

Electronic Supplementary Information

A Versatile Ferrocene-Containing Material as p-Type Charge Generation Layer for High-Performance Full Color Tandem OLEDs

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Synthesis and characterization

Preparation of aminoferrocene

Iodoferrocene (2.5 g, 6.67 mmol), cuprous iodide (CuI, 128 mg, 0.67 mmol), ferric chloride (FeCl₃, 107 mg, 0.67 mmol), sodium hydroxide (NaOH, 540 mg, 13.3 mmol), aqueous ammonia (15 M, 30 ml), and ethanol (EtOH, 30 ml) were placed in a thick-wall reaction tube. The reaction tube was sealed under nitrogen atmosphere and then heated at 90 °C for 12 h. After the reaction was cooled to room temperature, aqueous sodium hydroxide solution (1.0 M, 150 ml) was added, then the mixture was filtered through Celite, and washed with 50 mL of ethyl ether. The gathered solution was further extracted by diethyl ether for three times. The combined organic phases were dried using anhydrous MgSO₄ and concentrated under vacuum. The resulting crude product was purified by column chromatography (eluent: ethyl acetate/n-hexane = 1/2 (v/v)) to give the pure aminoferrocene in 48% yield. ¹H NMR (400 MHz, CDCl₃, δ): 4.08 (s, 5H), 3.97 (t, *J* = 1.6, 2H), 3.82 (t, *J* = 1.6, 2H), 2.58 (br, 2H).

Preparation of (dibiphenylamino)ferrocene (DPAF)

An oven-dried seal tube was charged with aminoferrocene (300 mg, 1.5 mmol), 4-bromobiphenyl (1.05 g, 4.5 mmol), palladium acetate (17 mg, 0.075 mmol), and sodium tert-butoxide (NaO^tBu, 1.13 g, 11.8 mmol). After evacuation and back-filling with dry and pure nitrogen three times, a solution of tributylphosphine in *n*-hexane (0.1 mL, 10 wt%) and toluene (6

mL) were added *via* syringe. The reaction was heated to 110 °C for 72 h and then cooled to room temperature. The resulting mixture was filtered through a Celite and silica gel pad and the pad was further washed using ethyl acetate. Solvent was evaporated under reduced pressure and the residue was purified by column chromatography (hexane/ethyl acetate (4:1)) to afford the desired DPAF in 50% yield. ¹H NMR (400 MHz, CDCl₃, δ): 7.55-7.61 (m, 8H), 7.41-7.44 (m, 4H), 7.35-7.38 (m, 4H), 7.24-7.33 (m, 2H), 4.18 (s, 4H), 4.10 (t, *J* = 3.6 Hz, 2H), 4.05 (t, *J* = 3.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, δ): 146.7 (2 C), 140.6 (2 C), 135.7 (2 C), 128.8 (4 CH), 127.7 (4 CH), 126.9 (4 CH), 126.8 (4 CH), 124.5 (2 CH), 106.5 (1 C), 69.0 (5 CH), 64.0 (2 CH), 60.5 (2 CH); HRMS (EI) *m/z* : [M]⁺ calcd for C₃₄H₂₇FeN, 505.1493; found, 505.1495. Anal. calcd for C₃₄H₂₇FeN: C 80.80, H 5.38, Fe 11.05, N 2.77; found: C 80.93, H 5.21, N 2.86.

General considerations

¹H and ¹³C NMR spectra were characterized *via* a Varian Mercury 400 spectrometer. Mass spectroscopy measurements were carried out with a JEOL JMS-700 spectrometer. Elemental analysis was carried out on Elementar vario EL cube instrument. Differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) were measured on TGA 2050 and DSC Q10 equipments from TA Instruments under nitrogen flow at heating/cooling rates of 10 °C/min, respectively. UV–vis absorption spectrum was recorded using a Hitachi U-3300 spectrophotometer. PL spectrum was measured on a Hitachi F-4500 spectrophotometer. The electrochemical potentials of the materials were performed in the CH₂Cl₂ solutions containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) using a CH-600 potentiostat (CH-instrument). A three electrode configuration system was used with a Pt disc as the working electrode, a silver wire as the counter electrode, and an Ag/AgNO₃ electrode as reference electrode. The potential was reported relative to the Fc/Fc⁺ couple.

Device fabrication and measurements

All tandem OLEDs were prepared on patterned glass substrates coated with indium tin oxide (ITO) with a sheet resistance of 15 Ω /sq. Prior to device fabrication, the ITO substrates were subjected to a routine cleaning process, then dried with nitrogen, and pretreated with UV-ozone exposure. All the organic and inorganic layers were thermally deposited on the substrate at a base pressure of 1×10^{-6} torr. The deposition rate for organic compounds is 1–2 \AA /s. The Al/LiF cathode was deposited by evaporation of LiF with a deposition rate of 0.1 \AA /s and then by evaporation of Al metal at a rate of 5 \AA /s. For the doping of organic layers, the evaporation rates of two materials were monitored independently by using two quartz-crystal monitors. The effective area of the emitting diode is 9.00 mm². Current, voltage, and light intensity measurements were taken simultaneously using a Keithley 2400 source meter and a Newport 1835-C optical meter equipped with a Newport 818-ST calibrated silicon photodiode. Electroluminescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer.

Device structures of RGB single-unit and tandem OLEDs

G1: ITO/NPB (30 nm)/TCTA (20 nm)/TCTA: TPBi: 4% Ir(ppy)₃ (30 nm)/TPBi (60 nm)/TPBi: 6% LiF (5 nm)/Al (100 nm).

G2: ITO/NPB (30 nm)/TCTA (20 nm)/TCTA: TPBi: 4% Ir(ppy)₃ (30 nm)/TPBi (60 nm)/TPBi: 6% LiF (5 nm)/Al (1 nm)/C₆₀ (4 nm)/DPAF (1 nm)/MoO₃ (1 nm)/NPB (30 nm)/TCTA (20 nm)/TCTA: TPBi: 4% Ir(ppy)₃ (30 nm)/TPBi (60 nm)/LiF (1 nm)/Al (100 nm).

R1: ITO/NPB (30 nm)/TCTA (20 nm)/TCTA: Bebq₂: 4% Ir(piq)₂(acac) (30 nm)/Bebq₂ (50 nm)/Bebq₂: 6% LiF (5 nm)/Al (100 nm).

R2: ITO/NPB (30 nm)/TCTA (20 nm)/TCTA: Bebq₂: 4% Ir(piq)₂(acac) (30 nm)/Bebq₂ (50 nm)/Bebq₂: 6% LiF (5 nm)/Al (1 nm)/C₆₀ (4 nm)/DPAF (1 nm)/MoO₃ (1 nm)/NPB (30 nm)/ TCTA (20 nm)/TCTA: Bebq₂: 4% Ir(piq)₂(acac) (30 nm)/Bebq₂ (60 nm)/ LiF (1 nm)/Al (100 nm).

B1: ITO/NPB (30 nm)/mCP (10 nm)/mCP: TmPyPB: 5% FIrpic (30 nm)/TmPyPB (60 nm)/TmPyPB: 6% LiF (5 nm)/Al (100 nm).

B2: ITO/NPB (30 nm)/mCP (10 nm)/mCP: TmPyPB: 5% FIrpic (30 nm)/TmPyPB (60 nm)/TmPyPB: 6% LiF (5 nm)/Al (1 nm)/C₆₀ (4 nm)/DPAF (1 nm)/MoO₃ (1 nm)/NPB (30 nm)/mCP (10 nm)/mCP: TmPyPB: 5% FIrpic (30 nm)/TmPyPB (60 nm)/LiF (1 nm)/Al (100 nm).

G3: ITO/NPB (30 nm)/TCTA (20 nm)/TCTA: TPBi: 4% Ir(ppy)₃ (30 nm)/TPBi (60 nm)/TPBi: 6% LiF (5 nm)/Al (1 nm)/C₆₀ (4 nm)/DPAF (1 nm)/NPB (30 nm)/TCTA (20 nm)/TCTA: TPBi: 4% Ir(ppy)₃ (30 nm)/TPBi (60 nm)/LiF (1 nm)/Al (100 nm).

G4: ITO/NPB (30 nm)/TCTA (20 nm)/TCTA: TPBi: 4% Ir(ppy)₃ (30 nm)/TPBi (60 nm)/TPBi: 6% LiF (5 nm)/Al (1 nm)/C₆₀ (4 nm)/MoO₃ (1 nm)/NPB (30 nm)/TCTA (20 nm)/TCTA: TPBi: 4% Ir(ppy)₃ (30 nm)/TPBi (60 nm)/LiF (1 nm)/Al (100 nm).

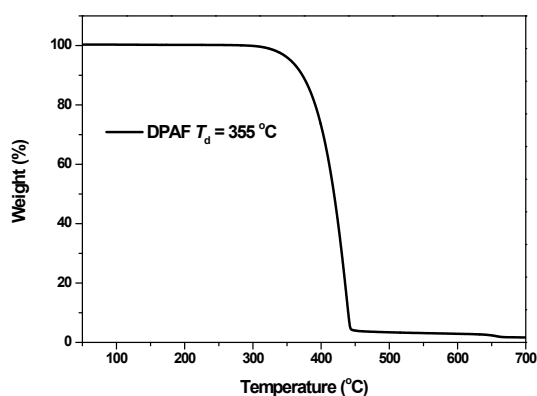


Figure S1. TGA profile of DPAF measured under N₂.

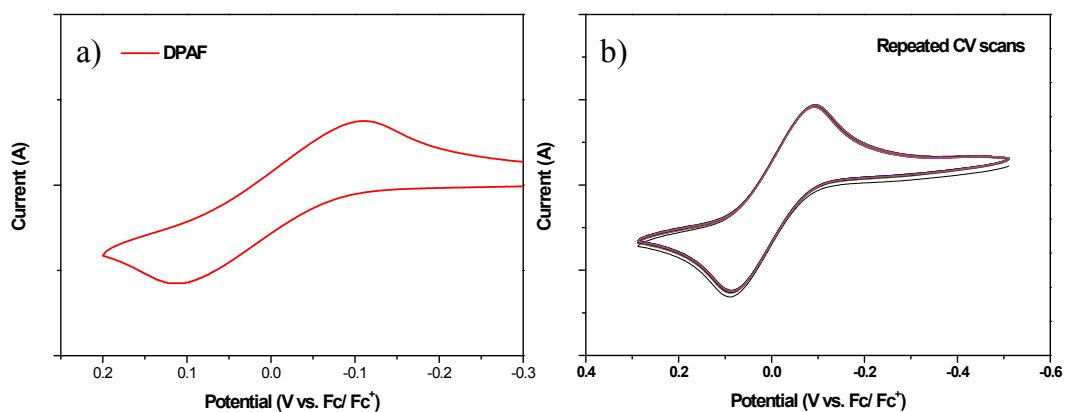


Figure S2. (a) Cyclic voltammogram curve and (b) repeated CV scans (20 cycles) of DPAF.

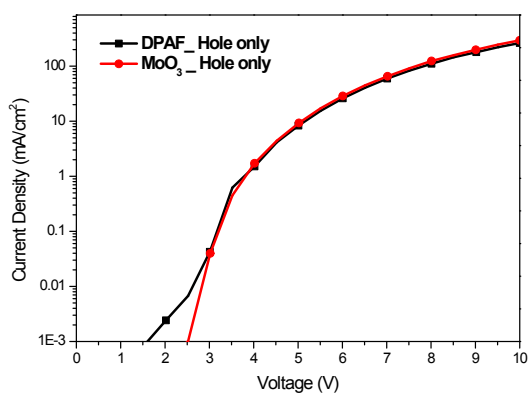


Figure S3. J-V curves of hole-only devices of DPAF and MoO₃.

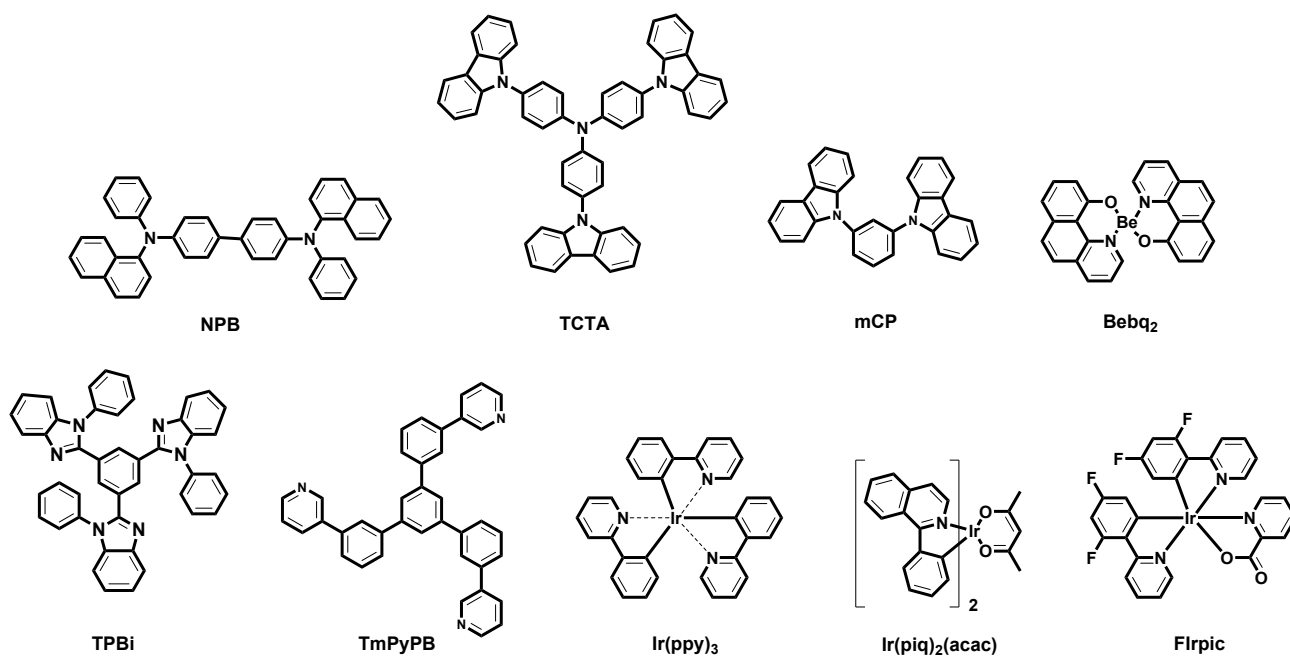


Figure S4. Chemical structures of materials for tandem OLEDs.

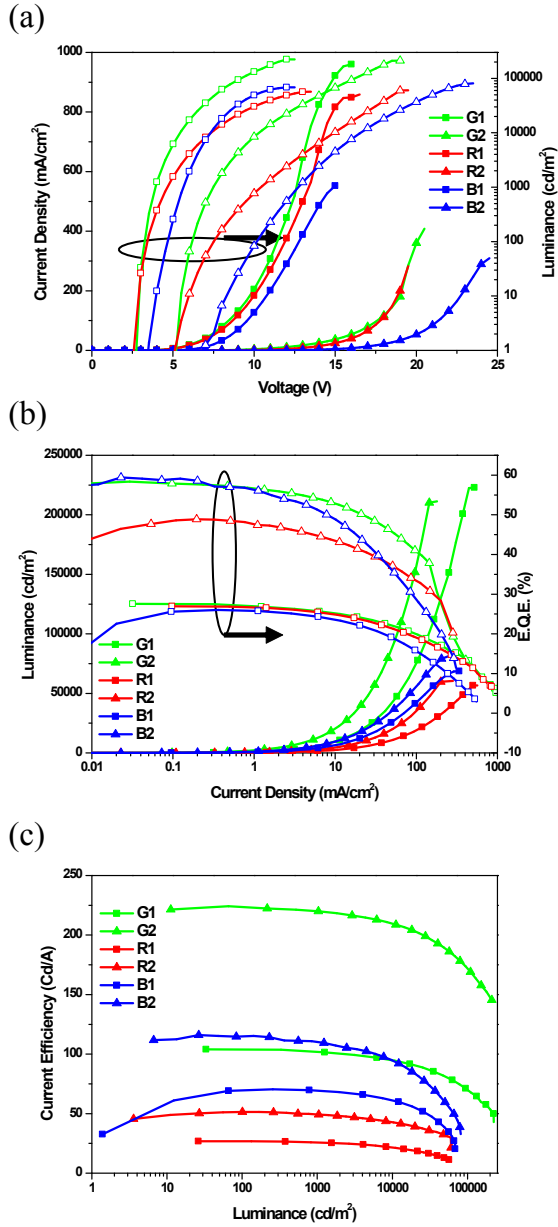


Figure S5. Performance of the GRB devices. (a) Current density-voltage-luminance characteristics. (b) Plots of EQE and luminance as a function of current density. (c) Current efficiency vs. luminance curves.

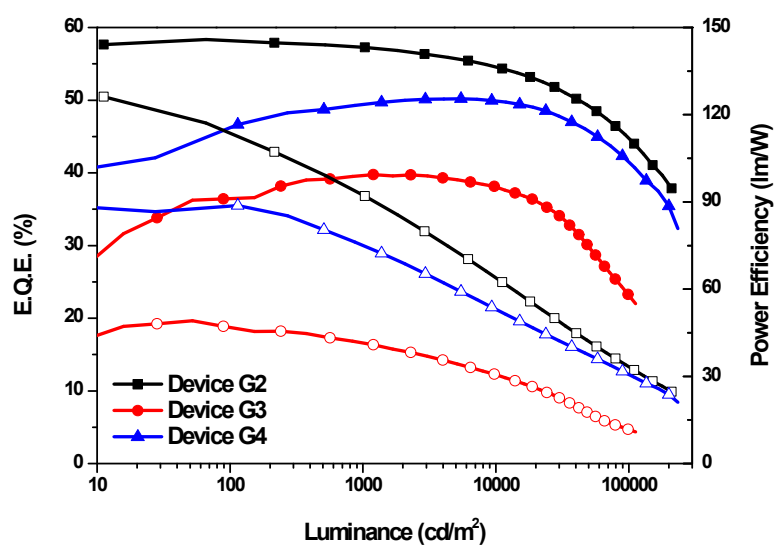


Figure S6. EL characteristic plots of EQE (solid) and power efficiency (open) vs. luminance for device G2-4.

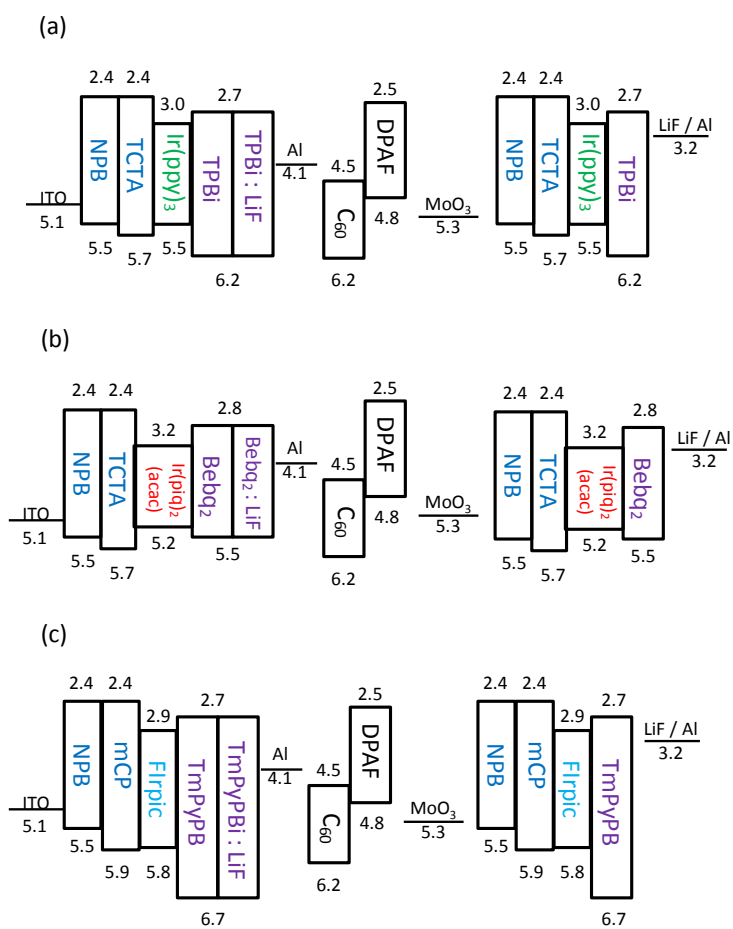


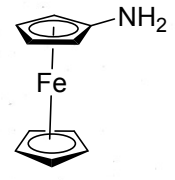
Figure S7. Energy level diagrams of the RGB tandem OLEDs


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ACQUISITION exp dof 0
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in 1.985 dmf 280
at 23864 PROCESSING
sw 6886.0 wifile
fb 3400 proc ft
se 4 tn not used
tper 56
pw 6.0 werr
d1 1.000 wexp
tof 0 wbe
nt 100 wnt
ct 4
alock n
gain not used
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in n
dp y
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rfp 2899.1
sh 2
ins 100.000
nm cdc ph

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4.100
3.874
3.819
2.585
1.550



¹H NMR in CDCl₃

