Declaration

I hereby declare that the work presented in this thesis titled *'Formazan-Based Metal Complexes for Applications in Resistive Switching and Electrocatalysis'* submitted to the Indian Institute of Technology Jodhpur in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy, is a bonafide record of the research work carried out under the supervision of Dr. Ramesh K. Metre. The contents of this thesis, in full or in parts, have not been submitted to, and will not be submitted by me to, any other Institute or University in India or abroad for the award of any degree or diploma.



Sunita
P19CY008

Certificate

This is to certify that the thesis titled *'Formazan-Based Metal Complexes for Applications in Resistive Switching and Electrocatalysis'*, submitted by Sunita (P19CY008) to the Indian Institute of Technology Jodhpur for the award of the degree of Doctor of Philosophy, is a bonafide record of the research work done by her under my supervision. To the best of my knowledge, the contents of this report, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Ramesh K. Metre
Ph. D. Thesis Supervisor
Date:

Abstract

Drawing inspiration from nature, the concept of redox-active ligands explores the catalytic potential of earth-abundant metals like iron and copper despite their preference for one-electron redox reactions. Unlike traditional spectator ligands, redox-active ligands offer energetically accessible levels for reduction or oxidation, enabling oxidation state changes to occur either exclusively at the ligand or synergistically at both the ligand and metal. The incorporation of redox-active ligands presents numerous benefits, such as facilitating continuous multielectron transfer, regulating electron-deficient transition states, and enabling single-electron changes in the redox state of the metal center. In this context, we have meticulously adapted redox-active formazan-based ligands to explore a broad spectrum of applications, encompassing resistive switching memory, antibacterial properties, and electrocatalysis. Formazans boast a rich history in chemistry, where deprotonation generates monoanionic chelating N-donor ligands called "formazanates." The synthesis of formazan ligands provides a straightforward route to formazanate-based complexes with tunable electronic and steric characteristics. Complexes featuring a formazanate ligand typically exhibit a narrow HOMO–LUMO gap, resulting in energetically accessible π*-orbitals. This property renders formazanate complexes redox-active, enabling reversible storage of electrons in a ligand-based manner within these compounds. The utilization of formazanate-based ligands in coordination with base metal ions has initiated a novel research domain, expanding the range of applications in the design of magnetic, optical, and intriguing electrical materials. This is achieved by leveraging the distinctive optoelectronic properties and adaptable electrochemistry offered by formazanate ligands. The primary focus of this thesis lies in the synthesis of formazanate-based ligands, their corresponding metal complexes, and their diverse applications, ranging from resistive switching memory to antibacterial activity and electrocatalysis. An ionic organotin complex was prepared using a 2-pyridine substituted formazan ligand and investigated for its application in solid-state non-volatile write once read many (WORM) memory devices, demonstrating a high switching on-off ratio. Furthermore, distorted octahedral bis(formazanate) zinc complexes were used in the fabrication of a memory device that intriguingly exhibited non-volatile resistive switching memory behavior. The bis(formazanate) iron complexes displayed extensive redox behavior during the cathodic sweep in cyclic voltammetry analysis and were realized as electroactive cathode materials for the electrocatalytic H_2O_2 reduction in one-compartment H_2O_2 fuel cell. Later, a mono(formazanate) mercury complex was prepared and was further studied as an antimicrobial agent.

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List of Symbols

Symbol	*Description*
μ	micro
α	Alpha
β	Beta
γ	Gamma
λ	Wavelength
δ	Chemical shift
ν	Frequency
K_B	Boltzmann constant
δ	Chemical shift
V	Volume
°	Degree
%	Percentage
Φ	Work function
q	Charge
θ	Theta
A	Absorbance
ϵ	Molar extinction coefficient
c	Concentration
s	Second
h	Hour
τ	Addison's parameter
π	Pi
σ	Sigma
Å	Angstrom
I	Current
mV	Millivolt
mA	Miliampere
eV	Electron volt
1D	One-dimensional
2D	Two-dimensional
ρ	Rho
V	Potential

List of Abbreviations

Abbreviation	*Full form*
AP	Amidophenolates
Cat	Catecholates
mnt	Dithiolenes
tdt	1,2-benzenedithiolates
abt	2-amidothiophenolates
CIF	Crystallographic information file
FC	Ferrocene
Por	Porphyrin
HCl	Hydrochloric
TD-DFT	Time-dependent density functional theory
HOMO	Highly occupied molecular orbital
LUMO	Lowest Unoccupied molecular orbital
FMO	Frontier molecular orbital
GMV	Gomphrena mosaic virus
TMV	Mosaic virus
HIV	Human immunodeficiency viruses
TEMPO	(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl
ROP	Ring-opening polymerization
PLA	Polylactide
SCO	Spin Crossover
FTIR	Fourier Transform Infra-red
SC-XRD	Single-Crystal X-ray Diffraction
NMR	Nuclear Magnetic Resonance
HRMS	High-Resolution Mass Spectrometry
TGA	Thermogravimetric Analysis
XPS	X-Ray Photoelectron Spectroscopy
EPR	Electron paramagnetic resonance
CV	Cyclic voltammetry
WORM	Write once read many
DRAM	Dynamic random access memory
RRAM	Resistive random access memory
MIM	Metal-insulator-metal
SRAM	Static random access memory
HRS	High resistive state
LRS	Low resistive state
RS	Resistive switching
RFID	Radio frequency identification
NDR	Negative differential resistance
ITO	Indium tin oxide
FTO	Fluorine-doped tin oxide
PVP	Poly (4-vinylpyridine)
AFM	Atomic Force Microscopy
SCLC	Space charge limited conduction
CF	Conductive filament
TE	Top electrode
BE	Bottom electrode
TMC	Transition metal complex
OMC	Organometallic complex
EDOT	3,4-ethylenedioxythiophene
LLCT	Ligand to ligand charge transfer
ALD	Atomic layer deposition
NBO	Natural bonding orbital
DCM	Dichloromethane
CCDC	Cambridge Crystallographic Data Centre