

Highly Efficient Ultra-Deep Blue Organic Light-Emitting Diodes with a Wet- and Dry-Process Feasible Cyanofluorene Acetylene Based Emitter

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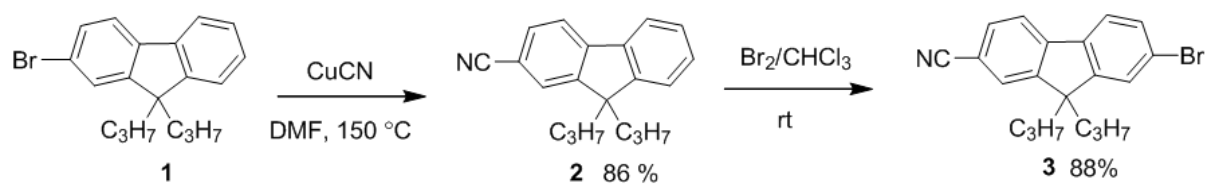
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Scheme S1: Synthesis of 7-bromo-9,9-dipropyl-9H-fluorene-2-carbonitrile (3);

The synthesis starts from cyanation of 2-bromo-9,9-dipropyl-9H-fluorene (**1**) with 2 eq. of copper cyanide in DMF at reflux condition to give 9,9-dipropyl-9H-fluorene-2-carbonitrile (**2**) in 86% yield. The compound 7-bromo-9,9-dipropyl-9H-fluorene-2-carbonitrile was obtained with a good yield of 88% by regioselective bromination of **2** at C-7 with 4 eq. of bromine in chloroform solvent at room temperature.

A mixture of 2-bromo-9,9-dipropyl-9H-fluorene (3.29 g, 10 mmol) and CuCN (1.79 g, 20 mmol) dissolved in 50 mL of DMF were sequentially charged into a two neck flask under N₂ atmosphere and heated to reflux for 24 h. Pour the reaction mixture into aqueous ammonia solution, stirred for 1h, and filtered the precipitate. The crude was purified by column chromatography adsorbed on silica gel using hexane/dichloromethane (2:1) as an eluant. White solid; Yield (2.36 g, 86%); mp 123 °C; IR (KBr, cm⁻¹) 2215 ($\nu_{C\equiv N}$); ¹H NMR (CDCl₃, 500.13 MHz) δ 7.75 (t, $J = 7.5$ Hz, 2H), 7.62 (d, $J = 8.5$ Hz, 2H), 7.36-7.42 (m, 3H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 151.6, 151.6, 145.9, 139.3, 131.5, 129.1, 127.5, 126.7, 123.3, 121.0, 120.4, 120.0, 110.1, 55.8, 42.6, 17.3, 14.5; HRMS calcd for C₂₀H₂₁NNa [M+Na]⁺ m/z 298.1572, found 298.1560.

To a stirred solution of 7-bromo-9,9-dipropyl-9H-fluorene-2-carbonitrile (2.75 g, 10 mmol) in dry chloroform (30 mL) was added bromine (6.39 g, 40 mmol) added drop wise at room temperature. The reaction mixture was stirred at room temperature for 12 h. Added aqueous sodium thiosulfate solution to reaction mixture and extracted the organic layer with chloroform, dried with anhydrous Na₂SO₄, the volatiles were removed by vacuum. White solid; Yield (3.11 g, 88%); mp 126-128 °C; IR (KBr, cm⁻¹) 2220 ($\nu_{C\equiv N}$); ¹H NMR (CDCl₃, 500.13 MHz) δ 7.73 (d, $J = 16.0$ Hz, 1H), 7.62 (dd, $J = 8.0$ Hz, 1.5 Hz, 1H), 7.59 (d, $J = 12.5$ Hz, 2H), 7.50-7.51 (m, 2H), 1.92-1.98 (m, 4H), 0.68-0.70 (m, 6H), 0.55-0.67 (m, 4H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 153.7, 151.3, 144.7, 138.3, 131.7, 130.8, 126.7, 126.7, 123.4, 122.3, 120.5, 119.8, 110.6, 56.2, 42.5, 17.3, 14.5; HRMS calcd for C₂₀H₂₀NBr [M]⁺ m/z 376.0677, found 376.0668.



Scheme S1. Synthesis of substituent block, 7-bromo-9,9-dipropyl-9H-fluorene-2-carbonitrile.

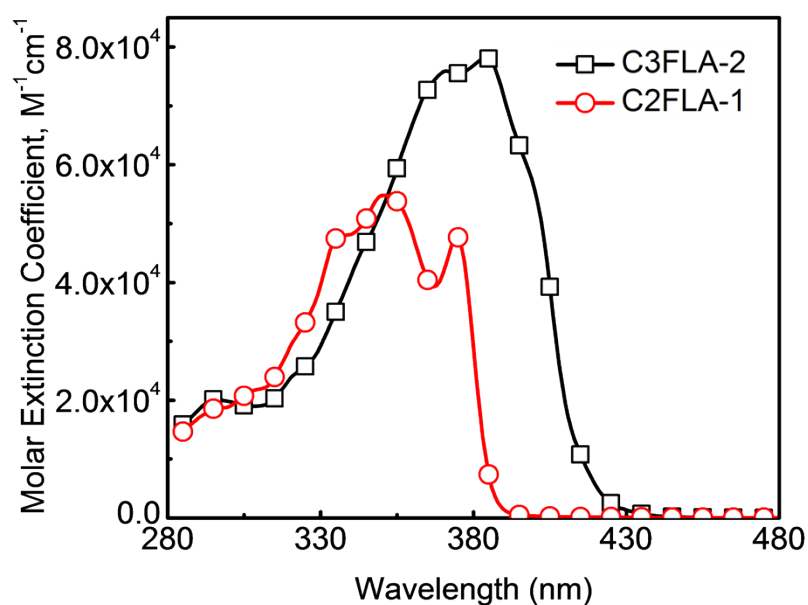


Figure S1. Absorption spectra of the C3FLA-2 and C2FLA-1 recorded in toluene solution.

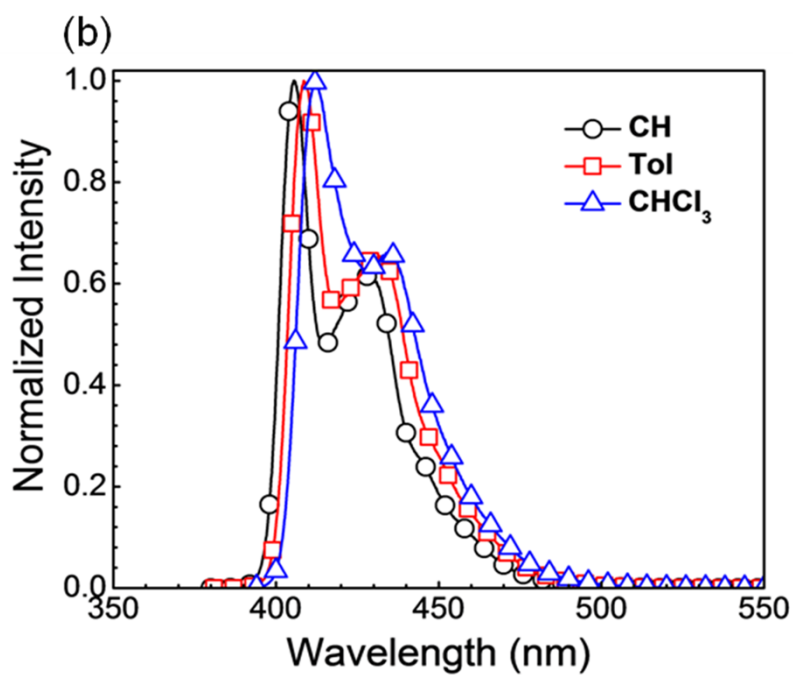
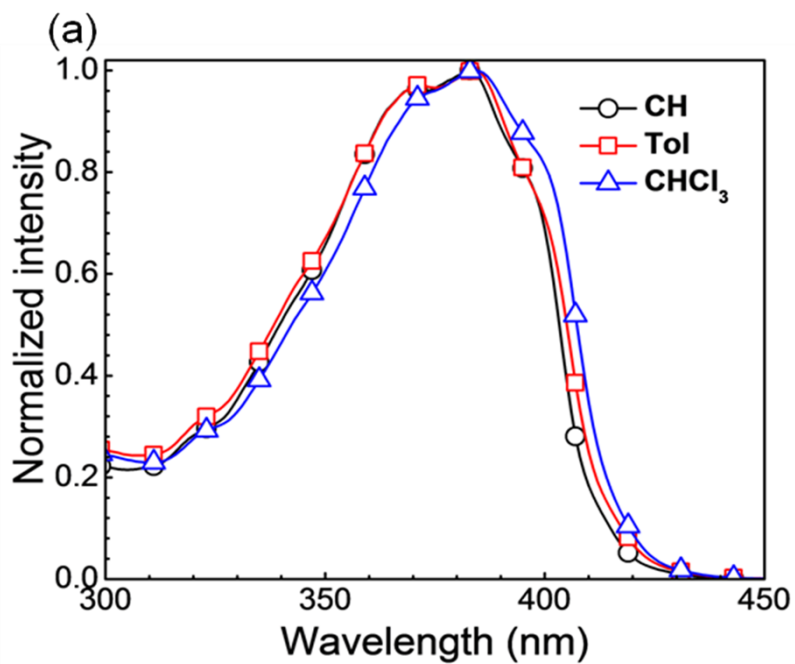


Figure S2. Normalized (a) absorption spectra and (b) emission spectra of C3FLA-2 emitter recorded in cyclohexane (CH), toluene (Tol) and chloroform (CHCl₃) solvents.

Table S1. Computed vertical transition energies, adiabatic ionization potential (I_p), ground state dipole moments (μ_g), oscillator strength (f), absorption wavelength (λ_{abs}), HOMO, LUMO, and energy band gap (E_g) of C3FLA-2 and C2FLA-1 by using B3LYP theory.

Dye	E_a , [eV]	I_p [eV]	f	μ_g [D]	HOMO [eV]	LUMO [eV]	E_g [eV]	λ , [nm]	Transitions
C2FLA-1 (vacuum)	0.99	-	1.71	7.98	-5.44	-1.99	3.45	393.7	HOMO \rightarrow LUMO (99%)
			0.32					318.8	HOMO \rightarrow LUMO+1(61%)
C2FLA-1 (Toluene)	-	6.48	1.34	6.34	-5.02	-1.94	3.09	452.2	HOMO \rightarrow LUMO (99%)
			0.95					343.8	HOMO-1 \rightarrow LUMO (61%), HOMO \rightarrow LUMO+1 (36%)
			0.22					311.2	HOMO \rightarrow LUMO+4 (96%)
C3FLA-2 (vacuum)	1.48	-	3.17	0.86	-5.39	-2.12	3.16	440.3	HOMO \rightarrow LUMO (97%)
			0.60					333.4	HOMO \rightarrow LUMO+2 (51%), HOMO-1 \rightarrow LUMO+1 (44%)
C3FLA-2 (Toluene)	-	6.23	3.36	0.97	-5.40	-2.23	3.28	433.3	HOMO \rightarrow LUMO (96%)
			0.63					326.6	HOMO \rightarrow LUMO+2 (50%), HOMO-1 \rightarrow LUMO+1 (44%)
			0.12					0.97	HOMO-1 \rightarrow LUMO+1 (52%), HOMO \rightarrow LUMO+2 (42%)

Table S2. Hole and electron mobility of the CBP, Spiro-2CBP, TCTA, and SimCP2 hosts.

Host	Hole mobility [cm ² /Vs]	Electron mobility [cm ² /Vs]	Electric field [V/cm]	Ref.
CBP	2×10^{-3}	3×10^{-4}	5.0×10^{-6}	56
Spiro-2CBP	10^{-3}	-	-	57
TCTA	3×10^{-4}	10^{-8}	5.0×10^{-6}	56
SimCP2	6.4×10^{-4}	4.6×10^{-4}	1.6×10^{-5}	58

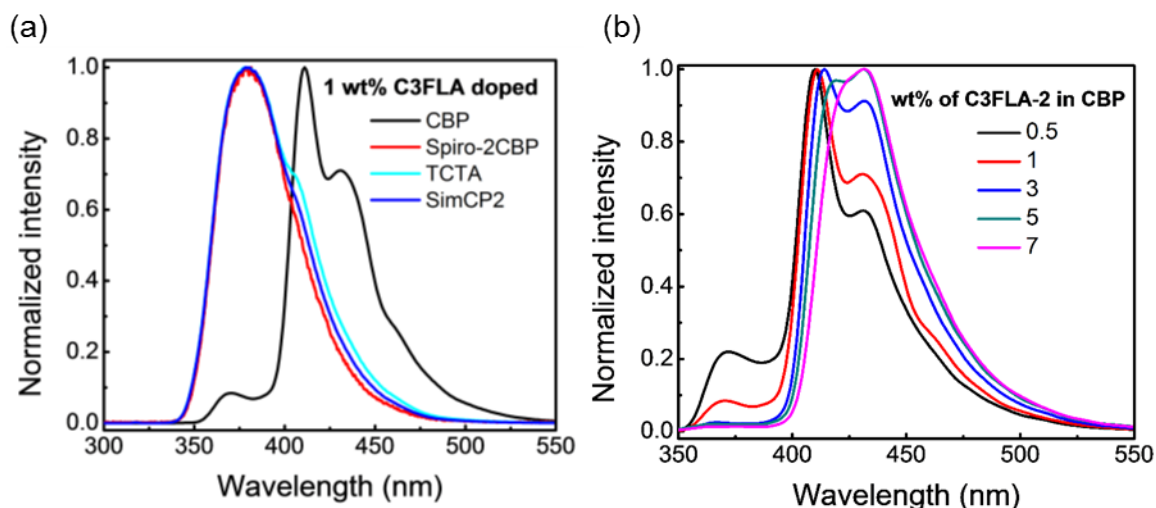


Figure S3. Normalized PL spectra of (a) 1 wt% C3FLA-2 doped in four different hosts, CBP, Spiro-2CBP, TCTA and SimCP2, and (b) 0.5 to 7 wt% of C3FLA-2 doped in the CBP host. All spectra have been recorded in THF at room temperature.

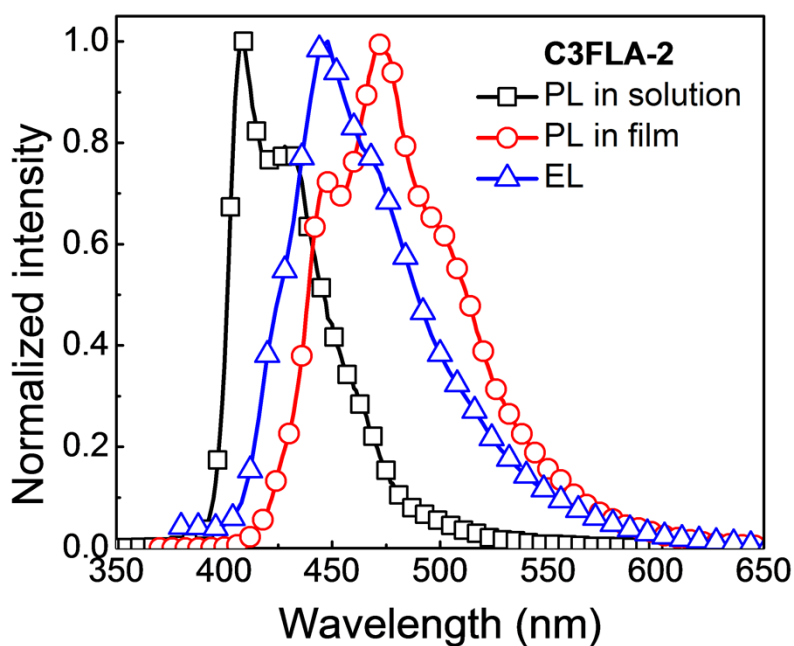


Figure S4. Normalized PL spectra and EL spectrum of deep-blue emitter, C3FLA-2, in solution (toluene) and solid state films. As compared with PL-spectrum of C3FLA-2 in toluene, the solid state EL- and PL-spectra show an extremely strong red-shift due to the emitter segregation.

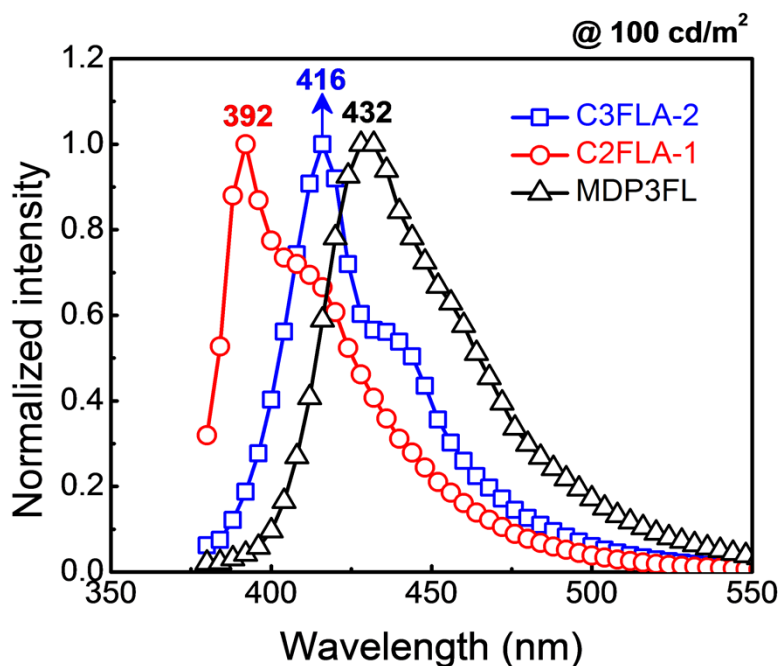


Figure S5. Normalized EL spectra of 1 wt% C3FLA-2, C2FLA-1 and MDP3FL emitters doped in CBP host.

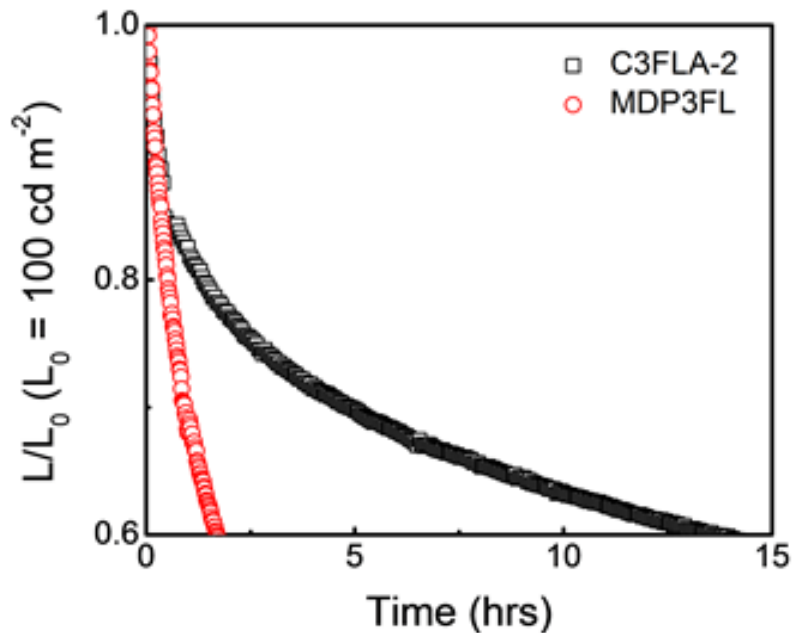


Figure S6. Operational lifetime of the novel deep-blue emitter C3FLA-2 based ultra-deep blue OLED driven under constant current with an initial luminance of 100 cd m⁻² at room temperature, a fluorene trimer based typical deep-blue emitter MDP3FL was also studied for comparison.

EQE calculation

(1) First, we calculate the # of emitted photons at each brightness obtained from the PR655 spectra scan at different wavelengths 380 nm to 780 nm of EL spectra.

(a) We have calculated the one photon energy at each wavelength using spectral distribution function ($W/m^2 \times cr$)

Where, W : Watt or (J/s); m^2 = emissive area; and cr = solid angle

(i) One photon energy at 380 nm = $(hc/380 \times 10^{-9})$ Joule

(ii) One photon energy at x nm = $(hc/x \times 10^{-9})$ Joule

Where, x is wavelength in nm.

(b) To calculate the # of photons at each wavelength (e. g. 380, 384, 388.....780 nm) by using following equation.

(i) # of photons at 380 nm = $(6.5333 \times 10^{-28})/(hc/380 \times 10^{-9})$

(ii) # of photons at x nm = $(6.5333 \times 10^{-28})/(hc/x \times 10^{-9})$

Where, 6.5333×10^{-28} is total energy in (per unit second per unit area per unit solid angle) contributed by all photons at 380 nm

Finally, we sum-up the number of photons obtained at each wavelength,

Total number of photon at particular luminance, which was obtained from PR655 = # of photons at 380 nm + # of photons at 384 nm + + # of photons at 780 nm

(2) After that calculated the # of electrons at each current density obtained in experiment-

As we have mentioned above that the current density measured in mA/cm²

Where, Current = mA

We have converted the unit from mA to Coulomb/s (1 mA = 0.001 Coulomb/s), which can use for the number of electron calculation

Emissive area of device = cm²

Then, we use the Faraday constant, because it is established that 1 Faraday = 96,494 Coulomb (1 Faraday also known as charge carried by 1 mole of electron, which is 96,494 Coulomb/mole)

So, 1 mA/cm² current density = $1 \times [0.001 \text{ (Ampere)}/96494 \text{ (Coulomb/mole)}] \times 6.02 \times 10^{23}$ (# of electrons/mole) = 6.23×10^{15}

of electrons = Current density at each point from experimental data $\times 6.23 \times 10^{15}$

Finally, we calculated the EQE at each luminance (n) as follows-

$$EQE_n = \frac{\text{\# of photon at } n \text{ luminance}}{\text{\# of electron at } n \text{ luminance}}$$

Where, n = each luminance value corresponding to each current density values, which were measured by PR655 and Keithley 2400 electrometer.