

# Semiconductor Metal–Organic Frameworks: Future Low-Bandgap Materials

Muhammad Usman, Shruti Mendiratta, and Kuang-Lieh Lu\*

Metal–organic frameworks (MOFs) with low density, high porosity, and easy tunability of functionality and structural properties, represent potential candidates for use as semiconductor materials. The rapid development of the semiconductor industry and the continuous miniaturization of feature sizes of integrated circuits toward the nanometer (nm) scale require novel semiconductor materials instead of traditional materials like silicon, germanium, and gallium arsenide etc. MOFs with advantageous properties of both the inorganic and the organic components promise to serve as the next generation of semiconductor materials for the microelectronics industry with the potential to be extremely stable, cheap, and mechanically flexible. Here, a perspective of recent research is provided, regarding the semiconducting properties of MOFs, bandgap studies, and their potential in microelectronic devices.

## 1. Introduction

Metal–organic frameworks (MOFs) represent a new class of crystalline inorganic–organic hybrid materials with uniform pore structures, high stability, and tunable metrics.<sup>[1–7]</sup> Due to these unique characteristics, MOFs have been exclusively studied for their applications in gas storage, sensing, chemical separations, catalysis, drug delivery, biomedical imaging, and as precursors for preparing carbon and metal oxides.<sup>[6,7]</sup> Similarly, the magnetic, optical, and ferroelectric behaviors of MOFs have been a topic of scientific interest for more than a decade.<sup>[8]</sup> These interests include the synthesis and design of new structural topologies, and the addition of more and more functionalities, expanding the dimensions of applications of MOFs very rapidly toward the electronics industry. The utilization of MOFs in electronics was first proposed by Allendorf and co-workers.<sup>[9]</sup> They provided a roadmap for the implementation of MOFs in microelectronics devices.<sup>[9,10]</sup> A few reports on the dielectric behavior of MOFs as interlayer dielectrics components for integrated circuit design have also appeared.<sup>[11]</sup> However, studies relating to the semiconducting behavior of MOFs are still in their initial stages, and further investigations are highly desired.<sup>[12]</sup>

Dr. M. Usman, Dr. S. Mendiratta, Prof. K.-L. Lu  
Institute of Chemistry  
Academia Sinica  
Taipei 115, Taiwan  
E-mail: kllu@gate.sinica.edu.tw

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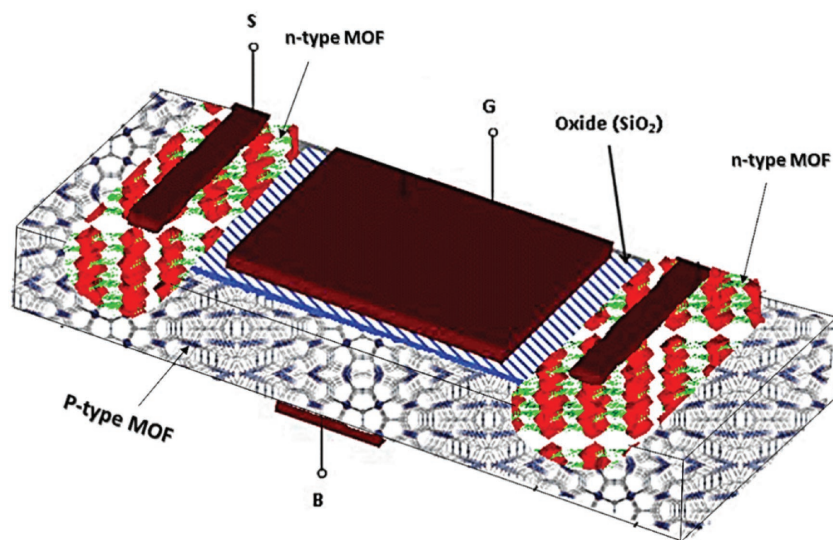
### 1.1. The Need for Novel Semiconductor Materials

Since the inception of the semiconductor industry, silicon (Si) and some III–V group metals have largely been used as semiconductors because of their unique properties, such as good mechanical strength, high thermal stability, and good compatibility with substrates and other related materials used.<sup>[13]</sup> However, the international technology roadmap for semiconductors (ITRS) proposed that, with the rapid development of ultralarge-scale integration (ULSI) technology, these traditional materials (e.g., Si, Ge, III–V compounds, SiC, GaAs, and GaN, etc.) have reached their functional limits. As stated in Moore's law,

the number of active devices on an integrated circuit (IC) has been exponentially increasing, approximately doubling every two years.<sup>[14]</sup> In order to keep pace with this advancing technology, the performance of ICs can be enhanced by increasing the transistor speed, or reducing the transistor size by packing more transistors onto a chip.<sup>[15]</sup> This decrease in size of the transistor is also associated with a decrease in the size of the interconnecting components. Therefore, the development of new semiconductor materials for industry applications is needed.<sup>[16]</sup> Organic polymers are currently being investigated as new semiconducting materials.<sup>[17]</sup> Some new techniques have also been introduced, which involve placing graphene (carbon-based material) on top of inorganic hexagonal boron nitride to incorporate a nonzero bandgap to the graphene, allowing it to function as a semiconductor.<sup>[18]</sup> Similarly in MOFs, the organic linker can impart semiconducting behavior to an inorganic node (the metal). The systematic design of transistors with semiconductor MOFs as an active component is drawn here for various integrated circuits (**Figure 1**). The presence of a functional organic component along with an inorganic counterpart, the easy tunability of the structural properties, and their multifunctionality make MOFs more versatile than organic or inorganic semiconductors for developing efficient semiconducting materials.<sup>[12]</sup> Experimental and theoretical investigations of MOFs as semiconductors are analyzed in this highlight.

## 2. Semiconducting MOFs

Metal–organic frameworks are generally considered to be poor conductors because the linking organic groups are mostly



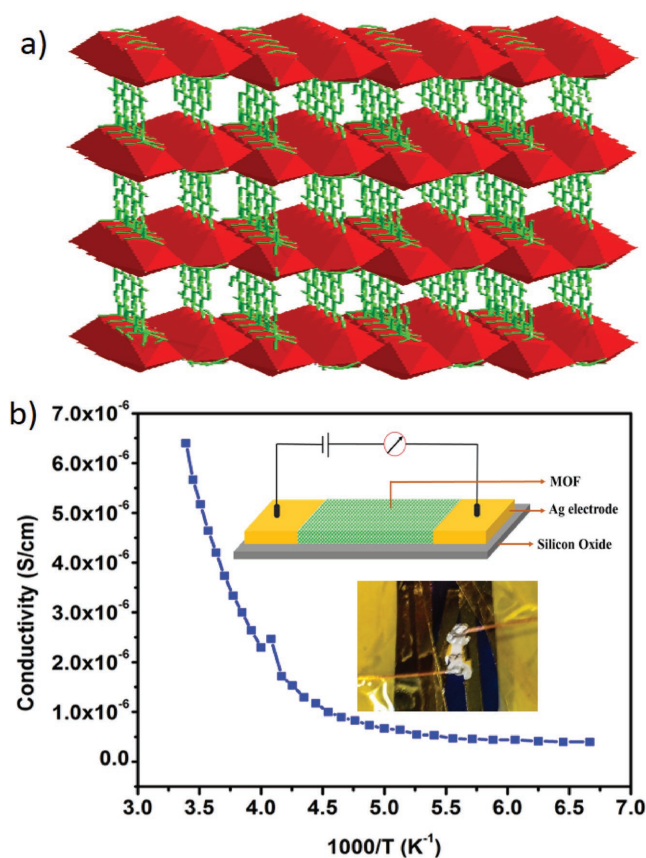
**Figure 1.** A systematic diagram showing MOFs as n- and p-type semiconductors for the design of metal-oxide-semiconductor field-effect transistor (MOSFET).

insulators with small  $\pi$ -orbital conjugation. However, following the roadmap for implementing MOFs in microelectronic devices by Allendorf, considerable efforts have been expended in recent years to incorporate electrical conductivity in MOFs.<sup>[9,10]</sup> There are some reports related to discovering the proton-conduction pathway in MOFs for battery applications. It has been reported that MOFs can provide proton-conducting behavior through well-designed pores and metal-oxide chain networks.<sup>[19]</sup> The highest proton conduction for MOFs has been reported to be around the order of  $10^{-2}$  S cm<sup>-1</sup> at 90% relative humidity and 85 °C.<sup>[20]</sup> Hydrogen-bonding interactions between the metallic bridges and water molecules in MOFs can also play important roles in proton conduction. However, solvent molecules can only support the proton conduction in MOFs, and do not provide much assistance in providing the electrical conductivity. In order to achieve electrical conduction paths in MOFs, Dinca et al. reported a new approach in which the oxygen atoms in metal–oxygen chains of existing MOFs were replaced isomorphically with sulfur atoms, thereby giving rise to infinite metal–sulfur chains with the potential to enable charge transport.<sup>[21]</sup> Later in 2013, Allendorf et al. established the tunable electrical conductivity in HKUST-1 thin films by incorporating a 7,7,8,8-tetracyanoquinodimethane (TCNQ) molecule inside the crystal framework.<sup>[22]</sup> High electrical conductivity has also been reported for Cu<sub>3</sub>(HITP)<sub>2</sub> (HITP = 2,3,6,7,10,11-hexaiminotriphenylene) and Ni<sub>3</sub>(HITP)<sub>2</sub>, where the crystal structures of these conducting 2D Cu- and Ni-based MOFs were found to be similar to that for semiconducting metal–organic graphene.<sup>[23]</sup> In progress toward the development of semiconductor MOFs, semiconductor@MOF core-shell structures were reported to have various properties. For example, Cu<sub>3</sub>(BTC)<sub>2</sub>@TiO<sub>2</sub> core-shell and ZnO@ZIF-8 nanorod structures were designed for photovoltaic applications.<sup>[24]</sup> It is believed that the semiconductor@MOFs heterostructures have promising applications in many electronic devices.

The semiconducting behavior of MOFs has been a topic of interest for the past several years. However, still, there are

only few reports regarding their intrinsic semiconductor properties, where most have only used Zn and Mg as metal nodes.<sup>[12a-c]</sup> Semiconductor Mn-based MOFs have been reported with activation energy  $E_a = 0.70 (\pm 0.03)$  eV.<sup>[12c]</sup> The semiconducting mechanism in the Mn-MOFs, [Mn( $\mu$ -Pz)( $\mu$ -Cl)<sub>2</sub>]<sub>n</sub> (Pz = pyrazine) was due to the delocalization and excitation of the  $\pi$ -electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the  $\pi$ -molecular orbitals.

Lu and co-workers also synthesized a 3D Sr-based semiconductor MOF (Figure 2).<sup>[25]</sup> In this case, the metal–organic network was designed using the s-block element strontium (Sr) as an inorganic node, which is naturally occurring as a nonradioactive element. The bandgap and semiconducting properties of the 3D Sr-based metal–organic framework {[Sr(Hbtc)(H<sub>2</sub>O)]}<sub>n</sub> (H<sub>3</sub>btc = 1,3,5-benzenetricarboxylic acid) were investigated. The Sr-MOF formed a 3D structure with the



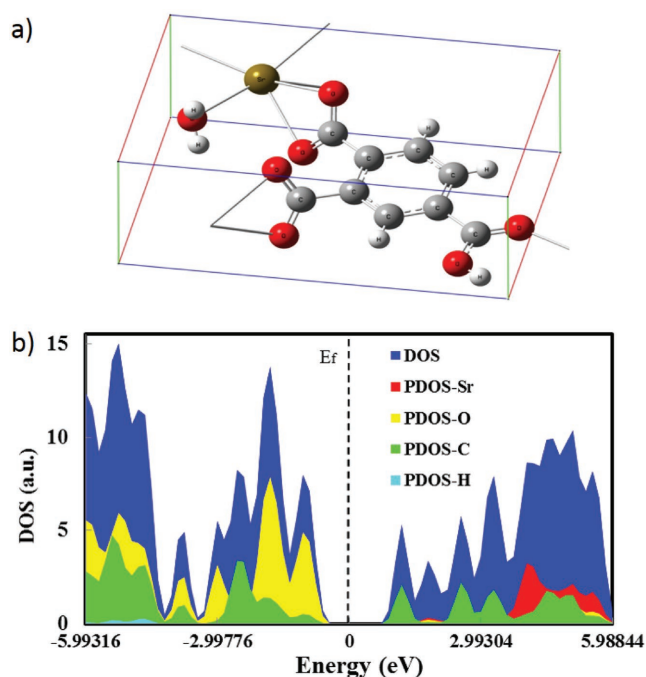
**Figure 2.** a) Three-dimensional layered structure of a Sr-based MOF connected through pillar ligands. b) Arrhenius plot for temperature-dependent DC conductivity. Schematic diagram and a photograph of a device designed using Sr-based MOF are shown as insets. Reproduced with permission.<sup>[25]</sup> Copyright (2015), American Chemical Society.

organic ligand functioning as a bridge between two metallic oxide layers (Figure 2a). The crystal structure of this MOF is quite similar to that of the famous semiconductor MoS<sub>2</sub>, with the advantageous support of an organic linker between the layers. The electrical conductivity of this compound was reported to be in the range of 10<sup>-6</sup> (S cm<sup>-1</sup>). Interestingly, the conductivity of the Sr-based MOF increases exponentially with annealing temperature, and the conductivity obeys an Arrhenius plot ( $\sigma$  vs 1/T), indicating its semiconducting transport behavior (Figure 2b). Temperature-dependent conductivity data indicated that a major part of the conductivity is due to the contribution of thermally generated carriers and a variable-range hopping mechanism. Alvaro et al. also reported the semiconductor behavior of the well-known MOF-5, having a bandgap of 3.4 eV.<sup>[12a]</sup> The photostability of the MOF-5 revealed that it was stable to light, and charge separation occurred upon the absorption of light on the ligand-to-metal charge-transfer band. Photogenerated delocalized electrons living in the microsecond time scale and capable of reducing the electron acceptors were observed by laser flash photolysis. Additional experimental evidence supporting the semiconducting behavior of MOF-5 was the oxidation of N,N,N',N'-tetramethyl-p-phenylenediamine to its corresponding radical cation by the generation of holes in the MOF-5. Moreover, the electrical properties suggest that the MOFs are suitable candidates for use as semiconductor materials for potential microelectronics applications.

### 3. Bandgap Investigation

As mentioned above, MOFs are generally considered to be insulating materials with a high bandgap. However, various simulation techniques have been applied in attempts to optimize their bandgap to the lower values that are required for semiconductors. MOFs are a type of hybrid crystalline material with both organic and inorganic components; hence, it is important to choose an appropriate simulation basis set, suitable for describing the electronic structure of the organic linkers, as well as for the metallic nodes. For most reported MOFs, density functional theory (DFT) has been applied to calculate the energy for the HOMO–LUMO levels for the periodic structure of the MOFs. In order to investigate the bandgap relationship with the crystal structure of the MOFs, MFU-4-type MOFs have been investigated.<sup>[12d]</sup> Volkmer et al. reported three techniques for engineering the bandgap of MOFs. It was proposed that increasing the conjugation of the linkers will lead to a higher valence-band (HOMO) energy; hence, the bandgap can be reduced. Selecting appropriate metal nodes at octahedral coordination sites with their unoccupied d-orbitals below the LUMO of the organic linker will also decrease the bandgap. In order to further control the bandgap, the organic linker can be modified with various functional groups (–NH<sub>2</sub>, –OH, –CH<sub>3</sub>, –Cl), which may donate 2p electrons to the aromatic linker, resulting in a band shift.<sup>[26]</sup> DFT calculations have shown that the bandgap for Zr–UiO-66 MOFs decreased from 3.1 eV to 2.2 eV when the benzenedicarboxylate (bdc) linker was functionalized by nitro (bdc–NO<sub>2</sub>) and amino (bdc–NH<sub>2</sub>) groups.<sup>[27]</sup>

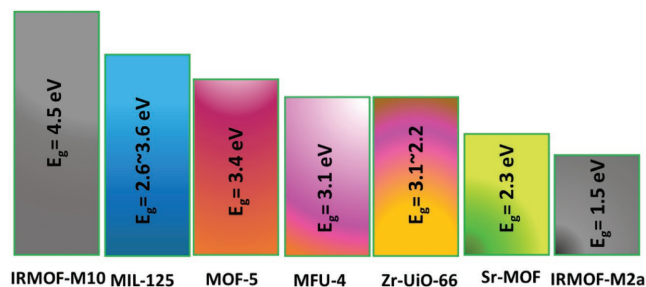
Lu et al. also investigated the theoretical data for a 3D semiconductor Sr-based MOF (Figure 3).<sup>[25]</sup> Starting with the



**Figure 3.** a) Optimized crystal structure of Sr-based MOF. b) Total (DOS) (blue area) and partial density of states (PDOS) (other colored area). The dashed line at zero energy represents the Fermi level ( $E_F$ ). Reproduced with permission.<sup>[25]</sup> Copyright (2015), American Chemical Society.

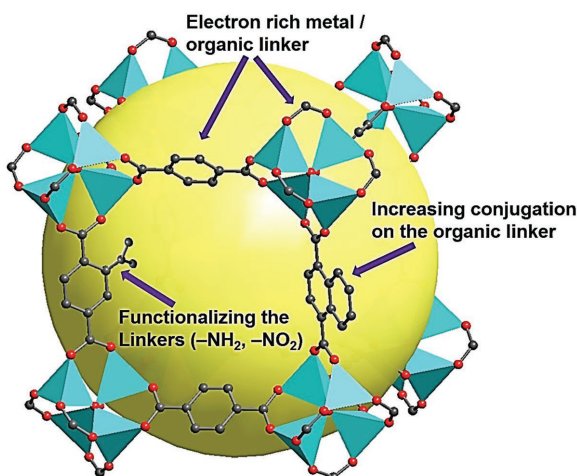
experimentally determined unit cells of the Sr-based MOF, DFT calculations were performed with generalized gradient approximations (GGA), as parameterized by Perdew, Burke, and Ernzerhof (PBE) for exchange-correlation functions and projector augmented-wave (PAW) potentials. The smallest bandgap was found to be indirect ( $\Gamma \rightarrow X$ ), between the  $\Gamma$  point in the valence band and the X point in the conduction band, being 2.04 eV (Figure 3).

The bandgap energy of the Sr-based semiconductor MOF was comparably lower than the reported values for MOF-5 ( $E_g = 3.4$  eV) and ZIF-8 ( $E_g = 5.5$  eV) and very close to the reported value for IRMOF-M2a.<sup>[12a,28]</sup> Bandgap comparisons are shown in Figure 4 for the reported semiconductor MOFs.



**Figure 4.** Bandgap comparison between some of the reported MOFs. IRMOF-10 = {M<sub>4</sub>O(L)<sub>3</sub>}, L = 4,4'-biphenyldicarboxylate; MIL-125 = {Ti<sub>8</sub>O<sub>8</sub>(OH)<sub>4</sub>(L)<sub>6</sub>}, L = 1,4-benzenedicarboxylate (bdc); MOF-5 = {Zn<sub>4</sub>O(1,4-benzenedicarboxylate)<sub>3</sub>}; MFU-4 = {M<sub>2</sub>Zn<sub>4</sub>(L)<sub>4</sub>(L')<sub>6</sub>}, (M = Co(II) or Zn; L = chloride or acac; L' = 1,2,3-benzotriazole); Zr–UiO-66 = {Zr<sub>6</sub>O<sub>6</sub>(OH)<sub>4</sub>(L)<sub>12</sub>}, L = 1,4-benzenedicarboxylate; Sr–MOF = {Sr(L)(H<sub>2</sub>O)<sub>n</sub>}, L = 1,2,4-benzenetricarboxylate.





**Figure 5.** Systematic diagram for reducing bandgap by adjusting the energy levels in MOF-5 type semiconductors.

From the current research on semiconductor MOFs, it can be concluded that to achieve an efficient semiconductor MOF, the bandgap can be decreased by: i) increasing the conjugation in the linker, ii) selecting electron-rich metal nodes and organic molecules, and iii) functionalizing the linker with nitro and amino groups (Figure 5).

#### 4. Challenges and Prospects

As discussed above, experimental results and theoretical calculations provide strong evidence to show that MOFs might be a suitable choice for use as new semiconductor materials in microelectronics. However, the integration of semiconductor MOFs in active devices is at a very early stage of development. The fundamental issues of MOFs related to thin-film fabrication, contact formation, controlling leakage current, and circuit design need to be addressed. Recently, comparable technologies have become available for growing thin films of MOFs on various substrates. Current advancements in the research area of MOF thin-film growth permit MOFs to be used as an active electronics component. Then come issues related to device integration, such as compatibility between MOF-related processing and substrate materials, followed by the development of interfacial layers to enhance MOF adhesion. Hence, with the tunability of the structural properties, having the advantageous properties of both organic and inorganic components, and multifunctionality, MOFs will be a better replacement for traditional semiconductor materials in the microelectronics industry. The incorporation of metal–sulfur chains and certain confined molecules, such as TCNQ, might provide a means to achieve charge transfer and enhance conductivity. Bandgap engineering can be performed by structure modification by increasing the conjugation in the linker, the appropriate functionalization of organic linkers and through suitable metal selection. Furthermore, given that the chemical and electronic properties of MOF-based materials differ considerably from those of classical semiconductors, gaining an in-depth understanding of the electron-transport mechanisms of MOF-based semiconductors

may offer new avenues. MOFs as semiconductors would permit new types of industrial materials to be synthesized, for use in photovoltaic devices, solar cells, electroluminescent devices, field-effect transistors, and sensors. The foregoing results discussed in this article will provide an effective pathway toward remarkable applications of MOFs as semiconductors for the fabrication of microelectronics devices in the future.

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