Supporting Information (SI)

Green multi-resonance induced thermally activated delayed fluorescence emitters containing phenoxazine units with highly efficient electroluminescence

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1. General information

All reagents and anhydrous solvents were commercially available and used without further purification. NMR measurements were conducted on BRUKER AVANCE III 400 MHz spectrometer. Chemical shifts of ^{1}H and $^{13}CNMR$ signals were quoted to tetramethylsilane ($\delta = 0.00$) and $CDCl_3$ ($\delta = 77.0$) as internal standards, respectively. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on a Bruker Daltonics Autoflex III spectrometer using dithranol as the matrix. Thermogravimetric analysis (TGA) curves were performed on a METTLER TOLEDO TG/SF-1100 analyzer under a N_2 atmosphere at a heating rate of 10℃ min^{-1}. Cyclic voltammetry measurements were conducted on MPI-A multifunctional electrochemical and chemiluminescent system (Xi'an Remex Analytical Instrument Co. Ltd., China) at room temperature, with a polished Pt plate as the working electrode, platinum thread as the counter electrode and Ag-$AgNO_3$ (0.1 M) in the solution (CH_3CN:DCM=1:1) as the reference electrode, tetra-n-butylammonium perchlorate (0.1 M) was used as the supporting electrolyte, using Fc^+/Fc as the internal standard, the scan rate was 0.1 V/s. Absorption spectra were measured on a Shimadzu UV-3100 spectrophotometer and photoluminescence spectra were measured from a Hitachi F-4600 photoluminescence spectrophotometer. The absolute photoluminescence quantum yields (absolute PLQY were measured via an integrating sphere) of the compounds were measured with HORIBA Fluorolog-3 fluorescence spectrometer. The decay lifetimes of the compounds were measured with Edinburgh Instruments FLS980 spectrometer. The density functional theory (DFT) and the time-dependent density functional theory (TD-DFT) calculations at the B3lyp/6-31G(d) level with a solvent effect using the SMD model were performed by Gaussian 09. The computational geometry data were appended to the end of the Supporting Information.

Analysis of Rate Constants: The rate constants of radiative decay ($k_{r,S}$) and nonradiative decay ($k_{nr,S}$) from S1 to S0 states, the rate constants of intersystem crossing (k_{ISC}) and reverse intersystem crossing (k_{RISC}) were calculated from the following six equations:

$$k_p = 1/\tau_p \quad \text{Eq. (1)}$$

$$k_d = 1/\tau_d \quad \text{Eq. (2)}$$

$$k_{r,S} = \Phi_p k_p + \Phi_d k_d \approx \Phi_p k_p \quad \text{Eq. (3)}$$

$$k_{nr,S} = \frac{1 - \Phi_{PL}}{\Phi_{PL}} k_{r,S} \quad \text{Eq. (4)}$$

$$k_{ISC} = k_p - k_{r,S} - k_{nr,S} \quad \text{Eq. (5)}$$

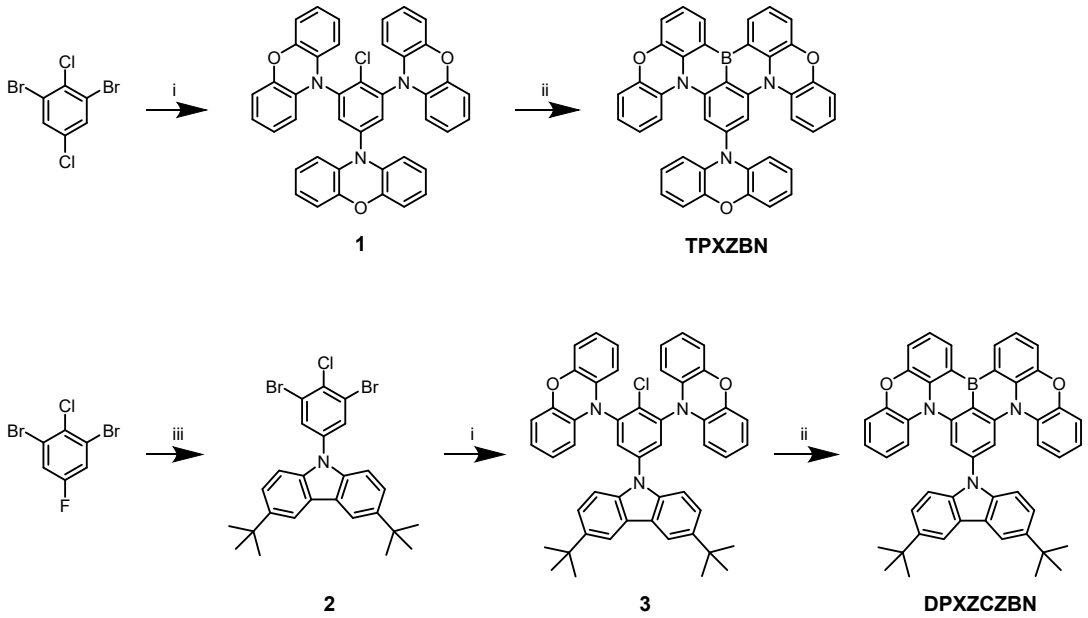
$$k_{RISC} = (k_p k_d \Phi_d)/(k_{ISC} \Phi_p) \quad \text{Eq. (6)}$$

The τ_p and τ_d represent the prompt and decay fluorescence lifetime, which determined from transient PL spectra. The k_p and k_d represent the decay rate constants for prompt and delayed fluorescence, respectively. Φp and Φd indicate prompt and delayed fluorescence components and can be distinguished from the total ΦPL by comparing the integrated intensities of prompt and delayed components in the transient PL spectra. [1]

References

1. H. Tao, Z. Lisi, L. Nengquan, H. Zhongyan, C. Xiaosong, X. Zhengqi, S. Gong, C. Zhou, C. Zhong and C. Yang, *Chem. Eng. J.* 2021, **426**.131169-131177.

2. Synthesis and Characterization



Scheme S1 Synthetic procedure of the precursors and compounds: i) 1. *t*-BuLi, *t*-BuPh, 0 ℃, 30 min, then 0 ℃, 2 h; 2. BBr_3, -40 ℃, 0.5 h, then RT, 0.5 h; 3. NEt(*i*-Pr)$_2$, 0 ℃, then 120 ℃, 12 h. ii) Cs_2CO_3, DMF, 150 ℃, 12 h; iii) $Pd_2(dba)_3$, SPhos, NaO*t*Bu, toluene, 90 ℃, 12 h.

Synthesis of 1 (TPXZCl, 10,10',10''-(2-chlorobenzene-1,3,5-triyl)tris(10*H*-phenoxazine)): 1,3-Dibromo-2,5-dichlorobenzene (4.8 g, 15.7 mmol) was added to a mixture of 10*H*-phenoxazine (6.4 g, 34.9 mmol), $Pd_2(dba)_3$ (0.3 g, 0.3 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 1.0 g, 2.4 mmol), NaO*t*Bu (5.3 g, 55.4 mmol) in toluene (150 mL) under a nitrogen atmosphere. After stirring at 90 ℃ for 12 h, the mixture was filtered with a pad of diatomite (eluent: dichloromethane). After evaporation, the mixture was purified by recrystallization from dichloromethane/hexane to afford **3** as white solid (yield = 2.6 g, 34%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.691 (s, 2H), 6.77-6.69 (m, 18H), 6.13-6.09 (m, 2H), 5.94-5.91 (m, 4H). ^{13}C NMR (101MHz, Chloroform-*d*) δ 144.27, 143.92, 141.86, 141.23, 138.96, 136.43, 133.19, 132.14, 123.55, 123.51, 122.56, 122.40, 116.23, 116.17, 113.14, 112.36.

Synthesis of TPXZBN: TPXZBN was synthesized according to the same procedure as for DPXZCZBN by using **3** (2.4 g, 3.6 mmol) instead **2** precursor. TPXZBN was obtained as yellow solid (yield = 0.4 g, 19%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 6.4 Hz, 2H), 7.63 (s, 2H), 7.49 (d, *J* = 7.6 Hz), 7.32-7.23 (m, 4H), 7.13 (dd, *J* = 1.6, 8 Hz, 2H), 7.09-7.05 (m, 2H), 6.97-6.93 (m, 2H), 6.74-6.66 (m, 6H), 6.17 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.38, 147.18, 144.02, 143.77, 136.83, 133.83, 130.61, 128.39, 126.24, 125.82, 123.72, 123.34, 122.06, 118.43, 117.86, 117.65, 115.53, 113.30, 109.42. HRMS (ESI): m/z $[M+H]^+$ Calcd. for $C_{42}H_{25}BN_3O_3$: 630.1897. Found 630.1983. Anal. Calcd for $C_{42}H_{25}BN_3O_3$: C, 80.14; H, 3.84; N, 6.68. Found: C, 79.32; H, 4.09; N, 6.26 (B and O are not analyzed by elemental analysis).

Synthesis of 2 (BrClCz, 3,6-di-*tert*-butyl-9-(3,5-dibromo-4-chlorophenyl)-9*H*-carbazole): 3,6-Di-*tert*-butyl-9*H*-carbazole (5.6 g, 20.0 mmol) and cesium carbonate (18.3 g, 56.0 mmol) were dissolved in DMF (110 mL) at room temperature under a nitrogen atmosphere. After stirring for 30 min, 1,3-dibromo-2-chloro-5-fluorobenzene (5.8 g, 20.0 mmol) was added to the solution. The mixture was stirred at 150 ℃ for 12 h. After cooling to room temperature, the reaction mixture was poured into a large amount of water. The product was extracted with dichloromethane for several times. The combined organic layer was dried with anhydrous $MgSO_4$. After filtration and evaporation, the crude product was purified by column chromatography on silica gel (eluent: DCM/PE = 1:20 , v/v) to afford **1** as white solid (yield = 5.3 g, 48%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12(d, *J* = 1.6 Hz, 2H), 7.85 (s, 2H), 7.50 (dd, *J* = 2, 8.4 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 1.47 (s, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143, 138.44, 138.01, 130.42, 124.13, 124.04, 123.82, 116.51, 108.87, 34.78, 31.94.

Synthesis of 3 (DPXZClCZ, 10,10'-(2-chloro-5-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-1,3-phenylene)bis(10*H*-phenoxazine)): 3,6-Di-*tert*-butyl-9-(3,5-dibromo-4-chlorophenyl)-9*H*-carbazole (6.1 g, 11.1 mmol) was added to a mixture of 10*H*-phenoxazine (4.2 g, 23.3 mmol), $Pd_2(dba)_3$ (0.5 g, 0.6 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 0.7 g, 1.7 mmol), NaO*t*Bu (3.7 g, 38.6 mmol) in toluene (120 mL) under a nitrogen atmosphere. After stirring at 90 ℃ for 12 h, the mixture was filtered with a pad of diatomite (eluent:

dichloromethane). After evaporation, the crude product was purified by silica gel (eluent: DCM/PE = 1:10, v/v) to afford **2** as gray solid (yield = 5.1 g, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 1.2 Hz, 2H), 7.92 (s, 2H), 7.51-7.44 (m, 4H), 6.78-6.72 (m, 12H), 6.05-6.01 (m, 4H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.29, 143.83, 140.83, 139.92, 137.93, 132.28, 130.55, 124.24, 124.12, 123.60, 122.27, 116.62, 116.07, 112.44, 108.88, 34.78, 31.88.

Synthesis of DPXZCZBN: A solution of *tert*-butyllithium in pentane (1.3 M, 18 mL, 23.4 mmol) was added slowly to a solution of **2** (3.9 g, 5.2 mmol) in *tert*-butylbenzene (200 mL) at 0 ℃ under a nitrogen atmosphere. After stirring at 60 ℃ for 2 h, pentane was removed in vacuo. After addition of boron tribromide (4.8 mL, 12.5 mmol) at -40 ℃, the reaction mixture was stirred at room temperature for 30 min. *N*,*N*-Diisopropylethylamine (NEt(*i*-Pr)$_2$, 14.8 mL, 20.0 mmol) was added at 0 ℃ and then the reaction mixture was allowed to room temperature. The reaction mixture was stirring at 120 ℃ for 12 h. After cooling to room temperature, the reaction mixture was poured into an aqueous solution of sodium bicarbonate. After filtration with a pad of diatomite (eluent: dichloromethane) and evaporation in vacuo, the mixture was purified by silica gel (eluent: Toluene/PE = 1:5, v/v) to afford crude product. After further purification with preparation thin liquid chromatography and recrystallization from DCM/methanol, **DPXZCZBN** was obtained as yellow solid (yield = 0.6 g, 15%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 2H), 8.07 (d, *J* = 7.6 Hz, 2H), 7.79 (s, 2H), 7.56 (d, *J* = 8 Hz, 2H), 7.51-7.46 (m, 4H), 7.26-7.21 (m, 4H), 7.10 (dd, *J* = 0.8, 8 Hz, 2H), 7.02 (t, *J* = 7 Hz, 2H), 6.90 (t, *J* = 8 Hz, 2H), 1.470 (s, 18H). ^{13}C NMR(101 MHz, Chloroform-*d*) δ 149.48, 147.33, 143.20, 142.81, 138.96, 137.00, 130.87, 128.40, 125.67, 123.69, 123.62, 118.65, 117.80, 117.55, 116.42, 116.39, 109.36, 106.20, 34.81, 31.99. HRMS (ESI): m/z $[M+H]^+$ Calcd. for $C_{50}H_{40}BN_3O_2$: 726.3286. Found 726.3291. Anal. Calcd for $C_{42}H_{25}BN_3O_3$: C,82.75; H, 5.56; N, 5.79. Found: C, 82.50; H, 5.58; N, 5.64 (B and O are not analyzed by elemental analysis).

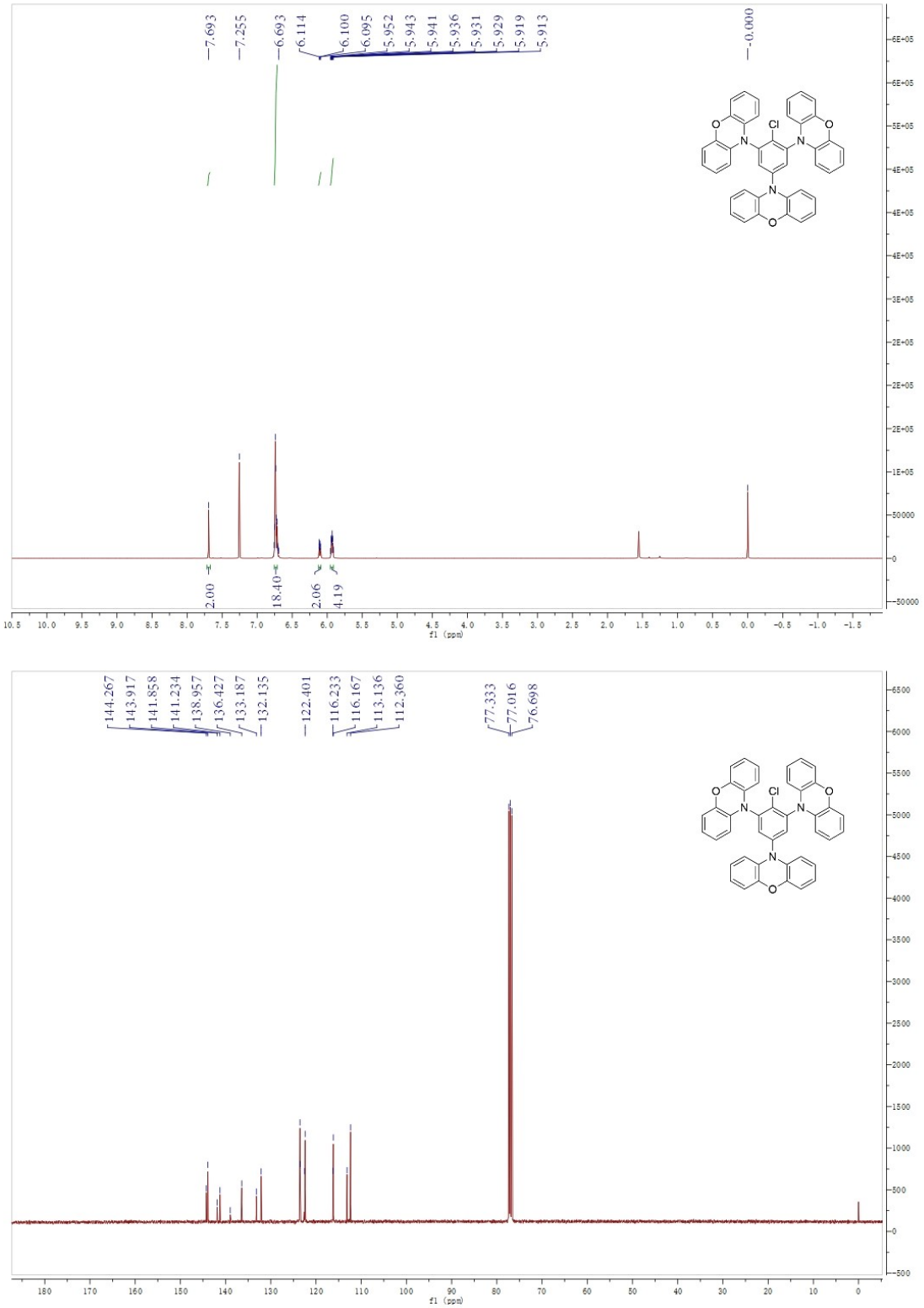


Fig. S1 ^{1}H and ^{13}C NMR spectra of **1** (TPXZCl) in chloroform-*d*.

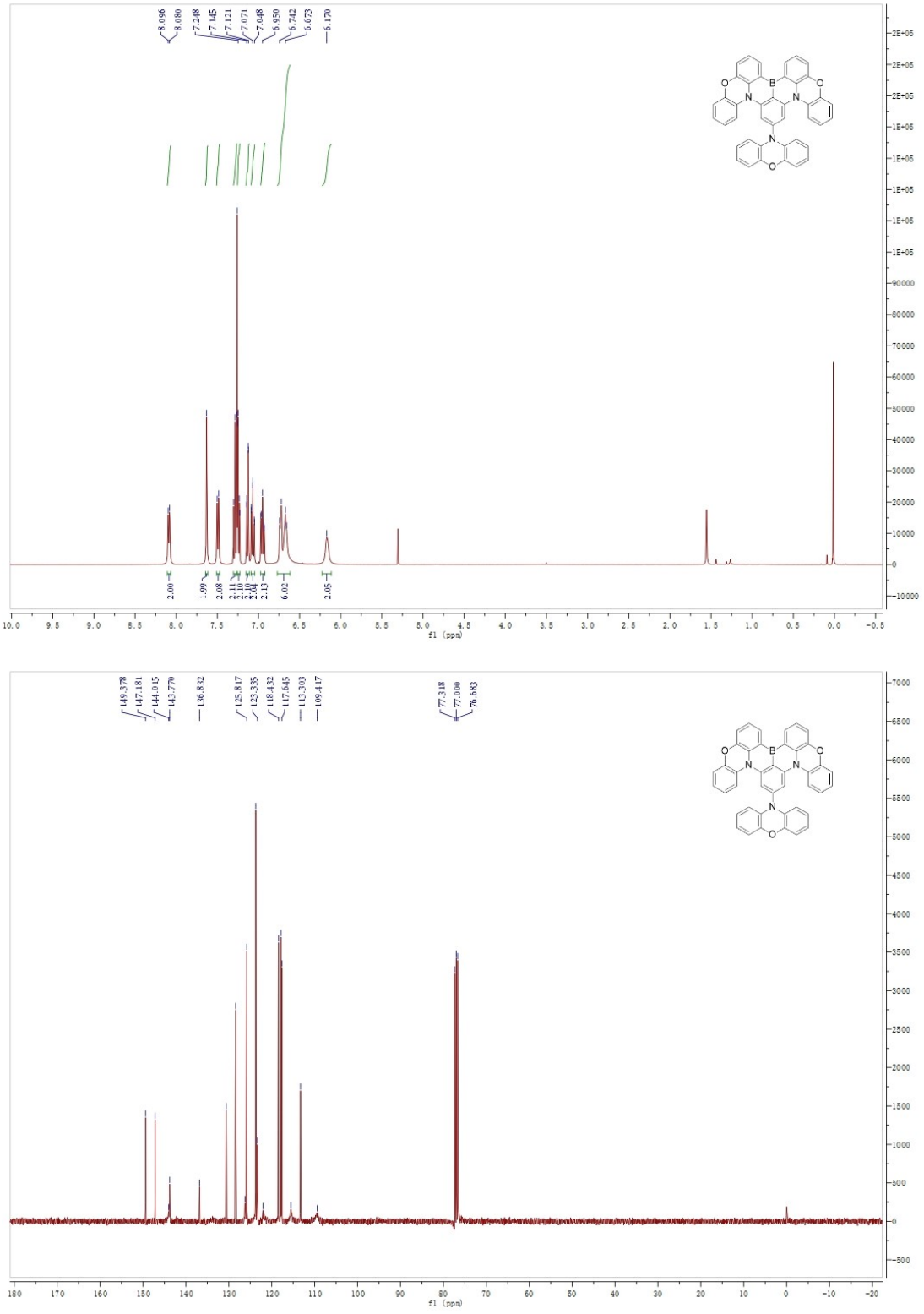


Fig. S2 ^{1}H and ^{13}C NMR spectra of TPXZBN in chloroform-*d*.

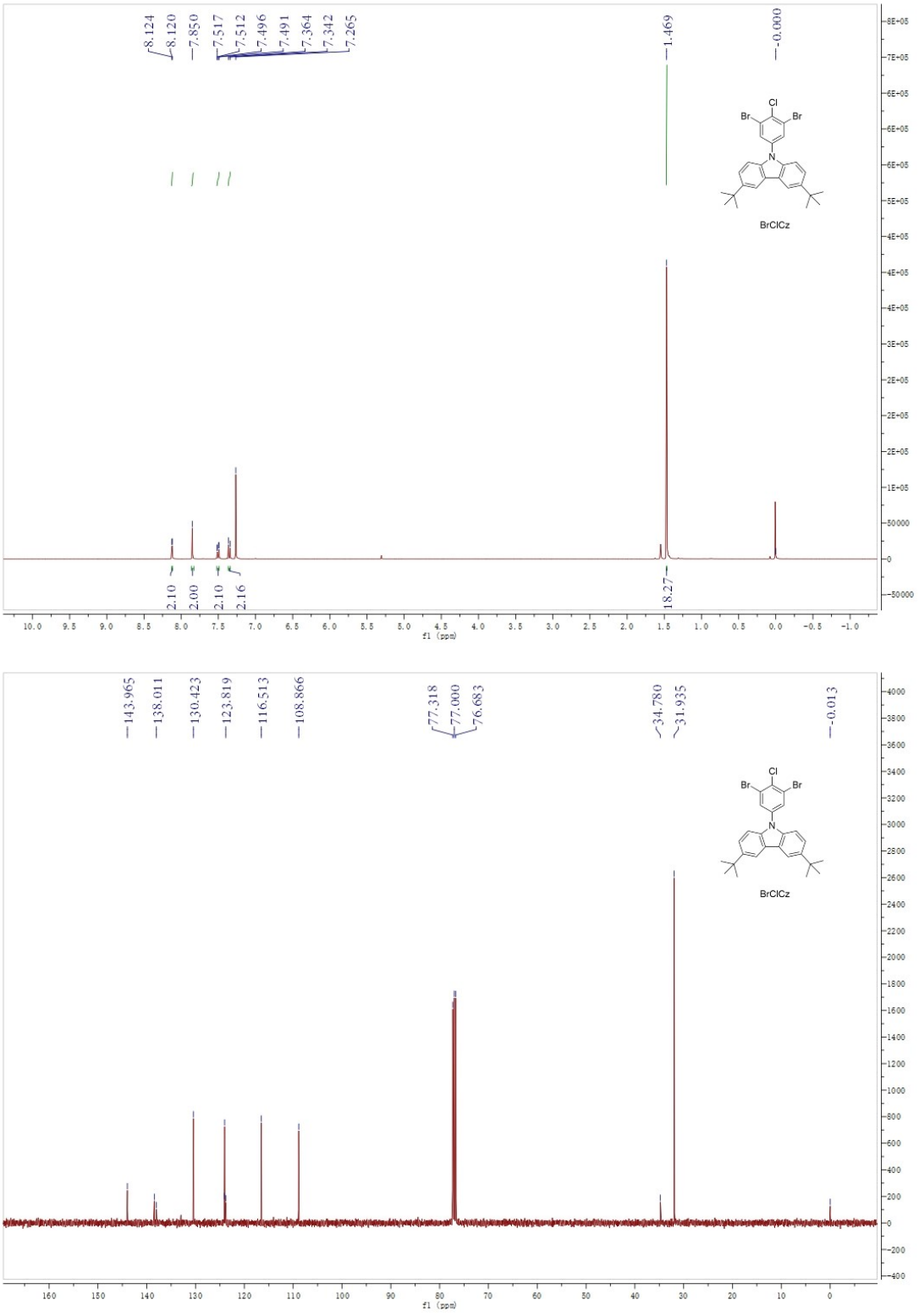


Fig. S3 ^{1}H and ^{13}C NMR spectra of **2** (BrClCz) in chloroform-*d*.

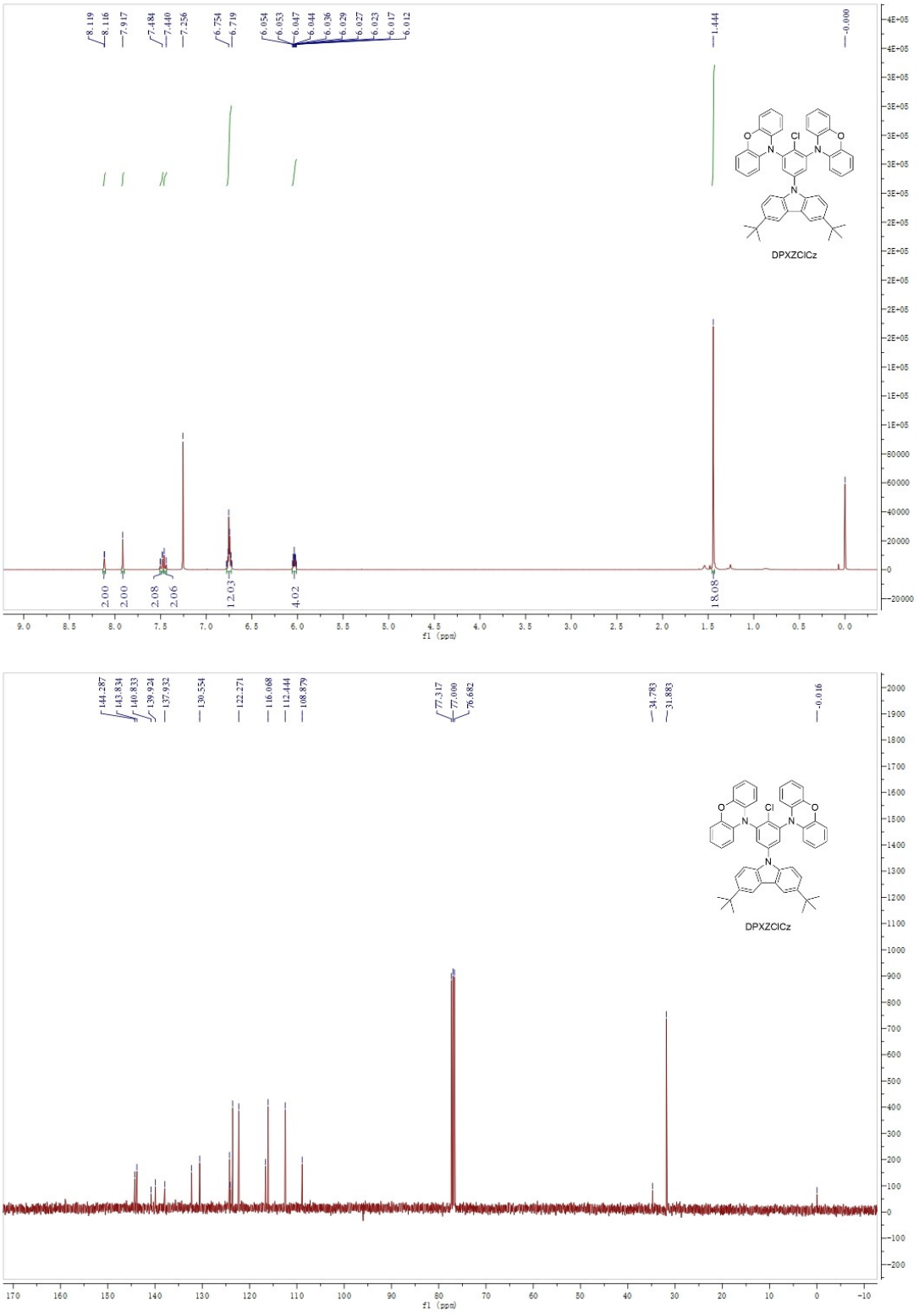


Fig. S4 ^{1}H and ^{13}C NMR spectra of **3** (DPXZClCZ) in chloroform-*d*.

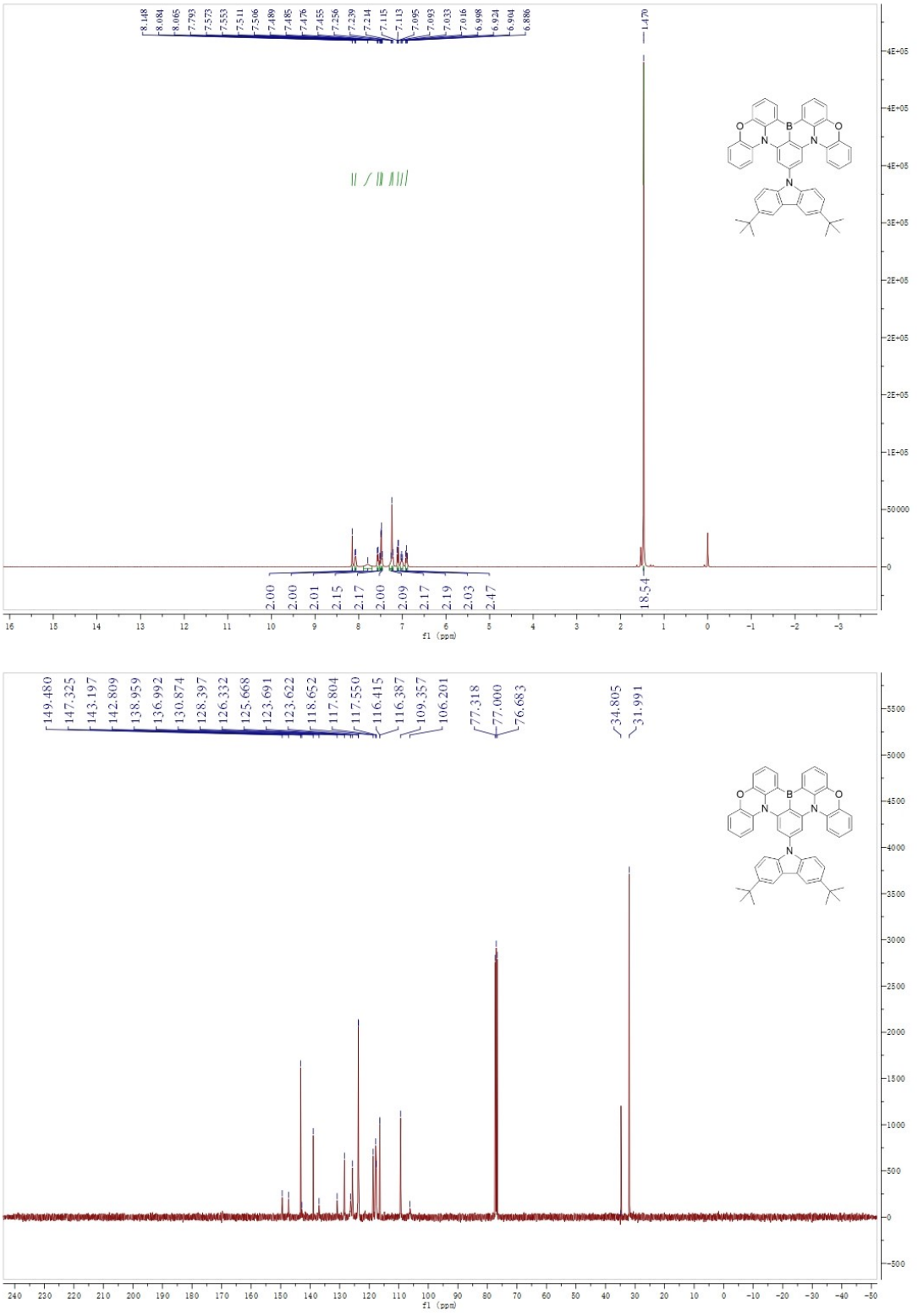


Fig. S5 ^{1}H and ^{13}C NMR spectra of DPXZCZBN in chloroform-*d*.

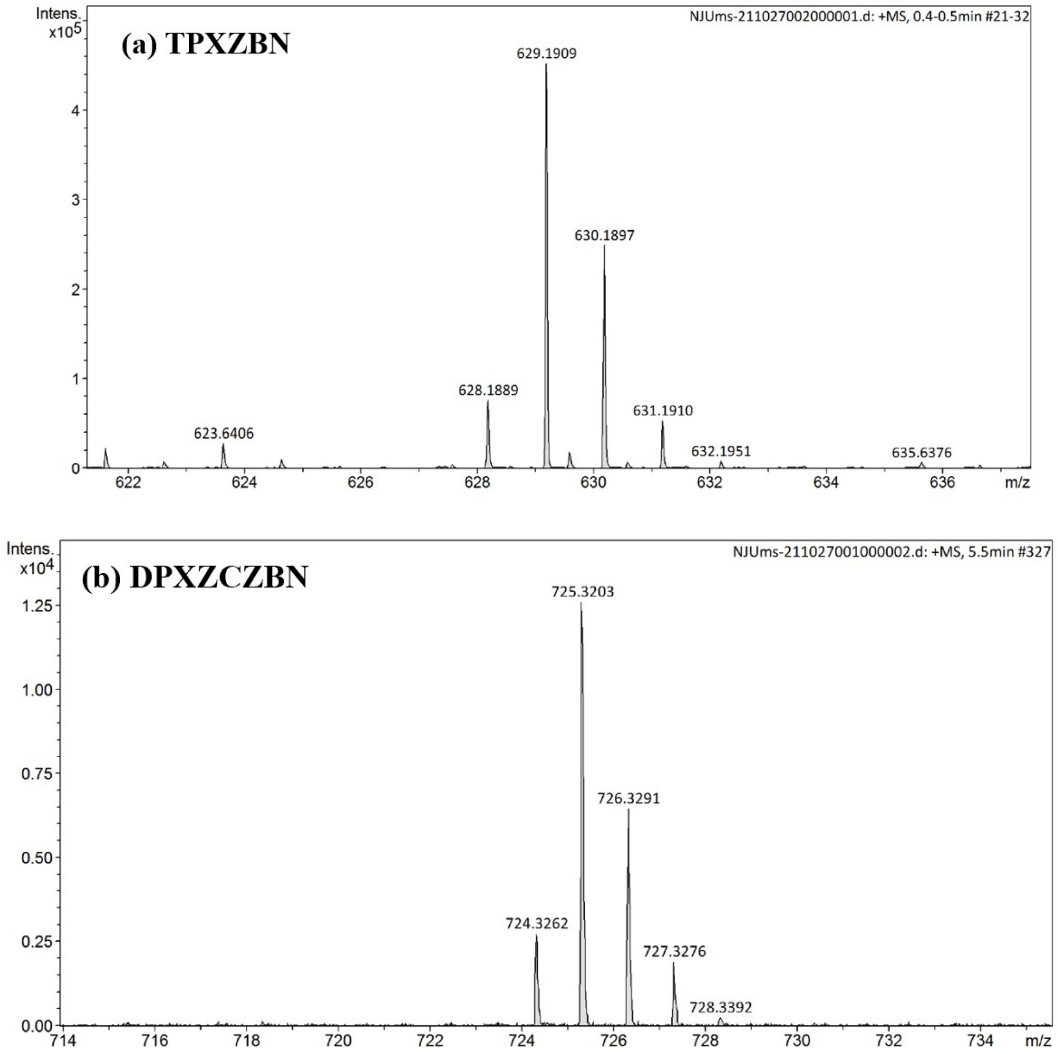


Fig. S6 HRMS spectra of (a) TPXZBN and (b) DPXZCZBN compounds.

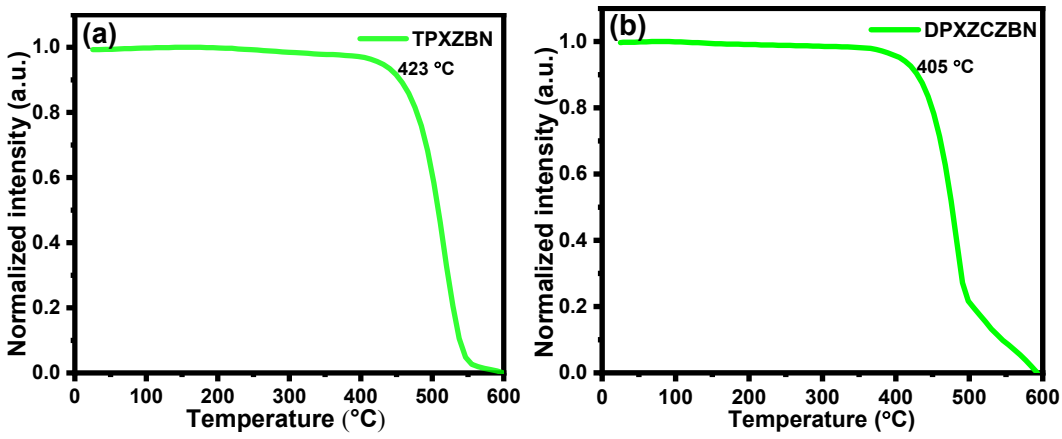


Fig. S7 TGA thermogram curves of (a) TPXZBN and (b) DPXZCZBN at a heating rate of 10 °C min^{-1} under N_2.

3. Photophysical measurements

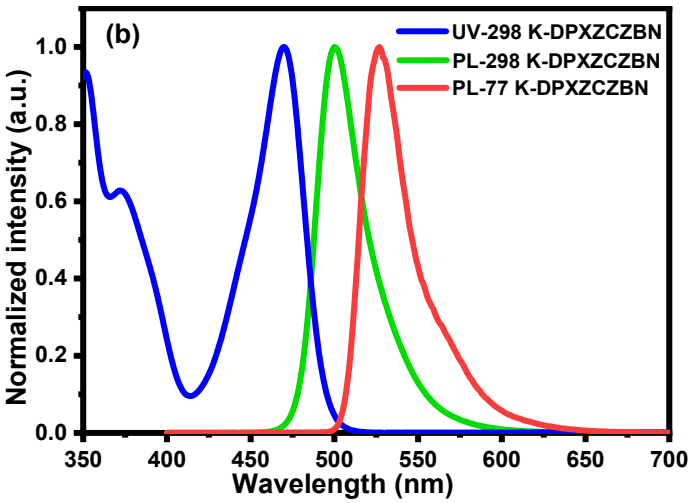


Fig. S8 UV-vis absorption, fluorescence and phosphorescence (77 K) spectra of DPXZCZBN measured in toluene solutions (10^{-5} M).

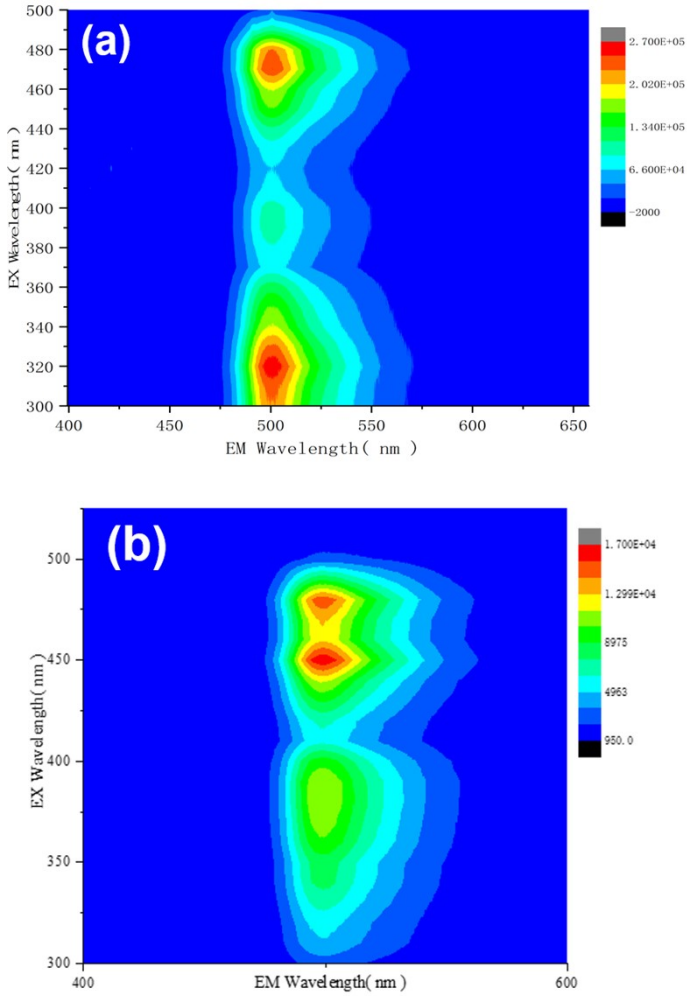


Fig. S9 Three-dimensional fluorescence maps of (a) TPXZBN (b) DPXZCZBN at 298 K (10^{-5} M in toluene).

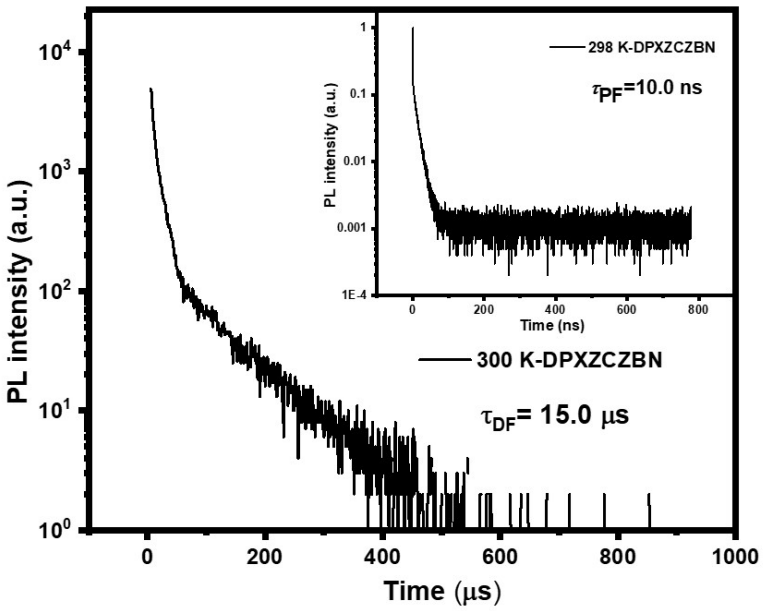


Fig. S10 The delayed fluorescence lifetime curves of 5 wt% doping concentration of DPXZCZBN in mCBP deposited film.

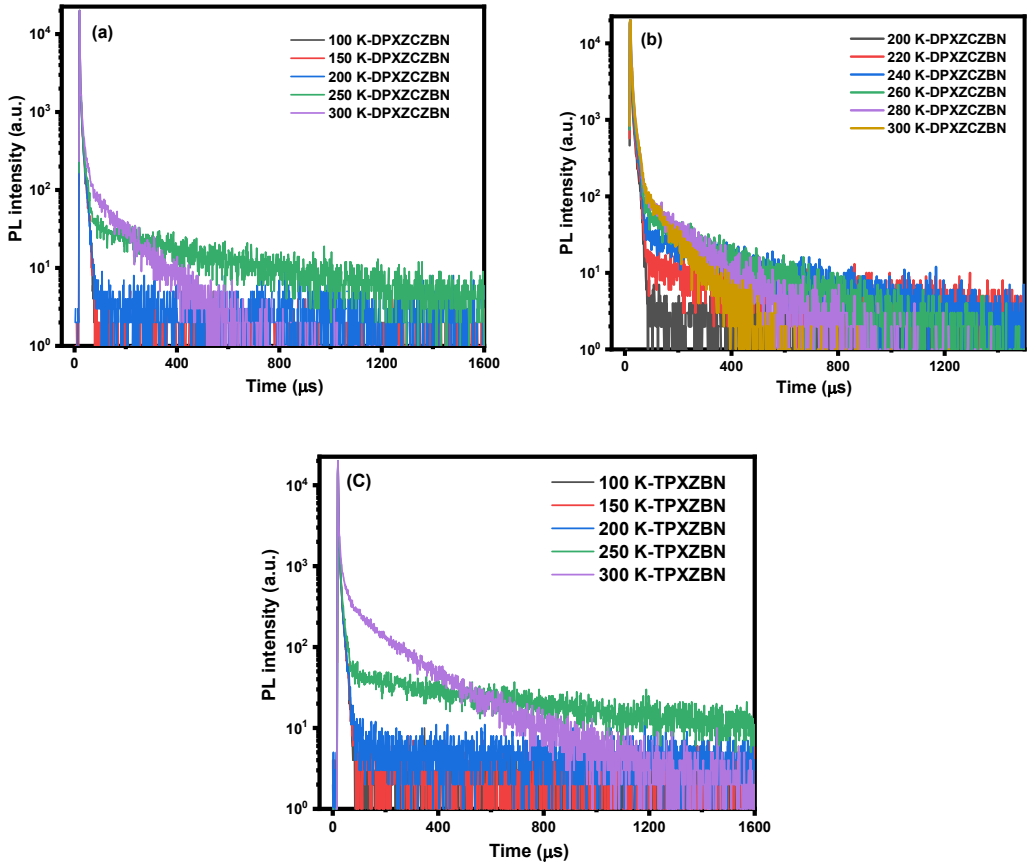
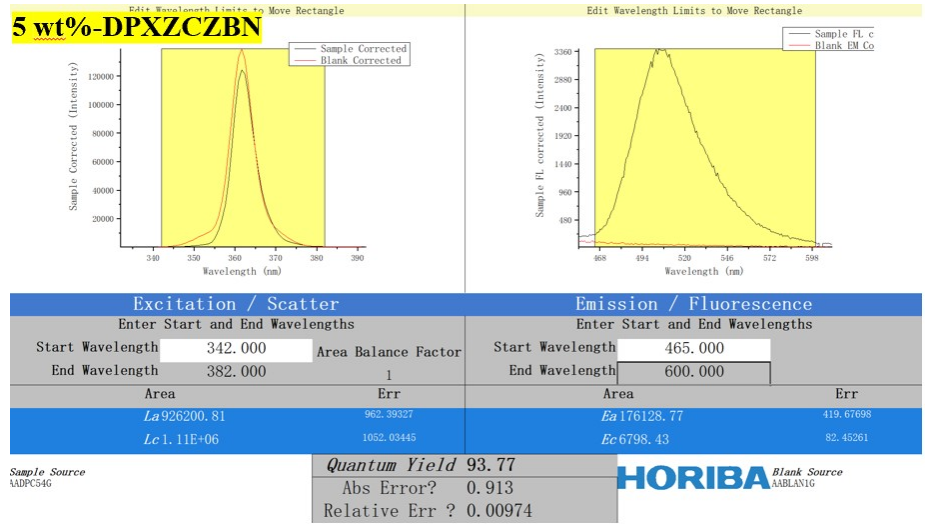


Fig. S11 The delayed fluorescence lifetime curves of 5 wt% doping concentration of (a)(b) DPXZCZBN and (c) TPXZBN in mCBP deposited films at various temperatures.



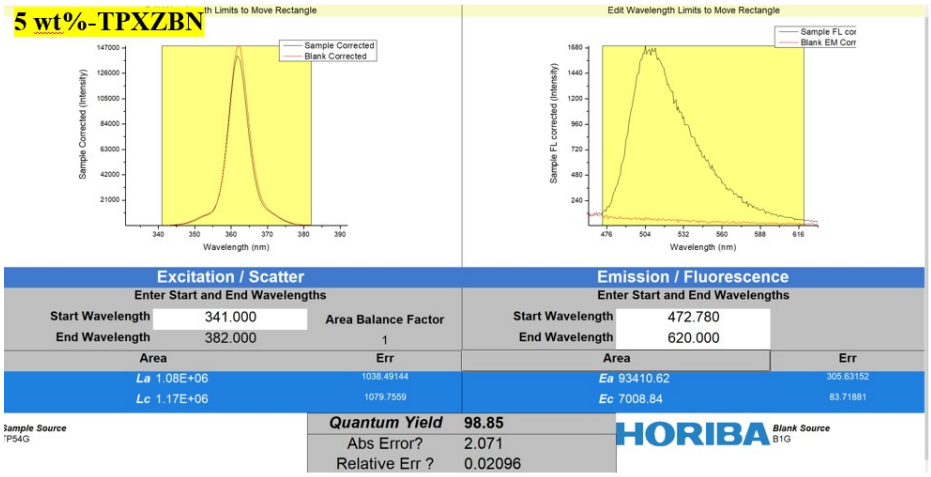
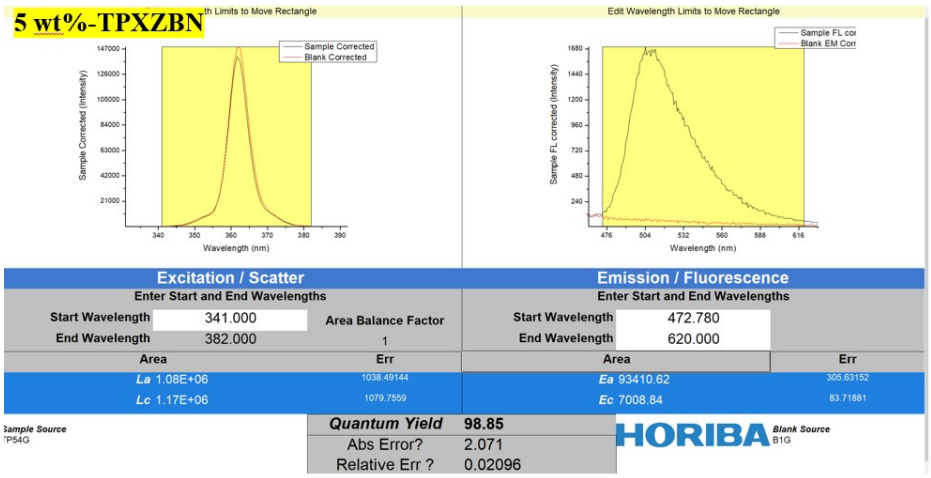


Fig. S12 PLQYs of TPXZBN/DPXZCZBN in mCBP deposited films with 5 wt% doping concentration.



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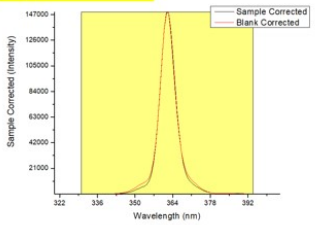

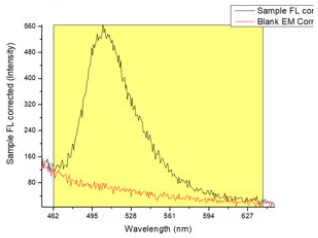

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Lc	1.17E+06	1081.69179	*Ec*	8492.18	92.15301

Quantum Yield	87.63	
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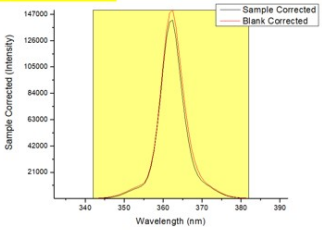
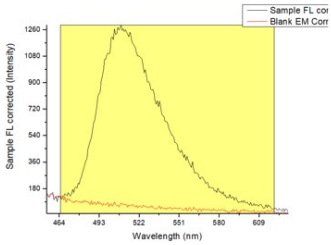
Relative Err ?	0.06682	

Sample Source TP159G

HORIBA *Blank Source* B1G

30 wt%-TPXZBN





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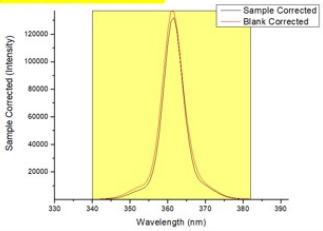
La	1.11E+06	1054.58302	*Ea*	75886.34	275.47475
Lc	1.20E+06	1097.34104	*Ec*	8126.73	90.14835

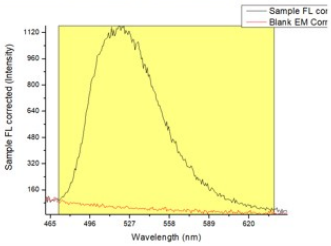
Quantum Yield	73.64	
Abs Error?	1.675	
Relative Err ?	0.02275	

Sample Source TP305G

HORIBA *Blank Source* B1G

50 wt%-TPXZBN





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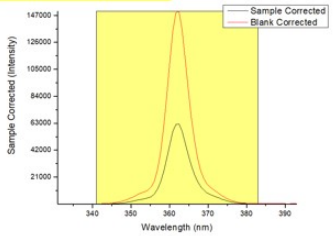
Lc	1.10E+06	1050.08006	*Ec*	7137.69	84.48482

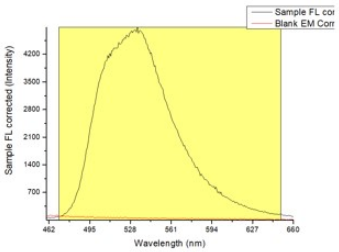
Quantum Yield	66.98	
Abs Error?	1.279	
Relative Err ?	0.0191	

Sample Source TP505G

HORIBA *Blank Source* B1G

70 wt%-TPXZBN





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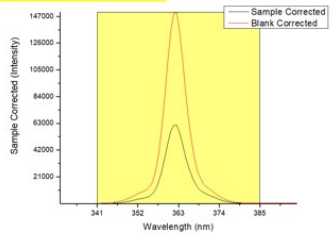
La	513963.41	716.91242	*Ea*	355813.86	596.50135
Lc	1.18E+06	1085.67112	*Ec*	7916.29	88.97356

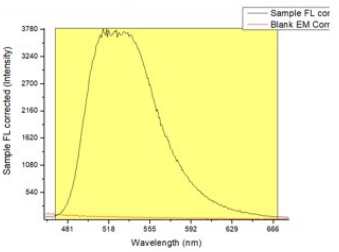
Quantum Yield	**52.34**
Abs Error?	0.149
Relative Err ?	0.00285

Sample Source TP704G

HORIBA ***Blank Source*** B1G

90 wt%-TPXZBN





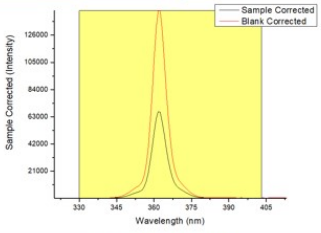
Excitation / Scatter			Emission / Fluorescence		
Enter Start and End Wavelengths			Enter Start and End Wavelengths		
Start Wavelength	341.000	Area Balance Factor	Start Wavelength	470.000	
End Wavelength	385.000	1	End Wavelength	670.000	
Area		Err	Area		Err
La	511239.87	715.0104	*Ea*	294693.35	542.85665
Lc	1.18E+06	1086.01535	*Ec*	8199.39	90.55049

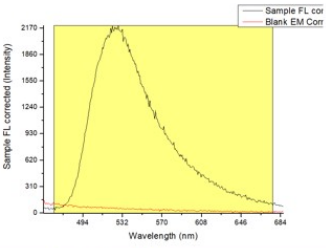
Quantum Yield	**42.88**
Abs Error?	0.136
Relative Err ?	0.00318

Sample Source TP903G

HORIBA ***Blank Source*** B1G

Pure film-TPXZBN





Excitation / Scatter			Emission / Fluorescence		
Enter Start and End Wavelengths			Enter Start and End Wavelengths		
Start Wavelength	330.060	Area Balance Factor	Start Wavelength	466.420	
End Wavelength	403.010	1	End Wavelength	676.490	
Area		Err	Area		Err
La	543487.01	737.21571	*Ea*	172784.45	415.67349
Lc	1.14E+06	1065.95047	*Ec*	8355.36	91.40764

Quantum Yield	**27.74**
Abs Error?	0.139
Relative Err ?	0.00502

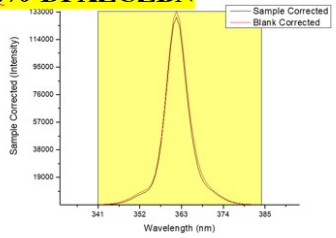
Sample Source TPpure3G

HORIBA ***Blank Source*** B1G

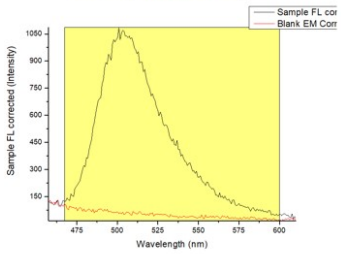
[redacted]

Edit Wavelength Limits to Move Rectangle

15 wt%-DPXZCZBN



Edit Wavelength Limits to Move Rectangle



Excitation / Scatter			Emission / Fluorescence		
Enter Start and End Wavelengths			Enter Start and End Wavelengths		
Start Wavelength	341.000	Area Balance Factor	Start Wavelength	467.550	
End Wavelength	384.000	1	End Wavelength	600.000	
Area		Err	Area		Err
La 1.02E+06		1007.86576	*Ea* 56105.82		236.86666
Lc 1.08E+06		1039.52231	*Ec* 6406.59		80.04116

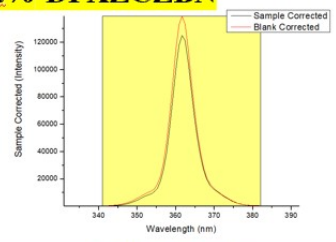
Quantum Yield	76.68
Abs Error?	2.317
Relative Err ?	0.03021

Sample Source DPC154G

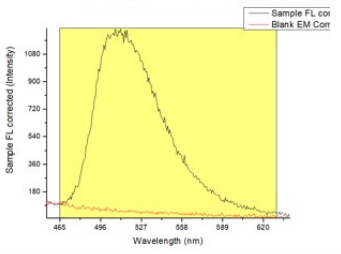
HORIBA *Blank Source* B1G

Edit Wavelength Limits to Move Rectangle

30 wt%-DPXZCZBN



Edit Wavelength Limits to Move Rectangle



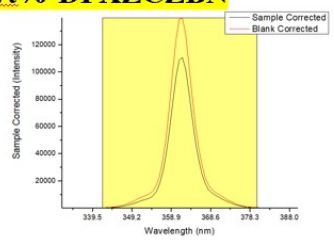
Excitation / Scatter			Emission / Fluorescence		
Enter Start and End Wavelengths			Enter Start and End Wavelengths		
Start Wavelength	341.000	Area Balance Factor	Start Wavelength	465.000	
End Wavelength	382.060	1	End Wavelength	630.000	
Area		Err	Area		Err
La 983066.64		991.49717	*Ea* 80318.53		283.40524
Lc 1.10E+06		1049.33738	*Ec* 7260.07		85.20605

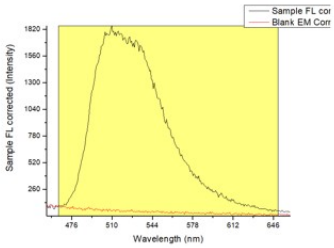
Quantum Yield	61.89
Abs Error?	1.133
Relative Err ?	0.01831

Sample Source DPC304G

HORIBA *Blank Source* B1G

50 wt%-DPXZCZBN





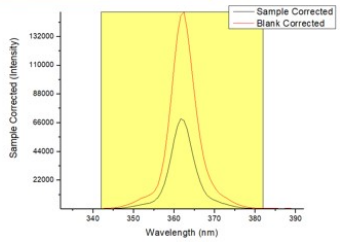
Excitation / Scatter			Emission / Fluorescence		
Enter Start and End Wavelengths			Enter Start and End Wavelengths		
Start Wavelength	342.000	Area Balance Factor	Start Wavelength	465.000	
End Wavelength	380.000	1	End Wavelength	650.000	
Area		Err	Area		Err
La	841067.69	917.09743	*Ea*	134540.05	366.79701
Lc	1.08E+06	1038.22976	*Ec*	7434.40	86.22296

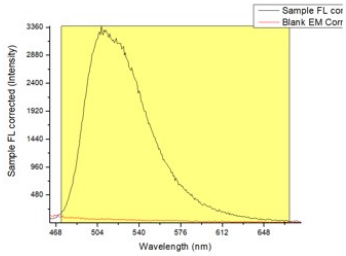
Quantum Yield	**53.66**
Abs Error?	0.500
Relative Err ?	0.00931

Sample Source DPC504G

HORIBA ***Blank Source*** B1G

70 wt%-DPXZCZBN





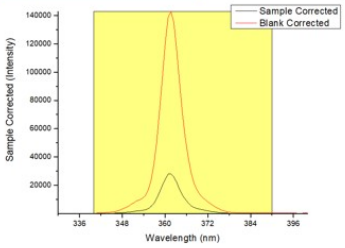
Excitation / Scatter			Emission / Fluorescence		
Enter Start and End Wavelengths			Enter Start and End Wavelengths		
Start Wavelength	342.000	Area Balance Factor	Start Wavelength	472.780	
End Wavelength	382.000	1	End Wavelength	670.000	
Area		Err	Area		Err
La	531647.63	729.14171	*Ea*	220184.09	469.23777
Lc	1.21E+06	1099.45816	*Ec*	8386.06	91.57545

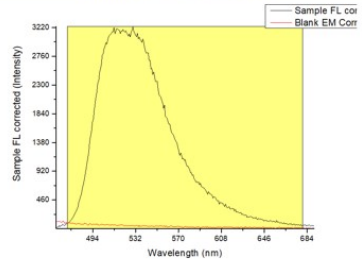
Quantum Yield	**31.28**
Abs Error?	0.124
Relative Err ?	0.00398

Sample Source DPC705G

HORIBA ***Blank Source*** B1G

90 wt%-DPXZCZBN



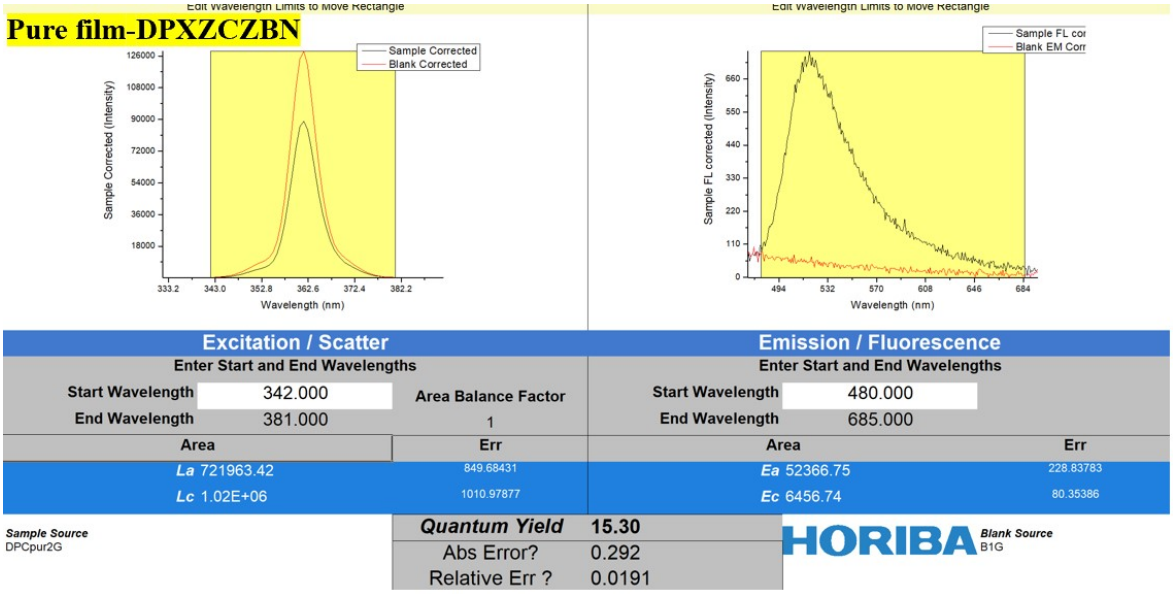


Excitation / Scatter			Emission / Fluorescence		
Enter Start and End Wavelengths			Enter Start and End Wavelengths		
Start Wavelength	340.000	Area Balance Factor	Start Wavelength	471.660	
End Wavelength	390.000	1	End Wavelength	680.000	
Area		Err	Area		Err
La	225668.04	475.0453	*Ea*	252375.07	502.36945
Lc	1.14E+06	1067.19894	*Ec*	7891.36	88.83331

Quantum Yield	**26.77**
Abs Error?	0.063
Relative Err ?	0.00235

Sample Source DPC906G

HORIBA ***Blank Source*** B1G



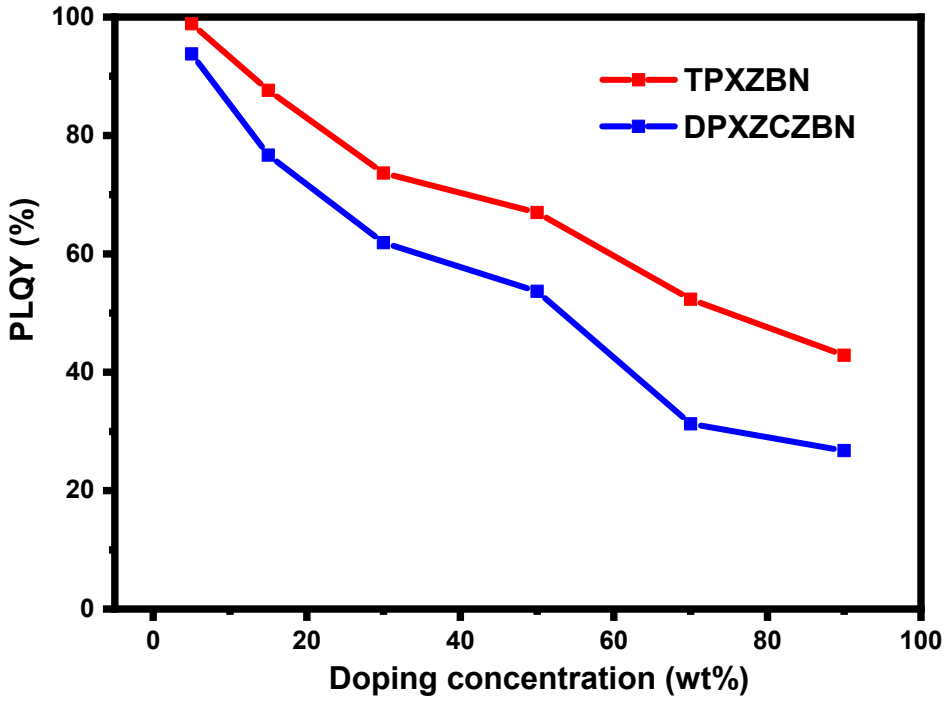


Fig. S13 PLQYs of TPXZBN/DPXZCZBN in mCBP deposited films with different doping concentrations.

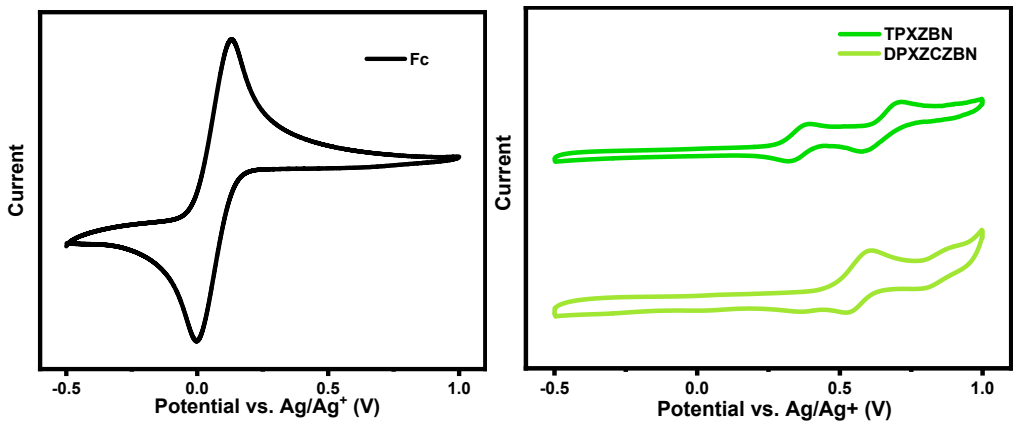


Fig. S14 Cyclic voltammogram curves of TPXZBN and DPXZCZBN in CH_3CN solutions.

6. Computational detail and geometry data

(a) (b) (c)

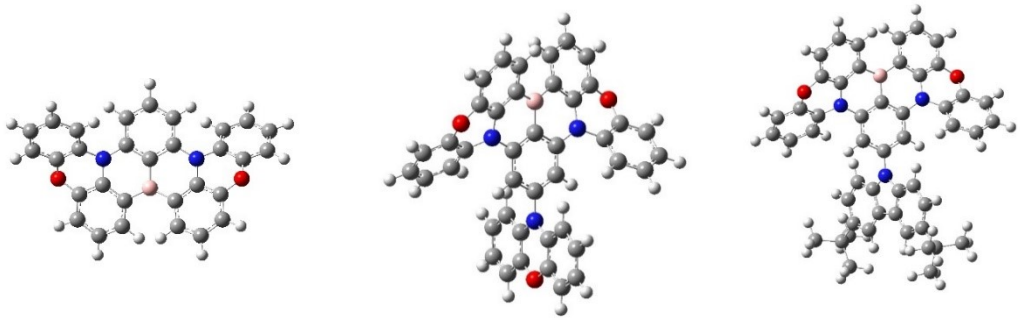


Fig. S15 The optimized structures of (a) PXZ-BN, (b) TPXZBN and (c) DPXZCZBN compounds calculated at the B3LYP/6-31g(d) level of theory.

	LUMO+2	LUMO+1	LUMO	HOMO	HOMO-1	HOMO-2
PXZ-BN	-0.29 eV	0.61 eV	-1.54 eV	-4.81 eV	-5.27 eV	-6.17 eV
TPXZBN	-0.46 eV	-0.78 eV	-1.69 eV	-4.66 eV	-4.95 eV	-5.35 eV
DPXZCZBN	-0.61 eV	-0.71 eV	-1.64 eV	-4.91 eV	-5.23 eV	-5.33 eV

Fig. S16 Frontier molecular orbitals of several molecular structures calculated at the B3LYP/6-31g(d) level of theory.

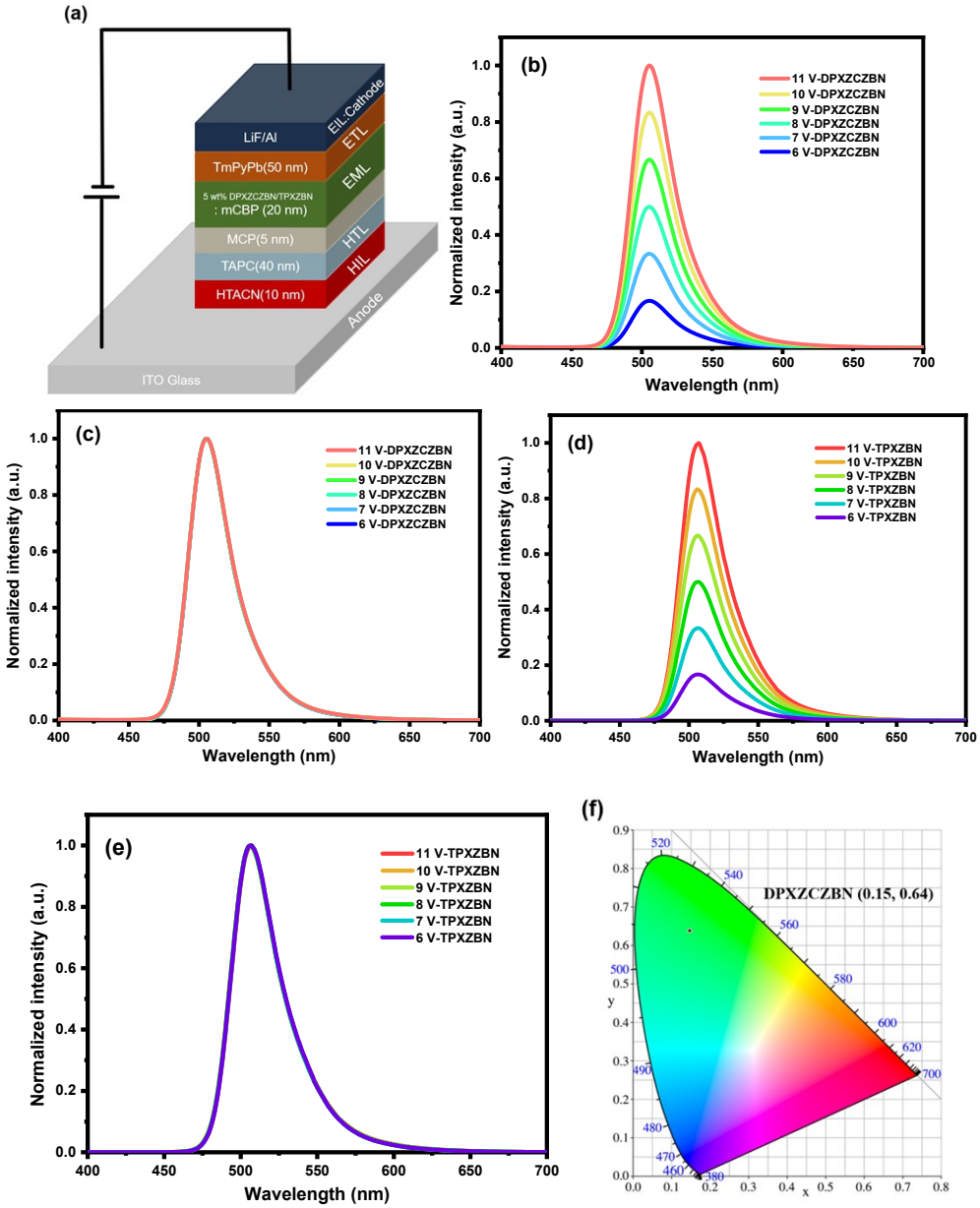


Fig. S17 (a) The energy level diagram of the devices. (b)(c) Normalized EL spectra of DPXZCZBN-based device measured at various voltages. (d)(e) Normalized EL spectra of TPXZBN-based device measured at various voltages. (f) CIE (x, y) coordinates.

Table S1 Cartesian coordinates of aforementioned complexes.

PXZ-BN			
Atom	x	y	z
C	0.00005	3.22266	-0.00005
C	-1.21598	2.55023	-0.08875
C	-1.22402	1.14772	-0.05751
C	0	0.42293	-0.00002
C	1.22405	1.14769	0.05746
C	1.21605	2.55019	0.08868
H	0.00007	4.30977	-0.00006
H	-2.13544	3.1118	-0.19522
H	2.13553	3.11174	0.19512
N	2.42958	0.42625	0.11188
N	-2.42957	0.42631	-0.11194
C	2.45496	-0.92399	0.52332
C	3.67007	-1.42693	1.02357
C	1.31301	-1.7559	0.47245
C	3.77362	-2.73126	1.47493
C	1.44235	-3.07795	0.95743
C	2.64488	-3.5621	1.45098
H	4.72687	-3.07493	1.86467
H	0.5653	-3.71737	0.9694
H	2.71914	-4.57857	1.82664
C	3.67712	0.95386	-0.33857
C	3.80525	1.9152	-1.34871
C	4.85015	0.41088	0.20782
C	5.06499	2.38138	-1.72831
H	2.91849	2.30525	-1.83349
C	6.10822	0.86442	-0.17187
C	6.21789	1.87095	-1.13148
H	5.13744	3.14106	-2.50107
H	6.9827	0.41458	0.28777
H	7.19857	2.23554	-1.42229
C	-3.6771	0.9539	0.33859
C	-4.85013	0.41096	-0.20783
C	-3.80521	1.91514	1.34882
C	-6.1082	0.86444	0.17194
C	-5.06496	2.38127	1.7285
H	-2.91845	2.30515	1.83363
C	-6.21786	1.87088	1.13165
H	-6.98269	0.41463	-0.28772
H	-5.13739	3.14087	2.50134
H	-7.19853	2.23543	1.42252
C	-2.45497	-0.92393	-0.52337
C	-1.31306	-1.75587	-0.47248
C	-3.6701	-1.42682	-1.02363
C	-1.44244	-3.07792	-0.95744
C	-3.77369	-2.73116	-1.47496

C	-2.64498	-3.56204	-1.45098
H	-0.56541	-3.71737	-0.9694
H	-4.72695	-3.07481	-1.8647
H	-2.71927	-4.57851	-1.82662
O	-4.77923	-0.60842	-1.13232
O	4.77926	-0.6086	1.1322
B	-0.00002	-1.0978	-0.00001

DPXZCZBN			
Atom	x	y	z
C	1.79844123	-1.15410269	-0.41196822
C	2.52311988	-0.00000864	0.00001492
C	1.79844622	1.1540853	0.41200646
C	0.39632183	1.14098799	0.43606516
C	-0.27907109	-0.00000007	0.00001468
C	0.39631606	-1.1409938	-0.43603026
H	-0.17443331	1.97642498	0.81921536
H	-0.17444485	-1.97642244	-0.81918873
N	2.5184634	2.28407529	0.8326953
N	-1.70422771	0.00000545	0.00000873
N	2.51845748	-2.28409421	-0.8326597
C	1.98906019	3.61051911	0.79790623
C	2.52397833	4.55140098	1.69085566
C	1.03056825	4.04888351	-0.12336122
C	2.06122821	5.86169639	1.73137937
C	0.5560228	5.36075413	-0.08390258
H	0.64784542	3.36265825	-0.86855407
C	1.0553348	6.26502491	0.85333669
H	2.50399438	6.54626553	2.44798649
H	-0.2041548	5.67042612	-0.79474797
H	0.68302312	7.28439863	0.89005189
C	3.86585174	2.17863128	1.24466499
C	4.36379527	3.17834178	2.1002455
C	4.69960745	1.10807475	0.84819222
C	5.66634415	3.13630599	2.5676021
C	6.01890373	1.07965974	1.35607797
C	6.49912695	2.07123279	2.19865637
H	6.00736714	3.92148893	3.23523876
H	6.65814508	0.24002816	1.10220667
H	7.51368748	2.02576312	2.58387506
C	1.98906436	-3.61054301	-0.79786626
C	2.52396545	-4.55141486	-1.69083707
C	1.03060812	-4.04892717	0.12342988
C	2.06122002	-5.8617121	-1.73136214
C	0.5560697	-5.36080033	0.08397268
H	0.64790872	-3.36271567	0.86864672

C	1.05535518	-6.26505651	-0.85329447
H	2.50397091	-6.54627204	-2.44798756
H	-0.20408062	-5.67048581	0.79484129
H	0.683049	-7.28443218	-0.89000985
C	3.86583527	-2.17864057	-1.24466185
C	4.69959359	-1.10807978	-0.84820608
C	4.36376488	-3.17834203	-2.10026101
C	6.01887605	-1.07965047	-1.35612676
C	5.66630033	-3.13629144	-2.56765396
C	6.49908462	-2.07121374	-2.19872483
H	6.65811667	-0.24001467	-1.10226746
H	6.00731168	-3.92146778	-3.23530431
H	7.51363403	-2.02573339	-2.58397141
C	-2.52481849	-0.81068657	0.78989766
C	-3.88018884	-0.51860608	0.50662808
C	-2.18504266	-1.75756337	1.75918988
C	-4.89811369	-1.19949599	1.18944469
C	-3.21854608	-2.41447535	2.41889101
H	-1.1490145	-1.96899115	2.0041441
C	-4.58651217	-2.16110334	2.15390954
H	-5.93141771	-0.96374559	0.95955913
H	-2.95101371	-3.1497443	3.17236039
C	-2.52480587	0.81070513	-0.78988563
C	-2.18501519	1.75757278	-1.75918147
C	-3.88018081	0.51864166	-0.50661991
C	-3.21850845	2.41448376	-2.41889961
H	-1.14898347	1.96899075	-2.00412924
C	-4.89809506	1.199538	-1.18944575
C	-4.58647847	2.16112416	-2.15392682
H	-2.95096459	3.14974851	-3.17236898
H	-5.9314029	0.96379636	-0.95956775
O	3.54492708	4.19843932	2.54574242
O	3.54489824	-4.19844804	-2.54573874
B	4.04360589	-0.00000704	0.00000392
C	-5.66522113	-2.93949317	2.93306857
C	-7.09219928	-2.53723085	2.51665414
C	-5.50105114	-4.45556428	2.67267465
C	-5.5131339	-2.66446141	4.44782323
H	-7.29195216	-1.47646554	2.70820126
H	-7.28033407	-2.73398928	1.4547131
H	-7.82376053	-3.11700129	3.09176129
H	-4.51985771	-4.82346714	2.99236708
H	-6.26194235	-5.02443641	3.2220005
H	-5.61162733	-4.68675964	1.60653731
H	-6.27546574	-3.21235074	5.01617182
H	-4.53313095	-2.97582739	4.82572205
H	-5.63039428	-1.5968782	4.66843397
C	-5.66517604	2.93951195	-2.93310308

C	-5.51332652	2.66415975	-4.44782375
C	-7.09215737	2.53753097	-2.51642855
C	-5.50075353	4.45561039	-2.67302769
H	-4.53333617	2.975322	-4.82592187
H	-5.63075703	1.59654788	-4.66820555
H	-6.27566476	3.21203435	-5.01617791
H	-7.280155	2.73459217	-1.45451956
H	-7.82371116	3.11723809	-3.09160907
H	-7.29205704	1.47673863	-2.70767375
H	-6.26162432	5.02448696	-3.22237727
H	-5.61116927	4.68703271	-1.606923
H	-4.5195412	4.82330005	-2.99290855

TPXZBN			
Atom	x	y	z
C	-0.63390359	1.22469968	-0.05489387
C	-1.35804591	0.00035586	-0.00000549
C	-0.63466292	-1.22443405	0.05485209
C	0.76843957	-1.21806103	0.08203595
C	1.44271616	-0.00051638	-0.00001706
C	0.76919442	1.21744782	-0.08209471
H	1.34091427	-2.13024488	0.18611544
H	1.34224178	2.12927119	-0.18617863
N	-1.3529659	-2.42827528	0.11361551
N	2.87825908	-0.00094827	0.00001612
N	-1.35146205	2.42898557	-0.11364472
C	-0.81859439	-3.68090619	-0.31942274
C	-1.36010907	-4.84867628	0.23889452
C	0.14832551	-3.81763619	-1.32298238
C	-0.8988107	-6.10956894	-0.12161138
C	0.62234961	-5.08001381	-1.68316065
H	0.53952415	-2.93745291	-1.81861084
C	0.113462	-6.22694897	-1.07387023
H	-1.34722399	-6.97989221	0.34710458
H	1.38776915	-5.15854241	-2.44938606
H	0.48455385	-7.20959768	-1.34918005
C	-2.70297713	-2.45257952	0.52881565
C	-3.20348007	-3.66479769	1.03839102
C	-3.53572996	-1.31130527	0.47446929
C	-4.5072977	-3.76590396	1.49247808
C	-4.85715339	-1.43843502	0.96159497
C	-5.33945379	-2.63860772	1.462297
H	-4.84929571	-4.71680948	1.88924972
H	-5.4968464	-0.56163444	0.96999598
H	-6.35533489	-2.71180358	1.83956868
C	-0.8162588	3.68130352	0.3192762
C	-1.35711037	4.84939017	-0.23902099
C	0.15082894	3.81746321	1.32275029

C	-0.89497836	6.11000725	0.12138283
C	0.62567489	5.07955639	1.68284118
H	0.54149663	2.93704446	1.81838646
C	0.11746386	6.22678593	1.07353488
H	-1.34289376	6.98059485	-0.34732032
H	1.39120001	5.15763521	2.44900722
H	0.48920804	7.20921297	1.34875621
C	-2.70149613	2.45412124	-0.52874964
C	-3.53494213	1.31335718	-0.47434954
C	-3.20128063	3.6666277	-1.03834319
C	-4.85630374	1.44126971	-0.96143885
C	-4.50505259	3.76851176	-1.49238961
C	-5.33788976	2.64172038	-1.4621638
H	-5.49653334	0.56486006	-0.96977732
H	-4.84648409	4.71961591	-1.88917413
H	-6.35374063	2.71552791	-1.83939784
C	3.58858809	0.04047079	1.21493602
C	4.99655366	0.04145753	1.18622831
C	2.95612977	0.07641757	2.46305768
C	5.73875031	0.08306488	2.35758261
C	3.70389187	0.11751952	3.64472191
H	1.87307659	0.0642659	2.51016699
C	5.09423308	0.1223484	3.59877121
H	6.82179521	0.08267753	2.27978917
H	3.18415238	0.14352656	4.59830867
C	3.58864967	-0.04259296	-1.21485448
C	2.95625347	-0.07826177	-2.463012
C	4.99661296	-0.04409436	-1.18605939
C	3.70406913	-0.11960487	-3.64463487
H	1.8732079	-0.06569361	-2.5101857
C	5.73886371	-0.08597042	-2.3573701
C	5.09440511	-0.12496104	-3.59859959
H	3.18437684	-0.14541308	-4.59825316
H	6.82190427	-0.08599049	-2.27951255
O	-2.38568339	-4.77214817	1.15571337
O	-2.38283346	4.77348457	-1.15571703
B	-2.87977216	0.00083628	0.00007719
H	5.68125869	0.15410055	4.51169938
H	5.68147301	-0.15690653	-4.51149398
O	5.70260369	-0.00145988	0.00010678

Table S2 The chemical structures and energy gaps of PXZ-BN, DPXZCZBN and TPXZBN.

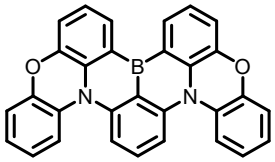
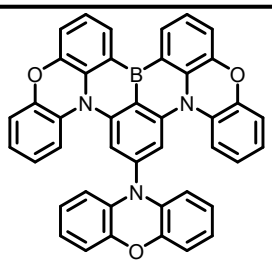
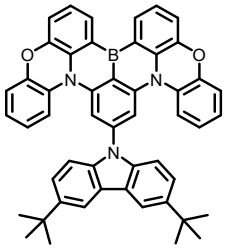
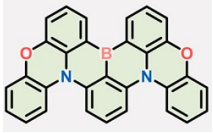
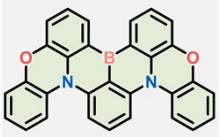
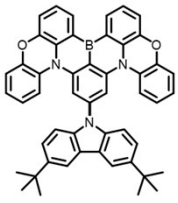
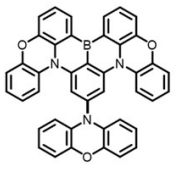
	PXZ-BN	TPXZBN	DPXZCZBN
Structure			
E_{HOMO}	-4.81 eV	-4.66 eV	-4.91 eV
E_{LUMO}	-1.54 eV	-1.69 eV	-1.64 eV
E_{gap}	3.27 eV	2.97 eV	3.27 eV

Table S3 The photophysical properties of the reported PXZ-BN/2PXZBN materials and TPXZBN / DPXZCZBN compounds investigated in this work.

Emitter	λ_{em} [nm]	λ_{ph} [nm]	FWHM [nm]	PLQY [%]	τ_{PF} [ns]	τ_{DF} [μs]	$EQE_{max/100/1000}$ (%)	FWHM [nm]
 PXZ-BN	502	540	38	90	8.2	90.7	23.3/19.9/11.3	47
 2PXZBN	504	-	34	84	6.8	25.3	17.7/15.3/7.4	60
 TPXZBN	502	537	33	94	7.4	27.1	21.3/19.6/17.4	37
 DPXZCZBN	500	527	32	99	10.0	15.0	19.2/18.8/17.2	36