Understanding the structure-optical property relationship in new organic materials: Design, synthesis and OLED applications

A Thesis

submitted

by

Sunil Kumar (Roll No: D11020)

for the award of the degree of

Doctor of Philosophy

School of Basic Sciences
Indian Institute of Technology Mandi

September, 2016

To the memories of Asha

&

To my beloved Parents

Indian Institute of Technology Mandi
Mandi, Himachal Pradesh – 175001

भारतीय प्रौद्योगिकी संस्थान मण्डी
मण्डी, हिमाचल प्रदेश, 175001

Declaration by the Research Scholar

This is to certify that the thesis entitled "**Understanding the structure-optical property relationship in new organic materials: Design, Synthesis and OLED applications**", submitted by me to the Indian Institute of Technology Mandi for the award of the degree of Doctor of Philosophy is a bonafide record of research work carried out by me under the supervision of Dr. Subrata Ghosh. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

In keeping with the general practice of reporting scientific observation, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

Mandi 175001
Date: Signature of Research Scholar

Indian Institute of Technology Mandi, V.P.O. Kamand, Tehsil Sadar, Near Kataula, Parashar, Road, Mandi, Himachal Pradesh 175005. Telephone No.01905-237927, Fax: 01905-237942, Email: subrata@iitmandi.ac.in

Indian Institute of Technology Mandi
Mandi, Himachal Pradesh – 175001

भारतीय प्रौद्योगिकी संस्थान मण्डी
मण्डी, हिमाचल प्रदेश, 175001

Thesis Certificate

This is to certify that the thesis entitled "**Understanding the structure-optical property relationship in new organic materials: Design, Synthesis and OLED applications**", submitted by Mr. Sunil Kumar to the Indian Institute of Technology, Mandi for the award of the degree of Doctor of Philosophy is a bonafide record of research work carried out by him under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

In keeping with the general practice of reporting scientific observation, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

Mandi 175001

Research Guide

Indian Institute of Technology Mandi, V.P.O. Kamand, Tehsil Sadar, Near Kataula, Parashar, Road, Mandi, Himachal Pradesh 175005. Telephone No.01905-237927, Fax: 01905-237942, Email: subrata@iitmandi.ac.in

Acknowledgements

While pursuing my Ph.D degree, I met many people who encouraged me during ups and downs and provided continuous support of their experience and knowledge throughout this journey. First and foremost I would like to thank my advisor Dr. Subrata Ghosh for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of research, writing of this thesis and to grow as a researcher. I could not have imagined having a better mentor for my doctoral study in IIT Mandi.

I also want to express my everlasting gratitude to the stimulating discussions of Doctoral committee members, Dr. P. F. Siril, Dr. V. Krishnan, Dr. P. C. Parameshwaran, Dr. P. C. Ravikumar and Dr. Dilip A.D who continually conveyed a spirit of adventure in regard to research and scholarship. I am grateful to well-known Professors for reviewing the manuscripts and thesis in spite of their busy schedule. I am also grateful to UGC for the financial support during the tenure. I shall ever remain grateful to all of them.

I would also like to express my deep gratitude to my teachers Dr. C.Bhaskar, Dr. S. Bhaskar and Dr. Poonam Patiyar. I am blessed that I met them in early stage of my education and I am still learning the science and how to live life every day from them.

I express my sincere thanks to the Director, IIT Mandi for his support and encouragements, especially, the research facilities at Advanced Materials Research Center (AMRC), IIT Mandi is gratefully acknowledged. It is a nice experience to work with Dr. Rik Rani Koner, Dr. Chayan Kanti Nandi, and Dr. Suman Kalyan Pal. Thanks to our collaborators Dr. Ritu Srivastava (NPL, Delhi), Dr. Punita Singh (NPL Delhi), Prof. J. H. Juo (NTHU,

Taiwan), Meenu Singh (Ph.D Student, NTHU, Taiwan) and Puspendra Kumar (Ph.D Student, IIT Mandi) for performing OLED device studies and theoretical studies.

It was nice to share times with friends like Chaudhary, Reena Sharma, Venketeswarulu, Rajkumar, Abhishek Gupta, Nagaraju, Anu, Ashish, Gourab Dey, Reena, Diksha, Tripti, Prateep, Dushyant and Sunil in institution campus. I have absolutely no hesitation in specially conveying warm thanks to my close friends Chander Kant, Harivansh, Anshul, Anurudh, Atul, Rahul, Gulshan, Parminder, Pankaj, Sindhu K and Shilpa who supported me whole heartedly with their amazing love, support and advice. I thankfully acknowledge my friend Sougata Sinha with whom I started my research carrier. I would be failing in my duties if I do not thank my brotherly friends Navneet Singh and Mohit Chawla. You provided eternal optimism and encouragement in me.

At last but not the least, thanks to my parents, brother and Asha, what I am today is just because of them. Words will be less to describe the support, encouragement and unconditional love provided by my family.

Table of Contents

Abbreviations

A……..…….……acceptor

ACQ……..aggregation caused quenching

Ag……..silver

AIE…….aggregation induced emission

CE…….…….current efficiency

CIE…….……commission internationale de l'eclairage

CT……..……charge transfer

CV……..cyclic voltammetry

D……..……...……..donor

DCM……...dichloromethane

DMF…….....dimethylformamide

DMSO……...dimethylsulfoxide

EA……..……..……..electron acceptor

ED ……..……..…… electron donor

EL……..electroluminescence

EM ……..……..…….electromagnetic

HTL……..……..……hole transport layer

EML……..……..emission layer

EQE…….……..……external quantum efficiency

ESI…….electronspray ionization

ETL……...……electron transport layer

eV……..electron volt

Fc……..……..ferrocene

HIL……..hole injection layer

HOMO……highest occupied molecular orbital

HRMS…….…high resolution mass spectrometry

ICP-OES…….…….. inductively-coupled plasma-optical emission spectroscopy

ITO……..……indium tin oxide

J-V-L……..current density-voltage-luminescence

KBr…….Potassium bromide

LUMO…….lowest unoccupied molecular orbital

m.p……..melting point

NMR……..nuclear magnetic resonance

OLED……....organic light emitting diode

ORTEP…….oak ridge thermal ellipsoid plot

PE……..……..power efficiency

PLQY…….... photoluminescence quantum yield

QY……..……..…… quantum yield

SSL...……..……..……solid state lighting

TD-DFT……...time-dependent density functional theory

T_g…….……..glass transition temperature

TGA…….……..thermo gravimetric analysis

UV……..……..……ultraviolet

Vis……...visible

3-D…….three dimensional

λ_{ex}……..……..excitation wavelength

λ_{em}…….emission wavelength

Abstract

Organic materials provide advantages such as design flexibility, cost effective synthesis and tuning of optical properties and thus the organic semiconducting materials have been the subject of active research and widely applied in the areas of organic light-emitting diodes, field-effect transistors, nonlinear optics, photovoltaic devices, biological fluorescent probes, and so on. The commercialization of high efficiency organic light-emitting diodes (OLED) has revolutionized solid state lighting and display technologies. The future of OLEDs depends on the availability of solid state emissive organic materials having efficient quantum yield and balanced charge carrier transport properties. Although many emissive organic materials have been developed and many useful display and lighting products based on OLED devices are available in the market there remains a wide scope to study structure based optical properties and their underlying emission mechanisms. Aggregation of luminophores affects luminescence efficiency of organic materials. Therefore, the research of luminescent solid state organic materials has been and continues to be one of the hot topics for research community. In this regard, our focus has been to develop efficient solid state emitters through chemical structure engineering. In order to make a useful contribution to the literature, new organic frameworks were synthesized and their photophysical properties were studied deeply.

This thesis seeks to understand the optical properties of OLED materials in solid state and provides a systematic study to tether the emission property in solid state to the coumarin derivatives which are known to lack emission in solid state despite of their tremendous emission property in solutions. This is accomplished through the manipulation of intermolecular interactions at molecular level and packing arrangement in the solid state. It was also found that through careful manipulation of the intermolecular interactions and packing arrangement, tuning of emission color

could be achieved through simple design strategies. The practical applications of acquired strategy are the white and green emitting diodes. The understandings at molecular level were further utilized to explore other material designs for other color emitters in visible region.

This thesis also seeks to introduce synthetic techniques towards the development of new dual state emitters and deep blue emitters. The understanding of intramolecular charge transfer process in consort with molecular geometry along with the molecular level understanding of intermolecular interactions and packing arrangement helped to develop organic materials with blue and green emission. The developed green emitters was found to have dual state emission characteristic. As a result of these design strategies, the green and deep blue emitters were obtained and corresponding green and blue emitting diodes were fabricated. The positive aspect of the present thesis is the theoretical simulation to study the designed architectures. The experimental findings were well supported by density functional theory (DFT) calculations and also, the DFT calculations were used to design materials in the present study. The support of theoretical calculations to the experimental results and vice versa proved the importance of theoretical studies in material designs.

Hence, a combination of synthetic development, molecular level understanding, theoretical studies and device applications led to understand of the key issues associated with the solid state emitters particularly those which are used as emitters in OLEDs.