 2:1$). The product was dissolved in 40 mL AcOH and then 10 mL HCl was added. The mixture was stirred under 120 °C for 2 h. After cooling to room temperature, the mixture was filtered to get crude product. Afterward, the product was purified by silica-gel column chromatography (Petroleum ether: CH₂Cl₂ = 4:1), and 3MeCz-BO (1.27 g, yield of 57.0%) was obtained as a white solid. ¹H NMR (400 MHz, THF- d_8) δ 8.36 (d, J = 2.3 Hz, 2H), 7.99 (dt, J = 7.8, 1.5 Hz, 2H), 7.60 - 7.33 (m, 6H), 7.24 (d, J = 8.4 Hz, 2H), 7.21 - 7.15 (m, 1H), 7.09 (d, J)= 1.9 Hz, 1H), 7.06 - 6.91 (m, 4H), 6.38 (dd, J = 8.5, 1.9 Hz, 1H), 6.30 (d, J = 2.1 Hz, 1H), 6.22 (d, J= 1.5 Hz, 1H), 5.75 (s, 2H), 2.57 (s, 6H), 2.29 (s, 3H), 2.05 (d, J = 8.3 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-d) & 158.32, 157.84, 155.14, 145.22, 140.44, 139.94, 139.02, 133.91, 133.88, 131.35, 131.02, 130.96, 130.10, 128.78, 128.58, 128.36, 128.16, 127.61, 127.47, 126.86, 126.48, 124.54, 124.20, 122.22, 121.94, 120.31, 119.70, 119.48, 117.90, 117.71, 113.57, 111.62, 108.51, 56.27, 21.63, 21.24, 20.92, 20.73. HRMS (APCI) *m/z* calcd. for C₅₄H₃₈BNO₂ [M+H]⁺: 744.3069, found: 744.3068.

Elemental analysis: calcd. for C₅₄H₃₈BNO₂: C, 87.21%; H, 5.15%; N, 1.88%, found: C, 87.24%; H, 5.09%; N, 1.94%.



Fig. S1. ¹H NMR spectrum of compound 1 in Acetone- d_6 .



Fig. S2. ¹³C NMR spectrum of compound 1 in Chloroform-*d*.



Fig. S3. HRMS spectrum of compound 1.



Fig. S4. ¹H NMR spectrum of compound 2 in Acetone- d_6 .



Fig. S5. ¹³C NMR spectrum of compound 2 in Chloroform-*d*.



Fig. S6. HRMS spectrum of compound 2.



Fig. S7. ¹H NMR spectrum of compound 3 in Acetone- d_6 .



Fig. S8. ¹³C NMR spectrum of compound 3 in Chloroform-d.



Fig. S9. HRMS spectrum of compound 3.



Fig. S10. HRMS spectrum of compound 4.



Fig. S11. ¹H NMR spectrum of 1MeCz-BO in THF-*d*₈.



Fig. S12. ¹³C NMR spectrum of 1MeCz-BO in Chloroform-d.







Fig. S14. ¹H NMR spectrum of 2MeCz-BO in THF- d_8 .



Fig. S15. ¹³C NMR spectrum of 2MeCz-BO in Chloroform-d.



Fig. S16. HRMS spectrum of 2MeCz-BO.



Fig. S17. ¹H NMR spectrum of 3MeCz-BO in THF- d_8 .



Fig. S18. ¹³C NMR spectrum of 3MeCz-BO in Chloroform-d.



Fig. S19. HRMS spectrum of 3MeCz-BO.

Thermal Stability Measurement.



Fig. S20. TGA curves at a heating rate of 10 °C min⁻¹ under N₂.

Electrochemical measurement.



Fig. S21. (a) Cyclic voltammetry (CV) curves of three compounds. CV curves for 4 cycles of 1MeCz-BO (b), 2MeCz-BO (c), and 3MeCz-BO (d).

X-Ray Crystallography

compound	1MeCz-BO	2MeCz-BO	3MeCz-BO
CCDC Number	2402467	2402468	2402469
Empirical formula	C52 H34 B N O2	C53 H36 B N O2	C54 H38 B N O2
Formula weight	715.61	729.64	743.66
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
T (K)	293	293	293
space group	P b c a	P 21/n	P b c a
a/Å	9.7393(2)	16.7191(13)	8.8277(3)
b/Å	24.5507(5)	8.8730(5)	27.8654(9)
c/Å	30.8103(7)	26.3102(17)	31.7860(12)
a/ °	90	90	90
β/ °	90	101.453(7)	90
γ/ °	90	90	90
V/Å ³	7366.9(3)	3825.5(5)	7819.0(5)
Z	8	4	8
density, g/cm ³	1.290	1.267	1.263
F (000)	2992.0	1528.0	3120.0
R1 (all data)	0.0572	0.1170	0.0888
wR2 (all data)	0.1528	0.3542	0.1672

Table S1. The single crystal X-ray crystallographic data of 1MeCz-BO, 2MeCz-BO and 3MeCz-BO.



Fig. S22. Packing mode of single crystal structures of 1MeCz-BO (a), 2MeCz-BO (b), and 3MeCz-BO (c).



Fig. S23. ORTEP diagram of the molecular structure of 1MeCz-BO. Thermal ellipsoids are shown at 50% probability.



Fig. S24. ORTEP diagram of the molecular structure of 2MeCz-BO. Thermal ellipsoids are shown at 50% probability.



Fig. S25. ORTEP diagram of the molecular structure of 3MeCz-BO. Thermal ellipsoids are shown at 50% probability.

Theoretical calculations.

Atomic	Coo	rdinates (Angstr	oms)	Atomic	ic Coordinates (Angstroms)		
type	Х	Y	Z	type	Х	Y	Z
N	-3.3511	0.7510	2.1231	С	2.1126	-0.7706	-3.1506
С	-0.2726	-0.0723	-1.7996	С	0.4665	3.4622	-3.0703
С	-0.0539	-1.3036	-2.2707	С	-0.2166	4.6162	-3.1562
С	-0.9936	-2.2157	-1.9514	С	-1.3170	4.7565	-2.3976
С	-2.1013	-1.9606	-1.2138	С	-1.7303	3.7658	-1.5926
С	-2.2274	-0.6740	-0.8403	С	3.2638	-1.2295	-3.6785
С	-1.3434	0.3034	-1.0945	С	4.3509	-0.4565	-3.8223
С	-2.5972	-0.2554	2.3760	C	4.3366	0.8281	-3.4305
С	-1.4879	0.0708	3.0459	C	3.1960	1.3089	-2.9094
С	-1.5842	1.3884	3.2095	C	0.2506	5.7245	-4.0696
С	-2.7409	1.7712	2.6291	C	5.5511	1.7140	-3.5710
С	-2.7804	-1.5404	2.0496	Н	-0.7470	-3.2268	-2.3105
С	-1.8686	-2.4602	2.4126	Н	-3.1230	-0.3340	-0.3295
С	-0.7618	-2.1048	3.0854	Н	-2.0242	-3.5214	2.1584
С	-0.5573	-0.8189	3.4114	Н	-0.0210	-2.8697	3.3724
С	-0.7150	2.2037	3.8209	Н	0.3477	-0.5197	3.9621
С	-1.0005	3.5113	3.8684	Н	0.2148	1.8266	4.2746
С	-2.1363	3.9455	3.3047	Н	-0.3114	4.2173	4.3605
С	-2.9849	3.0951	2.6996	Н	-2.3703	5.0240	3.3411
С	-4.4523	0.6002	1.4667	Н	-3.8659	3.5900	2.2828
С	-4.8420	-0.6252	1.0209	Н	-5.1402	2.6377	1.4118
С	-4.0330	-1.8763	1.3141	Н	-7.0730	2.3017	0.2100
С	-5.3026	1.5954	1.1378	Н	-6.2700	-1.7973	-0.0337
C	-6.4348	1.4308	0.4372	Н	-5.1443	-1.3633	3.8560
C	-6.7968	0.2178	0.0043	Н	-6.6297	-2.9060	5.0492
C	-5.9770	-0.7942	0.3151	Н	-7.2214	-5.0524	4.0526
C	-4.9271	-2.6952	2.2144	Н	-6.3421	-5.6948	1.8838
C	-5.2501	-3.8704	1.6615	Н	-5.2902	-5.9425	-0.0853
C	-4.6123	-3.9897	0.4848	Н	-3.9101	-5.9407	-2.0776
C	-3.8499	-2.9092	0.1956	Н	-2.5034	-4.1483	-2.5759
C	-5.4079	-2.3373	3.4140	Н	-8.6446	0.9181	-0.9443
C	-6.2236	-3.1838	4.0622	Н	-7.8121	-0.4292	-1.7927
C	-6.5506	-4.3645	3.5105	Н	-8.7192	-0.7408	-0.2602
C	-6.0656	-4.7172	2.3080	Н	1.3648	3.3195	-3.6892
C	-4.6624	-5.0663	-0.3082	Н	-1.8976	5.6929	-2.4397
C	-3.8914	-5.0704	-1.3991	Н	-2.6421	3.9084	-0.9874
C	-3.0821	-4.0303	-1.6461	Н	3.3164	-2.2837	-4.0012
C	-3.0068	-2.9201	-0.8740	Н	5.2667	-0.8897	-4.2575
С	-8.0593	-0.0154	-0.7885	Н	3.1607	2.3541	-2.5647
В	0.7714	1.0719	-2.1312	Н	-0.1043	6.7231	-3.7289
С	2.1106	0.5300	-2.7913	Н	1.3622	5.7738	-4.1142
C	0.0532	2.4852	-2.2506	Н	-0.1343	5.5517	-5.1004

 Table S2 Optimized Coordinates of 1MeCz-BO.

С	-1.0659	2.5989	-1.5051	Н	5.2733	2.7003	-4.0076
0	1.0431	-1.6303	-3.0294	Н	6.0122	1.8879	-2.5722
0	-1.5151	1.5989	-0.6734	Н	6.3266	1.2691	-4.2339

Table S3 Optimized Coordinates of 2MeCz-BO.

Atomic	Coo	rdinates (Angstro	oms)	Atomic	Coordinates (Angstroms)		
type	Х	Y	Z	type	Х	Y	Z
N	-4.0421	0.6136	1.1204	C	-2.8681	4.9477	-1.5519
C	-2.1548	0.0448	-2.6027	C	-3.6112	3.8375	-1.6667
С	-1.6422	-1.1877	-2.7436	C	1.5410	-1.1921	-1.5868
C	-2.4508	-2.2284	-2.4810	C	2.2979	-0.5070	-0.7172
C	-3.6957	-2.0416	-1.9999	С	2.0179	0.7736	-0.4234
C	-4.1478	-0.7793	-1.9026	C	0.9725	1.3525	-1.0385
C	-3.4084	0.3006	-2.2099	С	-0.6925	6.1502	-1.6973
C	-3.2272	-0.3738	1.1756	С	2.8586	1.5302	0.5774
C	-1.9624	-0.0012	1.3885	С	-0.1659	4.5000	1.9137
C	-2.0252	1.3253	1.4815	С	-0.0906	-3.1977	1.3586
C	-3.3203	1.6653	1.3230	Н	-2.0045	-3.2356	-2.5361
C	-3.4836	-1.6784	1.0340	Н	-5.1879	-0.5987	-1.5986
C	-2.4722	-2.5622	1.1153	Н	-2.6809	-3.6377	0.9965
C	-1.1987	-2.1732	1.3133	Н	0.0884	-0.5076	1.6199
C	-0.9406	-0.8616	1.4577	Н	0.0188	1.8310	1.7937
C	-1.0175	2.1836	1.6811	Н	-2.8059	4.9527	1.6476
C	-1.2796	3.4983	1.7304	Н	-4.5390	3.4535	1.3218
C	-2.5613	3.8775	1.6015	Н	-5.9884	2.4531	0.8747
C	-3.5528	2.9895	1.4079	Н	-8.2179	2.0333	0.4135
С	-5.2937	0.4157	0.8788	Н	-9.0240	-0.2519	0.0776
С	-5.7810	-0.8395	0.6789	Н	-7.4585	-2.0819	0.2419
С	-4.9015	-2.0687	0.7720	Н	-5.3273	-1.5753	3.5049
C	-6.2185	1.3932	0.7665	Н	-6.3237	-3.1853	5.0663
C	-7.5157	1.1857	0.4944	Н	-7.0004	-5.3938	4.2824
C	-7.9635	-0.0584	0.3073	Н	-6.6869	-6.0329	1.9567
C	-7.0817	-1.0584	0.4023	Н	-6.0932	-6.2860	-0.2496
C	-5.4699	-2.9286	1.8756	Н	-5.1217	-6.2388	-2.4767
C	-5.8447	-4.1403	1.4395	Н	-3.9810	-4.2871	-3.2772
C	-5.5310	-4.2593	0.1388	Н	0.0541	3.7012	-2.4299
C	-4.9842	-3.1200	-0.3317	Н	-3.3506	5.8944	-1.2585
C	-5.6331	-2.5753	3.1585	Н	-4.6953	3.9024	-1.4693
C	-6.1809	-3.4595	4.0075	Н	1.7749	-2.2508	-1.7894
С	-6.5557	-4.6749	3.5736	Н	3.1451	-1.0096	-0.2220
С	-6.3866	-5.0265	2.2877	Н	0.7267	2.3917	-0.7837
С	-5.6380	-5.3557	-0.6235	Н	0.2768	5.9170	-1.2007
С	-5.0900	-5.3339	-1.8463	Н	-0.4813	6.5600	-2.7111
С	-4.4509	-4.2360	-2.2795	Н	-1.1811	6.9484	-1.0948
С	-4.4093	-3.0986	-1.5560	Н	3.9438	1.3652	0.3901
В	-1.0920	1.2259	-2.6298	Н	2.6828	2.6284	0.5375
C	0.2242	0.6712	-1.9193	Н	2.6213	1.1836	1.6090

C	-1.7566	2.6197	-2.2401	Н	0.6936	4.2590	1.2474
С	-3.0851	2.6454	-2.0068	Н	-0.4853	5.5372	1.6669
0	-0.3163	-1.3342	-3.0565	Н	0.1897	4.4876	2.9689
0	-3.9233	1.5638	-2.1142	Н	-0.0462	-3.7548	0.3948
С	0.4880	-0.6228	-2.1995	Н	0.9102	-2.7392	1.5228
С	-1.0155	3.7370	-2.1711	Н	-0.2682	-3.9255	2.1827
С	-1.5510	4.9137	-1.8083				

 Table S4 Optimized Coordinates of 3MeCz-BO.

			-				
Atomic	Coo	rdinates (Angstre	oms)	Atomic	Coor	rdinates (Angstro	oms)
type	Х	Y	Z	type	Х	Y	Z
N	-2.9496	0.6024	1.1490	С	-1.8477	4.9795	-1.5717
С	-1.0970	0.0656	-2.5482	С	-2.5776	3.8564	-1.6344
С	-0.5744	-1.1606	-2.7053	С	2.6359	-1.0954	-1.6242
С	-1.3692	-2.2091	-2.4339	С	3.4027	-0.3840	-0.7850
С	-2.6227	-2.0342	-1.9722	C	3.1106	0.8975	-0.5068
С	-3.0920	-0.7774	-1.8821	C	2.0434	1.4507	-1.1079
С	-2.3551	0.3120	-2.1630	C	0.3038	6.2088	-1.8271
С	-2.1239	-0.3765	1.1884	C	3.9624	1.6857	0.4596
С	-0.8594	0.0098	1.3779	C	0.8943	4.5347	1.8634
C	-0.9346	1.3356	1.4726	C	1.0445	-3.1668	1.3073
С	-2.2361	1.6617	1.3393	Н	-0.9143	-3.2124	-2.4904
С	-2.3699	-1.6834	1.0491	Н	-4.1335	-0.6090	-1.5742
C	-1.3479	-2.5565	1.1106	Н	-1.5473	-3.6339	0.9929
С	-0.0750	-2.1540	1.2853	Н	1.2006	-0.4752	1.5683
С	0.1724	-0.8400	1.4263	Н	1.1092	1.8637	1.7423
С	0.0672	2.2054	1.6515	Н	-1.7521	4.9546	1.6518
С	-0.2089	3.5171	1.7057	Н	-3.4755	3.4351	1.3610
С	-1.4971	3.8820	1.6020	Н	-4.9233	2.4180	0.9408
С	-2.4824	2.9830	1.4286	Н	-7.1436	1.9785	0.5166
С	-4.2027	0.3916	0.9281	Н	-6.3443	-2.1254	0.3205
С	-4.6807	-0.8667	0.7325	Н	-4.1770	-1.6116	3.5501
С	-3.7881	-2.0872	0.8091	Н	-5.1370	-3.2378	5.1177
С	-5.1424	1.3556	0.8329	Н	-5.8067	-5.4480	4.3325
С	-6.4407	1.1306	0.5810	Н	-5.5224	-6.0727	1.9988
С	-6.8915	-0.1153	0.3949	Н	-4.9574	-6.3099	-0.2191
С	-5.9833	-1.0959	0.4763	Н	-4.0161	-6.2413	-2.4588
C	-4.3322	-2.9580	1.9164	Н	-2.9021	-4.2727	-3.2627
С	-4.7035	-4.1706	1.4795	Н	-8.9745	0.4986	0.0972
С	-4.4085	-4.2806	0.1737	Н	-8.4406	-0.9027	-0.8930
С	-3.8789	-3.1339	-0.2979	Н	-8.7554	-1.1046	0.8758
С	-4.4794	-2.6125	3.2033	Н	1.0568	3.7564	-2.5379
С	-5.0074	-3.5055	4.0556	Н	-2.3330	5.9246	-1.2781
C	-5.3784	-4.7218	3.6210	Н	-3.6537	3.9097	-1.3947
С	-5.2254	-5.0657	2.3310	Н	2.8804	-2.1543	-1.8132
C	-4.5165	-5.3732	-0.5940	Н	4.2685	-0.8659	-0.3016
С	-3.9852	-5.3394	-1.8241	Н	1.7886	2.4910	-0.8658

C	-3.3622	-4.2333	-2.2599	Н	1.2765	6.0062	-1.3235
С	-3.3232	-3.1001	-1.5302	Н	0.5084	6.5746	-2.8590
С	-8.3412	-0.4164	0.1042	Н	-0.1906	7.0293	-1.2605
В	-0.0578	1.2639	-2.6444	Н	5.0454	1.4876	0.2929
С	1.2850	0.7428	-1.9586	Н	3.8126	2.7839	0.3581
С	-0.7294	2.6544	-2.2559	Н	3.7088	1.3997	1.5059
С	-2.0475	2.6648	-1.9706	Н	1.7824	4.2580	1.2510
0	0.7464	-1.2916	-3.0456	Н	0.5789	5.5494	1.5317
0	-2.8731	1.5695	-2.0176	Н	1.2061	4.5967	2.9306
С	1.5603	-0.5526	-2.2214	Н	1.0824	-3.7141	0.3376
C	-0.0028	3.7831	-2.2393	Н	2.0423	-2.6991	1.4635
С	-0.5412	4.9592	-1.8789	Н	0.8853	-3.9044	2.1264



Fig. S26. The frontier molecular orbitals of 1MeCz-BO (a), 2MeCz-BO (b), and 3MeCz-BO (c).

Photophysical characterization.



Fig. S27. The transient photoluminescence decay curves of doped films in air and vacuum for 1MeCz-BO (a) and 2MeCz-BO (b).



Fig. S28. The transient photoluminescence decay curves test with microsecond flashlamp of doped films.



Fig. S29. The temperature-dependent transient photoluminescence decay spectra of the doped films for 1MeCz-BO (a) and 2MeCz-BO (b).



Fig. S30. The photoluminescence quantum yields of the doped films with different doped ratios for 1MeCz-BO, 2MeCz-BO, and 3MeCz-BO.

Table S5. The rate constants of exciton dynamics for 1MeCz-BO, 2MeCz-BO, and 3MeCz-BO.

				2		,) =	
	τ _p ^[a] [ns]	τ _d [a] [μs]	R _d ^[b] [%]	kp ^[c] [×10 ⁶ s ⁻¹]	k _d [c] [×10 ⁶ s ⁻¹]	Φ _p ^[d] [%]	Φ _d ^[d] [%]	k _{ISC} ^[e] [×10 ⁷ s ⁻¹]	k _{nr} ^[e] [×10 ⁶ s ⁻¹]
1MeCz-BO	22.9	14.1	24.0	4.37	0.71	62.9	19.8	1.05	5.75
2MeCz-BO	22.5	7.32	27.1	4.45	1.37	63.0	23.5	1.21	4.38
3MeCz-BO	20.2	4.73	29.4	4.98	2.12	58.9	29.4	1.65	3.87

[a] The lifetime of prompt and decay fluorescence. [b] Proportion of decay fluorescence. [c] Reciprocal of τ_p and τ_d . [d] Efficiencies of PF and DF. [e] Rate constants of intersystem crossing and non-radiation.

The quantum efficiencies and rate constants were calculated by the following equation. ^[5]

$$\Phi_{\rm p} = \Phi_{\rm PL} R_{\rm p} \tag{3}$$

$$\Phi_{\rm d} = \Phi_{\rm PL} R_{\rm d} \tag{4}$$

$$k_{\rm r} = \Phi_{\rm p} / \tau_{\rm p} \tag{5}$$

$$\Phi_{\rm PL} = k_{\rm r}/(k_{\rm r} + k_{\rm IC}) \tag{6}$$

$$\Phi_{\rm p} = k_{\rm r}/(k_{\rm r} + k_{\rm IC} + k_{\rm ISC}) \tag{7}$$

$$\Phi_{\rm IC} = k_{\rm IC} / (k_{\rm r} + k_{\rm IC} + k_{\rm ISC}) \tag{8}$$

$$\Phi_{\rm ISC} = k_{\rm ISC} / (k_{\rm r} + k_{\rm IC} + k_{\rm ISC}) = 1 - \Phi_{\rm p} - \Phi_{\rm IC}$$

$$\tag{9}$$

$$\Phi_{\rm RISC} = \Phi_{\rm d} / \Phi_{\rm ISC} \tag{10}$$

$$k_{\rm RISC} = (k_{\rm p} \, k_{\rm d} \, \Phi_{\rm d}) / (k_{\rm ISC} \, \Phi_{\rm p}) \tag{11}$$

$$k_{\rm p} = 1/\tau_{\rm p}; k_{\rm d} = 1/\tau_{\rm d}$$
 (12)

$$k_{\rm nr} = (1 - \Phi_{\rm PL}) k_{\rm r} / \Phi_{\rm PL} \tag{13}$$

Device Fabrication and Characterization.



Fig. S31. The EL characteristics of OLEDs device. EL spectra (a), J-V-L curves (b), and EQEsluminance curves (c) of 1MeCz-BO.

						0	
Device	λ _{EL} ^[a] (nm)	EQE _{max} [(%)	^{b]} CE _{max} ^{[c} (cd A ⁻¹)	[]] PE _{max} ^{[d}) (Im W ⁻¹	$ L_{max}^{[e]} $ (cd m ⁻²)	FWHM ^[f]) (nm)	CIE ^[g] (x,y)
1MeCz-BO (5%	420	3.2	3.2	2.4	340	39	0.168, 0.036
1MeCz-BO (10%	(6) 424	3.6	7.0	5.8	680	42	0.165, 0.037
1MeCz-BO (20%	(6) 430	6.1	11.7	10.2	1024	49	0.162, 0.048

Table S6. Device data of 1MeCz-BO with different doping ratios.

[a] The peak value of electroluminescence. [b] Maximum external quantum efficiency. [c] Maximum current efficiency. [d] Maximum power efficiency. [e] Maximum luminance. [f] Full width at half-maximum of electroluminescence peak. [g] Coordinates of Commission Internationale de L'Eclairage.



Fig. S32. The EL characteristics of OLEDs device. EL spectra (a), J-V-L curves (b), and EQEsluminance curves (c) of 2MeCz-BO.

Device	λ _{EL} ^[a] (nm)	EQE _{max} ^[b] (%)	CE _{max} ^[c] (cd A ⁻¹)	PE _{max^[d] (lm W⁻¹)}	L _{max} ^[e] (cd m ⁻²)	FWHM ^[f] (nm)	CIE ^[g] (x,y)
2MeCz-BO (5%)	428	4.0	3.6	3.3	400	46	0.165, 0.043
2MeCz-BO (10%)	432	6.3	11.8	9.6	905	47	0.165, 0.045
2MeCz-BO (20%)	436	8.6	17.1	14.9	1277	49	0.160, 0.050
2MeCz-BO (30%)	438	6.8	13.6	11.9	1368	50	0.153, 0.051

Table S7. Device data of 2MeCz-BO with different doping ratios.

[a] The peak value of electroluminescence. [b] Maximum external quantum efficiency. [c] Maximum current efficiency. [d] Maximum power efficiency. [e] Maximum luminance. [f] Full width at half-maximum of electroluminescence peak. [g] Coordinates of Commission Internationale de L'Eclairage.



Fig. S33. The EL characteristics of OLEDs device. EL spectra (a), J-V-L curves (b), and EQEsluminance curves (c) of 3MeCz-BO.

Device	λ _{EL} ^[a] (nm)	EQE _{max} ^[b] (%)	CE _{max} ^[c] (cd A ⁻¹)	PE _{max} ^[d] (Im W ⁻¹)	L _{max} ^[e] (cd m ⁻²)	FWHM ^[f] (nm)	CIE ^[g] (x,y)
3MeCz-BO (5%)	434	6.7	13.0	10.8	669	48	0.153, 0.045
3MeCz-BO (10%)	438	8.2	16.1	13.3	989	49	0.152, 0.046
3MeCz-BO (20%)	442	10.1	19.6	16.9	1334	50	0.151, 0.051
3MeCz-BO (30%)	444	9.3	18.8	16.4	1478	50	0.150, 0.054

Table S8. Device data of 3MeCz-BO with different doping ratios.

[a] The peak value of electroluminescence. [b] Maximum external quantum efficiency. [c] Maximum current efficiency. [d] Maximum power efficiency. [e] Maximum luminance. [f] Full width at half-maximum of electroluminescence peak. [g] Coordinates of Commission Internationale de L'Eclairage.

Thermal evaporated OLEDs.

As a comparison, 3MeCz-BO was also tested in thermally evaporated OLEDs, with the structure of ITO/ HAT-CN (10 nm)/TAPC (40 nm)/TCTA (10 nm)/mCP (10 nm)/DPEPO: 20 wt% emitter (20 nm)/PPF (5 nm)/TmPyPB (40 nm)/LiF (2 nm)/Al (100 nm). The EL properties of the evaporation device are shown in Fig. S34 and Table S9.

The evaporated device has an EQE_{max} of 7.3%, which is slightly lower than that of the solutionprocessed device. However, the evaporated device has a higher EQE at 1000 cd m⁻² and a lower efficiency roll-off. Furthermore, the evaporated device achieves nearly double luminance (2356 cd m⁻²) compared to the solution-processed device. Except for the EQE_{max} value, all other parameters indicate that the evaporation device is superior, which may be due to the different hole-transport, electron-blocking, and host materials.



Fig. S34. (a) EL spectrum of the thermal evaporation devices. (b) Current density-voltage-luminance (J-V-L) characteristics of the devices. (c) EQE versus luminance of the devices.

	There system and y of the properties of the devices for entreed bot											
3MeCz-BO	λ _{EL} ^[a] [nm]	EQE _{max} ^[b] [%]	EQE ₁₀₀₀ ^[b] [%]	L _{max} ^[c] [cd m ⁻²]	FWHM ^[d] [nm]	CIE ^[e] [x,y]						
Solution	442	10.1	5.2	1334	50	0.151, 0.051						
Evaporation	442	7.3	5.8	2356	51	0.155, 0.056						

Table S9. Summary of EL properties of two devices for 3MeCz-BO

[a] The peak value of electroluminescence. [b] External quantum efficiency at maximum and 1000 cd m⁻². [c] Maximum luminance. [d] Full width at half-maximum of electroluminescence peak. [e] Coordinates of Commission Internationale de L'Eclairage.

Reference

- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Wallingford, CT, 2016.
- 2. T. Lu, F. Chen, J. Comput. Chem. 2012, 33, 580-592.
- 3. W. Humphrey, A. Dalke, K. Schulten, J. Mol. Graph. 1996, 14, 33-38.
- 4. P. Zuo, Y.-J. Yang, F.-M. Liu, J.-R. Wu, Q. Zheng, H.-T. Yuan, L.-S. Liao, D.-Y. Zhou, Z.-Q. Jiang, Adv. Opt. Mater. 2024, 12, 2400860.
- 5. K. Masui, H. Nakanotani, C. Adachi, Org. Electron. 2013, 14, 2721-2726.