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# **Electronic Supplementary Information**

# High-efficiency blue-green electroluminescence from sublimable cationic iridium(III) complexes with a pyrazole-type ligand

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## Structural characterization methods

<sup>1</sup>H-NMR and <sup>19</sup>F-NMR spectra were recorded on a JOEL JNM-ECA600 NMR spectrometer. ESI mass spectrometry was performed with Thermo Electron Corporation Finnigan LTQ. Single-crystal X-ray characterization was measured on a Bruker SMART APEX charge-coupled device (CCD) diffractometer equipped with graphite monochromatized  $Mo_{K\alpha}$  radiation.

## Photophysical, electrochemical and thermal measurements

Absorption and photoluminescence (PL) spectra were characterized with an ultraviolet-visible spectrophotometer (Agilent 8453) and a fluorospectrophotometer (HITACHI, F-7000), respectively. Photoluminescence quantum yields (PLQYs) in degassed anhydrous acetonitrile solutions and neat film were measured at the excitation wavelength of 360 nm (Hamamutsu Photonics K. K., C9920-03). The excited state lifetimes were measured by a lifetime and steady state spectrometer (Edinburgh Instruments, FLS 980) with time-correlated single-photon counting technique at the peak emitting wavelength. Cyclic voltammetry was proved in oxygen-free anhydrous solutions on a Princeton Applied Research potentiostat/ galvanostat Model 283 voltammetric analyzer at a scan rate of 100 mV s<sup>-1</sup> with a platinum plate as the working electrode, a silver wire as the pseudo-reference electrode and a platinum wire as the counter electrode. Oxidation potentials were measured in N,N-dimethyl formamide with tetrabutylammonium perchlorate (40 mg mL<sup>-1</sup>) as the supporting electrolyte, while reduction potentials were performed in acetonitrile with tetrabutylammonium hexafluorophosphate (35 mg mL<sup>-1</sup>) as the supporting electrolyte. Ferrocene served as the internal standard. Thermal stability was measured by a thermogravimetric analyzer (TA Instruments Q5000) with a heating rate of 10°C min<sup>-1</sup> under nitrogen flows.

#### Quantum chemical calculations

Theoretical calculations on the ground and excited electronic states were performed by DFT and TD-DFT, respectively, at the B3LYP level, with double-ξ quality basis sets for carbon, hydrogen, nitrogen, fluorine (6-31G\*), and iridium (LANL2DZ). The inner core electrons of iridium(III) were replaced by an effective core potential (ECP), with outer core of 5s<sup>2</sup> 5p<sup>6</sup> electrons and the 5d<sup>6</sup> valence electrons. All the theoretical calculations were performed with a Gaussian 09 software package using a spin-restricted formalism.

#### **Device fabrication and evaluation**

OLEDs were grown on cleaned, ultraviolet-ozone-treated and indium-tin-oxide-coated glass substrates, with a sheet resistance of about 20  $\Omega$  per sq. Each functional layer was fabricated thereon successively by vacuum evaporation deposition under a low pressure below 5×10<sup>-4</sup> Pa. Each device shows an active area of 3.0×3.0 mm<sup>2</sup>. Current density-luminance-voltage (*J-L-V*) characteristics were collected with Keithley 4200 semiconductor system, while electroluminescence (EL) spectra were recorded by a Photo Research PR705 spectrophotometer. Device measurements were carried out at room temperature in the ambient air without further encapsulations.



Figure S1. The synthetic routes of complexes 1-4.



Figure S2. The single-crystal structures of complex **2**: (a)  $[Ir(ppz)_2(pzpy)]^+$ , (b)  $[B(dCF_3Ph)_4]^-$ . Here the thermal ellipsoids are drawn at 30% probability. The solvent molecules and hydrogen atoms have been omitted for clarity. The unlabeled atoms are carbon atoms.



Figure S3. The single-crystal structures of complex **4**: (a)  $[Ir(ppz)_2(Phpyim)]^+$ , (b)  $[B(dCF_3Ph)_4]^-$ . Here thermal ellipsoids are drawn at 30% probability. The solvent molecules and hydrogen atoms have been omitted for clarity. The unlabeled atoms are carbon atoms.



Figure S4. The absorption spectra of complexes **1-4** in anhydrous acetonitrile solutions ( $1 \times 10^{-5}$  mol L<sup>-1</sup>).





Figure S5. The excited state lifetimes of complexes **1-4** in solid films at room temperature.

Figure S6. Excited state lifetimes of complexes 1-4 in acetonitrile glass at 77 K.



Figure S7. Cyclic voltammetry in oxygen-free anhydrous solutions with the potentials recorded *versus* the ferrocenium/ ferrocence ( $Fc^+/Fc$ ) couple.



Figure S8. Thermogravimetric analysis for complexes 1-4 under nitrogen-flow conditions.



Figure S9. Molecular orbital surfaces of (a) the HOMO, (b) the LUMO of  $[Ir(ppz)_2(pzpy)]^+$  and (c) the HOMO, (d) the LUMO of  $[Ir(ppz)_2(Phpyim)]^+$ , corresponding to an isocontour value of  $|\Psi| = 0.02$ . All the hydrogen atoms are omitted for clarity.



Figure S10. Device characteristics of complex 1. (a) J-V; (b) L-V and (c) CE-L curves; (d) PE-L curves.



Figure S11. Device characteristics of complex **2**. (a) *J-V*; (b) *L-V* and (c) CE-*L* curves; (d) PE-*L* curves.



Figure S12. Device characteristics of complex **3**. (a) *J-V*; (b) *L-V* and (c) CE-*L* curves; (d) PE-*L* curves.



Figure S13. Device characteristics of complex **4**. (a) *J-V*; (b) *L-V* and (c) CE-*L* curves; (d) PE-*L* curves.

Cation	Triplet States	E <sub>calculated</sub> <sup>[a]</sup> [eV]	$\lambda_{calculated}^{[b]}$ [nm]	Dominant Excitations <sup>[c]</sup>	Dominant Character	Assignment
[lr(ppz)(pzpy)]+	T <sub>1</sub>	2.57	482	H → L (100 %)	d <sub>π</sub> (Ir)-π(ppz) →π*(pzpy)	MLCT/LLCT
		3.10	399	H → L+1 (40.0%)	d <sub>π</sub> (Ir)-π(ppz) → π*(pzpy)	MLCT/LLCT
	T <sub>2</sub>			H-3 → L (30.2%)	d <sub>π</sub> (Ir)-π(ppz) →π*(pzpy)	MLCT/LLCT
				H-4 → L (22.9%)	d <sub>π</sub> (Ir)-π(ppz) →π*(pzpy)	MLCT/LLCT
	T <sub>1</sub>	2.42	512	H → L (100%)	d <sub>π</sub> (Ir)-π(ppz) →π*(pyim)	MLCT/LLCT
[lr(ppz)(Phpyim)]+	T <sub>2</sub>	2.84	436	H-3 → L (42.2%)	d <sub>π</sub> (Ir)-π(ppz) →π*(pyim)	MLCT/LLCT
				H-6 → L (36.3%)	d <sub>π</sub> (Ir)-π(pyim) →π*(pyim)	MLCT/ILCT
				H-2 → L (18.7%)	d <sub>π</sub> (Ir)-π(ppz) →π*(pyim)	MLCT/LLCT

Table S1. Triplet excited states of [Ir(ppz)<sub>2</sub>(pzpy)]<sup>+</sup> and [Ir(ppz)<sub>2</sub>(Phpyim)]<sup>+</sup> from quantum chemical calculations by TD-DFT.

[a] Calculated excitation energy for the triplet excited states. [b] Calculated wavelength. [c] H denotes the HOMO and L denotes the LUMO, respectively, and the percentage is the contribution of each excitation.

	Ratio [%]	V <sub>on</sub> <sup>a)</sup> [V]	J <sup>b)</sup> at 5 V [A m <sup>-2</sup> ]	Max CE <sup>c)</sup> [cd A <sup>-1</sup> ]	CE <sup>c)</sup> at 10 <sup>3</sup> cd m <sup>-2</sup> [cd A <sup>-1</sup> ]	Max EQE <sup>d)</sup> [%]	Max PE <sup>e)</sup> [lm W <sup>-1</sup> ]	Max L <sup>f)</sup> [cd m <sup>-2</sup> ]	$\lambda_{ extsf{el}}^{ extsf{g})}$ [nm]	CIE <sup>h)</sup> ( <i>x, y</i> )
1	1.9	2.6	388.1	9.9	8.6	5.0	8.9	5.0×10 <sup>3</sup>	476	(0.21,0.32)
	2.2	2.6	475.9	11.2	10.0	5.5	10.5	5.1×10 <sup>3</sup>	478	(0.20,0.32)
	2.9	2.6	261.6	11.4	10.4	5.9	10.5	5.6×10 <sup>3</sup>	476	(0.19,0.30)
	3.9	2.7	311.2	6.1	4.7	3.0	5.3	4.1×10 <sup>3</sup>	476	(0.20, 0.30)
2	1.1	2.8	441.6	9.2	4.0	4.3	7.3	1.2×10 <sup>4</sup>	480	(0.22,0.35)
2	1.5	2.7	361.0	10.8	9.3	5.4	9.2	6.2×10 <sup>3</sup>	478	(0.22,0.32)
	2.4	3.1	303.4	10.5	8.7	5.0	8.2	6.0×10 <sup>3</sup>	482	(0.21,0.33)
	2.7	3.2	290.9	9.3	8.3	4.4	7.5	5.9×10 <sup>3</sup>	484	(0.22,0.34)
	0.6	2.5	427.5	20.9	19.8	8.2	18.8	1.0×10 <sup>4</sup>	500	(0.26, 0.44)
J	0.8	2.6	453.6	29.4	26.4	10.8	30.4	1.5×10 <sup>4</sup>	506	(0.27,0.48)
	1.1	2.8	378.8	27.5	24.5	10.7	28.1	1.3×10 <sup>4</sup>	500	(0.25, 0.44)
	1.5	2.6	504.2	22.1	20.9	8.9	19.5	1.2×10 <sup>4</sup>	500	(0.25, 0.43)
4	1.8	2.8	198.1	23.6	23.0	8.5	19.6	9.7×10 <sup>3</sup>	496	(0.27, 0.48)
	2.2	2.8	437.6	29.8	27.7	10.8	28.4	1.4×10 <sup>4</sup>	500	(0.27, 0.49)
	2.8	2.9	411.4	31.1	27.3	11.3	29.1	1.5×10 <sup>4</sup>	500	(0.27, 0.50)

Table S2. Detailed Device characteristics of complexes 1-4.

3.5	3.0	197.1	25.4	21.5	9.3	23.4	1.2×10 <sup>4</sup>	500	(0.27 <i>,</i> 0.48)
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<sup>a)</sup> x, doping concentration; <sup>b)</sup> J, current density; <sup>c)</sup> CE, current efficiency; <sup>d)</sup> EQE, external quantum efficiency; <sup>e)</sup> PE, power efficiency; <sup>f)</sup> L, luminance; <sup>g)</sup>  $\lambda_{EL}$  electroluminescent wavelength; <sup>h)</sup> CIE, Commission Internationale de l'Elairage.