Electronic Supplementary Information (ESI)

Ultra-Stable Green Emission from an Oxygen-Bridged Boron-Based TADF Emitter with Unprecedented Resistance to Concentration Quenching

Zhongxin Zhou, Jie Pan, Yixuan Pu, Changheng Guan,

Jiacheng Pan, WeiGuo Zhu,* and Yu Liu*

[a]*School of Materials Science and Engineering, Jiangsu Engineering Laboratory of Light-Electricity-Heat Energy-Converting Materials and Applications, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, National Experimental Demonstration Center for Materials Science and Engineering, Changzhou University, Changzhou 213164, China*

Email addresses:

(Z. Wu) wuzhonglian@jsut.edu.cn

(Y. Liu) liuyu03b@126.com

‡ These authors contributed equally to this work.

Table of Contents

1. Experimental Section

1.1. General experimental methods

Materials Unless otherwise specified, most of the solvents and reagents are commercially available (TCI, energy chemical) and used without further purification. Suzuki reaction were conducted under an N_2 atmosphere using the aard Schlenk line techniques to avoid the oxidation of the reactants by oxygen. Flash column chromatography and preparative TLC were carried out using silica gel. All the ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III 400 and 500 MHz NMR spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard. High-resolution mass spectra were performed using auto flex MALDI-TOF mass spectrometer. Thermogravimetric analysis (TG-DTA) was performed by Bruker TG-DTA 2400SA with a heating rate of 10 ºC min-1 from 25 ºC to 600 ºC under nitrogen atmosphere. the temperature at 5% weight loss was used as the decomposition temperature (T_d). At room temperature, cyclic voltammograms (CV) were performed by the electrochemical workstation CHI630E, the oxidation potential (*E*ox) was tested using the purified dry dichloromethane as the solvent and 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the electrolyte. Using platinum wire as the counter electrode, Ag/AgCl as the reference electrode, a platinum spar (0.8 mm) working electrode, and ferrocene (Fc/Fc^+) as the internal standard, the cyclic voltammetry curves were measured by a scanning speed at 100 mV/s. UV-Vis absorption spectra of the two NIR-TADF materials were obtained at room temperature using a Shimadzu UV-2600, The photoluminescence (PL) spectra were recorded on Edinburgh FLS1000, while time-resolved measurements were carried out using time-correlated single-photon counting (TCSPC) spectrometer (Edinburgh FLS1000), and EPL 450 laser were used as excitation source, and delayed life VPL450 laser in the Edinburgh Transient Fluorescence Spectrometer. Fluorescence and phosphorescence spectra at 77K were measured in degassed toluene using an Edinburgh FLS1000 transient fluorescence spectrophotometer. The photoluminescence quantum yields (PLQYs) were recorded with an integrating sphere coupled with Edinburgh FLS1000 under ambient condition.

Quantum chemical calculations were performed with Gaussian 09 program, in which density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed at the

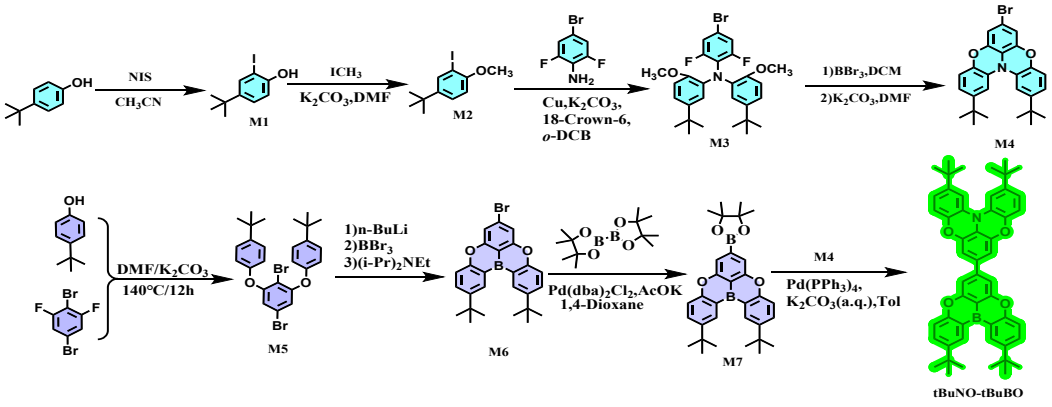
B3LYP/6-31g (d, p) level. The optimal geometries, as well as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for both emitters were obtained by DFT calculations. The excited states (S_n and T_n states) and NTOs (natural transition orbitals) were obtained by TD-DFT calculations.

1.2. Device fabrication and measurement

The structure of the doped devices is ITO/PEDOT:PSS (40 nm)/TAPC:emitter (x wt%, 40 nm)/TmPyPB (40 nm)/LiF (1.2 nm)/Al (120 nm). All devices with the emitting layers (EMLs) based on CBP doped with emitter, with different doping concentrations of 5 wt%, 10 wt%, 20 wt%, 40 wt% and 100 wt%, respectively. The PEDOT:PSS is used as a hole injection layer, the TmTyPB is used as an electron transport layer (ETL) and a hole blocking layer (HBL), and LiF is used as an electron injection layer. The films of PEDOT:PSS(40nm) were spin-coated on precleaned ITO glass substrates and annealed at 150 °C for 20 min. Then the light emitting layer and the layer of TmPyPb was evaporated onto the active layer. Finally, the LiF/Al layer was deposited on the top of the emitting layer. In order to prevent degradation and emission quenching caused by oxygen and water, all the above operations are performed in a nitrogen atmosphere or a vacuum state (1×10^{-4} Pa), and the OLED is encapsulated before characterization. The EL spectra and current density(*J*)–voltage(*V*)–radiance(*R*) curves were obtained using a PHOTORESEARCH Spectra Scan PR735 photometer and a KEITHLEY 2400 Source Meter constant current source at room temperature. The EQE values were calculated by assuming a Lambertian distribution.

2. Synthesis details

The chemical raw materials, catalysts, and solvents used were purchased from commercial suppliers and do not require further purification.



Scheme S1. Synthetic routes of tBuNO-tBuBO.

2.1. *Synthesis of 4-(tert-butyl)-2-iodophenol* (M1)

Add 4- (tert butyl) phenol (100 g, 665.7 mmol, 1 eq), N-iodobutyrimide (NIS, 149.8 g, 665.7 mmol, 1 eq), p-toluenesulfonic acid (TsOH, 114.5 g, 665.7 mmol, 1 eq), and acetonitrile solution (CH_3CN, 300.0 mL) to a 500 mL single necked flask. Avoid light and stir at room temperature for 6 h. Stop the reaction, pour the reaction solution into 300 mL of ice water, add 300 mL of saturated sodium sulfite solution, and stir vigorously for 10 minutes. Separate the organic phase, remove the acetonitrile solution under reduced pressure, and dry under vacuum at 60 ℃ to obtain 173.9 g of dark red viscous liquid with a yield of 94.61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.63 (s, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 5.30 (s, 1H), 1.27 (s, 9H).

2.2. *Synthesis of 4-(tert-butyl)-2-iodo-1-methoxybenzene* (M2)

Add 4- (tert butyl) -2-iodophenol (M1, 150 g, 543.2 mmol, 1.0 eq), iodomethane (CH_3I, 92.37 g, 650.76 mmol, 1.2 eq), potassium carbonate ($K_2CO_3$114.5 g, 665.7 mmol, 1.5 eq), and N, N-dimethylformamide solution (DMF, 300.0 mL) to a 500 mL single necked flask, and stir the reaction at room temperature for 12 h. Stop the reaction, pour the reaction solution into 800 mL of water, extract with DCM three times (100 mL * 3), combine the organic phases, and wash with water five times (500 mL * 5). Separate the organic phase, dry with magnesium sulfate, filter to remove magnesium sulfate, remove DCM under reduced pressure, purify by rapid column chromatography using DCM as the developing agent, and vacuum dry at 60 ℃ to obtain 128.7 g of colorless viscous liquid with a yield of 82.54%. ^{1}H NMR (400 MHz, $CDCl_3$)δ7.77 (s, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 1H), 3.86 (s, 3H), 1.28 (s, 9H).

2.3. *Synthesis of 4-bromo-N,N-bis(5-(tert-butyl)-2-methoxyphenyl)-2,6-difluoroaniline* (M3)

Under a nitrogen atmosphere, a 1000 mL single necked flask was filled with 4- (tert butyl) -2-iodo-1-methoxybenzene (M2, 100 g, 344.67 mmol, 2.5 eq), 4-bromo-2,6-difluoroaniline (28.68 g, 137.87 mmol, 1 eq), activated copper powder (Cu, 35.05 g, 511.48 mmol, 4 eq), potassium carbonate (K_2CO_3, 95.26g, 689.35 mmol, 5 eq), 18-crown-6 (9.11g, 34.47 mmol, 0.1 eq), and N, N-dimethylformamide solution (DMF, 500.0 mL). The mixture was heated to 180 ℃ and stirred for 72 h. Stop the reaction, cool to room temperature, filter by suction, and wash the filter cake with 300 mL DCM. Collect the filtrate and remove the organic solvent by vacuum distillation. Pour the residue into 300 mL of water, extract with DCM three times (50 mL * 3), combine the organic phases, and wash with water five times (100 mL * 5). Separate the organic phase, dry with

magnesium sulfate, filter to remove magnesium sulfate, remove DCM under reduced pressure, purify by column chromatography using PE: DCM=2:1 as the developing agent, and vacuum dry at 60 ℃ to obtain 61.27 g of white solid with a yield of 83.45%. ^{1}H NMR (400 MHz, $CDCl_3$)δ7.06 (dd, *J* = 8.5, 2.3 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 2.2 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.56 (s, 6H), 1.20 (s, 18H).

2.4. *Synthesis of 7-bromo-2,12-di-tert-butylbenzo[5,6][1,4]oxazino[2,3,4-kl]phenoxazine* (M4)

Under a nitrogen atmosphere, a 500 mL double necked flask was filled with 4-bromo-N, N-bis (5-(tert butyl) -2-methoxyphenyl) -2,6-difluoroaniline (50 g, 93.90 mmol, 1 eq) and a dry dichloromethane solution (DCM, 300.0 mL). The mixture was cooled to 0 °C, and boron tribromide (BBr_3, 51.75 g, 206.58 mmol, 2.2 eq) was slowly added. The reaction was allowed to recover to room temperature and stirred for 12 hours. The reaction mixture was quenched in 500 mL of ice water, extracted three times with DCM (50 mL * 3), and the organic phases were combined and washed three times with water (200 mL * 3). Separate the organic phase, dry with magnesium sulfate, filter to remove magnesium sulfate, and remove DCM under reduced pressure to obtain a gray white solid residue that does not require further treatment and can be used directly in the next step. In a nitrogen atmosphere, a 500 mL double necked flask was filled with a gray white solid residue and a potassium carbonate (K_2CO_3, 38.93 g, 281.7 mmol, 3 eq), N, N-dimethylformamide solution (DMF, 300.0 mL). The mixture was heated to 120 °C and stirred for 12 h. The reaction was stopped, cooled to room temperature, and the reaction mixture was poured into 800 mL of water to precipitate a large amount of white solid. The mixture was vigorously stirred for 30 minutes, filtered, and the filter cake was washed with distilled water (1500 mL) without further purification. The filter cake was vacuum dried at 60 °C to obtain 42.41 g of white solid with a yield of 97.25%. ^{1}H NMR (400 MHz, $CDCl_3$)δ7.36 (s, 2H), 6.92 (dd, *J* = 8.5, 1.7 Hz, 2H), 6.85-6.80 (m, 2H), 6.64 (s, 2H), 1.28 (s, 18H). MALDI-TOF MS (mass m/z): 464.120. Calcd for $C_{26}H_{26}BrNO_2$: 464.119.

2.5. *Synthesis of 4,4'-((2,5-dibromo-1,3-phenylene)bis(oxy))bis(tert-butylbenzene)* (M5)

Under a nitrogen atmosphere, a 250 mL single-necked flask was added with 2, 5-dibromo-1.3-difluorobenzene (M4, 30 g, 110.34 mmol), 4-tert-butylphenol (33.15 g, 220.68 mmol), and potassium carbonate (K_2CO_3, 45.75 g). 331.02 mmol), dry N-methylpyrrolidone (NMP, 100.0 mL). Heat to 200 ℃, and stir for reaction overnight. Stopped the reaction, cooled to room

temperature. The reaction solution was poured into 100 mL of distilled water and drained, and the filter cake was washed with 20 mL of methanol solution and dried under vacuum at 60 °C to obtain a white solid M5. The yield of M5 was 83.18%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.7 Hz, 4H), 6.99 (d, *J* = 8.7 Hz, 4H), 6.73 (s, 2H), 1.35 (s, 18H).

2.6. *Synthesis of 7-bromo-2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene* (M6)

Under a nitrogen atmosphere, M5 (30 g, 56.36 mmol) and toluene (Tol, 200 mL) were added to a 500 mL double-mouthed flask and pre-cooled at low temperature for 30 minutes. Then, n-BuLi (2.4 mol/L, 72.26 mmol, 30 mL) was slowly dropped in. After the low-temperature reaction for 1 hour, it was moved to the trial reaction for 2 hours. Pre-cool at low temperature for 30 minutes, slowly add boron tribromide (BBr_3, 90.17 mmol, 8.6 mL) drop by drop, react at low temperature for 1 hour, then move to room temperature for 3 hours of reaction; Pre-cool at low temperature for 10 minutes, slowly add NN-diisopropyl ethylamine (DIPEA, 140.89 mmol, 25 mL) dropdown, react at low temperature for 10 minutes, and then move to room temperature for 2 hours of reaction; Heat up to 120 ℃ and reflux for 24 hours. Stop the reaction, cool to room temperature, pour into 300 mL of methanol, vacuum filter, vacuum dry at 60 ℃, and obtain 16.5 g of white solid (M6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.36 (s, 2H), 1.48 (s, 18H).

2.7. *Synthesis of 2,12-di-tert-butyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene* (M7)

Under a nitrogen atmosphere, M6 (10 g, 21.68 mmol), 4,4,4',4',5,5',5' -octamethyl-2,2'-bi (1,3, 2-dioxaborane) (6.61 g, 26.02 mmol), and potassium acetate (AcOK) were added to a 250 mL single-necked flask. 10.64 g, 108.41 mmol), [1,1 '-bis (diphenylphosphine) ferrocene] palladium dichloride (II) (Pd(dppf)Cl_2, 0.476 g, 0.65 mmol), and dried dioxane (Diox, 120 mL) were heated to 110 °C and refluxed for 24 h. Stop the reaction, cool to room temperature, extract three times (20 mL*3) with DCM, combine the organic phase, and wash three times (30 mL*3). The organic phase was separated. Magnesium sulfate was used for drying, and magnesium sulfate was filtered out, and DCM was removed under reduced pressure. Column chromatography separation and purification were carried out with PE: DCM = 3:1 as the developing agent, and vacuum drying was conducted at 60 ℃. 10.5 g of white solid (M7) was obtained, with a yield of 95.28%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.75 (s, 2H), 7.79 (dd, *J* = 8.8, 2.5 Hz, 2H), 7.57 (s, 2H), 7.49 (d, *J* =

8.8 Hz, 2H), 1.46 (s, 18H), 1.37 (s, 12H).

2.8. *Synthesis of 2,12-di-tert-butyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene* (tBuNO-tBuBO)

Under a nitrogen atmosphere, M4 (4.64 g, 10 mmol), M7 (5.60 g, 11 mmol), potassium carbonate aqueous solution (K_2CO_3, 10 mL, 2 mol/L, 20 mmol), Tetrakis(triphenylphosphine) palladium ($Pd(PPh_3)_4$, 578 mg, 0.5 mmol), and 40 mL of toluene were added to a 200 mL single necked flask. Raise the temperature to 110 °C and continue the reaction for 24 hours. Stop the reaction, cool to room temperature, remove THF under vacuum distillation, extract with dichloromethane (3 × 30mL), collect the organic phase and sequentially wash with water, dry, and vacuum distill to remove the solvent. Using petroleum ether/dichloromethane (5:1) as the eluent, the remaining material was separated by column chromatography to obtain 5.83 g of bright yellow solid (tBuNO tBuBO). The yield was 76.1%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 2H), 7.77 (dd, *J* = 8.8, 2.5 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.42 (s, 2H), 7.32 (s, 2H), 6.90 (s, 6H), 1.49 (s, 18H), 1.31 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.77, 156.83, 145.90, 145.00, 144.69, 143.92, 143.69, 135.06, 130.34, 129.18, 127.29, 119.11, 116.95, 115.84, 111.11, 109.06, 105.16, 76.20, 75.99, 75.77, 33.55, 33.51, 30.53, 30.42. MALDI-TOF MS (mass m/z): 765.400 . Calcd for $C_{52}H_{52}BNO_4$: 765.400

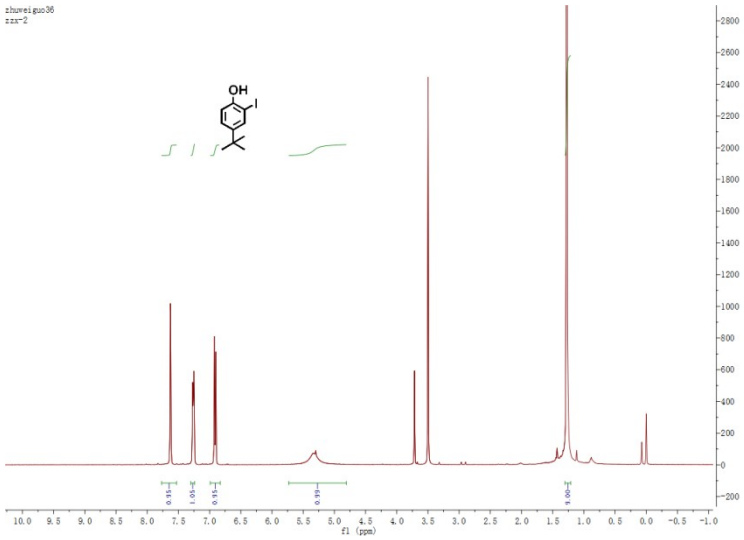


Fig. S1 ^{1}H NMR spectrum of **M1** in $CDCl_3$

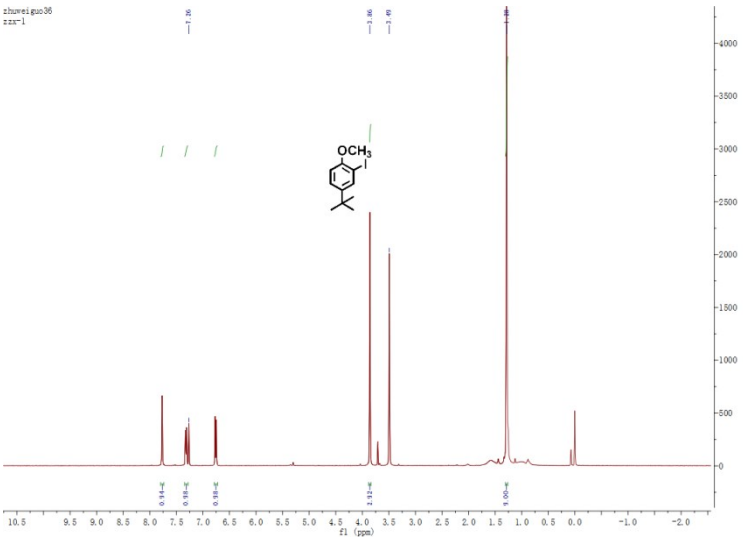


Fig. S2 ^{1}H NMR spectrum of **M2** in $CDCl_3$

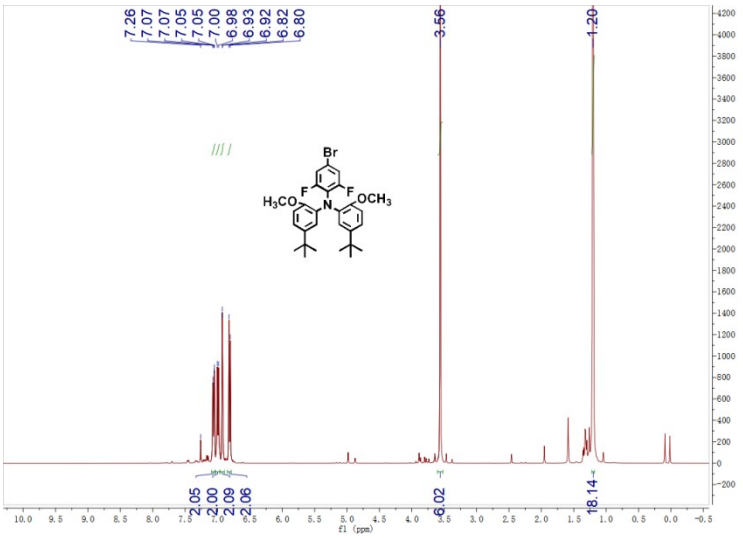


Fig. S3 ^{1}H NMR spectrum of **M3** in $CDCl_3$

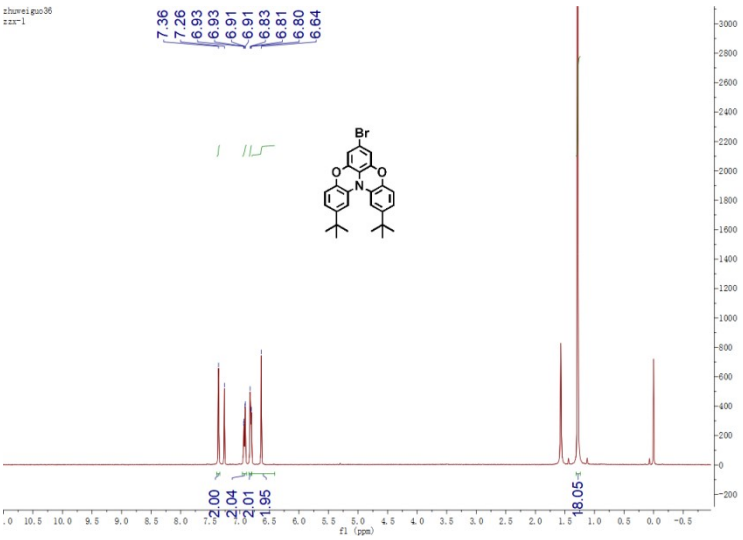


Fig. S4 ^{1}H NMR spectrum of **M4** in $CDCl_3$

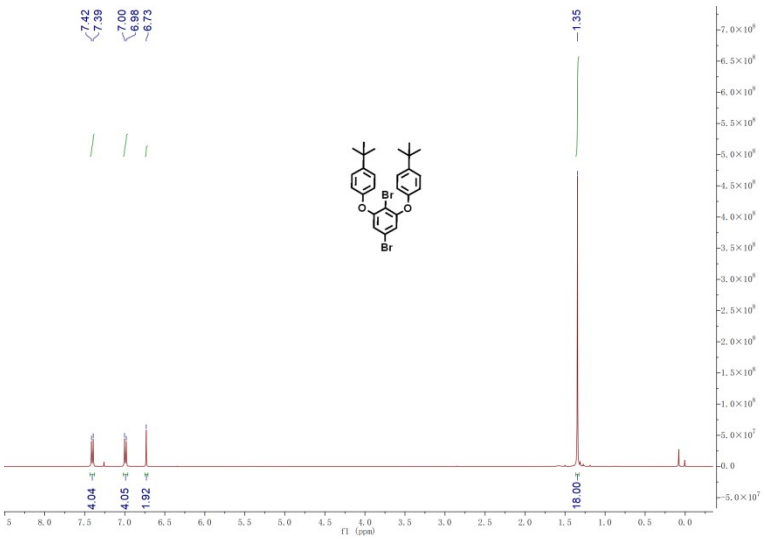


Fig. S5 ^{1}H NMR spectrum of **M5** in $CDCl_3$

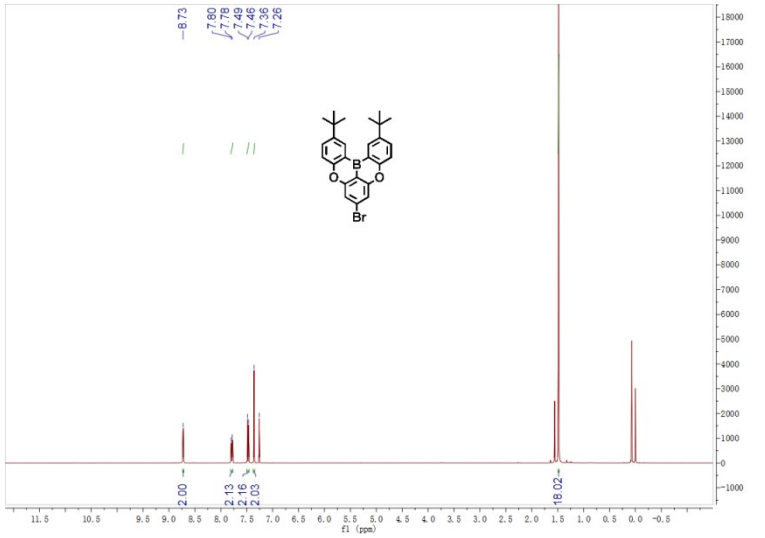


Fig. S6 ^{1}H NMR spectrum of **M6** in $CDCl_3$

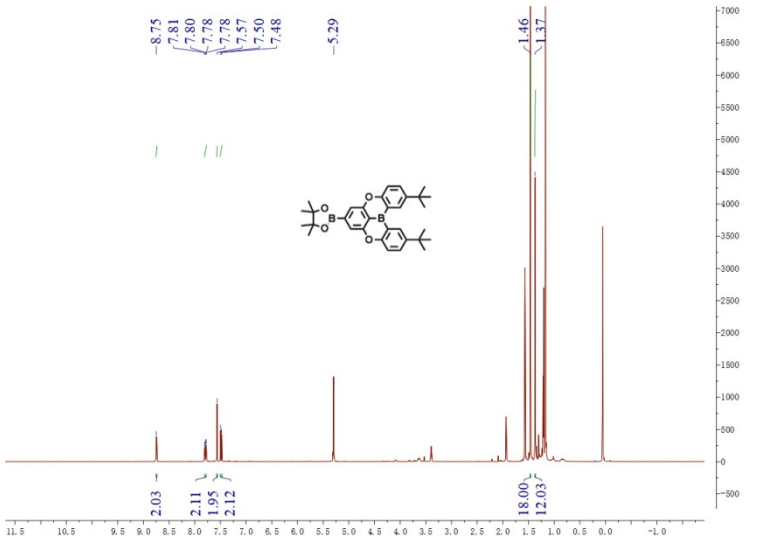


Fig. S7 ^{1}H NMR spectrum of **M7** in CD_2Cl_2

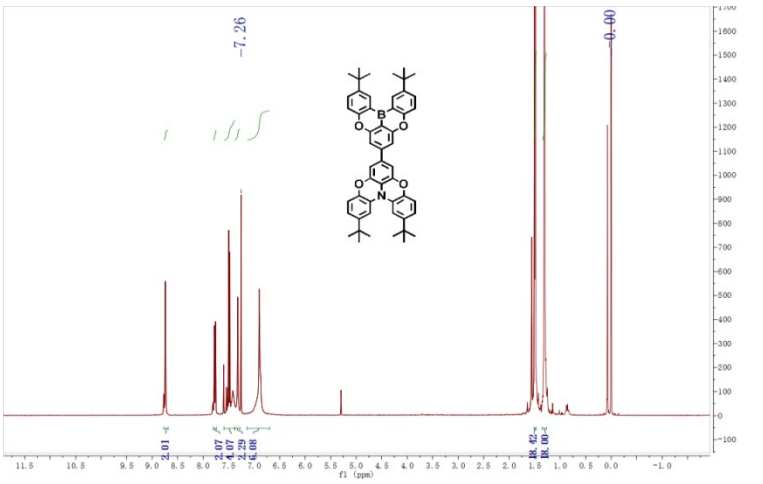


Fig. S8 ^{1}H NMR spectrum of **tBuNO-tBuBO** in $CDCl_3$

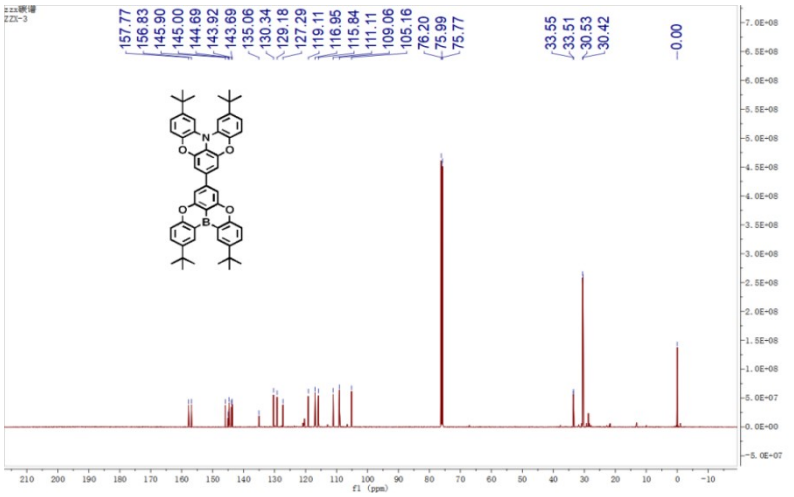


Fig. S9 ^{13}C NMR spectrum of **tBuNO-tBuBO** in $CDCl_3$

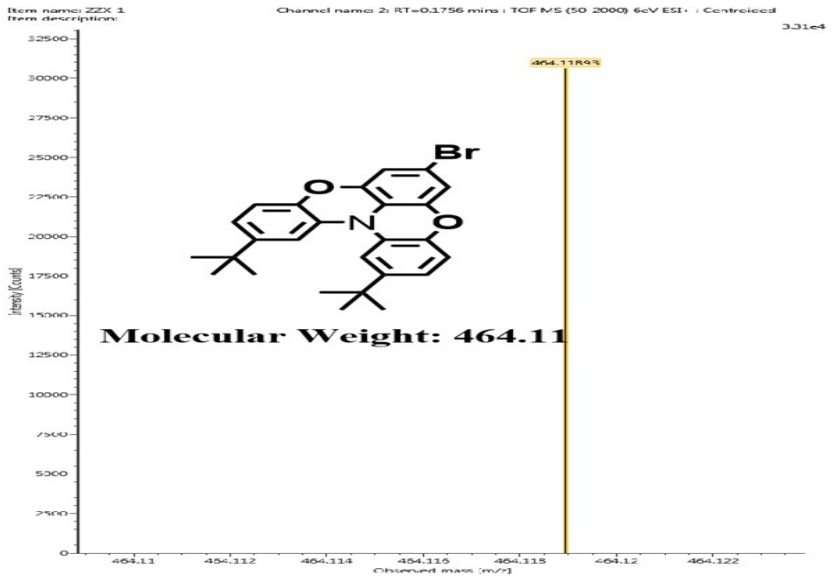


Fig. S10 MALDI-TOF-MS spectrum of **M4**

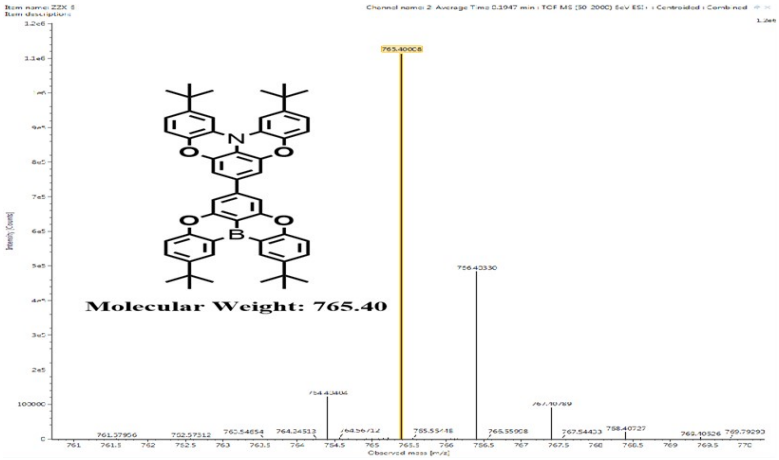


Fig. S11 MALDI-TOF-MS spectrum of **tBuNO-tBuBO**.

3. Thermogravimetric analysis and electrochemical properties.

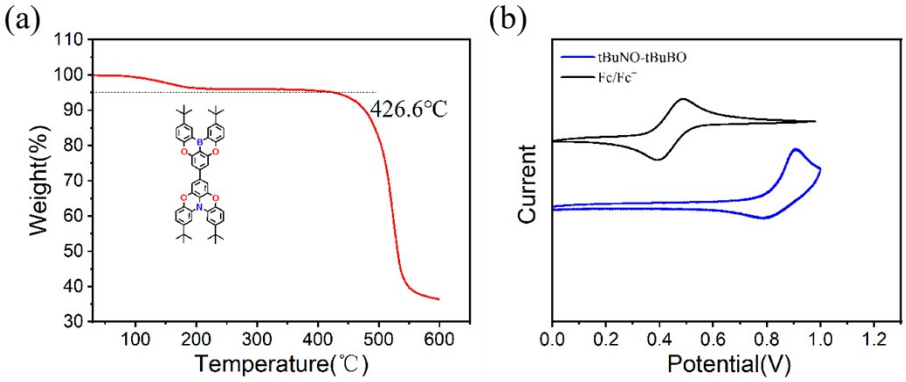


Fig. S12 TGA (a) analysis and CV(b) curves of the tBuNO-tBuBO.

4. Theoretical Simulation

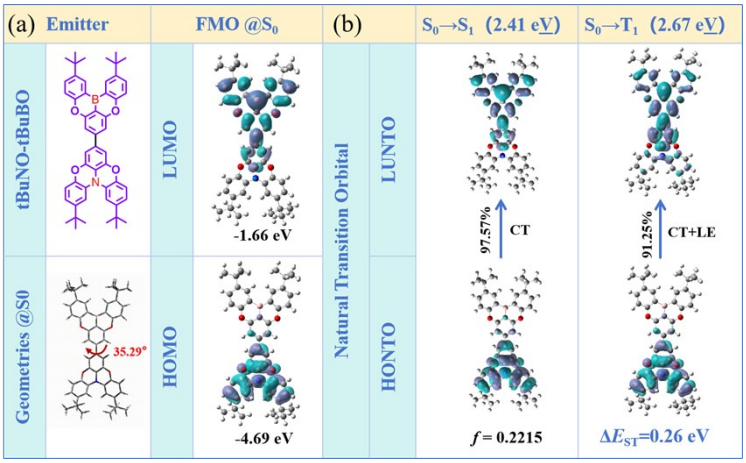


Fig. S13 (a) Molecular structure, HOMO and LUMO spatial distribution and energy levels of tBuNO-tBuBO. (b) Natural Transition Orbital pairs for the representative excited states (S_1 and T_1) of the tBuNO-tBuBO.

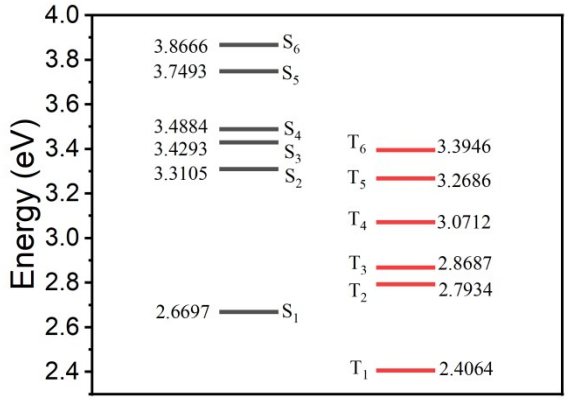


Fig. S14 Energy diagrams of tBuNO-tBuBO and the energy levels were calculated based on TD-DFT calculation at B3LYP/6-31G (d) level.

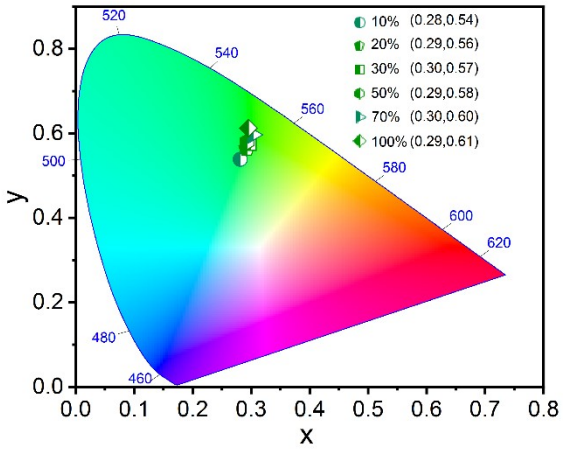


Fig. S15 CIE coordinates of tBuNO-tBuBO-based devices at different doping ratios.

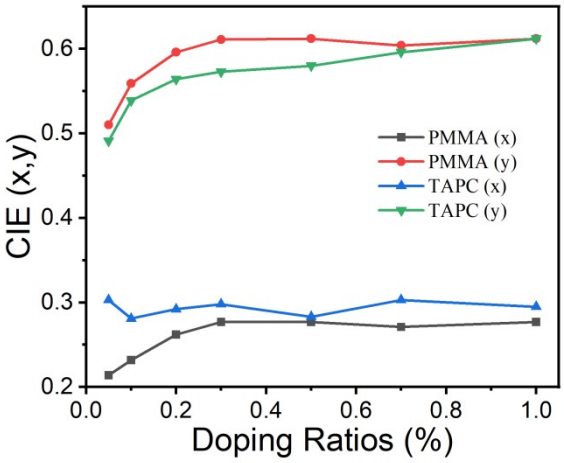


Fig. S16 CIE coordinates of tBuNO-tBuBO:PMMA film and tBuNO-tBuBO:TAPC-based devices at different doping ratios.

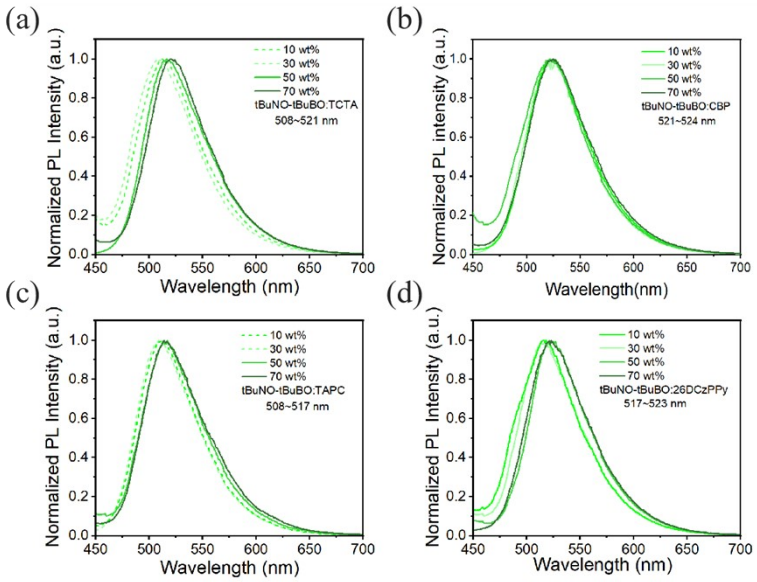


Fig. S17 PL curves of tBuNO-tBuBO: TCTA(a), tBuNO-tBuBO: CBP(b), tBuNO-tBuBO: TAPC(c), tBuNO-tBuBO:26DCzPPy(d) at different doping concentrations.

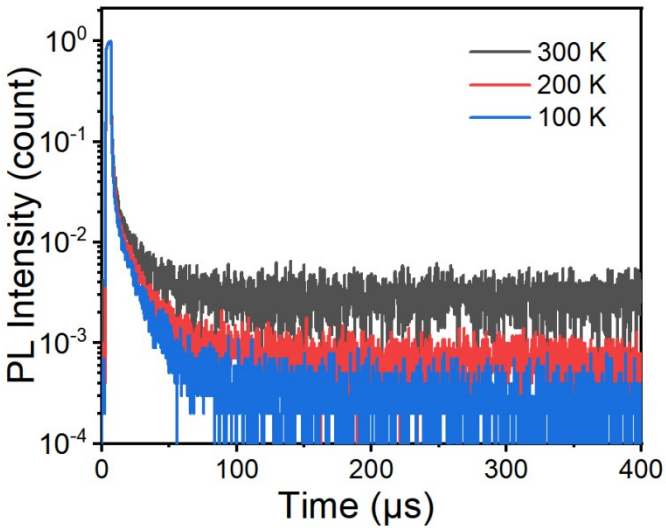


Fig. S18 Transient PL attenuation spectra of PMMA doped with (10 wt%) tBuNO tBuBO at varying temperatures (100~300K).

Table.S1 Natural Transition Orbital (NTO) analysis of tBuNO-tBuBO

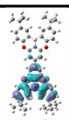
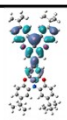
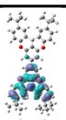
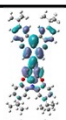
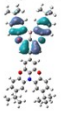
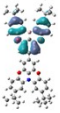
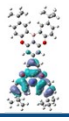
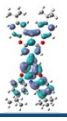
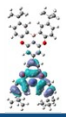
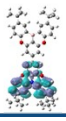
	Singlets				Triplets			
	Hole		Particle		Hole		Particle	
$S_0 \rightarrow S_1$		CT 97.57%		$S_0 \rightarrow T_1$		CT+LE 91.25%	
$S_0 \rightarrow S_2$		LE 97.08%		$S_0 \rightarrow T_2$		LE 96.71%	
$S_0 \rightarrow S_3$		LE+CT 95.57%		$S_0 \rightarrow T_3$		LE 83.47%	

Table S2 Energy levels of the first four frontier molecular orbitals of tBuNO-tBuBO simulated with the DFT method.

Emitter	S_1 (eV)	T_1 (eV)	T_2 (eV)	T_3 (eV)	T_4 (eV)	$f(S_0\text{-}S_1)$
tBuNO-tBuBO	2.67	2.41	2.79	2.87	3.07	0.2215

Table S3 Crystal data and structure refinement for tBuNO-tBuBO

CCDC Deposition Number	2483512
Empirical formula	$C_{52}H_{52}BNO_4$
Formula weight	765.75
Temperature/K	170
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.7113(9)
b/Å	10.2649(6)
c/Å	34.421(2)
α/°	90
β/°	91.181(4)
γ/°	90
Volume/Å^3	4137.0(5)
Z	4
ρ_{calc}g/cm^3	1.229
μ/mm^{-1}	0.594
F(000)	1632.0
Crystal size/mm^3	0.11 × 0.04 × 0.03
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.136 to 127.54

Index ranges	-13 ≤ h ≤ 13, -11 ≤ k ≤ 11, -40 ≤ l ≤ 39
Reflections collected	26622
Independent reflections	6667 [R_{int} = 0.0896, R_{sigma} = 0.0618]
Data/restraints/parameters	6667/36/566
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0647, wR_2 = 0.1590
Final R indexes [all data]	R_1 = 0.0973, wR_2 = 0.1866
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.30

Table S4 Photophysical parameters of tBuNO-tBuBO

Compound	λ_{PL}（nm）	τ_p/Φ_p[b] (ns/%)	τ_d/Φ_d[c] (μs/%)	k_p[d] ($10^8 s^{-1}$)	k_d[e] ($10^4 s^{-1}$)	k_{ISC}[f] ($10^7 s^{-1}$)	k_{RISC}[g] ($10^4 s^{-1}$)	k_r[h] ($10^7 s^{-1}$)	k_{nr}[i] ($10^6 s^{-1}$)
tBuNO-tBuBO[a]	495	5.4/53.11	36.3/29.89	1.85	2.75	9.94	5.96	7.62	2.11
10%tBuNO-tBuBO:PMMA Film	513	4.7/68.68	26.5/31.32	2.13	3.77	6.66	5.49	14.01	5.85

[a]tBuNO-tBuBO in toluene (10^{-5} mol/L) [b]Prompted lifetime (τ_p) and Quantum efffciency (Φ_p) and its proportion. [c]Delayed fluorescence (τ_d) lifetime and Quantum efffciency (Φ_d). [d]k_p is the rate constant of prompt fluorescence. [e]k_d is the rate constant of delayed fluorescence. [f]k_{ISC} is the rate constants of ISC. [g]k_{RISC} is the rate constant of RISC; [h]k_r is the rate constants of radiative. [i]k_{nr} is the rate constants of non-radiative.

Table S5 PL data of tBuNO-tBuBO:PMMA films with different doping ratios

tBuNO-tBuBO (wt%)	10%	20%	30%	50%	70%	100%
λ_{PL} (nm)	513	520	522	522	523	523
PLQY (%)	96	94	92	89	86	83
FWHM (nm)	73	68	68	68	67	67