Final Report of the Work Carried Out Under Interdisciplinary Projects in Sciences

(Approval No.: G/No.DST Purse/ 12-13/1674 dated 6/6/12; Total Grant 1,00,000/-)

"Synthesis of Materials Based on Mixed Ligand Complexes and their Evaluation as Solid-State Electroluminescent Devices"

Submitted by

Dr. Kirankumar R. Surati Principle Investigator Department of Chemistry Sardar Patel University V.V.Nagar (Gujarat)-388 120

Dr. K. D. Patel
Co-Investigator
Department of Physics
Sardar Patel University
V.V.Nagar (Gujarat)-388 120

Sardar Patel University Vallabh Vidyanagar 388120

Final report of the work done on the interdisciplinary research project (Report to be submitted by 15/04/2013)

- 1. University Reference: No. G/No.DST Purse/ 12-13/1674 dated 6th June 2012
- 2. Period of report from: 05/06/2012 to 31/03/2013
- 3. Title of research project: "Synthesis of Materials Based on Mixed Ligand Complexes and their Evaluation as Solid-State Electroluminescent Devices"
- 4. (a) Name of the Principle Investigator: Dr. Kirankumar R. Surati
 - (b) Deptt. Where work has progressed: Department of Chemistry, S. P. University.
- 5. Effective date of starting of the project: 05/06/2012
- 6. Grant approved and expenditure incurred during the period of the report
- (a) Total amount approved: Rs.80,000/-
- (b) Total expenditure: Rs. 64,972/-
- (c) Report of the work done: (Please attach five pages in a separate sheets) (Encloser 1)
- (i) Brief objective of the project:

The present work mainly deals with following objectives

- > To synthesis and characterization of novel mixed ligand complexes of Schiff base pyrazolone and ancillary ligand with Ir(III) and Zn(II) complexes
- > Photophysical properties measurement using absorption and photoluminescence spectra
- > Solid state conductance measurements for suitability of device
- > IV characteristics measurements for applicability of the device
- > Measurement of electrochemical properties using cyclic voltammetry
- > Fabrication of electroluminescent devices based on above mentioned mixed ligand complexes
- (ii) Work done so far and results achieved (in the following format)
- (a) Definition of problem handled:

The present work mainly deals with the synthesis of novel coordination compounds having iridium (III) as metal ion. All the Schiff base pyrazolone ligands are design in such way that one can tune the triplet level of the ligands to match the level of metal ions. Importantly, the design can improve the photoluminescence quantum efficiency of coordination compounds. All sets of

study can find the soup of the material in fabrication of solid state electroluminescent devices. The first solid-state electroluminescent device from a transition metal complex was reported in 1996 by the MIT group [1]. Since then, tremendous progress has been achieved in the performance of these devices, [2–11] which today is close to that of the best organic light-emitting diodes. As with every new class of electroluminescent materials, questions arise regarding (i) the ultimate limits of their efficiency, (ii) their response time, (iii) the availability of multiple colours, as well as (iv) their lifetime in devices. Transition metal complexes have emerged as promising candidates for applications in solid-state electroluminescent devices. These materials serve as multifunctional chromophores, into which electrons and holes can be injected, migrate and recombine to produce light emission. Their device characteristics are dominated by the presence of mobile ions that redistribute under an applied field and assist charge injection.

Due respect with above mention fact and the importance of these materials, the present proposal mainly deals with designing novel class of mixed ligands coordination compounds of with Schiff base pyrazolone ligands. All the compounds are plan to characterized and evaluate their properties for solid state electroluminescence devices.

b) Methodology adapted:

i. Approach /Strategy

Tuning of the photophysical properties of iridium (III) and zinc(II) complexes has received considerable attention because of a series of applications. Numerous iridium (III) and Zn(II) compounds have been reported giving efficient electroluminescence in the red, green and blue spectral region. The synthesis and photophysical characterization of novel ruthenium and osmium complexes have been published [9, 12-14], though still it is very important to understand the role of coordinating ligand and its effect on the electroluminescence. The present work is planned to focus on mixed ligand complex of iridium (III) and zinc (II) the effect of Schiff pyrazolone ligands along with various bipyridine derivatives. Further, some strategies of tuning the emitting color involve changing the degree of conjugation in the structure of cyclometalating and ancillary ligands at the complexes [15, 16]. The ancillary ligand is associated with metal to ligand charge transfer (MLCT) transition and plays a more passive role in determining the nature of the exited state. The pyrazolone base ligand with iridium (III) and zinc (II) complexes are also

lead to fine tuning of its emission color by orbital engineering with the d-orbitals metal ion and enhance the luminance efficiency.

Thus, Schiff base pyrazolone (scheme 1) series are plan to synthesize as novel ancillary ligands substitute for R_1 and R_2 represents different substitution at given position. As consequence series of ruthenium and osmium complexes are obtained with elevated efficiency and tuning of its emission color.

$$R_3$$
C R_3 OH

Scheme 1 (Where $R_1 = -CH_3$, $-C_6H_5$, $-C_6H_4Cl$; $R_2 = H$, CH_3 , SO_3H , Cl; $R_3 = Various primary amine)$

- ii. Schematic representation of the method/ Design of the device
- The fabrication of device includes a standard spine coating or vacuum-vapor deposition process. The emitting area is 2 x 2 mm and device are formed on the same Glass subtract. 4,4-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (NPB) the hole transporter is deposited on the indium tin oxide (ITO) coated glass. The NPB layer is followed by a layer of 4,4'-N,N'-dicarbazole-biphenyl(CBP) doped with mixed ligand complexes. Layer of TPBi to serve as the hole-blocker and electro-transporter or tri-(8-hydroxyquinoline) alluminum(III) (Alq₃) as the electron-transporter and Mg: Ag/Ag as the cathode, are deposited.

c) Detailed work and d) Results and Conclusion

Synthesis of Schiff base ligands

All the Schiff base compounds were derived from pyrazolone base compounds with various primary amines (Scheme 1).

Synthesis of Ir(III) and Zn(II) complexes

All the Ir(III) and Zn(II) metal complexes were synthesized with 3:1 and 2:1 ligands in methanol /metal ratio respectively. The representative compounds have been synthesized and their general structure is given below (Scheme 2).

Scheme 2: Some representative complexes to be synthesized in this proposed work

Experimental

All the compounds will be characterized by spectroscopy and crystallography study. Elemental analysis (C, H, N) will be performed on a model 2400 Perkin–Elmer elemental analyzer. Infrared (IR) spectra will be recorded on a model RX 1 FTIR Perkin–Elmer as KBr pellets. ¹H NMR spectra will be recorded on Bruker AV 400 MHz using suitable deuterated solvent and TMS as internal reference. The electronic spectra will be recorded on a model Perkin Elmer Lambda 35 UV–VIS spectrometer. The photoluminescence will be recorded on Edinburgh Instruments FLSP 920 system at BARC, Mumbai. Mass spectra (EI)/(FAB) of the compounds will be recorded at SAIF, CDRI, Lucknow. Specific conductivity of the Schiff base complexes will be measured on a model Elico CM 180 conductivity meter.

X-Ray single crystallogtraphic analysis of the synthesized compounds will be performed on Bruker SMART equipped with CCD area-detector diffractometer, equipped with low temperature device.

Characterization and Luminescence properties

All the compounds are synthesized and characterised by spectroscopy and studied the crystal structure of some Schiff base ligands (Coded as PMP-BA, MCPMP-T and MCPMP-BA shown in **Figure1**). PMBP-PAA and the corresponding coordination compounds of Ir(III) and Zn (II) have not yet been crystallized. We are presently working on it by slow evaporation.

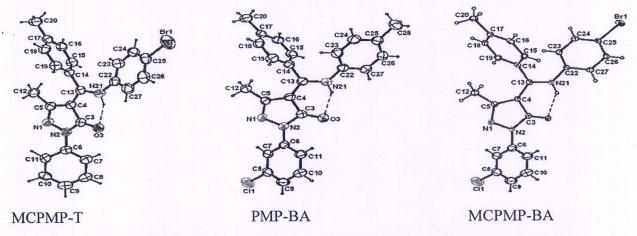


Figure 1: ORTEP diagram of some of our synthesized Schiff base ligands

I have studied the UV-vis absorption spectra of all the complexes (**Figure2**), where, spin-allowed metal-to-ligand charge transfer band (1 MLCT), spin –forbidden 3 MLCT and spin-orbital coupling enhanced ${}^{3}\pi - \pi^{*}$ transition have been detected. The formally spin-forbidden 3 MLCT gains the intensity through the strong spin-orbital coupling on the Iridium centre.

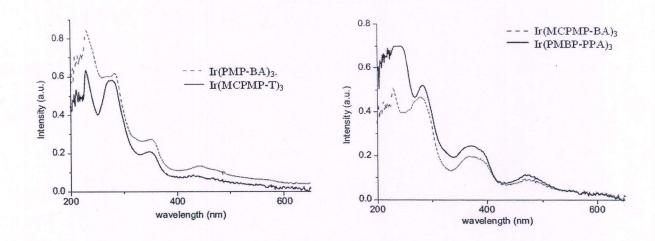
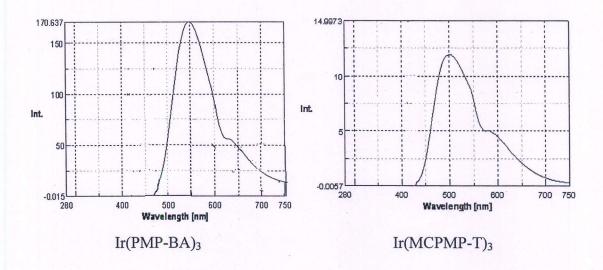


Figure 2: Electronic spectra of some of the synthesized complexes

The emission maxima for Ir(PMP-BA)₃, Ir(MCPMP-T)₃, Ir(MCPMP-BA)₃ and Ir(PMBP-PPA)₃ appeared at 550 nm, 500 nm, 500 nm and 600 nm, respectively with good phosphorescence in 10^{-5} M CH₂Cl₂ solution. As an achievement towards the study on the Structure-Activity-Relationship of these materials, we have been able to establish the relation between pyrazolone scaffolds by changing the substitution pattern (i.e. R₁, R₂ & R₃) to its photoluminescence property. Further, it is equally important to study the effect of neutral ligands such as bipyridyl derivatives in the present context.

The Photoluminescence spectra of Ir(III) Schiff base complexes shown in given figure below.



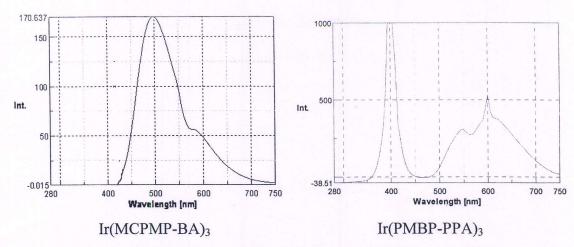


Figure 3: Photoluminescence spectra of Ir(III) Schiff base complexes

My major strength is in the synthesis of Schiff base ligands with desired properties by designing the molecule with proper adjustment of chromophore and lumophore. In addition to that we are working on tuning of OLEDs by modified the Schiff base pyrazolone with electron donor and electron accepter groups.

e) Details of publications (including conference presentations):

Oral presentation of research paper "Highly efficient Phosphorescent Iridium (III) and Zn(II) Mixed Ligand Complexes for OLEDs Application" at International Union of Materials Research Societies- International Conference on Electronic Materials 2012 (IUMRS-ICEM-12) which is to be held on 23rd -28th September 2012 at Pacifico Yokohama, Japan. (This visit support under DST, International Travel Support (ITS) Ref. No.SR/ITS/ 2929/2012-2013 & 16/08/2012).

iii. Has the progress been according to original plan of work and towards achieving the objective?

Yes, but unfortunately not to the extent I have proposed in the original proposal, due to the insufficient grant allotted to do this work.

iv. Please indicate the difficulties, if any, experienced in implementing the project:

There is no big difficulty encountered during the project tenure except budgetary allotment.

v. If project has not been completed, please indicate the reasons: N.A.

vi. Any other information which would help in evolution of work done on the project. :

The data generated under this project are useful as preliminary background for future research project consider under the DST, Technology System Development (TSD). It also establishes interdisciplinary approach to work across the barrier of subject.

Date: 04/05/2013

08000

SIGNATURE OF THE PRINCIPLE **INVESTIGATOR** (STAMP)

Dr. Kirankumar R. Surati

Assistant Professor, Assistant Professor,
Department of Chemistry,
Sardar Patel University,
V. V. Nagar-388120
Gujarat (INDIA)
E-mail: kiransurati@yahoo.co.in

SIGNATURE OF THE **CO-INVESTIGATOR**

HEAD OF THE DEPARTMENT

Head of the Chemistry Department Sardar Patel University Vallaigh Vidyanager-388120 Rujarat State, (Insta)