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Supporting Information

For

Blue heteroleptic iridium(III) complexes for OLEDs: simultaneous optimization of color purity and efficiency

Ying Lan,[a] Di Liu,[a,b]* Jiuyan Li,[a]* Yongqiang Mei,[a] Houru Tian[a]

[a] State Key Laboratory of Fine Chemicals, College of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian, 116024, China.

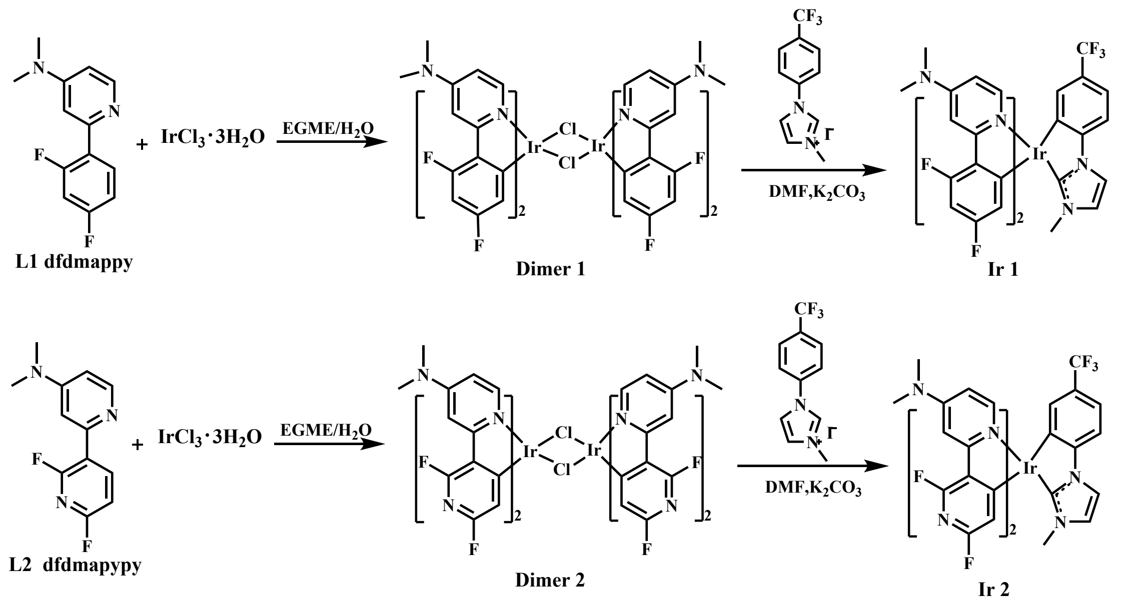
E-mail: liudi@dlut.edu.cn, jiuyanli@dlut.edu.cn.

[b] State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, 510640, China.

Contents

1. Experimental Section

Synthesis of Ir(III) complexes



Scheme S1. Chemical structures and synthetic routes for **Ir1** and **Ir2**.

Synthesis of iridium complexes Ir1 and Ir2. $IrCl_3$•$3H_2O$ (0.24 mmol) and the cyclometalating ligand L1/L2 (0.52 mmol) was dissolved in 2-ethoxyethanol/H_2O (6/2 mL). The mixture was stirred in N_2 atmosphere for 24 h at 110 °C. After cooling to room temperature, deionized water (20 mL) was added into the reaction mixture to get the yellow cyclometalated Ir(III) μ-chlorobridged dimer precipitation. The precipitate was collected by filtration and washed with water. Without further purification, the dimer1/dimer2 (0.08 mmol), ancillary ligands L3 (0.22 mmol) and K_2CO_3 (0.24 mmol) in DMF (8 mL) were heated at 100 °C for 12 h in N_2 atmosphere. Finally the solvent was removed under reduced pressure and the residue was extracted with dichloromethane (50 mL). And the product was obtained by column chromatography on silica gel.

Ir1: yellow power, yield: 48%. [1]H-NMR (DMSO-d_6, 400 MHz, δ[ppm]): 8.09 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.41-7.22 (m, 5H), 7.18 （d, *J* = 8.0 Hz, 1H), 6.82 (s, 1H), 6.71-6.47 (m, 2H), 6.46-6.30 (m, 2H), 6.10 (d, *J* = 8.4 Hz, 1H), 5.81 (d, *J* = 8.4 Hz, 1H), 3.22-2.87 (m, 15H). HRMS (ESI, *m/z*) : 884.2044 (calc. 884.2049). Anal. Calcd for $C_{37}H_{30}F_7IrN_6$: C, 50.28; H, 3.42; N, 9.51. Anal. Found: C, 50.16; H, 3.46; N, 9.46.

Ir2: yellow power, yield: 35%. [1]H-NMR (DMSO-d_6, 400 MHz, δ[ppm]): 8.15 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.40-7.30 (m, 3H), 7.26 （d, *J* = 6.8 Hz, 3H), 6.76 (s, 1H), 6.54-6.40 (m, 2H), 6.12 (s, 1H), 5.81 (s, 1H), 3.22-2.95 (m, 15H). HRMS (ESI, m/z) : 886.1944 (calc. 886.1954). Anal. Calcd for $C_{35}H_{28}F_7IrN_8$: C, 47.45; H, 3.19; N, 12.65. Anal. Found: C, 47.54; H, 3.22; N, 12.60.

2. Supplemental Tables and Figures

Table S1 Related triplet states of complexes **Ir1** and **Ir2** calculated from the TD-DFT method.

Complex	State	*E* [eV]	Dominant excitation	character
Ir1	T_1	3.10	H → L (35.2%), H-3→ L+1 (17.8%) H-4→ L+1 (14.8%)	^{3}MLCT/^{3}LLCT/^{3}LC
	T_2	3.11	H → L+1 (23.0%), H-3 → L (17.4%), H → L+1 (10.0%)	^{3}MLCT/^{3}LLCT/^{3}LC
Ir2	T_1	3.21	H → L+1 (42.0%), H-3 → L+1 (25.1%)	^{3}MLCT/^{3}LLCT/^{3}LC
FIrpic	T_1	2.91	H-1 → L+2 (28.2%), H → L+2 (13.0%) H → L (10.3%)	^{3}MLCT/^{3}LLCT/^{3}LC

Table S2 Surface distributions for HOMO/HOMO-3 and LUMO/LUMO+1 involved in the transitions for complexes Ir1 and Ir2. H and L denote HOMO and LUMO, respectively.

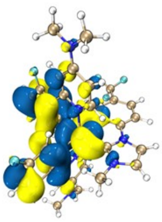
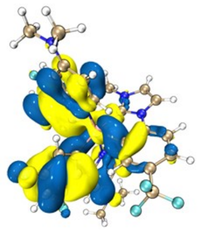
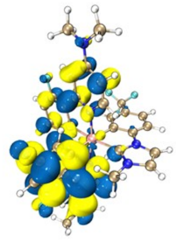
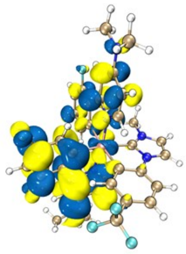
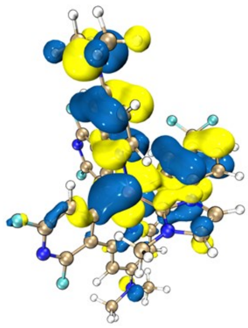
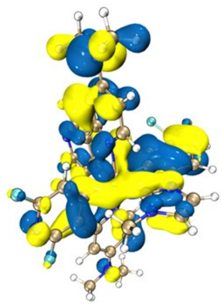
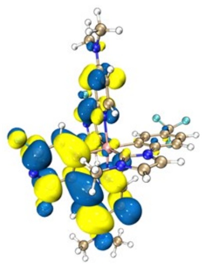
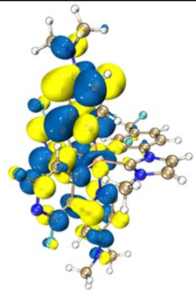
	H	H-3	L	L+1
Ir1				
Ir2				

Table S3 Calculated energies of the lowest triplet excited states (T_1) for complexes Ir1 and Ir2.

Complex	ΔE (T_1-S_0) [cm^{-1}, nm] [a]
Ir1	23529, 425
Ir2	23474, 426

[a] Energy difference between the lowest triplet excited state (T_1) and the ground state (S_0) at the corresponding optimized geometries.

Table S4 Comparison between the state-of-the-art blue OLEDs with CIE_y around 0.2 known in literatures and the OLEDs of this work.

Emitters	EL (λ_{max} ,nm)	EQE [a] [%]	CIE (x, y)	Ref.
$(dfpysipy)_2Ir(pic)$	-	29.0/23.2	(0.14, 0.19)	1
$(dfpysipy)_2Ir(mpic)$	-	31.9/24.7	(0.14, 0.19)	1
$(dfpysipy)_2Ir(fptz)$	-	19.5/-	(0.15, 0.18)	1
pic	-	15.5/-	(0.14, 0.18)	2
bor	-	22.6/-	(0.15, 0.20)	2
$Ir(pep)_3$		7.6/-	(0.15, 0.19)	3
$Ir(pmp)_3$		10.8/-	(0.15, 0.19)	3
$Ir(Me\text{-}pep)_3$	450	15.2/-	(0.15, 0.19)	3
$[Ir(mimb)(pzpyOph^F)]$	-	19.7/-	(0.15, 0.24)	4
$[Ir(mimb)(pzpy^{Bu}Oph^F)]$	-	20.7/-	(0.15, 0.24)	4
FCNIr	454	20.4 / 11.9	(0.14, 0.19)	5
FCNIrpic	-	25.1/ 23.1	(0.14, 0.18)	6
Ir(dbfmi)	-	18.6/ 6.2	(0.15, 0.19)	7
(fpmi)2Ir(dmpypz)	458	17.1/ 15.1	(0.13, 0.16)	8
(mpmi)2Ir(dmpypz)	464	15.4/ 13.6	(0.13, 0.18)	8
$[Ir(dfpypy)_2(POXD)]$	-	6.0/-	(0.16, 0.20)	9
$m\text{-}IrS^{Me}$	457	17.1/-	(0.14, 0.19)	10
TzIr	458	27.8/24.4	(0.144, 0.177)	11
Ir1	**462**	**28.0/20.8**	**(0.16, 0.21)**	**This work**
Ir2	**465**	**16.4/12.9**	**(0.16, 0.20)**	**This work**

[a] Values are given in the order of maximum and then at 1000 cd m^{-2}.

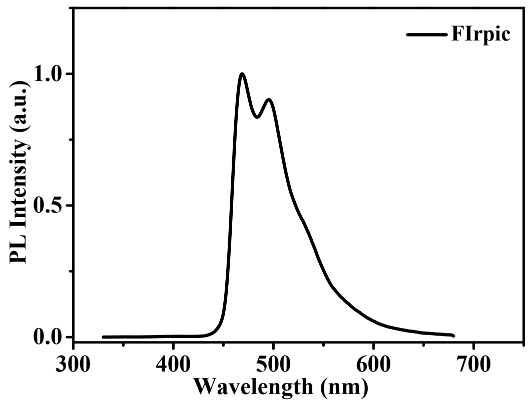


Fig. S1 PL spectra of complexes **FIrpic** in CH_2Cl_2 solution (10^{-5} mol L^{-1}) at RT.

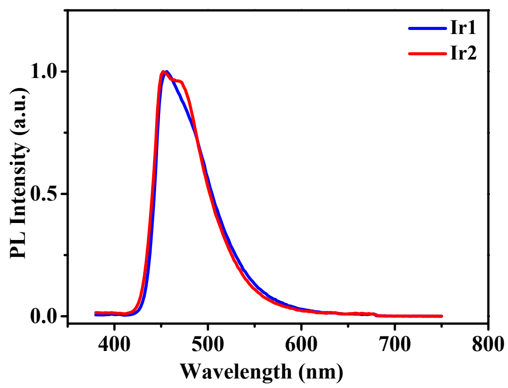


Fig. S2 PL spectra of **Ir1**and **Ir2** in the 5 wt % doped PPF films.

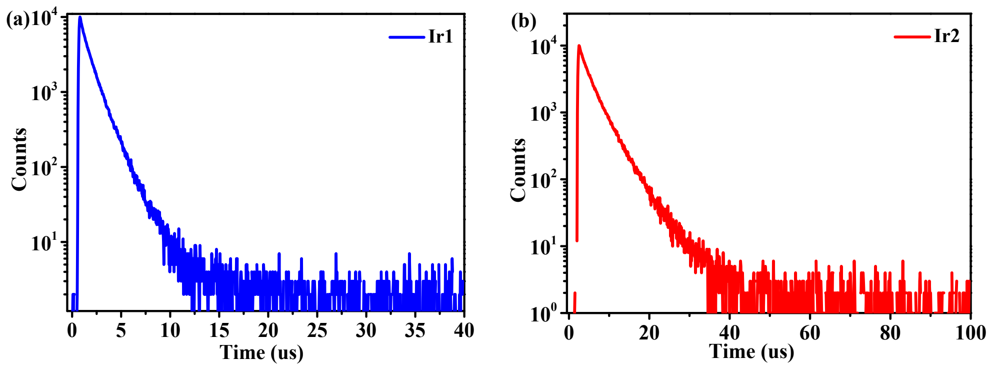


Fig. S3 Transient PL decay curves of **Ir1** and **Ir2** in 5 wt% doped PPF films. (excited at 380 nm).

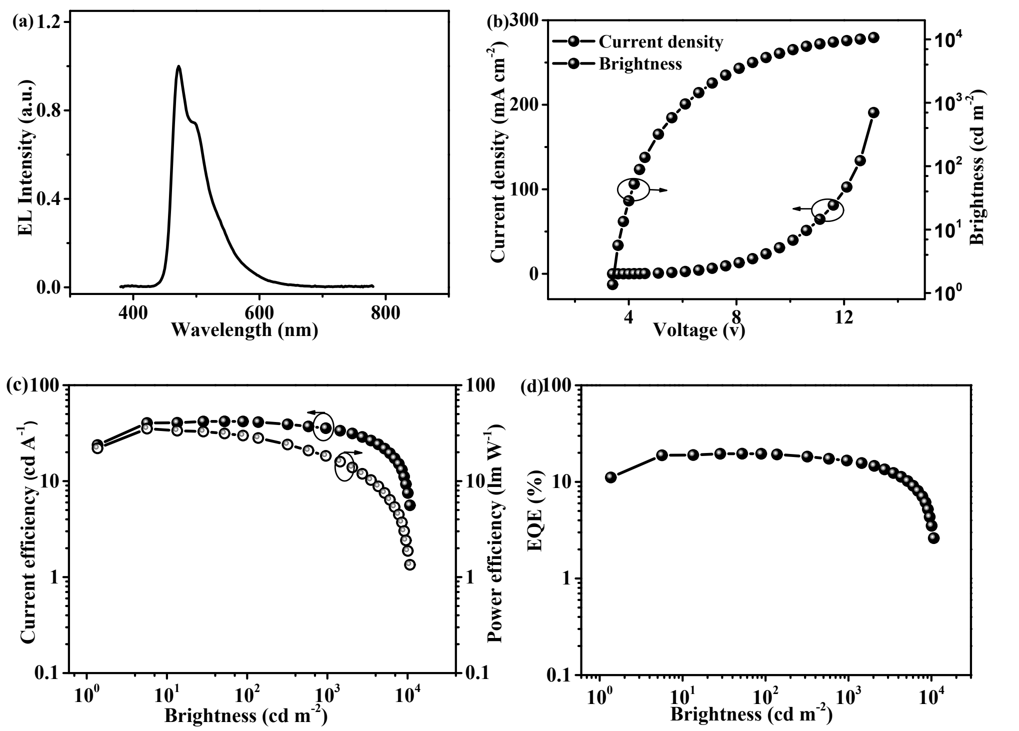


Fig. S4 The performance of the reference device based on FIrpic: (a) EL spectra (b) current density-voltage-brightness (*J*-*V*-*B*) characteristics and (c) CE and PE vs luminance curves and (d) EQE-luminance curves.

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