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Photophysical and electrochemical properties of heteroleptic tris-cyclometallated Ir(III) complexes

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Abstract

Some new heteroleptic tris-cyclometallated iridium(III) complexes have been synthesized and fully characterized. Among these iridium(III) complexes, bis(1-phenylpyrazolato-$N,C^{2'}$)iridium(III)[5-(2′-pyridyl)tetrazolate] (**3**) and bis(3-methyl-1-phenylpyrazolato-$N,C^{2'}$)iridium(III)[5-(2′-pyridyl)tetrazolate] (**4**) show excellent quantum yields at room temperature, the electron density being perturbed by introducing the pyridyltetrazole ligand, making $k_r > k_{nr}$. This destroys the concept of phenylpyrazole based iridium complexes.

Keywords: Iridium; Tris-cyclometallated; Photophysical properties; Electrochemical properties

1. Introduction

The photophysical properties of bis- and tris-cyclometallated complexes of Ir(III) have been investigated extensively [1–5]. An attractive application of these complexes is in the field of organic light-emitting diodes (OLEDs), where they have been used as phosphorescent dopants in the emitting layer [6–9]. Ir(III) complexes often exhibit favorable photophysical properties for OLEDs, including short phosphorescent lifetimes, high quantum efficiencies and good stability. In these devices, the singlet and triplet excited states that are created during charge recombination are trapped in the dopant, where effective intersystem crossing leads to efficient electrophosphorescence at room temperature.

fac-Tris(1-phenylpyrazolato-$N,C^{2'}$)iridium(III)($Ir(ppz)_3$) is noted for its high LUMO level and strong emission at 77 K ($\lambda_{max} = 414$ nm) [10–12]. An efficient white OLED is fabricated by using this complex as an electron blocking material to confine exciton recombination to the doped luminescent layer. The strongly temperature-dependent photoluminescent (PL) efficiency of $Ir(ppz)_3$ is a fatal drawback for OLEDs. Evidently, $Ir(ppz)_3$ decays non-radiatively by thermal population of a higher lying non-emissive excited state at room temperature.

Another application of *N*-phenylpyrazole iridium complexes focuses on their blue phosphorescence at room temperature, due to their exceedingly high energy gaps [13,14]. After adding fluorine substitutes to the phenyl ring of *N*-phenylpyrazole (2C^N) and using the more electron-withdrawing pyridyltriazolate as the third N^N chelating anion, all of the iridium complexes exhibit blue emissions at 455–469 nm and relatively weak emission intensities ($\Phi \sim 10^{-3}$) in degassed CH_2Cl_2 [13]. Another report mentions that after introducing 2-phenylpyridine or 2-(2′,4′-difluorophenyl)-pyridine to *N*-phenylpyrazole based iridium complexes, the quantum yields of the iridium complexes are moderate to high ($\Phi \sim 0.82$–0.77) [14]. Evidently, the pyrazole moiety is associated with the increase in k_{nr} and subsequent drop in quantum yield.

In this work, we have synthesized a series of iridium complexes that have *N*-phenylpyrazole for the C^N site and the strong electron-withdrawing ligand 5-(2′-pyridyl)tetrazole for the N^N site or acetylacetone for the O^O site [8,15]. The asymmetric character of these ligands

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is expected to disturb the HOMO and LUMO of the metal complexes, and afford a subtle color tuning via substituting either pyrazolate, tetrazolate or acetylacetonate sites.

2. Experimental

2.1. General information and materials

All materials including the *N*-phenylpyrazole ligands were obtained from Aldrich, Acros or TCI and were used without further purification. 5-(2′-Pyridyl)tetrazole is a known compound and can be prepared easily in one step from commercially available 2-cyanopyridine and sodium azide [16]. Scheme 1 outlines how the iridium dimers were synthesized by the method reported by Nonoyama and were utilized for preparing a series of $(C^N)_2Ir(O^O)$ or $(C^N)_2Ir(N^N)$ complexes [17,15]. All synthetic procedures and manipulations involving $IrCl_3 \cdot H_2O$ and other Ir(III) species were carried out under N_2.

Column chromatography was carried out using 70–230 mesh silica gel. ^1H NMR and ^{13}C NMR spectra were recorded in CD_2Cl_2 solution on Bruker Avance-300 (300 MHz) or AMX-400 (400 MHz) NMR spectrometers with tetramethylsilane (TMS) as the internal standard; all chemical shifts were reported in ppm from TMS. Elemental analyses were performed on a Heraeus CHN-RAPID elemental analyzer and Elementar vario EL III analyzer. The EI-Mass spectra were recorded on Bruker APEX II and VG 70-250S spectrometers. HRMS spectra were obtained using a MAT-95XL high resolution mass spectrometer. The UV–Vis spectra were measured in a 1.0×10^{-5} M CH_2Cl_2 solution on an Agilent 8453 spectrophotometer, and the photoluminescence spectra were recorded in a 1.0×10^{-5} M CH_2Cl_2 solution with a HITACHI model F-2500 fluorescence spectrophotometer.

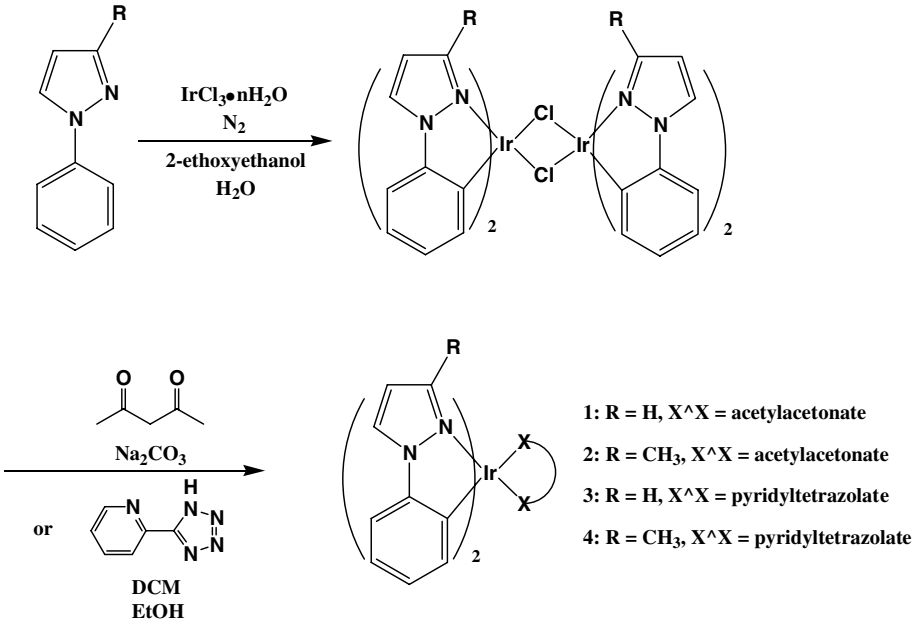
2.2. General information for the preparation of the iridium complexes

Scheme 1 outlines the synthetic process for an example of the iridium complexes $(C^N)_2Ir(O^O)$ or $(C^N)_2Ir(N^N)$. Detailed procedures of the preparation, the ^1H NMR spectra and chemical analysis data of the iridium complexes are given afterwards.

2.3. Synthesis of bis(1-phenylpyrazolato-*N*,$C^{2'}$)iridium(III)(acetylacetonate) (**1**)

The dimer $[(C^N)_2IrCl]_2$ was synthesized according to a previous report [17]. 1-Phenylpyrazole (1.22 g, 8.38 mmol) and iridium trichloride ($IrCl_3 \cdot nH_2O$, 1.0 g, 3.34 mmol) were dissolved in a 1:3 mixture of water and 2-ethoxyethanol. The mixture was refluxed at 110 °C for 24 h under a nitrogen atmosphere and then cooled to room temperature. After cooling, the product was isolated by filtration and washed with several portions of distilled water and then vacuum dried. The solid was collected by filtration and pumped to dry to give crude $[(1\text{-ppz})_2IrCl]_2$, 1.16 g (67.8%).

After cyclometallated Ir(III) μ-chloro-bridged dimers were obtained, 1.16 g of the dimer was dispersed in 2-ethoxyethanol in a flask, followed by addition of acetylacetone (0.56 g, 6.78 mmol) and sodium carbonate (1.32 g, 12.43 mmol), and the mixture was stirred under nitrogen for 15 min. After that, the mixture was refluxed at 126 °C for 15 h and then cooled to room temperature. The crude product was isolated by filtration and washed with distilled water, *n*-hexane and ether. (77% crude product yield) The crude product was chromatographed using ethyl acetate/*n*-hexane (1:1) to yield a yellow green powder, **1**. ^1H NMR (CD_2Cl_2, 400 MHz) δ 8.19 (s, 2H), 7.61 (s, 2H), 7.23 (d, $J = 7.7$ Hz, 2H), 6.92 (dd, $J = 7.7$, 7.5 Hz, 2H),



Scheme 1. Synthesis of the iridium(III) complexes.