Electronic Supporting Information

Tuning the Singlet-Triplet Energy Gap of AIE Luminogens: Crystallization-Induced Room Temperature Phosphorescence and Delay Fluorescence, Tunable Temperature Response, Highly Efficient Non-Doped Organic Light-Emitting Diodes

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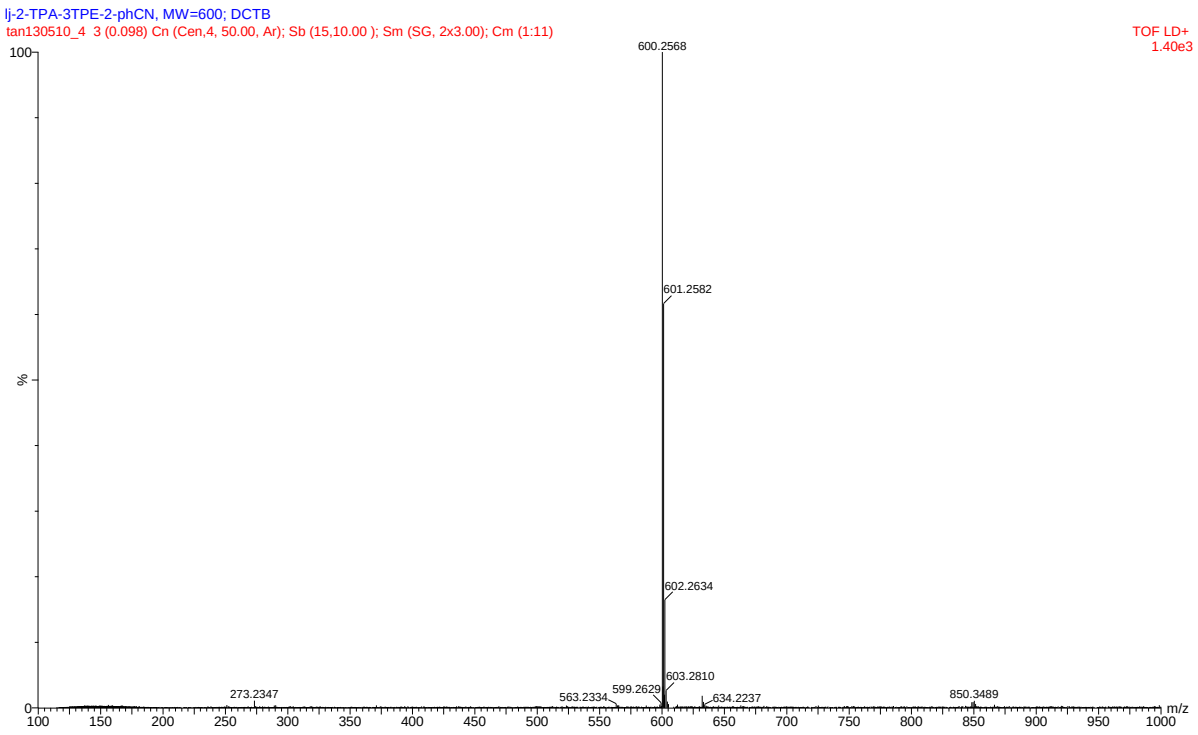

Fig. S1 MS spectrum of *o*-TPA-3TPE-*o*-PhCN.

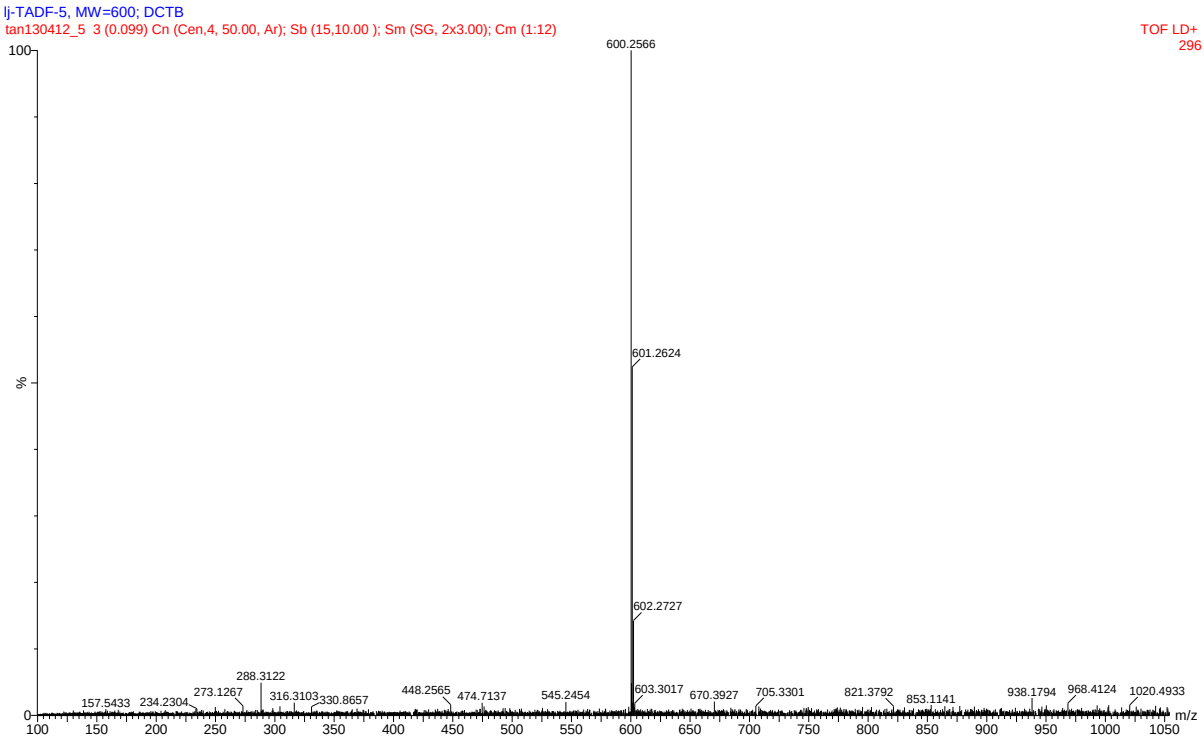

Fig. S2 MS spectrum of *o*-TPA-3TPE-*p*-PhCN.

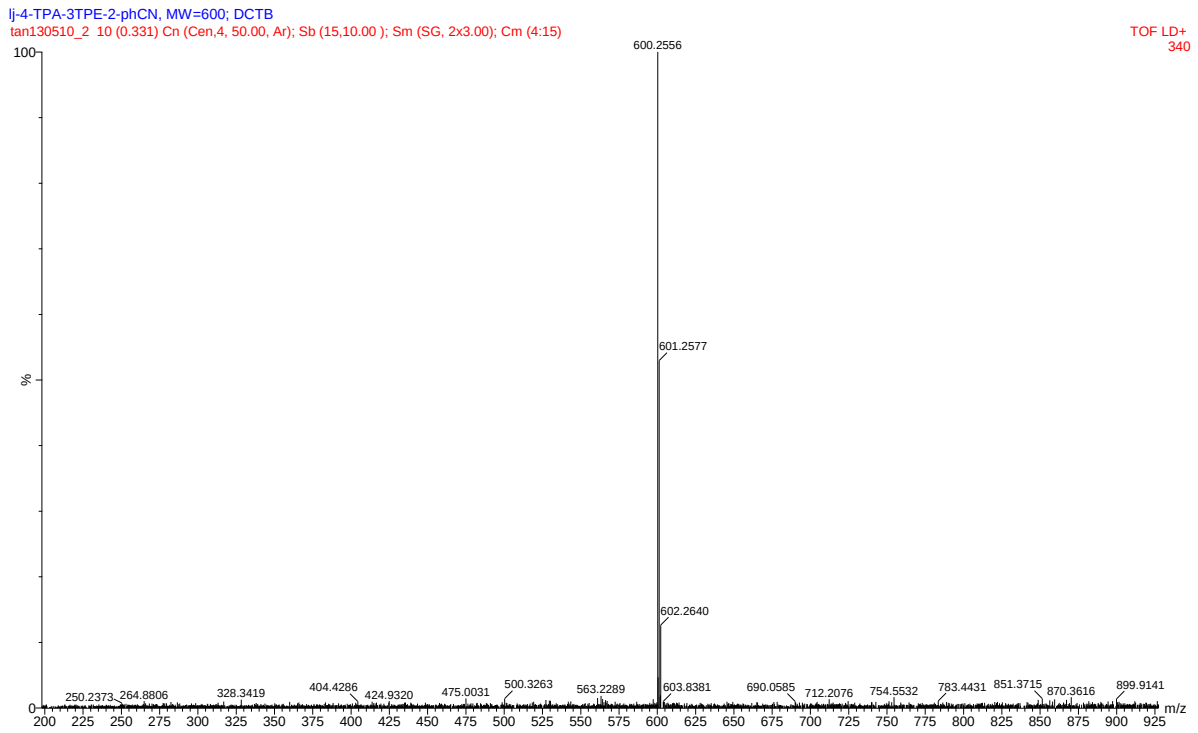

Fig. S3 MS spectrum of *p*-TPA-3TPE-*o*-PhCN.

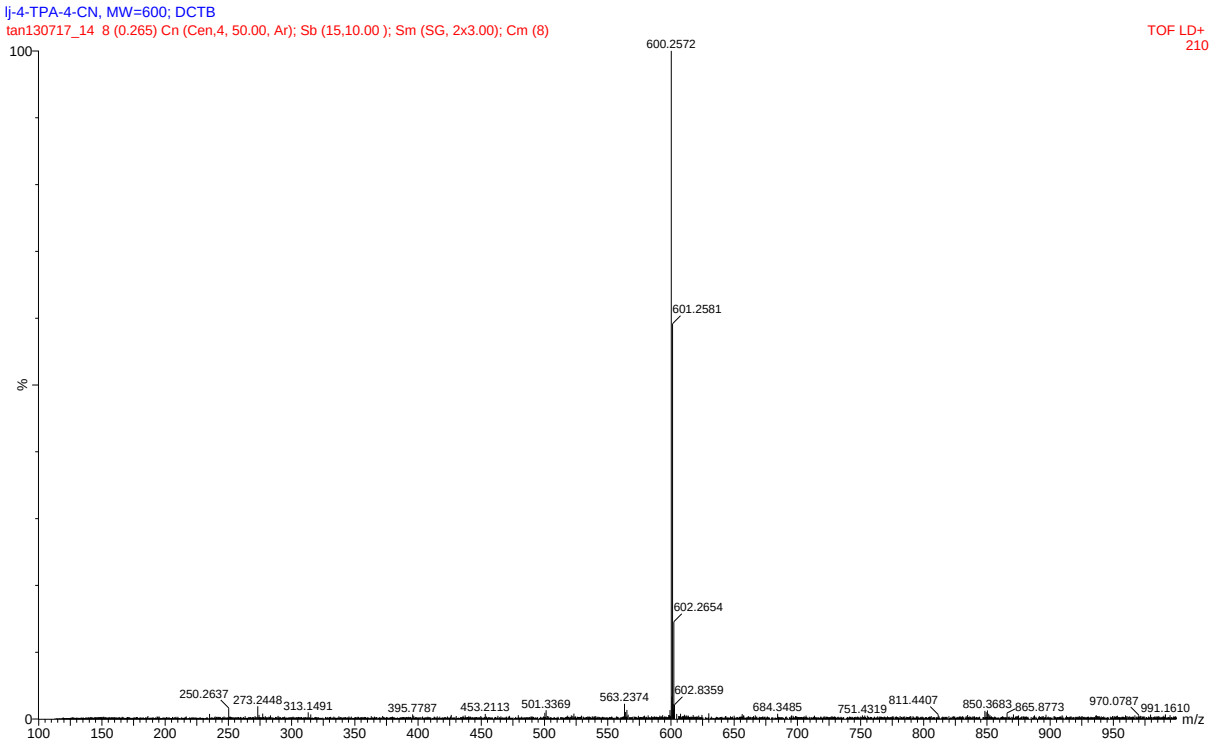

Fig. S4 MS spectrum of *p*-TPA-3TPE-*p*-PhCN.

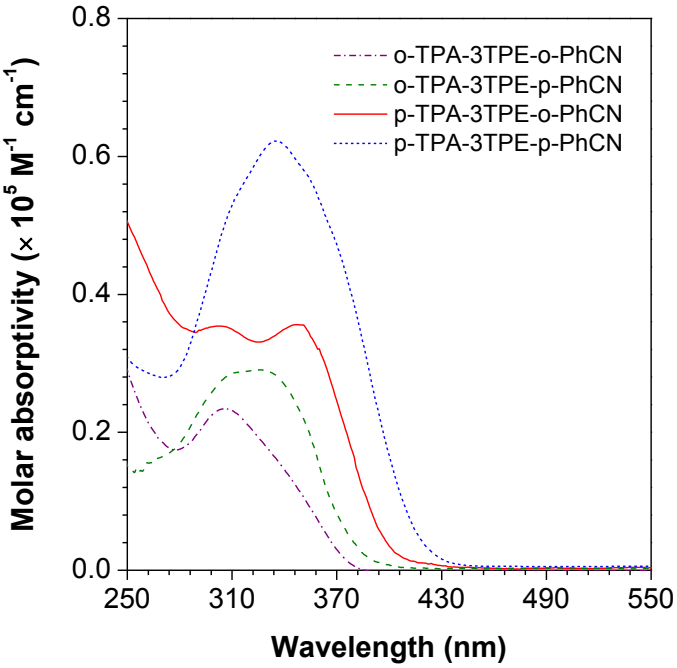

Fig. S5 UV absorption of D-3TPE-A molecules in THF.

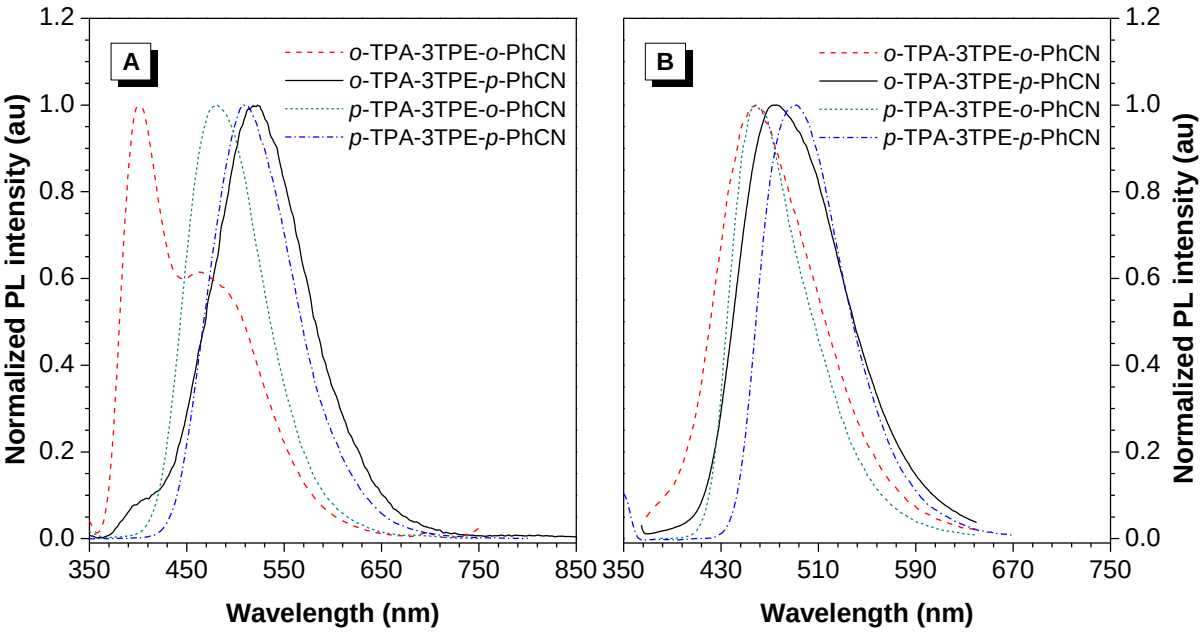

Fig. S6 Normalized PL spectra of D-3TPE-A molecules in (A) THF solution and (B) film state.

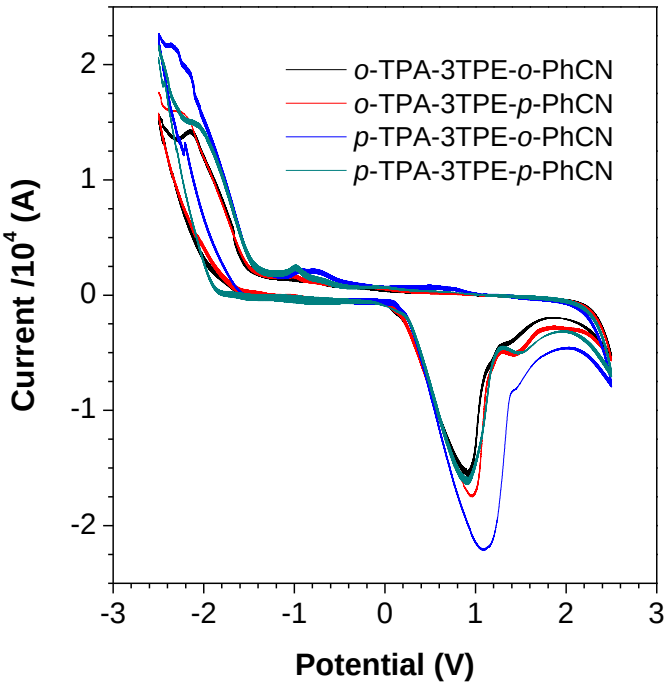

Fig. S7 Cyclic voltammogram of D-3TPE-A molecules measured in dichloromethane containing 0.1 M tetra-n-butylammonium hexafluorophosphate. Scan rate: 100 mV/s.

Table S1. Optical and thermal properties of D-3TPE-A molecules

	λ_{abs} (nm)	λ_{em} (nm)		Φ_F (%)	T_g/T_d	HOMO/LUMO	E_{opt}
	Soln	Soln	Film (τ)	Powder	(^oC)	(eV)	(eV)
o-TPA-3TPE-*o*-PhCN	306	402, 464	459 (7.2 ns)	23	68/340	-4.56/-1.28	3.28
o-TPA-3TPE-*p*-PhCN	324	520	474 (3.7 ns)	32	85/388	-4.59/-1.38	3.21
p-TPA-3TPE-*o*-PhCN	302, 348	488	459 (6.2 ns)	40	64/350	-4.62/-1.50	3.12
p-TPA-3TPE-*p*-PhCN	334	508	490 (5.7 ns)	42	73/356	-4.65/-1.73	2.92

Abbreviations: Soln = solution (10 μM in THF), λ_{em} = PL maximum wavelength, Φ_F = absolute fluorescence quantum yield measured using an integrating sphere, T_g = glass transition temperature, T_d = onset decomposition temperature, HOMO is estimated from the onset oxidation potential in cyclic voltammogram, LUMO is obtained by subtraction of the optical band gap from the HOMO energy level, E_{opt} = energy band gap determined from the onset of absorption spectra.

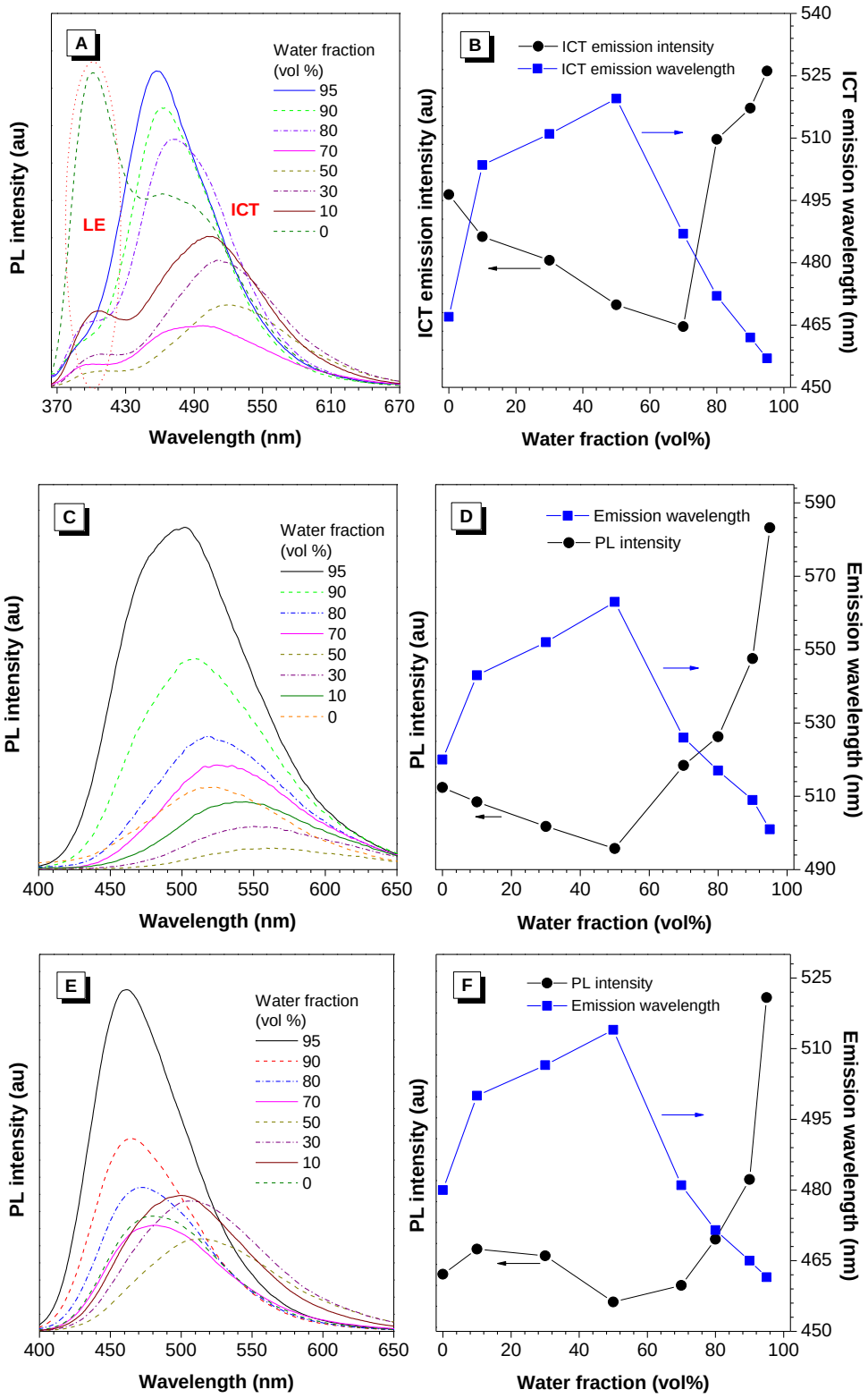

Fig. S8 PL spectra of (A) *o*-TPA-3TPE-*o*-PhCN, (C) *o*-TPA-3TPE-*p*-PhCN, and (E) *p*-TPA-3TPE-*o*-PhCN in THF/water mixtures with different water fractions at room temperature, excitation wavelength: 305, 340, and 350 nm, respectively. Dye concentration: 10 μM. Plots of PL intensity and emission wavelength versus water fraction of (B) *o*-TPA-3TPE-*o*-PhCN, (D) *o*-TPA-3TPE-*p*-PhCN, and (F) *p*-TPA-3TPE-*o*-PhCN. LE: local excited state emission; ICT: intramolecular charge transfer emission.

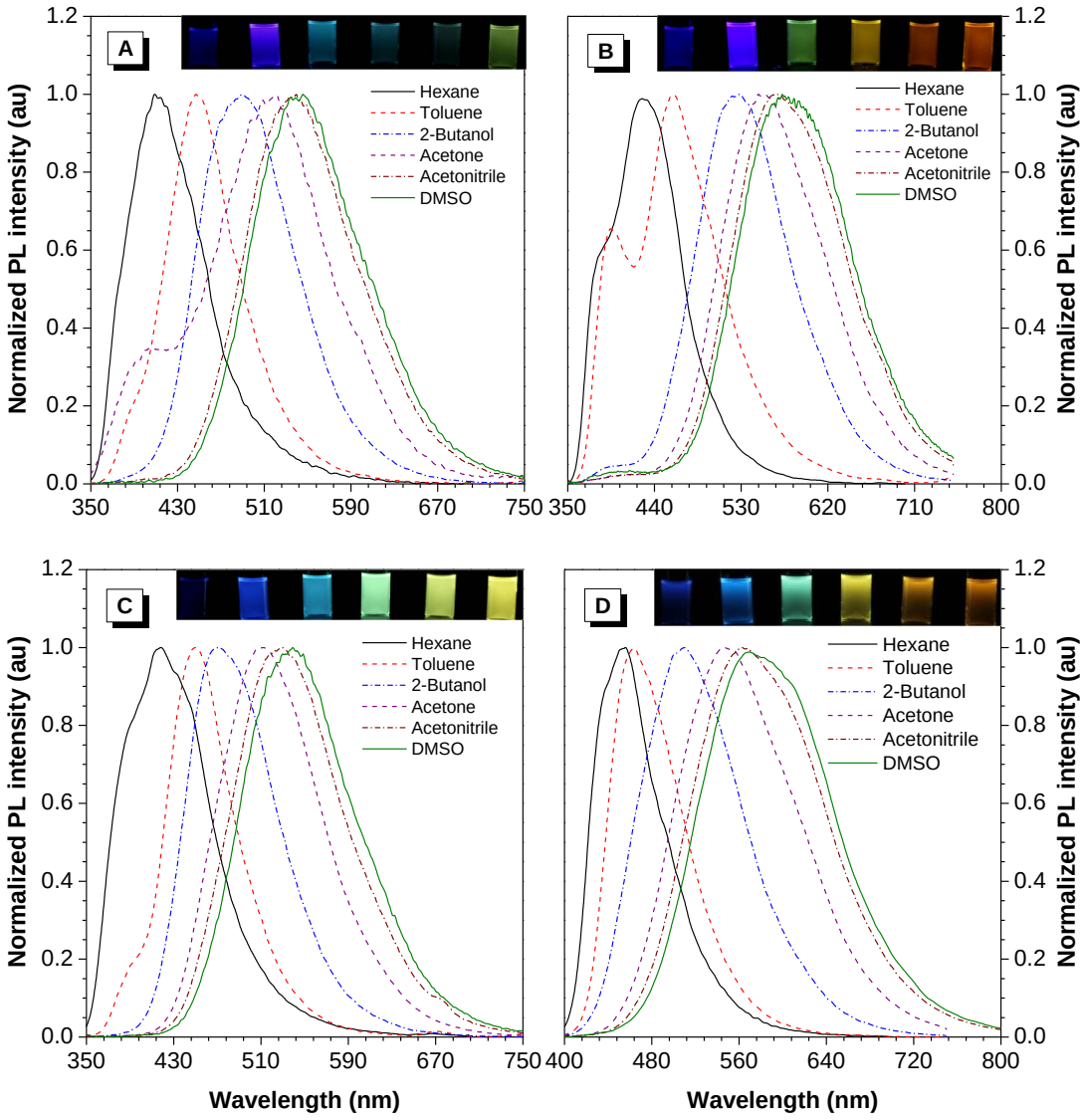

Fig. S9 Normalized PL spectra of (A) *o*-TPA-3TPE-*o*-PhCN, (B) *o*-TPA-3TPE-*p*-PhCN, (C) *p*-TPA-3TPE-*o*-PhCN and (D) *p*-TPA-3TPE-*p*-PhCN in different solvents. Concentration: 10 μM.

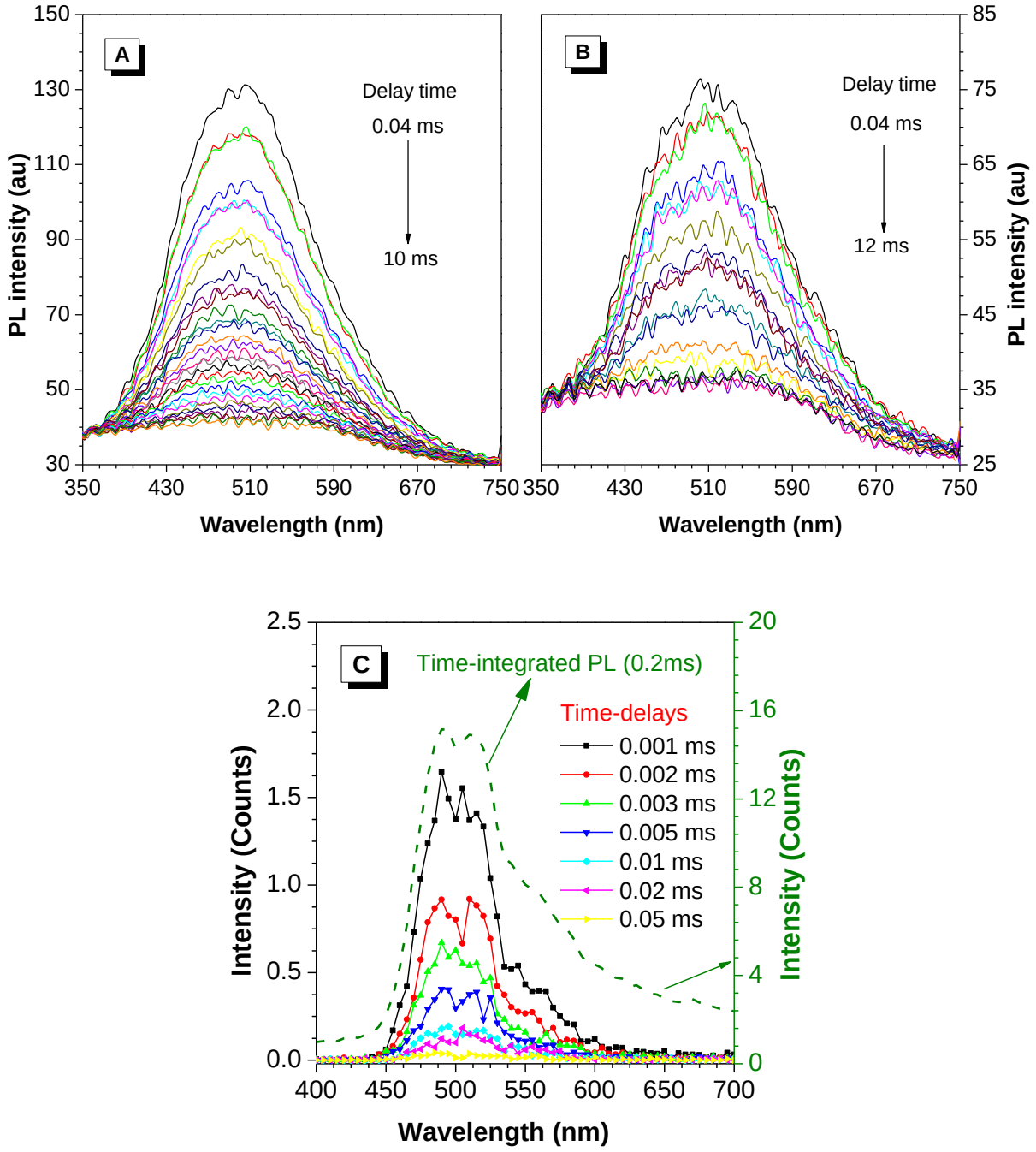

Fig. S10 Emission spectra with different delay times of crystals of (A) *o*-TPA-3TPE-*o*-PhCN, (B) *o*-TPA-3TPE-*p*-PhCN and (C) *p*-TPA-3TPE-*p*-PhCN at room temperature. (A) and (B) were obtained by time window method using a Perkin-Elmer LS 55 spectrofluorometer, (C) was measured via a time-resolved fluorescence spectrometer with the time resolution of 1 μs.

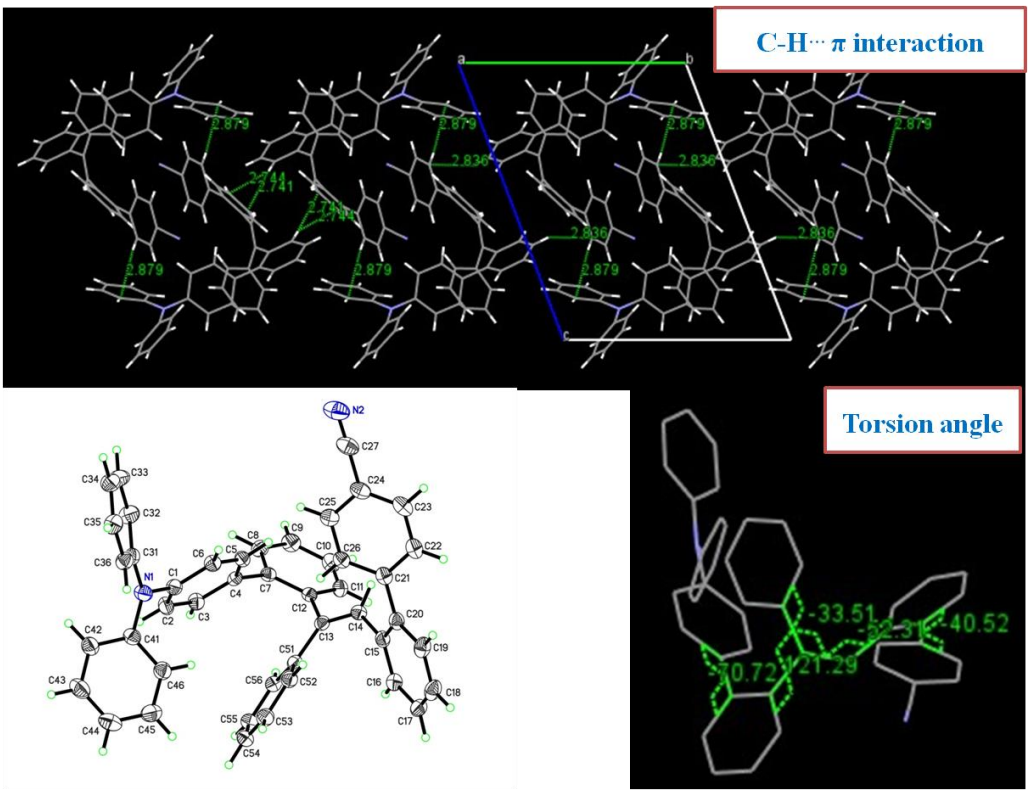

Fig. S11. Single crystal structure of *o*-TPA-3TPE-*o*-PhCN.

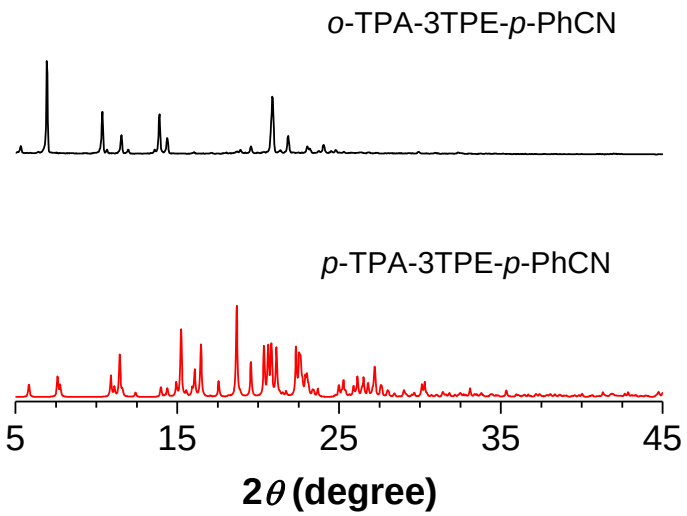

Fig. S12 Powder XRD patterns for microcrystals of *o*-TPA-3TPE-*p*-PhCN and *p*-TPA-3TPE-*p*-PhCN at room temperature, respectively.

Table S2. Crystal data and structure refinement for *o*-TPA-3TPE-*o*-PhCN.

Identification code	*o*-TPA-3TPE-*o*-PhCN	
Empirical formula	C45 H32 N2	
Formula weight	600.73	
Temperature	173.0(4) K	
Wavelength	1.5418 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.4790(3) Å	α= 68.455(6) °.
	b = 12.9948(8) Å	β= 84.347(4) °.
	c = 16.2781(11) Å	γ = 73.048(4) °.
Volume	1595.69(16) $Å^3$	
Z	2	
Density (calculated)	1.250 Mg/m^3	
Absorption coefficient	0.553 mm^{-1}	
F(000)	632	
Crystal size	0.40 x 0.18 x 0.05 mm^3	
Theta range for data collection	3.80 to 66.99 °.	
Index ranges	-10<=h<=6, -14<=k<=15, -19<=l<=19	
Reflections collected	9193	
Independent reflections	5563 [R(int) = 0.0333]	
Completeness to theta = 66.50 °	98.05 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.71036	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5563 / 0 / 424	
Goodness-of-fit on F^2	1.005	
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.1068	
R indices (all data)	R1 = 0.0469, wR2 = 0.1117	
Largest diff. peak and hole	0.198 and -0.172 e.$Å^{-3}$	

Table S3. Optical properties of D-3TPE-A molecules in *n*-hexane at 77 K and in crystals at RT

	λ_{em} (nm) (*n*-hexane at 77 K)		λ_{em} (nm) (Crystals at RT)		ΔE_{ST} (eV)
	FL	Delayed	FL	Delayed (τ)	
o-TPA-3TPE-*o*-PhCN	410	510	422	503 (105 μs)	0.59
o-TPA-3TPE-*p*-PhCN	430	510	452	506 (86 μs)	0.45
p-TPA-3TPE-*o*-PhCN	420	495	----	----	0.45
p-TPA-3TPE-*p*-PhCN	456	495	493	495 (14 μs)	0.21

λ_{em} = emission wavelength, ΔE_{ST} is estimated from the energy gap between the λ_{em} of fluorescence (FL) and phosphorescence (delayed) at 77 K.

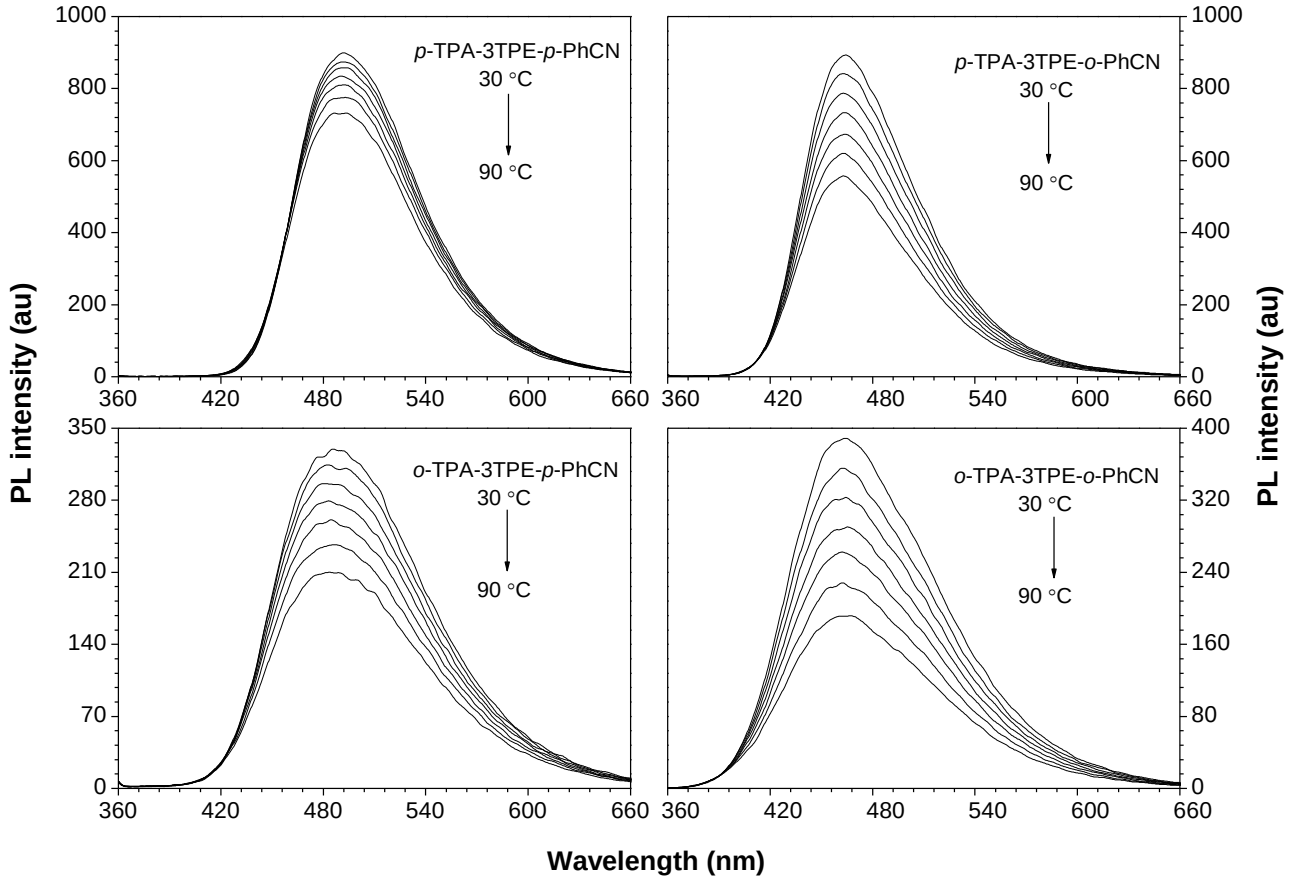

Fig. S13 Emission spectra of D-3TPE-A molecules in the thin film at different temperatures.

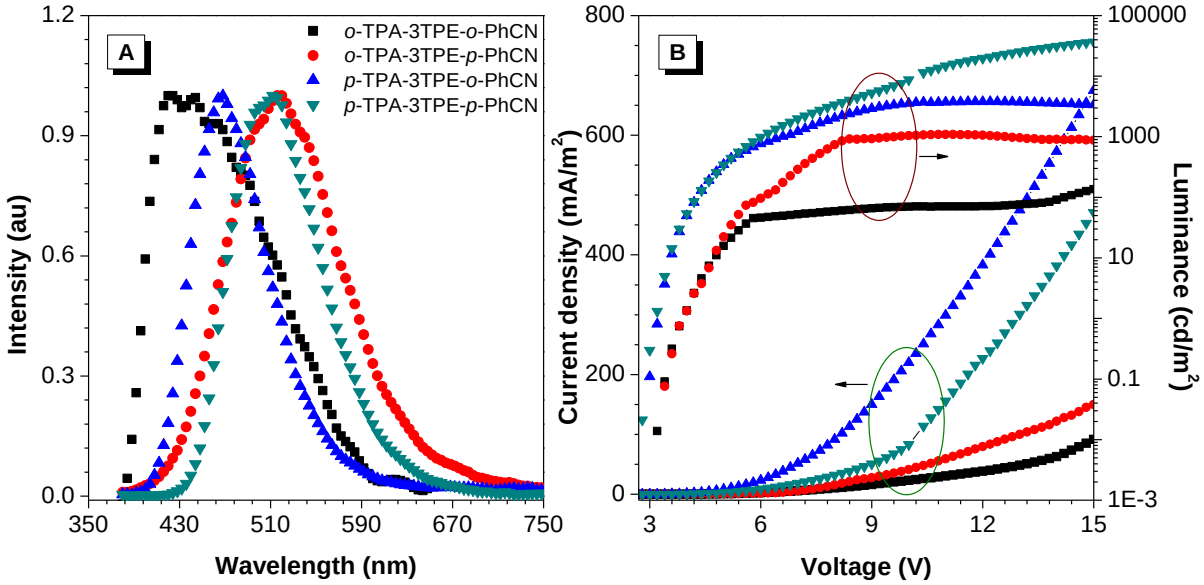

Fig. S14 (A) EL spectra and (B) change in luminance and current density with the applied bias of the EL devices based on D-3TPE-A molecules. The arrows indicate the attribution of the curves to the coresponding ordinates.

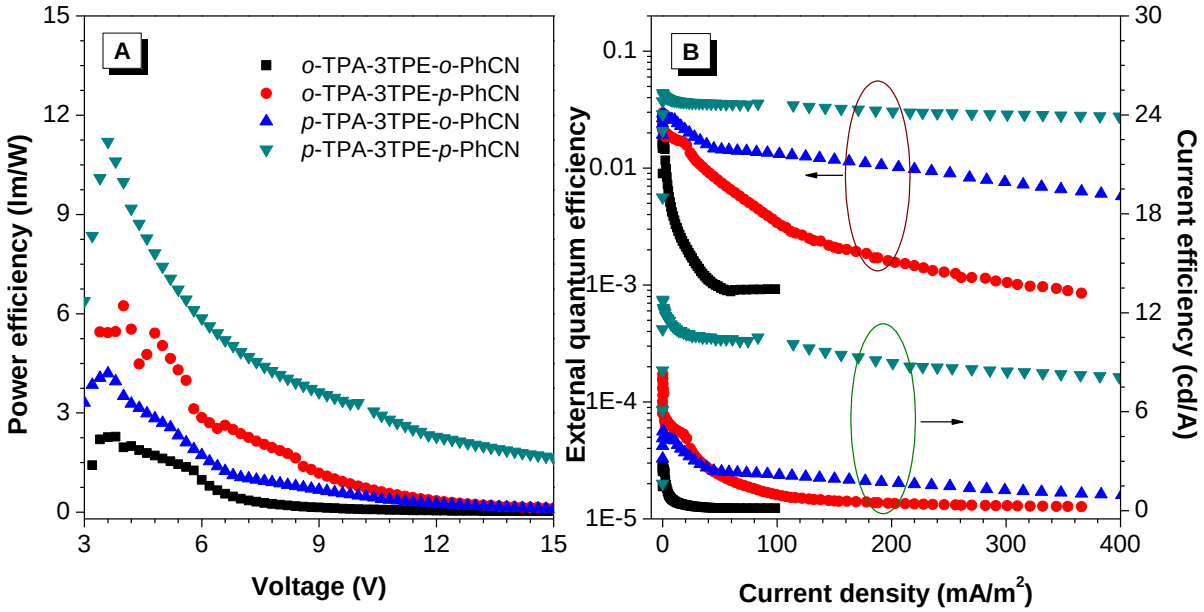

Fig. S15 Plots of (A) power efficiency *versus* voltage and (B) external quantum efficiency and current efficiency *versus* current density of the EL devices based on D-3TPE-A molecules. The arrows indicate the attribution of the curves to the coresponding ordinates.

Synthetic Procedures

***Preparation of o- or p-Triphenylaminobenzophenone* (*o*- or *p*-TPABP)**. Into a 150 mL two-necked round-bottom flask with a reflux condenser were placed 0.16 g (0.14 mmol) of $Pd(PPh_3)_4$, 2.40 g (8.3 mmol) of 4-(diphenylamino)phenylboronic acid and 1.81 g (6.92 mmol) of *o*,-bromobenzophenone (or *p*-bromobenzophenone). The flask was evacuated under vacuum and purged in dry nitrogen for three times. 60 mL of THF was then added, followed by the addition of 8 mL of saturated K_2CO_3 aqueous solution. The mixture was refluxed for 24 h, and then extracted with dichloromethane three times. The organic layers were combined and washed with brine twice. After solvent evaporation under reduced pressure, the crude product was purified on a silica-gel column using dichloromethane/hexane mixture (1:10 v/v) as eluent.

Characterization data of o-TPABP: A yellow solid was obtained in 70% yield. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 7.65 (m, 1H), 7.55 (m, 4H), 7.44 (d, 2H), 7.34 (t, 2H), 7.24 (t, 4H), 7.07 (d, 2H), 6.99 (t, 2H), 6.75 (d, 6H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 197.66, 146.42, 146.06, 139.43, 137.81, 136.57, 133.77, 132.20, 130.38, 129.53, 128.91, 128.77, 128.72, 128.39, 127.68, 126.80, 123.28, 122.90, 122.36. HRMS (MALDI-TOF): *m*/*z* 425.1784 (M+, calcd 425.1780).

Characterization data of p-TPABP: A yellow solid was obtained in 86% yield. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 7.79 (t, 4H), 7.74 (d, 2H), 7.67 (m, 3H), 7.56 (t, 2H), 7.32 (t, 4H), 7.10–7.02 (m, 8H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 195.68, 148.15, 147.27, 144.15, 137.76, 135.50, 133.00, 132.56, 131.00, 130.16, 129.97, 129.03, 128.46, 126.50, 125.05, 124.11, 123.04. HRMS (MALDI-TOF): *m*/*z* 425.1770 (M+, calcd 425.1780).

Preparation of diethyl 2- or 4-bromobenzylphosphonate. Into a 15 mL Schlenk tube was placed 3 g (12 mmol) of 2 or 4-benzylbromide. The flask was evacuated under vacuum and purged with dry nitrogen for three times. 3 mL of triethyl phosphite was added, then the mixture was refluxed overnight. The solvent was evaporated under reduced pressure and the crude product was used for further reaction without purification.

Preparation of o or p-TPA-3TPE-o or p-Br. Into a 25 mL Schlenk tube were placed 0.2 g (1.8 mmol) of *t*-BuOK, 0.5 g (1.2 mmol) of *o* or *p*-TPABP. The flask was evacuated under vacuum and purged with dry nitrogen for three times. Then 0.38 g (1.5 mmol) of diethyl 2 or

4-bromobenzylphosphonate in 10 mL of THF was added, followed by stirring at 50 ℃ overnight. The mixture was quenched by 1 M NH_4Cl aqueous solution, and then extracted with dichloromethane three times. The organic layers were combined and washed with brine twice. After solvent evaporation under reduced pressure, the crude product was purified on a silica-gel column using hexane as eluent.

***Characterization data of o-TPA-3TPE-o-Br*:** A white solid was obtained in 79% yield. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 7.44 (t, 2H), 7.21 (m, 7H), 7.12–6.96 (m, 9H), 6.84 (d, 4H), 6.79 (t, 3H), 6.66 (d, 2H), 6.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 147.64, 146.23, 144.53, 142.45, 140.95, 139.34, 138.44, 136.35, 132.67, 131.31, 130.81, 130.64, 130.31, 130.05, 129.86, 129.34, 128.74, 127.97, 127.75, 127.69, 127.39, 124.54, 124.22, 124.02, 123.75, 123.12. HRMS (MALDI-TOF): *m*/*z* 579.1430 (M+2, calcd 577.1405).

Characterization data of o-TPA-3TPE-p-Br: A yellow solid was obtained in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.43–7.38 (m, 2H), 7.37–7.31 (m, 3H), 7.24–7.19 (m, 6H), 7.17–7.08 (m, 4H), 7.01–6.90 (m, 6H), 6.86–6.79 (m, 6H), 6.70 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 147.64, 147.57, 146.33, 146.15, 143.40, 142.86, 142.64, 141.02, 139.90, 138.26, 136.76, 136.55, 135.76, 131.43, 131.35, 131.28, 131.17, 130.55, 130.34, 130.07, 129.98, 129.85, 129.14, 128.46, 128.37, 127.81, 127.66, 127.34, 124.65, 124.16, 124.06, 123.76, 123.73, 123.12, 120.41. HRMS (MALDI-TOF): *m*/*z* 579.1393 (M+2, calcd 577.1405).

Characterization data of p-TPA-3TPE-o-Br: A yellow solid was obtained in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.58–7.55 (m, 2H), 7.52–7.47 (m, 3H), 7.44–7.41 (m, 2H), 7.36 (m, 2H), 7.33–7.26 (m, 6H), 7.20–7.11 (m, 8H), 7.07–7.04 (m, 2H), 6.95–6.92 (m, 2H), 6.85 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 147.59, 147.25, 144.06, 143.95, 142.84, 141.10, 140.10, 139.57, 139.40, 138.12, 138.03, 134.37, 134.32, 132.40, 131.40, 131.35, 131.12, 130.65, 129.25, 128.43, 128.28, 128.23, 128.06, 128.01, 127.88, 127.60, 127.50, 127.48, 127.11, 126.63, 126.51, 126.37, 126.24, 125.16, 124.47, 123.88, 123.71, 122.97, 122.92. HRMS (MALDI-TOF): *m*/*z* 579.1398 (M+2, calcd 577.1405).

Characterization data of p-TPA-3TPE-p-Br: A yellow solid was obtained in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.65 (m, 1H), 7.55 (m, 4H), 7.44 (d, 2H), 7.34 (t, 2H), 7.24 (t, 4H), 7.07 (d, 2H), 6.99 (t, 2H), 6.75 (d, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 147.62,

147.35, 147.29, 143.16, 142.98, 141.38, 139.89, 139.66, 138.38, 136.39, 136.33, 134.31, 131.13, 131.08, 131.04, 130.77, 130.25, 129.28, 128.81, 128.26, 127.90, 127.77, 127.72, 127.68, 127.57, 126.87, 126.73, 126.44, 126.37, 124.48, 124.41, 123.93, 123.72, 123.00, 122.96, 120.54. HRMS (MALDI-TOF): *m*/*z* 579.1387 (M+2, calcd 577.1405).

Preparation of o or p-TPA-3TPE-o or p-PhCN. Into a 25 mL Schlenk tube were placed 100 mg (0.17 mmol) of *o* or *p*-TPA-3TPE-*o* or *p*-Br, 38 mg (0.26 mmol) of 4-cyanophenylboronic acid, and 10 mg (0.05 mmol) of $Pd(PPh_3)_4$. The flask was evacuated under vacuum and purged with dry nitrogen for three times. 5 mL of distilled THF was then added, followed by addition of 1 mL of saturated K_2CO_3 aqueous solution. The mixture was refluxed for 24 h. The reaction was quenched with saturated NH_4Cl solution, and then extracted with dichloromethane three times. The organic layers were combined and washed with brine twice. The solvent was evaporated under reduced pressure and the crude product was purified on a silica-gel column using ethyl acetate/hexane mixture (1:10 v/v) as eluent.

Characterization data of o-TPA-3TPE-o-PhCN: A white solid was obtained in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.58 (t, 2H), 7.42–7.38 (m, 5H), 7.28–7.15 (m, 9H), 7.01–6.95 (m, 11H), 6.84 (d, 2H), 6.62 (d, 2H), 6.54 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 147.46, 146.18, 144.34, 142.87, 141.22, 139.51, 139.43, 136.28, 136.23, 131.68, 130.78, 130.62, 130.04, 129.87, 129.83, 129.44, 129.08, 129.04, 128.07, 127.95, 127.84, 127.30, 127.21, 126.97, 126.39, 124.25, 123.77, 123.60, 122.44, 118.87, 110.44. HRMS (MALDI-TOF): *m*/*z* 600.2568 (M+, calcd 600.2565).

Characterization data of o-TPA-3TPE-p-PhCN: A yellow solid was obtained in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.71–7.60 (m, 4H), 7.46–7.33 (m, 6H), 7.26–7.09 (m, 12H), 7.00–6.88 (m, 10H), 6.79 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 147.70, 146.31, 146.16, 145.06, 145.03, 144.14, 143.36, 143.20, 142.95, 141.49, 141.22, 139.95, 138.50, 138.14, 138.01, 136.97, 136.39, 135.67, 132.54, 132.53, 131.38, 130.97, 130.30, 130.24, 130.17, 130.07, 130.00, 129.90, 129.79, 129.41, 129.02, 129.00, 128.28, 127.90, 127.85, 127.66, 127.49, 127.29, 126.94, 126.85, 126.71, 126.66, 123.84, 123.78, 123.75, 122.43, 122.38, 118.94, 110.64. HRMS (MALDI-TOF): *m*/*z* 600.2566 (M+, calcd 600.2565).

Characterization data of p-TPA-3TPE-o-PhCN: A yellow solid was obtained in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.59 (m, 2H), 7.48–7.38 (m, 6H), 7.31–7.20 (m, 12H), 7.15–7.11 (m, 7H), 7.04 (m, 3H), 6.97 (d, J = 8 Hz, 1H), 6.80 and 6.75 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm):147.59, 147.34, 147.29, 146.07, 143.74, 143.55, 143.06, 141.32, 140.05, 139.58, 139.42, 139.30, 138.04, 136.04, 135.93, 134.25, 131.86, 130.92, 130.86, 130.54, 130.02, 129.96, 129.72, 129.66, 129.28, 128.32, 128.23, 128.12, 127.99, 127.82, 127.57, 127.48, 127.33, 127.28, 127.22, 126.61, 126.34, 126.27, 126.14, 124.49, 124.44, 123.84, 123.67, 123.00, 118.99, 110.42, 110.31. HRMS (MALDI-TOF): *m*/*z* 600.2556 (M+, calcd 600.2565).

Characterization data of p-TPA-3TPE-p-PhCN: A yellow solid was obtained in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.57–7.47 (m, 4H), 7.37–7.32 (m, 5H), 7.30–7.21 (m, 8H), 7.17–7.12 (m, 6H), 7.06 (m, 3H), 6.95 (m, 1H), 6.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 147.58, 147.31, 145.01, 143.45, 143.27, 143.18, 141.41, 140.12, 139.67, 138.63, 138.03, 136.97, 134.25, 132.54, 130.81, 130.30, 130.22, 129.28, 128.84, 128.28, 127.94, 127.82, 127.75, 127.69, 127.57, 127.31, 127.22, 126.74, 126.69, 126.37, 124.49, 124.42, 123.87, 123.70, 123.01, 118.96, 110.67. HRMS (MALDI-TOF): *m*/*z* 600.2572 (M+, calcd 600.2565).