

Combination of TADF and Exciplex Emission for Efficient “Warm-White” OLEDs

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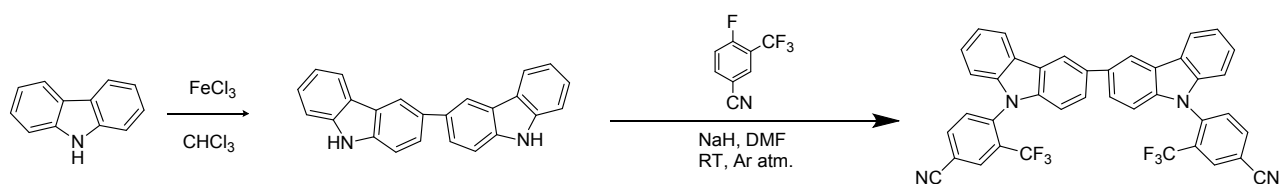
Supplementary material

Details of synthesis and identification

The melting points were determined in open capillaries with a digital melting point Electrothermal MEL-TEMP apparatus. All reactions and purity of the synthesized compounds were monitored by TLC using Silica gel 60 F 254 aluminum plates (Merck). NMR spectroscopy was carried out on a Bruker Avance 400 NMR spectrometer. The residue signal of CDCl₃ (7.26 ppm for ¹H NMR and 77.16 ppm for ¹³C NMR, respectively) was used as internal standard. Attenuated total reflection infrared (ATR IR) spectra were recorded using a Bruker VERTEX 70 spectrometer. MS data was recorded on UPLC-MS Acquity Waters SQ Detector 2.

Synthesis

The synthetic route of the compound $p\text{CNBCzoCF}_3$ is shown in Scheme 1. First of all, by Friedel-Crafts reaction using FeCl_3 as Lewis acid catalyst $9H,9'H-3,3'$ -bicarbazole was synthesized. Afterwards one symmetric bipolar material has been designed and synthesized with $3,3'$ -bicarbazole core. The compound $p\text{CNBCzoCF}_3$ was synthesized at room temperature in argon atmosphere via a nucleophilic substitution reaction with sodium hydride and 4-fluoro-3-(trifluoromethyl)benzonitrile. The chemical structure of the target compound was confirmed via ^1H , ^{13}C and ^{19}F nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FT-IR) and mass spectrometry (MS) measurements.

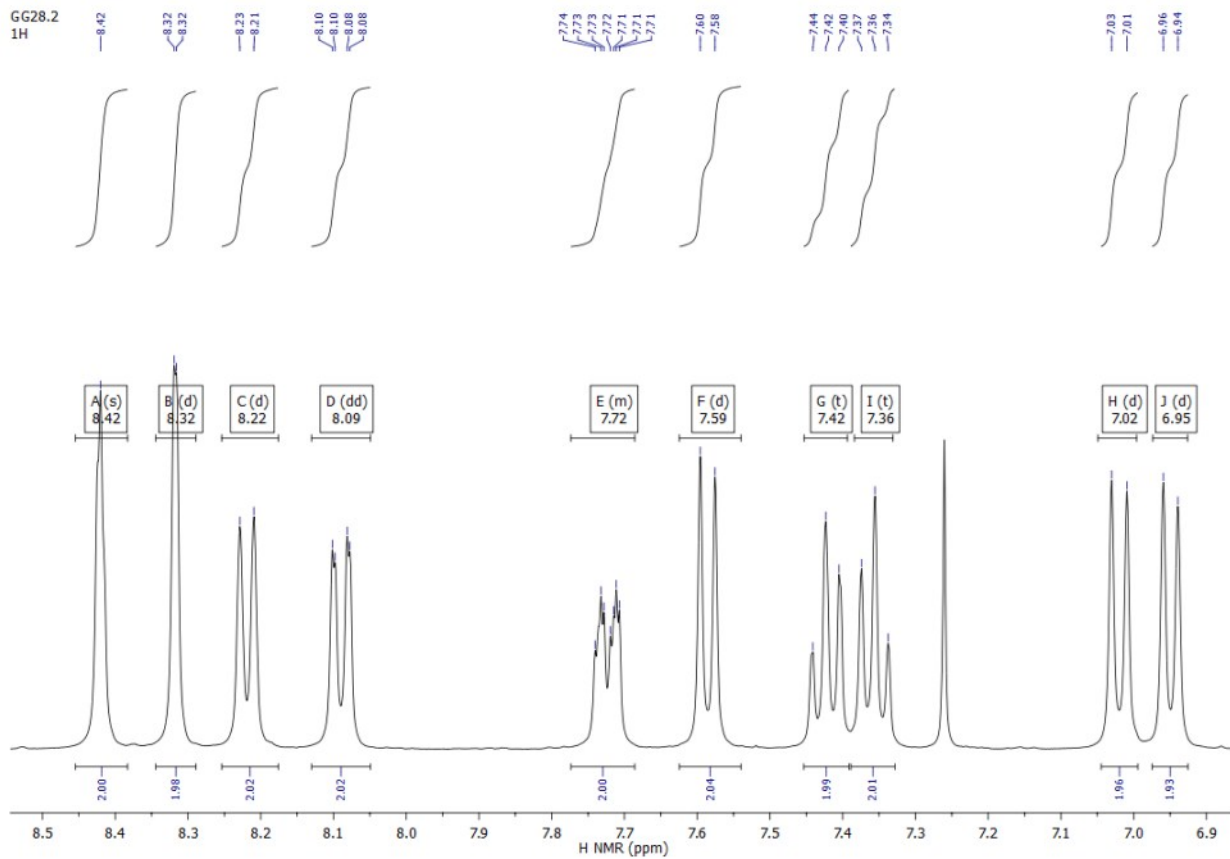


Scheme S1. Synthetic route and chemical structure of the target compound **4,4'-(9H,9'H-[3,3'-bicarbazole]-9,9'-diyl)bis(3-(trifluoromethyl)benzonitrile) ($p\text{CNBCzoCF}_3$)**.

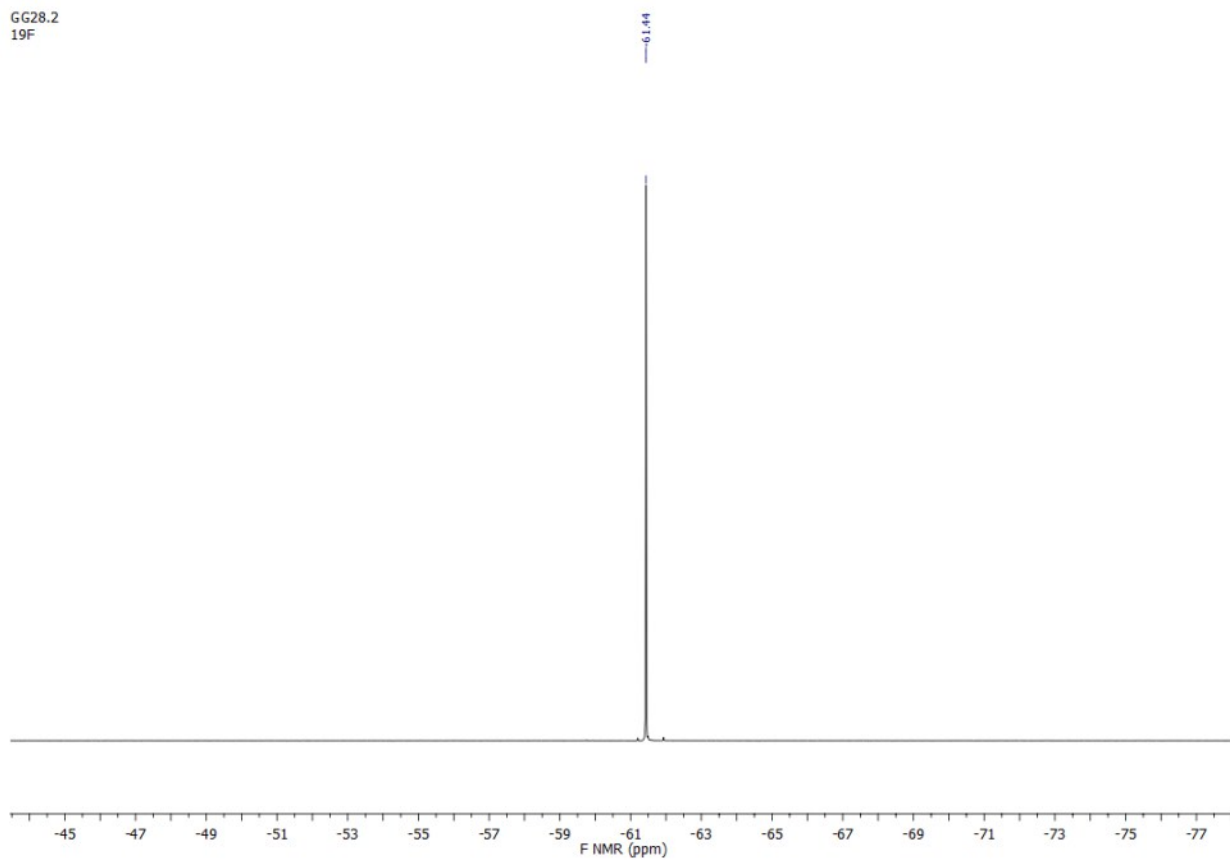
A mixture of the *N*-unsubstituted bicarbazole (0.50 g, 1.5 mmol), sodium hydride (NaH) (0.22g, 9.0 mmol) and 4-fluoro-3-(trifluoromethyl)benzonitrile (0.68g, 3.6 mmol) were dissolved in dimethylformamide (DMF) under argon atmosphere. The reaction mixture was mixed at room temperature for 20 hours. When the reaction completed, the mixture was poured into water and there was infused a small amount of saturated sodium hydroxide (NaOH) because of coagulation. Afterwards the crude product was filtered and purified by column chromatography (silica, DCM/Hex=1/1 as eluent). The target compound $p\text{CNBCzoCF}_3$ was obtained as yellowish powder after recrystallization from hot methanol. Yield: 0.30g (25%), melting point 294-295°C.

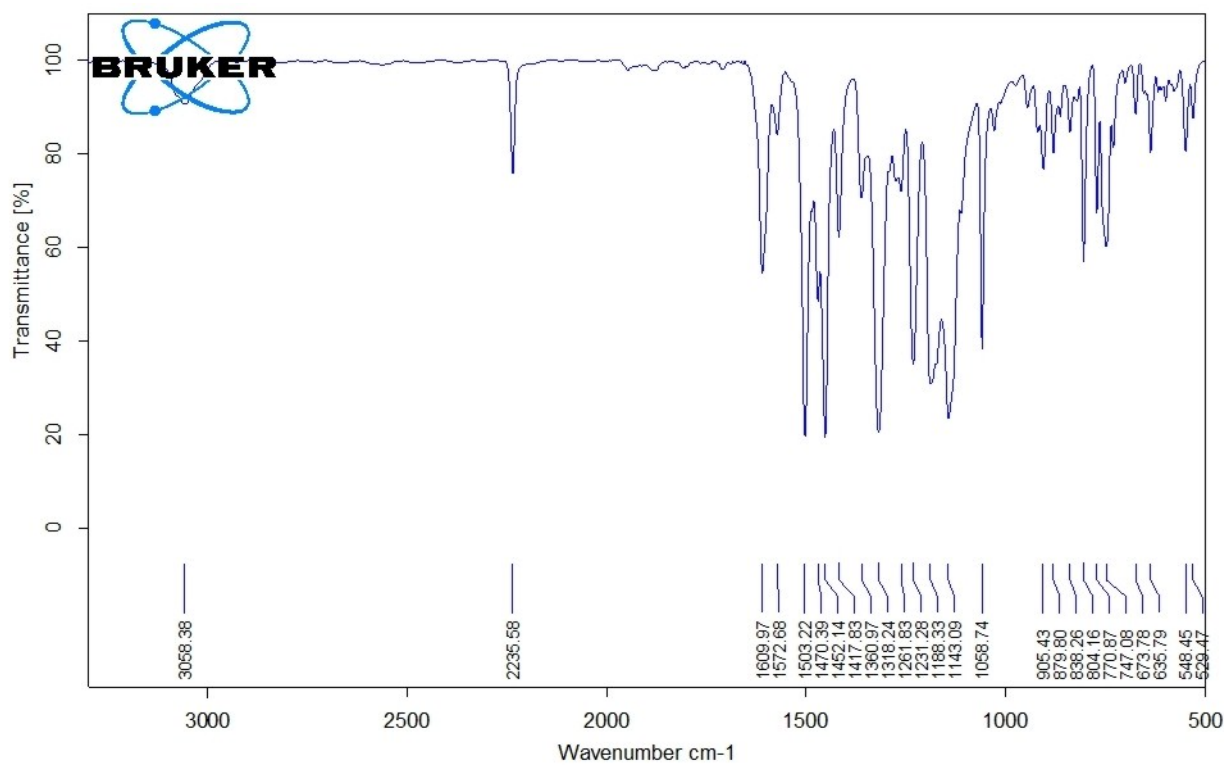
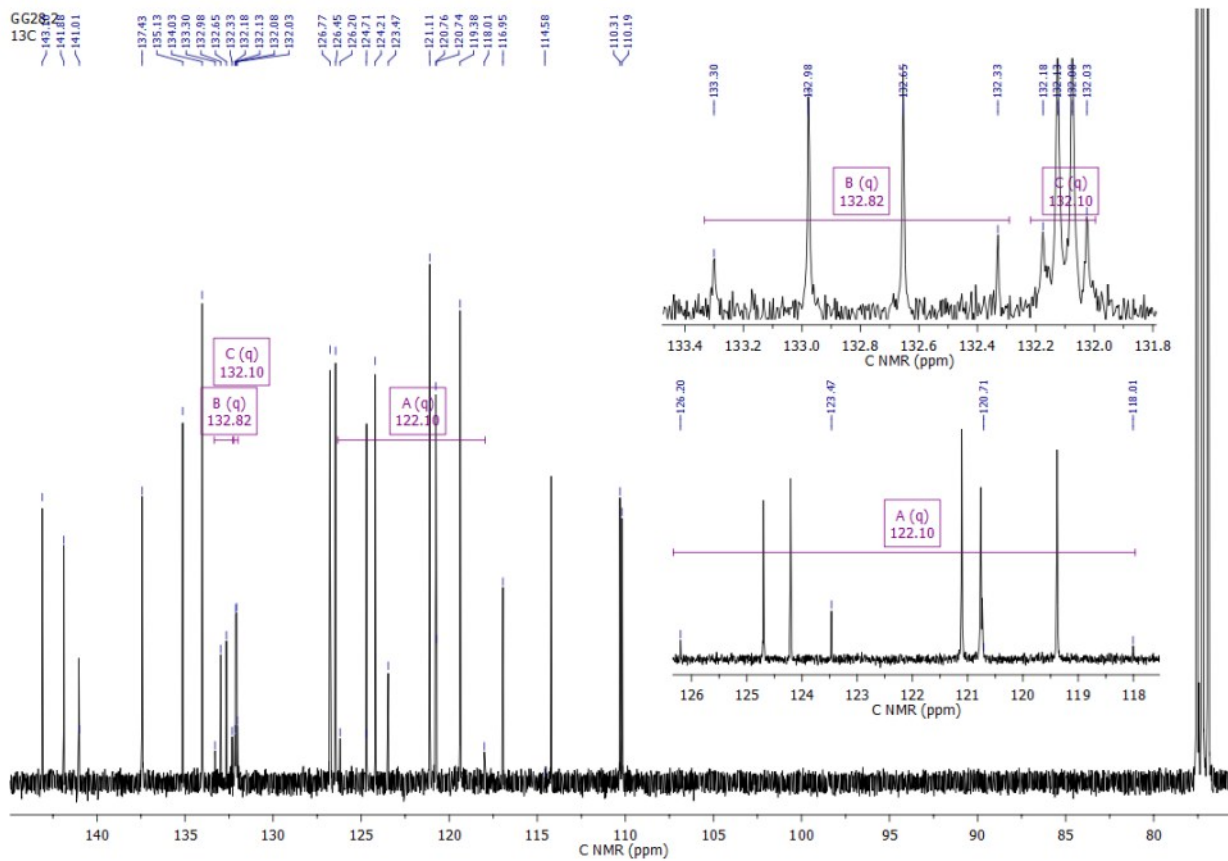
^1H NMR (400 MHz, CDCl_3) δ 8.42 (s, 2H), 8.32 (d, $J = 1.1$ Hz, 2H), 8.22 (d, $J = 7.7$ Hz, 2H), 8.09 (dd, $J = 8.1, 1.5$ Hz, 2H), 7.77 – 7.69 (m, 2H), 7.59 (d, $J = 8.1$ Hz, 2H), 7.42 (t, $J = 7.2$ Hz, 2H), 7.36 (t, $J = 7.2$ Hz, 2H), 7.02 (d, $J = 8.4$ Hz, 2H), 6.95 (d, $J = 8.1$ Hz, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -61.44. ^{13}C NMR (101 MHz, CDCl_3) δ 143.1, 141.9, 141.0, 137.4, 135.1, 134.0, 132.8 (q, $J = 32.5$ Hz), 132.1 (q, $J = 5.1$ Hz), 126.8, 126.5, 124.7, 124.2, 121.1, 122.1 (q, $J = 275$ Hz), 120.8, 119.4, 116.9, 114.6, 110.3, 110.2.

GG28.2
1H



GG28.2
19F





*p*CNBCzoCF₃ IR (KBr): 3058, 2235, 1069, 1503, 1470, 1318, 1231, 1188, 1143, 1058, 804, 770, 747.

MS of $p\text{CNBCzoCF}_3$ is following:

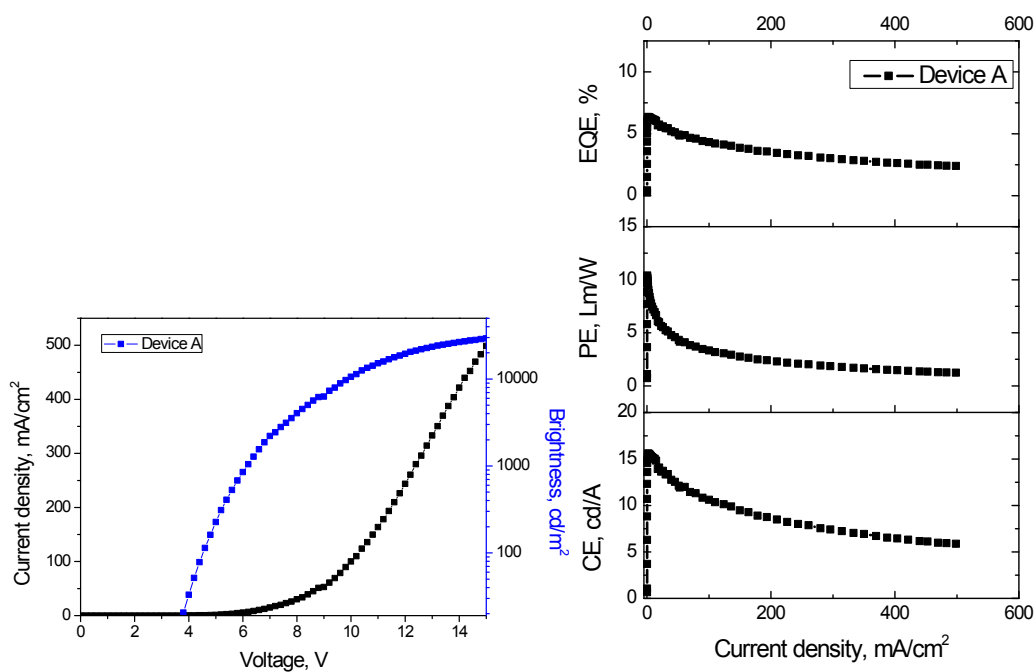
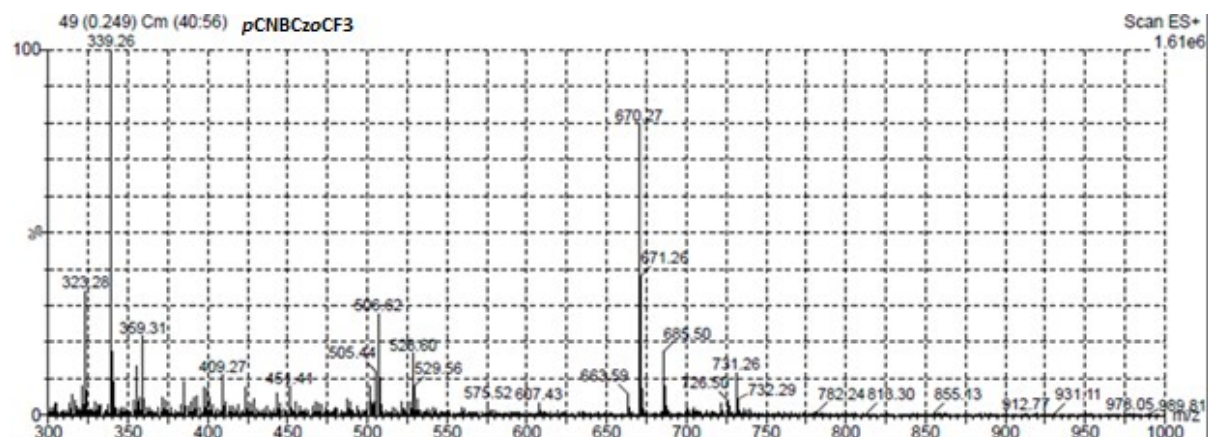


Fig. S1. Current density vs. voltage, luminance vs. voltage characteristics (a). Current efficiency vs. current density characteristic and current density vs. power and quantum efficiency characteristics of the fabricated Device A(b).

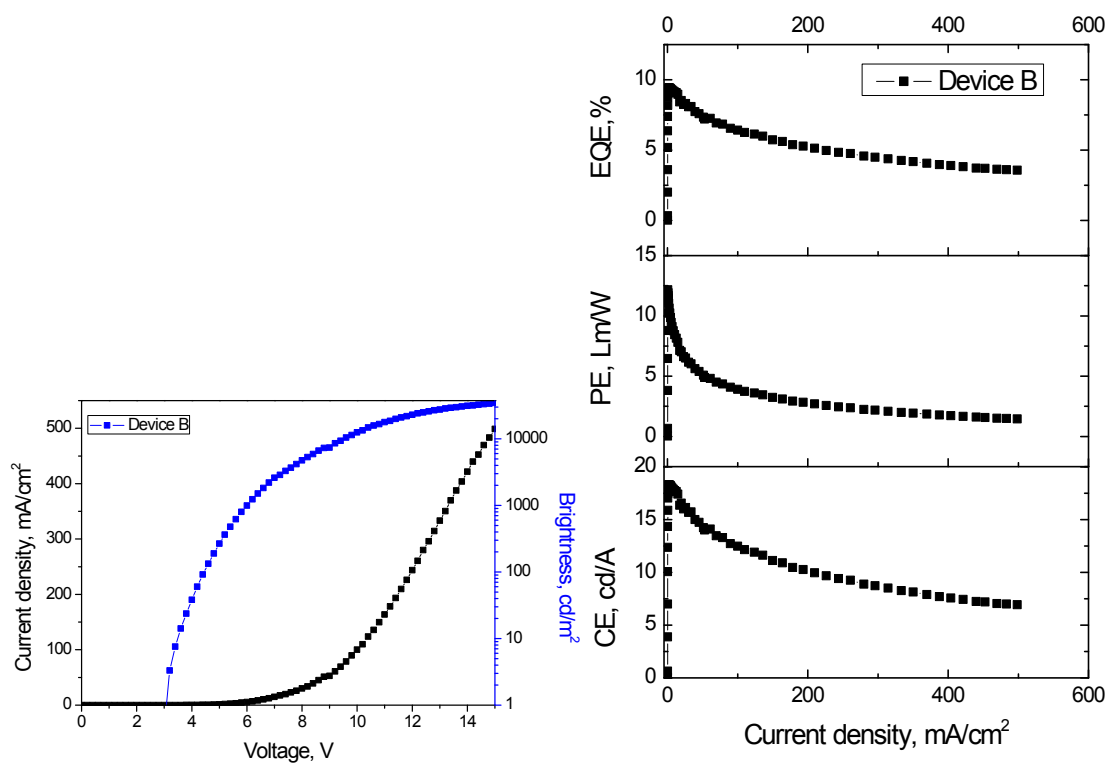


Fig. S2. Current density vs. voltage, luminance vs. voltage characteristics (a) and current efficiency vs. current density characteristic and current density vs. power and quantum efficiency characteristics (b) of the fabricated Device B.

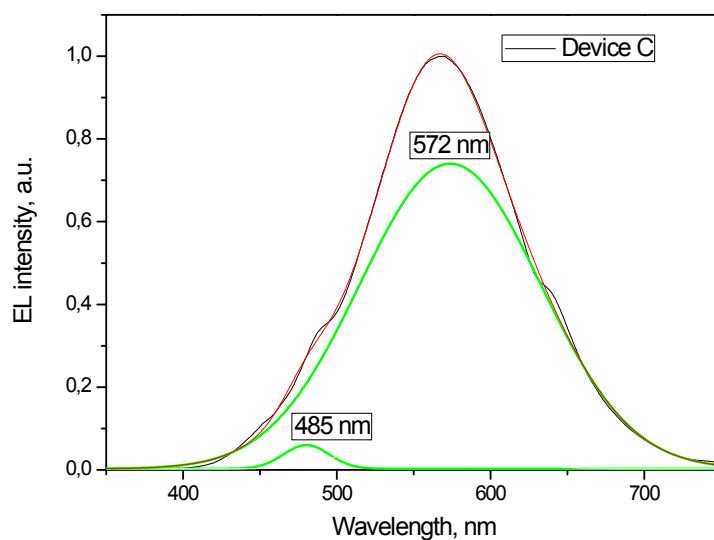


Fig. S3. Decomposed range in Gauss(Gaussian)

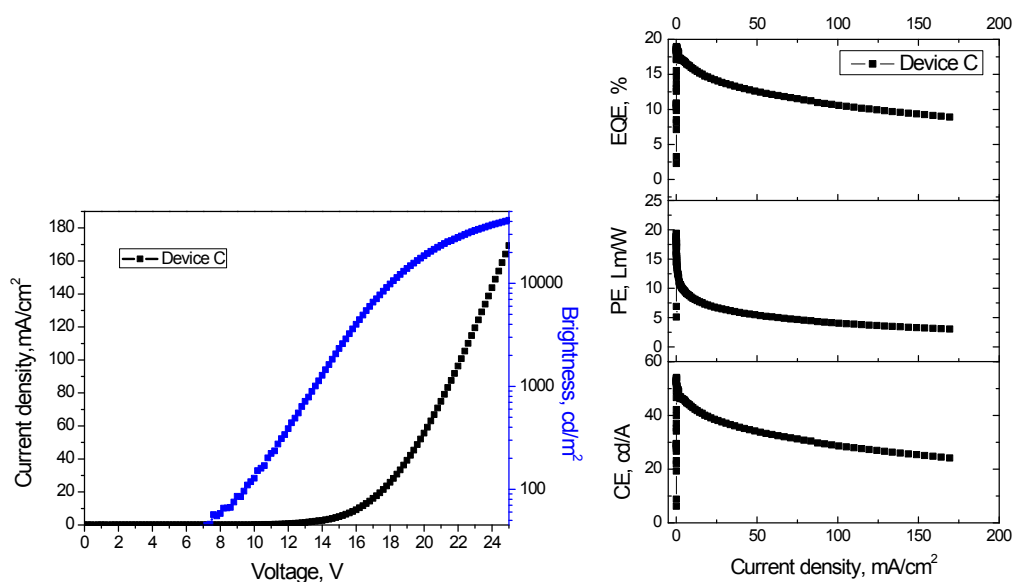


Fig. S4. Current density-voltage, luminance-voltage (a) and current efficiency vs power efficiency vs external quantum efficiency -current density characteristics (b) for the device C.

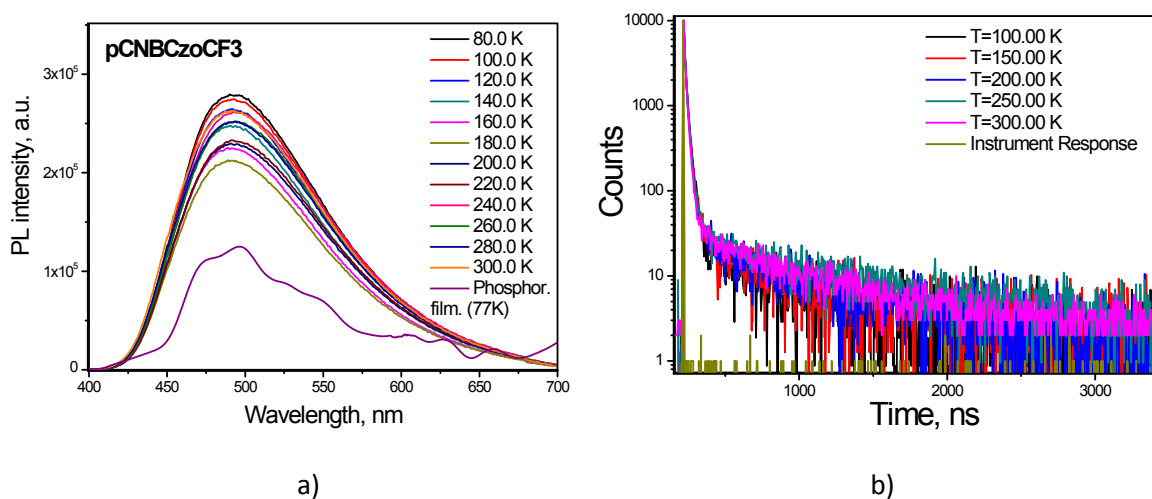


Fig. S5. PL spectra film (recorded at different temperatures) and phosphorescence spectrum (recorded at 77K and delay 50 ms after excitation) for pCNBCzoCF₃ film (a); time-decays of PL (recorded at different temperatures) for pCNBCzoCF₃ film.