

Supporting Information

Design of Pyridinylphosphinate-based Blue Iridium Phosphors for High-Efficiency Organic Light-emitting Diodes

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1. General Descriptions

1.1 Materials and measurements.

All reagents and chemicals were purchased from commercial sources and used without further purification. ^1H and ^{31}P NMR spectra were measured on a Bruker AM 400 spectrometer. Mass spectra (MS) were obtained with ESI-MS (LCQ Fleet, Thermo Fisher Scientific). High resolution mass spectra (HRMS) were measured with a LTQ-Orbitrap XL (ThermoFisher, U. S. A.). Absorption and photoluminescence spectra were measured on a UV-3100 spectrophotometer and a Hitachi F-4600 photoluminescence spectrophotometer, respectively. The decay lifetimes were measured with an Edinburgh Instruments FLS-920 fluorescence spectrometer. The phosphorescence quantum yields were determined in nitrogen degassed CH_2Cl_2 at 298 K against *fac*-Ir(ppy) $_3$ as a reference ($\Phi_p = 0.40$). Cyclic voltammetry measurements were conducted on a MPI-A multifunctional electrochemical and chemiluminescent system (Xi'an Remex Analytical Instrument Ltd. Co., China) at room temperature, with a polished Pt plate as the working electrode, platinum thread as the counter electrode and Ag-AgNO $_3$ (0.1 M) in CH_3CN as the reference electrode, *tetra*-n-butylammonium perchlorate (0.1 M) was used as the supporting electrolyte, using Fc^+/Fc as the internal standard, the scan rate was 0.1 V/s.

1.2 Theoretical calculation.

The density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were carried out with Gaussian 09 software package. The geometries of the ground state (S0) were fully optimized with the B3LYP exchange-correlation functional using the LANL2DZ basis set for iridium atom and the 6-31G** basis set for the other atoms both in vacuum and in CH_2Cl_2 (C-PCM27 solvent model). Vibrational frequency calculations were performed to validate that they are minima on potential energy surface. On the basis of the optimized S0 molecular structures in solvent, TD-DFT calculation was performed. Solvent effect was also considered by using C-PCM model. Frontier molecular orbitals were visualized using Gauss View, and their quantified compositions in percentage on different parts were given by QMForge.

1.3 Fabrication and measurements of OLEDs.

Indium-tin-oxide (ITO) coated glass with a sheet resistance of 10 Ω/sq was used as the anode

substrate. Prior to film deposition, patterned ITO substrates were cleaned with detergent, rinsed in de-ionized water, dried in an oven, and finally treated with oxygen plasma for 5 minutes at a pressure of 10 Pa to enhance the surface work function of ITO anode (from 4.7 to 5.1 eV). All the organic layers were deposited with the rate of 0.1 nm/s under high vacuum ($\leq 2 \times 10^{-5}$ Pa). The doped layers were prepared by co-evaporating dopant and host material from two individual sources, and the doping concentrations were modulated by controlling the evaporation rate of dopant. MoO₃, LiF and Al were deposited in another vacuum chamber ($\leq 8.0 \times 10^{-5}$ Pa) with the rates of 0.01, 0.01 and 1 nm s⁻¹, respectively, without being exposed to the atmosphere. The thicknesses of these deposited layers and the evaporation rate of individual materials were monitored in vacuum with quartz crystal monitors. A shadow mask was used to define the cathode and to make ten emitting dots (with the active area of 10 mm²) on each substrate. Device performances were measured by using a programmable Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a silicon photodiode. The EL spectra were measured with a calibrated Hitachi F-7000 fluorescence spectrophotometer. Based on the uncorrected EL fluorescence spectra, the Commission Internationale de l'Eclairage (CIE) coordinates were calculated using the test program of Spectrascan PR650 spectrophotometer. The EQE of EL devices were calculated based on the photo energy measured by the photodiode, the EL spectrum, and the current pass through the device.

2. Supplementary data

Table S1. HOMO and LUMO electron cloud density distribution of each fragment of the Ir(III) complexes.

Complex	Orbital	Energy/eV (experiment)	Energy/eV (Calculated)	Composition (%)		
				Main	Ir	Ancillary Ligands
(dfppy)₂Ir(PPP)	HOMO	-5.95	-5.72	42.37	53.23	4.40
	LUMO	-3.00	-1.67	86.22	4.25	9.53
(dfppy)₂Ir(PPP)	HOMO	-6.08	-6.14	32.89	58.12	8.99
	LUMO	-3.03	-1.85	90.96	4.52	4.52
(FCN)₂Ir(PPP)	HOMO	-6.02	-6.12	41.08	53.35	5.57
	LUMO	-3.05	-1.97	91.54	4.52	3.94

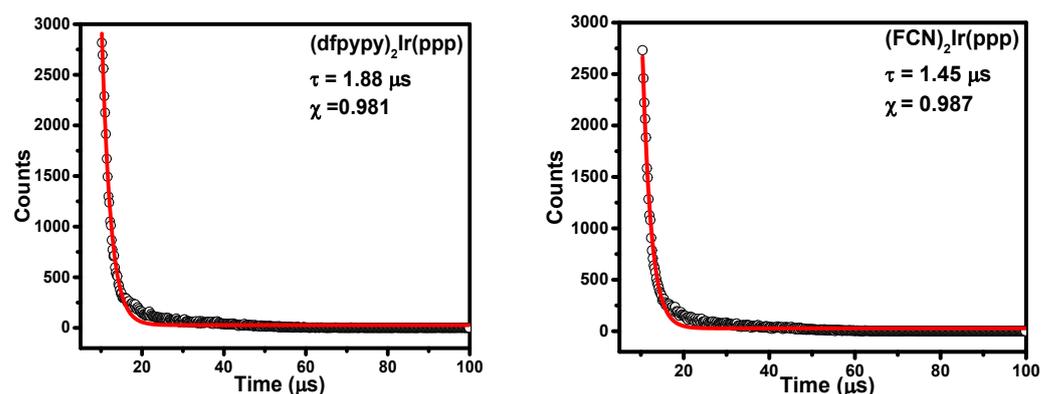


Fig. S1. The lifetime curves of both iridium complexes.

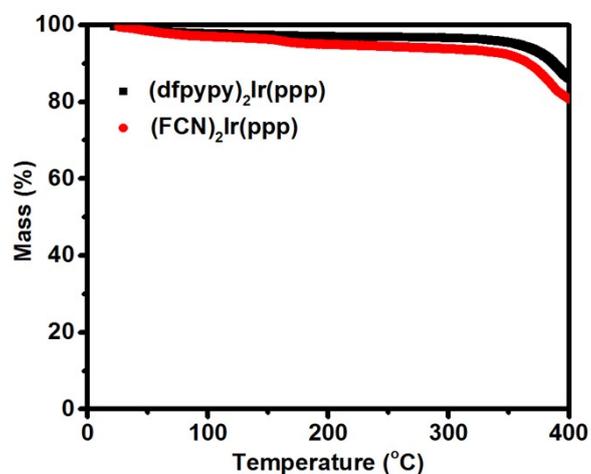
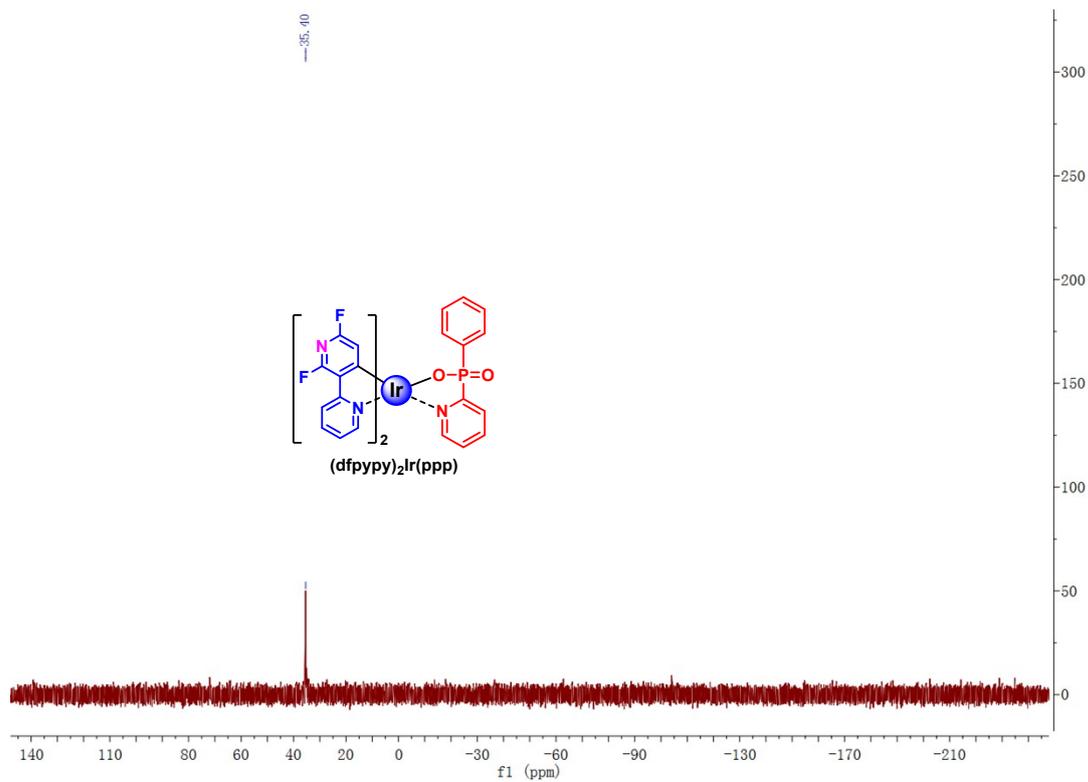
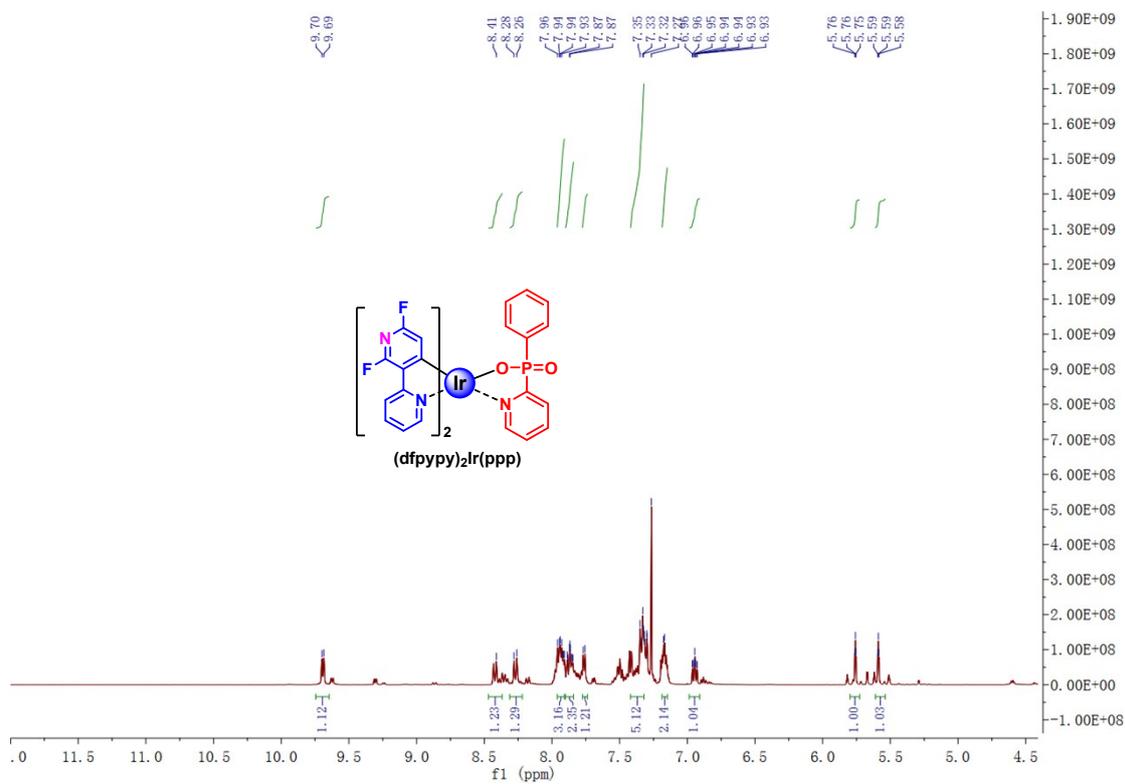
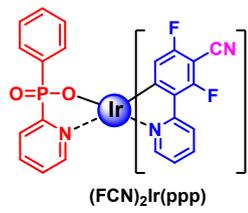
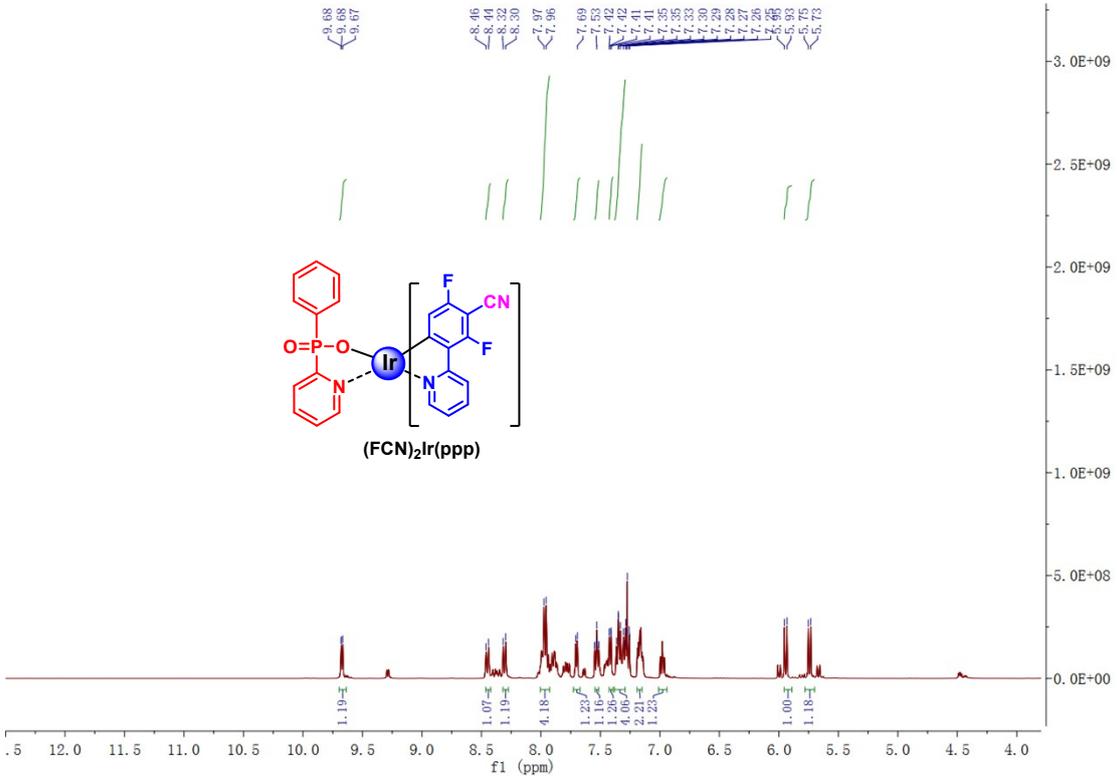
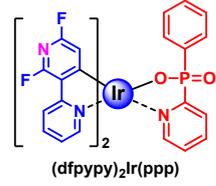
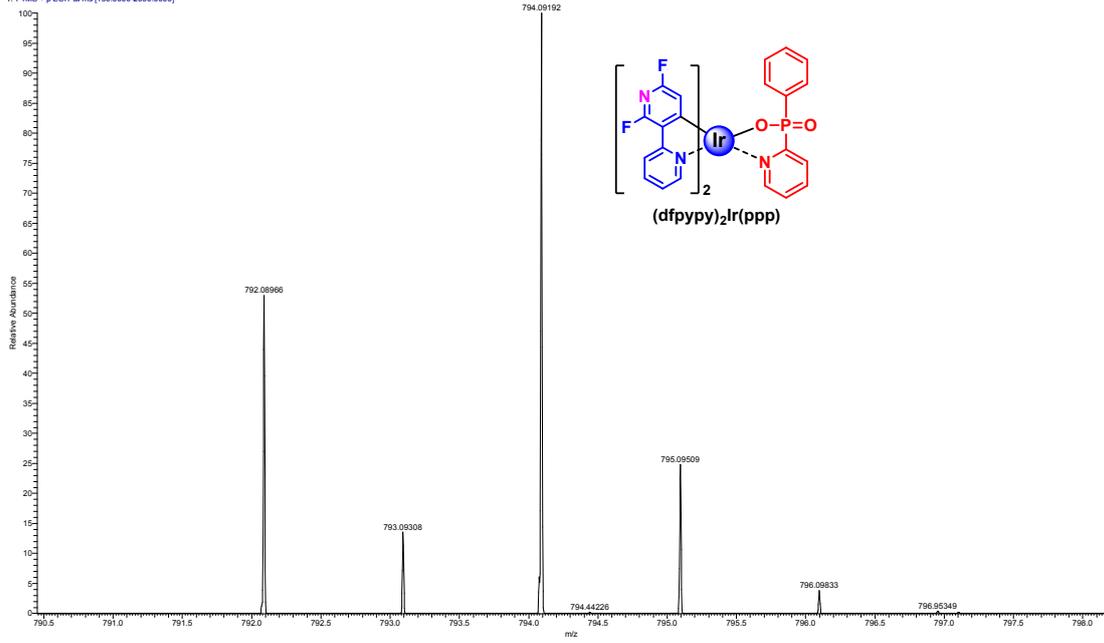


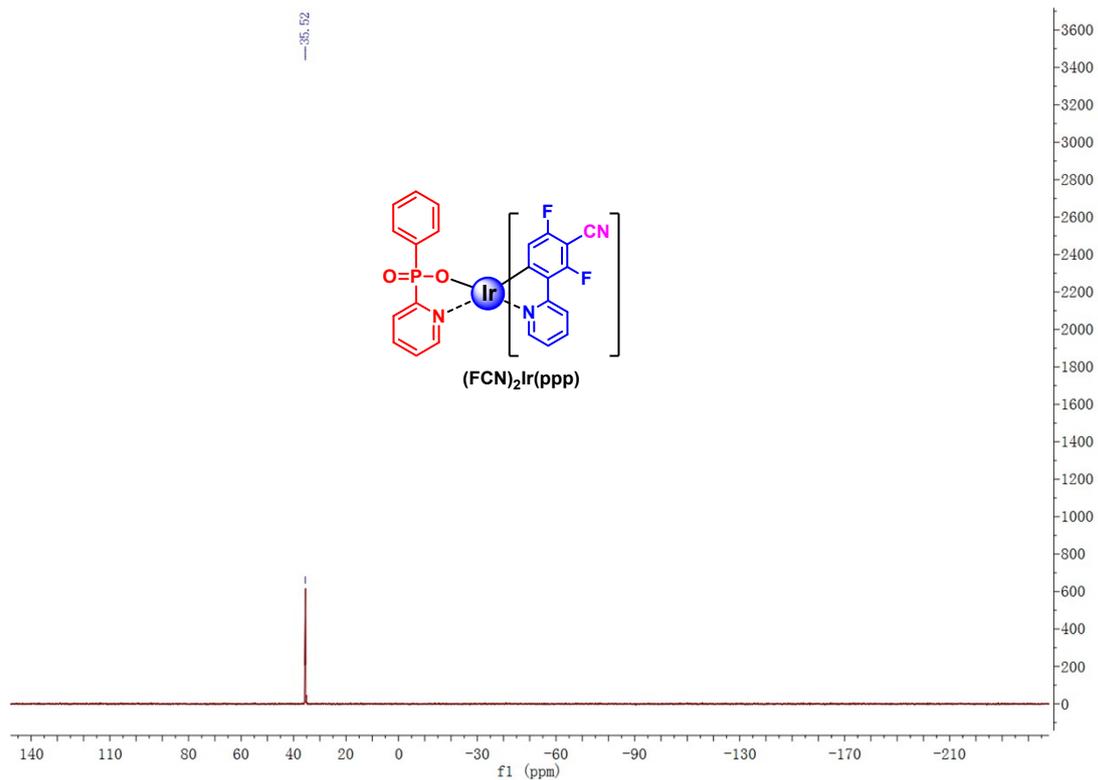
Fig. S2. Thermogravimetric analysis (TGA) of **(dfppy)₂Ir(PPP)** and **(FCN)₂Ir(PPP)**.

NMR and MS spectra of $(dfppy)_2Ir(ppp)$ and $(FCN)_2Ir(ppp)$.



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