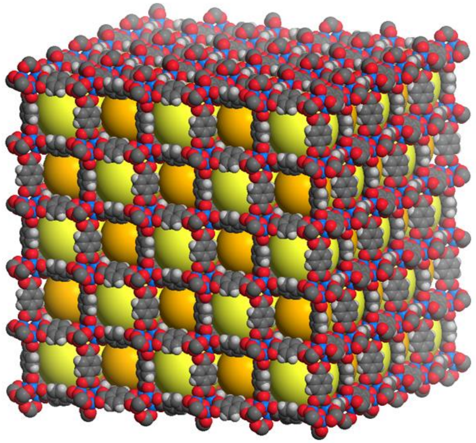
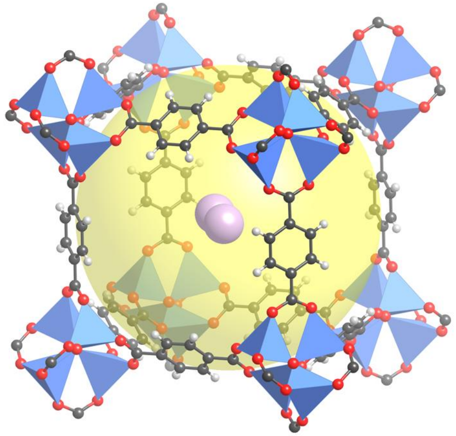
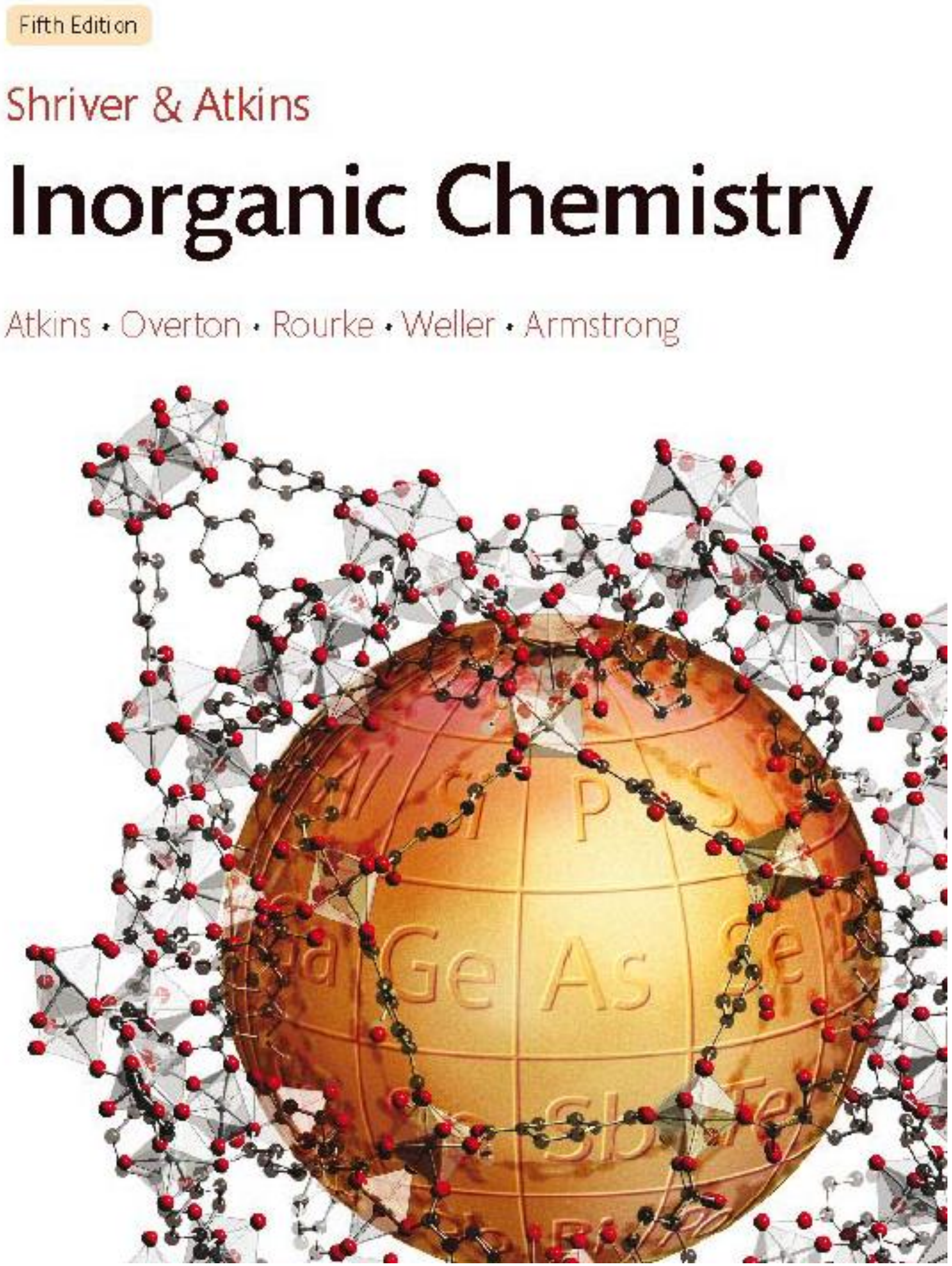
Metal Organic Frameworks



Tony Francis
Assistant Professor
Department of Chemistry
St. Mary's College, Manarcaud



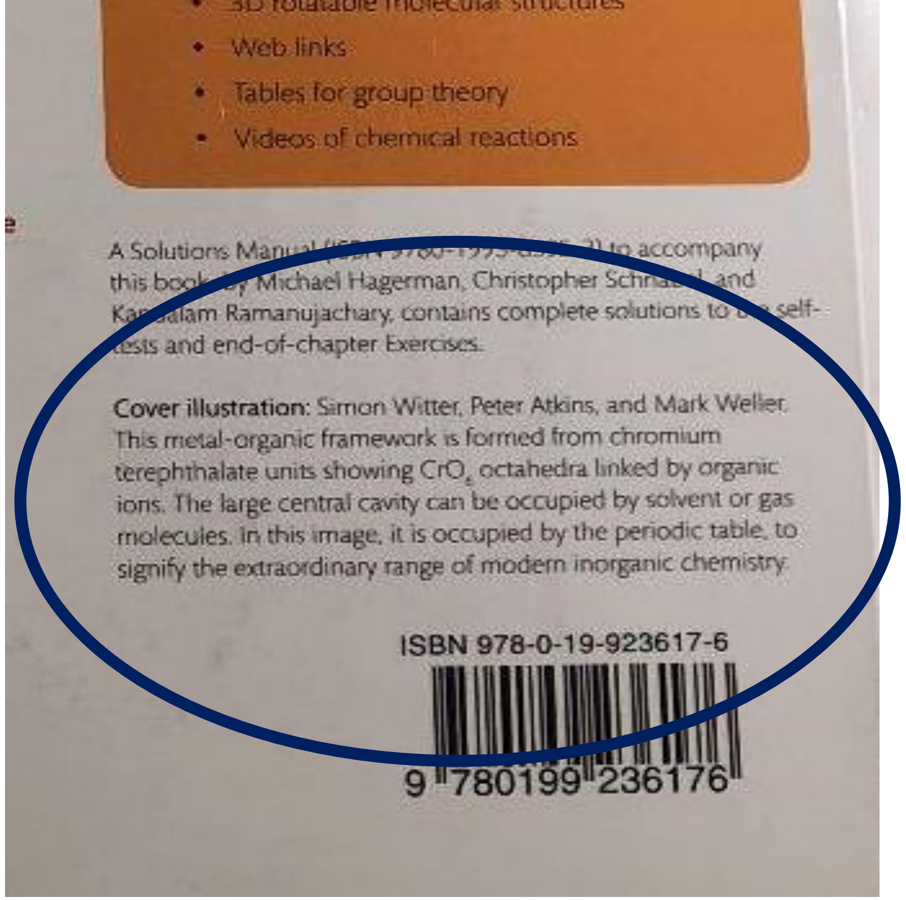


Fifth Edition

Shriver & Atkins

Inorganic Chemistry

Atkins • Overton • Rourke • Weller • Armstrong



- 3D rotatable molecular structures
- Web links
- Tables for group theory
- Videos of chemical reactions

A Solutions Manual ([illegible]) to accompany this book by Michael Hagerman, Christopher Schn[illegible] and Ka[illegible]alam Ramanujachary, contains complete solutions to [illegible] self-tests and end-of-chapter Exercises.

Cover illustration: Simon Witter, Peter Atkins, and Mark Weller. This metal-organic framework is formed from chromium terephthalate units showing CrO_6 octahedra linked by organic ions. The large central cavity can be occupied by solvent or gas molecules. In this image, it is occupied by the periodic table, to signify the extraordinary range of modern inorganic chemistry.

ISBN 978-0-19-923617-6

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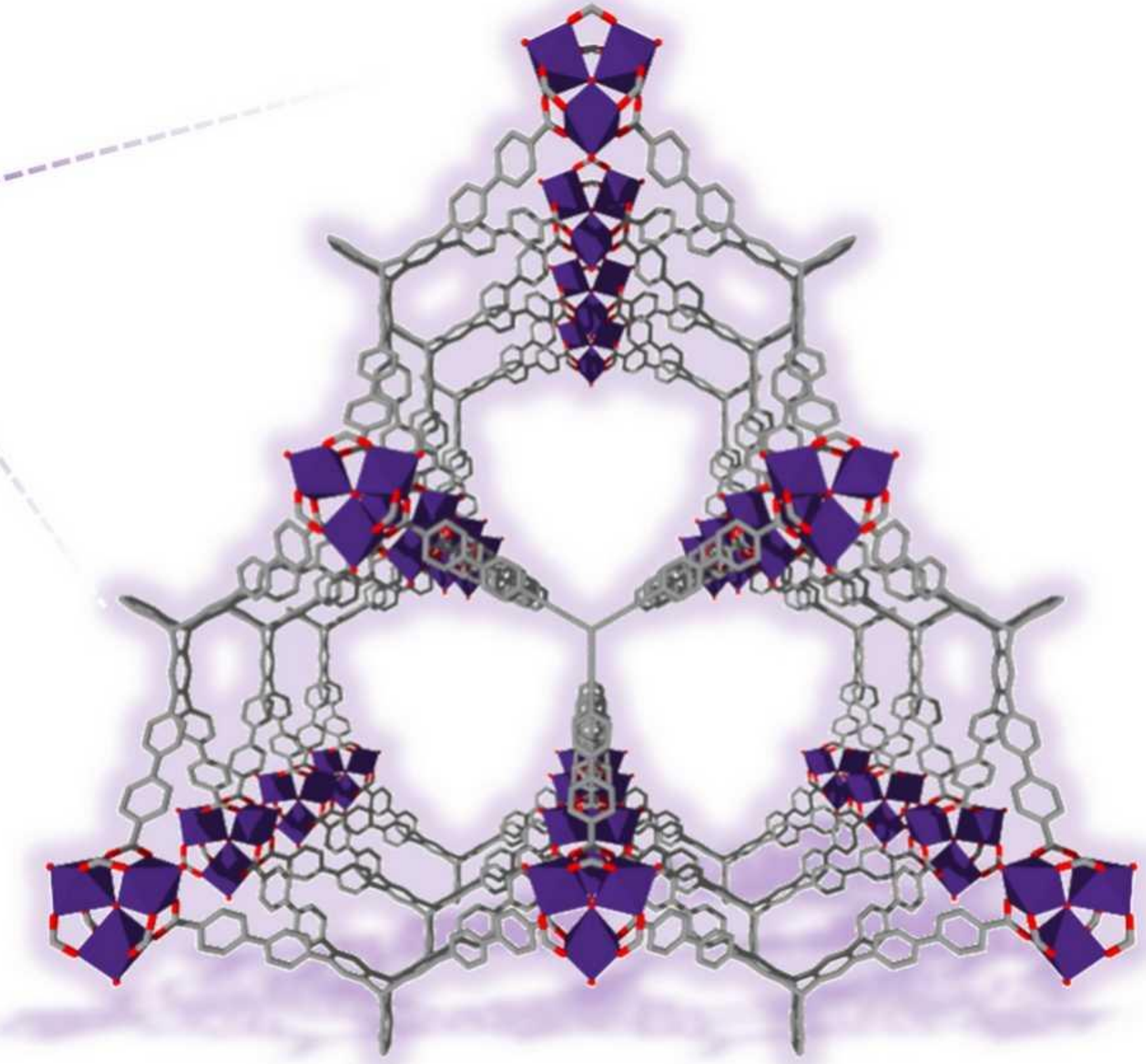
The metal organic framework (MOF), a crystalline compound, looks like simple table salt. It actually has the highest internal surface area of any known substance on the planet; If unfolded, a single MOF could cover a football field. It’s also the most porous material known to man. These are qualities that could make MOFs the key to better hydrogen cars and carbon capture and storage technology in the future.

≡

Volume of six M&M



Surface area = $7310\ m^2/g$ = 1.3 football field

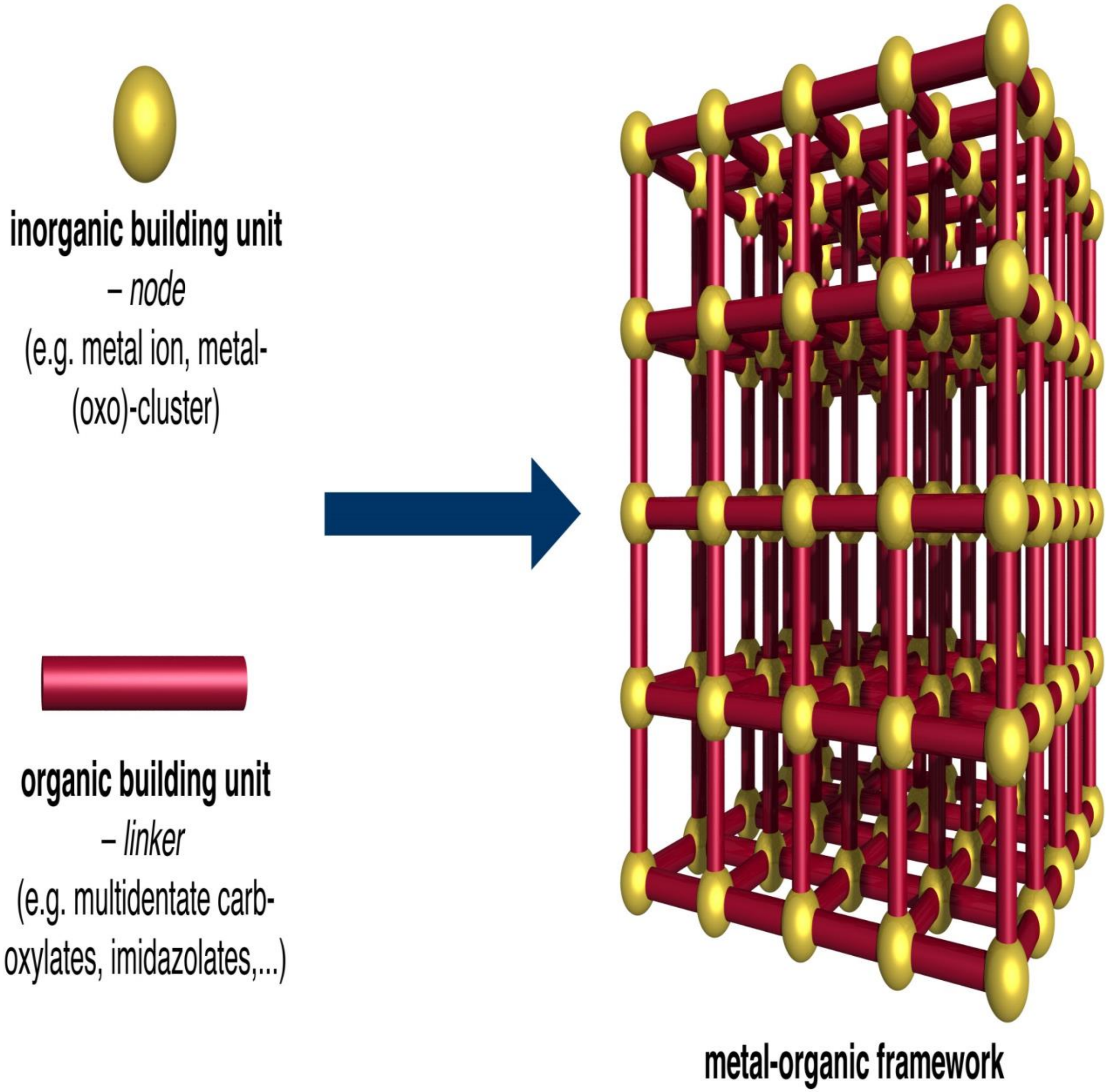
Metal organic Frameworks

- ❑ Metal-organic frameworks (MOFs) or coordination polymers are a class of porous polymeric material, consisting of metal ions linked together by organic bridging ligands through coordination bonds.
- ❑ MOFs have attracted tremendous attraction over the past years owing to their excellent properties including ultrahigh porosity with enormous surface areas and tunable pore size, shapes and functionalities.

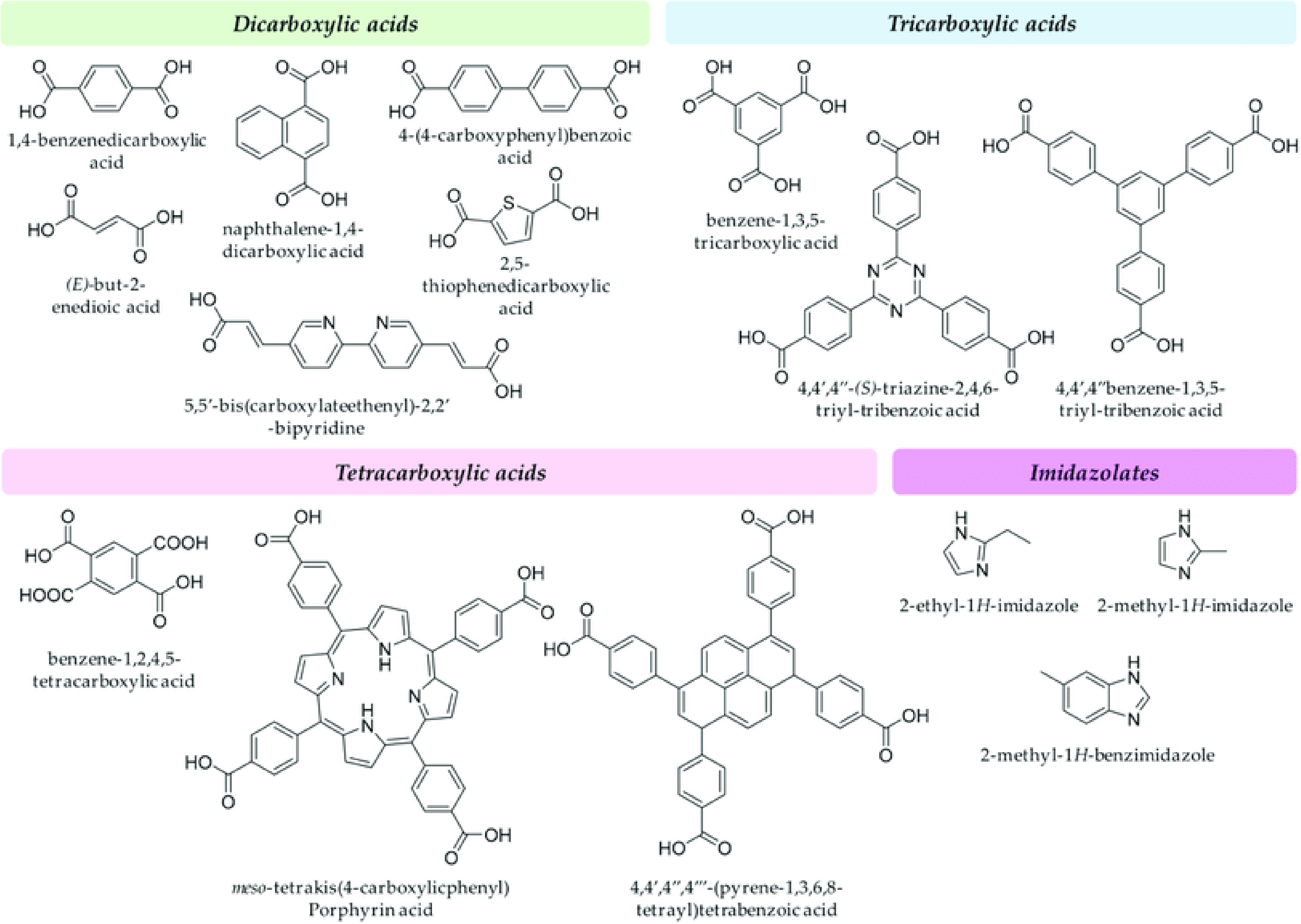
A metal-organic framework (MOF) material can be thought of as the composition of two major components: a metal ion (or cluster of metal ions) and an organic molecule called a linker (or bridging ligands)

Metal ions + Organic units (linkers/bridging ligands) ⟶ Coordination polymers or MOF materials

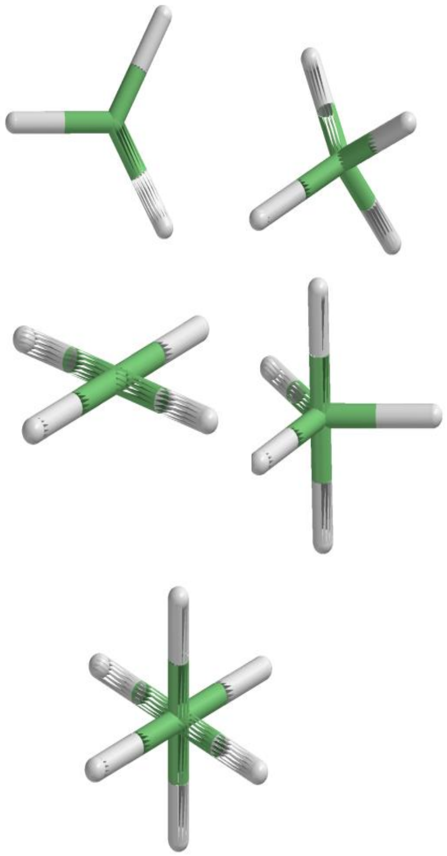
The organic ligands or linkers are groups that can donate multiple lone pairs of electrons (polydendate) to the metal ions, whereas the metal ions are made up with vacant orbital shells that can accept these lone pairs of electrons to form a metal-organic framework material.



Common Ligands Used in the synthesis of MOF



Metal centre or cluster (inorganic part)

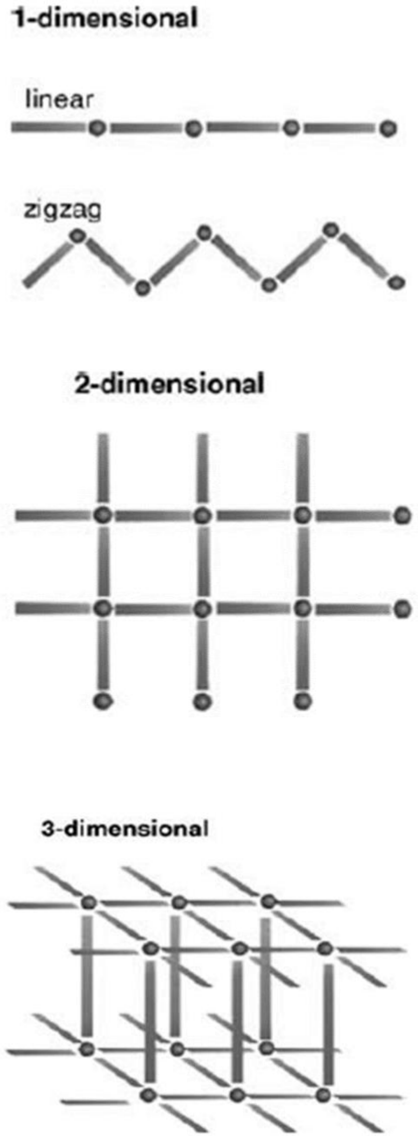


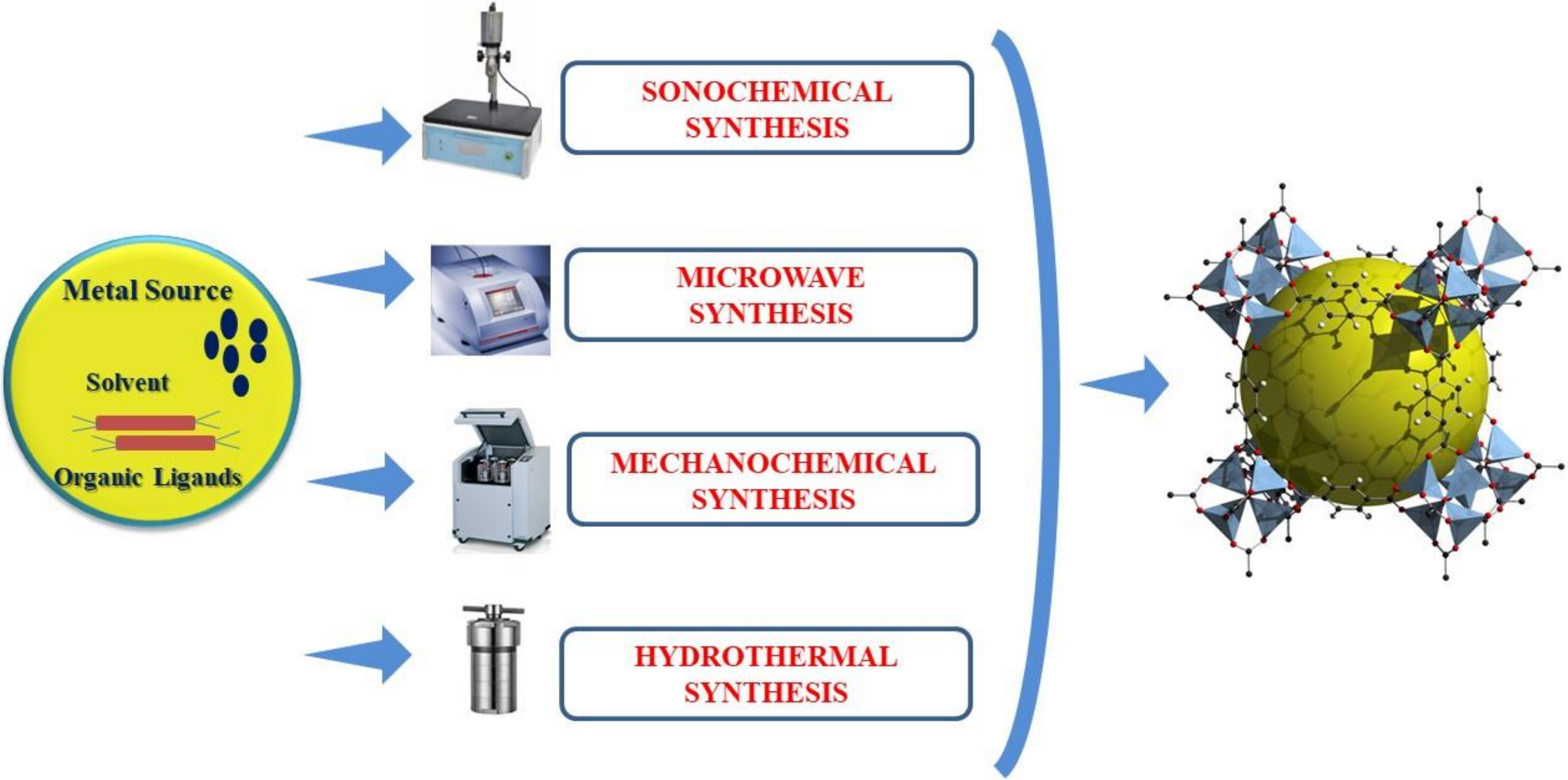
+

Linker (organic part)

→

Metal Organic Framework (coordination polymer)





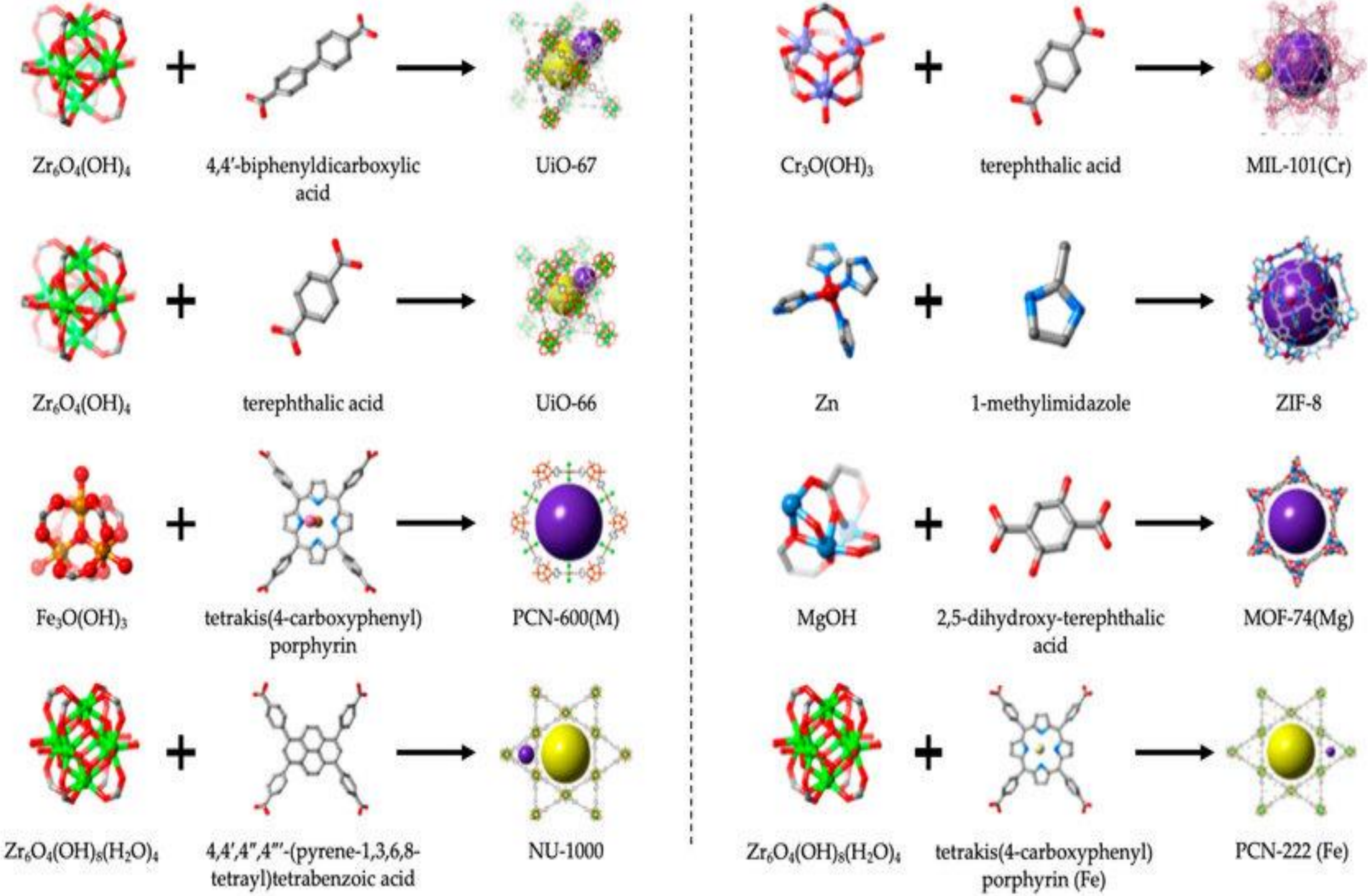
SONOCHEMICAL SYNTHESIS

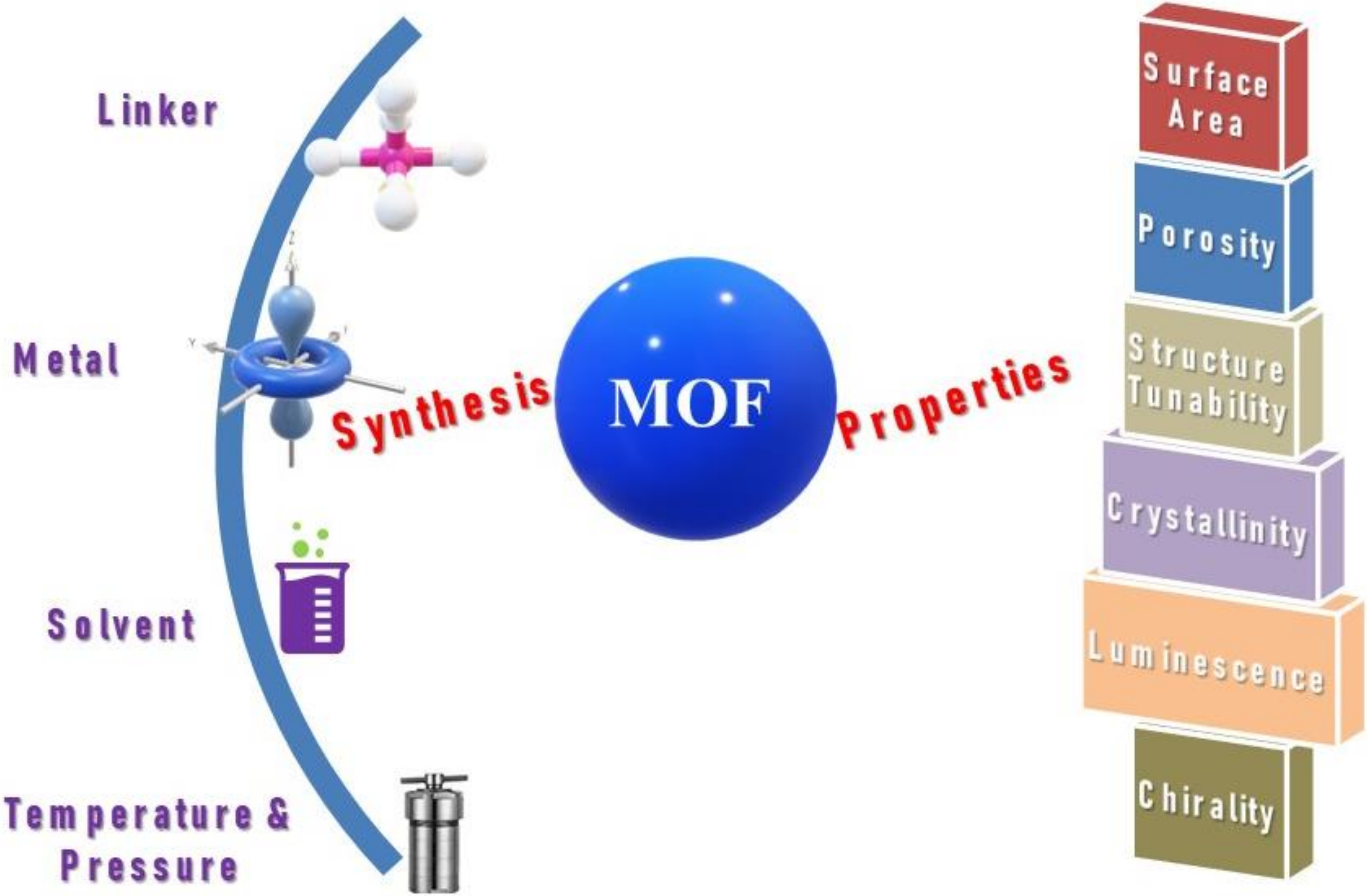
MICROWAVE SYNTHESIS

MECHANOCHEMICAL SYNTHESIS

HYDROTHERMAL SYNTHESIS

Some Famous MOFs





Linker

Metal

Solvent

Temperature & Pressure

Synthesis

MOF

Properties

Surface Area

Porosity

Structure Tunability

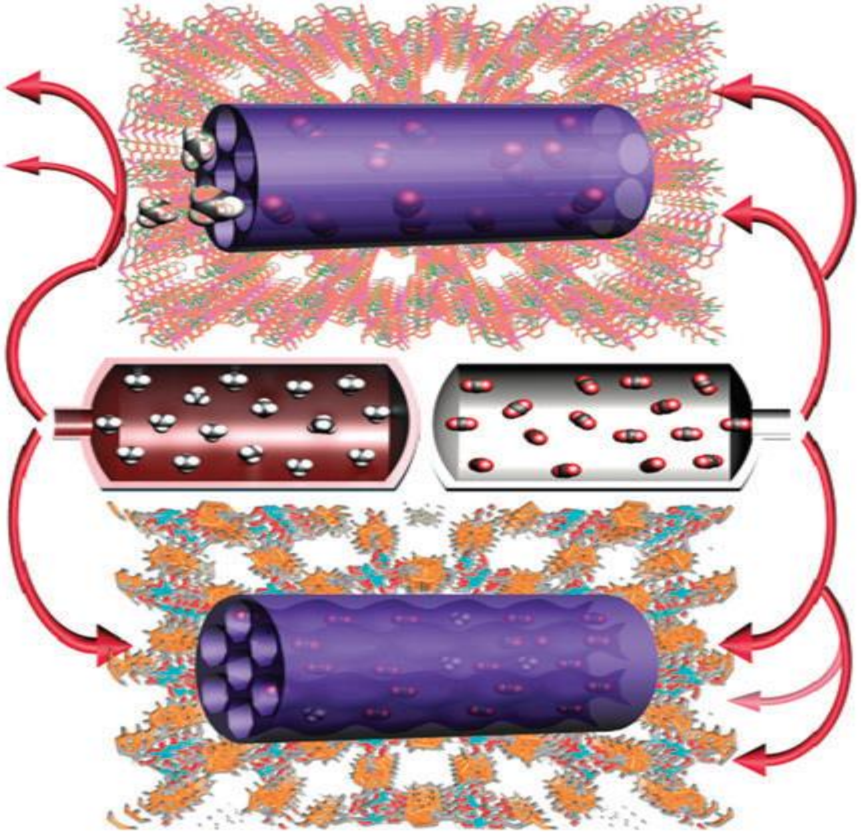
Crystallinity

Luminescence

Chirality

Applications of MOFs

- Gas storage
- Heterogeneous catalysis.
- Gas purification
- Light emitting device
- Gas separation
- Luminescent Sensors
- Drug Delivery
- Catalysis



Historical developments in MOF chemistry

- 1965 : Birth year of MOF
- 1990: Interest in porous coordination polymers & MOFs
- 1995 : The term MOF was popularized by Omar Yaghi
- 1997: 3D Mof was reported by Kitagawa
- 1999 : Synthesis of MOF 5 & HKUST-1
- 2002 : The concept of Isoreticular chemistry.

MOFs are a class of porous materials composed of metal nodes and organic linkers. Their modular nature allows for great synthetic tunability, affording both fine chemical and structural control. With creative synthetic design, properties such as porosity, stability, particle morphology, and conductivity can be tailored for specific applications. . MOFs are promising materials for many different applications, such as gas storage and separation, environmental conservation, heterogeneous catalysis, luminescent materials and biomedical materials. Since the emergence of several representative MOF compounds such as MOF-519 and HKUST-1,20 more than 20 000 MOF structures have been reported and studied to date. Due to the extraordinarily large extent of variability of both metal-containing units and organic linkers, it appears that an inexhaustible amount of MOFs could theoretically be designed and synthesized

The two main components of MOF are metal centers and organic linkers which are connected to each other by coordination bonds to form a network topology .These porous materials can be classified into three types namely one dimensional (1D), two dimensional (2D), three dimensional (3D) MOFs depending on the connectivity and geometry of metals and ligands in space . The ligands used for the synthesis of MOF should be rigid, planar & symmetrical . Symmetrically substituted organic ligands are usually preferred because crystal growth can occur in a more uniform & symmetrical fashion . MOF can be synthesized by various methods like electrochemical methods, microwave methods, sonochemical methods and hydrothermal methods . The high porosity and enormous internal surface area of MOFs, together with extraordinary degree of variability for both the organic and inorganic components of the structures, make MOFs a subject of interest for potential applications in clean energy . More significantly, these are interesting storage media for gases such as hydrogen and high capacity adsorbents to meet various separation and catalysis needs

Metal Organic Frameworks by Post-Synthetic Modification (PSM)

Post-synthetic modification (PSM) of metal–organic framework (MOF) compounds is a useful technique for preparing new MOFs that can exhibit or enhance many of the properties of the parent MOFs. PSM can be carried out by a number of approaches such as modifying the linker (ligand) and/or metal node, and adsorption/exchange of guest species. The surface environment of the MOF can be modified to increase structural stability as well as introducing desired properties. There is considerable scope in widening the applications of the MOF with compatible metal or ligand employing the PSM.

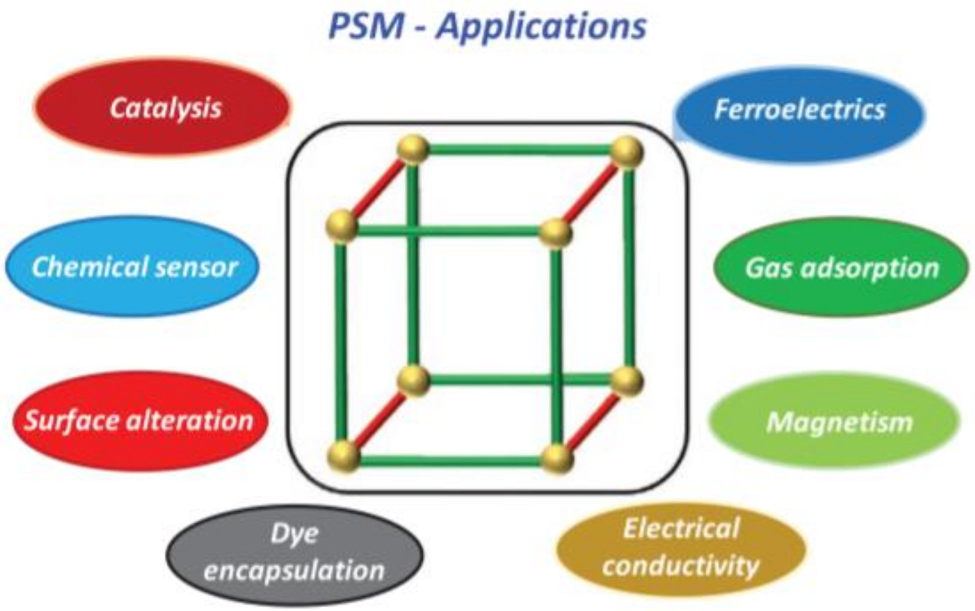
PSM of MOFs is a significant area of research which demands a careful approach to the design and execution of various methods . It is a promising and widely used strategy for generating novel scaffolds exhibiting improved properties compared to the parent frameworks. The principal aspect of this technique lies in the fact that the developed frameworks are mostly unattainable through de novo synthesis. It is also to be noted that the outcome can be controlled to an extent which is not at all possible for the conventional synthesis process.

The new chemical and physical properties installed in the MOFs by the change in their chemical composition have opened novel opportunities in exploiting numerous areas of application

The post-synthetic treatments, generally, result without altering the original topology and structure of the compound via a single crystal to single-crystal (SCSC) transformation. MOF materials are particularly attractive for the PSM due to two factors:

i) the labile nature of the coordination bonds between the metal and the ligand units, which is helpful for the metal ions in the bond detachment from the parent ligand in the framework as well as the bond formation with the incoming ligands,

ii) the porous nature and the accessibility of guest molecules to the framework, which determines stability of parent MOFs toward PSM.



Diverse fields of applications of post-synthetically modified MOFs.

- **Metal-Based Modification**

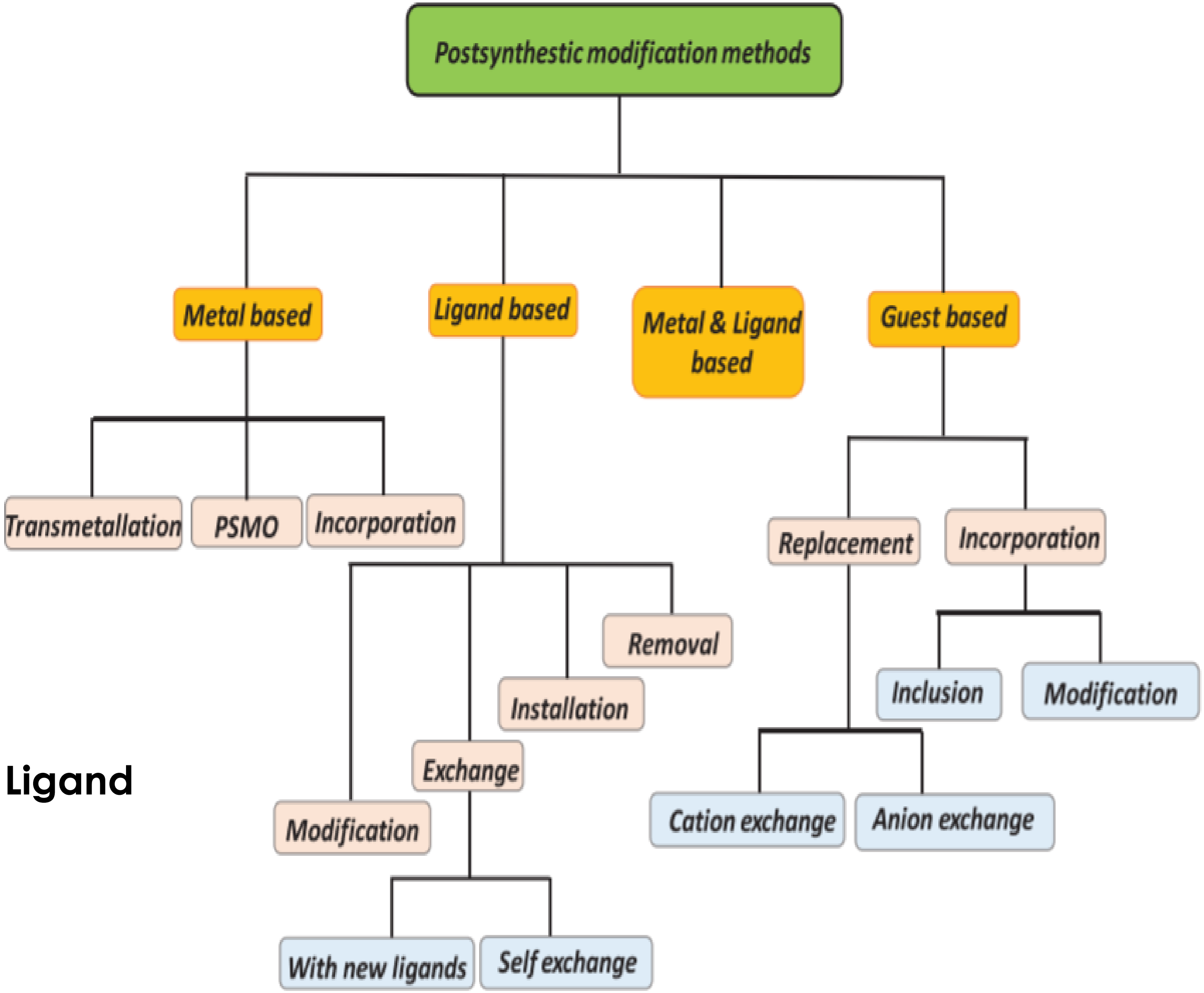
Transmetalation (Metal Exchange)
Epitaxial Growth on the Surface
Metal Incorporation (Metal Doping)
Metal Exchange Followed by Oxidation

- **Ligand-Based PSM in MOFs**

Ligand Modification in MOFs
Ligand Exchange in MOFs
Ligand Installation
Ligand Removal/Ligand Labilization

- **Simultaneous Exchange of Metal and Ligand**
- **Guest-Based PSM in MOF**

Guest Replacement



Metal exchange

Post-synthetic modification techniques can also be used to exchange an existing metal ion in a prefabricated MOF with a new metal ion by metal ion exchange. The complete metal metathesis from an integral part of the framework has been achieved without altering the framework or pore structure of the MOF. Similarly to post-synthetic ligand exchange post-synthetic metal exchange is performed by washing prefabricated MOF crystals with solvent and then soaking the crystal in a solution of the new metal. Post-synthetic metal exchange allows for a simple route to the formation of MOFs with the same framework yet different metal ions.

Ligand exchange

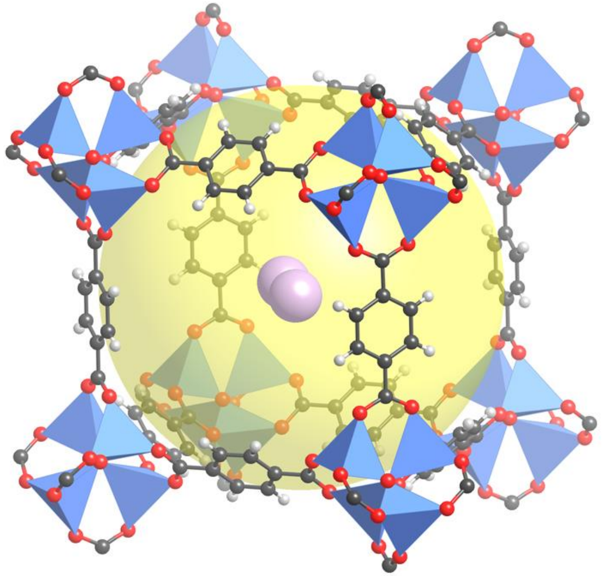
Post-synthetic modification techniques can be used to exchange an existing organic linking group in a prefabricated MOF with a new linker by ligand exchange or partial ligand exchange. This exchange allows for the pores and, in some cases the overall framework of MOFs, to be tailored for specific purposes. Some of these uses include fine-tuning the material for selective adsorption, gas storage, and catalysis. To perform ligand exchange prefabricated MOF crystals are washed with solvent and then soaked in a solution of the new linker. The exchange often requires heat and occurs on the time scale of a few days. Post-synthetic ligand exchange also enables the incorporation of functional groups into MOFs that otherwise would not survive MOF synthesis, due to temperature, pH, or other reaction conditions, or hinder the synthesis itself by competition with donor groups on the loaning ligand.

Characterization

- FT-IR, UV-Visible, P-XRD
- CHN analysis, PL spectra, TGA
- SEM and TEM
- Single crystal XRD
- Computational methods
- BET surface area analyser

Gas Storage

With appropriate framework design, many MOFs possess surface area and pore volume much larger than conventional adsorbents such as activated carbons and zeolites, which imply that MOFs are promising materials for gas storage. Nevertheless, the adsorbent is potentially useful only when its adsorption amount is larger than that of an empty container. For example, MOFs with large pore volumes can always adsorb very large amounts of nitrogen gas at 77 K, but it is not useful because an empty container can store more liquid nitrogen at 77 K, or a gas cylinder working at above 100 bar can easily store much gaseous nitrogen at room temperature. Similarly, MOFs may adsorb more CO2 than an empty cylinder at room temperature at the low pressures, but they are not considered as good CO2 storage medium because CO2 can be liquefied easily without excess pressurization.



Carbon capture

Because of their small, tunable pore sizes and high void fractions, MOFs are a promising potential material for use as an adsorbent to capture CO_2 . MOFs could provide a more efficient alternative to traditional amine solvent-based methods in CO_2 capture from coal-fired power plants.

MOFs could be employed in each of the main three carbon capture configurations for coal-fired power plants: pre-combustion, post-combustion, and oxy-combustion. In post-combustion carbon capture, the flue gas from the power plant would be fed through a MOF in a packed-bed reactor setup. Flue gas is the gas exiting to the atmosphere via a flue, which is a pipe or channel for conveying exhaust gases from a fireplace, oven, furnace, boiler or steam generator. Quite often, the flue gas refers to the combustion exhaust gas produced at power plants.

In carbon capture and storage (CCS) facilities, which capture carbon dioxide from polluting plants (i.e. coal-fired power plants) and store it, a significant amount of energy is wasted trying to catch CO2. Instead of simply capturing all the greenhouse gas, CCS facilities first have to chemically separate CO2 from gases like nitrogen and water vapor that also get spewed into the air.

It is generally 40 to 60 °C with a partial pressure of CO_2 at 0.13 - 0.16 bar. CO_2 can bind to the MOF surface through either physisorption, which is caused by Van der Waals interactions, or chemisorption, which is caused by covalent bond formation. Once the MOF is saturated with CO_2, the CO_2 would be removed from the MOF through either a temperature swing or a pressure swing. This process is known as regeneration. In a temperature swing regeneration, the MOF would be heated until CO_2 desorbs. To achieve working capacities comparable to the amine process, the MOF must be heated to around 200 °C. In a pressure swing, the pressure would be decreased until CO_2 desorbs.

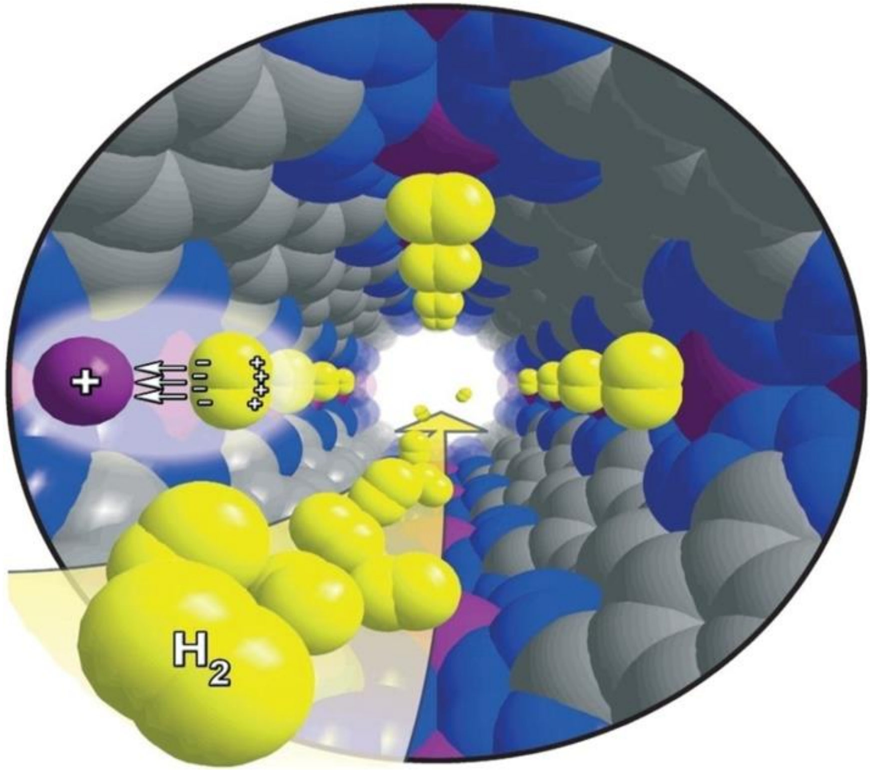
In addition to their tunable selectivities for different molecules, another property of MOFs that makes them a good candidate for carbon capture is their low heat capacities. Monoethanolamine (MEA) solutions, the leading method for capturing CO_2 from flue gas, have a heat capacity between 3-4 J/g K since they are mostly water. This high heat capacity contributes to the energy penalty in the solvent regeneration step, i.e., when the adsorbed CO_2 is removed from the MEA solution. MOF-177, a MOF designed for CO2 capture, has a heat capacity of 0.5 J/g K at ambient temperature.

In a collaborative project sponsored by the U.S. DOE, MOFs were shown to separate 90% of the CO_2 from the flue gas stream using a vacuum pressure swing process. The MOF Mg(dobdc) has a 21.7 wt% CO_2 loading capacity. Estimations showed that, if a similar system would be applied to a large scale power plant, the cost of energy would increase by 65%, while a U.S. NETL baseline amine-based system would cause an increase of 81% (the U.S. DOE goal is 35%). The cost of capturing CO_2 would be \$57 / ton CO_2 captured, while for the amine system the cost is estimated to be \$72 / ton CO_2 captured. The project estimated that the total capital required to implement such project in a 580 MW power plant would be \$354 million.

MOFS USED AS HYDROGEN STORAGE MATERIALS

In the past few decades, global dependency on the fossil fuel energy has caused tremendous ecological crisis. Nowadays, worldwide interest is focused on using a clean burning substitute for fossil fuels, due to both economic and environmental reasons. Among the various alternative energy strategies, utilizing hydrogen energy is a promising method due to its high efficiency, reversibility and environmental-friendliness. Hydrogen is a promising clean carrier for storage, transportation and conversion of energy in the 21st century.

However, the storage of hydrogen in a safe and economical manner is considered to be a bottleneck in the application of an on-board power supply. The storage of this lightweight fuel is one of the most important challenges impeding its practical application, which calls for storing and releasing hydrogen in the proper capacity and condition with fast kinetics and favorable reversibility. The US Department of Energy 2010 targets (revised in 2009 Feb.) for a hydrogen storage system are: a capacity of 4.5 wt% and 28 g H_2/L, a lifetime of 1000 cycles at ambient conditions; The 2015 targets are: a capacity of 5.5 wt% and 40 g H_2/L, a lifetime of 1500 cycles.

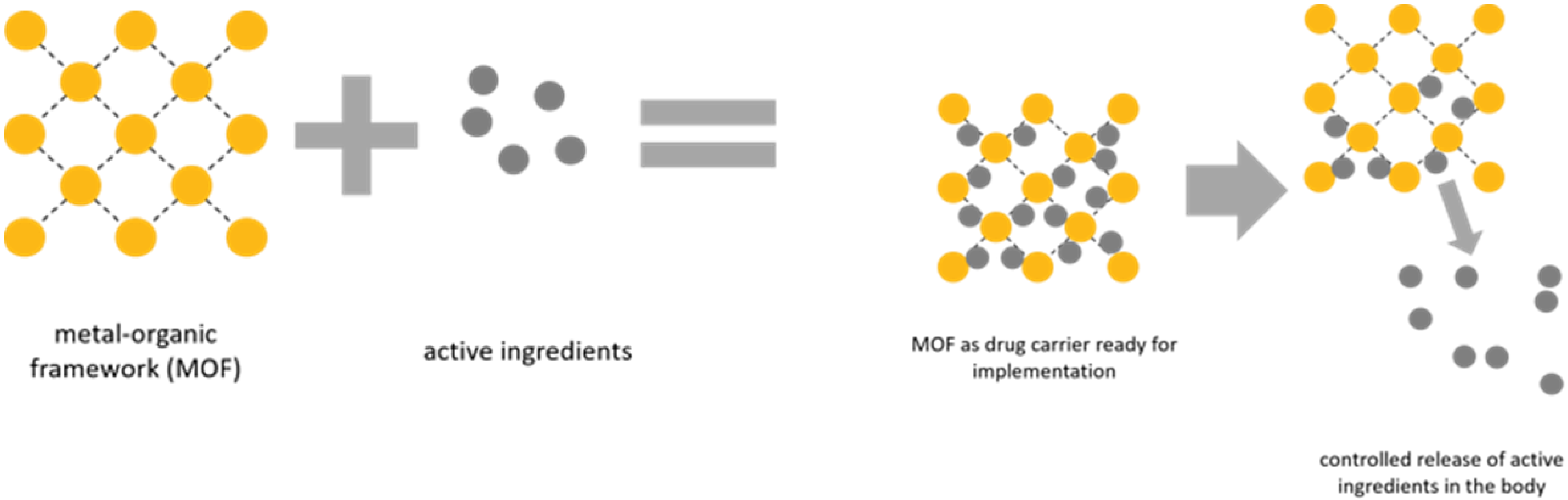


By far, there exist mainly two kinds of hydrogen storage materials. One of them is storage based on chemisorption, including metal hydrides and complex hydrides. The other kind is based on physisorption, including active carbon, zeolites and metal organic frameworks (MOFs). The chemisorption materials, such as magnesium, usually have large hydrogen storage capacities but show bad reversibility and weak kinetic properties. While the Physisorption materials is another significant approach for storing hydrogen. Comparing with the chemisorption materials, the physisiorption materials show rapid kinetic properties and excellent reversibility at low temperatures because of the weak interaction between hydrogen molecules and the materials. Physisorption on large surface area materials is considered as a promising approach for storing hydrogen. Furthermore, comparing with other porous materials such as zeolites and active carbon, some MOFs (Metal-organic frameworks) show promising results for hydrogen adsorption at low temperatures under appropriate pressures.

The low framework density, the high specific surface area, especially the controllable crystal structure have made MOFs be a favourable research interest. By crystal engineering[7], both the pore size and the electronic and chemical nature of the interior surface, on which H_2 molecules will be adsorbed, can be modified by careful designs.

Drug Delivery

Drug delivery (DD) is gaining enormous applauses from every corner of the medical world because of its controlled, localized delivery of drugs, which, not only increased the efficiency of the treatment but also reduces the side effects. NMOFs are scale-down materials obtained from metal organic framework (MOFs), and are self-assemblies of metal ions as coordination centers and organic ligands, which act as linkers between the metal centers. These hybrid nano materials comprising the properties of both organic and inorganic systems open a new pathway in the biomedical fields, especially for drug delivery. They are able to provide biocompatibility and high capacity of drug uptake due to the presence of organic groups such as carboxylates, imidazolates, amines, sulfonates, pyridyl, phenolates, phosphonates and the controlled drug release was achieved by the presence of inorganic moieties. They serve as excellent nano-carriers for the delivery of imaging contrast agent, chemotherapeutics and retroviral drugs. The incorporation of bio-medically relevant materials into NMOFs mainly involves two common methods or strategies: direct incorporation during NMOFs

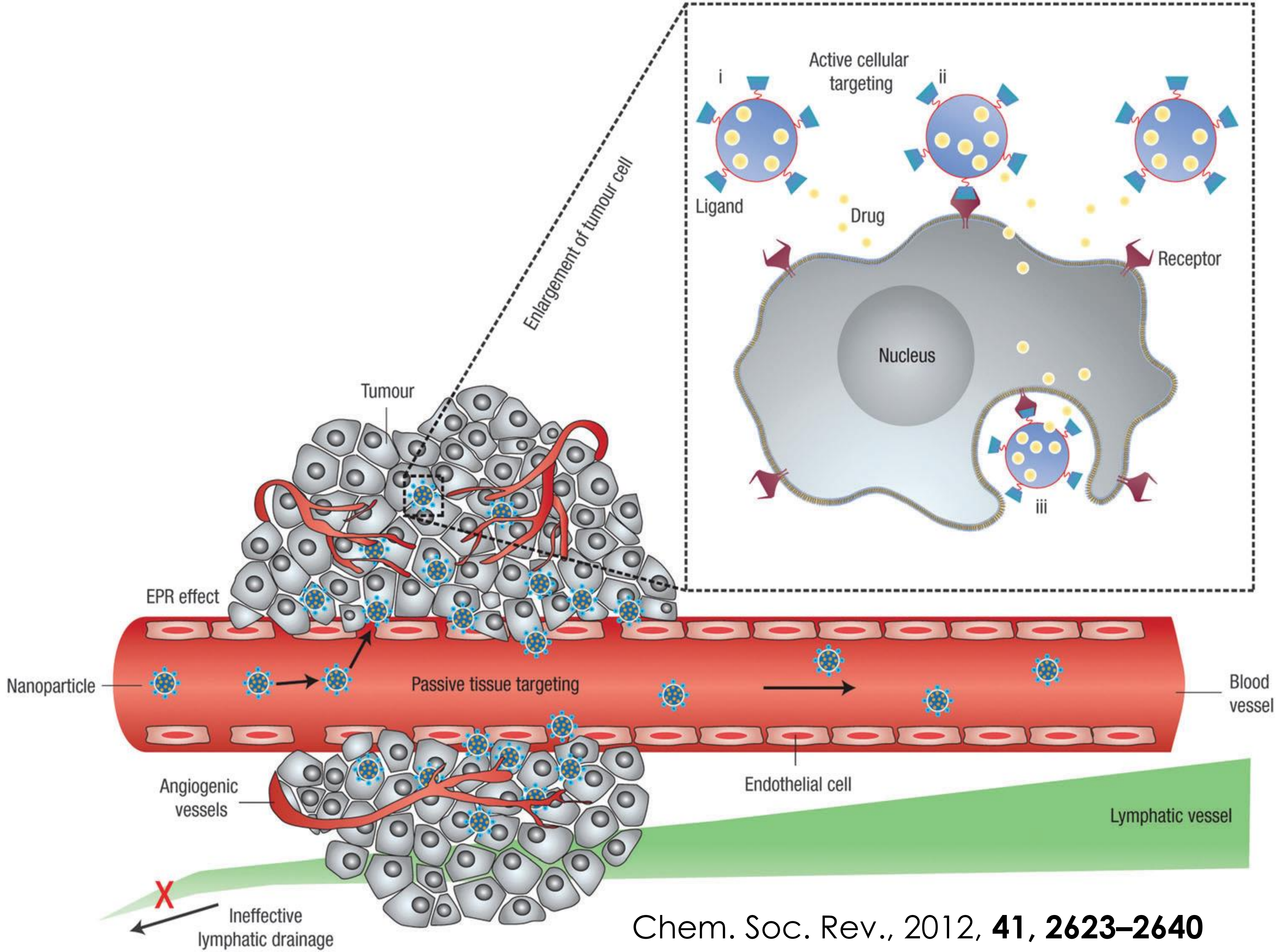


synthesis and the second method is by entrapping the active molecule into the NMOF pores by post-synthetic loading. The first one involves direct incorporation of bio-molecules like proteins, peptides etc. as a constituent part of the frameworks, these MOFs are also known as Bio-MOFs (Bioactive Metal Organic Frameworks) . In this method, by assembling bio-medically relevant agents like these metal ions (Gd^{3+}, Fe^{2+}, Fe^{3+}, Zn^{2+} etc.) with bridging ligands to form NMOFs and the delivery was achieved by the framework degradation.

In the latter case, the bio-medically relevant agents are incorporated into the NMOF pores after the synthesis operates by two methods; covalent and non-covalent encapsulation. Non-covalent loading in MOFs was first demonstrated on bulk phase and obtained better loading of up to 1.4 g of ibuprofen/ g of MOF . In the non-covalent method, the problem is that the encapsulation is reversible and this may lead to premature release of the active group. In the post-synthetic covalent case, the release of active agents will only be released by the decomposition of NMOF. This method makes use of the orthogonal functional groups within the frameworks of porous NMOFs, which are used to covalently attach active agents.

Nano MOFs for anti-tumor treatment

Around the world there are millions of people suffering from different forms of cancer. In Europe itself in each year around 3 million people are diagnosed with this dreadful disease making it the second death causing pathological condition . The main problem faced by cancer treatment is the delivery of drugs to specified sites. Earlier limitations while using conventional drugs for targeted drug delivery can be solved to an extent by the entry of nanomedicines. The advantage of using nanomedicines was further more structured when NMOFs, were used as a potential drug delivery system. The upper hand possessed by the nanoparticle drug delivery systems is their passive target towards the tumor cells by enhanced permeability and retention (EPR) effect.

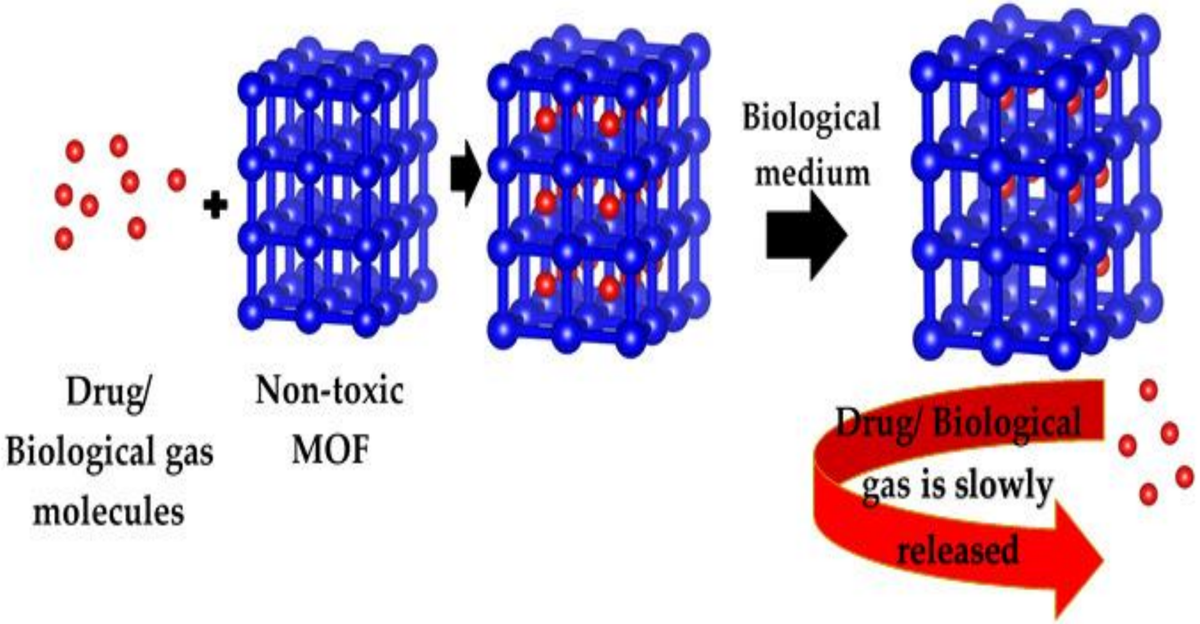


Chem. Soc. Rev., 2012, **41, 2623–2640**

REQUIREMENTS FOR AN EFFICIENT DRUG DELIVERY VEHICLE

They should be :-

- Non-toxic
- Biocompatible
- High drug loading capacity
- Control release and avoid the "burst effect"
- Control matrix degradation and engineer its surface
- Be small enough to allow intravenous injection
- Be detectable by various imaging techniques



Biomedical imaging and sensing

In contrast to inorganic nanomaterials used for biomedical sensing and imaging, MOFs are biodegradable by nature and are able to use biocompatible metals and linkers. These advantages are yet to be fully applied to pharmaceutical and medical applications.

MOFs can be applied in intracellular or in vivo imaging:

- MR imaging (MRI)
- Computer tomography (CT)
- MRI and CT dial-mode imaging
- Intracellular bio-imaging