



## Note

## Phosphorescence of iridium(III) complexes with 2-(2'-pyridyl)-1,3,4-oxadiazoles

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## ARTICLE INFO

## Article history:

Received 29 April 2012

Received in revised form 23 July 2012

Accepted 27 July 2012

Available online 3 August 2012

## Keywords:

Iridium

1,3,4-Oxadiazole

Ligand

Complex

Cyclometalation

Phosphorescence

## ABSTRACT

Cationic bis-cyclometalated iridium(III) complexes  $[(C^{\wedge}N)_2Ir(N^{\wedge}N)](PF_6)$  with 2-(2'-pyridyl)-5-R-1,3,4-oxadiazoles ( $N^{\wedge}N$ ; R = 1-adamantyl, mesityl, *N*-diphenylamino) have a redox gap of 2.58–2.68 V and exhibit orange–red phosphorescence in argon-saturated dichloromethane solution with a maximum, quantum yield, and excited-state lifetime of 613–644 nm, 2–6%, and 90–280 ns.

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## 1. Introduction

Tuning of the photophysical properties of phosphorescent cationic iridium(III) complexes  $[(C^{\wedge}N)_2Ir(N^{\wedge}N)]^+$  can be achieved by changing the cyclometalating  $C^{\wedge}N$  and neutral  $N^{\wedge}N$  ligands [1–10]. Here, we report phosphorescent cationic Ir(III) complexes with alkyl, aryl, or diarylamino substituted 2-(2'-pyridyl)-1,3,4-oxadiazoles—a class of easy-to-make neutral  $N^{\wedge}N$  ligands rarely used in coordination chemistry (Scheme 1) [11–16]. 1,3,4-Oxadiazole is an electron-deficient heterocycle that finds application as an electron-transport group in organic electronics [17,18]. We note that several research labs recently investigated neutral [19–21] and cationic [22,23] Ir(III) complexes with 1,3,4-oxadiazole-modified cyclometalating ligands.

## 2. Results and discussion

Three new  $N^{\wedge}N$  ligands **L1–L3** were prepared by reaction of 5-(2'-pyridyl)-1H-tetrazole with an acyl chloride in pyridine at reflux (Scheme 1) [24]. We chose bulky 1-adamantyl (**L1**) and mesityl (**L2**) groups to reduce solid state interaction and to increase solubility of the complexes. We chose a diphenylamino group (**L3**) because it facilitates hole-transport in electroluminescent metal complexes [25]. The reaction of **L1–L3** with  $[(ppy)_2Ir(\mu-Cl)]_2$  ( $ppy = N, C^{2'}\text{-2-phenylpyridyl}$ ) gave three new Ir(III) complexes  $[(ppy)_2Ir(N^{\wedge}N)](PF_6)$ , **1–3**, after purification by column chromatography

on silica (Scheme 1). All new compounds were characterized by elemental analysis,  $^1H$ ,  $^{13}C$ , and  $^{19}F$  NMR spectroscopy, and mass spectrometry.

Fig. 1 shows the X-ray structure of **3**. The Ir(III) ion is in a distorted octahedral  $[(C^{\wedge}N)_2Ir(N^{\wedge}N)]^+$  coordination environment. The two nitrogen atoms of the  $C^{\wedge}N$  ligands are in trans-position to each other. The Ir–( $C^{\wedge}N$ ) bonds are shorter than the Ir–( $N^{\wedge}N$ ) ones are (Table 1). The Ir–N ( $N^{\wedge}N$ ) bond to oxadiazole is shorter than that to pyridine by 0.032 Å (Table 1). The dihedral angles between the rings of the ligands are 6.22° (pyridyl and oxadiazole,  $N^{\wedge}N$ ) and 1.45° or 13.15° (phenyl and pyridine,  $C^{\wedge}N$ ). The cations of **3** do not participate in face-to-face  $\pi$ – $\pi$  stacking, and have the minimum inter-metallic Ir···Ir distance 9.090(2) Å.

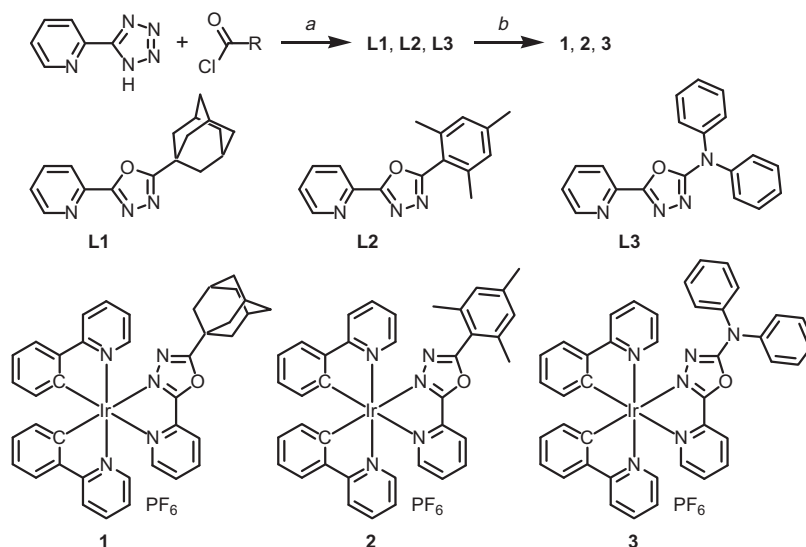
Redox potentials of **1–3** (relative to  $Fc^+/Fc$  [26]) were measured with cyclic voltammetry in acetonitrile and DMF and were found to be solvent-independent (Fig. 2 and Fig. S1, Supporting information). The complexes exhibit a reversible/quasi-reversible reduction of  $N^{\wedge}N$  ligand at –1.73 to –1.64 V; an irreversible oxidation of Ir–phenyl fragment at 0.93–0.98 V; and the redox gap,  $\Delta E = E^{ox} - E_{1/2}^{red}$ , 2.58–2.68 V (Table 2). The observed variation of reduction potentials, **3** (–1.73 V) < **1** (–1.68 V) < **2** (–1.64 V), reflects the electron-donor strength of substituents in the  $N^{\wedge}N$  ligand: diphenylamino (**3**) > 1-adamantyl (**1**) > mesityl (**2**).

**1–3** exhibit more positive redox potentials than does the reference complex  $[(ppy)_2Ir(2,2'\text{-bipyridine})](PF_6)$ , –1.77 and 0.84 V in DMF [27] or –1.78 and 0.88 V in acetonitrile [28]; therefore, we conclude that 1,3,4-oxadiazole is a stronger electron-acceptor [17,18] and a weaker  $\sigma$ -electron-donor than is the pyridine.

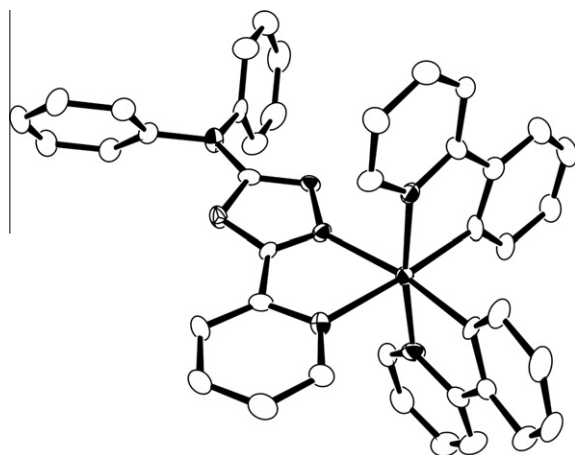
Ligands **L1–L3** are white solids; their electronic absorption spectra exhibit bands at  $\lambda < 375$  nm that are enhanced and

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**Scheme 1.** Synthesis of new ligands and Ir(III) complexes: (a) pyridine, under argon, reflux; (b)  $[(C^N)_2Ir(\mu-Cl)]_2$ , under argon, 40 °C, dichloromethane/methanol,  $KPF_6$ .



**Fig. 1.** Structure of **3** (CCDC 878933; 50% probability ellipsoids; H atoms and  $PF_6^-$  anion are omitted; ORTEP). Heteroatoms are shown as octant ellipsoids: Ir and N, black; O, clear.

**Table 1**  
Bond lengths (Å) in **3**<sup>a</sup>.

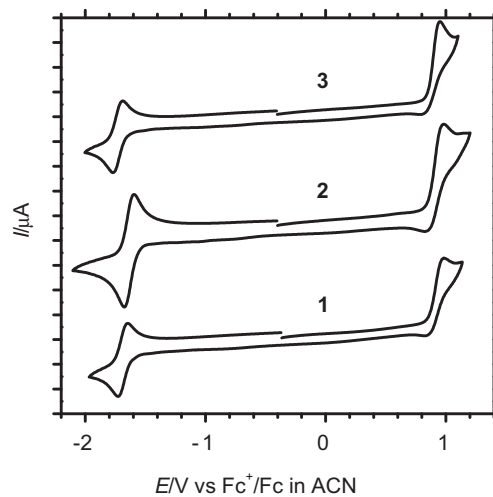
C <sup>^</sup> N		N <sup>^</sup> N	
Ir–C	Ir–N	Ir–N(py) <sup>b</sup>	Ir–N(oda) <sup>b</sup>
2.000(5)	2.040(6)	2.195(5)	2.163(5)
2.022(6)	2.064(5)		

<sup>a</sup> Each row corresponds to one ligand in the complex.

<sup>b</sup> N(py) and N(oda) are nitrogen atoms of pyridine and 1,3,4-oxadiazole, respectively.

red-shifted when 1-adamantyl group in **L1** is replaced with aromatic (mesityl or diphenylamino) and charge-transfer (diphenylamino-to-oxadiazole) chromophores in **L2** and **L3** (Fig. 3 and Table 3).

The complexes are yellow (**1**) or orange (**2**, **3**) solids; their electronic spectra in dichloromethane (Fig. 4, Table 3, and Fig. S2, Supporting information) display an (Ir–phenyl)-to-(N<sup>^</sup>N) charge transfer transition at  $\lambda > 450$  nm with molar absorption coefficients ( $\epsilon$ ) of less than  $10^3$  M<sup>-1</sup> cm<sup>-1</sup> [5]. The charge-transfer (MLCT, ILCT)



**Fig. 2.** Cyclic voltammograms of **1–3** in acetonitrile (glassy carbon electrode, 0.1 M  $NBu_4PF_6$ , 100 mV/s). The unit on the vertical axis is 10  $\mu$ A. CVs of **1–3** in DMF are shown in the Supporting information.

**Table 2**  
Redox properties<sup>a</sup>.

Complex	Solvent	$E_{1/2}^{red}/V^b$	$E^{ox}/V^c$	$\Delta E/V^d$
<b>1</b>	DMF	–1.68 (98) <sup>e</sup>	0.96	2.64
	ACN	–1.68 (78)	0.98	2.66
<b>2</b>	DMF	–1.64 (88)	0.94	2.58
	ACN	–1.64 (78)	0.98	2.62
<b>3</b>	DMF	–1.73 (83)	0.93	2.66
	ACN	–1.73 (83)	0.95	2.68

<sup>a</sup> In acetonitrile (ACN) or DMF. Relative to  $Fc^+/Fc$ . Error:  $\pm 50$  mV. On glassy carbon working electrode, with 0.1 M  $(NBu_4)PF_6$ , at scan rate 100 mV/s. The anodic/cathodic peak separation for the standard,  $Fc^+/Fc$  couple, was 78–88 mV.

<sup>b</sup> Reversible process (unless stated otherwise). The anodic/cathodic peak separation is given in brackets.

<sup>c</sup> Irreversible process. The return wave was observed in acetonitrile with anodic/cathodic peak separation of more than 150 mV at 100 mV/s. The oxidation peak potential is reported.

<sup>d</sup>  $\Delta E = E^{ox} - E_{1/2}^{red}$ .

<sup>e</sup> Quasi-reversible process; the anodic/cathodic peak separation is given in brackets.

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