Electronic Supplementary Information

Benzene-cored AIEgens for deep-blue OLEDs: high performance without hole-transporting layers, and unexpected excellent host for orange emission as a side-effect

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‡ *The authors contributed equally to this work.*

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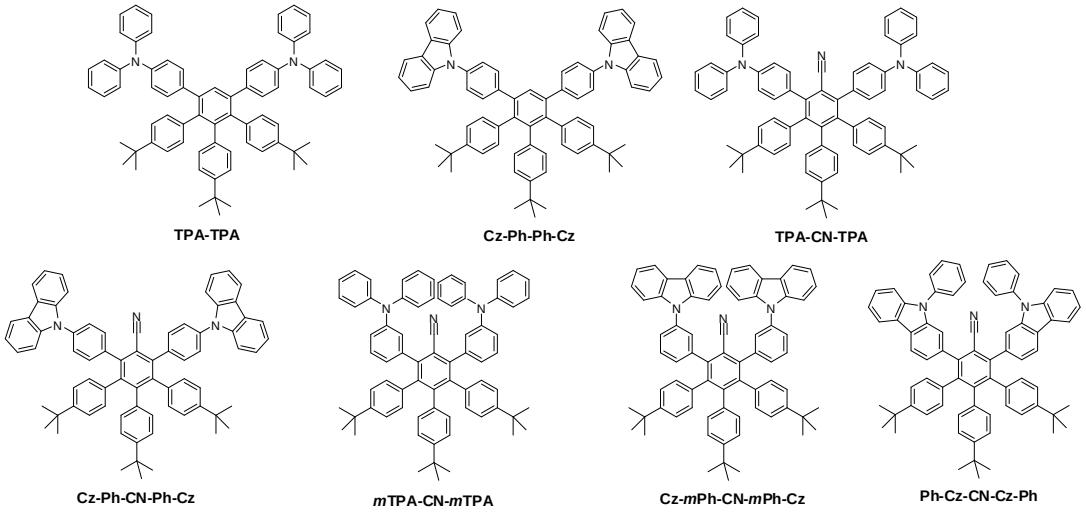


Chart S1. Chemical structures of the previous deep-blue luminogens.

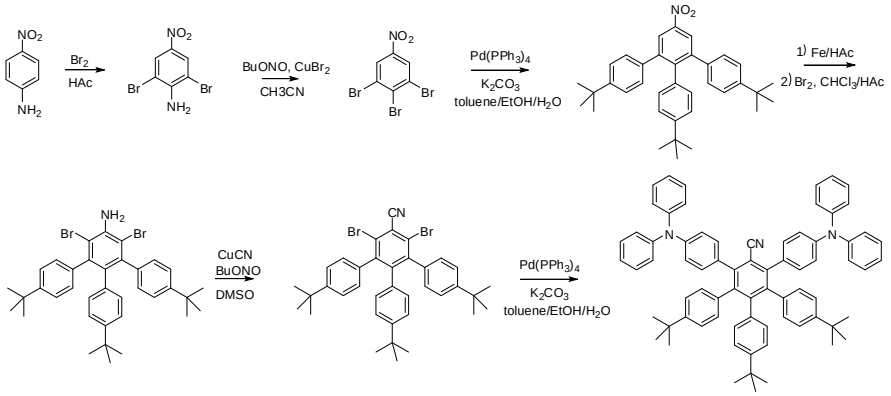


Chart S2. Synthetic routes of the synthesis of TPA-CN-TPA.

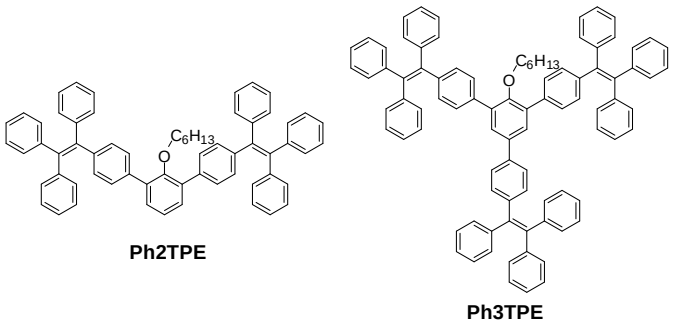
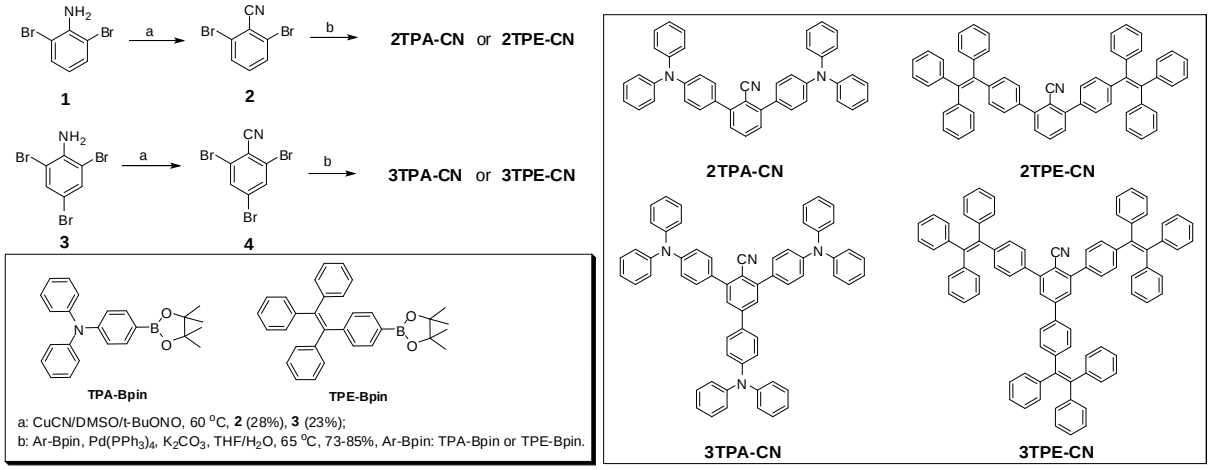


Chart S3. Chemical structures of Ph2TPE and Ph3TPE.



Scheme S1. Chemical structures and synthetic routes of the previous four luminogens.

Preparation of compounds:

2,6-Dibromoaniline (**1**) and 2,4,6-tribromoaniline (**3**) were commercial available. All other chemicals and reagents were obtained from commercial sources and used as received without further purification. Solvents for chemical synthesis were purified according to the standard procedures.

*Synthesis of 2,6-dibromobenzonitrile (**2**)*: CuCN (117 mg, 1.3 mmol) and **1** (249 mg, 1.0 mmol) was added to a stirred anhydrous DMSO (40 mL) at 50 ^{o}C to form a clear solution, then followed by the addition of *tert*-butyl nitrite (0.357 mL, 3.0 mmol). The resultant mixture was allowed to stir for 2 h, then poured into 1 M HCl (100 mL) and extracted with chloroform. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using chloroform/petroleum ether as eluent to give a pale yellow solid in the yield of 26% (68 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.66-7.64 (d, J = 8.1 Hz, 2H), 7.34-7.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 134.1, 131.7, 126.7, 118.7, 115.8. MS (EI), m/z: 259.50 ([M^+], calcd for $C_7H_3Br_2N$, 258.86). Anal. Calcd for $C_7H_3Br_2N$: C, 32.22; H, 1.16; N, 5.37. Found: C, 32.36; H, 1.24; N, 5.33.

*Synthesis of 2,4,6-tribromobenzonitrile (**4**)*: The synthetic procedure was similar to that of **2**.

3 (327 mg, 1.0 mmol) reacted with CuCN (117 mg, 1.3 mmol), by the addition of *tert*-butyl nitrite (0.357 mL, 3.0 mmol) to yield **4** (23%, 77 mg, a pale yellow solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.61 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 134.6, 128.1, 127.0, 117.8, 115.4. MS (EI), m/z: 338.49 ([M^+], calcd for $C_7H_2Br_3N$, 336.77). Anal. Calcd for $C_7H_2Br_3N$: C, 24.74; H, 0.59; N, 4.12. Found: C, 24.99; H, 0.73; N, 4.27.

Typical Procedure for the Synthesis of Luminogens.

*Synthesis of **2TPA-CN***: A mixture of 2,6-dibromobenzonitrile (103 mg, 0.4 mmol), 4-Bpin-triphenylamine (0.74 g, 2.0 mmol), $Pd(PPh_3)_4$ (30 mg) and potassium carbonate (1.10 g, 8.0 mmol) in toluene (8.0 mL), EtOH (2.0 mL) and distilled water (4.0 mL), was refluxed for 24 h under nitrogen in a 100 mL Schlenk tube. After quenched by water, the mixture was extracted with chloroform. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using chloroform/petroleum ether as eluent to afford the product as white solid in the yield of 76% (179 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.62-7.58 (m, 1H), 7.46-7.40 (m, 6H), 7.32-7.29 (m, 8H), 7.19-7.13 (m, 12H), 7.09-7.04 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.2, 147.3, 146.6, 132.1, 131.8, 129.8, 129.3, 128.1, 125.0, 123.4, 122.2, 118.4, 109.4. MS (EI), m/z: 589.68 ([M^+], calcd for $C_{43}H_{31}N_3$, 589.25). Anal. Calcd for $C_{43}H_{31}N_3$: C, 87.58; H, 5.30; N, 7.13. Found: C, 87.32; H, 5.53; N, 7.02.

*Synthesis of **3TPA-CN***. The synthetic procedure was similar to that of **2TPA-CN**. 2,4,6-tribromobenzonitrile (101 mg, 0.3 mmol) reacted with 4-Bpin-triphenylamine (550 mg, 1.5 mmol), in the presence of $Pd(PPh_3)_4$ (30 mg) and potassium carbonate (1.24 g, 9.0 mmol), to yield **3TPA-CN** (70%, 174 mg, a pale yellow solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.60 (s, 2H), 7.51-7.48 (m, 6H), 7.32-7.30 (m, 10H), 7.19-7.13 (m, 20H), 7.10-7.05 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.4, 148.2, 147.3, 147.2, 147.0, 144.3, 132.3, 132.0, 129.8, 129.3, 128.0, 126.2, 125.0, 124.8, 123.4, 123.0, 122.3, 118.7, 107.4. MS (EI), m/z: 832.52 ([M^+], calcd for $C_{61}H_{44}N_4$, 832.36). Anal. Calcd for $C_{61}H_{44}N_4$: C, 87.95; H, 5.32; N,

6.73. Found: C, 87.73; H, 5.57; N, 6.61.

*Synthesis of **2TPE-CN***. The synthetic procedure was similar to that of **2TPA-CN**. 2,6-dibromobenzonitrile (259 mg, 1.0 mmol) reacted with 4-Bpin-tetraphenylethene (1.37 g, 3.0 mmol), in the presence of $Pd(PPh_3)_4$ (30 mg) and potassium carbonate (2.76 g, 20 mmol) to yield **2TPE-CN** (74%, 563 mg, a light yellow solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.60 (m, 1H), 7.39-7.37 (d, J = 7.5 Hz, 2H), 7.31-7.28 (m, 4H), 7.14-7.05 (m, 34H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 146.5, 144.0, 143.5, 141.7, 140.2, 136.6, 131.9, 131.4, 131.3, 128.5, 128.2, 128.0, 127.7, 127.6, 127.5, 126.6, 126.5, 117.6, 110.1. MS (EI), m/z: 763.81 ([M^+], calcd for $C_{59}H_{41}N$, 763.32). Anal. Calcd for $C_{59}H_{41}N$: C, 92.76; H, 5.41; N, 1.83. Found: C, 92.96; H, 5.70; N, 1.96.

*Synthesis of **3TPE-CN***. The synthetic procedure was similar to that of **2TPA-CN**. 2,4,6-tribromobenzonitrile (168 mg, 0.50 mmol) reacted with 4-Bpin-tetraphenylethene (1.14 g, 2.5 mmol), in the presence of $Pd(PPh_3)_4$ (30 mg) and potassium carbonate (2.07 g, 15 mmol) to yield **3TPE-CN** (71%, 387 mg, yellow solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.54 (s, 2H), 7.40-7.37 (d, J = 8.1 Hz, 2H), 7.33-7.30 (d, J = 8.7 Hz, 4H), 7.12-7.06 (m, 51H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 146.9, 144.3, 144.2, 144.1, 143.5, 143.4, 143.3, 141.7, 140.2, 140.0, 136.6, 132.0, 131.8, 131.7, 131.4, 131.3, 131.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 126.8, 126.7, 126.6, 126.4, 117.8, 108.6. MS (MALDI-TOF), m/z: 1093.37 ([M^+], calcd for $C_{85}H_{59}N$, 1093.46). Anal. Calcd for $C_{85}H_{59}N$: C, 93.29; H, 5.43; N, 1.28. Found: C, 93.06; H, 5.46; N, 1.33.

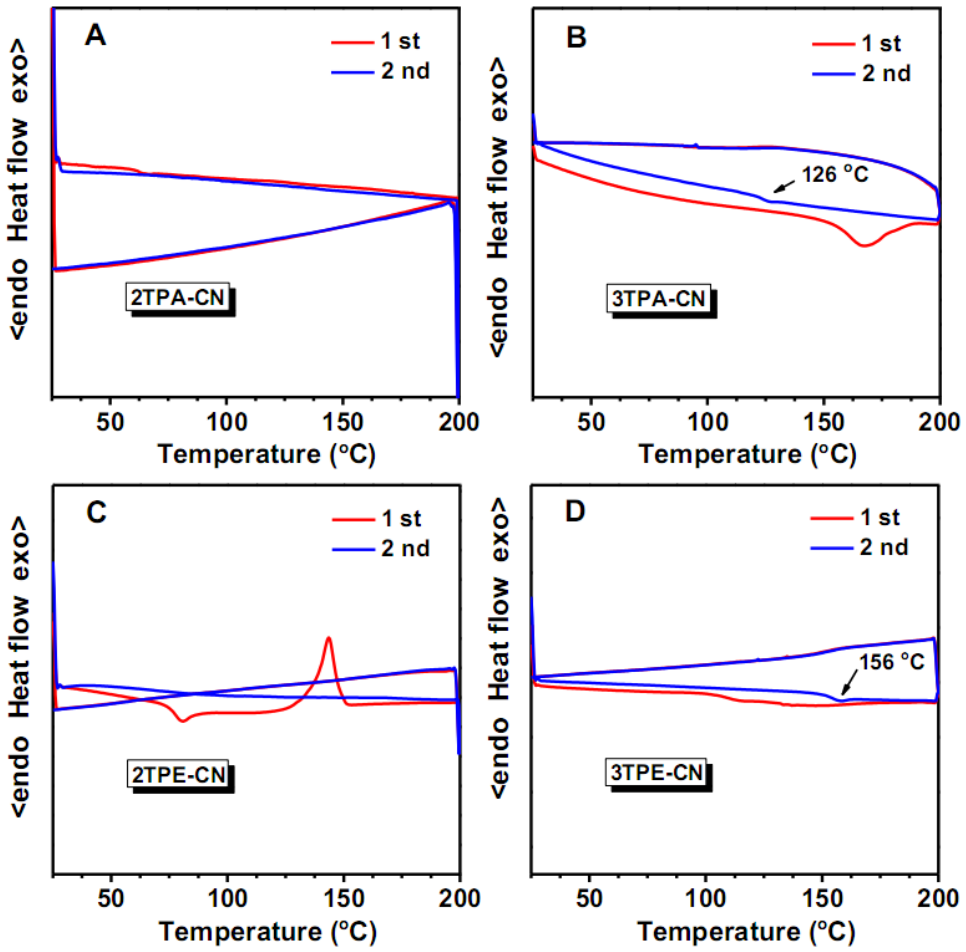


Figure S1. DSC curves of the four luminogens recorded under N_2 at a heating rate of 10 ^{o}C/min. (A: **2TPA-CN**; B: **3TPA-CN**; C: **2TPE-CN**; D: **3TPE-CN**)

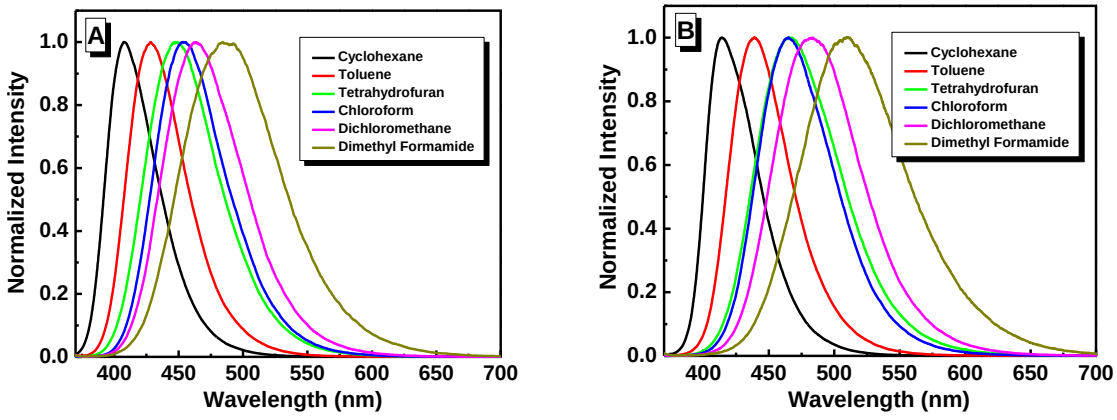


Figure S2. PL spectra of **2TPA-CN** (A) and **3TPA-CN** (B) in various solvents (~10 μM).

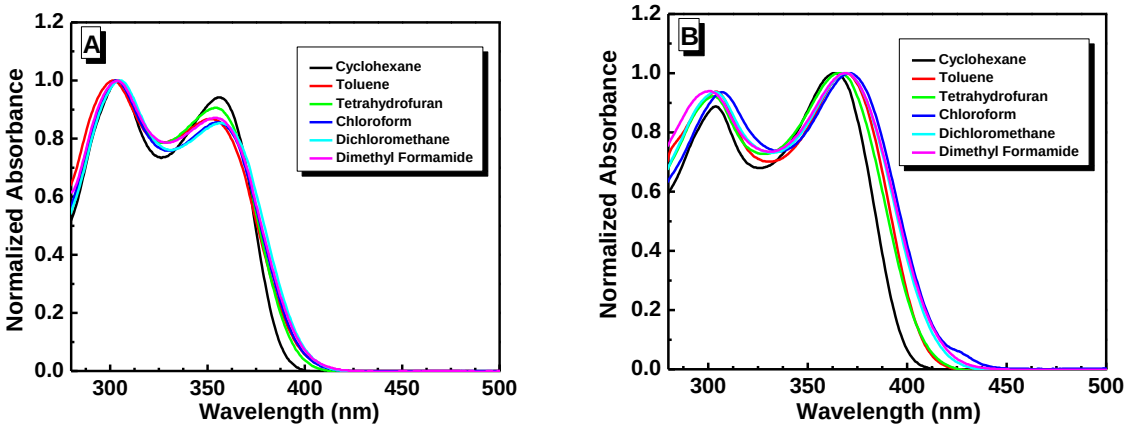


Figure S3. UV-vis spectra of **2TPA-CN** (A) and **3TPA-CN** (B) in various solvents (~10 μM).

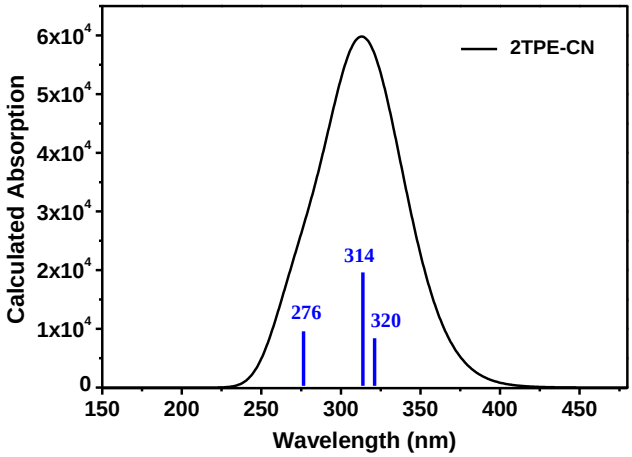


Figure S4. Calculated UV spectrum of **2TPE-CN**.

Table S1. Absorption wavelengths and oscillator strength of **2TPE-CN** evaluated by the TD-DFT (CAM-B3LYP/6-31G (d)) calculation.

Excitation energies	Absorption[nm] (oscillator strength)	Assignments (%)
3.87 eV	320.07 (0.42)	HOMO-1→LUMO+1 (41) HOMO→LUMO (41) HOMO→LUMO+2 (10)
3.95 eV	313.67 (0.99)	HOMO-1→LUMO (34) HOMO-1→LUMO+2 (15) HOMO→LUMO+1 (44)
4.49 eV	276.02 (0.47)	HOMO-2→LUMO (22) HOMO→LUMO (17) HOMO→LUMO+2 (29)

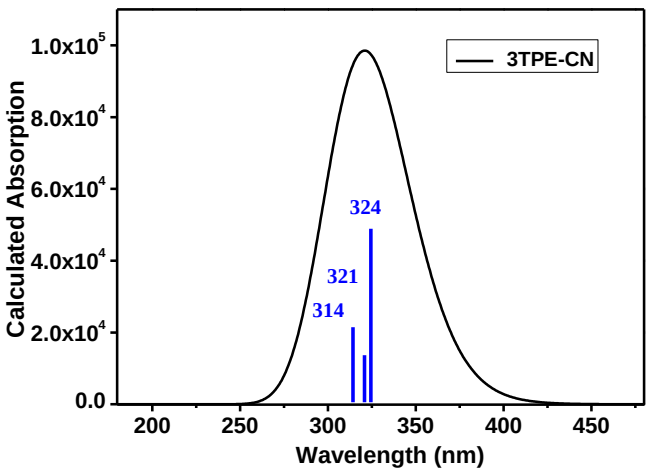


Figure S5. Calculated UV spectrum of **3TPE-CN**.

Table S2. Absorption wavelengths and oscillator strength of **3TPE-CN** evaluated by the TD-DFT (B3LYP/6-311G (d, p)) calculation.

Excitation energies	Absorption[nm] (oscillator strength)	Assignments (%)
3.83 eV	323.86 (1.44)	HOMO-2→LUMO (54) HOMO-2→LUMO+2 (17) HOMO-2→LUMO+3 (11) HOMO-1→LUMO+2 (6) HOMO→LUMO+1 (3)
3.86 eV	321.27 (0.38)	HOMO-1→LUMO+1 (35) HOMO→LUMO (23) HOMO→LUMO+2 (24)
3.95 eV	314.16 (0.64)	HOMO-1→LUMO (19) HOMO-1→LUMO+2 (19) HOMO→LUMO+1 (41)

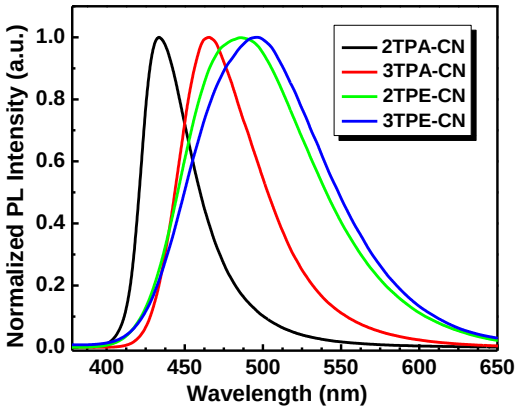


Figure S6. PL spectra of the films.

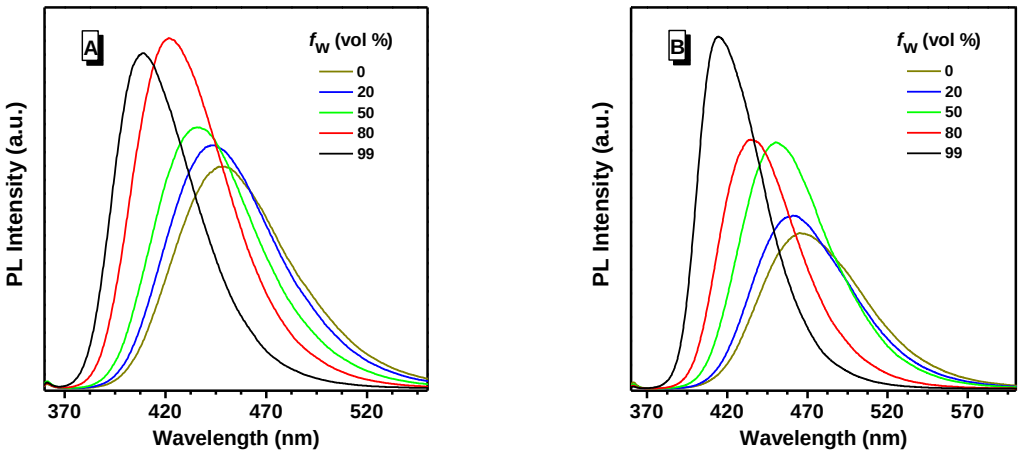


Figure S7. PL spectra of **2TPA-CN** (A) and **3TPA-CN** (B) in THF/cyclohexane mixtures with different cyclohexane fractions. Concentration: ~10 μM.

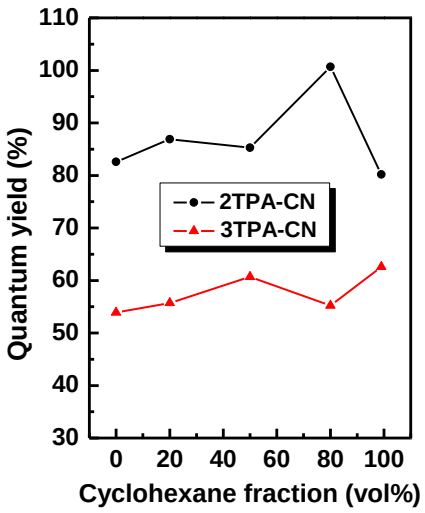


Figure S8. Quantum yields of **2TPA-CN** and **3TPA-CN** in THF/cyclohexane mixtures with different cyclohexane fractions.

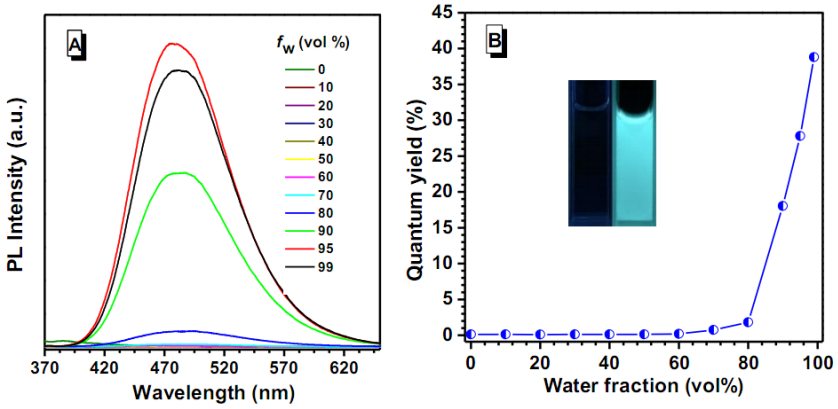


Figure S9. (A) PL spectra of **2TPE-CN** in THF/H_2O mixtures with different water fractions (f_w). (B) Plots of fluorescence quantum yields determined in THF/H_2O solutions using 9,10-diphenylanthracene (Φ = 90% in cyclohexane) as standard versus water fractions. Inset in (B): photos of **2TPE-CN** in THF/water mixtures (f_w=0 and 99%) taken under the illumination of a 365 nm UV lamp.

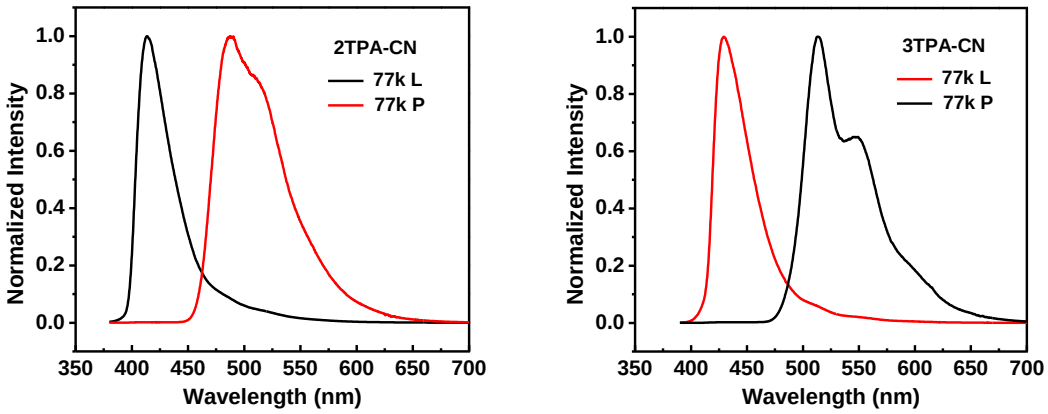


Figure S10. Luminescence (L) and phosphorescence (P) spectra of **2TPA-CN** and **3TPA-CN** at 77 K in a frozen 2-methyl-THF matrix. Concentration: ~10^{-3} M.

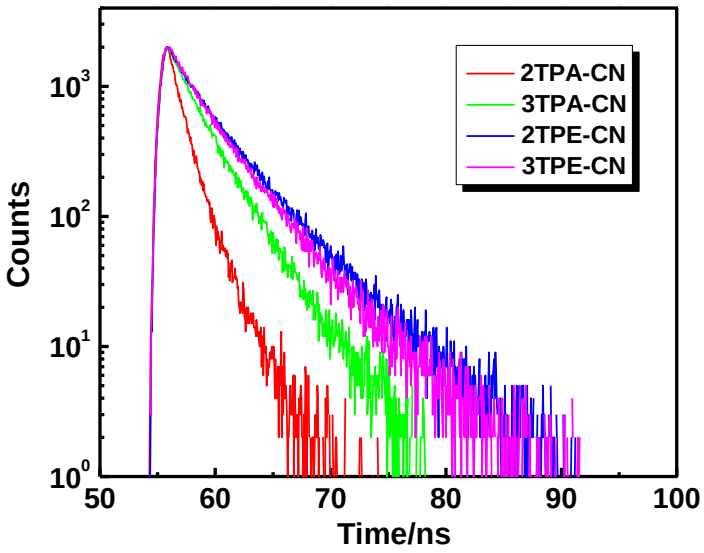


Figure S11. Emission decay of the four luminogens in oxygen-free toluene solution at room temperature.

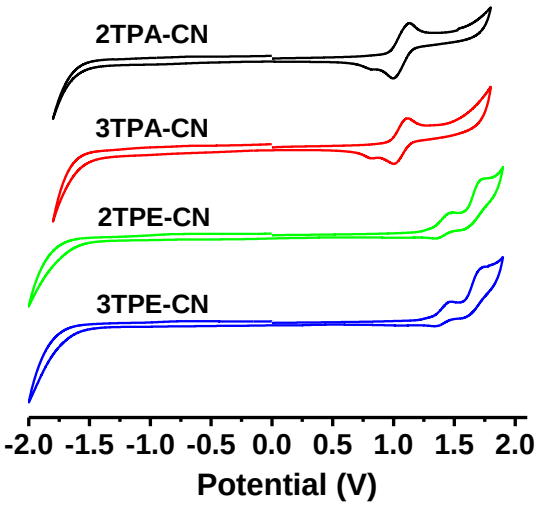


Figure S12. Cyclic voltammograms recorded in dichloromethane.

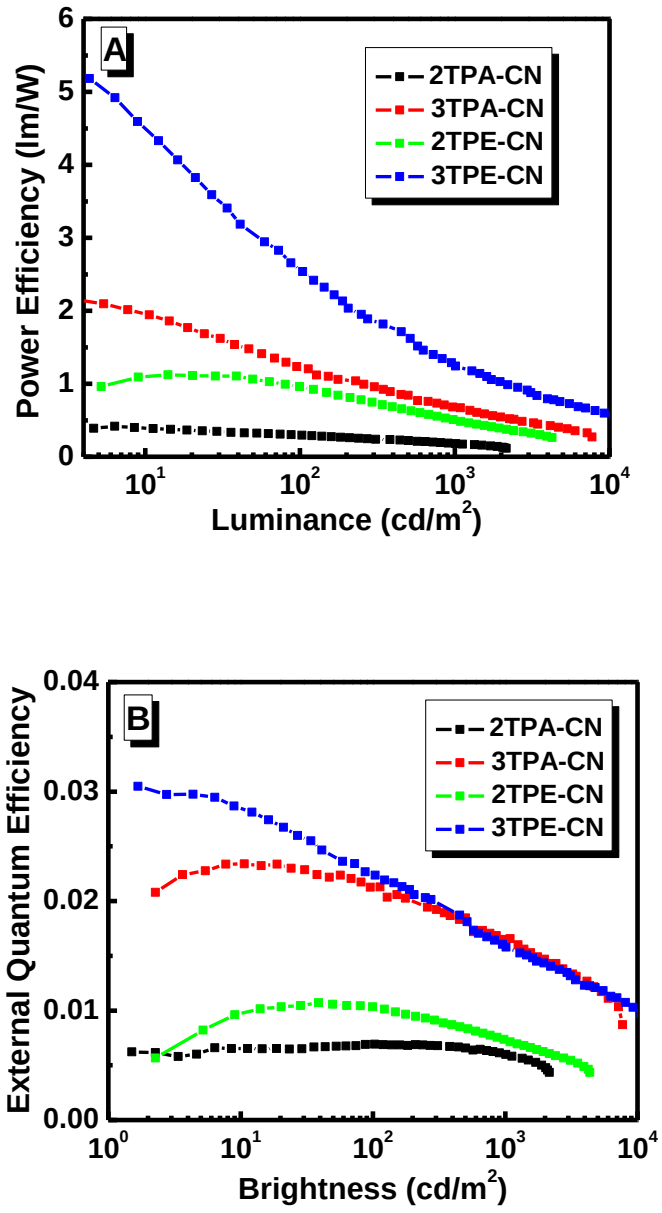
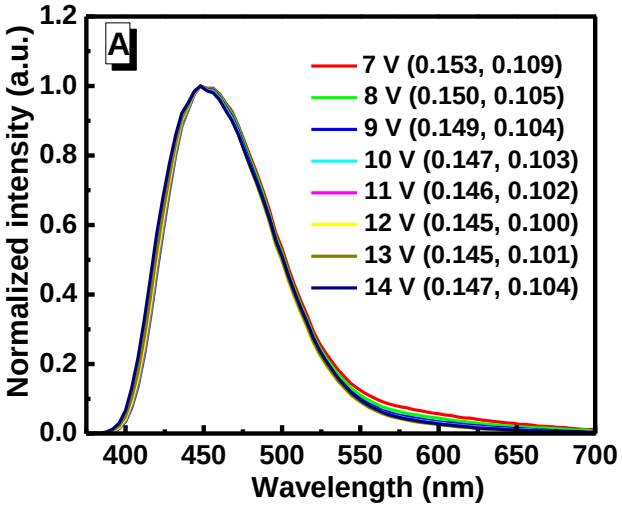
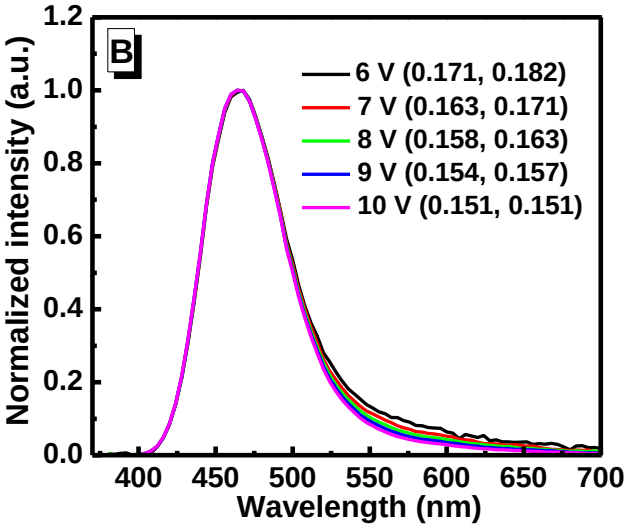
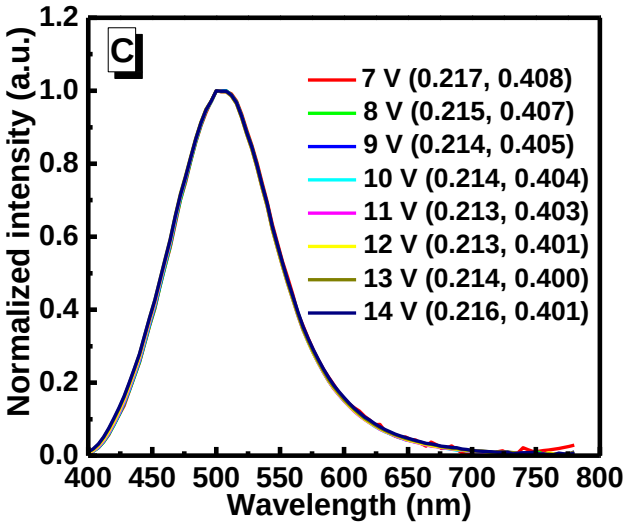


Figure S13. (A) Power efficiency-luminance characteristics and (B) External quantum efficiency-luminance characteristics of the four luminogens. Device configurations: ITO / MoO_3 (10 nm) / NPB (60 nm) / mCP (15 nm)/ X (30 nm) / TPBi (30 nm) / LiF (1 nm) / Al.


A
7 V (0.153, 0.109)
8 V (0.150, 0.105)
9 V (0.149, 0.104)
10 V (0.147, 0.103)
11 V (0.146, 0.102)
12 V (0.145, 0.100)
13 V (0.145, 0.101)
14 V (0.147, 0.104)
Normalized intensity (a.u.)
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
400
450
500
550
600
650
700


B
6 V (0.171, 0.182)
7 V (0.163, 0.171)
8 V (0.158, 0.163)
9 V (0.154, 0.157)
10 V (0.151, 0.151)
Normalized intensity (a.u.)
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
400
450
500
550
600
650
700


C
7 V (0.217, 0.408)
8 V (0.215, 0.407)
9 V (0.214, 0.405)
10 V (0.214, 0.404)
11 V (0.213, 0.403)
12 V (0.213, 0.401)
13 V (0.214, 0.400)
14 V (0.216, 0.401)
Normalized intensity (a.u.)
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
400
450
500
550
600
650
700
750
800

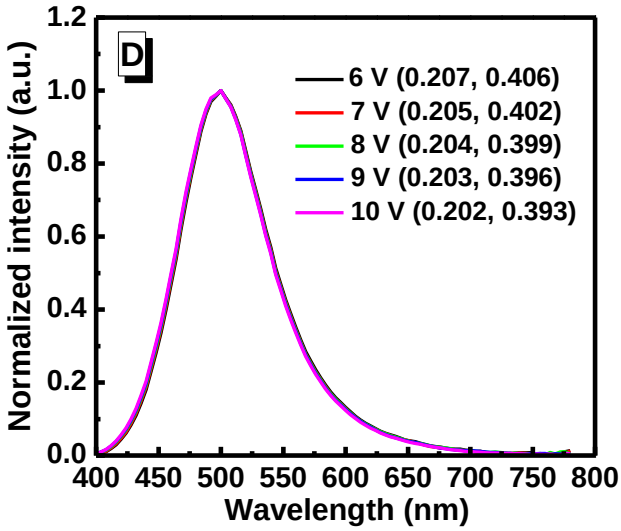
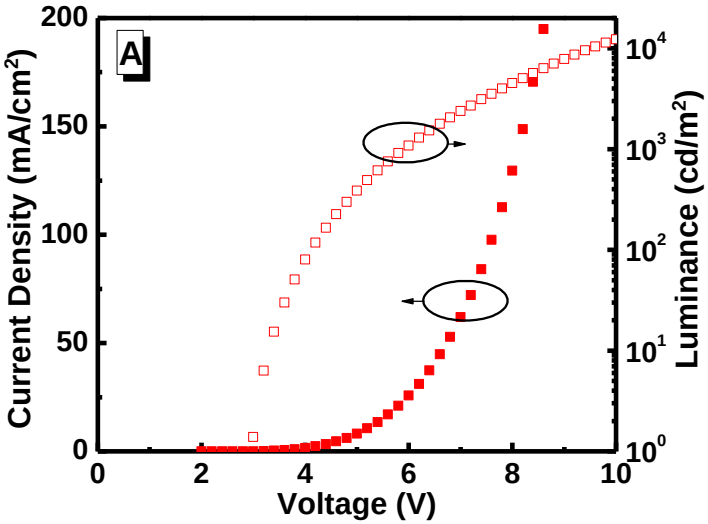
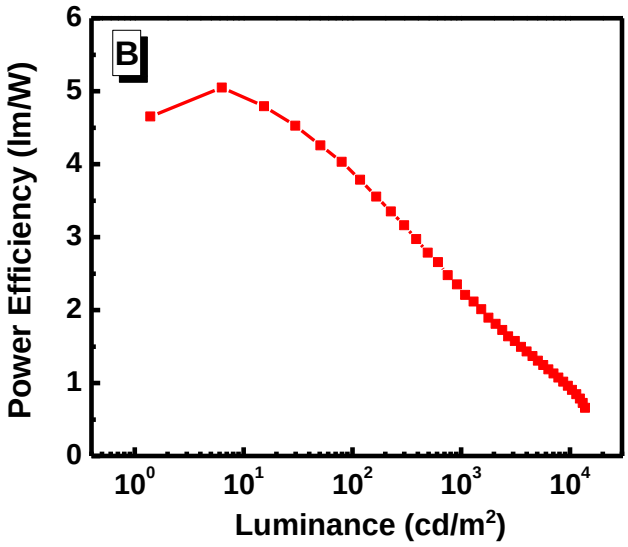


Figure S14. EL spectra of EL devices at different applied voltages of **2TPA-CN** (A), **3TPA-CN** (B), **2TPE-CN** (C) and **3TPE-CN** (D). Device configurations: ITO / MoO_3 (10 nm) / NPB (60 nm) / mCP (15 nm)/ X (30 nm) / TPBi (30 nm) / LiF (1 nm) / Al.


A
Current Density (mA/cm²)
Luminance (cd/m²)
Voltage (V)
0
50
100
150
200
0
2
4
6
8
10
10⁰
10¹
10²
10³
10⁴


B
Power Efficiency (lm/W)
Luminance (cd/m²)
0
1
2
3
4
5
6
10⁰
10¹
10²
10³
10⁴

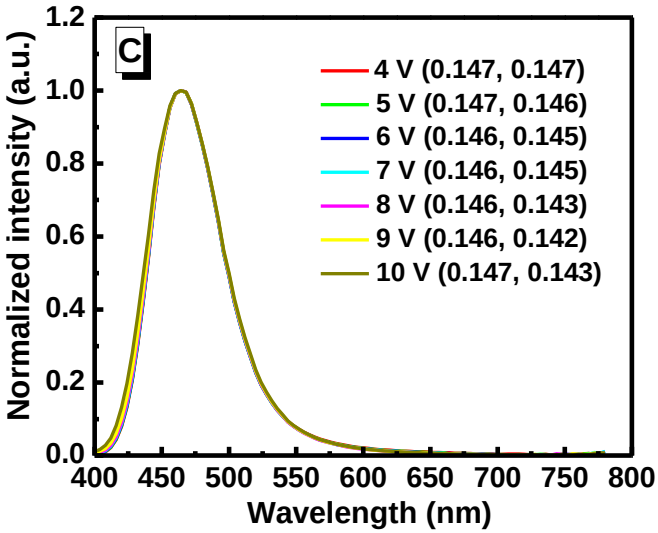
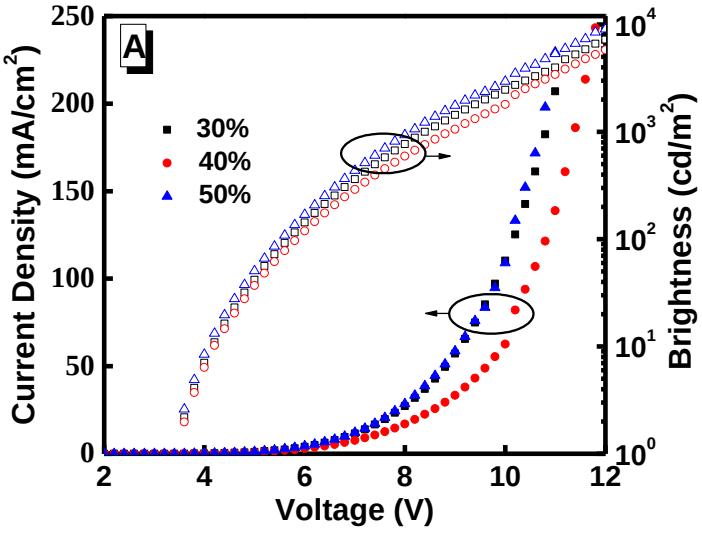
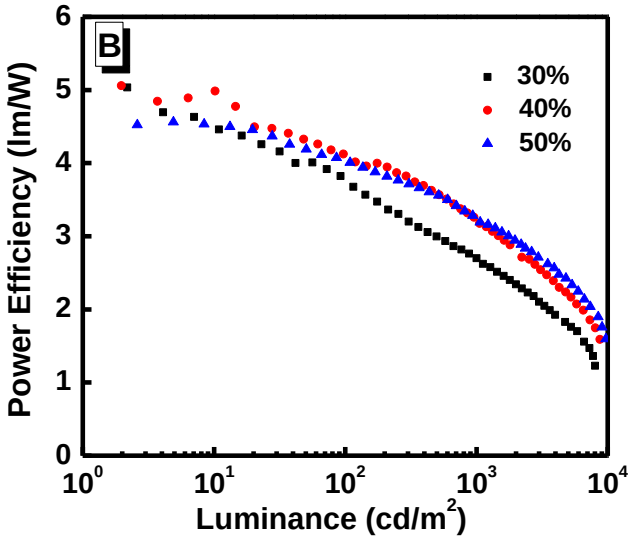


Figure S15. (A) Current density-voltage-luminance characteristics, (B) Power efficiency-luminance characteristics and (C) EL spectra of EL device at different applied voltages. Device configurations: ITO / MoO_3 (10 nm) / **3TPA-CN** (70 nm) / TPBi (30 nm) / LiF (1 nm) / Al.


A
30%
40%
50%
Current Density (mA/cm^2)
Brightness (cd/m^2)
Voltage (V)
0
50
100
150
200
250
2
4
6
8
10
12
10^0
10^1
10^2
10^3
10^4


B
30%
40%
50%
Power Efficiency (lm/W)
Luminance (cd/m^2)
0
1
2
3
4
5
6
10^0
10^1
10^2
10^3
10^4

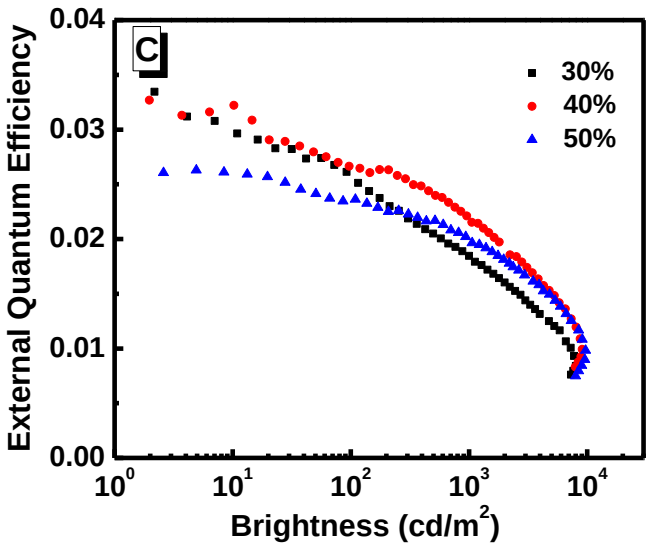
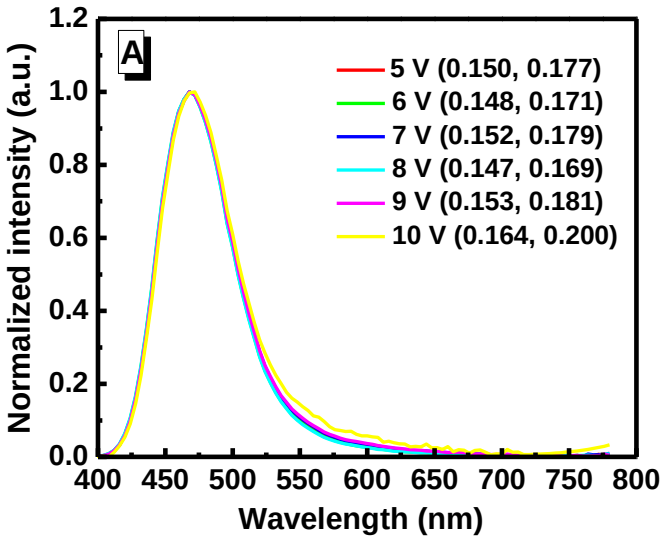


Figure S16. (A) Current density-voltage-luminance characteristics, (B) Power efficiency-luminance characteristics and (C) External quantum efficiency-luminance characteristics. Device configurations: ITO / MoO_3 (10 nm) / NPB (60 nm) / mCP (10 nm) / BmPyPb: x% **3TPA-CN** (20 nm) / BmPyPb (10 nm) /TPBi (35 nm) / LiF (1 nm) / Al.



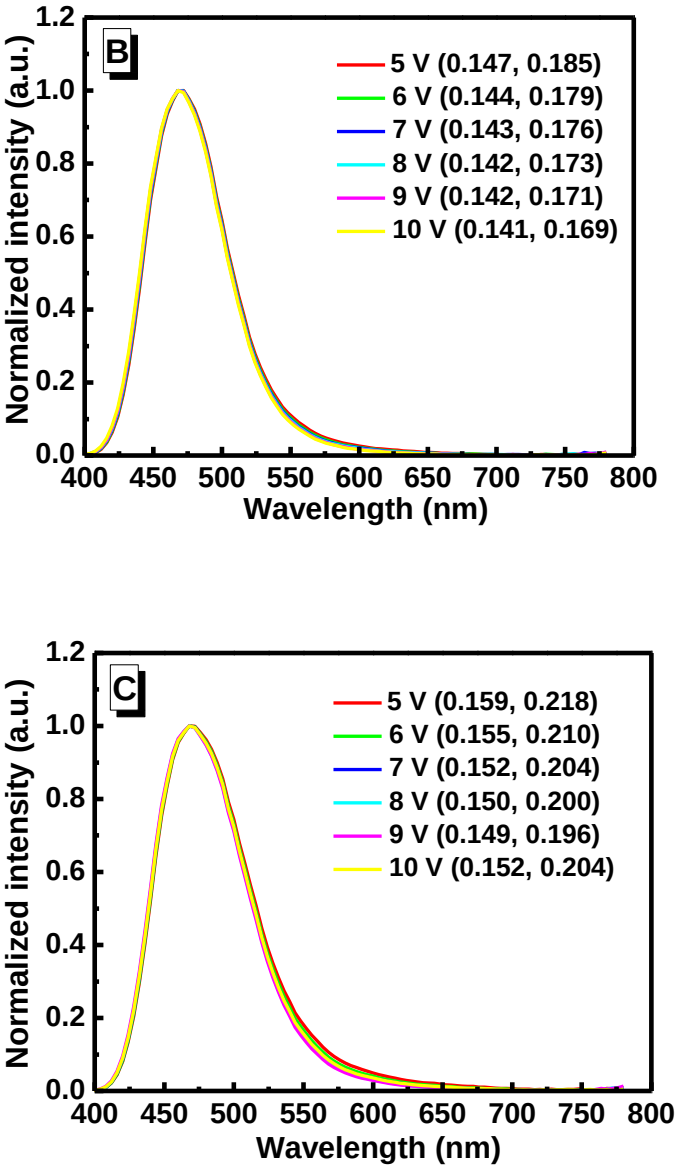
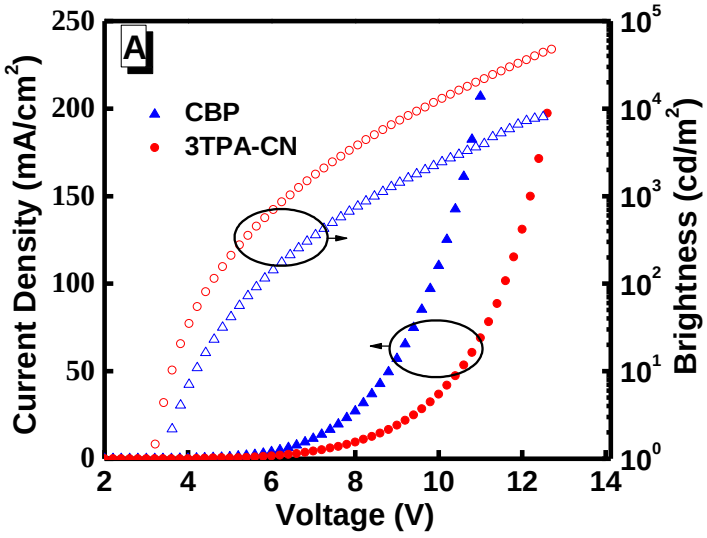
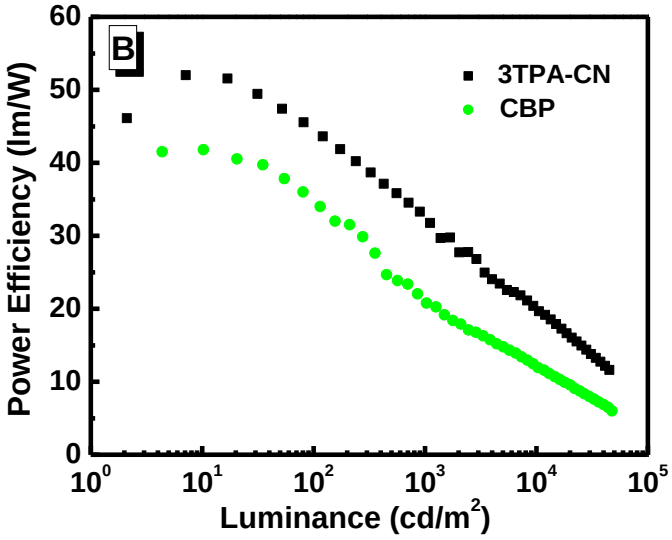


Figure S17. EL spectra of doped devices at different applied voltages. Device configurations: ITO / MoO_3 (10 nm) / NPB (60 nm) / mCP (10 nm) / BmPyPb: x% **3TPA-CN** (20 nm) / BmPyPb (10 nm) /TPBi (35 nm) / LiF (1 nm) / Al. (A: 30%; B: 40%; C: 50%)


A
CBP
3TPA-CN
Current Density (mA/cm^2)
Brightness (cd/m^2)
Voltage (V)
0
50
100
150
200
250
2
4
6
8
10
12
14
10^0
10^1
10^2
10^3
10^4
10^5


B
3TPA-CN
CBP
Power Efficiency (lm/W)
Luminance (cd/m^2)
0
10
20
30
40
50
60
10^0
10^1
10^2
10^3
10^4
10^5

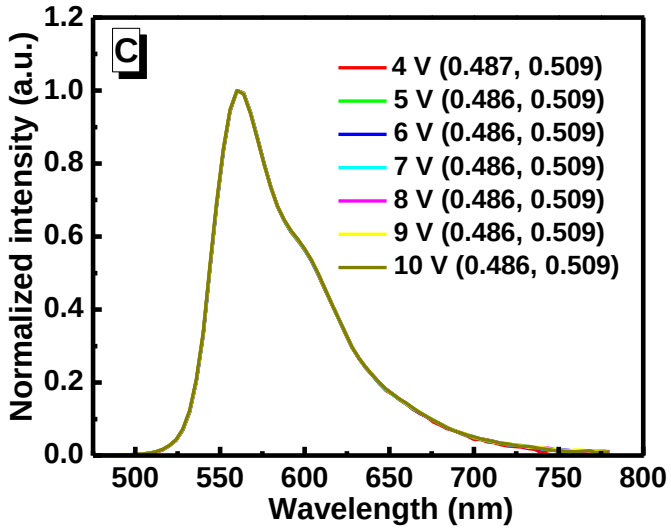


Figure S18. (A) Current density-voltage-luminance characteristics, (B) Power efficiency-luminance characteristics and (C) EL spectra of the device with CBP as the host. Device configurations: ITO / MoO_3 / NPB (60 nm) / mCP (10 nm) / CBP:PO-01 (20 nm, 10 wt%) / TPBI (40 nm) / LiF (1 nm) / Al.