Supporting Information

High-efficient Blue Multiple Resonance Emitter with Enhanced Horizontal Emitting Dipole Orientation Based on Indolocarbazole

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1. Experimental Section

1.1 General Information. All commercially available reagents were used as received unless otherwise stated. All reactions were carried out using Schlenk techniques under a nitrogen atmosphere. 600 MHz ^{1}H NMR spectra were measured by a JEOL JNM-ECS600 spectrometer at room temperature in deuterated dichloromethane and chloroform respectively with tetramethyl silane as the internal standard. MALDI-TOF-MS data was performed on a Shimadzu AXIMA Performance MALDI-TOF instrument in positive detection modes. Elemental analyses were performed on a flash EA 1112 spectrometer.

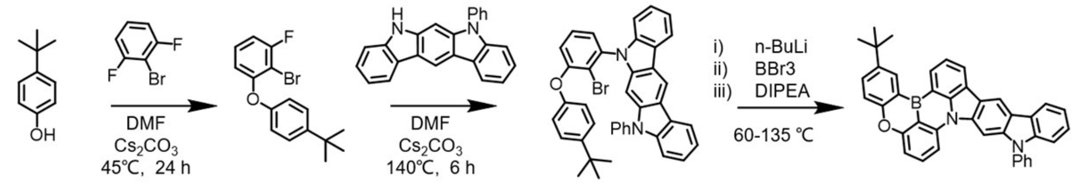
1.2 Single-Crystal Structure. Diffraction data were collected on a Rigaku MM007HF diffractometer using the ω-scan mode with graphite-monochromator Mo•Kα radiation. The structure determination was solved with direct methods using the SHELXTL programs and refined with full-matrix least squares on F^2. The corresponding CCDC reference number (2328700) and the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1.3 Computational methods. The calculations were performed with the Gaussian 09 package, using the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) method with the B3LYP hybrid functional. The structures were optimized using DFT (S_0 states) or TD-DFT (S_1 and T_1 state) methods with a 6–31G(d) basis set. And the TD-DFT calculation of Franck-Condon spectra have been performed according to the literature using the Gaussian 16 package[1]. And the vibrationally-resolved electronic emission spectra was obtained based on Franck-Condon spectra with the program keyword demanding outputting each vibration that contribute more than 0.1% to the whole spectrum.

1.4 Photoluminescence Property Measurements. Organic films for optical measurements were fabricated by thermal evaporation under high vacuum onto clean quartz substrates. UV-vis absorption spectra were recorded by an Agilent 8453 spectrophotometer. Steady State fluorescence spectra, fluorescence lifetime, and quantum efficiency were carried out with Edinburgh fluorescence spectrometer (FLS1000) with an integrating sphere. The excitation wavelength for fluorescence and phosphorescence measurement are 365 nm and 410 nm, respectively. Transient spectra for prompt part were collected with a 365 nm picosecond pulsed LED (EPL 365), while the delayed part was collected with a 320 nm pulse width tuning laser (VPL 320). And angle-resolved and polarization-resolved PL measurement was carried out by the molecular orientation measurement system (C14234-11, Hamamatsu Photonics) using a sample with a 10-nm-thick film doped with 1% emitter.

1.5 Device fabrication and measurement of EL characteristics. All compounds were subjected to temperature-gradient sublimation under high vacuum before use. OLEDs were fabricated on the ITO-coated glass substrates with multiple organic layers sandwiched between the transparent bottom indium-tin-oxide (ITO) anode and the top metal cathode. Before device fabrication, the ITO glass substrates were pre-cleaned by ion-free water. All material layers were deposited by vacuum evaporation in a vacuum chamber with a base pressure of 10^{-6} torr. The deposition system permits the fabrication of the complete device structure in a single vacuum pump-down without breaking vacuum. The deposition rate of organic layers was kept at 0.08- 0.12 nm s^{-1}. The doping was conducted by co-evaporation from separate evaporation sources with different evaporation rates. The current density, voltage, luminance, external quantum efficiency, electroluminescent spectra and other characteristics were measured with a Keithley 2400 source meter and an absolute EQE measurement system in an integrating sphere at the same time. The EQE measurement system is Hamamatsu C9920-12, which equipped with Hamamatsu PMA-12 Photonic multichannel analyzer C10027-02 whose longest detection wavelength is 1100 nm.

1.6 Synthesis



1 2 IDCzBNO

Scheme S1. Synthetic procedure of **IDCzBNO**.

Synthesis of 2-bromo-1-(4-(tert-butyl)phenoxy)-3-fluorobenzene (1): 4-(tert-butyl)phenol (3.0 g, 19.97 mmol) and Cs_2CO_3 (20.0 g, 61.38 mmol) were dissolved in DMF (150 mL) at room temperature. After stirring for 30 min, 2-bromo-1,3-difluorobenzene (12.0 g, 61.38 mmol) was added to the solution. The mixture was stirred at 45 °C for 24 h. Then the reaction mixture was poured into a large amount of water. The product was extracted with dichloromethane. The crude product was purified by column chromatography on silica gel (petroleum ether/ dichloromethane = 95:5, v/v) to afford 1 as a while solid (yield = 5.12 g, 79.3%). ^{1}H NMR (600 MHz, Methylene Chloride-d2) δ 7.38 – 7.36 (m, 2H), 7.25 – 7.10 (m, 1H), 6.95 – 6.85 (m, 3H), 6.70 – 6.65 (m, 1H), 1.31 (s, 9H).

Synthesis of 5-(2-bromo-3-(4-(tert-butyl)phenoxy)phenyl)-7-phenyl-5,7-dihydroindolo[2,3-b]carbazole (2): 5-phenyl-5,7-dihydroindolo[2,3-b]carbazole (3.09 g, 9.28 mmol) and Cs_2CO_3 (10.0 g, 30.69 mmol) were dissolved in DMF (120 mL) at room temperature. After stirring for 30 min, 2-bromo-1-(4-(tert-butyl)phenoxy)-3-fluorobenzene (3.0 g, 9.28 mmol) was added to the solution. The mixture was stirred at 140 °C for 8 h. Then the reaction mixture was poured into a large amount of water. The product was extracted with dichloromethane. The crude product was purified by column chromatography on silica gel (petroleum ether/ dichloromethane = 80:20, v/v) to afford 1 as a while solid (yield = 4.91 g, 83.3%). ^{1}H NMR (600 MHz, Methylene Chloride-d2) δ 8.86 (d, J = 2.7 Hz, 1H), 8.25 (dd, J = 7.6, 2.7 Hz, 2H), 7.59 – 7.57 (m, 4H), 7.44 – 7.27 (m, 10H), 7.06 (dt, J = 7.6, 3.4 Hz, 2H), 6.97 (dt, J = 10.3, 3.1 Hz, 3H), 1.34 (d, J = 2.7 Hz, 9H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.59, 154.55, 146.73, 141.54, 141.48, 141.13, 141.09, 140.49, 138.32, 137.61, 130.85, 130.81, 130.40, 129.83, 128.32, 127.42, 127.30, 126.73, 126.18, 125.99, 123.84, 123.76, 121.43, 120.71, 120.67, 120.45, 118.73, 118.64, 117.86, 116.51, 112.88, 110.08, 109.75, 89.46, 34.65, 31.81. MALDI-TOF: Calculated: 635.61, Found: 636.06.

Synthesis of IDCzBNO: A solution of n-butyllithium in pentane (8.85 mL, 2.4 M, 21.24 mmol) was added slowly to a solution of 5-(2-bromo-3-(4-(tert-butyl)phenoxy)phenyl)-7-phenyl-5,7-dihydroindolo[2,3-b]carbazole (4.5 g, 7.08 mmol) in xylene (150 mL) at 0 ºC under a nitrogen atmosphere. After stirring at 60ºC for 2 h, boron tribromide (2.05 mL, 21.24 mmol) was added at –40 ºC, and the reaction mixture was stirred at room temperature for 0.5 h. N,N-Diisopropylethylamine (6.17 mL, 34.40 mmol) was added at 0 ºC and then the reaction mixture was allowed to warm to room temperature. After stirring at 135 ºC for 8 h, the reaction mixture was cooled to room temperature. The reaction mixture was quenched by ethanol. And the mixture was evaporated under reduced pressure. The crude product IDCzBNO was purified by column chromatography on silica gel (petroleum ether/ dichloromethane = 85:15 v/v) and recrystallized from dichloromethane and methanol as a yellow powder (1.19 g, yield: 29.7%). ^{1}H NMR (600 MHz, Methylene Chloride-d_2) δ 8.73 (d, J = 2.5 Hz, 1H), 8.68 – 8.65 (m, 2H), 8.31 (dd, J = 7.3, 1.1 Hz, 1H), 8.20 (dt, J = 7.6, 1.0 Hz, 1H), 8.17 (d, J = 0.7 Hz, 1H), 7.86 (dd, J = 8.3, 0.6 Hz, 1H), 7.74 (ddd, J = 8.6, 2.4, 0.9 Hz, 1H), 7.72 – 7.67 (m, 5H), 7.61 – 7.56 (m, 2H), 7.42 – 7.37 (m, 3H), 7.34 – 7.31 (m, 1H), 7.14 (dd, J = 8.1, 0.7 Hz, 1H), 1.50 (d, J = 0.9 Hz, 9H). ^{13}C NMR (151 MHz, Methylene Chloride-d_2) δ 159.05, 157.59, 145.11, 143.94, 142.14, 141.99, 141.28, 139.15, 137.72, 133.86, 131.53, 131.15, 130.68, 130.25, 127.83, 127.18, 125.69, 124.54, 123.37, 122.73, 122.07, 121.03, 120.22, 119.99, 119.67, 117.19, 111.89, 109.67, 109.12, 107.00, 95.05, 34.52, 31.46. MALDI-TOF: Calculated: 564.23, Found: 564.13.

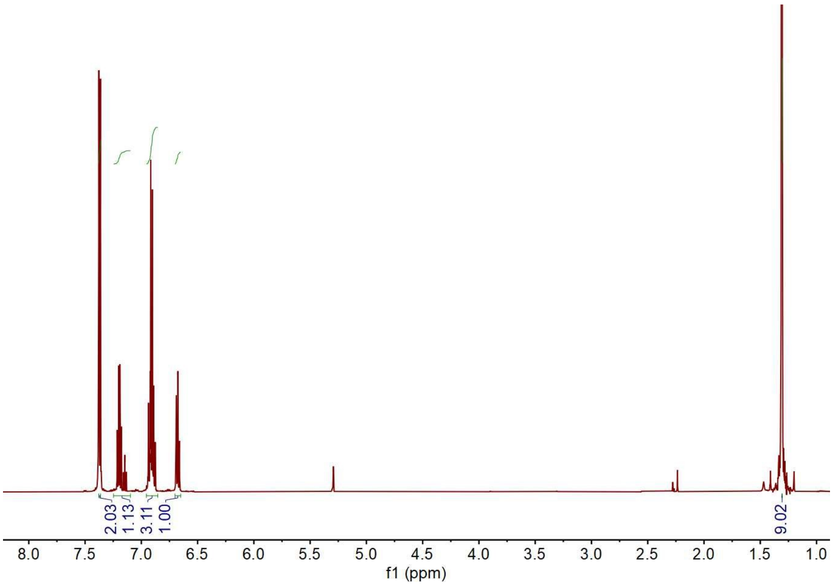


Fig.S1. ^{1}H NMR spectrum of **Compound 1** in CD_2Cl_2.

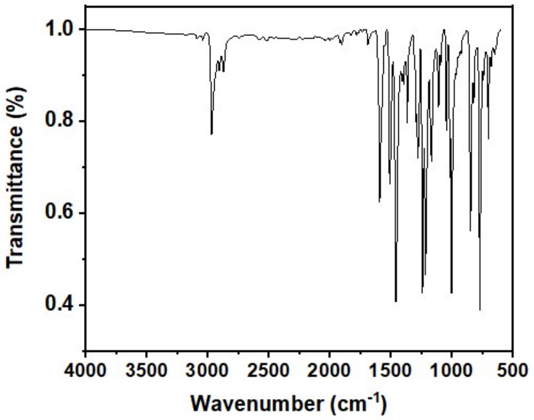


Fig. S2. IR spectrum of Compound 1.

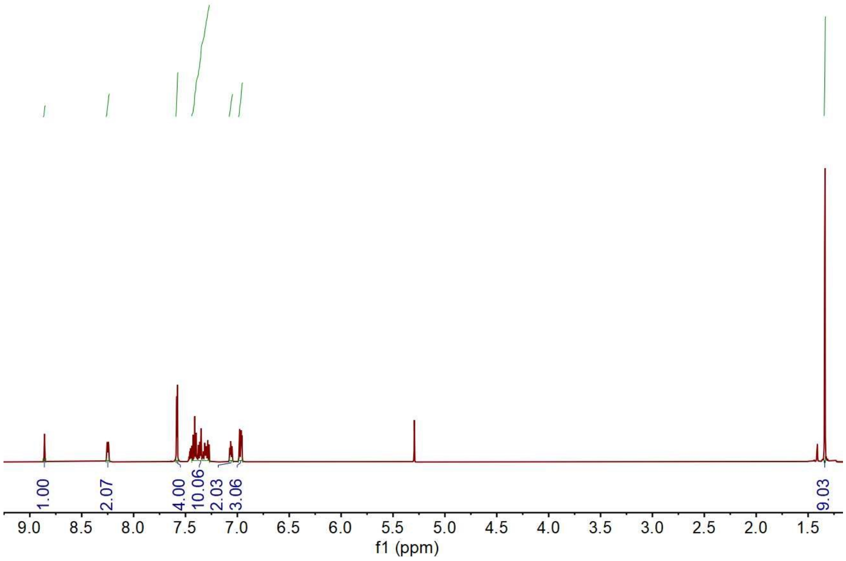


Fig.S3. The ^{1}H NMR spectrum of **Compound 2** (600 MHz, CD_2Cl_2, 25 °C).

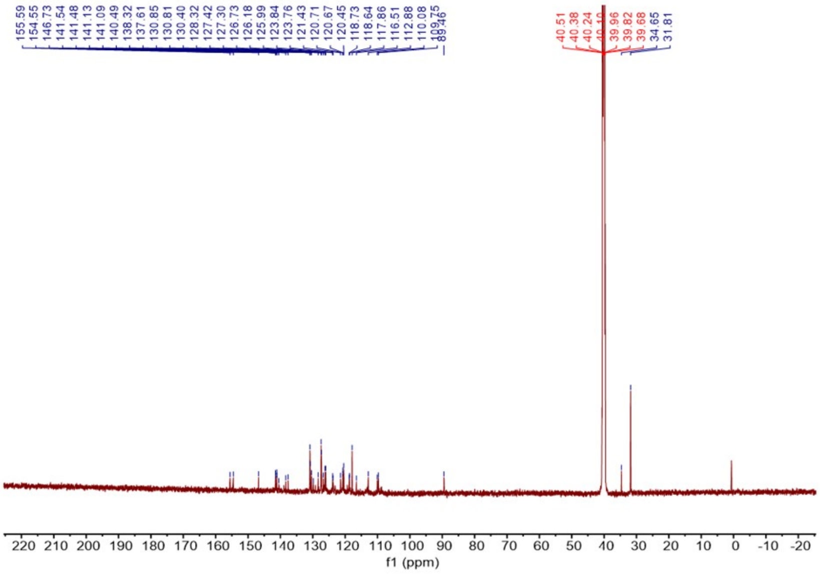


Fig. S4. ^{13}C NMR spectrum of **Compound 2** in DMSO-d_6.

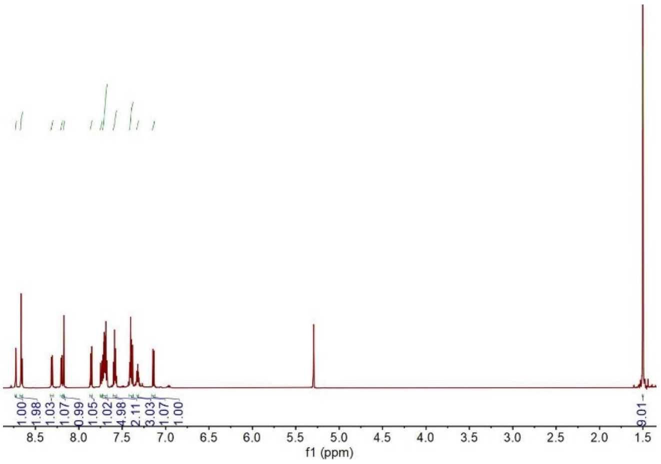


Fig.S5. ^{1}H NMR spectrum of **IDCzBNO** (600 MHz, CD_2Cl_2, 25 °C).

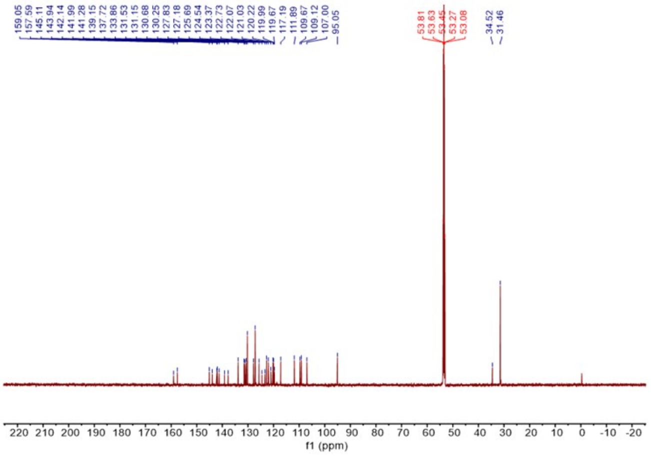


Fig. S6 ^{13}C NMR spectrum of **IDCzBNO** in Methylene Chloride-d_2.

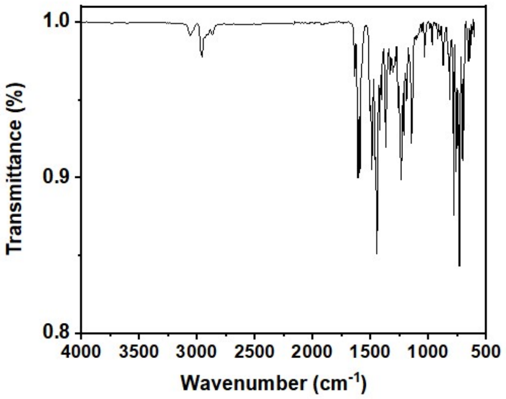


Fig. S7. IR spectrum of **IDCzBNO**.

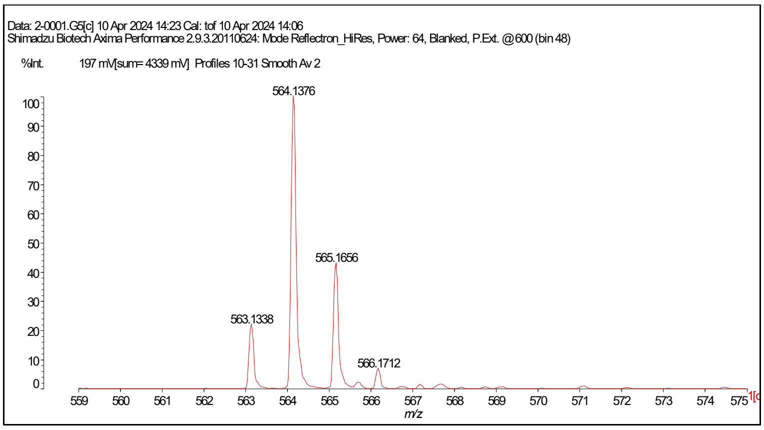


Fig. S8. MALDI spectrum of **IDCzBNO.**

2. Other supplementary figures and tables

Table S1. Crystal Data and Structure Refinement of **IDCzBNO**.

	IDCzBNO
empirical formula	C40H29BN2O
formula wt	564.46
crystal system	triclinic
T (K)	170.00(10)
space group	P -1
a/Å	7.2013(2)
b/Å	20.0452(7)
c/Å	20.4197(8)
α/ °	109.263(2)
β/ °	90.040(3)
γ/ °	95.032(3)
V/Å3	2770.49(7)
Z	4
density, g/cm^3	1.353
F (000)	1184
θ range/Å	1.744 to 27.497

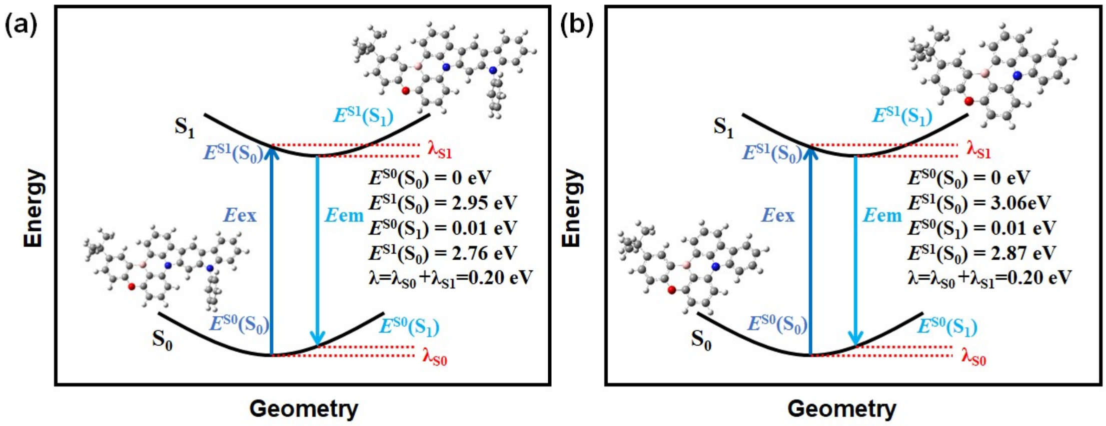


Fig.S9. Optimized S_0 and S_1 structures, single-point energies and reorganization energies of IDCzBNO (a) and CzBNO (b).

Table S2. Summary of TD-DFT calculations for **IDCzBNO** and **CzBNO** at the S_0 and S_1 structures at theB3LYP/6-31G(d) level.

Compound	Optimized Structure	Transition	Wavelength (nm)	Energy (eV)	Oscillator Strength
IDCzBNO	S_0	$S_0 \rightarrow S_1$	420.51	2.9484	0.4601
		$S_0 \rightarrow T_1$	476.20	2.6036	0.0000
	S_1	$S_1 \rightarrow S_0$	451.63	2.7452	0.3618
	T_1	$T_1 \rightarrow S_0$	476.22	2.6035	0.0000
CzBNO	S_0	$S_0 \rightarrow S_1$	405.74	3.0558	0.3414
		$S_0 \rightarrow T_1$	470.81	2.6334	0.0000
	S_1	$S_1 \rightarrow S_0$	431.40	2.8740	0.2666
	T_1	$T_1 \rightarrow S_0$	496.36	2.4979	0.0000

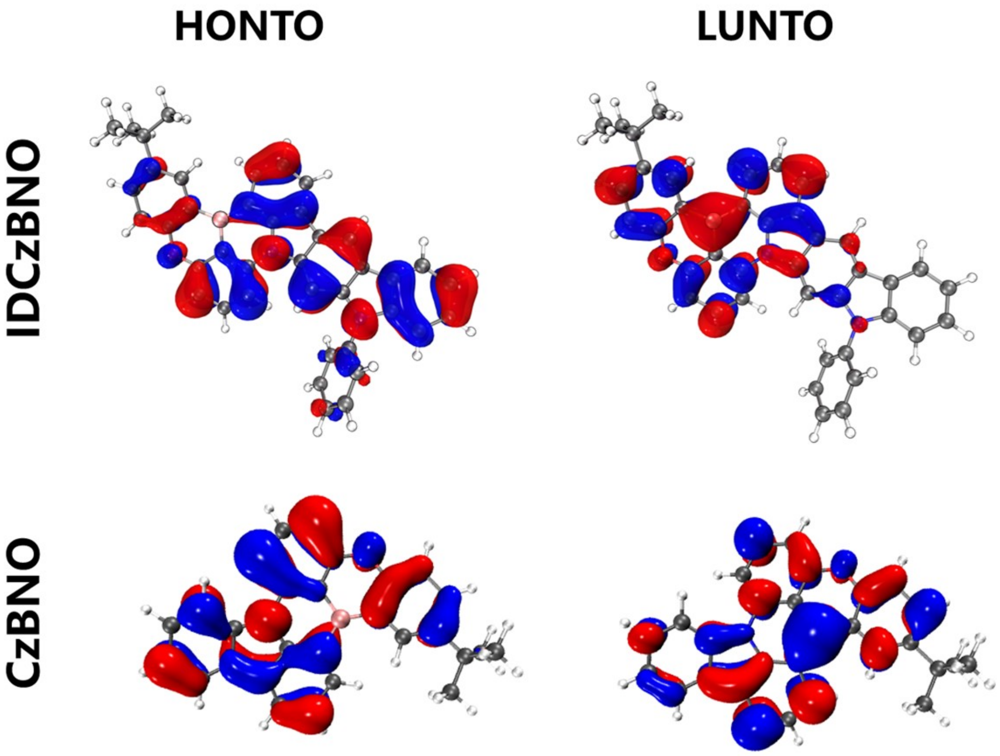


Fig.S10. HONTO, LUNTO distributions of IDCzBNO and CzBNO S_1 states obtained using B3LYP/6-31G(d) calculations. NTO means "Natural transition orbital".

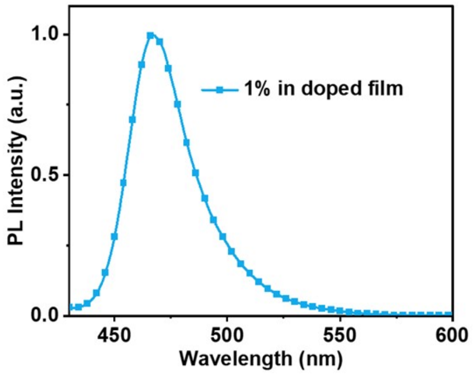


Fig. S11. PL Spectra of IDCzBNO in 1% doped film.

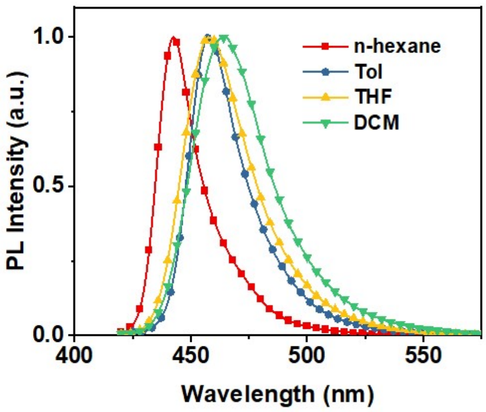


Fig.S12. Normalized fluorescence spectra of **IDCzBNO** in different solutions.

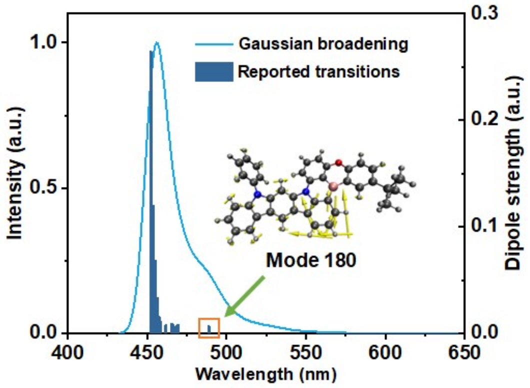


Fig.S13. Vibrationally-resolved electronic emission spectra analysis of **IDCzBNO** and the related vibration mode.

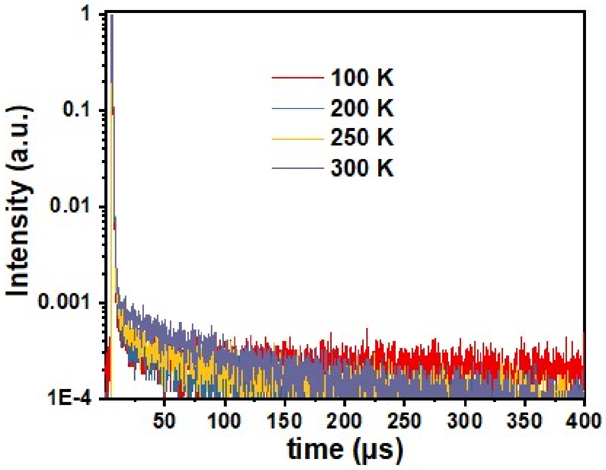


Fig. S14. Transient decay spectra at 100-300 K in the measuring time scale of 400 μs for IDCzBNO in the doped films at a concentration of 1%.

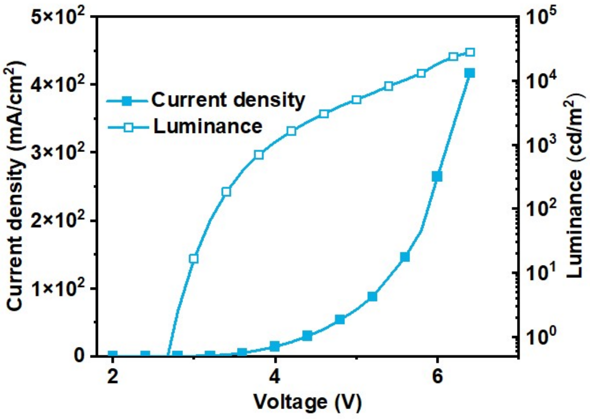


Fig.S15. Current density-voltage-luminance characteristics of **IDCzBNO** devices.

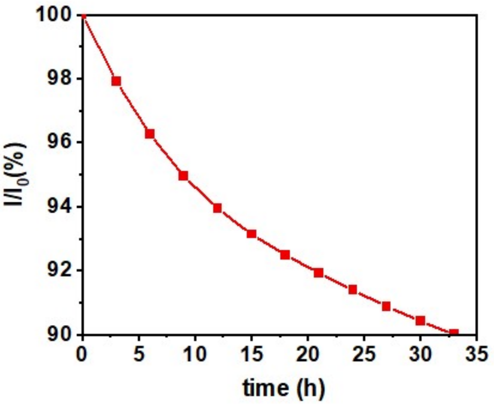


Fig. S16. Lifetime of the P-type devices based on IDCzBNO measured at 1,062 cd/m^2.

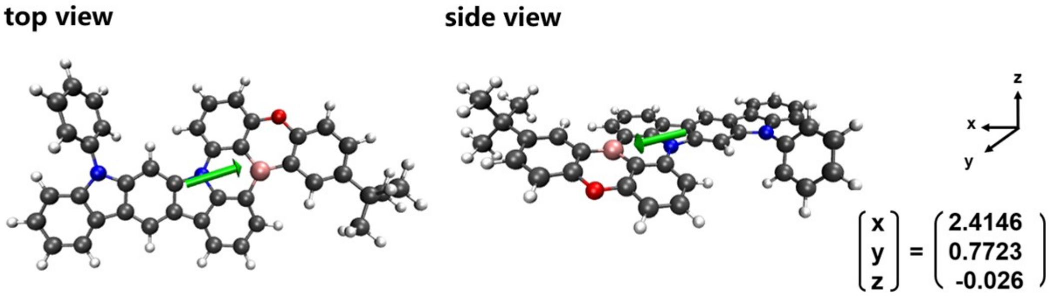


Fig.S17. Calculated transition dipole moment between the S_1 and S_0 states.

3. Reference

1 F. Santoro, R. Improta, A. Lami, J. Bloino, V. Barone, *The Journal of Chemical Physics* 2007, 126, 084509.