Electronic supplementary information

Tetraphenylbenzene-based AIEgens: the Horizontally Oriented Emitters for highly Efficient Non-doped Deep Blue OLEDs and Host for High-Performance Hybrid WOLEDs

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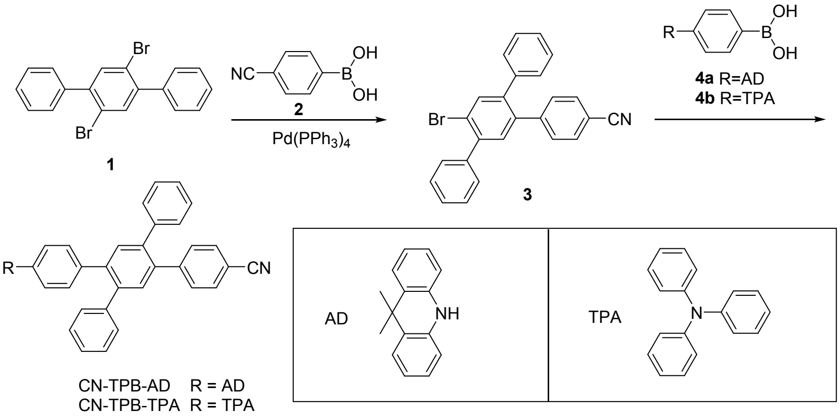
1. Materials and Instruments

All the chemicals and reagents were purchased from commercial sources and used as received without further purification. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 500 spectrometer in deuterated dichloromethane. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. TGA analysis was carried out on a TA TGA Q5000 and DSC analysis was performed on a DSC Q1000 under dry nitrogen at a heating rate of 10 ^{o}C min^{-1}. UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. Photoluminescence spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. Fluorescence quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. Fluorescence lifetimes were determined with a Hamamatsu C11367-11 Quantaurus-Tau time-resolved spectrometer. The frontier orbitals, energy levels of singlet and triplet states of the molecules based on the ground state geometries were calculated at B3LYP/6-31G(d,p) by Gaussian 09 program. Cyclic voltamogramms were measured on a CHI 610E A14297 in a solution of tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) in dichloromethane at a scan rate of 100 mV s^{-1}.

2. Synthesis

Synthesis of 4'-bromo-5'-phenyl-[1,1':2',1''-terphenyl]-4-carbonitrile (**3**)



Scheme S1 Synthetic routes to the CN-TPB-AD and CN-TPB-TPA.

Compound **1** (6.0 g, 15.5 mmol), [1] anhydrous potassium carbonate (6.4 g, 46.5 mmol) and $Pd(PPh_3)_4$ (895 mg, 0.8 mmol) were added into a 250 mL two neck round bottom flask under N_2 protection, then 1,4-dioxane (105 mL) and water (15 mL) were injected into the flask. The compound **2** (2.50 g, 17.0 mmol) dissolved in 45 mL 1,4-dioxane was added dropwise into the flask within 4.5 h. The reaction solution was stirred at 80 °C for 10 h. After cooling to room temperature, the solution was poured into water and extracted with dichloromethane (DCM) for three times, and then organic phase was combined and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by a silica gel column chromatography using petroleum ether (PE)/DCM (2:1 v/v) as eluent. White solid of compound **3** was obtained in 53% yield (3.38 g). ^{1}H NMR (500 MHz, CD_2Cl_2), δ (TMS, ppm): 7.15 (m, 2H), 7.26-7.29 (m, 5H), 7.39 (s, 1H), 7.41-7.51 (m, 7H), 7.80 (s, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2), δ (TMS, ppm): 145.75, 142.48, 141.85, 140.93, 139.71, 138.77, 135.74, 133.60, 132.50, 130.38, 130.05, 129.00, 128.81, 128.61, 128.13, 123.10, 119.38, 111.39.

Synthesis of 4'-(4-(10,10-dimethyl-9,10-dihydroanthracen-9-yl)phenyl)-5'-phenyl-[1,1':2',1''-terphenyl]-4-carbonitrile (CN-TPB-AD)

CN-TPB-AD was synthesized by similar procedures as **3** from the reagents of **4a** and **3** in 83% yield. ^{1}H NMR (500 MHz, CD_2Cl_2), δ (TMS, ppm): 7.69 (s, 1H), 7.58 (d, 2H), 7.56 (t, 1H), 7.47 (t, 4H), 7.40 (t, 1H), 7.38 (t, 1H), 7.33-7.25 (m, 10H), 7.22 (d, 1H), 7.20 (s, 1H), 6.97 (m, 4H), 6.26 (m, 2H), 1.66 (m, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2), δ (TMS, ppm): 145.89, 140.86, 140.43, 140.25, 140.20, 139.88, 138.22, 132.76, 132.46, 132.43, 131.82, 130.62, 129.96, 129.88, 128.27, 128.03, 127.14, 127.08, 118.84, 110.50. HRMS ($C_{46}H_{34}N_2$): *m/z* 614.2722 (M^+, calcd 614.2731).

Synthesis of 4'''-(diphenylamino)-2',5'-diphenyl-[1,1':4',1'':4'',1'''-quaterphenyl]-4-carbonitrile (CN-TPB-TPA)

CN-TPB-TPA was synthesized by similar procedures as **3** from the reagents of **4b** and **3** in 89% yield. ^{1}H NMR (500MHz, CD_2Cl_2), δ (TMS, ppm): 7.59 (s, 1H), 7.55 (t, 1H), 7.53 (t, 1H), 7.51 (d, 3H), 7.48 (d, 2H), 7.37 (t, 1H), 7.35(t, 1H), 7.26 (m, 14H), 7.22 (m, 2H), 7.10 (m, 6H), 7.03 (m, 2H). ^{13}C NMR (125

MHz, CD_2Cl_2), δ (TMS, ppm): 148.04, 147.76, 146.35, 141.17, 140.67, 140.38, 140.22, 139.59, 139.90, 138.21, 134.57, 133.13, 132.19, 130.27, 129.68, 128.64, 127.29, 126.40, 124.85, 124.16, 123.43, 119.26, 110.81. HRMS ($C_{49}H_{34}N_2$): *m/z* 650.2722 (M^+, calcd 650.2746).

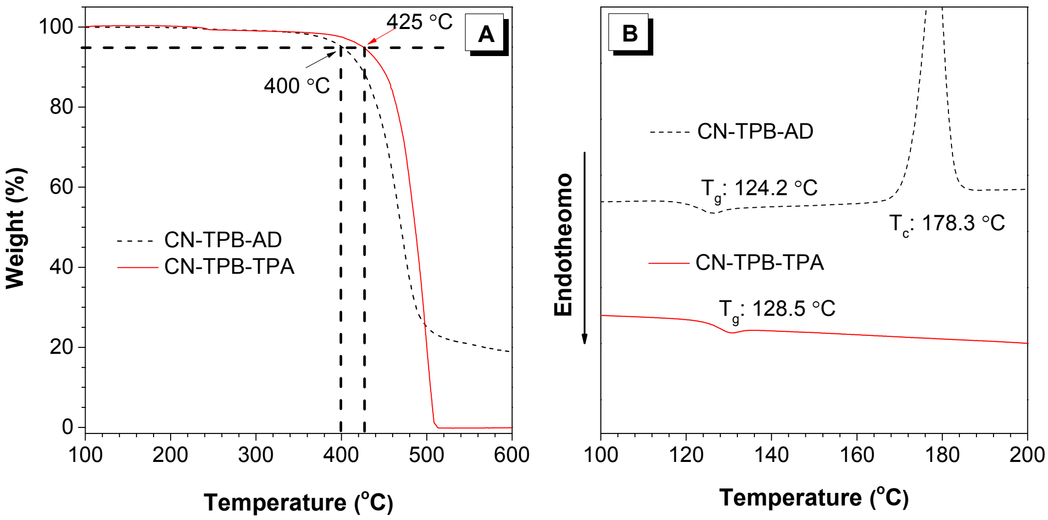


Fig. S1. TGA thermograms (A) and DSC curve (B) of CN-TPB-AD and CN-TPB-TPA recorded under nitrogen at a heating rate of 10 °C/min.

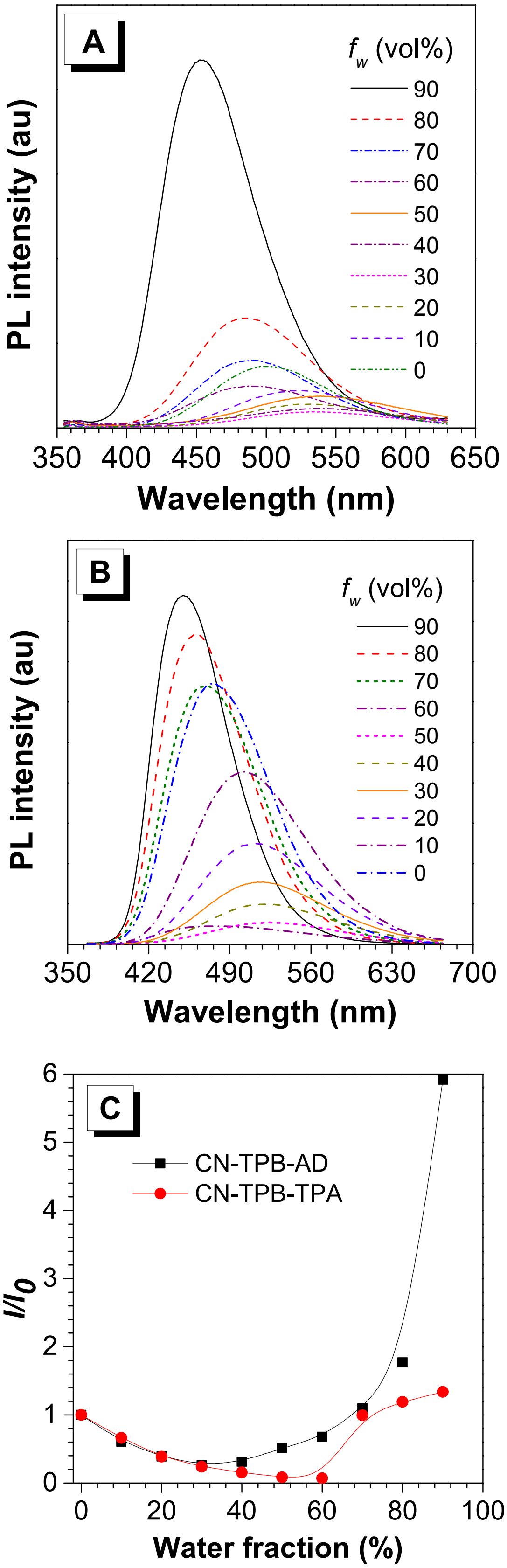


Fig. S2. (A) PL spectra of CN-TPB-AD, (B) CN-TPB-TPA in THF/water mixtures with different water fractions. (C) Plots of I/I_0 of CN-TPB-AD and CN-TPB-TPA versus water fractions in THF/water mixtures. Concentration: 10 μM.

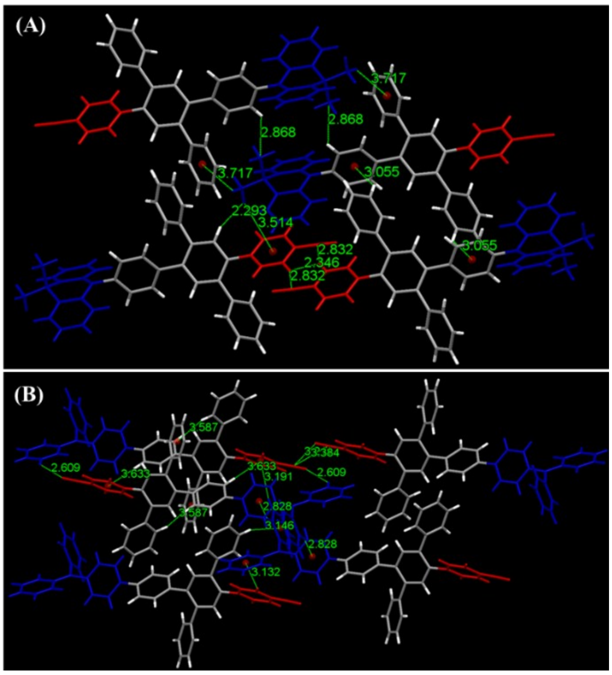


Fig. S3. The hydrogen-binding interactions in (A) CN-TPB-AD and (B) CN-TPB-TPA crystals.

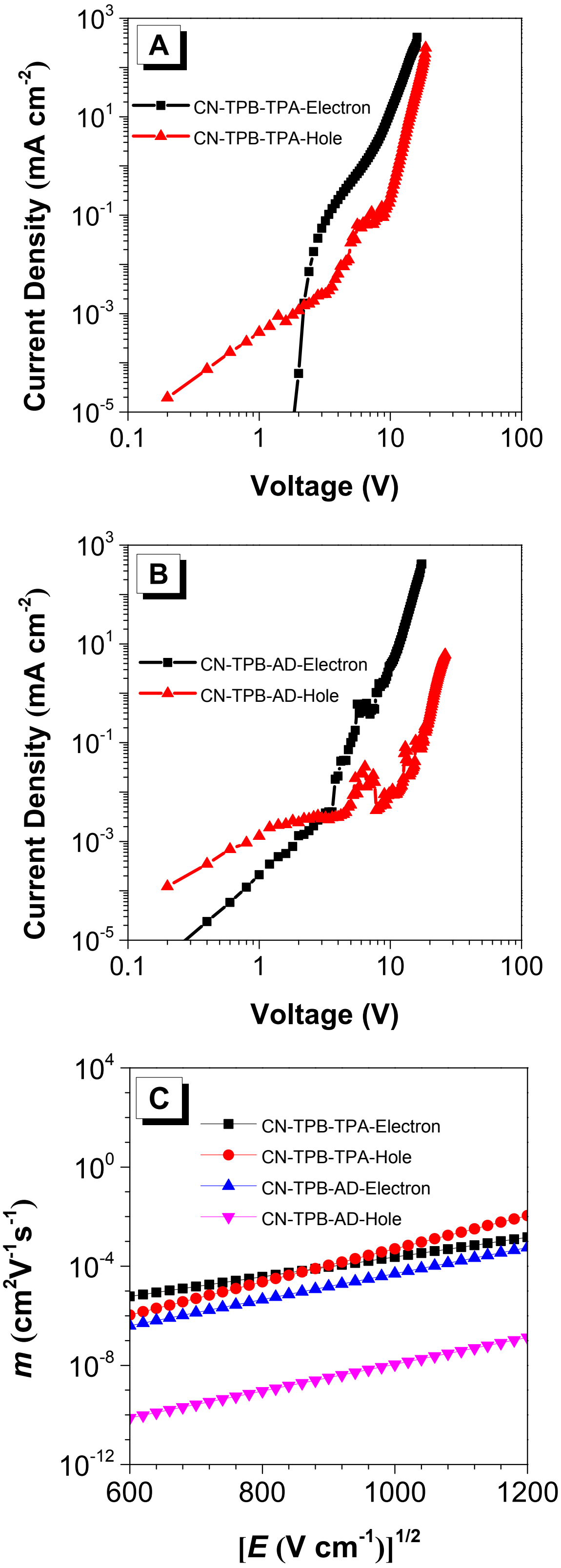


Fig. S4. Double logarithmic plots of current density versus applied voltage of the (A) devices B3 and B4 as well as (B) devices B1 and B2. (C) The hole- and electron-mobility of CN-TPB-AD and CN-TPB-TPA under different electrical fields.

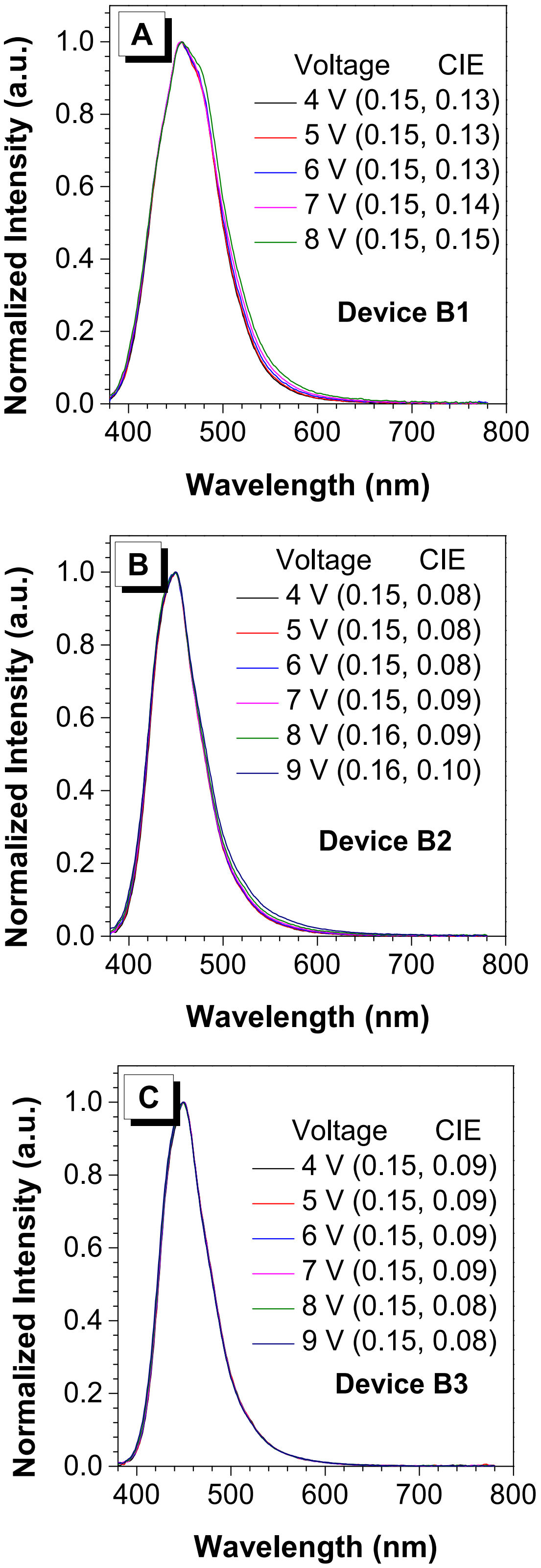


Fig. S5. EL spectra at various luminance of devices (A) B1, (B) B2, and (C) B3.

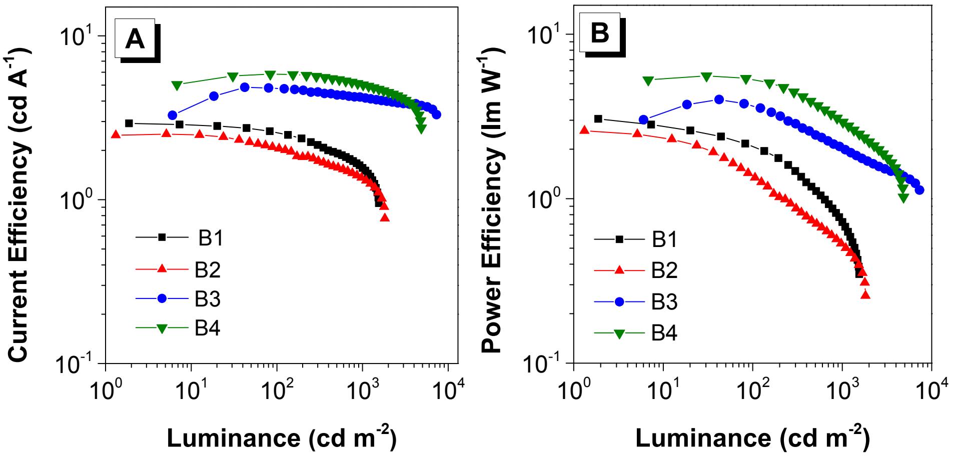


Fig. S6. Forward-viewing (A) CE and (B) PE as a function of luminance for B1-B4

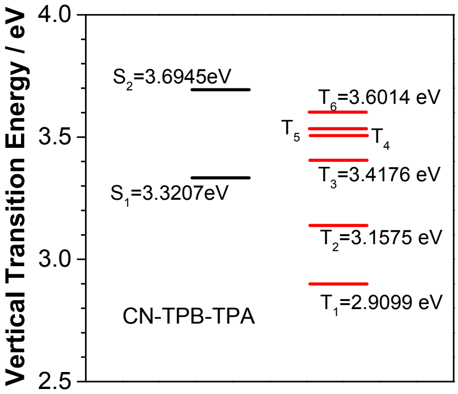


Fig. S7. The calculated energy levels of singlet and triplet states of CN-TPB-TPA based on DFT.

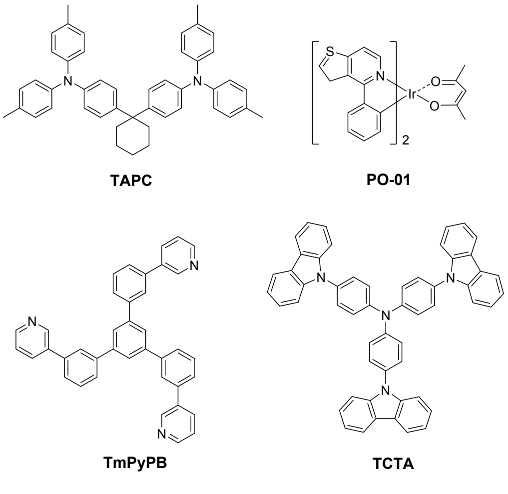


Fig. S8. The chemical structures of compounds used in the devices.

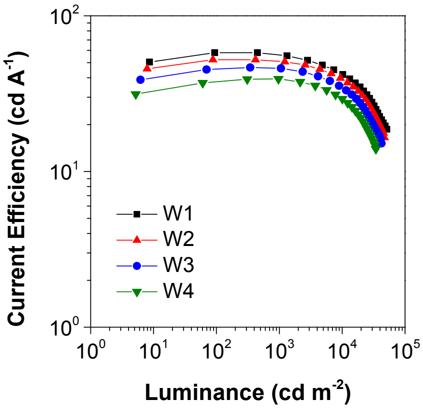


Fig. S9. Forward-viewing CE as a function of luminance for devices W1-W4.

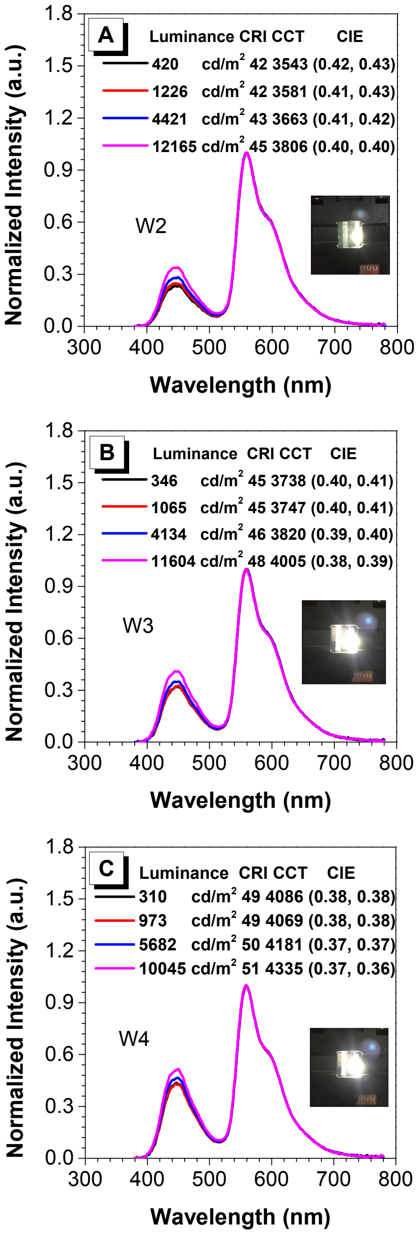


Fig. S10. EL spectra at various luminance of (A) device W2, (B) device W3 and (C) device W4.

Reference

1. A. Steiner and K. Y. Amsharov, *Angew. Chem. Int. Ed.*, 2017, **56**, 14732-14736.