

Optical and electroluminescent properties of a new Ir(III) complex — *fac*-tris[2,5-di(4-methoxyphenyl)pyridinato-C,N]iridium(III)

Mao-Liang Xu^{a,b,c}, Tian-Le Li^{a,b}, Wen-Lian Li^{a,*}, Zi-Ruo Hong^a, Zhong-Wei An^c, Qun Zhou^c

^a Key Laboratory of Excited State processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, PR China

^b Graduate School of the Chinese Academy of Sciences, Beijing, 100039, PR China

^c Xi'an Modern Chemistry Research Institute, Xi'an 710065, PR China

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Abstract

In this study, a new Ir(III) complex containing 2,5-di(4-methoxyphenyl)pyridine ligand was synthesized. The Ir(III) complex of intense green photophosphorescence emission showed its potential for organic electroluminescence (EL). EL devices were fabricated based on the Ir(III) complex. A maximum external quantum efficiency of 9.0% corresponding to a luminance efficiency of 36 cd/A and a peak luminance of 35 000 cd/m² were achieved, respectively, which is higher than that of the device based on *fac*-tris(phenylpyridine)iridium (Ir(ppy)₃) under the same conditions. The *Commission Internationale de L'Eclairage* coordinates (0.36, 0.62) for the device were independent of current density.

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1. Introduction

Organic light-emitting devices (OLEDs), which consist of organic thin films and exhibit light emission under electric current excitation, are expected to be one of the most promising candidates for flat panel display. After Tang reported the efficient double-layer OLEDs, different types of fluorescent materials have been studied and tremendous progress has been made in the past decades [1,2]. Due to the spin-independent electron–hole recombination, formation ratio of singlet excitons to triplet excitons is about 1:3. Because the triplets are intrinsically non-luminescent according to the spin conservation rule, only small fraction (~25%) of singlet excitons produce electrofluorescence in small molecular materials [3]. A large part of triplet energy is wasted via radiationless decay at room temperature, setting an upper limit to internal quantum efficiency of 25%. To overcome this obstacle by employing the phosphorescent materials, both singlets and triplets in OLEDs may participate in electrolumi-

nescence (EL) emission and hence the phosphorescent OLEDs show higher quantum efficiencies than those based on fluorescent materials. For example, Baldo et al. reported a highly efficient OLEDs using phosphorescent materials such as Pt- and Ir-complexes [4,5]. By employing the phosphorescent materials, the internal quantum efficiency can theoretically reach 100% [6] and emission color can be tuned by modifying the phenylpyridine ligand [7]. The complexes based on *fac*-tris(phenylpyridine)iridium (Ir(ppy)₃) skeleton have such a simple molecular structure and excellent luminescent properties that many efforts are still focusing on chemical modification of this type of complexes for better electrophosphorescent performance [8–11].

In this report, a new tris-orthometalated Ir(III) complex, *fac*-tris[2,5-di(4-methoxyphenyl)pyridinato-C,N]iridium(III) [Ir(d-moppy)₃], was synthesized and used as a triplet emitter in EL device.

Incorporation into the aromatic ring of a substituent, which enlarges the system of conjugated double bonds (such as phenyl group), brings about a bathochromic shift of the absorption spectrum, a hyperchromic effect. Moreover, the methoxy group is expected to enhance the quantum yield [12].

* Corresponding author. Tel.: +86 431 6176345; fax: +86 431 4638283.

E-mail address: wllioel@yahoo.com.cn (W.-L. Li).

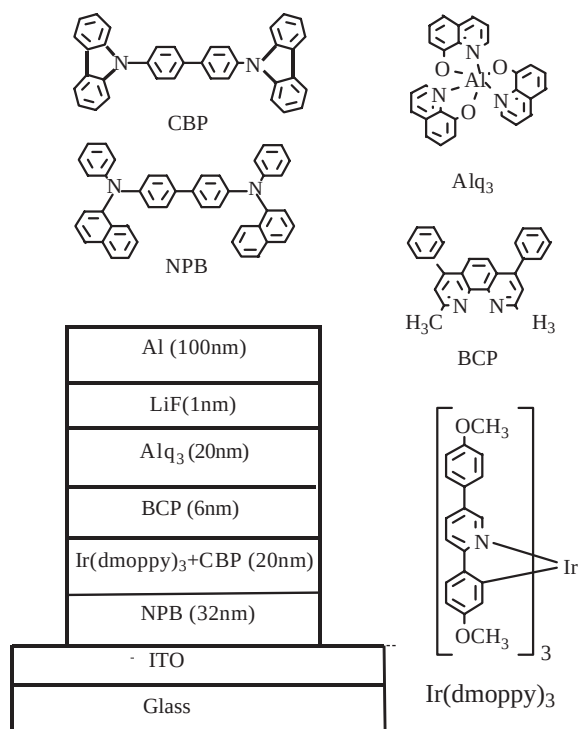


Fig. 1. Configuration of the device and chemical structures of materials used.

So, introducing methoxy group on the 4-position of phenyl ring and methoxyphenyl group on the 5-position of pyridyl ring based on $\text{Ir}(\text{ppy})_3$ is supposed to result in an influence on the highest occupied molecular orbital (HOMO) and emitting triplet metal-to-ligand charge-transfer ($^3\text{MLCT}$) state with a subsequent impact on the properties of photophysics and electrochemistry.

2. Experimental details

2,5-di(4-methoxyphenyl)pyridine (dmoppyH) was synthesized according to literature procedure [13]. $\text{Ir}(\text{ppy})_3$, bathocuproine (BCP), 4,4'- N,N' -dicarbazole-biphenyl (CBP), tris(8-hydroxyquinolinato)aluminum(III) (Alq_3), and 4,4'-bis[N -(1-naphthyl)- N -phenyl-amino]biphenyl (NPB) were obtained from Aldrich, and purified with train sublimation prior to devices processing. ^1H NMR (nuclear magnetic resonance) spectra were recorded on Bruker Avance 300 MHz instrument. Elemental analyses were performed on VarioEL III CHNS instrument. Absorption spectra were measured on UV–VIS–NIR scanning spectrophotometer. Photoluminescence (PL) spectra were measured with an F-4500 Fluorescence Spectrometer. Cyclic voltammetry experiments were performed with a MCP-1 electrochemical analyzer (JiangFen Co., China). EL spectra were recorded on a HITACHI MPF-4 Fluorescence Spectrophotometer. Brightness–current–voltage measurements were made simultaneously using a 3645 DC power supply combined with a 1980A Spot Photometer. External quantum efficiency was calculated from the luminance, current density, and EL spectrum under an assumption of Lambertian emission.

2.1. Synthesis and characterization of $\text{Ir}(\text{dmoppy})_3$

$\text{Ir}(\text{dmoppy})_3$ was synthesized by heating a mixture of $\text{Ir}(\text{acac})_3$ and dmoppyH at 220 °C in glycerol under N_2 for 24 h in 55% yield [14]. After purification, the compound was obtained as a yellow powder. Analysis found: C, 63.99; H, 4.025; N, 3.833. Calculations found: C, 64.39; H, 4.519; N, 3.954. ^1H NMR (300 MHz CDCl_3) δ (ppm): 7.66 (m, 9H), 7.57 (d, 3H), 7.07 (d, 6H), 6.75 (d, 6H), 6.45 (t, 6H), 3.70 (s, 9H), 3.51 (s, 9H).

The ^1H NMR data show ten coupled spins for the aromatic protons indicated a facial arrangement of the orthometalated dmoppy ligands. A meridional configuration of the ligands would result in 30 coupled spins for the tris-ligated complex [15]. The three ligands in the complex are magnetically equivalent due to the threefold symmetry axis of the molecule.

2.2. Device fabrication using phosphorescent $\text{Ir}(\text{dmoppy})_3$

Fig. 1 shows the chemical structures of materials used and the device configuration of the indium–tin oxide (ITO)/NPB/ $\text{Ir}(\text{dmoppy})_3$:CBP/BCP/ Alq_3 /LiF/Al. The multilayered devices consisted of a 32-nm-thick NPB as a hole transport layer, a 20-nm-thick 6% $\text{Ir}(\text{dmoppy})_3$ -doped CBP as an emitting layer, a 6-nm-thick BCP as hole blocking layer, a 20-nm-thick Alq_3 as electron transport layer, and a 1-nm-thick LiF layer followed by 100 nm aluminium cathode.

The devices were successively deposited onto an ITO-coated glass substrate with a sheet resistance of 60 $\Omega/\square$ in high vacuum of 5×10^{-4} Pa during one pump down. Prior to use, the ITO glass substrates were rinsed and degreased by sonication in a detergent solution, distilled water, and acetone. The substrates were treated by UV-ozone for 30 min just before loading into a vacuum chamber [16]. The emissive area of the device defined by the overlapping area of the cathode and the anode was 15 mm². In addition, as a comparative test, an EL device with the same structure was also fabricated with $\text{Ir}(\text{ppy})_3$

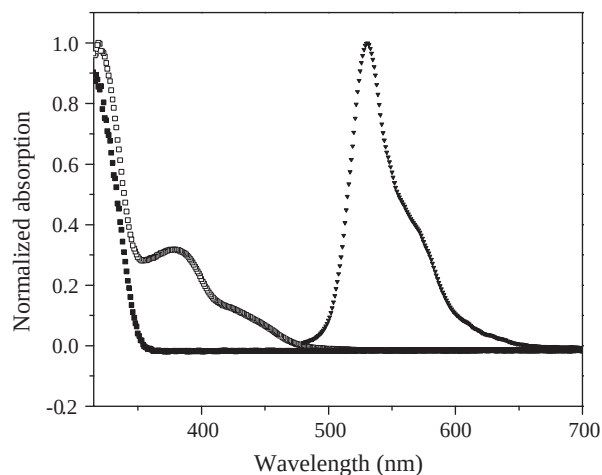


Fig. 2. The absorption spectra of the ligand dmoppyH (■) and the complex $\text{Ir}(\text{dmoppy})_3$ (□) and the PL spectrum of the complex $\text{Ir}(\text{dmoppy})_3$ (▼) in CH_2Cl_2 .

Table 1
Photophysical and electrochemical data of Ir(dmppy)₃ and Ir(ppy)₃

	Absorbance, [λ^a (nm) (log ϵ)]	λ_{em}^a (nm)	Φ_{PL}^a	Redox (mV) ^b , $E_{1/2}$
Ir(ppy) ₃	283(4.86), 341(4.00), 375(4.09), 405(3.92), 4.56(3.44), 4.87(3.08)	512	0.40 ^c	700
Ir(dmppy) ₃	318(4.98), 379(4.52), 4.25(4.12), 455(3.80)	531	0.41	678

^a Measured in CH₂Cl₂ solution at ambient temperature with the concentration of 10^{−5} mol/L.

^b Measured in CH₂Cl₂ at a concentration of 10^{−3} M and scan rate was 80 mV s^{−1}, values are reported relative to Ag/AgCl, supporting electrolyte was 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate.

^c Ir(ppy)₃ used as the reference for Φ_{PL} .

as emitter instead of the new Ir-complex. All the measurements were carried out in air at room temperature.

3. Results and discussion

Fig. 2 shows the absorption spectra of the ligand dmppyH and the complex Ir(dmppy)₃, and the PL spectrum of the complex Ir(dmppy)₃ in CH₂Cl₂ solution.

The intense absorption band at 330 nm can be assigned to spin allowed ¹(π – π^*) transition, and the band at around 390 nm corresponded to spin-allowed *meta*-ligand charge transfer band (¹MLCT). Weak absorption at 460 nm was assigned to the formally spin-forbidden ³MLCT transition, similar to reported value of Ir(ppy)₃ [15].

The peak wavelength is sensitive not only to the property but also to the position of the substituent [8]. By changing the substituents and their position, the peak wavelength of phosphorescent emissions can be tuned. In this work, substitution of a electron-donating group (methoxyl) onto the 4-position of the phenyl ring seems to raise both the lowest unoccupied molecular orbital (LUMO) and HOMO levels [17] resulting in no change in the emission spectrum. However, incorporation of a weakly electron-withdrawing group (4-methoxyphenyl) [18] onto the 5-position of the pyridyl ring

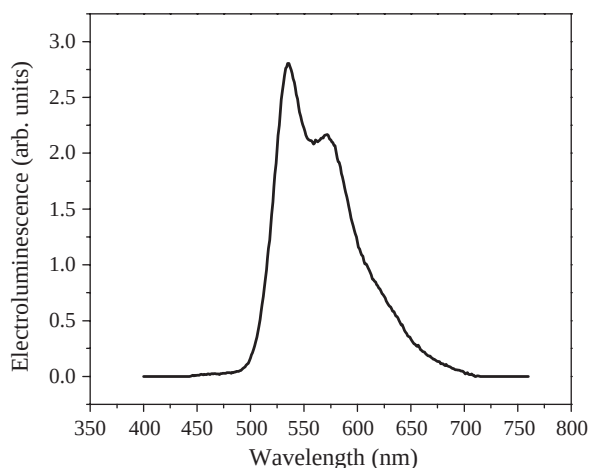


Fig. 3. The EL spectrum of the device ITO/NPB/Ir(dmppy)₃:CBP/BCP/Alq3/LiF/Al.

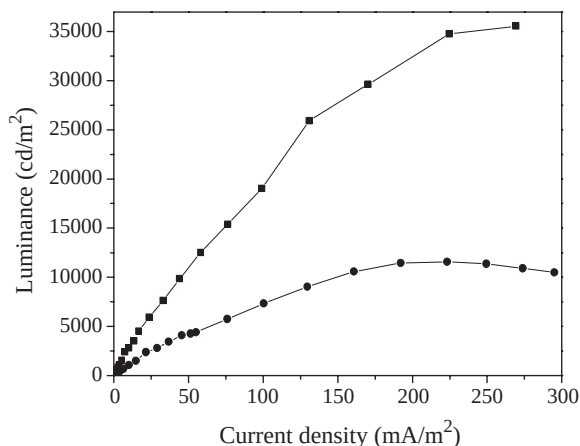


Fig. 4. Luminance versus current–density characteristics of Ir(ppy)₃- (●–), and Ir(dmppy)₃-doped (■–) devices.

lowered the LUMO level slightly, and hence a 20-nm red shifted was observed comparing to that of Ir(ppy)₃. The new Ir-complex exhibits intense green phosphorescence in CH₂Cl₂ solution, its PL quantum yield was 0.41 relative to Ir(ppy)₃ (Φ_{PL} =0.4 [19]). The photophysical and electrochemical data of Ir(dmppy)₃ are summarized in Table 1.

To investigate the electronic effects caused by the addition of methoxy and methoxyphenyl groups, cyclic voltammetry experiments were carried out for Ir(dmppy)₃ and Ir(ppy)₃. No reduction waves were measured in the complexes up to −3.0 V in our instrument and conditions; only the oxidation potentials were obtained, which can be attributed to the oxidation of the iridium (III). Incorporating electron-withdrawing group (such as 4-methoxyphenyl) on the phenylpyridine gives an increase in the oxidation potential, but introduction of strong electron-donating group (such as methoxy) into the ligand leads to a largely decreased value [20], so the Ir(dmppy)₃ containing the two groups shows slightly lower oxidative potential than Ir(ppy)₃, indicating the relative ease of oxidation.

The EL spectrum with a peak at 535 nm was shown in Fig. 3, corresponding to a green light emission, which is consistent with that of the PL. The *Commission Internationale de*

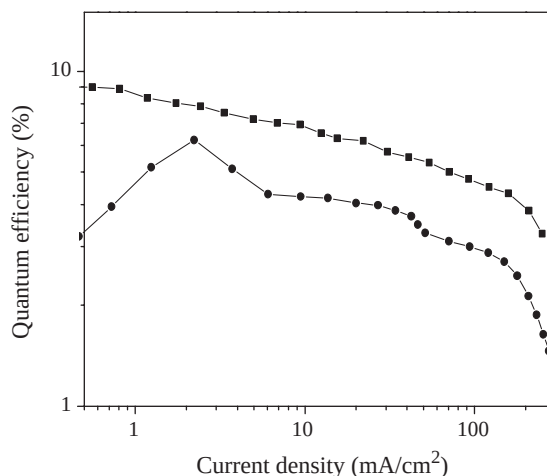


Fig. 5. External quantum efficiency versus current–density characteristics of Ir(ppy)₃- (●–), and Ir(dmppy)₃-doped (■–) devices.

L'Eclairage color coordinates were $x=0.36$, $y=0.62$, which were current density-independent. There are on characteristic emission peaks from CBP or Alq₃, indicating that the emission originates from the emissive layer.

The brightness of the devices at 20 mA/cm² are 5300 cd/m² and 2240 cd/m² for Ir(dmoppy)₃ and Ir(ppy)₃, respectively. The device based on Ir(dmoppy)₃ exhibits higher brightness, reaching the maximum luminance of 35 000 cd/m² at 270 mA/cm², see Fig. 4. The phosphorescent material Ir(dmoppy)₃ having a lower oxidation potential can serve as effective hole trap in OLEDs [21], resulting in the increase of driving voltage, so the turn-on voltage of Ir(dmoppy)₃-doped device was relatively higher than that of the device based on Ir(ppy)₃.

Fig. 5 shows the external quantum efficiency as the function of current density for the devices doped with Ir(dmoppy)₃ and Ir(ppy)₃. For Ir(dmoppy)₃-doped device, a maximum external quantum efficiency of 9.0% was obtained at 0.2 mA/cm². The device showed a gradual decrease of η_{ext} with increasing current density, which was attributed to triplet–triplet annihilation [22,23]. Nevertheless, at $J=1$, 10, 50 mA/cm², the device efficiency remained as high as 8.6%, 6.9%, and 5.5%, which is higher than the device based on Ir(ppy)₃ under the same conditions.

4. Conclusion

In conclusion, we synthesized a new iridium complex with 2,5-di(4-methoxyphenyl)-pyridine ligand. The device based on the Ir(dmoppy)₃ showed intense green emission with a peak wavelength of 535 nm; the maximum external quantum efficiency of 9.0% and luminance efficiency of 36 cd/A were achieved, which are higher than that of Ir(ppy)₃ under the same conditions. We believe the efficiency can be further enhanced by choosing a suitable host material or optimization of the device structure.

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