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Design and Synthesis of Heteroleptic Iridium (III) Phosphors for Efficient Organic Light Emitting Devices

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Abstract

The phosphorescent emitters are essential to realize energy-efficient display and lighting panels. The solution processability is of particular interest for large-scale and low-cost production. Here, we present a series of the heteroleptic iridium (Ir) complexes, Ir(ppy)₂L1, Ir(ppy)₂L2, and Ir(ppy)₂L3, using the new ancillary ligands, including 1-(2-chlorophenyl)-5-hydroxy-3-methyl-1H-pyrazole-4-carbaldehyde (L1), 5-hydroxy-3-methyl-1-(p-tolyl)-1H-pyrazole-4-carbaldehyde (L2), and 5-hydroxy-3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde (L3). Their photophysical and electrochemical properties were systematically characterized, followed by comparing with those predicted by density functional theory (DFT) simulations using hybrid functionals. Among the three phosphors synthesized, Ir(ppy)₂L1 exhibits the highest photoluminescence quantum yield ($\Phi_{PL} = 89\%$), with an exciton lifetime of 0.34 μ s. By using 4,4'-bis(carbazole-9-yl)biphenyl as the host material, we demonstrate high current efficiencies of 64 cd A⁻¹ and 40 cd A⁻¹ at 100 cd m⁻² in its vacuum-evaporated and solution-processed organic light-emitting devices, respectively, revealing the promise for large-area light sources.

Introduction

In spite of the fact that the organic light emitting diodes (OLEDs) technology has been successfully commercialized for more than one decade,¹⁻³ advanced research in understanding and engineering its performance index remains active to meet requirements of different applications, such as solid-state lightings and flat panel displays. Specifically, three main strategies have been utilized to enhance the device efficiencies, including: (i) molecular design of new high-quantum-yield emitters, bipolar hosts, and high-mobility transport materials,⁴⁻⁶ (ii) the new device architectures that promotes carrier recombination and confinement within the emissive layer,³ and (iii) the techniques that induces an efficient light out-coupling.^{3,7,8} In terms of the emitters, the phosphorescent organometallic compounds have been considered as a promising candidate, since one can in principle, harvest 100% of the excitons through a strong spin-orbit coupling (SOC) induced by the heavy metals, such as iridium (Ir), platinum (Pt), osmium (Os) and ruthenium (Ru).^{9,10} The phenylpyridine complexes of iridium are of particular interest based on the observations of fast intersystem crossing (ISC) and relatively short exciton lifetime (τ),¹¹ which result from the strong triplet metal-to-ligand charge transfer (³MLCT).¹² Recent findings in designing new Ir-based phosphors have further suggested that both cyclometalated and ancillary ligands profoundly influence the photophysical and electrochemical characteristics.¹³ Since the first demonstration of phosphorescent OLED in 1998 using a homoleptic iridium complex of *fac*-tris[2-phenylpyridinato-C2,*N*]iridium(III) (Ir(ppy)₃),¹⁴ several homoleptic and heteroleptic iridium complexes have been synthesized and employed in devices.^{3,4,15} For example, Kim et al. reported a maximum power efficiency (η_{PE}) of 22.6 lm W⁻¹ with a homoleptic *tris*-cyclometalated Ir(III) complex.¹⁶ Xu et al. reached η_{PE} of 43.6 lm W⁻¹ with a bis-cyclometalated iridium complex containing an organic ligand trifluoromethyl substituted bipyridine (2',6'-bis-(trifluoromethyl)-2,3'-bipyridine).¹⁷ A series of Ir complexes

with the tetra(4-trifluoromethylphenyl) imidodiphosphinate (tfmtpip), tetraphenylimidodiphosphinate (tpip), and trifluoromethylphenyl-pyridine (tfmppy) organic ligands have been demonstrated, which resulted the high performance OLED devices.¹⁸ Jou et al. reported a η_{PE} of 61 lm W⁻¹ using a heteroleptic iridium phosphor bis [5-methyl-8-trifluoromethyl-5*H*-benzo(c) (1,5)naphthyridin-6-one]iridium(pyrazinecarboxylate) (Ir(3-CF₃BNO)₂(prz)) in the wet-processed OLEDs.¹⁹ Tong et al. also demonstrated a high photoluminescence quantum yield (Φ_{PL}) of 72% and a η_{PE} of 35.5 lm W⁻¹ with the iridium complex, using two organic ligand groups, 1,3-difluoro-4,6-di(pyridin-2-yl) benzene and 2-(5-trifluoromethyl-1*H*-pyrazol-3-yl)-6-(4-trifluoromethylphenyl) pyridine.²⁰ Zhang et al. designed a green heteroleptic Ir complex, Ir(ppy)₂(POXD), by using an ancillary ligand *N*-(5-phenyl-1,3,4-oxadiazol-2-yl)-diphenyl phosphinic amide. The Ir(ppy)₂(POXD) emitter shows a η_{PE} of 42.5 lm W⁻¹ for dry-processed OLED device.²¹

The light emitting devices are often fabricated by thermally evaporating or spin-coating the phosphorescent emitters in a layer-by-layer manner.^{3,12} Nevertheless, very few emitters can exhibit high efficiencies with both processes.²² Considering the fact that the deposition process of an emitter largely depends on the thermal stability and solubility,²² there is a clear need to devise the new Ir-complexes that enable high-efficiency devices with versatile process methods, in order to address the challenges associated with the low-cost, roll-to-roll fabrication of OLEDs. Here, we designed and synthesized a series of heteroleptic iridium complexes by employing the typical 2-phenylpyridine cyclometalated ligand with three new ancillary ligands, including 1-(2-chlorophenyl)-5-hydroxy-3-methyl-1*H*-pyrazole-4-carbaldehyde (**L1**), 5-hydroxy-3-methyl-1-(p-tolyl)-1*H*-pyrazole-4-carbaldehyde (**L2**) and 5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**L3**). The synthesized complexes, namely, Ir(ppy)₂L1, Ir(ppy)₂L2, and Ir(ppy)₂L3,

possess high solubility in common organic solvents and proper thermal behavior, which allow facile film formation through the solution processes or thermal evaporation. Among the three materials considered, we achieve the best efficiencies with the Ir(ppy)₂L1 green emitter, with a current efficiency (η_{CE}) of 64 cd A⁻¹ and a η_{PE} of 48 lm W⁻¹, at 100 cd m⁻², in the thermal-evaporated devices. Moreover, we report comparable efficiencies in the solution-processed devices (η_{CE} = 46 cd A⁻¹ and η_{PE} = 29 lm W⁻¹ at 1000 cd m⁻²), confirming the potential in large-area OLED technology.

Results and discussion

Design and synthesis

In order to develop the phosphorescent emitters that are compatible with both solution and dry processes, the molecular design concepts are outlined as follows. First, a pyrazole-based chelation motif, which significantly enhances the solubility in the common organic solvents without compromising the thermal stability during evaporation,²³ Next, an electron-withdrawing chlorine atom (-Cl), an electron-donating methyl group (-CH₃), and a relatively electroneutral hydrogen atom (-H), are bound to the phenyl tail (see **Scheme 1**), corresponding to the **L1**, **L2**, and **L3** ancillary ligands used in this report, respectively. Such variation of ligand structure is anticipated to modulate the electron density around the Ir(III) center, which may allow us to tune the photophysical and electrochemical properties of Ir(III) complexes. Accordingly, we indeed observed a slightly deep highest occupied molecular orbital (HOMO) level in Ir(ppy)₂L1, but did not find a notable difference between Ir(ppy)₂L2 and Ir(ppy)₂L3. In addition, the electron-withdrawing nature of **L1** also leads to a degree of blueshift in the emission wavelength.

The ancillary ligands (**L1**, **L2**, and **L3**) were synthesized following the protocols reported in literature.^{24,25} The Ir(III) complexes were prepared by the Nonoyama route (see **Scheme 1**).²⁶

Scheme 1. Synthetic route of the green iridium complexes, $\text{Ir(ppy)}_2\text{L1}$, $\text{Ir(ppy)}_2\text{L2}$, and $\text{Ir(ppy)}_2\text{L3}$.

Thermal properties

The thermal behavior of the Ir(III) complexes, $\text{Ir(ppy)}_2\text{L1}$, $\text{Ir(ppy)}_2\text{L2}$, and $\text{Ir(ppy)}_2\text{L3}$ were characterized by using the differential scanning calorimetry (DSC) and the thermogravimetric analysis (TGA) techniques. As shown in **Table 1**, the glass transition temperatures (T_g) of the novel Ir(III) complexes are ranged from 235 °C to 254 °C, and their thermal decomposition temperatures (T_d) are ranged from 282 °C, to 301 °C, corresponding to a 5% weight loss (see **Fig. S1** and **Fig. S2**). The appropriate thermal stability of the Ir(III) complexes prevents a degree of degradation during thermal evaporation,²⁷ which is prerequisite for the dry-processed devices.

Table 1. Photophysical, electrochemical, and thermal characteristics of the novel cyclometalated heteroleptic phosphor $\text{Ir(ppy)}_2\text{L1}$, compared with those of the other two emitters $\text{Ir(ppy)}_2\text{L2}$ and $\text{Ir(ppy)}_2\text{L3}$.

Emitter	λ_{abs} [nm]	λ_{PL} [nm]			E_T^b [eV]	Φ_{PL}^c (%)	τ_{avg}^d (μs)		$K_r(\times 10^7)$		$K_{\text{nr}}(\times 10^6)$		T_g^e [°C]	T_d^f [°C]	E_g^g [eV]	HOMO/LOMO [eV]
		Sol.	Film	Phos. ^{a)}			300 K	77K	300K	77K	300K	77K				
$\text{Ir(ppy)}_2\text{L1}$	262, 283	511	516	500, 533	2.48	89	0.117	0.34	7.61	0.26	9.44	0.326	235	301	2.43	-4.70 / -2.27
$\text{Ir(ppy)}_2\text{L2}$	265, 283	512	518	499, 534	2.49	42	0.198	0.13	2.12	0.32	29.3	4.38	254	288	2.48	-4.90 / -2.42
$\text{Ir(ppy)}_2\text{L3}$	260, 302	512	516	497, 533	2.50	41	0.272	0.17	1.51	0.24	21.7	3.46	251	282	2.46	-4.88 / -2.42

^{a)}Phosphorescence emission at 77K, ^{b)}triplet energy, ^{c)}photoluminescence quantum yield, ^{d)}average exciton lifetime, ^{e)}glass transition temperature, ^{f)}decomposition temperature, ^{g)}optical bandgap.

Photophysical properties

Figure 1 presents the absorption (Abs) and photoluminescence (PL) spectra of Ir(ppy)₂L1, Ir(ppy)₂L2, and Ir(ppy)₂L3. The solution and film spectra correspond to the acetonitrile solution and the spin-coated sample, respectively. All the complexes show a strong absorbance in the UV region (< 380 nm), which corresponds to the ligand-centered (LC) π - π^* transitions.^{28,29} In the visible region, with increasing the wavelength, we assign the absorption peaks to the mechanisms of the singlet metal-to-ligand charge transfer (¹MLCT),²⁸ the spin-orbit coupling enhanced ³ π - π^* transition, and the spin-forbidden triplet MLCT (³MLCT). A strong ³MLCT is observed due to an efficient singlet-triplet mixing, a clear signature of the Ir(III) complexes.³⁰

Figure 1. Absorption (Abs) spectra, photoluminescence (PL) spectra (in solution and film), and phosphorescence spectra (at 77K) of the green iridium complexes, (a) $\text{Ir(ppy)}_2\text{L1}$, (b) $\text{Ir(ppy)}_2\text{L2}$, and (c) $\text{Ir(ppy)}_2\text{L3}$.

The PL spectra are centered at 511 nm for $\text{Ir(ppy)}_2\text{L1}$ and 512 nm for $\text{Ir(ppy)}_2\text{L2}$ and $\text{Ir(ppy)}_2\text{L3}$, and there is a small degree of bathochromic shift observed among the samples considered (see **Fig. 1**). It is noteworthy that all the synthesized compounds show excellent solubility in the commonly-used solvents, including acetonitrile, chloroform, dichloromethane, and toluene, as reflected by their strong and consistent PL spectra (**Fig. S3**), demonstrating the

versatility and promise for solution processing.³¹ The PL spectra of Ir complexes in the solid state thin films show a redshift 5 ± 1 nm compared to those in the solution. At a low temperature (77 K), the PL spectra of all the three Ir complexes show the multiple vibronic emission peaks (Fig.1).

Table 1 summarizes the Φ_{PL} s and the average exciton lifetimes (τ_{avg}) for the synthesized compounds at different conditions. The quantum yield was determined using the relative method calibrated by the typical green phosphor, Ir(ppy)₃, which possess a Φ_{PL} of 40% in acetonitrile.^{32,33} Among the three emitters synthesized, the Φ_{PL} for Ir(ppy)₂L1 is the highest and about two-fold higher than that for Ir(ppy)₃. We suppose that the high Φ_{PL} results from the more rigid carbon-chlorine bond, compared to the carbon-hydrogen bond in Ir(ppy)₃.³⁴ Compared to the PL spectra at room temperature, the low-temperature ones exhibit two additional peaks, which correspond to the triplet emission, owing to an efficient intersystem crossing (ISC).^{32,35} The triplet-energies (E_T) were therefore determined to be 2.48 eV, 2.49 eV, and 2.50 eV for Ir(ppy)₂L1, Ir(ppy)₂L2, and Ir(ppy)₂L3, respectively. The extracted τ_{avg} of all the three emitters range between 0.117 and 0.272 μ s at room temperature, and are increased up to 0.13 to 0.34 μ s at 77 K. The radiative rate constant (k_r) and non-radiative rate constant (k_{nr}) are estimated from the Φ_{PL} and τ_{avg} by using the equations $k_r = \Phi_{PL}/\tau$ and $\Phi_{PL} = k_r/(k_r + k_{nr})$.³⁶ In particular, Ir(ppy)₂L1 emitter exhibits nearly threefold increase of τ_{avg} at 77 K, resulting from a reduction of triplet exciton quenching. At room temperature, Ir(ppy)₂L1 also has a short excited state lifetime of 0.117 μ s that yields k_r of 7.61×10^7 s⁻¹ and k_{nr} of 9.44×10^6 s⁻¹ (**Table 1**). A slower non-radiative recombination rate leads to a strong ISC of singlet excited states that results in a high internal quantum efficiency. This fact is also reflected from the rate constants at low temperature ($k_r = 2.62 \times 10^6$ s⁻¹ and $k_{nr} = 3.26 \times 10^5$ s⁻¹). **Table 1** also summarizes the extracted k_r and k_{nr} for Ir(ppy)₂L2 and Ir(ppy)₂L3 counterparts. On the other hand, for Ir(ppy)₂L2 and Ir(ppy)₂L3, k_{nr} is higher than k_r , thereby resulting in a low Φ_{PL} .

Electrochemical properties

We characterize the electrochemical properties of the Ir complexes by the cyclic voltammetry (CV) in nitrogen atmosphere at room temperature. The HOMO energy level is determined using the oxidation potential, as shown in **Fig. S4**. The information allows us to estimate the lowest unoccupied molecular orbital (LUMO) energy with the optical bandgap (E_g), as determined by the room-temperature PL spectrum. **Table 1** presents the calculated energy bandgaps, HOMO and LUMO levels for the complexes considered. Note that the HOMO level for Ir(ppy)₂L1 is about 0.2 eV shallow relative to the other two counterparts, owing to the electron-withdrawing chlorine atom (R1, see **Scheme 1**) in the phenyl ring of the ancillary ligand.³⁷ The emission spectrum of the Ir(III) complexes is dominated by the ppy ligands, whereas the effect of the ancillary ligand is negligible. The electron-withdrawing/electron-donating nature of the substituent in ancillary ligand, on the other hand, mainly affects $d-\pi$ orbital hybridization of Ir atom and therefore changes the HOMO and LUMO energy levels.³⁸ The oxidation potential in Ir(ppy)₂L1 is about 0.1 eV higher than that in the other two, consistent with the DFT-calculated values (**Fig.2**).

Figure 2. Hybrid HSE06 calculations for energy frontier levels (HOMO, LUMO) for (a) Ir(ppy)₂L1, (b) Ir(ppy)₂L2, and (c) Ir(ppy)₂L3. Spin up (Up), spin down (Dw) and non-magnetic (NM) spin-solutions are shown in cyan, violet and faint brown, respectively. A comparison with

the experimental results (Exp) in blue is included at the first column to each system. Energy states are relative to the vacuum level (Evac) at 0 eV. The spatial electron distributions (isosurface cutoff $3.12 \times 10^{-4} \text{ e/\AA}^3$) of the HOMO and LUMO states of the closest set of calculations to the experimental results is shown aside each system. Yellow and blue isosurfaces show positive and negative charge densities, respectively.

Theoretical simulation

In order to gain a better insight into the electronic structures and photophysical characteristics of the green Ir(III) molecules, we performed first-principles density functional theory (DFT) calculations including hybrid functionals (see Methods for details). We took a fractional component of the exact exchange from the Hartree-Fock (HF) theory hybridized with the DFT exchange correlation potential at the level of the range-separated HSE06 hybrid functional. Such approach has been observed to improve the physical and chemical properties, as well as optical excitations of several compounds at a relative good balance between accuracy and time-consuming simulations.³⁹ Calculations have included spin-polarized effects as they were observed to be important in the analysis of the electronic properties. **Fig. 2** shows the HSE06 energy frontier levels (HOMO, LUMO) for Ir(ppy)₂L1, Ir(ppy)₂L2 and Ir(ppy)₂L3 systems at different spin solutions. Interestingly, large variations of the position of the HOMO and LUMO energy states are observed relative to the experimental results depending on the spin-polarization included in the simulations. Non-magnetic solutions tend to underestimate the HOMO-LUMO gap for all molecules by several hundreds of meV's, with the best agreement for Ir(ppy)₂L1, Ir(ppy)₂L2 and Ir(ppy)₂L3 on spin down, spin up and spin up polarizations, respectively. These magnetic solutions are also more energetically stable than the non-magnetic ones, with energy well above room temperature in the range of 0.815 eV to 0.356 eV per molecular unit (see **Table 2**). A magnetic moment of 1.0 μ_B per unit cell is developed at each Ir(III) complex. The charge density plots for the HOMO and LUMO states also show the distribution of the orbitals at

different parts of the Ir(III) complexes. They tend to be spread out over the entire molecule at the HOMO level but with less contribution at the radical side at the LUMO state where the different binding groups take place, e.g. chloro and methyl (**Fig. 2**). Such inhomogeneous charge distribution induces the appearance of dipole moments as large as 6.56 Debye for Ir(ppy)₂L1 (**Table 2**). The Bader analysis plotted in **Fig. 3** show that most of the atoms nearby Ir gain charge, which includes O and N atoms. This suggests that the charge balance between Ir and its near neighbors induce the appearance of the dipole moment in the molecule. This is agreement with recent angle-dependent photoluminescence measurements for similar Ir(III) complexes.⁴⁰ We have also simulated the optical properties for all three molecules as shown in **Fig. S5**. The highest absorption peaks in the experimental results at 298 nm, 260 nm and 259 nm for Ir(ppy)₂L1, Ir(ppy)₂L2 and Ir(ppy)₂L3, respectively, can be well described by the x-component of the absorption spectra. These peaks correspond to an excitation in the ultraviolet of 4.37 eV (Ir(ppy)₂L1), 4.35 eV (Ir(ppy)₂L2) and 4.64 eV (Ir(ppy)₂L3), which also have large dipole transition elements (see **Tables S1-S3** in SI).

Figure 3. Isosurfaces of the Bader analysis performed for (a) Ir(ppy)₂L1, (b) Ir(ppy)₂L2, and (c) Ir(ppy)₂L3 at HSE06 hybrid level. The gradient scale shows the variation of the Bader charge, $Q(\text{electrons})$, for specific atoms in the oligomers. Positive (negative) magnitudes of $Q(\text{electrons})$ show charge depletion (accumulation). Notice that O (red) and N atoms (blue) gain charge, while Ir atoms loose.

Table 2. Calculated magnetic energies ΔE through the energy difference between spin-polarized and non-spin-polarized calculations and magnitudes of the electric dipole moment (Debye) at

HSE06 hybrid level and for Ir(ppy)₂L1, Ir(ppy)₂L2, and Ir(ppy)₂L3. Non-magnetic (NM) and spin-polarized (SP) simulations are shown per unit cell.

Molecule	ΔE (eV)	Dipole Moment (Debye)	
		NM	SP
Ir(ppy) ₂ L1	-0.815	5.535	6.564
Ir(ppy) ₂ L2	-0.714	6.357	6.073
Ir(ppy) ₂ L3	-0.356	4.433	4.977

Table 3. Effect of Ir complexes on the fabrication process, operating voltage (OV), power efficiency (η_{PE}), current efficiency (η_{CE}), EQE (η_{EQE}), CIE color coordinates and maximum luminance by doping the various concentrations in the CBP host.

Emitter	Process	wt% of emitter in CBP host	OV (V) @ 100 / 1,000 cd/m ²	η_{PE} (lm/W)	η_{CE} (cd/A)	η_{EQE} (%)	CIE _{x,y} Coordinates	Maximum luminance (cd/m ²)
Ir(ppy) ₂ L1	Solution	5	4.1/5.2	29.6/19.6	38.9/32.3	10.3/9.0	(0.28,0.63)	11990
		10	4.1/5.0	30.3/29.2	39.6/46.4	10.7/12.6	(0.29,0.63)	10380
		15	4.1/5.0	28.5/26.0	37.3/41.7	10.1/11.3	(0.29,0.63)	10810
	Dry	5	4.1/5.1	31.3/26.6	41.0/42.6	10.5/11.5	(0.30,0.63)	15270
		10	4.2/5.5	47.7/31.0	63.7/54.7	17.4/15.2	(0.31,0.63)	20970
		15	4.2/5.5	40.2/26.0	54.2/46.5	14.8/12.7	(0.31,0.63)	20580
Ir(ppy) ₂ L2	Solution	5	4.5/5.6	11.6/10.4	16.7/18.4	4.6/5.1	(0.29,0.63)	7824
		10	4.7/5.9	11.1/9.1	16.4/17.1	3.7/4.5	(0.29,0.63)	7615
		15	4.7/6.1	8.7/6.9	13.1/13.4	3.2/3.5	(0.30,0.63)	6328
Ir(ppy) ₂ L3	Solution	5	5.0/5.8	6.4/10.4	10.2/19.0	3.1/5.9	(0.26,0.55)	10700
		10	5.5/6.6	3.6/9.3	6.4/19.5	1.8/5.6	(0.29,0.61)	12130
		15	5.3/6.6	2.6/6.5	4.5/13.6	1.3/3.8	(0.29,0.62)	10130

Electroluminescent characteristics

The OLEDs based on the new Ir(III) complexes were fabricated and characterized. **Fig. 4a** presents the device architectures and energy levels used in the solution-processed samples. The current density-voltage-luminance (J - V - L) characteristics, together with the calculated η_{CE} and η_{PE} as a function of L , are shown in **Figs. 4b, 4c, and 4d**, respectively. The solution-processed sample of Ir(ppy)₂L1, with an architecture of ITO/PEDOT:PSS/EML (5 wt% Ir(ppy)₂L1 +

CBP)/TPBi/LiF/Al, show η_{CE} of 32.3 cd A⁻¹ and η_{PE} of 19.6 lm W⁻¹ at 1000 cd m⁻², and by increasing the weight concentration to 10 wt%, which is determined to be the optimal concentration, a considerable degree of enhancement in efficiencies is achieved (η_{CE} = 46.4 cd A⁻¹ and η_{PE} of 29.2 lm W⁻¹). The device performance is slightly reduced by further increasing the concentration, probably due to a more significant degree of self-quenching.

Figure 4. Solution-process OLEDs based on 10 wt% Ir complexes in the CBP host. (a) Schematic energy-levels diagram, (b) $J-V-L$ characteristics, (c) current efficiency as a function of luminance, Inset: electroluminescence spectra (d) power efficiency as a function of luminance.

The device characteristics for the solution-processed Ir(ppy)₂L1, Ir(ppy)₂L2, and Ir(ppy)₂L3 at different concentrations are summarized in **Table 3**. Clearly, Ir(ppy)₂L1 is the best emitter among the three compounds considered here. In combination with the photophysical characteristics determined earlier, we attribute the superior performance to the following mechanisms: (i) a high Φ_{PL} of 89%, (ii) a proper exciton lifetime that allows effective ISC and prevents triplet quenching, and (iii) a high radiative rate constant that implies an efficient triplet metal to ligand charge transfer (³MLCT) and triplet ligand-centered transition (³LC). All three devices showed EL emission at 512 nm, which is consistent with the PL of Ir(ppy)₂L1, Ir(ppy)₂L2, and Ir(ppy)₂L3 (see inset **Fig. 4c**).

Figure 5. Comparison of dry- and solution-processed OLED devices based on Ir(ppy)₂L1 emitter. (a) Schematic energy-levels diagram of dry-processed device. (b) *J-V-L* characteristics, (c) current efficiencies as a function of luminance, Inset: normalized EL spectra. (d) power efficiencies as a function of luminance, Inset: large area ETH logo device operating at 5 V (active area ~ 2 cm²).

The outstanding performance of the Ir(ppy)₂L1 based solution-processed devices encourages us to test the dry-processed samples. **Fig. 5a** shows the device architecture considered and the energy levels, with a typical trilayer structure comprised of a 30 nm di-[4-(*N*, *N*-ditolyl-amino)-phenyl]cyclohexane (TAPC) as HTL, a 25 nm EML containing Ir(ppy)₂L1 in CBP with a controlled concentration (5, 10, and 15 wt%), and a 35 nm 1,3-bis(3,5-dipyrid-3-yl-phenyl)benzene (BmPyPB) ETL. The *J-V-L* characteristics are shown in **Fig. 5b** and **Table 3**. The EL spectrum for the dry-processed device is consistent with that for the solution-processed one. In addition to the fact that high η_{CE} of 63.7 cd A⁻¹ and η_{PE} of 47.7 lm W⁻¹ are achieved at 100 cd m⁻², in particular, the device shows only a 16% roll-off in η_{CE} at 1000 cd m⁻². The dry-processed device show 61%, 58%, and 63% higher in η_{CE} , η_{PE} , and η_{EQE} , respectively, compared to the solution-processed counterparts (**Fig. 5c** and **5d**). We attribute the enhanced device performance to: (i) a high hole mobility in the TAPC HTL, (ii) a high LUMO level (-2.0 eV) in the TAPC HTL that results in an efficient electron confinement,^{41,42} (iii) a high electron mobility in the BmPyPB ETL, and (iv) a deep HOMO level in the BmPyPB layer that results in an efficient hole confinement.³ In addition, as shown in **Fig. 5b**, the dry-processed device shows a nearly two-fold increase in L_{max} relative to that in the solution-processed OLED device. Both devices demonstrate an identical EL emission at 512 nm (inset: **Fig. 5c**).

Figure S6 shows the operational lifetime (t_{50}), referring to the duration before the luminance drops to 50% of the initial value, in the OLED devices using Ir(ppy)₂L1 and conventional Ir(ppy)₃. The Ir(ppy)₂L1-based device (ITO/PEDOT:PSS/TAPC/EML (Ir(ppy)₂L1

+ CBP)/BmPyPB/LiF/Al) shows a t_{50} value of 2.5 hours with an initial luminance (L_0) of 1097 cd m^{-2} . On the other hand, the Ir(ppy)_3 device was tested at a higher L_0 ($t_{50} = 1.46$ hours at L_0 of 1754 cd m^{-2}). We extrapolate and estimate the t_{50} values at $L_0 = 100 \text{ cd m}^{-2}$ to be 146.5 hours and 190.2 hours, for $\text{Ir(ppy)}_2\text{L1}$ and Ir(ppy)_3 devices, respectively. The performance of electrical stability is comparable.

Conclusion

In summary, we synthesize new heteroleptic Ir(III) complexes, $\text{Ir(ppy)}_2\text{L1}$, $\text{Ir(ppy)}_2\text{L2}$, and $\text{Ir(ppy)}_2\text{L3}$ by introducing new ancillary ligands. In particular, the complex based on the 1-(2-chlorophenyl)-5-hydroxy-3-methyl-1*H*-pyrazole-4-carbaldehyde (L1) ligand, shows a high Φ_{PL} of 89% in solution and excellent solubility in the commonly-used polar solvents. We demonstrate its solution- and dry-processed light emitting devices, with highest current efficiencies of 46 cd A^{-1} and 64 cd A^{-1} , respectively. We believe that with further optimization in device architecture, $\text{Ir(ppy)}_2\text{L1}$ would be a promising candidate for the efficient phosphorescent OLED devices.

Experimental

Materials and Characterizations

Iridium (III) chloride hydrate, 2-phenyl pyridine and 2-ethoxyethanol (Sigma-Aldrich), 1-phenyl-3-methyl-2-pyrazoline-5-one (Merck) were used as received. The organic solvents and other reagents were used after purification using the standard protocols.^{43, 44} All the reactions were carried out in nitrogen atmosphere with the Schlenk line. The nuclear magnetic resonance (NMR) spectra were collected using a Bruker 400 MHz Spectrometer (**Fig. S7-S9**). Deuterated

dimethyl sulfoxide (DMSO- d_6) was used as solvent for the measurement and calibration for the residual peak of the deuterated solvent (δ 2.52 for ^1H NMR). The high resolution mass spectra (HR-MS) of the complexes were taken with the Shimadzu LCMS-2010 Spectrometer (**Fig. S10**). The FT-IR Spectra were taken with the Infrared Spectrophotometer MB-3000 (**Fig. S11**).

Synthesis of $\text{Ir}(\text{ppy})_2\text{L1}$: A mixture of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.35 g, 1 mmol) and ppy (0.4 g, 2.20 mmol) in a mixture of 2-ethoxyethanol and water (20 mL, 3 : 1, v/v) was refluxed under nitrogen for 48 h. The reaction mixture was then cooled down to room temperature and water (10 mL) was added. The mixture was filtered and the residue was washed with water (20 mL) and ethanol (20 mL). The crude dichloro-bridged diiridium complex (0.57 g), $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$, was collected without further purification after it was dried out. A solution of ligand 1-(2-chlorophenyl)-5-hydroxy-3-methyl-*1H*-pyrazole-4-carbaldehyde (**L1**) (0.1 g, 0.4 mmol) and the dichloro-bridged diiridium complex $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (0.21 g, 0.2 mmol) in 2-ethoxyethanol (20 mL) was refluxed in the presence of Na_2CO_3 under nitrogen for 24 h in dark. After cooling to room temperature, the mixture was precipitated while stirring. The precipitate of complex **1** was filtered and washed with ethanol (20 mL) as an eluent: yellow solid; yield (0.19 g, 68%).

Spectral data: IR (KBr pellet cm^{-1}) 1620 ($-\text{HC}=\text{O}$); ^1H NMR (400 MHz, d_6 -DMSO, δ [ppm]): 8.90 (s, 1H, $-\text{CHO}$), 8.55 (d, $J=4.4$ Hz, 1H), 8.41 (d, $J=6.8$ Hz, 1H), 8.18-8.12 (m, 2H), 7.98-7.93 (m, 2H), 7.71 (d, $J=6.8$ Hz, 1H), 7.65 (d, $J=7.2$ Hz, 1H), 7.41-7.31 (m, 6H), 6.83-6.52 (m, 4H), 6.12 (d, $J=6.8$ Hz, 1H), 5.98 (d, $J=6.8$ Hz, 1H), 2.19 (s, 3H, $-\text{CH}_3$).; ^{13}C NMR(APT) (100 MHz, DMSO, δ) : 179.47, 167.83, 154.43, 150.46, 148.74, 148.46, 145.76, 145.49, 144.60, 144.40, 144.17, 138.89, 138.55, 133.44, 132.87, 131.06, 130.37, 130.23, 130.16, 129.01, 128.88, 128.26, 124.43, 123.17, 123.06, 121.46, 121.19, 119.50, 119.50, 119.41, 106.95, 13.31. HR-MS calcd for

$C_{33}H_{24}O_2N_4$ $^{193}IrCl$ $[M + H]^+$ m/z 736.14, found 736.91.; Anal. calcd. for $C_{33}H_{24}ClIrN_4O_2$: C 53.83, H 3.29, N 7.61; found: C 53.14, H 3.22, N 7.85.

Synthesis of $[Ir(ppy)_2L2]$: The synthesis of $Ir(ppy)_2L2$ was similar to that of $Ir(ppy)_2L1$ except that the ancillary ligand **L1** was replaced by 5-hydroxy-3-methyl-1-(p-tolyl)-1H-pyrazole-4-carbaldehyde (**L2**). The $Ir(ppy)_2L2$ as an eluent: yellow solid; in yield (0.18 g, 63%).

Spectral data: IR (KBr pellet cm^{-1}) 1624 ($-HC=O$); 1H NMR (400 MHz, d_6 -DMSO, δ [ppm]): 8.89 (s, 1H, $-CHO$), 8.55 (d, $J=5.2$ Hz, 1H), 8.43 (d, $J=5.2$ Hz, 1H), 8.17 (t, $J=6.8$ Hz, 2H), 7.96 (d, $J=7.2$ Hz, 1H), 7.92 (d, $J=8$ Hz, 1H), 7.53 (d, $J=8$ Hz, 2H), 7.43-7.34 (m, 4H), 7.01 (d, $J=8$ Hz, 2H), 6.81 (t, $J=7.6$, 2H), 6.67 (d, $J=4$ Hz, 2H), 6.13 (d, $J=7.6$ Hz, 2H), 2.21 (s, 3H, $-CH_3$), 2.19 (s, 3H, $-CH_3$); ^{13}C NMR(APT) (100 MHz, DMSO, δ) : 179.51, 167.89, 167.72, 159.96, 150.29, 148.55, 148.27, 145.80, 145.32, 144.41, 144.20, 144.35, 138.88, 138.72, 136.75, 134.18, 133.37, 129.54, 128.99, 124.49, 124.41, 123.40, 132.22, 121.46, 121.36, 119.51, 119.42, 108.12, 20.79, 13.26.; HR-MS calcd for $C_{34}H_{27}O_2N_4$ ^{193}Ir $[M + H]^+$ m/z 716.14, found 716.97.; Anal. calcd for $C_{34}H_{27}IrN_4O_2$: C 57.05, H 3.80, N 7.83; found: C 56.67, H 3.50, N 7.91.

Synthesis of $[Ir(ppy)_2L3]$: The synthesis of $Ir(ppy)_2L3$ was similar to that of $Ir(ppy)_2L1$ except that the ancillary ligand **L1** was replaced by 5-hydroxy-3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde (**L3**). The $Ir(ppy)_2L3$ as an eluent: yellow solid; yield (0.18 g, 64%).

Spectral data: IR (KBr pellet cm^{-1}) 1624 ($-HC=O$); 1H NMR (400 MHz, d_6 -DMSO, δ [ppm]): 8.91 (s, 1H, $-CHO$), 8.57 (d, $J=5.2$ Hz, 1H), 8.44 (d, $J=5.2$ Hz, 1H), 8.17 (t, $J=6.6$, 2H), 7.97-7.91 (m, 2H), 7.73 (d, $J=7.6$ Hz, 2H), 7.67 (d, $J=8$ Hz, 2H), 7.39 (m, 2H), 7.22 (t, $J=7.8$ Hz, 2H), 7.06 (t, $J=7.4$ Hz, 1H), 6.82 (t, $J=7.4$ Hz, 2H), 6.66 (m, 2H), 6.14 (t, $J=7.8$ Hz, 2H), 2.23 (s, 3H, $-CH_3$); ^{13}C NMR(APT) (100 MHz, DMSO, δ) : 179.69, 167.84, 167.70, 160.18, 150.59, 148.56, 148.30, 145.78, 145.32, 144.27, 144.22, 139.16, 138.91, 138.76, 133.33, 132.85, 129.17, 129.03,

124.97, 124.49, 123.45, 123.25, 121.50, 121.40, 119.56, 119.31 108.15, 13.30.; HR-MS calcd for $C_{33}H_{25}O_2N_4$ ^{193}Ir $[M + H]^+$ m/z 702.16; found 702.97.; Anal. calcd for $C_{33}H_{25}IrN_4O_2$: C 56.48, H 3.59, N 7.98; found: C 56.14, H 3.36, N 8.01.

Characterizations

The ultraviolet-visible (UV-vis) absorption spectra were taken using the JASCO V670 spectrometer. The photoluminescence (PL) spectra were recorded using the Horiba Fluorolog 3 spectrometer with a Xe lamp as the excitation source. The phosphorescence spectra of Ir complexes were also recorded using Horiba Fluorolog 3 spectrometer equipped with liquid nitrogen dewar assembly. The exciton lifetime of Ir(III) complexes were measured using a time-correlated single photon counting (TCSPC) setup, equipped with a SPC-130-EM counting module (Becker & Hickl GmbH) and an IDQ-ID-100-20-ULN avalanche photodiode (Quantic) for recording the decay traces. The emission of the films was excited by a 355 nm (frequency-tripled emission of Nd:YAG laser Duetto Time-Bandwidth Products) laser pulses with a repetition of 72 kHz triggering TCSPC counting module through an electronic delay generator (DG535 from Stanford Research Systems). The emission was filtered out from scattered laser light by long-pass filter at 400 nm. The cyclic voltammograms (CVs) were collected on a CHI660E electrochemical workstation. The thermal behavior of Ir(III) complexes were characterized using Mettler-Toledo DSC822e differential scanning calorimeter (DSC) in the range of 100 -300 °C and Mettler-Toledo thermogravimetric analyzer (TGA/SDTA 851) in the range of 50 - 600 °C at heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

Theoretical Methods

Theoretical calculations were performed using the DFT formalism as implemented in the Vienna *ab initio* simulation package (VASP)⁴⁵ and Castep.⁴⁶ For all systems a 25 Å × 25 Å × 25 Å box

was used to ensure a vacuum gap of at least 10 Å in all directions. A grid of $1 \times 1 \times 1$ k-sampling was used in all calculations. The three systems were optimized in CASTEP using a 500 eV plane wave energy cutoff in a spin polarised calculation using the Perdew-Burke-Ernzerhof (PBE)⁴⁷ functional and pseudopotentials from the inbuilt C9 pseudopotential library. Once the initial optimization was completed the novel ligand (L1, L2 or L3 dependent on the system) was rotated with respect to the rest of the molecule, which was kept fixed, in order to find the most stable geometry. This was done in 10° intervals. The lowest energy configurations from these were further optimized until all forces were less than 0.01 eV/Å to generate the final structures. The convergence tolerance for total energy used in these calculations was 1×10^{-5} eV/atom. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm was used to perform the optimizations.⁴⁸ The final geometries from this process were transferred to VASP. These calculations used PAW pseudopotentials^{49,50} and a cutoff energy of 434 eV via the PREC = Accurate setting. Total forces were checked and found to be still below the chosen force cutoff limit. An implicit solvation model⁵¹ was used to reproduce the effects of an acetonitrile solvent. To do this a relative permittivity of 36.64 was used. This was found to have minor effects on the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels. The HOMO/LUMO eigenvalues were calculated first using the PBE functional and then using the Heyd-Scuseria-Ernzerhof hybrid functional (HSE06).⁵² This hybrid functional was used as it provides a correction to the PBE functional at the direct exchange term of the exchange-correlation potential. This resulted in better agreement with the experimental data for the frontier energy states (HOMO, LUMO) and optical absorption spectra.

Materials, fabrication, and characterization of OLEDs

Materials: Patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of $15 \Omega/\square$ were purchased from Lumtech Corp. The hole injection material poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT: PSS) was purchased from Heraeus (Clevios AI 4083). Highly pure sublimed grade hole transporting material di-[4-(*N,N*-ditolyl-amino)-phenyl]cyclohexane (TAPC), electron transporting materials, 2,2',2''-(1,3,5-benzinetriyl)-*tris*(1-phenyl-1-*H*-benzimidazole) (TPBi) and 1,3-bis(3,5-dipyrid-3-yl-phenyl)benzene (BmPyPB), and a molecular host material 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP) were also purchased from Lumtech Corp. The electron injection materials lithium fluoride (LiF) (99.98%) was purchased from Acros Organics. Moreover, 99.999% pure Aluminum (Al) ingots were purchased from Kurt J. Lesker Co. Ltd. The sublimed-grade transport and host materials were used directly without further purification.

Device fabrication: For solution-process devices, firstly, a 35 nm aqueous solution of PEDOT:PSS hole transporting layer (HTL) is spin-coated (4000 rpm for 20s) on pre-cleaned ITO coated glass substrates. Then PEDOT:PSS layer is annealed at 125°C for 30 min. in ambient atmosphere. Later on these substrates were transferred into a glove box for subsequent deposition. The green emission layers (EMLs), consisting mixtures of 5, 10, and 15 wt% synthesized Ir(III) complexes, including Ir(ppy)₂L1, Ir(ppy)₂L2, and Ir(ppy)₂L3, together with the CBP host, were then spin-coated at 2500 rpm for 20 s. Finally, these substrates were transferred into a high vacuum chamber for succeeding layers, a 35 nm TPBi as electron-transporting layer (ETL), and a 1 nm LiF as electron injection layer, which were deposited by thermal evaporation at 1×10^{-7} mbar. Finally, a 100 nm Al cathode layer was evaporated with a shadow mask that results an active area of 25 mm². On the other hand, the dry-processed phosphorescent samples were prepared by sequentially depositing of ITO (120 nm)/TAPC (40

nm)/EML (20 nm)/BmPyPB (35 nm)/LiF (1 nm)/Al (100 nm) using the thermal evaporation. Before thermal evaporation, the EMLs were prepared by the solution-premixing of 5, 10, and 15 wt% of Ir(ppy)₂L1 emitter in to the CBP host matrix.

Device characterization: Current density-voltage-luminance (*J-V-L*) characteristics of the OLEDs were measured using a Keithley 2400 source meter and a Konica Minolta CS100 luminance meter. The electroluminescence (EL) spectra of all the devices were recorded by using a Photo Research PR 655 spectrometer. The external quantum efficiency, η_{EQE} , was then estimated by calculating the total number of emitted photons divided by the total number of injected electrons, based on the assumption of the Lambertian-type emission pattern.

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Supporting Information

Thermal, photophysical, and electrochemical characteristics, DFT calculation for the optical absorption and corresponding energy levels, NMR, mass and IR spectra of Ir (III) complexes with supplementary tables including calculated dipole transition matrix elements α (a.u.), and excitation energies ΔE for Ir (III) complexes are supplied as Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI:

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We design and synthesize a heteroleptic iridium (Ir) complex, Ir(ppy)₂L1, using an ancillary ligand, 1-(2-chlorophenyl)-5-hydroxy-3-methyl-1*H*-pyrazole-4-carbaldehyde (L1). The photophysical and electrochemical properties were systematically characterized, followed by comparing with those predicted by density functional theory simulations. By using 4,4'-bis(carbazole-9-yl)biphenyl as the host material, we demonstrate high current efficiencies of 64 cd A⁻¹ and 40 cd A⁻¹ at 100 cd m⁻² in its vacuum-evaporated and solution-processed organic light-emitting devices.