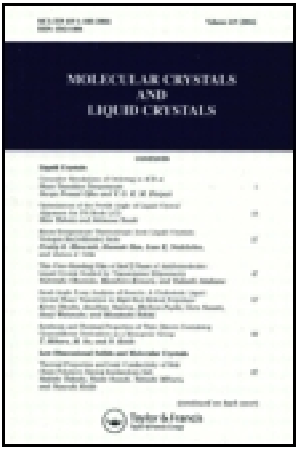

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Novel Green Phosphorescent Materials with Various Substituted Acetylacetonate Ligands for Organic Electroluminescent Device

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Version of record first published: 18 Oct 2010

To cite this article: Dong-Uk Kim, Seoung-Hey Paik, Sung-Hoon Kim, Yoon-Heung Tak, Yoon-Soo Han, Sang-Dae Kim, Ki-Dong Kim, Hui-Jin Ju, Hee-Wan Moon & Tae-Jeong Kim (2004): Novel Green Phosphorescent Materials with Various Substituted Acetylacetonate Ligands for Organic Electroluminescent Device, Molecular Crystals and Liquid Crystals, 424:1, 111-117

To link to this article: http://dx.doi.org/10.1080/15421400490505974

Mol. Cryst. Liq. Cryst., Vol. 424, pp. 111–117, 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490505974

NOVEL GREEN PHOSPHORESCENT MATERIALS WITH VARIOUS SUBSTITUTED ACETYLACETONATE LIGANDS FOR ORGANIC ELECTROLUMINESCENT DEVICE

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Novel green phosphorescent materials, IR-PPA1, IR-PPA2 and IR-PPA3 were synthesized as emission dopants for electroluminescent(EL) devices. Four kinds of devices were fabricated and the structures of devices were ITO/NPD/IR-PPA1(6%), IR-PPA2(6%), IR-PPA3(6%) or IR-PPY(6%) in CBP/BCP/Alq/LiF/Al, where IR-PPY was used as a reference material for comparison. Novel phosphorescent materials, IR-PPA1, IR-PPA2 and IR-PPA3 represented the luminances of 3930 cd/m^2, 3220 cd/m^2 and 2620 cd/m^2, and their external quantum efficiencies, about 9.4%, 7.8% and 6.4% in 11 mA/cm^2

Received 1 October 2003; accepted 19 January 2004.

This work was supported by grant No. R05-2000-000-00071-0 (2002) from the Basic Research Program of the Korea Science & Engineering Foundation.

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of current density in the EL devices, respectively. The maximum of EL spectra of novel emission dopants were detected at 532 nm in the IR-PPA1 device, and 525 nm in the IR-PPA2 device and 530 nm in the IR-PPA3 device.

Keywords: electroluminescent device; green phosphorescent; iridium complex

INTRODUCTION

A lot of studies have been conducted for commercial application of full color electroluminescent (EL) display since Kodak's study in 1987 [1–3]. Especially, recently phosphorescent materials for EL devices have been studies on improving EL efficiencies [4]. The strong spin-orbital coupling of the heavy metals can lead to high efficiency phosphorescence in EL devices. This study was focused on developing novel green phosphorescent materials for the EL devices. IR-PPY material has been known as an excellent green phosphorescent material for an emission layer in EL device. Based on this molecular structure, we designed novel green phosphorescent materials. These materials were composed by an iridium as a metal and two phenylpyridine and one 2,4-pentandione derivatives such as 3-methyl-2, 4-pentanedione, 2-acetylcyclopentanone and 2-acetylcyclohexanone as organic ligands. The molecular structures of these materials revealed in Figure 1. As the IR-PPY material, these phosphorescent materials are expected to exhibit high emitting efficiency due to using emission from both singlet and triplet excited states through the iridium as a heavy metal atom. In this paper the syntheses of IR-PPA1, IR-PPA2 and IR-PPA3 as well as their emission characteristics will be described through the comparative studies with IR-PPY.

EXPERIMENTAL

Syntheses of IR-PPA1, IR-PPA2 and IR-PPA3

Synthesis of [(ppy)$_2$IrCl]$_2$. A mixture of $Na_3IrCl_6 \cdot xH_2O$ (47.4 mg, 0.10 mmol) and 2-phenylpyridine (32.6 mg, 0.21 mmol) in 2-ethoxyethanol (5 ml) was stirred under reflux for 16 h. After cooling the reaction mixture to room temperature, the yellow precipitate was filtered off and washed with water, followed by two portions of ethanol (5 ml). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.22 (d, 4H), 7.84 (d, 4H), 7.71 (t, 4H), 7.46 (d, 4H), 6.73 (dd, 8H), 6.53 (t, 8H), 5.91 (t, 8H).

Synthesis of IR-PPA1. A mixture of [(ppy)$_2$IrCl]$_2$ (83.6 mg, 0.078 mmol), 3-methyl-2,4-pentanedione (22.8 mg, 0.2 mmol) and potassium carbonate (82.9 mg, 0.6 mmol) in 2-ethoxyethanol (5 ml) was stirred under reflux for 1 h. After cooling the reaction mixture to room temperature,

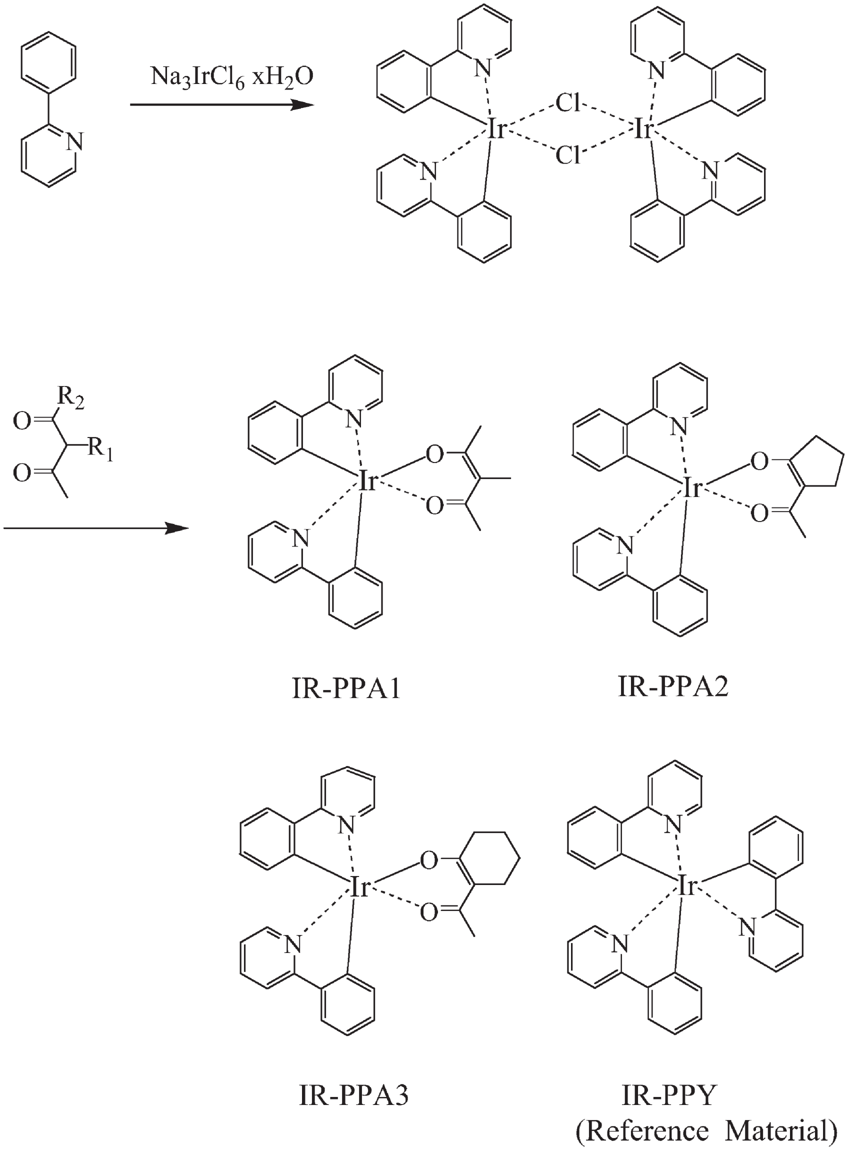

FIGURE 1 Synthetic route, and molecular structures of IR-PPA1, IR-PPA2, IR-PPA3 and IR-PPY.

the yellow precipitate was filtered off and washed with water, followed by two portions of methanol (5 ml). The crude product was chromatographed on silicagel with a dichloromethan as an eluent to give a yellow solid

(81.3 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (d, 2H), 7.85 (d, 2H), 7.51 (t, 2H), 7.54 (d, 2H), 7.13 (t, 2H), 6.80 (t, 2H), 6.68 (t, 2H), 6.26 (d, 2H), 2.17(s, 3H), 1.78 (s, 6H). MS (EI, m/z): Calcd for $C_{28}H_{25}IrN_2O_2$: 613.73. Found: 614.25

Synthesis of R-PPA2. The title compound was prepared in the same manner as described above for IR-PPA1 by simply replacing monoanionic ligand with 2-acetylcyclopentanone (25.2 mg, 0.2 mmol). Usual work-ups followed by filteration and the crude product was chromatographed on silica gel with a dichloromethan as an eluent to give a yellow solid (71.3 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (m, 2H), 7.83 (m, 2H), 7.60 (m, 2H), 7.52 (m, 2H), 7.11 (m, 2H), 6.78 (m, 2H), 6.69 (m, 2H), 6.25 (m, 2H), 2.64 (t, 2H, J = 7.2 Hz), 2.14 (m, 2H), 1.83 (s, 3H), 1.74 (m, 2H). MS (EI, m/z): Calcd for $C_{29}H_{25}IrN_2O_2$: 625.74. Found: 626.00

Synthesis of IR-PPA3. The title compound was prepared in the same manner as described above for IR-PPA1 by simply replacing monoanionic ligand with 2-acetylcyclohexanone (28.0 mg, 0.2 mmol). Usual work-ups followed by filteration and the crude product was chromatographed on silicagel with a dichloromethan as an eluent to give a yellow solid (90.0 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (m, 2H), 7.83 (m, 2H), 7.60 (m, 2H), 7.52 (m, 2H), 7.11 (m, 2H), 6.78 (m, 2H), 6.69 (m, 2H), 6.25 (m, 2H), 2.37 (m, 2H), 2.17 (m, 2H), 1.87 (s, 3H), 1.60 (m, 4H). MS (EI, m/z): Calcd for $C_{30}H_{27}IrN_2O_2$: 639.76. Found: 640.00

FABRICATION OF DEVICE

Organic layers and a metal electrode were formed by conventional vacuum-vapor deposition method on the ITO coated glass. 4,4′ -bis[*N*-(1-napthyl)-*N*-phenyl-amino] biphenyl (NPD) and LiF were adopted as a hole injection layer and an electron injection layer. NPD, 2,9-dimethyl-4,7-diphenyl-1, 10-phenanthroline (BCP) and tris-(8-hydroxyquinoline) aluminum (Alq_3) were used for the hole injection layer, the hole blocking layer and the electron injection layer, respectively. 6% IR-PPA1, 6% IR-PPA2 or 6% IR-PPA3 in 4,4′ -N,N′ -dicarbazole-biphenyl (CBP) host matrix as the emitting layer was made by co-deposition method, where the IR-PPA dopant was adopted for comparison with IR-PPA1, IR-PPA2 and IR-PPA3. Indium Tin Oxide (ITO) was used for an anode electrode and aluminum (Al) as a cathode electrode. Four types of devices were fabricated: (a) the device with IR-PPA1 (IR-PPA1 device), ITO/NPD/IR-PPA1(6%) in CBP/BCP/Alq/LiF/Al; (b) the device with IR-PPA2 (IR-PPA2 device), ITO/NPD/IR-PPA2(6%) in CBP/BCP/Alq/LiF/Al; (c) the device with IR-PPA3 (IR-PPA3 device), ITO/NPD/IR-PPA3(6%) in CBP/BCP/Alq/LiF/Al. (d) the device with

IR-PPY (IR-PPY device), ITO/NPD/IR-PPY(6%) in CBP/BCP/Alq/LiF/Al. The thicknesses of layers in EL devices was ITO/NPD(45 nm)/IR-PPA1 (6%), IR-PPA2(6%), IR-PPA3(6%) or IR-PPY(6%) in CBP(30 nm)/BCP (10 nm)/Alq(40 nm)/LiF(1 nm)/Al(150 nm).

RESULT AND DISCUSSION

Novel three phosphorescent materials, IR-PPA1, IR-PPA2 and IR-PPA3 were synthesized according to the methods illustrated in Figure 1. Their molecular structures were identified through spectroscopic techniques such as NMR spectroscopy and MS spectrometry.

Four kinds of devices with IR-PPA1, IR-PPA2, IR-PPA3 and IR-PPY were fabricated and their layer structures and thickness were precisely controlled to compare each other. Current densities of 11 mA/ cm^2 were measured at voltages of 7.54, 6.24, 7.34 and 8.35 with devices of IR-PPA1, IR-PPA2, IR-PPA3 and IR-PPY, respectively. In Figure 2 the luminances of 3930 cd/m^2 and 3220 cd/m^2 and 2620 cd/m^2 at 11 mA/cm^2 were observed in IR-PPA1, IR-PPA2 and IR-PPA3 devices, respectively, while the IR-PPY case was 2250 cd/m^2 at the same current density. This means that the luminances of IR-PPA1, IR-PPA2 and IR-PPA3 are not less than that of IR-PPY, and the novel pentandione derivatives as ligands for heavy-metal complexes play excellent roles in EL devices. The current density-external quantum efficiency characteristics demonstrated in Figure 3. External quantum efficiencies in four kinds of devices exhibit slow decreases with

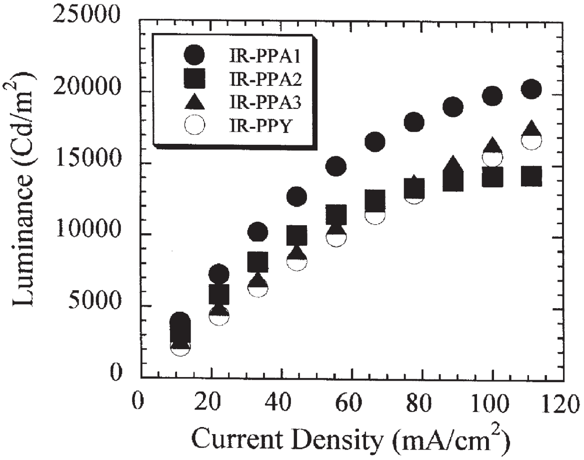

FIGURE 2 Luminance and current density characteristics in IR-PPA1, IR-PPA2, IR-PPA3 and IR-PPY device.

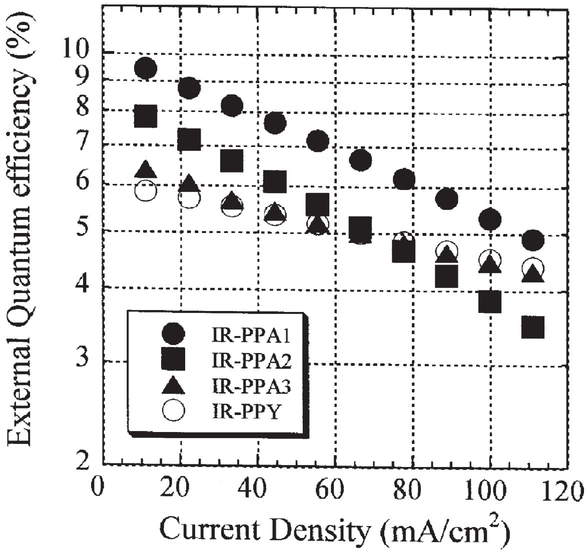

FIGURE 3 External quantum efficiency and current density characteristics in IR-PPA1, IR-PPA2, IR-PPA3 and IR-PPY device.

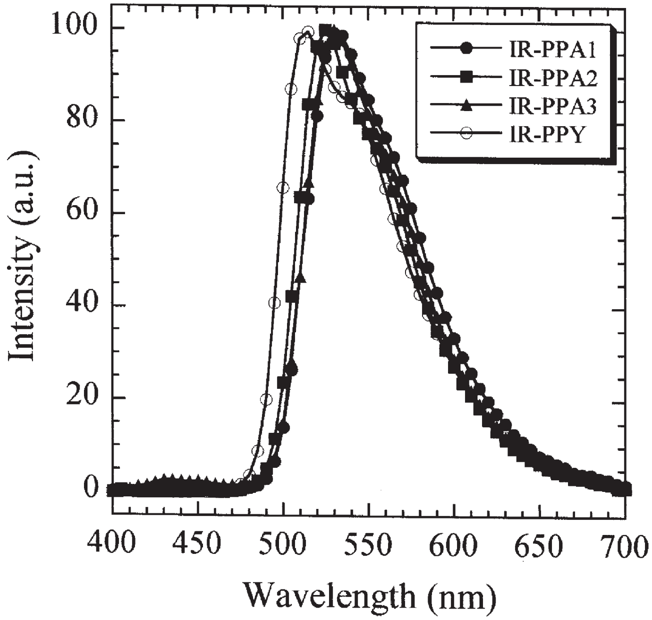

FIGURE 4 EL spectra of IR-PPA1, IR-PPA2, IR-PPA3 and IR-PPY device.

increasing current. In the same current density of 11 mA/cm^2, the external quantum efficiencies of IR-PPA1, IR-PPA2, IR-PPA3 and IR-PPY devices are 9.4%, 7.8%, 6.4% and 5.8%, respectively. These higher quantum efficiencies of the devices with IR-PPA1, IR-PPA2 and IR-PPA3 may be due to minimizing the quenching of triplet excitons through the substitution of 2,4-pentandion derivatives instead of a phenylpyridine ligand of IR-PPY. The maximum intensities of EL spectra were detected at 532 nm (IR-PPA1), 525 nm (IR-PPA2), 530 nm (IR-PPA3) and 514 nm (IR-PPY), which showed in Figure 4. CIE (Commision Internationalde I'Eclairage) coordinates show $x = 0.37$, $y = 0.60$ (IR-PPA1), $x = 0.34$, $y = 0.62$ (IR-PPA2) and $x = 0.35$, $y = 0.60$ (IR-PPA3), while the IR-PPY reveals the coordinate, $x = 0.32$, $y = 0.61$. The EL spectra of IR-PPA1, IR-PPA2 and IR-PPA3 are estimated as somewhat red shift than that of IR-PPY.

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