Supporting Information

Multifunctional Oxadiazole-based Ultraviolet-emitting Materials used as Host for Multicolor Phosphorescence

Lizhi Chu, Chenglin Ma, Li Zhang, Yannan Zhou, Jingru Song, Qikun Sun, Shi-Tong Zhang*, Wenjun Yang, Shanfeng Xue*

L. Chu, C. Ma, L. Zhang, Y. Zhou, J. Song, Dr. Q. Sun, Prof. W. Yang, Prof. S. Xue
Key Laboratory of Rubber-Plastics of Ministry of Education/Shandong Province (QUST), School of Polymer Science & Engineering, Qingdao University of Science & Technology, 53-Zhengzhou Road, Qingdao 266042, P. R. China
E-mail: sfxue@qust.edu.cn
Prof. S.-T. Zhang
State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China.
E-mail: stzhang@jlu.edu.cn

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SI-1 Measurements

NMR spectra were recorded on a Mercury 500 spectrometer. The chemical shift for each signal was reported in ppm units. The MALDI-TOF-MS mass spectra were measured using an AXIMA-CFRTM plus instrument. The dates of thermal gravimetric analysis (TGA) are from Perkin-Elmer thermal analysis system with the temperature of 50-800°C under a heating rate of 10 °C /min and the nitrogen atmosphere. The dates of Differential scanning calorimetry (DSC) are from NETZSCH (DSC-204) instrument with the temperature of 50-350 °C at a heating rate of 20 °C /min and a nitrogen flow rate of 80 mL/min. Cyclic voltammetry (CV) analysis of the materials was recorded on a three-electrode cell with tetra-n-butylammonium hexafluorophosphate (TBAPF6, 0.1 m in acetonitrile) as the supporting electrolyte. Two platinum wires were used as counter electrode and reference electrode. The scan rate is 100 mV/s, and all the potentials were corrected to the ferrocene/ferrocene $^{+}$ (Fc/Fc^{+}) standard under room temperature. The oxidation curve is obtained by dissolving the product and electrolyte in dichloromethane (DCM), and the reduction curve is obtained in N, N-Dimethylformamide (DMF). The single crystals of two molecules are obtained from the sublimation. Single-crystal X-ray diffraction data were collected by Rigaku RAXIS-PRID diffractometer. UV-vis absorption spectra were measured on a Hitachi U-4100 spectrophotometer. Fluorescence and low temperature phosphorescence measurements were measured on a Hitachi F-4600 spectrophotometer. The PLQYs were carried out using a FLS980 spectrometer. The lifetimes of films were measured on an Edinburgh FLS-980 with an EPL-375 optical laser. The DFT calculations were carried out with the Gaussian 09 B.01 Package at the level of PBE0/6-31g (d, p) and BMK/6-31g (d, p). ITO-coated glass with a sheet resistance of 15-20 Ω square–1 was used as the substrate. Before device fabrication, the ITO glass substrates were cleaned with acetone, Hellmanex^{TM} III and deionized water, dried 6h in an oven at 120 °C, the substrates were treated by O_2 plasma for 7 minutes to improve the hole injection ability of ITO. Finally transferred to a vacuum deposition system with a pressure of < 1.6×10^{-4} Pa. The current–voltage–luminance characteristics were measured by using a Keithley source measurement unit (Keithley 2450 and LS-160), EL spectra were measured with Flame-S (Serial Number: FLMS16791, Range: >350 nm). EQEs were calculated from the luminance, current density, and EL spectrum, all the results were measured in the forward-viewing direction without using any light out-coupling technique. The lifetime of the device at 1000 cd m^{-2} is deduced by Formula S1.

$$L_0^n \times LT_{50} = constant \qquad \text{Formula S1}$$

EQEs were calculated from the luminance, current density, and EL spectrum, all the results were measured in the forward-viewing direction without using any light out-coupling technique. According to equation following (Formula S2).

$$EQE = \frac{\pi \cdot L \cdot e}{683 \cdot I \cdot h \cdot c} \cdot \frac{\int_{380}^{780} I(\lambda) \cdot \lambda \cdot d\lambda}{\int_{380}^{780} I(\lambda) \cdot K(\lambda) \cdot d\lambda}$$

Formula S2

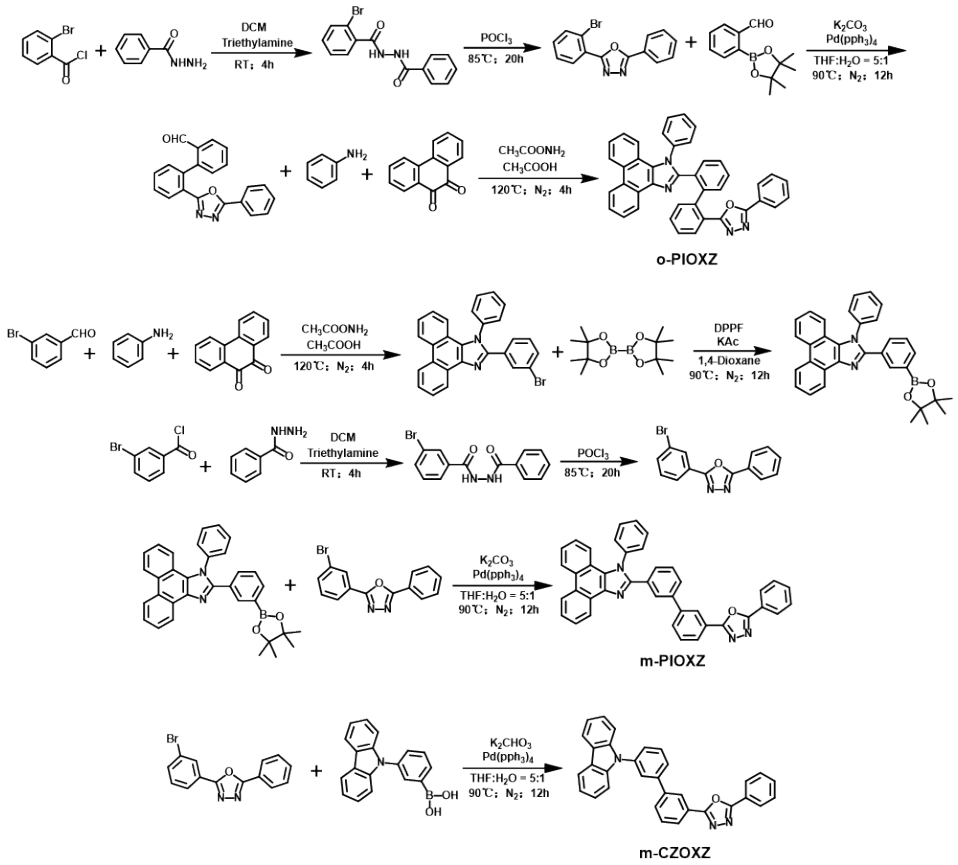
where L (cd m^{-2}) is the total luminance of the device, I (A) is the current, λ (nm) is EL wavelength, I(λ) is the relative EL intensity at each wavelength and is obtained by measuring the EL spectrum, K(λ) is the Commision International de L'Eclairage chromaticity (CIE) standard photopic efficiency function, e is the charge of an electron, h is the Planck's constant, c is the velocity of light.

The efficiency roll-offs of blue OLED device were calculated from maximum EQE and the EQE at luminescence of 1000 cd m−2. According to equation following (Formula S3):

$$\eta = \frac{EQE_{max} - EQE_{1000}}{EQE_{max}}$$

Formula S2

SI-2 Experimental section



Scheme S1. The detailed synthesis routes of o-PIOXZ, m-PIOXZ, and m-CZOXZ.

Synthesis of 2-phenyl-5-(2'-(1-phenyl-1H-phenanthro[9,10-d] imidazol-2-yl)-[1,1'-biphenyl]-2-yl)-1,3,4-oxadiazole (o-PIOXZ):

2-Bromobenzoyl chloride (0.6 mL, 4.55 mmol) was dissolved in 50 mL dichloromethane. Then the benzoyl hydrazide (0.63 g, 4.63 mmol) was dissolved in 20 mL dichloromethane, and 2 mL triethylamine was added. Then the benzoyl hydrazide solution was slowly added dropwise to the dichloromethane system of 2-Bromobenzoyl chloride, and the reaction was carried out at room temperature for 4 h. After the reaction was completed, the mixture was removed by a rotary evaporator, purified by evaporation crystallization with anhydrous ethanol, and finally filtered and dried to obtain the qOXZ-2Br (1.28 g, yield 86%). And then qOXZ-2Br (1 g, 3.13 mmol) was added to 15 mL of $POCl_3$ solvent and the resulting solution was refluxed in a closed system in a nitrogen atmosphere at 85 °C for 20 h. After the reaction was completed, the solution was cooled to room temperature, and then the solution was added dropwise to water to quench $POCl_3$. The mixed solvent was washed with water and dichloromethane. The organic phase was dried and filtered by $MgSO_4$, OXZ-2Br (0.50 g, yield 53%) can be purified by column chromatography with petroleum ether/dichloromethane (1/3; v/v). And then OXZ-2Br (1 g, 3.32 mmol), 2-formylphenylboronic acid pinacol ester (0.925 g, 3.98 mmol) and K_2CO_3 (0.69

g, 4.99 mmol) were dissolved in THF (50 mL) and water (10 mL), and Pd (PPh_3)$_4$ (0.15 g, 0.13 mmol) was added at 90 °C in N_2 for 24 h. The excess THF was removed by a rotary evaporator after cooled down, the mixture was washed with water and dichloromethane, and then OXZ-Ph-CHO (0.52 g, yield 48%) can be purified by column chromatography with petroleum ether/dichloromethane (1/3; v/v). And then a mixture of phenanthrenequinone (1.04 g, 5.01 mmol), aniline (1.87 g，20.04 mmol), OXZ-Ph-CHO (1.63 g，5.00 mmol), ammonium acetate (1.93 g, 25.05 mmol), and acetic acid (50 mL) was refluxed at 120 °C for 4 h under nitrogen. After cooling to room temperature, the system was poured into 200 mL cold water and separated by vacuum suction filtration. and then o-PIOXZ (1.55 g, yield 55%) can be purified by column chromatography with dichloromethane. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.74 (dd, J = 8.0, 1.4 Hz, 1H), 8.70 (d, J = 8.4 Hz, 1H), 8.66 (d, J = 8.2 Hz, 1H), 8.27 (dd, J = 8.2, 1.4 Hz, 1H), 7.84 (dd, J = 7.7, 1.3 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.62 (ddd, J = 8.5, 7.1, 1.5 Hz, 1H), 7.55 (td, J = 7.6, 1.3 Hz, 1H), 7.50 – 7.36 (m, 7H), 7.35 – 7.30 (m, 2H), 7.26 (d, J = 1.4 Hz, 0H), 7.25 – 7.22 (m, 1H), 7.18 (dd, J = 7.8, 1.2 Hz, 1H), 7.10 (ddd, J = 8.2, 7.0, 1.1 Hz, 1H), 7.04 (d, J = 7.8 Hz, 1H), 6.96 (dddd, J = 10.3, 8.8, 5.1, 1.6 Hz, 2H), 6.87 (dt, J = 9.0, 2.2 Hz, 2H), 6.42 – 6.35 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 163.95, 150.45, 140.67, 139.17, 137.13, 132.64, 132.14, 131.35, 130.92, 130.91, 130.38, 129.42, 129.39, 129.15, 128.89, 128.74, 128.71, 128.53, 128.46, 128.18, 127.97, 127.57, 127.28, 127.20, 126.78, 126.09, 125.55, 124.79, 124.00, 123.45, 123.00, 122.87, 120.69. MALDI-TOF MS (mass m/z): calcd for C41H26N4O, 590.2107; found, 591.2186 [M + H] $^+$.

Synthesis of 2-phenyl-5-(3'-(1-phenyl-1H-phenanthro[9,10-d] imidazol-2-yl)-[1,1'-biphenyl]-3-yl)-1,3,4-oxadiazole (m-PIOXZ):

A mixture of phenanthrenequinone (1.04 g, 5.01 mmol), aniline (1.87 g, 20.04 mmol), 3-bromobenzaldehyde (0.93 g, 5.01 mmol), ammonium acetate (1.93 g, 25.05 mmol), and acetic acid (50 mL) was refluxed at 120 °C for 4 h under nitrogen. After cooling to room temperature, the system was poured into 200 mL cold water and separated by vacuum suction filtration, and then PPI-3Br (2.09 g, yield 93%) can be purified by column chromatography with petroleum ether/dichloromethane (1/2; v/v). Then, a solution of PPI-3Br (2.00 g, 4.45 mmol), 4,4,4“,4”,5,5,5“,5”-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (1.36 g, 5.34 mmol), Pd(dppf)$_2$Cl$_2$ (0.10 g, 0.14 mmol), and KOAc (1.31 g, 13.35 mmol) in degassed 1, 4-dioxane (50 mL) was stirred at 90 °C for 12 h under nitrogen. The excess 1, 4-dioxane was removed by a rotary evaporator after cooled down, the mixture was washed with water and dichloromethane, and then PPI-3B (1.66 g, yield 75%) can be purified by column chromatography with petroleum ether/dichloromethane. And then 3-Bromobenzoyl chloride (0.6 mL, 4.55 mmol) was dissolved

in 50 mL dichloromethane. Then the benzoyl hydrazide (0.63 g, 4.63 mmol) was dissolved in 20 mL dichloromethane, and 2 mL triethylamine was added. Then the benzoyl hydrazide solution was slowly added dropwise to the dichloromethane system of 2-Bromobenzoyl chloride, and the reaction was carried out at room temperature for 4 h. After the reaction was completed, the mixture was removed by a rotary evaporator, purified by evaporation crystallization with anhydrous ethanol, and finally filtered and dried to obtain the qOXZ-3Br (1.21 g, yield 83%). And then qOXZ-3Br (1 g, 3.13 mmol) was added to 15 mL of $POCl_3$ solvent and the resulting solution was refluxed in a closed system in a nitrogen atmosphere at 85 °C for 20 h. After the reaction was completed, the solution was cooled to room temperature, and then the solution was added dropwise to water to quench $POCl_3$. The mixed solvent was washed with water and dichloromethane. The organic phase was dried and filtered by $MgSO_4$, purified by n-hexane evaporation crystallization, and finally filtered and dried to obtain OXZ-3Br (0.72 g, yield 76%). And then OXZ-3Br (1.00 g, 3.32 mmol), PPI-3B (1.98 g, 3.98 mmol), and K_2CO_3 (0.69 g, 5.00 mmol) were soluble in THF (50 mL) and water (10 mL), and dropped into $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol) at 90 °C for 24 h under N_2. The excess THF was removed by a rotary evaporator after cooled down, the mixture was washed with water and dichloromethane, and then m-PIOXZ (1.70 g, yield 87%) can be purified by column chromatography with dichloromethane. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.90 (dd, J = 8.0, 1.3 Hz, 1H), 8.76 (d, J = 8.4 Hz, 1H), 8.70 (d, J = 8.3 Hz, 1H), 8.22 – 8.13 (m, 3H), 8.09 (dt, J = 6.5, 2.0 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.70 – 7.63 (m, 5H), 7.62 – 7.48 (m, 9H), 7.42 (t, J = 7.8 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.23 (dd, J = 8.4, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 164.74, 150.46, 141.67, 139.81, 138.80, 131.83, 131.25, 130.47, 130.37, 130.10, 129.54, 129.36, 129.20, 129.14, 128.98, 128.34, 128.23, 127.59, 127.34, 127.23, 127.02, 126.35, 125.92, 125.70, 125.49, 125.01, 124.49, 124.15, 123.93, 123.17, 123.04, 122.78, 120.94. MALDI-TOF MS (mass m/z): calcd for C41H26N4O, 590.2107; found, 591.2176 $[M + H]^+$.

Synthesis of 2-(3'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-3-yl)-5-phenyl-1,3,4-oxadiazole (m-CZOXZ):

A mixture of OXZ-3Br (1 g, 3.32 mmol), (3-(9*H*-carbazol-9-yl) phenyl) boronic acid (1.14 g, 3.98 mmol), and K_2CO_3 (0.69 g, 5.00 mmol) were soluble in THF (50 mL) and water (10 mL), and dropped into $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol) at 90 °C for 24 h under N_2. The excess THF was removed by a rotary evaporator after cooled down, the mixture was washed with water and dichloromethane, and then m-CZOXZ (1.28 g, yield 83%) can be purified by column chromatography with dichloromethane. 1H NMR (500 MHz, Chloroform-d) δ 8.16 (ddd, J =

8.1, 6.7, 1.8 Hz, 5H), 7.87 (t, J = 1.9 Hz, 1H), 7.84 – 7.69 (m, 3H), 7.62 (t, J = 7.7 Hz, 2H), 7.57 – 7.40 (m, 7H), 7.35 – 7.28 (m, 2H). 13C NMR (101 MHz, Chloroform-d) δ 141.89, 141.22, 140.86, 138.50, 131.84, 130.59, 130.44, 129.84, 129.12, 127.04, 126.60, 126.28, 126.09, 125.81, 125.56, 124.73, 123.86, 123.50, 120.44, 120.14, 109.77. MALDI-TOF MS (mass m/z): calcd for C32H21N3O, 463.1685; found, 464.1763 $[M + H]^+$.

SI-3 Supporting Figures

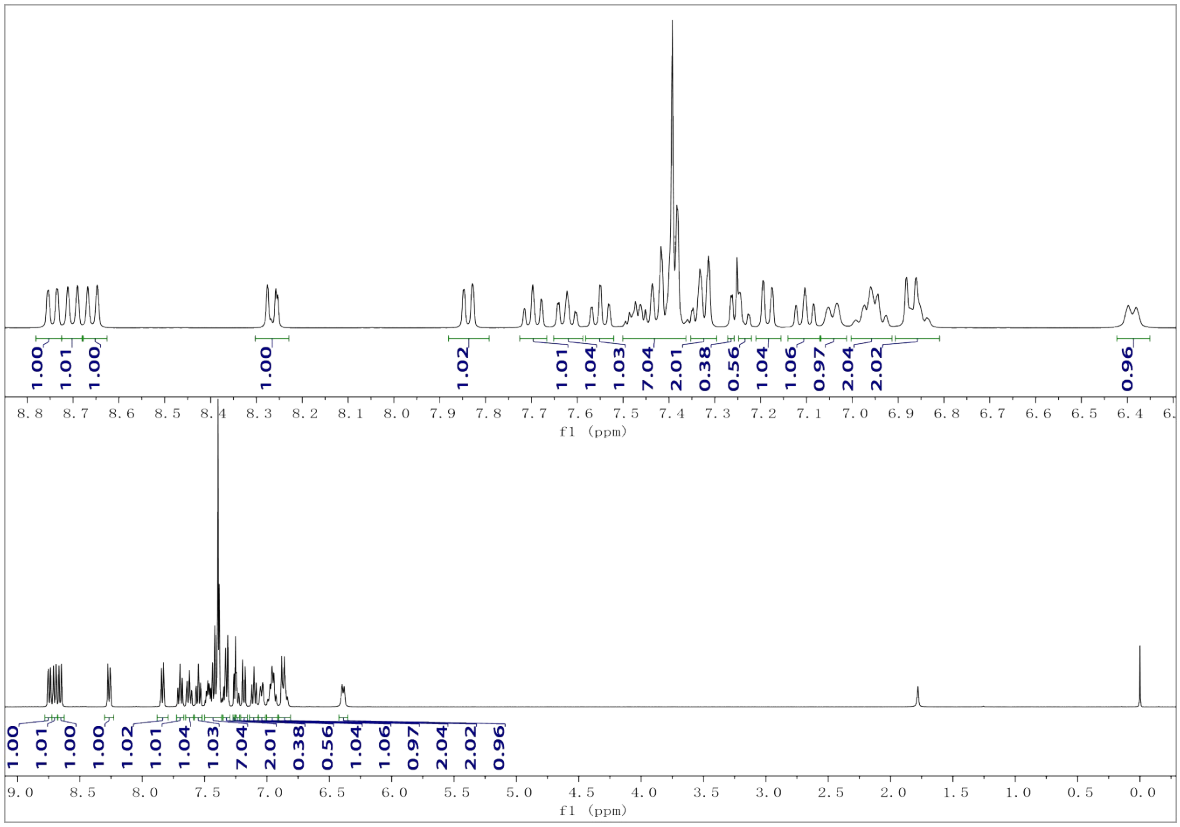


Fig S1. ^{1}H NMR spectrums of o-PIOXZ in $CDCl_3$.

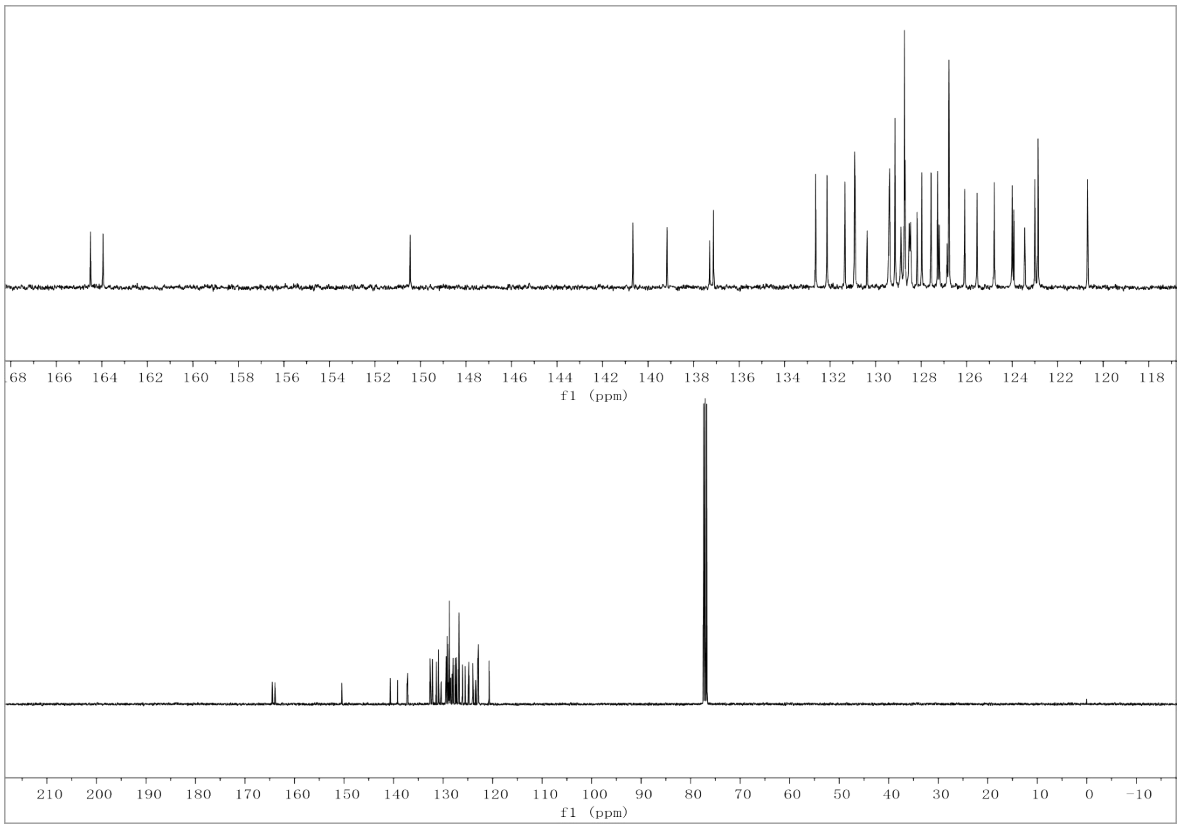


Fig S2. 13C NMR spectrums of o-PIOXZ in $CDCl_3$.

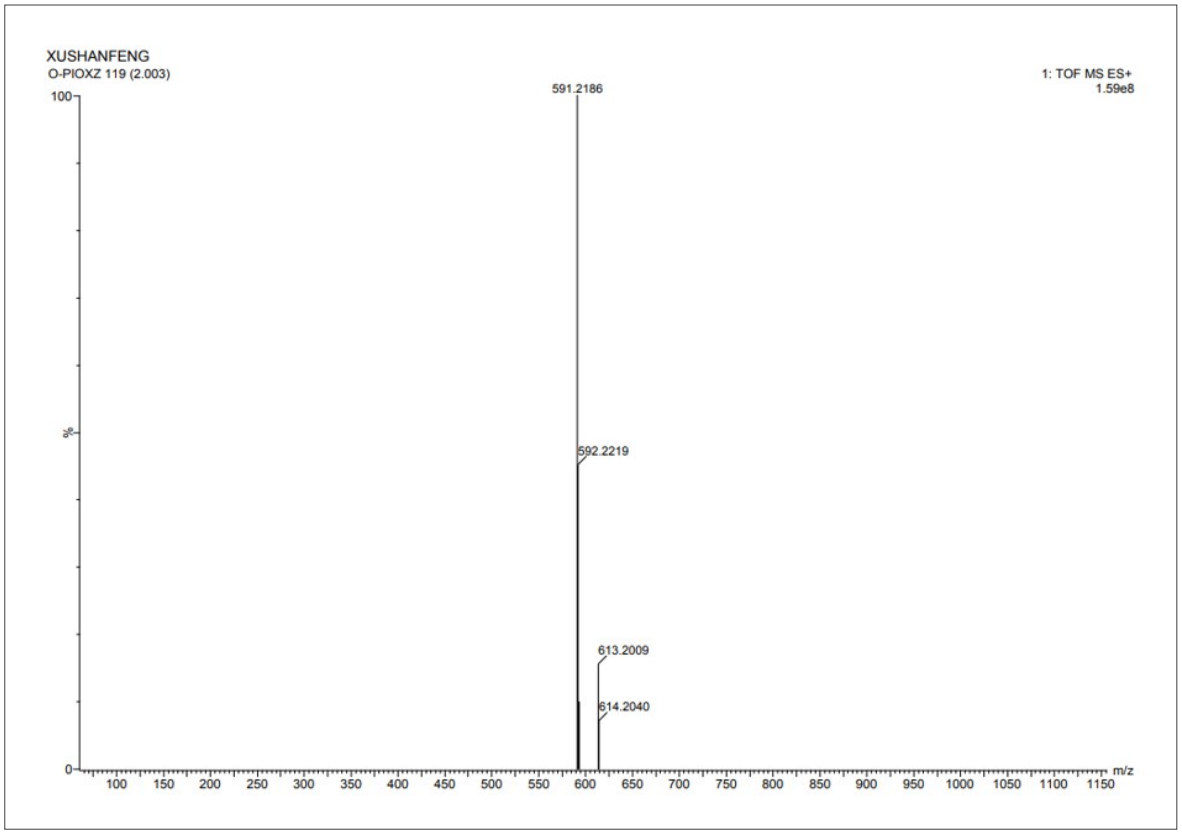


Fig S3. Mass Spectrum $[M + H]^+$ of o-PIXOZ.

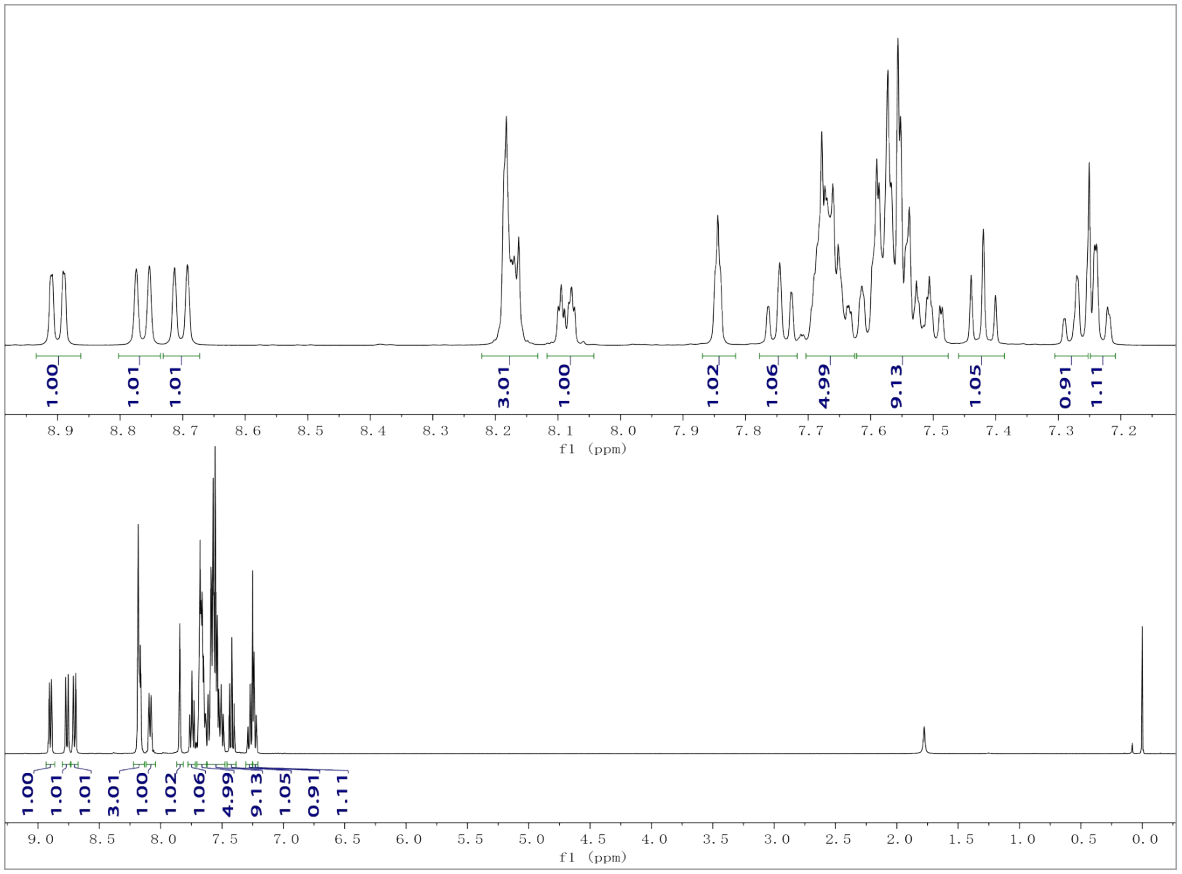


Fig S4. ^1H NMR spectrums of m-PIOXZ in $CDCl_3$.

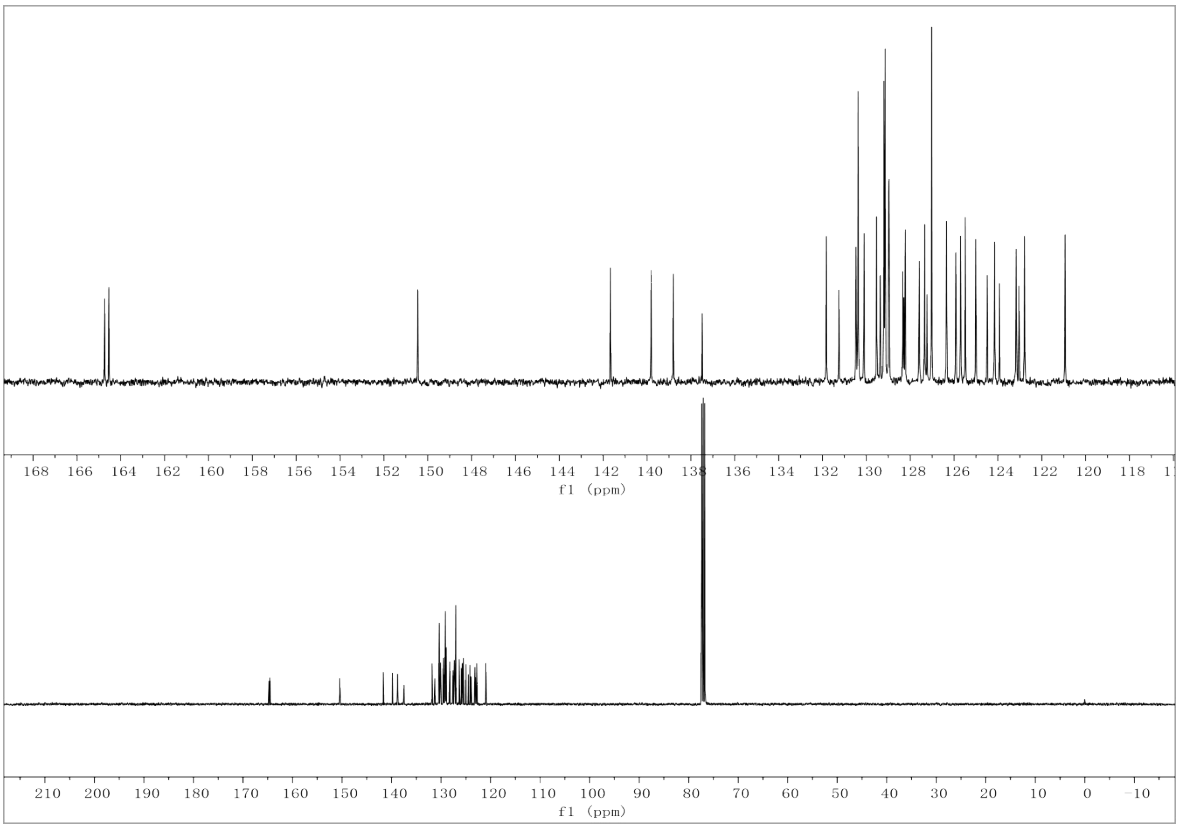


Fig S5. 13C NMR spectrums of m-PIOXZ in $CDCl_3$.

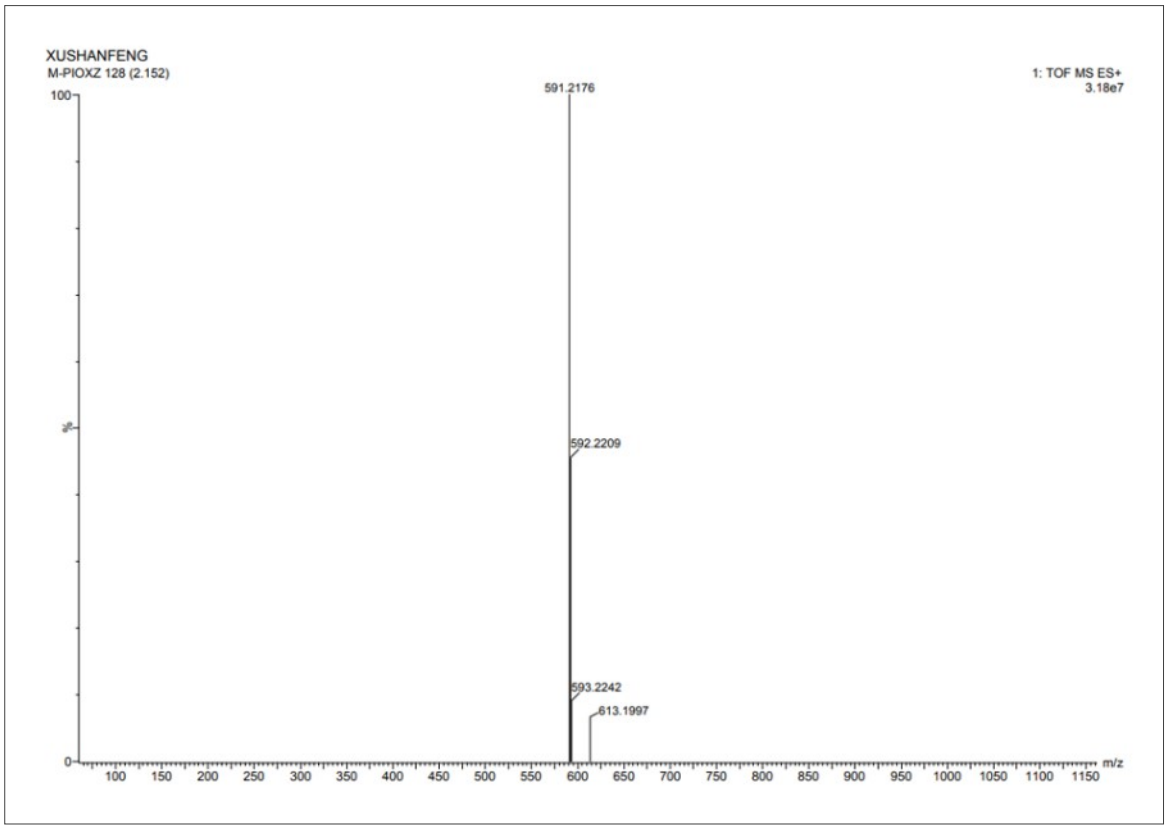


Fig S6. Mass Spectrum $[M + H]^+$ of m-PIXOZ.

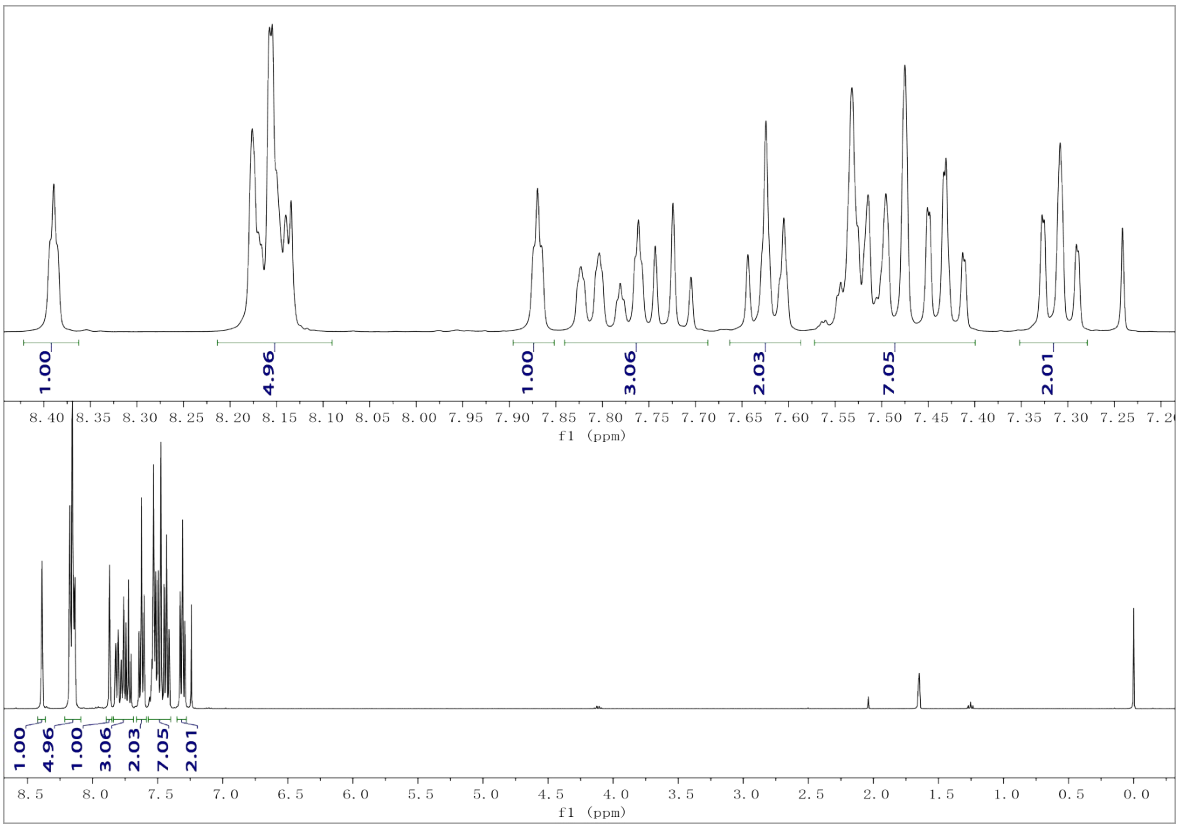


Fig S7. ^{1}H NMR spectrums of m-CZOXZ in $CDCl_3$.

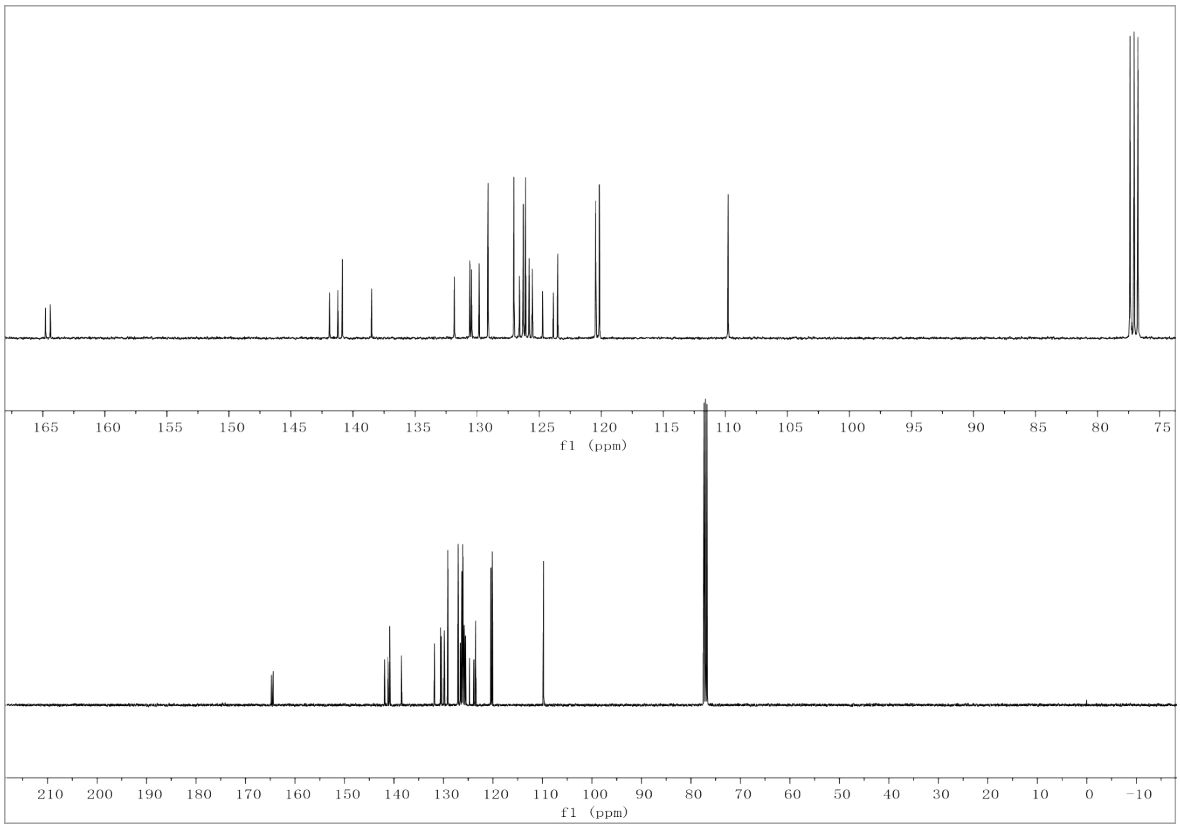


Fig S8. 13C NMR spectrums of m- CZOXZ in $CDCl_3$.

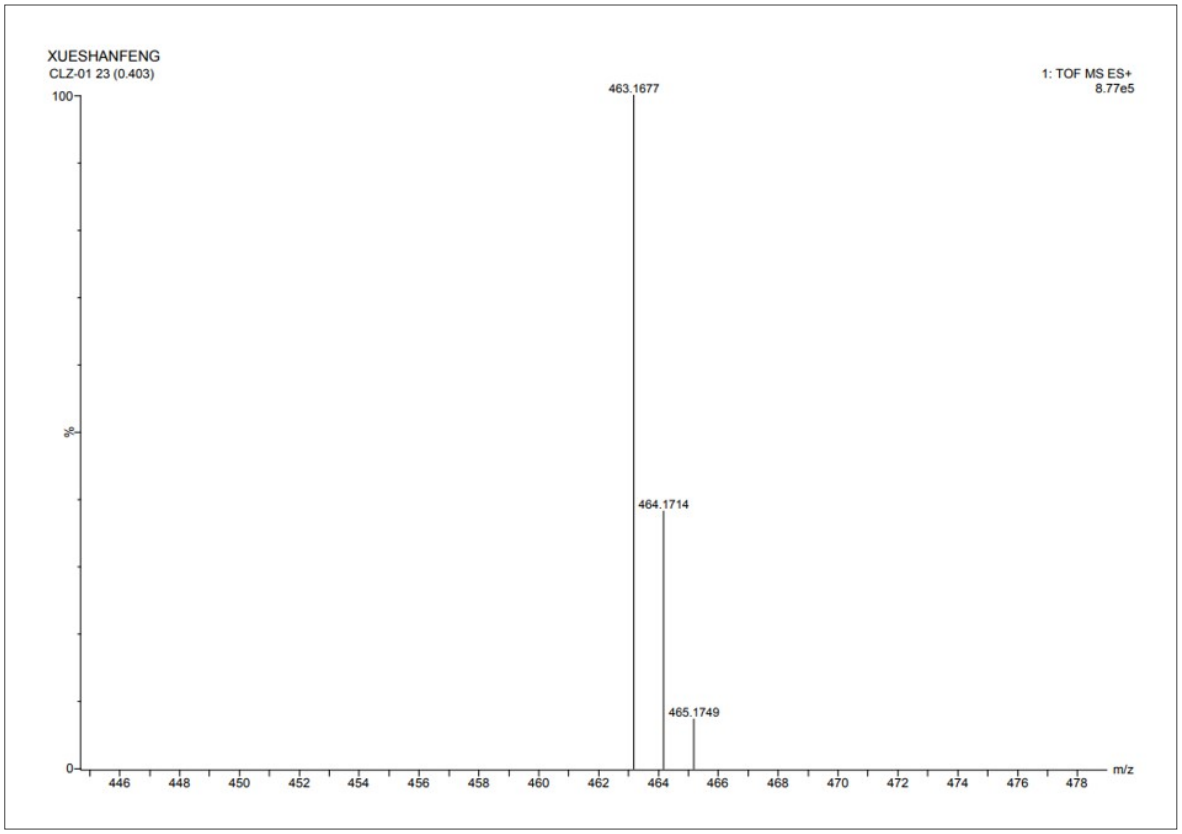


Fig S9. Mass Spectrum $[M + H]^+$ of m- CZOXZ.

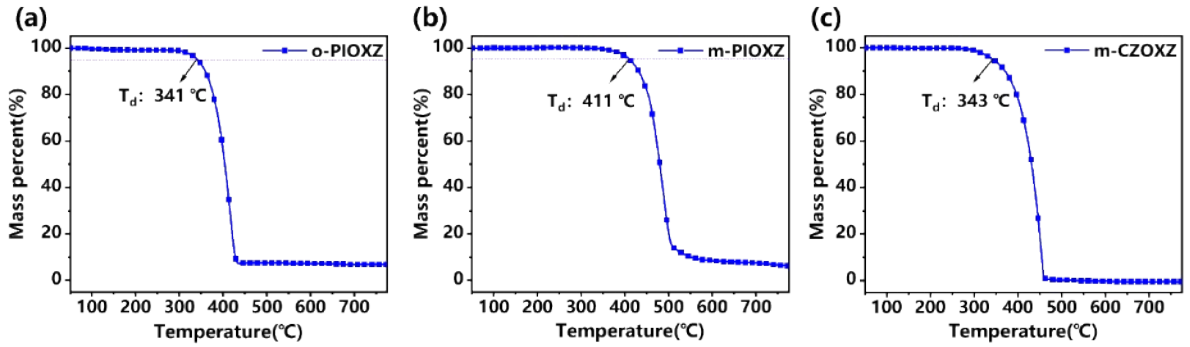


Fig S10. The TGA graphs of a) o-PIOXZ, b) m-PIOXZ, and c) m-CZOXZ.

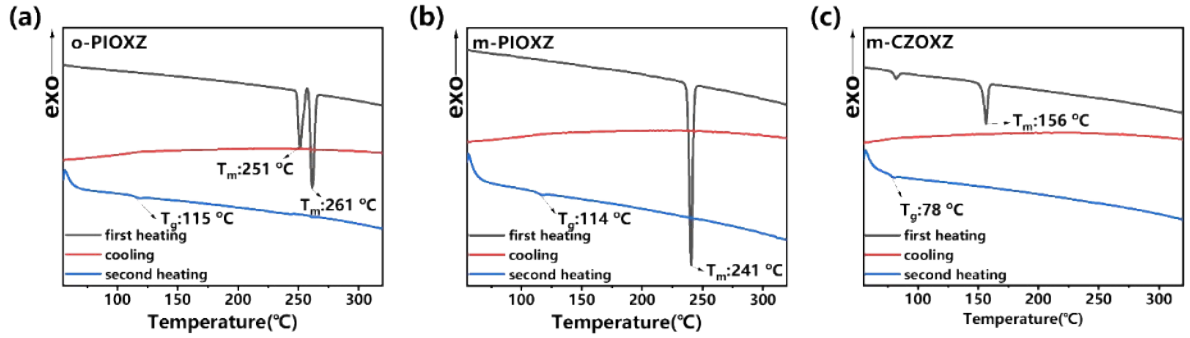


Fig S11. The DSC graphs of a) o-PIOXZ, b) m-PIOXZ, and c) m-CZOXZ.

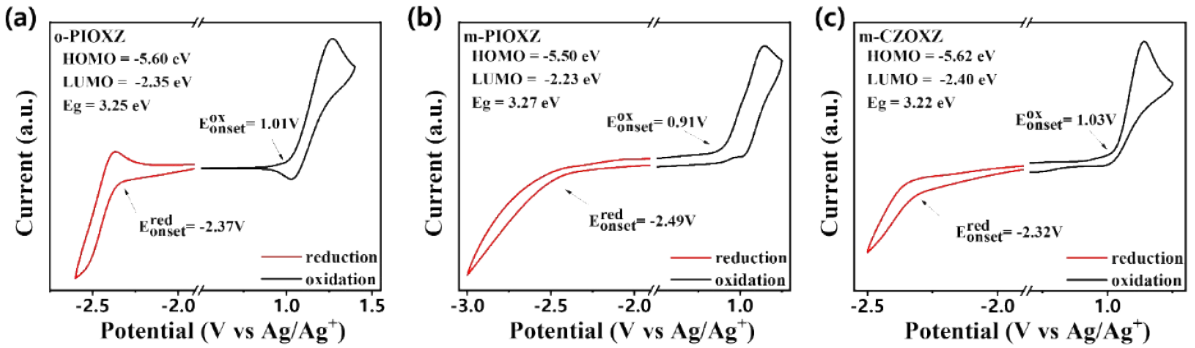


Fig S12. The cyclic voltammetry curve of the a) o-PIOXZ, b) m-PIOXZ, and c) m-CZOXZ in dichloromethane solution (oxidation section) and DMF solution (reduction section).

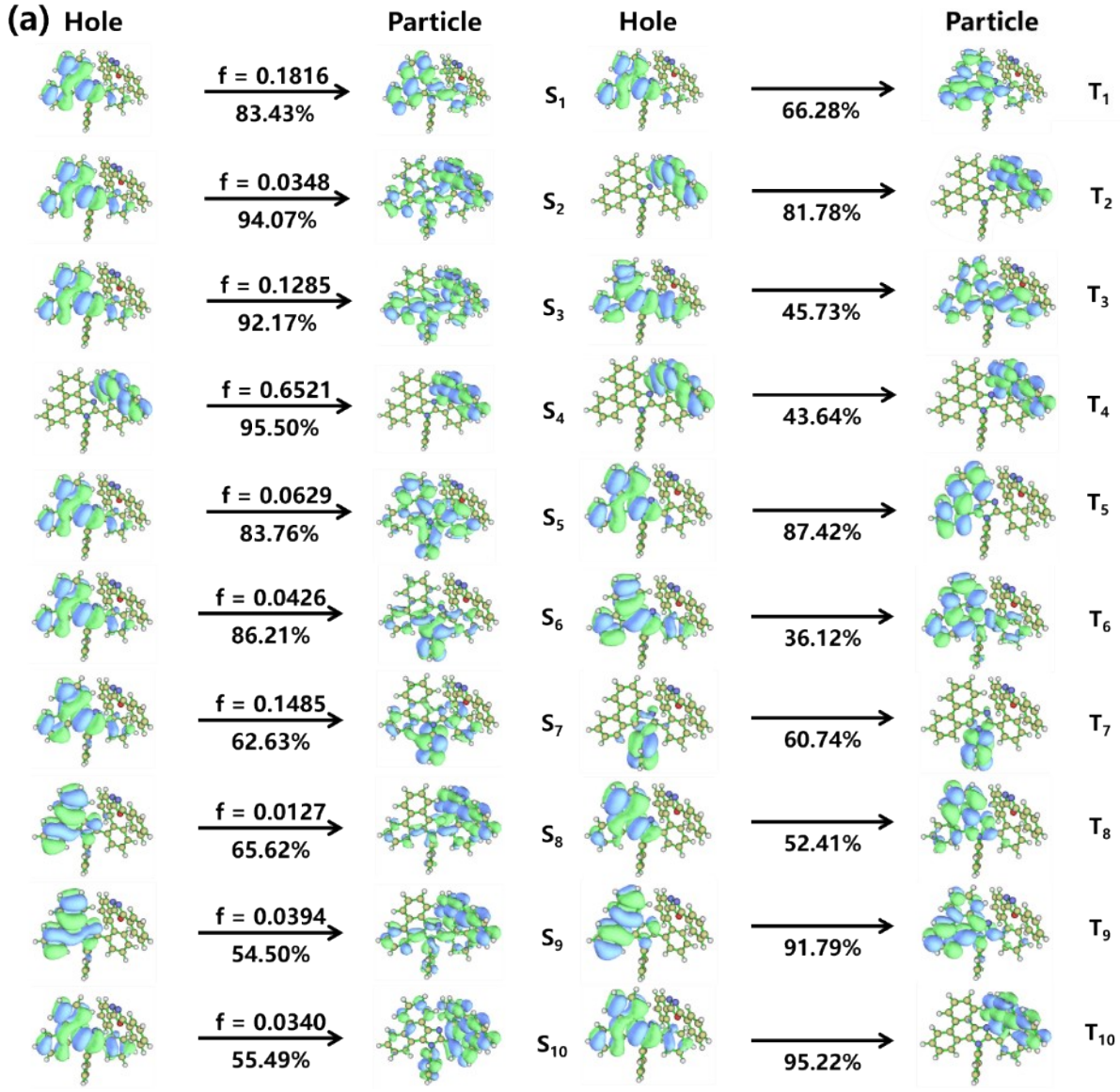


Fig S13. NTOs describing the transition characters of the S_1-S_{10} and T_1-T_{10} states in o-PIOXZ.

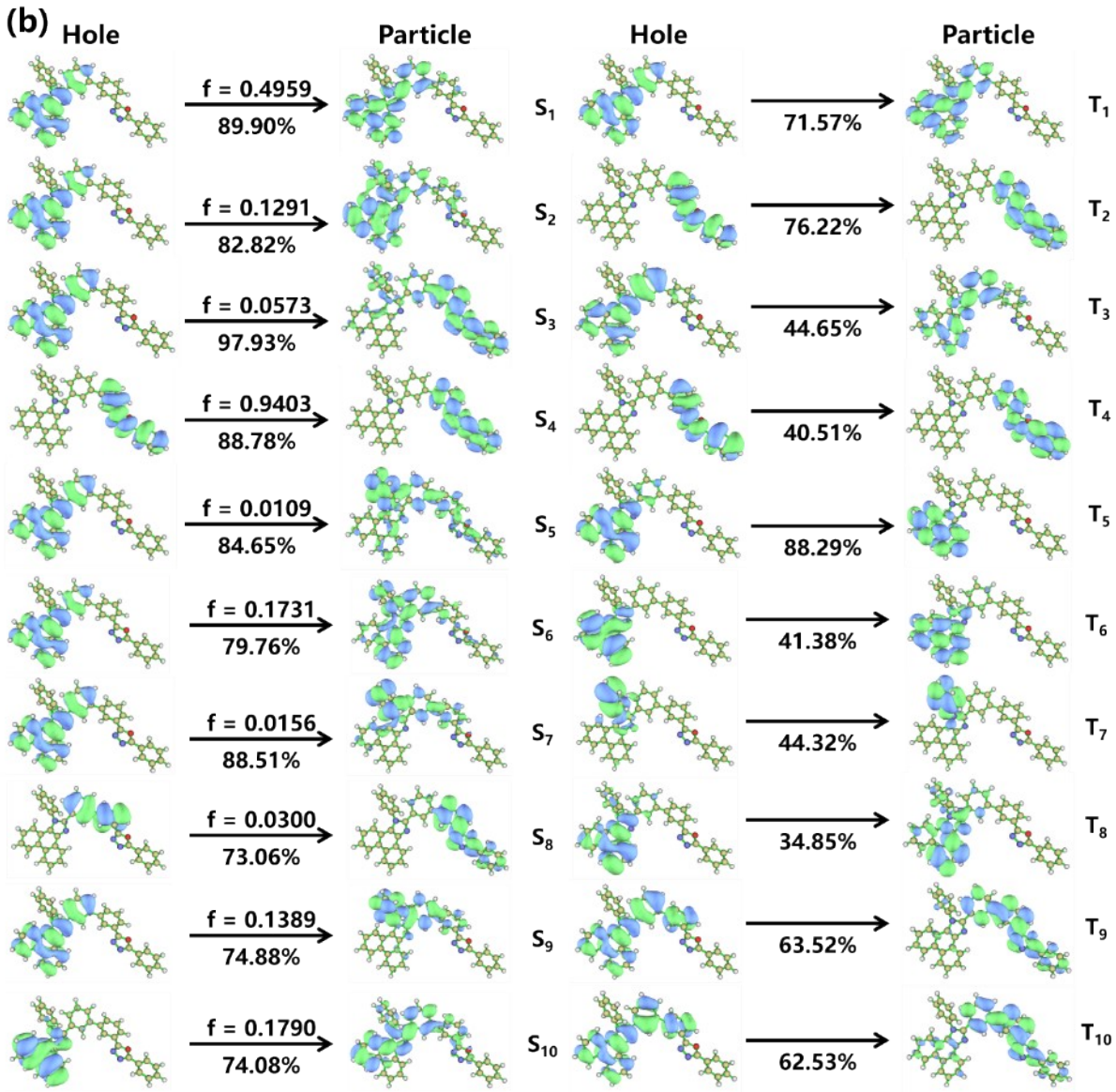


Fig S14. NTOs describing the transition characters of the S_1-S_{10} and T_1-T_{10} states in m-PIOXZ.

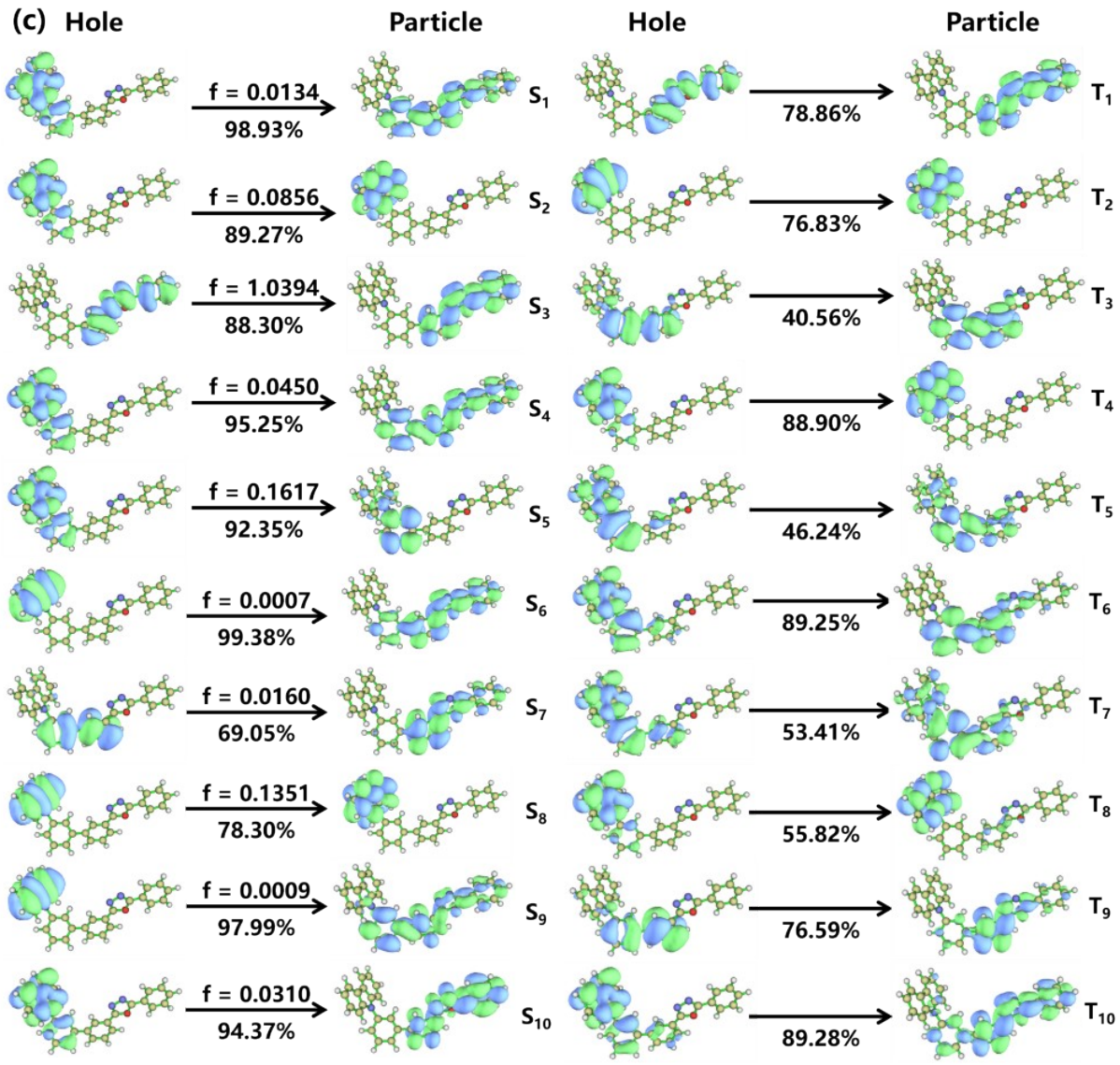


Fig S15. NTOs describing the transition characters of the S_1-S_{10} and T_1-T_{10} states in m-CZOXZ.

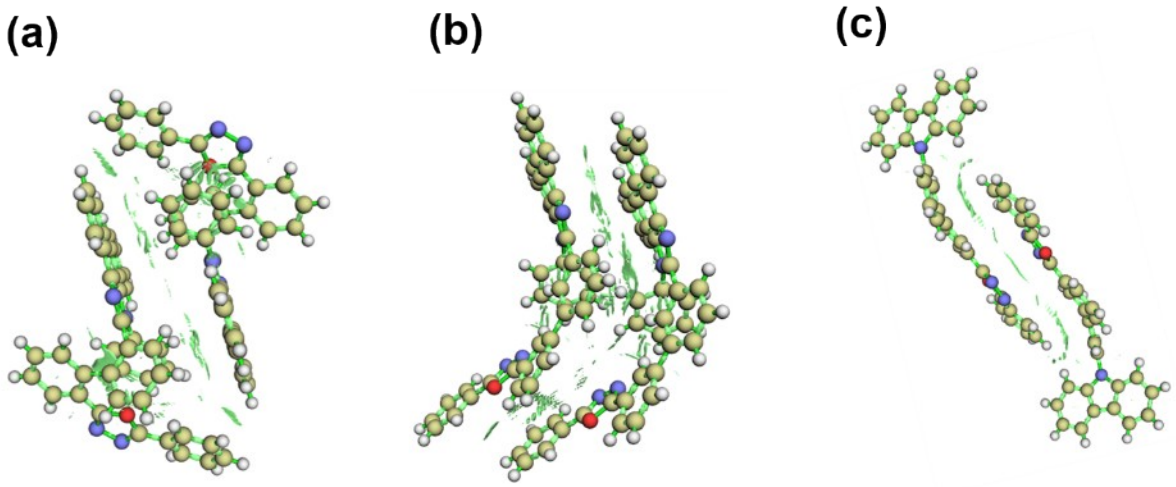


Fig S16. Intramolecular interactions for a) o-PIOXZ, b) m-PIOXZ, and c) m-CZOXZ molecule.

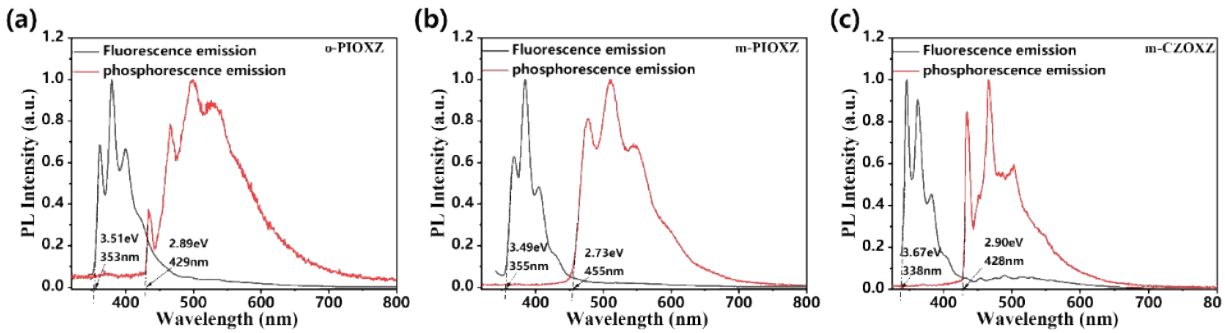


Fig S17. Normalized fluorescence and phosphorescence spectra of a) o-PIOXZ, b) m-PIOXZ, and c) m-CZOXZ in toluene solution (10^{-5} M) at 77 K.

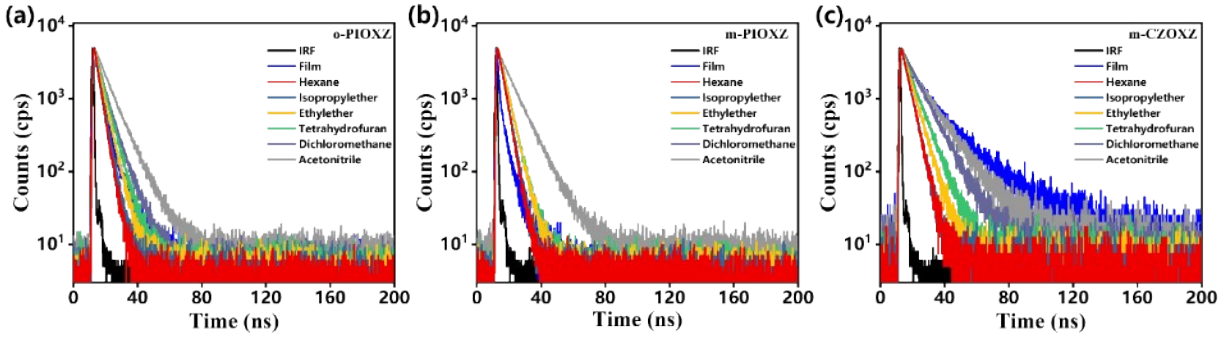


Fig S18. Transient PL spectra of a) o-PIOXZ, b) m-PIOXZ, and c) m-CZOXZ.

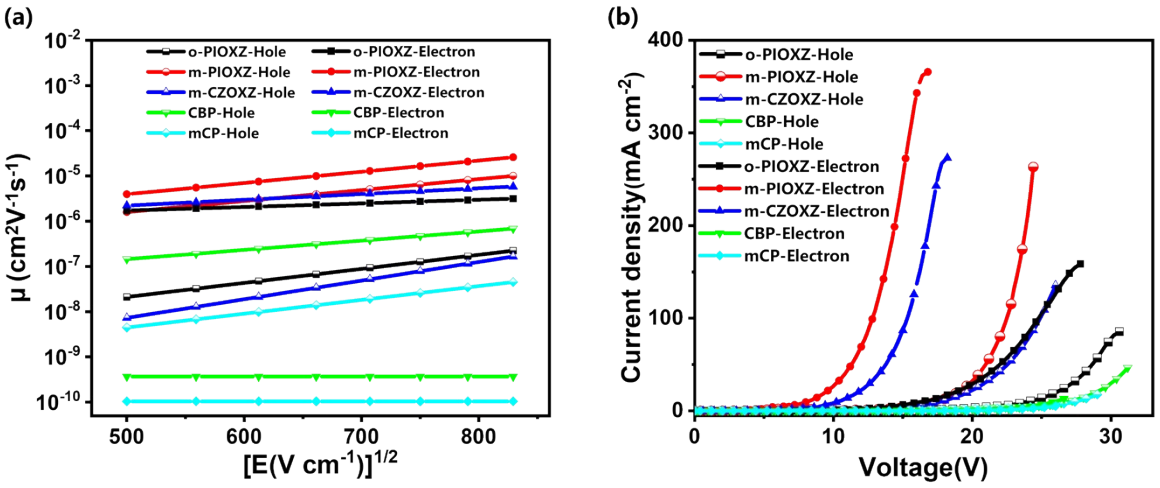


Fig 19. a) Electron field intensity-mobility curves and b) current density–voltage curves of m-PIOXZ, o-PIOXZ, m-CZOXZ, CBP, and mCP.

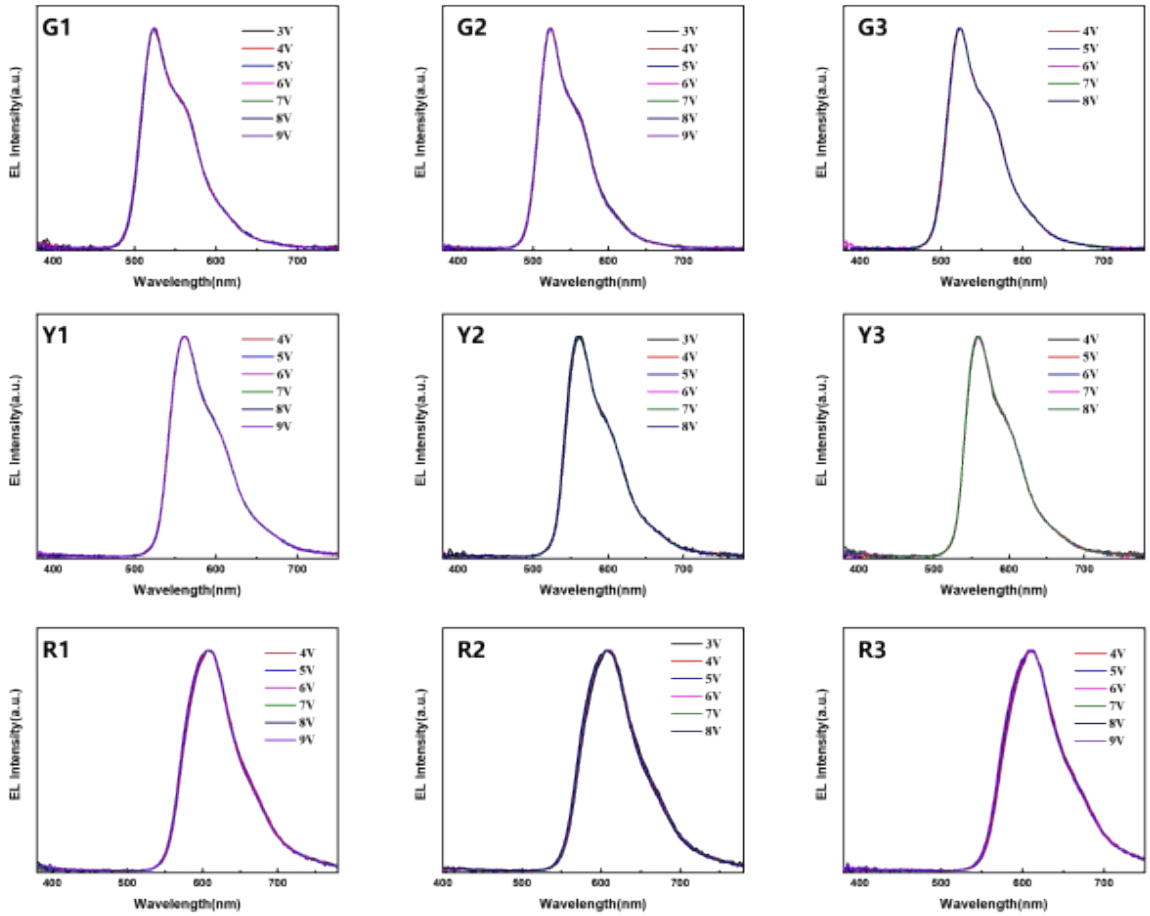


Fig S20. Normalized EL spectra at different voltages.

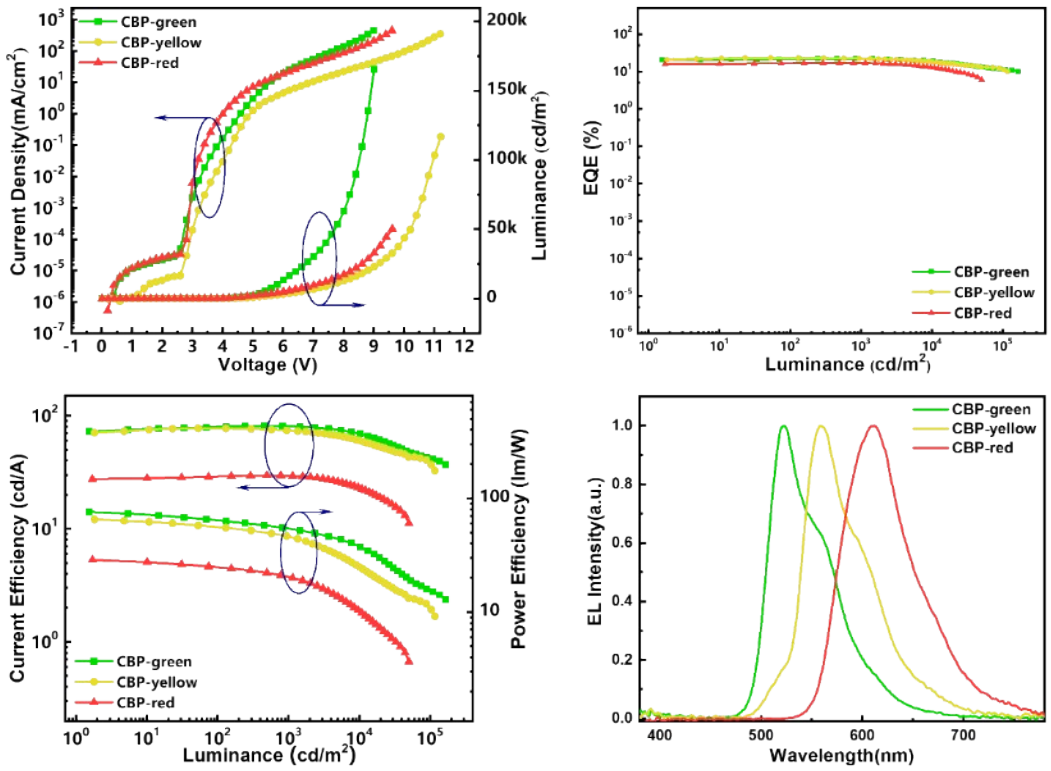


Fig S21. a) Current density-voltage-luminance curves; b) EQE-luminance curves; c) Current efficiency-luminance-power efficiency curves; d) The EL spectrum at EQE_{max}. Green, Red, Yellow are manufactured with CBP as the host.

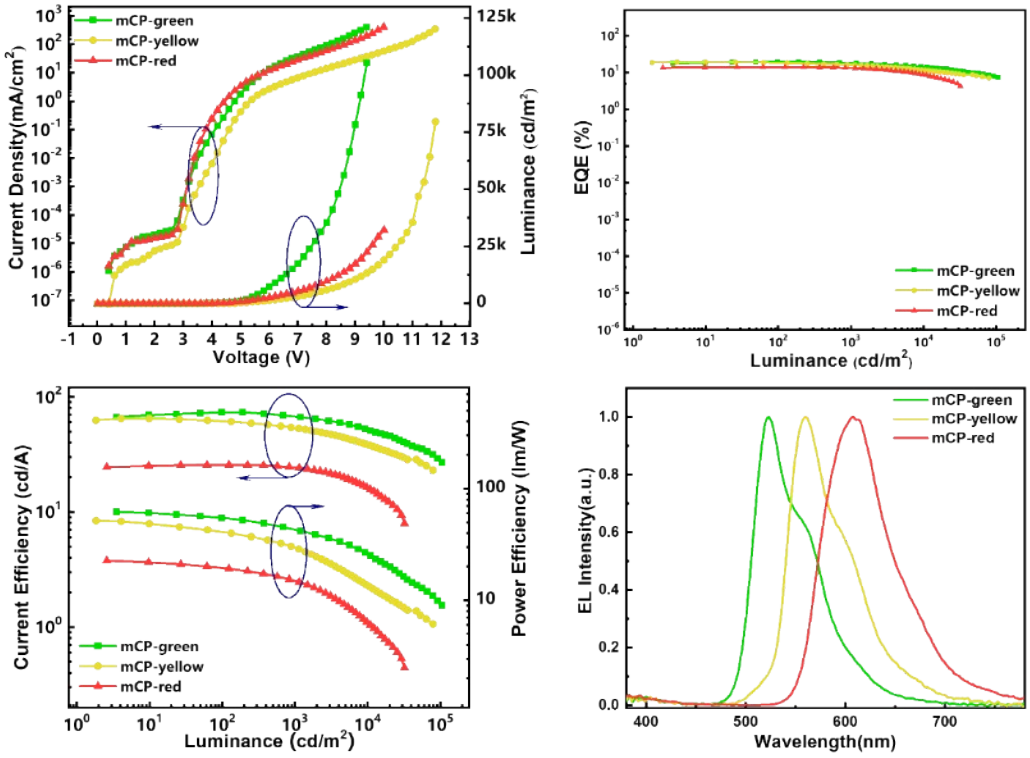


Fig S22. a) Current density-voltage-luminance curves; b) EQE-luminance curves; c) Current efficiency-luminance-power efficiency curves; d) The EL spectrum at EQE_{max}. Green, Red, Yellow are manufactured with mCP as the host.

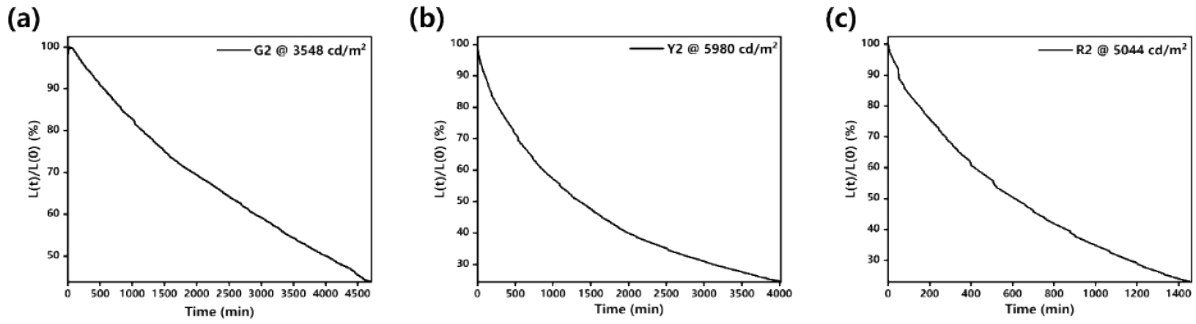


Fig S23. Luminance decay curves of device G2 at 3548 cd/m², device Y2 at 5980 cd/m², and device R2 at 5044 cd/m².

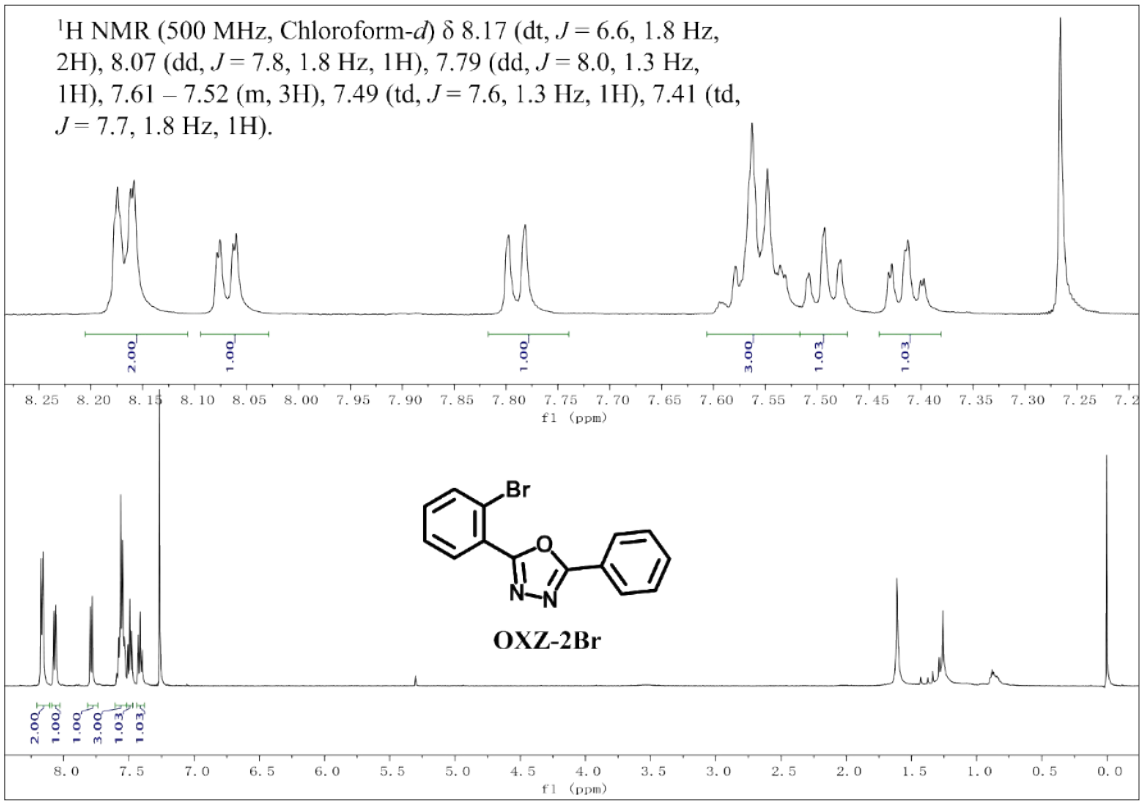


Fig S24. ^{1}H NMR spectrums of OXZ-2Br in $CDCl_3$.

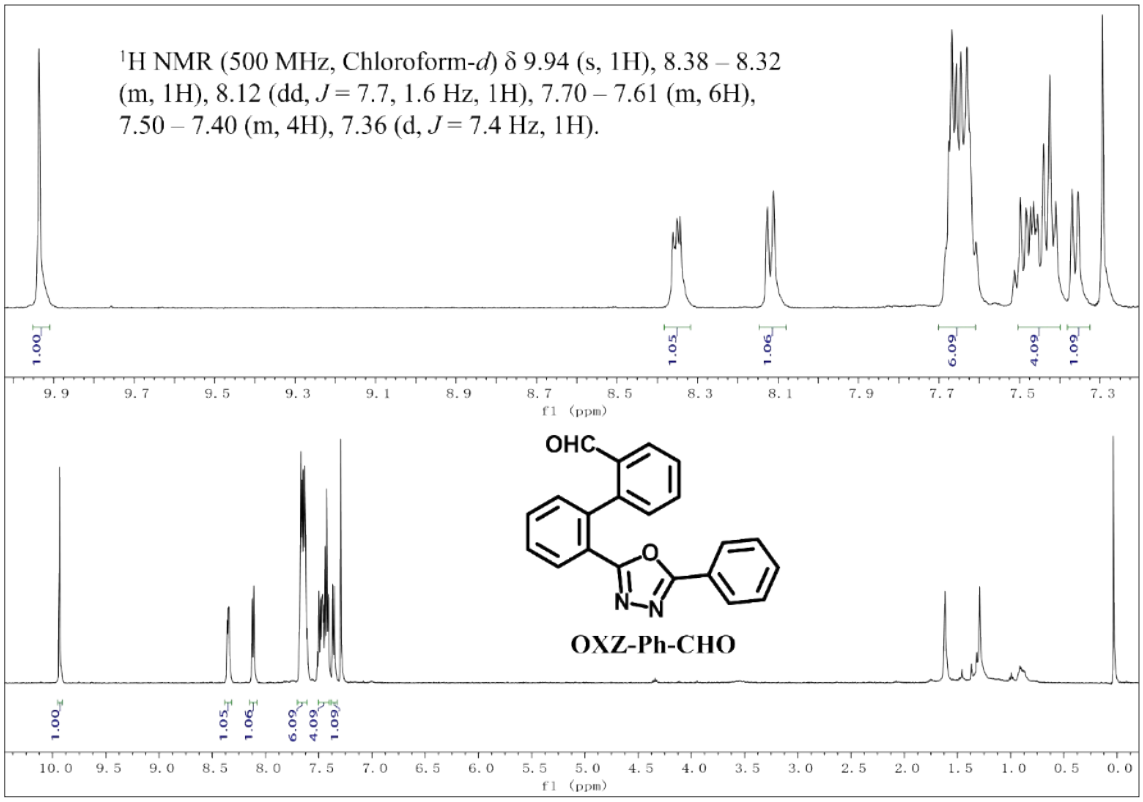


Fig S25. ^{1}H NMR spectrums of OXZ-Ph-CHO in $CDCl_3$.

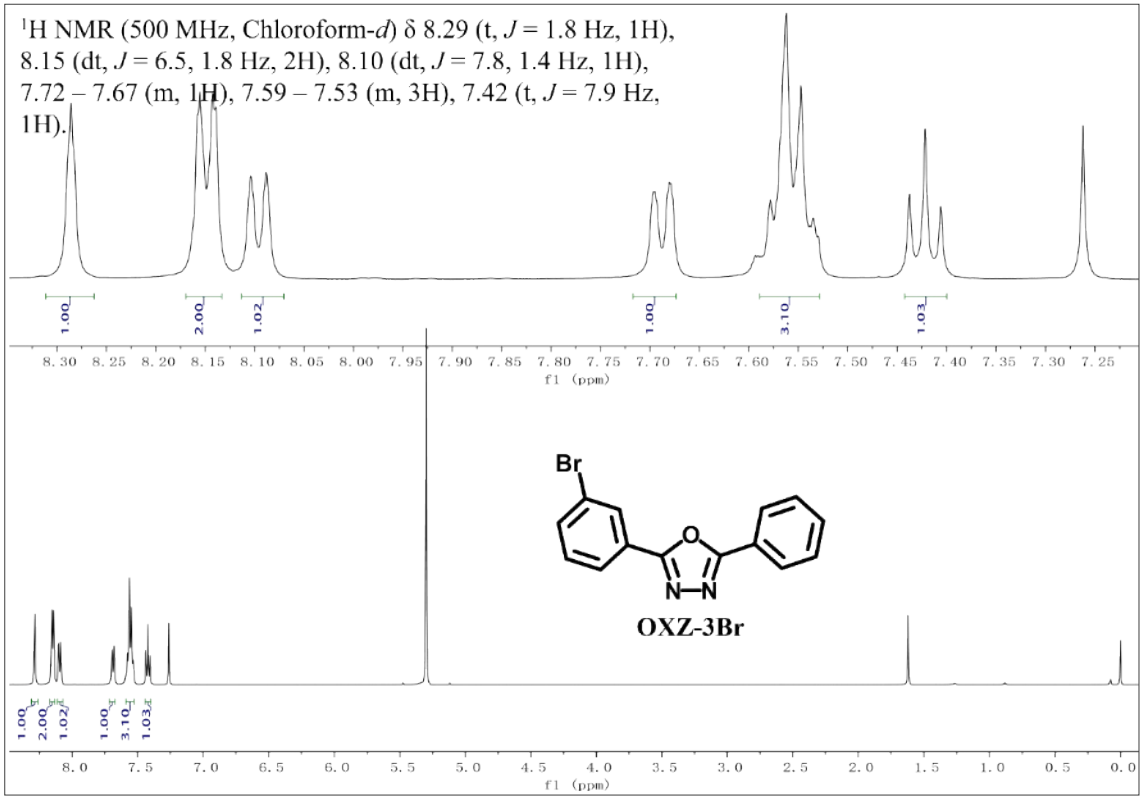


Fig S26. ^{1}H NMR spectrums of OXZ-3Br in $CDCl_3$.

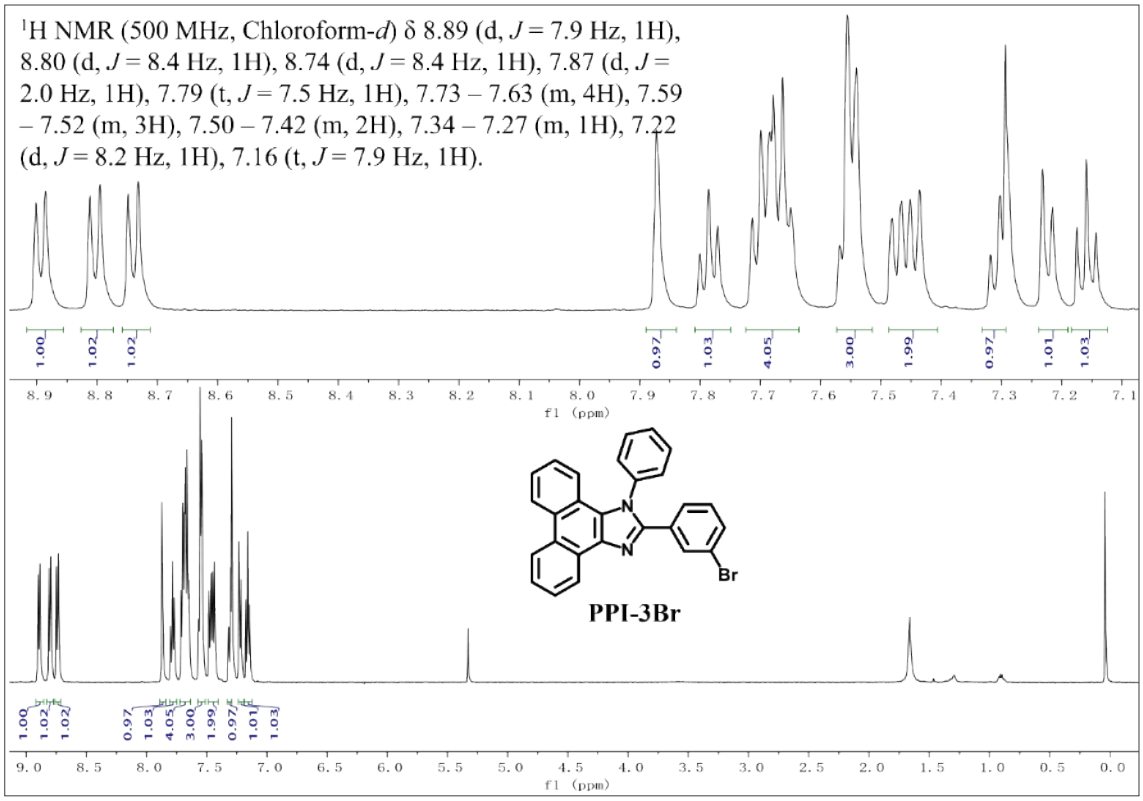


Fig S27. ^{1}H NMR spectrums of PPI-3Br in $CDCl_3$.

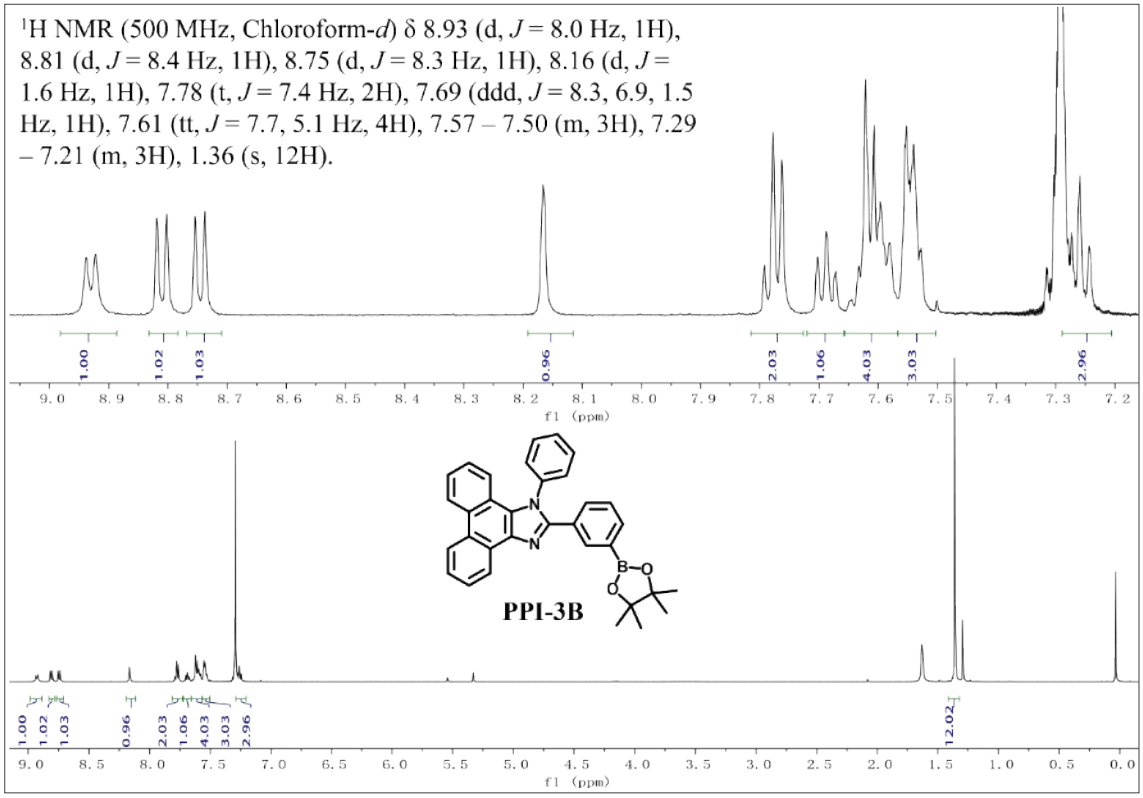


Fig S28. ^{1}H NMR spectrums of PPI-3B in $CDCl_3$.

SI-4 Supporting Tables

Table S1. The lifetime of G2, Y2, and R2 doped devices.

Devices	LT_{50} [h]	LT_{50} (@ 1000 cd/m²) [h]
G2 (@ 3548 cd/m²)	67.75	583
Y2 (@ 5980 cd/m²)	20.92	437
R2 (@ 5044 cd/m²)	9.95	156

Table S2. EL performance of PhOLEDs based on CBP and mCP hosts.

Devices [a)]	V_{on} [V]	L_{max} [cd/m²]	CE_{max} [cd/A⁻¹]	PE_{max} [lm/W]	EQE_{max} [%]	$EQE_{roll\text{-}off}$ [%]	λ_{EL} [nm]	CIE (x,y)
G-C	3.0	165459	81.22	75.94	21.99	0.70	522	(0.31,0.63)
G-m	3.4	105288	73.30	61.76	19.72	7.79	523	(0.31,0.63)
Y-C	3.4	116865	77.26	65.25	23.13	4.35	559	(0.47,0.51)
Y-m	3.8	79645	64.86	51.64	19.44	16.91	560	(0.47,0.51)
R-C	3.0	50345	29.58	28.69	16.74	0.86	612	(0.61,0.38)
R-m	3.4	32173	25.64	22.64	14.00	5.27	607	(0.60,0.39)

[a)] CBP and mCP are the host materials for G-C and G-m, R-C and R-m, and Y-C and Y-m devices, respectively.

Table S3. Crystal data for o-PIOXZ and m-PIOXZ.

Compound	o-PIOXZ	m-PIOXZ	m-CZOXZ
Chemical formula	$C_{41}H_{26}N_4O$	$C_{41}H_{26}N_4O$	$C_{32}H_{21}N_3O$
Formula weight	590.66	590.66	463.52
Crystal system	Triclinic	Triclinic	monoclinic
a/Å	10.3270(13)	5.5050(1)	53.653(3)
b/Å	11.0712(14)	19.8183(3)	9.1100(6)
c/Å	13.0992(17)	27.3727(4)	11.0235(7)
α/°	93.047(2)	90	90
β/°	92.234(2)	95.443(1)	95.524(3)
γ/°	102.161(2)	90	90
Unit cell volume/ Å3	1460.1(3)	2972.89(8)	5363.0(6)
Temperature/K	100	298	303
Space group	P -1	P 21/n	C 2/c
Z	2	4	8
Density (calculated) /g cm^{-3}	1.344	1.320	1.148
F(000)	616.0	1232.0	1936.0
Index ranges	-12 =< h =< 12 -13 =< k =< 10 -15 =< l =< 15	-6 =< h =< 6 -23 =< k =< 23 -32 =< l =< 32	-63 =< h =< 63 -10 =< k =< 10 -13 =< l =< 13
Reflections measured	5147	5503	4736
Completeness to theta = 72.13°	99.1%	99.4%	99.6%
Min. and max. transmission	0.6514 and 0.7456	0.4868 and 0.7531	0.4868 and 0.7531
Data / restraints / parameters	5101/0/416	5471/0/415	4718/0/325
Goodness-of-fit on F^2	0.955	1.047	1.047
Final R_1 values ($I > 2\sigma(I)$)	0.0355	0.1050	0.0759
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0960	0.0390	0.1942
Final R_1 values (all data)	0.0471	0.1050	0.0921
Final $wR(F^2)$ values (all data)	0.0981	0.0480	1.047
CCDC number	2410469	2410470	2413461