Supporting Information

Narrowband Blue Emission with Insensitivity to Doping Concentration from Oxygen-Bridged Triarylboron-based TADF Emitter: Nondoped OLEDs with High External Quantum Efficiency up to 21.4%

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Table of Contents

- 1. Experimental Section
- 1.1 General Information
- **1.2 Theoretical Calculations Method**
- **1.3 Device Fabrication and Characterization**
- 1.4 Synthesis of Materials
- 2. Supplementary Figures and Tables
- 3. References

1. Experimental Section

1.1 General Information

¹H NMR (500 MHz), ${}^{13}C{}^{1}H$ NMR (125 MHz), and ${}^{19}F{}^{1}H$ NMR (470 MHz) spectra were recorded on Bruker AV 600 NMR instrument at ambient temperature using deuterated solvents. Chemical shifts were given parts per million (ppm) relative to tetramethylsilane ($\delta = 0$ ppm). High-resolution mass spectra (HRMS) were measured on a Bruker maxis UHR-TOF mass spectrometer. Thermogravimetric analysis (TGA) of final products were measured using a PerkinElmer Instruments (Pyris1 TGA) at a heating rate of 10 °C/min from 30 to 800 °C under nitrogen atmosphere. The UV-vis absorption spectra were recorded using a UV-3100 spectrophotometer. Photoluminescence spectra and phosphorescence spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer with xenon lamp as the light source. The absolute PL quantum yields were determined on a Quantaurus-QY measurement system (C9920-02, Hamamatsu Photonics) using an integrating sphere system under nitrogen flow. The lifetimes of fluorescence and delayed fluorescence were undertaken on PicoQuant Fluotime300. Cyclic voltammetry experiments were performed on a CHI600 electrochemical analyzer (Chenhua, China) with a three-electrode cell configuration consisting of platinum counter electrode, an Ag/AgCl reference electrode and glassy carbon electrode used for the working electrode, respectively. During the electrochemical measurements, nitrogen-purged CH₃CN was used for the oxidation scan with tetra-n-butylammonium hexafluorophosphate (0.1 M in CH₃CN) as the supporting electrolyte, and redox potentials were obtained at a scan rate of 100 mV s⁻¹.

1.2 Theoretical Calculations Method

Geometrical and electronic properties of the ground-state were carried out by B3LYP density functional method including 6-31G (d, p) basis set using Gaussian 09 software package. HOMO and LUMO were visualized with Gaussview 5.0. The properties of excited states were then performed by Time-dependent DFT (TD-DFT) calculations

with PBE1PBE functional and basis set 6-31G (d, p).

1.3 Device Fabrication and Characterization

Patterned ITO glass substrates were cleaned sequentially with acetone, deionized water and isopropyl alcohol in an ultrasonic cleaner, then dried with N₂ flow and finally transferred into a vacuum chamber for deposition. Both 8-hydroxyquinolinolato-lithium (Liq) as electron injection layer and aluminum (Al) as cathode layer were deposited by thermal evaporation at 5×10^{-5} Pa. Additionally, the organic layers were deposited at the rates of 0.2-3 Å/s. After the organic film deposition, Liq and Al layer were deposited with rates of 0.1 and 3 Å/s, respectively. The emitting area of the device is about 0.09 cm². The current density-voltage-luminance (*J-V-L*), *L-EQE* curves and electroluminescence spectra were measured using a Keithley 2400 source meter and an absolute EQE measurement system (C9920-12, Hamamatsu Photonics, Japan).

1.4 Synthesis of Materials

All reagents and solvents were purchased from commercial sources and used without further purification. All reactions were performed under nitrogen conditions using anhydrous solvents. The final products were first purified by column chromatography, and then further refined by temperature gradient vacuum sublimation.



Scheme S1. Synthetic routes of target compounds.

Synthesis of BrPhenol: A mixture of 1,5-dibromo-2,4-difluorobenzene (5.4 g, 20.0 mmol), 4-tert-butylphenol (7.5 g, 50.0 mmol), and potassium carbonate (13.8 g, 100.0 mmol) in dry *N*-Methylpyrrolidone (100 mL) was performed for 12 h at 170 °C under nitrogen atmosphere. When cooling to room temperature, the reaction mixture was extracted with ethyl acetate:petroleum ether (v:v=1:1) and water. The collected organic layers were dried over anhydrous Na₂SO₄ and then evaporated under reduced pressure. The crude product was further purified using silica gel chromatography with petroleum ether as eluent to afford **BrPhenol** as a white powder with 86% yield. ¹H NMR (500 MHz, CDCl₃, δ): 7.86 (s, 1.0H); 7.31-7.28 (m, 4.0H); 6.85-6.82 (m, 4.0H); 6.58 (s, 1.0H); 1.28 (s, 18.0H). ¹³C{¹H} NMR (125 MHz, CDCl₃, δ): 154.0; 153.8; 146.8; 136.9; 126.7; 117.5; 111.7; 108.9; 34.3; 31.4.

Synthesis of tBuDCzPhenol: 3,6-di-tert-butylcarbazole (1.4 g, 5.0 mmol), iodocopper (38 mg, 0.2 mmol), sodium *tert*-butoxide (0.58 g, 6.0 mmol), and 1,10-phenanthroline (54 mg, 0.3 mmol) were added to a solution of **BrPhenol** (1.1 g, 2.0 mmol) in dry mesitylene. Then the mixture was performed for 24 h at 160 °C under nitrogen atmosphere. When cooling to room temperature, the mixture was extracted

with dichloromethane and water. And the combined organic layers were evacuated to dryness and the resulting product was purified by column chromatography on silica gel (eluent: dichloromethane/petroleum ether = 1:4) to afford **tBuDCzPhenol** as a white solid with 80% yield. ¹H NMR (500 MHz, CDCl₃, δ): 8.01 (d, *J*=2.0 Hz, 4.0H); 7.67 (s, 1.0H); 7.46 (dd, *J*₁=2.0 Hz, *J*₂=8.5 Hz, 4.0H); 7.29 (d, *J*=8.5 Hz, 4.0H); 7.05-7.02 (m, 4.0H); 6.97 (s, 1.0H); 6.70-6.67 (m, 4.0H); 1.44 (s, 36.0H); 1.16 (s, 18.0H). ¹³C{¹H} NMR (125 MHz, CDCl₃, δ): 153.9; 153.0; 146.7; 142.6; 139.3; 130.9; 126.0; 123.4; 123.3; 123.2; 118.1; 116.1; 110.6; 109.5; 34.7; 34.1; 32.1; 31.3.

Synthesis of TDBA-Cz: To a solution of tBuDCzPhenol (0.9 g, 1.0 mmol) in dry tert-butylbenzene (10 mL), tert-butyllithium (1.3 M, 1.5 mL, 2.0 mmol) was added drop by drop at 0 °C. After stirring for 2 h at 60 °C, the reaction mixture was cooled to 0 °C and boron tribromide (0.2 mL, 2.0 mmol) was added, then the reaction mixture was allowed to room temperature and stirred for 1 h. N,N-diisopropyl-ethylamine (0.4 mL, 2.0 mmol) was added at 0 °C and then the mixture was allowed to room temperature and stirred for 1 h. After stirring for 24 h at 140 °C, the mixture was then quenched by slow addition of 5 mL N,N-diisopropyl-ethylamine. The resulting mixture was extracted with dichloromethane and water, and then the combined organic layer was concentrated by evaporation under reduced pressure. The residue was further purified by silica gel chromatography (eluent:dichloromethane/petroleum ether = 1:4) to afford **TDBA-Cz** as a yellow powder with 35% yield. ¹H NMR (500 MHz, CDCl₃, δ): 8.81 (d, J=2.5 Hz, 2.0H); 8.19 (d, J=2.0 Hz, 4.0H); 8.13 (s, 1.0H); 7.68 (dd, $J_1=2.5$ Hz, J₂=9.0 Hz, 1.0H); 7.44 (dd, J₁=1.5 Hz, J₂=8.5 Hz, 4.0H); 7.22 (d, J=8.5 Hz, 4.0H); 7.09 (d, *J*=9.0 Hz, 2.0H); 1.48 (s, 18.0H); 1.47 (s, 36.0H). ¹³C{¹H} NMR (125 MHz, CDCl₃, δ): 158.1; 151.6; 145.8; 142.8; 139.8; 133.6; 132.0; 130.1; 123.6; 123.5; 118.5; 118.4; 116.2; 109.7; 34.8; 34.6, 32.1; 31.5. HRMS (ESI, m/z, [M+H]+): calcd. for C₆₆H₇₃BN₂O₂: 937.5765, found: 937.5022.

Synthesis of DBA-Cz: 3,6-di-tert-butylcarbazole (1.2 g, 4.2 mmol), tris(dibenzylideneacetone)dipalladium (183 mg, 0.2 mmol), sodium *tert*-butoxide (0.48 g, 5.0 mmol), and tri-*n*-butylphosphoniumtetrafluorobor (116 mg, 0.4 mmol) were

added to a solution of **DBA-2Br** (0.8 g, 2.0 mmol) in dry toluene. Then the mixture was performed for 24 h at 110 °C under nitrogen atmosphere. When cooling to room temperature, the mixture was extracted with dichloromethane and water. And the combined organic layers were evacuated to dryness and the resulting product was purified by column chromatography on silica gel (eluent: dichloromethane/petroleum ether = 1:4) to afford **DBA-Cz** as a yellow solid with 10% yield. ¹H NMR (500 MHz, CDCl₃, δ): 8.66 (d, *J*=2.5 Hz, 2.0H); 8.06 (d, *J*=1.5 Hz, 4.0H); 7.91 (t, *J*=8.0 Hz, 1.0H); 7.84 (dd, *J*₁=1.5 Hz, *J*₂=9.0 Hz, 2.0H); 7.77 (d, *J*₁=8.5 Hz, 2.0H); 7.37 (d, *J*=8.0 Hz, 2.0H); 7.29 (d, *J*=9.0 Hz, 4.0H); 7.23 (dd, *J*₁=1.5 Hz, *J*₂=8.5 Hz, 4.0H); 1.48 (s, 18.0H); 1.47 (s, 36.0H). ¹³C {¹H} NMR (125 MHz, CDCl₃, δ): 159.1; 157.4; 142.7; 139.5; 135.3; 133.2; 132.6; 131.9; 123.6; 123.3; 120.1; 116.2; 108.9; 108.9; 34.7; 32.0. HRMS (ESI, m/z, [M+H]⁺): calcd. for C₅₈H₅₇BN₂O₂: 825.4513, found: 825.4503.

2. Supplementary Figures and Tables



Figure S1. ¹H NMR spectrum of compound BrPnenol (CDCl₃).



Figure S2. ¹³C NMR spectrum of compound BrPnenol (CDCl₃).



Figure S3. ¹H NMR spectrum of compound tBuDCzPhenol (CDCl₃).



Figure S4. ¹³C NMR spectrum of compound tBuDCzPhenol (CDCl₃).



Figure S5. ¹H NMR spectrum of compound TDBA-Cz (CDCl₃).



Figure S6. ¹³C NMR spectrum of compound TABA-Cz (CDCl₃).



Figure S7. ¹H NMR spectrum of compound DBA-Cz (CDCl₃).



Figure S8. ¹³C NMR spectrum of compound DBA-Cz (CDCl₃).



Figure S9. TGA curve of TDBA-Cz.



Figure S10. TGA curve of DBA-Cz.



Figure S11. HOMO and LUMO distributions and the calculated ΔE_{ST} for **TDBA-Cz** and **DBA-Cz**.

Figure S12. CV curve of TDBA-Cz.

Figure S13. CV curve of DBA-Cz.

Table S1. Emission wavelengths and FWHMs for TDBA-Cz in different solvents.

TDBA-Cz	<i>n</i> -hexane	toluene	EA	DCM
λ_{em}	449	460	468	476
FWHM	36	43	50	57

DBA-Cz	<i>n</i> -hexane	toluene	EA	DCM
λ_{em}	432	447	463	479
FWHM	19	38	63	72

Table S2. Emission wavelengths and FWHMs for DBA-Cz in different solvents.

Figure S14. PL spectra of TDBA-Cz in DPEPO films with different doping concentration.

Table S3. Emission wavelengths and FWHMs for TDBA-Cz in DPEPO films with

TDBA-Cz	10%	20%	30%	50%	100%
λ_{em}	456	455	456	458	462
FWHM	46	41	41	41	41

different doping concentration.

Figure S15. PL spectra of DBA-Cz in DPEPO films with different doping concentration.

Table S4. Emission wavelengths and FWHMs for DBA-Cz in DPEPO films with

DBA-Cz	10%	20%	30%	50%	100%
λ_{em}	450	458	469	486	494
FWHM	47	54	72	82	75

different doping concentration.

Figure S16. PLQY of TDBA-Cz and DBA-Cz in DPEPO films with different doping

concentration.

Figure S17. Temperature-dependent transient PL decay of **TDBA-Cz** and **DBA-Cz** in neat film from 77 to 300 K.

Figure S18. Single crystal structure (a and b) and packing diagrams of **TDBA-Cz** (c and d) (CCDC: 2130844).

Figure S19. EL performances of the TADF-OLEDs based on DBA-Cz. a) EL spectra.b) EQE versus luminance curves. c) Current density and luminance versus voltage characteristics.

Emitter	Dopant Ratio	V _{on} [V]	$\lambda_{ m EL}$ [nm]	FWHM [nm]	EQE [%]	CE [cd/A]	CIE (x,y)
	10%	2.5	467	50	30.3	34.4	0.136, 0.147
DBA-	20%	2.6	471	51	29.3	41.4	0.136, 0.183
Cz	50%	2.9	474	55	16.2	28.6	0.147, 0.259
	100%	4.6	478	63	11.3	28.5	0.170, 0.312

Table S5 EL data of the OLEDs based on DBA-Cz

Figure S20. CIE coordinates of TDBA-Cz and DBA-Cz-based devices at different doping ratios.

Figure S21. Device lifetime data of (a) **TDBA-Cz** and (b) **DBA-Cz** devices with the doping concentrations of 10 wt%, 50 wt%, and 100 wt% measured at initial luminance of 100 nit.

EML Emitter	V _{on} [V]	$\eta_{c,max}$ [cd/A]	λ _{em} [nm]	FWHM [nm]	EQE [%]	Process	Ref.
TB-tCz	3.68	2.19	416	44	8.21	Solution	[1]
TB-tPCz	3.54	5.61	428	42	15.8	Solution	[1]
2	3.5	33.6	474	59	21.3	Vacuum	[2]
BBFCz	3.5	2.88	416	42	6.8	Solution	[4]
1	3.6	30.1	473	57	20.7	Vacuum	[5]
3	4.4	25.7	473	59	17.4	Vacuum	[5]
B-oCz	4.4	11.6	463	60	8	Solution	[6]
B-oTC	3.9	37.3	474	56	19.1	Solution	[6]
sAC- sDBB	3.1	19.3	452	51	22.5	Vacuum	[7]
TDBA-Cz	2.4	31.5	467	45	21.4	Vacuum	This Work

Table S6. The summary of EL performance of non-doped blue OLEDs reported inliteratures on the premise of FWHM less than 60 nm.

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