



Light-emitting materials from cyclometalated heteroleptic iridium(III) complexes—A physicochemical study

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ABSTRACT

Phosphorescent studies of 2-arylimidazole heteroleptic cyclometalated iridium(III) complexes with picolinic acid as the ancillary ligand were made. The observed experimental data reveal that these complexes possess dominantly $^3\text{MLCT}$ and $^3\pi\text{--}\pi^*$ excited states and the solvent shift of these complexes is interpreted by Reichardt–Dimroth and Marcus solvent functions. The results are consistent with prior assignments on the absorption band to a metal-to-ligand charge transfer excited state associated with chelating ligand. Emission kinetic studies exploited that the radiative transition (k_r) increases with increasing λ_{em} .

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1. Introduction

Recently, the synthesis of luminescent transition metal complexes has attracted much attention due to their favorable optical and electrical properties, making them in general perfect candidates for electro-optical applications such as organic light-emitting diodes (OLEDs), solar cells, and optical sensors [1,2]. For OLED application which is believed to be a promising candidate for the next generation display technology, organometallic complexes possessing heavy transition metal cores are highly desired [3,4]. The strong spin–orbit coupling effectively promotes intersystem crossing as well as enhances the subsequent emissive decay from triplet excited state to ground state, facilitating strong phosphorescence by harvesting both singlet and triplet excitons within OLEDs. Since the internal quantum efficiency can theoretically be achieved as high as 100%, these heavy-metal containing emitters are thus superior to fluorescent ones in OLED applications [5–12].

In this series, phosphorescent iridium(III) complexes are particularly promising because of their favorable short excited state lifetimes, well-suited energy levels, thermal stability, and environmental inertness. The strong appeal and desire for better emitters, along with the need for a deeper understanding on the correlation between structural processes and photophysical properties, has pushed a continuous progress in the design of phosphorescent Ir(III) complexes. In exploring high efficient phosphorescent

emitters and moving toward materials with the required color gamut for full color displays, a good harvest of high-performance Ir(III) complexes covering the whole visible region has been achieved, and the correlation between cyclometalated ligand structures and emission character is well established.

Our interest in the development of highly efficient phosphors for applications in OLEDs prompted us to synthesize heteroleptic iridium complexes and investigate their photophysical properties. In the present study the methoxy group as electron releasing moiety was chosen due to the emission of iridium complexes that comes from phosphorescence with triplet character of both ligand centered ($\pi\text{--}\pi^*$) and MLCT (metal-to-ligand charge transfer) transitions. The phosphorescence is strongly affected by the triplet energy of the *ortho*-chelating $\text{C}\dot{\text{N}}$ ligands and the methoxy group could play a key role in the alteration of the triplet energy. Incorporating the methoxy group as a substituent in the imidazole ring has an influence on the HOMO/LUMO level, as well as $^3\text{MLCT}$ state of the complexes. Herein we described the results of our systematic investigation on synthesis, X-ray, structural characterization, photophysical properties and electrochemical behaviour of cyclometalated iridium complexes.

2. Experimental

2.1. Materials and methods

Iridium(III) trichloride trihydrate ($\text{IrCl}_3\cdot 3\text{H}_2\text{O}$, Sigma–Aldrich Ltd.), 2-ethoxyethanol ($\text{H}_5\text{C}_2\text{OC}_2\text{H}_4\text{OH}$, S.D. fine) and all other reagents were used without further purification.

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2.2. Optical measurements and composition analysis

The ultraviolet–visible (UV–vis) spectra of the phosphorescent Ir(III) complexes were measured in an UV–vis spectrophotometer (Perkin Elmer Lambda 35) and corrected for background absorption due to solvent. Photoluminescence (PL) spectra were recorded on a Perkin Elmer LS55 fluorescence spectrometer. The solid-state emission spectra were recorded on fluoromax2 (ISA SPEX) Xenon-Arc lamp as a source. NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. MS spectra (EI and FAB) were recorded on a Varian Saturn 2200 GCMS spectrometer. Cyclic voltammetry (CV) analyses (Table S1) were performed by using CHI 630A potentiostat electrochemical analyzer. Measurements of oxidation and reduction were undertaken using 0.1 M tetra(*n*-butyl)ammoniumhexafluoro-phosphate as a supporting electrolyte, at scan rate of 0.1 V s⁻¹. The potentials were measured against an Ag/Ag⁺ (AgCl) reference electrode using ferrocene/ferrocenium (Cp₂Fe/Cp₂Fe⁺) as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram.

2.3. General procedure for the synthesis of ligands

The various substituted 2-arylimidazole ligands were prepared from an unusual four component assembling of butan-2,3-dione, ammonium acetate, *m*-anisidine and substituted aryl aldehyde as shown in Scheme S1 [13–21].

2.4. General procedure for the synthesis of iridium complexes

The 2-arylimidazole based cyclometalated iridium complexes **1–3** were synthesized via Nonoyama route [22] (Scheme S2).

The yield and the NMR data are given in Supplementary material.

3. Results and discussion

3.1. Photophysical properties

The absorption bands of complexes (**1–3**) show two kinds of bands (Fig. 1). The intense band observed around 250 nm (Table 1) in the ultraviolet part of the spectrum can be assigned to the allowed ligand centered ($\pi-\pi^*$) transitions [23] and somewhat weaker bands are also observed in the lower part of energy ($\lambda_{\text{max}} < 330$ nm). The band position, size and extinction coefficient of the bands observed in the range 330–425 nm suggest that these are MLCT transitions (¹MLCT and ³MLCT) [24,25]. According to our previous papers [19–21], weak bands located at longer wavelength

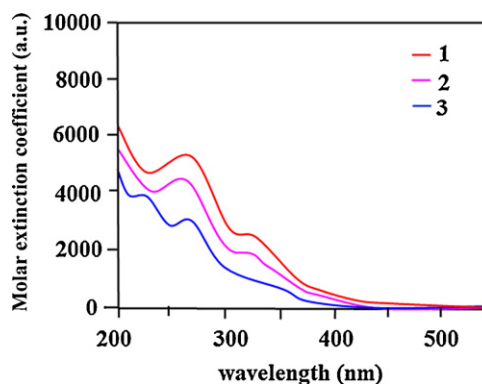


Fig. 1. The UV–vis absorption spectra of the complexes **1** and **2** in CH₂Cl₂.

Table 1
Photophysical properties of iridium complexes **1–3**.

Complex	Quantum yield (Φ)	Lifetime (μs) 298 K	k_r (μs^{-1})	k_{nr} (μs^{-1})
Ir(dmpti)(pic), 1	0.30	1.2	0.25	0.58
Ir(fpdmti)(pic), 2	0.38	1.0	0.38	0.62
Ir(dmdpi) ₂ (pic), 3	0.25	1.9	0.13	0.39

have been assigned to the ¹MLCT $\leftarrow S_0$ and ³MLCT $\leftarrow S_0$ transitions of iridium complexes. Thus the broad absorption shoulders at 382 and 425 nm observed for **1** are likely to be ascribed to the ¹MLCT $\leftarrow S_0$ and ³MLCT $\leftarrow S_0$ transitions, respectively. The intensity of the ³MLCT $\leftarrow S_0$ transition is close to that of ¹MLCT $\leftarrow S_0$ transition, suggesting that ³MLCT $\leftarrow S_0$ transition is strongly allowed by S–T mixing of spin–orbit coupling [12] and similar observations are made for complexes **2** and **3**. Absorption in the range of around 330 nm for complexes (**1–3**) corresponds to the transition of the ¹MLCT state as evident from its extinction coefficient of the order 10³. The absorption like long tail toward lower energy and higher wavelength around 388 nm is assigned to ³MLCT transition and gains intensity by mixing with the high lying ¹MLCT transition through the spin–orbit coupling (Fig. 2) of iridium(III) [17]. Both singlet MLCT (¹MLCT) and triplet MLCT (³MLCT) bands are typically observed for these complexes in all solvents. In order for these iridium(III) complexes to be useful as phosphor EL devices, strong spin–orbit coupling must be present to efficiently mix the singlet and triplet excited states. Clear evidences for mixing of the singlet and triplet excited states are seen in the absorption of these complexes.

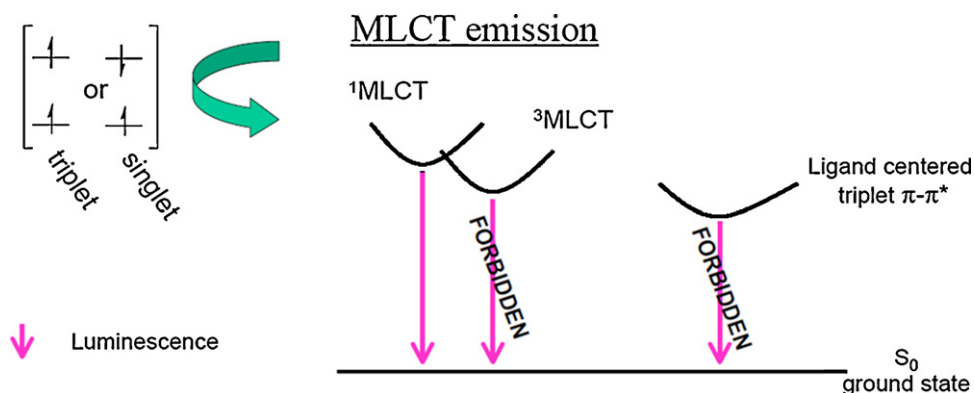


Fig. 2. Spin–orbit coupling of heavy-metal facilitated triplet emission.

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