

# Synthesis, characterization, photophysical and electrochemical properties of new phosphorescent dopants for OLEDs

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## Abstract

New heteroleptic iridium(III) complexes of 2-(*p*-substituted-phenyl)-pyridine were synthesized and characterized. These complexes have two cyclometalated ligands ( $C^{\wedge}N$ ) and a bidentate ancillary ligand (LX), that is,  $(C^{\wedge}N)_2Ir(LX)$ . LX was either acetylacetonate or 5-nitro-8-hydroxy quinolate. Substitution on the *p*-phenyl of  $C^{\wedge}N$  ligands was used to alter the electronic properties of these complexes. The  $(C^{\wedge}N)_2Ir(acac)$  complexes show phosphorescence with good quantum yields and microsecond lifetimes and also show photoluminescence over a wide visible range ( $\lambda_{max} = 503\text{--}620\text{ nm}$ ). The HOMO level and triplet energy level of these complexes were also determined. These data indicate their potential use as emitting materials for organic light emitting diodes, OLEDs.

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Organic light emitting devices (OLEDs) have become very attractive mainly due to their potential use in flat panel displays,<sup>1,2</sup> and for oxygen sensing purposes.<sup>3</sup> Heavy metal complexes, particularly those containing Pt and Ir have attracted considerable attention as they can induce inter system crossing by strong spin–orbit coupling, leading to mixing of the singlet and triplet excited states.<sup>4</sup> The spin forbidden nature of radiative relaxation becomes allowed in heavy metal complexes, and hence results in high phosphorescence efficiency. Homoleptic and heteroleptic iridium(III) complexes have been studied extensively resulting in improved materials for device purposes.<sup>5,6</sup> OLEDs prepared with Ir(III) complexes as dopants are the most efficient OLEDs reported having nearly 100% internal phosphorescence efficiency.<sup>7</sup>

For practical applications such as display technology, tuning of emission in the visible spectrum is required. A powerful color tuning has been obtained by employing different cyclometalating ligands ( $C^{\wedge}N$ ) in Ir(III) complexes.<sup>8,9</sup> Structural change or chemical modification of

the cyclometalating ligand should alter the phosphorescent properties of the iridium(III) complexes. Alternatively, heteroleptic Ir(III) complexes having ancillary ligands such as acetylacetonate, and picolinate were synthesized.<sup>10</sup> The emission properties in most of the heteroleptic complexes are still dominated by cyclometalating ligands. Also, the electron-donating or electron-withdrawing character of the ancillary ligand in heteroleptic complexes can be used as a tool to increase or decrease the electron density on the metal center which subsequently will affect the emission and the lifetime of the excited state.

In the literature, several structurally different cyclometalating ligands, namely, 2-phenylpyridine, 2-thienylpyridine, 2-quinolinylypyridine, 2-benzothienylpyridine were used to achieve wide range emission of Ir(III) complexes.<sup>9</sup> Iridium(III) complex of 2-phenylpyridine, that is,  $Ir(ppy)_2(acac)$  has been studied extensively.<sup>5</sup> In this project, we aimed to tune a wide range of emission by very simple chemical modification of the 2-phenylpyridine ligand in Ir(III) complexes. Herein, we report the synthesis, characterization, photophysical, and electrochemical properties of iridium(III) complexes **1–4** of 2-(*p*-methoxy/acetyl-phenyl)-pyridine having acetylacetonate or 5-nitro-8-hydroxy-quinolate as the ancillary ligand. These easily achieved

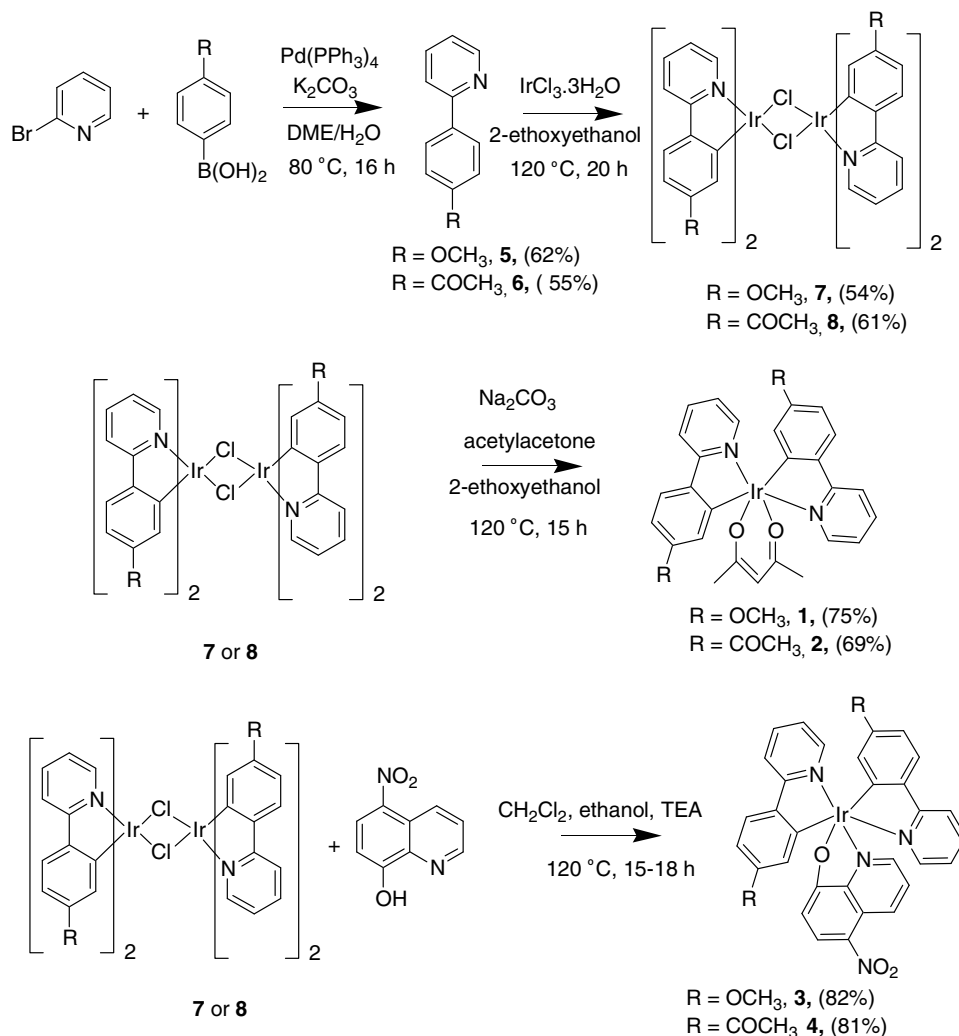
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modifications of the ligands alter the photophysical and electrochemical properties of Ir(III) complexes. Electrochemical study of **1–4** shows the effect of different ligands on the  $E_{\text{HOMO}}$  and triplet energy levels.

Ir(III) complexes **1–4** were synthesized as outlined in Scheme 1. New cyclometalated ligands were synthesized by Suzuki–Miyaura coupling<sup>11</sup> of 2-bromopyridine and aryl boronic acids catalyzed by  $\text{Pd}(\text{PPh}_3)_4$  in a biphasic aqueous solution of  $\text{K}_2\text{CO}_3$  and DME. Reflux of the reaction mixture at 80 °C for 16 h and purification of the crude product by column chromatography gave pure ligands, **5–6**, in good yields. Cyclometalating ligands **5–6** were used to prepare the  $\mu$ -chloro bridged precursors **7–8**. A solution of **5** or **6** (2.3 equiv) and iridium chloride (1.0 equiv) in 2-ethoxyethanol was refluxed for 20 h at 120 °C. The solvent was evaporated, and the solid residue was washed several times with methanol to afford pure **7–8**. Iridium(III) complexes **1** and **2** were prepared by allowing **7** or **8** to react with acetylacetonate in 2-ethoxyethanol at 120 °C for 15–18 h. The solvent was evaporated by vacuum distillation and the crude product was washed four times with methanol to afford **1** (yellow solid) and **2** (orange solid) in 75%

and 69% yields, respectively. Complexes **3–4** were synthesized using a recently reported synthetic method.<sup>12</sup>  $\mu$ -Chloro bridged **7** or **8** and 5-nitro-8-hydroxyquinoline were refluxed in a mixture of dichloromethane, ethanol, and triethylamine at 80 °C for 16–20 h under a nitrogen atmosphere. The evaporation of the solvent followed by washing with ethanol afforded pure **3–4** as orange solids in ~80% yield. Compounds **1–8** were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and ES-MS techniques.<sup>13–15</sup> All compounds **1–8** were stable in air for several days.

Compounds **1** and **2** showed intense absorptions from  $\pi$ - $\pi^*$ ,  $^1\text{MLCT}$ , and  $^3\text{MLCT}$  transitions. Compounds **3** and **4** showed an intense absorbance at 450–462 nm, which is attributed to the quinolinolate ligand (Table 1). Deaerated dilute solutions of **1–4** in toluene were used to record the emission spectra. Excitation of **1–4** at 450 nm gave emission in the green to red region (Fig. 1). A considerable bathochromic shift was observed in the emissions from **1–4**. Iridium complex **1** emits at 503 nm while **4** shows emission at 620 nm. Phosphorescence quantum yields ( $\phi_{\text{PL}}$ ) were obtained with respect to rhodamine 6G.<sup>16</sup>  $\phi_{\text{PL}}$  of **1–2** were higher as compared to **3–4**. Ir(III) complexes



Scheme 1. Synthetic scheme for compounds **1–8**.

Table 1  
Photophysical and electrochemical data of **1–4**

Complexes	Absorbance (nm) ( $\log \epsilon$ )	PI <sub>sol</sub> (nm)	$\phi_{\text{sol}}^{\text{a}}$	$\tau^{\text{b}}$ ( $\mu\text{s}$ )	S <sub>0</sub> –T <sub>1</sub> <sup>c</sup> (eV)	E <sub>HOMO</sub> (eV)	T <sub>1</sub> <sup>d</sup> (eV)
Ir(ppy) <sub>2</sub> (acac)	345 (3.8), 412 (3.4), 460 (3.3), 497 (3.0)	516	0.34	1.6	—	—	—
<b>1</b>	371 (3.8), 407 (3.6), 434 (3.0), 482 (3.0)	503	0.23	1.1	2.51	–5.21	–2.70
<b>2</b>	366 (3.3), 407 (3.2), 439 (3.1), 505 (3.1)	569	0.11	1.7	2.25	–5.37	–3.12
<b>3</b>	349 (3.6), 462 (3.8)	620	<0.1	12.1	2.04	–5.37	–3.33
<b>4</b>	322 (4.1), 450 (4.2)	619	<0.1	13.7	2.04	–5.50	–3.46

<sup>a</sup> Quantum yield in toluene.

<sup>b</sup> PI (Photoluminescence) life time.

<sup>c</sup> Determined from the PI spectrum.

<sup>d</sup> Triplet energy level.

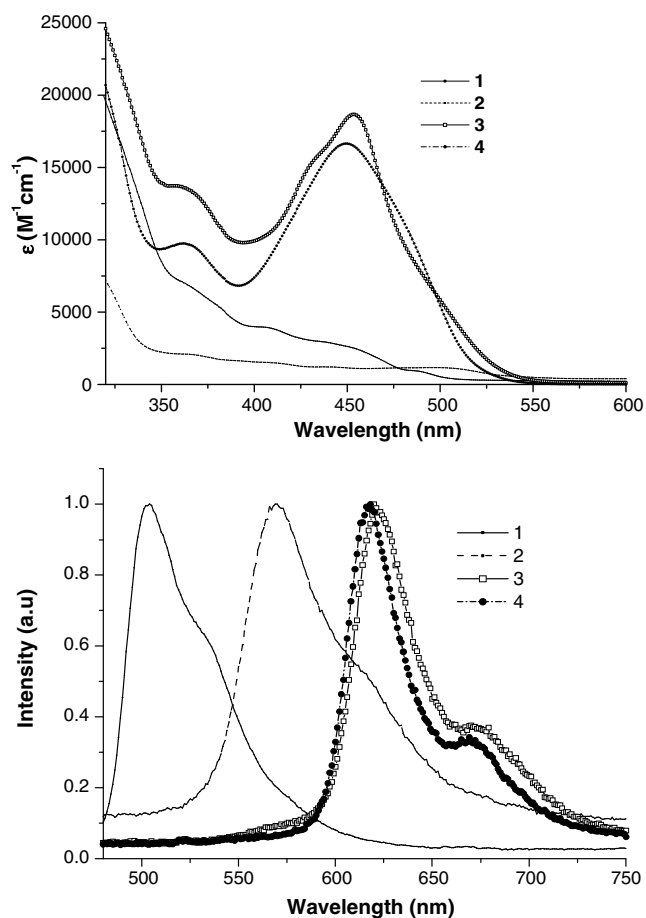


Fig. 1. Absorption (top) and emission (bottom) spectra of **1–4** recorded in toluene ( $\lambda_{\text{ex}} = 450 \text{ nm}$ ).

**1–4** show single photoluminescence life times ( $\sim 1\text{–}14 \mu\text{s}$ , Table 1).

Solution electrochemistry methods provide an insight on the HOMO and LUMO levels and stability of the radical anion/cations. Complexes **1–4** were characterized by reversible oxidation in cyclic voltammetry in acetonitrile (concn [**1–4**]  $\sim 1 \text{ mM}$ , tetrabutylammonium hexafluorophosphate  $0.1 \text{ M}$  as supporting electrolyte). The peak potential was determined versus ferrocene as an internal standard. Complexes **1–4** were not reducible in the electrochemical range accessible in acetonitrile (Fig. 2). The HOMO levels of **1–4** were determined from the corre-

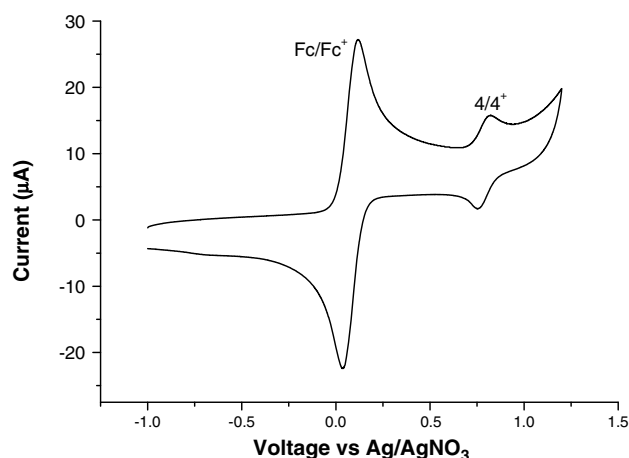


Fig. 2. Cyclic voltammogram of **4** recorded in acetonitrile (scan rate =  $0.2 \text{ V/s}$ ).

sponding oxidation peak potentials. The  $E_{\text{HOMO}}$  values of **1–4** were calculated using as earlier reported equation<sup>17,18</sup> and are listed in Table 1. The HOMO levels of **1–4** lie in the range of  $-5.2$  to  $-5.5 \text{ eV}$ . The triplet energy levels of **1–4** promise the potential use of these compounds as triplet harvesters to produce green to red emissions in OLEDs.

In conclusion, new heteroleptic Ir(III) complexes of 2-*p*-phenylpyridine were synthesized and characterized. Photophysical studies of these complexes show emission maxima in the green to red region. Electrochemical properties were evaluated to determine the HOMO levels and triplet levels of these compounds which suggest that they may serve as green-red emitters in OLEDs.

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### References and notes

- Burroughes, J. H.; Bradley, D. D. C.; Brown, A. B.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

2. (a) Muller, D. C.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wledermann, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerhotz, K. *Nature* **2003**, *421*, 829; (b) Shinar, J. *Organic Light-Emitting Devices*; Springer: New York, 2003.
3. DeRosa, M. C.; Hodgson, D. J.; Enright, G. D.; Dawson, B.; Evans, C. E. B.; Crutchley, R. J. *J. Am. Chem. Soc.* **2004**, *126*, 7619.
4. (a) Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Nature* **2000**, *403*, 750; (b) Montes, V. A.; Perez-Bolivar, C.; Agarwal, N.; Shinar, J.; Anzenbacher, Jr. P. *J. Am. Chem. Soc.* **2006**, *128*, 12436.
5. Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Lee, H.-E.; Adachi, C.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4304.
6. Adachi, C.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. *Appl. Phys. Lett.* **2000**, *78*, 1704.
7. Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *J. Appl. Phys.* **2001**, *90*, 5048.
8. Tsuboyama, A.; Iwawaki, H.; Furugori, M.; Mukaide, T.; Kamatani, J.; Igawa, S.; Moriyama, T.; Miura, S.; Takiguchi, T.; Okada, S.; Hoshino, M.; Ueno, K. *J. Am. Chem. Soc.* **2003**, *125*, 12971.
9. Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2001**, *40*, 1704.
10. Yeh, S.-J.; Wu, M.-F.; Chen, C.-T.; Song, Y.-H.; Chi, Y.; Ho, M.-H.; Hsu, S.-F.; Chen, C. H. *Adv. Mater.* **2005**, *17*, 285–289.
11. Miyaura, N. In *Metal-Catalyzed Cross-Coupling Reactions*; De Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004.
12. Kappaun, S.; Sax, S.; Eder, S.; Moller, K. C.; Waich, K.; Niedermair, F.; Saf, R.; Mereiter, K.; Jacob, J.; Mullen, K.; List, E. J. W.; Slugovc, C. *Chem. Mater.* **2007**, *19*, 1209–1211.
13. *Characterization data for ligand 5*:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.85 (s, 3H,  $\text{OCH}_3$ ), 6.98 (d, 2H,  $J = 9.0$  Hz, aryl), 7.15–7.17 (m, 1H, 3-pyridyl), 7.65–7.71 (m, 2H, 4,5-pyridyl), 7.93 (d, 2H,  $J = 9.0$  Hz, aryl), 8.63 (d, 1H,  $J = 5.0$  Hz, 2-pyridyl);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  55.31, 114.13, 119.89, 121.41, 128.17, 132.01, 137.82, 149.52, 157.07, 161.43. Elemental Anal. Calcd for  $\text{C}_{12}\text{H}_{11}\text{NO}$ : C, 77.81; H, 5.99; N, 7.56. Found: C, 76.55; H, 6.25; N, 7.81.
14. *Synthesis of Ir(III) complex, 1*: In a reaction vessel,  $\mu$ -dichloro-bridged compound **7** (0.050 g, 0.041 mmol),  $\text{Na}_2\text{CO}_3$  (0.048 g, 0.045 mmol), and acetylacetone (12  $\mu\text{L}$ ) were stirred in 2-ethoxyethanol (2.0 mL) under an inert atmosphere. The reaction mixture was refluxed at 120  $^\circ\text{C}$  for 20 h. The solvent was evaporated to afford a yellow precipitate which after several washings with methanol afforded pure compound **1** as a green solid (0.041 g, 75%).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.84 (s, 6H,  $\text{CH}_3$  of acac), 3.56 (s, 6H,  $\text{OCH}_3$ ), 5.31 (s, 1H), 5.72 (s, 2H), 6.48 (s, 2H), 7.15 (m, 2H), 7.55 (d, 2H,  $J = 8.5$  Hz), 7.76–7.80 (m, 4H), 8.47 (d, 2H, 2-pyridyl,  $J = 5.0$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  28.08, 53.50, 106.29, 107.92, 125.06, 136.22, 137.91, 146.53, 149.71, 151.61, 159.73, 163.93, 168.23, 184.55; ES-MS ( $m/z$ ) calcd for  $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}_4\text{Ir}$ , 659.7528; found 659.8218 ( $\text{M}^+$ ), 560.7508 ( $\text{M}^+ - \text{acac}$ ).
15. *Synthesis of Ir(III) complex, 4*:  $\mu$ -Dichloro-bridged compound **8** (0.032 g, 0.025 mmol) and 5-nitro-8-hydroxy-quinoline (0.012 g, 0.065 mmol) were dissolved in a mixture of ethanol (1.0 mL), dichloromethane (2.0 mL), and triethylamine (0.5 mL), and refluxed at 80  $^\circ\text{C}$  under an inert atmosphere for 18 h. The precipitate obtained was filtered and washed with ethanol to give pure compound **4** as an orange solid (0.031 g, 77%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.33 (s, 3H,  $\text{CH}_3$ ), 2.38 (s, 3H,  $\text{CH}_3$ ), 6.81 (s, 1H), 6.95 (t, 1H,  $J = 10$  Hz), 7.05 (t, 1H,  $J = 10$  Hz), 7.23–7.26 (m, 1H), 7.48–7.58 (m, 4H), 7.75 (d, 2H,  $J = 10$  Hz), 7.80–7.86 (m, 4H), 8.00 (d, 1H,  $J = 10$  Hz), 8.05 (d, 1H,  $J = 10$  Hz), 8.65 (d, 1H,  $J = 10$  Hz), 8.70 (d, 1H,  $J = 10$  Hz), 9.55 (d, 1H,  $J = 10$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  26.86, 115.78, 120.21, 122.37, 123.87, 124.38, 125.91, 127.55, 129.68, 131.36, 132.07, 132.99, 135.39, 137.42, 137.77, 142.82, 147.05, 148.61, 149.17, 166.61, 167.71, 177.82, 198.86; ES-MS ( $m/z$ ) calcd for  $\text{C}_{35}\text{H}_{25}\text{N}_4\text{O}_5\text{Ir}$ , 774.1454; found 774.9623 ( $\text{M}^+$ ), 584.9683.
16. Kubin, R. F.; Fletcher, A. N. *J. Lumin.* **1982**, *27*, 455.
17. Mishra, A.; Nayak, P. K.; Ray, D.; Patankar, M. P.; Narasimhan, K. L.; Periasamy, N. *Tetrahedron Lett.* **2006**, *47*, 4715.
18. Andrade, B. W. D.; Datta, S.; Forrest, S. R.; Djurovich, P.; Polikarpov, E.; Thompson, M. E. *Org. Electron.* **2005**, *6*, 11.