

Supporting Information

Synthesis and Characterization of Triple-Azacrown Ethers Containing Fluorene-Cored Derivative: Application as Electron Injection Layer for Significantly Enhanced Performance of PLEDs

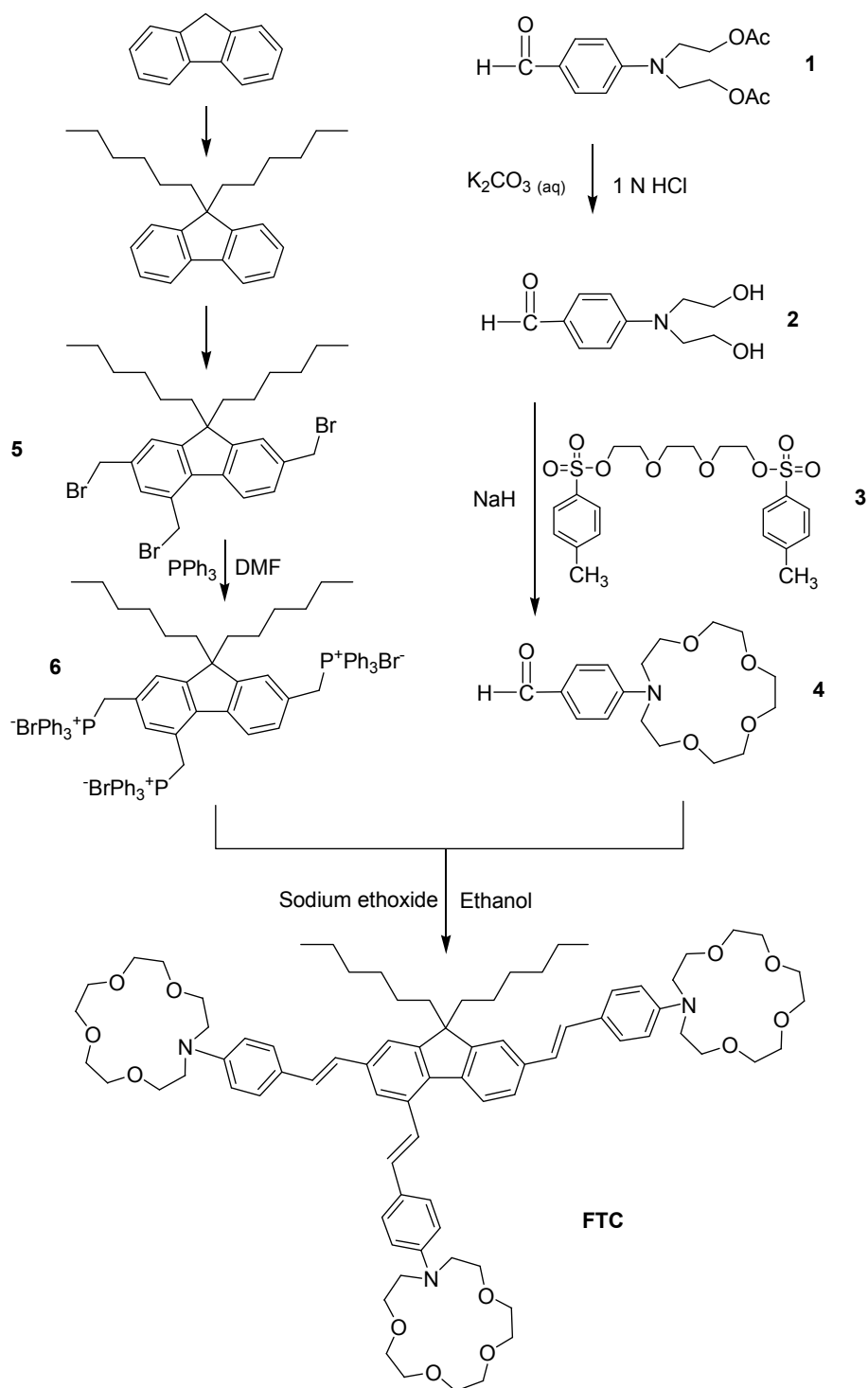
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4-Bis(2-hydroxyethyl)amino)benzaldehyde (2)

A mixture of 4-(Bis(2-acetoxyethyl)amino)benzaldehyde (10 g, 34 mmol), methanol (150 mL) and sodium carbonate solution (10.9 g, 102 mmol) was stirred at room temperature overnight. Few drops of 1N HCl were added to the mixture; and then the methanol was removed by rotary evaporation. The mixture was extracted with chloroform and the organic layer was dried (MgSO₄) and concentrated under reduced pressure. The residue was purified by column chromatography eluted with ethyl acetate to give **2** (4.9 g, 69.5 %). ¹H NMR (300 MHz, CDCl₃, TMS, 25 °C): δ 9.62 (s, H, -CHO) 7.63-7.66 (d, 2H, *J* = 9.0 Hz, Ar-H), 6.68-6.71 (d, 2H, *J* = 9.0 Hz, Ar-H), 3.86-3.89 (t, 4H, *J* = 9.8 Hz, -CH₂-), 3.65-3.68 (t, 4H, *J* = 9.7 Hz, -CH₂-), 3.40-3.45 (d, 2H, *J* = 16.4 Hz, -OH). Anal. Calcd. for C₁₁H₁₅NO₃ (%): C, 63.14; H, 7.23; N, 6.69. Found: C, 63.07; H, 7.28; N, 6.59.



Scheme S1. Synthetic procedures of **FTC**.

Triethyleneglycol Ditosylate (3)

Mixture of *p*-toluenesulfonyl chloride (5.75 g, 0.03 mol), triethylene glycol (1.5 g, 0.01

mol) and THF (15 mL) was mechanically stirred at 0 °C. Aqueous solution of KOH (16 M, 4 mL) was added portion wise to the mixture within 1 h and then stirred at room temperature for 7 h. The mixture was poured into ice water, the appearing white precipitate was collected by filtration and re-crystallized from methanol/water to afford white crystal of **3** (3.214 g, 70%, m.p. 81-83 °C). ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): 7.25-7.79 (m, 8H, aromatic region), 4.1 (m, 4H), 3.6 (m, 4H), 3.5 (s, 4H), 2.4 (s, 6H). FT-IR (KBr, cm⁻¹): 1600 (aromatic ring), 1129 (C-O-C), 1175 (sulfonate). Anal. Calc. for C₂₀H₂₆O₈S₂: C, 52.39; H, 5.72. Found: C, 52.37; H, 5.72.

4-(Monoaza-15-crown-5)benzaldehyde (4)

A mixture of compound **2** (0.4 g, 2.09 mmol) and NaH (0.8 g, 60 % in mineral oil, 20 mmol) in dried THF (300 mL) was refluxed under nitrogen atmosphere for 30 min. The mixture was added dropwise with a solution of compound **3** (1.0 g, 2.1 mmol) in THF (200 mL) and then stirred at 70 °C for 2 days. After adding an aqueous solution of H₂SO₄ (2 M, 50 mL), the THF was removed by rotary evaporation. The mixture was then extracted with chloroform and the organic layer was dried (MgSO₄) and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: acetone/*n*-hexane = 3/2) to give **4** (0.3 g, 44.49 %). ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ 9.73 (s, H, -CHO) 7.70-7.73 (d, 2H, *J* = 8.8 Hz, Ar-H), 6.71-6.74 (d, 2H, *J* = 8.7 Hz,), 3.52 (m, 4H, crown ether), 3.77-3.80 (m, 16H, crown ether). Anal. Calcd. for C₁₇H₂₅NO₅ (%): C, 63.14; H, 7.79; N, 4.33. Found: C, 62.68; H, 7.77; N, 4.14. FT-IR (KBr, cm⁻¹): ν 2798 (-CH aldehyde), 1667 (-CHO stretch), 1124 (C-O stretch).

2,4,7-Tri(bromomethyl)-9,9-dihexylfluorene (5)

Into the mixture of 9,9-dihexylfluorene (3.25 g, 9.5 mmol) and paraformaldehyde (9.3g, 0.31 mole) under ice bath was added drop-wise with HBr aqueous solution (33 wt%). The mixture was stirred at 70 °C for 2 day under nitrogen atmosphere, poured into ice water and extracted with CH₂Cl₂. After removal of CH₂Cl₂ by a rotary evaporator, the residues were purified by column chromatography using *n*-hexane/toluene (10/1, v/v) as eluent to afford colorless liquid of **5**. (4.19 g, 72%) ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ 7.87-7.89 (d, 1H, *J* = 8 Hz), 7.3-7.4 (m, 2H, ArH), 7.30-7.35 (m, 2H, ArH), 4.8 (s, 2H, -CH₂-), 4.5 (s, 2H, -CH₂-), 4.6 (s, 2H, -CH₂-), 1.93-1.97 (m, 4H, -CH₂-), 0.56-1.25 (m, 22H, -CH₂-). Anal. Calc. for C₂₈H₃₇Br₃: C, 54.83; H, 6.08. Found: C, 54.41; H, 6.01.

2,4,7-Tri[methylene(triphenylphosphonium bromide)]-9,9-dihexylfluorene (6)

To a mixture of compound **5** (4.3 g, 7.5 mmol) and triphenylphosphine (15.7 g, 59.8 mmol) and DMF (60 ml) was stirred at 100 °C for 2 days under nitrogen atmosphere. The mixture was poured into excess of benzene and the appearing solid was collected by filtration, which was dried it in vacuo at 100 °C to get the desired product **6** (8.7 g, 82.5 %). ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ 7.84~7.52 (m, 45H, Ar-H), 7.12 (s, 1H, Ar-H), 6.96 (s, 2H, Ar-H), 6.87 (s, 1H, Ar-H), 6.71 (s, 1H, Ar-H), 5.56~5.52 (d, 2H, *J* = 16Hz, -CH₂Br), 5.35~5.31 (d, 2H, *J* = 16 Hz, -CH₂Br), 5.16~5.12 (d, 2H, *J* = 16Hz, -CH₂Br), 1.43~1.33 (m, 4H, -CH₂-), 1.15~1.1 (m, 4H, -CH₂-), 0.95~0.79 (m, 14H, -CH₃- and -CH₂-), 0.046 (m, 4H, -CH₂-). Anal. Calc. for C₈₂H₈₂Br₃P₃: C, 70.3; H, 5.9. Found: C, 70.1; H, 5.99.

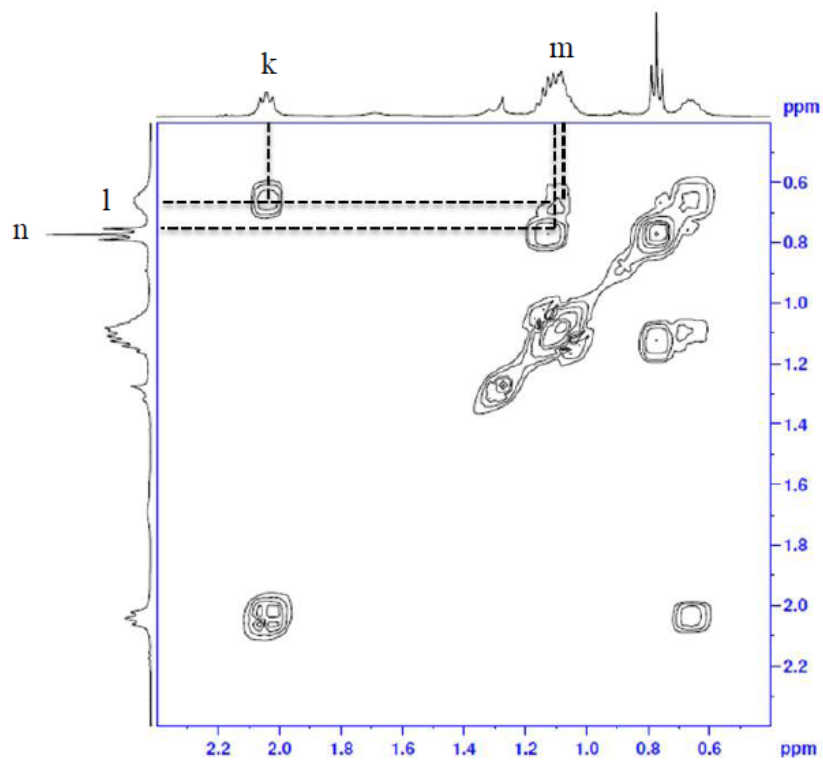


Figure S1 COSY spectrum of FTC (0.4~2.4 ppm).

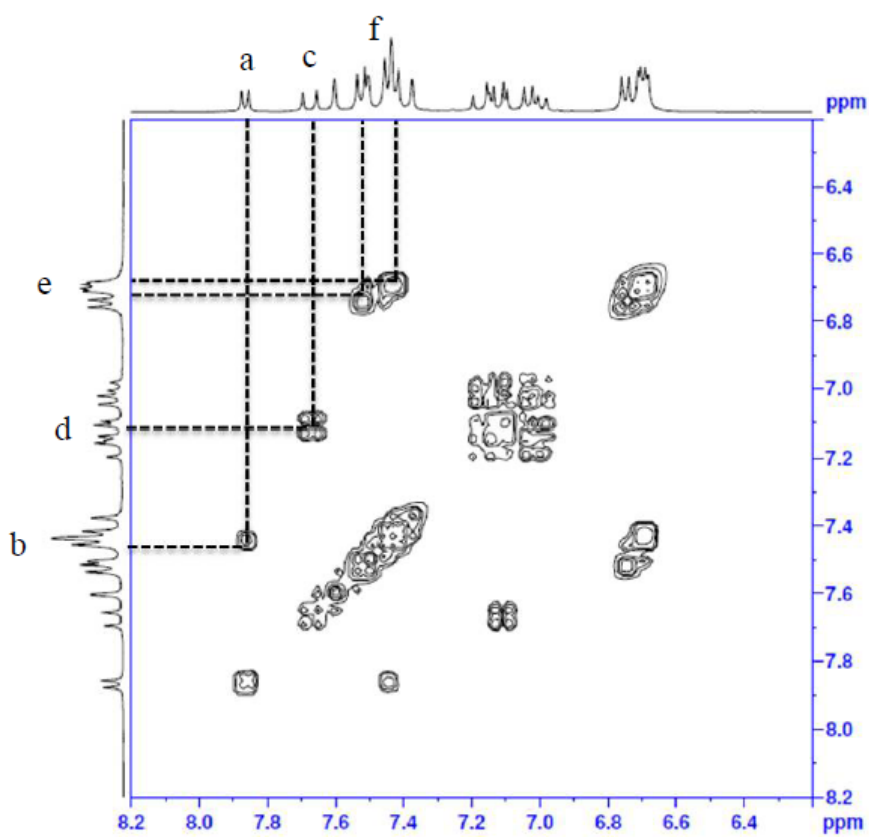


Figure S2 COSY spectrum of FTC (6.2~8.2 ppm).

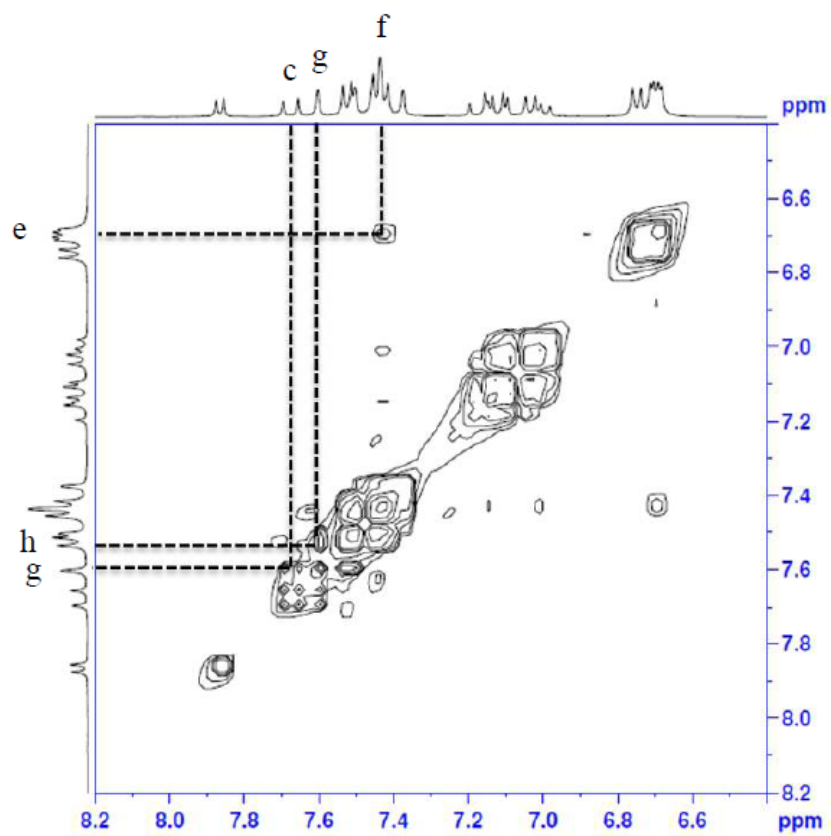


Figure S3 NOESY spectrum of FTC (6.4~8.2 ppm).

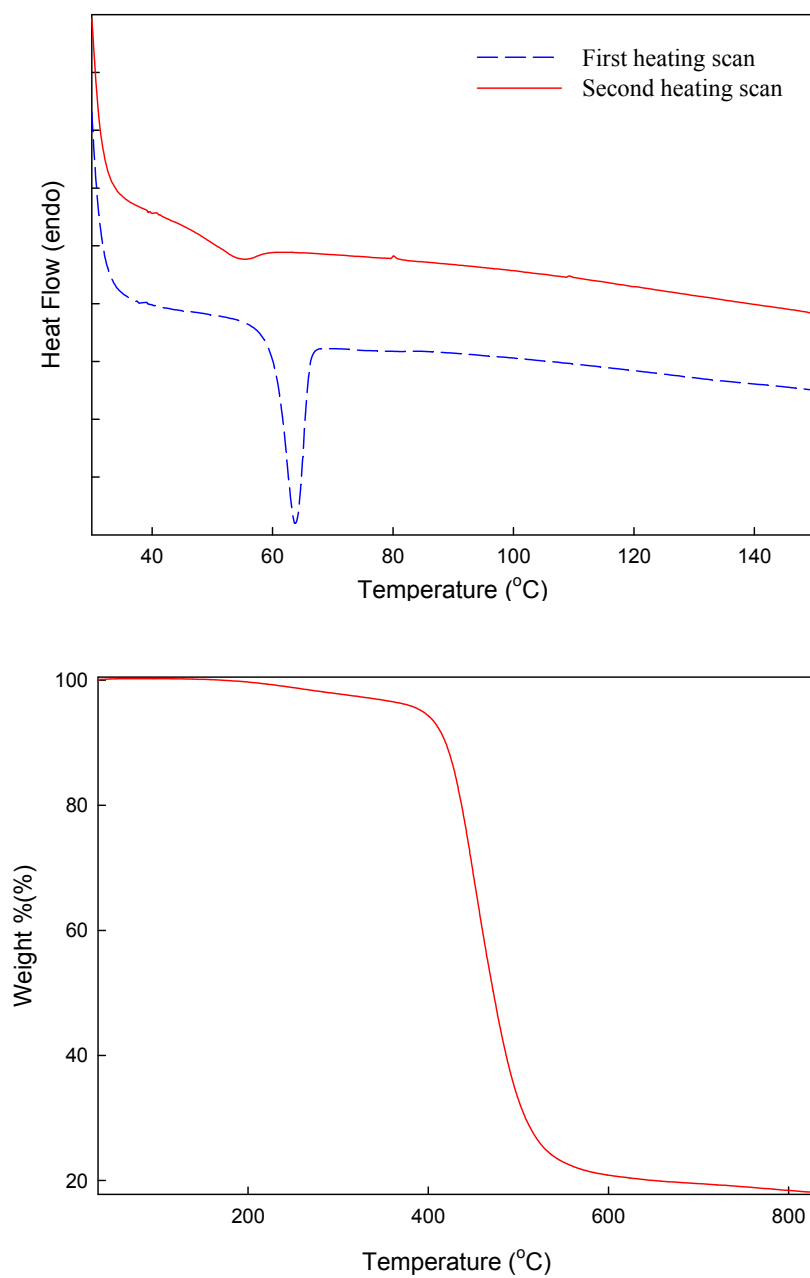


Figure S4 (a) Differential scanning calorimetric curves of **FTC** obtained from the first and second scan with a heating rate of 10 °C/min. (b) Thermogravimetric analysis of **FTC** with heating rate of 10 °C/min under nitrogen atmosphere.

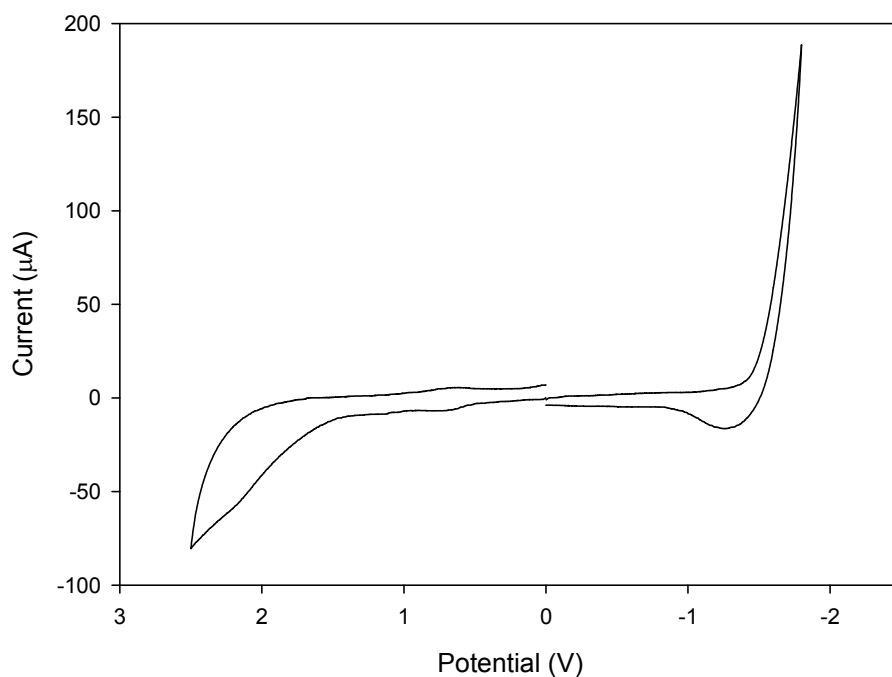


Figure S5 Cyclic voltammogram of FTC in 0.1 M $n\text{-Bu}_4\text{NClO}_4$; scan rate: 100 mV/s.

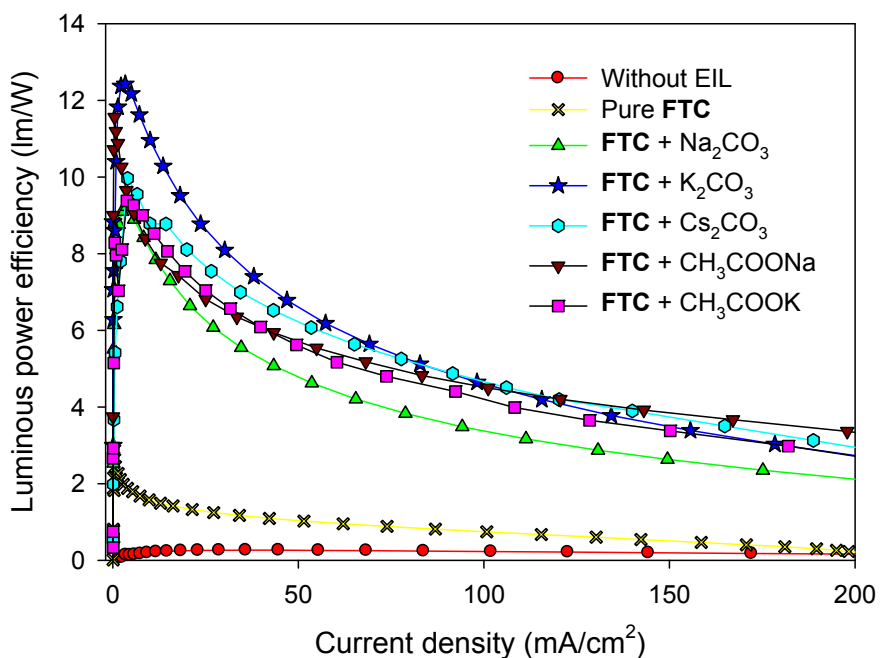


Figure S6 Luminous power efficiency versus current density characteristics of PLEDs. Device structure: ITO/PEDOT:PSS/PF-Green-B/EIL/Al.

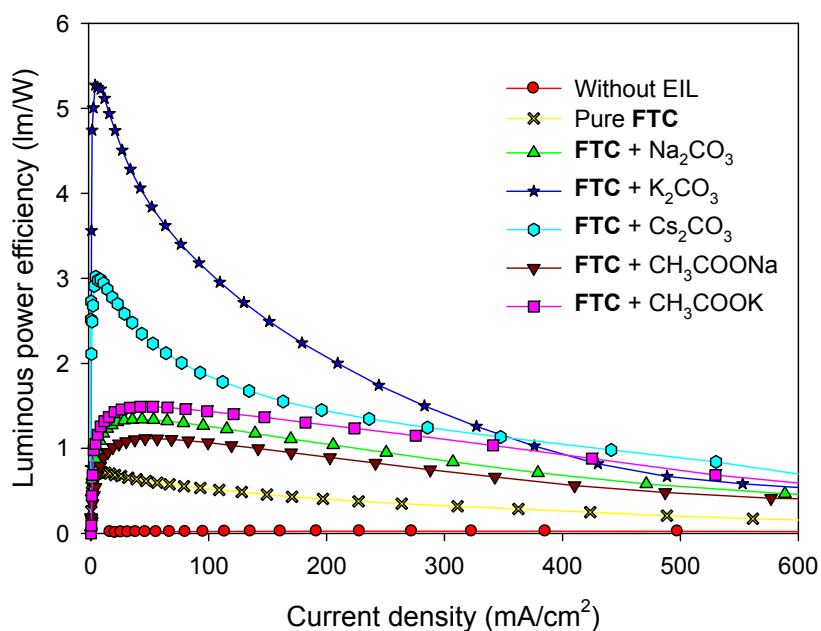


Figure S7 Luminous power efficiency versus current density characteristics of PLEDs. Device structure: ITO/PEDOT:PSS/ HY-PPV/EIL/Al.

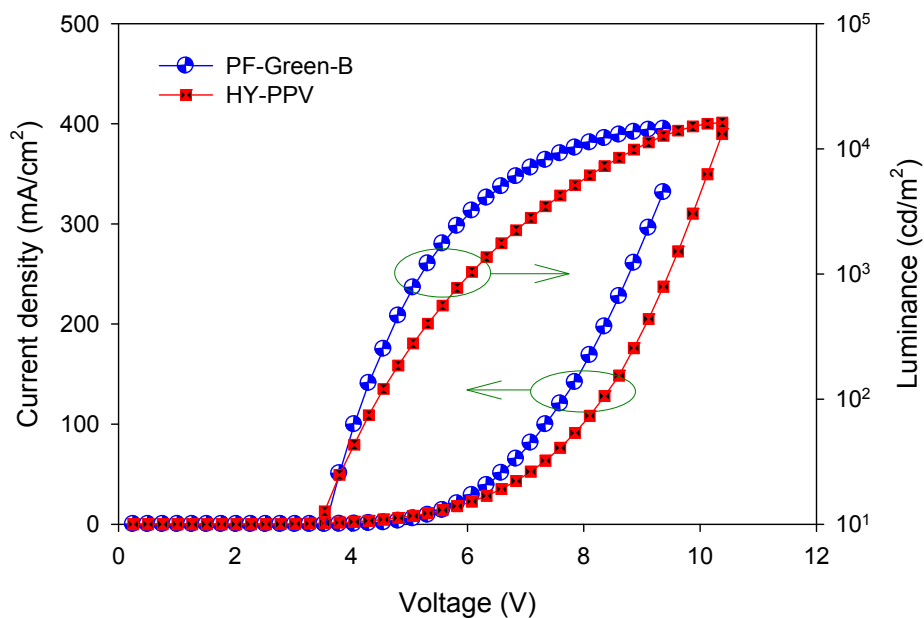


Figure S8 Luminance versus voltage and current density versus voltage characteristics of PLEDs. Device structure: ITO/PEDOT:PSS/PF-Green-B or HY-PPV/LiF/Al.

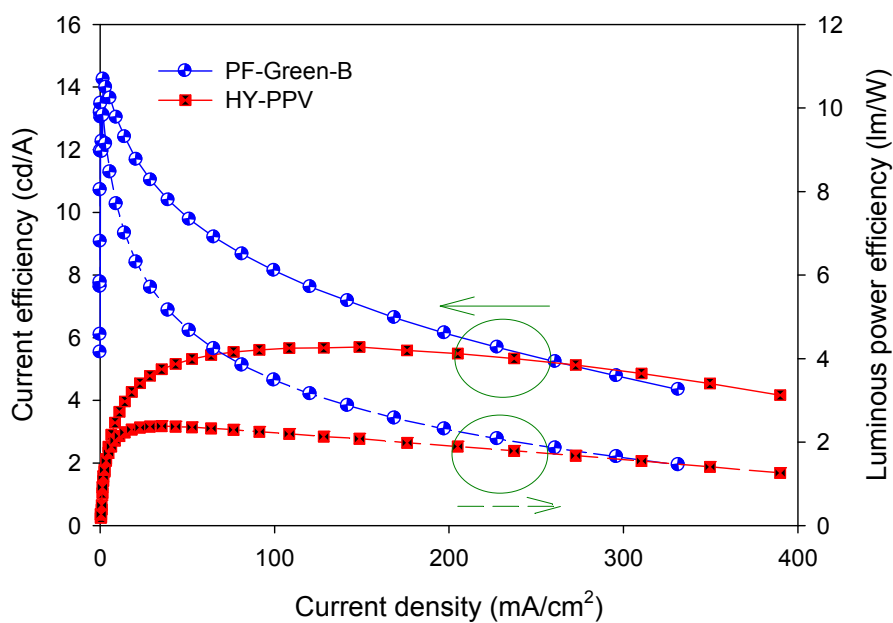


Figure S9 Current efficiency versus current density and luminous power efficiency versus current density characteristics of PLEDs. Device structure: ITO/PEDOT:PSS/PF-Green-B or HY-PPV/LiF/Al.

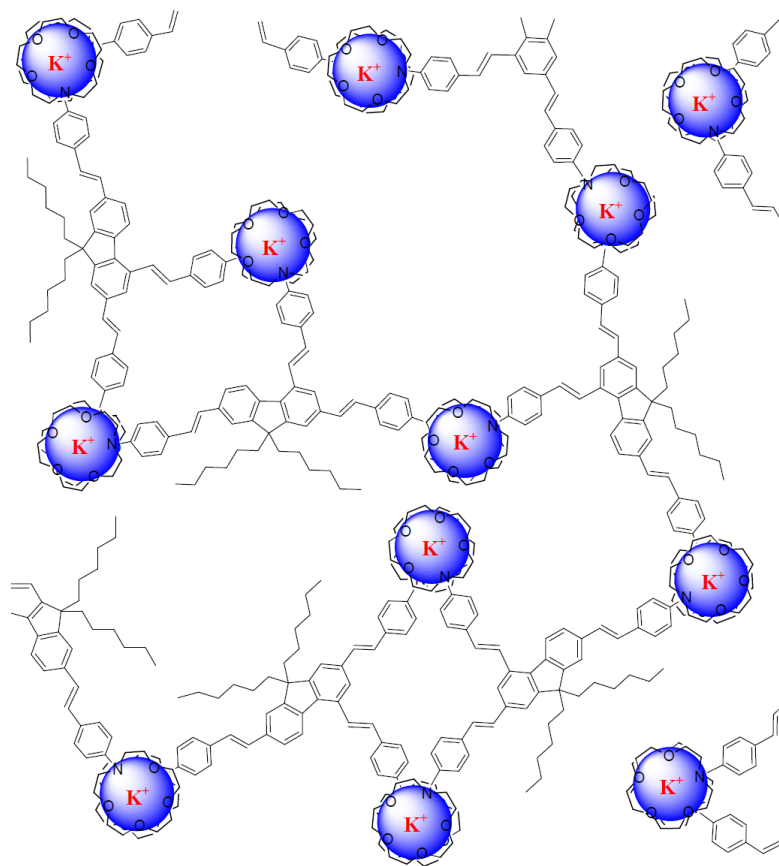


Figure S10 The proposed chemical structure of doped FTC.