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Chapter

Coordination Polymer Frameworks for Next Generation Optoelectronic Devices

Hemali Rathnayake and Sheeba Dawood

Abstract

Metal–organic frameworks (MOFs), which belong to a sub-class of coordination polymers, have been significantly studied in the fields of gas storage and separation over the last two decades. There are 80,000 synthetically known MOFs in the current database with known crystal structures and some physical properties. However, recently, numerous functional MOFs have been exploited to use in the optoelectronic field owing to some unique properties of MOFs with enhanced luminescence, electrical, and chemical stability. This book chapter provides a comprehensive summary of MOFs chemistry, isoreticular synthesis, and properties of isoreticular MOFs, synthesis advancements to tailor optical and electrical properties. The chapter mainly discusses the research advancement made towards investigating optoelectronic properties of IRMOFs. We also discuss the future prospective of MOFs for electronic devices with a proposed roadmap suggested by us. We believe that the MOFs-device roadmap should be one meaningful way to reach MOFs milestones for optoelectronic devices, particularly providing the potential roadmap to MOF-based field-effect transistors, photovoltaics, thermoelectric devices, and solid-state electrolytes and lithium ion battery components. It may enable MOFs to be performed in their best, as well as allowing the necessary integration with other materials to fabricate fully functional devices in the next few decades.

Keywords: MOF, coordination polymers, optoelectronics, isoreticular MOF, semiconducting MOFs

1. Introduction

Over last few decades, crystalline microporous materials, from zeolites, to coordination polymers and its subclass, metal organic frameworks (MOFs) have gained enormous attention in the scientific community due to their structural versatility and tailorable properties like nanoscale porosity, high surface area, and functional density [1, 2]. Metal organic frameworks have evolved in last few years as a revolutionary material that are self-assembled nanostructure [3, 4] built from metal ions and organic ligands. The first MOF, MOF-5 or IRMOF-1 ($Zn_4O(BDC)_3$) reported by Omar M. Yaghi was used in gas adsorption applications accounting to its high surface area of 2900 m^2/g [5, 6]. To date, 80,000 MOFs [7] have been reported owing to its diverse structure, compositions, tunable porosity, specific surface area, [8] ease of

functionalization, unsaturated metal sites [9] and biocompatibility [10] . As a result, MOFs were used in a wide range of applications such as gas storage and separation, drug delivery and storage, chemical separation, sensing, catalysis, and bio-imaging [3, 7, 11–13]. In terms of structural orientation, the coordination bonding between a metal ion and organic ligand results in the formation of extended networks of one, two, and three-dimensional framework with potential voids [6, 14]. The coordination bonding facilitated through a suitable molecular approach, involving reticular synthesis, provides the flexibility to alter the pore size and transform its structure, targeting specific applications. Thus, utilizing the advantage of various combinations of metal-ligands and interaction of metal-ligands, MOFs are ideal candidates in the field of material science, offering an attractive property of structural tunability, providing a pathway to introduce and tailor intrinsic characteristics, such as optical, electrical, and magnetic properties.

There has been a growing interest exploring MOF as emerging semiconducting materials to meet the current demand in the electronic devices [15]. In particular, the electronic characteristics such as electrical, optical, and magnetic properties of MOFs have become an interesting topic of research attributing to their applications in microelectronic and optical devices. The implementation of MOFs in the electronic industry was first reported by Allendorf and co-workers [16]. MOF-5 with Zn_4O metal nodes and orthogonally interconnected six units of terephthalate is the most-studied MOF as a semiconductor. In 2007, Garcia and co-workers reported on the semiconducting behavior of MOF-5 synthesized at room temperature, with a bandgap of 3.4 eV [17]. Since then, intense research has been carried out to develop MOFs with semiconducting properties, opening new research domains for the scientific community in nanoscience.

The presence of narrow band gap structure either direct or indirect and charge mobility contribute to the semiconducting behavior of MOFs. To design MOFs with semiconducting behavior, significant amount of research is ongoing to identify the general structural requirements for enhancing the orbital overlapping between the building components. The main advantage of MOFs is the ability to tune the crystalline structure and functionality through phenomenal conceptual approaches such as rational designing and synthetic flexibility. In reticular chemistry, which is also known as rational designing, the coordination bonding between metal node and organic ligand provides an understanding of atomic positions precisely contributing to determine the fundamental structure–property relationships. Thus, the crystalline structure of MOFs consists of self-assembled ordered nanostructure with defined organized spatial space that is constructed via coordination chemistry between the building components.

Moreover, the sub-angstrom knowledge of atomic positions helps to eliminate any disorder in the structure that contributes to poor mobility in the structure. Considering synthetic flexibility, the electronic properties of MOFs could be tailored, resulting in potential applications such as a photovoltaic device tuned for solar cells, electroluminescent devices, field effect transistors, spintronic devices, and sensors. These developments have led many researchers to explore electrical, magnetic, and optical properties of MOFs [15, 18, 19]. However, the electrical properties of MOFs and integration of them in micro-electronic devices is still at an early stage and remain under research when compared to other types of existing conducting materials [4, 15] due to their insulating character. Although MOFs possess the properties of both organic and inorganic counterparts, they behave as electrical insulators or poor electrical conductors due to the poor overlapping between the π-orbitals of organic ligands and d-orbitals of the metal ion [20]. Yet, MOFs serving as an interface between (inorganic) hard and (organic) soft materials provide an opportunity for adapting various structure–property relationships that

is related to wide range of parameters such as choice of metal ion, organic linker, and molecular designing approach. In general, the structure–property relationship in MOFs is a consequence of cooperative mechanism, i.e. the interaction between the metal and ligand, which could be readily identified by taking advantage of the knowledge of their detailed atomic structure, enabling fine tuning of their functionalities [7, 11]. According to the literature, Bastian Hoppe and his co-workers reported Cu-2, 3, 6, 7, 10, 11-hexahydroxytriphenylene (Cu_3hhtp_2-MOF), a copper-based graphene-like framework with inherent electrical conductivity about 0.045 S cm^{-1} [21]. MOFs with electrical conductivity higher than 0.1 S cm^{-1} was achieved by Talin and co-workers [22]. Thus, the designing of MOFs with conducting or semiconducting properties is necessary to enhance the sensitivity of electrical or demonstrate a sensing concept; but rarely have MOFs been an integral part of an actual device [23].

The purpose of this chapter is to provide comprehensive discussion on optoelectronic MOFs developed up to date and identify focus points to bring MOFs with optoelectronic properties for the realization of integrating MOFs into actual devices for electronic device applications. We first provide a MOFs chemistry and isoreticular synthesis advancements to make isoreticular MOFs (IRMOFs) with tailored optical and electronic properties. Then we summarize the current state of MOF research relevant to optoelectronics, particularly discussing the synthesis, electronic structure, and photophysical properties of three selected IRMOFs (IRMOF-1, 8, and 10). Finally, we propose a MOFs-device roadmap, focusing on MOF-based field-effect transistors, photovoltaics, thermoelectric devices, and solid-state electrolytes and lithium ion battery components.

2. Chemistry of MOFs

2.1 Dimensional classification and evolution of MOFs

Coordination polymers are organic–inorganic hybrid materials where organic moieties are bonded to metal ion or metal clusters via coordination bonds. The energy of such bonding is usually between 50 and 200 KJ mol^{-1}. Apart from strong coordination bonding, weaker interaction such as hydrogen bonds, van der Waal forces and π-π interactions also influence the formation of coordination polymers. Depending on the geometry, coordination polymers are classified into three subclasses: (1) One-dimensional (1-D) coordination polymers, (2) Two-dimensional (2-D) coordination polymers, and (3) Three-dimensional coordination polymers (**Figure 1**).

The coordination polymer assembled from organic ligand and metal ion into three dimensional hierarchical crystalline structures is often regarded as metal organic framework. Since then, the term coordination polymer and metal organic
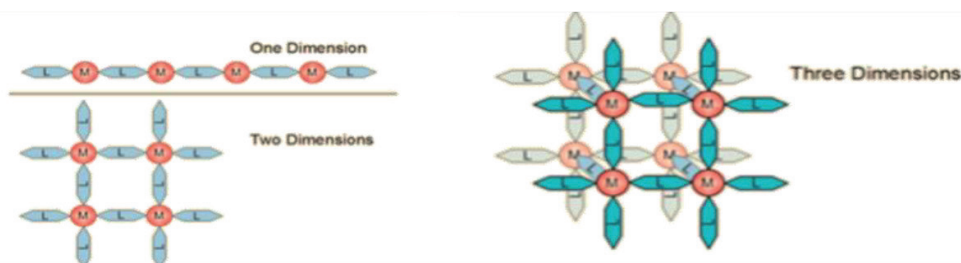
Figure 1.
Dimensional structures of coordination polymers.

framework have been used interchangeably. The term MOFs was first introduced by Omar Yaghi in 1995 [4, 9]. The framework of MOFs is either porous or non-porous. However, the porosity of MOFs was reported to be reversible due to various environmental factors (temperature, pressure, light intensity) contributing to the weak intermolecular interactions between building components. Thus, efforts have been made to modulate the strong structural rigidity that could incorporate permanent porosity. Based on this, in 1998 Kitagawa classified MOFs into three categories; 1st, 2nd, and 3rd generation coordinated network. Among three generations of coordinated networks, 3rd generation coordinated networks were defined to have permanent porosity with structural flexibility [10]. This led to numerous applications and implementation of coordinated networks in the gas storage community. The intermolecular interaction between organic ligand and metal ions, choice of building units, crystallization, environment, and guest molecules determine the crystal structural rigidity and dimensionality of MOF's coordination network. This major advance in the field of coordination polymer depicted that coordinated networks of MOFs could be modified and developed in a highly periodic manner, with a defined understanding of the crystalline structure, porosity, and chemical functionality. Thus, the ability to design and control the arrangement of metal ions with extended organic spaces in three-dimensional fashion led to the origin of the term reticular chemistry which was first introduced by Yaghi and coworkers [4].

With the variability of organic and inorganic components and their interaction, the freedom of modulating the structure of MOFs into highly ordered hierarchical structures with tunable pore volume and adjustable surface area has become feasible that made MOFs stand out compared to the other porous materials. Taking advantage of one of these hallmarks of MOFs i.e. designing of topologically diverse structures with desirable properties has been explored extensively attracting wide range of applications in gas storage, separation, catalysis, sensing and drug delivery [5]. Since 1990s, this area of chemistry has experienced tremendous growth in the field of material science and modern chemistry [4]. The flexibility with geometry, size, and functionality led to the "design" of a large number of MOFs. The organic units are generally ditopic or polytopic organic carboxylates, linked to metal-containing units, such as transition metals (e.g., Cu, Zn, Fe, Co, and Ni), alkaline earth elements (e.g. Sr., Ba), p-block elements (e.g. In, Ga), and actinides (e.g. U, Th) [6]. A major advance in the chemistry of MOFs came in 1999 with the invention of two structures i.e. MOF-5 (IRMOF-1) and HKUST-1 [11] reported by Omar et al. and Chui et al., respectively. Subsequently, in the coming years around 2002, the flexible and non-flexible structures of MIL-88/53 [12] was reported by Ferey et al.

2.2 Reticular chemistry and isoreticular MOFs

The demand for the synthesis of new materials to perform highly specific and cooperative functions has been increasing rapidly in parallel with advanced technology [13, 14]. Recently, the field of metal organic framework has evolved significantly due to its practical and conceptual approach to design and develop the target material. Intrinsically, the reticular chemistry is described as the process of assembly of molecular building blocks held together by strong bonding that pattern into periodic arrays of the ordered net like structures [13–16]. Some of the advantages of this approach are: (1) Molecular approach, which provides the ability to design and control the structure of frameworks [17]; (2) Bonding in which the strong bonding between the building blocks could impart superior functionalities like thermal and chemical stability into the framework; and (3) Engineered crystallinity, which is based on the type of the interactions (intermolecular or intramolecular) design and synthesis with controlled and desired properties.

After the introduction of the parent MOF, MOF-5, taking advantage of reticular chemistry that includes reticulating metal ions and organic carboxylate, the group of Omar M. Yaghi synthesized a new class of materials called IRMOFs. Thus, the theory of isoreticular chemistry was established in the year 2002 with the development of IRMOFs. These class of materials were developed to improve the surface area and pore volume by incorporation of different topological linkers. In IRMOF, IR stands for isoreticular, which means it is a series of MOFs with the same topology, but different pore size [14, 20, 22, 23]. A series of different IRMOFs share similar *pcu* topology of IRMOF-n (n = 1–16). As shown in the **Figure 2**, the pore volume and porosity vary with the variation in the organic linker. Applying the concept of isoreticular chemistry, various kinds of MOFs were developed.

2.3 Synthetic advancements of MOFs

The conceptual approach of designing and assembling a metal–organic framework follows reticular synthesis and is based upon identification of how building blocks come together to form a net, or reticulate. The synthesis of MOFs is often regarded as "design" which implies to construct, built, execute, or create according to the target material. The synthesis approach for a new MOF should follow several factors asides from the geometric principles that are considered during its design. Among such factors, by far the most important is the maintenance of the integrity of the building blocks. A great deal of research effort has been demonstrated on the synthesis of a novel organic link and synthesis conditions that are mild enough to maintain the functionality and conformation of organic ligand, yet reactive enough to establish the metal–organic bonds. In situ generation of a desired secondary subunit (SBU) is required carful design of synthetic conditions and must be compatible with the mobilization and preservation of the linking units [24]. Typically, this is achieved by precipitation of the product from a solution of the precursors where solubility is a necessary attribute of the building blocks but is quite often circumvented by using solvothermal techniques [24].
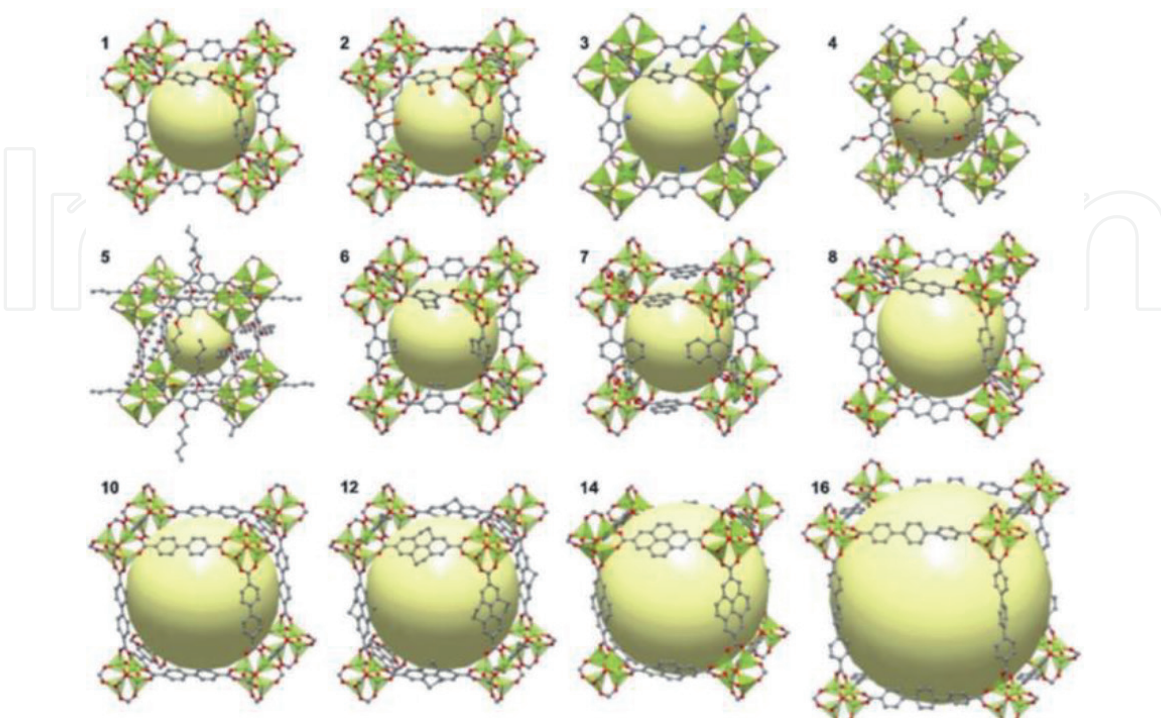
Figure 2.
Crystal structures of IRMOFs-n series [n = 1–16]. The non-interpenetrated structures from
(n = 1,2,3,4,5,6,7,8,10,12,14,16). The yellow sphere represents the pore volume. Zn atoms are in green, O in red,
C in gray, Br atoms in Orange, and amino groups in blue [17].

Traditional goal of MOF synthesis is to obtain high quality single crystal for deducing the structure and understand the crystal packing, geometry, and pore volume with respect to the organic ligand's length. Thus, prior to begin elucidating the concept of reticular synthesis, most early studies were exploratory and early stage synthesis has mainly involved simple, highly soluble precursors, and labile metal ions of the late transition series. The polymerization that leads to make 3D-network of MOFs needs an assembly process where an insoluble entity is quickly formed that precludes recrystallization. Fortunately, it differs in the degree of reversibility of the bond formation event, allowing detachment of incoherently matched monomers followed by reattachment with continued defect free crystal growth. The framework assembly occurs as a single synthetic step, where all of the desired attributes of the target material constructs by the building blocks. This often requires a combinatorial approach, which involves subtle changes in concentration, solvent polarity, pH, or temperature. Any subtle changes in these parameters leads to poorer quality crystals, reduced yields, or the formation of entirely new phases [24].

Augmenting simple crystal growth processes used to grow simple inorganic salts, early efforts of producing highly crystalline MOFs involved the slow introduction of the building blocks to reduce the rate of crystallite nucleation. Methods included slow evaporation of a solution of the precursors, layering of solutions, or slow diffusion of one component solution into another through a membrane or an immobilizing gel [24]. During the nucleation stage, the ligand deprotonation prior to the coordination onto metal ion is catalyzed introducing a volatile amine gradually via vapor diffusion. Just as for many of the polar solvents used, suitable choice of base is necessary to avoid competitive coordination with the organic links for the available metal sites. While in some cases, blocking of metal coordination sites is necessary for the formation of a particular SBU. However, this approach has generally been regarded as leading to low-dimensional structures that are less likely to define an open framework.

With the need for more robust frameworks, having larger pore volumes and higher surface area, introducing bulker, longer length organic linkers are necessary, but greater difficulties in crystal growth were encountered. Thus, later, solvothermal techniques were found to be a convenient solution to overcome this challenge and have largely benefit over often time-consuming methods involving slow coupling of the coordinating species. The typical solvothermal method combines the precursors as dilute solutions in polar solvents such as water, alcohols, acetone or acetonitrile and heated in sealed vessels such as Teflon-lined stainless-steel bombs or glass tubes, generating autogenous pressure. The crystal growth process is enhanced by using mixed solvent systems where the solution polarity and the kinetics of solvent-ligand exchange can tune to achieve rapid crystal growth. It has found that, exposing the growing framework to a variety of space-filling solvent molecules may also be an effective way to stabilize its defect-free construction as they efficiently pack within the defined channels [24]. For deprotonation of the linking molecule alkyl formamides and pyrrolidinones have been particularly useful, as they are also excellent solubilizing agents.

In recent years, modifying the solvothermal method, there are several rapid synthesis methods were proposed by researchers to develop MOF crystals within a short duration of time. Some of the external parameters implemented to develop MOFs include the use of Microwave energy (Microwave synthesis), [25] Ultrasonic waves (Sonochemical synthesis), Mechanical energy (Mechano-chemical synthesis) and electrical energy (Electrochemical synthesis). The synthetic strategies developed up to date to make different type of MOFs are summarized in the **Table 1** along with reaction conditions [26]. Additionally, a surfactant driven-templating method, [22] a CO_2-expanded liquid route, [27] a post-synthetic method, [28] and an ionic liquid-based method [29] are developed to create hierarchical mesoporous microstructures and thin films of MOFs [25, 27–29].

Synthesis method	Reaction time	Temperature (K)
Slow evaporation	7 days to 7 months	298
Sonochemical method	30–180 mins	272–313
Solvothermal method	48–96 hours	353–453
Mechano-chemical method	30 min to 2 hours	298
Electrochemical method	10–30 mins	273–303
Microwave Synthesis	4 mins to 4 hours	303–373

Table 1.
Synthesis methods developed up to date to make MOFs.

3. $Zn_4O(L)_3$-based isoreticular MOFs with cubic topology for optoelectronics

3.1 Road map to electrically conductive MOFs

In the area of MOFs, the main desire is to design MOFs with optoelectronic properties and to optimize the charge transport mechanism suitable for developing electronic devices. Although numerous applications of MOFs with different types of synthesis methods are being investigated, a versatile and scalable synthesis approach for the preparation of MOFs with semiconducting properties for optoelectronic devices are still in the early stage and a little research work so far done towards tailoring MOFs structure–property relationship to use as active materials in optoelectronic devices, such as solar cells, field-effect transistors, and photoluminescence devices.

To introduce MOFs as semiconducting materials, tuning of band gap such as lowering the bandgap or increasing the charge mobility is required. This tunability is again dependent upon the type of interaction i.e. Intermolecular interaction: metal ion and the organic ligand or Intramolecular interaction - π stacking [18]. The two key factors responsible for poor electrical conductivity in MOFs are: (1) the insulating character of organic ligand and (2) due to poor overlapping between the π-orbitals of organic ligand and d-orbitals of metal ions [16]. The common strategies for constructing MOFs with electrical conductivity involves three possible charge pathways.

Pathway 1: A long range of charge transport in this pathway is facilitated through bonds. This mechanism is promoted by interaction between ligand π and metal d orbital [16]. This mechanism is based on the tunneling of electron between the donor and acceptor portions of the framework. Typically, the electrical conductivity in the range 10^{-7} to 10^{-10} S cm^{-1} is considered as insulator. This is caused due to poor overlapping between the metal ion and organic linker as the electronegative nature of oxygen atom in the carboxylate group of the linker is so high that it requires high voltage for tunneling of the electrons [30]. Various MOFs that exhibit conductivity through this mechanism have been reported, of which $[[Cu_2(6\text{-}Hmna)\ (6\text{-}mn)]\cdot NH_4]_n$, a copper-sulfur based MOF constructed from 1,6-Hmna = 6-mercaptonicotinic acid, 6-mn = 6-mercaptonicotinate shows highest electrical conductivity of 10.96 S/cm (**Table 2**).

Pathway 2: In this pathway, the charge transport is facilitated through space via π stacked aromatic ligands which was proposed as an alternative to through bond strategy. This mechanism typically promotes electron hopping mechanism by employing electroactive molecules [16, 30]. TTF-TCNQ i.e. tetrathiafulvalene-tetracyano quinomethane is one of the MOFs that demonstrate metallic conductivity

Materials	Mechanism	Conductivity (Scm^{-1})	Charge carrier	Mobility $(\text{cm}^2\text{V}^{-1}\text{S}^{-1})$	Ref.
Metals Cu Au Fe	Tunneling	6.5×10^5 4.1×10^5 1.0×10^5	e	46	[31]
Organic polymers Polyacetylene Polythiophenes Rubrene	Charge transfer (electron hopping)	10–9 1975	h	1–10 4	[31]
TTF-TCNQ $Ni_3 (HITP)_2$ $Zn_2 (TTFTB)$	Through-space	700 40 4.0×10^{-6}	h or e	48.6 0.2	[16, 31, 32]
$Cu_3(BTC)_2$-TCNQ NU-901-C60	Guest molecule	0.07 1×10^{-3}	h		[33, 34]
$Fe_2(DSBDC)$ $\{[Cu_2(6\text{-Hmna})(6\text{-mn})] \cdot NH_4]_n$ $Cu [Ni(pdt)2]$	Through-bond	1×10^{-6} 10.96 1×10^{-4}			[18, 35–37]

Table 2.
Significant progress in the last few years made towards developing electrically conductive MOFs and their conductive properties compared with conventional metals.

(shown in the **Table 2**) through-space (π-π stacking) mechanism [38]. Recently, TTF-based ligand consisting of benzoate spacers is used to develop Zn based MOF reported by Dincă et al. These MOFs shows columnar stacks of TTF (3.8 Å) with the charge mobility of a magnitude that resembles some best conductive organic polymers [35, 36].

Pathway 3: The other alternative strategy to increase the conductivity of MOFs is via incorporating an appropriate guest molecule within the MOF. These molecules can activate long range delocalization either through bonds or through space or that can inject mobile charge carriers by oxidizing or reducing the organic ligand and metal ions [16, 30] NU-901, a MOF consisting of $Zr_6 (\mu_3\text{-O})_4 (\mu_3\text{-OH})_4 (H_2O)_4 (OH)_4$ nodes and tetratopic 1,3,6,8-tetrakis (p- benzoate) pyrene (TBAPy4-) linkers. These materials were chosen for the encapsulation of C_{60}. After installation of C_{60}, the NU-901-C_{60} shows electrical conductivity higher than that of NU-901 (shown in the **Table 2**). As per reports, the donor-acceptor interactions between TBAPy4-/C_{60} contribute to the electrical conductivity of the framework [32, 38].

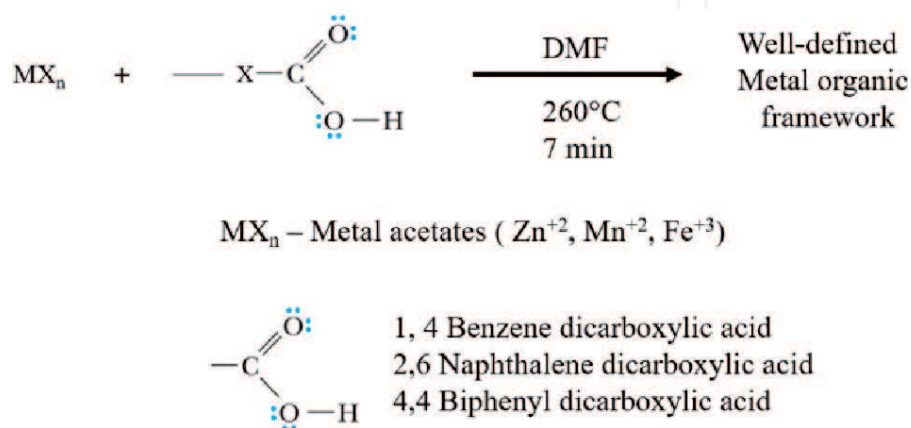### 3.2 Synthesis and optoelectronic properties of IRMOF-1

IRMOF-1, which is commonly known as MOF-5, invented by Yaghi and co-workers [39] in 1996, has become one of mostly studied MOF with promising application in high capacity hydrogen storage [40, 41]. MOF-5, consists of Zn_4O units connected by linear 1,4-benzenedicarboxylate units to form a cubic network, having the primitive cubic unit cell. Syntheses demonstrated for MOF-5 in which the starting materials are mixed in solution at ambient temperature. Subsequent addition of triethylamine promotes the deprotonation of the organic linker to precipitate MOF-5. Depending on the addition of base either slowly by diffusion as described in the original synthesis method [39] or rapidly as an aliquot [42] the product can be either single crystal mixtures, which must be mechanically separated, or microcrystalline powders. The ambient temperature synthesis method described above following the fast addition of base, is easy to scale up. However,

metal precursor, zinc nitrate poses potential safety concerns, especially for large-scale production. Furthermore, reports of such synthetic conditions have been largely limited to MOF-5 and IRMOF-8 [42–44].

Later, a rapid, simple, room-temperature high yielding synthesis method was introduced by Yaghi and co-workers that can apply to make a wide range of new MOFs, including IRMOF-0, which uses acetylenedicarboxylate as the linker [45]. This synthesis method follows a room temperature synthesis, wherein separate N,N-dimethylformamide (DMF) solutions of terephthalic acid (BDC) with triethylamine and zinc acetate dihydrate are prepared, then the zinc salt solution is added to the organic solution with rapid stirring at ambient temperature. Upon immediately of the formation of a white powder followed by 2.5 hours of reaction time, pure MOF-5 is collected and confirmed by powder XRD. The same synthesis without a base (triethylamine) has also yielded pure MOF-5, confirming that addition of a base is unnecessary when zinc acetate is used as a source of Zn (II) in the MOF-5 synthesis [45].

This synthesis method has later modified by Rathnayake et.al to make IRMOFs (IRMOF-1, 8, and 10) by cutting down the reaction time from 2.5 hours to 7–9 minutes [23]. As depicted in **Figure 3**, our group is able to make a wide range of hierarchical microstructures of highly crystalline MOFs, including IRMOF-1. Microstructures of IRMOF-1 prepared from the modified solvothermal method (**Figure 3**), are visualized using scanning electron microscope and are depicted in **Figure 4(a)**. Crystal structure of IRMOF-1, retrieved by matching its simulated XRD with experimental powder XRD is depicted in **Figure 4(b)**, and follows cubic lattice cell, which belongs to Fm3m cubic space groups. The electron density potential distribution modeled from VESTA (**Figure 4(c)**) evidences that the electron potential is localized on Zn_4O clusters and there is no electron delocalization with the organic linkers, confirming no orbital overlap for energy transfer through metal–ligand charge transfer processes.

As a first member of isoreticular series, IRMOF-1 has explored for luminescence due to ZnO quantum dots behavior, which has been believed, contributing to luminescence. The ZnO QD absorption and emission spectra from electronic transitions have been investigated, suggesting that that the luminescent behavior of IRMOF-1 arises from a $O_2 - Zn^+ \rightarrow O - Zn^+$ charge-transfer transition within each tetrahedral Zn_4O metal cluster, which has been described as a ZnO-like QD [46]. The photoluminescence emissions of IRMOF-1 with intensity peak maximum at 525 nm, was ascribed to energy harvesting and LMCT from 1,4-benzenedicarboxylate (BDC) linked to the Zn_4O cluster. The nature of the luminescence transitions in IRMOF-1 nanoparticles has been investigated by Tachikawa et al. where the


MX_n – Metal acetates (Zn^{+2}, Mn^{+2}, Fe^{+3})

1, 4 Benzene dicarboxylic acid
2,6 Naphthalene dicarboxylic acid
4,4 Biphenyl dicarboxylic acid

Figure 3.
Reaction scheme for synthesis of Isoreticular MOFs using modified solvothermal method followed by solvent driven self-assembly.
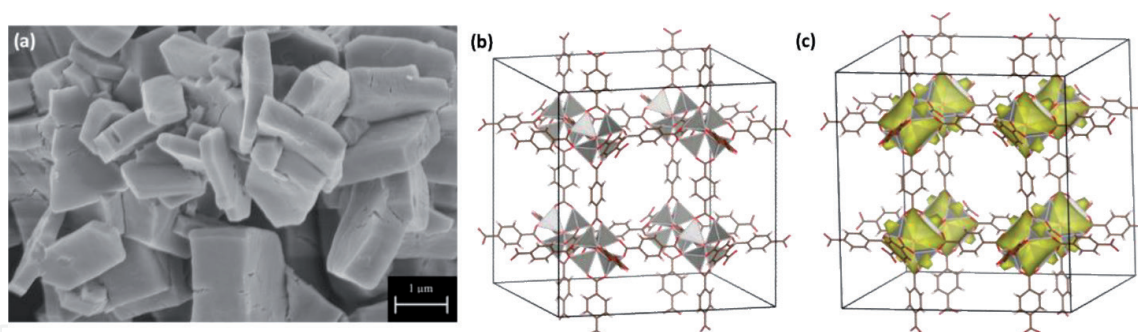
Figure 4.
(a) A SEM image of IRMOF-1 microstructures, (b) crystal structure of IRMOF-1 retrieved from crystallographic open database, and (c) electron density potential distribution of IRMOF-1 modeled from VESTA.

transition responsible for the green emission of IRMOF-1 is similar to that of ZnO [47]. Therefore, the emission observed in IRMOF-1 has been speculated to originate from the ZnO QD not from the ligand. However, Further investigations demonstrated that ZnO impurities in the material gave rise to the emission assigned to the quantum dot like luminescence and that pure MOF-5 displays a luminescence behavior that is more closely relevant to that of the ligand. [9] However, the exact nature of the luminescence of MOF-5 is still under dispute with ligand– ligand charge transfer, [10] ligand-centered, [9] and ligand–metal charge transfer [11] mechanisms as primary suggestions.

In an on-going study, our group has been investigating optoelectronic behavior of IRMOF-1. As depicted in **Figure 5**, UV–vis absorption spectrum shows absorption vibrionic features similar to the linker with two absorptions peaks at 208 nm and 240 nm along with a shoulder peak at 285 nm. The emission spectrum collected by exciting at 240 nm exhibits linker-based emission with three well-resolved vibrionic transitions at 328 nm, 364 nm, and 377 nm. We observed a small high energy shoulder peak at 464 nm, which corresponds to an excitonic transition of Zn_4O nodes. However, we have no observed a longer wavelength emission peak at 525 nm, which has claimed in prior studies to energy harvesting and LMCT from 1,4-benzenedicarboxylate (BDC) linked to the Zn_4O cluster. Therefore, our findings support that IRMOF-1's luminescence comes from linker emission rather than the charge transfer processes. This further excludes the emission originating from the ZnO quantum dots like clusters of Zn_4O. The optical band gap calculated from the UV–visible spectrum on-set is found to be 3.97 eV. There are no experimental band gaps reported for IRMOF-1 up to date.
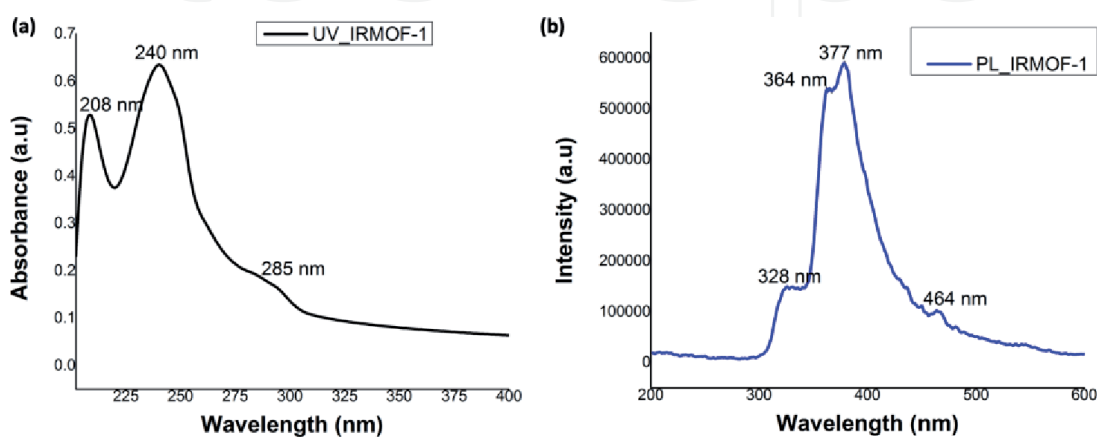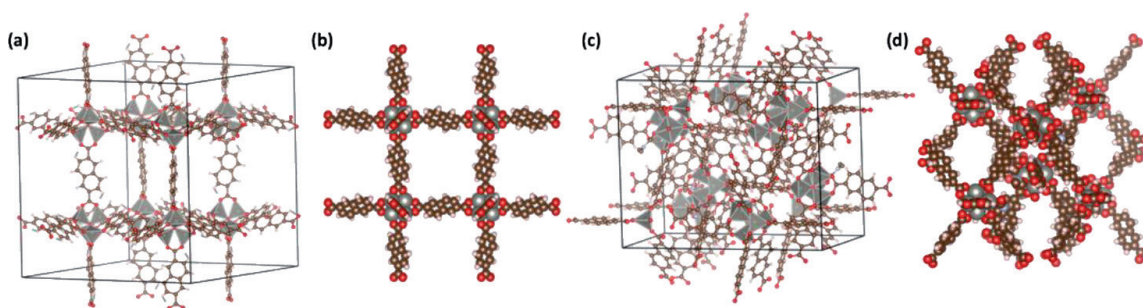

Figure 5.
Photophysical properties of IRMOF-1 – (a) UV–visible spectrum and (b) photoluminescence spectrum in solution (ethanol).

### 3.3 Synthesis and optoelectronic properties of IRMOF-8

Significant research efforts have demonstrated successful synthesis of a variety of isoreticular MOFs (IRMOFs) with the formula of $Zn_4O(L)_3$ (where L is a rigid linear dicarboxylates) using traditional solvothermal method, which uses zinc nitrate as metal precursor and the respective organic ligands in an amide-based solvent system. These IRMOFs follow the same cubic topology as the prototypical MOF-5, a framework with octahedral $Zn_4O(CO_2)_6$ clusters, which are linked along orthogonal axes by phenylene rings [3, 26, 48, 49]. This family of IRMOFs-n (n = 1–16) gained significant attention in gas storage community due to its high pore volume and surface area. Among the IRMOFs series, IRMOF-1 and 8 have been extensively studied for gas adsorption and photoluminescence properties [39, 50, 51] but have not explored their optoelectronic properties until recently.

IRMOF-8 is constructed from the linkage of basic zinc acetate clusters and naphthalene-2,6-dicarboxylic acid units (NDC). Originally reported IRMOF-8 with non-interpenetrated cubic crystal lattice has only been extensively studied for gas sorption and storage applications [50, 51]. Later, a number of interpenetrated phases of $Zn_4O(ndc)_3$-based systems have been discovered [52–54]. Although the synthesis of interpenetrated IRMOF-8 (INT-IRMOF-8) are similar to that of IRMOF-8, the possibility that typical solvothermally synthesized IRMOF-8 contains at least a significant amount of an interpenetrated phase. There are modified synthesis methods have been introduced to make fully non-interpenetrated IRMOF-8 [55] and INT-IRMOF-8 [23, 55]. The crystal structures of non-interpenetrated IRMOF-8 and INT-IRMOF-8 along with their space filling structures, acquired from the Crystallographic Open Database (COD) and generated using VESTA are depicted in **Figure 6**.

Recently, our group has introduced a modified solvothermal synthesis method, which involves a solvent polarity driven self-assembly process to make hierarchical microstructures of INT- IRMOF-8, exhibiting promising optoelectronic properties for the first time [23]. Instead using zinc nitrate as the metal precursor, the synthesis we developed utilizes zinc(II)acetate as the metal precursor. Hierarchical microstructures of INT-IRMOF-8 nanocrystals can be prepared in high yield in the presence of minimum volume of dimethyl formamide by mixing zinc(II) precursor with naphthalene-2,6-dicarboxylic acid at room temperature followed by subjecting to solvothermal annealing at 260°C for 7 minutes [23]. Microstructures visualized under TEM (**Figure 7(b)**) reveal that they are hierarchical layers of self-assembled nanocrystals with randomly arranged voids among the nanocrystals. The wide-angel X-ray scattering (WAXS) pattern along with the selective area electron diffraction (SAED) pattern have shown that the microstructures are made from self-assembled nanocrystals of INT-IRMOF-8, which exhibits lamella packing pattern (**Figure 7(c)** and **(d)**), benefiting for optoelectronic behavior.

Figure 6.
Crystal structures of: (a) non-interpenetrated IRMOF-8 and (b) its space filling view, (c) INT-IRMOF-8 and (d) its space filling view.
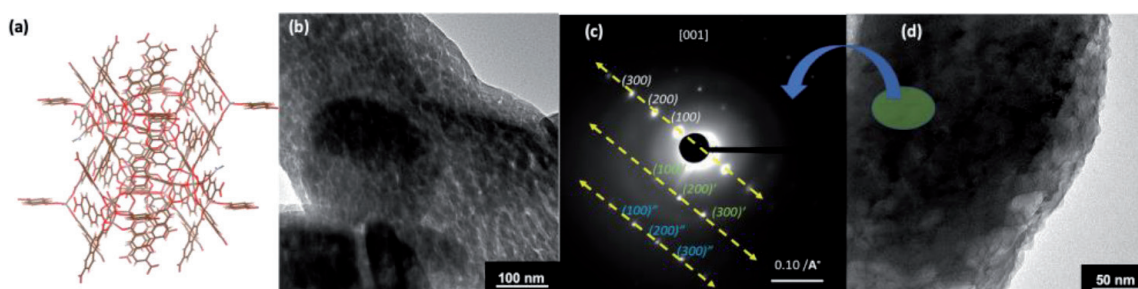
Figure 7.
*(a) Interpenetrated view of INT-IRMOF-8's crystal structure; (b) a TEM image of a microstructure; (c) the SAED pattern of a microstructure taken from the TEM under dark field diffraction mode along with (d) a TEM image of the respective microstructure. [**Figure 7** is re-created from the original data].*

The photophysical properties of INT-IRMOF-8 exhibit mainly linker based optical properties. The presence of high intensity absorption peak set from 220 nm to 360 nm, which corresponds to vibronic π-π* absorption transitions of naphthalene core, evidencing the linker-based absorption, resulting from the lack of favorable spatial and energetic overlap of the metal and the ligand orbitals [21, 49]. Typically, MOFs' photoluminescence behavior arises as a result of different types of charge transfer processes, which include metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), ligand–ligand charge transfer (LLCT), ligand-centered luminescence, and metal-to-metal charge transfer (MMCT) processes [56]. However, this metal-centered luminescence depends on the metal type, ligand type, and their spatial orientations. The emission spectrum of INT-IRMOF-8 microstructures exhibits three emission bands, in which vibrionic transitions corresponds to only linker-based emission with no indication of additional emissions due to any charge transfer processes. The optical band gap reported for INT-IRMOF-8 is 2.82 eV [23] and the theoretical band gap reported in the past for non-interpenetrated IRMOF-8 was ranged from 2.83 eV to 3.27 eV [57]. There are no experimental band gaps reported for IRMOF-8 up to date.

The charge transfer ability of IRMOF-8 for the first time is evaluated by our group. The average electrical conductivity of INT-IRMOF-8 microstructures was ranged from 3.98×10^{-2} to 2.16×10^{-2} S cm^{-1}, which is higher than the electrical conductivities reported for most MOFs (<10^{-10} S/cm). The interpenetrated structure, high crystallinity, and narrow band gap contribute to the to the electrical conductivity of hierarchical structures of INT-IRMOF-8 nanocrystals.

### 3.4 Synthesis and optoelectronic properties of IRMOF-10

Among the series of IRMOFs (IRMOF 1–16) introduced by Yaghi and coworkers [58–60], several IRMOFs have shown effective selective preconcentration properties, including IRMOF-10 [61–64].

Compared to IRMOF-1, physicochemical, optical, and electronic properties of IRMOF-10 with its 4,4′-biphenyldicarboxylate linkers has received much less attention. IRMOF-10 was first synthesized by Yaghi and coworkers [50, 58–60], Owing to its higher surface area and larger pore sizes, use of IRMOF-10 for gas absorption and separation and hydrogen storage have been widely investigated, but scarce attention has been paid to other properties of IRMOF-10, such as structural stability, optical and electrical properties, electronic structure, and chemical bonding. The first publication about biphenyl MOFs already anticipated the major challenges related to Zn-biphenyl MOFs: the growth of single-crystals and interpenetration. A structure from single-crystal XRD of non-functionalized IRMOF-10 is not yet available. A single-crystal X-ray structure analysis of a non-interpenetrated

IRMOF-10 derivative was not reported until the breakthrough of the group of Telfer, which showed how interpenetration can be effectively suppressed by using thermolabile protecting groups in the synthesis of amino-MOFs [65]. Following the modified solvothermal synthesis method introduced by Rathnayake et al., microstructures of non-interpenetrated IRMOF-10 was successfully synthesized, and crystal structure was confirmed by matching the powder XRD traces with the simulated XRD pattern. The microstructures morphology is depicted in **Figure 8(a)** and crystal structure retrieved from the Crystallographic Open Database is depicted in **Figure 8(b)**. IRMOF-10's single crystal structure reveals three-dimensional coordination framework, formed by periodic arrangement of Zn(II) atoms, which is tetrahedrally coordinated by four oxygen atoms from four biphenyl linker units, following the unit formula of $Zn_4O(L)_3$ with cubic topology as IRMOF-1.

The electron potential density localization surrounding the metal oxide nodes and organic linker units in IRMOF-10's unit cell reveals the electron density distribution with respect to the biphenyl conjugation length. As shown in **Figure 8(c)**, the electron potential is delocalized within metal oxide nodes and bi-phenyl units, and partial distribution of charges has increased around bi-phenyl units compared to naphthalene units of IRMOF-8. Thus, the findings suggest that linker length has more pronounced effect on the individual material's electronic band structure and density of state, providing clear visualization on the localization of electronic potential within the crystal lattice. The delocalization of electron density potential through biphenyl linkers evidences its potential to be used as optoelectronic materials. Thus, exploring its electronic structure, band gap, optical, and electrical properties is a major interest to the materials science community. However, despite computational investigations on theoretical prediction of optoelectronic properties, [66] there are no experimental investigations on IRMOF-10's optoelectronic behavior has been conducted up to date.

The equilibrium solid-state structure, electronic structure, formation enthalpy, chemical bonding, and optical properties of IRMOF-10 have investigated with density functional calculations. Electronic density of states and band structures study have shown that the band gap for the IRMOF-10 is ranged from 2.9 eV to 3.0 eV, resulting in a nonmetallic character [66]. Until now, there are no experimental studies available to verify theoretical predictions on IRMOF-10's electronic structure. The calculated optical properties of IRMOF-10 provide useful information for future experimental exploration. The optical properties (dielectric function, refractive index, absorption coefficient, optical conductivity s(v), reflectivity, and electron energy-loss spectrum of the IRMOF-10 have computed in the past, [66] but there is no experimental investigation conducted up to date.
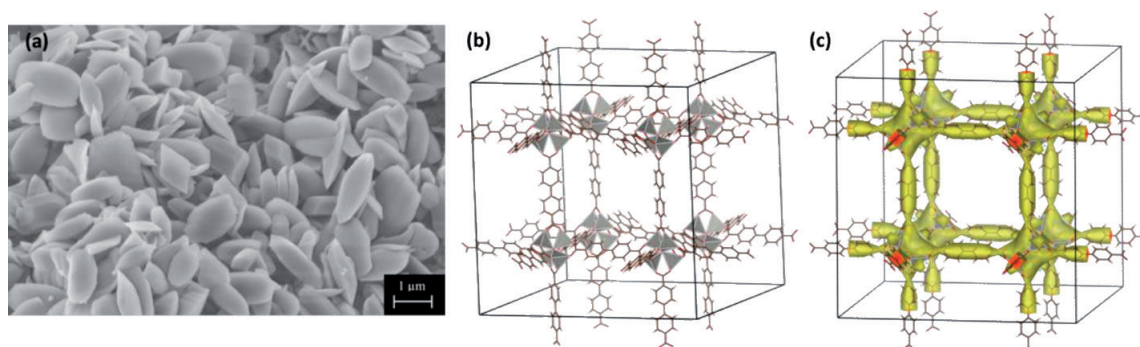
Figure 8.
(a) A SEM image of IRMOF-10 microstructures, (b) crystal structure of IRMOF-10 retrieved from crystallographic open database, and (c) electron density potential distribution of IRMOF-10 modeled from VESTA.
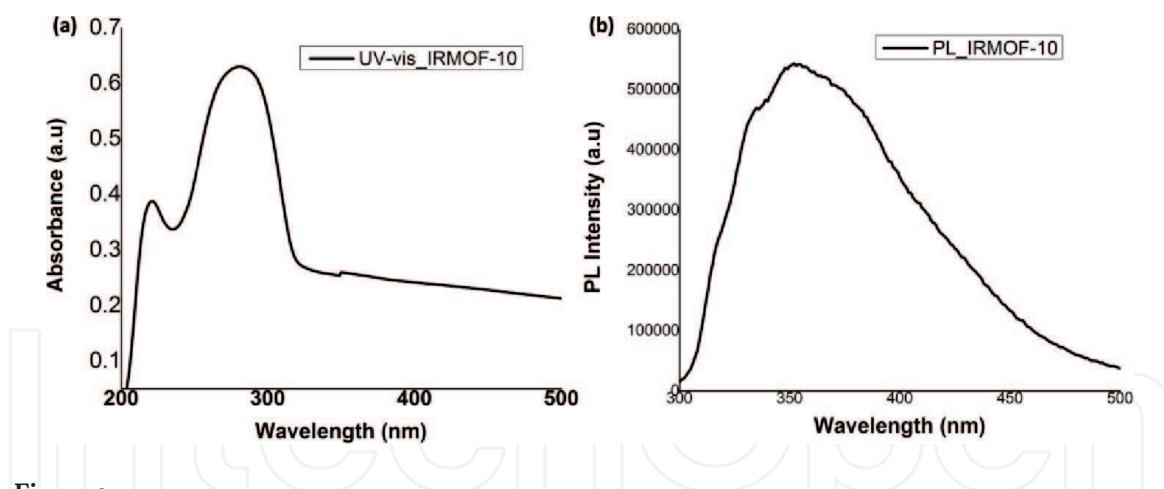
Figure 9.
Photophysical properties of IRMOF-10 – (a) UV–visible spectrum and (b) photoluminescence spectrum in solution (ethanol).

Recently, our group has studied optoelectronic behavior of non-interpenetrated IRMOF-10. As shown in **Figure 9**, we explored the photophysical properties of non-interpenetrated IRMOF-10 and calculated its optical band gap. IRMOF-10 exhibits linker-based absorption with absorption maximum at 282 nm along with a shoulder peak at 222 nm. IRMOF-10 shown blue luminescence with broader emission ranged from 310 nm to 450 nm along with the emission maximum at 353 nm. The optical band gap calculated from the UV–visible spectrum on-set is 3.80 eV, which is narrower than the optical band gap of IRMOF-1 and larger than the theoretical band gap predicted from computational analysis.

In summary, the conjugation length of the organic linker in IRMOFs contributes to the semiconducting properties rather than the periodic pattern or the distances between the Zn_4O clusters. The conjugation length of organic linkers of IRMOF-1, 8, and 10 described here differs from one aromatic unit (benzene) to one and half aromatic unit (naphthalene) to two aromatic units (biphenyl). The resonance effect arises due to the conjugation speaks directly to the photophysical behavior and optical band structure characteristics, reflecting a clear trend in narrowing the band gap with gradual increase in the conjugation length of the ligand. The dramatic change in the optical band gap upon changing the organic linker in the MOF structure has also been reported in the past [66]. Thus, these studies evidences that the semiconducting properties of MOFs strongly depends on the resonance effects from the organic linker [67].

4. Future prospective

With a growing demand for continuous miniaturization and functional scaling, the complementary metal-oxide semiconductor (CMOS) platform continues to drive advances in integrated circuits (IC), nanoelectronics and information processing technologies. While it is now possible to produce an amazing array of nanoscale materials and morphologies, the assembly and integration of these nanostructures into ordered arrays, with other materials, remain key challenges. Moore's Second Law projects a need for new, high throughput fabrication approaches that can produce useful and defect free nanostructures for future silicon-based CMOS related technologies. Recent advances in nanomaterial synthesis enable new families of emerging research materials (ERMs) that show potential for extending and augmenting existing CMOS technology, with respect to wafer level manufacturability, uniformity, reliability, performance and cost, and they warrant additional

research focus and verification. The integration of More-than-Moore, application specific, materials and structures on a CMOS platform leverages the best of both technologies, though this added complexity also challenges the extensibility of conventional fabrication and patterning methods. Consequently, there remains a need for simple fabrication methods that can create two- and three-dimensional ordered functional nanostructures, which can adapt to a wide variety of materials, patterning, and application needs.

Highly crystalline microstructures of MOFs have been paving the path, addressing the current challenges in fabrication needs that create two- and three-dimensional ordered structures and which are adaptable to a wide variety of materials specific applications. These nanoscale building blocks, and their assemblies combine the flexibility, conductivity, transparency, and ease of processability of soft matter (organic) with electrical, thermal, and mechanical properties of hard matter (inorganic). They offer a new window for fine-tuning structural nodes with known geometries and coordination environments. With respect to the fabrication of ordered nanoscale structures, MOFs have several advantages. First, since they are themselves a highly ordered self-assembled nanostructure, as a result of their crystallinity, their pore dimensions are completely defined, making knowledge of atomic positions possible. Second, the nanoporosity of their structure results from geometric factors associated with the bonding between their inorganic and organic components, enabling rational template design [68]. Third, unlike the conventional template materials, MOFs possess a high degree of synthetic flexibility with potentially widely tunable electrical, optical, and mechanical properties. Surely, the development of simple, versatile low-cost methodologies for the design, production, and nanoscale manipulation of innovative functional organic–inorganic hybrid building blocks will provide a powerful new capability for designing, integrating, and patterning new nanoscale materials with tunable properties onto a CMOS platform. Recent milestones of MOFs in photovoltaic, optical and chemical sensing, and field effect transistors highlight the potential of these materials for future electronic devices, heterogeneous platforms, non-traditional patterning opportunities [16, 69–71].

Interest in using these materials in fields such as gas storage [72], separations [73], [sensing [21], and catalysis [74] is rapidly accelerating. The advantages of MOFs for above applications are promising due to the wide range of possibilities of the rational design inherited in these materials. Thus, superior properties and new understanding with respect to the interaction of small molecules with nanoporous materials are being achieved. Although most MOFs are found to be dielectrics, a few semiconducting frameworks are known [23, 37, 75, 76]. The theoretical predictions conduced up to date on variety of MOFs suggest that there are possible MOFs with semiconducting properties [77–79] . MOFs that are magnetic [80], ferroelectric [81, 82], proton-conducting [83–86], and luminescent [87, 88] are also known. Additionally, their porosity creates the potential to introduce non-native functionality to a given structure by infusing the accessible volume with a second molecule or material. Moreover, because the chemical environment within the pore can be modified, it is possible to tailor the interface between the MOF and a templated material to stabilize specific materials or nanostructures. Consequently, MOFs and the coordination polymers of crystalline nanoporous frameworks possess many of the properties of an ideal template.

Despite the endless possibilities for how MOFs could be used for device applications, when using MOFs for semiconductor microelectronic devices such as sensors, field-effect transistors, light harvesting and absorbing, light-emitting diodes, thermoelectric devices, energy storages and lithium ion batteries, and scintillators, it is necessary to understand how these materials function within the device and how

they will interface with other functional and structural elements. Therefore, this section focuses on providing a future prospective for advances that must be made for their realization in electronic devices. A possible MOF-device roadmap, which identifies MOFs applications in electronic devices along with machine learning for new MOFs developments and MOFs database screening for novel properties is depicted in **Figure 10**. Our intention of providing this roadmap is to stimulate future endeavors of MOFs roadmap for electronic industry by translating current MOFs basic research agenda into applied research in the future. The roadmap that we identified here is created by combining the prospective previously provided by Allendorf et al., focusing five major fields pertinent to device fabrication [89]. These previously proposed areas include: (1) Fundamental Properties, (2) Thin film growth and processing, (3) MOFs hybrid and multilevel structures, (4) Device integration, and (5) Manufacturing issues. Our prospective for the proposed potential MOF-device roadmap particularly concentrated on member-specific applications in electronic industry, where functional density of MOFs can be utilized in subcategories of a wide variety of electronic devices. As the MOF-based optoelectronic field is fairly new and fall within the basic research stage, our roadmap is structured based on MOFs relative progress made so far and build upon the future road map comparing with the progress made in the field of organic electronics.

Exploring electronic properties, such as electronic structure, band gap, conductivity, electron, and hole mobilities, and dielectric constants of MOFs need to be one of the priority areas in the next decades and must be understood. Additionally, understanding lattice defects and their relationship to electronic properties must be explored combining theoretical and experimental approaches as they likely will limit the ultimate performance of a device. The field-effect transistor (FETs), which is the basic device building block for modern electronics, dictates the materials properties relevant to electronic applications. The FET performance is determined by the carrier mobility, source and drain contact resistance, and the capacitance of the gate electrode. Si is the preeminent materials for FET fabrication because of its bandgap of 1.1 eV, high carrier mobility, availability of multiple n- and p-type dopants, environmental stability, stable oxide, and high terrestrial abundance. However, Si based device fabrication requires enormous capital investment and Si is not compatible with a variety of low cost, flexible, transparent, and low melting
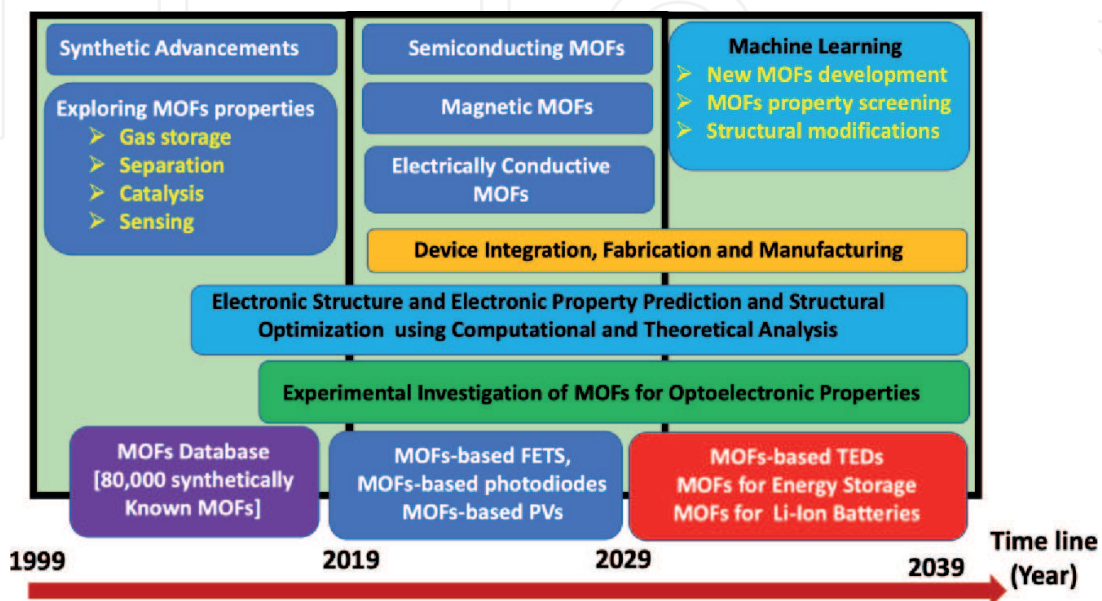
Figure 10.
A possible MOF-device roadmap for electronic industry proposed by Rathnayake.

temperature substrates. For these reasons, alternative materials including polymers, organic molecules, and more recently nanotubes and nanowires have been gaining a lot of attention for various emerging applications. The long-range crystalline order of MOFs implies that charge transport through delocalized conduction and valence bands typical of crystalline inorganic semiconductors is possible. Emergence of delocalized bands in MOFs will require that the π orbitals in the linker groups overlap effectively with the metal d orbitals. Such overlap is absent in the majority of synthetically known MOFs where carboxylate oxygen atoms are coordinated to the metal center through σ bonds. Therefore, most MOFs are electrical insulators. This barrier needs to be overcome in next decades, perhaps by synthesizing novel MOFs using higher order conjugated linkers and increasing the functional density of the MOFs. Modifying the linker structure could lead to better charge transfer between linker and the metal cations of the framework. One possible route has suggested replacing the carboxylate terminating linkers with isocyanide groups [89]. It has been shown that, Prussian Blue, a mixed valence crystalline compound with Fe(II) and Fe(III) ions coordinated with isocyanide ligands, is electrically conducting [90]. Another approach, suggested by Allendorf et al., is to introduce conducting phases into the MOF channels [89]. Some other approaches have been taken place to enhance electronic transport properties of MOFs by introducing other conductive nanomaterials, inorganic oxides, polymers, and carbon nanotubes into MOFs framework [91–93].

Atomic level fundamental understanding that cannot be obtained readily from experimental methods, is necessary to address MOFs electronic band structure, density of state, band gap, and electron and hole mobilities. There has been increasing accuracy of predictive results using molecular dynamics (MD) force fields (FF) and DFT approximations for various MOFs' property studies [94–100]. Density Functional Theory (DFT) methods using periodic boundary conditions have been popular for predicting the electronic structure of MOFs [57, 67, 101, 102]. However, DFT-based computational calculations are underestimate excited state energies by about a factor of two. Adapting high-accuracy methods, such as Quantum Monte Carlo (QMC), DFT + U, and GW are not feasible for systems with large numbers of electrons. For example, practical QMC calculations currently could not apply to the systems that exceed 1000 electrons. One formula unit of IRMOF-1 has 760 electrons and 106 atoms. Owing to these limitations in current computational approaches, MOFs are much more challenging than traditional electronic materials with much smaller unit cells. The computational methods for predicting properties of MOFs are at an early stage of development, in particularly for predicting electronic properties of MOFs [57, 101]. Developing simple and rapid analytical approaches are not only a necessary tool to experimental investigations but also can be used as an accelerate investigation and predictive tool by themselves to screen semiconducting MOFs from the database of synthetically known MOFs. Such analytical approaches combined with computational studies will eventually enable the design of machine learning approaches for large-scale screening of existing and hypothetical MOF structures for specific applications [103–105].

MOFs are also showing promise in their use as electrolytes due to their low electronic conductivity, tunable polarity, and high porosity [106]. There are many ways that MOFs have been employed to elevate the downfalls of current electrolytes. For example, they have been using as hosts for liquid electrolyte solutions or ionic liquids [107, 108]. However, the drying of the electrolyte solution within the MOFs presents an issue since the ion transport is mostly achieved by the solvent molecules within the electrolyte rather than by the MOF itself. Furthermore, MOFs is used as a filler to reduce the crystallinity of SPEs [107, 108]. However, up to date MOFs have not been explored to be used as a solid electrolyte excepts in a composite form [109].

One way to achieve this is designing lithium-based metal organic frameworks (Li MOF) where excess lithium is transferred through the defects in the MOF structure. However, research regarding Li MOFs as solid electrolytes is currently lacking. The majority of MOF/electrolyte studies are only focused on employing MOFs as a host of ionically conductive materials rather than utilizing MOFs as solid-state electrolytes. Therefore, we identified this area of research in the proposed roadmap to stimulate investigating the potential of Li-based MOFs as solid electrolytes. There are different types of Li-MOFs already developed [110–112], but many of them are designed for applications other than battery electrolytes. We believe that Li- MOF structures can be tuned for lithium transport. Overall, Li MOFs show potential for the use as solid ionic conductors and much research should be performed to explore their possibility for solid state electrolytes and battery components.

Exploring thermoelectric properties of MOFs emerges five years ago along with exploring the electronic properties of MOFs by systematic structural modifications and introducing guest molecules onto MOFs. The first thermoelectric property measurements on MOFs has introduced by Erikson in 2015 [113]. then, up to date, there have been less than ten publications in thermoelectric MOFs, thus this field of research is relatively new. Highly nanoporous MOFs are promising since porosity can reduce the lattice thermal conductivity. The effect the conjugation length of the organic linker that tailors the pore dimension for lattice thermal conductivity must be investigated. The thermoelectric figure of merit that measures the efficiency of a thermoelectric device can be improved by decreasing the lattice thermal conductivity. It is believed that changing the conjugation length or the complexity of the organic linker changes phonon scattering, thereby changing the lattice thermal conductivity [77, 114]. The ligand modifications can be successfully achieved by isoreticular synthesis approaches. Also, increasing the porosity of MOFs increases phonon scattering that also reduces thermal conductivity [114]. Therefore, in order to utilize MOFs as active materials in thermoelectric devices, understanding the contribution of phonon vibrations to lattice thermal conductivity is essential and must be investigated. Directing future research on thermoelectric MOFs towards experimentally investigating thermoelectric properties of MOF based thin films to find ways of decreasing thermal conductivity by structural modifications to the organic ligand is beneficial.

In order to use MOFs as photoactive layer for energy harvesting and conversion, MOFs should possess decent light harvesting capability in the region from visible light to near-infrared (NIR). As the material's light-harvesting window is primarily determined by its band gap, synthesizing a MOF with a semiconducting band gap that can absorb light in the solar spectrum should be a requirement for it to serve as the photoactive material. Given that the electronic configuration of MOFs is contributed by both the constituent metal ion and the organic linker, the resultant bandgap and semiconducting properties of MOFs can thus be tailored by their structural design and engineering. Since most MOFs possess large band gap due to lack of overlap between metal ion and the organic linker and low degree of conjugation, they cannot effectively absorb light in the solar spectrum. The ligand center of MOFs plays a dominant role in its resulting light harvesting behavior [77, 114]. Tailoring the structure and its composition, MOFs charge transfer processes can be improved to enable the photocurrent of MOFs and fulfilling the photoactive functions.

To effectively reduce the band gap of MOFs and enrich their semiconducting properties for photovoltaic applications, three strategies can be implemented and have been identified [115]. These strategies are: (1) selecting electron rich metal nodes and conjugated-based organic molecules, (2) enhancing the conjugation of the organic linker, and (3) functionalizing the organic linker with

electron-donating groups, such as hydroxyl, nitro, and amino groups. Additionally, facilitating electron delocalization through guest-mediated p-donor/acceptor stacks can also effectively diminish the band gaps of the materials [115]. Besides narrowing the band gap, electronic structure that contributes the semiconducting properties of MOFs also play a vital role as sufficient dissociation of the photoexcitons generated in the MOFs is required to produce a reasonable photocurrent. In this regard, MOFs exhibit critical barriers to use as the photoactive materials directly and impedes its progress in photovoltaic applications to date. However, up to date, besides acting as the photoactive materials, the MOFs has been contributing to the photovoltaic community by serving as functional additives or interlayers to improve the performance and stability of the derived solar cell devices. In order to utilize MOFs for photoactive layer in photovoltaics, it is necessary to design electrically conductive MOFs. The research efforts developing more functional conducting MOFs are required in the coming decade.

5. Conclusions

Owing to synthetic processability using reticular chemistry, MOFs offer unusual properties paving the path for many opportunities and their use in optoelectronic devices. Their use in devices so far is limited to sensors and gas storage. However, MOFs field is moving towards exploring their optical and electrical properties to use in electronic devices. There are many MOFs with tunable bandgap, both ultralow-k and high-k dielectric constants, varied magnetic properties, luminescence, and a few with semiconducting behavior, suggesting MOFs as emerging material with unique properties exceeding any other class of materials. Combining the solvothermal synthesis method with self-assembly processes, we can achieve highly ordered nanoporous structures with precise dimensionality that creates the potential for electronics and self-assembly with atomic-scale resolution and precision. In order to become MOFs for electronic devices, many challenges must be solved, and electronic structures of MOFs should be revealed. The MOFs-device roadmap should be one meaningful way to reach MOFs milestones for optoelectronic devices and will enable MOFs to be performed in their best, as well as allowing the necessary integration with other materials to fabricate fully functional devices.

Acknowledgements

Conflict of interest

There is no conflict of interest to declare.

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