

*Dedicated to*  
*Maa & Lt. Baba*



# TEZPUR UNIVERSITY

(A Central University Established by an Act of Parliament)  
Napaam, Tezpur-784028, Sonitpur, Assam,  
India

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## DECLARATION

I, do hereby declare that the thesis entitled “*Methodological Development for Sensing of Fluoride ion in Aqueous Medium Using Organic Probe Molecules,*” submitted to the Department of Chemical Sciences, Tezpur University, under the School of Sciences is a record of original research work carried out by me. All sources of assistance have been assigned with due acknowledgment. I, also declare that neither this work as a whole nor any part of it has been submitted to any other University or Institute for any kind of degree, diploma, or award.

Place: Tezpur University, Tezpur

Date: 10/12/24

*Bikash Ch. Mushahary*  
(Bikash Ch. Mushahary)



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## CERTIFICATE OF SUPERVISOR

This is to certify that the thesis entitled "*Methodological Development for Sensing of Fluoride ion in Aqueous Medium Using Organic Probe Molecules*" submitted to Tezpur University, in the Department of Chemical Sciences, under the School of Sciences, in partial fulfillment for the award of the degree of Doctor of Philosophy in Science is a record of research work carried out by **Mr. Bikash Chandra Mushahary**, under my supervision and guidance.

All help received by him from various sources have been duly acknowledged. No part of this thesis has been reproduced elsewhere for award of any other degree.

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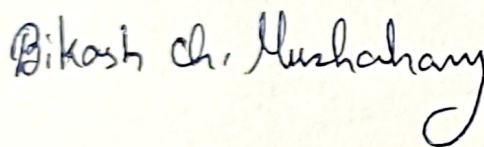


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The committee recommends for the award of the degree of Doctor of Philosophy.

**Principal Supervisor**

**External Examiner**

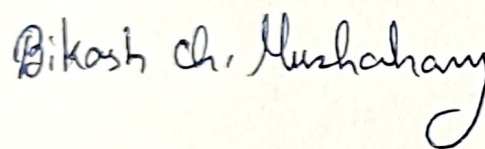
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## ***PREFACE***

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*The need for a methodology that can effectively detect fluoride ions in aqueous environments using specially designed probes is substantial. While many organic probes perform well in organic solvents, few exhibit comparable efficiency in water. The challenges stem from fluoride's high enthalpy of hydration, which hinders its interaction with the sensor's recognition unit. To address these obstacles, a transition metal-mediated approach is explored. In this method, a metal ion binds to the designed probes in a fluoride-rich environment, indirectly facilitating fluoride detection by stabilizing the conjugate base formed in the presence of fluoride through the creation of stable in-situ metal complexes. Additionally, a fluoride ion-assisted displacement of dye molecules (fluorescein and perylene tetracarboxylate) from aluminum complexes of the respective dye is demonstrated as an effective colorimetric and fluorometric chemodosimeter for sensing of fluoride in 100% water. In conclusion, this thesis explores methodologies for enhancing the fluoride sensing affinity of chemical sensors in aqueous environments, thereby enabling practical applications in real life situations.*



**(Bikash Ch. Mushahary)**

**Place:** Tezpur University, Tezpur

**Date:** 10-12-2024

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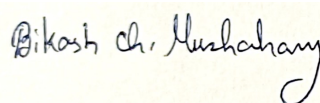
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**(Bikash Ch. Mushahary)**

**Place:** Tezpur University, Tezpur

**Date:**

## ***LIST OF ABBREVIATION AND SYMBOLS***

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$\delta$ ppm	Chemical shift in parts per million
$\mu$ L	Micro liter(s)
$\mu$ M	Micro molar
mM	Mili molar
Abs	Absorbance
AcO	Acetate
Aq	Aqueous
B3LYP	Becke, 3-parameter, Lee–Yang–Parr
CPCM	Conductor-like Polarizable Continuum Model
CT	Charge Transfer
CV	Cyclic Voltammetry
DFT	Density Functional Theory
DMSO	Dimethyl sulfoxide
DPV	Differential Pulse Voltammetry
EPR	Electron Paramagnetic Resonance
Equiv.	Equivalent
FT-IR	Fourier Transform Infrared
H-bonding	hydrogen bonding
HOMO	Highest Occupied Molecular Orbital
ICT	Intramolecular Charge Transfer
LCMS	Liquid Chromatography Mass Spectrometry
LC-MS	Liquid Chromatography-Mass Spectroscopy
LMCT	Ligand to Metal Charge Transfer
LOD	Limit of Detection
LUMO	Lowest Unoccupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
MeCN	Acetonitrile

<i>MeOH</i>	<i>Methanol</i>
<i>MLCT</i>	<i>Metal to Ligand Charge Transfer</i>
<i>NBO</i>	<i>Natural Bond Orbital</i>
<i>NMR</i>	<i>Nuclear Magnetic Spectroscopy</i>
<i>ppb</i>	<i>parts per billion</i>
<i>ppm</i>	<i>parts per million</i>
<i>PTC</i>	<i>Perylene Tetracarboxylate</i>
<i>SPADNS</i>	<i>5-Dihydroxy-3-(4-Sulfophenylazo)-2,7-Naphthalenedisulfonic Acid trisodium salt</i>
<i>TBA</i>	<i>Tetrabutylammonium</i>
<i>TBAF</i>	<i>Tetrabutyl ammonium fluoride</i>
<i>TDDFT</i>	<i>Time-Dependent Density Functional Theory</i>
<i>TLC</i>	<i>Thin Layer Chromatography</i>
<i>TMS</i>	<i>Tetramethyl silane</i>
<i>TRPL</i>	<i>Time Resolved Photoluminescence Spectroscopy</i>
<i>UV-Vis</i>	<i>UV-Visible</i>
<i>WHO</i>	<i>World Health Organization</i>
<i>TBA</i>	<i>Tetrabutylammonium</i>
<i>WHO</i>	<i>World Health Organization</i>
<i>ISE</i>	<i>Ion Selective electrode</i>

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