Table of Contents

Abstract **i**

Declaration **vii**

Certificate **viii**

Acknowledgements **x**

Contents **xiii**

List of tables **xix**

List of figures **xxi**

List of abbreviations **xxix**

List of symbols **xxx**

Chapter 1: Introduction **1-39**

1.1 Metal organic framework (MOF) 1

1.2.1 Electrically conducting MOF 4

1.2.1 Intrinsically Conducting MOF 4

1.2.2 Extrinsically Conducting MOF 5

1.2.2.1 Guest for extrinsically conducting MOF 6

1.3 Strategy to impart modification in structure or microstructure of MOF 8

1.4 Mechanism of charge transport in MOF 10

1.5 Applications of conducting MOF 13

1.5.1 Energy storage device 13

1.5.2 Energy conversion 15

1.5.3 Electrochemical sensors 15

1.5.3.1 Potentiometric sensors 17

1.5.3.2 Amperometric sensors 18

1.5.3.3 Voltametric sensors 18

1.5.3.4 Impedometric sensors 19

1.5.4 Electrochemical biosensors 19

1.5.4.1 Antibody based 21

1.5.4.2 Enzyme based 21

1.5.4.3 Aptamer based 22

1.6 Scope of the thesis 22

Chapter 2: Experimental procedures and characterization techniques 40-68

2.1 Introduction 40
2.1.1 Physical properties of the materials 41
2.2 Materials Used 43
2.2.1 Synthesis of MOF: UiO-66 43
2.2.2 In Situ Polymerization of PEDOT 44
2.2.3 Synthesis of PEDOT 45
2.2.4 Synthesis of Ag_2O nanoparticles (NP) 45
2.2.5 Synthesis of Ag_2O infiltrated UiO-66 MOF (S1(MOF)) 46
2.2.6 Synthesis of Ag_2O anchored UiO-66 MOF (S2(MOF)) 47
2.3. Fabrication of working electrode 48
2.3.1 S1(MOF)/S2(MOF) on ITO coated glass 48
2.3.2 PEDOT@UiO-66 on ITO coated glass 48
2.3.3 UiO-66 MOF fabricated on ITO coated glass for SHI irradiation experiment 48
2.3.4 Fabrication of pristine and irradiated UiO-66 with biomolecules 49
2.4. Preparation of the analyte solution for electrochemical sensing 49
2.4.1 Preparation of Cd^{2+} and Hg^{2+} solution 49
2.4.2 Preparation of Catechol (CT) and hydroquinone (HQ) solutions 49
2.5. Characterization techniques 50
2.5.1 Powder X-ray diffraction 50
2.5.2 Fourier transformed Infrared spectroscopy 51
2.5.3 Raman spectroscopy 52
2.5.4 Scanning electron microscopy 53
2.5.5 High resolution transmission electron microscopy 55
2.5.6 N2 adsorption-desorption measurements 56
2.5.7 Current-voltage (I-V) characteristics 57
2.6 Evaluation of electrochemical properties 58

2.6.1 Cyclic voltammetry (CV) 58
2.6.2 Electrochemical impedance spectroscopy (EIS) 59
2.6.3 Differential pulse voltammetry (DPV) 62
2.7 Conclusions 63

Chapter 3: Structural, morphological, vibrational characteristics of Ag_2O and PEDOT incorporated UiO-66 Metal Organic Frameworks **69- 92**

3.1 Introduction 69
3.2 Structural and morphological analysis of the Ag_2O@UiO-66 71
3.2.1 Structural characterization 71
3.2.2 Morphological Characterization 72
3.2.2.1 Field emission scanning electron microscopy 72
3.2.2.2 Transmission electron microscopy 75
3.2.3 BET surface area and pore size distribution 77
3.3 Structural and morphological investigation of PEDOT@UiO-66 79
3.3.1 Structural features 79
3.3.2 Morphological features 80
3.3.2.1 Transmission electron microscopy 80
3.3.2.2 Field emission scanning electron microscopy 81
3.3.3 BET surface area and pore size analysis 83
3.3.6 Molecular stretching and Raman active modes 85
3.4 Conclusions 87

Chapter 4: Electrical transport properties of Ag_2O and PEDOT incorporated UiO-66 Metal Organic Frameworks **93- 110**

4.1 Introduction 93
4.2 Carrier transport phenomena of (S1(MOF) and S2(MOF)) 94
4.2.1 *I-V* characteristics 94
4.2.2 Temperature dependent conductivity studies 99
4.3 Carrier transport phenomena and temperature dependency of PEDOT@UiO-66 100

4.3.1 *I-V* characteristics 100
4.3.2 Temperature dependent conductivity studies 104
4.4 Conclusion 106

Chapter 5: Application of Ag_2O incorporated UiO-66 in electrochemical sensing of heavy metal ions **111- 136**

5.1 Introduction 111
5.2 Electrochemical properties of S1(MOF) and S2(MOF) coated working electrode 113
5.2.1 Cyclic Voltammetry 114
5.2.2 Electrochemical impedance spectroscopy (EIS) 118
5.3 Optimization of electrochemical conditions for sensing 120
5.4 Electrochemical sensing of Hg^{2+} and Cd^{2+} individually and simultaneously by S1(MOF) and S2(MOF) coated working electrode 121
5.4.1 Individual sensing of Cd^{2+} and Hg^{2+} 121
5.4.2 Simultaneous sensing of Cd^{2+} and Hg^{2+} by the electrodes 125
5.4.3 Selectivity study for the electrodes 128
5.4.4 Stability and reproducibility features of the electrodes 129
5.4.5 Real sample analysis 131
5.5 Conclusions 132

Chapter 6: Application of PEDOT@UiO-66 MOF in electrochemical sensing of organic environmental contaminants **137-150**

6.1 Introduction 137
6.2 Electrochemical Properties of PEDOT@UiO-66 coated working electrode 139
6.2.1 Cyclic Voltammetry 139
6.2.2 Electrochemical Impedance Spectroscopy 142
6.3 Optimization of sensing parameters 144
6.3.1 Cyclic Voltammetry in presence of analytes HQ and CT 144
6.3.2 Effect of pH on the redox reactions 146

6.4 Analysis of individual and simultaneous electrochemical sensing of Catechol (CT) and Hydroquinone (HQ) using PEDOT@UiO-66 working electrode 147
6.4.1 Sensing of HQ and CT individually 147
6.4.2 Simultaneous sensing of HQ and CT by PEDOT@UiO-66 MOF 149
6.4.3 Selective determination of HQ and CT from their mixtures 150
6.4.4 Selectivity, Stability, repeatability and reproducibility 152
6.4.5 Real Sample analysis 155
6.5 Conclusions 156

Chapter 7: Swift heavy ion (SHI) irradiation effect on structural, morphological, and electrical behaviour of UiO-66 MOF and biosensing application **160- 187**

7.1. Introduction 160
7.2 SHI irradiation experiment on UiO-66 MOF fabricated on ITO coated glass 162
7.3 Structural and morphological features 162
7.3.1 X-ray diffraction studies 162
7.3.2 Fourier-transformed IR spectroscopy (FTIR) 164
7.3.3 Raman spectroscopy 165
7.3.4 Morphological study 167
7.4 *I-V* characteristics 169
7.5 Electrochemical performances of irradiated samples 170
7.5.1 Cyclic Voltammetry and EIS studies 170
7.5.2 Scan rate varying CV 173
7.6 Modification of the electrodes by immobilizing biomolecules. 175
7.7 Analytical performance mouse IgG immobilized N^{5+} irradiated UiO-66 electrodes 177
7.7.1 Sensing of Goat anti-mouse IgG 177
7.7.2 Reproducibility of Goat anti-mouse IgG detection using UiO-66-5 x 10^{11}-Gu-IgG-BSA 180
7.7.3 Selectivity test on UiO-66-5 x 10^{11}-Gu-IgG-BSA for Goat anti- 182

mouse IgG
7.7.4 Stability 183
7.8 Conclusion 183

Chapter 8: Conclusions and Future Direction **188- 192**
8.1 Conclusions 188
8.2 Future direction 191