



## Review

## Cyclometallated iridium complexes for conversion of light into electricity and electricity into light

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## ABSTRACT

This brief review describes applications of cyclometallated iridium complexes for energy saving organic light-emitting devices (OLED's) and energy generating molecular photovoltaic cells. The first part consists of a short overview of the methods to modulate emitted color and quantum yield in neutral and ionic complexes for light-emitting diodes. And in the second part, we report initial results of cyclometallated iridium complexes for solar cell applications.

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## 1. Introduction

Climatologists are pointing to global warming threatening our planet and some fossil fuels like oil are coming close to their overall production peak. Therefore, in a political shift for a sustainable world, developed and developing countries are taking actions on energy issues, aiming for a reduction of worldwide energy consumption and increase of the production of energy originating from renewable sources.

Lighting applications account for about 19% of the electricity consumption of the world, therefore low energy consumption devices such as organic light-emitting devices (OLEDs), have been considered as the most promising solution for decreasing overall energy consumption. In this respect iridium(III) cyclometallated complexes are attracting wide spread interest because of their unique photophysical properties [1]. In order to solve the second target, it is important to note that the obvious main energy source for renewable energy is coming from the sun. In that respect, dye-sensitized solar cells (DSSC) are considered as being the most promising solution for harnessing the energy of the sun and converting it into electrical energy. Using ruthenium complexes 11% power

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conversion efficiency under AM1.5 conditions have been obtained [2]. In dye-sensitized solar cells ruthenium has without any doubt the lion share of the studied dyes [3]. However, recently other metal complexes as well as metal-free organic dyes are testing the supremacy of ruthenium [4]. Iridium complexes are far from competing with ruthenium, however iridium complexes exhibited some interesting behavior worthwhile having a closer look at them [5]. We will shortly review the iridium complexes, which are useful in energy saving (light-emitting diodes) and energy generating (dye-sensitized solar cells) applications.

## 2. Cyclometallated iridium complexes for OLED applications

The last decade witnessed an explosion of the number of reported luminescent cyclometallated iridium(III) complexes. This widespread interest originates from their wide color tunability and high phosphorescence quantum yield, which make them very attractive for application in organic light-emitting diodes (OLEDs). Neutral iridium cyclometallated complexes have been used extensively in OLEDs and obtained up to 19% external quantum efficiencies, using multilayered structure for charge injection, transport, and light emission [6]. This long standing record has been broken recently with devices exhibiting more than 20% external quantum efficiencies. They rely on the use of newly developed host materials with improved charge transporting capabilities [7].

Simplified working principle of OLED is shown in Fig. 1. A layer of emissive material is sandwiched between a cathode and an anode. When the device is biased, holes are injected in the HOMO level of the material and electron are injected in the LUMO level. Both electron and hole will be transported to the other electrode. If a hole and an electron are passing close enough from each other, they may interact and finally recombine to lead to an exciton, which will deactivate by emitting light. In order to improve injection and transporting properties in the device, multilayer architectures are usually used.

### 2.1. General photophysical properties

In metal complexes there are three types of excited states: (a) metal-centered (MC) excited states, from the promotion of an electron from  $t_{2g}$  to  $e_g$  orbitals; (b) ligand-centered (LC) states that are  $\pi-\pi^*$  transitions; (c) metal-to-ligand charge transfer states (MLCT), which can be understood with the aid of an energy level diagram shown in Fig. 2. Singlet-singlet absorptions are an electronic transition from metal  $t_{2g}$  orbitals to empty ligand orbitals or centered on the ligand, that is from  $\pi$  orbitals to empty  $\pi^*$  orbitals, without spin change, which are allowed and are identified by large extinction coefficients. On the contrary, singlet-triplet absorptions are transitions with spin change and are forbidden, therefore associated with small extinction coefficients. However, a singlet state may be involved in spin flip, which is called intersystem crossing

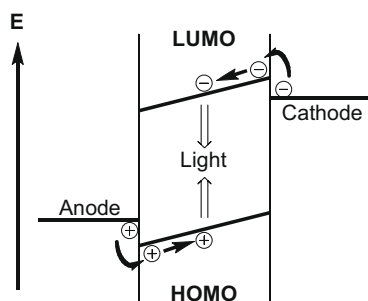


Fig. 1. Operating principles of OLED.

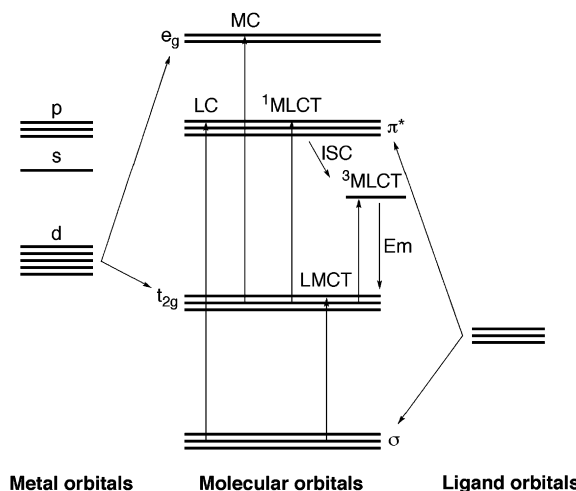


Fig. 2. Schematic and simplified molecular orbital diagram for an octahedral  $d^6$  metal complex involving 2-phenylpyridine ( $C_3$  symmetry)-type ligands in which various possible transitions are indicated.

(ISC), resulting in an excited triplet state. The radiative process of a singlet and triplet excited states to a singlet ground state are termed fluorescence and phosphorescence, respectively. In cyclometallated iridium complexes, the excited triplet state, which is responsible for phosphorescence, is a combination of the LC and the MLCT triplet excited state, that is a mixed (triplet) excited state. As iridium complexes possess strong spin-orbit coupling, excited singlet states can undergo efficient ISC into the triplet state resulting in high phosphorescence quantum yields. However, not all the complexes are highly luminescent because of the different deactivation pathways. The choice of iridium metal is of special interest for a number of reasons: (a) because of its quasi-octahedral geometry one can introduce specific ligands in a controlled manner; (b) the photophysical and the electrochemical properties of iridium complexes can be tuned in a predictable way; (c) the iridium metal possess stable and accessible oxidation and reduction states; and (d) cyclometallated iridium complexes are known to have highest triplet quantum yields.

### 2.2. Neutral tris-cyclometallated iridium complexes

Tris-cyclometallated iridium complexes are neutral complexes of the type  $Ir(C^{\wedge}N)_3$ . The archetype of such complexes is  $Ir(ppy)_3$  ( $ppy = 2$ -phenylpyridine), where the coordination of  $ppy$  ligand to metal is analogous to that found in 2,2'-bipyridine except that one nitrogen is replaced by carbon anion. The absorption spectra of  $[Ir(ppy)_3]$  display strong ligand-to-ligand (LC,  $\pi-\pi^*$ ) and MLCT transitions in the UV and the visible region, respectively. The MLCT transition bands are lower in energy than the LC  $\pi-\pi^*$  transitions. The excited triplet state shows strong phosphorescence in the green region at around 515 nm, with an excited state lifetime of 2  $\mu s$  [8]. Since the analysis of the spectral properties of  $Ir(ppy)_3$  complex using DFT by Hay, it is known that the HOMO in tris-phenylpyridine  $Ir(III)$   $[Ir(ppy)_3]$  is principally composed of  $\pi$  orbitals of the phenyl ring and the metal  $d$ -orbitals. The pyridine is formally neutral and is the major contributor to the LUMO in the  $[Ir(ppy)_3]$  complex [9]. In a practical approximation, the emission maximum of luminescent iridium complexes is determined principally by the HOMO-LUMO gap. An effective strategy to tune the emission color in  $Ir(III)$  complexes relies on the selective stabilization or destabilization of the HOMO and/or LUMO of the complex. Watts et al. synthesized several substituted  $ppy$ -based neutral iridium complexes (Table 1) [8,10].

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