Supplementary Information (SI) for Journal of Materials Chemistry C.

Mechanochemical synthesis of carbazole isomer Phosphor with Mechanofluorochromic and AIE Properties

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All the starting materials, unless otherwise indicated, were obtained from commercial suppliers and were used without further purification. All the compounds were purified by column chromatography. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AVANCE III 500 NMR instrument with $CDCl_3$ and DMSO-d_6 as solvents and tetramethylsilane (TMS) as internal standard at room temperature. ESI high resolution mass spectrometry analysis was performed on a Waters Xevo G2 Qt mass spectrometer. Prompt and delayed photoluminescence spectra were measured on a Hitachi F-4700 fluorescence spectrometer and an Edinburgh Instruments FLS1000 fluorescence spectrophotometer. Absolute PL quantum yields (PLQY) were determined with an integrating sphere spectrometer C11347 (Hamamatsu, Japan). UV-Vis absorption spectra were measured on a UV-3600 Shimadzu spectrophotometer. Single Crystal X-ray diffraction data were collected using a Bruker D8 Quest diffractometer (Cu Kα, λ= 1.54178 Å). Indexing and data integration were performed using APEX4 (Difference Vectors method).

Absorption correction was performed by multiscan method implemented in SADABS. Space groups were determined using XPREP implemented in APEX4. Structures were solved using SHELXL-2014 (direct methods) and refined using SHELXL-2014 (full-matrix least-squares on F^2) with anisotropic displacement contained in APEX4 program packages. Hydrogen atoms on carbon and nitrogen were calculated in ideal positions with isotropic placement parameters set to 1.2 × U_{eq} of the attached atoms. All chemical structures were optimized at the level of B3LYP/6-31G and the excited energies were calculated by the time-dependent density functional theory (TD-DFT) method at the level of B3LYP at the 6-31G (p, d). All the calculations were performed within Gaussian 09 software package.

3-(4-bromophenyl)-2-methyl-1H-benzo[g]indole (Br-Bd).

1-Naphthylhydrazine hydrochloride (0.975 g, 5 mmol), 4-bromophenylacetone (0.173 g, 5.5 mmol), oxalic acid (1.6 g, 17.5 mmol), dimethylurea (0.7 g, 7.5 mmol), and 100 ul of acetic acid were added to a 30 ml jar of ball milling. Four small steel balls of 10 mm diameter were then added to the jar. The reaction jar was fixed to a ball mill, the frequency of the ball mill was set to 30 HZ, the reaction time was set to 2 h, and the product was ground in air at room temperature for two hours, cooled down to room temperature, and then washed with water and filtered to obtain the solid crude product. The crude product was purified by silica gel column, using petroleum ether to ethyl acetate 10:1 as eluent to obtain the beige pure product. Yield: 87%. The compound structure of Br-Bd has been identified and reported in the previous work[1, 2].

3-(4-bromophenyl)-9H-carbazole (Br-Cz).

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (1 g, 3.4 mmol), 1,4-dibromobenzene (1 g, 4.24 mmol), K_2CO_3 (23 mg, 0. 17 mmol), $(PPh_3)_2PbCl_2$ (36 mg, 0.05 mmol), DMF (20 ml) were added to a 50 mL Shrek bottle and the mixed solution was refluxed at 80 ℃ for 12 h in a nitrogen atmosphere. After the reaction, the resulting mixture was cooled to room temperature and the solvent was washed through saturated brine and ethyl acetate twice. The solvent obtained was removed under reduced pressure. The crude product was purified by silica gel column using petroleum ether to DCM 1:1 as eluent to give the pure product as a white powder. Yield: 60%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25, 8.25, 8.13, 8.12, 7.63, 7.63, 7.62, 7.61, 7.59, 7.58, 7.50, 7.48, 7.46, 7.45, 7.43, 7.28, 7.28, 7.27, 7.27, 7.26.

2-methyl-3-(4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-4-yl)-1H-benzo[g]indole (Bd-TPE).

Br-Bd (0.336 g, 1 mmol), 4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane (0.550 g, 1.2 mmol), Pd $(PPh_3)_4$ (0. 029 g, 2.5 mmol%), K_2CO_3 (0.040 g, 30 mol%) were added to a reaction flask, vacuumed and aerated with nitrogen three times, 10 mL of DMF was added and the reaction was carried out at 85° for 12 h. The reaction was cooled to room temperature and then extracted with water and ethyl acetate. The crude product was purified on a silica gel column and petroleum ether-ethyl acetate 10:1 was used as eluent to give a pure white product. Yield: 85%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74, 8.02, 8.00, 7.95, 7.93, 7.81, 7.79, 7.78, 7.75, 7.74, 7.73, 7.72, 7.68, 7.66, 7.56, 7.54, 7.53, 7.45, 7.43, 7.42, 7.26, 2.66. ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.83, 143.80, 143.78, 142.65, 141.14, 140.67, 138.70, 138.10, 134.42, 131.83, 131.46, 131.38, 130.28, 129.78, 129.58, 129.50, 128.91, 127.78, 127.71, 127.65, 126.94, 126.50, 126.42, 126.04, 125.43, 123.60, 123.53, 121.31, 120.78, 119.21, 119.11, 116.12, 77.27, 77.02, 76.76, 12.70.

3-(4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-4-yl)-9H-carbazole (Cz-TPE).

Similar to Bd-TPE, CZ-TPE is a white powder. Yield: 90%. ^{1}H NMR (500 MHz, DMSO) δ 11.33, 8.50, 8.24, 8.22, 7.84, 7.82, 7.76, 7.74, 7.74, 7.72, 7.58, 7.56, 7.55, 7.53, 7.52, 7.50, 7.42, 7.41, 7.39, 7.20, 7.18, 7.17, 7.17, 7.15, 7.14, 7.13, 7.12, 7.11, 7.08, 7.06, 7.04, 7.03, 7.00, 6.99, 3.33, 2.50. ^{13}C NMR (126 MHz, DMSO) δ 143.73, 143.69, 142.71, 141.24, 140.75, 140.67, 139.87, 138.00, 137.66, 131.81, 131.22, 131.15, 130.71, 128.43, 128.35, 128.28, 127.46, 127.28, 127.15, 127.07, 127.00, 126.24, 126.12, 124.91, 123.65, 123.11, 120.96, 119.16, 118.60, 111.83, 111.57, 40.56, 40.39, 40.23, 40.06, 39.89, 39.73, 39.56.

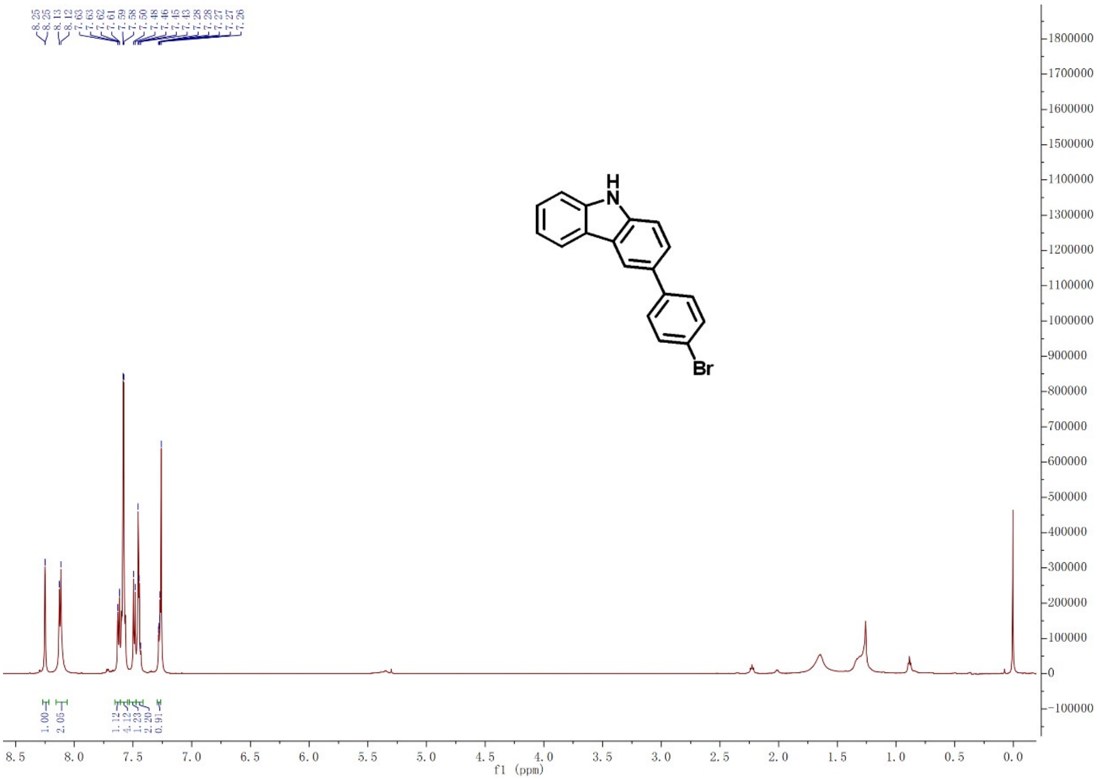

Figure S1. ^1H NMR spectrum of Cz-Br in $CDCl_3$.

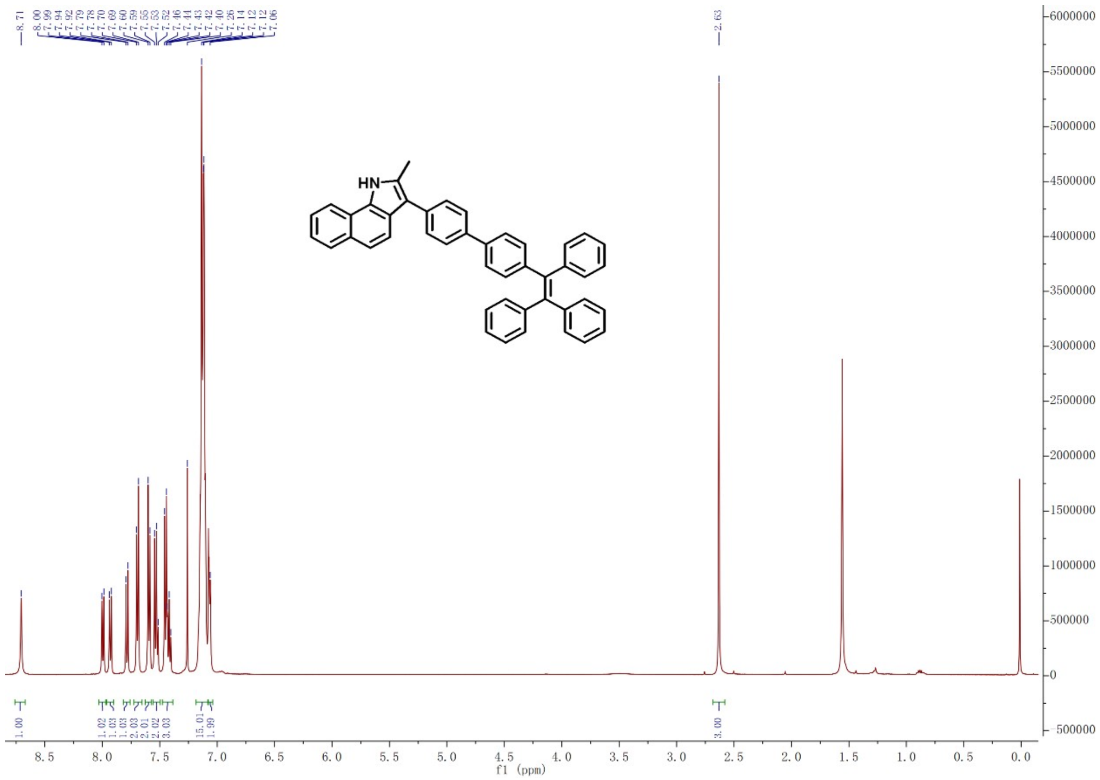

Figure S2. ^{1}H NMR spectrum of Bd-TPE in $CDCl_3$.

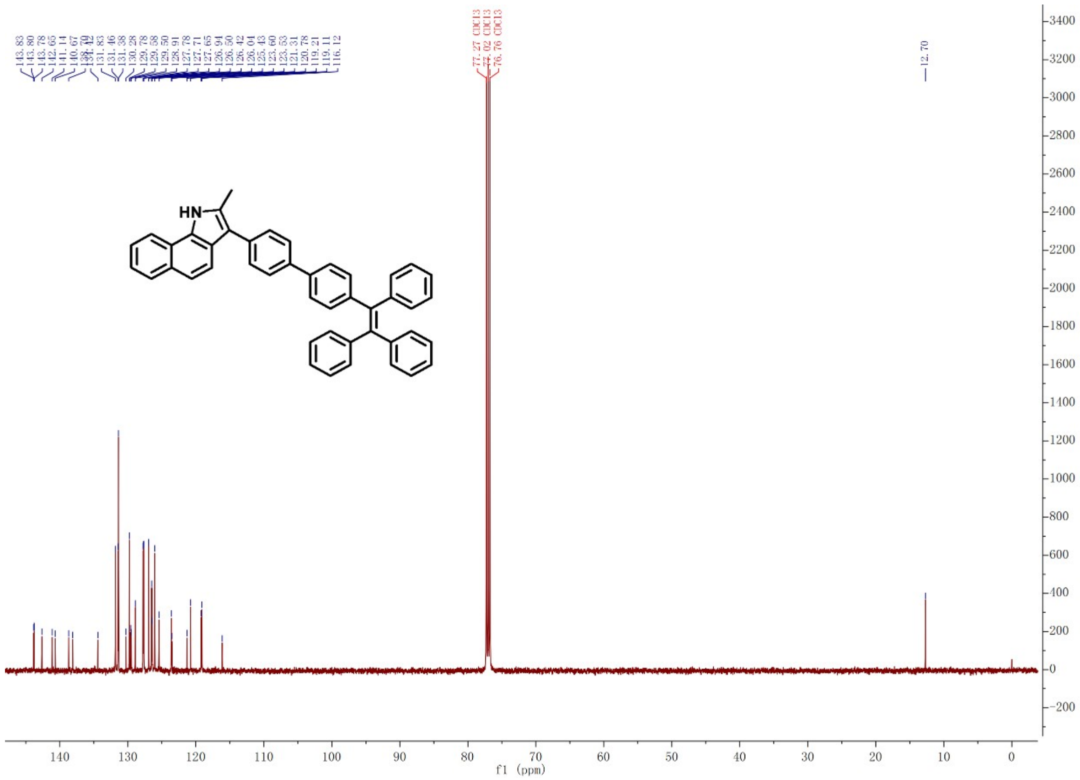

Figure S3. ^{13}C NMR spectrum of Bd-TPE in $CDCl_3$.

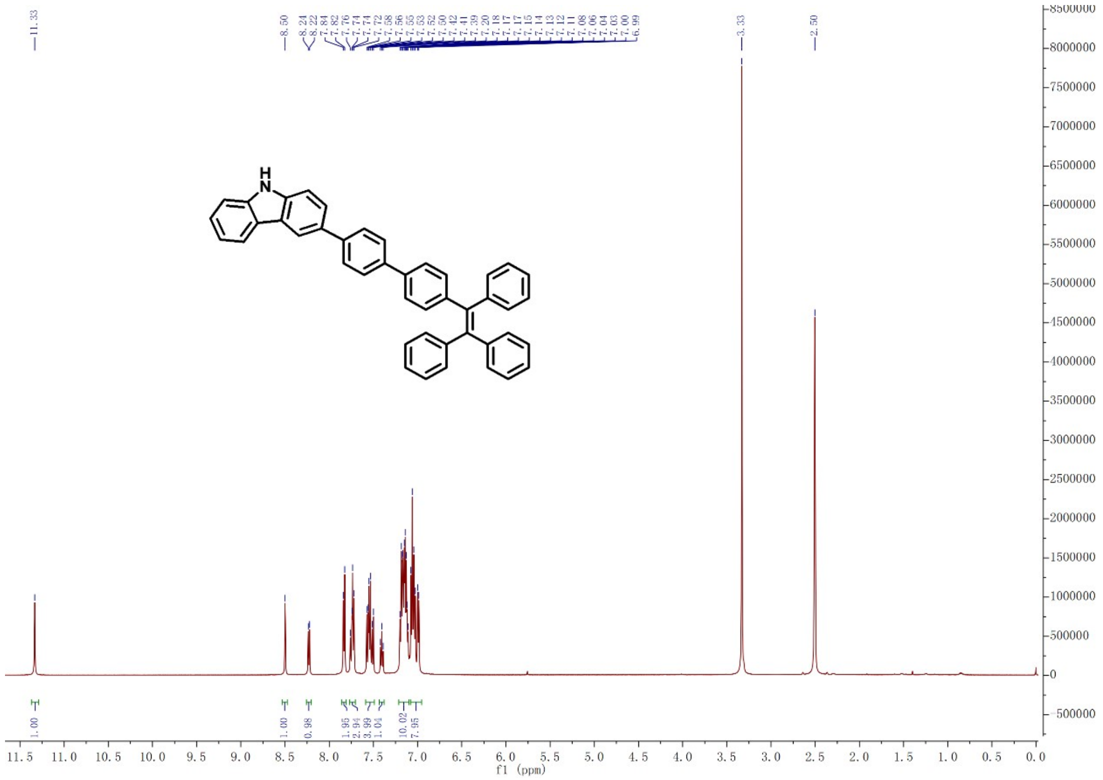

Figure S4. ^{1}H NMR spectrum of Cz-TPE in DMSO-d_6.

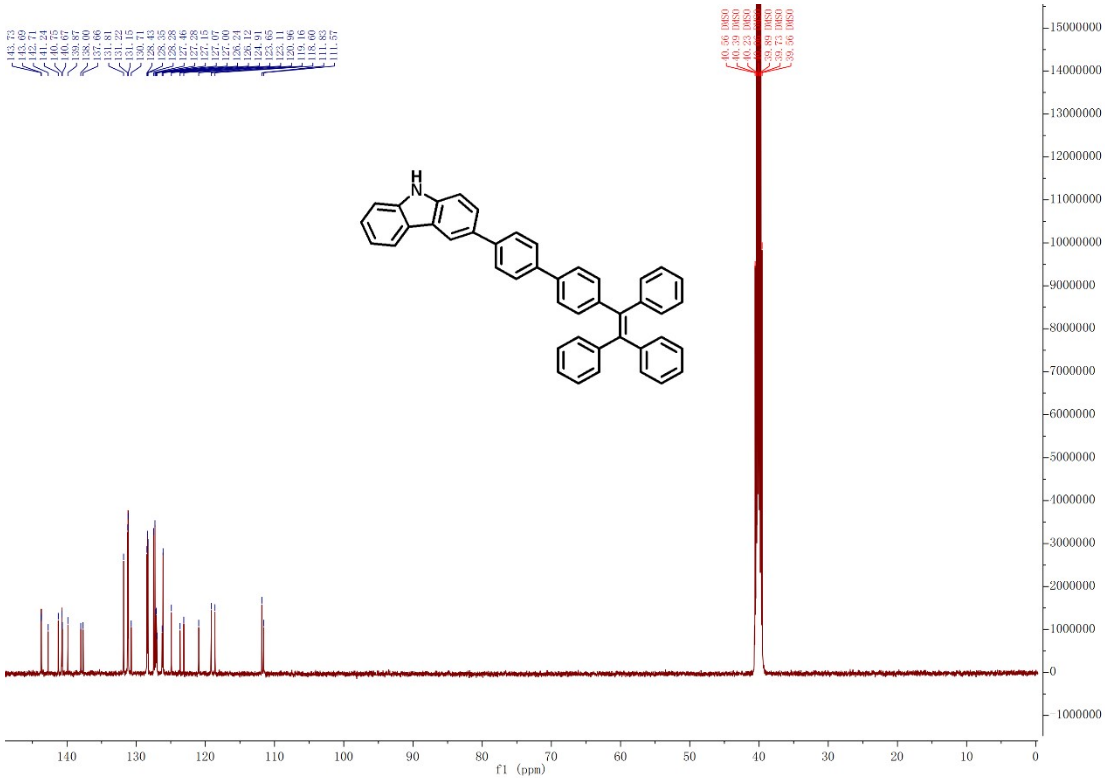

Figure S5. ^{13}C NMR spectrum of Cz-TPE in DMSO-d_6.

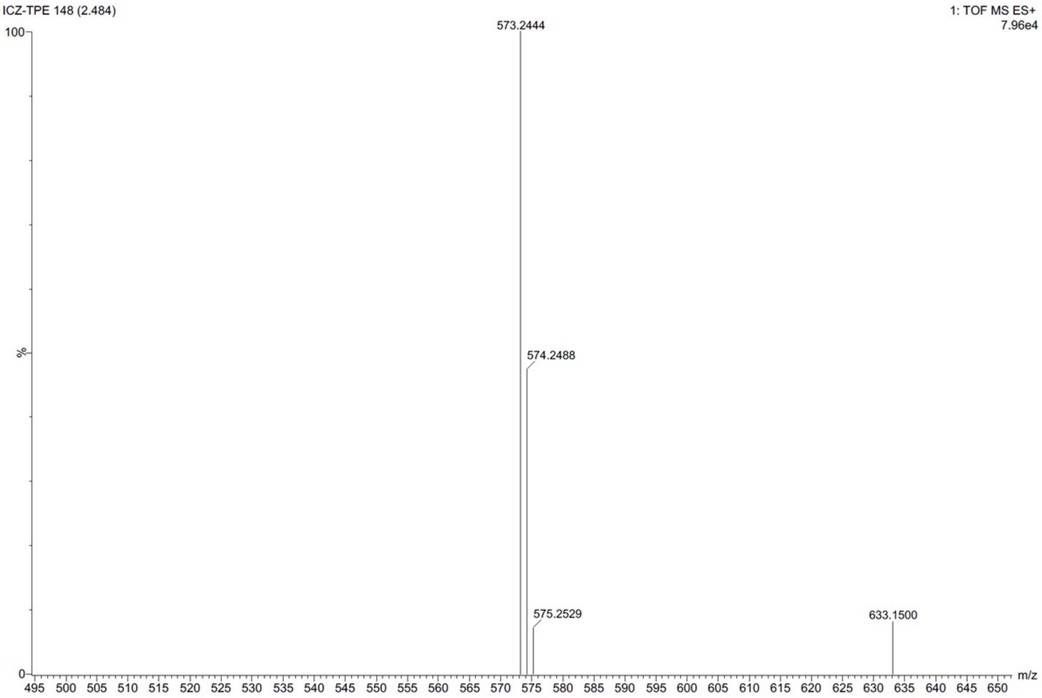

Figure S6. HR-MS spectrum of Cz-TPE.

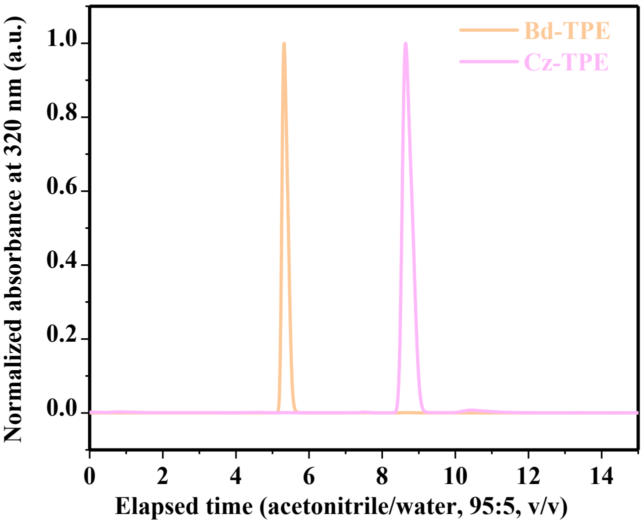

Figure S7. The HPLC spectra of Bd-TPE and Cz-TPE were monitored at 320 nm using acetonitrile: water as eluent in the ratio of 95:5 (v/v).

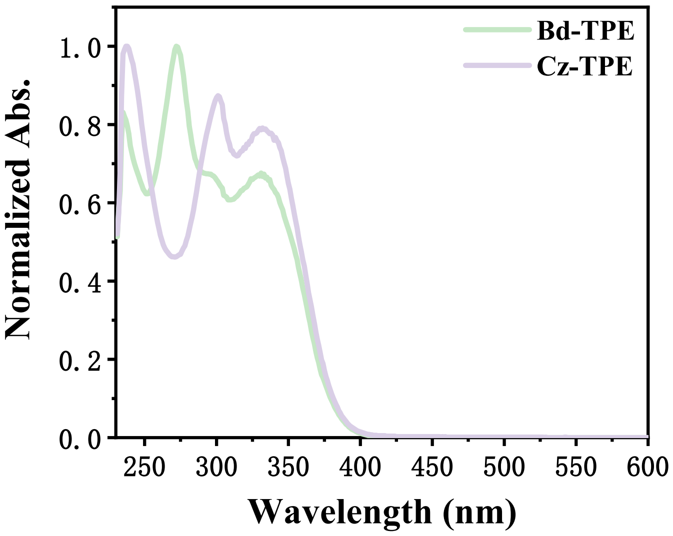

Figure S8. Absorption spectra of Bd-TPE and Cz-TPE.

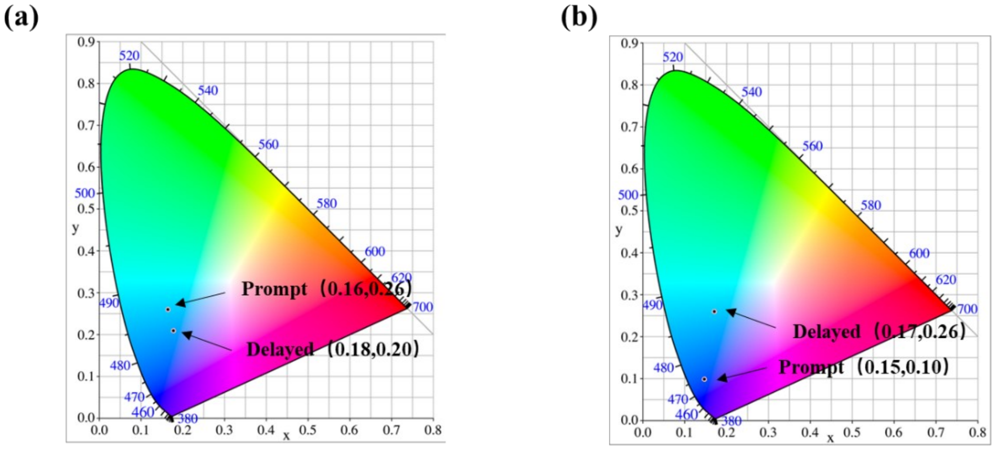

Figure S9. Prompt and Delayed CIE coordinates of (a) Bd-TPE@PVA and (b)) Cz-TPE@PVA.

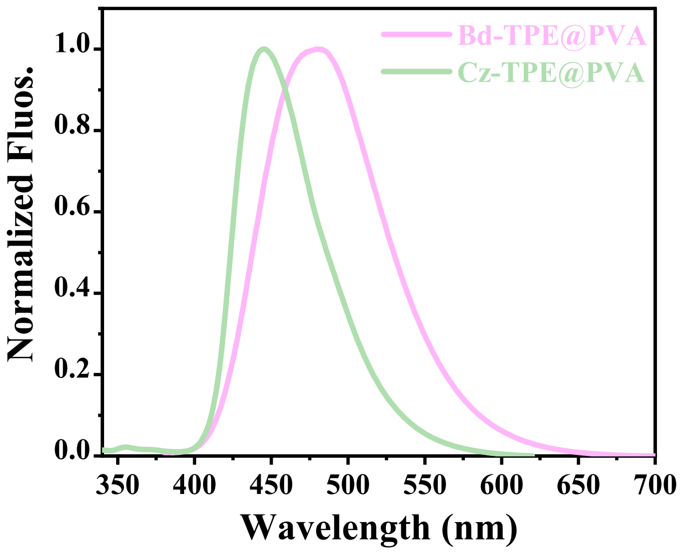

Figure S10. Prompt PL spectra of Bd-TPE@PVA and Cz-TPE@PVA at RT.

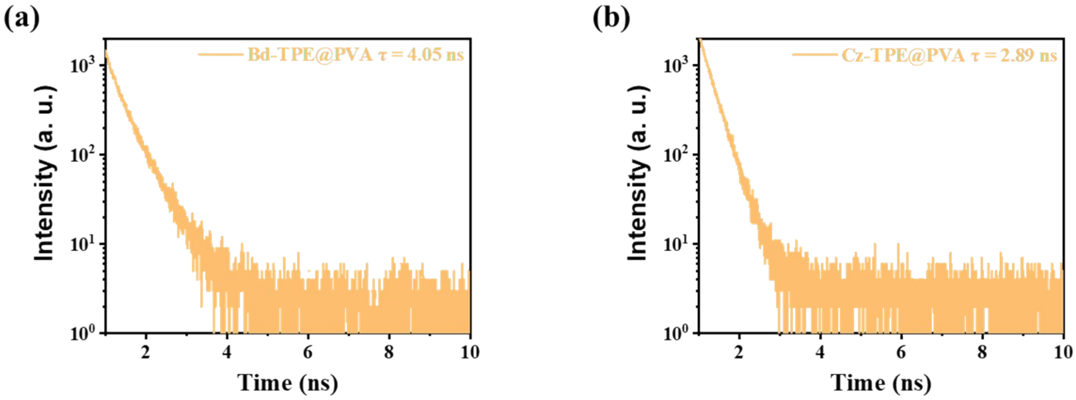

Figure S11. Fluorescence lifetime curves of Bd-TPE@PVA (a) and Cz-TPE@PVA (b) films under 320 nm emission excitation.

Table S1. Detailed data of the **Bd-TPE and Cz-TPE** single crystal.

Identification code	Bd-TPE	Cz-TPE
CCDC Number	2414152	2414154
Empirical formula	$C_{45}H_{33}N$	C44H31N
Formula weight	587.72	573.70
Temperature/K	273.15	273.15
Crystal system	triclinic	monoclinic
Space group	P-1	Cc
a/Å	10.6646(3)	5.370
b/Å	11.8273(4)	62.292
c/Å	14.1548(4)	9.513
α/°	93.2030(10)	90
β/°	95.6450(10)	104.33
γ/°	112.3870(10)	90
Volume/Å^3	1634.35(9)	3083.1
Z	2	4
ρ_{calc}g/cm^3	1.194	1.236
μ/mm^{-1}	0.519	0.538
F(000)	620.0	1208.0
Crystal size/mm^3	0.12 × 0.1 × 0.08	0.12 × 0.1 × 0.08
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
Theta range for data collection	8.126° to 133.04°	5.674° to 133.462°
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 14$, $-16 \le l \le 16$	$-6 \le h \le 6$, $-6 \le k \le 74$, $-11 \le l \le 11$
Reflections collected	18124	5338
Independent reflections	5680 [R_{int} = 0.0675, R_{sigma} = 0.0639]	5208 [R_{int} = 0.0649, R_{sigma} = 0.0630]
Data/restraints/parameters	5680/0/416	5208/20/513
Goodness-of-fit on F^2	1.060	0.925
Final R indexes [I>=2σ (I)]	R_1 = 0.0542, wR_2 = 0.1475	R1 = 0.0820, wR2 = 0.2208
Final R indexes [all data]	R_1 = 0.0722, wR_2 = 0.1578	R1 = 0.1064, wR2 = 0.2503

Table S2. The singlet and triplet excited state transition configurations of **Bd-TPE** monomer. The matched excited states that contain the same orbital transition components of S_1 are shown in bold.

Excited State	Energy (eV)	Transition configuration (%）
T_1	2.2959	H -> L 60.4%, H-2 -> L 14.2%, H-1 -> L 10.9%
T_2	2.7773	H -> L+1 19.6%, H-2 -> L 13.2%, H-1 -> L+2 12.0%, H -> L+2 7.1%, H-1 -> L+1 7.0%, H-3 -> L 6.0%, H-2 -> L+2 5.3%, H -> L 5.3%
T_3	2.8609	H-1 -> L+2 28.7%, H -> L+1 12.8%, H-2 -> L+2 8.4%, H-1 -> L+1 6.9%, H-2 -> L+1 6.8%, H-3 -> L 6.0%
S_1	3.2593	**H -> L 96.7%**
T_4	3.3497	H-1 -> L+1 20.6%, H-1 -> L 19.1%, H -> L+4 14.8%, H-3 -> L 7.2%, H-1 -> L+4 7.0%
T_5	3.4719	H -> L+5 9.3%, H -> L+3 9.1%, H-2 -> L+5 5.6%, H-4 -> L 5.5%, H-9 -> L 5.1%
T_6	3.4977	H -> L+2 35.9%, H-2 -> L+1 11.1%, H-2 -> L+2 10.7%, H -> L+1 9.6%, H-1 -> L+4 8.9%, H-1 -> L+2 6.8%
T_7	3.5675	H-2 -> L 12.5%, H -> L+1 8.2%, H-1 -> L+4 5.6%
S_2	3.6049	H-1 -> L 89.6%, H-2 -> L 5.8%

Table S3. The singlet and triplet excited state transition configurations of **Cz-TPE** monomer. The matched excited states that contain the same orbital transition components of S_1 are shown in bold.

Excited State	Energy (eV)	Transition configuration (%）
T_1	2.3595	H -> L 62.5%, H-1 -> L 21.9%
T_2	2.9073	H -> L+2 28.2%, H-1 -> L 14.9%, H -> L+1 9.3%, H-3 -> L 8.8%, H -> L 7.4%
T_3	3.1923	H-2 -> L+1 34.5%, H -> L+1 10.0%, H-1 -> L+2 8.7%, H-2 -> L+2 6.8%
T_4	3.2904	H-1 -> L+1 41.6%, H -> L+1 22.0%, H -> L+2 12.5%
S_1	3.3818	**H -> L 96.6%**
T_5	3.4796	H -> L+3 13.3%, H -> L+4 8.0%, H-1 -> L+3 7.4%, H-10 -> L 5.9%
T_6	3.5133	H-1 -> L+2 18.3%, H-2 -> L+1 13.8%, H-1 -> L 7.3%, H -> L+6 5.7%
T_7	3.6426	H-11 -> L 6.5%, H -> L+11 5.8%, H-6 -> L 5.8%, H-5 -> L+9 5.4%

1. X. Xu, X. Guo, Z. Chen, D. Ding, K. Liu, S. Su, L. Yu and M. Sun, *Small* 2025, **21**, 2405639.
2. H. Lv, X. Xu, J. Li, X. Huang, G. Fang and L. Zheng, *Angew. Chem. Int. Ed.*, 2022, **61**, e202206420.