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

A Thesis

Submitted for the Degree of

DOCTOR OF PHILOSOPHY

In the School of Basic Sciences

By

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18th October, 2016

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)

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Date: 18th October, 2016

Name: Manisha Devi

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: 18th October, 2016

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Manisha Devi

Table of Contents

Abbreviations

Symbols

Φ	Quantum Yield
λ_{em}	Position of the Emission Maximum
λ_{ex}	Position of the Excitation Maximum
ε	Molar Extinction Coefficient
τ	Life Time
δ	Chemical Shift

Solvents

CH_3CN/ACN	Acetonitrile
$CHCl_3$	Chloroform
CCl_4	Carbon tetrachloride
CH_2Cl_2/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

TRIS	Tris(hydroxymethyl)-aminomethane

Mechanisms

AIE	Aggregation-Induced Emission
CHEF	Chelation Enhanced Fluorescence Signaling
CT	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

^{13}C NMR	Carbon Nuclear Magnetic Resonance
^{1}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

I	Fluorescence Intensity in the Presence of Analyte
I_o	Fluorescence Intensity in the Absence of Analyte
HOMO	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
μM	Micromolar
mM	Milimolar
nM	Nanomolar
^oC	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.