Supporting Information

Synergistic Optimization of MR-TADF Materials via Rigid Skeleton and Charge Delocalization for Enhanced Photoluminescence and Electroluminescence Performance

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1. Instrumentation and materials.

All of the reagent and solvent were obtained from commercial sources and directly used without any further purification. ¹H and ¹³C NMR spectra were measured on a Bruker ARX 500 NMR spectrometer and reported as parts per million (ppm) from the internal standard TMS. Highresolution mass spectra were recorded on a MICROTOF-Q III instrument. Absorption and photoluminescence spectra were measured on a Shimadzu UV-3100 and a Hitachi F-4600 photoluminescence spectrophotometer, respectively. Cyclic voltammetry measurements were conducted on a MPI-A multifunctional electrochemical luminescent system (Xi'an Remex Analytical Instrument Ltd. Co., China) at room temperature with a polished Pt plate as the working electrode, platinum thread as the counter electrode and Ag-AgNO₃ (0.1 M) in CH₃CN as the reference electrode, tetra-n-butylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte, respectively, using Fc^+/Fc as the internal standard, the scan rate was 0.1 V/s. The absolute photoluminescence quantum yields via an integrating sphere and the decay lifetimes of the compounds were measured with HORIBA Fluorolog-3 fluorescence spectrometer. The thermogravimetric analysis (TGA) curve was performed on a Pyris 1 DSC under nitrogen at a heating rate of 10 °C min⁻¹. The ground state calculations are based on optimized structure using Gaussian 09 by density functional theory (DFT) using the B3LYP functional with the 6-31G(d,p) basis set; excited state calculations were conducted by time-dependent density functional theory (TD-DFT) with B3LYP functional with the 6-31G(d,p) basis set.

Indium-tin-oxide (ITO) coated glass with a sheet resistance of 10 Ω sq⁻¹ was used as the anode substrate. Prior to film deposition, patterned ITO substrates were cleaned with detergent, washed by de-ionized water, dried and treated with oxygen plasma for 10 minutes at a pressure of 10 Pa to enhance the surface work function of ITO anode (from 4.7 to 5.1 eV). All the organic layers were

deposited with the rate of 0.1 nm/s under high vacuum ($\leq 9 \times 10^{-5}$ Pa). The doped layers were prepared by co-evaporating dopant and host material from two individual sources, and the doping concentrations were modulated by controlling the evaporation rate of dopant. LiF and A1 were deposited in another vacuum chamber ($\leq 1.0 \times 10^{-4}$ Pa) with the rates of 0.01 and 1 nm/s, respectively, without being exposed to the atmosphere. The thicknesses of these deposited layers and the evaporation rate of individual materials were monitored in vacuum with quartz crystal monitors. A shadow mask was used to define the cathode and to make ten emitting dots (with the active area of 10 mm²) on each substrate. Device performances were measured via using a programmable Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a silicon photodiode. The EL spectra were measured with a Hitachi F-4600 spectrophotometer. Based on the uncorrected EL fluorescence spectra, the Commission International e de l'Eclairage (CIE) coordinates were calculated using the test program of Spectra scan PR650 spectrophotometer. The EQE of EL devices were calculated based on the photo energy measured by the photodiode, the EL spectrum, and the current pass through the OLED.

2. Experimental section

The synthesis details of two materials are described in the following:

2.1 Preparation procedure for OFBr

4-(*tert*-butyl)phenol (2.0 g, 13.3 mmol), 2-bromo-1,3-difluorobenzene (2.7 g, 14.0 mmol) and Cs₂CO₃ (6.5 g, 20.0 mmol) were dissolved in DMF (35 mL) at room temperature. Then the mixture was stirred at 160 °C for 16 h. After cooling to room temperature, the reaction mixture was poured into a large amount of water. The product was extracted with dichloromethane, and the combined organic layer was dried over anhydrous MgSO₄. After evaporation, the product was purified by column chromatography (PE/DCM= 8/1, v/v) to get the OFBr as a white solid (1.6 g, yield: 37%). ¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.38 (m, 2H), 7.20 (td, *J* = 8.3, 6.4 Hz, 1H), 6.96 (dd, *J* = 9.2, 2.4 Hz, 2H), 6.91 (td, *J* = 8.2, 0.8 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 1.35 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 161.37 (s), 159.41 (s), 156.14 (d, *J* = 3.4 Hz), 153.85 (s), 147.08 (s), 128.41 (d, *J* = 9.5 Hz), 126.75 (s), 126.32 (s), 118.43 (s), 115.94 (s), 34.40 (s), 31.48 (s). HRMS (MALDI-TOF, m/z): [M]+ calcd for C₁₆H₁₆BrFO, 323.205; found, 323.476.

2.2 Preparation procedure for OYCzBr

5,12-dihydroindolo[3,2-a]carbazole (0.5 g, 2.0 mmol), OFBr (0.7 g, 2.2 mmol) and Cs_2CO_3 (1.0 g, 3.0 mmol) were dissolved in DMF (10 mL) at room temperature. Then the mixture was stirred at 160 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into a large

amount of water. The product was extracted with dichloromethane, and the combined organic layer was dried over anhydrous MgSO₄. After evaporation, the product was purified by column chromatography (PE/DCM= 4/1, v/v) to get the OYCzBr as a white solid (0.4 g, yield: 36%). ¹H NMR (500 MHz, CDCl₃) δ 8.29 (d, *J* = 7.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.42 (m, 6H), 7.36 – 7.30 (m, 2H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.15 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.08 (dd, *J* = 17.2, 8.6 Hz, 3H), 1.38 (s, 9H). HRMS (MALDI-TOF, m/z): [M]+ calcd for C₃₄H₂₇BrN₂O, 559.507; found, 559.848.

2.3 Preparation procedure for OYCzPhBr

A mixture of iodobenzene (0.9 g, 4.5 mmol), OYCzBr (1.3 g, 2.3 mmol) in 5 mL 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one (DMPU) in a sealed tube were heated to 200 °C overnight with Cu powder (32.0 mg, 0.5 mmol) as catalyst, 18-crown-6 (240.0 mg, 1 mmol) as phase transfer catalyst, and K₂CO₃ (1.5 g, 10.5 mmol) as base. The resulting mixture was washed with 20 mL three times and extracted with 20 mL dichloromethane before dried with Na₂SO₄. The product OYCzPhBr was obtained through column chromatography with eluent of petroleum ether as white solid (yield = 1.1 g, 75%). ¹H NMR (500 MHz, CDCl₃) δ 8.25 – 8.17 (m, 2H), 7.71 (d, *J* = 18.4 Hz, 5H), 7.52 – 7.45 (m, 3H), 7.40 – 7.29 (m, 4H), 7.25 (dd, *J* = 13.4, 4.7 Hz, 1H), 7.15 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.12 – 7.04 (m, 4H), 6.86 – 6.81 (m, 1H), 5.97 (dd, *J* = 8.0, 4.3 Hz, 1H), 1.38 (s, 9H). HRMS (MALDI-TOF, m/z): [M]+ calcd for C₄₀H₃₁BrN₂O, 635.605; found, 635.912.

2.4 Preparation procedure for OYCzPhBN

To a solution of OYCzPhBr (1.0 g, 1.6 mmol) in *tert*-butylbenzene was slowly added *n*-BuLi (2.5 M in hexane, 1.9 mL, 4.8 mmol) at -5 °C. After reacting for 2 h at 80 °C, BBr₃ (0.5 mL, 4.8 mmol) was slowly added at -35 °C, and then the mixture was stirred at room temperature for 0.5 h. After addition of NEt(*i*-Pr)₂ (0.9 mL) at -5 °C, the reaction mixture was further stirred at 140 °C for 18 h. After cooling to room temperature, the reaction mixture was carefully quenched by addition of saturated brine. The product was extracted with dichloromethane, and the combined organic layer was dried over anhydrous Na₂SO₄. After filtration and evaporation, the crude product was purified by column chromatography on silica gel (eluent: hexane/chloroform = 7:1, v/v) and recrystallization from chloroform/methanol to afford OYCzPhBN as a yellow solid (yield = 0.2 g, 22%). ¹H NMR (500 MHz, CD₂Cl₂) δ 9.88 (s, 1H), 9.32 (s, 1H), 8.60 (d, *J* = 7.7 Hz, 2H), 8.50 – 8.43 (m, 3H), 8.38 (d, *J* = 1.9 Hz, 1H), 8.09 (t, *J* = 8.2 Hz, 1H), 7.77 (s, 5H), 7.48 (ddd, *J* = 25.8, 12.9, 6.2 Hz, 4H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.17 (d, *J* = 8.0 Hz, 1H), 1.59 (s, 9H). HRMS (MALDI-TOF, m/z): [M]+ calcd for C₄₉H₂₀BN₂O, 564.495; found, 564.849.

2.5 Preparation procedure for CzFBr

3,6-di-*tert*-butyl-9*H*-carbazole (2.8 g, 10.0 mmol), 2-bromo-1,3-difluorobenzene (2.7 g, 14.0 mmol) and Cs₂CO₃ (6.5 g, 20.0 mmol) were dissolved in DMF (35 mL) at room temperature. Then the mixture was stirred at 160 °C for 16 h. After cooling to room temperature, the reaction mixture was poured into a large amount of water. The product was extracted with dichloromethane, and the combined organic layer was dried over anhydrous MgSO₄. After evaporation, the product was purified by column chromatography (PE/DCM= 10/1, v/v) to get the CzFBr as a white solid (2.3 g, yield: 51%). ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, *J* = 1.7 Hz, 2H), 7.52 – 7.46 (m, 3H), 7.36 – 7.29 (m, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 1.50 (s, 18H). HRMS (MALDI-TOF, m/z): [M]+ calcd for C₂₆H₂₇BrFN, 452.411; found, 452.666.

2.6 Preparation procedure for CzYCzBr

The relevant reaction routes refer to the synthesis of OYCzBr. The product was purified by column chromatography (PE/DCM= 4/1, v/v) to get the CzYCzBr as a white solid, and directly used for the next reaction step.

2.7 Preparation procedure for CzYCzPhBr

The relevant reaction routes refer to the synthesis of OYCzPhBr. The product was purified by column chromatography (PE/DCM= 10/1, v/v) to get the CzYCzPhBr as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 8.28 (d, *J* = 8.5 Hz, 1H), 8.19 (dd, *J* = 5.1, 3.0 Hz, 3H), 7.81 – 7.68 (m, 8H), 7.54 (ddd, *J* = 22.3, 8.6, 1.9 Hz, 2H), 7.41 – 7.30 (m, 4H), 7.23 – 7.14 (m, 4H), 6.86 (t, *J* = 7.6 Hz, 1H), 5.97 (d, *J* = 8.1 Hz, 1H), 1.50 (d, *J* = 7.4 Hz, 18H). HRMS (MALDI-TOF, m/z): [M]+ calcd for C₅₀H₄₂BrN₃, 764.811; found, 765.202.

2.8 Preparation procedure for CzYCzPhBN

The relevant reaction routes refer to the synthesis of OYCzPhBN. The product was purified by column chromatography (PE/DCM= 10/1, v/v) to get the CzYCzPhBN as a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 9.65 (s, 1H), 9.02 (s, 1H), 8.49 (d, *J* = 8.3 Hz, 1H), 8.31 (dd, *J* = 28.5, 8.2 Hz, 2H), 8.20 (d, *J* = 8.6 Hz, 1H), 7.93 – 7.83 (m, 2H), 7.74 – 7.65 (m, 7H), 7.61 – 7.55 (m, 1H), 7.49 (dd, *J* = 6.2, 2.7 Hz, 2H), 7.45 – 7.30 (m, 6H), 7.24 (s, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.10 (d, *J* = 8.0 Hz, 1H), 1.64 (s, 8H), 1.57 (s, 3H), 1.31 (d, *J* = 25.9 Hz, 7H). HRMS (MALDI-TOF, m/z): [M]+ calcd for C₅₀H₄₀BN₃, 693.701; found, 694.058.

3. NMR spectra





Fig. S4 ¹H NMR spectrum of OYCzPhBr in CDCl₃.







3. Thermal gravimetric analyzer



4. Absorption and emission performance

4.1 Photophysical data of OYCzPhBN and CzYCzPhBN

Table S1. Photophysical	data of the OYCzPhBN a	nd CzYCzPhBN.
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Compound	$\lambda_{abs}{}^{a}$	$\lambda_{PL}{}^{b}$	FWHM [◦]	S_1^d	T_1^e	$\Delta E_{\rm ST}^{\rm f}$	$arPsi_{ ext{PL}}{}^{ ext{g}}$	$ au_{ m p}{}^{ m h}$	$ au_{ m d}{}^{ m h}$	$k_{ m f}{}^{ m i}$	$k_{\rm ISC}{}^{\rm i}$	$k_{\rm RISC}^{i}$
	[nm]	[nm]	[nm]	[eV]	[eV]	[eV]	[%]	[ns]	[µs]	$[10^8 \text{ s}^{-1}]$	$[10^8 \text{ s}^{-1}]$	$[10^5 \text{ s}^{-1}]$
OYCzPhBN	434	448	20	2.76	2.53	0.23	89	2.57	4.83	3.1	0.8	1.3
CzYCzPhBN	469	491	19	2.54	2.42	0.12	92	1.65	2.78	4.7	1.3	3.0

^aAbsorption peak at room temperature measured in toluene solution $(5.0 \times 10^{-5} \text{ M})$. ^bEmission peak at room temperature measured in toluene solution $(5.0 \times 10^{-5} \text{ M})$. ^cFull width at half maximum of emission spectrum for PL spectrum. ^dCalculated by the fluorescence spectrum at room temperature. ^cCalculated by the phosphorescence spectrum at 77 K. ^fEstimated by S₁ and T₁. ^gAbsolute photoluminescence quantum yield measured in doped film. ^bprompt decay and delayed fluorescence lifetime in doped film. ⁱRate constant of fluorescence radiative decay (S₁ \rightarrow S₀): $k_f = \Phi_{p} / \tau_p$; Rate constant of ISC (S₁ \rightarrow T₁); $k_{ISC} = (1 - \Phi_p) / \tau_p$; Rate constant of RISC (T₁ \rightarrow S₁); $k_{RISC} = \Phi_d / (k_{ISC} \cdot \tau_p \cdot \tau_d \cdot \Phi_p)$.

4.2 UV-vis spectra of two emitters in various solvents



Fig. S10 UV-vis spectra of OYCzPhBN (a) and CzYCzPhBN (b) in various solvents.

4.3 PL spectra of two emitters in various solvents



Fig. S11 PL spectra of OYCzPhBN (a) and CzYCzPhBN (b) in various solvents.



4.4 PL spectra of two emitters in various solvents

Fig. S12 Fluorescence and phosphorescence spectra of CzYCzPhBN (a) and OYCzPhBN (b) at 77K

5. Cyclic voltammogram curves



Fig. S13 Cyclic voltammogram curves of OYCzPhBN (a) and CzYCzPhBN (b) and ferrocene measured in CH₃CN/DCM containing 0.1 M *tetra-n*-butylammonium hexafluorophosphate

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Molecule	$E_{(Fc/Fc^+)}^{a}(V)$	$E_{\text{ox,onset}^{a}}(V)$	$E_{\rm g,opt}^{\rm b} ({\rm eV})$	$E_{\rm HOMO}^{\rm c}({\rm eV})$	$E_{\rm LUMO}^{\rm d} ({\rm eV})$
OYCzPhBN	0.48	1.38	2.76	-5.70	-2.94
CzYCzPhBN	0.48	1.02	2.48	-5.34	-2.86

Table S2. Electrochemical properties of OYCzPhBN and CzYCzPhBN

^aThe onset of oxidation curve; ^bOptical gap (1240/ λ_{onset}); ^c E_{HOMO} = -[$Eox - E_{(Fc/Fc^+)} + 4.8$] eV; ^d E_{LUMO} =($E_{HOMO} + E_{g,opt}$).

6. Calculation

S ₁ -geom		E	xperiment	al value	B3LYI	P/6-31G(d	l,p) So	CS-CC2/co	c-pVDZ
	S ₁ [eV]	T ₁ [eV]	$\Delta E_{ m ST}$ [eV]	S ₁ [eV]	T ₁ [eV]	$\Delta E_{ m ST}$ [eV]	S ₁ [eV]	T ₁ [eV]	$\Delta E_{ m ST}$ [eV]
OYCzP hBN	2.76	2.53	0.23	3.03	2.59	0.44	3.24	3.10	0.14
CzYCz PhBN	2.54	2.42	0.12	2.85	2.45	0.40	3.03	2.92	0.11

Table S3. Comparison of ΔE_{ST} values of two MR-TADF materials under different calculation methods

Geometry Optimization:

The ground-state (S_0) geometries of both MR-TADF emitters were fully optimized in vacuo using density functional theory (DFT) with the B3LYP functional and the 6-31G(d,p) basis set in Gaussian 09.

The first excited-state (S_1) geometries were optimized using time-dependent DFT (TD-DFT) at the same level of theory (B3LYP/6-31G(d,p)), ensuring consistency for subsequent excited-state calculations.

Excited-State Calculations:

Vertical excitation energies and electronic properties (e.g., singlet-triplet energy gaps, ΔE_{ST}) were computed using the SCS-CC2/cc-pVDZ method via the MRCC-2022 software package. This approach accounts for multi-reference character and provides reliable estimates for MR-TADF systems.

All calculations were performed on the S_0 -optimized geometries unless explicitly stated otherwise (e.g., emission energies derived from S_1 -optimized structures).

Transparency & Reproducibility:

The Cartesian coordinates of all optimized geometries (S_0 and S_1) are now provided in the revised SI as follows:.

OYCzPhBN: the coordinates of S₀ state

Symbolic Z-matrix:

Charge = 0	Multiplicity	y = 1	
Ν	-0.4608	2.46435	0.1277
В	2.03451	1.01223	-0.14525
С	3.0695	3.29807	-0.54477
С	3.02547	4.67216	-0.7882
С	1.78397	5.29694	-0.76827
С	0.61077	4.59532	-0.4786
С	0.67788	3.22639	-0.19037
С	1.92117	2.53539	-0.26159
С	4.52154	1.3957	-0.35965
С	-1.7575	2.89214	0.47671
С	-2.62036	1.76002	0.50211
С	-1.80247	0.59803	0.18361
С	-0.47189	1.06886	0.03833
С	3.48699	0.47582	-0.10584
С	3.88951	-0.85061	0.18901
С	5.21718	-1.27168	0.20386
С	6.20116	-0.30278	-0.09464
С	-1.98112	-0.7906	0.02619
С	-0.84201	-1.63568	-0.15012
С	0.44881	-1.11514	-0.2109
С	0.68616	0.26734	-0.12058
С	-2.21012	4.1556	0.87023
С	-3.54583	4.29655	1.2429
С	-4.41315	3.19801	1.24803
С	-3.95479	1.9312	0.8964
Ν	-3.12469	-1.58877	0.03277
С	-2.73745	-2.93182	-0.13418
С	-1.33048	-2.9967	-0.23885
С	-3.53669	-4.0727	-0.22014
С	-2.89452	-5.29893	-0.39224
С	-1.4952	-5.3846	-0.48218
С	-0.70707	-4.23817	-0.40954

С	-4.47861	-1.1677	-0.1419
С	-5.43337	-1.48398	0.83029
С	-6.76329	-1.10339	0.64286
С	-7.13831	-0.40431	-0.50663
С	-6.18175	-0.09326	-1.47586
С	-4.85356	-0.48149	-1.30203
С	5.64292	-2.71509	0.52909
С	4.43928	-3.62737	0.83096
С	6.56825	-2.71313	1.76936
С	6.40733	-3.31009	-0.67757
Н	3.93906	5.2135	-1.00591
Н	1.71724	6.35747	-0.99171
Н	-0.33512	5.11167	-0.53468
Н	3.11324	-1.56141	0.4377
Н	7.25084	-0.58047	-0.10119
Н	1.27871	-1.79758	-0.35549
Н	-1.54561	5.00447	0.93997
Н	-3.90569	5.2727	1.55339
Н	-5.44699	3.32681	1.55323
Н	-4.6244	1.08497	0.95648
Н	-4.61728	-4.01151	-0.15608
Н	-3.49155	-6.20352	-0.45815
Н	-1.02514	-6.35438	-0.61313
Н	0.37405	-4.30645	-0.48858
Н	-5.12654	-2.0114	1.72754
Н	-7.50286	-1.34643	1.3995
Н	-8.17203	-0.10383	-0.64693
Н	-6.4698	0.44671	-2.37248
Н	-4.10495	-0.25301	-2.05341
Н	3.75745	-3.69776	-0.02308
Н	4.79257	-4.63899	1.0548
Н	3.86881	-3.27779	1.69756
Н	7.46885	-2.11388	1.60552
Н	6.88728	-3.7339	2.00799

Н	6.04947	-2.30627	2.64359
Н	6.72507	-4.33562	-0.4585
Н	5.77241	-3.33427	-1.56936
Н	7.30293	-2.73022	-0.91987
С	5.86832	1.01292	-0.36827
Н	6.62936	1.75672	-0.58023
0	4.30828	2.72625	-0.62346

OYCzPhBN: the coordinates of S_1 state

Symbolic Z-matrix:

Charge =	0 Multiplici	ty = 1	
Ν	0.1059	-1.2176	-0.4896
В	-2.4476	-0.3929	0.2151
С	-3.1912	-2.7306	-0.3023
С	-2.8271	-3.9817	-0.6396
С	-1.5676	-4.3146	-0.9362
С	-0.5997	-3.395	-0.8897
С	-0.822	-2.1207	-0.5159
С	-2.1335	-1.8752	-0.2541
С	-4.7134	-1.2272	0.4425
С	1.3908	-1.3124	-0.5398
С	1.957	-0.0876	-0.5363
С	0.9723	0.8208	-0.552
С	-0.1164	0.0451	-0.3821
С	-3.9411	-0.1653	0.6927
С	-4.4416	0.9444	1.2573
С	-5.7505	1.0725	1.5526
С	-6.5405	0.0202	1.2619
С	0.9004	2.1691	-0.6458
С	-0.2813	2.6869	-0.2712
С	-1.3799	1.9648	-0.0274
С	-1.2944	0.6347	-0.1393
С	2.243	-2.3577	-0.5057
С	3.5765	-2.1977	-0.4914

С	4.1067	-0.9705 -0.4333
С	3.2834	0.0852 -0.4222
Ν	1.7118	3.1334 -0.9285
С	1.1282	4.245 -0.6321
С	-0.123	4.0079 -0.2053
С	1.4464	5.5472 -0.7762
С	0.6	6.523 -0.4025
С	-0.6169	6.2349 0.0818
С	-0.9984	4.9529 0.1633
С	2.866	3.033 -1.4879
С	3.8828	3.9123 -1.3615
С	5.0602	3.7753 -1.9928
С	5.2683	2.743 -2.8193
С	4.2766	1.8623 -2.9988
С	3.1128	2.0172 -2.3471
С	-6.3447	2.3379 2.1838
С	-5.3114	3.4606 2.4358
С	-6.9764	1.9784 3.5466
С	-7.4271	2.9175 1.2459
Н	-3.5039	-4.8344 -0.6819
Н	-1.3298	-5.3491 -1.2433
Н	0.3568	-3.7748 -1.2546
Н	-3.7477	1.7589 1.4838
Н	-7.6184	0.0546 1.4756
Н	-2.3193	2.4588 0.2407
Н	1.9425	-3.4054 -0.4043
Н	4.2441	-3.0752 -0.4385
Н	5.1966	-0.8356 -0.3345
Н	3.7346	1.0735 -0.2598
Н	2.3753	5.9034 -1.2389
Н	0.8899	7.5807 -0.5282
Н	-1.3116	7.0428 0.3656
Н	-2.0129	4.7062 0.5131
Н	3.8406	4.75 -0.6515

Н	5.8712	4.5033	-1.82
Н	6.2299	2.6251	-3.3451
Н	4.4135	1.0218	-3.7003
Н	2.3283	1.2909	-2.617
Н	-4.8321	3.8054	1.4914
Н	-5.7917	4.358	2.8876
Н	-4.5162	3.1433	3.1477
Н	-7.8119	1.2501	3.4536
Н	-7.397	2.8788	4.049
Н	-6.2182	1.5342	4.2313
Н	-7.8612	3.8563	1.6583
Н	-6.9996	3.1558	0.2452
Н	-8.2797	2.2209	1.0894
С	-6.0095	-1.0891	0.7334
Н	-6.65975	-1.9145	0.53147
0	-4.4064	-2.3881	-0.0158

CzYCzPhBN: the coordinates of S_0 state

Symbolic Z-matrix:

Charge = 0	Multiplicity = 1
Ν	-3.142 -1.1744 -0.03934
Ν	1.57807 -2.24145 0.4273
В	-0.4307 -0.18636 0.22026
С	-2.12848 -2.14271 0.05689
С	-2.42567 -3.51263 0.04985
С	-1.38479 -4.43376 0.05398
С	-0.05351 -4.03777 0.12803
С	0.24826 -2.6758 0.25793
С	-0.77895 -1.68839 0.1847
С	-2.89042 0.17511 0.21691
С	-4.09981 0.89848 0.24877
С	-5.15479 -0.04846 -0.06277
С	-4.53717 -1.31152 -0.26742
С	2.73685 -2.9884 0.73078

С	3.87604 -2.14706 0.57387
С	3.38145 -0.82997 0.19951
С	1.96701 -0.92046 0.19916
С	-6.52993 0.10683 -0.22396
С	-7.33341 -0.9747 -0.61263
С	-6.69133 -2.20085 -0.85781
С	-5.31425 -2.38641 -0.70035
С	-1.63359 0.76511 0.38832
С	-1.65552 2.1492 0.67965
С	-2.83227 2.90824 0.76032
С	-4.06332 2.26051 0.52372
С	3.90989 0.44205 -0.09705
С	3.02857 1.55647 -0.2579
С	1.64535 1.411 -0.16584
С	1.06023 0.15432 0.06428
С	2.86672 -4.28812 1.23184
С	4.1436 -4.76663 1.52161
С	5.27435 -3.96228 1.3409
С	5.1456 -2.6527 0.88625
Ν	5.22133 0.8914 -0.25093
С	5.19611 2.27518 -0.50677
С	3.85534 2.71991 -0.50652
С	6.26061 3.14239 -0.75706
С	5.95922 4.48465 -0.98761
С	4.63313 4.94816 -0.97508
С	3.57637 4.07176 -0.73858
С	6.38619 0.09992 -0.48895
С	7.48425 0.20691 0.37119
С	8.63569 -0.54092 0.11918
С	8.68956 -1.39769 -0.98251
С	7.59147 -1.49942 -1.83985
С	6.44236 -0.74565 -1.60226
С	-2.82959 4.41509 1.08843
С	-1.40953 4.96634 1.31687

С	-3.65225 4.66367 2.37533
С	-3.4652 5.20039 -0.08365
С	-8.85336 -0.78205 -0.7746
С	-9.45966 -0.32944 0.57502
С	-9.56544 -2.07689 -1.20955
С	-9.1268 0.30047 -1.84575
Н	-3.44323 -3.86758 0.0618
Н	-1.6176 -5.49292 -0.00367
Н	0.72452 -4.78118 0.05498
Н	-6.9702 1.08522 -0.05597
Н	-7.2691 -3.0535 -1.1936
Н	-4.8908 -3.34565 -0.95936
Н	-0.70784 2.6373 0.86578
Н	-4.99136 2.82335 0.56001
Н	1.01425 2.28322 -0.29841
Н	2.00773 -4.90672 1.44659
Н	4.25133 -5.77323 1.91396
Н	6.25897 -4.3506 1.58239
Н	6.02271 -2.02645 0.8041
Н	7.28546 2.78888 -0.77261
Н	6.76844 5.18241 -1.18101
Н	4.43133 5.99955 -1.15529
Н	2.55144 4.43125 -0.73891
Н	7.42386 0.86165 1.23436
Н	9.48595 -0.45937 0.78924
Н	9.58381 -1.98313 -1.17257
Н	7.63046 -2.16133 -2.69941
Н	5.5879 -0.81066 -2.26771
Н	-0.78009 4.85329 0.42802
Н	-1.46419 6.035 1.54788
Н	-0.90938 4.47242 2.15615
Н	-4.68992 4.33438 2.2663
Н	-3.66638 5.73209 2.61849
Н	-3.21865 4.12755 3.22594

Н	-3.47678 6.27335 0.13868
Н	-2.89714 5.05113 -1.00782
Н	-4.49729 4.88991 -0.27179
Н	-9.02333 0.61212 0.92145
Н	-10.54065 -0.17955 0.47615
Н	-9.29077 -1.08234 1.35196
Н	-9.20735 -2.43339 -2.18089
Н	-10.6402 -1.89117 -1.30285
Н	-9.43151 -2.88112 -0.47873
Н	-10.20521 0.45281 -1.96651
Н	-8.68371 1.26328 -1.57466
Н	-8.71494 0.00365 -2.81592

CzYCzPhBN: the coordinates of S_1 state

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1				
Ν	-4.4064	-2.3881	-0.0158	
Ν	0.1059	-1.2176	-0.4896	
В	-2.4476	-0.3929	0.2151	
С	-3.1912	-2.7306	-0.3023	
С	-2.8271	-3.9817	-0.6396	
С	-1.5676	-4.3146	-0.9362	
С	-0.5997	-3.395	-0.8897	
С	-0.822	-2.1207	-0.5159	
С	-2.1335	-1.8752	-0.2541	
С	-4.7134	-1.2272	0.4425	
С	-6.0095	-1.0891	0.7334	
С	-6.5441	-2.2581	0.3872	
С	-5.5335	-3.0206	-0.0737	
С	1.3908	-1.3124	-0.5398	
С	1.957	-0.0876	-0.5363	
С	0.9723	0.8208	-0.552	
С	-0.1164	0.0451	-0.3821	
С	-7.8276	-2.6314	0.4682	

С	-8.2058	-3.8544	0.0581
С	-7.224	-4.6285	-0.438
С	-5.9408	-4.2291	-0.5077
С	-3.9411	-0.1653	0.6927
С	-4.4416	0.9444	1.2573
С	-5.7505	1.0725	1.5526
С	-6.5405	0.0202	1.2619
С	0.9004	2.1691	-0.6458
С	-0.2813	2.6869	-0.2712
С	-1.3799	1.9648	-0.0274
С	-1.2944	0.6347	-0.1393
С	2.243 -	2.3577	-0.5057
С	3.5765	-2.1977	-0.4914
С	4.1067	-0.9705	-0.4333
С	3.2834	0.0852	-0.4222
Ν	1.7118	3.1334	-0.9285
С	1.1282	4.245	-0.6321
С	-0.123	4.0079	-0.2053
С	1.4464	5.5472	-0.7762
С	0.6 6	.523 -0	0.4025
С	-0.6169	6.2349	0.0818
С	-0.9984	4.9529	0.1633
С	2.866	3.033 -	1.4879
С	3.8828	3.9123	-1.3615
С	5.0602	3.7753	-1.9928
С	5.2683	2.743	-2.8193
С	4.2766	1.8623	-2.9988
С	3.1128	2.0172	-2.3471
С	-6.3447	2.3379	2.1838
С	-5.3114	3.4606	2.4358
С	-6.9764	1.9784	3.5466
С	-7.4271	2.9175	1.2459
С	-9.6731	-4.2898	0.1414
С	-10.1502	-4.2084	1.6087

С	-9.9257	-5.7361	-0.3419
С	-10.5317	-3.3525	-0.7359
Н	-3.5039	-4.8344	-0.6819
Н	-1.3298	-5.3491	-1.2433
Н	0.3568	-3.7748	-1.2546
Н	-8.5728	-1.9282	0.8672
Н	-7.4548	-5.634	-0.8235
Н	-5.2866	-4.97 ·	-0.976
Н	-3.7477	1.7589	1.4838
Н	-7.6184	0.0546	1.4756
Н	-2.3193	2.4588	0.2407
Н	1.9425	-3.4054	-0.4043
Н	4.2441	-3.0752	-0.4385
Н	5.1966	-0.8356	-0.3345
Н	3.7346	1.0735	-0.2598
Н	2.3753	5.9034	-1.2389
Н	0.8899	7.5807	-0.5282
Н	-1.3116	7.0428	0.3656
Н	-2.0129	4.7062	0.5131
Н	3.8406	4.75 -	0.6515
Н	5.8712	4.5033	-1.82
Н	6.2299	2.6251	-3.3451
Н	4.4135	1.0218	-3.7003
Н	2.3283	1.2909	-2.617
Н	-4.8321	3.8054	1.4914
Н	-5.7917	4.358	2.8876
Н	-4.5162	3.1433	3.1477
Н	-7.8119	1.2501	3.4536
Н	-7.397	2.8788	4.049
Н	-6.2182	1.5342	4.2313
Н	-7.8612	3.8563	1.6583
Н	-6.9996	3.1558	0.2452
Н	-8.2797	2.2209	1.0894
Н	-10.1136	-3.1748	2.0174

Н	-11.2056	-4.5482	1.7118
Н	-9.5237	-4.8527	2.2669
Н	-9.6632	-5.8688	-1.4159
Н	-11.0008	-6.0114	-0.2495
Н	-9.3579	-6.4797	0.2621
Н	-11.6039	-3.6525	-0.7211
Н	-10.4947	-2.2942	-0.3954
Н	-10.1902	-3.3761	-1.7959

6. Device characterization



Fig. 14 The device structure and chemical structures of each functional layer molecules.

Device	$\lambda_{\rm EL}{}^{\rm a}$ [nm]	FWHM ^b [nm]	V _{on} ^c [V]	L _{max} ^d [cd m ⁻²]	CE° [cd A ⁻¹]	EQE ^f [%]	$CIE^{g}(x,y)$
D-CzYCzPhBN	484	23	3.2	8392	48.2/23.7/21.6/9.7	35.0/17.2/15.8/7.1	0.09, 0.26
D-OYCzPhBN	447	25	3.4	2607	6.1/5.0/2.4/1.1	10.8/8.8/4.2/2.0	0.15, 0.05

Table S4. Device performances of HF-OLEDs.

^aThe electroluminescence peak. ^bFull width at half maximum of electroluminescence spectrum. ^cTurn-on voltage at 1 cd m⁻². ^dMaximum luminance. ^eMaximum current efficiency and current efficiency at 10, 100 and 1000 cd m⁻². ^fMaximum external quantum efficiency and external quantum efficiency at 10, 100 and 1000 cd m⁻². ^gCommission Internationale de l'Éclairage color coordinates measured at 10 mA cm⁻².