# Development of New Fluorescent Chemosensors for Various Analytes and Their Evaluation as Molecular Logic Gates

A Thesis

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In the School of Basic Sciences

By

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(D11021)

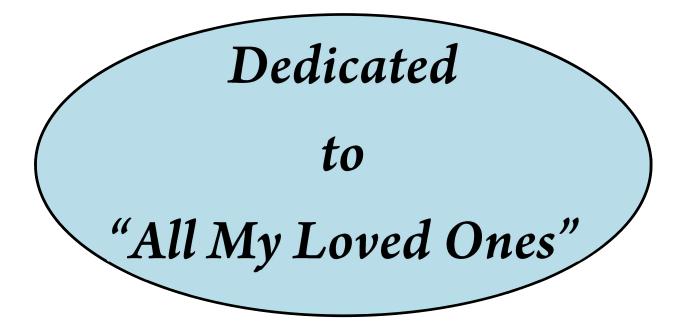


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### **Declaration by the Research Scholar**

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.

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### **Declaration by the Research Advisor**

I hereby certify that the entire work in this Thesis has been carried out by *Manisha Devi*, 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 of Diploma.

Signature:

Name of the Guide: Dr. Pradeep C. Parameswaran Date: 18<sup>th</sup> October, 2016

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## Abbreviations

### Symbols

Φ	Quantum Yield
$\lambda_{em}$	Position of the Emission Maximum
$\lambda_{ex}$	Position of the Excitation Maximum
3	Molar Extinction Coefficient
τ	Life Time
δ	Chemical Shift
	Solvents
CH <sub>3</sub> CN/ACN	Acetonitrile
CHCl <sub>3</sub>	Chloroform
CCl <sub>4</sub>	Carbon tetrachloride
CH <sub>2</sub> Cl <sub>2</sub> /DCM	Dichloromethane
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DIPEA	N,N-diisopropylethylamine
EtOH	Ethanol
MeOH	Methanol
TEA	Triethylamine
THF	Tetrahydrofuran
	Chemicals
BTC	Benzene-1,3,5-tricarbonyl chloride
BODIPY	Boron dipyrromethane difluoride
CDI	1,1-carbonyldiimidazole
EDTA	Ethylenediaminetetraacetic acid
HEPES	4-(2-hydroxethyl)-1-piperaineethanesulfonic acid
HPB	2-(2'-hydroxyphenyl)benzoxazole
HoBt	1-hydroxybenzotriazole
NBD	Nitro-benzoxadiazole

ABBERIVATIONS		
TRIS	Tris(hydroxymethyl)-aminomethane	
Mechanisms		
AIE	Aggregation-Induced Emission	
CHEF	Chelation Enhanced Fluorescence Signaling	
СТ	Charge Transfer	
EET	Electronic Energy 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	
PICT	Planar Intra-molecular Charge Transfer	
PET	Photoinduced Electron Transfer	
TICT	Twisted Intra-molecular/Intermediate Charge Transfer	
Instruments		
<sup>13</sup> C NMR	Carbon Nuclear Magnetic Resonance	
<sup>1</sup> H NMR	Proton Nuclear Magnetic Resonance	
HR-MS	High Resolution Mass Spectrometry	
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy	
FT-IR	Fourier Transform Infrared Spectroscopy	
TEM	Transmission Electron Microscopy	
SEM	Scanning Electron Microscopy	
STEM	Scanning Transmission Electron Microscopy	
TGA	Thermogravimetric Analysis	
DLS	Dynamic Light Scattering	
DRS	Diffuse Reflectance Spectroscopy	
UV-Vis	Ultraviolet-Visible	
AAS	Atomic Absorption Spectroscopy	

	Others
Ι	Fluorescence Intensity in the Presence of Analyte
Io	Fluorescence Intensity in the Absence of Analyte
НОМО	Highest Occupied Molecular Orbital
HPLC	High Performance Liquid Chromatography
LOD	Low Detection Limit
LUMO	Lowest Unoccupied Molecular Orbital
NIR	Near-Infrared
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
PDI	Polydispersity Index
WBCs	White Blood Cells
LMGs	Low Molecular Mass Gelators
RMS	Root-mean-square
μΜ	Micromolar
mM	Milimolar
nM	Nanomolar
°C	Degree Celsius
m.p.	Melting Point
CCDC	Cambridge Crystallographic Data Centre
DFT	Density Functional Theory
CPU	Central Processing Unit

#### Abstract

In recent years, the detection and quantification of biologically and environmentally important ions and small molecules have emerged as significant goals in the field of supramolecular chemistry. Among the various chemosensors used for these purposes, fluorescent chemosensors have attracted particular attention because of their high sensitivity and potential for *in vitro* and *in vivo* analyses. A fluorescent chemosensor is a molecular system in which the physicochemical properties of a fluorophore moiety vary upon interaction with a chemical species so that a change in fluorescence is produced. Fluorescent chemosensors have several advantages over other optical sensors because of their versatility, high selectivity/sensitivity, reliability & reproducibility, low detection limit (LOD), low cost, non-invasive nature and potential for real-time analyses. Fluorescent chemosensors are often explored towards other applications as well, such as the construction of molecular logic gates. This is because, the chemosensors exhibit large differences in their photophysical properties in "OFF" and "ON" states, which can therefore be treated as "0" and "1" states, enabling their applications in molecular logic operations.

In the present thesis, a series of fluorescent chemosensors based on different fluorescent platforms have been developed towards the detection of various small molecules, cations and anions. The photophysical and binding properties of these new fluorescent chemosensors have been explored in detail and possible mechanisms of their binding interactions with analytes have been established through spectroscopic studies. Some of the fluorescent chemosensor have been explored towards their bio-imaging and molecular logic gates applications as well.