

Supporting Information

A Novel Bipolar Phosphorescent Host for Highly Efficient Deep-Red OLEDs at Wide Luminance Range of 1000-10000 cd m⁻²

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General Information

Materials obtained from commercial suppliers were used without further purification. Anhydrous hexane was distilled with sodium benzophenone ketyl under nitrogen atmosphere and degassed by the freeze-pump-thaw method. All glassware, syringes, magnetic stirring bars and needles were dried in a convection oven for at least 4 h. Reactions were monitored with thin layer chromatography (TLC). Commercial TLC plates (Silica gel 60 F254, Merck Co.) were visualized under UV light at 254 and 365 nm. Silica column chromatography was done with silica gel 60 G (particle size 5~40 μm, Merck Co.). ¹H NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer with tetramethylsilane as an internal standard. Mass spectra were measured on a GC/MS mass spectrometer. Elemental analyses were performed on a flash EA 1112 spectrometer. Absorption spectra were obtained using a Shimadzu UV-2550 UV-vis spectrometer. PL spectra were recorded on a Perkin-Elmer LS-55 fluorescence spectrometer with a Xe arc lamp excitation source. All solvents were degassed via three freeze-pump-thaw cycles. Emission lifetime experiments were performed by the time-correlated single-photon counting (TCSPC) system under right-angle sample geometry. A 379 nm picosecond diode laser (Edinburgh Instruments EPL375, repetition rate 20 MHz) was used to excite the samples. The PL emission was collected by a photomultiplier tube (Hamamatsu H5783p) connected to a TCSPC board (Becker&Hickel SPC-130). The time constant of the instrument response function (IRF) is ca. 220 ps. Electrochemical measurements were performed with a BAS 100W Bioanalytical electrochemical work station, using Pt working electrode, platinum wire as auxiliary electrode, and a porous glass wick Ag/Ag⁺ as reference electrode. The voltammograms were referenced to the ferrocene/ferrocenium couple and the scan rate was 100 mV s⁻¹. Due to the limitation^{S1} in measuring reduction potentials in the range of -2.7 V to -3.5 V in CH₂Cl₂, we obtained only

the oxidation potential for three phosphors, and no reduction wave was detected within the electrochemical window of dichloromethane. The HOMO levels of phosphors were calculated from the onset of the oxidation potential in the cyclic voltammetry (CV) wave. The bandgap (E_g) of them were calculated from their absorption edge of the UV-vis spectra. The LUMO levels of them were determined by considering the difference between their HOMO level and the corresponding E_g . The time-of-flight (TOF) technique involves generation of carriers near one electrode with a short pulse of light and observation of the current displaced in the external circuit by the motion of the carriers through the sample. The sample for TOF measurement was prepared on the glass substrate covered with indium tin oxide (ITO) layer with the structure of [ITO/phosphor (1 μm)/Al]. An intense short duration (5-6 ns) light pulse from a frequency-tripled (355 nm) Nd:YAG laser was incident at one side of the sample to generate photocarriers. The sample was mounted in a vacuum and the measurement was made at the electric field of $5.0 \times 10^5 \text{ V cm}^{-1}$ at 293 K.

Single Crystal Structure

The single crystal suitable for X-ray structural analysis was obtained by vacuum sublimation. Diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the ω -scan mode with graphite-monochromator Mo•K α radiation. The structure was solved with direct methods using the SHELXTL programs and refined with full-matrix least-squares on F^2 .^{S2} Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. The corresponding CCDC reference number (CCDC: 1400002) and the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Theoretical Calculations

The ground state geometries were fully optimized by the density functional theory (DFT)^{S3} method with the Becke three-parameter hybrid exchange and the Lee-Yang-Parr correlation functional^{S4} (B3LYP) and 6-31G** basis set using the Gaussian 03 software package.^{S5}

Fabrication of the OLEDs and EL Measurements

The general architecture of the multilayer diodes is as follows. The ITO (indium-tin oxide) coated glass substrates (20 Ω /square) were first cleaned in ethanol, acetone, and soap ultrasonic baths. All organics were purified by gradient sublimation and thermally evaporated

at a rate of 1.0 \AA s^{-1} at a pressure of ca. $3.5 \times 10^{-4} \text{ Pa}$. A LiF layer (0.5 nm) was deposited at a rate of 0.2 \AA s^{-1} . The Al cathode was deposited at a rate of 10 \AA s^{-1} and the active area of the diode segments was $2 \times 3 \text{ mm}^2$. EL spectra and brightness-current density-voltage characteristics were measured by combining a Spectrascan PR-650 spectrophotometer with a computer-controlled direct-current power supply Keithley model 2400 voltage-current source under ambient conditions at room temperature.

Synthesis

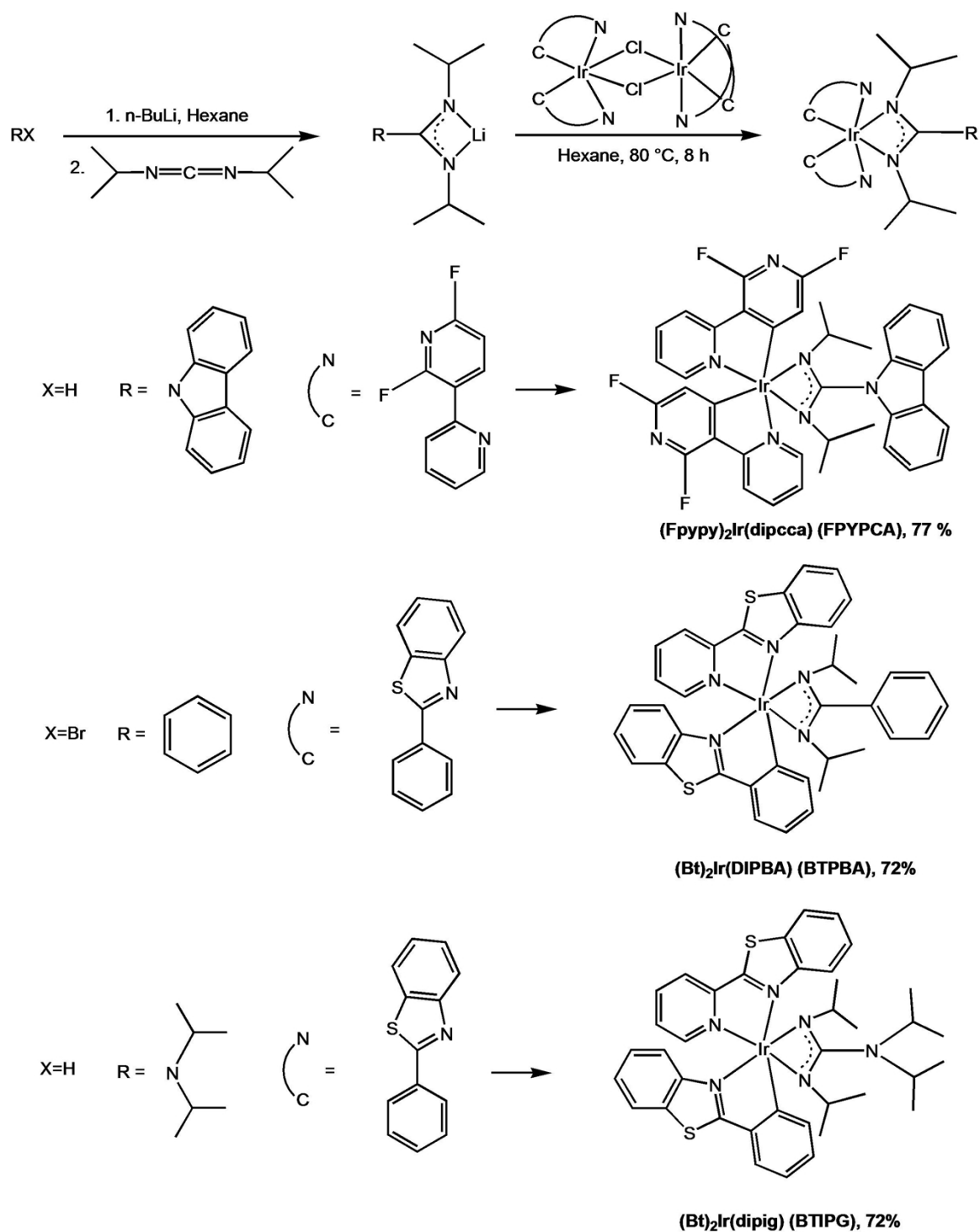
Materials: $[(F_2\text{ppy})_2\text{Ir}(\mu\text{-Cl})_2]$ and $[(\text{Bt})_2\text{Ir}(\mu\text{-Cl})_2]$ were synthesized according to a modified Nonoyama procedure,^{S6} by refluxing $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (2.5 g, 7 mmol) with 2.5 equiv of the ligands (3.3 g of 2',6'-difluoro-2,3'-bipyridine or 3.6 g of 2-phenylbenzothiazole) in a 3:1 (v/v) mixture of 2-methoxyethanol and water for 6-7 h. The reaction mixture was cooled to room temperature and water was added to precipitate the product. The resulting mixture was filtered and the precipitate was then washed with hexane and ethyl ether several times to provide $[(F_2\text{ppy})_2\text{Ir}(\mu\text{-Cl})_2]$ and $[(\text{Bt})_2\text{Ir}(\mu\text{-Cl})_2]$ in 85% and 82% yields, respectively.

$(F_2\text{ppy})_2\text{Ir}(\text{dipcca})$ (FPYPCA), $(\text{Bt})_2\text{Ir}(\text{dipba})$ (BTPBA) and $(\text{Bt})_2\text{Ir}(\text{dipig})$ (BTIPG): A hexane solution of n-BuLi (0.20 mL x 2.5 M) was added to carbazole (83 mg, 0.5 mmol) or diisopropylamine (50 mg, 0.5 mmol) or bromobenzene (78 mg, 0.5 mmol) in hexane (10 mL) under argon. The reaction mixture was stirred at room temperature for 30 min, and then added dropwise to N,N-diisopropylcarbodiimide (63 mg, 0.5 mmol). The colorless solution was stirred for another 30 min, and then added dropwise to $[(F_2\text{ppy})_2\text{Ir}(\mu\text{-Cl})_2]$ (304 mg, 0.25 mmol) or $[(\text{Bt})_2\text{Ir}(\mu\text{-Cl})_2]$ (323 mg, 0.25 mmol) in hexane solvent (20 mL). After stirring at 80 °C for 8 h, the reaction mixture was cooled to room temperature. The solvent was evaporated under vacuum, and the product was washed with Et_2O (20 mL) three times to give a powder $(F_2\text{ppy})_2\text{Ir}(\text{dipcca})$ (FPYPCA) (77%), $(\text{Bt})_2\text{Ir}(\text{dipba})$ (BTPBA) (72%) and $(\text{Bt})_2\text{Ir}(\text{dipig})$ (BTIPG) (72%).

(F₂pypp)₂Ir(dipcca) (FPYPCA): ¹H NMR (500 MHz, CDCl₃) δ 9.56 (d, *J* = 5.5 Hz, 2H), 8.39 (d, *J* = 8.3 Hz, 2H), 8.11 (d, *J* = 7.7 Hz, 2H), 8.03 (t, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 6.5 Hz, 2H), 7.53 – 7.47 (m, 4H), 7.32 (t, *J* = 5.5 Hz, 2H), 5.76 (s, 2H), 3.13 (dt, *J* = 12.4, 6.2 Hz, 2H), 0.67 (d, *J* = 6.3 Hz, 6H), -0.08 (d, *J* = 6.2 Hz, 6H). Elemental analysis: found C, 53.95%; H, 3.80%; N, 11.23%; calc. for C₃₉H₃₂F₄IrN₇: C, 54.03%; H, 3.72%; N, 11.31%. MS m/z: 867.01 [M⁺] (calc. 867.24).

(Bt)₂Ir(dipba) (BTPBA): ¹H NMR (500 MHz, CDCl₃) δ 9.20 (d, *J* = 8.3 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 8.1 Hz, 4H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.29 (m, 3H), 7.18 (d, *J* = 6.7 Hz, 2H), 6.82 – 6.76 (m, 2H), 6.60 (t, *J* = 7.1 Hz, 2H), 6.48 (d, *J* = 7.7 Hz, 2H), 3.36 (dt, *J* = 12.6, 6.3 Hz, 2H), 0.58 (d, *J* = 6.4 Hz, 6H), -0.17 (d, *J* = 6.2 Hz, 6H). Elemental analysis: Found: C, 57.47; H, 4.35; N, 6.98; calc. for C₃₉H₃₅IrN₄S₂: C, 57.40; H, 4.32; N, 6.87. MS m/z: 817.64 (M⁺) (calc. 818.21).

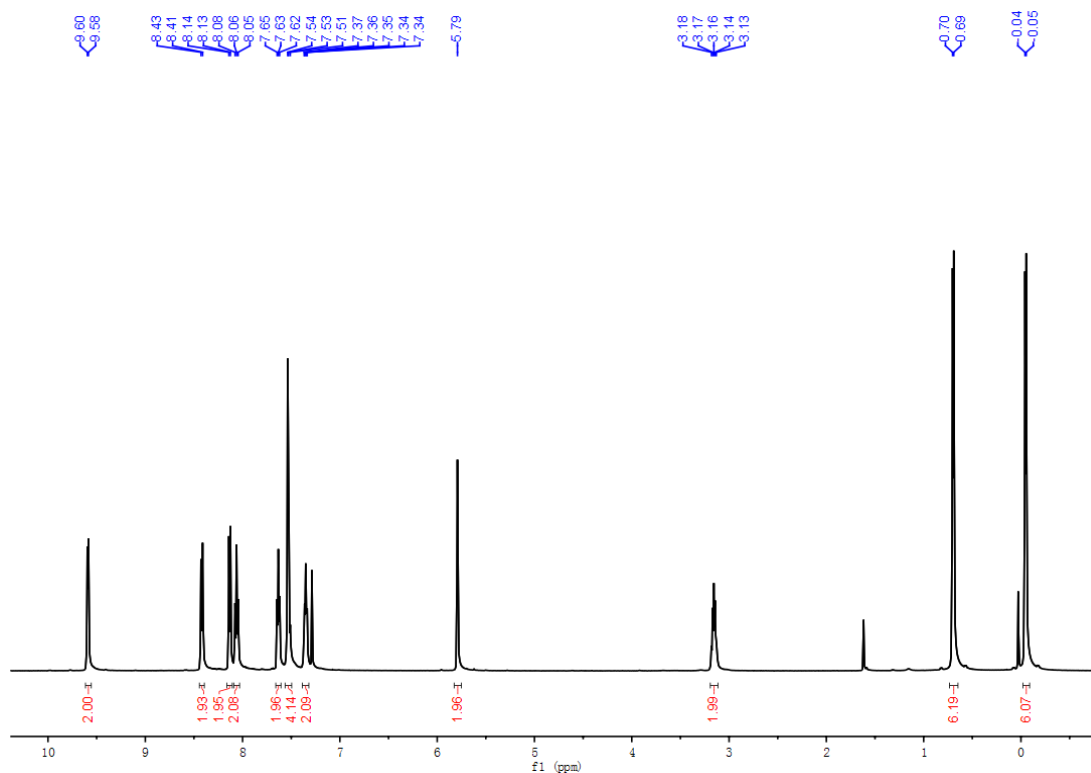
(Bt)₂Ir(dipig)(BTIPG): ¹H NMR (500 MHz, CDCl₃) δ 9.12 – 9.06 (m, 2H), 7.90 – 7.86 (m, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.43 (p, *J* = 6.5 Hz, 4H), 6.75 (t, *J* = 7.3 Hz, 2H), 6.57 (t, *J* = 7.1 Hz, 2H), 6.40 (d, *J* = 7.7 Hz, 2H), 3.80 (dt, *J* = 12.7, 6.3 Hz, 2H), 3.60 (dt, *J* = 13.9, 6.9 Hz, 2H), 1.28 (d, *J* = 7.0 Hz, 6H), 1.01 (d, *J* = 6.8 Hz, 6H), 0.82 (d, *J* = 6.3 Hz, 6H), -0.05 (d, *J* = 6.3 Hz, 6H). Elemental analysis: Found: C, 55.71; H, 5.34; N, 8.20; calc. for C₃₉H₄₄IrN₅S₂: C, 55.82; H, 5.29; N, 8.35. MS m/z: 838.82 (M⁺) (calc. 839.27).



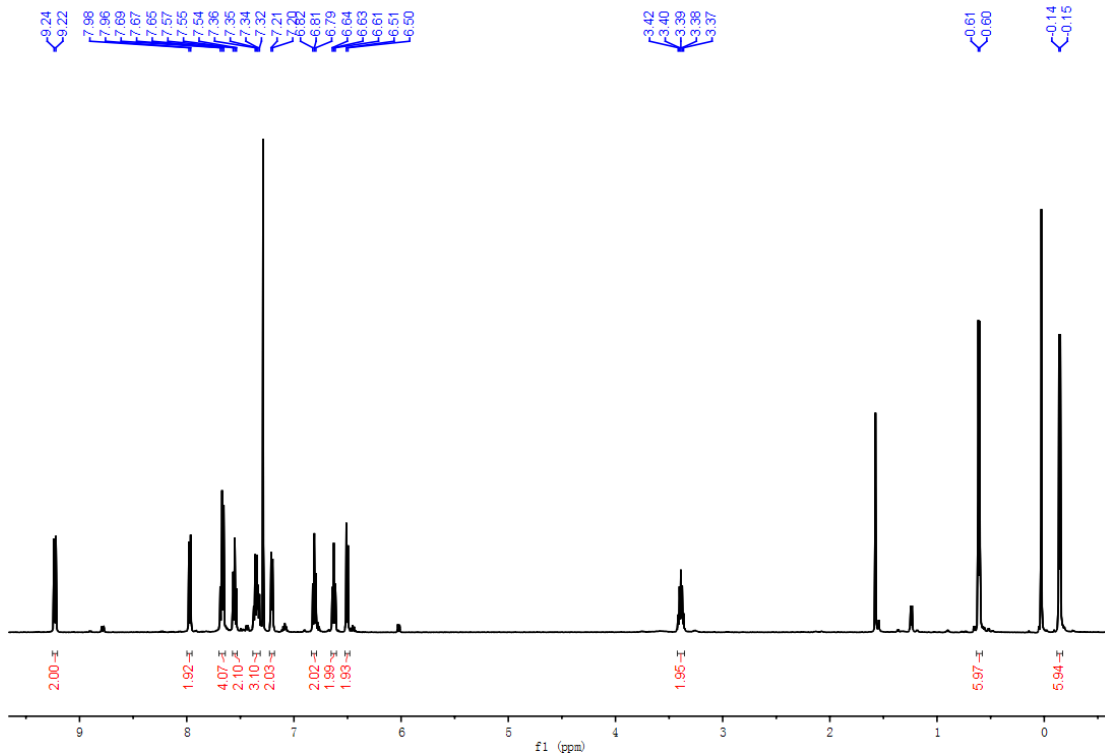
S-Scheme 1. Synthetic procedure and structures of **FPYPCA**, **BTPBA** and **BTIPG**.

S-Table 1. Crystal data and structure refinement parameters for **FPYPCA**.

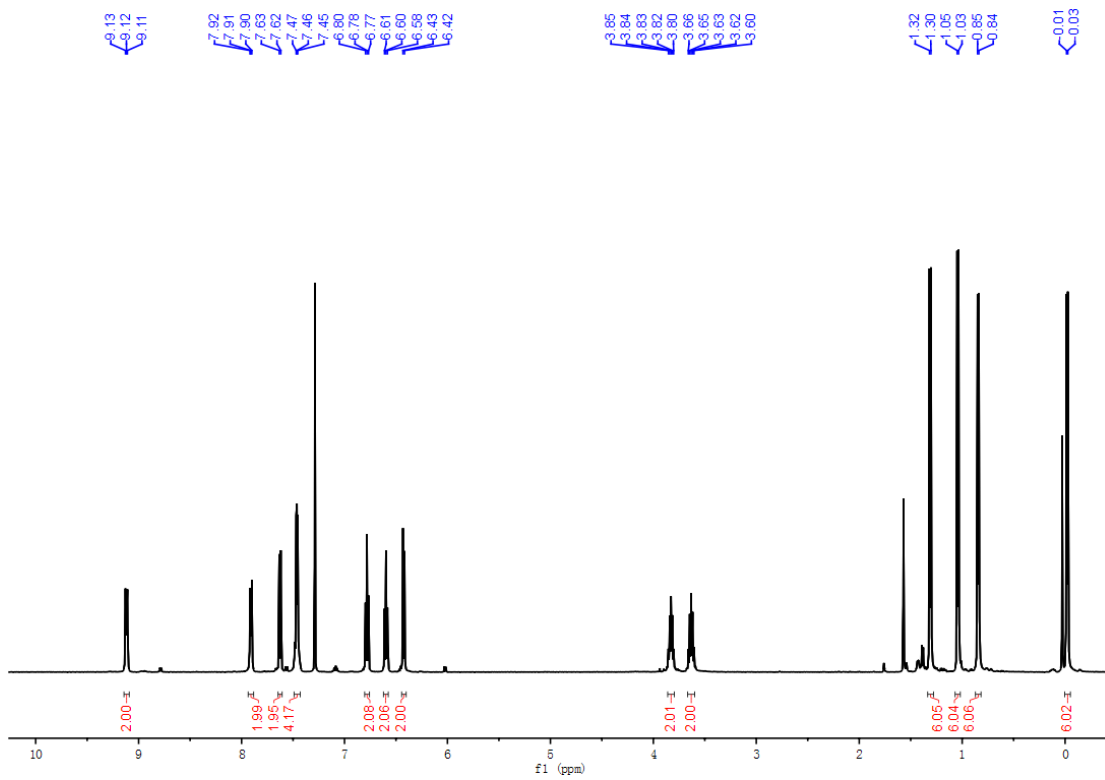
| Complexes | FPYPCA |
|--|------------------------------------|
| Formula | $C_{39}H_{32}F_4IrN_7 \cdot CH_4O$ |
| molecular weight | 898.98 |
| crystal system | Triclinic |
| space group | P -1 |
| crystal size mm ³ | 0.34 * 0.26 * 0.22 |
| a [Å] | 11.9138(9) |
| b [Å] | 12.3154(9) |
| c [Å] | 14.3549(11) |
| α [o] | 99.444(1) |
| β [o] | 98.544(1) |
| γ [o] | 116.930(1) |
| V [Å ³] | 1791.9(2) |
| Z | 2 |
| ρ_{calc} [g/cm ³] | 1.666 |
| temp (K) | 293(2) |
| μ [mm ⁻¹] | 3.790 |
| reflections collected | 9649 |
| independent reflections | 6193 |
| RF, Rw(F ²) (all data) | 0.0502, 0.1211 |
| RF, Rw(F ²) [I > 2 σ (I)] | 0.0410, 0.0999 |
| GOF | 1.117 |
| CCDC | 1400002 |



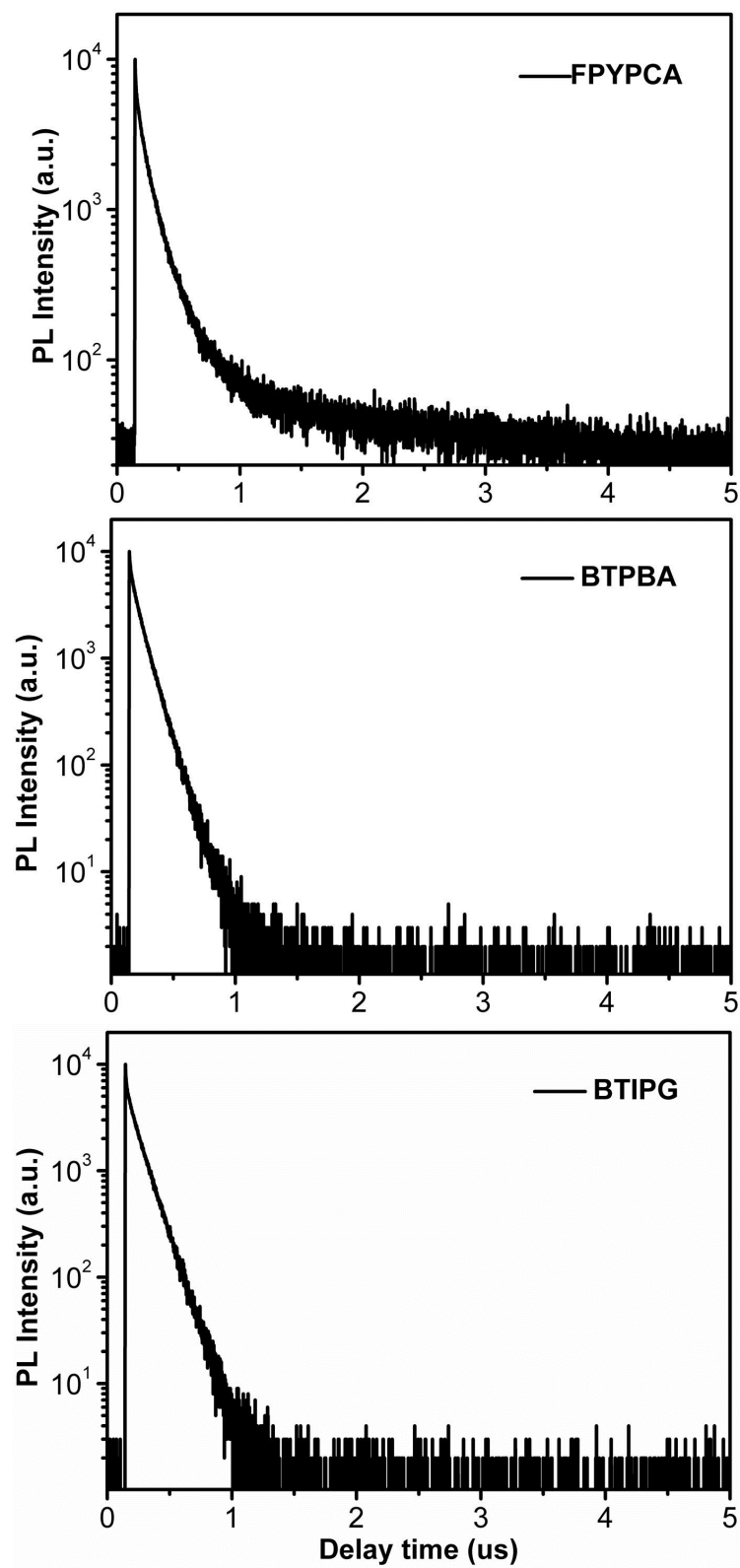
S-Fig. 1. ¹H NMR spectrum of FPYPCA in CDCl₃.



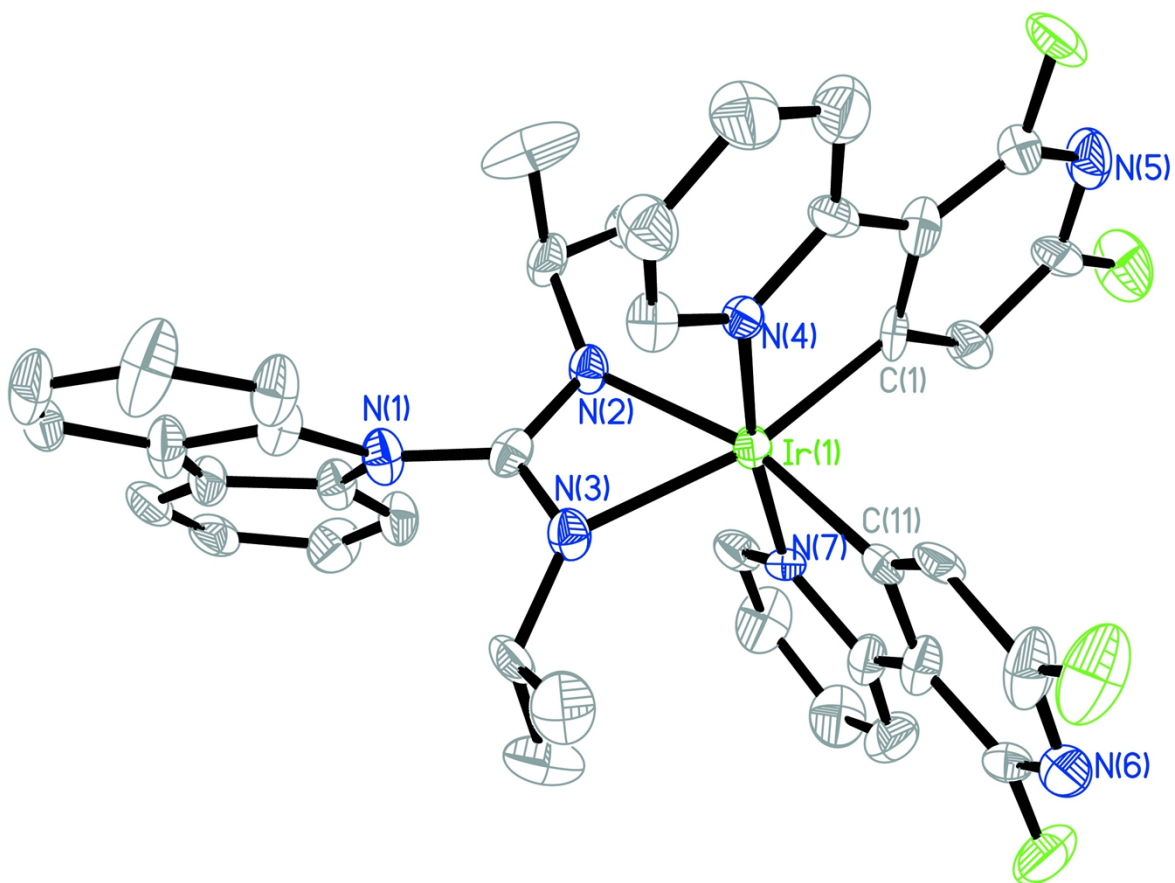
S-Fig. 2. ^1H NMR spectrum of BTPBA in CDCl_3 .



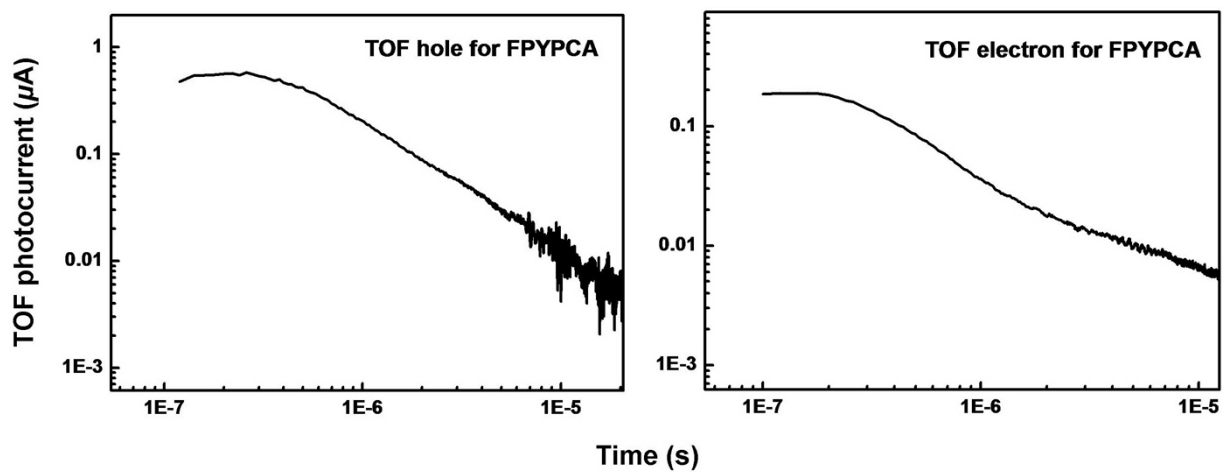
S-Fig. 3. ^1H NMR spectrum of BTIPG in CDCl_3 .



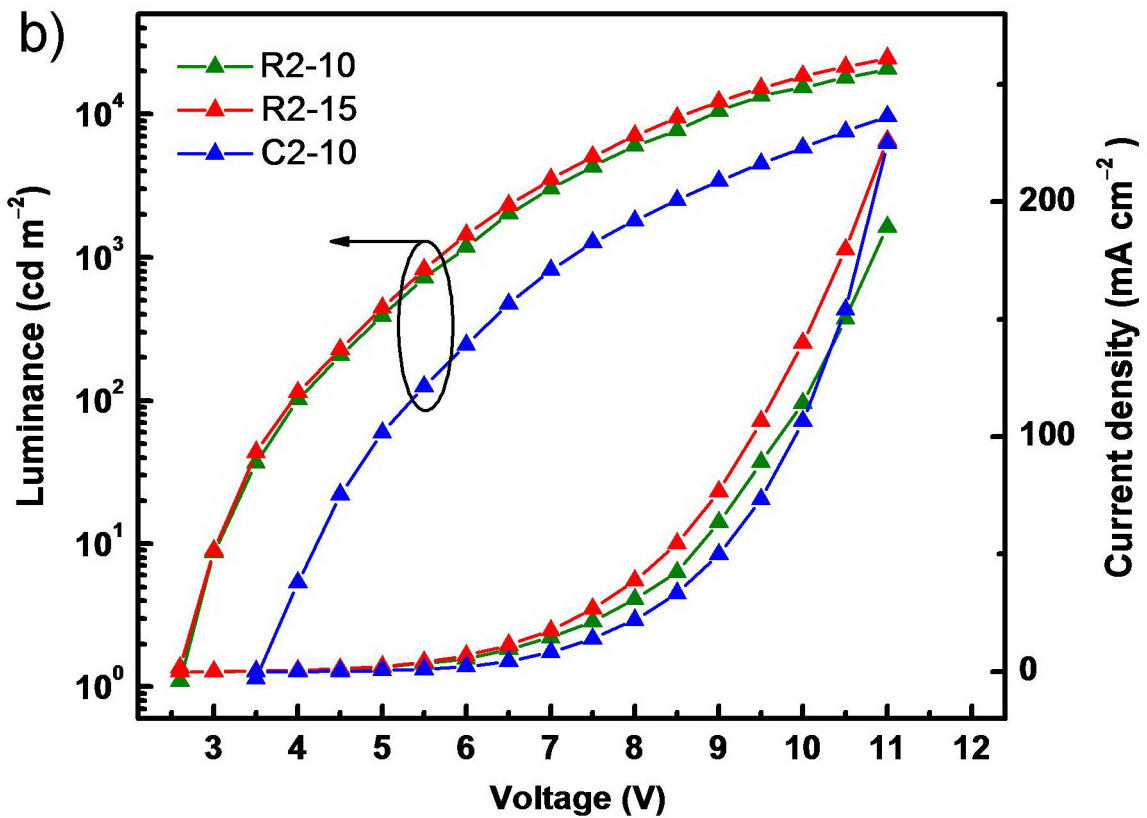
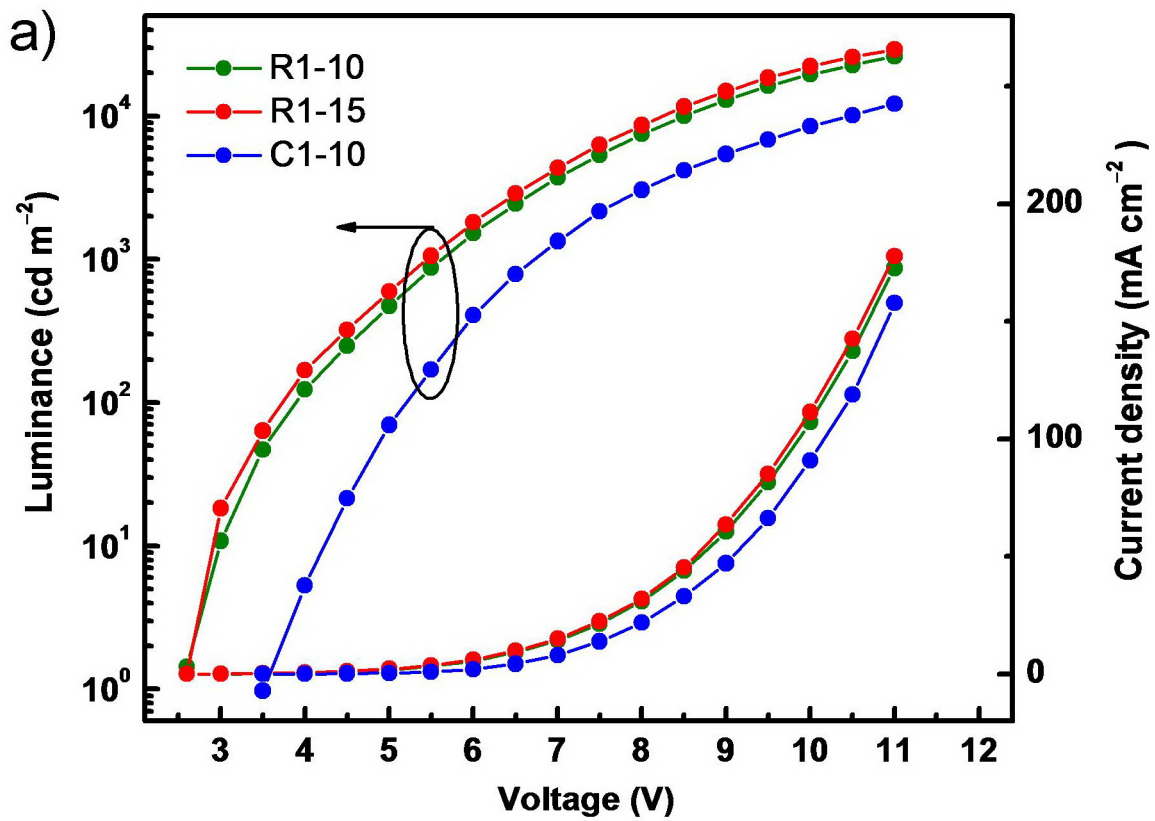
S-Fig. 4. Transient PL spectra of FPYPCA, BTPBA and BTIPG.



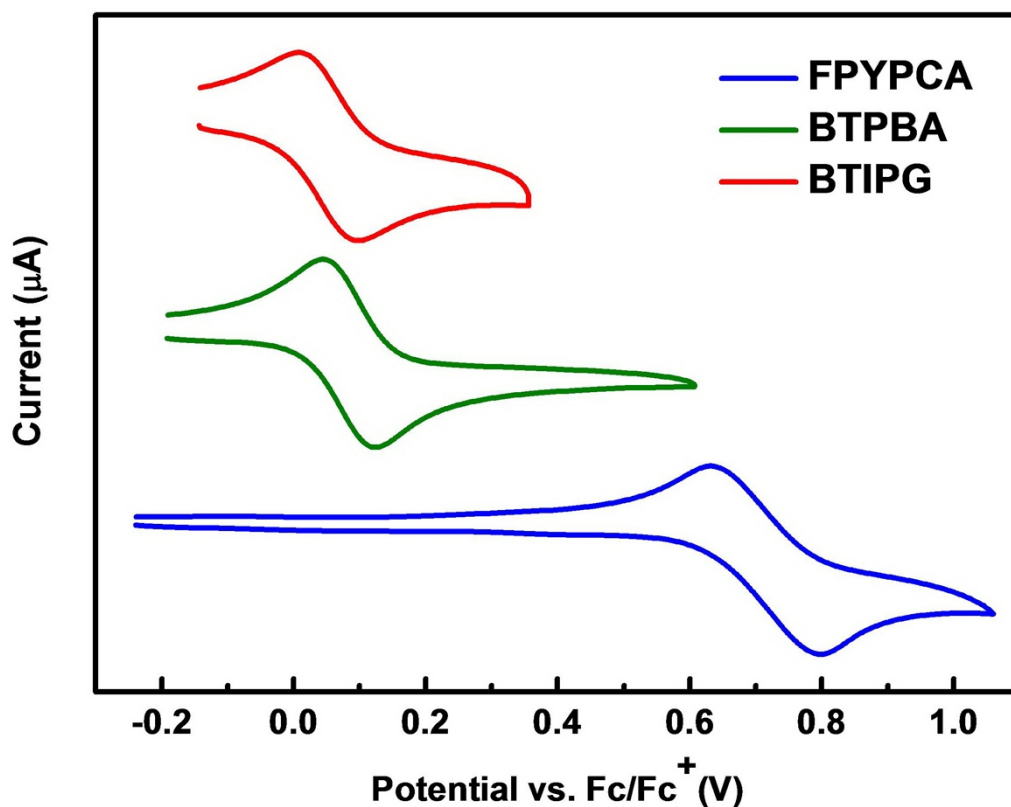
S-Fig. 5. ORTEP diagram of FPYPCA with thermal ellipsoids shown at 50% probability level.



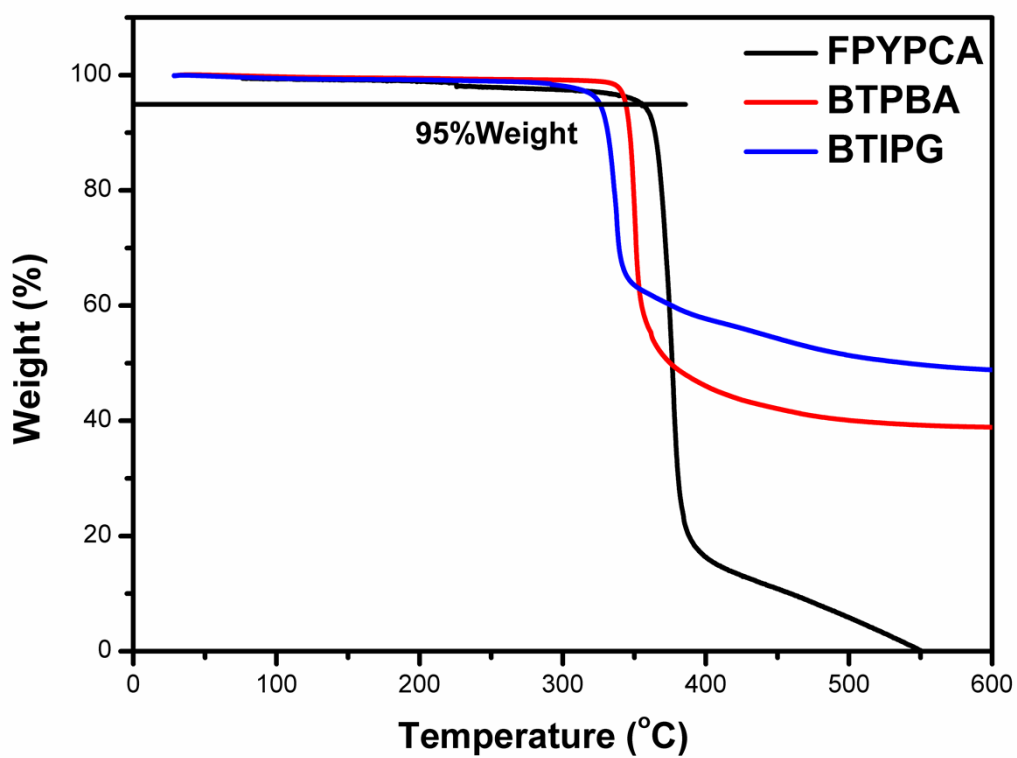
S-Fig. 6. Typical time of flight transient FPYPCA.



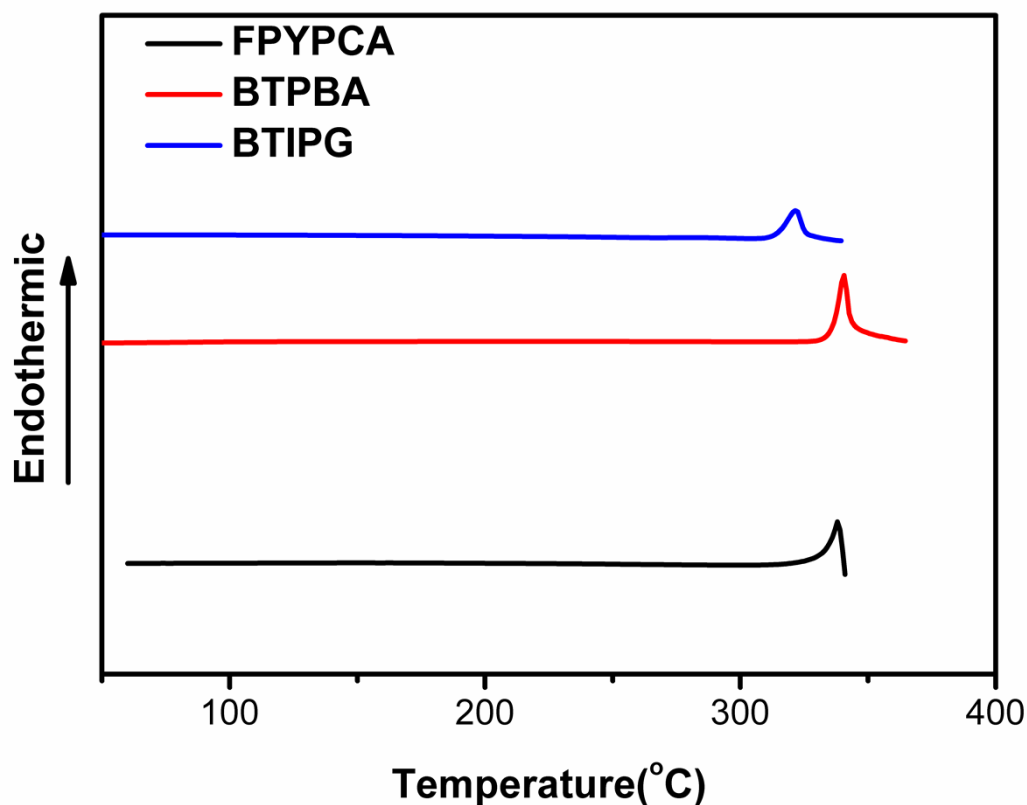
S-Fig. 7. Current density-voltage-luminance (J - V - L) curves of a) R1-10, R1-15, and C1-10, and b) R2-10, R-15 and C2-10.



S-Fig. 8. Cyclic voltammograms of FPYPCA, BTPBA and BTIPG in CH₂Cl₂ for oxidation.



S-Fig. 9. TGA graphs of FPYPCA, BTPBA and BTIPG.



S-Fig. 10. DSC graphs of FPYPCA, BTPBA and BTIPG.

SI-References:

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