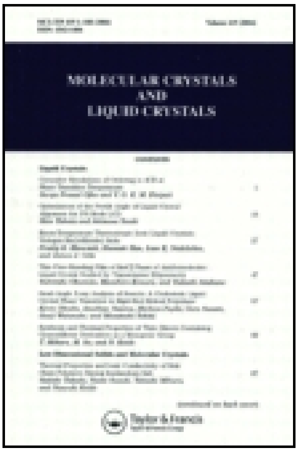

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Solution Processed Green Phosphorescent Organic Light-Emitting Diodes Based on Phenylpyridine Derivatives Using Small Molecule Host

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Solution Processed Green Phosphorescent Organic Light-Emitting Diodes Based on Phenylpyridine Derivatives Using Small Molecule Host

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A novel cyclometalated ligand 2-(2,4-dimethoxyphenyl)-5-trifluoromethylpyridine (MeO_2CF_3ppy), and its complexes bis*[2-(2,4-dimethoxy-phenyl)-5-trifluoromethyl pyridinato-N,$C^{2'}$]iridium acetylacetonate ($(MeO_2CF_3ppy)_2Ir(acac)$) and* bis*[2-(2,4-Dimethoxy-phenyl)-5-trifluoromethyl pyridinato-N,$C^{2'}$]iridium pyrazolate ($(MeO_2CF_3ppy)_2Ir(prz)$) were synthesized, respectively. Trifluoromethyl (CF_3) and dimethoxy group (MeO_2) were introduced into main ligand for color tuning. The green emitting PhOLEDs, based on ITO/PEDOT:PSS (40 nm)/TCTA:TPBi:Ir(III) complex (80 nm)/Bphen (20 nm)/LiF (0.7 nm)/ Al (120 nm) were fabricated. The solution-processed PhOLEDs based on $(MeO_2CF_3ppy)_2Ir(acac)$ exhibited a maximum quantum efficiency of 3.40% and luminance efficiency 8.32 cd/A with CIE coordinate of (0.33, 0.63).*

Keywords Solution-process; PhOLEDs; Iridium(III) complex

Introduction

Since Tang's group investigated electroluminescent devices based on tris(8-hydroxyquinoline) aluminum (Alq_3) in 1987, organic light-emitting diodes (OLEDs) have been attracted great attention [1]. In recent years, there are increasing numbers of solution-processed OLEDs fabricated from fluorescent polymers or dendrimers [2,3]. However, the performances exhibit only low efficiencies in most cases. A lot of efforts have been directed to phosphorescent materials in order to obtain high efficiencies [4]. For instances, OLEDs using phosphorescent materials such as iridium or platinum complexes as the emitting materials were reported, which showed a much higher efficiency than those using fluorescent emitting materials [5,6]. In particular, phosphorescent OLED (PhOLED) materials offer the possibility of developing highly efficient OLEDs, since they are able

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to achieve emission from both the singlet and triplet excited states. Therefore, an internal quantum efficiency of up to 100% is theoretically possible. Many research groups have been fabricated by simultaneous or sequential thermal vapor deposition with several organic layers [7,8]. However, the thermal vapor deposition process for fabricating PhOLEDs is relatively complicated and expensive, particularly if large area substrates are used. On the other hand, solution based methods have the potential to facilitate rapid and low-cost processing and can be extended to large area substrates. In order to practical OLEDs, there have been continuous efforts to develop cyclometalated Ir(III) complexes with finely tuned color emissions. For example, modifying the chemical structure as well as the substituent groups of the cyclometalated ligand give a significant tuning of phosphorescence [9,10]. Thus, cyclometalated ligand is modified by incorporating a trifluoromethyl and dimethoxy group on the pyridine and phenyl ring to produce effect on the emission wavelength of the Ir(III) complexes. In this paper, we report a synthesis, electrochemical, photophysical, and electroluminescent (EL) of Ir(III) complexes containing phenylpyridine (ppy) derivative for the fabrication of solution-processed PhOLEDs.

Experimental

Characterization

^{1}H-NMR spectra was recorded on a Varian Mercury Plus 300 MHz spectrometer and the chemical shifts were recorded in ppm units with $CDCl_3$ as the internal standard. The thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851e, DSC 822e analyzer under an N_2 atmosphere at a heating rate of 10°C/min. Cyclic voltametry (CV) was carried out with a CHI 600C potentiostat (CH Instruments) at a scan rate of 100 mV/s in a 0.1 M solution of tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) in anhydrous CH_2Cl_2. A platinum wire was used as the counter electrode and an $Ag/AgNO_3$ electrode was used as the reference electrode. UV-visible spectra were measured using a JASCO V-570 spectrophotometer. PL spectra and low-temperature fluorescence spectra were obtained using Hitachi F-4500 fluorescence spectrophotometer.

Materials

2,4-Dimethoxyphenyl boronic acid, 2-chloro-5-(trifluoromethyl)pyridine, tetrakis(triphenylphosphine)palladium(0), *n*-butyllithium (2.5 M solution in hexanes), acetylacetone, tetrabutylammonium hexafluorophosphate, 2-ethoxyethanol, and tetrahydrofuran (THF) were obtained from Aldrich Chem. Iridium(III) chloride trihydrate ($IrCl_3{\cdot}3H_2O$) was obtained from Acros organics. The materials were used without further purification, with the exception of THF, which was distilled from sodium/benzophenone under nitrogen.

Synthesis of 2-(2,4-Dimethoxyphenyl)-5-trifluoromethylpyridine (MeO_2CF_3ppy)

2,4-Dimethoxyphenyl boronic acid (2.20 g, 12.12 mmol) and 2-chloro-5-trifluoromethyl) pyridine (2.01 g, 11.02 mmol) were added to round bottom flask with reflux condenser and dissolved THF (50 mL). After aqueous K_2CO_3 (4 M, 10 mL) was delivered, then tetrakis(triphenylphosphine)palladium(0) (0.6 g, 0.55 mmol) was added and then reaction mixture was heated at 80°C for 24 h. The cooled crude mixture was poured onto brine and extracted with CH_2Cl_2 (50 mL × 3 times) then dried over anhydrous $MgSO_4$. Finally silica column purification (ethyl acetate:*n*-Hexane = 1:15) gave transparent liquid (3.00 g, 10.0 mmol) in quantitative yield. ^{1}H-NMR δ (ppm) 8.91 (s, 1H), 8.01 (d, J = 8.7, 1H), 7.91 − 7.86 (m, 2H), 6.65 (dd, J = 2.1, 8.4, 1H), 6.58 (d, J = 2.7, 1H), 3.88 (s, 6H). Yield: 82%

Synthesis of [(MeO$_2$CF$_3$ppy)$_2$Ir(μ-Cl)]$_2$

IrCl$_3$ □ xH$_2$O (1.41 g, 4.01 mmol) and (MeO$_2$CF$_3$ppy)$_2$ (3.00 g, 10.0 mmol) were dissolved in 2-ethoxy ethanol : H$_2$O = 15 mL : 5 mL, and refluxed at 135°C for 28 hr. After cooling, yellow precipitate was filtered and washed with ethanol and water. The washed product was 85% yield.

Synthesis of (MeO$_2$CF$_3$ppy)$_2$Ir(acac) or (MeO$_2$CF$_3$ppy)$_2$Ir(prz)

[(MeO$_2$CF$_3$ppy)$_2$Ir(μ-Cl)]$_2$ (1 g, 0.63 mmol), sodium carbonate (0.8 g, 7.56 mmol), and acetyl acetone (0.2 ml, 1.89 mmol) or 2-pyrazine carboxylic acid (0.24 mmol) were dissolved in 30 mL of 2-ethoxy ethanol. After degassed, the reaction vessel was maintained under nitrogen condition. Temperature was raised to 130 °C and the reaction mixture was stirred for 22 h. Then cooled crude mixture was poured into brine and extracted with CH$_2$Cl$_2$ (50 mL × 3 times) then dried over anhydrous magnesium sulfate. Silica column purification (dicloromethane:methanol = 2:1) gave yellow powder.

(MeO$_2$CF$_3$ppy)$_2$Ir(acac) ^{1}H-NMR δ (ppm) 8.6 (s, 2H), 8.48 (d, J = 9, 2H) 7.83 (dd, J = 2.4, 9, 2H), 6.01 (d, J = 2.4, 2H), 5.35 (d, J = 2.1, 2H), 5.24 (s, 1H), 3.90 (s, 6H), 3.50 (s, 6H), 1.81 (s, 6H). Anal. Calcd for: C: 46.31, H: 3.42, N: 3.27. Found: C: 46.61, H: 3.69, N: 3.10. Yield: 68%

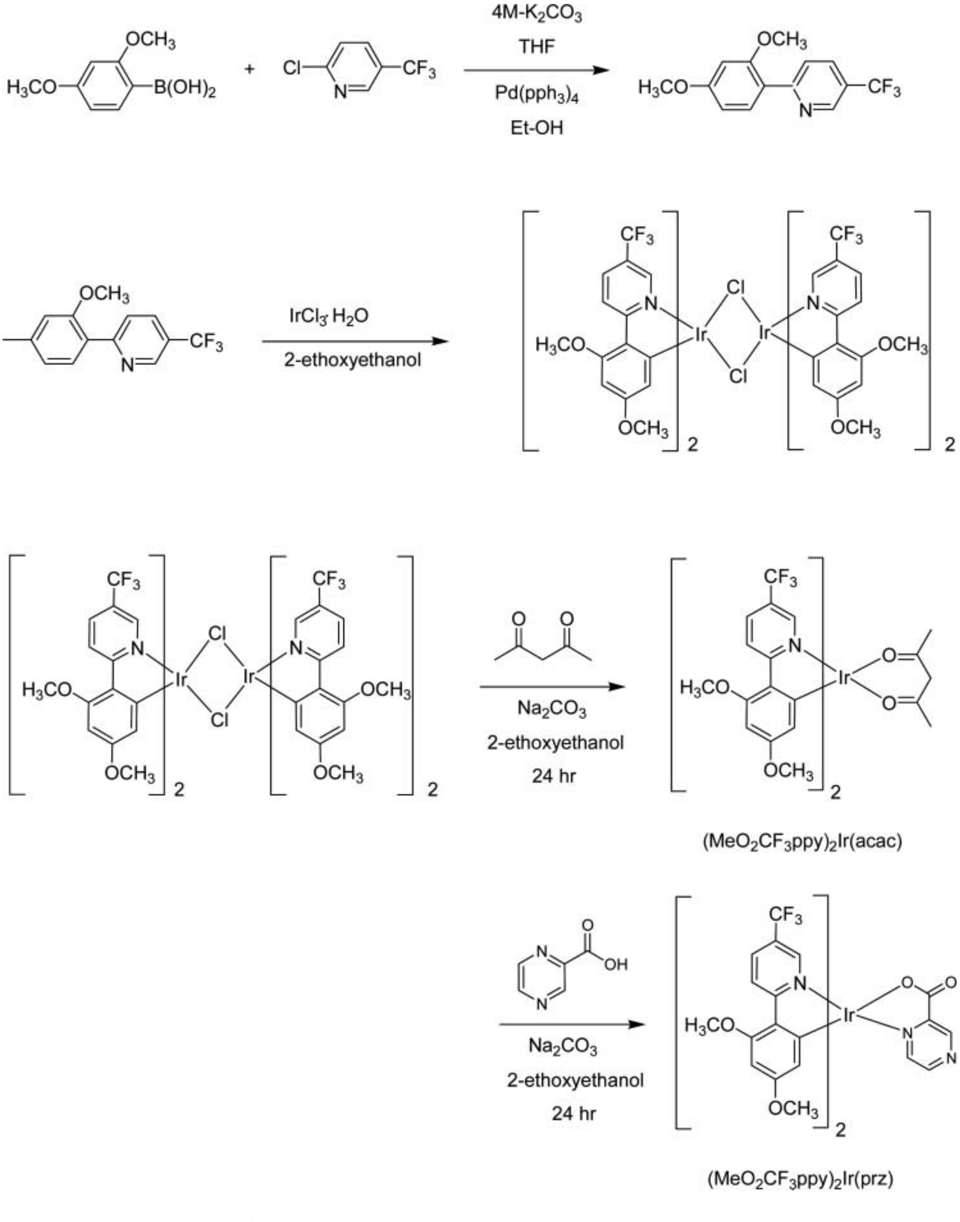
(MeO$_2$CF$_3$ppy)$_2$Ir(prz) ^{1}H-NMR δ (ppm) 9.50 (d, J = 1.2, 1H), 8.92 (d, J = 0.9, 1H), 8.73 (m, 2H), 8.65 (d, J = 9.3, 1H), 7.84(m, 2H), 7.76 (dd, J = 1.2, 2.7, 1H), 7.50 (s, 1H), 6.15 (d, 2.1, 1H), 6.08 (d, J = 2.4, 1H), 5.48 (d, J = 2.1, 1H), 5.21 (d, J = 2.1, 1H), 3.98 (s, 3H), 3.91 (s, 3H), 3.57 (s, 3H), 3.48 (s, 3H). Anal. Calcd for: C: 45.05, H: 2.86, N: 6.37. Found: C: 45.17, H: 3.66, N: 6.18. Yield: 77%

Fabrication of PhOLEDs and measurement

The PhOLEDs were fabricated in the configuration ITO/PEDOT:PSS (40 nm)/TCTA: TPBi:Ir(III) complex (80 nm)/BPhen (20 nm)/LiF (0.7 nm)/Al (120 nm). The PEDOT:PSS was spin-coated directly onto the patterned ITO glass and baked in air at 150°C for 10 min. The emitting layer was then spin-coated onto the PEDOT: PSS coated substrate from a mixed solution of TCTA and TPBi (weight ratio, 2:1), and doped with 8 wt% of (MeO$_2$CF$_3$ppy)$_2$Ir(acac) or (MeO$_2$CF$_3$ppy)$_2$Ir(prz). The emitting layer was then spin-coated onto the PEDOT: PSS coated substrate from a mixed solution of TCTA, TPBi and doped with (MeO$_2$CF$_3$ppy)$_2$Ir(acac) or (MeO$_2$CF$_3$ppy)$_2$Ir(prz). All solutions used in the PhOLEDs fabrication were filtered with 0.20 μm PTFE syringe filter. The emitting layer was then baked at 80°C for 30 min in glove box. Finally, as typical cathode, consisting of BPhen (20 nm)/LiF (0.7 nm)/Al (120 nm) was thermal vapor deposited with effective area of 4 mm^2 at a pressure 5×10^{-6} Torr. The film thickness was measured by using α-Step IQ surface profiler (KLA Tencor, San Jose, CA). EL spectra and current density-voltage-luminance (*J-V-L*) characteristics of PhOLEDs were measured with a programmable Keithley model 236 power source and spectrascan CS-1000 photometer, respectively. All measurements were carried out at room temperature under an ambient atmosphere.

Results and Discussion

General synthetic procedures used for the preparation of $(MeO_2CF_3ppy)_2Ir(acac)$ and $(MeO_2CF_3ppy)_2Ir(prz)$ are outlined in Scheme 1. The main ligand, 2-(2,4-dimethoxyphenyl)-5-trifluoromethylpyridine (MeO_2CF_3ppy) was prepared by Suzuki coupling method which is the palladium-catalyzed cross coupling between boronic acid and halide [11]. The cyclometalated iridium chloride-bridged dimers were synthesized from iridium trichloride hydrate with an excess of the main ligand using Nonoyama's method [12]. The



Scheme 1. Synthetic routes for Ir(III) complexes.

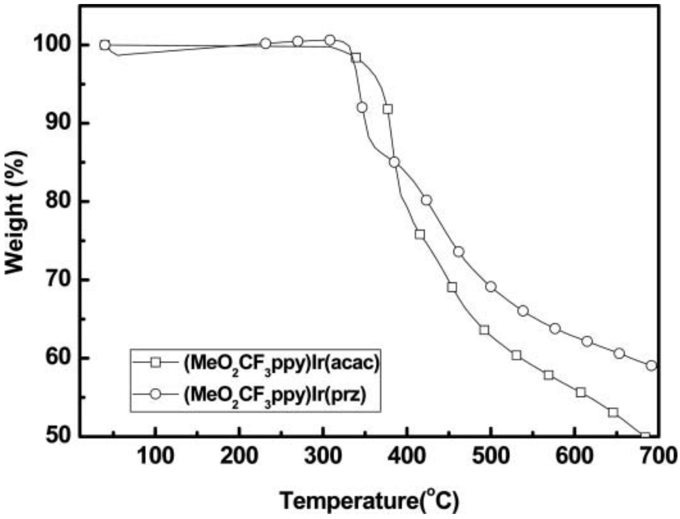


Figure 1. TGA trace of Ir(III) complexes measured at a scan rate of 10 °C/min under N_2.

Na_2CO_3-mediated ligand exchange reactions with acetylacetone and 2-pyrazine carboxylic acid (prz) ancillary ligands were carried out to give heteroleptic iridium complexes in quantitative yield. These two Ir(III) complexes were purified using silica column chromatography and recrystallization. The final products prior to device fabrication were characterized by ^{1}H- NMR spectroscopy and elemental analysis. The thermal properties of the Ir(III) complexes were measured by TGA and DSC under an N_2 atmosphere at a heating rate of 10°C/min as shown in Fig. 1 and results are summarized in Table 1. Two Ir(III) complex is thermally stable up to 340°C, as determined by TGA, which is beneficial to the long-term stability of the PhOLEDs devices fabricated from this material. Figure 2 displays the UV-visible absorption and photoluminescence (PL) spectra of the Ir(III) complex dissolved in CH_2Cl_2 solution. The photophysical factors of the Ir(III) complex is summarized in Table 1. The strong absorption bands between 300 nm and 400 nm in the UV region with distinct vibronic features are assigned to the spin- allowed $^1\pi$-π^* transition of the ligands in the Ir(III)complexes. These strong $^1\pi$-π^* absorption bands are accompanied by weaker

Table 1. Photophysical, electrochemical, and thermal data for synthesized Ir(III) complexes

Compound	T_d (°C)[a]	λ_{em} (nm)[b]	λ_{em} (nm)[c]	Φ_{pl} (%)[d]	HOMO LUMO (eV)[e]
$(MeO_2CF_3ppy)_2$ Ir(acac)	367	521	526	0.16	–5.35/−3.10
$(MeO_2CF_3ppy)_2$ Ir(prz)	341	613	555	0.10	–5.35/−2.90

[a] Temperature with 5% mass loss measure by TGA with a heating rate of 10°C/min under N_2.

[b] Maximum emission wavelength, measured in CH_2Cl_2 solution (298 K).

[c] Maximum emission wavelength, measured in PMMA film (298 K).

[d] Measured in 1×10^{-5}M degassed CH_2Cl_2 solution relative to $Ir(ppy)_3$(Φ_{pl} = 0.40) with 420 nm excitation.

[e] Determined from the half-wave potentials for oxidation and reduction.

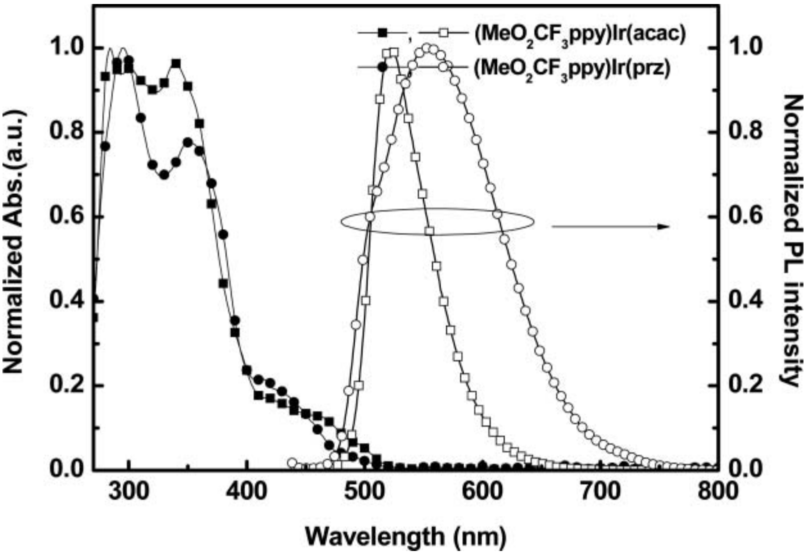


Figure 2. Absorption and PL spectra of the $(MeO_2CF_3ppy)_2Ir(acac)$ and $(MeO_2CF_3ppy)_2Ir(prz)$ in CH_2Cl_2 at 293 K.

and lower energy absorption bands well extending into the visible region, which can be correspond to an admixture of some ^{1}MLCT, ^{3}MLCT and $^3\pi$-π^* transitions. As a result, the absorption intensity of ^{1}MLCT and $^3\pi$-π^* transitions are enhanced by the spin-orbital coupling of the Ir(III) central ion. The solution state of PL spectra of $(MeO_2CF_3ppy)_2Ir(acac)$ and $(MeO_2CF_3ppy)_2Ir(prz)$ shows the maximum emission peaks at 520 and 542 nm, respectively, as shown in Fig. 2. The electrochemical behavior of the Ir(III) complexes was investigated by cyclic voltammetry. From the oxidation and reduction potentials, HOMO and LUMO energy levels of $(MeO_2CF_3ppy)_2Ir(acac)$ and $(MeO_2CF_3ppy)_2Ir(prz)$ were calculated to be −5.35 eV, and −3.10 to −2.90 eV, respectively. Figure 3 shows the relative HOMO and LUMO energy levels of the materials used to fabrication for PhOLEDs.

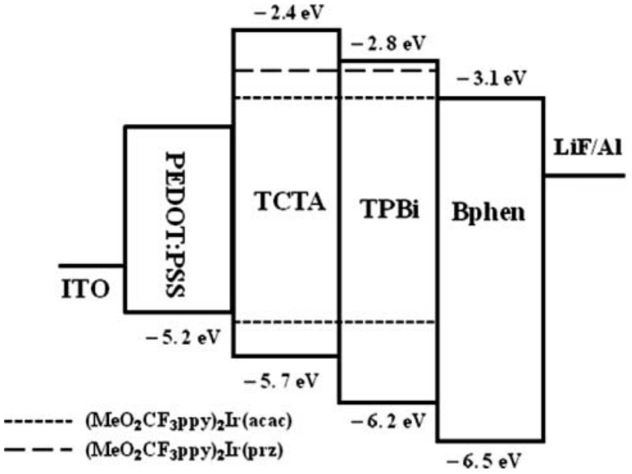


Figure 3. The relative HOMO/LUMO energy levels of the materials used for the PhOLEDs.

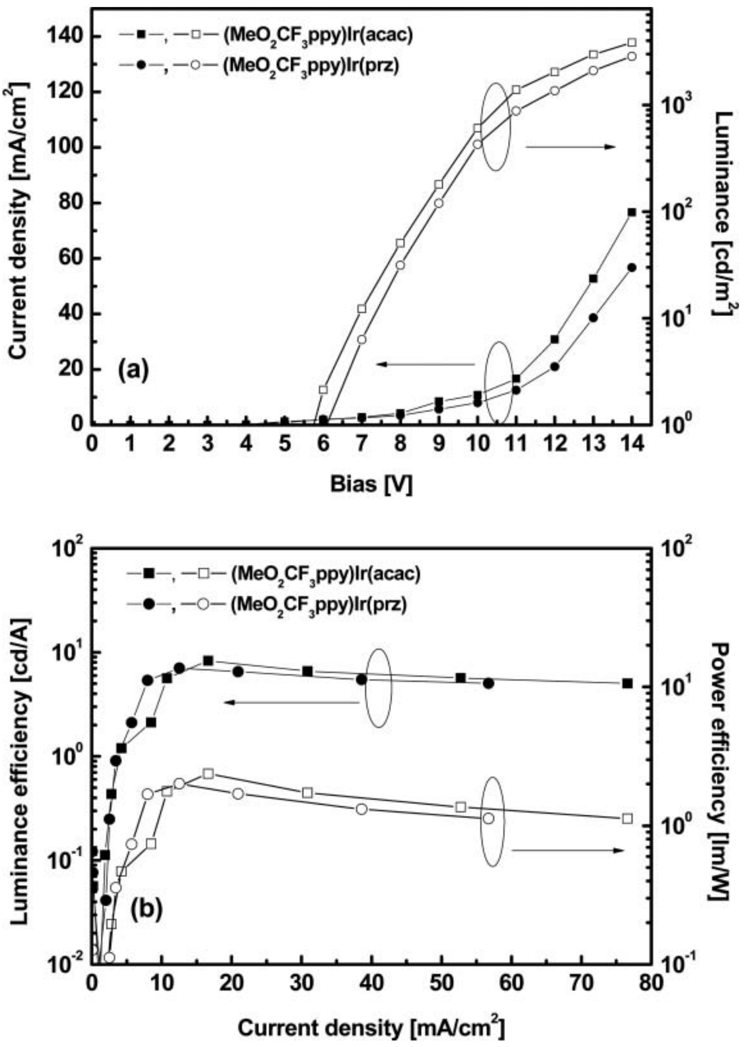


Figure 4. (a) Current density-voltage-luminance (*J-V-L*) and (b) luminance efficiency and power efficiency-current density characteristics of $(MeO_2CF_3ppy)_2Ir(acac)$ and $(MeO_2CF_3ppy)_2Ir(prz)$.

The energy level diagrams show that the energy levels of $(MeO_2CF_3ppy)_2Ir(acac)$ and $(MeO_2CF_3ppy)_2Ir(prz)$ (both HOMO and LUMO) lie above and below those of the host, respectively. Consequently, it is possible that Ir(III) complexes would be able to trap both electrons and holes in the emitting layer. Also, Bphen has a deep HOMO energy level and higher triplet energy level than Iridium(III) complexes and thus effectively confine triplet exciton within the emitting layer. Figure 4(a) displays the current density-voltage-luminance (*J-V-L*) characteristics of these PhOLEDs. The maximum luminance of the PhOLEDs using $(MeO_2CF_3ppy)_2Ir(acac)$ and $(MeO_2CF_3ppy)_2Ir(prz)$ exhibited 3,853 and 2852 cd/m^2, and their turn-on voltages were 5.5 and 6.1 V, respectively. The PhOLEDs with the $(MeO_2CF_3ppy)_2Ir(acac)$ exhibited a higher current density than that of those with the $(MeO_2CF_3ppy)_2Ir(prz)$ at the same voltage. The difference in current density of PhOLEDs produced from different electron injection barrier from Al cathode to emitting

Table 2. EL characteristics of PhOLEDs fabricated using Ir(III) complexes as a emitter

Compound	L_{max} (cd/m^2)	QE_{max} (%)	LE_{max} (cd/A)	PE_{max} (lm/W)	CIE(x,y)^a
$(MeO_2CF_3ppy)_2$ Ir(acac)	3853	3.40	8.32	2.37	0.33, 0.63
$(MeO_2CF_3ppy)_2$ Ir(prz)	2852	3.21	7.03	2.00	0.43, 0.53

[a] Recorded at current density 30 mA/cm^2.

layer. The LUMO energy levels of $(MeO_2CF_3ppy)_2$Ir(acac) and $(MeO_2CF_3ppy)_2$Ir(prz) have a −3.10 and −2.90 eV, respectively. As can be seen in Figure 3, the electrons are easily trapped by $(MeO_2CF_3ppy)_2$Ir(prz), due to the LUMO energy gap of 0.20 eV between Bphen and $(MeO_2CF_3ppy)_2$Ir(prz). However, the LUMO energy gap between Bphen and $(MeO_2CF_3ppy)_2$Ir(acac) is 0 eV, which is negligible with the LUMO energy level of $(MeO_2CF_3ppy)_2$Ir(acac). As a result, electrons are directly injected from Bphen to emitting layer without any energy barrier, leading to high current density. Figure 4(b) shows the luminance efficiency and power efficiency versus the current density characteristics and the PhOLED performances are summarized in Table 2. The maximum luminance efficiencies of the PhOLEDs using $(MeO_2CF_3ppy)_2$Ir(acac) and $(MeO_2CF_3ppy)_2$Ir(prz) were found to be 8.32 and 7.03 cd/A and their maximum power efficiencies were 2.37 and 2.00 lm/W, respectively. The most attractive feature of PhOLEDs was their slow decay of efficiency against the increase in current densities. For example, when using $(MeO_2CF_3ppy)_2$Ir(acac) as an emitter, the PhOLEDs exhibited an luminance efficiency of 5.63 cd/A at a low current density of 10.80 mA/cm^2. However, at a high current density of 76.58 mA/cm^2, the PhOLEDs exhibited a luminance efficiency of 5.08 cd/A. As a result, the efficiency roll-off depends on the effective electron and hole blocking ability by using LUMO of TCTA (2.4 eV) and a HOMO of Bphen (6.5 eV), respectively, resulting in the confinement of opposite charges within the emitting layer.

Conclusions

In conclusion, we synthesized a novel Ir(III) complexes with a phenylpyridine derivative, (MeO_2CF_3ppy) in order to fabricate solution processed PhOLEDs. The emission peak wavelength could be fine-tuned in green to greenish-yellow color range 510–540 nm by using suitable ancillary and cyclometalated ligands. The fabricated PhOLEDs with the configuration of ITO/PEDOT:PSS/TCTA:TPBi:Ir(III) complex/cathode exhibited maximum external quantum and luminance efficiency values of 3.40% and 8.32 cd/A, respectively.

Acknowledgements

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