

# Cyclometalated Ir(III) Complexes As Dopants For OLEDs

Tanima Hajra  
 Department of Chemistry  
 Rama University, Kanpur, India  
 tanima.hajra@gamil.com

**Abstract:** This review article comprises of a short summary on the history of Organic Light Emitting Diode (OLED) and its importance in display technology. It describes the use of heavy-metal [Pt(II), Ir(III), Os(II) etc.] organometallic complexes as dopants in the OLED fabrication. Special emphasis is given on cyclometalated Ir(III) complexes which are excellent phosphors with lifetime in microseconds at room temperature justifying their superiority over others.

**Keywords:** OLED, phosphorescence, cyclometalated, Ir.

## I. INTRODUCTION

The first ever widely used display technology was based on the cathode ray tube (CRT). It was the first workhorse of test and video display technology. The main components used in this technology are a negatively charged cathode, an electron gun, and a screen coated with a grid of phosphor dots. The electron gun shoots electrons down the tube and phosphors would glow when struck by such an electron beam. By the time this technology matured, brightness, resolution and contrast have been optimized and very good display properties could be extracted from such devices [1-3].

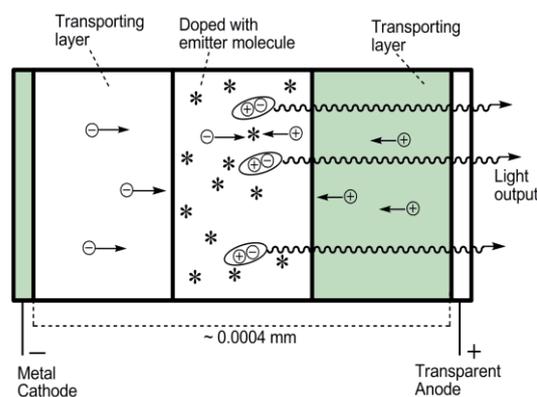
Just when the CRT era appeared to go on forever, a new technology, namely liquid crystal display (LCD) started to make its presence felt. The LCD platform uses a grid of liquid crystals. Three transistors are placed behind each such liquid crystal. A RGB (red-green-blue) spectrum is generated, the mix of which provides the full colour display [4-6]. The advantages of the LCD devices in terms of the compactness and slimness of the device along with a sharper color image allowed this technology to slowly displace those based on CRTs. However, in spite of their undeniable advantages, LCDs are not the perfect answer to display needs. LCD devices suffer from the disadvantages that since they are not self-illuminating they need *backlighting* which is an additional power drain. In addition, LCD devices suffer from viewing-angle dependent distortions [7-9].

Organic Light Emitting Diodes (OLEDs) are emerging as the primary challengers to LCDs and seem to have the potential to overcome the disadvantages of the latter [10,11]. OLEDs are

being increasingly looked upon as the most viable candidates for realizing *perfect* flat panel displays. OLEDs offer many advantages over LCDs. They are self-luminescent, therefore they do not need the requirement of back lighting. The display devices can be thinner, lighter and need low operating voltage than LCDs. Finally, properly designed OLED devices can be quite robust, provide purer color and wider viewing angle. The growing need for better display devices is the main driving force in the area of OLEDs [12-14].

## II. PRINCIPLE OF ELECTROLUMINESCENCE

OLED technology is based on the principle of electroluminescence, a phenomenon first discovered by Pope et al. in 1963 [15,16]. In the devices based on electroluminescence, holes and electrons are injected in the opposite sides of a planar multilayer thin film. These holes and electrons migrate through the thin film, to an interface (doped with emitter molecules) where they recombine to form radiative excited states called excitons that radiatively decay to produce luminescence from the device (Scheme 1).



Scheme 1. Schematic representation of the working principle of OLED.

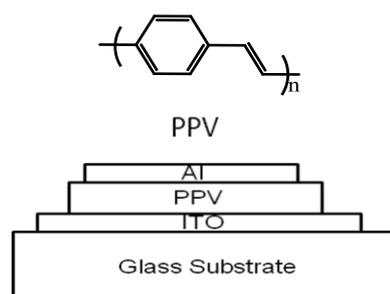
Depending on the nature of the emitter used OLEDs can be divided into two main categories viz., small molecule organic light emitting diodes (SMOLED) and polymer light emitting diodes (PLED). The first multilayer SMOLED device was fabricated by Tang and Vanslyke in the year 1987 where they

used a fluorescent molecule Alq<sub>3</sub> (Scheme 2) as the dopant<sup>3</sup> which emits green light ( $\lambda_{\text{max}}=550$  nm) with an external efficiency of ~1% [17].



Scheme 2. Device structure and molecular structure of dopants in the first SMOLED.

Subsequently, Friend and coworkers in the year 1990 developed a PLED, where an emissive conjugated polymer PPV (Scheme 3) was deposited by an inkjet printing technique.<sup>4</sup> PPV emits in the green-yellow region with an external efficiency 0.05% [18-20].



Scheme 3. Device structure and molecular structure of dopants in the first PLED.

The electrically generated exciton formed by electron-hole recombination can be either a singlet or a triplet with the singlet to triplet ratio being 1:3 as determined by theoretical predictions and experimental measurements. Organic molecules that emit light do so from singlet excited states, emission in such systems is then a spin-allowed process called fluorescence. Fluorescent materials used to fabricate OLEDs do not give detectable triplet emission (phosphorescence). Also, in such systems intersystem-crossing (ISC) between the triplet and singlet manifold is quite inefficient at room temperature. Thus, the *maximum* internal quantum efficiency for OLEDs based on fluorescence is limited to only 25%. By doping OLEDs with heavy metal phosphors, singlet-triplet limitation can be eliminated. The excitons are trapped at the phosphor where strong spin-orbit coupling induced by a heavy

metal ion leads to singlet-triplet state mixing leading to an efficient phosphorescent emission at room temperature. Thus, by introducing a heavy metal ion it is possible to harvest both the singlet as well as triplet excitons. This is the principle behind the use of organometallic complexes as phosphorescent dopants.

### III. INTRODUCTION TO PHOSPHORESCENT Ir (III) COMPLEXES

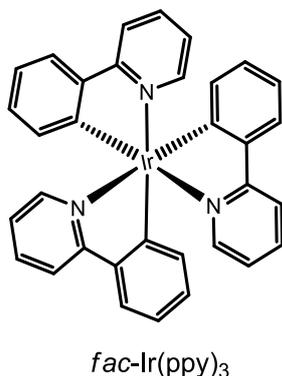
Organometallic complexes containing 4d and 5d transition metal ions serve as good candidates as phosphorescent dopants. The reason for this is the presence of strong spin-orbit coupling in such metal ions which leads to the mixing of singlet and triplet states, outriding the spin forbidden nature of radiative relaxation, resulting in high phosphorescence efficiencies [21-23].

Several studies are known in the literature that have focused on the design and the application of organometallic molecules which possess significant spin-orbit coupling. Square planar complexes of Pt(II),<sup>5-6</sup> Pd(II)<sup>7-8</sup> as well as octahedral complexes containing Ru(II),<sup>9-10</sup> Ir(III),<sup>11-12</sup> Os(II)<sup>13</sup> and Rh(III)<sup>14</sup> are the leading examples of such molecules as they exhibit highly efficient room temperature phosphorescence. Particularly, complexes containing Pt(II) and Ir(III) serve as efficient phosphorescent emitters. But, the main drawback of platinum complexes is that they have long phosphorescence lifetime which results in severe triplet-triplet annihilation at high current which eventually reduces the device efficiency [24,25].

Among all of these compounds, the most attractive choice appears to be organometallic complexes containing Ir(III) with a d<sup>6</sup> configuration. This is due to the presence of a very strong spin-orbit coupling present in such complexes. Organometallic Ir(III) complexes seem to be potential candidates for diverse applications in OLEDs,<sup>15</sup> LECs (Light-emitting electrochemical cells),<sup>16</sup> luminescent biological labels,<sup>17</sup> singlet oxygen sensitizers<sup>18</sup> etc.

### IV. SYNTHESIS AND STRUCTURE OF PHOSPHORESCENT Ir(III) COMPLEXES

The general structure of such cyclometalated Ir(III) complexes includes one core Ir atom with at least two anionic bidentate cyclometalating ligands (such as 2-phenylpyridine (ppy)). The bidentate ligand binds to the central metal ion through a C and a N atom. The remaining two coordination sites of Ir can be occupied by many ancillary ligands. If the ancillary ligand(s) and the cyclometalating ligand are the same then such complexes are homoleptic and if they are different then the complex is termed as heteroleptic. King *et al.* reported the tris-cyclometalated iridium



Scheme 4. First example of a Ir(III) cyclometalated phosphor used in OLEDs.

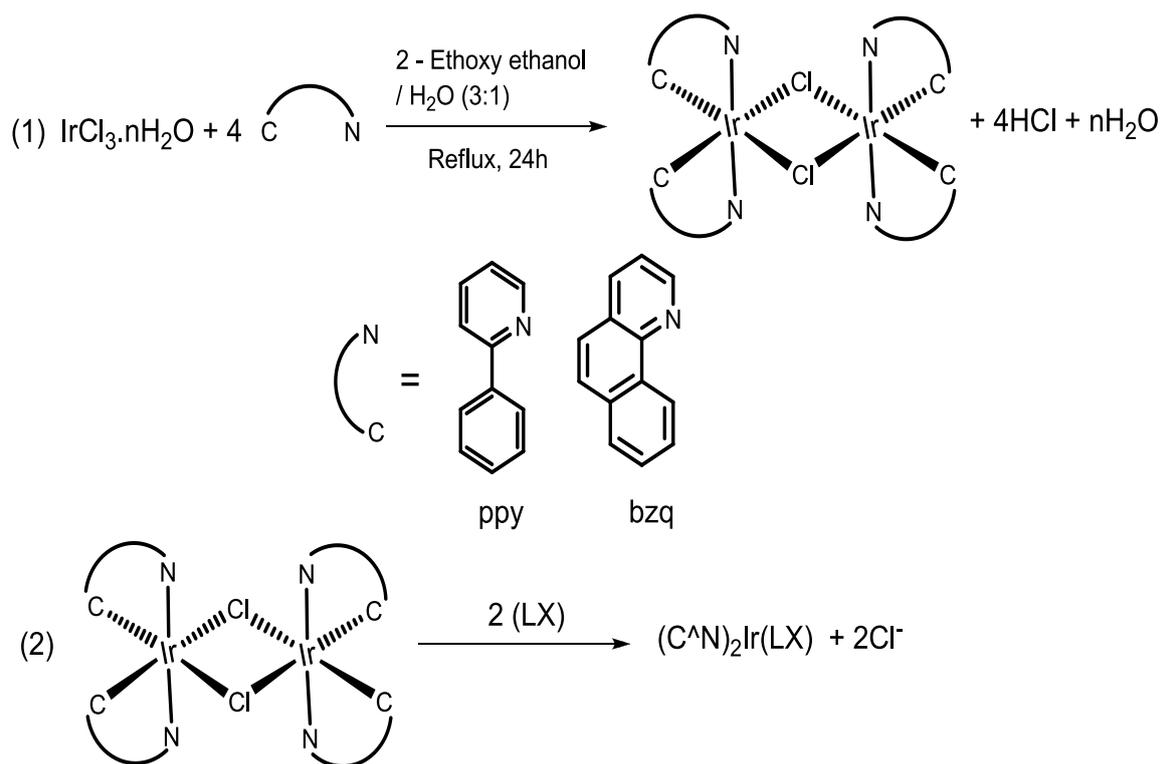
complex, *fac*-Ir(ppy)<sub>3</sub> in a low yield (~10%) as a byproduct in 1985 (Scheme 4). Subsequently, in 1999 Baldo *et al.* successfully developed an efficient green phosphorescent

OLED using the *fac*-Ir(ppy)<sub>3</sub> with the external efficiency ( $\eta_{\text{ex}}$ ) 8%.

The general synthesis of Ir(III) complexes involves a two-step procedure. The first step involves the now famous Nonoyama reaction where cyclometalating ligands are reacted with IrCl<sub>3</sub>·nH<sub>2</sub>O to give a chloro-bridged dinuclear Ir(III) complex [(C<sup>^</sup>N)<sub>2</sub>Ir]<sub>2</sub>(μ-Cl)<sub>2</sub> where C<sup>^</sup>N is the cyclometalating ligand.<sup>18</sup> The second step consists of *bridge-splitting* followed by substituting the chloride ligands by the ancillary ligand affording the final product (Scheme 5).

2-Phenylpyridine (ppy) is the most frequently used cyclometalating ligand. Other typical cyclometalating ligands (C<sup>^</sup>N) used are 2-(*p*-tolyl)pyridine (tpy), 2-(4,6-difluorophenyl)pyridine (dfppy), 1-phenylpyrazole (ppz) and 2-(4,6-difluorophenyl)pyrazole (dfppz) etc.

The ancillary ligand can be either a cyclometalating ligand (homoleptic) or a different kind (heteroleptic). The ancillary ligand can be generally chelating or non-chelating. Ligands such as acetylacetonates, pyrazoles, picolinates, triazolates and tetrazolates etc. have been extensively used ancillary ligands.

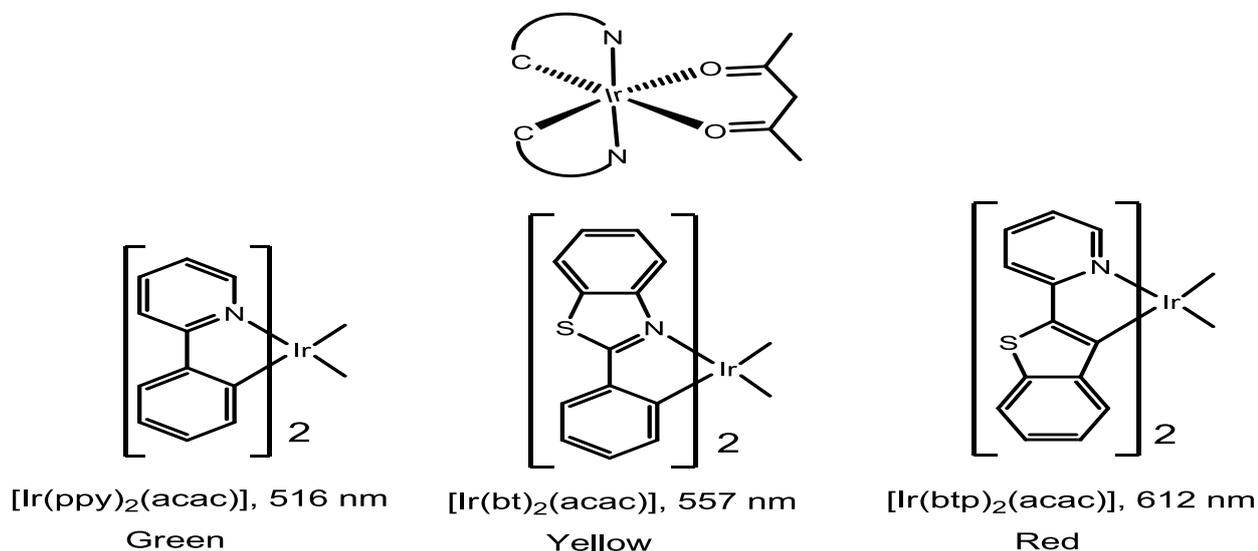


Scheme 5. The Nonoyama procedure for the preparation of the dinuclear chloride-bridged compound, [(C<sup>^</sup>N)<sub>2</sub>Ir]<sub>2</sub>(μ-Cl)<sub>2</sub> and subsequent bridge-splitting reaction with LX.

## V. COLOR TUNING OF THE CYCLOMETALATED Ir(III) COMPLEXES

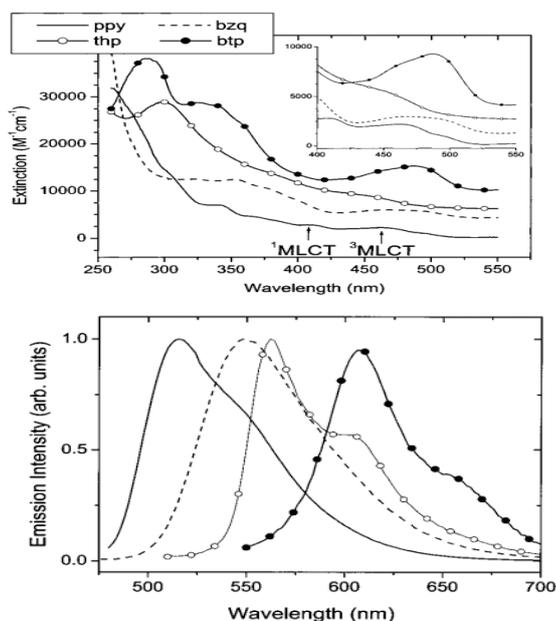
The most attractive feature of the cyclometalated Ir(III) complexes is that their emission color can be tuned over the whole visible spectrum<sup>20 - 22</sup> allowing their use for the construction of white light<sup>23</sup> or near-infrared emitters.<sup>24</sup>

This colour-tuning is possible by a meticulous selection of the cyclometalating as well as the ancillary ligand. For example, Thompson *et al.* used a series of cyclometalating ligands (Scheme 6) and ancillary ligand (acac) to vary the colour of the complexes from green to yellow to red.<sup>25</sup>



Scheme 6. Tuning of the color of  $\text{Ir}^{\text{III}}(\text{C}^{\wedge}\text{N})_2(\text{acac})$  complexes by changing the cyclometalating ligand.

Absorption and emission spectra of these compounds are shown in (Scheme 7).



Scheme 7. Absorption and emission spectra of cyclometalated  $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{acac})$  compounds ( $\text{C}^{\wedge}\text{N} = \text{ppy}, \text{thp}, \text{bzq}, \text{btp}$ ). (Reproduced from Ref. 25).

## VI. CONCLUSION

This article describes the synthesis, structures and photophysical properties of cyclometalated Ir(III) complexes. The potential applications of these compounds as dopants in OLEDs and LEECs are discussed. Though most luminophores are mononuclear heteroleptic (both neutral and cationic) complexes, di- and multinuclear complexes are proving to be superior alternatives. The ability to easily tune the luminescence spectra of organometallic complexes makes them attractive candidates for OLED materials.

## ACKNOWLEDGMENT

The author wish to thank Prof. V. Chandrasekhar, Director, NISER, Bhubaneswar and Dr. J. K. Bera, Professor, IIT Kanpur for introducing her to this field of work.

## REFERENCES

- [1] Castellano, J. A. Ed., Handbook of Display Technology, Academic Press, 1st Edition, 1992.

- [2] Pope, M., Kallmann, H., Magnante, P. *J. Chem. Phys.* 38: 2042, 1963.
- [3] Tang, C.W., Vanslyke, S.A. *Appl. Phys. Lett.* 51: 913, 1987.
- [4] Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burns, P. L., Holmes, A. B. *Nature.* 347: 539, 1990.
- [5] Lai, S.-W., Che, C.-M. *Top. Curr. Chem.* 241: 27, 2004.
- [6] Williams, J. A. G., Wilkinson, A. J., Whittle, V. L. *Dalton Trans.* 2081, 2008.
- [7] Wu, Q., Hook, A., Wang, S. *Angew. Chem. Int. Ed.* 39: 3933, 2000.
- [8] Deda, M. L., Ghedini, M., Aiello, I., Pugliese, T., Barigelletti, F., Accorsi, G. *J. Organometal. Chem.* 690: 857, 2005.
- [9] Baranoff, E., Collin, J.-P., Flamigni, L., Sauvage, J.-P. *Chem. Soc. Rev.* 33: 147, 2004.
- [10] Tung, Y.-L., Lee, S.-W., Chi, Y., Chen, L.-S., Shu, C.-F., Wu, F.-I., Carty, A. J., Chou, P.-T., Peng, S.-M., Lee, G.-H. *Adv. Mater.* 17: 1059, 2005.
- [11] Ragni, R., Orselli, E., Kottas, G. S., Omar, O. H., Babudri, F., Pedone, A., Naso, F., Farinola, G. M., De Cola, L. *Chem. Eur. J.* 15: 136, 2009.
- [12] Wong, W.-Y., Ho, C.-L. *Coord. Chem. Rev.* 694: 2661, 2009.
- [13] Chi, Y., Chou, P.-T. *Chem. Soc. Rev.* 36: 1421, 2007.
- [14] Indelli, M. T., Chiorboli, C., Scandola, F. *Top. Curr. Chem.* 280: 215, 2007.
- [15] Ulbricht, C., Beyers, B., Friebe, C., Winter, A., Schubert, U. S. *Adv. Mater.* 21: 4418, 2009.
- [16] Lowry, M.S., Bernhard, S. *Chem. Eur. J.* 12: 7970, 2006.
- [17] Lo, K. K.-W., Zhang, K. Y., Chung, C.-K., Kwok, K. Y. *Chem. Eur. J.* 13: 7110, 2007.
- [18] DeRosa, M. C., J. Hodgson, D., Enright, G. D., Dawson, B., Evans, C. E. B., Crutchley, R. J. *J. Am. Chem. Soc.* 126: 7619, 2004.
- [19] Nonoyama, M. *Bull. Chem. Soc. Jpn.* 47: 767, 1974.
- [20] Flamigni, L., Barbieri, A., Sabatini, C., Ventura, B., Barigelletti, F. *Top. Curr. Chem.* 281: 143, 2007.
- [21] Liang, B., Jiang, C. Y., Chen, Z.;Zhang, X. J., Shi, H. H., Cao, Y. *J. Mater. Chem.* 16: 1281, 2006.
- [22] Costa, R. D., Ortí, E., Bolink, H. J., Graber, S., Housecroft, C. E., Constable, E. C. J. *J. Am. Chem. Soc.* 132: 5978, 2010.
- [23] Sun, Y. R., Giebink, N. C., Kanno, H., Ma, B. W., Thompson, M. E., Forrest, S. R. *Nature.* 440: 908, 2006.
- [24] Mehlstäubl, M., Kottas, G. S., Colella, S., De Cola, L. *Dalton Trans.* 2385, 2008.
- [25] 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.* 123, 4304, 2001.