Development of New Schiff Base Derivatives as Fluorescent Chemosensors, NIR Emitters and Catalysts

A Thesis

Submitted for the Degree of

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By

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Dedicated

To

“All My Loved Ones”

Declaration by the Research Scholar

I hereby declare that the entire work embodied in this Thesis is the result of investigations carried out by me in the ***School of Basic Sciences,*** Indian Institute of Technology Mandi, under the supervision of ***Dr. Pradeep C. Parameswaran,*** and that it has not been submitted elsewhere for any degree or diploma. In keeping with the general practice, due acknowledgements have been made wherever the work described is based on finding of other investigators.

Place: Kamand (Mandi) Signature:

Date: Name: Abhishek Kumar Gupta

Declaration by the Research Advisor

I hereby certify that the entire work in this Thesis has been carried out by ***Mr. Abhishek Kumar Gupta,*** under my supervision in the ***School of Basic Sciences,*** Indian Institute of Technology Mandi, and that no part of it has been submitted elsewhere for any Degree or Diploma.

Signature:

Name of the Guide: Dr. Pradeep C. Parameswaran
Date:

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Abhishek Kumar Gupta

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Abbreviations

Symbols

Φ	Quantum Yield
K_b	Binding Constant
λ_{em}	Position of the Emission Maximum
λ_{ex}	Position of the Excitation Maximum
ε	Molar Extinction Coefficient
τ_{avg}	Average Life Time
δ	Chemical Shift
$t_{1/2}$	Half Life Time
E_g	Energy Gap

Solvents

$CHCl_3$	Chloroform
CH_2Cl_2/DCM	Dichloromethane
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
EtOH	Ethanol
MeOH	Methanol
TEA	Triethylamine
THF	Tetrahydrofuran

Chemicals

ATP	Adenosine-5'-triphosphate
CTP	Cytidine-5'-triphosphate
ADP	Adenosine diphosphate
AMP	Adenosine monophosphate
PPi	Potassium pyrophosphate
DFP	2,6-Diformylphenol
TRIS	Tris(hydroxymethyl)aminomethane
PA	Phenyl acetate

ABBREVIATIONS

BnOH	Benzyl alcohol
BnA	Benzyl acetate
EA	Ethyl acetate
IA	Isopropyl acetate
HA	Hexyl acetate
BuA	Butyl acetate
CO	Canola oil
MO	Methyl oleate
ML	Methyl linoleate
FAME	Fatty acid methyl ester
AIBN	Azobis(isobutyronitrile)
HEPES	4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid
BODIPY	Boron dipyrromethane difluoride
PMMA	Poly(methylmethaacrylate)
4-MTA	4-Methylthioaniline
Bu_4NPF_6	Tetrabutylammonium hexafluorophosphate
	Mechanisms
AIE	Aggregation Induced Emission
CT	Charge Transfer
ESIPT	Excited State Intramolecular Proton Transfer
FRET	Fluorescence Resonance Energy Transfer
ICT	Intramolecular Charge Transfer
MLCT	Metal Ligand Charge Transfer
eT	Electron Transfer
ET	Energy Transfer
PET	Photo-induced Electron Transfer
ILCT	Intra-Ligand Charge Transfer
	Instruments
^{13}C NMR	Carbon Nuclear Magnetic Resonance
^{1}H NMR	Proton Nuclear Magnetic Resonance

ABBREVIATIONS

^{31}P NMR	Phosphorus Nuclear Magnetic Resonance
HR-MS	High Resolution Mass Spectrometry
ESI-MS	Electron Spray Ionization Mass Spectrometry
FT-IR	Fourier Transform Infrared Spectroscopy
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
SCXRD	Single Crystal X-Ray Diffraction
CV	Cyclic Voltammetry
GC	Gas Chromatography
DLS	Dynamic Light Scattering
DRS	Diffuse Reflectance Spectroscopy
UV-Vis	Ultraviolet-Visible
AAS	Atomic Absorption Spectroscopy
FID	Flame Ionized Detector
	Others
I	Fluorescence intensity in the presence of analyte
Io	Fluorescence intensity in the absence of analyte
HOMO	Highest Occupied Molecular Orbital
HPLC	High Performance Liquid Chromatography
LUMO	Lowest Unoccupied Molecular Orbital
NIR	Near Infra-Red
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
μM	Micro-molar
mM	Milli-molar
nM	Nano-molar
Ns	Nano-second
K	Keto
E	Enol
^{o}C	Degree Celsius

ABBREVIATIONS

m.p.	Melting Point
CCDC	Cambridge Crystallographic Data Center
DFT	Density Functional Theory
CIFs	Complexation Induced Shifts
DL	Detection Limit
PPM	Parts Per Million
HRLs	Hydroxyl Rich Ligands
pH	Potential of Hydrogen
EDG	Electron Donating Group
EWG	Electron Withdrawing Group
ORTEP	Oak Ridge Thermal-Ellipsoid Plot

Abstract

Schiff base molecules are gaining attention in recent years because of their ability to form compounds that are relevant to diverse areas. Schiff bases possess excellent characteristics including structural similarities with biological substances, relatively simple synthetic procedures and synthetic flexibility that allow structural design as per the requirements. Schiff bases often act as excellent chelating agents and form a variety of complexes with transition metal ions. Because of these unique properties, Schiff bases are widely used in the development of molecular sensors, catalysts, molecular switches, optical data storage devices and bio-mimetic compounds. However, there are still many areas where Schiff bases have not yet been fully explored. For example, the development of chemodosimeters for the selective detection of cations, especially in presence of interfering cations, is still a challenging task. The selective detection of biological macro anions like adenosine triphosphate (ATP), cytidine triphosphate (CTP) etc. is also a difficult task because of the larger size of such anions. Similarly, studies on Schiff base derivatives as solid state near infra-red (NIR) emitters and multifunctional materials are scarce in the literature.

In the present thesis, we have tried to address some of the above issues by developing suitable Schiff base molecular systems. We have developed a pyrene based Schiff base chemodosimeter for the selective detection of Nb^{5+} ions in mixed aqueous media in presence of interfering cations and a series of hydroxyl-rich Schiff base receptors for the selective detection of macro anions like ATP and CTP in 100% aqueous environments. In continuation, we have developed a series of multifunctional zinc complexes for photo luminescent and catalytic applications using hydroxyl-rich compartmental Schiff base ligands. The photoluminescence properties of these zinc complexes were explored in solid state, solutions and in polymer matrix, which revealed their good potential as tunable solid state emitters. Some of these complexes acted as efficient catalysts for the transesterification of simple esters as well as vegetable oils revealing their potential in biodiesel generation. Finally, we have developed an extended pi-conjugated compartmental Schiff base molecule built on 2, 6-diformyl phenol derivatives that acted as deep red to NIR solid state emitter based on excited state intramolecular proton transfer (ESIPT) mechanism.