

NEWER METAL COMPLEXES FOR ORGANIC LIGHT EMITTING DEVICES

Project No. 40-51/2011(SR)

(July 2011 - 2014)



SPONSORED BY

UNIVERSITY GRANT COMMISSION, NEW DELHI

Dr. Pratap Singh Kadyan
Principal investigator



**DEPARTMENT OF CHEMISTRY
MAHARSHI DAYANAND UNIVERSITY
ROHTAK-124001, HARYANA**

Dec, 2014

EXECUTIVE SUMMARY

Summary of the UGC-Major Research Project entitled “Newer Metal Complexes For Organic Light Emitting Devices” Sanctioned to Dr Pratap Singh Kadyan, Professor, Department of Chemistry, Maharshi Dayanand University, Rohtak by University Grant Commission, New Delhi. [F. No. 40-51/2011(SR)]

Summary

In conclusion some N, O donating azomethine ligands with salicylaldehyde and different diamines had synthesized. Zinc and beryllium complexes were synthesized with these ligands. These complexes could be suitable emission source for fabrication of organic light emitting devices. These complexes showed high luminescence intensity under UV excitation. The color was tuned by using different bridging ligand as different derivatives of diamines. With increase in methyl group in bridging group there occurs blue shift in emission wavelength. The synthesized metal chelates showed excellent luminescent properties emitting blue light as reported here. Beryllium complexes emit at lower wavelength than zinc Schiff base complexes. The blue light emitting zinc complexes are less reported, synthesized zinc complexes can be used as blue light emitting materials for display applications.

We also synthesized some ternary metal complexes using N, O and N, N chelating agents as primary ligands and 8-hydroxyquinoline and its derivatives as secondary ligand. The metal complexes showed high luminescence intensity under ultraviolet-visible radiations excitation. Zinc, beryllium and magnesium metal complexes had synthesized. These complexes can be suitable emission source for fabrication of organic light emitting devices. Color tuning can be obtained by using these metal complexes for full color display applications.

Addition of different substituent on ligands had either increased or decreased the energy difference between the HOMO and LUMO of ligand moiety which promoted the energy transfer from ligand to metal thereby enhancing the photoluminescence. This trend could also be seen in the electroluminescence properties of the complexes. It was also noticed that emitted color could also be tuned by selecting either a suitable substituent in substituted 8-hydroxyquinoline or a metal ion for the synthesis of metal quinolates. It has happened due to changes in band gap between HOMO and LUMO of the metal quinolates. Based on these facts, we synthesized metal chelates using metals zinc, beryllium, magnesium etc. and suitably substituted 8-hydroxyquinoline and other ligands as discussed earlier. It is pertinent to mention here that increase in covalent character of metal ligand bond had also resulted in red shift of emission wavelength. Beryllium complexes emit at shorter wavelength as compared to the magnesium complexes and magnesium complexes emit at shorter wavelength as compared to the zinc complexes. Furthermore, emitted color was tuned by choosing the metal centre and suitably substituted 8-hydroxyquinolines. It is also noteworthy that excitation wavelength of the complex

was red shifted when electron donating group is introduced in phenoxide moiety particularly at 5 and 7 positions of quinoline ring and vice versa. It is due to increase in electron density in HOMO of the phenoxide ring. As a result, HOMO is destabilized which in turn decrease the band gap between HOMO and LUMO hence excitation wavelength is red shifted. This was in accordance with the reports available in the literature. A series of metal chelates so synthesized showed excellent luminescent properties as reported here.

We have also fabricated seven organic light emitting devices using different complexes as emissive materials and these materials were found to be efficient for OLEDs applications.

1. Organic light emitting devices containing mixed-ligand zinc complexes, i.e., 2-(2-hydroxyphenyl)benzothiazolato-5,7-dichloro-8-hydroxyquinolinatozinc(II) [ZnBTZ(Cl₂q)], 2-(2-hydroxyphenyl)benzothiazolato-5,7-dimethyl-8-hydroxyquinolinatozinc(II) [ZnBTZ(Me₂q)], 2-(2-hydroxyphenyl)benzothiazolato-2-carbonitril-8-hydroxyquinolinatozinc(II) [ZnBTZ(CNq)] and 2-(2-hydroxyphenyl)benzothiazolato-5-chloro-8-hydroxyquinolinatozinc(II) [ZnBTZ(Clq)] as emissive layer were fabricated and characterized. The electroluminescence spectra show peak emission centered at 532 nm, 572 nm, 541 nm and 552 nm respectively, for these materials. The emitted light has chromaticity with Commission Internationale d'Eclairage coordinates $x = 0.35$ and $y = 0.56$ for ZnBTZ(Cl₂q), $x = 0.49$ and $y = 0.47$ for ZnBTZ(Me₂q), and $x = 0.48$ and $y = 0.40$ for ZnBTZ(CNq), $x = 0.39$, $y = 0.56$ for ZnBTZ(Clq) complex. The results showed that there is mixed ligand complex are also good light emitting materials and it is observed that attaching on electron withdrawing groups as on phenol ring results in blue shift and addition of electron donating group phenol ring result in red shift.
2. Mixed ligand complex (2-(2-Pyridyl)benzimidazolato)2-methyl-8-hydroxyquinolinatozinc(II) [ZnPBIMEq] was found to be efficient green light emitting material. The device emitted light at 532 nm with CIE coordinates at $x = 0.34$, $y = 0.40$. The maximum brightness was found 2639 cd/m² at 12 V.
3. Organic electroluminescent (EL) devices were fabricated using the Schiff base zinc metal complexes Bis(salicylidene)propylene-1,3-diaminatozinc(II) [Zn(salpen)] and Bis(salicylidene)butylene-1,4-diaminatozinc(II) [Zn(salbutene)]. The device emitted bright bluish green light with emission peaks at 512 nm and 513 nm for [Zn(salpen)] and [Zn(salbutene)] respectively.
4. The turn-on voltages of the fabricated devices were found to be having low values from 8-16 V. The intensity of luminance and brightness of the devices increased with increase of applied voltages.
5. The current efficiency and power efficiency of the fabricated devices were found to be good as 1.18, 1.32, 1.40 Cd/A and 0.40, 0.32, 0.30 lm/W, respectively.

6. The synthesized metal complexes may be used in future as important and efficient emissive materials in fabrication of organic light emitting devices.

Objective of the Project

The metal complexes have attracted a great attention in the electronic industry because of their potential applications in organic light emitting devices shortly known as OLEDs. These materials find applications in electronic technological fields especially in flat panel display technology. The possible commercial use for them may be in lap-top computers, mobile phones, in automobile sectors like car dashboards, in advertisement panels and also in architectural market like decorative lighting etc. Elegant in their simplicity, OLED displays offer the thinnest profile of any colour flat panel technology. The whole assembly can be very small as little as 2 mm in depth that can replace the heavy and bulky cathode-ray tube of the display systems. Enormous work to synthesize the materials especially preparing organic hybrid materials complexing with metal ions is in progress throughout the world. Specialists working in this field have paid their attention towards making materials used for OLEDs producing photoluminescence with high quantum yield and with good stability in the devices.

Introduction and research focus

The phenomenon of the emission of the light from any material under excitation by photons or bombardment of electrons or by passage of an electric current is called luminescence and this is a low temperature process. Luminescence may be divided into two kinds: phosphorescence or fluorescence. Phosphorescent materials produce the emission of light which continue for a considerable time after the excitation source has been withdrawn, upto several seconds or longer. Phosphorescence can be produced by mainly three kinds of excitation, i.e. photoluminescence (PL) under excitation of photons, cathodoluminescence (CL) under bombardment of electrons and electro-luminescence (EL), by passing an electric current through a specimen. Electroluminescence can be produced by inorganic as well as organic materials. The electroluminescent with good quantum efficiency can be used for the fabrication of EL devices. An electro-luminescent cell has a layer of a phosphor, a binder and an inert filler between a pair of electrodes, the filler being inorganic materials such as TiO_2 or ZrO_2 or titanates. Here the phosphorescent material can be inorganic type such as ZnS , $(\text{Zn,Cd})\text{S}$ or other similar materials. Electroluminescent devices based on organic materials are of considerable interest owing to their attractive characteristics and potential applications to flat panel displays.

The metal chelates containing both oxygen and nitrogen donors in the organic molecules are the prominent materials in this area. The driving force in investigating the metal chelates compounds with oxygen and nitrogen donors is mostly due to the early discovery of the aluminum complex of 8-hydroxyquinoline, Alq_3 .

Alq_3 is used as an emissive material, which emits in the green region with a broad emission peak at 530nm. Other EL colours can be obtained by doping a small amount of specific

guest molecules in Alq₃ or by choosing different organic fluorescent materials as emitters. In some cases, doping can enhance luminance efficiency by reducing non-radiative decay. Doping of highly fluorescent organic dyes have shown a tremendous efficiency enhancement with good colour tuning properties¹⁻⁷. Since then, tremendous progress has been made in the field of organic electro-luminescence particularly in the last few years and commercialization activity is well underway.

To this date, Alq₃ is still the most widely used as electron transport and the host emitting material. This is because the compound is thermally and morphologically stable to be evaporated into thin film, easily synthesized and purified and is a good fluorescent emitter as a green colour. But, it has also several shortcomings such as mobility, bandgap and the ashing problem during sublimation. Studies on its molecular parking⁸, photodegradation⁹, electron drift mobility¹⁰, transport phenomenon,¹¹ excited state¹², fluorescence¹³ and electric field dependent quenching of EL¹⁴ are still in progress.

Attempts have been made to improve the quantum efficiency, thermal stability and thin film morphology of Alq₃ by structural modifications. For example, tris(5-hydroxymethyl-8-quinolinato)aluminum¹⁵ has been reported to form more uniform amorphous thin film than Alq₃ by slow vacuum deposition and the material emits green light with better efficiency. Bis(5,7-dichloro-8-quinolinato)-(8-quinolinolato)aluminum [Alq(Clq)₂]¹⁶ indicates that the red shift increases linearly as the number of Clq ligands increases. Another tridentate (salicylidene-0-amino-phenolato)(8-quinolinolato)aluminum [Al(saph-q)]¹⁷ has been synthesized and reported to be more stable than Alq₃.

Other metal chelates with variety of metal ions such as Be, Mg, Ca, Sr, Sc, Y, Cu and Zn have also shown decent device performance and interesting fluorescent properties. Sano et.al.¹⁸ have prepared several kinds of 2:1 complexes with 8-hydroxyquinoline derivative with these metal ions. Amongst them the beryllium complexes (Beq₂) has been found to be the most fluorescent in the green region (520 nm) and the zinc complex Znq was found to have a strong yellow fluorescence at 556 nm. They have also synthesized bis(10-hydroxybenzo-8-quinolinato)beryllium (Be bq₂) which has a strong fluorescence at 515 nm with high melting point at 368°C and good electron transport properties. The luminance efficiency of 6.1 cd/A has been shown in a device. Another highly fluorescent beryllium complex bis[2-(2-hydroxyphenyl)pyridine]beryllium¹⁹ was found to emit in the blue (445 nm) with a voltage of 3V and maximum luminance efficiency reaching 3-8 cd/A and a maximum luminance of 15000 cd/m² at derive voltage of 12V. The diphenyl analog of Alq₃ (Ph₂Bq₂) have also been synthesized²⁰ and their solution photoluminescence was 15 nm shorter, but had high quantum efficiency than the corresponding Alq₃ derivatives. Lithium derivative, viz (8-hydroxyquinolato)lithium and (2-methyl-8-hydroxyquinolato)lithium have also been found to be useful emitter²¹ with good electron injection and transport properties.

Recently, aluminum and zinc chelates²² with 2-(2-hydroxyphenyl)-5-phenyloxadiazole and 1-phenyl-2-(2-hydroxyphenyl)benzimidazole have been found to be useful materials as they could serve as host electron transport emitters in the blue fluorescent region.

It has been observed recently that one of the key developments in the advancements of the OLED display technology is attributed to the discovery of the guest–host doped emitter system²³. The reason being that the host material with optimized transport and luminescent properties may be used together with fluorescent guest dopants leading to EL of desirable hues with high efficiencies. Doping principle has recently been used by exploiting highly phosphorescent materials leading to nearly 100% internal EL efficiency²⁴. Workers in this field have developed highly fluorescent RGB dopants alongwith excellent phosphorescent triplet emitters.²⁵⁻³²

References

1. E. Gurnee and R. Fernandez, US Patent, 1965, 3172862.
2. M. Pope, H. Kallman and P. Magnante, J. Chem. Phys. 1963, **38**, 2042.
3. C.W. Tang, US Patent 1982, 4356429
4. E.W. tang and S.A. Van Slyke, Appl. Phys. Lett., 1987, **51**, 913.
5. R. Friend, J. Burroughes and Bradley, WO patent 1990, **90**,13148.
6. R. Friend, J. Burroughes and D. Bradley, US Patent 1993, 5247190.
7. C.W. Tang, C.H. Chem. And R. Goswami, US Patent, 1988, 4769292.
8. M. Brinkmann, G. Gadret, C. Taliani, N. Masciochi, A. Sironi and M. Muccini, Synth. Met. 2001, **121**, 1499.
9. G. Yu, D. Shen, Y. Liu and D. Zhu, Synth. Met. 2001, **121** 1433.
10. B.J. Chem, W.Y. Lai, Z.Q. Gao, C.S. Lee, S.T. Lee and W.A. Gambling, Appl. Phys Lett. 1999, **75**, 4010.
11. M. Stobel, J. Staudigel, F. Stenber, J. Blassing, J. Simmerer, A Winnacker, H. Neuner, D. Metzendorf, H.H. Johannes and W. Kowalsky Synth. Met., 2000, **111**, 19.
12. M.D. Hall and H.B. Schlegel, Chem. Matr., 2001, **13**, 2632
13. M. Sugimoto, M. Anzai, K. Sakanoue and S. Sasaki, Appl. Phys. Lett. 2001, **79**, 2348.
14. J. Szymkowski, W. Stamper, J. Kalinowski and Z.H. Kafafi, Appl. Phys. Lett, 2002, **80**, 1465.
15. S. Yein, Y. Hua, S. Chem, X. Y. Hou and X. Xu, Synth. Met. 2002, **11**, 109.
16. H. Jang, L.M. Do, Y. Kim, J.G. Kin, T. Zyung and Y. Do, Synth. Met. 2001, **121**, 1669.
17. HY. Shao, Y. Que, N. X. Hu, and X. Hong, Chem. Lett., 2000, 1068.
18. T. Sano, Y. Nishio, Y. Hanada, H. Takahashi, T. Usuki and K. Shibata, J. Mater. Chem, 2000, **10**, 157.
19. Y. Lin, J. Guo, J. Feng, H. Zhang, Y. Li and Y. Wang, Appl. Phys. Lett., 2001, **78**, 2300.
20. S. Anderson, M. S. Weaver and A. J. Hudson, Synth. Met. 2000, **111**, 59.
21. C. Schmitz, H.W. Schmidt, M. Thelakkat, Chem. Matr., 2000, **12**, 3012.
22. S. Totils, K. Noda, H. Tanaka, Y. Taga and T. Tsutsui, Synth. Met., 2000, **111**, 393.
23. C.W. Tang, S.A. VanSlyke and C.H. Chem, J. Appl. Phys. 1989, **65**, 3610.
24. M.A. Baldo, M.E. Thompson and S.R. Forrest, Nature, 2000, **403**, 750
25. J. L. Fox and C.H. Chem, US Patent 1994, 4736032
26. K. Yamashita, J. Futenms, T. Mori and T. Mizutani, Synth. Met. 2000, **111**, 87
27. K.T. Tao, S Miyata, H. Sasabe, G.J. Zhang, T.Wada and M.H. Jiang, Appl. Phys. Lett., 2001, **78**, 279
28. M. Mitsuya, T. Suzuki, T. Koyama, H. Shirai and Y. Taniguchi, Appl. Phys. Lett., 2000, **77**, 3272.
29. J. Shi, C.W. Tang and C.H. Chem. US Patent 1999, 5935721
30. K. Okumoto, T. Ohara, T. Noda and Y. Shirota, Synth. Met., 2001, **121**, 1655.
31. M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S.Shibley, M.E. Thompson and S.R. Forrest, Nature, 1998, **395**, 151.
32. M.A. Baldo, S. Lamansky, P.E. Burrow, M.E. Thompson and S.R. Forrest, Appl. Phys. Lett. 1999, **75**, 4.

Outcomes of the UGC, Major Research Project [40-51/2011(SR)]

- 1) Work done during the project was also submitted in the form of one Ph.D thesis (Vandna Nishal-**Registration no.-05-IGR-922**) and she successfully obtained the Ph.D degree from the M. D. University, Rohtak-124001.
- 2) 4 research papers have already published in the international journal of the repute.
- 3) 7 research papers have already presented in the international/national conferences

➤ Paper published in International journal:

1. "Synthesis, Characterization, and Electroluminescent Characteristics of Mixed-Ligand Zinc(II) Complexes"
Journal of ELECTRONIC MATERIALS, Vol. 42, No. 6, 2013, Pages 973-978.
DOI: 10.1007/s11664-013-2477-3.
2. "Ternary zinc complexes as electron transport and electroluminescent materials"
Journal of Organometallic Chemistry, Vol. 740, 2013, Pages 116-122.
<http://dx.doi.org/10.1016/j.jorganchem.2013.04.032>
3. "n-Type ternary zinc complexes: Synthesis, physicochemical properties and organic light emitting diodes application" Journal of Organometallic Chemistry, Vol. 756, 2014, Pages 38-46. <http://dx.doi.org/10.1016/j.jorganchem.2014.01.022>.
4. "A new zinc-schiff base complex as an electroluminescent material"
Journal of Organic Semiconductors, Vol. 2, No. 1, 2014, Pages 15–20.
<http://dx.doi.org/10.1080/21606099.2014.942767>.

➤ Papers presented in the National/ International Conferences:

1. Paper entitled "Synthesis and Optical Characterization of New Aluminum Complex", in **NCTCBS-2011 Conference**, held at Department of Chemistry, M. D. University, Rohtak (HAR) on November 2-4, 2011.
2. Paper entitled "Synthesis and Optical Characterization of Bis(5-chloro,8-hydroxyquinolinato)mono{2-(2-pyridyl)benzimidazolato}aluminum(III) complex", in **SETMRC-2011 Conference**, held at Vikram University, Ujjain (M.P.) on November 25-26, 2011.
3. Paper entitled "Electroluminescent Characteristics of (2-(2-hydroxyphenyl)benzothiazolato)5,7-dichloro-8-hydroxyquinolinatozinc(II) Complex", in **IWPSD-2011 Conference**, held at IIT Kanpur (U.P.) on December 19-22, 2011.
4. Paper entitled "Synthesis and Electroluminescent Characterization of Tris(N-salicylidine-2-aminothiophenolato)Al(III) Complex", in **ICGTCS-2012, Conference** held at Udaipur (RAJ) on March 3-4, 2012.
5. Paper entitled "Optoelectronic Characterization of 2-(2-Hydroxyphenyl)benzothiazolato)5,7-dimethyl-8-hydroxyquinolinatozinc(II)", in **GC:NFCS-2012 Conference**, held at Kurukshetra University, Kurukshetra (HAR) on September 22-23, 2012.
6. Paper entitled "Electroluminescent Characterization of a mixed ligand zinc complex", in **First Tapsun Conference-2012**, held at NPL, New Delhi on December 4-5, 2012.
7. Paper entitled "Luminescent characteristics of zinc complexes for optoelectronic application", in **Advances in Chemical Sciences-2013 Conference**, held at Department of Chemistry, M. D. University, Rohtak (HAR) on March 1-2, 2013



UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI - 110 002.

PROFORMA FOR SUBMISSION OF INFORMATION AT THE SENDING THE
FINAL REPORT OF THE WORK DONE ON THE PROJECT

(TO BE SUBMITTED IN TRIPLICATE)

1	Name and address of the principal Investigator	Dr. Pratap Singh Kadyan Department of chemistry Maharshi Dayanand University Rohtak-124001
2	Name and Address of the institution	Office: Department of chemistry Maharshi Dayanand University Rohtak-124001 Residential: -do-
3	UGC Reference No & Date	40-51/2011(SR) 22 nd June, 2011
4	Date of Implementation	1st July, 2011
5	Tenure of the project	1st July 2011 to 30 June, 2014
6	Grant Allocated	Rs. 8,48,000/-
7	Grants received	I st Installment : 6,43,000/- II nd Installment: 1,64,000/- Total grant received : 8,07,000/- out of the 8,48,000/-
8	Final Expenditure	Rs. 7,61,931/-
9	Title of the project	"Newer Metal Complexes for Organic Light Emitting Devices"
10	Objectives of the project	Annexure -I
11	Whether objectives were achieved	YES
12	Achievements from the project	Annexure -II
13	Summary of the findings	Annexure -III
14	Contribution to the society	
15	Whether any Ph.D. Enrolled, if any, details	Vandna Nishal -(05-IGR-922) "Some Binary and Ternary Metal Complexes as Photoluminescent and Electroluminescent Materials"
16	No. of Publications out of the project work (Please Attached re-prints)	04


Dr. Pratap Singh Kadyan
Principal Investigator
[40-51/2011 (SR)]
Deptt. of Chemistry
M.D. University, Rohtak-124001

S.No.	Item	Amount Approved	Amount Released	Expenditure Incurred	Net balance now
1	Books & Journals	20,000	20,000/-	nil	20,000/-
2	Equipments	3,80,000	3,80,000/-	3,79,688/-	312/-
3	Honorarium	nil	nil	nil	nil
4	Contingency	30,000	27,000/-	26,788/-	212/-
5	Field Work/Travel	30,000	27,000/-	27,000/-	nil
6	Chemicals & Glassware	3,00,000	2,70,000/-	2,69,905/-	95/-
7	Hiring Services	50,000	45,000/-	20,550/-	24,450/-
8	Overhead	38,000	38,000/-	38000/-	nil
9	Any other items (please specify)	----	----	----	---
10	Staff (date of appointment) (fromto.....)	nil	nil	nil	nil
	Total	8,48,000/-	8,07,000/-	7,61,931/-	45,069/-

Certified that an amount of Rs. 7,61,931/- (Rupees -Seven lakhs sixty one thousands nine hundreds thirty one only) out of Rs. 8,07,000/- (Rupees -Eight lakhs seven thousands only) received from the University Grants Commission under the scheme of support for Major Research Project entitled "Newer Metal Complexes for Organic Light Emitting Devices" vide UGC letter No. F. 40-51/2011(SR) dated 22-06-2011 & 02-08-2014 has been utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions as laid down by the Commission.

PRINCIPAL INVESTIGATOR

(SIGNATURE WITH SEAL)

Dr. Pratap Singh Kadyan
Principal Investigator
[40-51/2011 (SR)]
Deptt. of Chemistry
M.D. University, Rohtak-124001

FINANCE OFFICER
Maharshi Dayanand University,
ROHTAK-124001 (HARYANA) INDIA
REGISTRAR/PRINCIPAL

(SIGNATURE WITH SEAL)

Registrar,
M.D. University
ROHTAK

Resident Senior Auditor,
Local Audit Haryana,
M.D.U., Rohtak.



UNIVERSITY GRANTS COMMISSION
 BAHADUR SHAH ZAFAR MARG
 NEW DELHI - 110 002.

(Utilization certificate)

Certified that an amount of Rs. 7,61,931/- (Rupees -Seven lakhs sixty one thousands nine hundreds thirty one only) out of Rs. 8,07,000/- (Rupees -Eight lakhs seven thousands only) received from the University Grants Commission under the scheme of support for Major Research Project entitled "Newer Metal Complexes for Organic Light Emitting Devices" vide UGC letter No. F. 40-51/2011(SR) dated 22-06-2011 & 02-08-2014 has been utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions as laid down by the Commission.

If as a result of check or audit objection, some irregularity is noticed at later stage, action will be taken to refund, adjust or regularize the objected amount.

Signature
 (Principal Investigator)

Dr. Pratap Singh Kadyan
 Principal Investigator
 [40-51/2011 (SR)]
 Deptt. of Chemistry
 M.D. University, Rohtak-124001

Signature
 (Finance Officer)

Seal/Stamp

Signature
 (Registrar)

Seal/Stamp

Jt. Director (Audit)

Joint Director
 Local Audit Haryana
 M.D. University, Rohtak