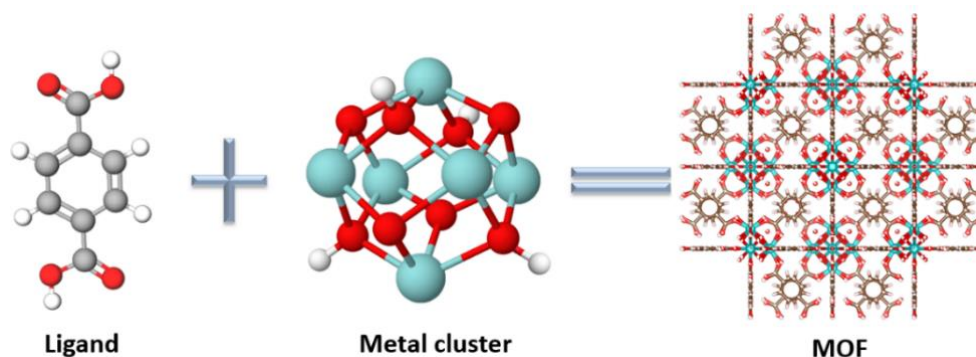


*“I walk slowly but never walked backward”- Abraham Lincoln*

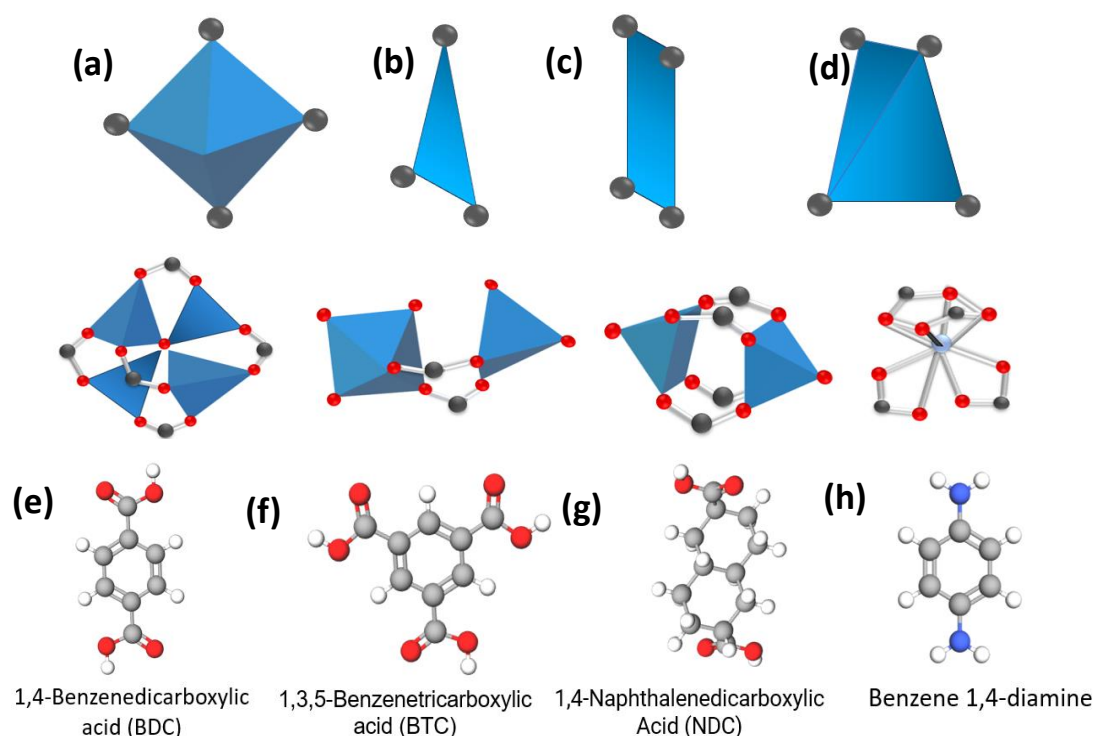
## 1.1 Metal organic frameworks (MOF)

Porous material has attracted a great deal of attention in the recent few decades from a variety of scientific disciplines, including physics, chemistry, material science and environmental science. The study of porous materials in physics has revealed fascinating phenomena pertaining to their structural and electrical characteristics [1]. The complex relationship between the porous architecture and physical behavior has prompted studies to understand new quantum effects and emergent phenomena in these materials. Comparably, research in chemistry has accelerated the investigation of designing, synthesizing and tuning porous materials with specific chemical functions. Porous materials offer a platform for the development of high-performance materials for applications such as catalysis, gas storage, sensing, drug delivery, and energy storage [2]. Research in porous architecture has sparked an interest in materials with better mechanical, thermal, and electrical properties. Metal organic Frameworks (MOFs) are a new class of hybrid porous material, also known as porous coordination polymers (PCPs), made up of metal nodes connected to organic linkers through coordination bonding, known for its fascinating properties like ultra-high surface area, tunable nanopores, ordered crystalline structure, high thermal stability etc. (Fig.1.1) [3]. Prof. Yaghi, a chemist, and materials scientist, laid the foundation for exploring the synthesis and properties of these innovative materials in late 1990s [4]. Since then, MOF research has flourished globally, with scientists exploring a vast array of MOF structures and applications [5].



**Fig.1.1.** Molecular diagram of UiO-66 MOF formation from 1,4- benzenedicarboxylic acid linker and  $Zr_6O_4(OH)_4$  metal cluster.

The fundamental component of MOFs is secondary building unit (SBU) which governs the geometry of the framework. The SBUs are typically metal nodes or clusters that are connected by organic linkers to create the three-dimensional network of the MOF [6]. The use of different SBUs in MOFs leads to distinct topologies due to the unique coordination environments, geometries, and connectivity patterns associated with each type of SBU [7]. The geometry and number of coordination site of the SBU is mainly determined by the type of metal used while porosity and rigidity of the MOF depends on the organic linker. Some of the possible SBU are shown in Fig. 1.2 (a, b, c, d,) as illustrated by Yaghi and group [8]. The structural illustration showing how molecular clusters, such as SBUs, shaped like squares, triangles, tetrahedrons, and octahedrons, are used to assemble crystalline MOFs. A fascinating characteristic of MOF is its structural tunability, which arises from different shapes and sizes of SBUs as well as length and orientation of the organic linker [9]. The usage of different combination of SBUs and organic linkers has contributed to the structural diversity of MOFs which in turn influence the properties like surface area, pore size, thermal stability, and chemical stability of the framework [10].



**Fig.1.2.** (a), (b), (c), (d) Illustrations of possible SBUs and (f), (g), (h), (i) organic linkers in MOF construction.

Some of the generally used organic linkers are based on carboxylic acid, organophosphorus compounds, salts of sulfonic acid, and heterocyclic compounds (Fig. 1.2 (e, f, g, h)). It is possible to create different MOFs with same topology with the only differences being in the kind and size of the linkers [11]. Such an example is the series of MOF composed of octahedral  $Zn_4O$  SBU connected to different dicarboxylic linkers, named as isorecticular MOFs (IRMOFs)[12]. Similarly, there are some other series of MOFs with same topology are available like MIL-series (Materials Institute Lavoisier), ZIF-series (Zeolitic imidazolate frameworks), UiO-series (University of Oslo) etc [13]–[15]. These series have been obtained by substituting the linker with a new one, which has kept the structural symmetry maintained in some cases, and in some other cases, the unit cell parameters have changed because of the length of the carbon chain. To enhance the versatility of MOFs and tailor them for diverse applications, researchers attach specific functional groups to the organic linkers, thereby introducing desired traits such as enhanced reactivity, selectivity, or affinity for certain molecules [16],[17]. Additionally, by employing post synthetic techniques, the accessible pores and active sites of metal clusters or linkers of the as-prepared MOFs can be artificially changed. As a result, with distinguished combination of SBUs and linkers a large variety of MOF with diverse structure, different pore sizes, morphologies and surface areas has been reported so far [18],[19]. Owing to the diverse characteristics of each MOF, researchers found a wide field of applications such as gas separation, absorption, sequestration, catalysis, sensing, etc [20]. MOFs can be synthesized through various routes, with hydrothermal or solvothermal methods being among the most commonly employed. In these processes, MOF precursors are allowed to react in a high-temperature aqueous or solvent environment, allowing controlled crystallization [21]. The hydrothermal/solvothermal approach offers a precise control over the MOF structure and properties, making it a versatile and widely used synthesis method in materials chemistry [22]. Moreover, layer-by-layer assembly, liquid phase self-assembly, physical/chemical exfoliation, and other techniques can be used to create MOFs with 1D, 2D, and 3D morphologies, which promotes the application of MOFs in electronics and electrochemical devices [23].

## 1.2 Electrically conducting MOF

MOFs in their conventional form are non-conductive due to low in charge carriers and absence of conductive pathways. They function as electrical insulators because of the linked inflexible metal ions and redox-inactive organic ligands, which raise the energy barrier for electron transfer. But, because of their high porosity and structural integrity MOFs have been serving unquestionably for the past 20 years in various applications. The MOFs have explored in some advanced applications like energy storage supercapacitors, batteries, fuel cells, oxygen evolution, hydrogen evolution, sensing etc [24]. All these applications involve electrochemical processes where MOF has to serve either as the electrode material or electrocatalysts or membrane. A crucial parameter to optimize the electrochemical performance of the active material is the charge transfer mechanism. However, the absence of electrical conductivity in the conventional pristine MOFs would suppress its efficiency to certain extent. Therefore, studies for introducing the conduction mechanism in MOF is still under active consideration [25]. Two important strategies employed by the researchers are by developing redox-active ligands or  $\pi$ -conjugated ligands and by encapsulating guest molecules into the framework. For convenience the MOFs obtained through the above-mentioned processes are termed as ‘intrinsically’ and ‘extrinsically’ conducting MOFs [26].

### 1.2.1 Intrinsically conducting MOF

The MOFs which possess electronic or protonic conductivities in its pristine form without any addition of external source are termed as intrinsically conducting MOF(ICMOF). Most of the ICMOFs are found to have a 2D morphology exhibiting a network of extended  $\pi$ -conjugated bonds. In 3D conducting MOFs, mainly the metal center provides the free-charge carriers and charge transport generally takes place via ‘through-bond’ processes[27]. Compared to the traditional MOFs and ICMOFs exhibits high electrical conductivity and decent charge mobility which endow them with rapid electron transfer and efficient ion transport [28]. The 2D ICMOF possess unique sheet-like structures with a large degree of anisotropy, exhibiting substantially large exposed surfaces, regular open channels, abundant active sites, and good mechanical property [29]. They adopt a graphite-like structure with 2D layer lattices formed via the planar coordination between metal

nodes and organic ligands. Furthermore, these 2D layers stack along the  $z$  axis by  $\pi$ - $\pi$  interactions and thus form regular and open nanochannels. Ligands of 2D ICMOM comprises highly planar and conjugated structures containing multitrophic ortho-substituted  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{SH}$ , functional groups, while the chelating centers are usually transition metal ions (Fe, Cu, Co, Ni or Pt, etc.) having unpaired electrons [30],[31]. It first forms a square-planar coordination geometry with strong  $d\pi$ - $P\pi$  orbital hybridization, and further extends over the in-plane direction through the metal-ligand interactions, leading to a high charge delocalization in 2D ICMOFs.

### 1.2.2 Extrinsicly conducting MOF

Minor alterations in the structure and compositions of Metal-Organic Frameworks (MOFs) bring about a significant transformation in their properties including conductivity. Even slight modifications can induce a remarkable shift in the electrical properties of these materials. Hence, MOF researchers have post-synthetically changed MOFs with guest molecules to tune and improve their electrical conductivity [32]. The encapsulation of guests into the pores of MOFs is the most widely adopted strategy to lower the energy barriers for charge transfer and realize conductivity in MOFs. The available pores of MOFs provide good platforms for loading guests via post synthetic modification. This process involves the addition of stoichiometric amount of new species into pre synthesized MOF. In order to create continuous charge transport channels and reach enhanced mobilities, higher guest loadings are usually required [33]. It is typical practice to incorporate guests with longer structures, like conductive polymers and inorganic oxides in order to attain a continuous path for charge transfer. Charge transfer mechanisms between the MOF framework and the guest are thought to be responsible for the increased conductivity since they produce free charge carriers[34]. This approach is beneficial as the adjustment between guest and the framework maximizes their synergistic effect. The MOFs with billion-fold increase in the conductivity can be realized through this process. In addition, when just a portion of the pores are filled with guests, the MOF's porous structure is preserved which maintains its large surface area [35]. To finely customize the transport properties of these materials, a promising strategy involves matching the reduction potentials of both the framework and guest, along with considering the sizes of the guest

molecules and the pores. This approach offers the potential for enhanced control and tailoring of the material's electrical characteristics.

### 1.2.2.1 Guest for extrinsically conducting MOF

**Conducting polymers:** Conducting polymers are a class of organic polymers that have the unique property of conducting electricity. Unlike traditional polymers, which are insulators, conducting polymers can carry an electrical charge due to the delocalized  $\pi$ -electrons within their molecular structure. The conductivity of undoped polymer ranges between  $10^{-6}$  to  $10^{-10}$  S  $\text{cm}^{-1}$ , which lies in the boundary region of semiconductor and insulators [36]. However, the conductivity of the polymer can be enhanced up to the metallic conductivity area by doping it with oxidative/reductive substituents or donor/acceptor radicals. For example,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{I}_2$ ,  $\text{Br}_2$ , and so on [37]. Some popularly known CPs are polyaniline (PANI), polypyrrole (PPy), polyazulene, PEDOT, polyaminonaphthalenes etc. The CPs can be easily processed through various methods of polymerization like oxidative, electrochemical, photochemical etc. The introduction of conductive polymer into the pores of MOF greatly enhances the conductivity of the material. The inclusion of CP in MOF can make it beneficial as an electrode substrate since it gives the electrode the conductive qualities it needs as well as the effective surface area for analyte accumulation. Moreover, loading CP with proper concentration into MOF will retain the porous nature of the MOF which is necessary for ion diffusion during the electrochemical process. Dhara et al. reported an intercalation of pyrrole monomers into the pores of Cd -  $\text{H}_2\text{NDC}$  = 2,6-naphthalenedicarboxylic acid based fluorescent 3D MOF. The monomer was polymerised by treating with iodine solution which enhanced the electrical conductivity nearly by 9-fold [38]. Abraira et al. demonstrated a confinement of conducting PEDOT inside the pores of iron-based MOF MIL-100. They found that the PEDOT@MIL-100(Fe) composite exhibits a 10 times higher electrical conductivity than the pristine CP which could be due to the nanoarrangement of PEDOT within the pores of MOF. They further investigated the electrochemical and electrochromic properties of the composite [39]. Another example of CP incorporated MOF is the work of Ouay et al. where they performed a controlled loading of EDOT monomer into the pores of MIL-101(Cr) MOF. They achieved a conductivity of  $1.1 \times 10^{-3}$  S  $\text{cm}^{-1}$  along with a higher surface area after the polymerization of PEDOT inside the pores of MOF [40].

**Metal nanoparticles (NPs) or nanoclusters (NCs):** In recent decades, metal nanoparticles (NPs) have received growing interest owing to their abundant active sites and high electrical conductivity, and hence they have been widely investigated in a broad range of applications, particularly in electrochemical sensing and catalysis [41]. The metal NPs are considered thermodynamically unstable due to their enormous surface areas and high surface energy. As a result, they often agglomerate, resulting in inefficient exposure of active areas, weakening their catalytic and conducting characteristics. Thus, an appropriate platform is required to avoid the aggregation in order to obtain the stability [42]. Since MOF has pores to accommodate guest, they are suitable for loading metal NPs or metal nanoclusters. This nanoscale confinement within the pores of MOF can induce change in the electronic property of the host-guest moieties. This change can create additional charge transport pathways within the framework structure in which electrons can hop between the metal nanoclusters through metal-metal interactions or through delocalized states within the MOF framework. As a result, overall conductivity of the system increases. For example, Grzybowski et al. infiltrated  $\text{AgNO}_3$  to the pores of rubidium  $\gamma$ -cyclodextrin MOF (Rb-CD-MOF) which enhanced the conductivity by 10000-fold magnitude [43]. They found that the charge transport would take place through tunnelling between the NCs. They also observed similar performance in NC loaded MIL-53 MOF. A metal NP encapsulated MOF was reported by the group of Zhang where they loaded platinum (Pt) NP in three different MOFs ZIF-8, ZIF-67 and UiO-66. They applied the material as a catalyst which exhibits good selectivity and a good conversion of energy in hydrogenation reaction[44] .

**Redox-active and other guest:** Many other materials ranging from organic to inorganic oxides, metallocarbene, metal oxides can also be integrated in the structure of MOF in order to obtain a high conductivity to ensure their uses in electronic or electrochemical applications. Organic species with C-H or C-C bonds infiltrated in MOFs are evident in the work of Goswami et al. [45]. They encapsulated  $\text{C}_{60}$  fullerene in Zr-tetrakis (p-benzoate) pyrene (TBAPy) MOF Nu-90. The composite has resulted an increase in conductivity from  $<10^{-14} \text{ S cm}^{-1}$  to  $\sim 10^{-3} \text{ S cm}^{-1}$  which is  $10^{11}$  times higher than the pristine Nu-90 [45]. A similar work was reported by the group of Kung et al. where they infiltrated the Zr-based MOF (Nu-1000) with Ni-bis(dicarbollide) to get a conductivity which is several orders higher than the guest free MOF [46]. An organic compound known as

7,7,8,8-tetracyanoquinodimethane (TCQN) is one of the most widely used guest material to enhance the conductivity from the infancy of generation of extrinsically conducting MOF. In 2013 the group of Talin et al. incorporated TCQN into a thin film Cu-BTC MOF which enhanced the electrical conductivity of the overall composite. Their investigation demonstrated that the high is a result of strong electronic interaction between the guest and binuclear copper nodes [47]. In the later years many reports on TCQN incorporated MOF have arrived [47]–[49]. There are also numerous studies available in the literature on how the addition of iodine or polyiodides altered electrical conductivity [48],[49].

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

To make MOF useful in areas like energy storage, photovoltaics, sensing, and catalysis, it is necessary to tailor its features, including band structure, conductivity, adsorption behaviour, and charge separation. Defect engineering is currently regarded as an essential technique for customising MOF's physicochemical characteristics. Defect engineering pertains to the intentional introduction of structural defects or irregularities into metal-organic frameworks (MOFs) with the aim of modifying their microstructural characteristics and optimising their performance for a range of applications [50]. Existence of defects in MOFs indicates the deviation from an ideal long range ordered crystalline structure. Point defects that usually formed in MOF are missing linker defect, missing cluster defect, modified linker defect, modified cluster defect etc. The defects in MOF can be created during the synthesis itself or they can be introduced in post-synthesis steps[51]. Approaches like modulator assisted synthesis, mixed linker synthesis are some of the “de novo” methods to impart defects during the synthesis of the crystal. Post-synthetic modification in the MOF structures has been carried out through various methods like ligand exchange methods, functionalization, grafting of polymers or foreign molecules, etching methods, harsh activation condition etc [52].

In polymers, oxides of metals and other carbon-based materials the structural modification and hence optical / electrical property tuning is most popularly carried out by a method known as energetic ion irradiation method. Factors like bond length, charge transfer between adjacent active sites, aromaticity, conjugation length, intermolecular interaction etc can influence the electrical properties of a materials to a great extent [53]. As a result,



one of the best ways to cause structural and microstructural changes in materials is through swift heavy ion (SHI) irradiation. It is used to modify the characteristics of many different kinds of materials, such as semiconductors, metals, and insulators. The energy of the ions, fluences and type of ions used for irradiation are the factors that play vital role in modifying the material property. When the energy of the ion is relatively low in few hundreds of keV they are used to modify the surface or interface of the materials [53].

**Swift heavy ion irradiation:** Swift Heavy Ion (SHI) irradiation is a technique of bombarding a target material with high energy heavy ion beams with energy range of few MeV to hundreds of MeV. During the bombardment, the energy of the fast-moving ions are transferred to the target material through two processes- elastic collision and inelastic collision. When the energy loss takes place through elastic collision the atoms of the target material get displaced and the method is referred as nuclear stopping. This is essentially nuclear energy loss,  $S_n = \left(\frac{dE}{dx}\right)_n$ . In inelastic collision the high energy heavy ions excite or ionize the atom by interacting with the electron density of the atoms in the target material. This process is mediated via electronic stopping power and energy loss during the process is called electronic energy loss,  $S_e = \left(\frac{dE}{dx}\right)_e$  [54]. In SHI irradiation, electronic stopping dominates over nuclear stopping in the energy range tens of MeV to hundreds of MeV. When a SHI traverse through a material medium, it creates a trail of electronic excitations and ionizations along its path due to its strong Coulomb field. This track consists of displaced lattice atoms and electrons, forming a long cylindrical core of charged ions. In certain cases, particularly when the electronic stopping power of the ions exceeds a critical threshold, the strong Coulombic repulsion between the highly charged ions leads to an explosion, termed as "Coulomb explosion" [55]. This results in the generation of a radial shock wave, where the electrostatic energy is converted into coherent atomic movements radially outward from the ion path. This radial expansion continues until the ions are screened by the conduction electrons in the material. This repulsion can lead to the ion breaking apart into multiple smaller fragments, releasing a significant amount of energy in the process. The fragments produced by Coulomb explosion can include charged particles such as ions and electrons as well as neutral species. In some cases, it can lead to the formation of nanoscale defects, such as vacancies, interstitials, and dislocations, within the material. These defects can significantly alter the material's structural, mechanical, and

electronic properties [56]. Another model that competes this process is known as thermal spike model where the kinetic energy is transmitted to the lattice by electron-phonon interaction which results in the increase in lattice temperature above its melting. The drop in temperature is again very rapid which causes amorphous ion tracks upon melt solidification [57]. Although both models are well-established and competitive, the Coulomb explosion model can be more important in insulators, whilst the thermal spike model is highly relevant to metals and semiconductors. SHI irradiation changes physical, chemical, optical, electrical properties of the target material by introducing defects in its structure. The material modification from SHI includes higher electronic conductivity, thermal stability, phase change (from crystalline to amorphous), enhanced electrochemical stability, change in optical properties, randomly placed pore formation and also crosslinking in polymer matrix etc. [58].

#### 1.4 Mechanism of charge transport in MOF

The factors influencing the conductivity of materials are charge carrier electrons ( $e$ ) and holes ( $h$ ) density ( $n$ ) and mobility( $\mu$ ) as given by-

$$\sigma = n_h e \mu_h + n_e e \mu_e \quad (1.1)$$

The material must have a large concentration of delocalised charge carriers say  $\sim 10^{15} \text{ cm}^{-3}$  in order to have a high charge density [59]. A MOF's organic ligands and metal ions have the potential to serve as sources of charge carriers. Metal clusters with unpaired electrons can contribute to the free charge carriers in MOF by making the metal site potentially redox-active. For example,  $\text{Cu}^{2+}$  with  $d^9$  configuration has an unpaired electron which can act as a source of free charge carrier [60]. To facilitate unpaired electron transport between metal ions or nodes, the organic ligands should be either redox-active compounds or stable radicals.

Band theory additionally reveals key strategies for raising a material's charge density. According to the band theory the orbitals of adjacent atoms or molecules overlap when they are arranged closely. As a result, overlapping of appropriate orbitals give rise to a band with continuous energy state. The forbidden energy states in between those continuous bands are called energy gap. This bandgap is also a determining factor for the

conduction in the materials. The term ‘valence band’ ( $E_v$ ) refers to the energy band of the outermost electron orbital. Conduction band ( $E_c$ ) refers to the energy band that is partially filled with electrons. In metallic conductors, these two bands overlap, and the Fermi level ( $E_F$ ) lies in between the bands, which allows the electrons to transfer freely. In semiconductors and insulators, the band gap is large hence the charge carriers are absent. The Fermi level in semiconductors and insulators lies in the band gap between the completely filled valence band and entirely empty conduction band. The difference between the lowest energy state of conduction band ( $E_{CL}$ ), or highest energy state valence band ( $E_{VH}$ ) and Fermi level is called activation energy ( $E_a$ ) –

$$E_a = E_F - E_{VH} = E_{CL} - E_F \quad (1.2)$$

Activation energy is the energy required to move charge carriers from the valence band to the conduction band [61]. The electrons in the valence band can be thermally activated by raising the temperature in order to attain the activation energy, thereby increasing the carrier density ( $n$ ). Now, the relation between carrier density, activation energy and temperature are given by the following relation-

$$n = n_o \exp\left(-\frac{E_a}{kT}\right) \quad (1.3)$$

In the eqn  $n_o$  refers to prefactor,  $k$  refers to the Boltzmann constant and  $T$  is the absolute temperature. Unlike intrinsic semiconductor in extrinsic semiconductor Fermi level does not lie at the middle of band gap rather it moves towards the conduction band or valence band depending upon the type of dopant [62]. Charge mobility is a key parameter that reflects how efficiently charges (electrons or holes) can move through a material. In the conducting MOFs, there are two main charge-transport regimes to consider: hopping transport and band transport [25]. In hopping transport mechanism charge carriers move through the material by hopping between localised states or sites with discrete energy levels. In this transport, the phenomenon mobility is determined by the hopping probability ( $P$ ), which is a function of the spatial distance ( $R$ ) and energy differential ( $E$ ) between consecutive hopping sites, as given by the equation-

$$P = \exp\left(-\alpha R - \frac{E}{kT}\right) \quad (1.4)$$

Here, constant  $\alpha$  is defined by the nature of hopping site. Because of this, the hopping transport depends on charge hopping between adjacent units with small energy difference and close spatial distance [59]. The band transport refers to the transport of charge carriers (electrons or holes) through delocalized states created by continuous coordination or covalent bonds within the framework. The orbital symmetry and energy level compatibility between the metal centres and organic ligands are critical for effective conduction. The mobility in band transport mechanism is dictated by the effective mass ( $m^*$ ) of delocalized charge carriers and the mean time ( $\tau$ ) between two consecutive charge-scattering events as shown in equation-

$$\mu = \frac{e\tau}{m^*} \quad (1.5)$$

Higher quantity of charge-scattering sites like defects, disorders, impurities or grain boundaries will result in smaller  $\tau$  which can reduce the mobility of the carriers. Contrarily, the smaller effective mass can contribute to higher mobility [61]. Effective mass is influenced by various factors such as band dispersion, crystal structure symmetry, and unit-cell features. A well-dispersed band, resulting from good orbital overlap, is crucial for achieving a low effective mass.

In intrinsically conducting MOF two strategies are seen to be employed to provide charge transfer pathways- “through bond” and “through space”. Both strategies have the potential to provide band transfer or hopping. The through-bond mechanism seeks to increase charge transmission by allowing the metallic node and organic ligand orbitals to overlap in the right energy and spatial patterns through covalent bonding. The extended charge-transfer channel created by the coordination and covalent bonds made up of metal and organic molecules improves the charge transfer in MOFs [63]. This mechanism is mainly observed in MOFs composed with redox active ligands or metal ions and 2D MOFs with long-range  $\pi$ -conjugation. For example, transition metal (Ni, Fe, Cu, Zn etc.) based 2D MOFs with electroactive ligands like hexahydroxytriphenylene (HHTP), hexaiminotriphenylene (HITP), bezehexathiol (BHT) etc [64]. The non-covalent bonds between the organic components of MOF such as  $\pi$ - $\pi$  stacking give rise to through-space carrier transport channels. Within MOFs, redox active fragments held together by metal ions and ligands at interplanar lengths of less than 3.5 Å would exhibit the aforesaid

mechanism of charge conduction. TCQN, tetrathiafulvalene (TTF) etc. based MOFs conducts current through this conduction mechanism [65].

The extrinsically conducting MOF takes advantage of the structure's inherent porosity, which allows for the integration of guest molecules and so boosts conductivity. When the guest molecule itself is conductive species, the conductivity of entire host-guest composite enhances as the guest will have their own charge carriers and pathways for charge conduction. If the guest molecules are redox active, they can give rise to charge carriers through creating conductive channels within the MOF skeleton or on the walls by guest-framework interaction. Guest molecules in MOFs can indeed serve as examples of through-bond charge transport, particularly when they are tightly coupled to the MOF framework. When these guest molecules are in close proximity to the framework, they easily interact with the metal ions or organic linkers, facilitating charge transfer through direct electronic interactions, rather than through-space charge transfer.

## 1.5 Applications of conducting MOF

### 1.5.1 Energy storage device

With time, the demand for energy storage device has increased to meet the need of alternative energy source. Electrochemical energy storage devices are systems that store energy through chemical reactions involving the transfer of electrons between electrodes and electrolytes. The researchers aim to explore improved electrode materials for electrochemical energy storage systems such as supercapacitors, Li-ion batteries, metal-sulphur batteries etc. Supercapacitors, are energy storage devices that store charges electrostatically (electric double layer capacitor (EDLC) or through chemical reaction (pseudo capacitor). They fill the gap between traditional capacitors and batteries, providing higher power density, faster charge and discharge rates, and longer cycle life. Thus, electrodes of the supercapacitor should have a sufficiently large surface area along with electrical conductivity for efficient functioning. Electrically conductive MOF with a synergistic combination of favourable features such as improved charge transport, precisely controlled porous structure, and large surface area show great promise as active materials for supercapacitors electrodes. Basically, 2D MOFs with inherent conductivity, MOF derived metal oxides, MOF composites with metal oxides, metal nanoparticles and

MXenes are utilised as supercapacitor electrode so far [66],[67]. For example, a  $\text{Cu}_3(2, 3, 6, 7, 10, 11\text{-hexahydroxytriphenylene})_2$  catecholate (Cu CAT) MOF reported by Hou et al. was used to develop a flexible supercapacitor electrode on polypyrrole membrane [68]. It resulted in a high capacitance of  $252.1 \text{ mF cm}^{-2}$  with an energy density of  $22.4 \text{ } \mu\text{Wh cm}^{-2}$  and a power density of  $1.1 \text{ mW cm}^{-2}$ . This case demonstrates the use of an intrinsically conducting MOF nanowire in supercapacitor electrode due to its large surface area and high conductivity. The MOF derived metal oxide nanocomposite was reported by Li et al. where they used Ni-MOF as a template to prepare  $\text{Ni (OH)}_2\text{-MnO}_2\text{@C}$  ternary composite which resulted in a high specific capacity of  $2.9 \text{ C cm}^{-2}$  ( $965.1 \text{ C g}^{-1}$ ) at a current density of  $2 \text{ mA cm}^{-2}$  along with high specific energy density of  $39.1 \text{ Wh kg}^{-1}$  with a power density of  $221.4 \text{ W kg}^{-1}$  [69]. Rajasekaran et al. describes a supercapacitor electrode material based on MOF composite with reduced graphene(rGO) and polyaniline (PANI) [70]. The samarium-based MOF/rGO/PANI composite resulted in a high specific capacitance of  $218 \text{ F g}^{-1}$  and specific power and energy are calculated to be  $59.3 \text{ Wh kg}^{-1}$  and  $581 \text{ W kg}^{-1}$ .

Metal-ion batteries (MIB), such as Li-ion and Na-ion, are rechargeable devices that have a higher energy density but a lower power density. In MIBs, charge-discharge phenomena take place when metal ions migrate from the electrolyte solution to the electrode to get intercalated in the crystal lattice of the electrode material and the stored metal ions are freed from the electrode material and returned to the electrolyte solution through a process known as de-intercalation[71]. Porous architectures, redox activity, and electrical conductivity are important considerations while developing high-performance electrode materials for MIBs. In the early years of 2000, researchers have explored the pristine MOF composed of Fe, Co, Mn, Ni and BDC or BTC linkers as anode material in Li-ion batteries [72]–[74]. Later on, MOF derived metal oxides and nanoporous carbon have caught much attention due to the ability of exchanging electrons rather than intercalation to enhance their conductivity [75],[76]. A Fe-based MOF was first reported in 2017 by the group of Jin et al. as active electrode for Li-ion batteries. They prepared a stable MIL-88B(Fe) with 1,4-dicarboxybenzene linker which exhibits high capacity of  $680 \text{ mA h g}^{-1}$  with current density  $200 \text{ mA g}^{-1}$  [77]. The example of a conductive MOF based Li-ion battery is reported by Sun et al. for anode material for hybrid capacitor-battery application. They prepared a 1D nanowire of Co-HHTP MOF that produces reversible

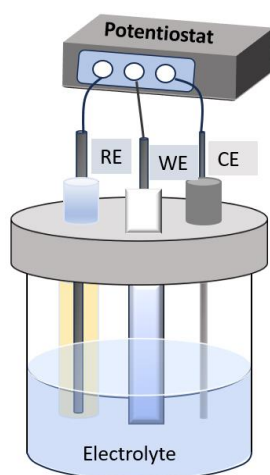
capacity of 435 mA h g<sup>-1</sup> at 1 A g<sup>-1</sup> and power density of 10 kW kg<sup>-1</sup> and with energy density of 64 W h kg<sup>-1</sup> [78]. Apart from Li-ion batteries, the MOF in its pristine or modified form has been exploited for cathode as well as anode material for Zn-ion, Na-ion, Li-S batteries [79],[80].

### 1.5.2 Energy conversion

Electrochemical energy conversion involves a process known as electrocatalysis which uses electricity to separate water molecules into their constituent elements, hydrogen and oxygen. Electrocatalyst are potentially used in oxygen evolution reaction (OER), hydrogen evolution reaction (HER), oxygen reduction reactions (ORR) etc. [81]. The application of these electrocatalytic processes say ORR is required in fuel cell as the fundamental reaction to dictate the conversion of fuel to electricity. During electrocatalytic water splitting OER and HER takes place in energy storage devices like metal-air battery. The electrocatalytic performance is evaluated by low overpotential, high current density with low Tafel slope [82]. The breaking of highly energetic O=O bonds during the ORR poses a significant challenge, requiring an efficient catalyst to overcome the kinetic sluggishness of the process. Owing to the advantage of tunable porous structure, open redox active sites, thermal and chemical stability MOF can be exploited as an electrocatalyst. Including pristine MOFs, porous carbon derived from MOF, bimetallic MOF have made significant progress as electrodes for energy conversion. Li et al. reported a bimetallic MOF composed of Fe-Co cluster and BDC ligands [83]. The composite u-CoFe<sub>0.5</sub>-BDC was prepared via ultrasonic treatment which resulted in an overpotential of 295 mV at a current density of 10 mA cm<sup>2</sup>. This was significantly higher than the commercial RuO<sub>2</sub> catalyst, while being cost-effective and stable. Zhang et al. developed a bifunctional electrocatalyst for ORR and OER for metal-air batteries. They derived a honeycomb-like FeS/Fe<sub>3</sub>C@NS-C-900 composite from a Fe-BTC MOF through pyrolysis. The composite has an excellent cyclic stability upto 1730 cycles at 2 mA/cm<sup>3</sup> when used as cathode material [84].

### 1.5.3 Electrochemical sensors

Chemical sensors represent sophisticated analytical tools employed for both qualitative and quantitative assessments of target specific species. These sensors operate through selective chemical reactions, allowing for precise identification and measurement of the



**Fig.1.3.** Three-electrode system with counter electrode (CE), reference electrode (RE) and working electrode (WE) in an electrolyte connected to a potentiostat.

target substance. As per the IUPAC definition, a chemical sensor is a device designed to convert chemical information, spanning from the concentration of a singular component to comprehensive composition analysis, into a practical and analytically useful signal [85]. Typically, a chemical sensor comprises two fundamental components: a receptor and a physicochemical transducer. The receptor is specifically designed to recognize and distinguish the analyte while the transducer converts the chemical information into a discernible and amplified analytical signal. Receptors are diverse and can be complex (macro)molecules that form highly specific interactions with the target analyte, or they can be activated or doped surfaces. Now, depending on the type of transducer employed the chemical sensors can be classified as, electrochemical sensor, optical sensor, mass sensitive sensor, calorimetric sensor etc. [86].

Electrochemical sensors typically consist of an electrode, where electrochemical reactions with the target analyte occur, and a transducer that converts these reactions into measurable electrical signals, such as voltage or current. The sensor's ability to generate a signal proportional to the concentration of the analyte makes it a valuable tool for various applications, including environmental monitoring, healthcare diagnostics, and industrial processes. Generally, electrochemical sensors use a three-electrode setup immersed in an electrolyte. An additional electrode called reference electrode along with the counter and working electrode completes the setup. The reference electrode maintains a constant



potential at the working electrode, ensuring that the electrochemical reactions being studied are not influenced by variations in the reference potential. The potential of the reference electrode serves as a reference point for the electrochemical reactions occurring at the working electrode. Generally used reference electrodes are calomel and Ag/AgCl. Auxiliary or counter electrodes can complete the circuit by allowing the current to pass without changing the potential at the reference. Platinum (Pt) wires are typically used as a counter electrode due to its inert nature. The working electrode is the electrode where the actual electrochemical reactions of interest take place in an electrochemical cell. It is the site where oxidation and reduction reactions occur, generating a measurable current or potential that is indicative of the studied electrochemical processes. Conventionally, glassy carbon electrode, carbon paste, gold/Pt are used as working electrodes [87]. However, traditional electrodes in direct electrochemical determinations encounter challenges like elevated overpotential, slow electrode kinetics, electrode surface fouling, limited selectivity, and low sensitivity. The primary issue with bare electrodes is the fouling of their surfaces, primarily caused by the adsorption of analyte molecules or their reaction byproducts. This fouling significantly compromises the stability of the electrode response. To alleviate these challenges, modifying the electrode surface with suitable modifiers offers a promising approach to mitigate issues related to stability and enhancement of overall electrochemical performance.

### 1.5.3.1 Potentiometric sensors

Potentiometric sensors are a type of chemical sensor that are based on the measurement of the potential difference, or voltage, between two electrodes in a solution. When an analyte undergoes redox reaction at the electrode-analyte interface which changes the potential of the electrode, that change quantifies the activity of the ions undergoing the electrochemical reaction. Commonly used potentiometric sensors are based on ion-selective electrodes. These electrodes exhibit selectivity for specific ions, allowing for targeted and precise measurements. In the traditional setup, these electrodes typically contain an ion selective permeable membrane which segregates the sample from the internal environment of the electrode. Of these two electrodes, one is the working electrode (dependent on the environment), while the other is the reference electrode. With the help of a solution that contains the particular ion of interest at a steady activity level, the reference electrode is

able to maintain a constant potential. The potential difference, or cell potential, can be directly associated with the dissolved ion concentration while the potential of the reference electrode remains fixed. Potentiometric sensors have been widely utilised to monitor pH change for many years.

### **1.5.3.2 Amperometric sensors**

In an amperometric sensor, current is measured while a constant potential is applied to drive the electrochemical redox reaction. The intensity of the measured current is proportional to the concentration of the analyte present. Two-electrode and, more conveniently, three-electrode systems are used in this process. The behaviour of the working electrode is the key factor in amperometric sensors. Therefore, much effort has been made to construct a working electrode to achieve significant sensitivity and stability. Noble metals and various carbon-based solid electrodes have found their way to serve in this method as solid electrodes. Nowadays, a widely adapted strategy to enhance performance is the deliberate chemical modification of the conventional electrode surface. The modifiers can be incorporated into the surface of the electrodes through chemisorption, physisorption, electrochemical deposition, electrochemical polymerization etc.

### **1.5.3.3 Voltametric sensors**

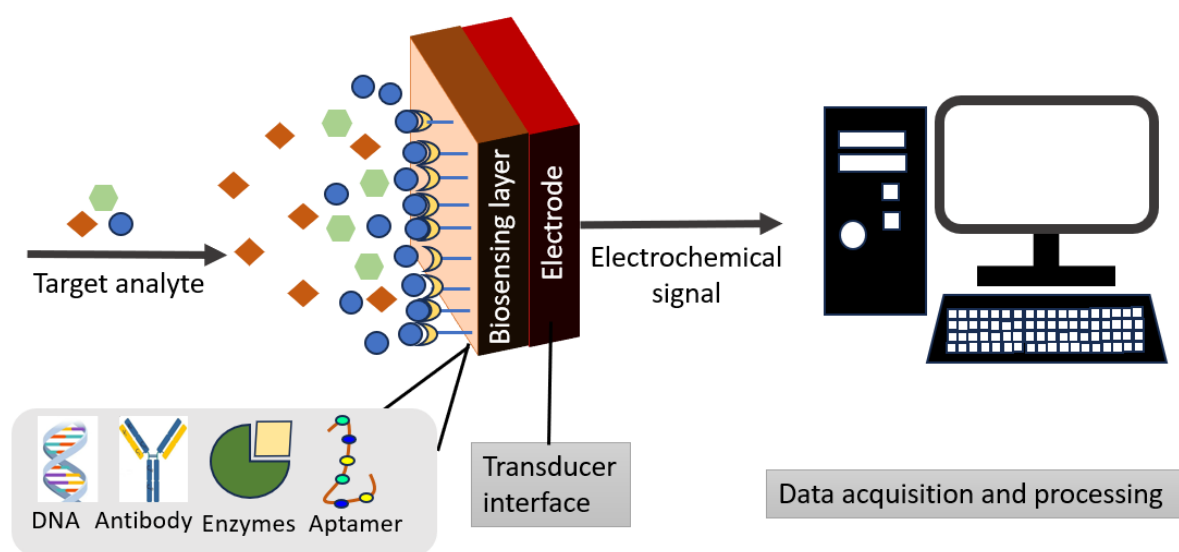
Voltammetry can be performed in a similar electrochemical setup as amperometry, the only difference is the potential is not constant in this method. The current is scanned within a potential window where the redox activity of the analytes is most likely to take place. Various voltametric techniques are cyclic voltammetry, differential pulse voltammetry, square wave voltammetry, stripping voltammetry etc. In these techniques the voltage is applied between the counter and the working electrode and the current is measured between reference and the working electrode. Due to the application of potential redox reaction occurs at the interface of electrolyte and electrode which in turn causes the charge transport to establish a current flow between the counter and working electrode. For a particular working electrode, the observed current response usually exhibits a peak or plateau that precisely matches the concentration of the electroactive component in the test solution.

#### 1.5.3.4 Impedimetric sensors

In impedimetric sensors the detection of analytes is characterized by the change in impedance of the circuit. It measures the impedance provided by the electrode and electrolyte solution to the flow of current between the counter and working electrode when the system is simulated by a small potential. Electrochemical impedance spectroscopy (EIS) is the most commonly used technique to measure impedance. The impedance of the system is analysed by varying the frequency of the potential in a range say 10 mHz to 100 kHz. This method is used because it delivers an enhanced sensitivity at lower concentration of the analytes.

#### 1.5.4 Electrochemical biosensors

The electrochemical biosensor is a sensing device that translates complex bioanalytical events into readable signal by using a biomolecule or bioinspired object as a bioreceptor [86]. In simple words when the receptor of the electrochemical sensor is composed of biological components like DNA, enzymes, proteins or antibodies the sensor is called as biosensor as illustrated in Fig. 1.4. The bioreceptors recognize bio analytes through a highly specific molecular interaction and transducer convert recognition event into an electrical signal in an electrochemical biosensor. Immobilization of biomolecules to the working electrode ensures the selectivity of the sensor to specific analytes. Moreover, use of electroanalytical technique discards the need of applying an additional electronic device for the analysis of biorecognition event. Biosensors were first introduced by Clark and Lyons to detect components present in the blood of patient during 1950-1970 [88]. Such biosensors are termed as first-generation (I gen) biosensors where bioreceptors are coupled or encapsulated in a membrane connected to the transducer. The analytes when diffuse through the membrane to transducer an electrical signal is produced which is the indication of detection. The limitation with I gen biosensor is that it requires high reaction potential for measuring the sensing signal. With time biosensor evolved to second generation (II gen) and third generation (III gen). In the II gen biosensors a mediator has been integrated in the bioreceptor layer or allowed to freely suspend in the electrolyte in order to reduce the requirement of high operational potentials and to obtain a better sensitivity. In the third generation (III gen) biosensor the electron transfer directly takes place between redox active bioreceptor layer and electrode. In this case the mediator and the bio molecules are



**Fig.1.4.** Schematic of a typical electrochemical biosensor setup.

**Table.1.1** Classification of biosensors according to the generation

Generation	Description	Advantage or drawback
I	Mediator less, employ enzymes like glucose oxidase, works by reducing oxygen to hydrogen peroxide	suffer from interference from compounds present in the sample matrix that can react with the enzyme or electrode surface, slow response time, Limited Stability
II	Mediators are immobilized, works at potential, advanced membranes are also used	Enhance sensitivity, reduces interference, Improved stability.  Mediator instability, mediator toxicity, complexity of fabrication are some disadvantages.
III	Mediator less- direct electron transfer between enzyme and electrode material, based on bio-electro catalysis, fast response.	Enhanced selectivity and sensitivity, multifunctionality, specific interaction with the antigens as biocompatible materials is used to modify the electrode.

immobilized together into the electrode which makes the electron transfer mechanism easier. Quicker reaction times are achieved by minimising the electron transfer distance between the mediator and the enzyme by their close proximity to the transducer surface. Different nanomaterials and nanocomposites have been explored in the recent years to accomplish the direct electron transfer mechanism. Important applications of these biosensors include environmental monitoring, food safety, and medical diagnostics. Based on the types of bioreceptors biosensors are classified into enzyme based, antibody based, aptamer based, whole cell based, nanoparticle based etc. The classification of biosensors depending on their generations are described in Table 1.1 with their benefits and advantages.

#### **1.5.4.1 Antibody based**

Antibodies are special class of protein produced in the living organism by the immune system in response to fight the foreign materials like pathogen or antigens which are composed of amino acids and plasma proteins. Antibodies, also known as immunoglobulins (Ig), possess a distinctive Y-shaped structure comprising two identical pairs of protein chains: heavy chains and light chains which are interconnected by disulfide bonds. This molecular architecture embodies two functional regions: the variable region (Fab) and the constant region (Fc) [89]. The variable region located at the tip of the Y-shaped structure of the antibody contains antigen-binding sites that confer specificity by recognising and binding to unique antigens. The multiplicity of amino acid sequences in this area supports the wide range of antibodies that can target several diseases. Conversely, the constant region, found at the base of the Y-structure, encompasses the crystallizable fragment (Fc), comprising constant domains from the heavy and light chains. The Fc region coordinates a number of effector activities that are essential for immune responses. Antibodies are classified into five groups depending on its constant region namely IgG, IgM, IgA, IgD and IgE [90]. Antibody based biosensors are commonly termed as immunosensors.

#### **1.5.4.2 Enzyme based**

Enzymes are catalyst which speed up a chemical reaction involving biological component. The enzyme-based biosensors work under principle of catalytic activity of the enzyme and

binding to the analyte. The enzymes have specific binding sites called binding pockets to interact with the analyte through a lock and key analogous mechanism.[91] Because of this particular interaction, the substrate and the enzyme's redox active site exchange electrons, forming the product. Further detection is based on measuring current response corresponding to the concentration and activity of the enzyme or analyte. One example of enzymatic biosensing is glucose detection by using glucose oxidase as enzyme.

#### 1.5.4.3 Aptamer based

Aptamers are single stranded sequence of RNA or DNA molecules which possess an amazing capacity to adapt to a variety of three-dimensional structures for binding with various targets. To interact with specific target molecules like peptides, protein complexes, pathogen, live cells or inorganic molecules, aptamers can mould themselves into different configurations from helices to loops to fit the surfaces of their chosen targets like jigsaw pieces [92]. Therefore, they have great selectivity and specificity towards binding targets. Aptamers can often tolerate a range of temperatures without losing their structural integrity. They can easily be synthesized in a laboratory. They follow a selection process known as Systematic evolution of ligands by exponential enrichment (SELEX) introduced by Tuerk, Gold, Ellington and Szostak [93]. Using this method, appropriate binding sequences are amplified after being initially extracted from big oligonucleotide libraries. Aptamers are seen to be used in diagnostic as well as therapeutic applications [94].

#### 1.6 Scope of the thesis

Since its discovery in 1995 by Professor Omar Yaghi and his research group, MOF has garnered widespread attention and popularity across various scientific disciplines, ranging from chemistry to material sciences [95]. The MOFs are three-dimensional network of metal nodes connected to monodentate or multidentate organic linkers via coordination bonds. The topology of the metal centre dictates the overall structure of a particular MOF. The aesthetic properties of MOFs are influenced by how specific metal components interact with the organic ligands. Interestingly, even if the organic linker maintains the same overall structure, slight variations in its size or shape can lead to a range of MOF structures that share a common underlying framework. Following the publication of the MOF-5 prototype composed of  $Zn_4O(BDC)_3$  [where BDC = 1,4-benzenedicarboxylate],

a great deal of research has been done to find other MOF types [96]. As of right now, over 20,000 different varieties of MOFs have been synthesised. The main attraction of the MOF is their highly ordered porous structure with an ultra-large specific surface area. Therefore, the majority of the early enthusiasm surrounding MOF materials was centred on its traditional uses as microporous materials for the storage of gases, separation of gases from mixtures, sequestrations etc. In the later years, as diverse MOF structures have been uncovered, their applications have expanded into numerous fields, including catalysis, drug delivery, sensing, and beyond [97]. In the earlier years, the MOF suffered the structural instability due to the weak coordination bonding between the ligand and the metal centre. These linkages can be prone to hydrolysis in the presence of moisture or water. Hydrolysis leads to the degradation of the framework, resulting in the collapse of the porous structure and loss of crystallinity. Thankfully, with the discovery of highly stable MOFs based on Zr, Fe, Cr with robust metal centres, the issue regarding the practical use of MOF has been resolved [11]. In spite of being multifunctional with versatility, most of the MOFs are less utilized in the field of energy storage, optoelectronics or electrochemistry as MOF is electrically insulating in nature because of lack of free charge carriers and restricted charge transport pathways [15]. In the meantime, two approaches have been surfaced to address this drawback. The first strategy was to produce an intrinsically conducting MOF by using redox active metal centers, redox active ligands,  $\pi$ -conjugated organic linkers, acceptor-donor pairs during the synthesis of MOF [98]. Nevertheless, these MOFs demonstrated fairly good electrical conductivity. There are few building blocks for these MOFs that are readily available, and they require expensive raw ingredients for synthetic methods. Till date, only a few numbers of intrinsically conducting MOFs are available in comparison with the large variety of structurally diverse conventional MOFs. Still the fundamental aspect behind the conduction mechanism of such MOF is questionable and very less reports can be found regarding its fundamental behavior like mobility, transport property etc. Moreover, employing this method has not enabled stable traditional MOFs to establish charge transfer pathways. The second approach involves the post synthetic modification of as synthesised MOF by loading guest materials into the framework which can be termed as extrinsically conducting MOF. Owing to its highly porous nature, the MOF offers a suitable platform for guest accommodation in their specific nanochannels where guest molecule shows unique

properties regarding their motion, charge transfer, electronic properties magnetic properties, phase transition etc. [99]. The extrinsically conducting MOF can be generated by adding other conducting materials like conducting polymers, metal nanoparticles, graphene, porous carbon, quantum dot etc. [100]. These guests then form charge transport pathways throughout the material through guest–guest or guest–framework interactions [101]. With controlled loading of guest into the pores can partially fill the pores by keeping the porosity of parent MOF intact and also can provide the charge carriers or charge transfer pathways to generate electrical conductivity. Inspired from earlier reported works on guest assisted conductivity in MOFs, the present work of the thesis aimed to develop an extrinsically conducting MOF by loading different guest molecules. Since Zr- based MOFs are established as highly stable MOF in aqueous media, UiO-66 has been selected as the host for loading guest through post-synthetic treatments for this thesis work. Research on the incorporation of metal nanoclusters and nanoparticles into MOFs has primarily focused on MOFs containing metals such as zinc, copper, and cobalt [102]. However, there has been limited exploration of using metal oxide nanoparticles (MONPs) as guests within MOF pores, despite their potential advantages. The MONPs offer greater stability compared to metal nanoparticles and demonstrate superior redox activity. These properties are particularly valuable for applications in the electrochemical field, which is the specific focus of this study. Despite the infancy in this area of research, the unique characteristics of MONPs make them promising candidates for enhancing the electrochemical performance of MOFs, warranting further exploration in applied research. Due to the cost effectiveness and easy processibility the metal oxide chosen for the host UiO-66 is silver oxide nanoparticle ( $\text{Ag}_2\text{O}$ ). Another suitable candidate for guest is conducting polymers because of their semiconducting nature, delocalized  $\pi$ -electrons, redox active behavior, high stability. PEDOT has emerged as one of the most widely studied conducting polymers, garnering significant attention from both academic and industrial sectors [103]. This is primarily attributed to its combination of relatively high conductivity and exceptional stability under ambient conditions. Furthermore, PEDOT exhibits potential to achieve transparency in the visible range, making it even more appealing for desired applications. Therefore, PEDOT was opted as another guest material to incorporate into the UiO-66 host.



A unique strategy apart from intrinsically conducting MOF or extrinsically conducting MOF for tuning the band structure or electronic behaviour of MOF is defect engineering. It involves deliberate introduction of structural imperfections or modifications to enhance specific properties or functionalities of the material. This approach can significantly impact various aspects on MOF performance, including porosity, stability, conductivity, catalytic activity, and gas sorption properties. SHI irradiation is a powerful technique used to create defects in materials by bombarding them with high-energy charge particles. When energetic ions penetrate into a material, they interact with the atomic nuclei and electrons, leading to the creation of various types of defects, such as vacancies, interstitials, dislocations, and Frenkel pairs. This energetic ion interaction can also cause electronic excitations and ionizations which leads to the creation of electron-hole (e-h) pairs. The migration and recombination of these carriers can contribute to the electrical behaviour of the MOF. Looking into these advantages of SHI the present work aimed to include the irradiation induced effects on the pristine MOF UiO-66. For that purpose, 60 MeV  $N^{5+}$  SHI of different fluences has been irradiated on UiO-66 to tune the conductivity.

Over the years electrically conducting MOFs have drawn interest as promising candidates for electrochemical sensing applications due to their unique properties [104]. These materials boast high surface areas, providing ample active sites for analyte adsorption and enhancing sensitivity. Additionally, their adjustable pore structures enable precise tuning of active site accessibility, leading to improved selectivity towards target analytes. Unlike traditional insulating MOFs, electrically conducting MOFs exhibit conductivity, facilitating efficient electron transfer during electrochemical reactions and resulting in rapid response times and enhanced signal-to-noise ratios. Moreover, these materials demonstrate excellent stability under various environmental conditions, ensuring long-term sensor performance. With the ability to be functionalized for specific applications, electrically conducting MOFs offer versatility in detecting a wide range of analytes with high sensitivity and selectivity. As research progresses, these materials are poised to drive advancements in electrochemical sensing for diverse fields such as environmental monitoring, healthcare diagnostics, and food safety [105]. Environmental contaminants pose significant threats due to their toxicity, bioaccumulation potential, disruption of ecosystems, persistence, and ability to spread over long distances. These

pollutants, which include industrial chemicals, heavy metals, pesticides, and other human-caused pollutants, can have a variety of harmful health consequences on people and wildlife. High atomic density metals, such as lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), and others, are heavy metal ions that have a propensity to accumulate in bodily tissues, organs, or living things when they are ingested, inhaled, or come into direct contact with the skin [106]. They can form bonds with proteins, enzymes and nucleic acids and interfere cellular activities, leading to dysfunction of organs. They can also induce oxidative stress by generating reactive oxygen species (ROS) within cells, which can damage cellular components like lipids, proteins, and DNA. Along with these organic environmental contaminants are also harmful for living organisms. Aromatic molecules called dihydroxybenzene isomers, such as hydroquinone, resorcinol, and catechol, are frequently found in a variety of consumer and commercial products [107]. Even though these substances have numerous uses, living things may be at risk from them. Catechol is a common ingredient in medications and insecticides that, at high amounts, can cause organ damage like respiratory problems, and skin irritation. Hydroquinone, utilized in skin-lightening products, can lead to skin irritation, allergic reactions, and ochronosis with prolonged use, and has been associated with potential carcinogenicity. Therefore, the detection of environmental contaminants is essential for protecting human health, safeguarding ecosystems and wildlife, ensuring regulatory compliance, and guiding pollution prevention and mitigation efforts. Furthermore, MOFs possess high surface areas and tunable pore structures, which provide ample space for the immobilisation of biomolecules such as enzymes, antibodies, or DNA strands.

Regarding the ongoing topic discussed above, the goal of this work is to develop extrinsically conducting MOFs to fabricate electrode materials for a sensing environmental contaminant and to irradiate UiO-66 with SHI for using the defected material as biosensing electrode. Thus, the work aspires to incorporate guest molecules Ag<sub>2</sub>O and PEDOT in UiO-66 through different post synthetic approaches. Since the conducting MOF produced will have different guests, they will be having affinities for different analytes. In this manner, the same MOF can be used as a selective detector for different analytes by varying the guest incorporated in it. Due to the SHI irradiation on UiO-66, structural as well as other properties of the pristine MOF could be altered. To verify the modifications developed as an influence of SHI irradiation, UiO-66 can be immobilised with an antibody

known as immunoglobulin G extracted from mouse (mouse IgG), which is a protein developed in a mouse by its defence mechanism upon the introduction of foreign species. The resulting bioreceptor/transducer component can be used for the detection of antigen goat anti-mouse IgG. The motivation behind the modification being produced in the MOF through different approaches is to enhance the functionality of the potential host so that it can offer a stable, sensitive and selective electrode for electrochemical and biosensing applications.

Being motivated from the above aspects, the following objectives have been set to address the thesis

- 1) To synthesize Zr based UiO-66 MOF and incorporating conducting polymers (PEDOT) and metal oxide nanoparticles (Ag) in their nanopores (Extrinsically conducting MOF).
- 2) To explore the electrical charge transport property and temperature dependent conductivity of Ag<sub>2</sub>O incorporated UiO-66 and PEDOT inserted UiO-66.
- 3) To fabricate Ag<sub>2</sub>O incorporated UiO-66 MOF in ITO coated glass electrodes for sensing inorganic environmental contaminants like Hg<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> etc. individually as well as simultaneously.
- 4) To fabricate PEDOT inserted UiO-66 MOF on ITO coated glass electrodes for sensing organic environmental contaminants like hydroquinone (HQ) and catechol (CT) individually as well as simultaneously.
- 5) To examine the SHI irradiation effect on UiO-66 MOF bombarded with high energy ions of different fluences and observe the change in the sensing parameters of the electrodes.

The complete work of this thesis has been compiled into the seven following chapters in accordance with the aforementioned goals. Further the materials and chemical reagents utilized to get the desired products and various synthesis procedures employed to obtain the products has been discussed in Chapter 2. The investigation regarding the structural, morphological, vibrational aspects of parent UiO-66 and modified UiO-66 with guests are discussed in Chapter 3. Then in Chapter 4, the electrical and carrier transport studies of guest loaded UiO-66 are discussed. In chapter 5 Ag<sub>2</sub>O loaded UiO-66 has been investigated for individual and simultaneous sensing of analytes Hg<sup>2+</sup> and Cd<sup>2+</sup>. In a

similar manner chapter 6 discusses the individual and simultaneous sensing of HQ and CT by PEDOT inserted UiO-66. The SHI irradiation induced effects on structural, morphological, electrical properties of UiO-66 and its application as biosensing electrode for anti-goat mouse IgG are highlighted in Chapter 7. Conclusive remarks on the of overall work performed for the thesis along with future perspective have been summarized in Chapter 8.

---

**Reference**

- [1] Kitagawa, S. Future Porous Materials. *Acc Chem Res.* **50**: 514–516 ,2017.
- [2] Bennett, T. D., Coudert, F.-X., James, S. L. & Cooper, A. I. The changing state of porous materials. *Nat Mater.* **20**: 1179–1187 ,2021.
- [3] Kirchon, A., Feng, L., Drake, H. F., Joseph, E. A. & Zhou, H.-C. From fundamentals to applications: a toolbox for robust and multifunctional MOF materials. *Chem Soc Rev.* **47**: 8611–8638 ,2018.
- [4] Zou, D., Liu, D. & Zhang, J. From Zeolitic Imidazolate Framework-8 to Metal-Organic Frameworks (MOFs): Representative Substance for the General Study of Pioneering MOF Applications. *Energy and Environmental Materials.* **1**: 209–220, 2018
- [5] Freund, R. *et al.* The Current Status of MOF and COF Applications. *Angewandte Chemie International Edition.* **60**: 23975–24001 ,2021.
- [6] Natarajan, S. & Mahata, P. Metal–organic framework structures – how closely are they related to classical inorganic structures? *Chem Soc Rev.* **38**: 2304 ,2009.
- [7] Butova, V. V, Soldatov, M. A., Guda, A. A., Lomachenko, K. A. & Lamberti, C. Metal-organic frameworks: structure, properties, methods of synthesis and characterization. *Russian Chemical Reviews.* **85**: 280–307 ,2016.
- [8] Schoedel, A. & Rajeh, S. Why design matters: From decorated metal-oxide clusters to functional metal-organic frameworks. in pp 1–55 of book Metal Oxide Frameworks, (2020).
- [9] Rungtaweeworanit, B., Diercks, C. S., Kalmutzki, M. J. & Yaghi, O. M. Spiers Memorial Lecture: : Progress and prospects of reticular chemistry. *Faraday Discuss.* **201**: 9–45 ,2017.
- [10] Furukawa, H., Cordova, K. E., O’Keeffe, M. & Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science. (1979)* **341**: ,2013.

- 
- [11] Soni 1, S., Bajpai 2, P. K. & Arora 2, C. A review on metal-organic framework: synthesis, properties and application. *Characterization and Application of Nanomaterials*. **2**: ISSN- 2578-1995,2018.
- [12] Mai, Z. & Liu, D. Synthesis and Applications of Isorecticular Metal–Organic Frameworks IRMOFs-  $n$  ( $n = 1, 3, 6, 8$ ). *Cryst Growth Des.* **19**: 7439–7462 ,2019.
- [13] Xuan Huynh, N. T., Chihaiia, V. & Son, D. N. Hydrogen storage in MIL-88 series. *J Mater Sci.* **54**: 3994–4010 ,2019.
- [14] Ryder, M. R. *et al.* Identifying the Role of Terahertz Vibrations in Metal–Organic Frameworks: From Gate-Opening Phenomenon to Shear-Driven Structural Destabilization. *Phys Rev Lett.* **113**: 215502 ,2014.
- [15] Yuan, S. *et al.* Stable Metal–Organic Frameworks: Design, Synthesis, and Applications. *Advanced Materials*. **30**: 1704303,2018.
- [16] Hao, J., Xu, X., Fei, H., Li, L. & Yan, B. Functionalization of Metal–Organic Frameworks for Photoactive Materials. *Advanced Materials*. **30**: 1705634,2018.
- [17] Cai, M. *et al.* Functionalization of MOF-5 with mono-substituents: effects on drug delivery behavior. *RSC Adv.* **10**: 36862–36872 ,2020.
- [18] Qin, Y., Hao, M., Wang, D. & Li, Z. Post-synthetic modifications (PSM) on metal–organic frameworks (MOFs) for visible-light-initiated photocatalysis. *Dalton Transactions.* **50**: 13201–13215 ,2021.
- [19] Tanabe, K. K. & Cohen, S. M. Postsynthetic modification of metal–organic frameworks—a progress report. *Chem. Soc. Rev.* **40**: 498–519 ,2011.
- [20] Rasheed, T., Rizwan, K., Bilal, M. & Iqbal, H. M. N. Metal–Organic Framework-Based Engineered Materials—Fundamentals and Applications. *Molecules*. **25**: 1598 ,2020.

- [21] Ko, S. *et al.* Synthesis of metal–organic frameworks (MOFs) and their application in the selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>. *New Journal of Chemistry*. **46**: 15758–15775 ,2022.
- [22] Stock, N. & Biswas, S. Synthesis of metal-organic frameworks (MOFs): Routes to various MOF topologies, morphologies, and composites. *Chemical Reviews*. **112**: 933–969, 2012
- [23] Beamish-Cook, J., Shankland, K., Murray, C. A. & Vaquero, P. Insights into the Mechanochemical Synthesis of MOF-74. *Cryst Growth Des*. **21**: 3047–3055 ,2021.
- [24] Liu, W. & Yin, X.-B. Metal–organic frameworks for electrochemical applications. *TrAC Trends in Analytical Chemistry*. **75**: 86–96 ,2016.
- [25] Xie, L. S., Skorupskii, G. & Dincă, M. Electrically Conductive Metal–Organic Frameworks. *Chemical Reviews*. **120** 8536–8580, 2020
- [26] Meng, H. *et al.* Conductive Metal–Organic Frameworks: Design, Synthesis, and Applications. *Small Methods*. **4**: 2000396, 2020.
- [27] De Lourdes Gonzalez-Juarez, M., Flores, E., Martin-Gonzalez, M., Nandhakumar, I. & Bradshaw, D. Electrochemical deposition and thermoelectric characterisation of a semiconducting 2-D metal-organic framework thin film. *J Mater Chem A Mater*. **8**: 13197–13206 ,2020.
- [28] Calvo, J. J., Angel, S. M. & So, M. C. Charge transport in metal-organic frameworks for electronics applications. *APL Materials*. **8**: 050901 ,2020.
- [29] Ge, K. *et al.* Facile Synthesis of Two-Dimensional Iron/Cobalt Metal–Organic Framework for Efficient Oxygen Evolution Electrocatalysis. *Angewandte Chemie - International Edition*. **60**: 12097–12102 ,2021.
- [30] Dou, J. H. *et al.* Atomically precise single-crystal structures of electrically conducting 2D metal–organic frameworks. *Nat Mater*. **20**: 222–228 ,2021.

- [31] Nath, N., Chakroborty, S., Pal, K., Barik, A. & Soren, S. Novel synthetic approach of 2D-metal-organic frameworks (MOF) for wastewater treatment. *Nanotechnology*. **34**: 442001 ,2023.
- [32] Yin, Z., Wan, S., Yang, J., Kurmoo, M. & Zeng, M.-H. Recent advances in post-synthetic modification of metal–organic frameworks: New types and tandem reactions. *Coord Chem Rev*. **378**: 500–512 ,2019.
- [33] Yang, S. *et al.* Enhancing MOF performance through the introduction of polymer guests. *Coord Chem Rev*. **427**: 213525 ,2021.
- [34] Wang, F., Wang, B., Hao, B., Zhang, C. & Wang, Q. Designable Guest-Molecule Encapsulation in Metal–Organic Frameworks for Proton Conductivity. *Chemistry – A European Journal*. **28**: 202103732,2022.
- [35] Li, G., Zhang, K., Zhao, H., Hou, L. & Wang, Y. Increased Electric Conductivity upon I<sub>2</sub> Uptake and Gas Sorption in a Pillar-Layered Metal–Organic Framework. *Chempluschem*. **82**: 716–720 ,2017.
- [36] Das, T. K. & Prusty, S. Review on Conducting Polymers and Their Applications. *Polym Plast Technol Eng*. **51**: 1487–1500 ,2012.
- [37] Jadhav, A. *et al.* Conducting Polymers and Their Composites. in pp 147–178 of book Contemporary nanomaterials in material Engineering applications, (2021).
- [38] Dhara, B. *et al.* Increase in Electrical Conductivity of MOF to Billion-Fold upon Filling the Nanochannels with Conducting Polymer. *J Phys Chem Lett*. **7**: 2945–2950 ,2016.
- [39] Salcedo-Abraira, P. *et al.* A highly conductive nanostructured PEDOT polymer confined into the mesoporous MIL-100(Fe). *Dalton Transactions*. **48**: 9807–9817 ,2019.
- [40] Le Ouay, B. *et al.* Nanostructuring of PEDOT in Porous Coordination Polymers for Tunable Porosity and Conductivity. *J Am Chem Soc*. **138**: 10088–10091 ,2016.



- [41] Mody, V., Siwale, R., Singh, A. & Mody, H. Introduction to metallic nanoparticles. *J Pharm Bioallied Sci.* **2**: 282 ,2010.
- [42] Jamkhande, P. G., Ghule, N. W., Bamer, A. H. & Kalaskar, M. G. Metal nanoparticles synthesis: An overview on methods of preparation, advantages and disadvantages, and applications. *J Drug Deliv Sci Technol.* **53**: 101174 ,2019.
- [43] Han, S. *et al.* Tunneling Electrical Connection to the Interior of Metal–Organic Frameworks. *J Am Chem Soc.* **137**: 8169–8175 ,2015.
- [44] Zhang, W. *et al.* Microenvironment of MOF Channel Coordination with Pt NPs for Selective Hydrogenation of Unsaturated Aldehydes. *ACS Catal.* **10**: 5805–5813 ,2020.
- [45] Goswami, S. *et al.* A porous, electrically conductive hexa-zirconium( IV)/(V) metal–organic framework. *Chem Sci.* **9**: 4477–4482 ,2018.
- [46] Talin, A. A. *et al.* Tunable Electrical Conductivity in Metal-Organic Framework Thin-Film Devices. *Science (1979).* **343**: 66–69 ,2014.
- [47] Schneider, C. *et al.* High electrical conductivity and high porosity in a Guest@MOF material: evidence of TCNQ ordering within Cu<sub>3</sub> BTC<sub>2</sub> micropores. *Chem Sci.* **9**: 7405–7412 ,2018.
- [48] Chen, X. *et al.* Seebeck Coefficient Measurements of Polycrystalline and Highly Ordered Metal-Organic Framework Thin Films. *ECS Journal of Solid State Science and Technology.* **6**: 150–153 ,2017.
- [49] Zeng, M.-H. *et al.* Rigid Pillars and Double Walls in a Porous Metal-Organic Framework: Single-Crystal to Single-Crystal, Controlled Uptake and Release of Iodine and Electrical Conductivity. *J Am Chem Soc.* **132**: 2561–2563 ,2010.
- [50] Fang, Z., Bueken, B., De Vos, D. E. & Fischer, R. A. Defect-Engineered Metal–Organic Frameworks. *Angewandte Chemie International Edition.* **54**: 7234–7254 ,2015.

- 
- [51] Dissegna, S., Epp, K., Heinz, W. R., Kieslich, G. & Fischer, R. A. Defective Metal–Organic Frameworks. *Advanced Materials*. **30**: 1704501 ,2018.
- [52] Xiang, W., Zhang, Y., Chen, Y., Liu, C. & Tu, X. Synthesis, characterization and application of defective metal–organic frameworks: current status and perspectives. *J Mater Chem A Mater*. **8**: 21526–21546 ,2020.
- [53] Levalois, M. & Marie, P. Damage induced in semiconductors by swift heavy ion irradiation. *Nucl Instrum Methods Phys Res B*. **156**: 64–71 ,1999.
- [54] Lang, M., Djurabekova, F., Medvedev, N., Toulemonde, M. & Trautmann, C. Fundamental Phenomena and Applications of Swift Heavy Ion Irradiations. in *Comprehensive Nuclear Materials*. 485–516 (Elsevier, 2020).
- [55] Fleischer, R. L., Price, P. B. & Walker, R. M. Ion Explosion Spike Mechanism for Formation of Charged-Particle Tracks in Solids. *J Appl Phys*. **36**: 3645–3652 ,1965.
- [56] Medvedev, N. *et al.* Frontiers, challenges, and solutions in modeling of swift heavy ion effects in materials. *J Appl Phys*. **133**: 100701,2023.
- [57] Kamarou, A., Wesch, W., Wendler, E., Undisz, A. & Rettenmayr, M. Swift heavy ion irradiation of InP: Thermal spike modeling of track formation. *Phys Rev B*. **73**: 184107 ,2006.
- [58] Lang, M., Devanathan, R., Toulemonde, M. & Trautmann, C. Advances in understanding of swift heavy-ion tracks in complex ceramics. *Curr Opin Solid State Mater Sci*. **19**: 39–48 ,2015.
- [59] Calvo, J. J., Angel, S. M. & So, M. C. Charge transport in metal–organic frameworks for electronics applications. *APL Mater*. **8**: 050901,2020.
- [60] Huang, X. *et al.* Superconductivity in a Copper (II)-Based Coordination Polymer with Perfect Kagome Structure. *Angewandte Chemie*. **130**: 152–156 ,2018.
- [61] Xie, L. S., Skorupskii, G. & Dincă, M. Electrically Conductive Metal–Organic Frameworks. *Chem Rev*. **120**: 8536–8580 ,2020.

- [62] John Singleton. *Band Theory and Electronic Properties of Solids (Oxford Master Series in Condensed Matter Physics)*. (OUP Oxford, United Kingdom: OUP Oxford., 2001).
- [63] Guo, L. *et al.* Conductive metal-organic frameworks: Recent advances in electrochemical energy-related applications and perspectives. *Carbon Energy*. **2**: 203–222 ,2020.
- [64] Liu, J. *et al.* 2D Conductive Metal–Organic Frameworks: An Emerging Platform for Electrochemical Energy Storage. *Angewandte Chemie International Edition*. **60**: 5612–5624 ,2021.
- [65] Schneider, C. *et al.* High electrical conductivity and high porosity in a Guest@MOF material: evidence of TCNQ ordering within Cu<sub>3</sub> BTC<sub>2</sub> micropores. *Chem Sci*. **9**: 7405–7412 ,2018.
- [66] Park, J. *et al.* Stabilization of Hexaaminobenzene in a 2D Conductive Metal–Organic Framework for High Power Sodium Storage. *J Am Chem Soc*. **140**: 10315–10323 ,2018.
- [67] Liang, Z., Qu, C., Guo, W., Zou, R. & Xu, Q. Pristine Metal–Organic Frameworks and their Composites for Energy Storage and Conversion. *Advanced Materials*. **30**: 1702891 ,2018.
- [68] Hou, R. *et al.* Integrated Conductive Hybrid Architecture of Metal–Organic Framework Nanowire Array on Polypyrrole Membrane for All-Solid-State Flexible Supercapacitors. *Adv Energy Mater*. **10**: 1901892 ,2020.
- [69] Li, J. *et al.* Hierarchically nanostructured Ni(OH)<sub>2</sub>–MnO<sub>2</sub>@C ternary composites derived from Ni-MOFs grown on nickel foam as high-performance integrated electrodes for hybrid supercapacitors. *Electrochim Acta*. **343**: 136139 ,2020.
- [70] Rajasekaran, S. *et al.* Sm-MOF/rGO/PANI composite as an electrode material for supercapacitor applications. *Electrochim Acta*. **467**: 143031 ,2023.

- 
- [71] Liang, Y., Dong, H., Aurbach, D. & Yao, Y. Current status and future directions of multivalent metal-ion batteries. *Nat Energy*. **5**: 646–656 ,2020.
- [72] Rambau, K., Musyoka, N. M., Palaniyandy, N. & Manyala, N. Manganese-Based Metal Organic Framework from Spent Li-Ion Batteries and its Electrochemical Performance as Anode Material in Li-ion Battery. *J Electrochem Soc*. **168**: 010527 ,2021.
- [73] Zhang, Y. *et al.* A nickel-based metal-organic framework: A novel optimized anode material for Li-ion batteries. *Mater Lett*. **161**: 712–715 ,2015.
- [74] Hu, X. *et al.* Cobalt-based metal organic framework with superior lithium anodic performance. *J Solid State Chem*. **242**: 71–76 ,2016.
- [75] Li, Y. *et al.* MOF-Derived Metal Oxide Composites for Advanced Electrochemical Energy Storage. *Small*. **14**: ,2018.
- [76] Zheng, G. *et al.* Fabrication of 2D Cu-BDC MOF and its derived porous carbon as anode material for high-performance Li/K-ion batteries. *Appl Surf Sci*. **559**: 149701 ,2021.
- [77] Jin, Y. *et al.* Fe-Based Metal-Organic Framework and Its Derivatives for Reversible Lithium Storage. *J Mater Sci Technol*. **33**: 768–774 ,2017.
- [78] Sun, J. *et al.* Conductive Co-based metal–organic framework nanowires: a competitive high-rate anode towards advanced Li-ion capacitors. *J Mater Chem A Mater*. **7**: 24788–24791 ,2019.
- [79] Park, J. *et al.* Stabilization of Hexaaminobenzene in a 2D Conductive Metal–Organic Framework for High Power Sodium Storage. *J Am Chem Soc* **140**: 10315–10323 ,2018.
- [80] Zhu, K., Wu, T., Sun, S., Wen, Y. & Huang, K. Electrode Materials for Practical Rechargeable Aqueous Zn-Ion Batteries: Challenges and Opportunities. *ChemElectroChem*. **7**: 2714–2734 ,2020.

- [81] Liu, X. *et al.* Electrochemical Hydrogen Generation by Oxygen Evolution Reaction-Alternative Anodic Oxidation Reactions. *Advanced Energy and Sustainability Research*. **3**: 2200005,2022.
- [82] Masa, J., Andronesco, C. & Schuhmann, W. Electrocatalysis as the Nexus for Sustainable Renewable Energy: The Gordian Knot of Activity, Stability, and Selectivity. *Angewandte Chemie International Edition*. **59**: 15298–15312 ,2020.
- [83] Li, F., Li, J., Zhou, L. & Dai, S. Enhanced OER performance of composite Co–Fe-based MOF catalysts *via* a one-pot ultrasonic-assisted synthetic approach. *Sustain Energy Fuels*. **5**: 1095–1102 ,2021.
- [84] Li, Y.-W. *et al.* Fe-MOF-Derived Efficient ORR/OER Bifunctional Electrocatalyst for Rechargeable Zinc–Air Batteries. *ACS Appl Mater Interfaces*. **12**: 44710–44719 ,2020.
- [85] Privett, B. J., Shin, J. H. & Schoenfish, M. H. Electrochemical Sensors. *Anal Chem*. **82**: 4723–4741 ,2010.
- [86] Kimmel, D. W., LeBlanc, G., Meschievitz, M. E. & Cliffel, D. E. Electrochemical Sensors and Biosensors. *Anal Chem*. **84**: 685–707 ,2012.
- [87] Hanrahan, G., Patil, D. G. & Wang, J. Electrochemical sensors for environmental monitoring: design, development and applications. *Journal of Environmental Monitoring*. **6**: 657 ,2004.
- [88] Harper, A. & Anderson, M. R. Electrochemical Glucose Sensors—Developments Using Electrostatic Assembly and Carbon Nanotubes for Biosensor Construction. *Sensors*. **10**: 8248–8274 ,2010.
- [89] Chiu, M. L., Goulet, D. R., Teplyakov, A. & Gilliland, G. L. Antibody Structure and Function: The Basis for Engineering Therapeutics. *Antibodies*. **8**: 55 ,2019.
- [90] Wu, A. M. & Senter, P. D. Arming antibodies: prospects and challenges for immunoconjugates. *Nat Biotechnol*. **23**: 1137–1146 ,2005.

- 
- [91] Wilson, G. S. & Hu, Y. Enzyme-Based Biosensors for in Vivo Measurements. *Chem Rev.* **100**: 2693–2704 ,2000.
- [92] Tombelli, S., Minunni, M. & Mascini, M. Analytical applications of aptamers. *Biosens Bioelectron.* **20**: 2424–2434 ,2005.
- [93] Gold, L. SELEX: How It Happened and Where It will Go. *J Mol Evol.* **81**: 140–3 ,2015.
- [94] Song, K.-M., Lee, S. & Ban, C. Aptamers and Their Biological Applications. *Sensors.* **12**: 612–631 ,2012.
- [95] Ji, Z., Wang, H., Canossa, S., Wuttke, S. & Yaghi, O. M. Pore Chemistry of Metal–Organic Frameworks. *Adv Funct Mater.* **30**: ,2020.
- [96] Schoedel, A., Li, M., Li, D., O’Keeffe, M. & Yaghi, O. M. Structures of Metal–Organic Frameworks with Rod Secondary Building Units. *Chem Rev.* **116**: 12466–12535 ,2016.
- [97] Kirchon, A., Feng, L., Drake, H. F., Joseph, E. A. & Zhou, H.-C. From fundamentals to applications: a toolbox for robust and multifunctional MOF materials. *Chem Soc Rev.* **47**: 8611–8638 ,2018.
- [98] Meng, H. *et al.* Conductive Metal–Organic Frameworks: Design, Synthesis, and Applications. *Small Methods.* **4**: 2000396, 2020.
- [99] Jiang, H.-L. & Xu, Q. Porous metal–organic frameworks as platforms for functional applications. *Chemical Communications.* **47**: 3351 ,2011.
- [100] Saha, R., Gupta, K. & Gómez García, C. J. Strategies to Improve Electrical Conductivity in Metal–Organic Frameworks: A Comparative Study. *Cryst Growth Des.* **24**: 2235–2265 ,2024.
- [101] Calvo, J. J., Angel, S. M. & So, M. C. Charge transport in metal-organic frameworks for electronics applications. *APL Materials.* **8**: 050901, 2020.

- 
- [102] Wang, X., Wang, Y. & Ying, Y. Recent advances in sensing applications of metal nanoparticle/metal–organic framework composites. *TrAC - Trends in Analytical Chemistry*. **143**: 116395, 2021.
- [103] Gueye, M. N., Carella, A., Faure-Vincent, J., Demadrille, R. & Simonato, J.-P. Progress in understanding structure and transport properties of PEDOT-based materials: A critical review. *Prog Mater Sci*. **108**: 100616 ,2020.
- [104] Liu, C. *et al.* Missing-Linker 2D Conductive Metal Organic Frameworks for Rapid Gas Detection. *ACS Sen.s* **6**: 429–438 ,2021.
- [105] Zou, X. *et al.* Recent advances of environmental pollutants detection via paper-based sensing strategy. *Luminescence*. **36**: 1818–1836 ,2021.
- [106] Peralta-Videa, J. R. *et al.* Nanomaterials and the environment: A review for the biennium 2008–2010. *J Hazard Mater*. **186**: 1–15 ,2011.
- [107] Meskher, H. & Achi, F. Electrochemical Sensing Systems for the Analysis of Catechol and Hydroquinone in the Aquatic Environments: A Critical Review. *Crit Rev Anal Chem*. **25**:1–14, 2022.