SUMMARY

OF

MINOR RESEARCH PROJECT

IN

PHYSICS

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Funding Agency : UGC

Sanction Amount : 1,20,000/-


Date of Implementation : February 11, 2010.

Duration of Project : 2 years. (11th February 2010 to 10th February 2012)

Title of the Project: “SYNTHESIS AND CHARACTERIZATION OF PHOSPHORESCENT MATERIALS FOR DISPLAY APPLICATION”.

Place of Work :- SHRI SHIVAJI EDUCATION SOCIETY AMRAVATI'S,

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1. Introduction: An organic light-emitting diode (OLED) is a special type of light-emitting diode (LED). An OLED is composed of at least one undoped organic layer that is put between two electrodes. Electrons and holes are injected from either side of the electrode, respectively. After applying a voltage, both carriers will drift towards the other side in the applied electrical field. When both electrons and holes meet at the bulk or the interface, they then recombine to form excitons, which will decay to produce light emission. In 1987, Tang et al. [3] reported OLEDs based on small organic molecules by thermal vacuum deposition and in 1990, at Cambridge University, Friend et al. [51] reported OLEDs based on solution-processed semiconducting polymers. These two pioneering works made a breakthrough in the OLED areas, and since then lots of papers on this subject were published. According to the materials used for OLEDs, OLEDs can be divided into two types: small-molecular OLEDs and polymer light-emitting diodes (PLEDs). Generally, an OLED refers to small-molecular OLED.

Since the first observation of organic electroluminescence (i.e. the generation of light by electrical excitation of an organic material) in the 1960s by applying hundreds of volts to an anthracene single crystal [1], in the recent decades the field of organic electronics has progressed enormously [2]. Boosted by the pioneering work of Tang and VanSlyke and the resulting worldwide activity in numerous research groups [3], the advances in the fields of device science, device fabrication as well as chemistry, physics and materials science have evolved organic light-emitting device (OLED) technology to a point where it is now an important competitor to liquid crystals and liquid crystal displays (LCDs) [4-8]. Consequently, the interest in OLED technology has been impressive and first commercial products based on small molecules and conducting polymer films are already available. The OLED market is still growing and a large expansion in market penetration has been forecasted [2]. The tremendous interest in OLEDs and displays made from these devices is especially caused by technological aspects such as low costs, the ease of fabrication using standard techniques (e.g. vacuum deposition or solution processing) [9-13], the possibility of realizing flexible or large-area displays, their use in lighting applications and the variety of organic materials providing emission wavelengths that cover wavelengths from the ultraviolet to near infrared [14-16].

Although OLEDs already meet the requirements for some practical applications in, e.g., portable electronics like cellular phones or digital cameras [5] with operating lifetimes up to 100,000 hours [16], the intrinsic limits of organic light-emitting devices have not been reached yet [17]. Therefore, further scientific efforts devoted to the design, engineering and fabrication of OLEDs also considering charge carrier injection, spin effects, interfaces, quenching processes, morphology changes or light extraction have to be undertaken in order to provide a step forward to the complete commercialization of this technology [2]. The design and synthesis of novel emitter materials plays an important role in commercialization of this technology. Therefore, the concepts of fluorescent and phosphorescent emitter materials are herein discussed putting special focus on phosphorescent iridium complexes (as prototypical example of dopants suitable for realizing high-performance electroluminescent devices).

Electro phosphorescent materials incorporating complexes of third-row transition-metal elements have attracted a great deal of attention because of their
potential applications as highly efficient electroluminescent (EL) emitters [18-28]. The strong spin-orbit coupling induced by the heavy metal promotes an efficient intersystem crossing from the singlet to the triplet excited state manifold, which then facilitates strong electroluminescence by harnessing both singlet and triplet excitons after the initial charge recombination.

EL devices based on these phosphors allow both singlet and triplet excitons to be harvested and the internal efficiency, theoretically, can reach as high as 100%[29]. For full-color display applications, red, green, and blue emitting materials that have sufficient luminous efficiency and proper chromaticity must be developed. The synthesis of efficient red emitters is intrinsically more difficult because their luminescence quantum yields tend to decrease as the emission wavelength increases in accordance with the energy gap law [30,49].

The cyclometalated iridium complexes used in EL devices are octahedral, with a 3 oxidation state, and exhibit strong phosphorescence primarily from a triplet metal-to-ligand charge-transfer (3MLCT) or a ligand-centered 3n–n* transition [21-23].

The emission colors from these complexes, which range from blue to red, are strongly dependent on the choice of the cyclometalating ligand[21-23]. Structural modifications of the ligands in Ir (III) complexes would affect the electro luminescence (EL) performance of phosphorescent OLEDs using them as dopants [24]. The purpose of the present study was the molecular design of highly efficient red phosphorescent emitters based on iridium (III) phenyl quinoline complex.

In full-color display applications, it is important to require a pure red emission. Although platinum complex (PtOEP) shows red emission at 650 nm (CIE) chromaticity coordinates of \((x, y) = (0.72, 0.29)\), the occurrence of triplettriplet (T–T) annihilation is inevitable at high currents due to its relatively long phosphorescent lifetime [29,30] which will lead to low electroluminescent (EL) efficiency at high current density.

Recently, the studies are focusing on the iridium complexes[31-37] with relatively short phosphorescent lifetime for the development of red OLEDs. The red emissions at 622 nm, 624 nm and 625 nm have been obtained in OLEDs employing iridium isoquinoline complex and 2-(9,9-di-n-octyl fluoren-2-yl)-4-phenyl quinoline (FPQ) complex. Some red emitting soluble phosphorescent iridium complexes are listed in table 1.1.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Ir complex</th>
<th>Soluble in</th>
<th>Emission wavelength (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>Ir(btp)(_2)(acac)</td>
<td>2-methyltetrahydrofuran</td>
<td>612 (PL)</td>
<td>22</td>
</tr>
<tr>
<td>2)</td>
<td>Ir(piq)(_3)</td>
<td>toluene</td>
<td>620</td>
<td>40</td>
</tr>
<tr>
<td>3)</td>
<td>Ir(DBQ)(_2)(acac)</td>
<td>CH(_2)Cl(_2)</td>
<td>618 (PL)</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Ir(MDQ)(_2)(acac)</td>
<td></td>
<td>608 (PL)</td>
<td></td>
</tr>
<tr>
<td>4)</td>
<td>Ir(piq)(_3)</td>
<td>1,2-dichlorobenzene</td>
<td>620</td>
<td>41</td>
</tr>
<tr>
<td>5)</td>
<td>Ir(piq)(_3)</td>
<td>1,2-dichlorobenzene</td>
<td>630</td>
<td>42</td>
</tr>
<tr>
<td>6)</td>
<td>Ir(C8piq)(_3)</td>
<td>p-xylene</td>
<td>621</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>Ir(4F5mpiq)(_3)</td>
<td></td>
<td>608</td>
<td></td>
</tr>
<tr>
<td></td>
<td>([F = Fluorine, M = Methyl])</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7)</td>
<td>Ir(C4-piq)(_3)</td>
<td>1,2-dichlorobenzene</td>
<td>619 or 617</td>
<td>39</td>
</tr>
<tr>
<td>8)</td>
<td>Ir(BPPa)(_3)</td>
<td>CH(_2)Cl(_2)</td>
<td>625 (PL)</td>
<td>44</td>
</tr>
</tbody>
</table>
| 9) | (piq)$_2$Ir(PO)  
   (nazo)$_2$Ir(PO)  
   (piq)Ir(PO)$_2$  
   (nazo)Ir(PO)$_2$ | CH$_2$Cl$_2$ | 652 (PL)  
   657 (PL)  
   591, 620 (PL)  
   690 (PL) | 45 |
|---|---|---|---|
| 10 | i) (Et-Cvz-PhQ)$_2$Ir(pic)  
   ii) (EO-Cvz-PhQ)$_2$Ir(pic)  
   iii) (EO-Cvz-PhQ)$_2$Ir(pic)N-O | 1,2-dichlorobenzene | 600 | 46 |
| 11 | (Ir[phq]$_2$acac  
 Ir[piq]$_2$acac | 1,2-dichlorobenzene | 596 and 597 | 47 |
| 12 | Ir[dbfiq]$_2$(bdp) | Toluene  
 Device | 640 (PL)  
 636 to 642 | 48 |

PL: Photoluminescence

### 2. The Present Project work

Even though organic light-emitting device (OLED) technology has evolved to a point where it is now an important competitor to liquid crystal displays (LCDs), further scientific efforts devoted to synthesized the materials to the design, engineering and fabrication of OLEDs are required for complete commercialization of this technology. Along these lines, the present work synthesis and characterization of iridium complexes for OLED technology putting special focus on fluorescent and phosphorescent emitter materials. Moreover, as a prototypical example of phosphorescent emitter materials, a brief discussion of iridium(III) complexes is enclosed concentrating on their synthesis, photo physical properties and approaches for realizing iridium based phosphorescent polymers.

The main aim of the present work is to synthesis of Iridium (III) based complexes for organic light emitting diode which are based on methyl, methoxy, chlorine-methyl, and chlorine substituted 2-4 diphénylquinoline ligands. On the basis of above mentioned problems, this project is focused on structural conformation, thermal stability and optical studies UV-vis absorption, photoluminescence and optical efficiency of the iridium based complexes. This is achieved by synthesizing 2, 4-diphenyl quinoline ligand by substituting styryl(methoxy, methyl and chloride) groups and then synthesizing corresponding iridium complexes. The chemical modification of the 2, 4-diphenyl quinoline by introducing the styryl (methoxy, methyl and chloride) group at the 2-position is expected to change the emitting wavelength of the complexes.

### 3. Conclusions

It is known that the HOMO of iridium(III) complexes is determined by the 5d orbital of Ir(III) with substantial mixing with the π orbital of the ligand and the LUMO is related to the π* orbital of the ligand [40].

Thus, One can modulate HOMO and LUMO values of Ir(III) complexes to tune the emission color by changing the structure of the ligands. Upon this point, we synthesized a series of new ligands with different substituents at Para-position of 2-phenyl ring in 2,4-diphenyl-quinoline (DPQ) unit. Corresponding bis-cyclometalated iridium(III) complexes were synthesized and their electrochemical, photo physical and electro phosphorescent properties were studied. With the above ideas, we have successfully synthesized phosphorescent iridium complexes Ir[DPQ]$_2$(acac),
Ir(OMe-DPQ)$_2$(acac), Ir(Cl-DPQ)$_2$(acac), Ir(OMe-MDPQ)$_2$(acac) and Ir(M-DPQ)$_2$(acac) by using 2-4 diphenyl quinoline (DPQ), OMe-DPQ, Cl-MDPQ, M-DPQ and CI-DPQ as a cyclometalating ligands and acetyl acetone (acac) as an ancillary ligand. The photo physical properties of iridium(III) complexes have received considerable attention because of a series of practical applications such as flat-panel displays.

The synthesized complexes are thermally very stable over a wide range of temperature and suitable for the use as red-emissive materials in solution processed organic devices, OLEDs. It is also very promising for applications in flexible organic devices.

For the fabrication of efficient phosphorescent OLEDs, the transition metal complex is typically used as emitting guest in a host material to avoid triplet-triplet annihilation or quenching effects associated with the relatively long excited state lifetimes. All the synthesized Iridium complexes shows orange-red to red colors emission in red spectral region.

As a consequence, phosphorescent iridium complexes have emerged as the most promising class for practical OLED applications and the number of new phosphorescent complexes with emission wavelengths covering the entire visible spectrum is still growing. The photo physical properties of Iridium complexes are summarized in table 4.1.

Table 4.1 Photo physical Properties of the Complexes in THF solution at room temperature

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ir(2,4-DPQ)$_2$(acac)</th>
<th>Ir(OMe-DPQ)$_2$(acac)</th>
<th>Ir(Cl-DPQ)$_2$(acac)</th>
<th>Ir(OMe-MDPQ)$_2$(acac)</th>
<th>Ir(M-DPQ)$_2$(acac)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Che.Form.</td>
<td>C$<em>{47}$H$</em>{35}$N$_2$O$_2$Ir</td>
<td>C$<em>{49}$H$</em>{39}$N$_2$O$_4$Ir</td>
<td>C$<em>{47}$H$</em>{35}$N$_2$O$_2$ClIr</td>
<td>C$<em>{49}$H$</em>{39}$O$_2$N$_2$ClIr</td>
<td>C$<em>{49}$H$</em>{39}$O$_2$N$_2$ClIr</td>
</tr>
<tr>
<td>Nature</td>
<td>crystalline</td>
<td>crystalline</td>
<td>crystalline</td>
<td>crystalline</td>
<td>crystalline</td>
</tr>
<tr>
<td>$\lambda$emi (nm)</td>
<td>615 nm</td>
<td>610nm</td>
<td>620nm</td>
<td>662nm</td>
<td>650nm</td>
</tr>
<tr>
<td>CIE Coordinates</td>
<td>(0.679, 0.318),</td>
<td>(0.661, 0.330)</td>
<td>(0.686, 0.309)</td>
<td>(0.713, 0.282)</td>
<td>(0.715, 0.283)</td>
</tr>
</tbody>
</table>

The physical and chemical properties of synthesized blue emitting organic phosphors materials 2,4-Diphenyl Quinoline (DPQ), OMe-DPQ, Cl-MDPQ, M-DPQ and CI-DPQ ligands (polymers) which is suitable as electron transport materials in OLEDs are summaries in Table 4.2.

Table 4.2 Physical and Chemical Properties 2, 4-DPQ and its substituted derivatives

<table>
<thead>
<tr>
<th>Compounds</th>
<th>2,4-DPQ</th>
<th>OMe-DPQ</th>
<th>CI-DPQ</th>
<th>Cl-MDPQ</th>
<th>M-DPQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Che.Form.</td>
<td>[C$<em>{21}$H$</em>{17}$N]</td>
<td>[C$<em>{22}$H$</em>{17}$NO]</td>
<td>[C$<em>{21}$H$</em>{16}$ClN]</td>
<td>[C$<em>{22}$H$</em>{16}$NCl]</td>
<td>[C$<em>{22}$H$</em>{17}$N]</td>
</tr>
<tr>
<td>Color</td>
<td>Off-white</td>
<td>Off-white</td>
<td>white</td>
<td>off-white</td>
<td>off-white</td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
<td>-----------</td>
<td>-------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>Nature</td>
<td>crystalline</td>
<td>crystalline</td>
<td>crystalline</td>
<td>crystalline</td>
<td>crystalline</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>383, 399 nm</td>
<td>385 nm</td>
<td>385 nm</td>
<td>338, 350nm</td>
<td>342, 346nm</td>
</tr>
<tr>
<td>$\lambda_{\text{emi}}$</td>
<td>436 nm</td>
<td>434 nm</td>
<td>450 nm</td>
<td>411 nm</td>
<td>406 nm</td>
</tr>
<tr>
<td>m.p.</td>
<td>114 °C</td>
<td>98 °C</td>
<td>111 °C</td>
<td>130.65 °C</td>
<td>103.59 °C</td>
</tr>
<tr>
<td>Onset</td>
<td>300 °C</td>
<td>298 °C</td>
<td>327 °C</td>
<td>126.14 °C</td>
<td>100.58°C</td>
</tr>
<tr>
<td>Td</td>
<td>338 °C</td>
<td>340 °C</td>
<td>345 °C</td>
<td>212 °C</td>
<td>233</td>
</tr>
<tr>
<td>Mol.Wt.</td>
<td>283.231</td>
<td>311.242</td>
<td>317.691</td>
<td>329.692</td>
<td>295.242</td>
</tr>
</tbody>
</table>

The present results on the electronic structure and optical properties of (DPQ), OMe-DPQ, CI-MDPQ, M-DPQ and CI-DPQ suggest that they can be expected to have improved nonlinear optical properties. The results of the present study show that the optical band gap of the 2, 4-DPQ and its substituted derivatives varies from 3.048 to 3.465 eV. We can thus expect enhanced and spectrally tunable photo electronic properties in the new polymeric compounds. The TGA, DTA and DSC study of the compound show good thermal stability. The introduction of the chlorine group into the backbone disrupt the copolanearity of aromatic units in chain packing which increases the between-chains spaces or free volume thus enhancing solubility and thermal stability.

In the present study, the essentials of OLED technology have been reviewed putting special focus the use of fluorescent and phosphorescent emitter materials. After discussion of the advantages of phosphorescent complexes doped into suitable host materials and the corresponding energy transfer processes, the synthesis and photo physical properties of phosphorescent iridium(III) complexes have been enclosed. It has been shown that this class of materials exhibits photo physical characteristics readily tuned by changes of the cyclometalating and/or ancillary ligands, thus being ideal candidates for applications in, e.g., full color displays.

### 4. Scope of the work

The scope of present study is that by using different strategies for incorporating iridium complexes into polymers can give phosphorescent polymers with reduced phase separation in combination with facilitated device fabrication (e.g. solution processing). The development of OLEDs has undoubtedly been empowered by different applications in display technology. As a consequence, tremendous scientific efforts have been devoted to this topic concentrating on the design, engineering and fabrication of OLEDs. For the fabrication of efficient phosphorescent OLEDs, the transition metal complex is typically used as emitting guest in a host material to avoid triplet-triplet annihilation or quenching effects associated with the relatively long excited state lifetimes [57]. Not surprisingly, numerous reports can be found in literature focusing on the synthesis and characterization of novel iridium, platinum or osmium based complexes for realizing highly efficient phosphorescent OLEDs [55-59]. Among these materials, phosphorescent iridium(III) complexes are anticipated to be the most promising candidates for practical applications.

### 5. Applications
1) Since the pioneering work of Baldo and co-workers showing that phosphorescent dyes (transition metal complexes with organic ligands or organometallic compounds) doped into appropriate host materials give improved OLEDs. The OLED will be a good candidate for the new generation of the solid-state lighting, in Flat-Panel Displays etc.

2) For the fabrication of efficient phosphorescent OLEDs, the transition metal complex is typically used as emitting guest in a host material to avoid triplet-triplet annihilation or quenching effects associated with the relatively long excited state lifetimes.

3) The interest in iridium compounds iridium(III) has especially been boosted by the different fields of application ranging from very efficient catalysts to important emitter materials in OLEDs.

4) The synthesized Iridium complexes with the emission in the red region are very promising for applications in flexible organic devices.

5) The cyclometalated Ir(III) complexes show high phosphorescent efficiencies and are one of the most promising classes of phosphorescent dyes used in organic light emitting diodes (OLEDs).

6. References


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