

## Coumarin-Based, Electron-Trapping Iridium Complexes as Highly Efficient and Stable Phosphorescent Emitters for Organic Light-Emitting Diodes

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Received November 10, 2009

A new class of coumarin-based iridium tris-cyclometalated complexes has been developed. These complexes are highly emissive, with emission colors ranging from green to orange-red. Besides modification of ligand structures, color tuning was realized by incorporation of ligands with different electrochemical properties in a heteroleptic structure. The organic light-emitting diodes (OLEDs) using these compounds as emissive dopants are highly efficient and stable. Unlike other Ir(III) phosphorescent dopants, these coumarin-based Ir(III) dopants can effectively trap and transport electrons in the emissive layer.

During the last two decades, luminescent Ir(III) complexes with extended  $\pi$ -systems have generated enormous interest because of their potential use in a variety of photonic applications, including photocatalysis,<sup>1</sup> photoelectrochemistry,<sup>2</sup> biological labeling,<sup>3</sup> and electroluminescence (EL).<sup>4</sup> One type of device that exploits the triplet-based emitting properties of cyclometalated Ir(III) complexes is the organic light-emitting diode (OLED). By employing triplet-based emitting materials where both singlet and triplet excitons participate, the internal quantum efficiency of OLEDs can reach as high as 100%.<sup>5</sup>

The most commonly used class of OLED phosphorescent emitters is the tris-cyclometalated iridium(III) complexes, utilizing the strong spin–orbital coupling of Ir to give efficient triplet emission. Concerning practical applications such as flat panel displays, tuning of the emission color to cover the entire visible spectrum is very desirable. Coumarin

dyes are efficient laser dyes fluorescing in the blue-green spectral region. Because of the synthetic possibilities of a large variety of coumarin derivatives, which would help realize easy tuning of energy gaps of the corresponding Ir complexes, the class of coumarin ligands seems to be a promising candidate for the preparation of organoiridium(III) complexes for a variety of photonic applications. We report herein on the development of highly emissive tris-cyclometalated iridium(III) complexes having electron-deficient coumarin or its aza-analogue structure in their ligands. Their electrochemical and photophysical properties and the application of these complexes as emissive dopants in OLEDs are presented.

The six cyclometalating ligands investigated in this work are listed in Figure 1. The four coumarin derivatives, 3-(2-pyridinyl)coumarin (*pc*), 6H-[2]benzopyrano[4,3-*b*]pyridin-6-one (*bppo*), *para*-fluoro-6H-[2]benzopyrano[4,3-*b*]pyridin-6-one (*f-bppo*), and 6H-[2]benzopyrano[4,3-*c*]isoquinolin-6-one (*bpio*) were prepared following literature procedures.<sup>6</sup> Subsequent treatment of these C<sup>^</sup>N cyclometalating ligands with IrCl<sub>3</sub>·*n*H<sub>2</sub>O in a refluxing ethoxyethanol:water mixture (3:1 in volume) afforded the respective chloride-bridged iridium dimers [Ir(C<sup>^</sup>N)<sub>2</sub>Cl]<sub>2</sub>. The anticipated homoleptic and heteroleptic Ir(III) tris-cyclometalated complexes (Ir(*ppy*)<sub>2</sub>*pc*, Ir(*pc*)<sub>2</sub>*ppy*, Ir(*ppy*)<sub>2</sub>*bppo*, Ir(*bppo*)<sub>2</sub>*ppy*, Ir(*bppo*)<sub>3</sub>, Ir(*f-bppo*)<sub>3</sub>, Ir(*pc*)<sub>2</sub>*piq*, and Ir(*piq*)<sub>2</sub>*bpio*) were then prepared from reactions involving these chloride-bridged dimers and the designated H(C<sup>^</sup>N) ligands (Supporting Information).

Tris iridium d<sup>6</sup> complexes with asymmetric cyclometalating ligands such as 2-phenylpyridine (*ppy*) can have either a facial (*fac*) or a meridional (*mer*) configuration. The meridional isomers usually show markedly different spectroscopic properties than do the facial forms, such as broad, red-shifted emission, lower quantum efficiencies and poor optical stability. Therefore, the facial forms are usually desired for photonic applications. The facial isomers comprising coumarin ligands *bppo* and *bpio* can be prepared directly in alcoholic solvents at elevated temperatures (> 180 °C). In the case of Ir(*ppy*)<sub>2</sub>*pc* and Ir(*pc*)<sub>2</sub>*ppy*, however, decomposition occurred under similar conditions, likely due to the instability

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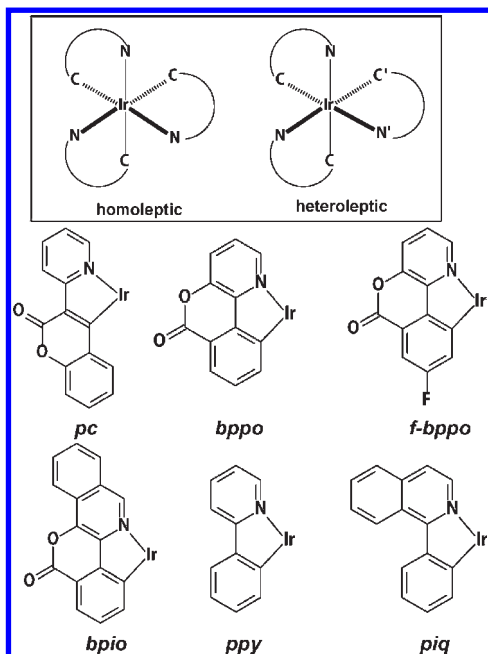
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**Figure 1.** Cyclometalating ligands used to prepare the Ir(III) complexes. Abbreviations used throughout the paper are listed below the C<sup>∧</sup>N fragments.

of ligand *pc* and its bis-cyclometalated Ir derivatives in alcoholic solvents at high temperatures. In order to obtain the facial isomers of Ir(*ppy*)<sub>2</sub>*pc* and Ir(*pc*)<sub>2</sub>*ppy*, their corresponding meridional isomers were first prepared at 120 °C. The meridional isomers were then converted to their facial counterparts by either sealing a sample of the isolated meridional isomer into a small ampule under high vacuum and placing the ampule in an oven with the temperature set above 300 °C for 12–16 h or refluxing a slurry of the *mer*-isomer in sulfonane for several hours.

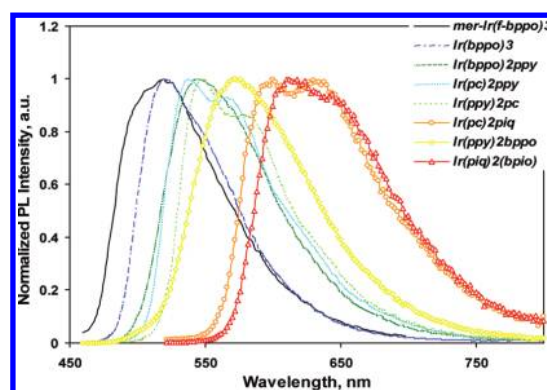
All eight compounds are air stable and sublime cleanly. The C<sub>3</sub> symmetry of *fac*-Ir(*bppo*)<sub>3</sub> is readily apparent from the very simple <sup>1</sup>H NMR spectrum, which displays only six resonances. However, Ir(*f-bppo*)<sub>3</sub> formed under the same reaction condition as *fac*-Ir(*bppo*)<sub>3</sub> has the meridional isomer as the principal product, indicating that a large kinetic barrier needs to be overcome to isomerize. The experimental result is consistent with the report that fluorinated ligands tend to favor meridional isomer formation even at elevated temperatures.<sup>7</sup> Efforts were made to convert *mer*-Ir(*bppo*)<sub>3</sub> to its facial form photochemically, and nearly complete conversion (> 95%) was observed under UV irradiation in less than 3 h.

The electrochemical properties of the eight tris-cyclometalated Ir (III) complexes were examined using cyclic voltammetry. A summary of the redox potentials, measured relative to the saturated calomel electrode (SCE), is listed in Table 1. The redox potentials of Ir(*ppy*)<sub>3</sub>, a commonly used phosphorescent dopant in OLEDs, are also included for comparison. All compounds showed a reversible one-electron oxidation process, with potentials of 0.9–1.4 V vs SCE, which can be assigned to the metal-centered oxidation. Multiple reversible, ligand-centered, one-electron reduction processes in the range of –1.6 to –1.9 V were also observed. Electrochemical analysis shows that the reduction and oxidation of

**Table 1.** Electrochemical<sup>a</sup> and Photophysical<sup>b</sup> Properties of the Coumarin-Based Ir Complexes and Ir(*ppy*)<sub>3</sub>

compound	1st oxidation potential (V vs SCE)	1st reduction potential (V vs SCE)	λ <sub>max</sub> (nm)	Φ <sub>PL</sub>
Ir( <i>ppy</i> ) <sub>2</sub> <i>pc</i>	1.06	–1.83	550	0.97
Ir( <i>pc</i> ) <sub>2</sub> <i>ppy</i>	1.33	–1.65	536	0.81
Ir( <i>ppy</i> ) <sub>2</sub> <i>bppo</i>	0.93	–1.79	570	0.82
Ir( <i>bppo</i> ) <sub>2</sub> <i>ppy</i>	1.09	–1.72	544	0.96
Ir( <i>bppo</i> ) <sub>3</sub>	1.23	–1.66	518	1.09
<i>mer</i> -Ir( <i>f-bppo</i> ) <sub>3</sub>	1.35	–1.60	520	0.76
Ir( <i>pc</i> ) <sub>2</sub> <i>piq</i>	1.08	–1.68	600	0.53
Ir( <i>piq</i> ) <sub>2</sub> <i>bpio</i>	0.92	–1.75	615	0.53
Ir( <i>ppy</i> ) <sub>3</sub>	0.75	–2.32	510	1

<sup>a</sup> Determined in 50%/50% v/v acetonitrile/toluene; scan rate 100 mV S<sup>–1</sup>; tetrabutylammonium hexafluorophosphate as supporting electrolyte; all electrochemical processes are reversible. <sup>b</sup> Measured in degassed dichloromethane solution at room temperature; all Φ<sub>PL</sub>'s are reported relative to Ir(*ppy*)<sub>3</sub>.



**Figure 2.** Photoluminescence spectra of coumarin-based Ir complexes (room temperature, degassed dichloromethane solution).

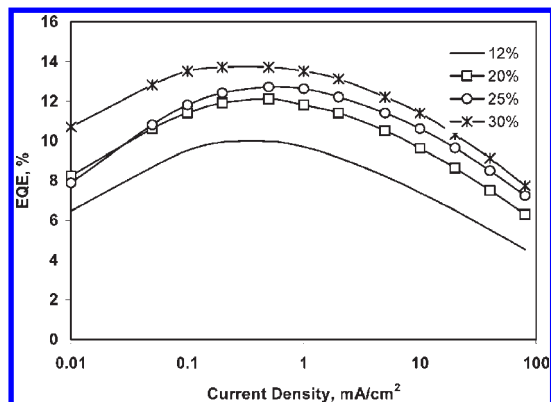
the coumarin-based Ir compounds occur at significantly less negative and more positive potentials, respectively, than are found for typical tris Ir(III) cyclometalated complexes used as phosphorescent emitters in OLEDs.<sup>7,8</sup> For example, the reduction and oxidation potentials of Ir(*bppo*)<sub>3</sub> are both shifted to more positive values by about 700 mV and 500 mV, respectively, relative to potentials found for Ir(*ppy*)<sub>3</sub>. The unique redox properties observed from this new class of Ir complexes are believed to result from the strong electron-withdrawing abilities of the coumarins, which suggest that these complexes may be mainly electron-trapping instead of hole-trapping when used as phosphorescent dopants in conventional OLED architectures, for example, in carbazole-based hosts.<sup>9</sup>

All eight coumarin-based Ir (III) compounds show strong luminescence. Their room-temperature solution (solvent: dichloromethane) quantum yields were measured relative to Ir(*ppy*)<sub>3</sub> [ $\phi_{\text{phos}}(\text{fac-Ir}(\text{ppy})_3) = 1.0$ ] and compiled in Table 1, together with the emission maxima. The emission spectra are shown in Figure 2. The emission colors given by these Ir complexes range from green to orange-red.

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**Figure 3.** EQEs as a function of current density and dopant concentration for devices having a light-emitting layer consisting of NPB doped with  $\text{Ir}(\text{ppy})_2\text{pc}$ .

The main approach employed herein to tune the emission energy of the Ir complexes has been incorporation of cyclometalating ligands with different electrochemical properties into one heteroleptic structure. For example, according to the DFT calculations, ligands *ppy* and *bppo* have similar triplet energies of 2.91 and 2.89 eV, respectively. Because the emission energy of homoleptic tris-cyclometalated Ir complexes is well correlated with the triplet energy of the cyclometalating ligand ( $C^{\wedge}N$ ),  $\text{Ir}(\text{ppy})_3$  and  $\text{Ir}(\text{bppo})_3$  have similar triplet energies, with their emission profiles positioned very closely to each other. However, the electrochemical data indicate that the HOMO and LUMO energies of  $\text{Ir}(\text{bppo})_3$  are 0.48 and 0.66 eV lower, respectively, than those of  $\text{Ir}(\text{ppy})_3$ , reflecting the strong  $\pi$ -electron-deficient character of the *bppo* ligand relative to the *ppy* ligand. To examine the effectiveness of ligand mixing on tuning the photophysical properties of the Ir complexes, one *bppo* ligand in  $\text{Ir}(\text{bppo})_3$  was replaced with *ppy* in  $\text{Ir}(\text{bppo})_2\text{ppy}$ , and a bathochromic shift of the  $\lambda_{\text{max}}$  from 518 to 544 nm was observed. When two *bppo* ligands in  $\text{Ir}(\text{bppo})_3$  were replaced by *ppy* in  $\text{Ir}(\text{ppy})_2\text{bppo}$ , further red-shifting of the emission to 560 nm occurred. This red shift with increasing number of *ppy* ligands was also accompanied by pronounced increases in the HOMO energies and relatively small increases in the LUMO energies. However, replacement of the final *bppo* ligand in  $\text{Ir}(\text{ppy})_2\text{bppo}$  with a *ppy* ligand to make  $\text{Ir}(\text{ppy})_3$  introduced a very strong blue shift in the emission energy rather than an additional red shift. These observations are explained by the DFT calculations that show that the HOMOs of these Ir complexes are principally composed of a mixture of the metal *d* orbitals with the phenyl  $\pi$  orbitals of the most electron-donating ligand, while the LUMOs mainly reside on the most electron-withdrawing ligand. Therefore, replacement of the strongly electron-withdrawing *bppo* with *ppy* in the heteroleptic complex significantly raises the HOMO energy but has a less pronounced effect on the LUMO energy, consequently leading to a decreased HOMO–LUMO gap and the resulting red shift in the emission energy. Replacement of the final *bppo* ligand with a *ppy*

ligand in  $\text{Ir}(\text{ppy})_3$  means the LUMO shifts from being on a *bppo* ligand to the much higher-energy LUMO on a *ppy* ligand, causing an increase in the HOMO–LUMO gap and the observed strong blue shift.

The OLEDs fabricated using these coumarin-based Ir(III) complexes as emissive dopants are highly efficient and stable. For example, with dopants  $\text{Ir}(\text{ppy})_2\text{pc}$ ,  $\text{Ir}(\text{pc})_2\text{ppy}$ ,  $\text{Ir}(\text{ppy})_2\text{bppo}$ , and  $\text{Ir}(\text{bppo})_2\text{ppy}$ , external quantum efficiency (EQE) as high as ~20–21%, and power efficacy above 45 lm/W can be realized at current density of 1  $\text{mA}/\text{cm}^2$  (Supporting Information). To investigate the electron-trapping/transporting ability of these coumarin-based Ir dopants in the emissive layer, a series of devices was fabricated in which the light emitting layer consists of the hole transporting host NPB (*N,N'*-di(naphthalen-1-yl)-*N,N'*-diphenylbenzidine) doped with  $\text{Ir}(\text{ppy})_2\text{pc}$ , where the  $\text{Ir}(\text{ppy})_2\text{pc}$  concentration was varied from 12% to 30%. The device structure was ITO |  $\text{CF}_x$  | HAT-CN (10 nm) | TAPC (85 nm) | NPB (10 nm) | NPB + *x* %  $\text{Ir}(\text{ppy})_2\text{pc}$  (20 nm) | SBFK (10 nm) | PADN (65 nm) | Bphen (10 nm) | LiF (0.5 nm) | Al (100 nm). (HAT-CN: 2,3,6,7,10,11-hexacyano-1,4,5,8,9,12-hexaazatriphenylene; TAPC: 1,1-bis-(4-bis(4-methylphenyl)-aminophenyl)-cyclohexane; SBFK: bis(9,9'-spirobifluorene-2-yl) ketone; PADN: 2-phenyl-9,10-di(2-naphthyl)anthracene; Bphen: 4,7-diphenyl-1,10-phenanthroline) (Supporting Information). In this set of devices, a steady increase of the EQE was observed, even at a very high  $\text{Ir}(\text{ppy})_2\text{pc}$  concentration of 30% (Figure 3). This observation contrasts with what is typically observed in phosphorescent OLEDs, where EQE loss often occurs when the dopant concentration surpasses 10% due to triplet–triplet annihilation. The EQE increase from 9.7% to 13.5%, as the  $\text{Ir}(\text{ppy})_2\text{pc}$  concentration increases from 12% to 30%, may suggest that part of the EQE improvement was brought about by improved charge balance in the emissive layer, thanks to the presence of a large amount of electron-transporting  $\text{Ir}(\text{ppy})_2\text{pc}$ , and this gain in EQE more than cancels out the EQE loss resulting from concentration quenching.

In conclusion, a new class of coumarin-based tris-cyclometalated iridium complexes has been developed. Besides modification of ligand structures, incorporation of ligands with different electrochemical properties in a heteroleptic structure has been demonstrated to be an effective tool for emission color tuning. The OLEDs based on these complexes are highly efficient and stable. The unique electron-trapping/transporting property of this dopant class could lead to novel device structure design in future OLED research.

**Acknowledgment.** The authors thank Drs. S. Huo, R. H. Young, J. C. Deaton, and D. Y. Kondakov for helpful discussions.

**Supporting Information Available:** Experimental and supporting results. This material is available free of charge via the Internet at <http://pubs.acs.org>.