

## Supporting Information

### Carbazole derivatives as electron transport and n-type acceptor materials for efficient organic light-emitting devices

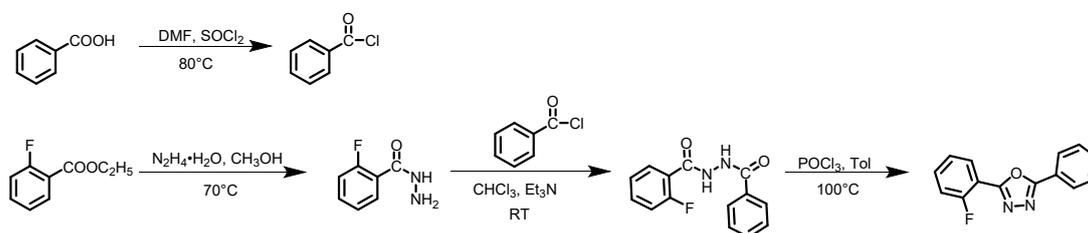
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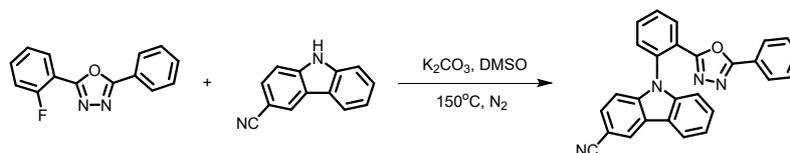
#### 1. Experimental section

##### 1.1 The synthetic routes of *o*-FOXD.



**Scheme S1.** The synthetic routes of *o*-FOXD. [1]

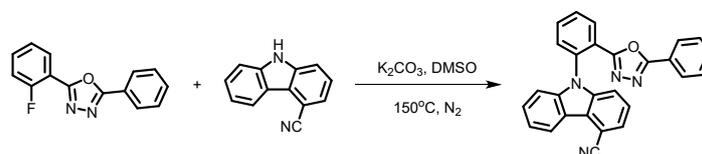
##### 1.2. The synthetic route of 3CNCzOXD and 4CNCzOXD.



**Scheme S2.** The synthetic routes of 3CNCzOXD.

A mixture of *o*-FOXD (0.50 g, 2.08 mmol), (9*H*)-carbazole-3-carbonitrile (0.48 g, 2.50 mmol) and  $K_2CO_3$  (1.44 g, 10.41 mmol) in dimethyl sulfoxide (DMSO) (5 mL) was stirred at 150°C for 24 h under an  $N_2$  atmosphere. After cooling to room temperature, the mixture was poured into water, filtered, and then purified by column chromatography over silica gel with dichloromethane/petroleum ether as the eluent to afford a white solid (Yield: 75%).  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (TMS, ppm) 8.90 (s, 1H), 8.49 (d,  $J = 6.6$  Hz, 1H), 8.40 (d,  $J = 9.0$  Hz, 1H), 8.01 (t,  $J = 7.8$  Hz, 1H), 7.97 – 7.92 (m, 1H), 7.89 (d,  $J = 6.6$  Hz, 1H), 7.74 (d,  $J = 6.2$  Hz, 1H), 7.52 (t,  $J = 7.8$  Hz, 1H), 7.48 – 7.43 (m, 1H), 7.38 (t,  $J = 7.0$  Hz, 3H), 7.22 – 7.16 (m, 3H), 7.10 (d,  $J = 8.2$  Hz, 1H);  $^{13}C$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  ppm: 164.21, 162.12, 143.43, 142.39, 134.62, 133.92, 132.70, 131.77, 131.40, 131.14, 130.11, 129.68, 128.36, 126.56, 126.35, 123.73, 123.05, 122.89, 122.39, 121.81, 121.75, 120.61, 111.13, 110.43, 102.35.; GC/MS ( $m/z$ ): calcd. for  $C_{27}H_{16}N_4O$ : 412.5; found: 412.1. Anal. calcd. for  $C_{27}H_{16}N_4$ : C 78.63, H 3.91, N 13.58%; found: C 78.56, H 3.88, N 13.67%.

##### 1.3. The synthetic route of 4CNCzOXD.



**Scheme S3.** The synthetic routes of 4CNCzOXD.

A mixture of *o*-FOX (0.50 g, 2.08 mmol), (9*H*)-carbazole-4-carbonitrile (0.48 g, 2.50 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.44 g, 10.41 mmol) in dimethyl sulfoxide (DMSO) (5 mL) was stirred at 150°C for 24 h under an N<sub>2</sub> atmosphere. After cooling to room temperature, the mixture was poured into water, filtered, and then purified by column chromatography over silica gel with dichloromethane/petroleum ether as the eluent to afford a white solid (Yield: 80%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ (TMS, ppm) 8.50 (t, *J* = 7.6 Hz, 2H), 8.05 – 8.00 (m, 1H), 7.94 (dd, *J*<sub>1</sub> = 13.8, *J*<sub>2</sub> = 6.2 Hz, 2H), 7.78 (d, *J* = 7.4 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.46 – 7.36 (m, 4H), 7.17 – 7.13 (m, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ ppm: 164.14, 162.11, 142.35, 141.47, 134.64, 133.88, 132.75, 131.94, 131.40, 131.15, 129.64, 128.95, 127.13, 126.48, 125.73, 123.09, 123.01, 122.85, 121.66, 121.09, 120.79, 118.93, 115.36, 110.69, 103.12. GC/MS (*m/z*): calcd. for C<sub>27</sub>H<sub>16</sub>N<sub>4</sub>O: 412.5; found: 412.1. Anal. calcd. for C<sub>27</sub>H<sub>16</sub>N<sub>4</sub>: C 78.63, H 3.91, N 13.58%; found: C 78.69, H 3.95, N 13.72%.

## 2. General procedures.

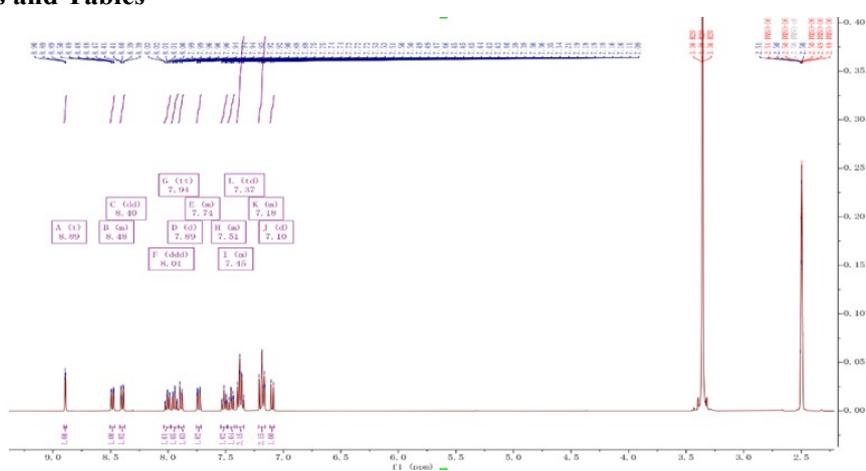
<sup>1</sup>H NMR spectra were recorded on a Bruker DMX-400 spectrometer in deuteriochloroform using tetramethylsilane (TMS; δ = 0 ppm) as an internal standard. Mass spectra were recorded using a Gas chromatography-mass spectrometry, GC/MS. Elemental analyses (EA) of C, H, N, and S were performed on a Vario EL III microanalyzer. Absorption spectra: Ultraviolet-visible (UV-Vis) absorption spectra of solution in dichloromethane and thin film on a quartz substrate were measured using Shimadzu UV-1780 recording spectrophotometer, and the photoluminescence (PL) spectra were recorded using a Hitachi F-7100 fluorescence spectrophotometer. Thermal gravimetric analysis (TGA) was undertaken with a METTLER TOLEDO TGA2 instrument. The thermal stability of the samples was determined by measuring their weight loss at a heating rate of 10°C min<sup>-1</sup> from 25 to 500°C using 3 mg sample under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit within the temperature range of 50 to 350°C, heating at a rate of 10°C min<sup>-1</sup> under N<sub>2</sub> atmosphere. Cyclic voltammetry (CV): The electrochemical cyclic voltammetry was conducted on a CHI voltammetric analyzer, in a 0.1 mol L<sup>-1</sup> acetonitrile solution of tetrabutylammonium hexafluorophosphate (n-Bu<sub>4</sub>NPF<sub>6</sub>) at a potential scan rate of 100 mV s<sup>-1</sup>. The conventional three electrode configuration consists of a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl wire pseudo-reference electrode. The polymer sample was coated on the platinum sheet of working electrode. The reference electrode was checked versus ferrocenium-ferrocene (Fc<sup>+</sup>/Fc) as internal standard as recommended by IUPAC (the vacuum energy level: -4.8 eV). All the solutions were deaerated by bubbling nitrogen gas for a few minutes prior to the electrochemical measurements. HOMO energy levels were calculated from the equation of  $E_{\text{HOMO}} = -(E_{\text{onset}}(\text{ox}) + 4.8)$  eV, and LUMO energy levels were deduced from the optical band gap ( $E_g$ ) values and HOMO levels.

## 3. OLED fabrication and measurements

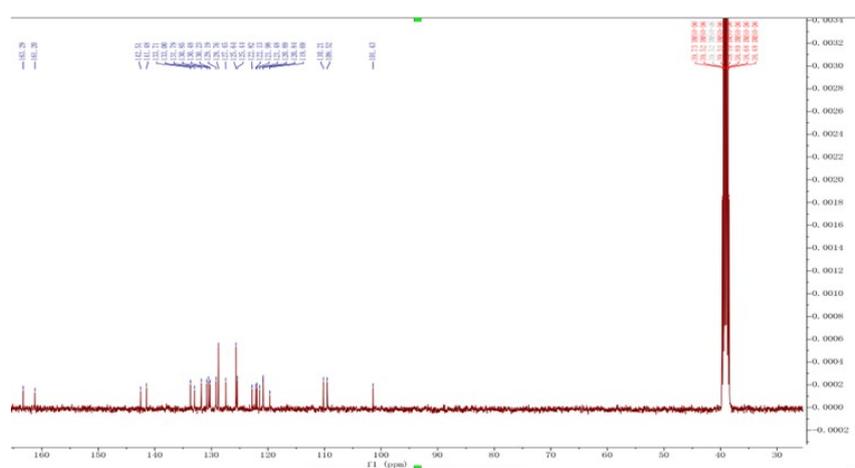
The electroluminescent devices were fabricated by vacuum deposition technology, and all functional layers were fabricated on pre-treated indium tin oxide (ITO) substrates. ITO glass substrates were successively cleaned by ultrasonic wave with detergent, alcohol, acetone and deionized water, then dried at 120°C in a vacuum oven for more than 60 min. Then the organic layers and electrodes were sequentially deposited. Electron-only devices (EOD) were fabricated with the configuration of Al (100 nm)/Liq (1 nm)/ETL (100 nm)/Liq (1 nm)/Al (100 nm). The device structure for ETMs were fabricated as ITO/HAT-CN (3 nm)/TAPC (40 nm)/TCTA (5 nm)/CBP (5 nm)/ CBP:(ppy)<sub>2</sub>Ir(acac) (15 nm)/ETL (40-70 nm)/Liq (1 nm)/Al (100 nm), and the

device structure for n-type acceptor in exciplex hosts were ITO/HAT-CN (3 nm)/TAPC (40 nm)/EML (45:45:10 wt%, 100 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm). In green phosphorescent devices, 3 nm of dipyrazino[2,3-*f*:2',3'-*h*]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HAT-CN) was deposited on ITO substrates as hole injection layer, followed by 40 nm of 4,4'-cyclohexylidenebis[*N,N*-bis(4-methylphenyl)aniline] (TAPC), 5 nm *N,N,N*-tris[4-(9-carbazolyl)phenyl]amine (TCTA), 5 nm of CBP as hole transporting layer. The thickness for electron transporting layer was optimized from 40 to 70 nm. Meanwhile, the 1 nm of Liq and hundred-nanometer of Al were considered as the cathode layers. Current density-voltage-luminance (*J-V-L*) characteristics were tested through using a Keithley source measurement unit (Keithley 2400 and Keithley 2000) and a calibrated silicon photodiode. In addition, the EL spectra were measured by a Spectra scan PR650 spectrophotometer. It should be noted that the measurements were carried out at room temperature under ambient condition.

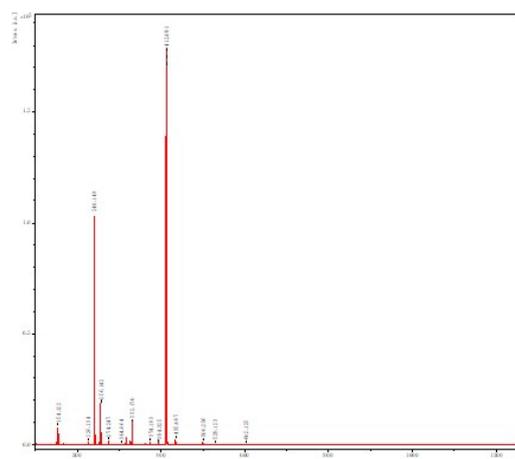
#### 4. Figures and Tables



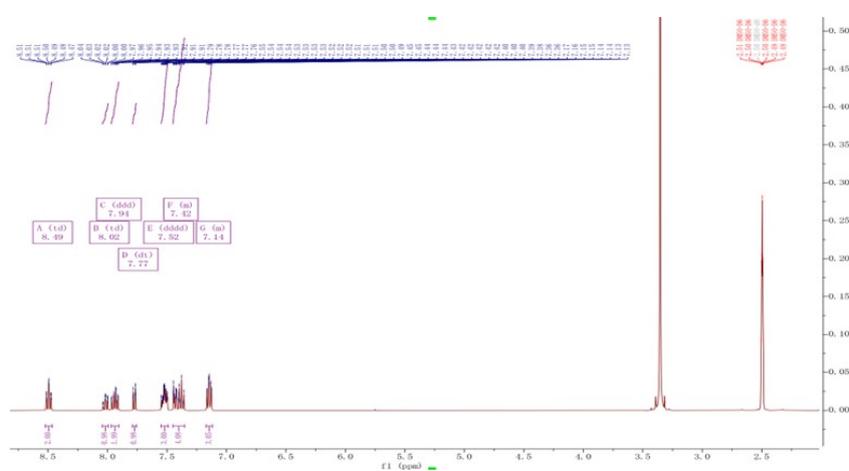
**Fig. S1.**  $^1\text{H}$  NMR spectra of the target compound 3CNCzOXD.



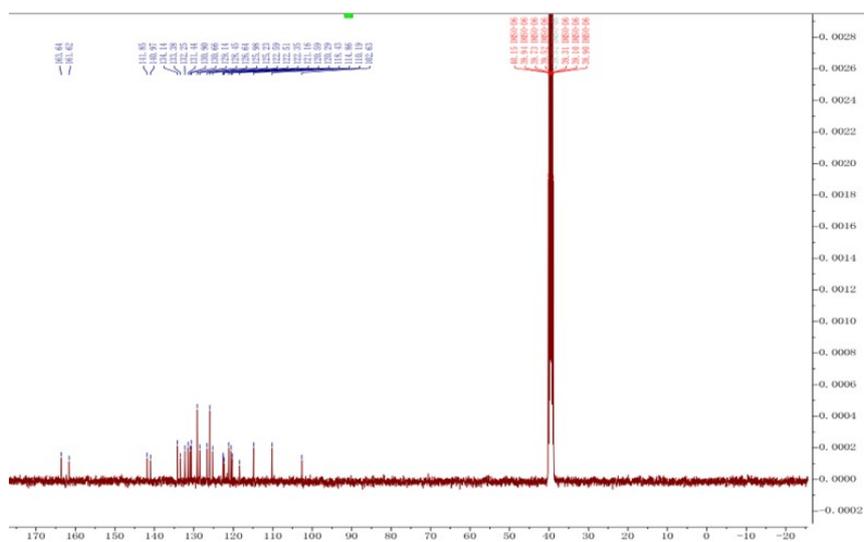
**Fig. S2.**  $^{13}\text{C}$  NMR spectra of the target compound 3CNCzOXD.



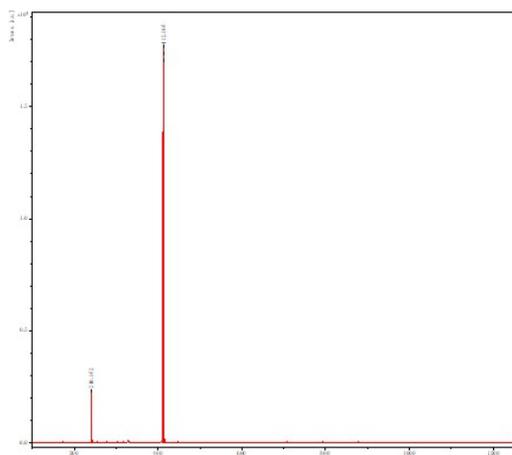
**Fig. S3.** GC/MS Mass spectrometry for the target compound 3CNCzOXD.



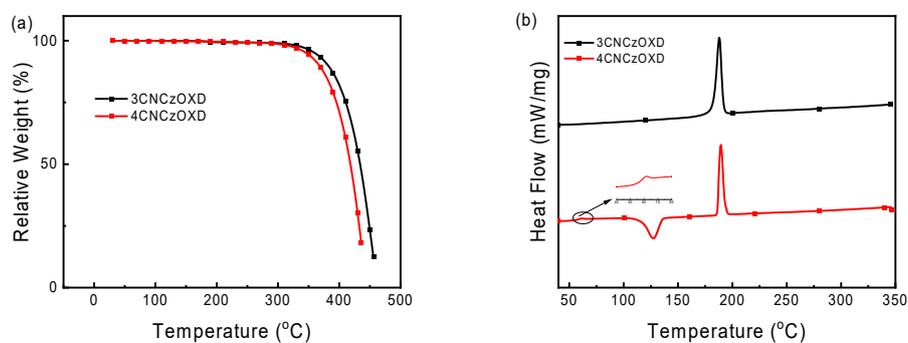
**Fig. S4.**  $^1\text{H}$  NMR spectra of the target compound 4CNCzOXD.



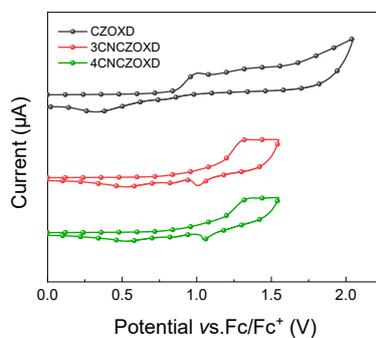
**Fig. S5.**  $^{13}\text{C}$  NMR spectra of the target compound 4CNCzOXD.



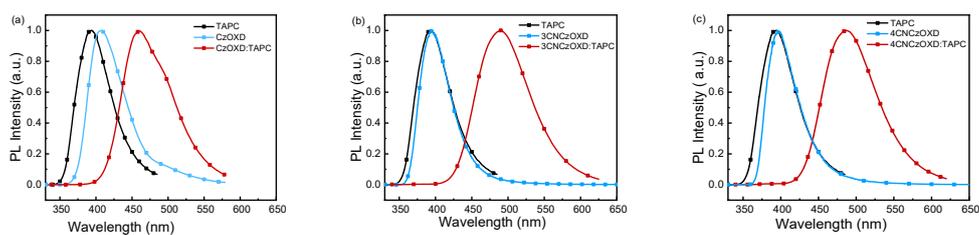
**Fig. S6.** GC/MS Mass spectrometry for the target compound 3CNCzOXD.

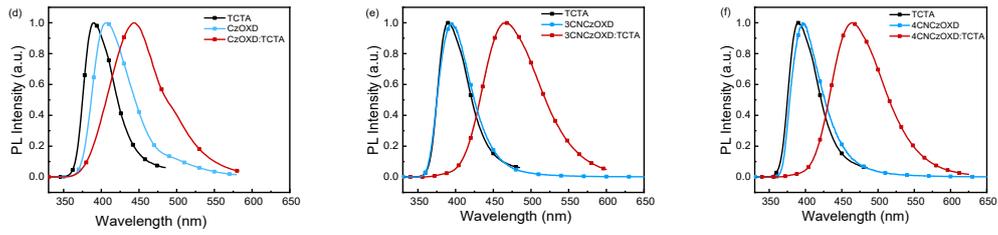


**Fig. S7.** (a) TGA and (b) DSC curves for Compounds 3CNCzOXD and 4CNCzOXD.

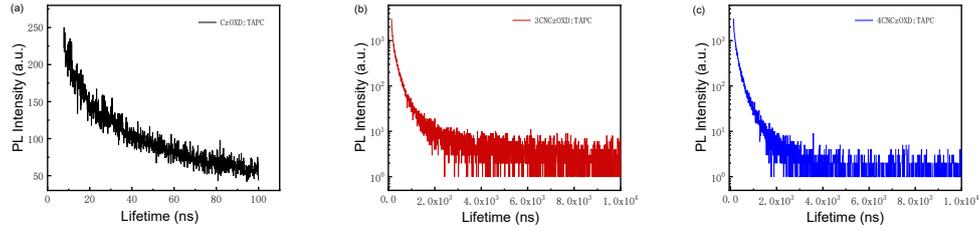


**Figure. S8.** Cyclic voltammograms of compounds 3CNCzOXD and 3CNCzOXD in  $\text{CH}_2\text{Cl}_2$  solution for oxidation scan.

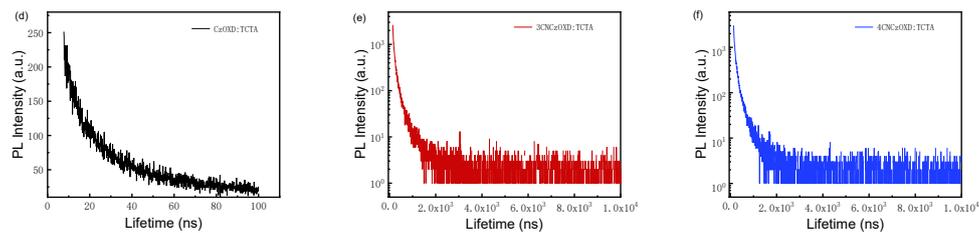




**Figure. S9.** The PL spectra of the electron donor, acceptor and corresponding exciplex in film state.



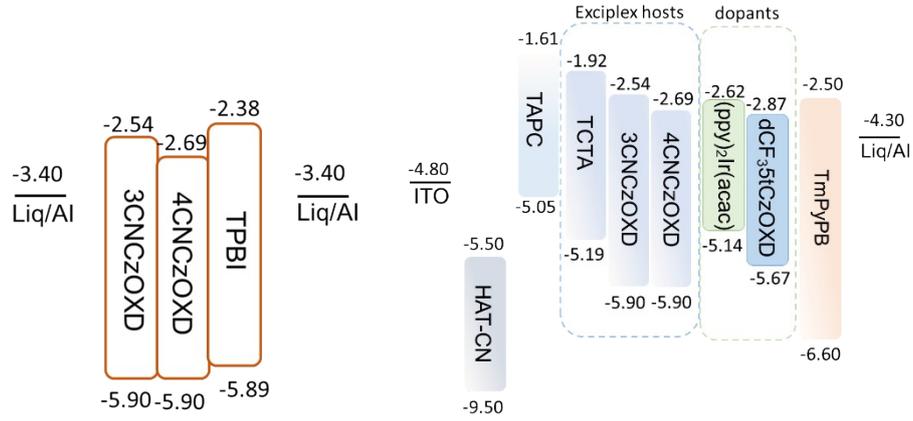
	CzOXD: TAPC	CzOXD :TCTA	3CNCzOX D: TAPC	3CNCzOX D: TCTA	4CNCzO XD:TAP C	4CNCzO XD:TCT A
PLQY/ % <sup>a</sup>	8.66	4.44	8.17	3.89	8.21	4.79
$\tau_p^b$ /ns	5.21/4.6%	6.78/16.4%	93/59%	55/61%	82/53%	52/60%
$\tau_d^c$ /ns	43.3/95.4%	30.7/83.6%	465/41%	290/39%	352/47%	261/40%



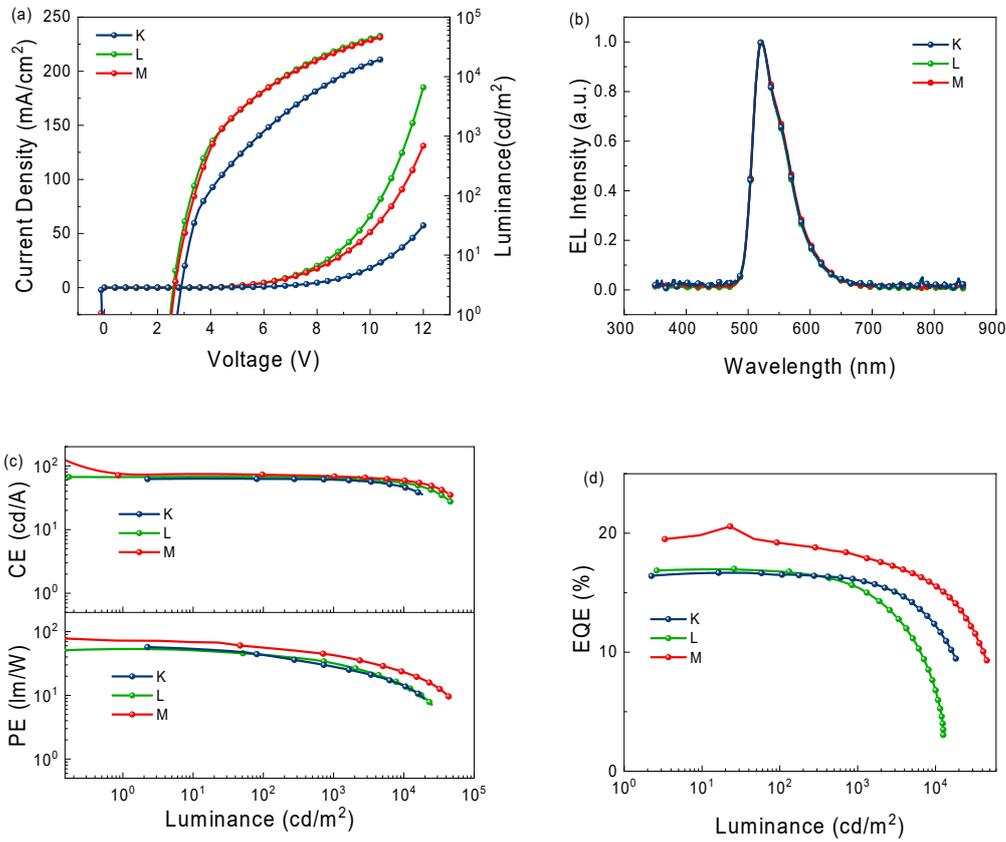
**Figure. S10.** Transient decay curves of exciplex emission in blended films.

**Table.S1.** Transient decay data for various exciplex emission.

<sup>a</sup> Photoluminescence quantum yield in blended films measured at ambient conditions. <sup>a</sup> The prompt fluorescence lifetime and the corresponding components. <sup>b</sup> The delayed fluorescence lifetime and the corresponding components.



**Figure. S10.** Device structure of electron-only devices and TADF and phosphorescent devices.



**Figure. S12.** (a)  $L$ - $V$ - $J$  characteristics, (b) EL spectra, (c) CE and PE versus luminance and (d) EQE versus luminance curves for devices K-M.

**Table.S2** Electroluminescence characteristics for the devices.

Device	EML	$V_{on}^{[a]}$ (V)	$L_{max}^{[b]}$ ( $cd/m^2$ )	CE <sup>[c]</sup> ( $cd/A$ )	PE <sup>[d]</sup> ( $lm/W$ )	EQE <sup>[e]</sup> (%)	$\lambda_{EL}^{[f]}$ (nm)
K	CzOXD: (ppy) <sub>2</sub> Ir(acac)	3.4	19340	63.0	57.3	16.7	522

L	3CNCzOXD: (ppy) <sub>2</sub> Ir(acac)	3.0	48880	68.0	68.3	18.0	521
M	4CNCzOXD: (ppy) <sub>2</sub> Ir(acac)	3.2	45670	77.0	71.7	20.6	522

[a] Turn-on voltage. [b] Maximum luminance. [c] Maximum current efficiency. [d] Maximum power efficiency. [e] Maximum external quantum efficiency. [f] Peak wavelength for EL emission.

#### Reference

- [1] D Hu, M Y Zhu, C S Shi, et al, Manipulating peripheral non-conjugated substituents in carbazole/oxadiazole hybrid TADF emitters towards high-efficiency OLEDs [J]. *J. Mater. Chem. C*, 2021,9, 13384-13391