
Supplementary information

High-efficiency, long-lifetime deep-blue organic light-emitting diodes

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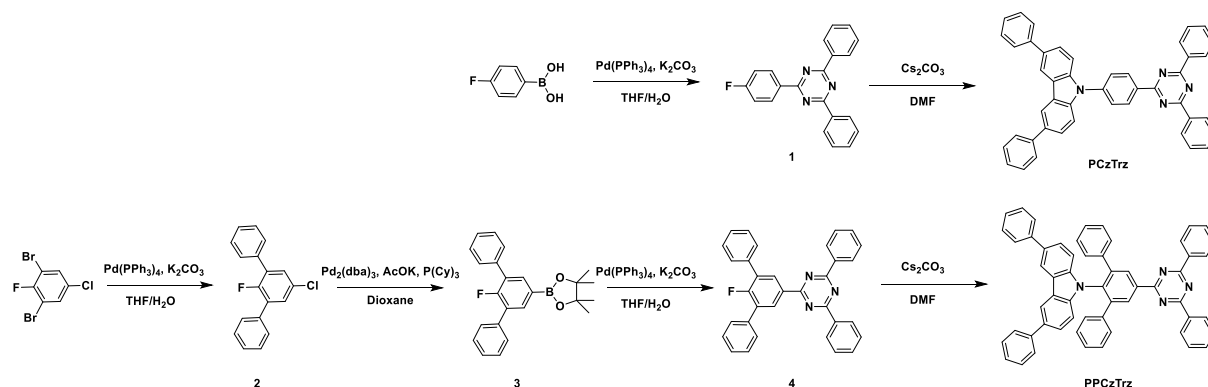
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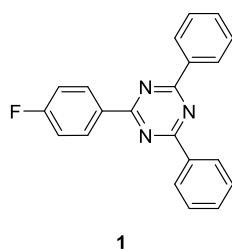
E-mail: so.jeon@samsung.com, hono.choi@samsung.com, leej17@skku.edu

Synthesis



Scheme S1. Synthetic route of PCzTrz and PPCzTrz TADF materials.

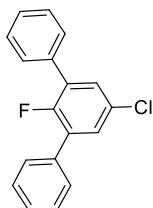
2-(4-Fluorophenyl)-4,6-diphenyl-1,3,5-triazine (1)



A mixture of (4-fluorophenyl)boronic acid (2.74 g, 19.61 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (5.0 g, 18.68 mmol), and tetrakis(triphenylphosphine)palladium(0) (1.08 g, 0.93 mmol, 5 mol %) in 30 mL of anhydrous tetrahydrofuran (THF) was refluxed under argon for 4 h. A solution of potassium carbonate (5.16 g, 37.35 mmol) in 30 mL of water was slowly added to the reaction mixture. After allowing it to cool to ambient temperature, the reaction mixture was extracted with dichloromethane and water. The organic layer was evaporated with a rotary evaporator. The product was purified by column chromatography using dichloromethane/*n*-hexane (1/1), and 5.09 g (yield 83 %) of 2-(4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (**1**) was obtained a white solid. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.79 (dd, *J* = 8.9, 5.6 Hz, 2H), 8.77 (dt, *J* = 8.3, 1.6 Hz, 4H), 7.62 (t, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 4H), 7.25 (t, *J* = 8.6 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 171.9, 170.9, 166.0 (*J* = 253.1 Hz), 136.3, 132.8,

132.6 ($J = 2.8$ Hz), 131.5 ($J = 9.0$ Hz), 129.2, 128.9, 115.9 ($J = 21.7$ Hz); ^1H , ^{13}C NMR data were in accordance with the literature. (*J. Am. Chem. Soc.*, **141**(41), 16388-16397 (2019)) ^{19}F NMR (470 MHz, CDCl_3) δ -108.1.

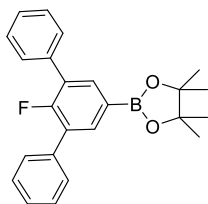
5'-Chloro-2'-fluoro-1,1':3',1''-terphenyl (**2**)



2

A mixture of phenylboronic acid (63.43 g, 520.22 mmol), 1,3-dibromo-5-chloro-2-fluorobenzene (50.00 g, 173.41 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-phos, 14.24g, 34.68 mmol), and tetrakis(triphenylphosphine)palladium(0) (20.04 g, 17.34 mmol, 10 mol %) in 300 mL of anhydrous THF was refluxed under argon for 16 h. A solution of potassium carbonate (95.87 g, 693.63 mmol) in 300 mL of water was slowly added to the reaction mixture. After allowing it to cool to ambient temperature, the reaction mixture was extracted with dichloromethane and water. The organic layer was evaporated with a rotary evaporator, and the product was purified by column chromatography using dichloromethane/*n*-hexane (1/1). The product was then rapidly recrystallized using only *n*-hexane by lowering the temperature below 5 °C using an ice bath. A large amount of white solid 5'-chloro-2'-fluoro-1,1':3',1''-terphenyl (**2**) was obtained in 83% yield. ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.53 (d, $J = 7.6$ Hz, 4H), 7.44 (t, $J = 7.5$ Hz, 4H), 7.38 (t, $J = 7.2$ Hz, 2H overlap), 7.37 (d, $J = 6.1$ Hz, 2H overlap); ^{13}C NMR (126 MHz, CDCl_3) δ 155.3 ($J = 249.3$ Hz), 135.0, 131.5 ($J = 16.7$ Hz, 2H overlap), 129.6 ($J = 3.5$ Hz), 129.5 ($J = 3.8$ Hz), 129.3 ($J = 2.7$ Hz), 128.8, 128.4; ^{19}F NMR (470 MHz, CDCl_3) δ -126.6.

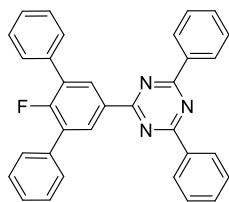
2-(2'-Fluoro-[1,1':3',1''-terphenyl]-5'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3)



3

5'-Chloro-2'-fluoro-1,1':3',1''-terphenyl (**2**) (40.66g, 143.81 mmol), bis(pinacolato)diboron (54.78 g, 215.71 mmol), potassium acetate (35.29 g, 359.52 mmol), tricyclohexylphosphine (4.03 g, 14.38 mmol), and tris(dibenzylideneacetone)dipalladium(0) (13.17 g, 14.38 mmol) were dissolved in 1,4-dioxane (290 mL) under a nitrogen atmosphere. The reaction mixture was stirred and refluxed for 20 h. The mixture was then filtered, diluted with toluene, and washed with water. The organic layer was dried over anhydrous MgSO_4 and evaporated with a rotary evaporator. The crude product was purified by column chromatography by dichloromethane/*n*-hexane (2/3) and the dried under vacuum to give 2-(2'-fluoro-[1,1':3',1''-terphenyl]-5'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**) (47.0 g, 87 %). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.88 (d, $J = 7.6$ Hz, 2H), 7.60 (d, $J = 7.9$ Hz, 4H), 7.43 (t, $J = 7.5$ Hz, 4H), 7.36 (t, $J = 7.0$ Hz, 2H), 1.34 (s, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.0 (d, $J = 254.2$ Hz), 137.1 (d, $J = 4.0$ Hz), 136.1, 129.5 (d, $J = 14.4$ Hz), 129.5, 129.5, 128.5, 127.8, 84.2, 25.1; ^{19}F NMR (470 MHz, CDCl_3) δ -119.8.

2-(2'-Fluoro-[1,1':3',1''-terphenyl]-5'-yl)-4,6-diphenyl-1,3,5-triazine (4)



4

A mixture of 2-(2'-fluoro-[1,1':3',1''-terphenyl]-5'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6) (30.20 g, 80.68 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (18.0 g, 67.23 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-phos, 5.52 g, 13.45 mmol), and tetrakis(triphenylphosphine)palladium(0) (3.89 g, 3.36 mmol, 5 mol %) in 110 mL of anhydrous tetrahydrofuran was refluxed under argon for 19 h. A solution of potassium carbonate (18.59 g, 134.47 mmol) in 110 mL of water was slowly added to the reaction mixture. After allowing it to cool to ambient temperature, the reaction mixture was extracted with toluene and water, and the organic layer was evaporated with a rotary evaporator. The product was purified by column chromatography using dichloromethane/*n*-hexane (1/1), and 30.0 g (93 %) of 2-(2'-fluoro-[1,1':3',1''-terphenyl]-5'-yl)-4,6-diphenyl-1,3,5-triazine (4) was obtained as a white solid. ¹H NMR (500 MHz, CD₂Cl₂) δ (ppm) 8.83 (d, *J* = 7.0 Hz, 2H), 8.75 (d, *J* = 6.9 Hz, 2H), 7.72 (d, *J* = 6.8 Hz, 4H), 7.62 (t, *J* = 6.8 Hz, 2H), 7.53-7.58 (m, 8H), 7.47 (t, *J* = 7.5 Hz, 2H); ¹³C NMR (126 MHz, CD₂Cl₂) δ 171.9, 170.9, 159.7 (d, *J* = 256.3 Hz), 136.3, 135.9, 132.8, 132.7 (d, *J* = 3.8 Hz), 131.1 (d, *J* = 4.4 Hz), 130.4 (d, *J* = 15.7 Hz), 129.6 (d, *J* = 2.5 Hz), 129.2, 128.9, 128.8, 128.3; ¹⁹F NMR (470 MHz, CDCl₃) δ -117.9

General procedure for S_NAr reaction synthesis of 9-(5'-(4,6-diphenyl-1,3,5-triazin-2-yl)-[1,1':3',1''-terphenyl]-2'-yl)-3,6-diphenyl-9H-carbazole (PPCzTrz) as a representative example

3,6-Diphenyl-9H-carbazole (10.32g, 17.41 mmol) and caesium carbonate (5.56 g, 31.66 mmol) were added to a solution of 2-(2'-fluoro-[1,1':3',1''-terphenyl]-5'-yl)-4,6-diphenyl-1,3,5-triazine

(10.00 g, 15.83 mmol) in *N,N*-dimethylformamide (DMF, 20 mL) at room temperature. The reaction mixture was stirred at 160 °C for 12 h. After allowing it to cool to room temperature, the reaction mixture was diluted with MeOH (200 mL) and filtered. The reaction mixture was carefully washed with water/MeOH (100/100 mL), and the resulting brown solid was collected by filtration. The crude product was purified by column chromatography using dichloromethane/*n*-hexane (1/3) as the eluent. The A solid was obtained, and the product was then recrystallized from toluene and finally dried under vacuum to give 9-(5'-(4,6-diphenyl-1,3,5-triazin-2-yl)-[1,1':3',1''-terphenyl]-2'-yl)-3,6-diphenyl-9*H*-carbazole (**PPCzTrz**) as a yellow crystal in 97 % yield (12.02 g). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 9.05 (s, 2H), 8.84 (dt, *J* = 7.0, 1.6 Hz, 4H), 8.25 (dd, *J* = 1.4, 0.5 Hz, 2H), 7.65-7.70 (m, 6H overlap), 7.62 (tt, *J* = 7.3, 1.3 Hz, 4H), 7.54 (dd, *J* = 8.5, 1.8 Hz, 2H), 7.46 (br. t, *J* = 7.8 Hz, 4H), 7.32 (tt, *J* = 7.4, 1.3 Hz, 2H), 7.19-7.21 (m, 4H), 7.13 (dd, *J* = 8.5, 0.4 Hz, 2H), 7.08-7.09 (m, 6H overlap); ¹³C NMR (126 MHz, CDCl₃): 172.5, 171.6, 143.9, 142.1, 141.6, 139.3, 137.7, 136.6, 136.1, 133.4, 133.3, 131.8, 129.6, 129.3, 129.3, 128.6, 128.6, 128.1, 127.5, 127.1, 125.8, 124.1, 118.9, 111.2; LC/MS: 779.31 [(*M* + *H*)⁺]. Anal. Calcd. for C₅₇H₃₈N₄: C, 87.89; H, 4.92; N, 7.19. Found: C, 87.8; H, 4.9; N, 7.2

9-(4-(4,6-Diphenyl-1,3,5-triazin-2-yl)phenyl)-3,6-diphenyl-9H-carbazole (PCzTrz)

The following procedure is the same as that used to synthesize **PPCzTrz**, except it uses 2-(4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (1.74 g, 5.32 mmol) as an acceptor and 3,6-diphenyl-9*H*-carbazole (2.04 g, 6.38 mmol) as a donor to synthesize **PCzTrz** (2.50 g, 75%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 9.03 (d, *J* = 8.6 Hz, 2H), 8.83 (d, *J* = 6.8 Hz, 4H), 8.42 (d, *J* = 1.5 Hz, 2H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.75 (dt, *J* = 7.1, 1.0 Hz, 4H), 7.71 (dd, *J* = 8.5, 1.8 Hz, 2H), 7.59-7.66 (m, 8H overlap), 7.49 (t, *J* = 7.8 Hz, 4H), 7.36 (tt, *J* = 7.9, 1.0 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃): δ 172.0, 171.1, 142.0, 141.7, 140.5, 136.3, 135.2, 134.3, 132.9, 130.9,

129.2, 129.1, 128.9, 127.5, 126.9, 126.7, 126.1, 124.7, 119.2, 110.6; LC/MS: 627.3 [(M + H)⁺].

Anal. Calcd. for C₅₁H₃₃N₅: C, 86.24; H, 4.82; N, 8.94. Found: C, 86.2; H, 4.8; N, 8.9

Experimental

Chemicals were purchased from Sigma-Aldrich Co., Tokyo Chemical Industry Co., and Wako Pure Chemical Industries Ltd., and used without further purification. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker ASCEND 500 at 500 MHz using CD₂Cl₂ and CDCl₃ as the solvent. The Liquid chromatograph mass spectrometer–ion trap–time of flight (LCMS-IT-TOF) was recorded using a Shimadzu spectrometer. The measurement conditions of the LCMS equipment were set as follows: acetonitrile and water for mobile phase solvents, 0.5 mL/min flow rate, and anhydrous tetrahydrofuran for the sampling solvent. Atmospheric pressure chemical ionization (APCI) was used for the ionization source. ACQUITY, CSH C18, 1.7 μm, 2.1 × 100 mm (Waters) was used for the column. Ultraviolet–visible (UV-Vis) spectra were obtained by means of a Varian model UV-Vis-NIR spectrophotometer 5000, and the fluorescence spectra were measured on a HITACHI F7000 spectrometer for the solution states. The UV-Vis absorption and solution photoluminescence (PL) emission spectra of materials were obtained from a dilute toluene solution (1 × 10⁻⁵ M), while the triplet energy values of the TADF materials were obtained from the PL spectra at 77 K using liquid nitrogen after delay time of 1 ms. To measure the glass transition temperature (T_g), differential scanning calorimeter (DSC) measurements was performed on a TA Instruments Q2000 under nitrogen at a heating rate of 10 °C/min from room temperature to 400 °C. Thermogravimetric-differential thermal analysis (TG-DTA) was performed using a TA Instruments Q5000 under flowing nitrogen at a heating rate of 10 °C/min from room temperature to 600 °C to detect the decomposition temperature (T_d, corresponding to 5% weight loss) of each TADF material. The energy levels were measured by using cyclic voltammetry (CV). Each material was dissolved in anhydrous

dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as an electrolyte to measure the oxidation, from which the highest occupied molecular orbital (HOMO) energy level was estimated. Glassy carbon was used as the working electrode, a platinum wire was used as the counter electrode, a saturated Ag/AgCl was used as the reference electrode, and ferrocene was used as the standard reference. All solutions were purged with nitrogen for 10 minutes before each experiment. The lowest unoccupied molecular orbital (LUMO) levels of each materials were estimated from the difference between the HOMO energy level and the optical band gap, which were estimated from the absorption edge of the UV-Vis spectra.

Methods

Device fabrication and measurements

Bottom-emitting devices were fabricated based on the device structure of indium tin oxide (ITO, 50 nm)/DNTPD (40 nm)/BPBPA (10 nm)/mCBP (10 nm)/EML (30 nm)/DBFTrz (5 nm)/ZADN (20 nm)/LiF (1.5 nm)/Al (200 nm), where DNTPD is $N^d, N^{d'}$ -bis[4-[bis(3-methylphenyl)amino]phenyl]- $N^d, N^{d'}$ -diphenyl-[1,1'-biphenyl]-4,4'-diamine, BPBPA is $N^d, N^d, N^{d'}, N^{d'}$ -tetra([1,1'-biphenyl]-4-yl)-[1,1'-biphenyl]-4,4'-diamine, mCBP is 3,3'-di(9H-carbazol-9-yl)-1,1'-biphenyl, DBFTrz is 2,8-bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[*b,d*]furan, ZADN is 2-[4-(9,10-di-naphthalen-2-yl-anthracen-2-yl)-phenyl]-1-phenyl-1*H*-benzoimidazole, and LiF is lithium fluoride. To evaluate the top-emitting devices, OLED devices were fabricated as follows: Ag-coated ITO (150 nm)/p-doped (3 wt%, NDP series, Novaled AG) N -([1,10-biphenyl]-4-yl)-9,9-dimethyl- N -(4-(9-phenyl-9Hcarbazol-3-yl)phenyl)-9H-fluoren-2-amine ((BCFA), 10 nm)/BCFA(107 nm)/mCBP (10 nm)/EML (30 nm)/DBFTrz (5 nm)/ZADN:LiQ (5:5, 30 nm)/Yb (1 nm)/codoped AgMg (13%, 13 nm)/CPL (70 nm). The emitting materials were deposited by co-evaporation of three or four materials at

the same time. The doping concentration was precisely controlled using a gold sensor. Three devices were fabricated to verify the reproducibility of the device data. The transient EL intensity was obtained using a function generator (Keysight 33622A), an oscilloscope (Yokogawa DL9140) connected to a photomultiplier tube (HAMAMATSU G1760001), and a current amplifier (DHPCA-100). The pulses that were applied to the device corresponded to $25\text{mA}/\text{cm}^2$ current density with a pulse width of $100\text{ }\mu\text{s}$. A vacuum thermal evaporation process was used in the device fabrication, and the devices were encapsulated for the device test. The device performance was analysed using a Keithley 2400 measurement system and a CS 2000 (Konica Minolta Inc.) spectroradiometer. We tested the lifetimes in dark conditions using a Polaronix (McScience Co.) lifetime measurement system equipped with an electrical source and photodiode as a detecting unit.

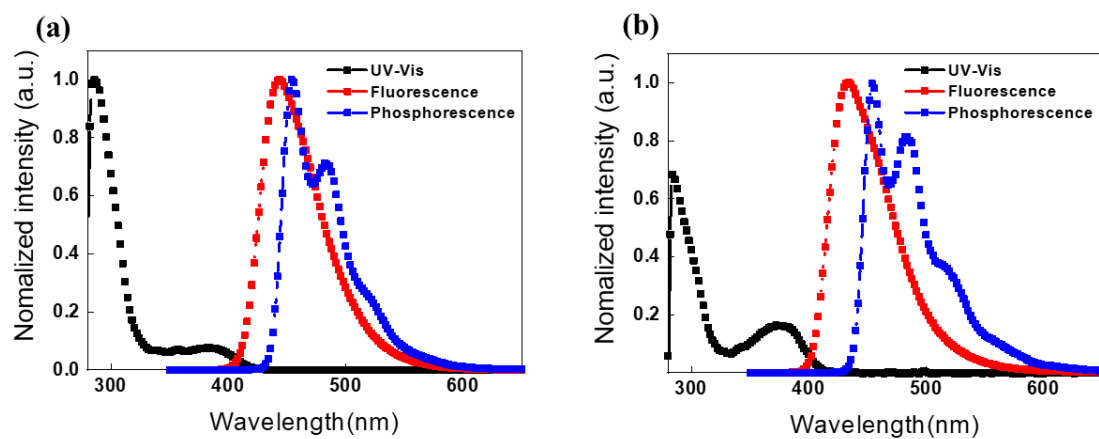


Figure S1. Ultraviolet-visible (UV-vis), fluorescence, and phosphorescence spectra. (a) PPCzTrz and (b) PCzTrz.

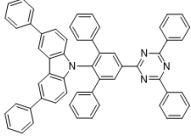
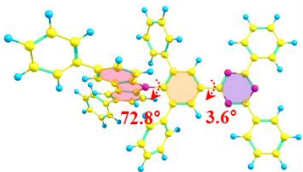
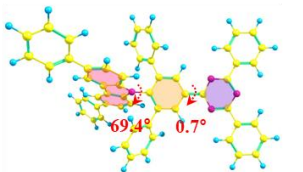
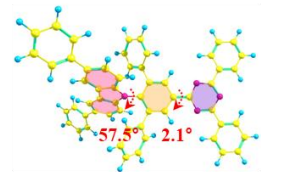
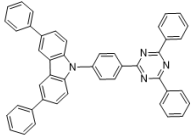
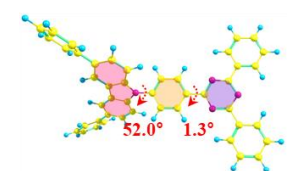
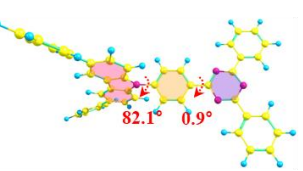
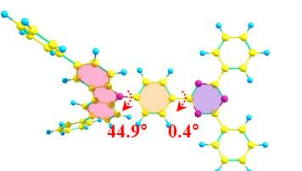
Compound	S ₀	S ₁	T ₁
PPCzTrz 			
PCzTrz 			

Figure S2. Optimized geometry of the PPCzTrz and PCzTrz in the ground and excited states.

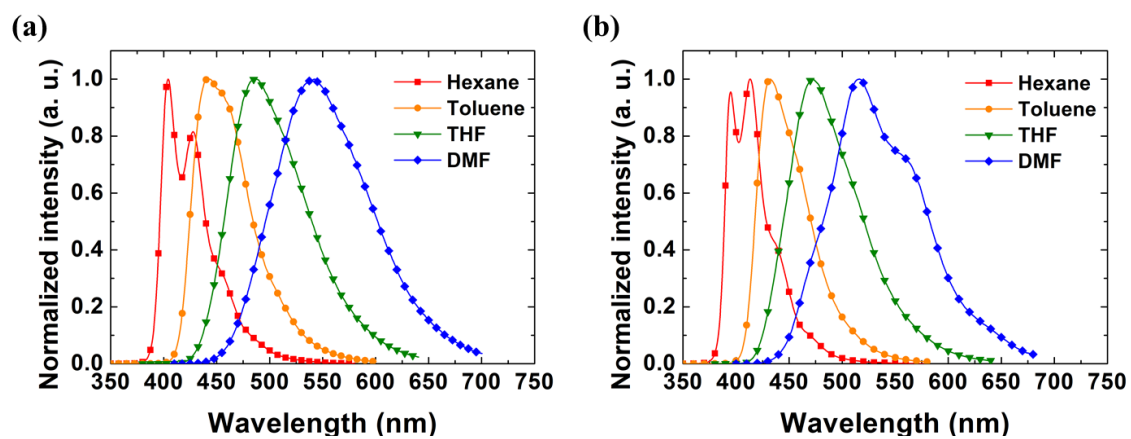


Figure S3. Normalized fluorescence spectra. (a) PPCzTrz and (b) PCzTrz in different solvents.

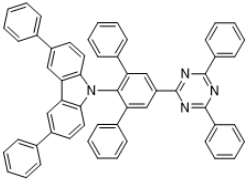
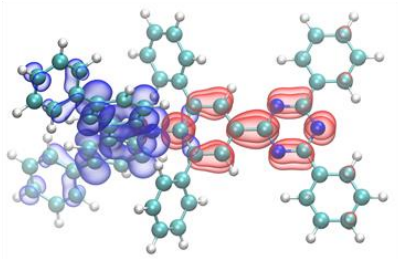
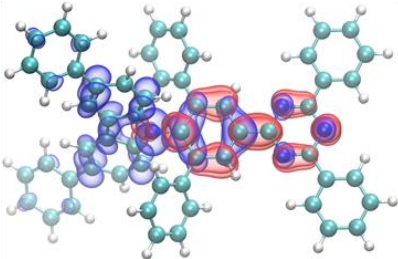
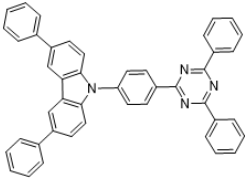
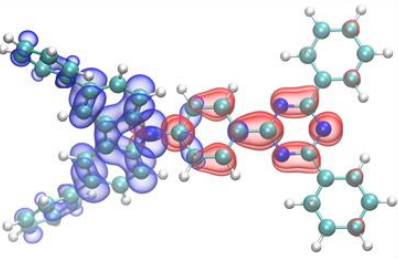
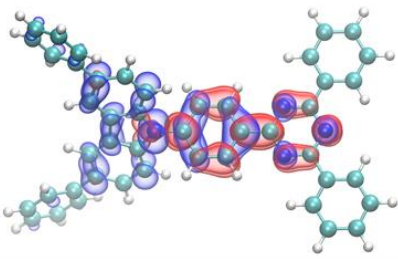
Compound	S_1	T_1
PPCzTrz 		
PCzTrz 		

Figure S4. The highest occupied (blue) and lowest unoccupied (red) natural transition orbitals for S_1 and T_1 states of the PPCzTrz and PCzTrz TADF emitters.

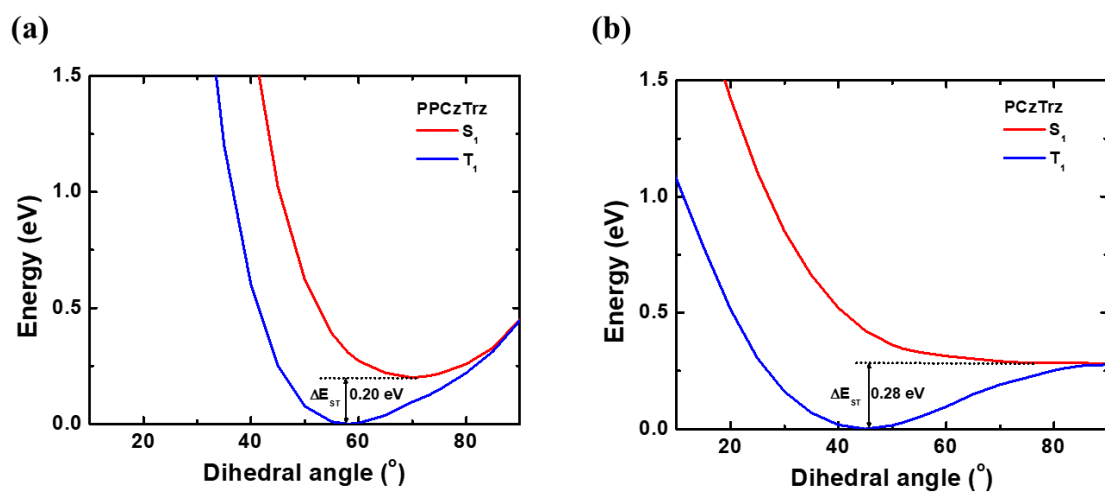


Figure S5. Energy curves for S₁ (red) and T₁ (blue) states. (a) **PPCzTrz** and (b) **PCzTrz** TADF emitters.

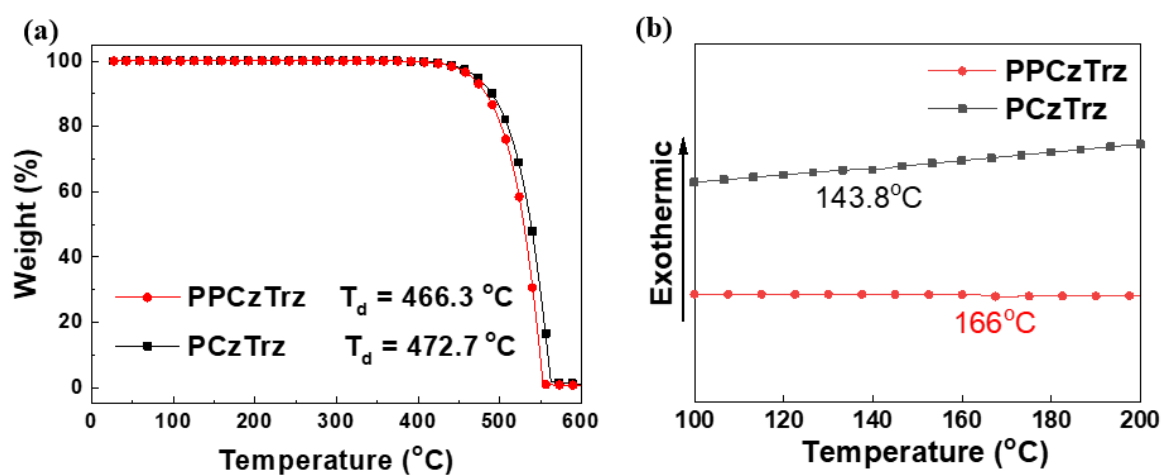


Figure S6. Thermal analysis characteristics. (a) TGA and (b) DSC traces of **PPCzTrz** and **PCzTrz** recorded under nitrogen at a heating rate of 10 °C/min.

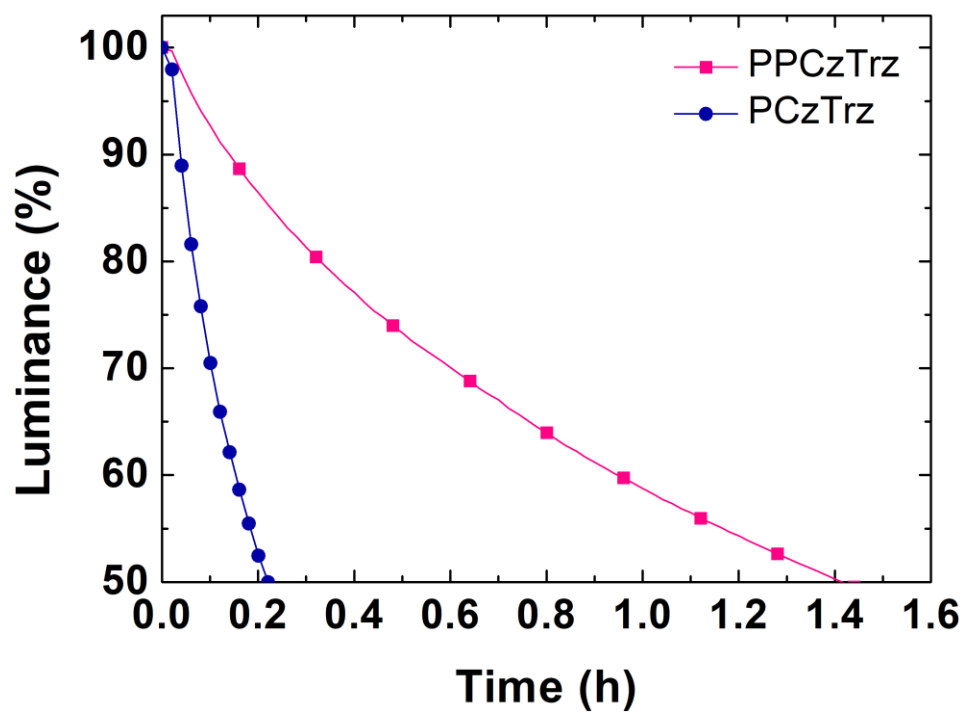


Figure S7. Device lifetime of the PPCzTrz- and PCzTrz-doped DPEPO devices at 1,000 cd/m².

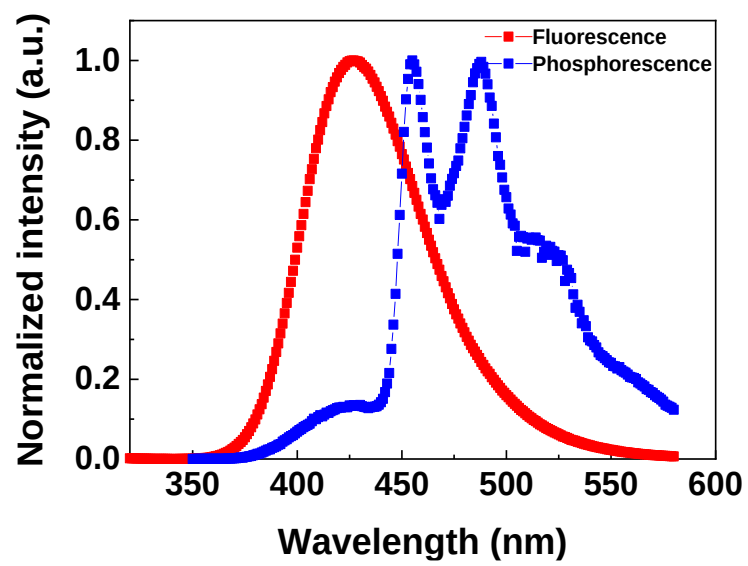


Figure S8. PL spectra of the oCBP:CNmCBPCN mixed host film.

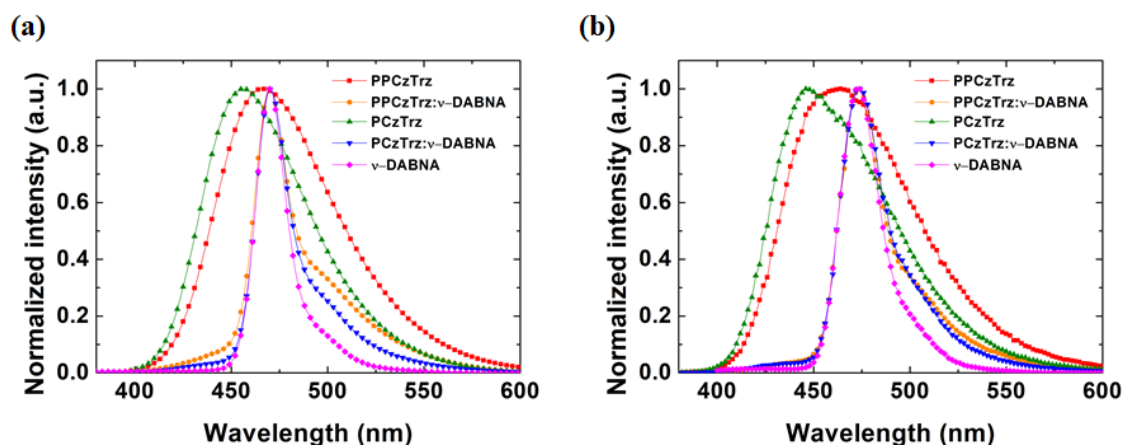


Figure S9. PL spectra. PPCzTrz (10 wt%), PPCzTrz:v-DABNA (10 wt%:1wt%), PCzTrz (10 wt%), PCzTrz:v-DABNA (10 wt%:1wt%), and v-DABNA (1wt%) in (a) DPEPO and oCBP:CNmCBPCN mixed host films.

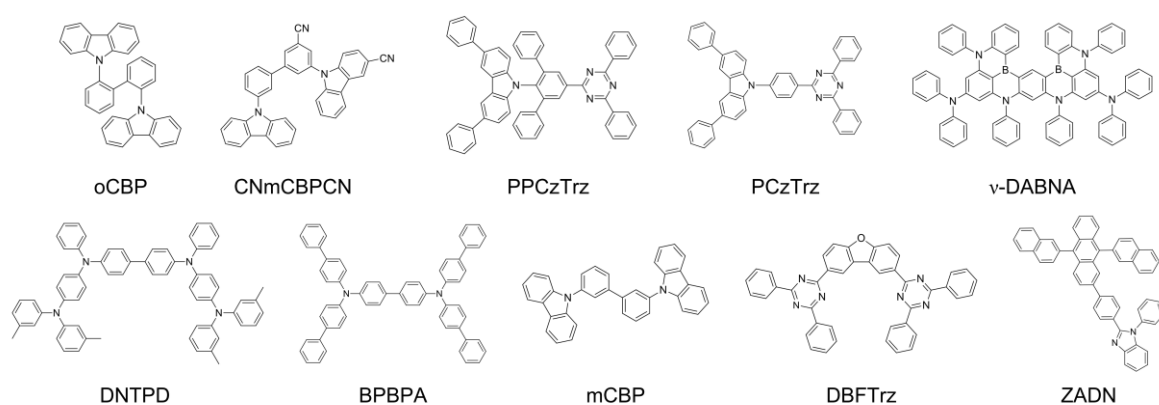


Figure S10. Chemical structure of the materials used for the device fabrication.

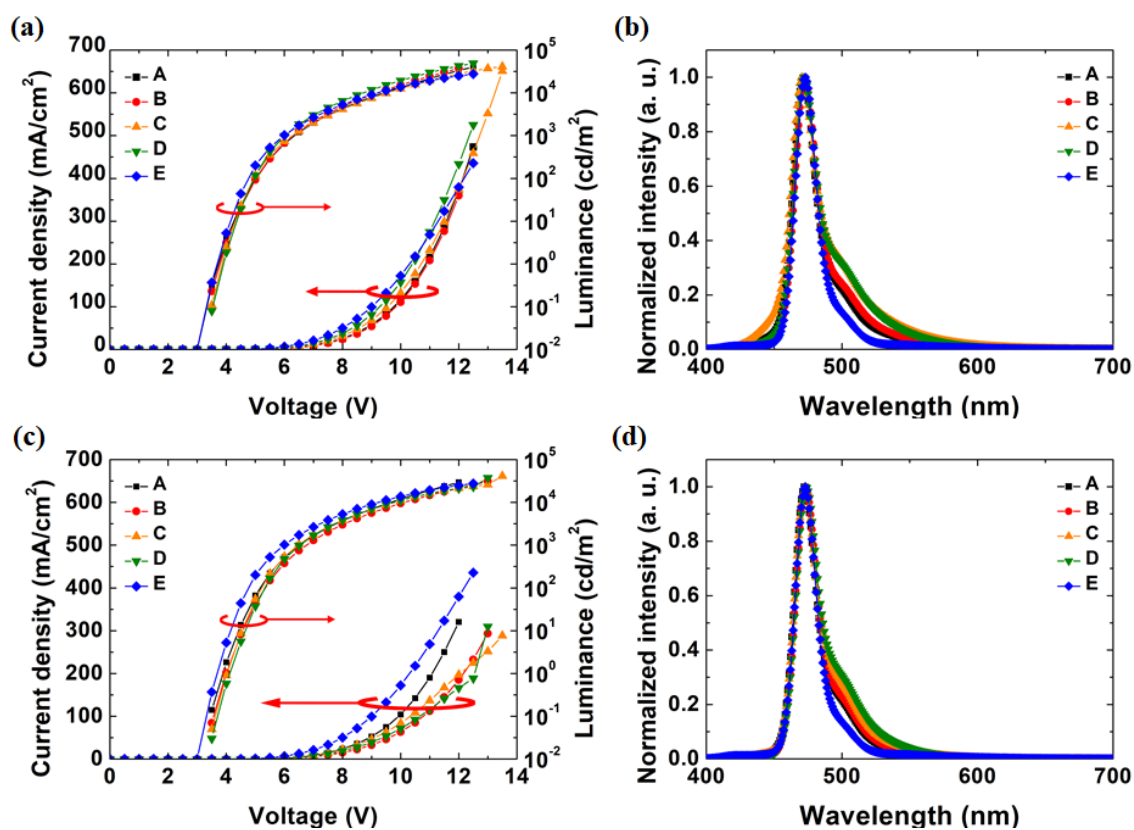


Figure S11. Data for the bottom-emitting devices. (a) Current density–voltage–luminance and (b) EL spectra of the PPCzTrz devices, and (c) current density–voltage–luminance and (d) EL spectra of the PCzTrz devices. (A:TADF(10 wt%):v-DABNA(0.5 wt%), B:TADF(10 wt%):v-DABNA(1.0 wt%), C:TADF(20 wt%):v-DABNA(0.5 wt%), D:TADF(20 wt%):v-DABNA(1.0 wt%), and E:v-DABNA(1.0 wt%))

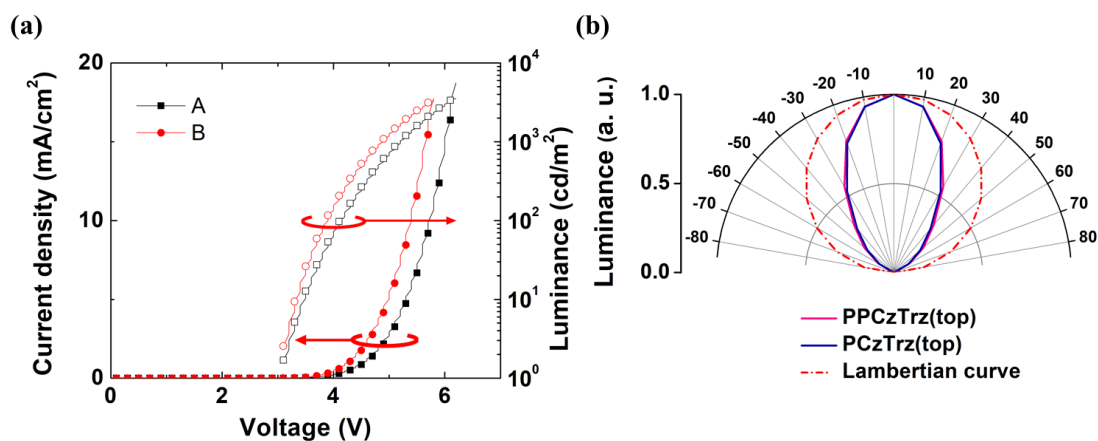


Figure S12. Device performances and lambertian emission pattern of the top-emitting OLEDs.

(a) Current density–voltage–luminance data (A:PPCzTrz(10 wt%):v-DABNA (1.0 wt%), B:PCzTrz (10 wt%):v-DABNA (1.0 wt%) in the oCBP:CNmCBPCN mixed host) (b) Angular distributions of EL intensity according to viewing angles relative to the Lambertian light emission pattern measured at a voltage of 4.0 V.

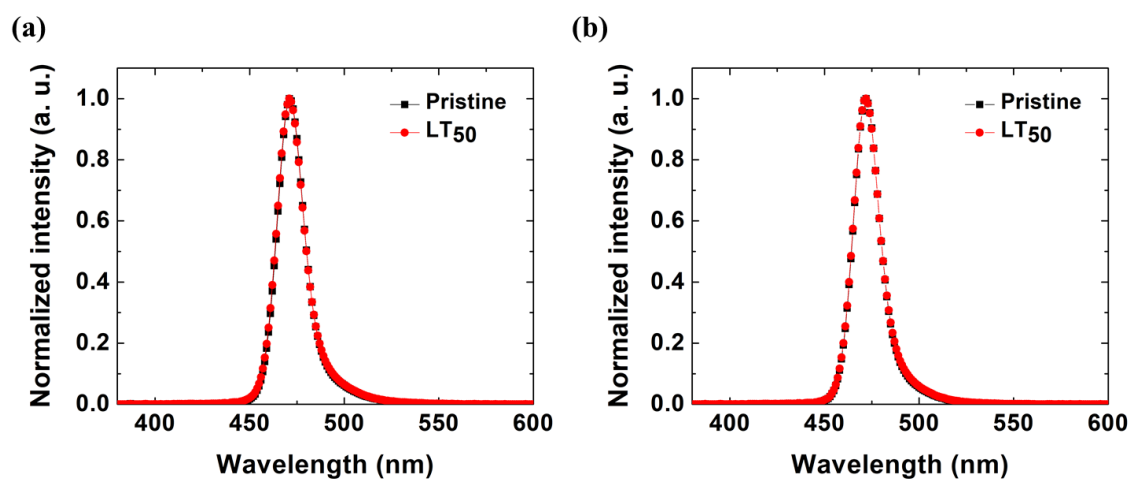


Figure S13. EL spectra of before and after device lifetime test. (a) PPCzTrz and (b) PCzTrz devices.

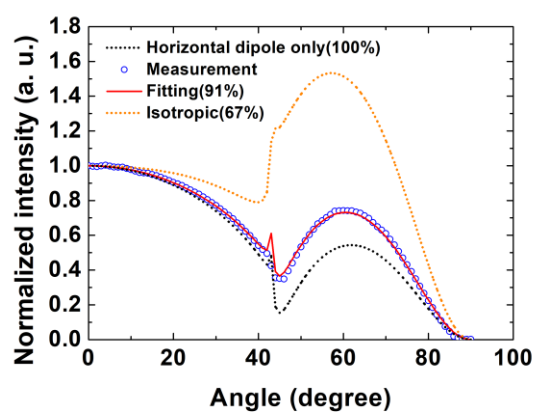


Figure S14. Anisotropic horizontal orientation value of the PPCzTrz: v-DABNA-doped emitting layer.

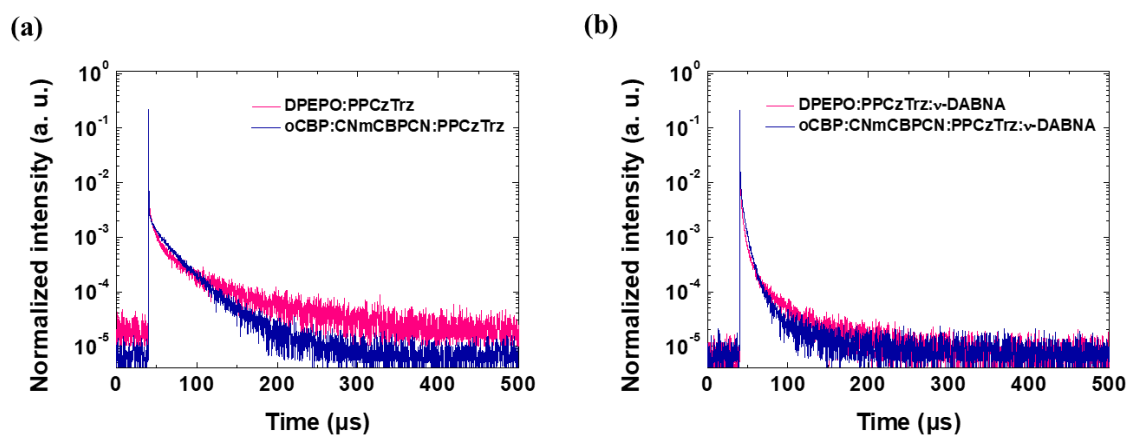


Figure S15. Transient PL decay data. (a) host:PPCzTrz and (b) host:PPCzTrz: v-DABNA films in the DPEPO and oCBP:CNmCBP hosts.

Table S1. Summarized photophysical properties of **PPCzTrz**, **PCzTrz**, and **v-DABNA**

	HOMO ^a (eV)	LUMO ^a (eV)	HOMO– LUMO gap (eV)	T _g ^b (°C)	T _d ^c (°C)	Singlet-energy onset (max) (eV)	Triplet-energy onset (max) (eV)	ΔE _{ST} onset (max) (eV)
PPCzTrz	-5.602	-2.657	2.945	166	466.3	3.00 (2.79)	2.84 (2.73)	0.16 (0.06)
PCzTrz	-5.609	-2.585	3.024	143.8	472.7	3.07 (2.86)	2.84 (2.73)	0.23 (0.13)
v-DABNA	-5.4	-2.8	2.6	-	-	2.66 (2.62)	2.64 (2.59)	0.02 (0.03)

^aMeasured from CV. ^b2nd heating scan value. ^cCorresponding to 5% weight loss.

Table S2. Summarized PLQY and transient PL characteristics of **PPCzTrz** and **PCzTrz**

	Φ_{total} (%)	Φ_{prompt} (%)	Φ_{TADF} (%)	τ_{p} (ns)	τ_{d} (μs)	$k_{\text{ISC}}^{\text{b}}$ (10^7s^{-1})	$k_{\text{RISC}}^{\text{b}}$ (10^4s^{-1})
PPCzTrz^a	93	36	57	30.0	25.0	5.67	8.02
PCzTrz^a	95	39	56	12.6	79.5	6.35	1.44

^a20 wt% doped film in DPEPO. ^bCalculated according to the method reported in the reference.¹

Table S3. Summarized device performance parameters of **PPCzTrz**, **PCzTrz**, and **v-DABNA** devices according to the doping concentration in the oCBP:CNmCBPCN mixed host.

PPCzTrz/ v-DABNA (wt%)	Voltage^a (V)	CE^a/CE_{max} (cd/A)	EQE^a/EQE_{max} (%)	CIE_x^b	CIE_y^b	λ_{max}^a (nm)	Roll-off^c (%)	LT₅₀^a (h)
A.10/0.5	6.3	22.9/33.3	21.8/30.3	0.13	0.17	472	28	110
B.10/1.0	6.4	28.9/39.7	25.2/33.0	0.13	0.20	473	24	151
C.20/0.5	6.2	18.2/32.3	14.4/23.9	0.14	0.21	472	40	94
D.20/1.0	6.0	25.6/43.1	19.5/30.9	0.14	0.23	472	37	152
E.0.0/1.0	6.3	14.6/30.3	17.7/33.2	0.13	0.14	473	46	41
PCzTrz/ v-DABNA (wt%)	Voltage^a (V)	CE^a/CE_{max} (cd/A)	EQE^a/EQE_{max} (%)	CIE_x^b	CIE_y^b	λ_{max}^a (nm)	Roll-off^c (%)	LT₅₀^a (h)
A.10/0.5	6.5	20.7/32.1	21.2/31.5	0.12	0.16	472	33	103
B.10/1.0	6.7	24.3/35.5	23.8/33.5	0.12	0.18	473	29	113
C.20/0.5	6.5	21.6/37.0	19.1/31.0	0.12	0.20	473	38	61
D.20/1.0	6.5	25.9/38.7	21.3/30.9	0.12	0.22	473	31	97
E.0.0/1.0	6.3	14.6/30.3	17.7/33.2	0.13	0.14	473	46	41

^aValues at luminance of 1,000 cd/m². ^bColour coordinates at a luminance of 1,000 cd/m². ^cRoll-off efficiency values from maximum luminance to 1,000 cd/m².

Table S4. The colour coordinate corrected current efficiency (CCE) values of the blue devices reported in the literatures.

Emitter	cd/A ^a	CIEy	CCE (cd/A)	Lifetime LT ₅₀ , (h)	Ref.
v-DABNA	31.2	0.11	283.6	N.A. ^b	2
t-DABNA	10.9	0.09	121.1	17 ^c	3
TDBA-Ac	8.51	0.06	141.8	N.A.	4
TDBA-DI	35.07	0.15	233.8	N.A.	4
TMCz-BO	29.8	0.18	165.6	N.A.	5
TMCz-3P	37.8	0.26	145.4	N.A.	5
CNImIr	43.1	0.27	159.6	4,364	6
Ir(cb) ₃	29.1	0.13	223.8	10,700 ^d	7
Pt(1-ptz)	27.3	0.28	97.5	0.5 ^e	8
(dfpysipy) ₂ Ir(mpic)/TBPe	18.0	0.19	94.74	N.A.	9
Ir(cb) ₃ /t-DABNA	23.4	0.115	203.5	293 ^c	3
CzAcSF/TBPe	23.7	0.23	103.1	N.A.	10
ACRSA/TBPe	27.0	0.30	90.00	N.A.	11
DMAC-DPS/BPPyA	14.5	0.16	90.63	N.A.	12
DMAC-DMT/BPPyA	12.9	0.11	117.3	N.A.	12
DMAC-DMT/BPPyA	18.3	0.15	122.0	N.A.	12
SPAC-DMT/BPPyA	5.8	0.11	52.73	N.A.	12
DMAC-DPS/t-DABNA	32.6	0.15	217.3	N.A.	13
5CzCN/TBPe	31.1	0.23	135.2	N.A.	14
PPCzTrz/v-DABNA	32.8	0.09	364	7,400^d	This work
PCzTrz/v-DABNA	38.9	0.09	432	6,100^d	This work

^aMaximum current efficiency

^bN.A. denotes that data was not assigned.

^cValues at a luminance of 200 cd/m²

^dValues at a luminance of 100 cd/m²

^eValues at a luminance of 500 cd/m²

Table S5. The external quantum efficiency (EQE) and lifetime of the real deep blue devices with a y colour coordinate <0.10 reported in the literatures.

Emitter	EQE_{max}	CIE_y	Lifetime LT₅₀, (h)	Ref.
t-DABNA	12.7	0.09	17	3
TDBA-Ac	21.5	0.06	N.A.	4
fac-Ir(pmp) ₃	10.1	0.09	N.A.	15
PtON7-dtb	24.8	0.08	N.A.	16
PXB-mIC	12.5	0.08	N.A.	17
DABNA-1	13.5	0.09	N.A.	18
PPCzTrz/v-DABNA	29.3	0.09	7,400	This work
PCzTrz/v-DABNA	34.4	0.09	6,100	This work

Table S6. Device performance of the bottom- and top-emitting OLEDs.

Bottom-emitting	Voltage ^a (V)	CE _{max} /CE ^a (cd/A)	EQE _{max} /EQE ^a (%)	CCE _{max} ^b (cd/A)	CIE ^c	Roll-off ^d (%)	LT ₅₀ ^a (h)	LT ₅₀ ^e (h)
PPCzTrz ^f	6.4±0.1	39.7±0.7/28.9±0.8	33.0±0.3/25.2±0.8	199±5	0.13,0.20	24	151±3	9,500±150
PCzTrz ^f	6.7±0.1	35.5±0.8/24.3±0.5	33.5±0.1/23.8±0.2	197±5	0.12,0.18	29	113±2	7,100±90
v-DABNA ^g	6.3±0.3	30.3±0.9/14.6±0.6	33.2±0.2/17.7±0.2	217±7	0.13,0.14	46	41±1	2,600±70
Top-emitting	Voltage ^a (V)	CE _{max} /CE ^a (cd/A)	EQE _{max} /EQE ^a (%)	CCE _{max} ^b (cd/A)	CIE ^c	Roll-off ^d (%)	LT ₅₀ ^a (h)	LT ₅₀ ^e (h)
PPCzTrz ^f	5.3±0.1	32.8±0.9/23.6±0.9	29.3±0.9/21.4±0.7	364±10	0.12,0.09	28	117±4	7,400±240
PCzTrz ^f	4.9	38.9±1.0/24.4±0.3	34.4±0.9/21.9±0.3	432±11	0.12,0.09	37	97±2	6,100±100

^aValues at luminance of 1,000 cd/m². ^bMaximum current efficiency divided by CIE y colour coordinate. ^cColour coordinates at 1,000 cd/m². ^dRelative reduction of EQE at 1,000 cd/m² from the maximum EQE. ^eConverted lifetime at an initial luminance of 100 cd/m² using an acceleration factor of 1.8. ^f**TED-TADF** device, 10 wt% of PPCzTrz and PCzTrz with 1 wt% of v-DABNA doped into the mixed host. ^gConventional TADF device, 1 wt% of v-DABNA doped into the mixed host.

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