8.1 Conclusions

The goal of this thesis work is to increase Zr-based MOF UiO-66's conductivity so that it can be used in electrochemical sensing applications. To accomplish that the host MOF UiO-66 was initially produced via solvothermal synthesis route and subsequently, post-synthetic modifications were performed on it through various means. The first approach to enhancing the electrical conductivity of UiO-66 was the introduction of guest molecules to the framework. To compare their effects on the host, guests from various origins namely, inorganic and organic kind were added to the system. For inorganic guest Ag_2O NP was chosen due to its easy processibility, semiconducting behaviour, good redox active properties and better stability as compared to their counter metal NPs. The Ag_2O NPs were loaded into as prepared UiO-66 through different methods. (i) In the first method, the $AgNO_3$ loaded with UiO-66 powder was reduced to Ag_2O by stirring the mixture in an acetonitrile solution. The resulting product was named S1(MOF). (ii) In the second approach, $AgNO_3$ was reduced during its inclusion in UiO-66 using a natural reducing agent extracted from banana root bulbs. This resulted in the production of Ag_2O-loaded UiO-66 known as S2(MOF). Both these methods resulted in Ag_2O NP incorporation in UiO-66 framework. Secondly, the organic guest incorporated into UiO-66 was PEDOT which followed *in-situ* polymerization of monomer EDOT in the presence of $FeCl_3$ within the pores of framework. The third approach to alter the electrical properties of UiO-66 was to impart post-synthetical modifications on UiO-66 by irradiating with 60 MeV N^+ ions with different fluences. The irradiation resulted in structural modifications in UiO-66 lattice which led to an enhancement in electrical and electrochemical performance. The irradiation modified UiO-66 electrodes were immobilized with mouse IgG for use in biosensing applications. This chapter presents the findings from the research that has been carried out and the observations that were made. The major findings of these three systems are summarized below-

- The guest loading into the framework through various approaches was quite effective as substantiated by the XRD, FTIR, FESEM, TEM, EDX results. The structural integrity of UiO-66 is suggested by the fact that, despite undergoing chemical treatments throughout both forms of guest loading, the parent MOF's structure remained unaltered. As the Ag_2O NPs were reduced via two different approaches they resulted in residing in different parts of the MOF. In S1(MOF) the Ag_2O NPs were present inside the pores of UiO-66 as depicted by the FESEM and TEM imaging. On the other hand, in S2(MOF) they were present on the surface of UiO-66 particles. These results were also supported with the findings of N_2 isotherm analysis and BET surface area measurements also. In case of PEDOT@UiO-66, octahedral pores of UiO-66 are believed to be partially filled with the PEDOT chains. One significant observation is that, even after guest loading, the material's total specific surface area remained high enough to warrant the electrochemical performance suitably. This implies that UiO-66 can accommodate inorganic as well as organic guest molecules in its framework while maintaining the microporous crystalline nature intact.

- The current-voltage and charge transport property investigations have demonstrated that the guest's inclusion into the UiO-66 framework has improved conductivity. In cases of S1(MOF) and S2(MOF) electrodes, the conductivity of UiO-66 has increased by order of 10. Ohmic and SCLC mechanisms are examined as possible conduction mechanisms for the charge transport phenomenon in these MOFs. The temperature dependence conductivity reveals the absence of thermionic emission of carriers as it decreases with temperature. In the PEDOT@UiO-66 the conformation of PEDOT transformed from benzoid to quinoid as result of confining it within the pores of UiO-66 which in turn increased the conductivity by 10 million-fold. The enhancement in current response was reflected in the current- voltage characteristics of the PEDOT@UiO-66 as compared to UiO-66 and PEDOT. The conduction mechanism that governed the carrier transport property of PEDOT@UiO-66 was assumed to be thermionic emission as analysed from the *I-V* data. The temperature dependence of conductivity profiles of PEDOT and PEDOT@UiO-66 characterize semiconducting features in the material following the Motts' variable range hopping (MVH) rule across the CP chains.
- The electrochemical studies on S1(MOF) and S2(MOF) after fabricating them on ITO electrodes have revealed that Ag_2O incorporation can enhance the electrochemical performance of UiO-66 by increasing the current response and reducing the charge transfer resistance. The S2(MOF), in fact offered a better current response than S1(MOF). The probable reason behind this fact is assumed to be the exposed redox active Ag_2O NPs present on the surface of UiO-66. The combination of diffusion controlled and surface adsorbed phenomena are analysed to govern adequate electrochemical reaction kinetics. The sensing aspects of S1(MOF) and S2(MOF) were examined with two analytes- Cd^{2+} and Hg^{2+}. Both the MOFs were able to detect heavy metal ions individually as well as

simultaneously because of presence of two different active sites that can bind to different analytes. When monitored Hg^{2+} and Cd^{2+} simultaneously, S2(MOF) electrode could detect analytes in nM (3 nM and 8 nM, respectively) concentration which is lower than the permissible concentration for Hg^{2+} and Cd^{2+} in drinking water recommended by WHO. The sensing of Hg^{2+} and Cd^{2+} both independently and simultaneously by S1(MOF) and S2(MOF) showed higher sensitivity towards the analytes as compared to the earlier reports. With the benefits of both improved performances and greener synthesis, S2 (MOF) is believed to be a better sensing candidate for simultaneous detection when compared to S1 (MOF). Moreover, both S1(MOF) and S2(MOF) were reliable for applying in real samples as they showed good recovery of 81.36% and 101.4% for the analytes.

- In PEDOT@UiO-66 the incorporation of PEDOT into the pores of UiO-66 potentially enhances the electrochemical properties which is governed by diffusion-controlled mechanisms. When organic molecule PEDOT was introduced into the framework it was able to distinguish the redox peaks of the hydroxybenzene isomers CT and HQ due to the synergistic effect of PEDOT and UiO-66. The electrode PEDOT@UiO-66 was able to detect the isomers individually as well. In a concentration range of 1 μM-300 μM PEDOT@UiO-66 detected HQ with a lower LOD of 0.338 μM and sensitivity of 1.809 μA μM cm^{-2}, and detected CT with LOD 2.84 μM and sensitivity 0.7 μA μM cm^{-2}. In addition, the PEDOT@UiO-66 can interact with the specified analyte even while other unwanted analytes are present, designating it as a selective electrode for the intended analyte. An interesting finding is that upon loading PEDOT in UiO-66, it provided a long-term stability to UiO-66 structure as well as electrochemical properties.
- Swift ion irradiation of 60 MeV ion of N^{5+} Zr-based MOF UiO-66 has influenced the structural, morphological and electrical properties which in turn influenced the biosensing behaviours. With different fluences the effect was different on the structure and so on the related properties. The first two fluences are assumed to impart defects like missing linker defect on the MOF structure. When irradiation was imposed with lower fluence of 10^{10} ions/cm^2 and 10^{11} ions/cm^2, only lower amount of defects have been formed which kept structure intact However, as the fluence is increased to 10^{12} ions/cm^2 the amount of defects increased which caused degradation in the structure by reducing the crystallinity. Studies using vibrational spectroscopy pointed to the development of missing linker defects in the UiO-66 lattice structures. This causes the granules to clump together, increasing in size with each fluence. Both the redox activities and electrical characteristics are impacted by

the agglomeration. The electrical transport enhanced with each fluence and dropped at 10^{12} ions/cm^2 which is the clear consequence of increasing disorder in the lattice structure. Due to the formation of defects the electroactive surface area increased which helped enhancing the electrochemical detection. As expected, electrode irradiated with 5 x 10^{11} ions/cm^2 outperformed all the other electrodes in electrochemical performance and sensing behaviour due its higher conductivity. It was able to detect the antigen with a low LOD of 4.13 ng mL^{-1} and sensitivity 0.205 μA ng^{-1} mL. Accordingly, the investigation suggests that SHI irradiation may induce defects in the crystal structure of MOF, which further contributes to improving the material's electroactive performance.

Future Prospects

The results of this research work demonstrated that structurally stable Zr-based UiO-66 is a good host for long-chain organic molecules as well as inorganic metal oxides. The inclusion of guest molecules into the framework have not dramatically altered the structural features of MOF, yet new features like enhancement in conductivity and electrochemical behaviour have been added. This opens up a range of opportunities, from basic research to understand the conduction mechanism in extrinsically conducting MOFs to energy storage applications such as supercapacitors and metal-ion battery cathodes and anodes. Fundamental aspects like the in-depth study of conduction mechanisms, measurement of mobility of charge carriers, band structure calculations, AC conductivity measurements, dielectric property, optoelectronic property, etc. can be carried out in the systems that are being developed for this thesis work.

The integration of silver oxide (Ag_2O) within MOFs holds promise for photovoltaic applications. Ag_2O, with its semiconducting properties and suitable bandgap, offers potential for light absorption and electron-hole pair generation essential for photovoltaic conversion. Incorporating Ag_2O into MOFs provides structural stability and enables efficient charge transport, facilitated by the MOF's porous architecture and high surface area. Tunable properties of Ag_2O@UiO-66 composites allow optimization of optical absorption and charge carrier mobility, essential for enhancing device performance. However, challenges such as interface optimization and long-term stability need addressing through further research to unlock the full potential of Ag_2O@UiO-66 composites in photovoltaics.

One key advantage of the PEDOT@UiO-66 system is its enhanced conductivity and structural stability, which enables its use in harsh environments and prolonged operation. This stability is crucial for applications where the material may be subjected to mechanical stress or chemical exposure. One of such applications is energy storage, where higher conductivity can facilitate efficient charge transport, improving the performance of batteries or supercapacitors. Additionally, in catalysis, the combination of conductivity and structural stability can enable efficient electron transfer processes, enhancing catalytic activity.

The effect of SHI irradiation on UiO-66 has been investigated in the Chapter 7 which gives an impression that irradiating with some particular fluences can result in desired modifications in the structure. Utilising advanced characterisation techniques is important to comprehend the detailed nature of defects, which may provide a clear picture of the sort of defects, be it missing linkers, missing clusters, or any other point defects. Future research is anticipated to produce important insights from a number of cutting-edge techniques, including BET analysis, neutron diffraction, anomalous diffraction, in-situ XRD, in-situ Raman, etc.

Given that SHI irradiation has been successful in producing defects in UiO-66, this suggests that guest-loaded UiO-66, such as S1 (MOF), S2 (MOF), and PEDOT@UiO-66, may be made susceptible to changes on applying high energy ions. Finally, electrodeposition or the formation of nanocomposites including gold nanoparticles or other conducting species such as PEDOT, graphene oxide, etc., can be done in the near future to improve the biosensing properties of SHI-irradiated UiO-66.