

Color Tuning Based on a Six-membered Chelated Iridium(III) Complex with Aza-aromatic Ligand

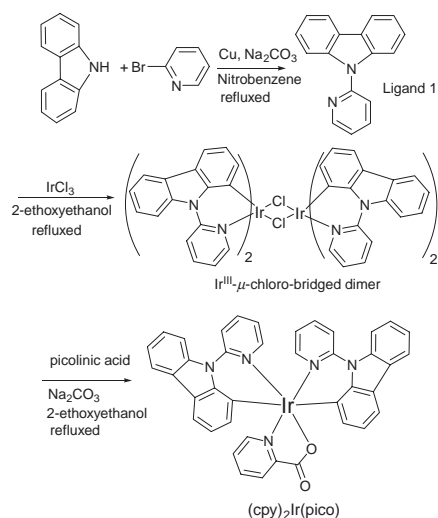
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(Received July 12, 2005; CL-050899)

A six-membered chelated iridium complex containing aza-aromatic ligand is prepared. Emission color tuning from yellow to deep red is observed for electroluminescent devices with different doping concentrations.

In the past few years, iridium(III) complexes as electrophosphorescent material were becoming increasingly important due to their high quantum yields of photoluminescence (PL) and electroluminescence (EL).¹ Most of the ligands reported in the iridium(III) complexes are based on the derivatives of *o*-pyridylarene, *o*-pyridylheterocycle, or 2-phenyloxazole.² Among them, phenylpyridine (ppy) structures (Figure 1a) are the most popular.¹ Recently, alkenylpyridines (Figure 1b) as organic ligands for phosphorescent iridium complexes were reported.^{2,3} All these iridium complexes were prepared in a five-membered chelated framework. Iridium complexes with six-membered chelated framework were rarely prepared.⁴ In this letter, a six-membered chelated iridium(III) complex containing aza-aromatic ligand as shown in Figure 1c is reported. The pyridine and carbazole units in the ligand are connected through a nitrogen atom. The conjugated electron pair on the nitrogen atom acts as a bridge and electron donor to form the π -type conjugation with the aryl groups. Thus, this molecule is also a conjugated structure like the alkenylpyridine ligand,⁵ which forms a six-membered chelated framework with metal center. This iridium complex possesses some interesting properties which are different from those of the common iridium complexes for organic light-emitting diodes (OLEDs).

The complex iridium(III) bis[2-(*N*-carbazolyl)pyridinato-*N,C*³] picolinate ((c_{py})₂Ir(pico)) was prepared according to the synthetic procedures shown in Scheme 1.⁶ Ligand 1 was prepared through the copper-catalyzed Ullmann reaction⁷ between carbazole and 2-bromopyridine. The Ir^{III}- μ -chloro-bridged dimer was prepared according to a similar procedure in the literature.^{4,8} Picolinic acid was chosen as the third ligand to produce the target complex. Although 2,4-pentanedione (Hacac) had also been tried as the third ligand, the precipitate possesses poor solubility in common solvents. The identification of the complex



Scheme 1. The synthetic route to (c_{py})₂Ir(pico).

was carried out by nuclear magnetic resonance (NMR) and MALDI-TOF mass spectroscopy.⁶ The MALDI-TOF mass spectroscopy shows a molecular ion peak at m/z 801, corresponding to [(c_{py})₂Ir(pico)]⁺, with fragment at m/z 679, corresponding to [(c_{py})₂Ir]⁺. The 5% decomposition temperature is at 360 °C under N₂ atmosphere.

Figure 2 displays the UV-vis absorption and emission spectra of the complex in the solid state and degassed CH₂Cl₂ solution (5×10^{-6} M). The complex possesses the similar absorption spectra in the solid state and solution. The strong absorption bands at ca. 300 nm ($\epsilon = 8.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) is assigned to the spin-allowed ¹ π - π^* transition of the cyclometallated aza-aromatic ligand. The next broad absorption bands around 360 nm ($\epsilon = 4.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) are ascribed to the contributions of the typical spin-allowed metal-to-ligand charge transfer ¹MLCT transition, the spin-forbidden ³MLCT transitions and the ³ π - π^* transitions. PL spectra of (c_{py})₂Ir(pico) was measured in degassed CH₂Cl₂ solution at room temperature giving very weak emission. Similarly, very weak emission was observed in other solvents. In sharp contrast, highly intense luminescence was obtained with λ_{max} at 538 nm in the recrystallized solid ($\Phi_{\text{PL}} = 5\%$), and the PL spectrum in CH₂Cl₂ solution shows redshift of about 10 nm, compared with that of the solid state. This solvent quenching phenomenon can be attributed to bipolar structure constructed with the electron-rich nitrogen atom and the electron-deficient metal center, so that rapid energy-transfer quenching, possibly incorporating internal conversion and solvent collision deactivation, takes places.⁹ Few iridium complexes for OLEDs show the similar solvent quenching effect.¹

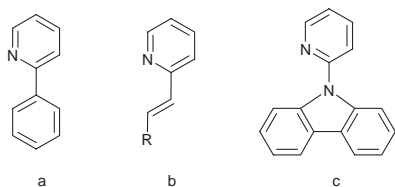


Figure 1. Ligands for the iridium complexes based on a) phenylpyridine ligand, b) alkenylpyridine ligand, and, c) aza-aromatic ligand.

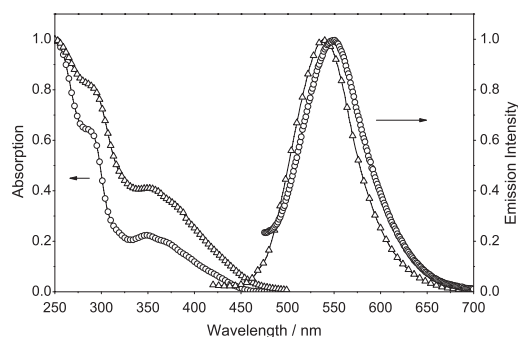


Figure 2. Normalized UV-vis absorption and PL spectra in the solid state (\square) and degassed CH_2Cl_2 (\circ) at room temperature. All spectra were normalized at their respective peak maximum.

Doped and undoped light-emitting devices based on the complex were fabricated.⁶ In device **A**, CBP was chosen as host with a doping concentration of 10 wt %. In device **B**, no host material was used. Figure 3 shows the EL spectra of the doped and undoped light-emitting devices at 12 V, together with the PL spectrum in the solid state. Compared with the PL spectrum, the EL spectrum of the undoped device **B** ($\lambda_{\text{max}} = 652 \text{ nm}$) has a significant red shift in electric field. In device **A**, by doping the complex to the CBP host, a significant blue shift occurs ($\lambda_{\text{max}} = 570 \text{ nm}$) compared with the undoped device **A**. These results may be referred to as the solid-state solvation effect (SSSE), which has been reported for other bipolar organic molecules in doped light-emitting devices.⁹ The conjugated electron pair on the nitrogen atom and metal center form a bipolar framework in the complex. By doping the polar complex into the triarylamine host, the local electric field in the film is changed. The intermolecular dipole-dipole interactions of host and guest result in these spectral shifts.^{9,10} Device **A** give a maximum brightness of 138 cd m^{-2} at $J = 282 \text{ mA cm}^{-2}$; and device **B** shows a maximum brightness of 2080 cd m^{-2} at $J = 445 \text{ mA cm}^{-2}$.

In conclusion, a six-membered chelated iridium complex containing aza-aromatic ligands is demonstrated. The complex possesses some different properties in comparison with the common iridium complexes for OLEDs. Significant solvent quench-

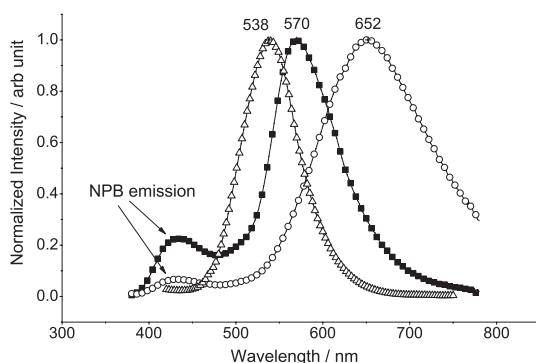


Figure 3. The PL spectrum in the solid state (\triangle) and electroluminescent spectra of device **A** (\blacksquare) and **B** (\circ) at 12 V: **A**. ITO/NPB (70 nm)/10 wt % complex in CBP (60 nm)/BCP (30 nm)/Mg-Ag (250 nm); **B**. ITO/NPB (30 nm)/complex without host (25 nm)/BCP (30 nm)/Mg-Ag (250 nm). All spectra were normalized at their respective peak maximum.

ing was observed for the complex. The devices based on the complex also possess solid-state solvation effect. Tuning of emission color is obtained with doped and undoped devices. Further study of photophysical properties and the optimization device based on the complex are under investigation.

This work was financially supported by the National Natural Science Foundation of China under Grants Nos. 60325412, 90406021, and 50428303 as well as the Shanghai Commission of Science and Technology under Grants Nos. 03DZ11016 and 04XD14002 and the Shanghai Commission of Education under Grant No. 2003SG03. RZh would also like to extend his gratitude to Fudan University and IAM for the 4th Graduate Creation Foundation (No. CQH2203001) and scholarships offered.

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