Supporting Information

Simple/Efficient Solution-Processed Emitting Systems Dominated by a Novel Bipolar Small-Molecule Iridium (III) Complex

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General information

Materials obtained from commercial suppliers were used without further purification. Tetrahydrofuran 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 2 hours. Reactions were monitored with thin layer chromatography (TLC). Commercial TLC plates (Silica gel 60 F254, Merck Co.) were developed and the spots were seen under UV light at 254nm and 365nm. Silica column chromatography was done with silica gel 60G (particle size 5-40 μm. Merck Co.). ^{1}H NMR spectrum was recorded on a Bruker AVANVE 500MHz 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. Solid state PL efficiencies were measured using an integrating sphere (C-701, Labsphere Inc.), with a 365 nm Ocean Optics LLS-LED as the excitation source, and the light was introduced into the integrating sphere through an optical fiber. Emission lifetime experiments were performed by the time-correlated single-photon counting (TCSPC) system under right-angle sample geometry. Electrochemical measurements were performed with a BAS 100W Bioanalytical electrochemical work station.

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•Kα radiation. The structure was solved with direct methods using the SHELXTL programs and refined with full-matrix least-squares on F^2. Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. The corresponding CCDC reference number (CCDC: 2073344) and the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Fabrication of the OLEDs and EL measurements

The ITO (indium-tin oxide) coated glass substrates (20Ω/square) were first cleaned in ethanol,

acetone, and soap ultrasonic baths. The hole-injecting layer (HIL), poly(3,4-ethylened ioxythiophene):poly-styrenesulfonate (PEDOT:PSS) was spin-coated onto the oxygen-plasma-treated ITO-coated glass substrate at 3000 rpm for 40 s, followed by annealing in air for 20 min at 135 ℃. The emitting layer (EML) was then spin-coated from chlorobenzene solvent and annealed at 80 ℃ for 20min in nitrogen atmosphere. All the vapor-deposition organics were purified by gradient sublimation and thermally evaporated at a rate of 1.0 Å s^{-1} at a pressure of ca. 3.5×10^{-4} Pa. A LiF layer was deposited at a rate of 0.2 Å s^{-1}.

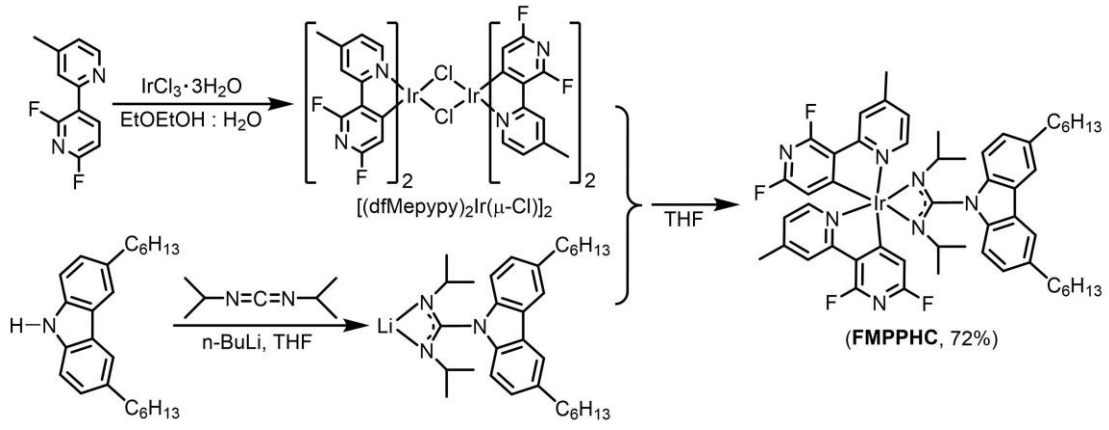
EL spectra and luminance-current density-voltage characteristics were measured by combining a Spectrascan PR-655 spectrophotometer with a computer-controlled direct-current power supply Keithley model 2400 voltage-current source under ambient conditions at room temperature.

Materials

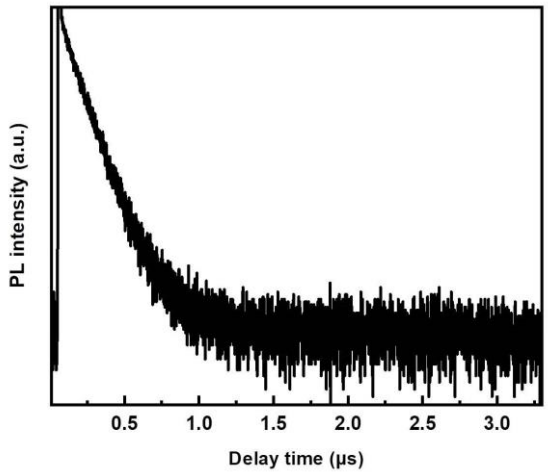
$[(dfMepypy)_2Ir(\mu\text{-}Cl)]_2$ were synthesized according to a modified Nonoyama procedure by refluxing $IrCl_3$ $3H_20$ (1.8 g, 5mmol) with 2.5 equiv of the ligands (2.4 g of 2',6'-difluoro-4-methyl-2,3'-bipyridine) in a 3:1 (v/v) mixture of 2-methoxyethanol and water for 8 hours. The reaction mixture was cooled to room temperature and water was added to precipitate the product. The resulting mixture was filtered and then washed with hexane and ethyl ether several times to provide $[(dfMepypy)_2Ir(\mu\text{-}Cl)]_2$ in 80% yields.

$(dfMepypy)_2Ir(diHepcca)$ (FMPPHC): A THF solution of n-BuLi (0.20ml×2.5M) was added to 3,6-dihexyl-9H-carbazole (170 mg, 0.5 mmol) in THF (10 ml) under argon. The reaction mixture was stirred at room temperature for 30 min, and then added dropwise to N,N-diisopropylcarbodiimide (65 mg, 0.5 mmol). The colorless solution was stirred for another 30 min, and then added to $[(dfMepypy)_2Ir(\mu\text{-}Cl)]_2$ (304 mg, 0.25 mmol) in THF solvent (20 ml). After stirring at room temperature for 8 hours, the solvent was evaporated under vacuum, and the product was washed with Et_2O (20 mL) three times to give a light green powder FMPPHC in 72% yields.

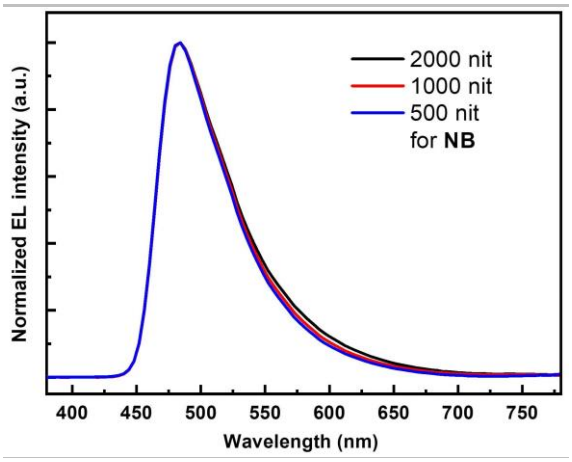
FMPPHC: MS:m/z 1063.32 (M+). Anal. Calcd for $C_{53}H_{60}F_4IrN_7$: C, 59.87; H, 5.69; F, 7.15; Ir, 18.08; N, 9.22 Found: C, 59.82; H, 5.73; F, 7.12. ^{1}H NMR (500 MHz, CDCl3) δ 9.38 (d, *J* = 5.8 Hz, 2H), 8.20 (s, 2H), 7.89 (s, 2H), 7.40 (d, *J* = 8.3 Hz, 4H), 7.33 (d, *J* = 8.3 Hz, 2H), 5.77 (s, 2H), 3.19 – 3.12 (m, 2H), 2.80 (t, *J* = 7.7 Hz, 4H), 2.75 (s, 6H), 1.78 – 1.71 (m, 4H), 1.43 (s, 4H), 1.36 (s, 8H), 0.92 (s, 6H), 0.66 (d, *J* = 6.1 Hz, 6H), -0.06 (d, *J* = 6.1 Hz, 6H).



S-Scheme 1. Synthetic procedure and structure of FMPPHC.



S-Figure 1. Transient PL spectra of FMPPHC.



S-Figure 2. EL spectra of **NB** at luminance level of 500, 1000 and 2000 cd m^{-2}.

S-Table 1. Crystal data and structure refinement for FMPPHC.

Identification code	FMPPHC
Empirical formula	$C_{53}H_{60}F_4IrN_7$
Formula weight	1063.28
Temperature/K	99.82
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.0004(17)
b/Å	27.109(3)
c/Å	10.5807(9)
α/°	90
β/°	99.688(4)
γ/°	90

Volume/Å^3	4806.7(8)
Z	4
ρ_{calc}g/cm^3	1.469
μ/mm^{-1}	2.837
F(000)	2160.0
Crystal size/mm^3	0.13 × 0.12 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.716 to 63.116
Index ranges	$-24 \leq h \leq 25$, $-39 \leq k \leq 39$, $-15 \leq l \leq 14$
Reflections collected	122072
Independent reflections	15167 [R_{int} = 0.0425, R_{sigma} = 0.0280]
Data/restraints/parameters	15167/0/594
Goodness-of-fit on F^2	1.446
Final R indexes [I>=2σ (I)]	R_1 = 0.0417, wR_2 = 0.1080
Final R indexes [all data]	R_1 = 0.0488, wR_2 = 0.1104
Largest diff. peak/hole / e Å^{-3}	3.02/-2.01