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Controlling through-space and through-bond intramolecular charge transfer in bridged D-D'-A TADF Emitters

Supporting information

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General Experimental.

All chemicals and reagents were used as received from commercial sources without purification. Solvents for chemical synthesis were purified by distillation. All chemical reactions were carried out under an argon or nitrogen atmosphere. NMR spectra were measured in CD_2Cl_2 or $CDCl_3$ through Varian (Utility 400) spectrometer at ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) respectively.

Thermogravimetric analysis (TGA) was undertaken with a TGA Q500 instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their 5% weight loss while heating at a rate of 10 ℃/min. Differential scanning calorimetry (DSC) analyses were performed on a TA Instrument DSC-2920 Low Temperature Difference Scanning Calorimeter at a heating rate of 10 ℃/min under nitrogen.

The electrochemical properties were probed from cyclic voltammetry (CV) with a CHI619B electrochemical analyzer, where the oxidation scans were carried out in CH_2Cl_2 solution (1.0 mM) containing 0.1 M of tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte and the reduction scans were carried out in argon-purged DMF solution (1.0 mM) containing 0.1 M of tetra-n-butylammonium perchlorate (TBAP) as a supporting electrolyte at a scan rate of 100 mV/s with the ferrocene/ferrocenium (Fc/Fc^+) as the internal standard. The conventional three-electrode configuration consists of a glassy carbon electrode, a platinum wire, and a saturated Ag/AgCl electrode as working, auxiliary, and reference electrodes, respectively. HOMO and LUMO levels were calculated from the oxidation / reduction half-wave potential with the formula: $E_{\mathrm{HOMO}} = -4.8 - (E_{\mathrm{onset}}^{\mathrm{oxi}} - E^{\mathrm{Fc/Fc+}})$ (eV) and $E_{\mathrm{LUMO}} = -4.8 - (E_{1/2}^{\mathrm{red}} - E^{\mathrm{Fc/Fc+}})$ (eV).

Crystallographic data were carried out at 200(2) K on a Oxford Gemini A CCD diffractometer using with Mo-Kα radiation ($\lambda = 0.71073$ Å). Cell parameters and data reduction were retrieved and refined manipulating CrysAlis Pro software on all reflections. The structures were solved and refined with SHELXL programs. The hydrogen atoms were included in calculated positions and refined using a riding mode.

Steady state: Photoluminescence measurements are obtained using concentrations of 20μML^{-1} solutions along with drop cast films on quartz substrates at 1% in zeonex and 10% by weight in the other hosts. A Jobin Yvon Horiba Fluoromax-3 and a spectrophotometer Shimadzu UV-VIS-NIR 3600, for emission and absorption measurements respectively. All spectral on-set energies are corrected using the Jacobian conversion of wavelengths to energies.[2]

Time Resolved: The time resolved measurements are obtained using a gated iCCD camera (250-950nm) system. Films were placed in a Janis Research VNF-100 cryostat and excited by a 150ps Nd:YAG laser (355nm).

OLED Fabrication and Characterization:

Organic materials and the indium tin oxide (ITO)-coated glass with sheet resistance of ~15 Ω/square were purchased from Lumtec and Shine Materials Technology. The ITO substrate was washed with deionized water and acetone in sequence, followed by treatment with UV-Ozone for 5 minutes. All organic materials were subjected to temperature gradient sublimation. The organic and metal layers were deposited onto the ITO-coated glass substrate by thermal evaporation and the device fabrication was completed in a single cycle without breaking the vacuum. The active area of the device was set to 2×2 mm^2, as defined by the shadow mask used for cathode deposition. Current density-voltage-luminance characterization was measured using a Keithley 238 current source-measure unit and a Keithley 6485 pico-ammeter equipped with a calibrated Si photodiode. The electroluminescent spectra were recorded using an Ocean Optics spectrometer.

Synthesis

Synthesis of 1-bromo-9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9*H*-carbazole (1BrCzT).

A solution of sodium hydride (60% in oil, 600 mg, 1.5 eq., 15.0 mmol) and 1-bromo-9*H*-carbazole (2.46 g, 1 eq., 10.0 mmol) in DMF (100 mL) was stirred at room temperature for 1 hour under argon atmosphere. 2-Chloro-4,6-diphenyl-1,3,5-triazine (2.67 g, 1.02 eq., 10.0 mmol) was then added to the solution at room temperature and refluxed for 16 hours. The mixture was poured into water and the precipitate was collected by filtration and washed with water and methanol to get the yellow colored solid **1BrCzT** (4.05 g, yield: 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dt, *J* = 8.0, 1.6 Hz, 4H), 8.51 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.08 (td, *J* = 8.0, 0.8 Hz, 2H), 7.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.67-7.57 (m, 6H), 7.53 (td, *J* = 8.0, 1.2 Hz, 1H), 7.43 (td, *J* = 8.0, 1.2 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 164.2, 141.2, 137.8, 135.6, 132.9, 131.8, 129.8, 129.3, 128.7, 127.6, 125.5, 124.0, 123.3, 120.1, 119.0, 113.9, 109.5; HRMS (m/z, FAB$^+$) calcd for $C_{27}H_{17}{}^{79}BrN_4$ 476.0637, found 476.0644; calcd for $C_{27}H_{17}{}^{81}BrN_4$ 478.0616, found 478.0612.

Synthesis of 4-(9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9*H*-carbazol-1-yl)-*N*,*N*-diphenylaniline (Ph_2TRZCzTPA).

1-Bromo-9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9*H*-carbazole (0.5 g, 1 eq., 1.05 mmol), (4-(diphenylamino)phenyl)boronic acid (0.464 g, 1.2 eq., 1.26 mmol), and $Pd_2(dba)_3$ (0.029 g, 3.0 mmol%) were mixed in a 25 mL two-neck bottle. The whole system was evacuated and purged with argon gas. The mixture was dissolved in dry toluene (10 mL), then $^tBu_3P$ (2.51 mL, 0.05 M in toluene, 12 mmol%) and degassed $K_2CO_{3\,(aq.)}$ (1.26 mL, 2.5 M in distilled water, 30 mmol%) was subsequently added. The mixture was refluxed (120 °C) under inert atmosphere for 14 hours. After completion of the reaction, it was cooled to room temperature (25 °C), and the mixture was extracted with dichloromethane. The combined organic layer was washed with brine and dried over $MgSO_4$ after which the solvent was removed by rotary evaporator. The crude product was purified by column chromatography on silica gel using the eluent system, hexane : dichloromethane = 5 : 1 and then with hexane : dichloromethane : toluene = 3 : 1 : 0.1 to obtain the pure product as a yellow solid **Ph_2TRZCzTPA** (0.202 g, yield: 30%). ^{1}H NMR (400 MHz, CD2Cl2) δ 8.63-8.60 (m, 4H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.16-8.10 (m, 2H), 7.64-7.60 (m, 2H), 7.57-7.50 (m, 7H), 7.44-7.40 (m, 1H), 7.27-7.24 (m, 2H), 7.10-7.05 (m, 4H), 6.91-6.87 (m, 2H), 6.75-6.72 (m, 4H), 6.54-6.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 165.0, 147.5, 146.3, 140.9, 136.9, 135.5, 134.9, 133.0, 130.0, 129.5, 129.3, 128.8, 128.7, 128.5, 128.0, 128.0, 127.3, 126.2, 124.5, 123.5, 123.1, 123.1, 122.9, 120.3, 118.9, 113.8; MS (m/z, FAB$^+$) 641.5 (9.17); HRMS (m/z, FAB$^+$) calcd for $C_{45}H_{31}N_5$ 641.2579, found 641.2576; anal. calcd for $C_{45}H_{31}N_5$: C, 84.22; H, 4.87; N, 10.91, found C, 84.49; H, 4.79; N, 10.97.

Synthesis of 4-(9*H*-carbazol-1-yl)-*N*,*N*-diphenylaniline (CzTPA).

1-Bromo-9*H*-carbazole (5 g, 1 eq., 20.3 mmol), (4-(diphenylamino)phenyl)boronic acid (7.05 g, 1.2 eq., 24.4 mmol), and $Pd_2(dba)_3$ (0.558 g, 0.03 eq., 0.61 mmol) were mixed in a 250 mL two-neck bottle. The whole system was evacuated and purged with argon gas. The mixture was dissolved in dry toluene (50 mL), then added $^tBu_3P$ (48.8 mL, 0.05 M in toluene, 0.12 eq., 2.44 mmol) and degassed $K_2CO_{3\,(aq.)}$ (30.5 mL, 2.5 M in distilled water, 3.6 eq., 73.1 mmol). The system was refluxed (115 ^oC) for 14 hours under inert atmosphere. After completion of the reaction, the mixture was cooled to room temperature (25 ^oC), and then extracted with dichloromethane. The combined organic layer was washed with brine, dried over $MgSO_4$ and then solvent was removed by rotary evaporator. The crude product was purified by column chromatography on silica gel using hexane : dichloromethane = 3 : 1 as the eluent to obtain the desired product as a white solid **CzTPA** (6.84 g, yield: 82%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 6H), 7.34 (t, *J* = 8.0 Hz, 6H), 7.19 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.90, 147.55, 139.69, 137.50, 133.10, 129.71, 129.70, 129.34, 126.19, 125.85, 124.99, 124.92, 124.39, 124.00, 123.89, 123.49, 120.77, 120.29, 119.85, 119.47; HRMS (ESI) m/z : [M^+] calcd for $C_{30}H_{22}N_2$ 410.1783, found 410.1769.

Synthesis of 4-(9-(4-(4,6-Diphenyl-1,3,5-triazin-2-yl)phenyl)-9*H*-carbazol-1-yl)- *N*,*N*-diphenylaniline (Ph_3TRZCzTPA).

4-(9*H*-carbazol-1-yl)-*N*,*N*-diphenylaniline (1 g, 1 eq., 2.44 mmol), 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (1.14 g, 1.2 eq., 2.92 mmol), $Pd_2(dba)_3$ (0.056 g, 0.025 eq., 0.061 mmol), and NaO^tBu (0.304 g, 1.3 eq., 3.17 mmol) were mixed in a 100 mL double neck round bottom flask and the system was evacuated then purged with argon gas. The mixture was dissolved in dry toluene (40 mL), refluxed (120 ^oC) under argon for 5 hours after $^tBu_3P$ (5 mL, 0.05M in toluene, 0.1 eq., 0.24 mmol) was added. After completion of the reaction, it was cooled to room temperature (25 ^oC), the salts were filtered off and washed with dichloromethane. After removal of the solvent by the rotary evaporator, the crude product was purified by column chromatography on silica gel using hexane : dichloromethane = 5 : 1 as the eluent to obtain the desired product as a yellow solid **Ph_3TRZCzTPA** (1.44 g, yield: 83%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.81 (dd, *J* = 1.6, 8.8 Hz, 4H), 8.72 (d, *J* = 8.0 Hz, 2H), 8.21-8.18 (m, 2H), 7.66-7.59 (m, 6H), 7.42 (dd, *J* = 4.0, 2.4 Hz, 4H), 7.33 (dd, *J* = 8.4, 2.4 Hz, 3H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.96 (t, *J* = 7.6 Hz, 4H), 6.81 (d, *J* = 8.0 Hz, 4H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 4.0 Hz, 2H), 6.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.84, 147.34, 146.25, 142.96, 142.12, 136.15, 134.28, 132.64, 129.80, 129.25, 129.07, 129.02, 128.85, 128.69, 127.89, 126.69, 126.27, 125.39, 124.61, 123.72, 122.81, 121.67, 120.61, 120.52, 120.19, 119.10, 110.19, 147.34, 142.96, 142.12, 136.15, 134.28, 132.64, 129.80, 129.25, 129.07, 129.02, 128.85, 128.69, 127.89, 126.69, 126.27, 125.39, 124.61, 123.72, 122.81, 121.67, 120.61, 120.52, 120.19, 119.10; HRMS (m/z, FAB^+) calcd for $C_{51}H_{35}N_5$ 717.2892, found 717.2898; anal. calcd for $C_{51}H_{35}N_5$:C, 85.33; H, 4.91; N, 9.76, found C, 85.48; H, 4.82; N, 9.91.

Synthesis of 1-(4-(9*H*-carbazol-9-yl)phenyl)-9*H*-carbazole (CzPK).

1-Bromo-9*H*-carbazole (3 g, 1.0 eq., 12 mmol)、9-(4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)phenyl)-9*H*-carbazole (5.402 g, 1.2 eq., 15 mmol) and $Pd(PPh_3)_4$ (0.7 g, 0.05 eq., 0.061 mmol) were mixed in a 250 mL two-neck bottle. The whole system was evacuated and purged with argon gas. The mixture was dissolved in dry toluene (60 mL), then added $^tBu_3P$ (24 mL, 0.05 M in toluene, 0.1 eq., 1.2 mmol) and $K_2CO_{3\ (aq.)}$ (22 mL, 2 M in distilled water, 3.6 eq., 44 mmol) was subsequently added. The system was refluxed (125 °C) for 14 hours under inert atmosphere. After completion of the reaction, the mixture was cooled to room temperature (25 °C), and then extracted with dichloromethane. The combined organic layer was washed with brine, dried over $MgSO_4$ and then solvent was removed by rotary evaporator. The crude product was purified by column chromatography on silica gel using the eluent system, hexane : dichloromethane = 5 : 1 and then with hexane : dichloromethane = 3 : 1 to obtain the desired product as a white solid **CzPK** (3.34 g, yield: 67%). ^1H NMR (400 MHz, CD_2Cl_2) δ 8.58 (s, 1H), 8.21 (dt, *J* = 8.0, 1.0 Hz, 2H), 8.17-8.14 (m, 2H), 7.97 (dt, *J* = 8.8, 2.2 Hz, 2H), 7.79 (dd, *J* = 6.6, 2.2 Hz, 2H), 7.58 (dd, *J* = 7.2, 1.2 Hz, 3H), 7.53-7.45 (m, 4H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.36-7.28 (m, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 141.4, 140.2, 138.6, 137.8, 137.5, 130.3, 128.3, 126.7, 126.6, 126.4, 124.8, 124.4, 124.0, 123.9, 120.9, 120.8, 120.6, 120.5, 120.3, 120.2, 111.4, 110.34; MS (m/z, FAB^+) 408.2 (4.41); HRMS (m/z, FAB^+) calcd for $C_{30}H_{20}N_2$ 408.1626, found 408.1622.

Synthesis of 1-(4-(9*H*-carbazol-9-yl)phenyl)-9-(4,6-diphenyl-1,3,5-triazin-2-yl)- 9*H*-carbazole (Ph_2TRZCzPhCz).

A solution of sodium hydride (60% in oil, 0.166 g, 1.7 eq., 4.16 mmol) and 1-(4-(9*H*-carbazol-9-yl)phenyl)-9*H*-carbazole (1 g, 1 eq., 2.45 mmol) in DMF (25 mL) was stirred at room temperature under argon for 1 hour. 2-Chloro-4,6-diphenyl-1,3,5-triazine (1.245 g, 1.9 eq., 4.65 mmol) was then added to the solution at room temperature and refluxed for 16 hours. The mixture was poured into water and the precipitate was collected by filtration then washed with water and methanol. The crude product was dissolved with dichloromethane then washed with pentane to afford the pure product as a yellow solid **Ph_2TRZCzPhCz** (0.92 g, yield: 59%). ^1H NMR (400 MHz, CD_2Cl_2) δ 8.60 (dd, *J* = 7.6, 1.6 Hz, 5H) 8.22 (tt, *J* = 5.3, 0.8 Hz, 2H), 8.05 (dd, *J* = 8.4, 0.8 Hz, 2H), 7.71-7.60 (m, 7H), 7.55 (qd, *J* = 7.1, 1.4 Hz, 5H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.29-7.20 (m, 4H), 7.09 (dd, *J* = 6.4, 2.0 Hz, 2H), 6.9 (s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 172.1, 165.1, 140.9, 140.7, 140.2, 136.8, 136.1, 135.3, 133.2, 129.5, 129.3, 129.0, 128.7, 128.6, 128.1, 127.5, 126.8, 126.0, 125.9, 123.6, 123.3, 123.2, 120.2, 120.1, 120.0, 119.6, 113.8, 109.8; MS (m/z, FAB^+) 639.2 (3.37); HRMS (m/z, FAB^+) calcd for $C_{45}H_{29}N_5$ 639.2423, found 639.2421; anal. calcd for $C_{45}H_{29}N_5$: C, 84.48; H, 4.57; N, 10.95, found C, 84.78; H, 4.49; N, 11.05.

Synthesis of 1-(4-(9*H*-carbazol-9-yl)phenyl)-9-(4-(4,6-diphenyl-1,3,5-triazin-2- yl)phenyl)-9*H*-carbazole (Ph_3TRZCzPhCz).

1-(4-(9*H*-carbazol-9-yl)phenyl)-9*H*-carbazole (1 g, 1 eq., 2.45 mmol), 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (1.14 g, 1.2 eq., 2.94 mmol), $Pd_2(dba)_3$ (0.056 g, 0.025 eq., 0.061 mmol) and NaO^tBu (0.306 g, 1.3 eq., 3.18 mmol) were mixed in a 100 mL double neck round bottom flask and the system was evacuated then purged with argon gas. The mixture was dissolved in dry toluene (50 mL), refluxed (125 °C) under argon for 14 hours after $^tBu_3P$ (5 mL, 0.05M in toluene, 0.1 eq., 0.25 mmol) was added. After completion of the reaction, it was cooled to room temperature (25 °C), the salts were filtered off and washed with dichloromethane. After removal of the solvent by the rotary evaporator, the crude product was purified by column chromatography on silica gel using hexane : dichloromethane = 3 : 1 as the eluent to obtain the desired product as a yellow solid **Ph3TRZCzPhCz** (1.45 g, yield: 83%). ^1H NMR (400 MHz, CD_2Cl_2) δ 8.75-8.71 (m, 6H), 8.27 (qd, *J* = 7.6, 1.2 Hz, 2H), 7.89 (dd, *J* = 7.4, 2.0 Hz, 2H), 7.65-7.43 (m, 14H), 7.40-7.36 (m, 1H), 7.28 (dd, *J* = 6.4, 2.0 Hz, 2H), 7.13 (d, *J* = 7.2 Hz, 2H), 6.96

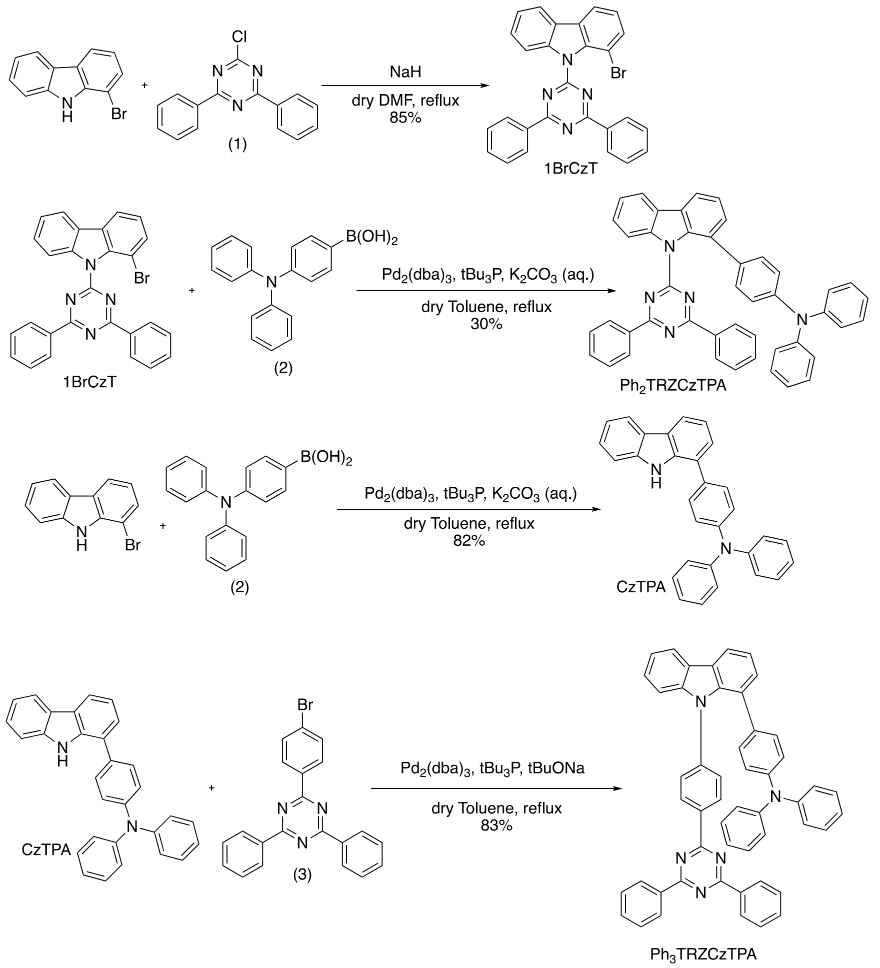
(s, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 172.3, 171.3, 143.3, 142.9, 141.1, 139.0, 138.4, 136.7, 136.6, 135.3, 133.2, 131.3, 130.0, 129.6, 129.5, 129.2, 128.5, 127.0, 126.7, 126.2, 124.2, 123.6, 121.3, 121.2, 120.8, 120.4, 120.3, 120.1, 110.8, 110.1; MS (m/z, FAB$^+$) 715.1 (1.75); HRMS (m/z, FAB$^+$) calcd for $C_{51}H_{33}N_5$ 715.2736, found 715.2736; anal. calcd for $C_{51}H_{33}N_5$: C, 85.57; H, 4.65; N, 9.78, found C, 85.63; H, 4.67; N, 9.86.

Synthesis of 9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9*H*-carbazole (CzTRZ).

A solution of carbazole (2 g, 1 eq., 11.96 mmol) and sodium hydride (60% in oil, 0.718 g, 1.5 eq., 17.94 mmol) in DMF (240 mL) was stirred at room temperature under argon for 1 hour. 2-Chloro-4,6-diphenyl-1,3,5-triazine (3.5 g, 1.1 eq., 13.16 mmol) was then added to the solution at room temperature and refluxed for 16 hours. The mixture was poured into water and the precipitate was collected by filtration and washed with water and methanol to get the white solid **CzTRZ** (4.53 g, yield: 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 10.8 Hz, 2H), 8.77 (dd, *J* = 7.6, 5.6 Hz, 4H), 8.10 (d, *J* = 7.2 Hz, 2H), 7.67-7.60 (m, 8H), 7.45 (t, *J* = 7.6 Hz, 2H); MS (m/z, FAB$^+$) 399.2 (10.68); HRMS (m/z, FAB$^+$) calcd for $C_{27}H_{18}N_4$ 398.1531, found 398.1534.

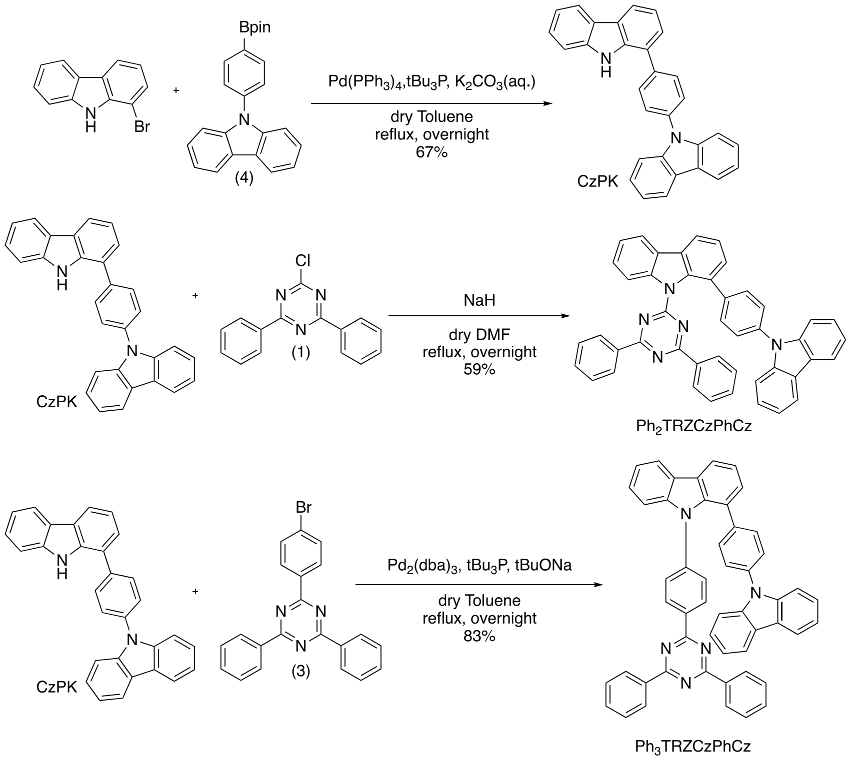
Supplementary Figures

Scheme S1 displays the synthetic routes towards **Ph$_2$TRZCzTPA** and **Ph$_3$TRZCzTPA**. The intermediate **1BrCzT** was obtained in 85% yield after treating 2-chloro-4,6-diphenyl-1,3,5-triazine **(1)** with 1-bromo-9*H*-carbazole in the presence of NaH in DMF at room temperature, while **Ph$_2$TRZCzTPA** was synthesized in 30% yield via the Suzuki coupling reaction between **1BrCzT** and (4-(diphenylamino)phenyl)boronic acid **(2)**. The intermediate **CzTPA** was synthesized in 82% yield via the Suzuki coupling reaction between 1-bromo-9*H*-carbazole and (4-(diphenylamino)phenyl)boronic acid **(2)**. **Ph$_3$TRZCzTPA** was synthesized in 83% yield via the Buchwald–Hartwig coupling reaction between **CzTPA** and 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine **(3)**.



Scheme S1. The synthetic routes of **Ph$_2$TRZCzTPA** and **Ph$_3$TRZCzTPA**.

Scheme S2 displays the synthetic routes towards **Ph$_2$TRZCzPhCz** and **Ph$_3$TRZCzPhCz**. The key intermediate **(CzPK)** was synthesized in 67% yield via the Suzuki coupling reaction between 1-bromo-9*H*-carbazole and 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole **(4)**. **Ph$_2$TRZCzPhCz** was obtained in 59% yield after treating **CzPK** with 2-chloro-4,6-diphenyl-1,3,5-triazine **(1)** in the presence of NaH in DMF at 150 ^{o}C. **Ph$_3$TRZCzPhCz** was synthesized in 83% yield via the Buchwald–Hartwig coupling reaction between **CzPK** and 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine **(3)**.



Scheme S2. The synthetic routes of **Ph_2TRZCzPhCz** and **Ph_3TRZCzPhCz**.

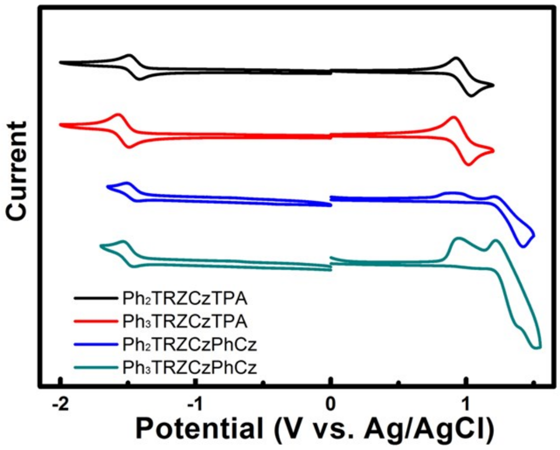


Figure S1. Cyclic voltammograms of **Ph_2TRZCzTPA**, **Ph_3TRZCzTPA**, **Ph_2TRZCzPhCz**, and **Ph_3TRZCzPhCz**.

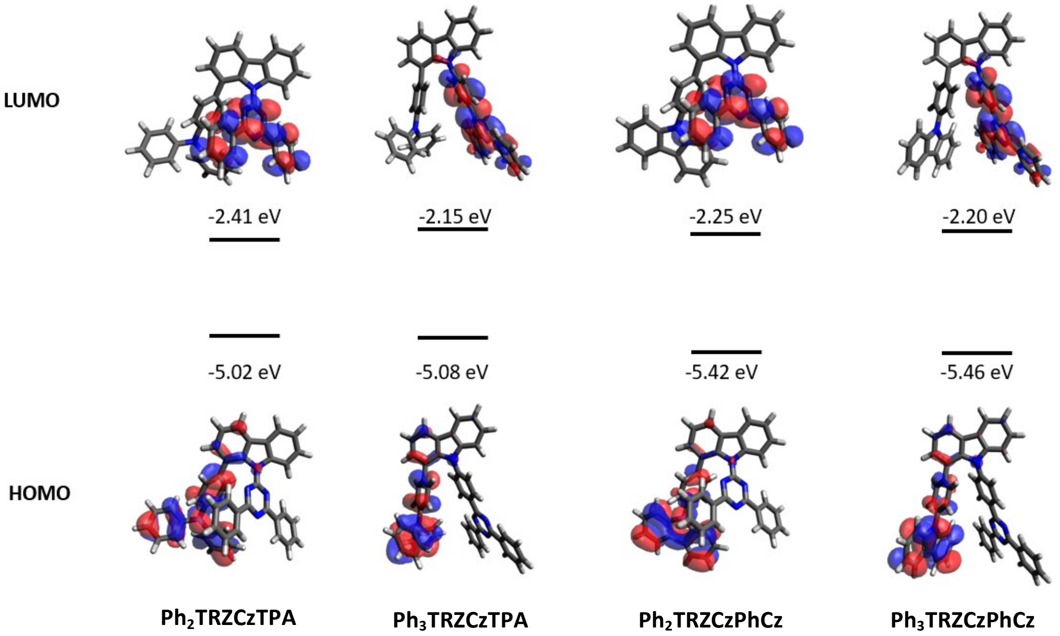
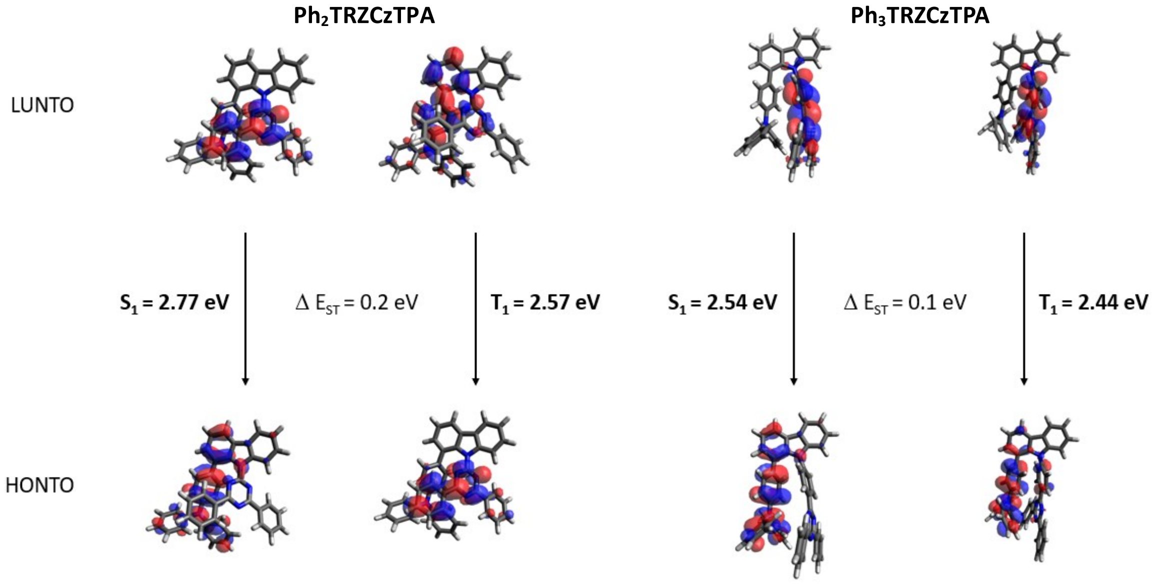


Figure S2. The calculated HOMO and LUMO orbital distributions and energy levels of **$\mathrm{Ph_2}$TRZCzTPA**, **$\mathrm{Ph_3}$TRZCzTPA**, **$\mathrm{Ph_2}$TRZCzPhCz**, and **$\mathrm{Ph_3}$TRZCzPhCz.**



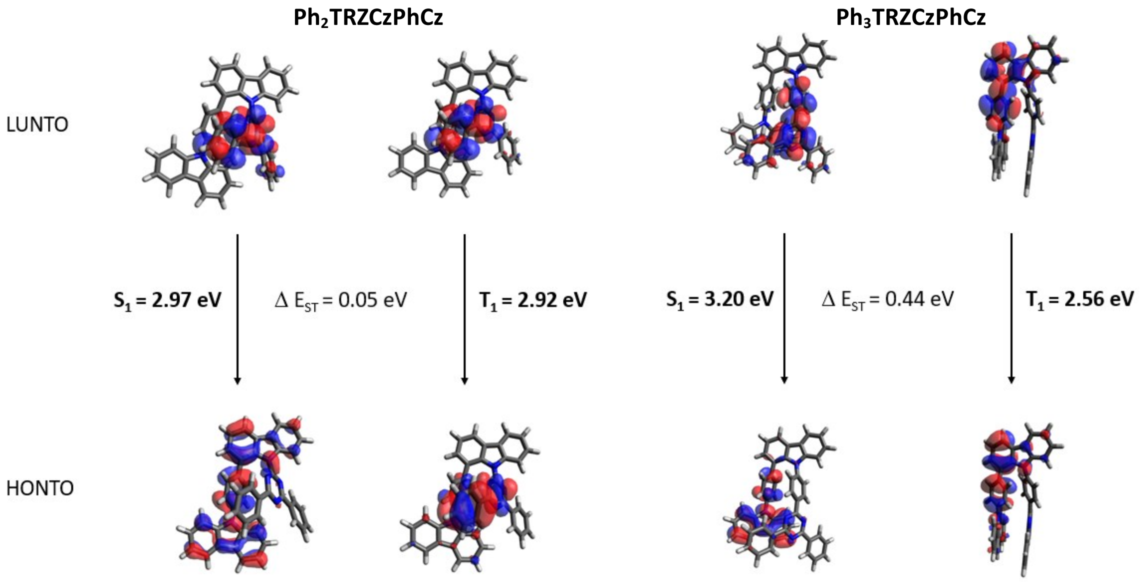
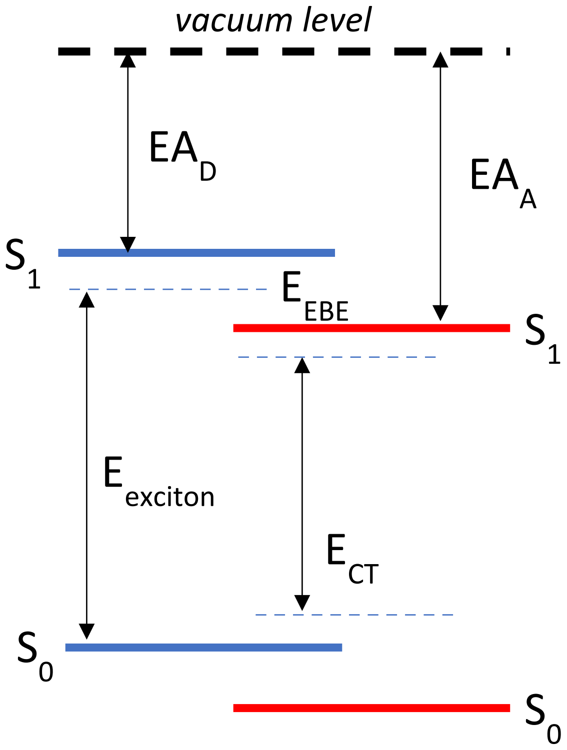


Figure S3. Nature Transition Orbital (NTO) of **Ph$_2$TRZCzTPA, Ph$_3$TRZCzTPA, Ph$_2$TRZCzPhCz**, and **Ph$_3$TRZCzPhCz** for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ transitions based on the optimized S_1 and T_1 geometries.



Scheme S3. Schematic representation of the driving force, $\Delta G_0 = EA_A - EA_D - \Delta E_b$ for CT formation in D A molecules; Where EA_D and EA_A are the electron affinity of A and D fragment respectively, and ΔE_b is the difference in binding energy between the initially created exciton and the charge separated state, $\Delta E_b = E_{exciton} - E_{CT}$. $\mathrm{E_{EBE}}$ is the exciton binding energy and $\mathrm{E_{CT}}$ represents the relaxed CT energy dependent on environment polarity/polarizability and conformational relaxation effects.

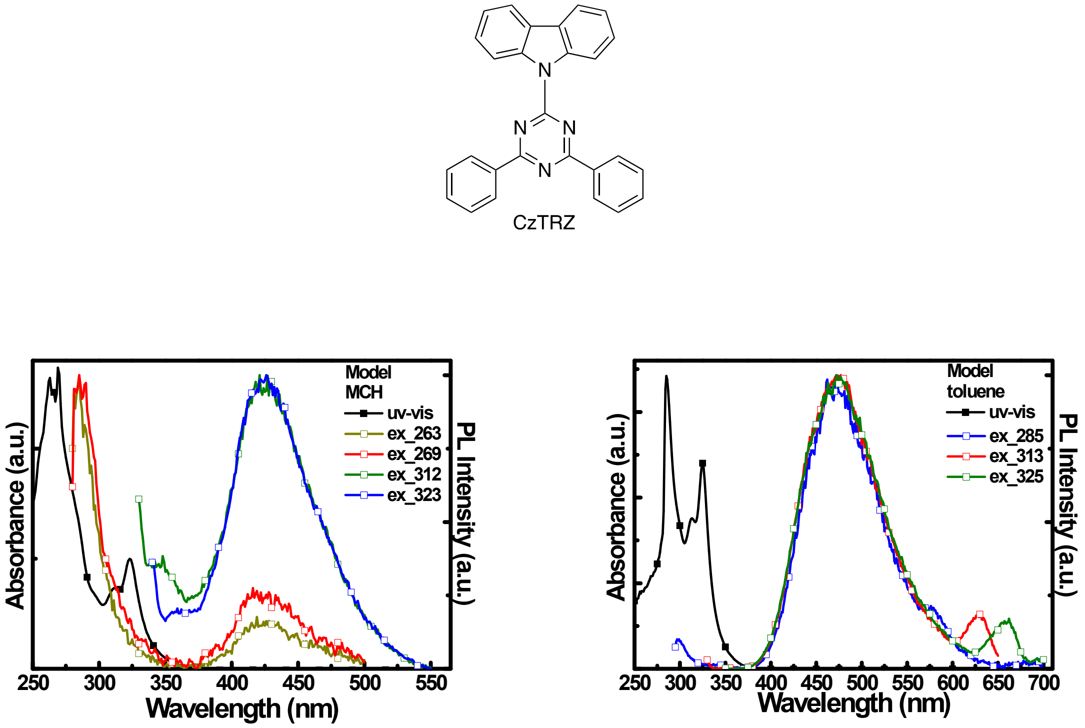


Figure S4. Structure of **CzTRZ** compound and its absorption and emission.

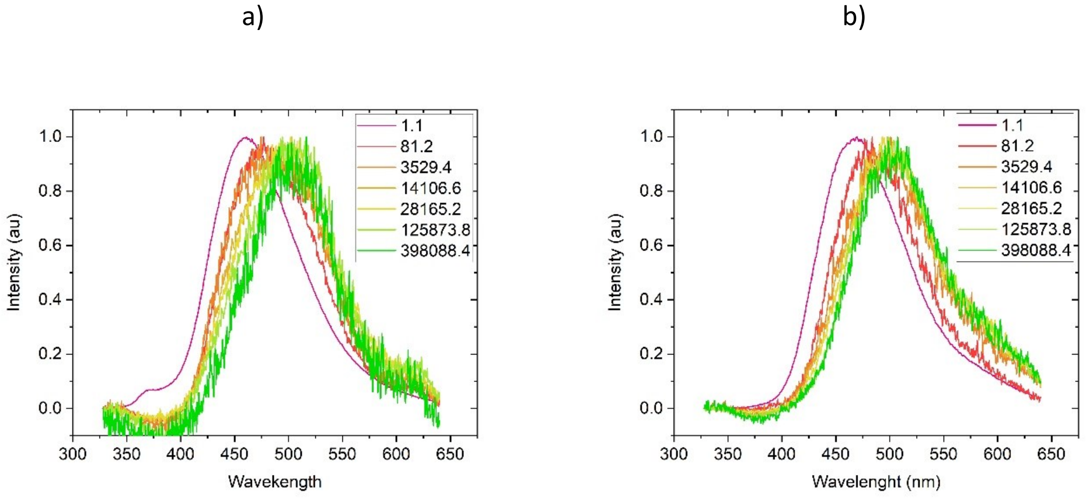


Figure S5. Representative time resolve spectra obtained for **Ph$_2$TRZCzPhCz** using a) mCBP and b) mCP as a host matrix, showing clear CT emission.

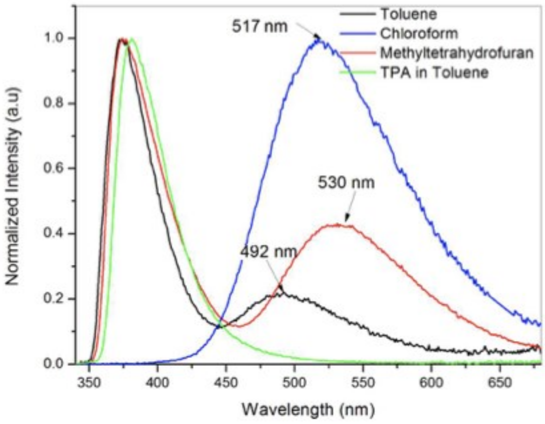


Figure S6. Solvent dependent emission spectra from the 1 to 1 CT complex formed between TPA and TRZ (1:1 ratio).

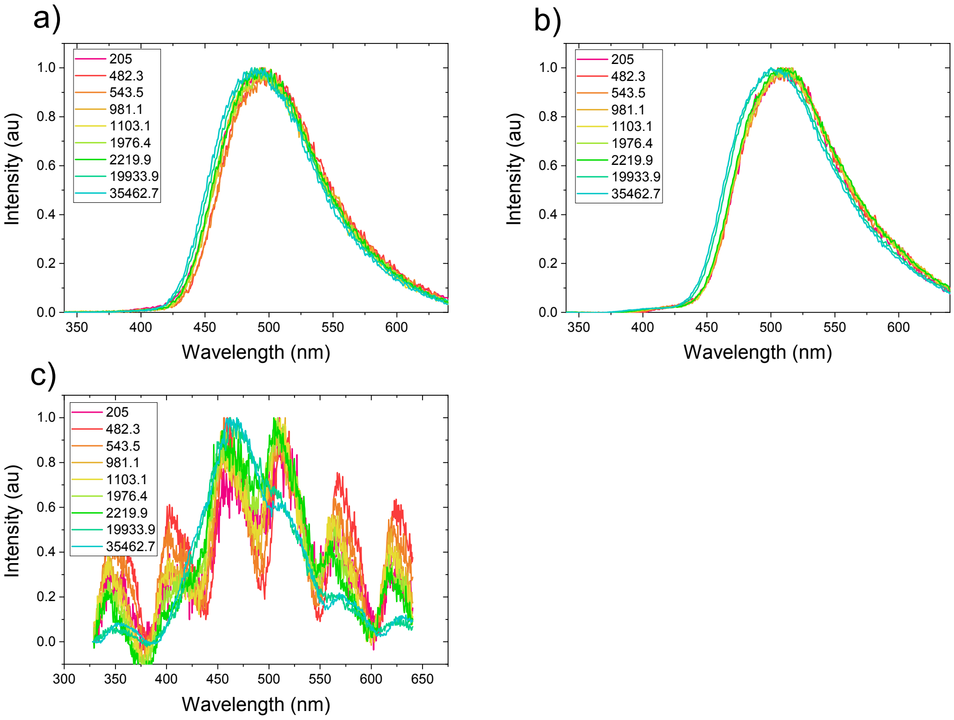


Figure S7. Evolution of the DF emission component from films (a) **Ph$_3$TRZCzTPA** , (b) **Ph$_2$TRZCzTPA** and (c) **Ph$_2$TRZCzPhCz**, using a Zeonex matrix, measured at 300 K, legends in ns.

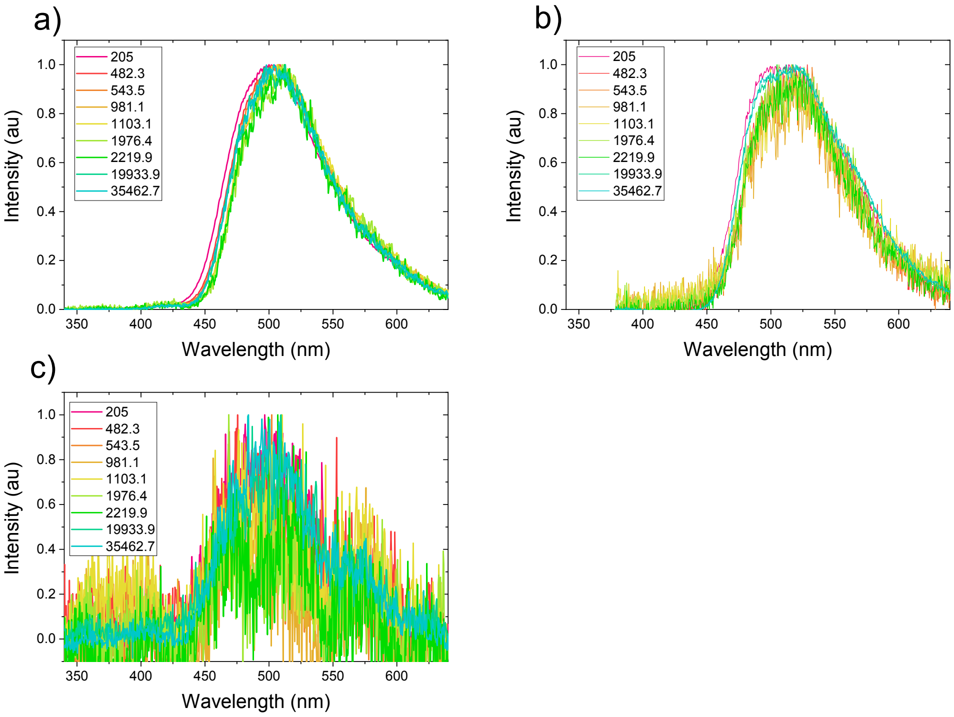


Figure S8. Evolution of the DF emission component from films (a) **Ph_3TRZCzTPA** , (b) **Ph_2TRZCzTPA** and (c) **Ph_2TRZCzPhCz**, using a Zeonex matrix, measured at 80 K, legends in ns.

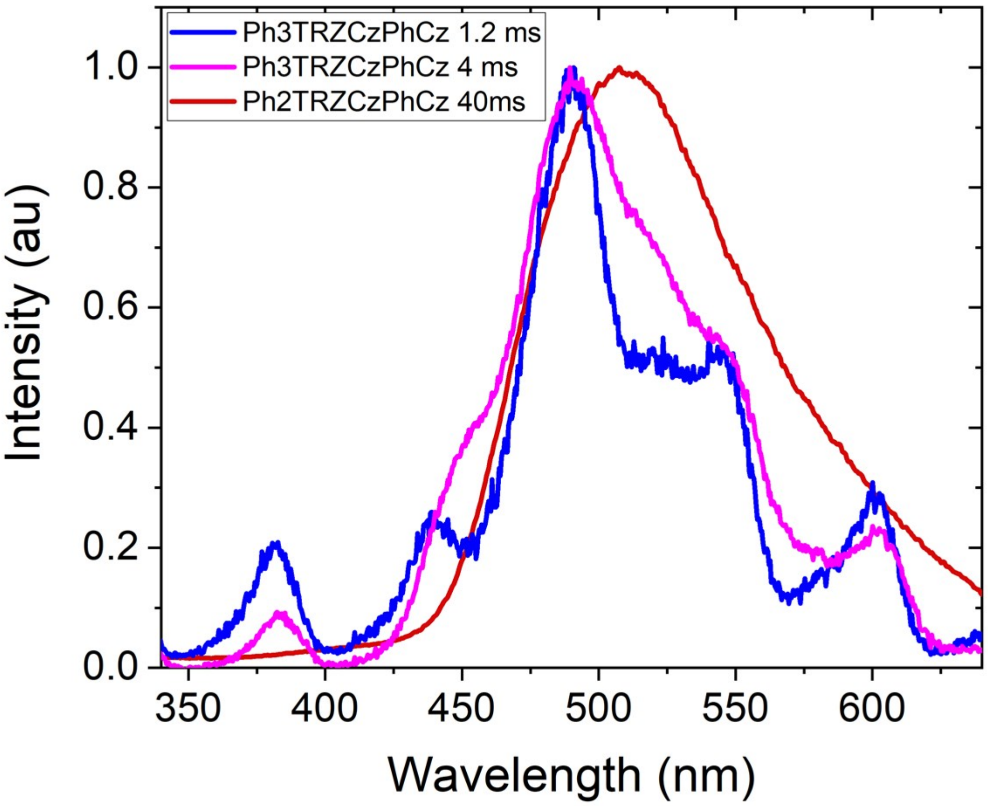


Figure S9. Comparison of the time evolution of the phosphorescence observed in **Ph_3TRZCzPhCz** in zeonex, showing time dependent dual phosphorescence.

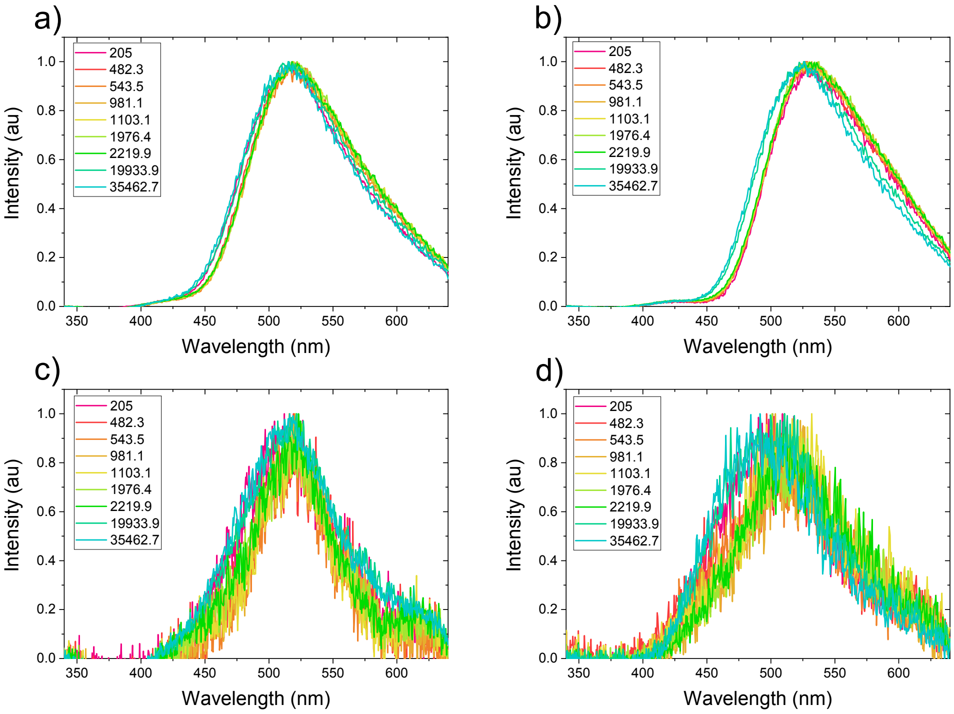


Figure S10. Evolution of the DF emission component from films (a) **Ph_3TRZCzTPA** , (b) **Ph_2TRZCzTPA**, (c) **Ph_2TRZCzPhCz** and (d) **Ph_3TRZCzPhCz** , using a DPEPO matrix, measured at 300 K, legends in ns.

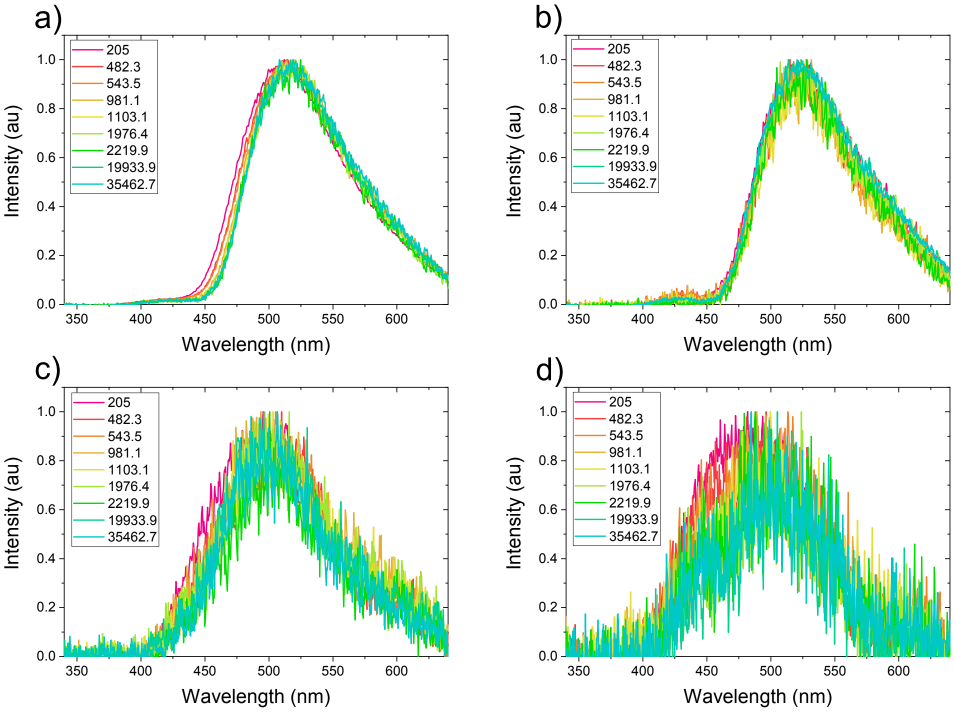
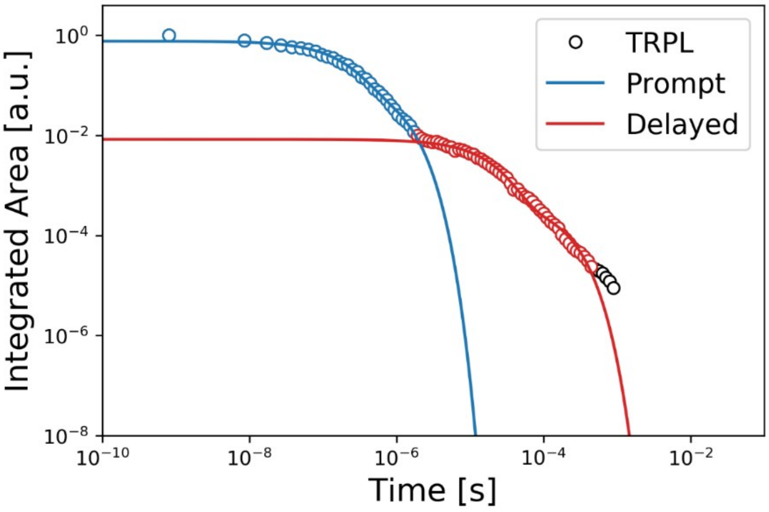
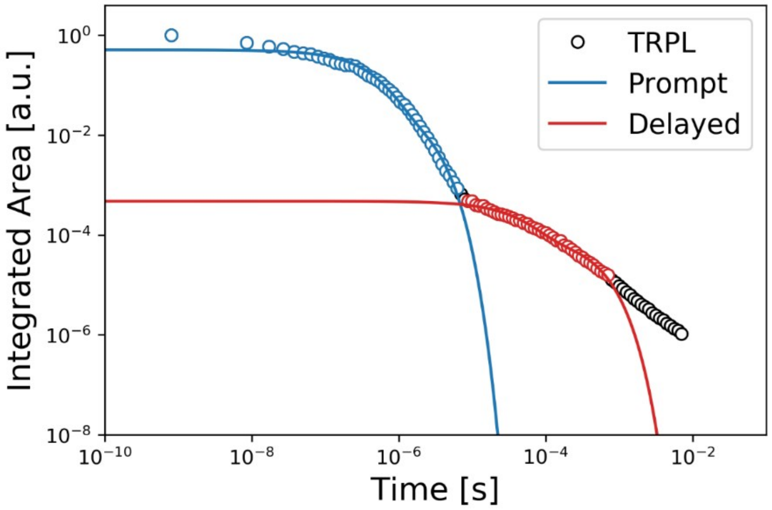


Figure S11. Evolution of the DF emission component from films (a) **Ph_3TRZCzTPA** , (b) **Ph_2TRZCzTPA**, (c) **Ph_2TRZCzPhCz** and (d) **Ph_3TRZCzPhCz** , using a DPEPO matrix, measured at 80 K, legends in ns.



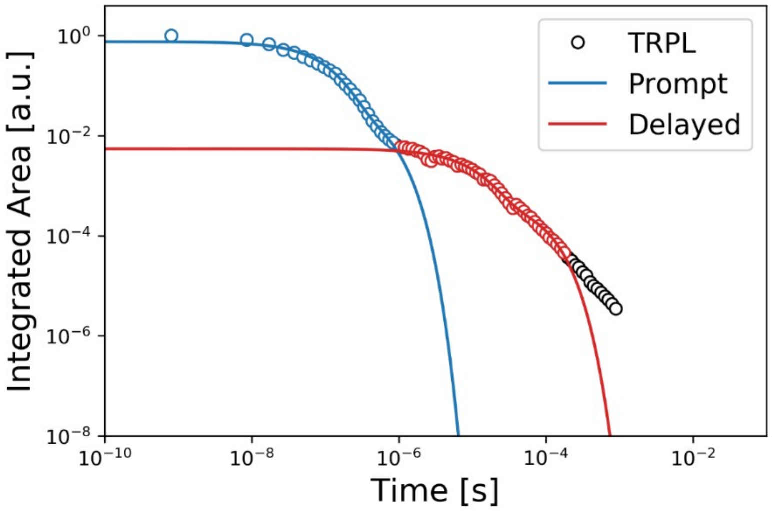
K_F	K_F Error	K_{ISC}	K_{ISC} Error	K_{rISC}	K_{rISC} Error
1558533	36695.3	1817959	473.5009	63112.24	1701.811

Figure S12. Decay and constant rates obtained using a kinetic model, for **Ph_3TRZCzTPA** using a DPEPO matrix at 300K.



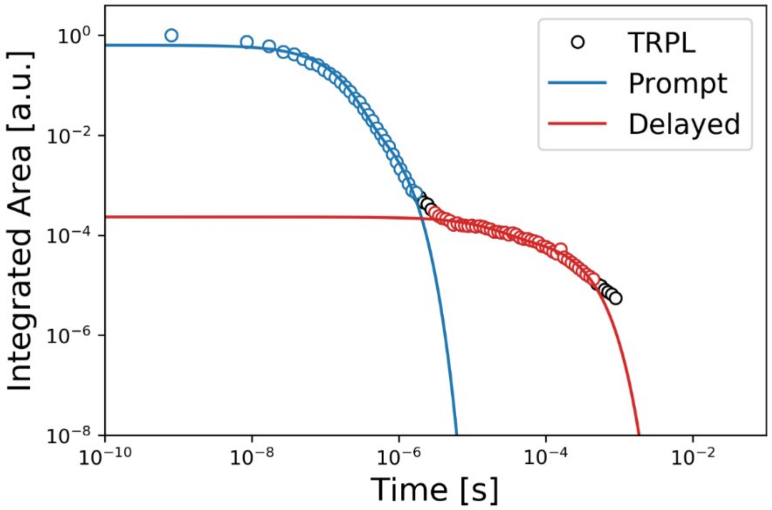
K_F	K_F Error	K_{ISC}	K_{ISC} Error	K_{rISC}	K_{rISC} Error
1520971	216202.1	1000000	1363.991	13759.69	1939.198

Figure S13. Decay and constant rates obtained using a kinetic model, for **Ph$_3$TRZCzTPA** using a DPEPO matrix at 80 K.



K_F	K_F Error	K_{ISC}	K_{ISC} Error	K_{rISC}	K_{rISC} Error
3715694	305297.2	4120833	287074.6	100360.2	6813.977

Figure S14. Decay and constant rates obtained using a kinetic model, for **Ph$_2$TRZCzTPA** using a DPEPO matrix at 300 K.



K_F	K_F Error	K_{ISC}	K_{ISC} Error	K_{rISC}	K_{rISC} Error
3515396	42875.89	1447948	121364.1	9122.475	717.5389

Figure S15. Decay and constant rates obtained using a kinetic model, for **Ph_2TRZCzTPA** using a DPEPO matrix at 80 K.

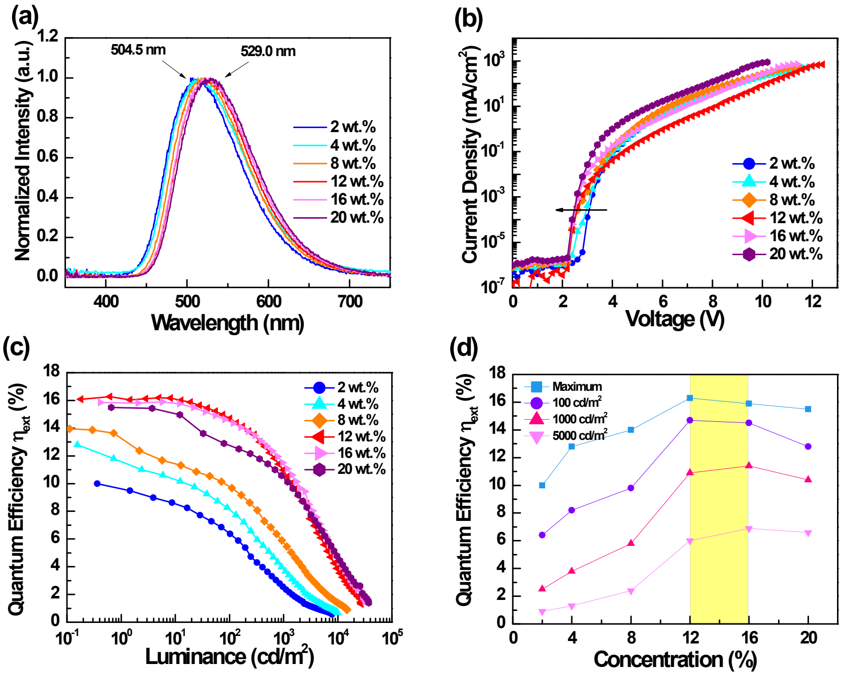


Figure S16. (a) EL spectra of Device A with different doping concentrations; (b) current density-voltage (*J*-*V*) curves; (c) external quantum efficiency vs. luminance; (d) external quantum efficiency vs. concentration for Device A with different **Ph_2TRZCzTPA** doping concentrations.

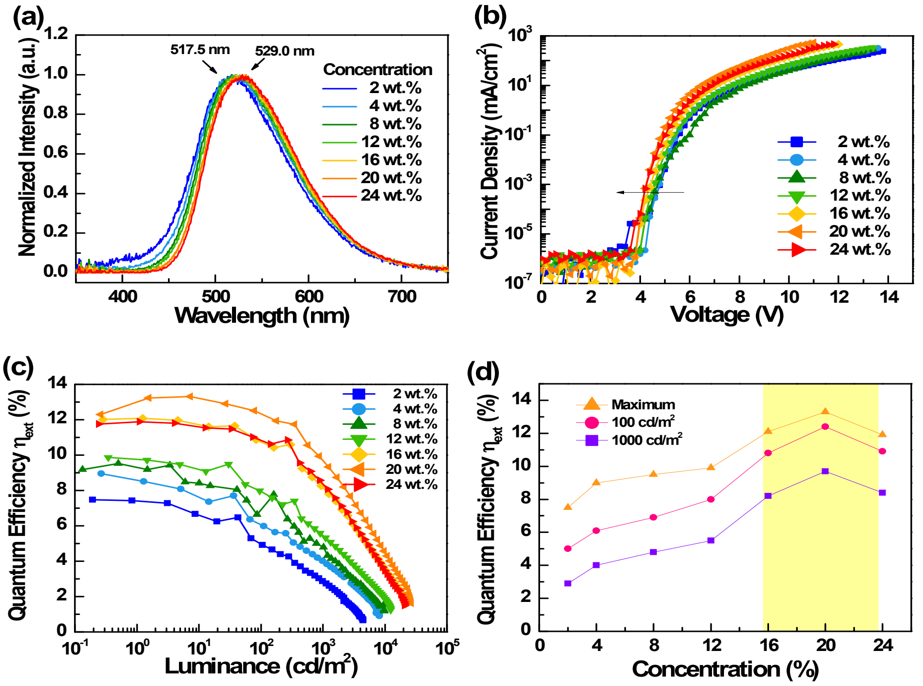


Figure S17. (a) EL spectra of Device A with different doping concentrations; (b) current density-voltage (*J*-*V*) curves; (c) external quantum efficiency vs. luminance; (d) external quantum efficiency vs. concentration for Device B with different **Ph_3TRZCzTPA** doping concentrations.

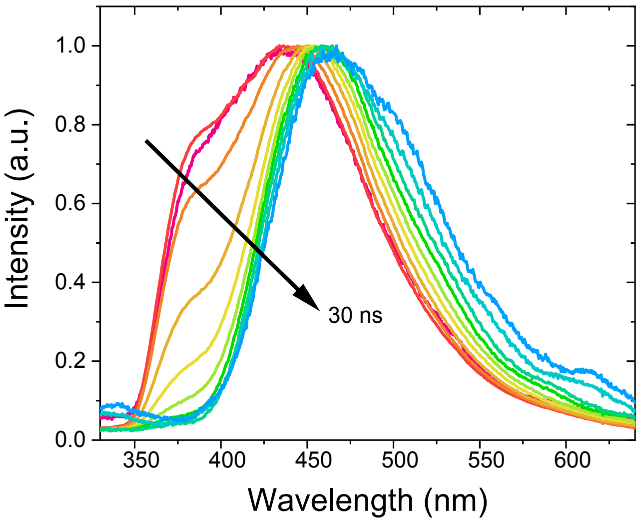


Figure S18. First 30 ns of the prompt emission of **Ph_2TRZCzPhCz** at RT using a zeonex matrix.

Supplementary Tables

Table S1. X-ray data and structure refinement parameters for **Ph_2TRZCzTPA**, **Ph_3TRZCzTPA**, **Ph_2TRZCzPhCz** and **Ph_3TRZCzPhCz** crystals.

	Ph_2TRZCzTPA	**Ph_3TRZCzTPA**	**Ph_2TRZCzPhCz**	**Ph_3TRZCzPhCz**
Empirical formula	$C_{45}H_{31}N_5$	$C_{51}H_{35}N_5$	$C_{45}H_{29}N_5$	$C_{51}H_{33}N_5$
Formula weight	641.75	717.84	639.73	715.82
Temperature	200(2) K	200(2) K	200(2) K	200(2) K
Wavelength	1.54178 Å	1.54178 Å	1.54178 Å	1.54178 Å
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P-1	Cc
a /Å	10.9783(5)	9.9987(3)	9.2085(2)	11.1684(3)
b /Å	11.3335(5)	12.2565(3)	11.6926(2)	47.1830(14)
c /Å	14.5816(7)	16.4287(4)	15.4348(3)	8.2066(2)
α /°	72.0231(16)	77.6247(7)	91.4859(7)	90
β /°	74.3813(17)	74.5072(7)	97.3274(7)	122.0067(7)
γ /°	81.0156(18)	73.7224(7)	104.3337(7)	90
Volume	1656.69(13) $Å^3$	1841.11(8) $Å^3$	1594.14(5) $Å^3$	3667.15(17) $Å^3$
Z	2	2	2	4
Density (calculated)	1.286 Mg/m^3	1.295 Mg/m^3	1.333 Mg/m^3	1.297 Mg/m^3
Absorption coefficient	0.595 mm^{-1}	0.595 mm^{-1}	0.618 mm^{-1}	0.597 mm^{-1}
F (000)	672	752	668	1496
Reflections collected	11146	14382	10684	13062
Independent reflections	6256 [R(int) = 0.0169]	7536 [R(int) = 0.0173]	6001 [R(int) = 0.0136]	7209 [R(int) = 0.0203]
Goodness-of-fit on F^2	1.042	1.025	1.054	1.068
R_1, wR_2 [I>2σ(I)]	0.0367, 0.0923	0.0370, 0.0960	0.0345, 0.0841	0.0438, 0.1142
R_1, wR_2 [all data]	0.0416, 0.0969	0.0393, 0.0986	0.0396, 0.0879	0.0444, 0.1157
Largest diff. peak and hole	0.222, -0.188 e.$Å^{-3}$	0.208, -0.204 e.$Å^{-3}$	0.222, -0.159 e.$Å^{-3}$	0.362, -0.220 e.$Å^{-3}$
CCDC number	1499013	2043941	2043942	2043943

Table S2. The data of theoretical DFT/TDTFT calculations

	HOMO (eV)	LUMO (eV)	λ_{S_1} (nm)	S_1 (eV)	T_1 (eV)	ΔE_{ST} (eV)
Ph$_2$TRZCzTPA	-5.02	-2.41	496	2.54	2.44	0.10
Ph$_3$TRZCzTPA	-5.08	-2.15	447	2.77	2.57	0.20
Ph$_2$TRZCzPhCz	-5.4	-2.25	417	2.97	2.92	0.05
Ph$_3$TRZCzPhCz	-5.46	-2.20	388	3.20	2.56	0.64

Table S3. EL characteristics of device A with different **Ph$_2$TRZCzTPA** doping concentrations.

conc. [wt.%]	V_{on}[a] [V]	L_{max} [cd/m^2]	EQE [%]	CE [cd/A]	PE [lm/W]	λ_{Peak}[d] [nm]	CIE[d] [x,y]
2	3.3	7,893 (11.6 V)	10.0[b], 6.4[c]	28.9[b], 18.6[c]	28.3[b], 12.2[c]	504.5	(0.28, 0.49)
4	3.2	9,907 (11.8 V)	12.8[b], 8.2[c]	37.7[b], 24.0[c]	39.5[b], 16.3[c]	513.5	(0.30, 0.50)
8	3.0	14,865 (11.4 V)	14.0[b], 9.8[c]	42.0[b], 29.5[c]	50.8[b], 21.4[c]	517.5	(0.30, 0.53)
12	2.9	27,158 (12.4 V)	16.3[b], 14.7[c]	49.7[b], 44.9[c]	59.3[b], 28.3[c]	521.5	(0.32, 0.55)
16	2.7	32,094 (11.4 V)	15.9[b], 14.5[c]	49.0[b], 44.7[c]	59.1[b], 34.2[c]	523.0	(0.33, 0.54)
20	2.6	37,385 (10.2 V)	15.5[b], 12.8[c]	47.7[b], 39.4[c]	57.7[b], 35.8[c]	529.0	(0.34, 0.55)

[a]Turn-on voltage measured at 1 cd/m^2; [b]Maximum Efficiency; [c]Measured at 10^2 cd/m^2; [d]Measured at 10^3 cd/m^2.

Table S4. EL characteristics of device B with different **Ph$_3$TRZCzTPA** doping concentrations.

conc. [wt.%]	V_{on}[a] [V]	L_{max} [cd/m^2]	EQE [%]	CE [cd/A]	PE [lm/W]	λ_{Peak}[d] [nm]	CIE[d] [x,y]
2	5.0	4,437 (13.8 V)	7.5[b], 5.0[c]	21.0[b], 14.0[c]	13.8[b], 7.1[c]	517.5	(0.29, 0.47)
4	4.9	8,183 (13.6 V)	9.0[b], 6.1[c]	25.5[b], 17.3[c]	16.7[b], 9.1[c]	517.5	(0.31, 0.50)
8	4.9	9,785 (13.4 V)	9.5[b], 6.8[c]	27.8[b], 20.0[c]	18.3[b], 9.7[c]	521.5	(0.32, 0.51)
12	4.7	12,367 (13.4 V)	9.9[b], 8.0[c]	29.0[b], 23.4[c]	19.8[b], 12.6[c]	523.0	(0.32, 0.52)
16	4.5	21,499 (12.0 V)	12.1[b], 10.8[c]	36.4[b], 32.5[c]	25.9[b], 18.8[c]	526.5	(0.33, 0.53)

20	4.4	26,434 (11.0 V)	13.3[b], 12.4[c]	40.3[b], 37.5[c]	28.6[b], 23.3[c]	529.0	(0.34, 0.54)
24	4.4	20,679 (11.8 V)	11.9[b], 10.9[c]	35.7[b], 32.6[c]	26.4[b], 19.4[c]	529.0	(0.34, 0.54)

[a] Turn-on voltage measured at 1 cd/m^2; [b] Maximum Efficiency; [c] Measured at 10^2 cd/m^2; [d] Measured at 10^3 cd/m^2.

References

1. Banerjee, A.; Maji, M. S.; A Brønsted Acid Catalyzed Cascade Reaction for the Conversion of Indoles to α-(3-Indolyl) Ketones by Using 2-Benzyloxy Aldehydes *Chem. Eur. J.* **2019**, *25*, 11521.