Electronic Supplementary Information

Highly efficient blue phosphorescent iridium(III) complexes with various ancillary ligands for organic light-emitting diodes

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1. General Experimental Information

All operations were performed under an inert nitrogen atmosphere using standard Schlenk unless otherwise stated. All solvents were used after distillation and stored over activated molecular sieves (5 Å). All reagents and chemicals were purchased from commercial sources and used without further purification. The NMR spectra were recorded with a Bruker spectrometer at ambient temperature. Mass spectra were obtained on SHIMADZU matrixassisted laser desorption/ionization time-of-flight mass pectrometer (MALDI-TOF-MASS). The UV-vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. Steadystate emission experiments at room temperature or 77 K were measured on an Edinburgh LFS-920 spectrometer. Excited-state lifetime studies were performed with an Edinburgh LFS-920 spectrometer with a hydrogen-filled excitation source. The data were analyzed by a software package provided by Edinburgh Instruments. The absolute quantum yields of the complexes were determined through an absolute method by employing an integrating sphere. The solution was degassed by three freeze-pump-thaw cycles. Cyclic voltammetry measurements were carried out in acetonitrile (5 \times 10⁻⁴ M) with a three-electrode cell configuration consisting of platinum working and counter electrodes and a Ag/AgNO₃ (0.01 M in CH₃CN) reference electrode at room temperature. Tetra-*n*-butylammonium hexafluorophosphate (0.1 M in CH_3CN) was used as the supporting electrolyte. The redox potentials were recorded at a scan rate of 100 mV/s and are reported with reference to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple.

2. X-Ray Crystallography Analysis

The X-ray diffraction data were collected on a Bruker Smart CCD Apex DUO diffractometer with graphite monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å) using the ω -2 ϑ scan mode. The data were corrected for Lorenz and polarization effects. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL-2000. All calculations and molecular graphics were carried out on a computer using the SHELX-2000 program package and Mercury. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center (CCDC). CCDC deposition numbers for **Ir1**, **Ir2**, **Ir3**, **Ir4** and **Ir6** are 1553323, 1553324, 1553325, 1553326 and 1553327, respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +441223336033; E-mail: deposit@ccdc.cam.ac.uk, or www: http://www.ccdc.cam.ac.uk).

3. EL Device Fabrication

Blue organic light-emitting diodes (OLEDs) based on Ir3, Ir4 and FIrpic were fabricated by spin-coating with a configuration of ITO/PEDOT:PSS (30 nm)/EML (40 nm)/TmPyPb (60 nm)/LiF (0.8 nm)/Al (100 nm). Prior to use, the patterned indium tin oxide (ITO) glass substrates were ultrasonically cleaned with detergent, alcohol and acetone, deionized water and then dried at 120 °C in a vacuum oven for more than one hour. After ultraviolet/ O_3 treatment for 4 min. Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) were spin-coated onto the cleaned ITO substrates at 3000 rpm for 60 s, and annealed for 20 min at 120 °C. The EML was prepared by spin-coating at 2000 rpm for 30 s, and annealed for 20 min at 80 °C in the glove box. The thickness of the EML is about 40 nm. Next, a 60 nm thickness 1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (TmPyPb), acting as a high triplet energy exciton blocking layer with electron transport properties, was deposited on the EML. Deposition rate of organic materials was 0.1 nm/s and vacuum pressure for thermal deposition was 5 \times 10⁻⁴ Pa. After deposition of the TmPyPb layer, a cathode consisting of 0.8 nm LiF and 100 nm Al was deposited at a rate of 0.01 nm/s for LiF and 0.1-0.4 nm/s for Al. The thickness of the films was controlled by a quartz thickness monitor. The emission area of the devices is 12 mm². The current-voltage-luminescence characteristics were measured by a Keithley 2602 source meter with a calibrated silicon photodiode. The electroluminescence spectra of the devices were analyzed with a spectrometer (PR655). The thickness of organic thin films was measured using a spectroscopic ellipsometry (α -SE, J.A. Wollam Co. Inc.). All the samples were measured directly after fabrication without encapsulation in ambient atmosphere at room temperature.

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Fig. S1 The enlarged view of ${}^{1}H$ NMR of Ir1 in CDCl₃.



Fig. S2 The enlarged view of $^{19}\mathsf{F}$ NMR of Ir1 in CDCl3.

complex	δ (ppm) $^{\scriptscriptstyle a)}$	³ J _{HF} (Hz) ^{a)}
	H ^{b)}	
lr1	6.53	12.00
lr2	5.97	11.20
lr3	6.09, 5.98	10.80, 10.80
Ir4	6.13, 5.89	11.20, 11.20
Ir5	6.16, 6.04	10.80, 11.20
lr6	6.13, 6.02	10.80, 11.20

Table S1. Selected chemical shifts and coupling constants of Ir1-Ir6.

^{a)} Recorded in CDCl₃; ^{b)} Protons adjacent to the C-Ir bonds of the complexs.

Complex	Absorption ^{a)}	Emission ^{b)}	Rigidochromic shift ^{c)}
	λ_{abs} [nm]	$\lambda_{ m em}[m nm]$	$\lambda_{\Delta}[nm]$
lr1	274, 344, 381	454, 488 (sh)	10
lr2	258, 293, 344, 380, 412	466, 503 (sh)	14
lr3	258, 277, 315, 366, 403	453, 486 (sh)	5
lr4	257, 284, 318, 376, 409	459, 493 (sh)	6
Ir5	254, 273, 313, 331, 368, 394	455, 489 (sh)	2
lr6	253, 276, 313, 368, 397	453, 486 (sh)	4

 Table S2. Absorption, luminescence data for Ir1-Ir6.

^{a)}At a concentration of 1.0×10^{-5} mol/L in CH₂Cl₂; ^{b)} At a concentration of 1.0×10^{-5} mol/L in 2-MeTHF glass matrix at 77 K, λ_{ex} = 365 nm; ^{c)} The difference between the PL peaks measured at room temperature and at 77 K.

Complex	lr1	lr2	lr3
Formula	$C_{36}H_{18}N_3F_{12}Ir$	$C_{30}H_{21}Cl_2F_8IrN_2O_2$	$C_{32}H_{16}F_{11}IrN_{6}$
Formula weight	912.73	856.59	885.71
Temperature/K	150.0	150.0	150.0
Crystal system	trigonal	orthorhombic	triclinic
Space group	R-3	Pccn	P-1
a/Å	15.6723(14)	22.103(9)	13.9402(19)
b/Å	15.6723(14)	15.658(6)	14.806(2)
c/Å	56.758(5)	17.759(7)	17.817(2)
α/°	90	90	78.953(3)
<i>в</i> /°	90	90	83.405(3)
γ/°	120	90	70.356(2)
V/Å ³	12073(2)	6146(4)	3394.1(8)
Z	6	8	4
$ ho_{calc}$ g/cm ³	0.753	1.851	1.733
μ/mm ⁻¹	1.700	4.599	4.026
F(000)	2640.0	3312.0	1704.0
Crystal size/mm ³	0.3×0.11×0.09	0.25×0.11×0.1	0.25×0.11×0.1
Radiation/Å	0.71073	0.71073	0.71073
ϑ/(°)	2.152 to 65.268	3.188 to 56.08	2.332 to 62.712
Reflections collected	47779	49493	30443
Data/restraints/ parameters	9816/0/313	7436/0/408	21283/6/901
GOF	1.076	1.067	1.055
R ₁ /wR ₂ [I>=2σ (I)]	0.0383/0.0857	0.0582/0.1190	0.0562/0.1183
R ₁ /wR ₂ [all data]	0.0556/0.0911	0.0845/0.1432	0.0966/0.1441
Largest diff. peak/hole / e Å ⁻³	5.40/-2.21	3.87/-3.65	5.34/-4.01

Table S3. Crystallographic data for Ir1, Ir2 and Ir3	3.
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Complex	lr4	lr6
Formula	$C_{30}H_{16}F_8IrN_3O_2$	$C_{30}H_{16}F_8IrN_7$
Formula weight	794.66	818.70
Temperature/K	150.0	150.0
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	12.913(5)	12.9273(17)
b/Å	14.715(6)	14.3788(19)
c/Å	17.797(8)	18.473(2)
α/°	78.336(10)	85.200(3)
<i>в</i> /°	84.328(10)	78.666(2)
γ/°	74.230(9)	89.935(3)
V/Å ³	3184(2)	3354.6(8)
Z	4	4
$ ho_{calc}$ g/cm ³	1.658	1.621
μ/mm ⁻¹	4.271	4.055
F(000)	1528.0	1576.0
Crystal size/mm ³	0.25×0.11×0.07	0.25×0.13×0.08
Radiation/Å	0.71073	0.71073
ϑ/(°)	2.926 to 51.996	2.256 to 52
Reflections collected	23679	24475
Data/restraints/ parameters	12464/0/793	13093/13/829
GOF	1.124	1.084
R ₁ /wR ₂ [I>=2σ (I)]	0.0292/0.0885	0.0295/0.0806
R_1/wR_2 [all data]	0.0370/0.0921	0.0341/0.0838
Largest diff. peak/hole / e Å ⁻³	1.03/-1.52	1.51/-2.57



Fig. S3 Cyclic voltammograms of Ir1-Ir6 under a scan rate of 100 mV/s.



Fig. S4 The η_c -*L* curves (a), η_p -*L* curves (b), *L*-*V* curves (c) and *J*-*V* curves (d) of the blue devices based on **Ir3** and **Ir4** in 5% and 15%.



Fig. S5 The *J-V* curves of the blue devices based on Ir3 and Ir4 in 10% and 20%.



Fig. S6 The η_c -*L* curves (a), η_p -*L* curves (b), *L*-*V* curves (c) and *J*-*V* curves (d) of the blue devices based on **Ir4** and FIrpic in 20%.

4. NMR and MALDI-TOF spectra











































