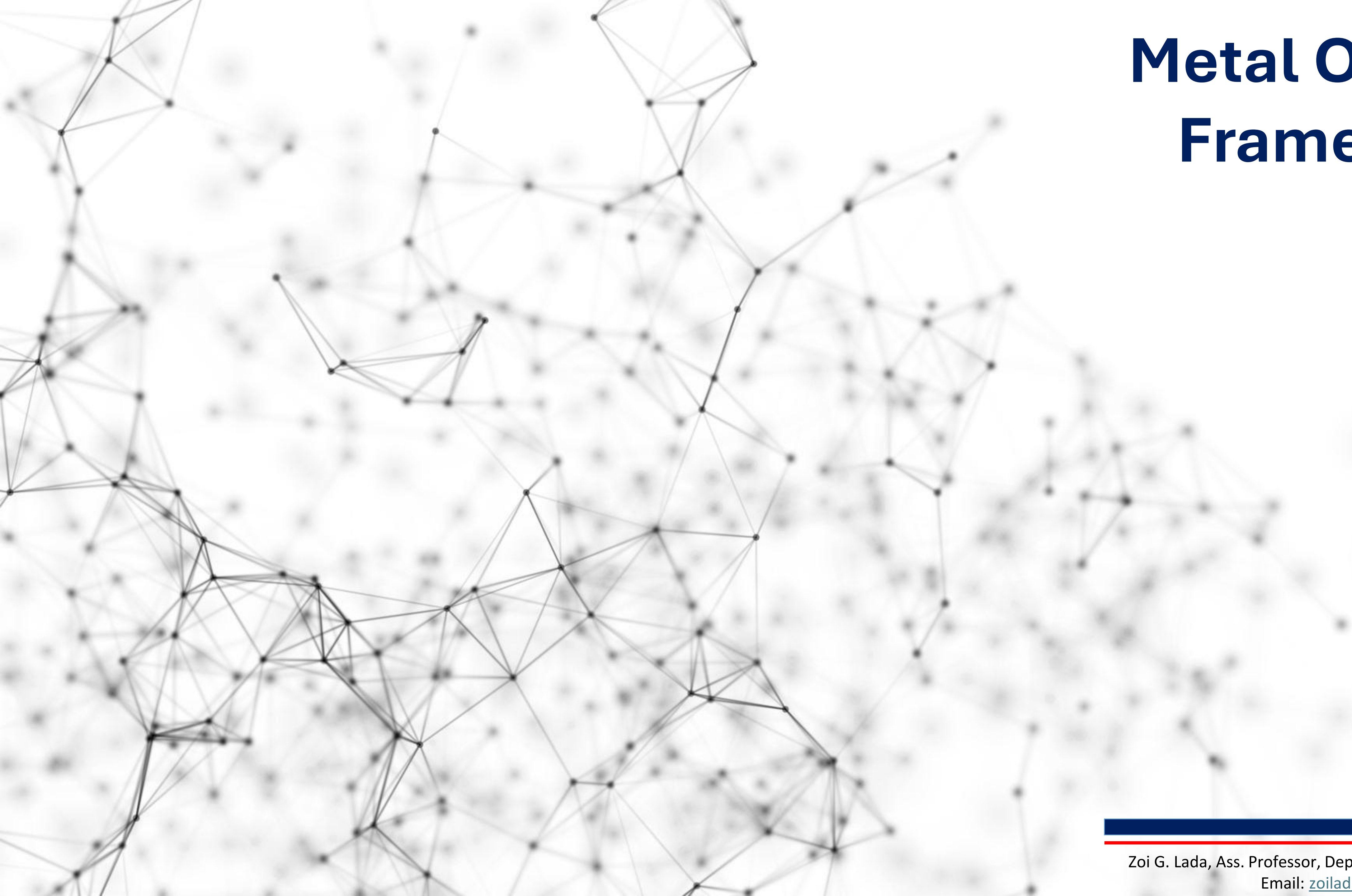


Metal Organic Frameworks

Zoi G. Lada, Ass. Professor, Dep. Chemistry, Un. Patras, Greece,
Email: zoilada@upatras.gr

Metal Organic Frameworks

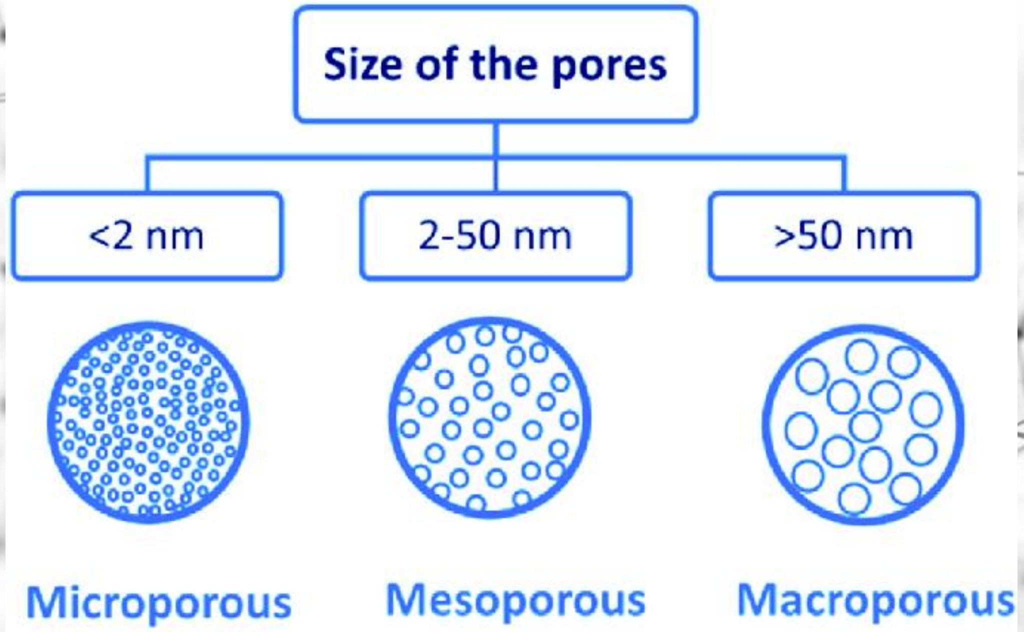
- **Nanoporous Materials (What are?, and types)**

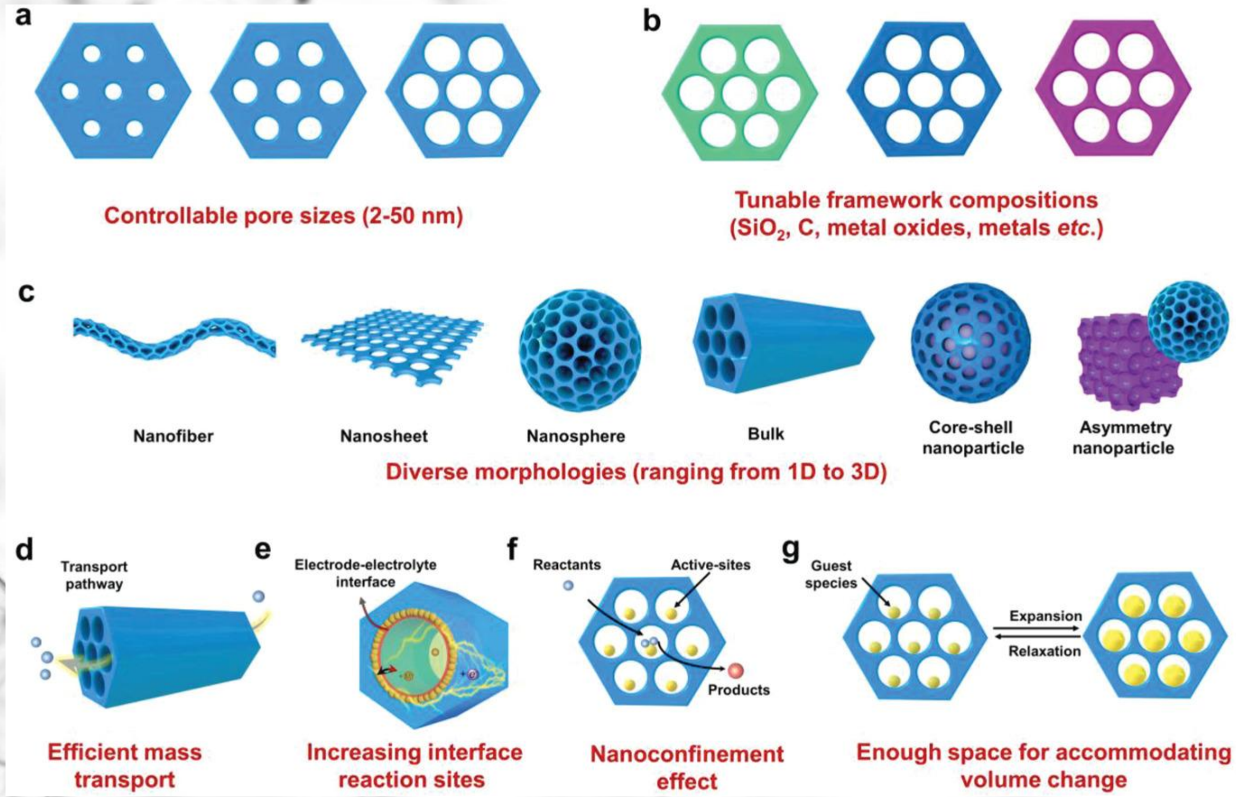
- **Review of Metal-Organic Frameworks**
    - Basic structure
    - Structural features
    - Important of pore size
    - Preparation of MOFs
    - Common ligands used for MOFs
    - Properties of MOFs
    - For better application
    - Synthesis method
    - Chemistry of MOFs
    - Applications of MOFs
        - Literature review
        - Conclusion and Scope for future work for MOFs

Metal Organic Frameworks

Nanoporous Materials (What are?, and types)

- **Consist of regular organic or inorganic structure, supporting a periodic porous system**
- Nanoporous materials are classified by their pore size: **microporous** (<2 nm), **mesoporous** (2–50 nm), and **macroporous** (>50 nm)
- **Nanofibers, nanosheets, nanospheres, etc**

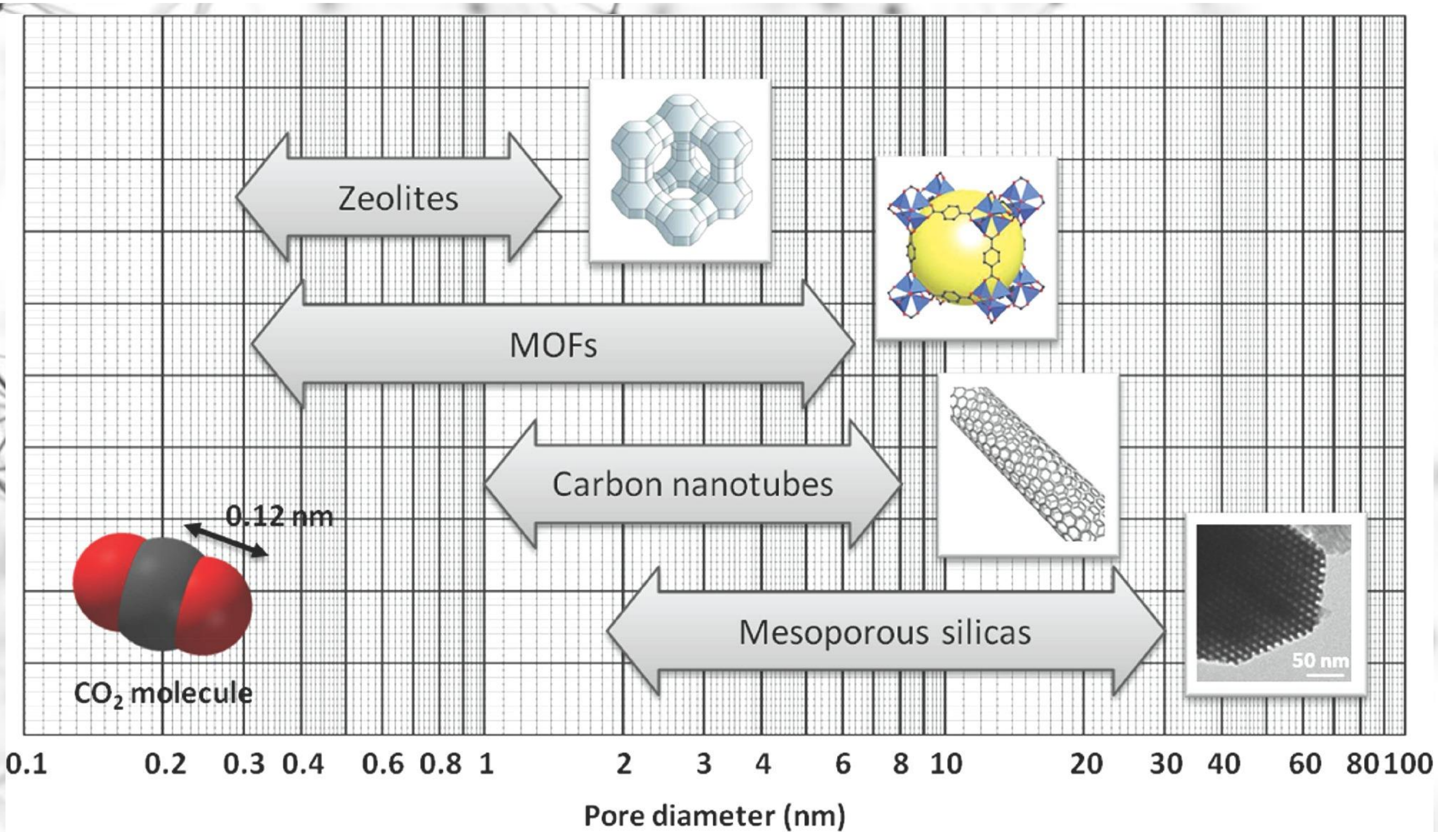




Metal Organic Frameworks

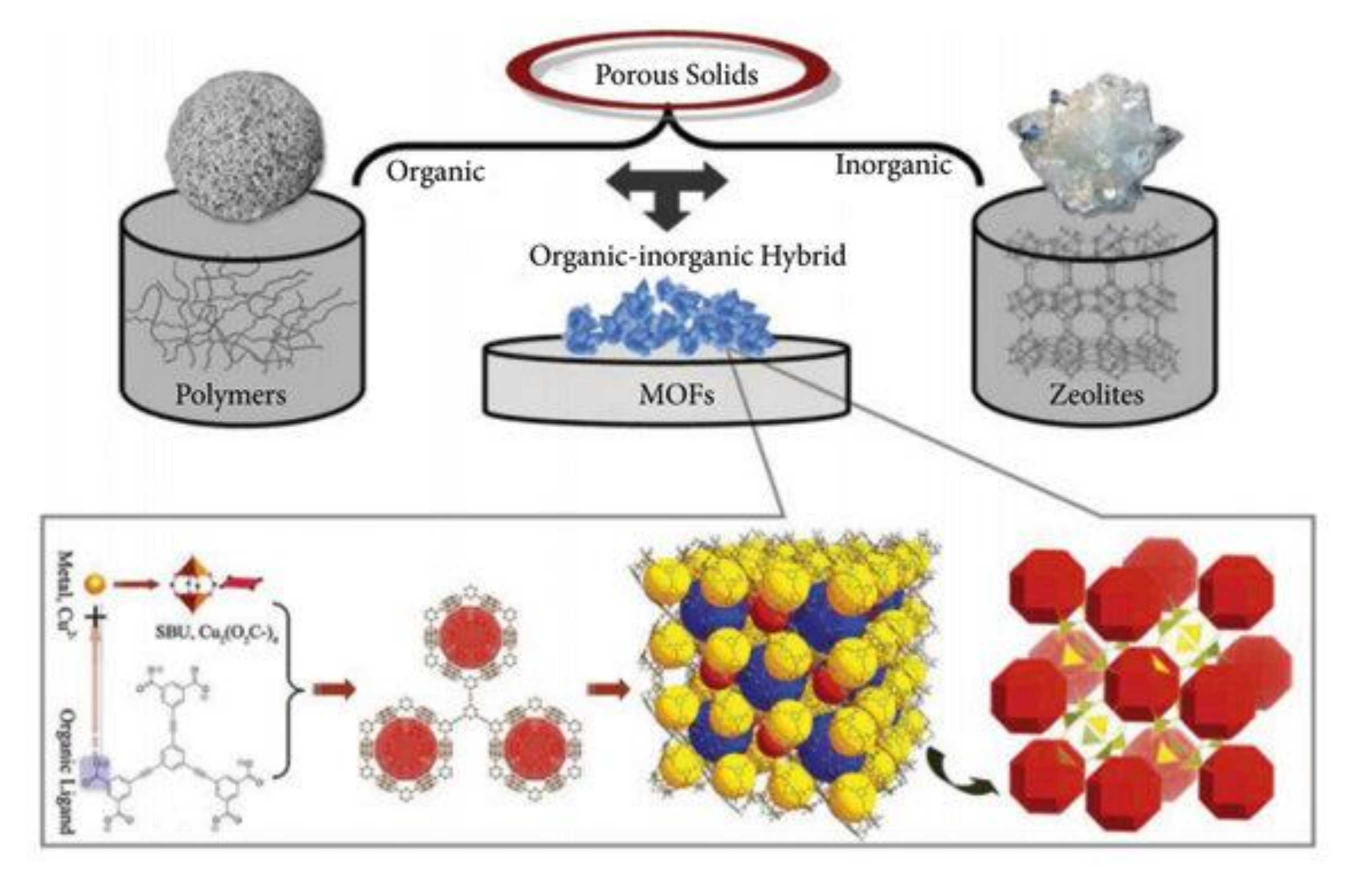
- **Nanoporous Materials (What are?, and types)**

Nanoporous materials are divided into categories:
Microporous materials like zeolites have very **small pores useful for selective catalysis and gas separation**
Mesoporous materials offer a balance with **larger pores for better accessibility while retaining high surface area**, making them useful for **drug delivery and catalysis with larger molecules**
Macroporous materials, with the **largest pores**, have the **easiest access but lower selectivity**



Metal Organic Frameworks

- Nanoporous Materials (What are?, and types)



Metal Organic Frameworks

- **Nanoporous Materials (What are?, and types)**

Publications in zeolites and MOFs

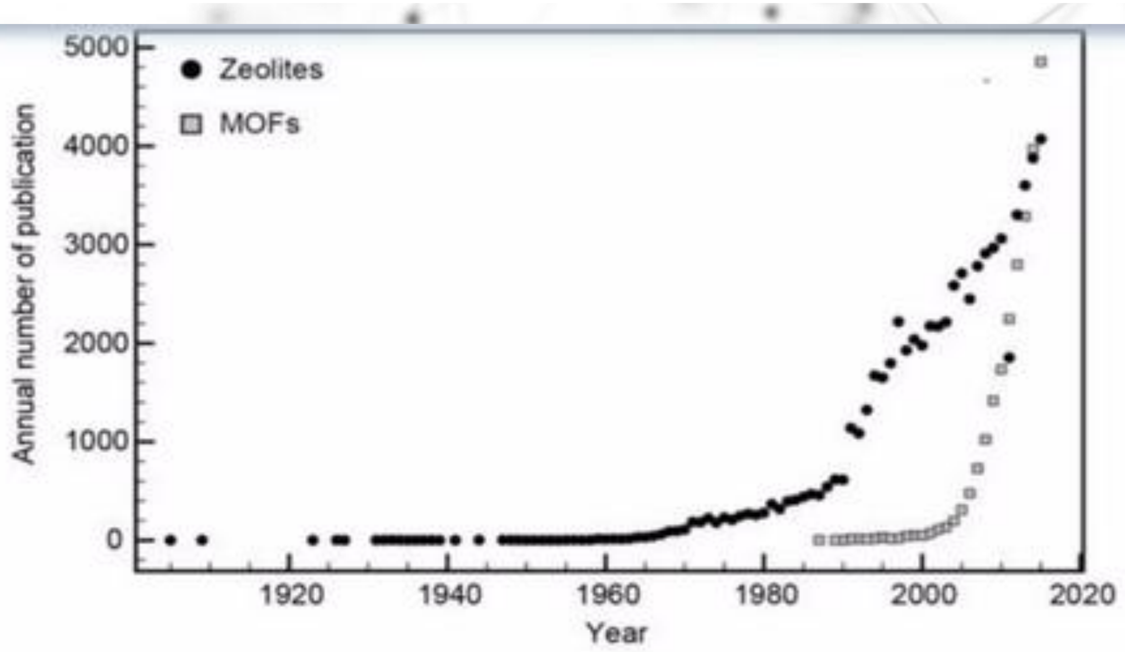


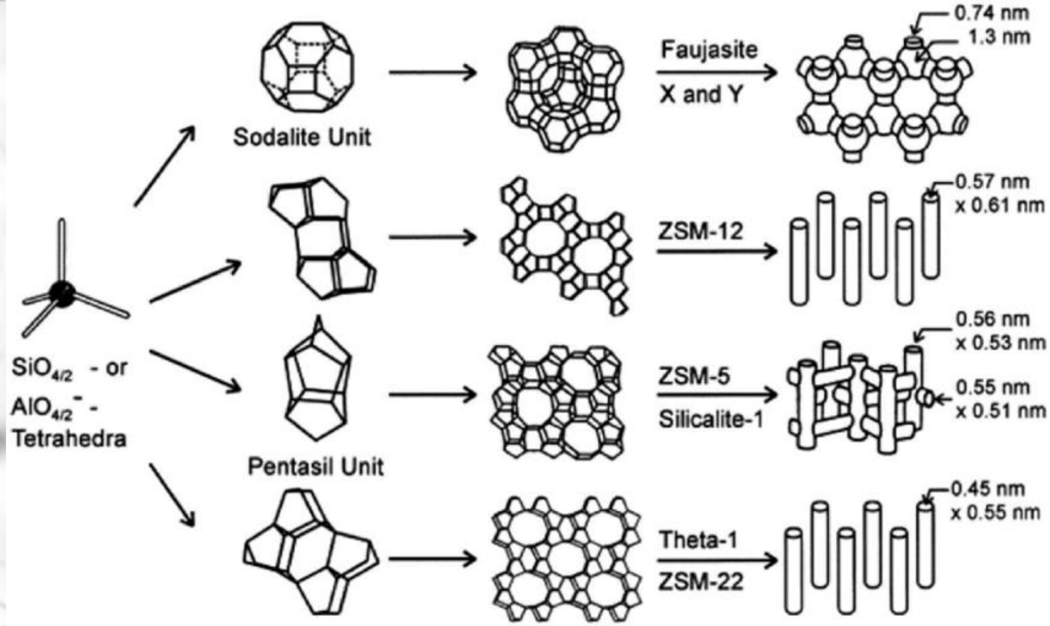
Figure 1. Number of publications on zeolites (black circles) and MOFs (gray squares) in given year.

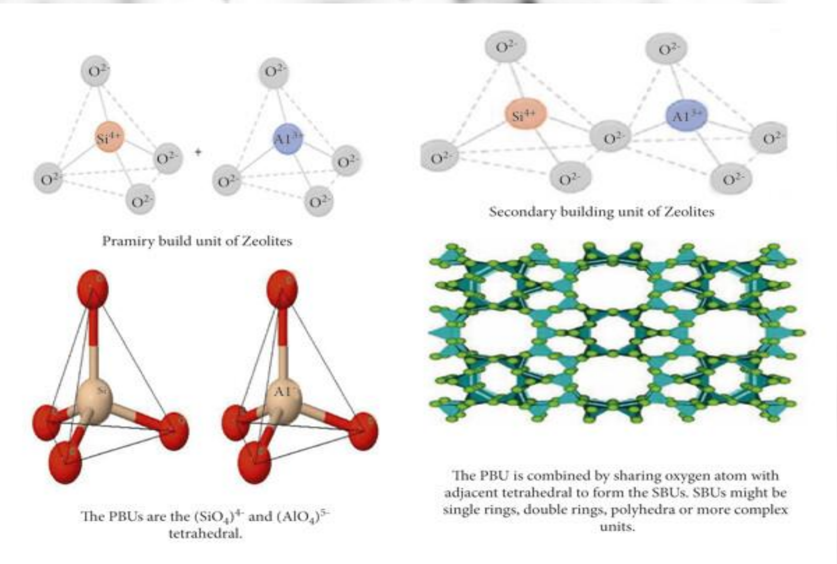
ZEOLITES: (INORGANIC NANOPOROUS COMPOUNDS)

- **Zeolites** are microporous crystalline solids with **well-defined structures**. Generally, they contain **silicon, aluminium** and **oxygen in their framework and cations**, **water and/or other molecules within their pores**.

- Zeolites form with many different crystalline structures, which have large open pores (sometimes referred to as cavities) in a very regular arrangement and roughly the same size as small molecules.

- The most interesting thing about zeolites is their **open, cage-like framework structure** and the way it can trap other molecules inside it.





Pramiry build unit of Zeolites

Secondary building unit of Zeolites

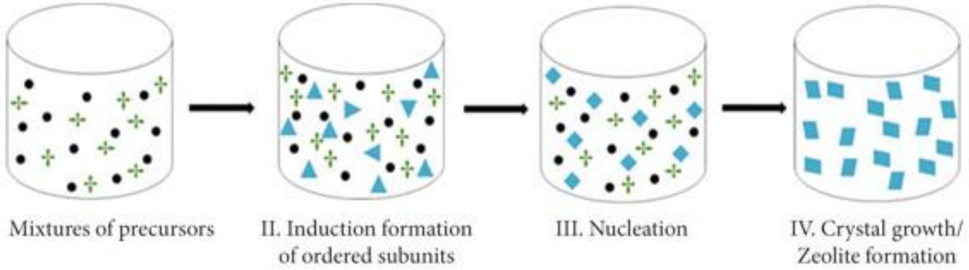
The PBUs are the $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ tetrahedral.

The PBU is combined by sharing oxygen atom with adjacent tetrahedral to form the SBUs. SBUs might be single rings, double rings, polyhedra or more complex units.

ZEOLITES: (INORGANIC NANOPOROUS COMPOUNDS)

Synthetic Approaches

Hydrothermal



The **ionothermal synthesis** method is characterized using **ionic solvent and template to avoid high pressure**, which is caused by water vapor. In 2004, Wang et al. reported the first synthesis of aluminophosphate and silico-aluminophosphate zeolites through the ionothermal method. This resulted in high efficient and high surface area zeolite.

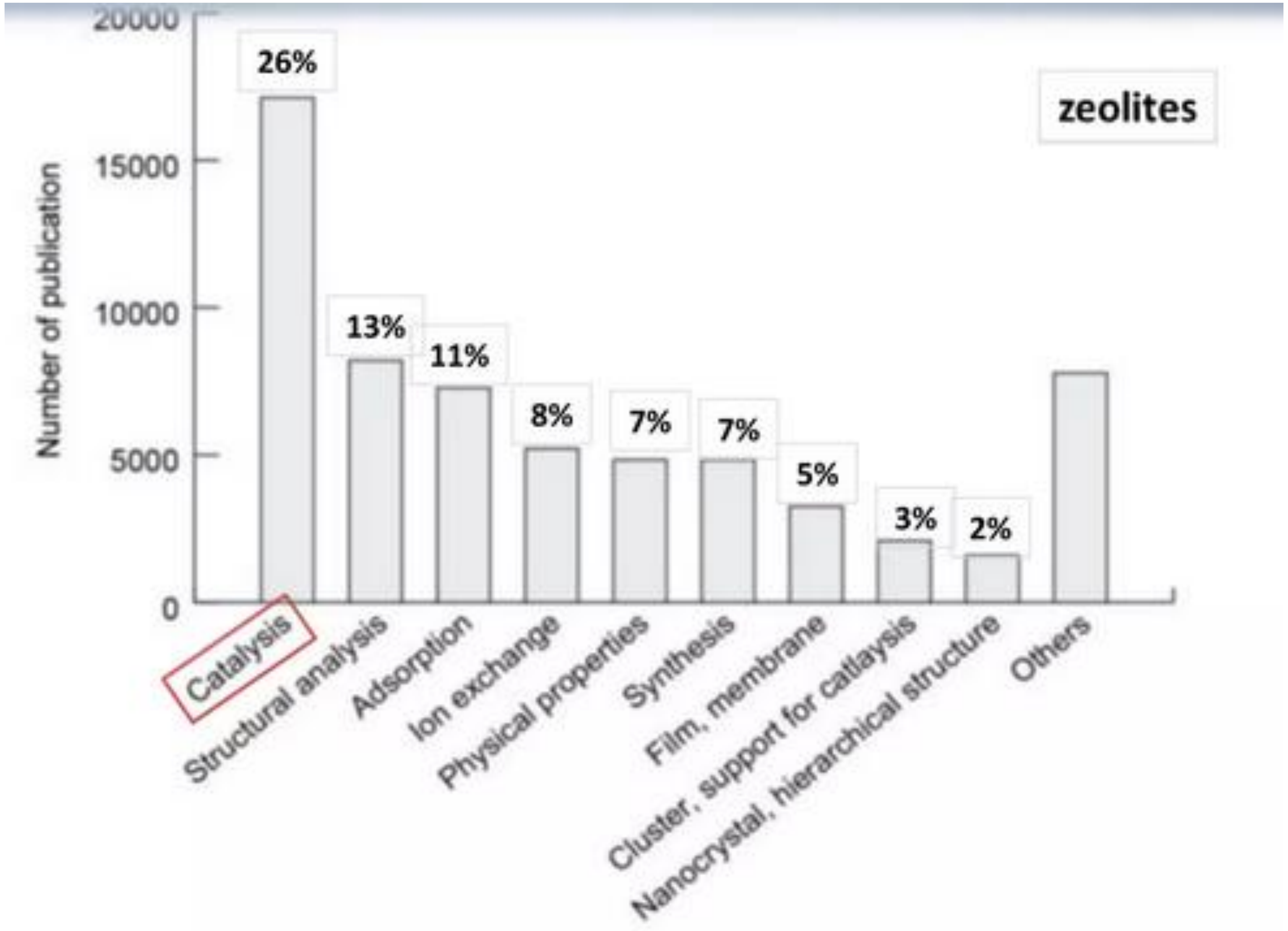
Green Synthesis Methods

The **microwave-assisted method** is characterized by having **mild reaction conditions and high crystallization rate**. This method has been developed to promote the nucleation rate of zeolites through increasing of the crystallization rate.

Cr-supported and TiO_2-doped photocatalytic natural zeolites through displacing of TiO_2 lattice with Ti^{4+} sites due to the close ionic radius of Ti^{4+} and Cr^{3+}. They bring **enhancement to the binding force of Cr/O/Ti through the increment of calcination temperature**. This **improves the photocatalytic activity** of the synthesized zeolites

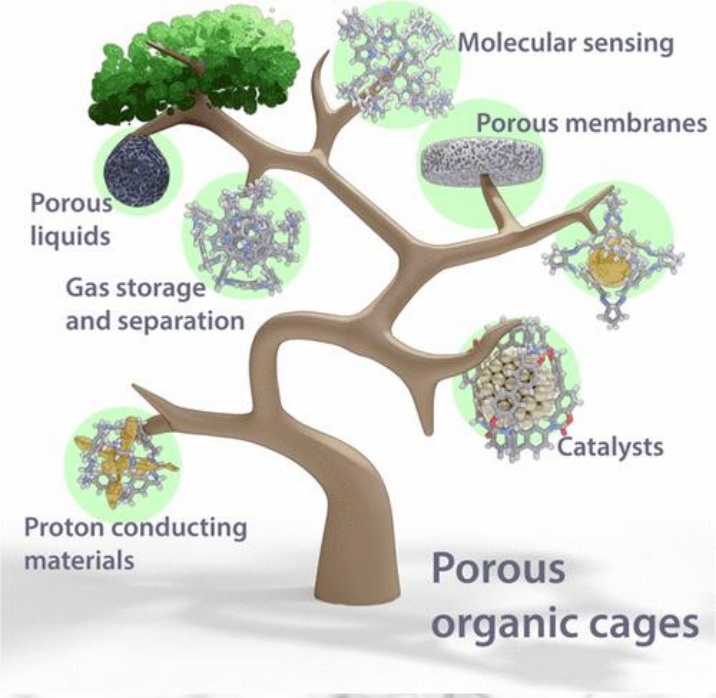
ZEOLITES: (INORGANIC NANOPOROUS COMPOUNDS)

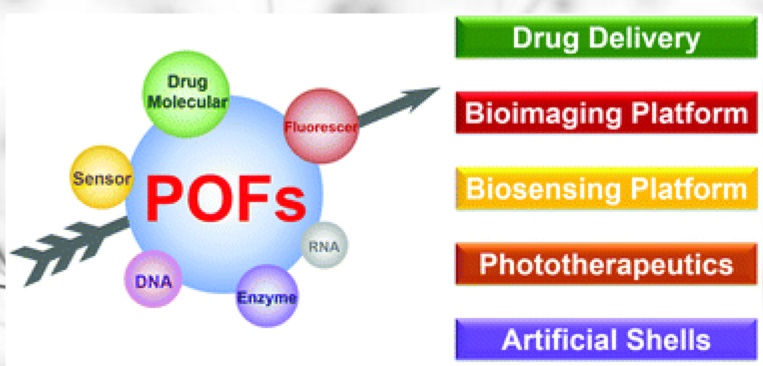
Publications in Zeolites



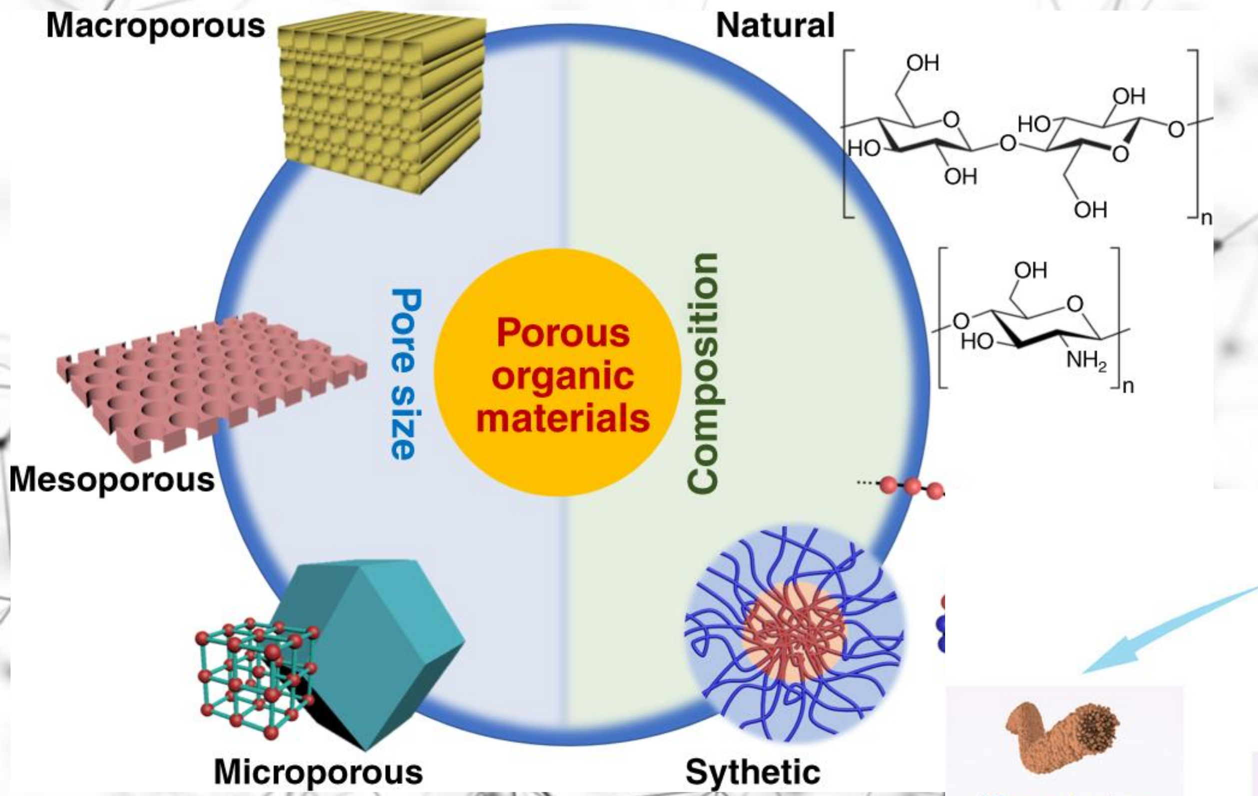
POFs: (ORGANIC NANOPOROUS COMPOUNDS)

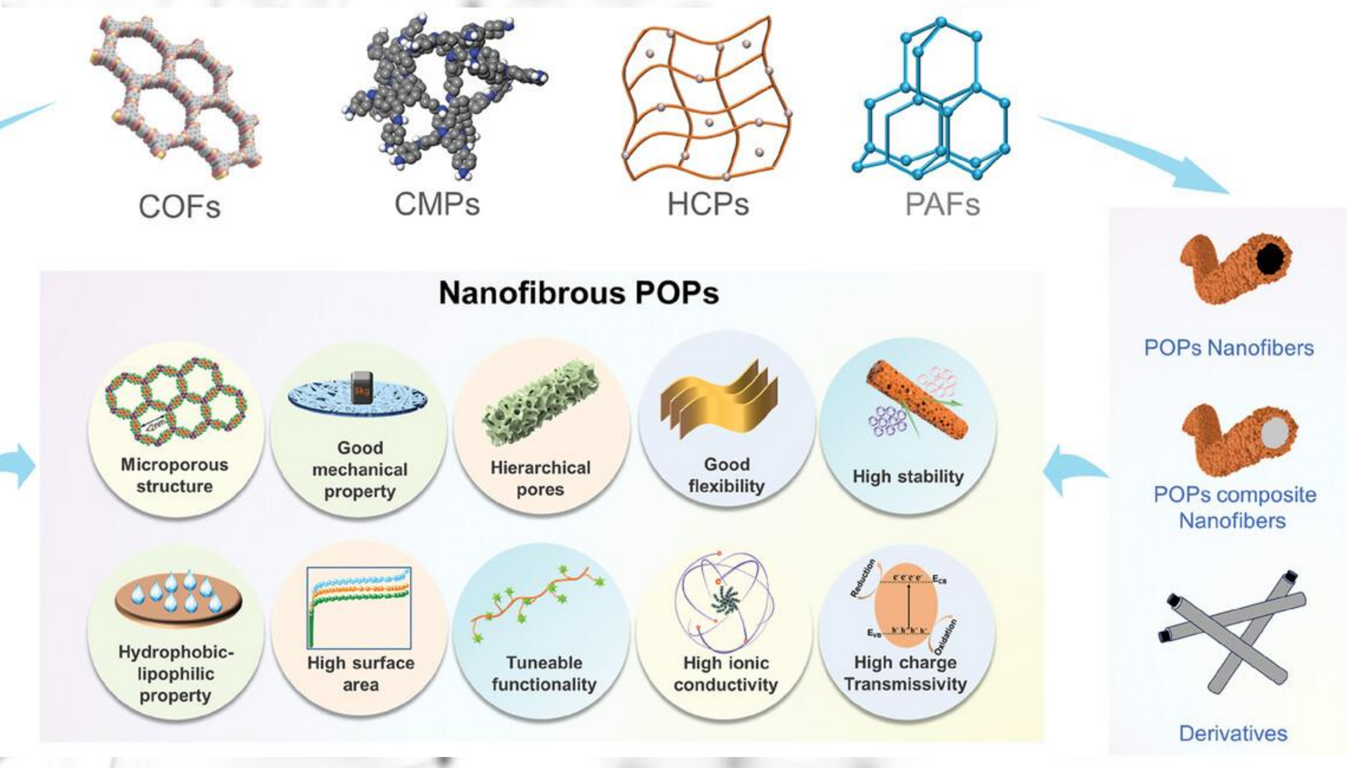
- **POFs are composed of different organic moieties linked by covalent bonds**, resulting in ordered and rigid structure
- **Exceptional thermal stabilities** and low frameworks densities
- **Exhibit permanent porosity and specific surface areas**
- **Application**: Gas storage, separation, catalysis, and etc





POFs: (ORGANIC NANOPOROUS COMPOUNDS)



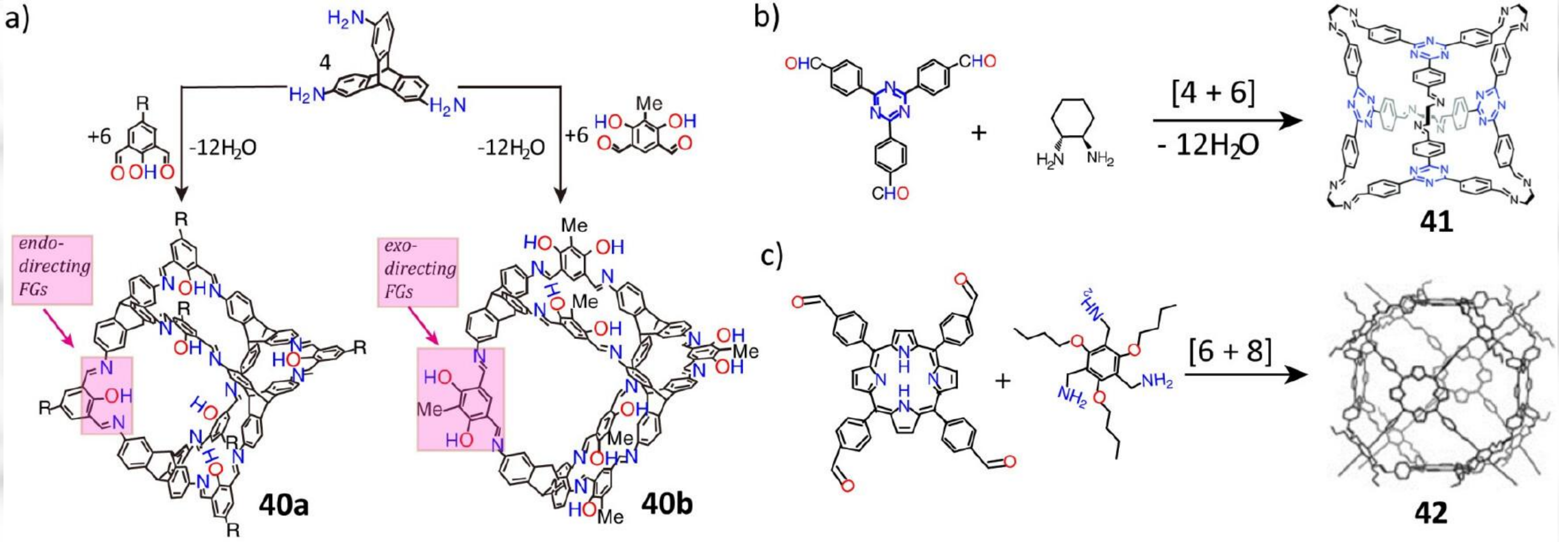


POFs: (ORGANIC NANOPOROUS COMPOUNDS)

Synthetic Approaches

1. Bottom-up Polymerization

- **Principle:** Controlled covalent bonding between organic monomers with defined geometry.
- **Common reactions:**
  - **Condensation reactions:** e.g., boronic acid trimerization, imine formation, triazine formation.
  - **Coupling reactions:** Suzuki, Sonogashira, Yamamoto couplings for PAFs and CMPs.
  - **Click chemistry:** azide–alkyne cycloaddition for mild, modular synthesis.
- **Solvothermal synthesis** is typical for crystalline COFs (temperature 80–200 °C, in mixed solvents such as dioxane/mesitylene or DMF).



POFs: (ORGANIC NANOPOROUS COMPOUNDS)

Synthetic Approaches

2. Template-assisted or Sol–Gel Methods

- Used for amorphous POFs to create meso-/macroporous structures.
- Soft or hard templates (e.g., micelles, silica nanoparticles) guide porosity.
- Template removed by calcination or chemical etching.

3. Mechanochemical Synthesis

- Solvent-free ball milling of monomers under controlled conditions.
- Environmentally friendly, scalable, and increasingly popular for COFs and CMPs.

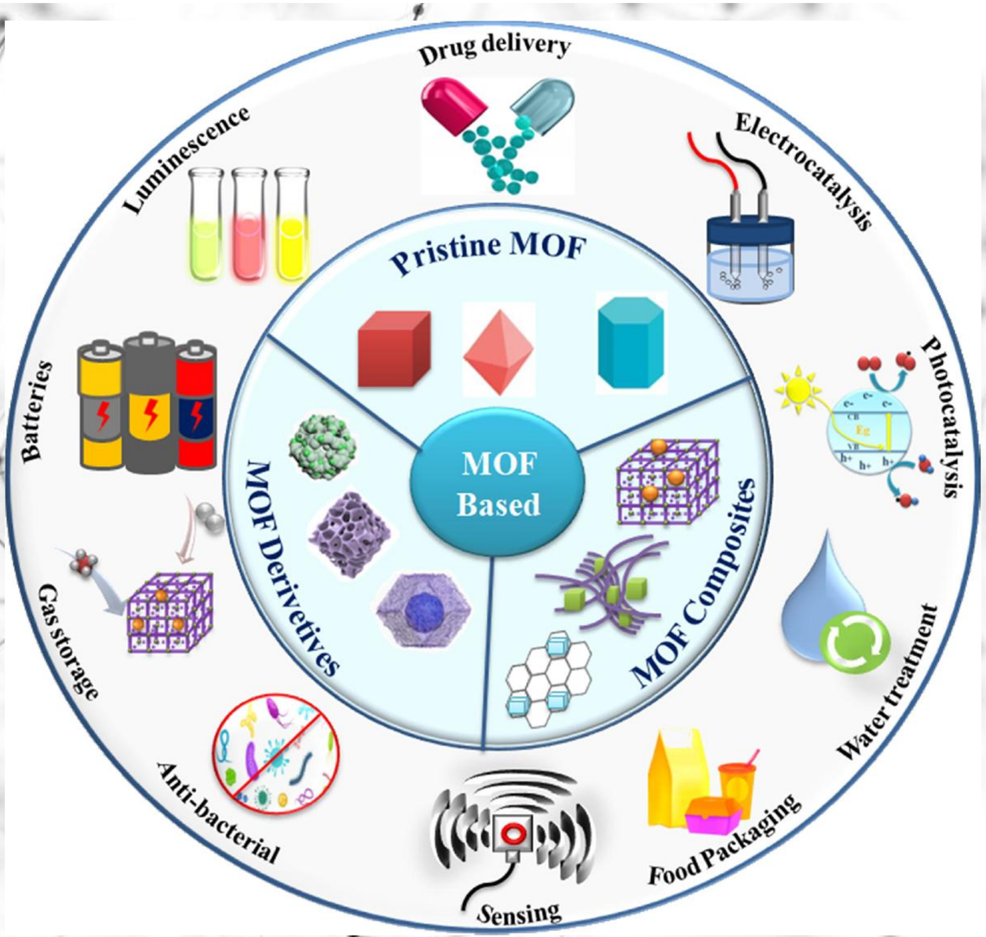
4. Post-synthetic Functionalization

- Surface modification (e.g., sulfonation, amination) to tune hydrophilicity or catalytic activity.
- Can introduce specific binding sites for gases, pollutants, or ions.

Metal Organic Frameworks

- Metal-Organic Framework, abbreviated to MOF, is a **Coordination Polymer** (or alternatively Coordination Network) **with an open framework containing potential voids**.

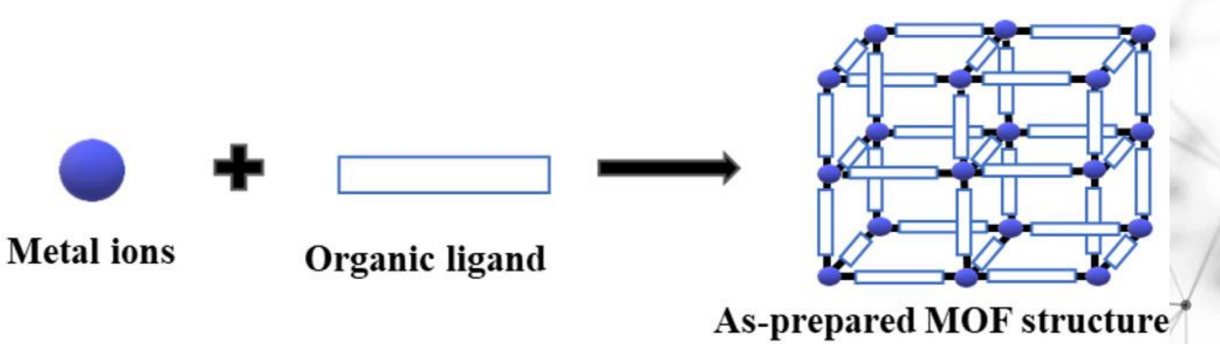
- MOFs are **self-assembled metal clusters with organic ligands**, are well known for their structure, permanent porosity, and tunable properties and have shown great prospect for various applications.

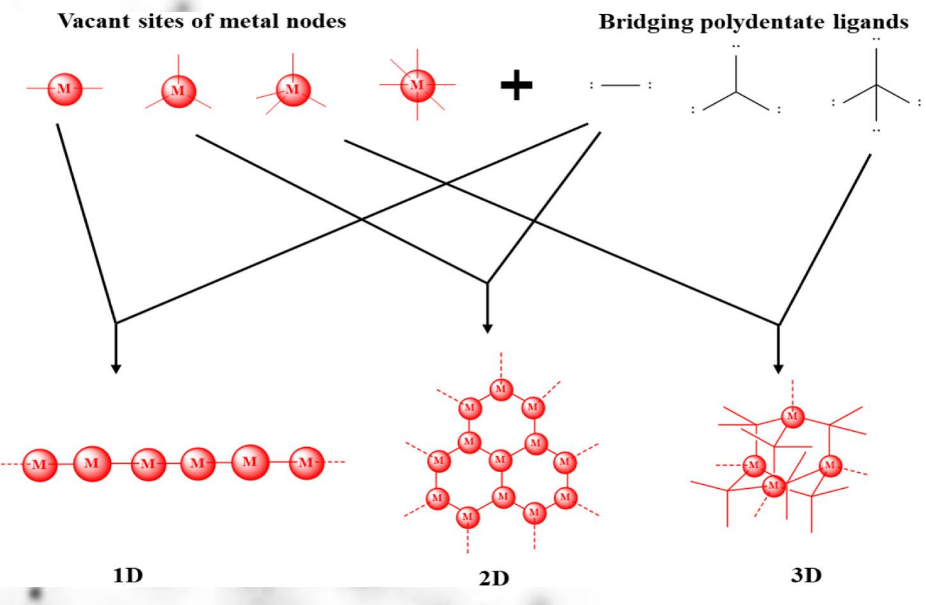


Metal Organic Frameworks

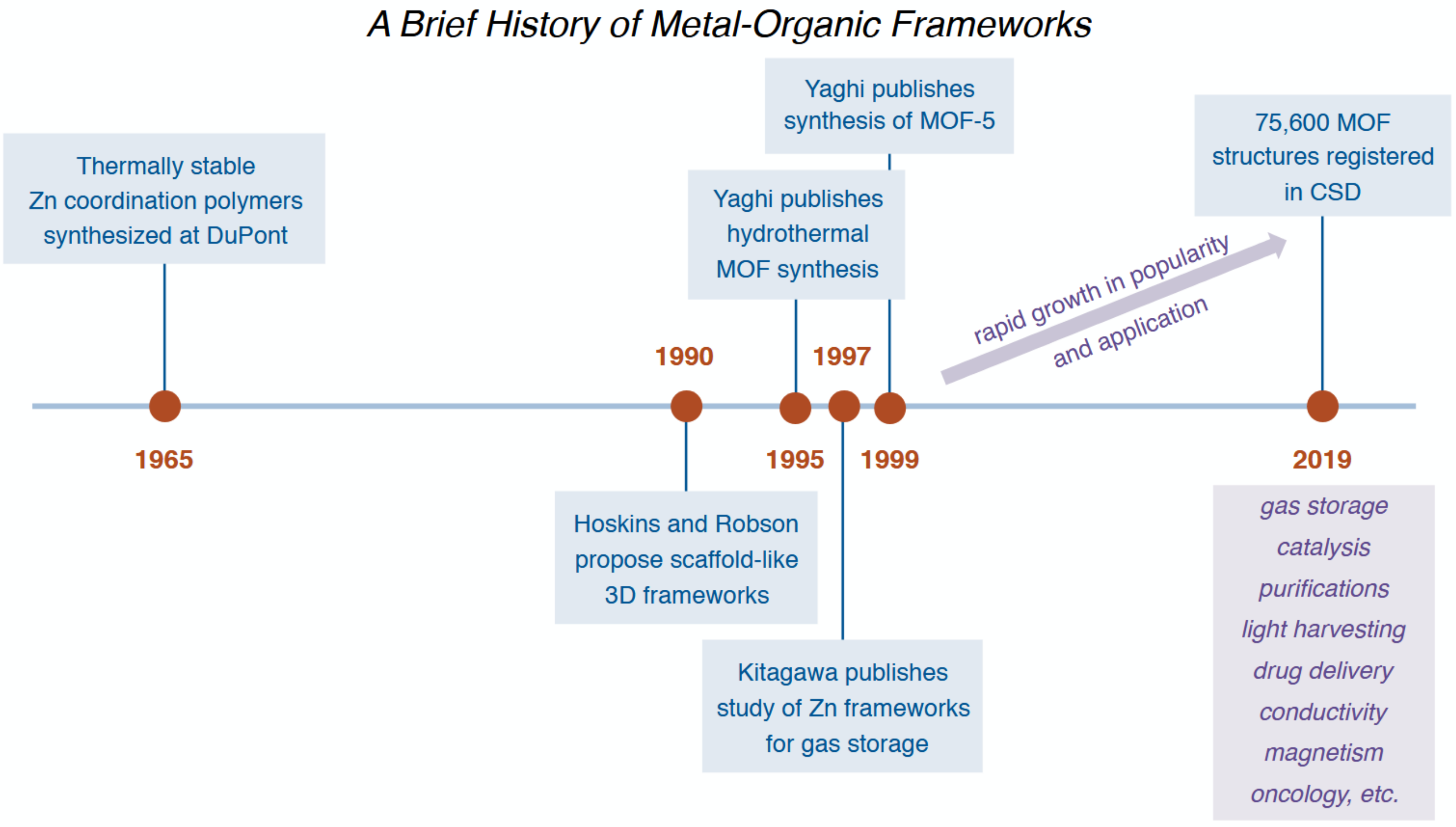
Basic structure

MOFs structures made up of inorganic nodes, which can either be single ions or clusters of ions, and organic linkers.





Metal Organic Frameworks



A Brief History of Metal-Organic Frameworks

1965
Thermally stable
Zn coordination polymers
synthesized at DuPont

1990
Hoskins and Robson
propose scaffold-like
3D frameworks

1995
Yaghi publishes
hydrothermal
MOF synthesis

1997
Kitagawa publishes
study of Zn frameworks
for gas storage

1999
Yaghi publishes
synthesis of MOF-5

*rapid growth in popularity
and application*

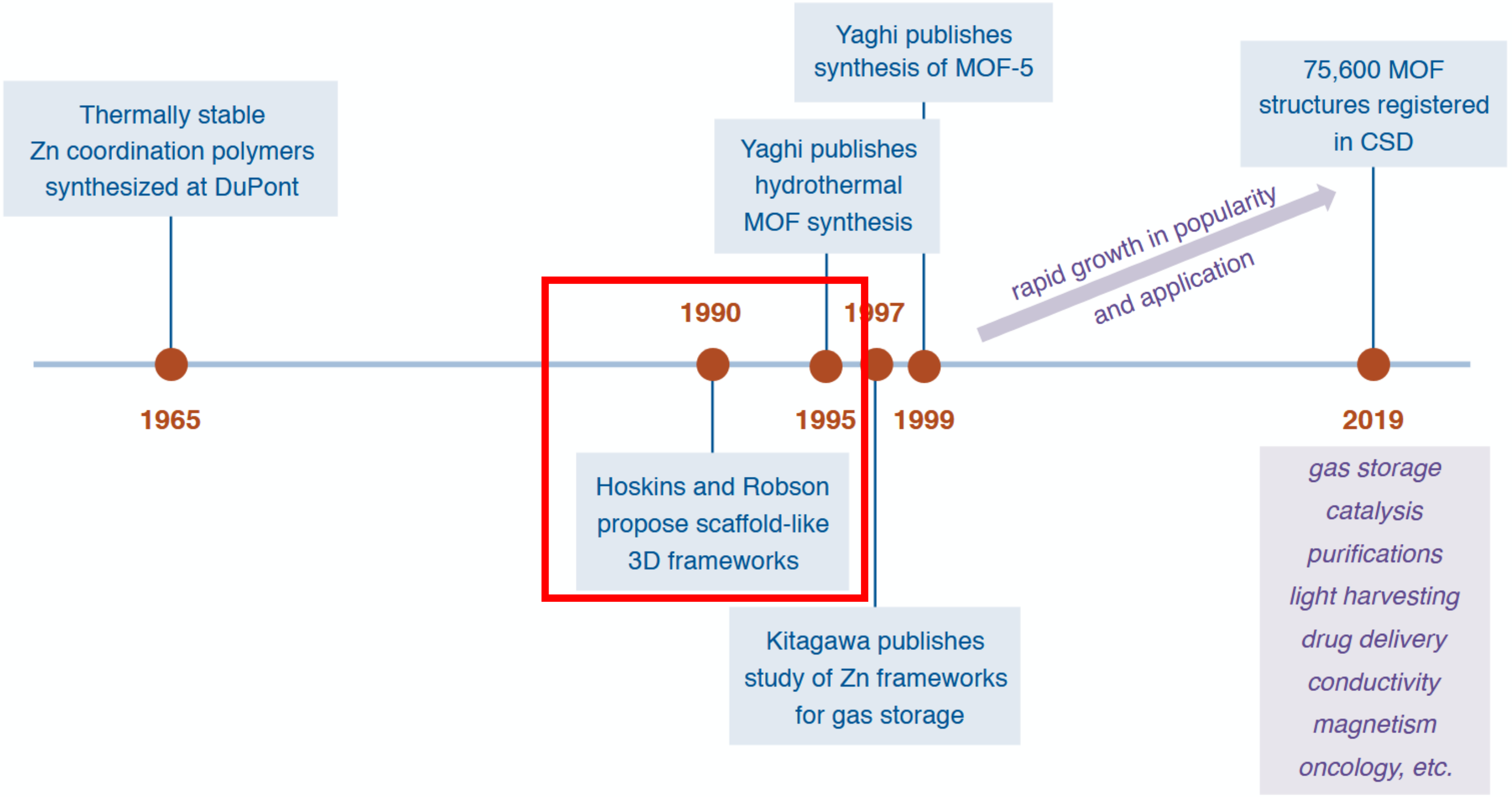
2019
75,600 MOF
structures registered
in CSD

gas storage
catalysis
purifications
light harvesting
drug delivery
conductivity
magnetism
oncology, etc.

Tomic, E. A. *J. Appl. Polym. Sci.* **1965**, *9*, 3745-3752.
Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546-1554.
Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1995**, *117*, 10401-10402.
Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem. Int. Ed.* **1997**, *36*, 1725-1727
Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276-279.
The Cambridge Crystallographic Data Centre. How Many MOFs are there in the CSD? https://www.ccdc.cam.ac.uk/ (Accessed Apr 20, 2019).

Metal Organic Frameworks

A Brief History of Metal-Organic Frameworks



1965
Thermally stable Zn coordination polymers synthesized at DuPont

1990
Hoskins and Robson propose scaffold-like 3D frameworks

1995
Yaghi publishes hydrothermal MOF synthesis

1997
Kitagawa publishes study of Zn frameworks for gas storage

1999
Yaghi publishes synthesis of MOF-5

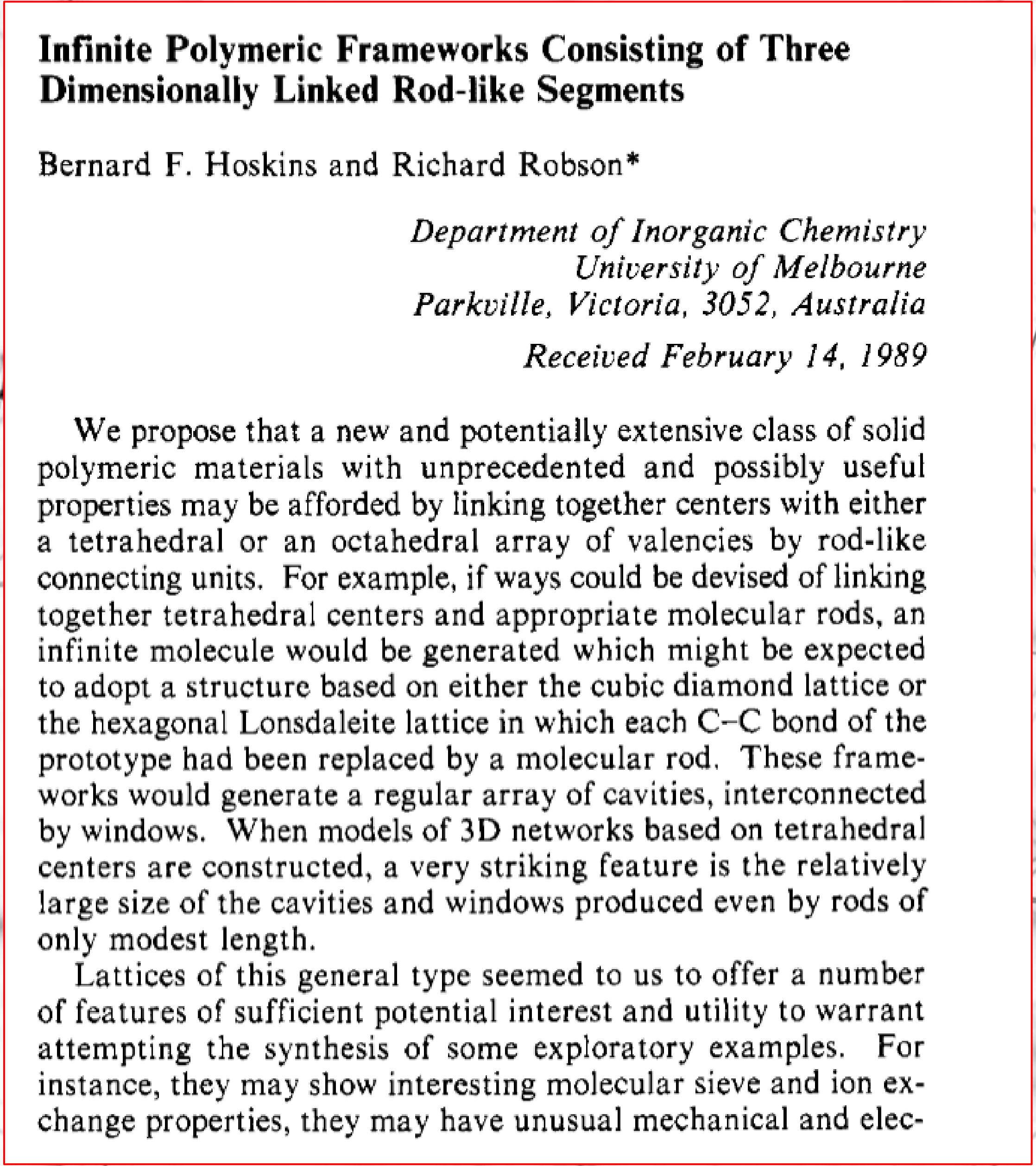
rapid growth in popularity and application

2019
75,600 MOF structures registered in CSD

gas storage
catalysis
purifications
light harvesting
drug delivery
conductivity
magnetism
oncology, etc.

Tomic, E. A. *J. Appl. Polym. Sci.* **1965**, *9*, 3745-3752.
Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546-1554.
Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1995**, *117*, 10401-10402.
Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem. Int. Ed.* **1997**, *36*, 1725-1727
Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276-279.
The Cambridge Crystallographic Data Centre. How Many MOFs are there in the CSD? https://www.ccdc.cam.ac.uk/ (Accessed Apr 20, 2019).

Metal Organic Frameworks



Infinite Polymeric Frameworks Consisting of Three Dimensionally Linked Rod-like Segments

Bernard F. Hoskins and Richard Robson*

Department of Inorganic Chemistry
University of Melbourne
Parkville, Victoria, 3052, Australia

Received February 14, 1989

We propose that a new and potentially extensive class of solid polymeric materials with unprecedented and possibly useful properties may be afforded by linking together centers with either a tetrahedral or an octahedral array of valencies by rod-like connecting units. For example, if ways could be devised of linking together tetrahedral centers and appropriate molecular rods, an infinite molecule would be generated which might be expected to adopt a structure based on either the cubic diamond lattice or the hexagonal Lonsdaleite lattice in which each C–C bond of the prototype had been replaced by a molecular rod. These frameworks would generate a regular array of cavities, interconnected by windows. When models of 3D networks based on tetrahedral centers are constructed, a very striking feature is the relatively large size of the cavities and windows produced even by rods of only modest length.

Lattices of this general type seemed to us to offer a number of features of sufficient potential interest and utility to warrant attempting the synthesis of some exploratory examples. For instance, they may show interesting molecular sieve and ion exchange properties, they may have unusual mechanical and elec-

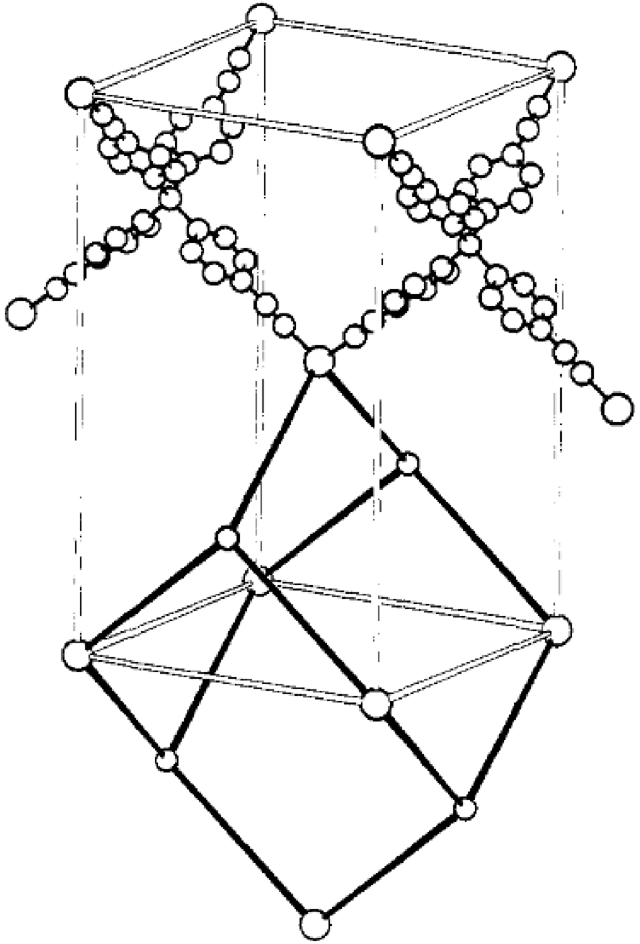
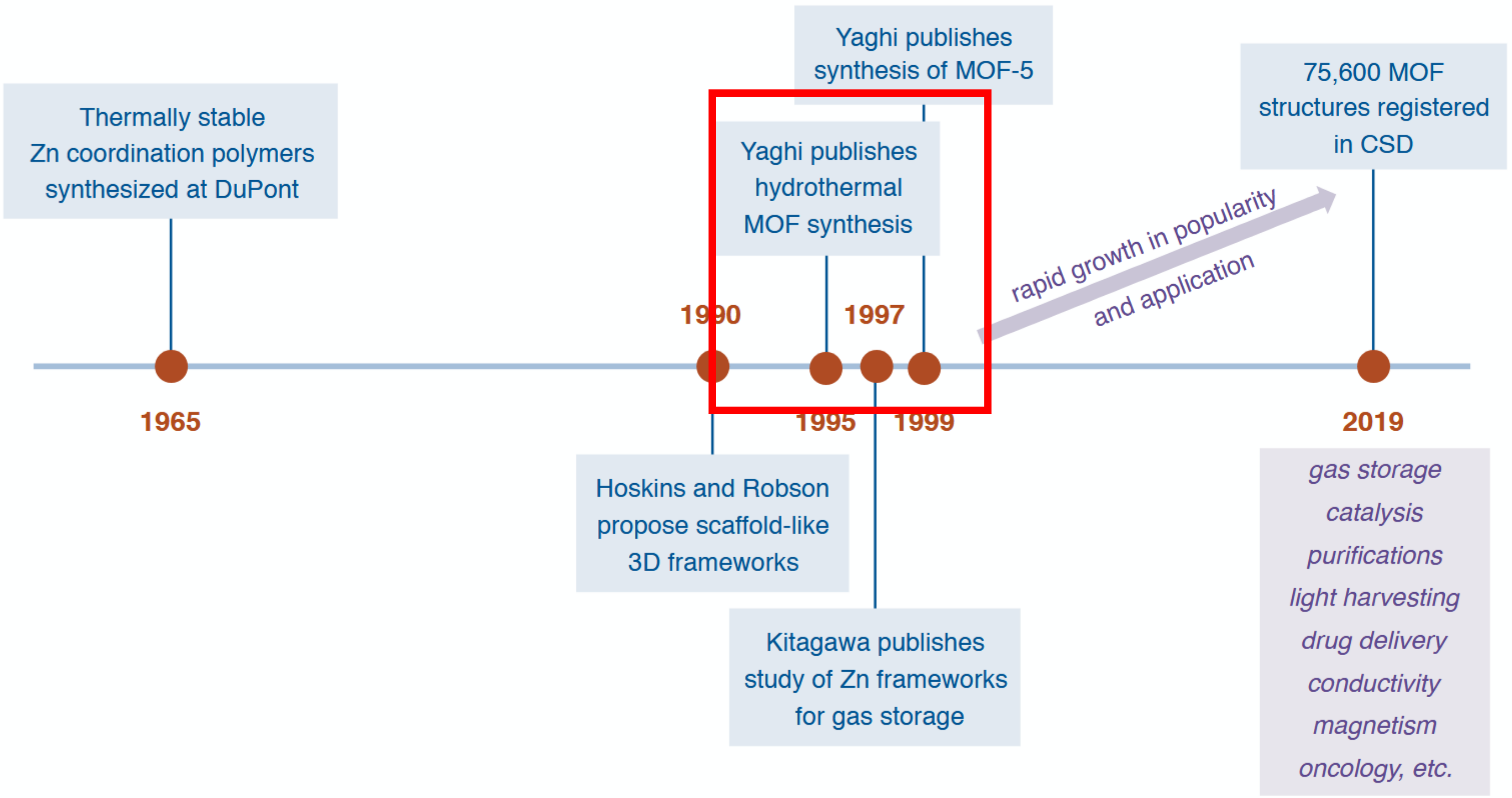


Figure 1. Structure of $\{Cu^{I}[C(C_6H_4{\cdot}CN)_4]\}_n^{n+}$ framework. One complete tetragonal unit cell together with parts of adjoining cells are shown; the larger circles denote the copper atoms. All $C{\cdot}C_6H_4{\cdot}CN{\cdot}Cu$ rods are 8.856 (2) Å long. An adamantane-like cavity with its center at the center of the bottom face of the complete unit cell is highlighted. Bond lengths: CuN, 2.03 (4) Å; C≡N, 1.05 (6) Å; CC distances normal.

Metal Organic Frameworks



A Brief History of Metal-Organic Frameworks

1965: Thermally stable Zn coordination polymers synthesized at DuPont

1990: Hoskins and Robson propose scaffold-like 3D frameworks

1995: Yaghi publishes hydrothermal MOF synthesis

1997: Kitagawa publishes study of Zn frameworks for gas storage

1999: Yaghi publishes synthesis of MOF-5

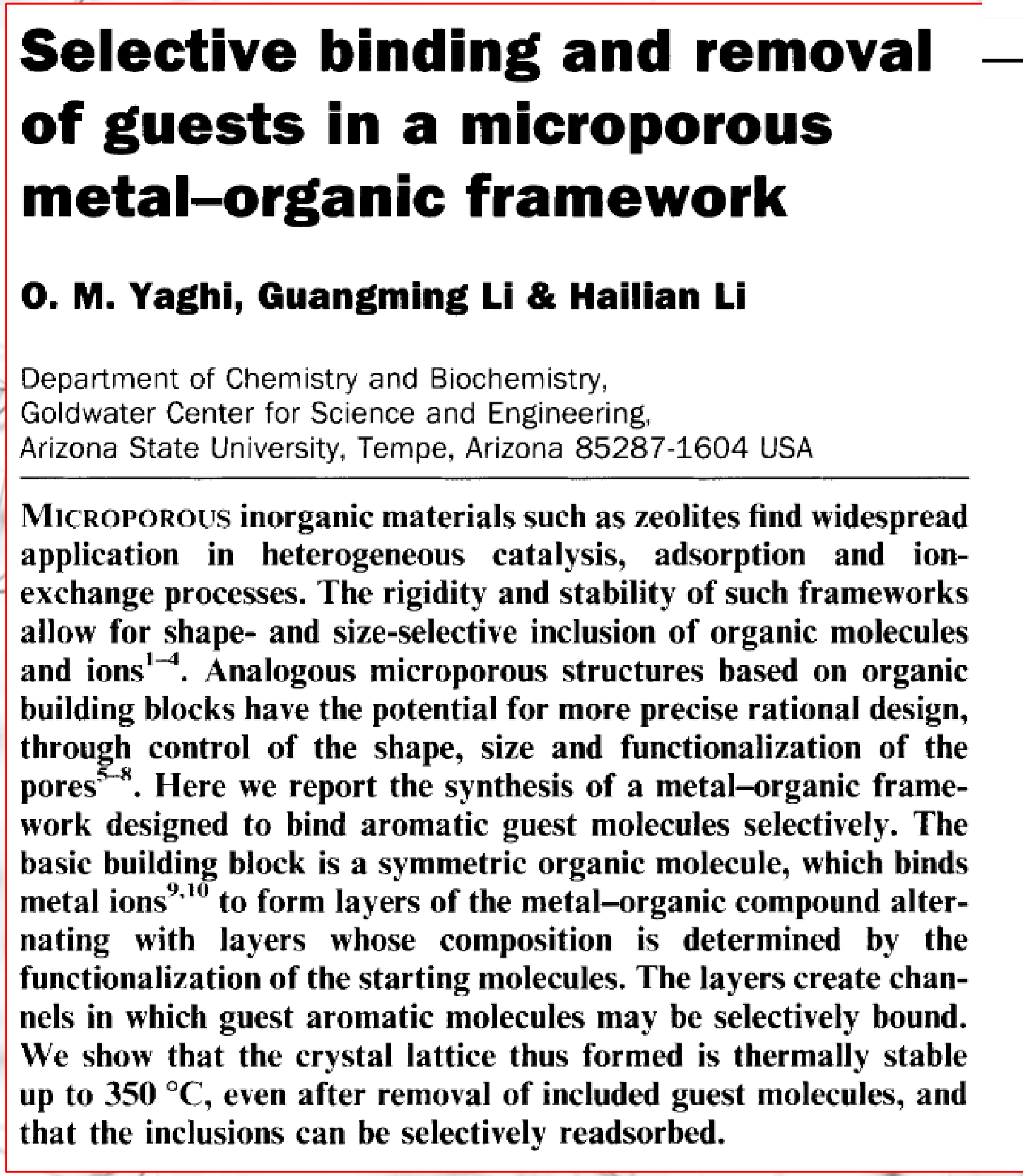
rapid growth in popularity and application

2019: 75,600 MOF structures registered in CSD

gas storage
catalysis
purifications
light harvesting
drug delivery
conductivity
magnetism
oncology, etc.

Tomic, E. A. *J. Appl. Polym. Sci.* **1965**, *9*, 3745-3752.
Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546-1554.
Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1995**, *117*, 10401-10402.
Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem. Int. Ed.* **1997**, *36*, 1725-1727
Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276-279.
The Cambridge Crystallographic Data Centre. How Many MOFs are there in the CSD? https://www.ccdc.cam.ac.uk/ (Accessed Apr 20, 2019).

Metal Organic Frameworks



Selective binding and removal of guests in a microporous metal–organic framework

O. M. Yaghi, Guangming Li & Hailian Li

Department of Chemistry and Biochemistry,
Goldwater Center for Science and Engineering,
Arizona State University, Tempe, Arizona 85287-1604 USA

MICROPOROUS inorganic materials such as zeolites find widespread application in heterogeneous catalysis, adsorption and ion-exchange processes. The rigidity and stability of such frameworks allow for shape- and size-selective inclusion of organic molecules and ions[1–4]. Analogous microporous structures based on organic building blocks have the potential for more precise rational design, through control of the shape, size and functionalization of the pores[5–8]. Here we report the synthesis of a metal–organic framework designed to bind aromatic guest molecules selectively. The basic building block is a symmetric organic molecule, which binds metal ions[9,10] to form layers of the metal–organic compound alternating with layers whose composition is determined by the functionalization of the starting molecules. The layers create channels in which guest aromatic molecules may be selectively bound. We show that the crystal lattice thus formed is thermally stable up to 350 °C, even after removal of included guest molecules, and that the inclusions can be selectively readsorbed.

nature

nature > letters > article

Letter | Published: 14 December 1995

Selective binding and removal of guests in a microporous metal–organic framework

O. M. Yaghi, Guangming Li & Hailian Li

Nature **378**, 703–706 (1995) | Cite this article

33k Accesses | **2670** Citations | **82** Altmetric | Metrics

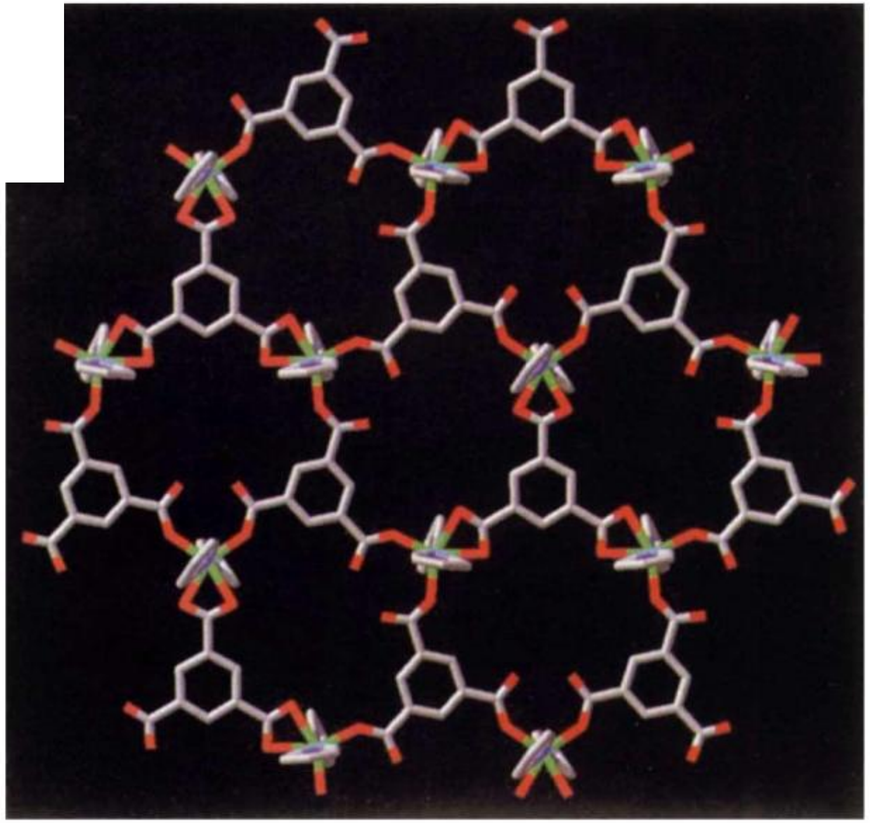
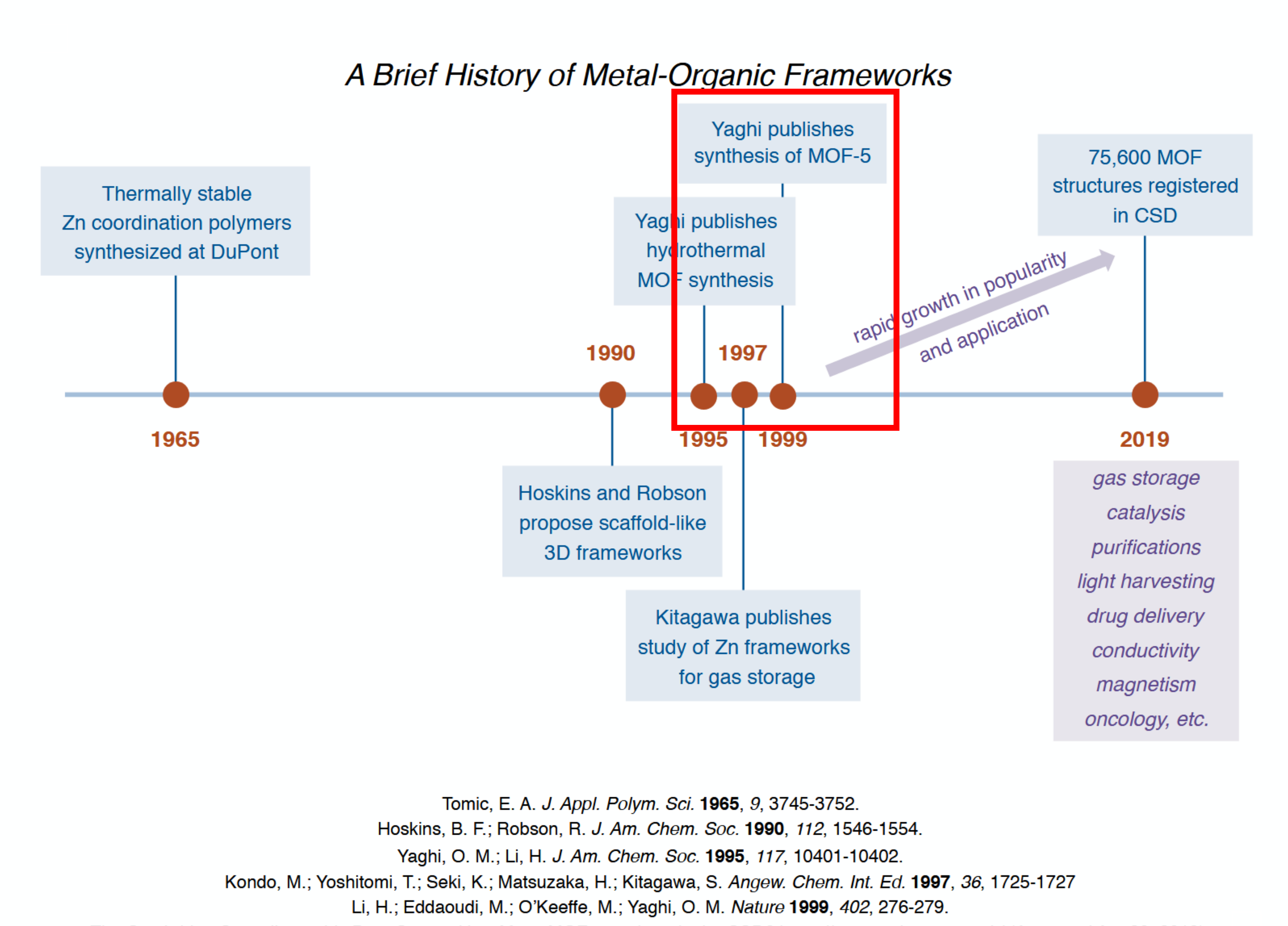


FIG. 2 A single layer of the extended porous network of $CoC_6H_3(COOH_{1/3})_3(NC_5H_5)_2 \cdot 2/3\ NC_5H_5$. The metal-carboxylate layer is shown approximately along the x–y plane: green, Co; red, O; blue, N; grey, C. Only one of the two preferred orientations about the Co–N bond is shown for the statistically disordered coordinated pyridine molecules. The hydrogen atoms on the pyridines and BTC units are omitted for clarity.

Metal Organic Frameworks



A Brief History of Metal-Organic Frameworks

1965
Thermally stable Zn coordination polymers synthesized at DuPont

1990
Hoskins and Robson propose scaffold-like 3D frameworks

1995
Yaghi publishes hydrothermal MOF synthesis

1997
Kitagawa publishes study of Zn frameworks for gas storage

1999
Yaghi publishes synthesis of MOF-5

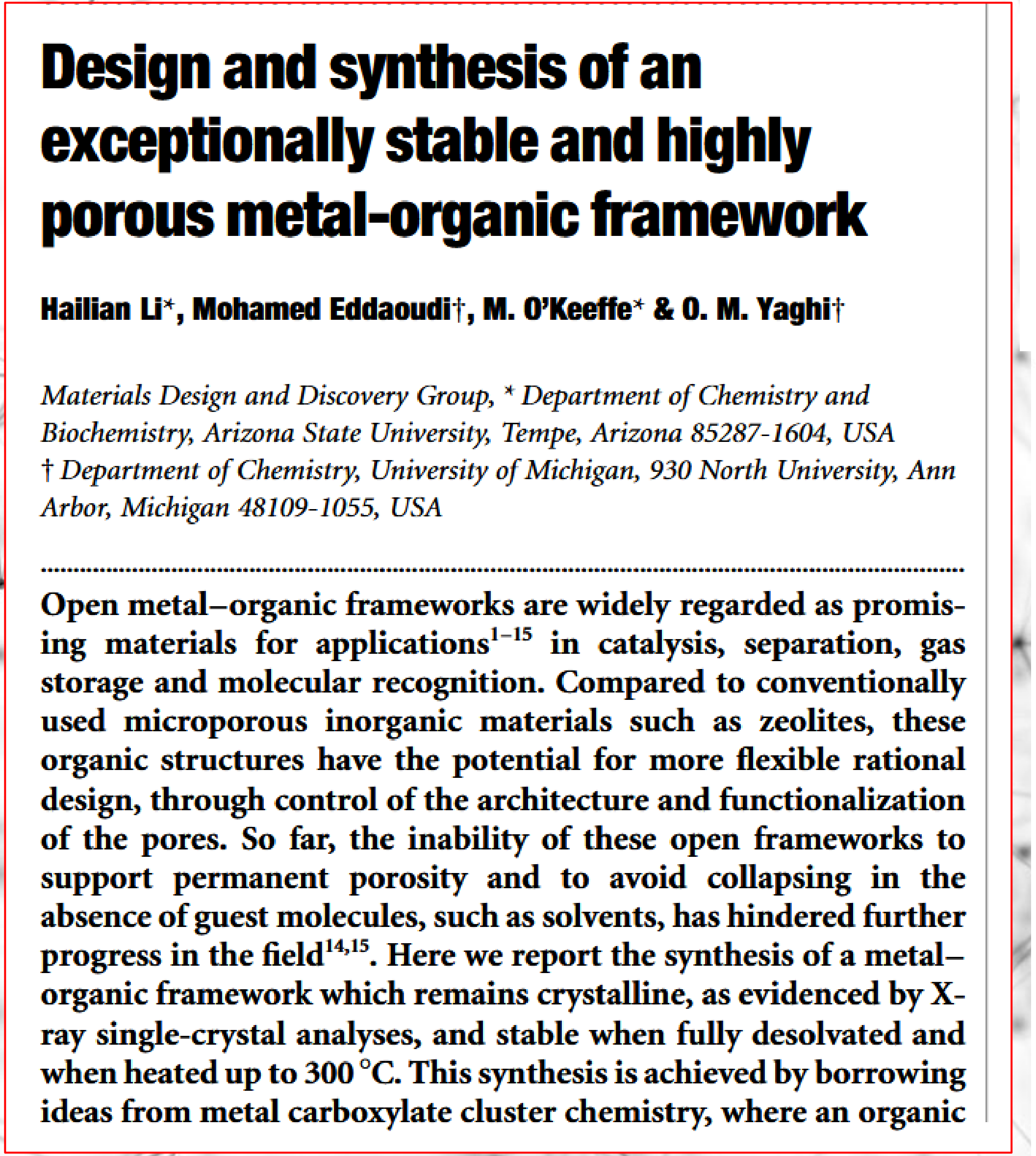
rapid growth in popularity and application

2019
75,600 MOF structures registered in CSD

gas storage
catalysis
purifications
light harvesting
drug delivery
conductivity
magnetism
oncology, etc.

Tomic, E. A. *J. Appl. Polym. Sci.* **1965**, *9*, 3745-3752.
Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546-1554.
Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1995**, *117*, 10401-10402.
Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem. Int. Ed.* **1997**, *36*, 1725-1727
Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276-279.
The Cambridge Crystallographic Data Centre. How Many MOFs are there in the CSD? https://www.ccdc.cam.ac.uk/ (Accessed Apr 20, 2019).

Metal Organic Frameworks

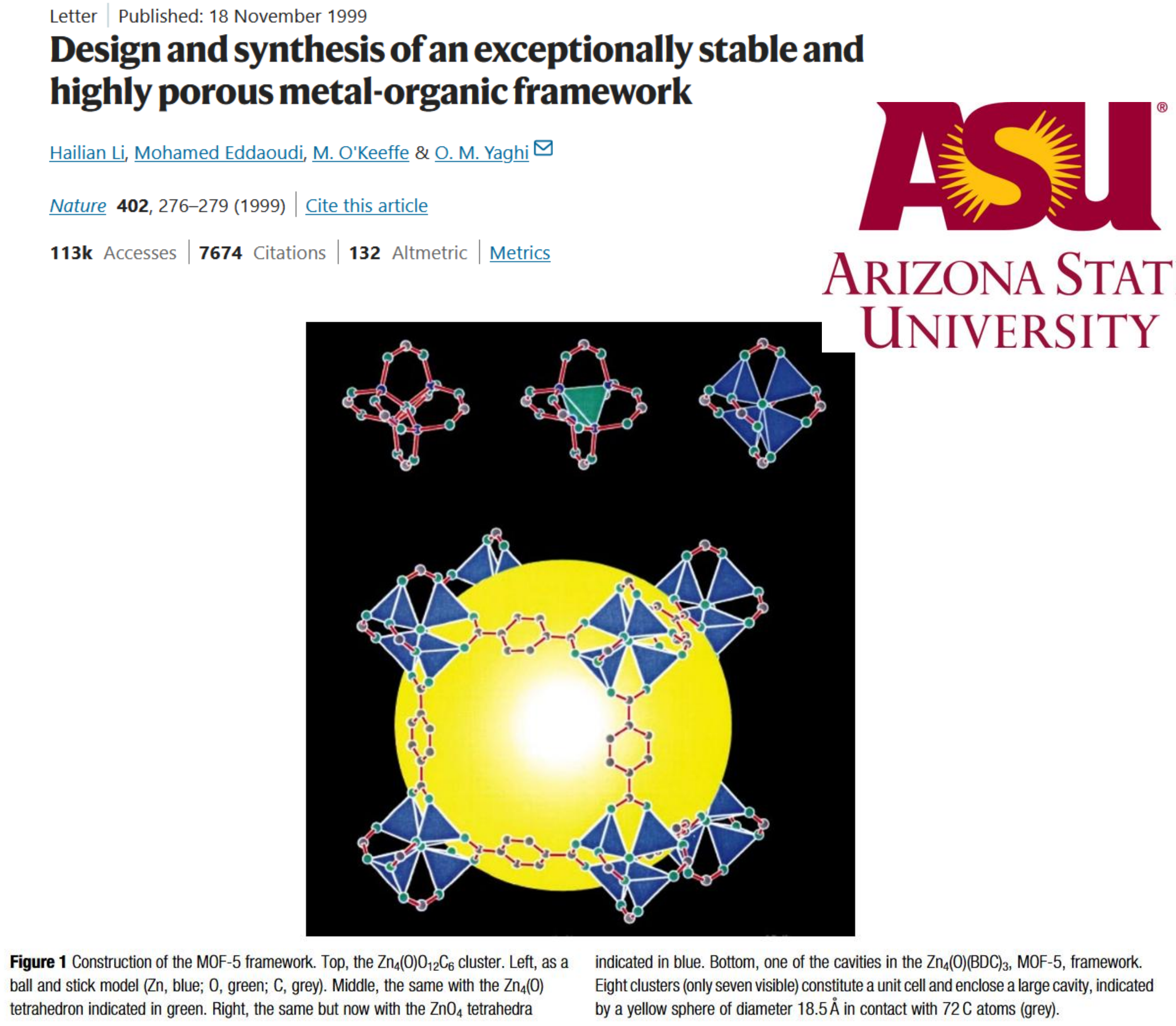


Design and synthesis of an exceptionally stable and highly porous metal-organic framework

Hailian Li*, Mohamed Eddaoudi†, M. O'Keeffe* & O. M. Yaghi†

*Materials Design and Discovery Group, * Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, USA*
† Department of Chemistry, University of Michigan, 930 North University, Ann Arbor, Michigan 48109-1055, USA

Open metal–organic frameworks are widely regarded as promising materials for applications[1–15] in catalysis, separation, gas storage and molecular recognition. Compared to conventionally used microporous inorganic materials such as zeolites, these organic structures have the potential for more flexible rational design, through control of the architecture and functionalization of the pores. So far, the inability of these open frameworks to support permanent porosity and to avoid collapsing in the absence of guest molecules, such as solvents, has hindered further progress in the field[14,15]. Here we report the synthesis of a metal–organic framework which remains crystalline, as evidenced by X-ray single-crystal analyses, and stable when fully desolvated and when heated up to 300 °C. This synthesis is achieved by borrowing ideas from metal carboxylate cluster chemistry, where an organic



Letter | Published: 18 November 1999

Design and synthesis of an exceptionally stable and highly porous metal-organic framework

Hailian Li, Mohamed Eddaoudi, M. O'Keeffe & O. M. Yaghi

Nature **402**, 276–279 (1999) | Cite this article

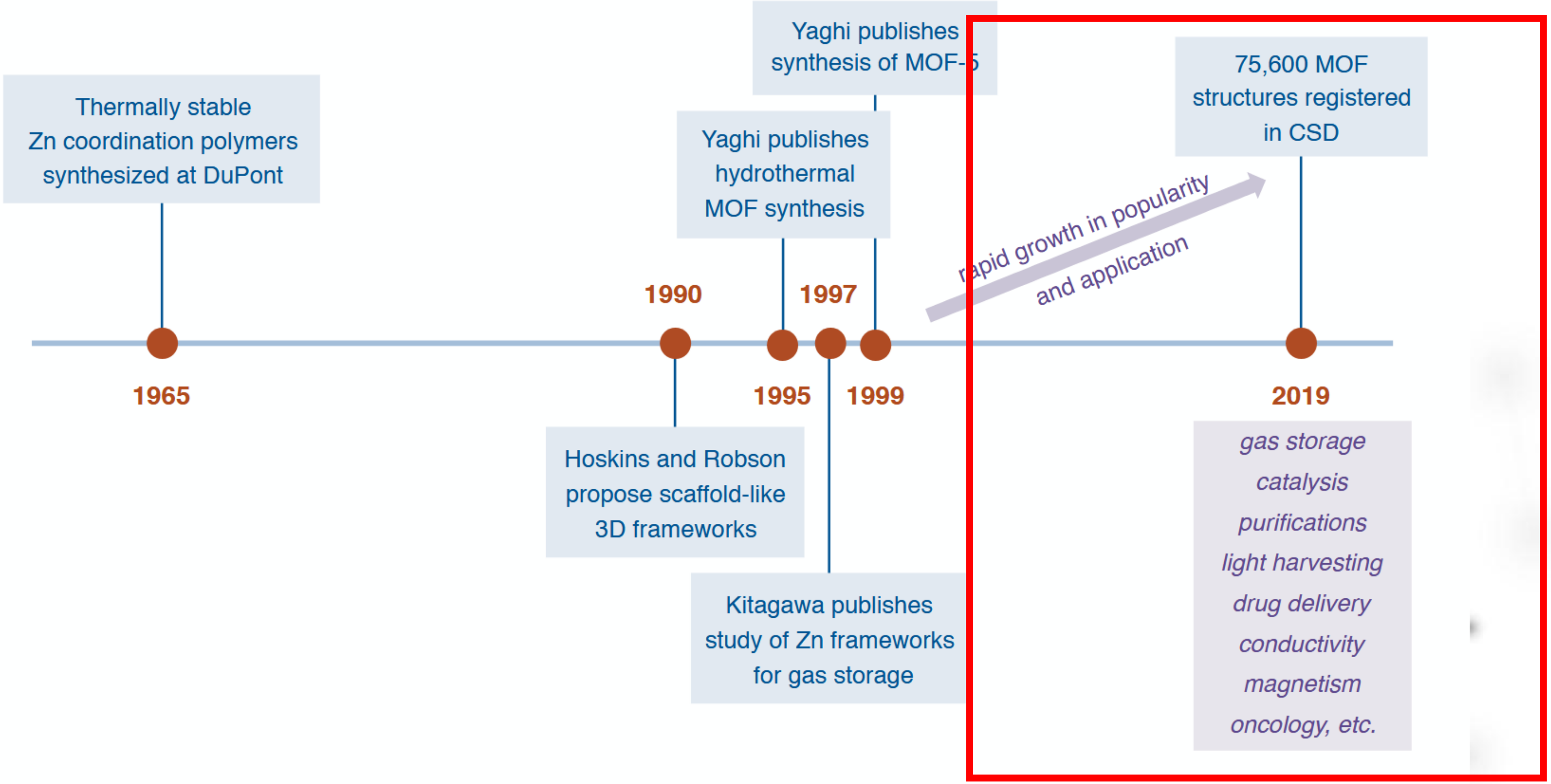
113k Accesses | **7674** Citations | **132** Altmetric | Metrics

Figure 1 Construction of the MOF-5 framework. Top, the $Zn_4(O)O_{12}C_6$ cluster. Left, as a ball and stick model (Zn, blue; O, green; C, grey). Middle, the same with the $Zn_4(O)$ tetrahedron indicated in green. Right, the same but now with the ZnO_4 tetrahedra indicated in blue. Bottom, one of the cavities in the $Zn_4(O)(BDC)_3$, MOF-5, framework. Eight clusters (only seven visible) constitute a unit cell and enclose a large cavity, indicated by a yellow sphere of diameter 18.5 Å in contact with 72 C atoms (grey).

ARIZONA STATE UNIVERSITY

Metal Organic Frameworks

A Brief History of Metal-Organic Frameworks



1965
Thermally stable Zn coordination polymers synthesized at DuPont

1990
Hoskins and Robson propose scaffold-like 3D frameworks

1995
Yaghi publishes hydrothermal MOF synthesis

1997
Kitagawa publishes study of Zn frameworks for gas storage

1999
Yaghi publishes synthesis of MOF-5

rapid growth in popularity and application

2019
75,600 MOF structures registered in CSD

gas storage
catalysis
purifications
light harvesting
drug delivery
conductivity
magnetism
oncology, etc.

Tomic, E. A. *J. Appl. Polym. Sci.* **1965**, *9*, 3745-3752.
Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546-1554.
Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1995**, *117*, 10401-10402.
Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem. Int. Ed.* **1997**, *36*, 1725-1727
Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276-279.
The Cambridge Crystallographic Data Centre. How Many MOFs are there in the CSD? https://www.ccdc.cam.ac.uk/ (Accessed Apr 20, 2019).

Metal Organic Frameworks

Why so many different applications?

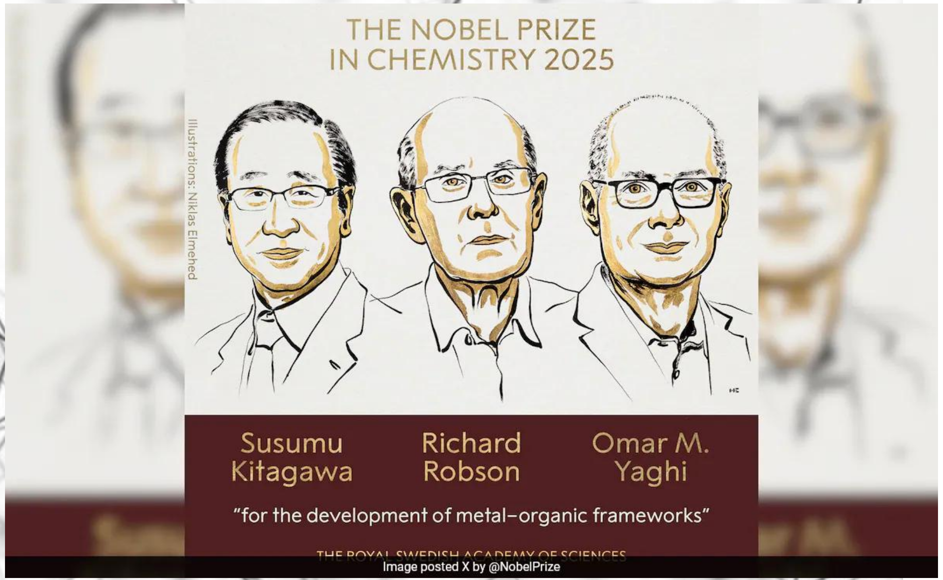
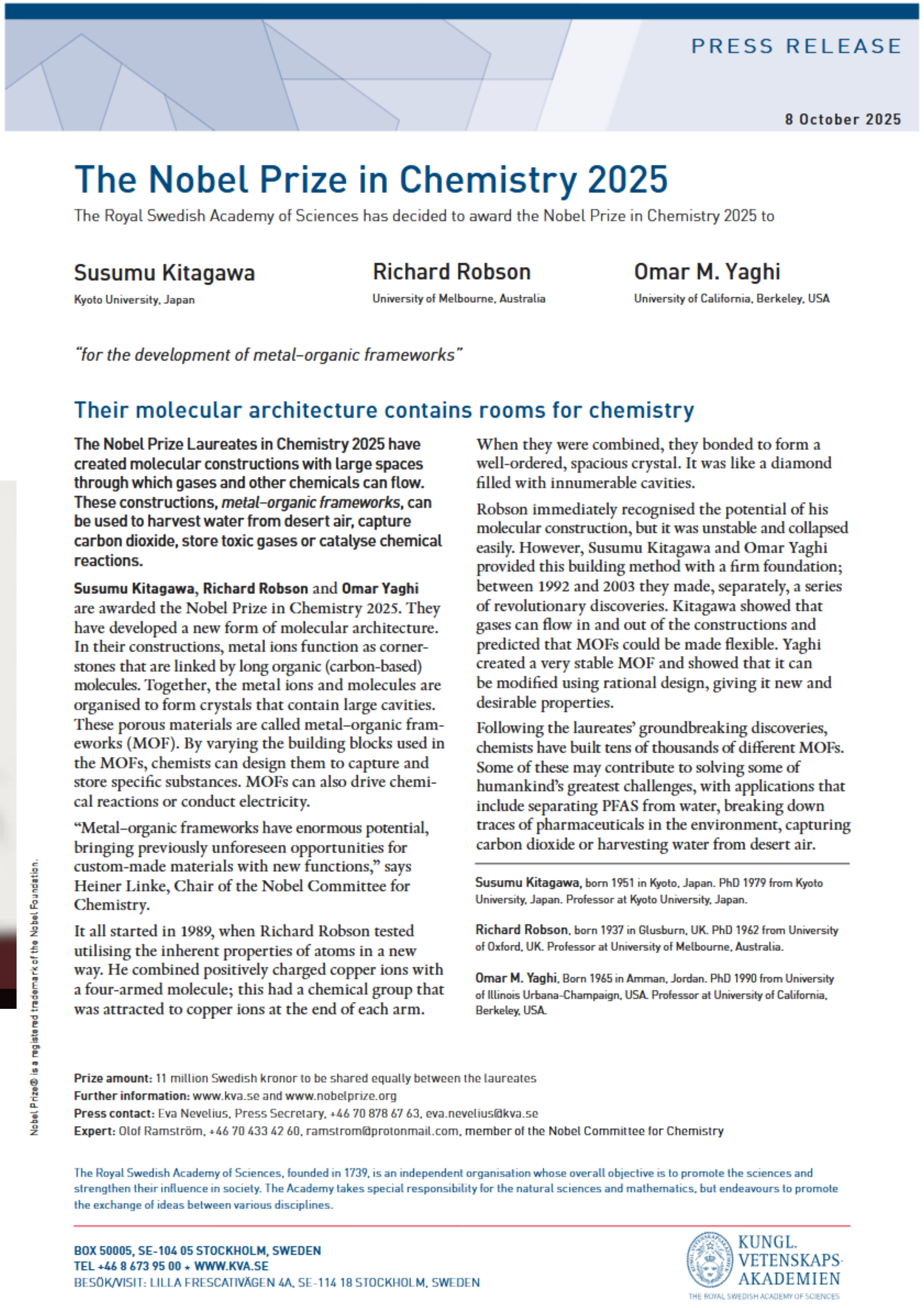


Image posted X by @NobelPrize



PRESS RELEASE

8 October 2025

The Nobel Prize in Chemistry 2025

The Royal Swedish Academy of Sciences has decided to award the Nobel Prize in Chemistry 2025 to

Susumu Kitagawa
Kyoto University, Japan

Richard Robson
University of Melbourne, Australia

Omar M. Yaghi
University of California, Berkeley, USA

"for the development of metal-organic frameworks"

Their molecular architecture contains rooms for chemistry

The Nobel Prize Laureates in Chemistry 2025 have created molecular constructions with large spaces through which gases and other chemicals can flow. These constructions, *metal–organic frameworks*, can be used to harvest water from desert air, capture carbon dioxide, store toxic gases or catalyse chemical reactions.

Susumu Kitagawa, Richard Robson and **Omar Yaghi** are awarded the Nobel Prize in Chemistry 2025. They have developed a new form of molecular architecture. In their constructions, metal ions function as cornerstones that are linked by long organic (carbon-based) molecules. Together, the metal ions and molecules are organised to form crystals that contain large cavities. These porous materials are called metal–organic frameworks (MOF). By varying the building blocks used in the MOFs, chemists can design them to capture and store specific substances. MOFs can also drive chemical reactions or conduct electricity.

"Metal–organic frameworks have enormous potential, bringing previously unforeseen opportunities for custom-made materials with new functions," says Heiner Linke, Chair of the Nobel Committee for Chemistry.

It all started in 1989, when Richard Robson tested utilising the inherent properties of atoms in a new way. He combined positively charged copper ions with a four-armed molecule; this had a chemical group that was attracted to copper ions at the end of each arm.

When they were combined, they bonded to form a well-ordered, spacious crystal. It was like a diamond filled with innumerable cavities.

Robson immediately recognised the potential of his molecular construction, but it was unstable and collapsed easily. However, Susumu Kitagawa and Omar Yaghi provided this building method with a firm foundation; between 1992 and 2003 they made, separately, a series of revolutionary discoveries. Kitagawa showed that gases can flow in and out of the constructions and predicted that MOFs could be made flexible. Yaghi created a very stable MOF and showed that it can be modified using rational design, giving it new and desirable properties.

Following the laureates' groundbreaking discoveries, chemists have built tens of thousands of different MOFs. Some of these may contribute to solving some of humankind's greatest challenges, with applications that include separating PFAS from water, breaking down traces of pharmaceuticals in the environment, capturing carbon dioxide or harvesting water from desert air.

Susumu Kitagawa, born 1951 in Kyoto, Japan. PhD 1979 from Kyoto University, Japan. Professor at Kyoto University, Japan.

Richard Robson, born 1937 in Glusburn, UK. PhD 1962 from University of Oxford, UK. Professor at University of Melbourne, Australia.

Omar M. Yaghi, Born 1965 in Amman, Jordan. PhD 1990 from University of Illinois Urbana-Champaign, USA. Professor at University of California, Berkeley, USA.

Prize amount: 11 million Swedish kronor to be shared equally between the laureates
Further information: www.kva.se and www.nobelprize.org
Press contact: Eva Nevelius, Press Secretary, +46 70 878 67 63, eva.nevelius@kva.se
Expert: Olof Ramström, +46 70 433 42 60, ramstrom@protonmail.com, member of the Nobel Committee for Chemistry

Nobel Prize® is a registered trademark of the Nobel Foundation.

The Royal Swedish Academy of Sciences, founded in 1739, is an independent organisation whose overall objective is to promote the sciences and strengthen their influence in society. The Academy takes special responsibility for the natural sciences and mathematics, but endeavours to promote the exchange of ideas between various disciplines.

BOX 50005, SE-104 05 STOCKHOLM, SWEDEN
TEL +46 8 673 95 00 • WWW.KVA.SE
BESÖK/VISIT: LILLA FRESCATIVÄGEN 4A, SE-114 18 STOCKHOLM, SWEDEN

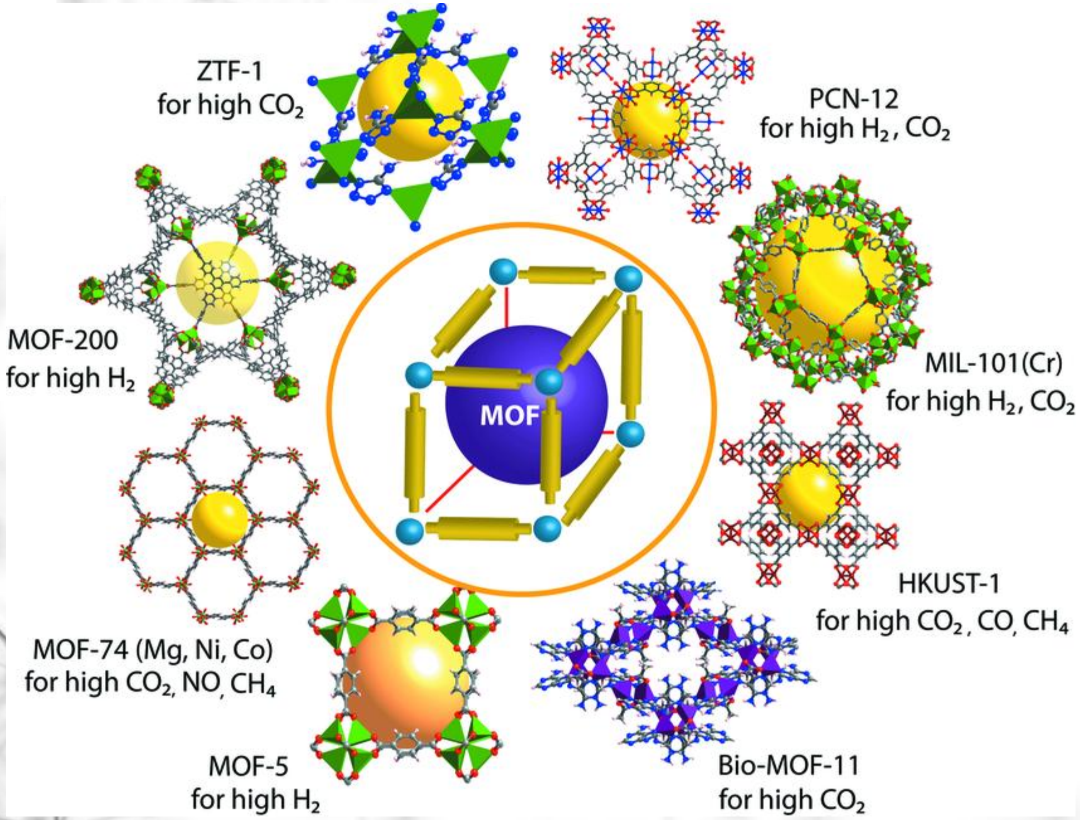
KUNGL. VETENSKAPS-AKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

Metal Organic Frameworks

Structural features

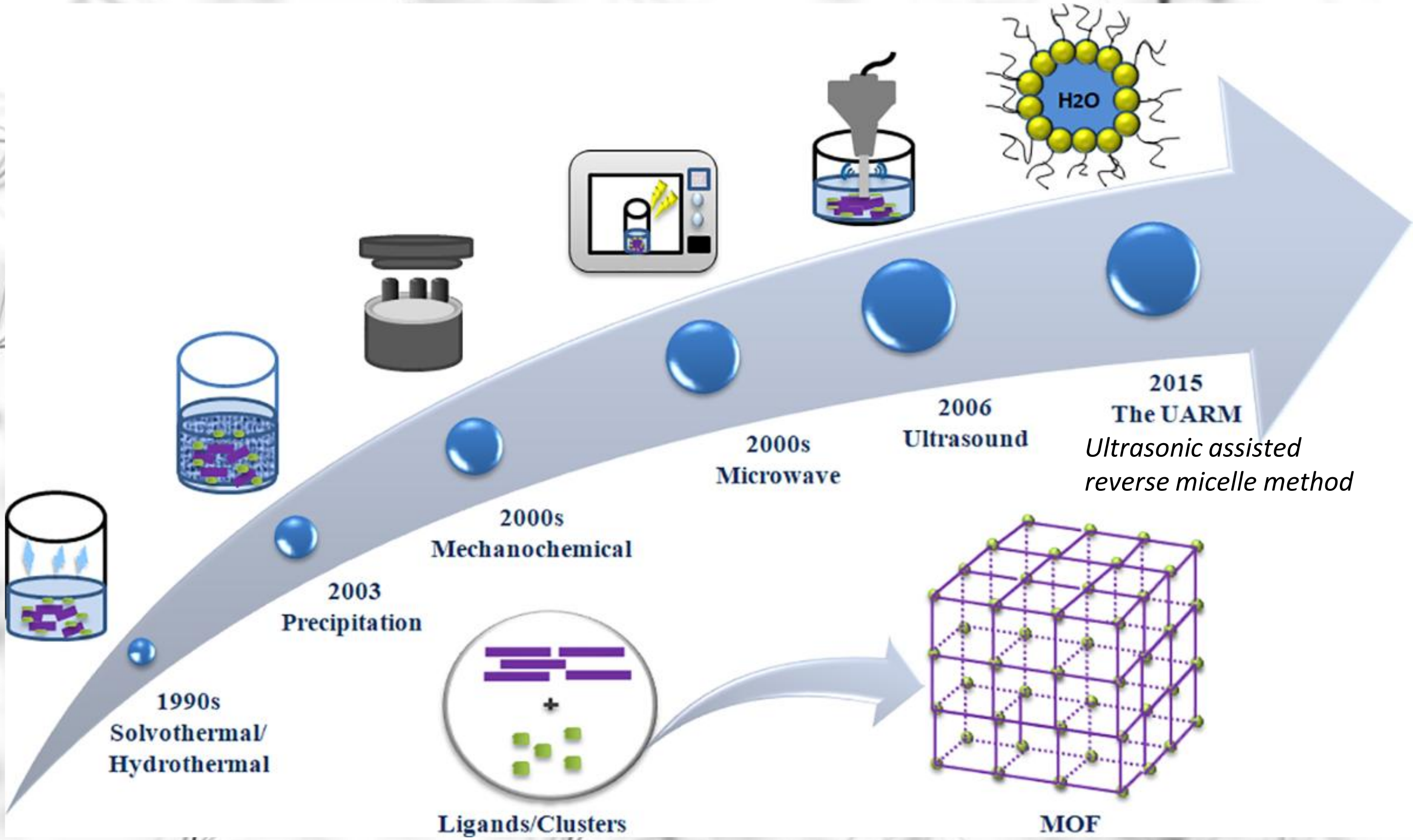
They contain potential voids which can be used for various application.

- Very low density
- Crystalline
- Large voids
- Significant van der Waals interaction



Metal Organic Frameworks

Synthetic Approaches



Ultrasonic assisted reverse micelle method

Routes To MOF

- Solvothermal/ Hydrothermal
- Microwave-Assisted
- Sonochemical
- Mechanochemical
- Electrochemical
- Discarded Material as a synthesis medium
- Water-Based (Green Synthesis)
- Ionic Liquid-Based
- Microfluidic
- Dry Gel Conversion

Metal Organic Frameworks

Synthetic Approaches

Different methods of synthesis of MOFs have been described:

Traditional synthesis:

I) **Hydrothermal/solvothermal** (special closed chemical reactors, boiling temperature of the solvent or above this boiling point, elevated pressure caused by solvent vapour or produced by a pump)

II) **non-solvothermal** (open flasks, below the solvent boiling point, at atmospheric pressure)

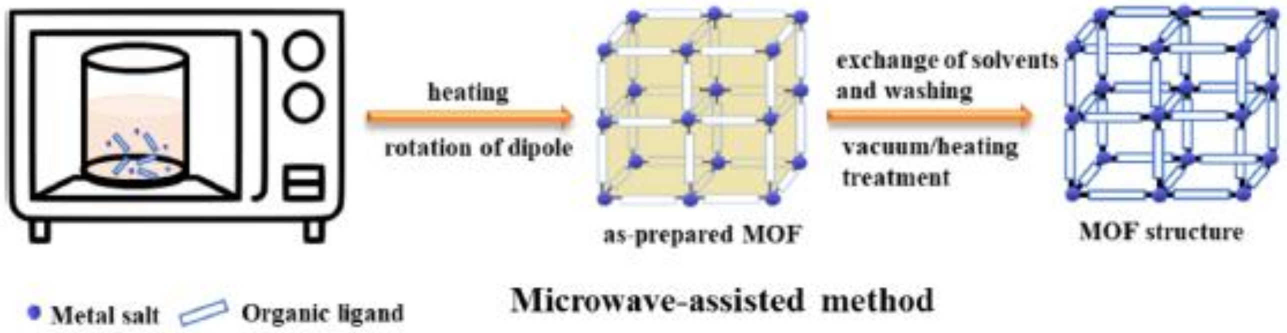
Notice: method II does not require complex equipment
Method I (Solvothermal synthesis) affords **higher yields and better crystallinity** of the product, but requires special equipment (autoclaves or sealed containers that can withstand increased pressure); in addition, the duration of the process should be taken into account (the synthesis can continue for several weeks and even months)

Metal Organic Frameworks

Synthetic Approaches

Microwave approach

Scheme 1. Microwave-Assisted Synthesis of MOF Structures

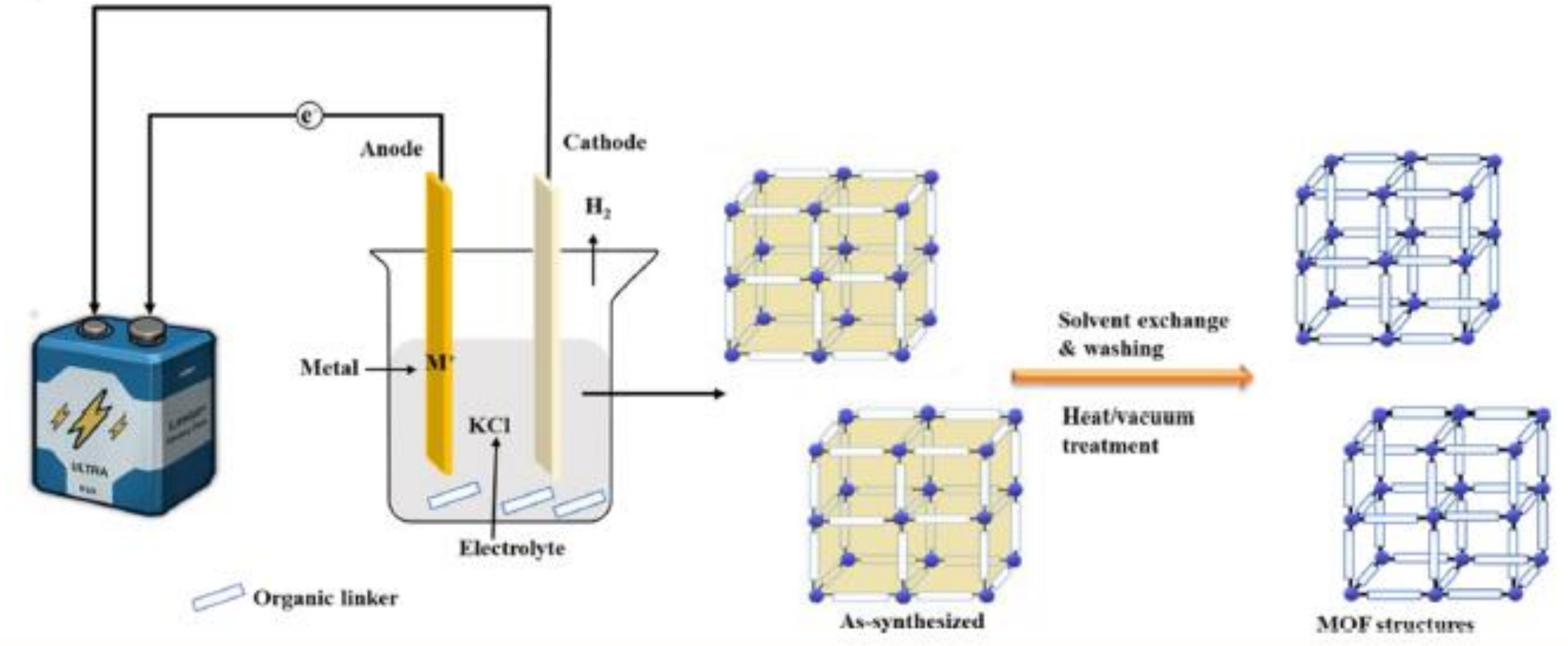


Metal Organic Frameworks

Synthetic Approaches

Electrochemical approach

Scheme 2. Electrochemical Synthesis of MOF Structures

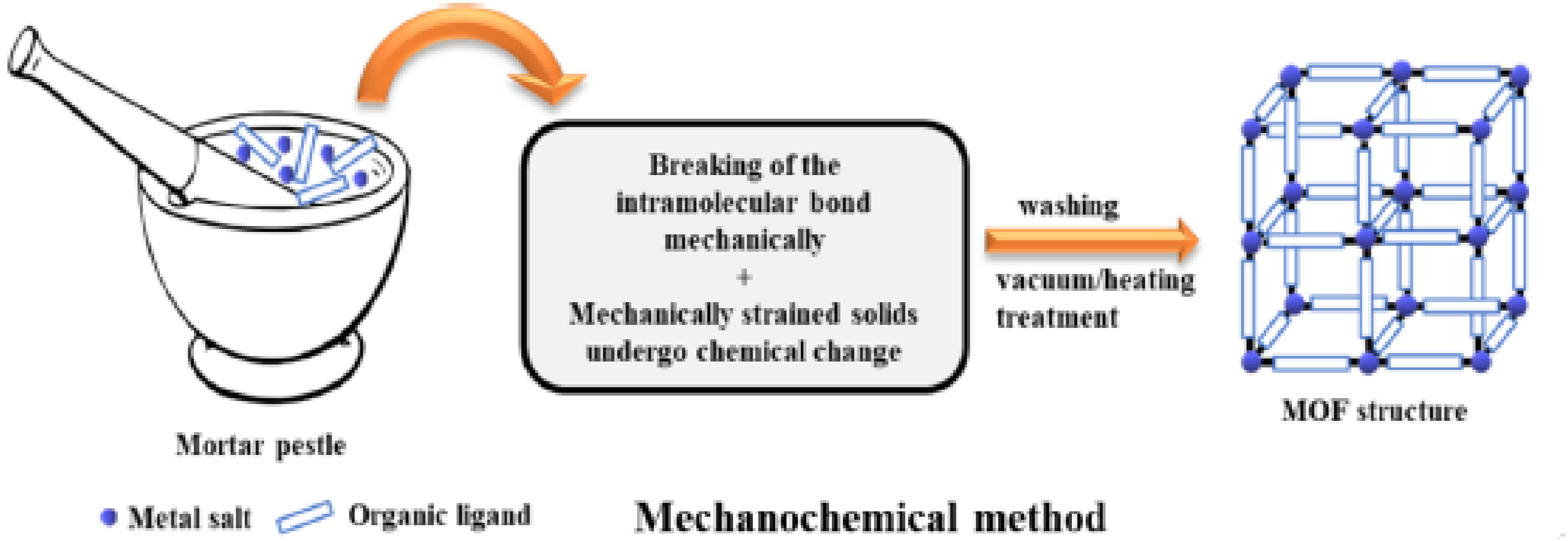


Metal Organic Frameworks

Synthetic Approaches

Mechanochemical approach

Scheme 4. Mechanochemical Synthesis of MOF Structures

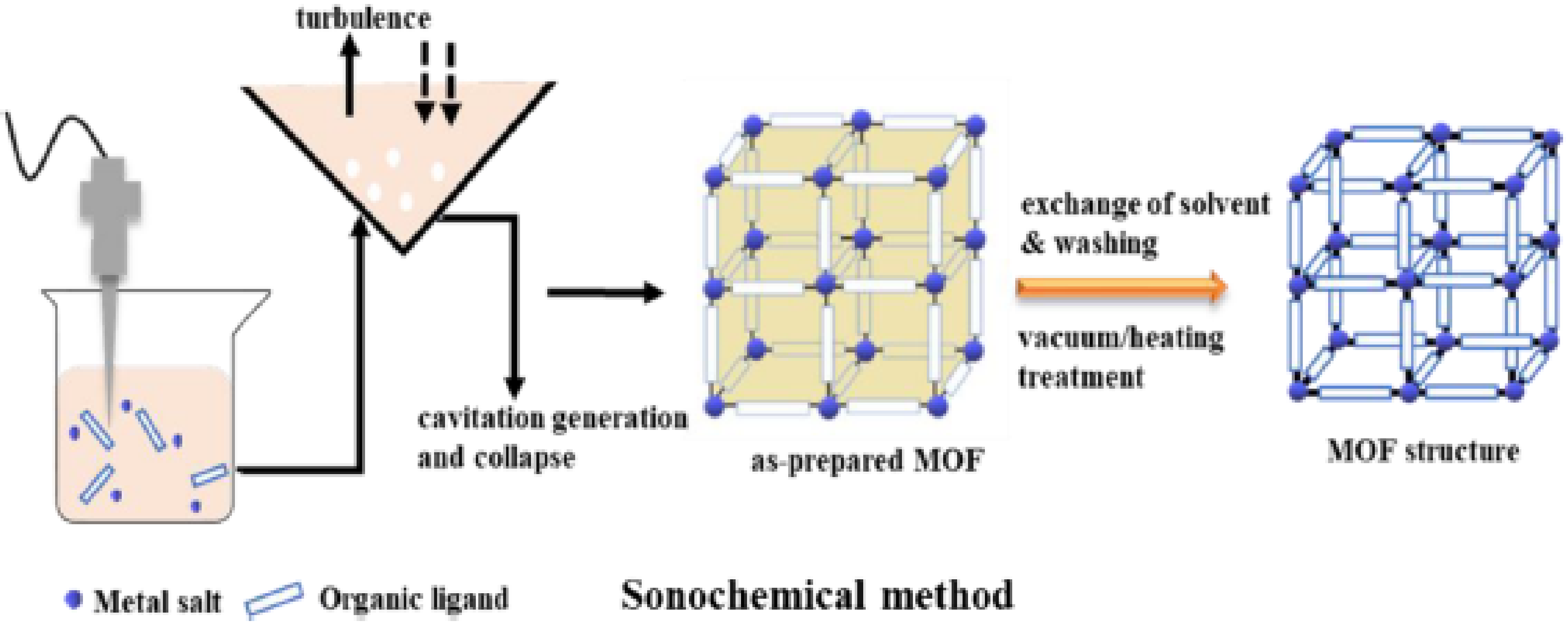


Metal Organic Frameworks

Synthetic Approaches

Sonochemical approach

Scheme 5. Sonochemical Synthesis of MOF Structures

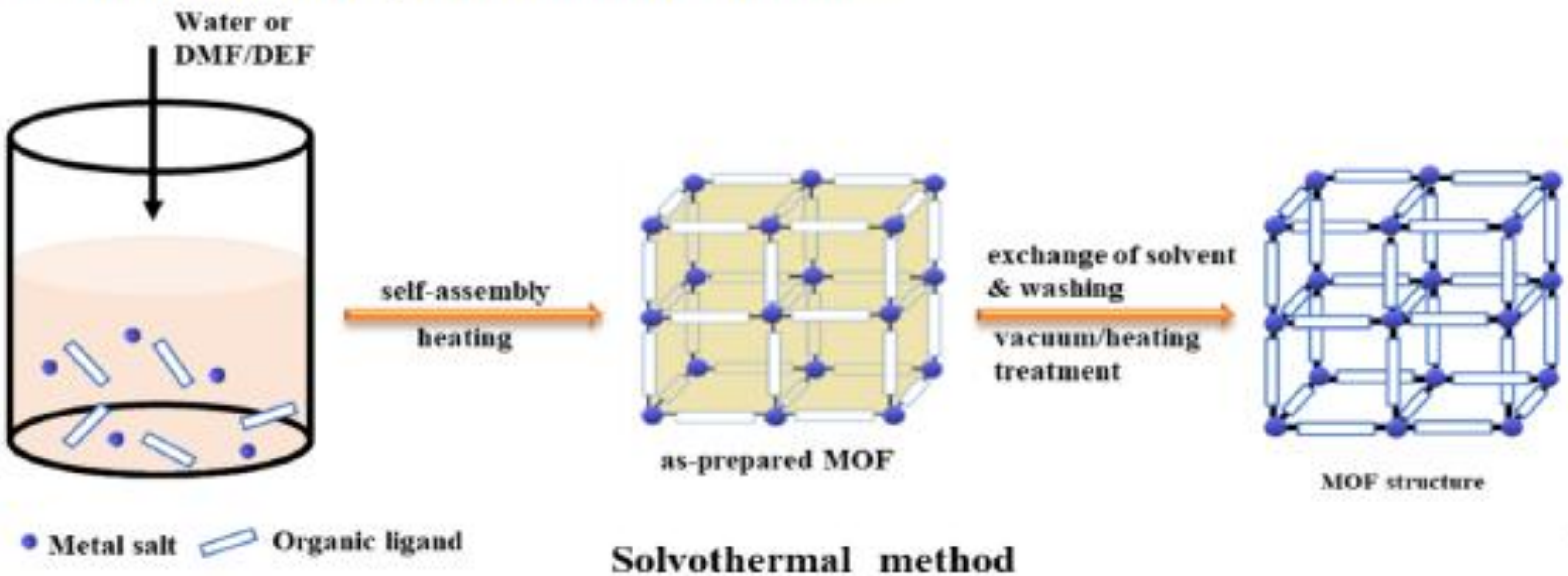


Metal Organic Frameworks

Synthetic Approaches

Conventional solvothermal approach

Scheme 3. Conventional Solvothermal Synthesis of MOF Structures

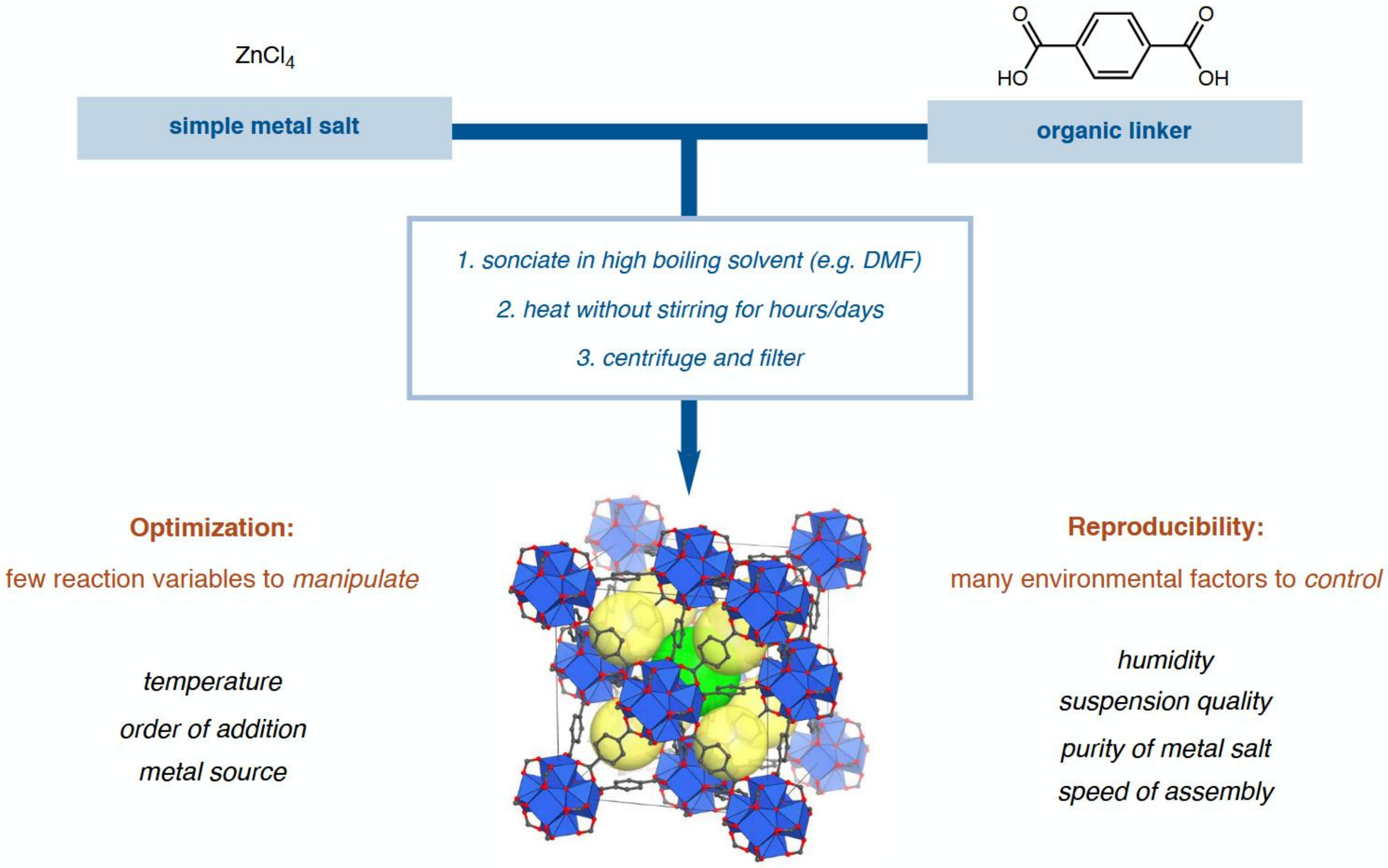


Solvothermal method

Metal Organic Frameworks

Synthetic Approaches

Conventional solvothermal approach



$ZnCl_4$

simple metal salt

organic linker

1. *sonciate in high boiling solvent (e.g. DMF)*
2. *heat without stirring for hours/days*
3. *centrifuge and filter*

Optimization:

few reaction variables to *manipulate*

temperature
order of addition
metal source

Reproducibility:

many environmental factors to *control*

humidity
suspension quality
purity of metal salt
speed of assembly

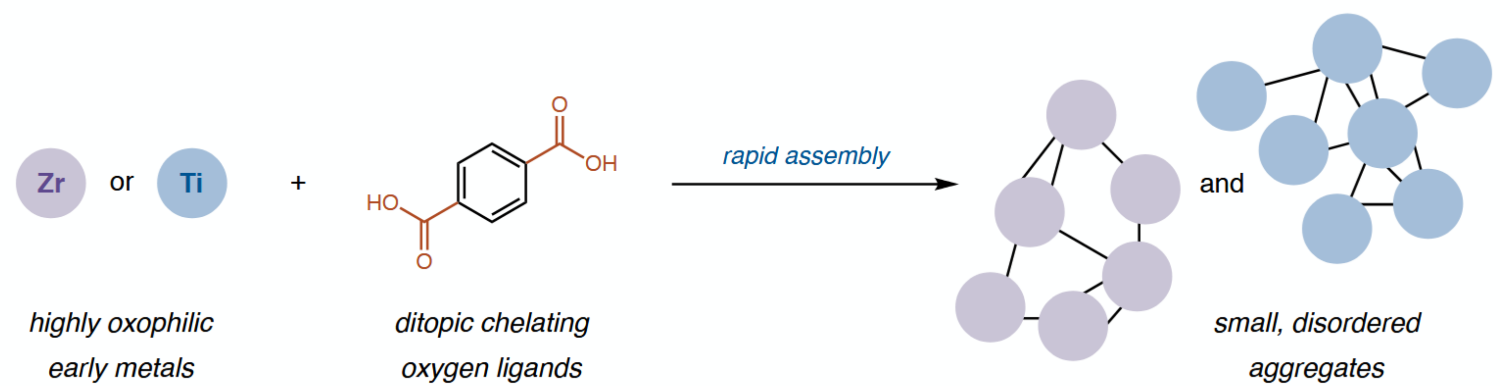
Howarth, A. J.; Peters, A. W.; Vermeulen, N. A.; Wang, T. C.; Hupp, J. T.; Farha, O. K. *Chem. Mater.* **2017**, *29*, 26-39.

Metal Organic Frameworks

Synthetic Approaches

Conventional solvothermal approach

Pitfalls of Uncontrolled Self-Assembly



How do we slow down self-assembly and control lattice quality?

Modulators promote order in MOF self-assembly

Metal Organic Frameworks

Synthetic Approaches

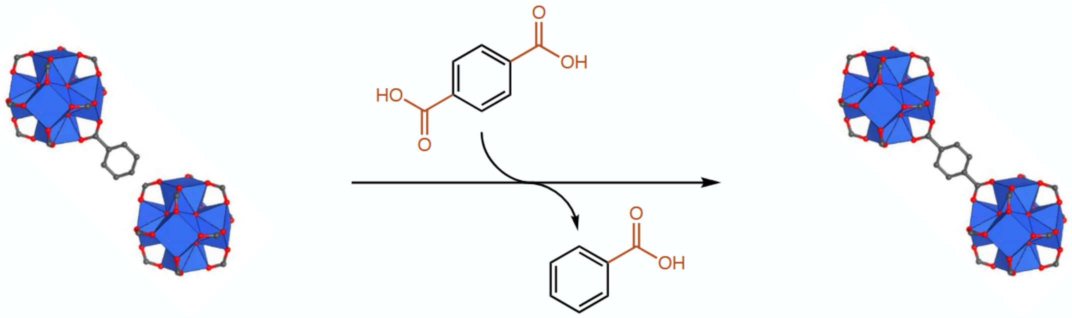
Conventional solvothermal approach

Modulators as Small Molecule Regulators of MOF Growth

Mechanisms of Action

1. Reversibly occupying coordination sites on metal clusters
2. Accelerating metal cluster formation

Case 1: Benzoic and acetic acids

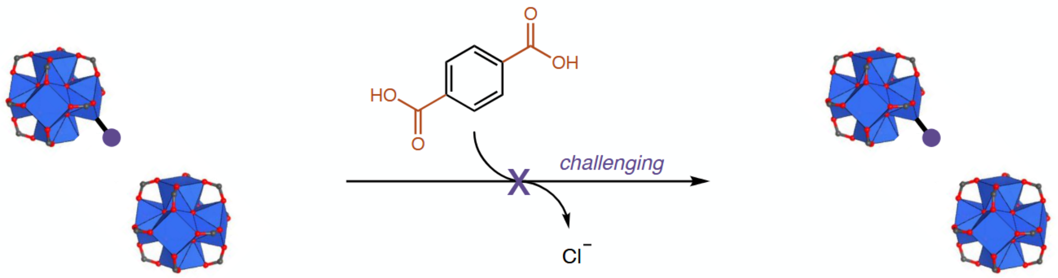


Monotopic coordination to metal clusters slows nucleation rate

Promotes ideal framework assembly

Shaate, A.; Roy, P.; Godt, A.; Lippke, J.; Waltz, F.; Wiebcke, M.; Behrens, P. *Chem. Eur. J.* **2011**, *17*, 6643-6651.

Case 2: Hydrochloric Acid



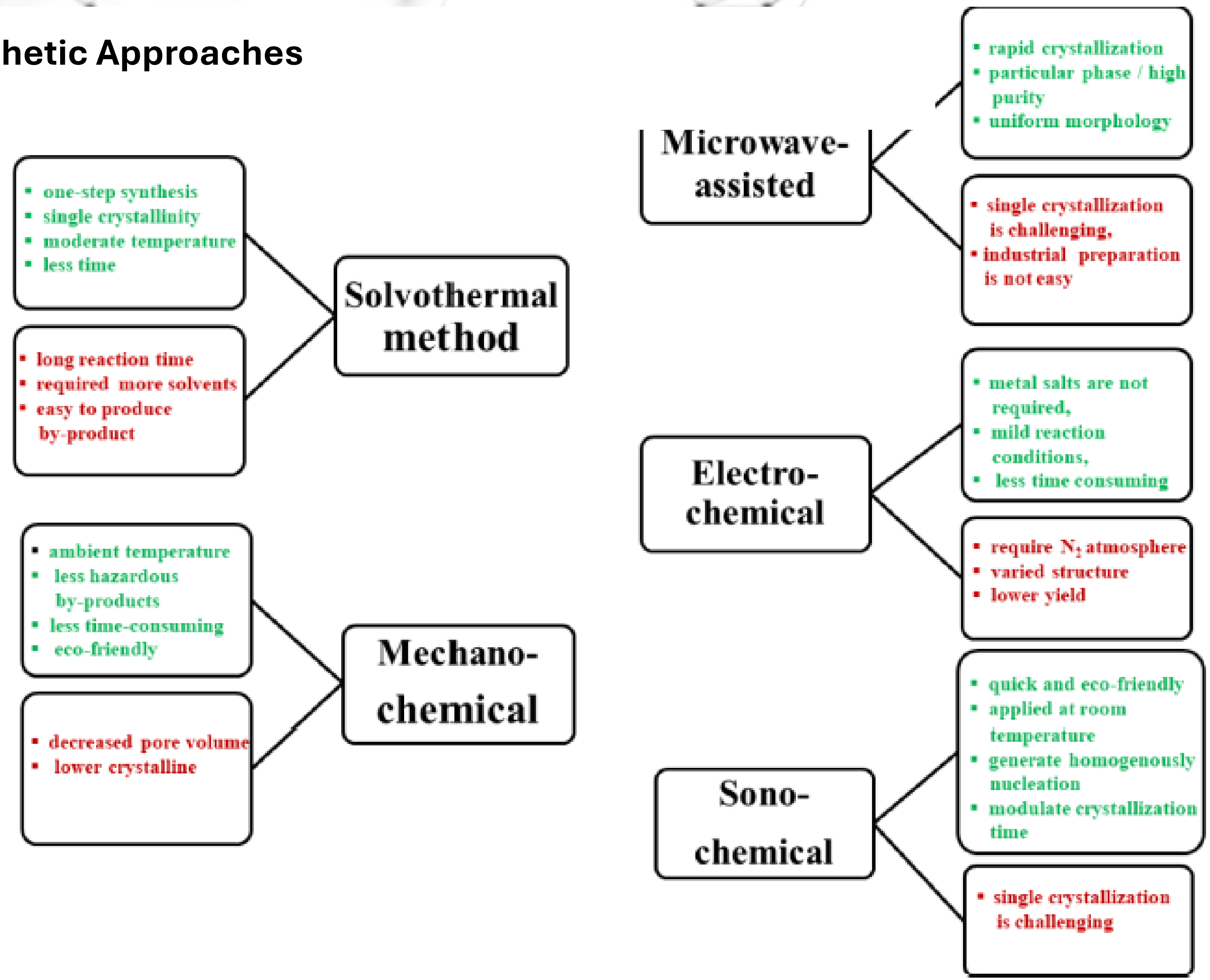
Neutralizes solvent (DMF) and promotes metal cluster formation

Creates missing linker defect sites
(not necessarily a bad outcome)

Katz, M. J.; Brown, Z. J.; Colon, Y, J.; Siu, P. W.; Scheidt, K. A.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K. *Chem. Commun.* **2013**, *49*, 9449-9451.

Metal Organic Frameworks

Synthetic Approaches



Solvothermal method

- one-step synthesis
- single crystallinity
- moderate temperature
- less time

- long reaction time
- required more solvents
- easy to produce by-product

Mechano-chemical

- ambient temperature
- less hazardous by-products
- less time-consuming
- eco-friendly

- decreased pore volume
- lower crystalline

Microwave-assisted

- rapid crystallization
- particular phase / high purity
- uniform morphology

- single crystallization is challenging,
- industrial preparation is not easy

Electro-chemical

- metal salts are not required,
- mild reaction conditions,
- less time consuming

- require N_2 atmosphere
- varied structure
- lower yield

Sono-chemical

- quick and eco-friendly
- applied at room temperature
- generate homogenously nucleation
- modulate crystallization time

- single crystallization is challenging

Metal Organic Frameworks

Synthetic Approaches

But most of the time, MOFs are synthesized by combining organic ligands and metal salts in **solvothermal** reactions at low temperatures (below 300°C), that:

➤ **Polar solvent:** Water, dialkyl formamides, dimethyl sulfoxide or acetonitrile.

➤ **The most important parameters of solvothermal:**

Temperature,
the source and concentration of metal salt and ligand (which can be varied across a large range),

the solubility of the reactants in the solvent,

the pH of the solution,

reaction time and etc.

Metal Organic Frameworks

Importance of pore size

- **Many potential applications of MOFs depends on the size and nature** of the available free volume or pores within the frameworks structure

- **Tuning of the pores is typically achieved by variation of the metal ions or organic ligands**

- **Lengthening the organic chains can lead to increased pore size but is often limited by a decrease in stability of the framework**

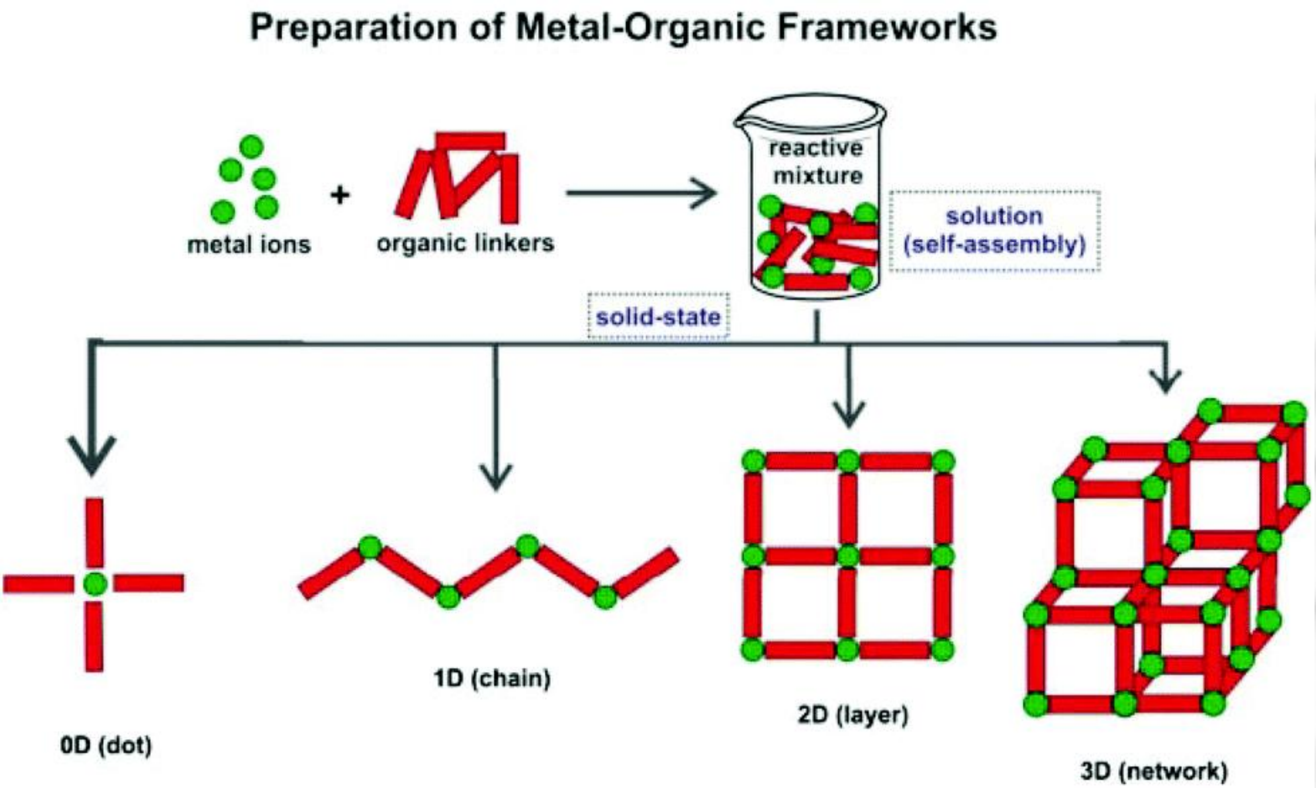
- **With no gas present,** the thermal conductivity decreases with increasing pore size. **In the presence of adsorbed gas**, MOFs with smaller pores experience reduced thermal conductivity due to phonon scattering introduced by gas crystal interactions

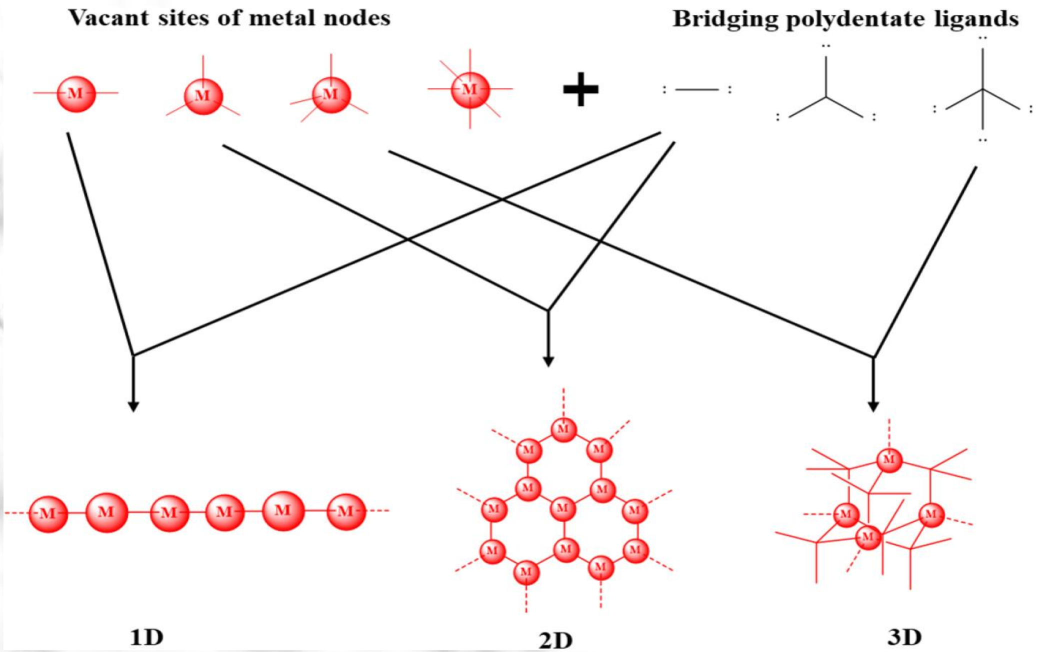
- **For larger pores (>1.7 nm), the adsorbed gas does not significantly affect thermal conductivity**

- **This difference is due to the decreased probability if gas-crystal collisions in larger pore structures**

Metal Organic Frameworks

Topology

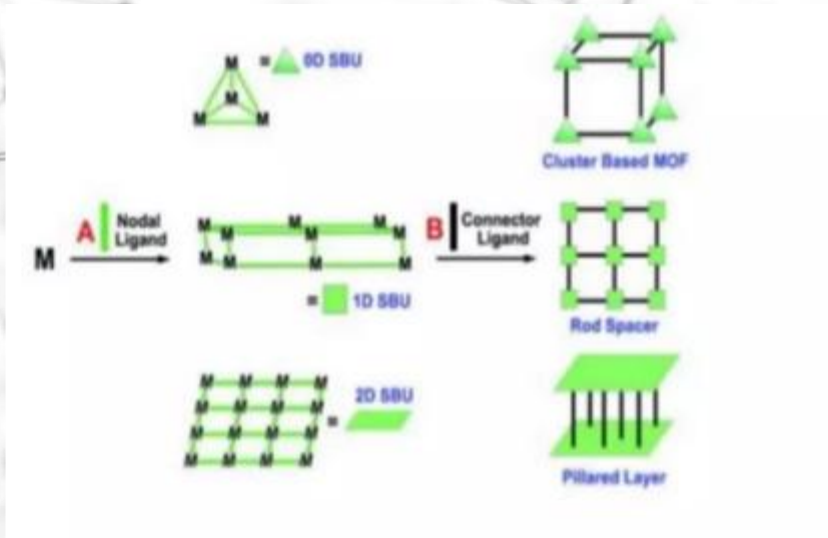


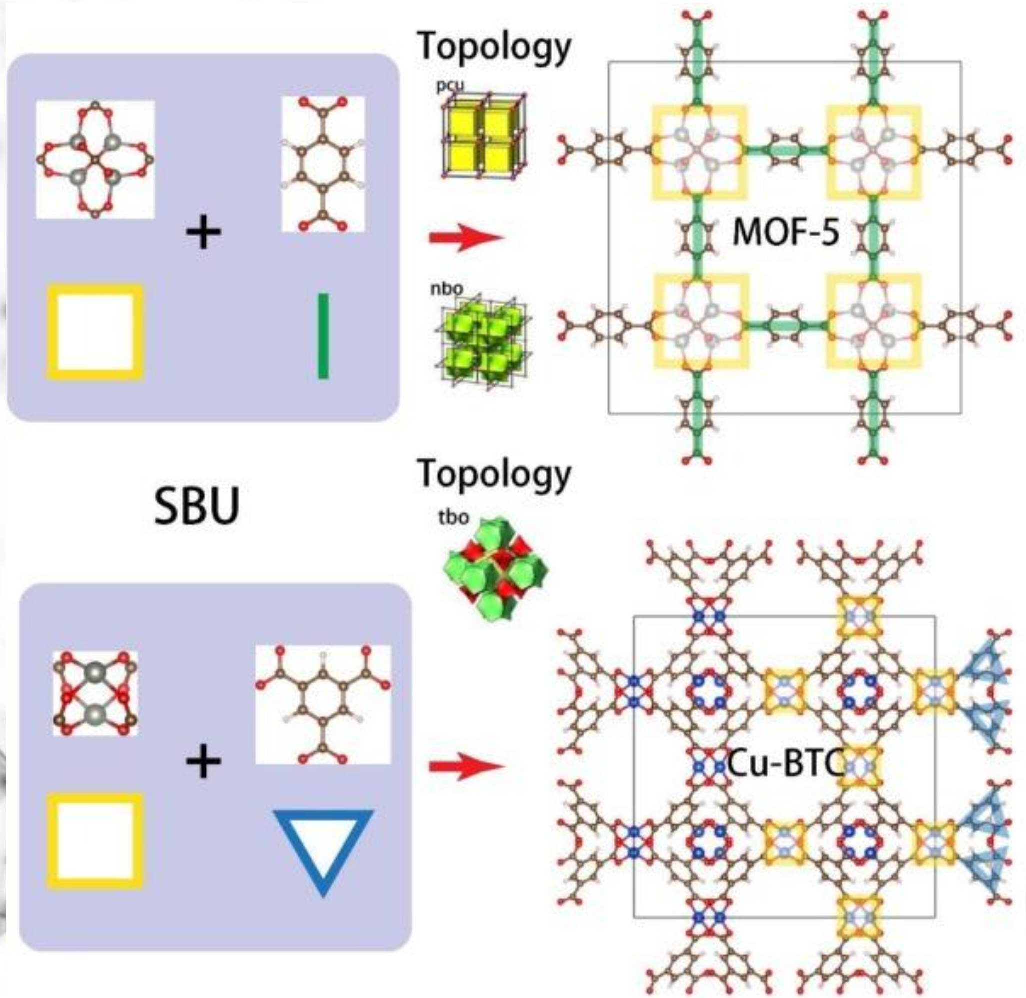


Metal Organic Frameworks

Topology

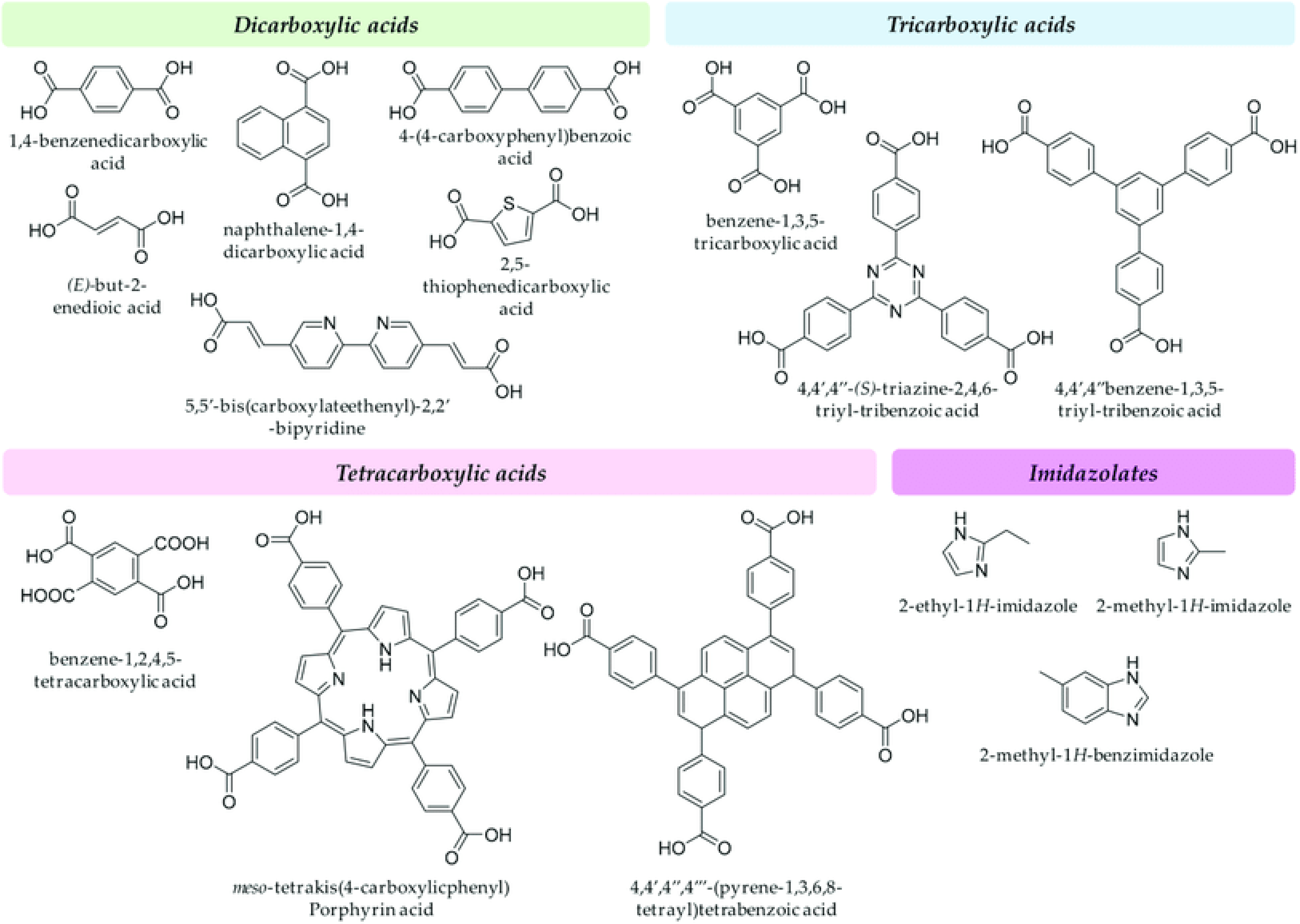
The coordination complex formed by the metal ions ad the donor atoms of the linker, termed the secondary building unit (SBU), dictates the final topology of the MOF framework

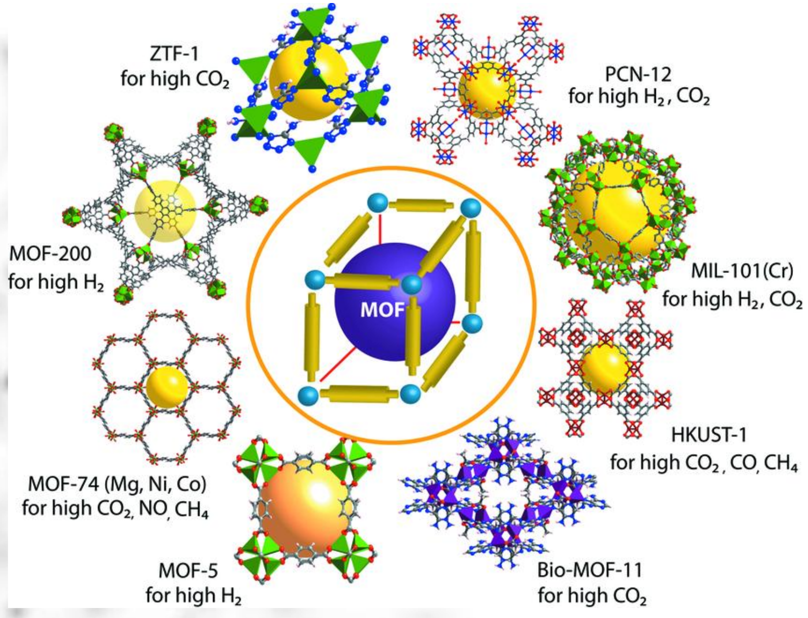




Metal Organic Frameworks

Common ligands used for MOFs





Metal Organic Frameworks

Properties of MOFs

- **The backbone of the compound is constructed from metal ions which act as connectors and organic bridging ligands as linkers.**

- **Readily accessible porosity.**

- **The coexistence of inorganic (hydrophilic) and organic (hydrophobic) moieties in structure may influence on adsorption properties.**

- Although most of MOFs are electrical insulators, several materials in this class have recently demonstrated **excellent electrical conductivity and high charge mobility**.

- The **thermal stability of MOFs** is determined by the coordination number and local coordination environment instead of framework topology.

- In general MOFs are poor thermal conductors with thermal conductivity that is similar to concrete.

Metal Organic Frameworks

For better application

- **Surface Area:** MOFs with higher surface area are more desirable.
- **Pore Size:** MOFs must have the proper pore size to allow uptake and release of analytes.
- **Stability:** MOFs must exhibit reasonable stability upon exposure to oxygen, moisture, the analytes of interest or changes in temperature.
- **Solubility:** MOFs should be insoluble in aqueous media.
- **Analyte interaction:** MOFs may exhibit special structural characteristics that may facilitate selective uptake and release of analytes.

Metal Organic Frameworks

Chemistry of MOFs

•The **organic linkers** used in MOFs are capable of connecting two metal oxide clusters (ditopic linkers)

•**Linkers with higher dimensionality can also be used**

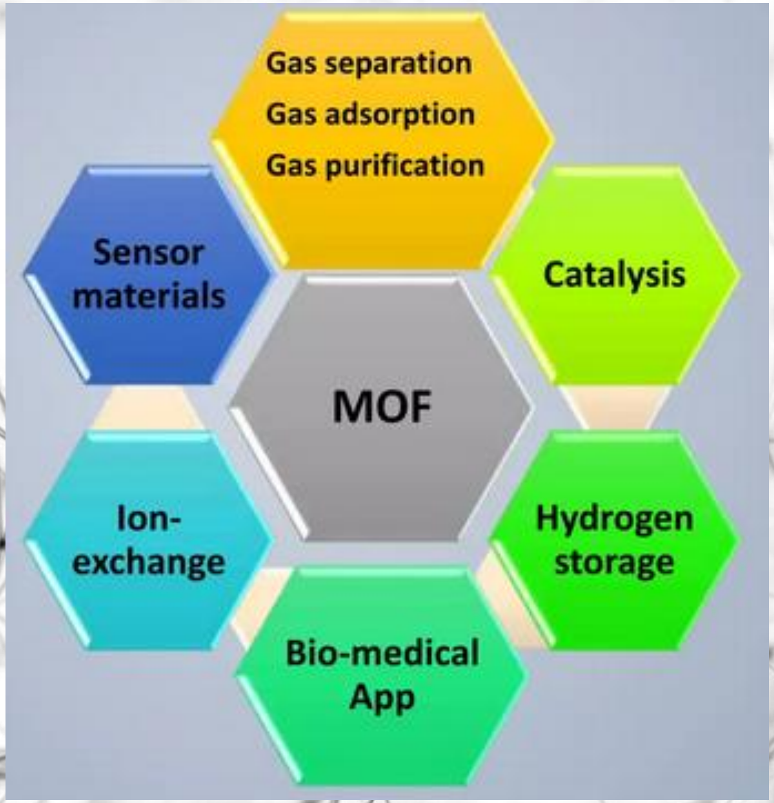
•**Organic ligands with rigid backbones are often preferred**, because the rigidity makes it **easier to predict the network geometry**, and in addition the rigidity also helps to sustain the open pore structure after the removal of the included solvent

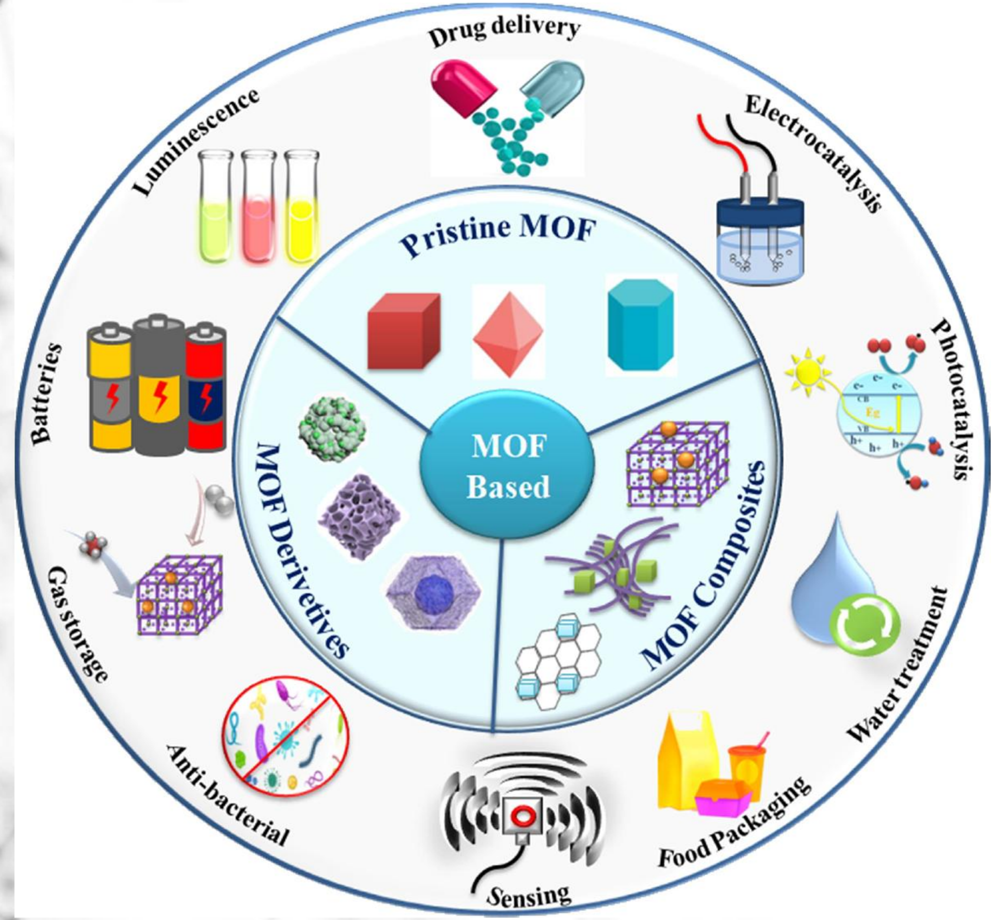
•**Transition metal ions are often used as the inorganic components of MOFs**. Different metal ions are well known to prefer different coordination numbers and geometries, such as linear, T- or Y-shaped, tetrahedral, square-planar, square-pyramidal, trigonal-bipyramidal, octahedral, trigonal-prismatic, and pentagonal-bipyramidal

•The bonds formed between the metal ions and donor atoms of the linker are strong and as a result, the extended network structure in the MOF is quite robust

Metal Organic Frameworks

Applications of MOFs





Metal Organic Frameworks

Publications of MOFs

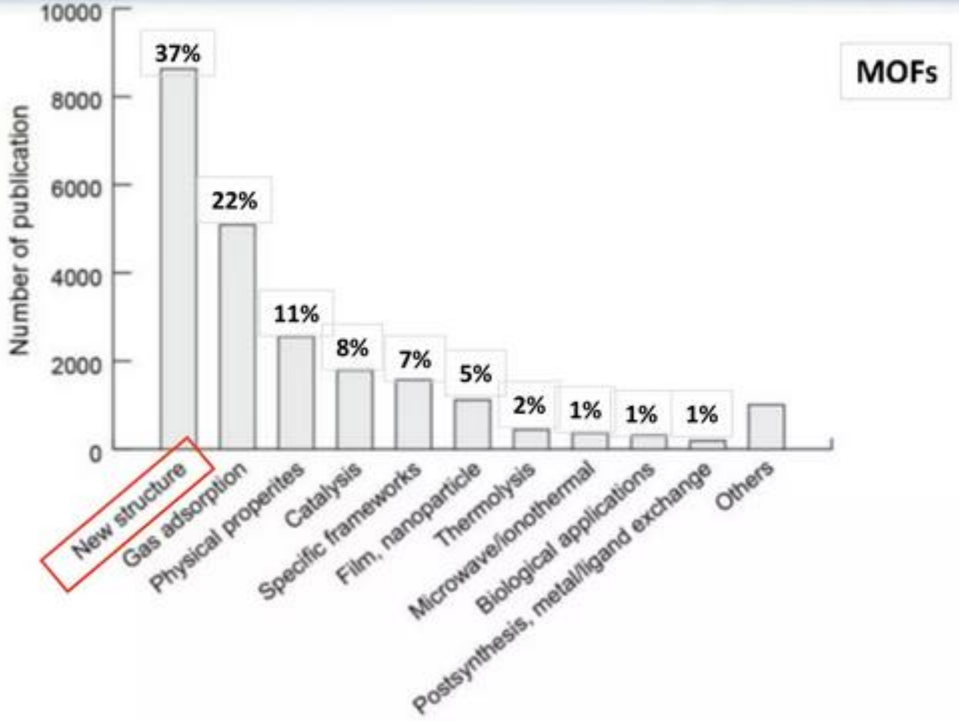
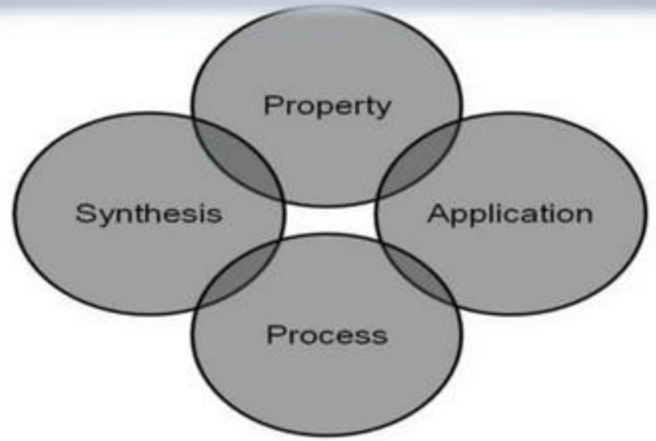


Figure 5. Research areas for MOFs from citation network analysis.



Scheme 2. Stages of material research.

Metal Organic Frameworks vs Zeolites

SYNTHESIS OF ZEOLITES:

- **Around 200 framework types of zeolites** have been synthesized and reported

- Primarily, zeolites have been synthesized using **hydrothermal methods**

- The lower number of framework structures of zeolites is due to the **low number of building unites and mystery in the self-assembly processes of zeolites**. In general, the synthesis of new framework structures is difficult to achieve

SYNTHESIS OF MOFs:

- The synthesis of new MOFs is widely studied because of the **variety in combinations of metal ions and bridging ligands**

- **These structures are important with regard to the surface area**. Likewise, the incorporation of functional building unites basically allows their molecular functionality to be adopted by porous materials

- Most of these are synthesized using **hydrothermal methods**, along with microwave or ionothermal synthetic methods

- Interest in them is also due to their **topological structures**, which are not found in inorganic salt or molecular crystals

Metal Organic Frameworks vs Zeolites

PROPERTIES OF ZEOLITES:

•**One of the most important properties of zeolites is their acidity**. Zeolites have Brostened acidic proton sites as counterparts to anionic frameworks, which can be introduced by the isomorphous substitution of Si(IV) by Al(III) atoms in the TO4 tetrahedral (T= Si, Al)

PROPERTIES OF MOFs:

•**Adsorptive properties are tunable in terms of pore functionalization**. MOF-74 can be synthesized with a variety of metal centers such as Zn^{2+}, Fe^{2+}, Co^{2+}, etc

•The H_2 adsorption heat is also tunable. These tunabilities in relation to the adsorption energy are particularly important for **gas separation based on interactions**

•The **flexibility of the framework** is specific for MOFs and has been shown as unique porous properties. This is because such porous materials change their structures in response to **guest adsorption**, making these materials useful for some applications

Metal Organic Frameworks vs Zeolites

APPLICATIONS OF ZEOLITES:

- **Catalytic applications** are more ideal for zeolites because of the use of robust frameworks and their acidic sites compared with MOFs. Acidic sites provide various organic reactivity such as cracking and isomerization. **Tons of zeolites have been used for the fluid catalytic cracking of heavy oils.**

- **Redox active sites** are introduced using metal site substitutes such as Ti and Sn. The redox activity can be used for epoxidation, and so on.

- Extra-framework cations such as Cu^{2+} and encapsulated clusters such as Pt clusters can also **be catalytic reaction sites.**

APPLICATIONS OF MOFs:

Gas adsorption applications as portable storage are more suitable for MOFS because of the light composition of formula weights.

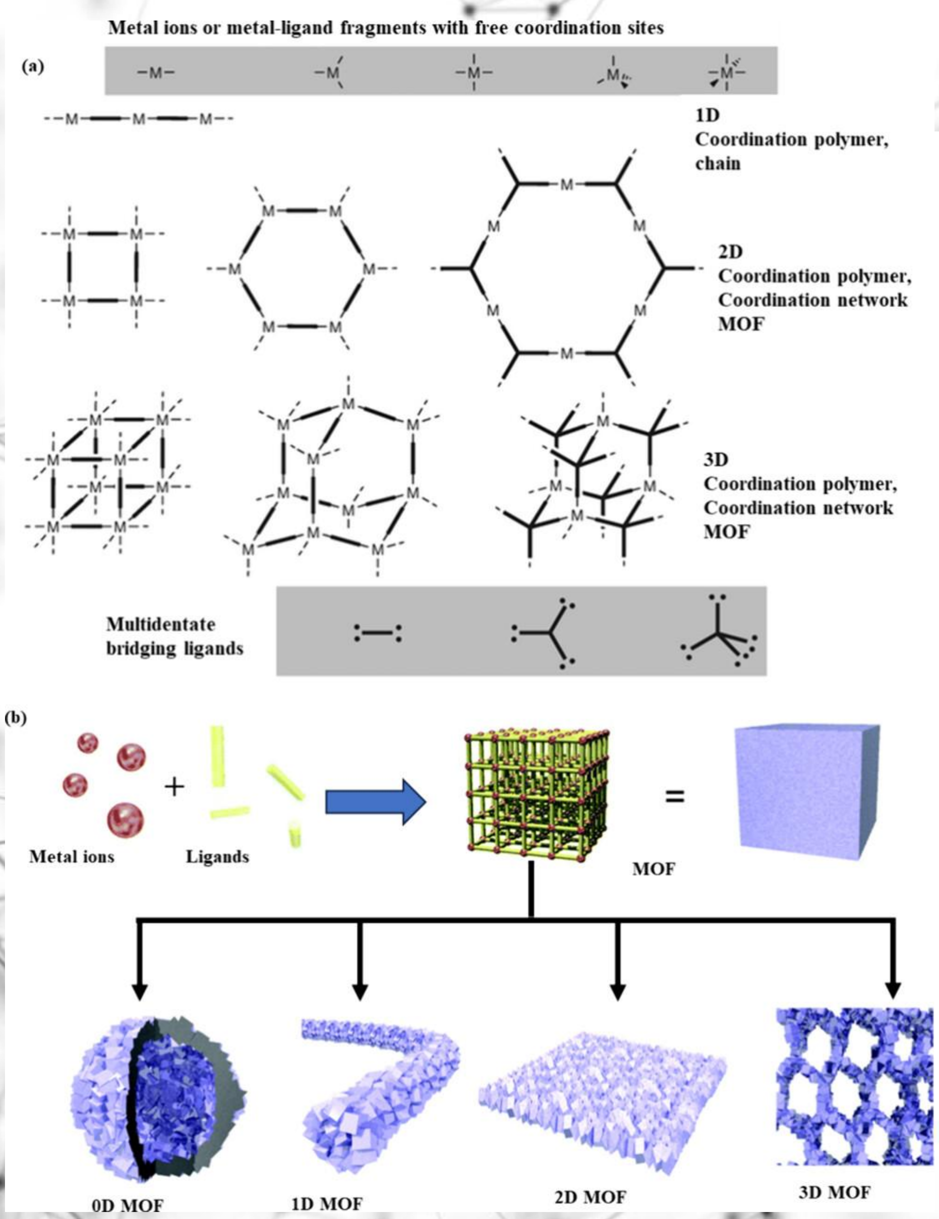
Hydrogen and methane gases are the general targets for gas storage as a demonstration of energy transport.

Gas separation applications have also been studied. Syn-gas can be contaminated with CO2. Therefore, CO2/CH4 or C2H6/CH4 separation has been studied.

…….

Metal Organic Frameworks

Why so many different applications?



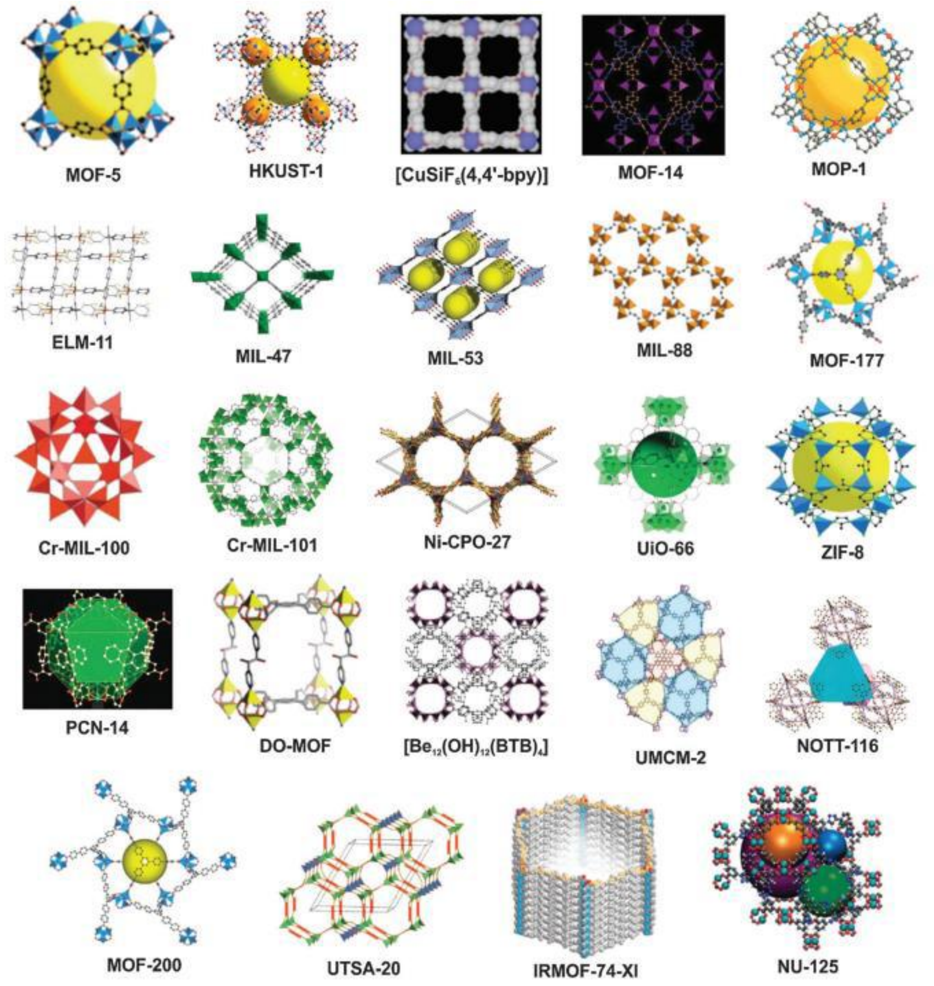
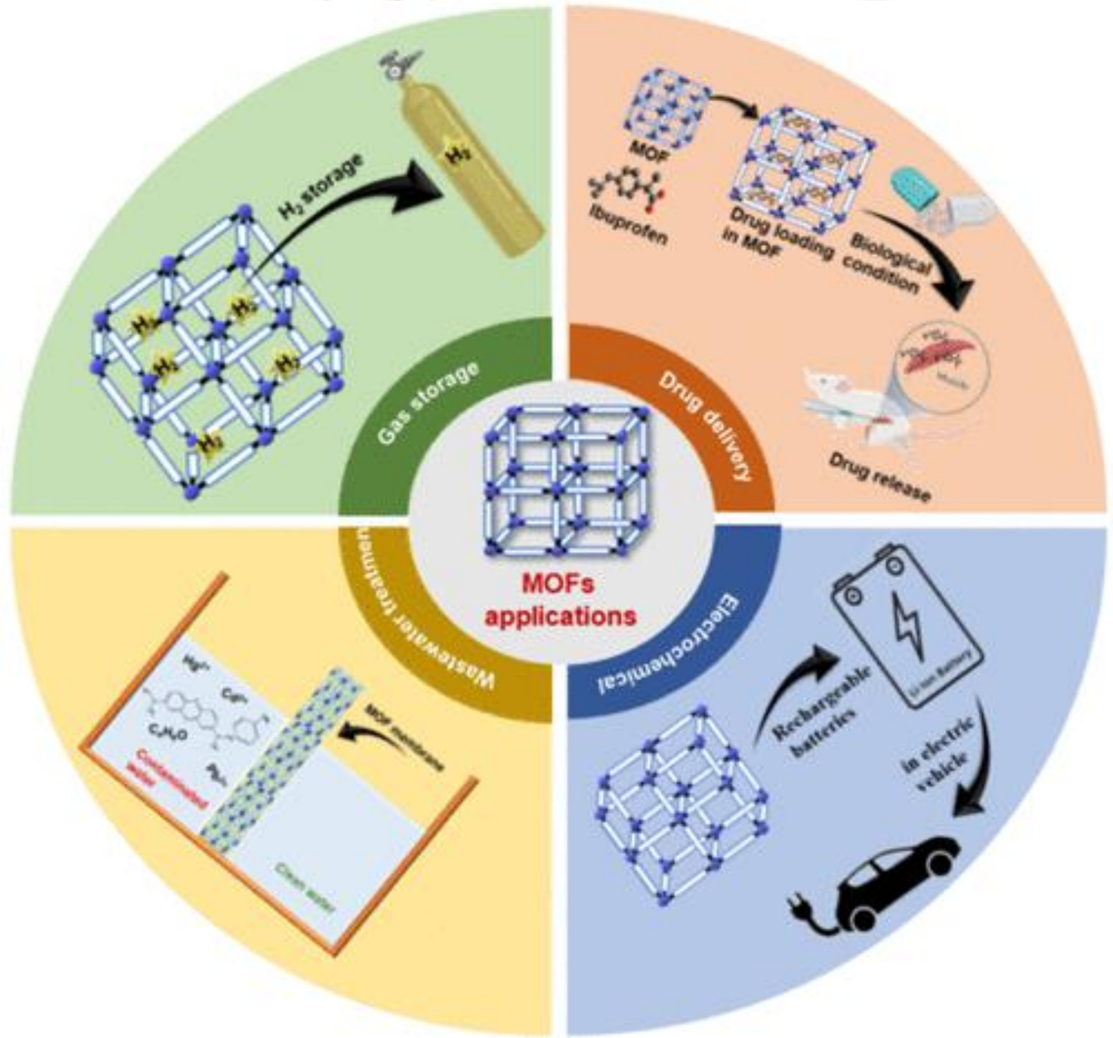


Fig. 3 Porous MOFs prepared by several research groups aiming the accommodation/retention of chemical species in their pores/channels.

Metal Organic Frameworks

Why so many different applications?



Metal Organic Frameworks

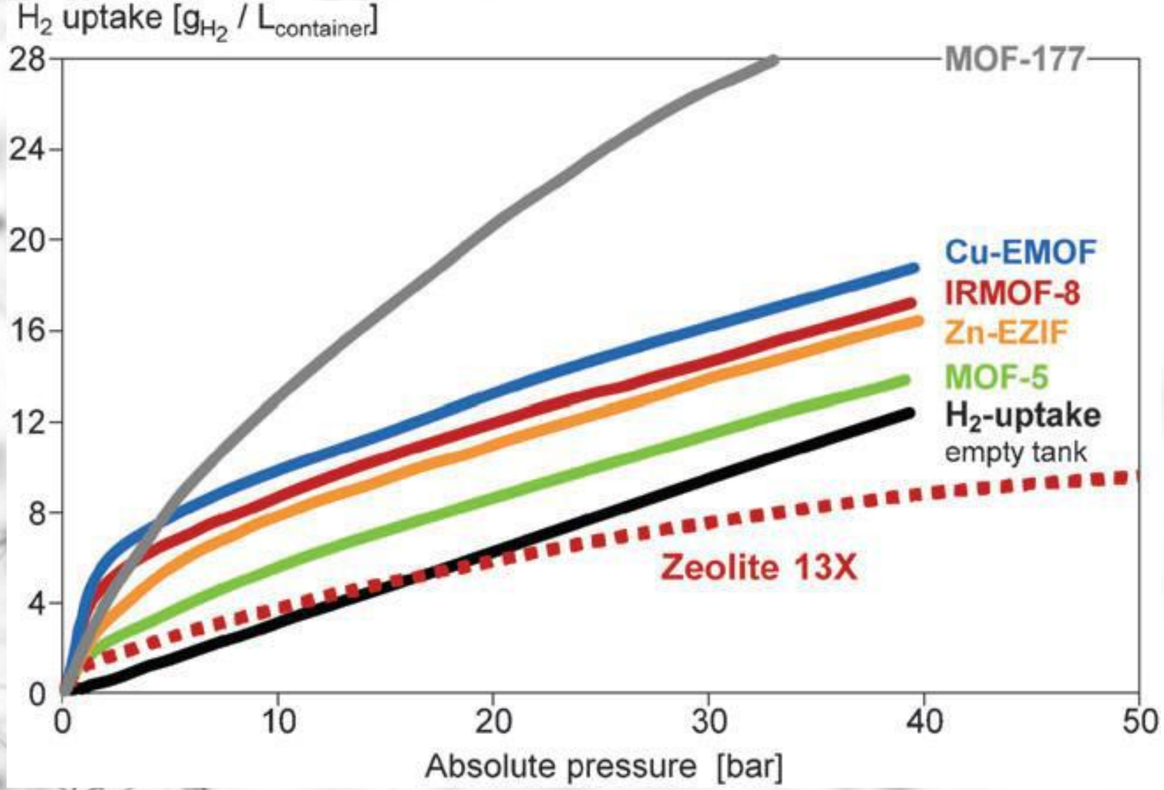
H_2 storage

Στόχος

40 (STP) $gH_2/L_{μέσου}$ (-40 έως -60°C, <100bar)

Ζεόλιθοι

<10 $gH_2/L_{μέσου}$



Chem. Soc. Rev. 2009, 38, 11284

Metal Organic Frameworks

CH_4 storage and transport

Στόχος

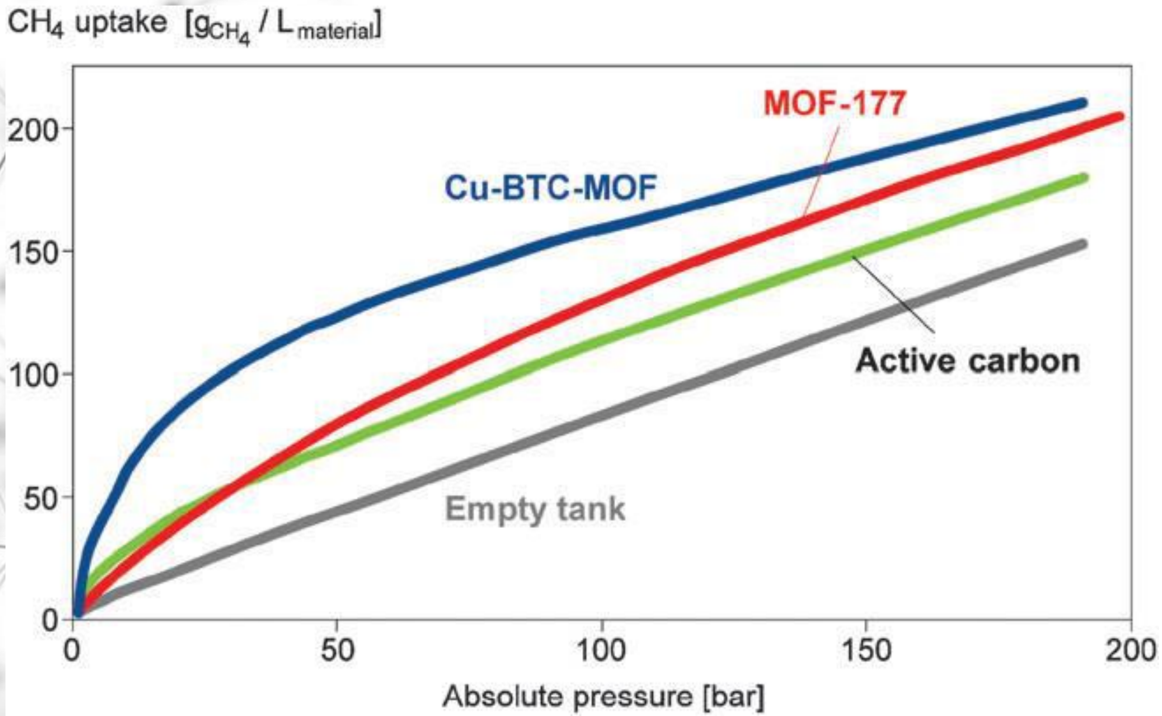
263 $gCH_4/L_{μέσου}$ (25 °C, 35 bar)

Ζεόλιθοι

<100 $gCH_4/L_{μέσου}$

Πορώδη Υλικά από Άνθρακα

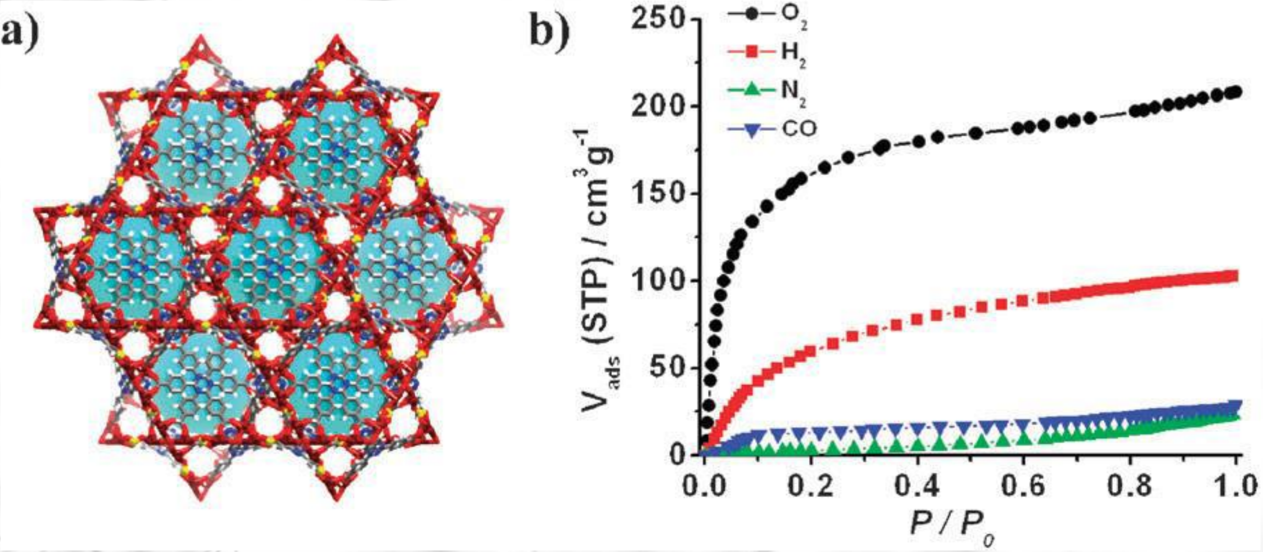
50-160 $gCH_4/L_{μέσου}$



Chem. Soc. Rev. 2009, 38, 11284

Metal Organic Frameworks

Selectivity in gas adsorption



PCN-17
(MOF Yb_{III})

77 K
O_2,~210 cm^3/g
H_2,~105 cm^3/g
N_2 και O_2,~20 cm^3/g

Chem. Soc. Rev. 2009, 38, 11284

SEMTE SCHOOL FOR ENGINEERING OF MATTER, TRANSPORT & ENERGY

Adsorption Simulations on Metal-Organic Frameworks for Air Separation

Sean McIntyre

Dr. Bin Mu and Bohan Shan

26th Annual Arizona/NASA Undergraduate Research Symposium

Sheraton Phoenix Airport Hotel Tempe

April 22, 2017

ASU/NASA Space Grant Program

ASU Arizona State University

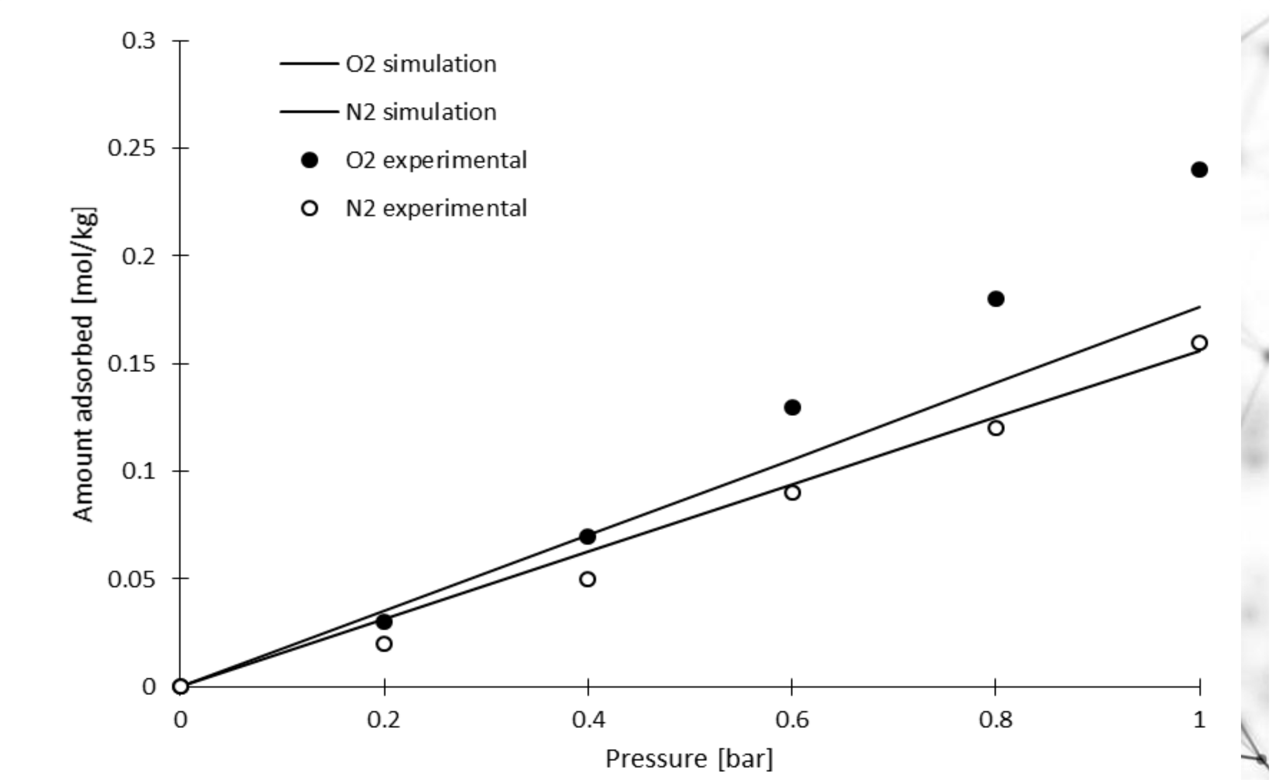
NASA

Methods

- Grand Canonical Monte Carlo (GCMC) adsorption simulations were executed using RASPA molecular software
    - Structural data of the material were defined using crystallographic information files
    - Universal force field and DREIDING force field parameters were utilized for atomistic interactions
        - Non-bonding van der Waals and electrostatic parameters
        - This is the conventional approach for adsorption simulations in MOFs

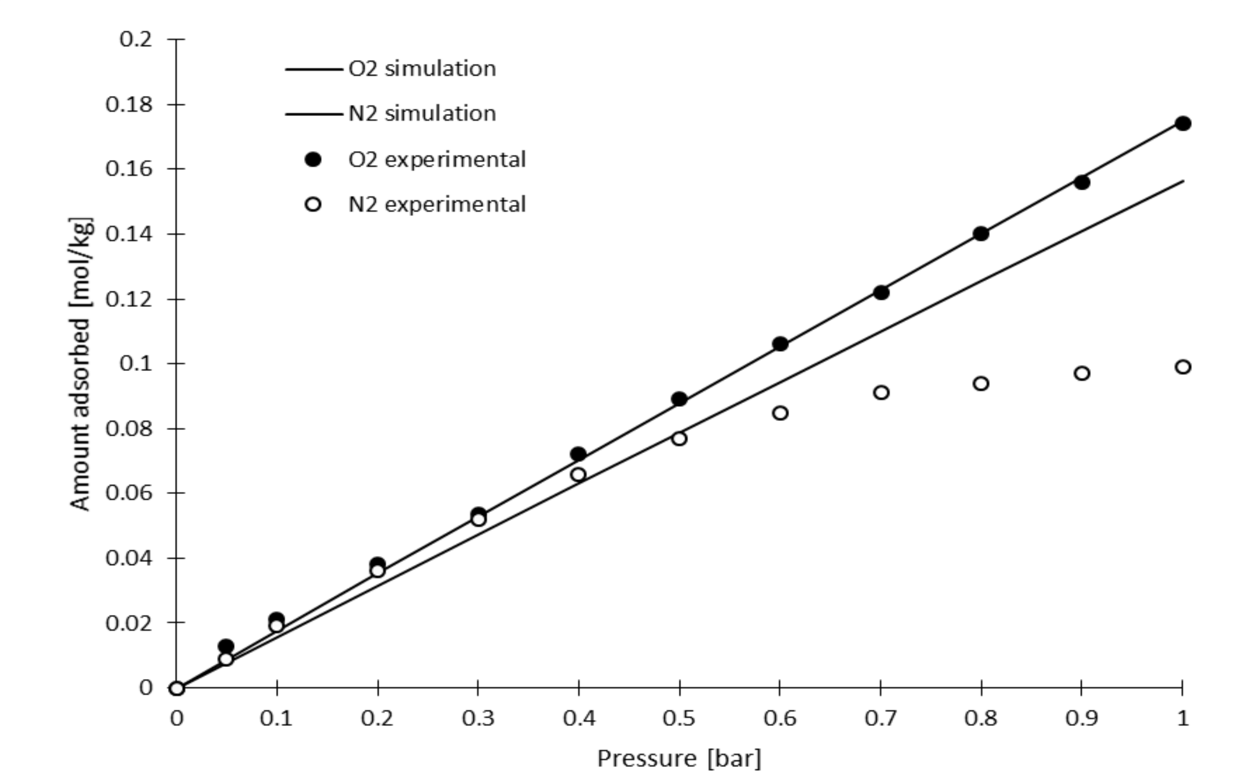
Results

UMCM-1 (Zn metal + btb ligand)



Mu, B., et al.; Gas Adsorption Study on Mesoporous Metal-Organic Framework UMCM-1; J. Phys. Chem. C 2010, 114, 6464–6471.

MOF-177 (Zn metal + btb ligand)

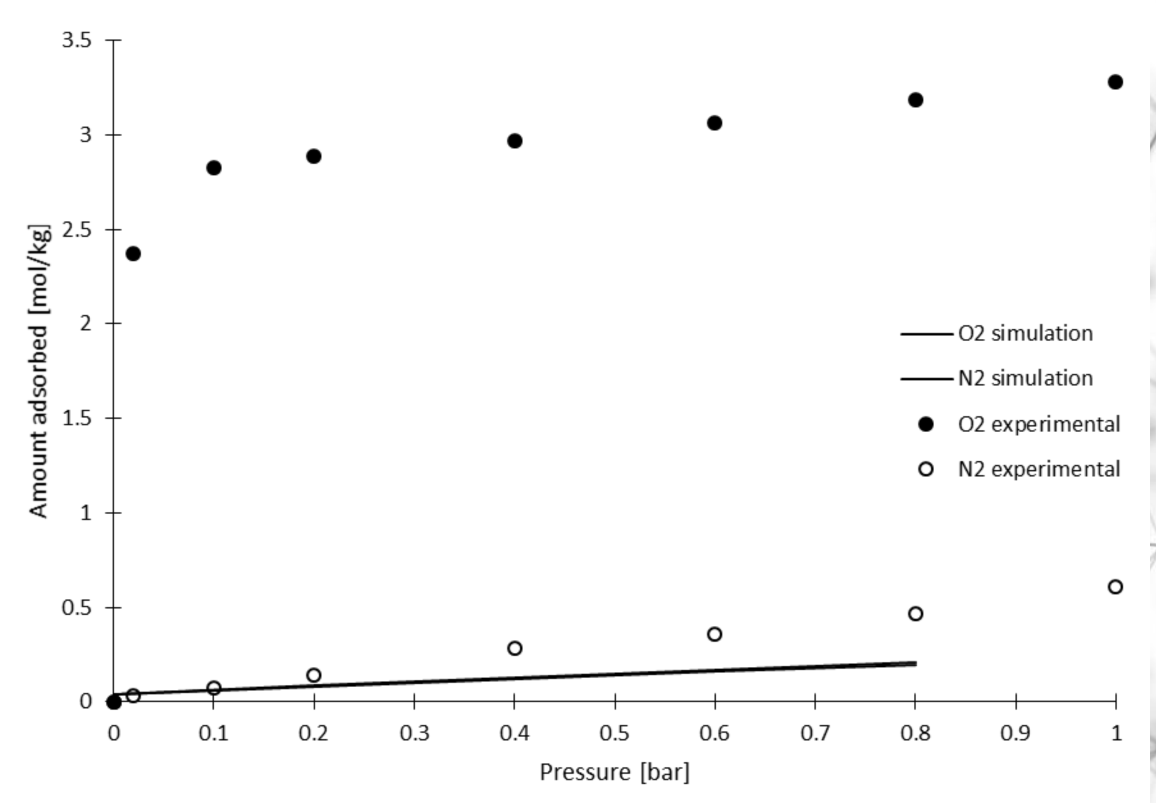


Li, Y., et al.; Gas Adsorption and Storage in Metal-Organic Framework MOF-177; Langmuir 2007, 23, 12937-12944

- Particularly accurate prediction of isotherms for these MOFs

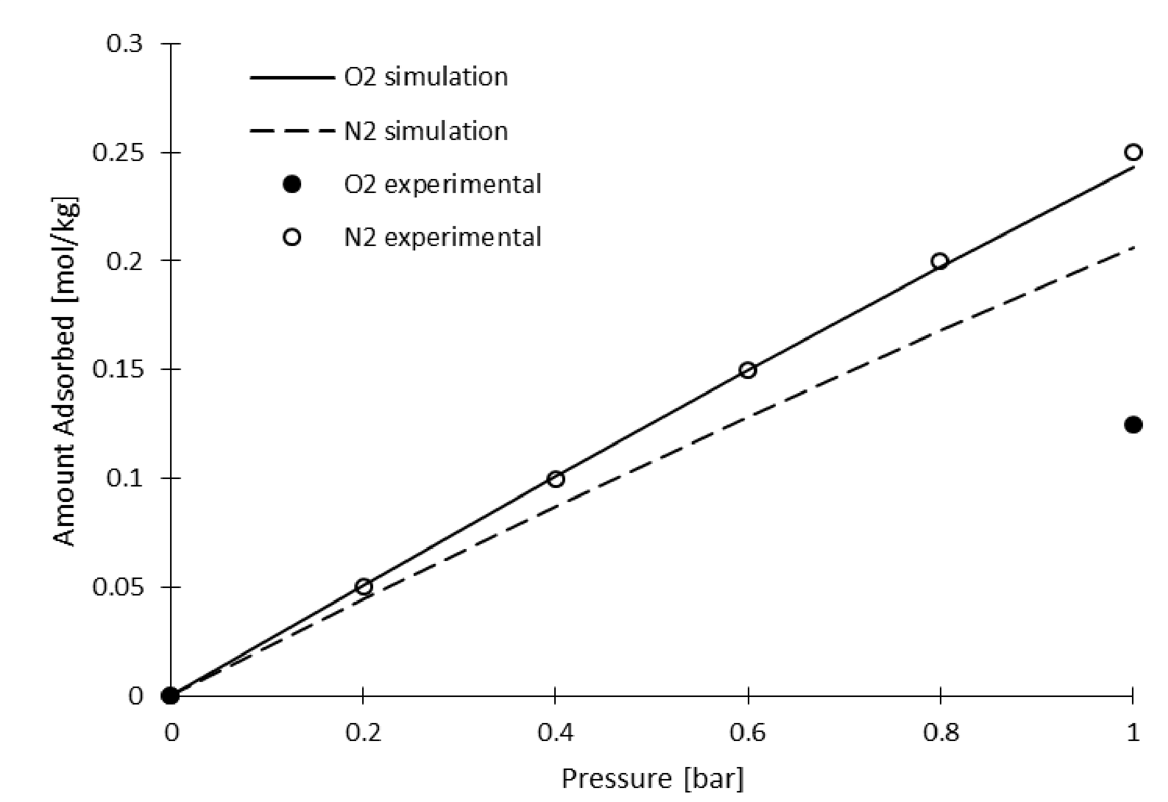
Results

MOF-74 (Fe metal + dobdc ligand)



Bloch, E.D., et al; Selective Binding of O2 over N2 in a Redox-Active Metal-Organic Framework with Open Iron(II) Coordination Sites; J. Am. Chem. Soc. 2011, 133, 14814–14822.

UiO-66 (Zr metal + bdc ligand)



Piscopo C.G., et al.; Positive effect of the fluorine moiety on the oxygen storage capacity of UiO-66 metal–organic frameworks; New J. Chem., 2016, 40, 8220–224.

- Reported heat of adsorption of MOF-74: -41 kJ/mol
- Simulation heat of adsorption: -12 kJ/mol

- Nitrogen selectivity not predicted

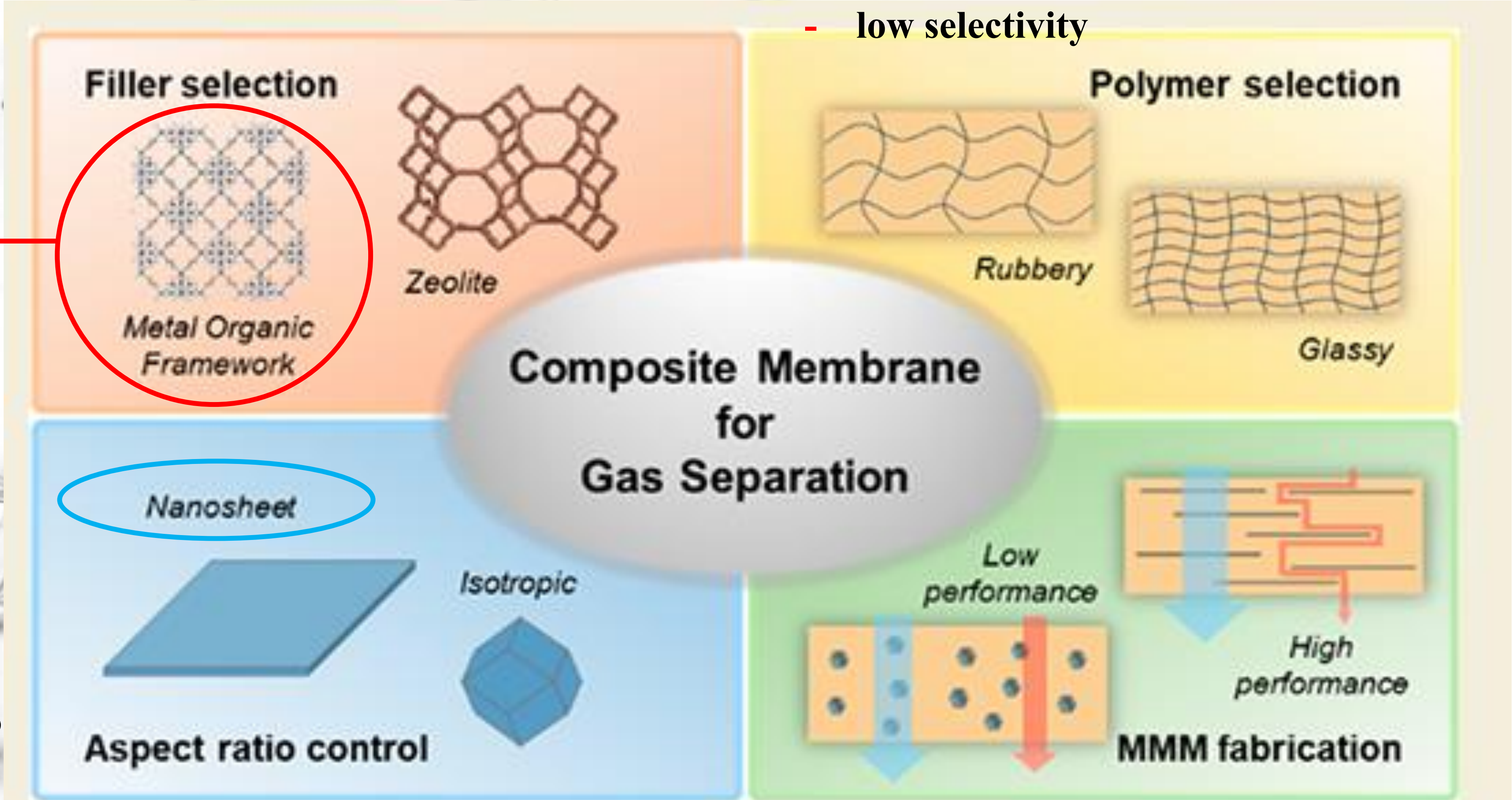
Conclusion

- Generic force fields adequately predicted physical adsorption of various MOFs
- The force fields must be modified in order to screen for nitrogen-selectivity or oxygen chemisorption
- Future work will involve the development and comparison of more advanced force field
  - Goal to propose a computationally-efficient means of screening for nitrogen-selectivity and chemisorption in MOFs

Metal Organic Frameworks

Selectivity in gas separation

\+ high permeability
\- low selectivity



tunable pores, high surface area, functionalizable

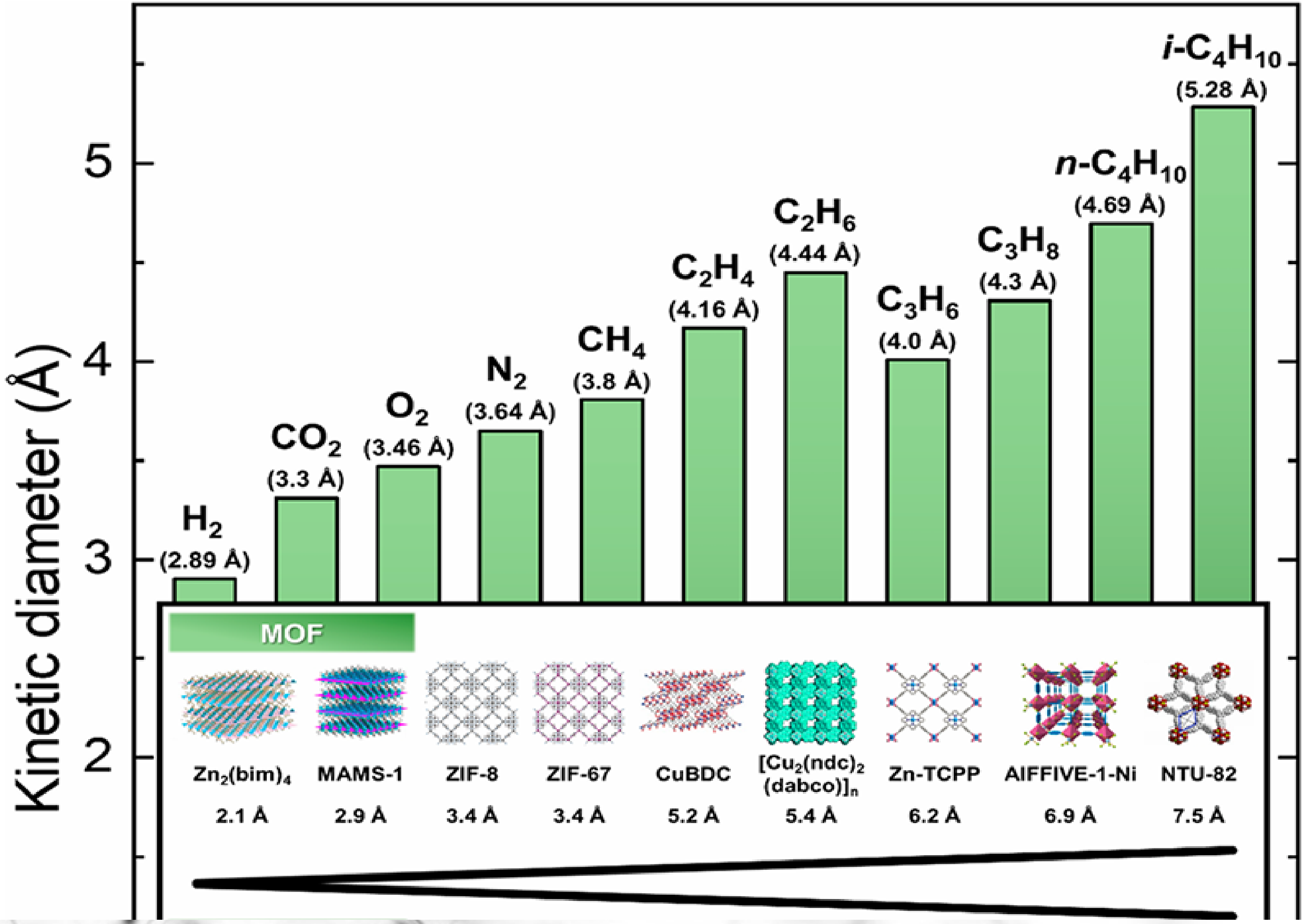
- high aspect ratio
- cover more area
- reduce defects
- promote selective transport

GOAL
Uniform dispersion, strong polymer–filler interaction, controlled thickness and orientation

Metal Organic Frameworks

Selectivity in gas separation

2D MOFS SELECTED FOR SEPERATION CO_2

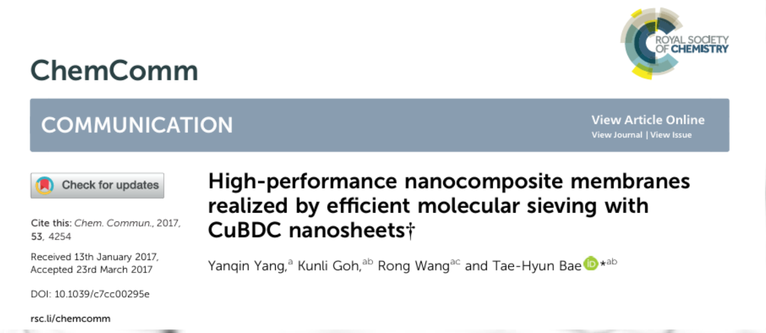


Kinetic diameters of industrially important gas molecules and examples of MOF prepared in the form of nanosheets or plates with high aspect ratio

Metal Organic Frameworks

Selectivity in gas separation

2D MOFS SELECTED FOR SEPERATION CO_2
ns - CuBDC



ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

High-performance nanocomposite membranes realized by efficient molecular sieving with CuBDC nanosheets†

Cite this: *Chem. Commun.*, 2017, 53, 4254

Received 13th January 2017,
Accepted 23rd March 2017

DOI: 10.1039/c7cc00295e

rsc.li/chemcomm

Yanqin Yang,[a] Kunli Goh,[ab] Rong Wang[ac] and Tae-Hyun Bae *[ab]

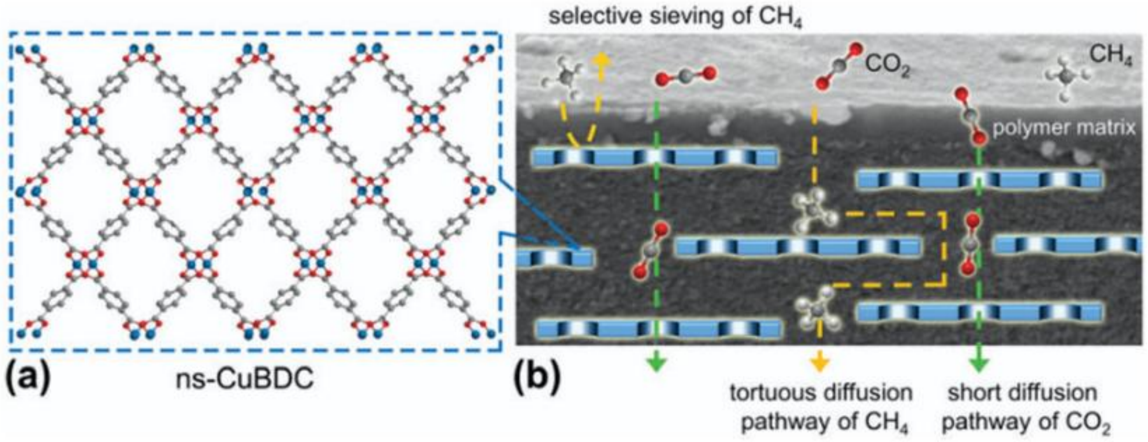
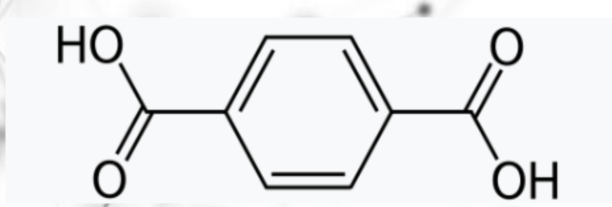
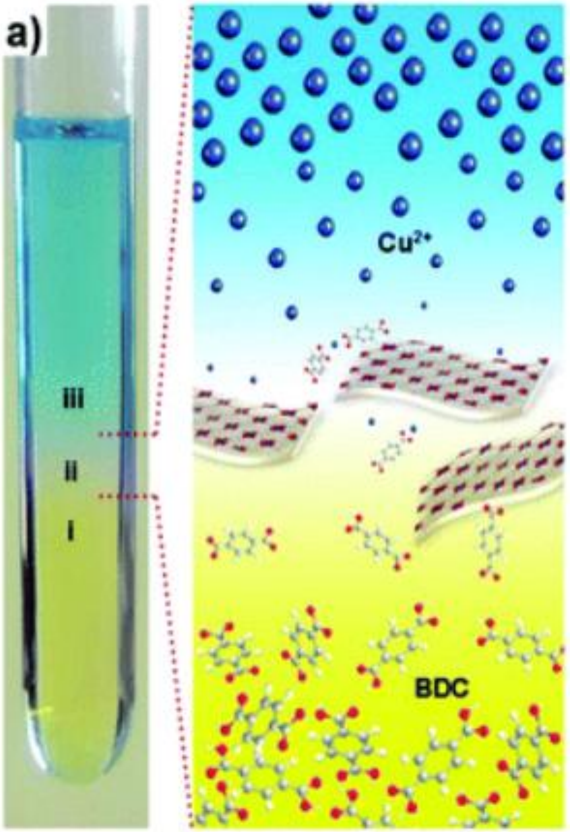


Fig. 1 (a) Chemical structure of ns-CuBDC. (b) Schematic illustration of a MMM containing a nanoporous layered filler with ideal orientation.



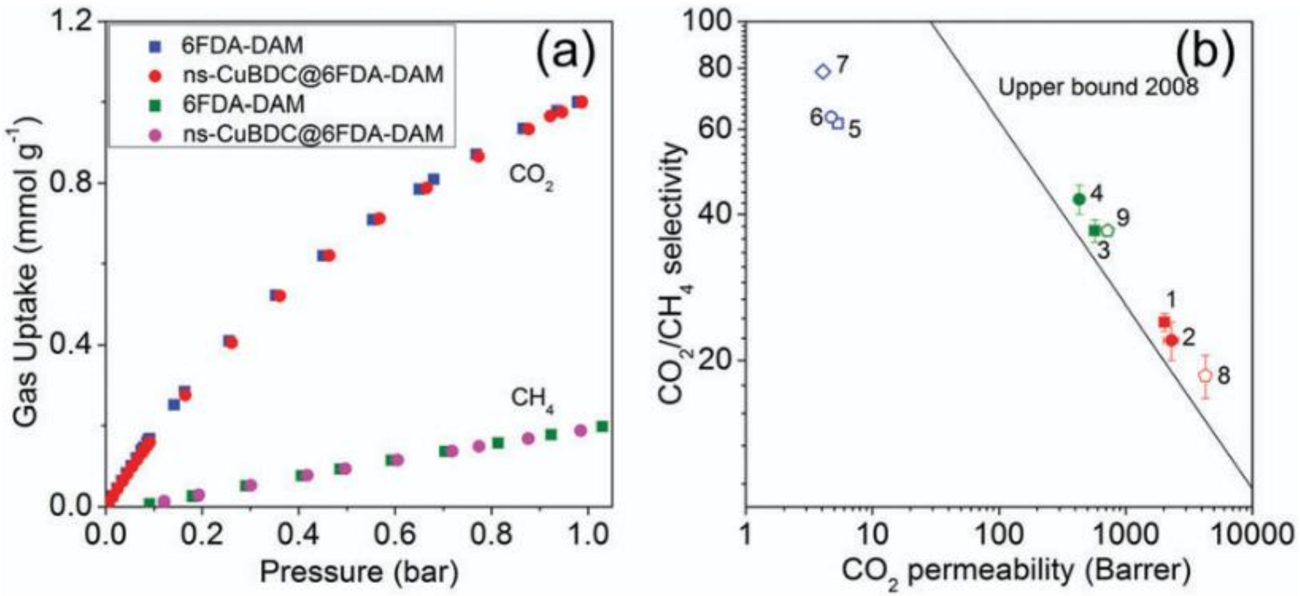
Linker

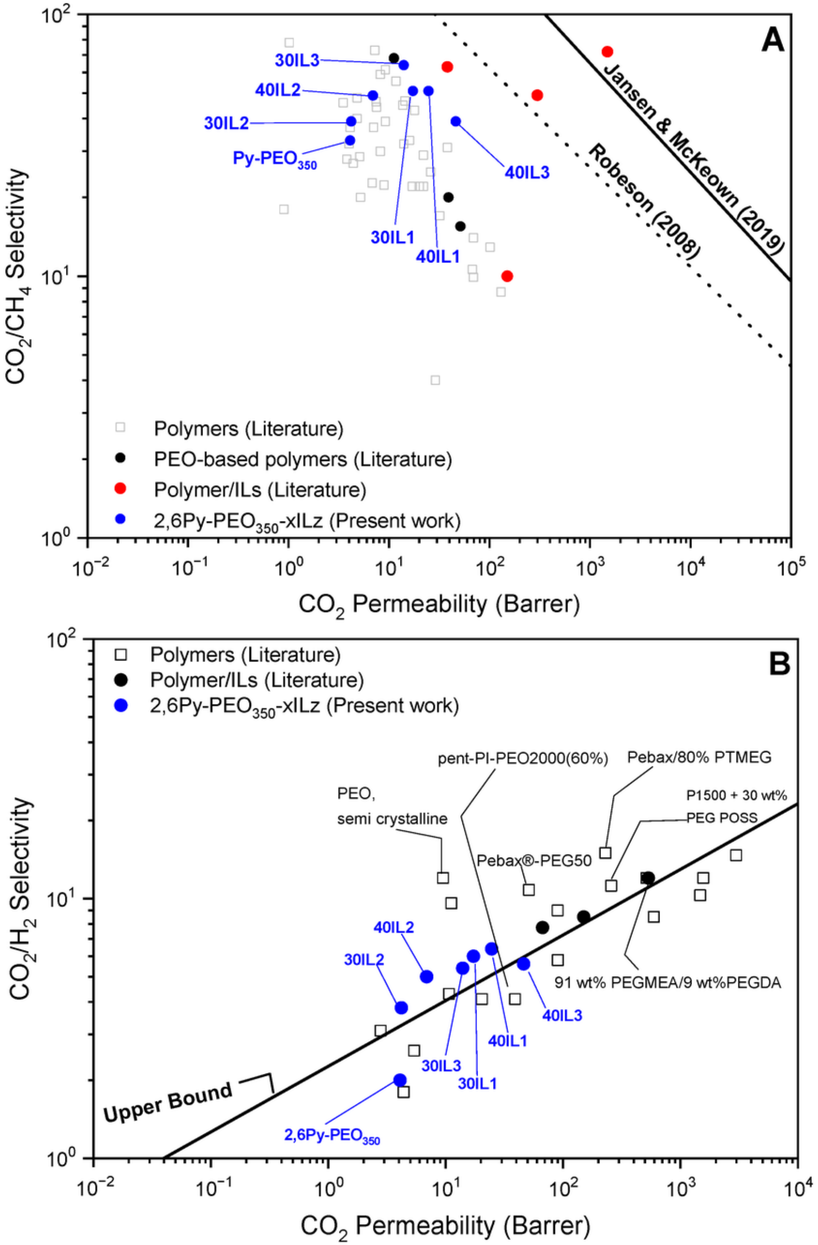


(a)Schematic illustration of the three-layer synthesis strategy. (i), the middle buffer layer (ii), and the Cu^{2+} ion layer (iii). (b) Crystalline structure of the 2D CuBDC MOF.

Metal Organic Frameworks

Selectivity in gas separation

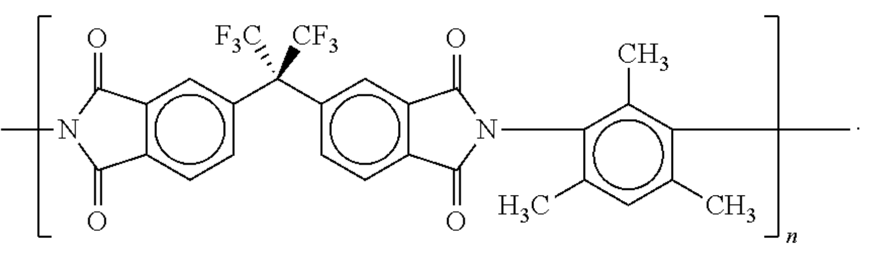




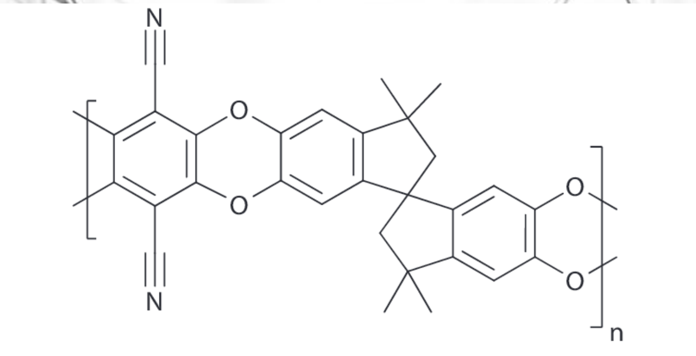
Metal Organic Frameworks

Selectivity in gas separation

Fabrication of mixed matrix membranes



Chemical structure of 6FDA-DAM



MMMs exhibited separation performances with high CO_2 permeability and decent CO_2/CH_4 selectivity

Metal Organic Frameworks

Selectivity in gas separation


Chemical Engineering Journal 481 (2024) 148294

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Mixed matrix membranes incorporating two-dimensional ZIF-8 nanosheets for enhanced CO_2/N_2 separation

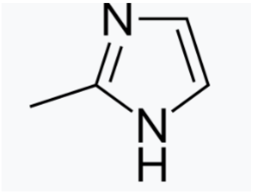
Sung Kuk Jeong [a,1], Jeong Yun Jeong [b,1], Semin Lim [a], Woo-Sik Kim [a], Hyuk Taek Kwon [b,*], Jinsoo Kim [a,*]

[a] Department of Chemical Engineering, Kyung Hee University, 1732 Deogyeong-daero, Giheung-gu, Yongin-si, Gyeong gi-do 17104, Republic of Korea

[b] Department of Chemical Engineering, Pukyong National University, 45 Yongso-ro, Nam-gu, Busan 48513, Republic of Korea

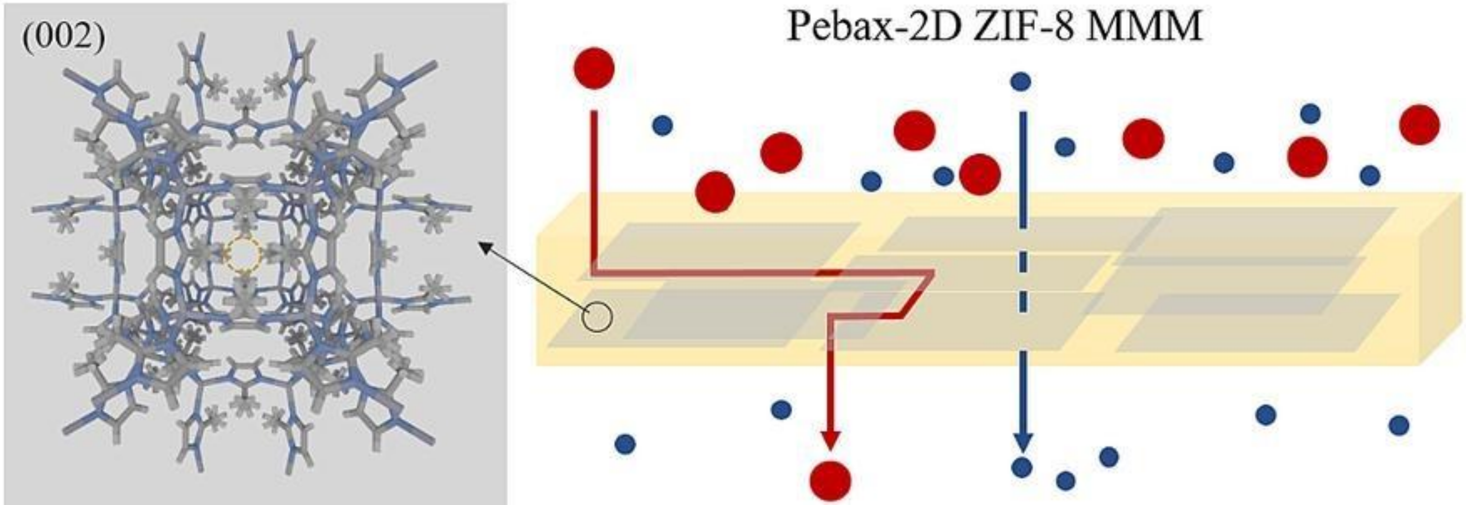
2D MOFS SELECTED FOR SEPERATION CO_2

➢ **2D ZIF-8 nanosheets**


2-Methylimidazole

Improved CO_2/N_2 separation possibly due to……

- *Enhanced molecular sieving through 4-membered windows smaller than conventional 6-membered window*
- *Increased transport tortuosity for less selective N_2 due to 2D morphology of the filler*



Metal Organic Frameworks

Selectivity in gas separation

Chemical Engineering Journal 481 (2024) 148294

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

ELSEVIER

Mixed matrix membranes incorporating two-dimensional ZIF-8 nanosheets for enhanced CO_2/N_2 separation

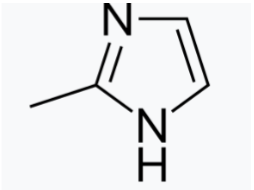
Sung Kuk Jeong [a,1], Jeong Yun Jeong [b,1], Semin Lim [a], Woo-Sik Kim [a], Hyuk Taek Kwon [b,*], Jinsoo Kim [a,*]

[a] Department of Chemical Engineering, Kyung Hee University, 1732 Deogyeong-daero, Giheung-gu, Yongin-si, Gyeong gi-do 17104, Republic of Korea

[b] Department of Chemical Engineering, Pukyong National University, 45 Yongso-ro, Nam-gu, Busan 48513, Republic of Korea

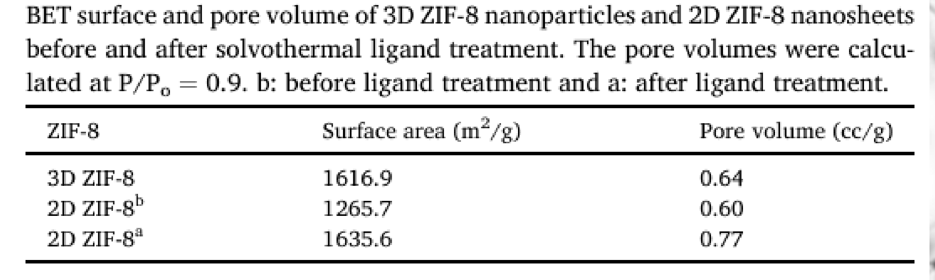
2D MOFS SELECTED FOR SEPERATION CO_2

- **2D ZIF-8 nanosheets**



2-Methylimidazole

0.36 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.8 g of 2-mIm were dissolved in an aqueous SDS solution (0.4 g of SDS in 45 mL of deionized water) and 5 mL of deionized water, respectively. Then, **the later was injected into the former under stirring for 1 min and the mixture were transferred into an autoclave**, which was kept at **120 °C** for 4 h.



BET surface and pore volume of 3D ZIF-8 nanoparticles and 2D ZIF-8 nanosheets before and after solvothermal ligand treatment. The pore volumes were calculated at $P/P_o = 0.9$. b: before ligand treatment and a: after ligand treatment.

ZIF-8	Surface area (m^2/g)	Pore volume (cc/g)
3D ZIF-8	1616.9	0.64
2D ZIF-8[b]	1265.7	0.60
2D ZIF-8[a]	1635.6	0.77

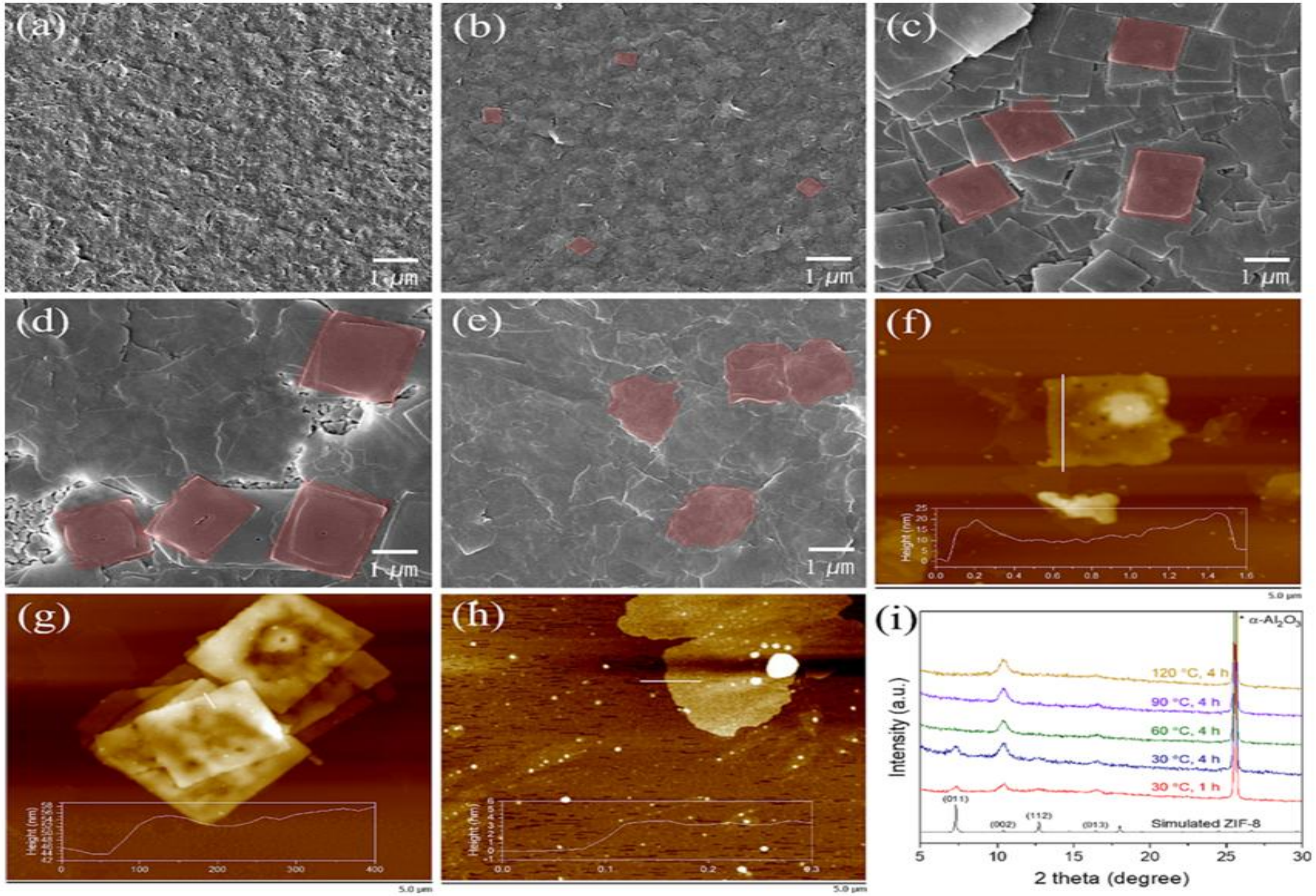
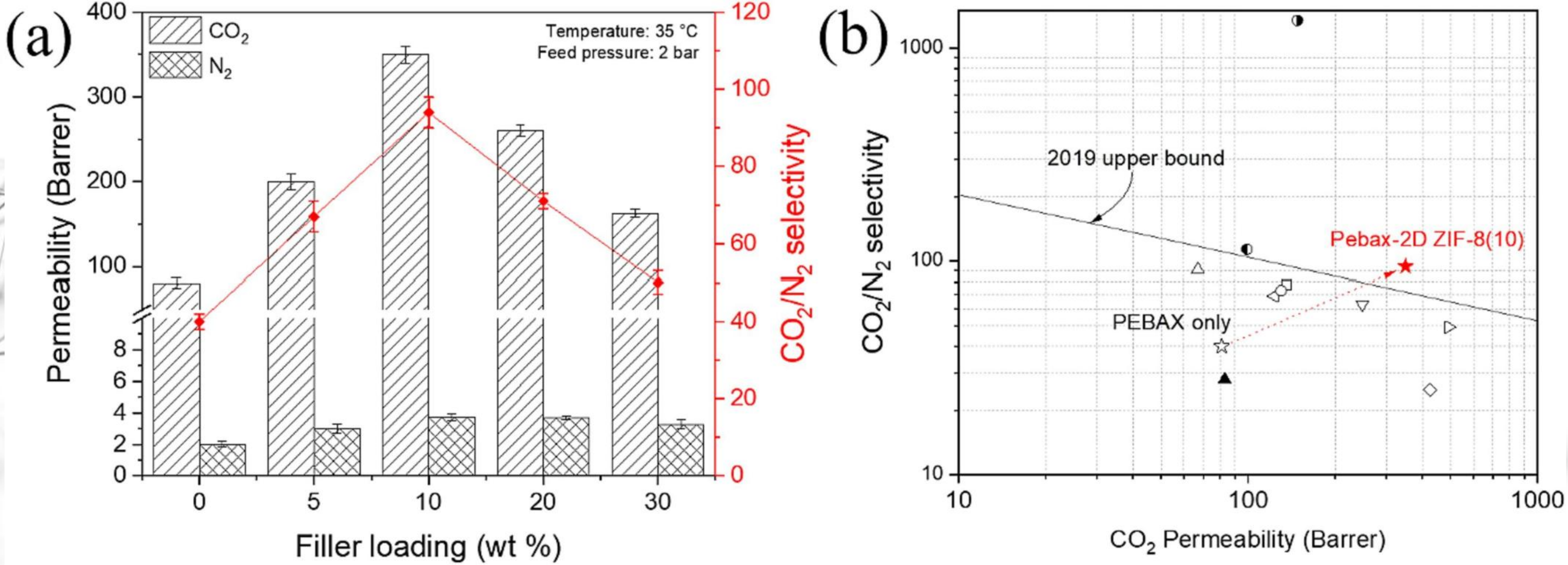


Fig. 1. Electron micrographs of 2D ZIF-8 nanosheets synthesized at 30 °C for 1 h (a), at 30 °C for 4 h (b), at 60 °C for 4 h (c), at 90 °C for 4 h (d), and at 120 °C for 4 h (e). AFM images of 2D ZIF-8 grown at 60 °C for 4 h (f), at 90 °C for 4 h (g), and at 120 °C for 4 h (h). XRD patterns of all synthesized 2D ZIF-8 nanosheets (i). Since as-synthesized 2D ZIF-8 nanosheets were severely aggregated after drying (Fig. S1), making analyses (SEM and XRD) difficult, porous α-Al_2O_3 substrates were used for oriented deposition of the 2D ZIF-8 nanosheets via capillary suction.

Metal Organic Frameworks

Selectivity in gas separation



Metal Organic Frameworks

Selectivity in gas separation

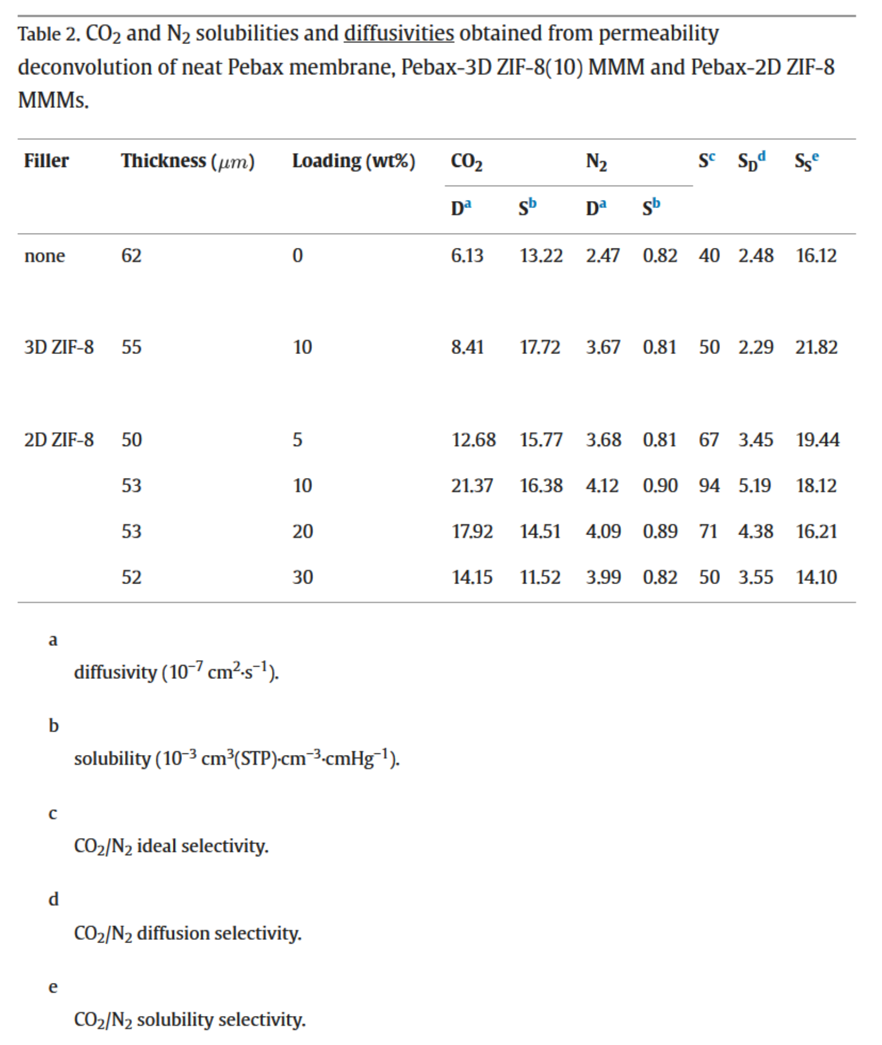


Table 2. CO_2 and N_2 solubilities and diffusivities obtained from permeability deconvolution of neat Pebax membrane, Pebax-3D ZIF-8(10) MMM and Pebax-2D ZIF-8 MMMs.

Filler	Thickness (μm)	Loading (wt%)	CO_2		N_2		S^c	$S_D{}^d$	$S_S{}^e$
			D^a	S^b	D^a	S^b			
none	62	0	6.13	13.22	2.47	0.82	40	2.48	16.12
3D ZIF-8	55	10	8.41	17.72	3.67	0.81	50	2.29	21.82
2D ZIF-8	50	5	12.68	15.77	3.68	0.81	67	3.45	19.44
	53	10	21.37	16.38	4.12	0.90	94	5.19	18.12
	53	20	17.92	14.51	4.09	0.89	71	4.38	16.21
	52	30	14.15	11.52	3.99	0.82	50	3.55	14.10

[a] diffusivity (10^{-7} $cm^2 \cdot s^{-1}$).

[b] solubility (10^{-3} $cm^3(STP) \cdot cm^{-3} \cdot cmHg^{-1}$).

[c] CO_2/N_2 ideal selectivity.

[d] CO_2/N_2 diffusion selectivity.

[e] CO_2/N_2 solubility selectivity.

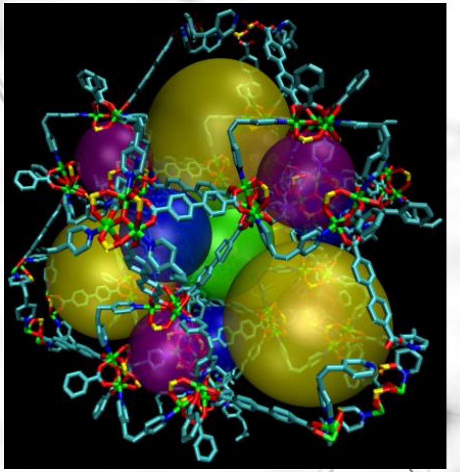
The Pebax-2D ZIF-8(10) shows relatively higher rate of increases in both diffusivity and solubility of CO_2 than those of N_2, leading to higher S_D (~5.2), S_S (~18.1)

The enhanced diffusion-based CO_2/N_2 separation was possibly enabled by the combined effect of the aforementioned increased tortuosity and molecular sieving capability of the nanoporous 2D ZIF-8 fillers

Hybrid Synergy with MOFs and Metal Phosphate Materials

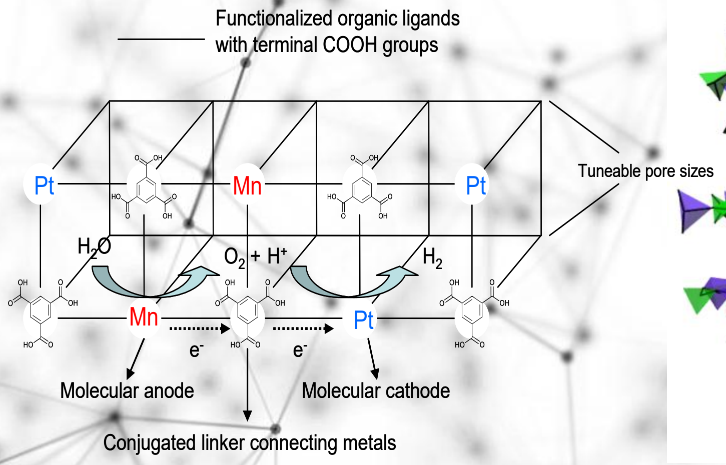
UNIVERSITY OF Southampton

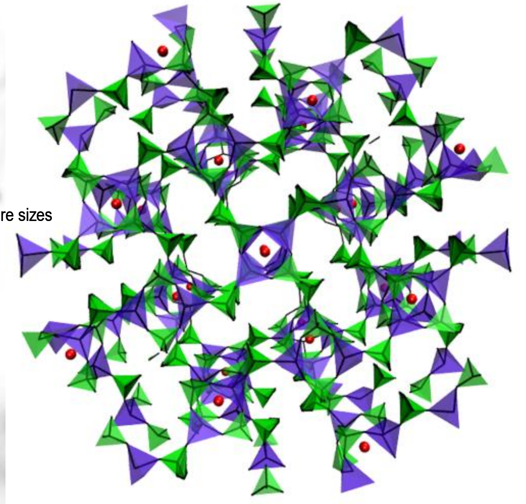
H_2 storage and CO_2 capture



MOF-500 - $[(Fe_3O)_4\ (SO_4)_{12}(BPDC)_6\ (BPE)_6]$

Photocatalytic Oxidation of Water





$[Co(II)\text{-}(PO_3F)]_4F[PO_2F_2]_2.H_2O$

H_2Storage and CO_2 capture

Gas release mechanisms

MOFs and ZIFS

- Hierarchical formation of pores (4 different cavity sizes)
- High tunability from organic linkers and metal centres
- Potential for functionalization and selectivity control

Synergy

Metal Phosphate Frameworks

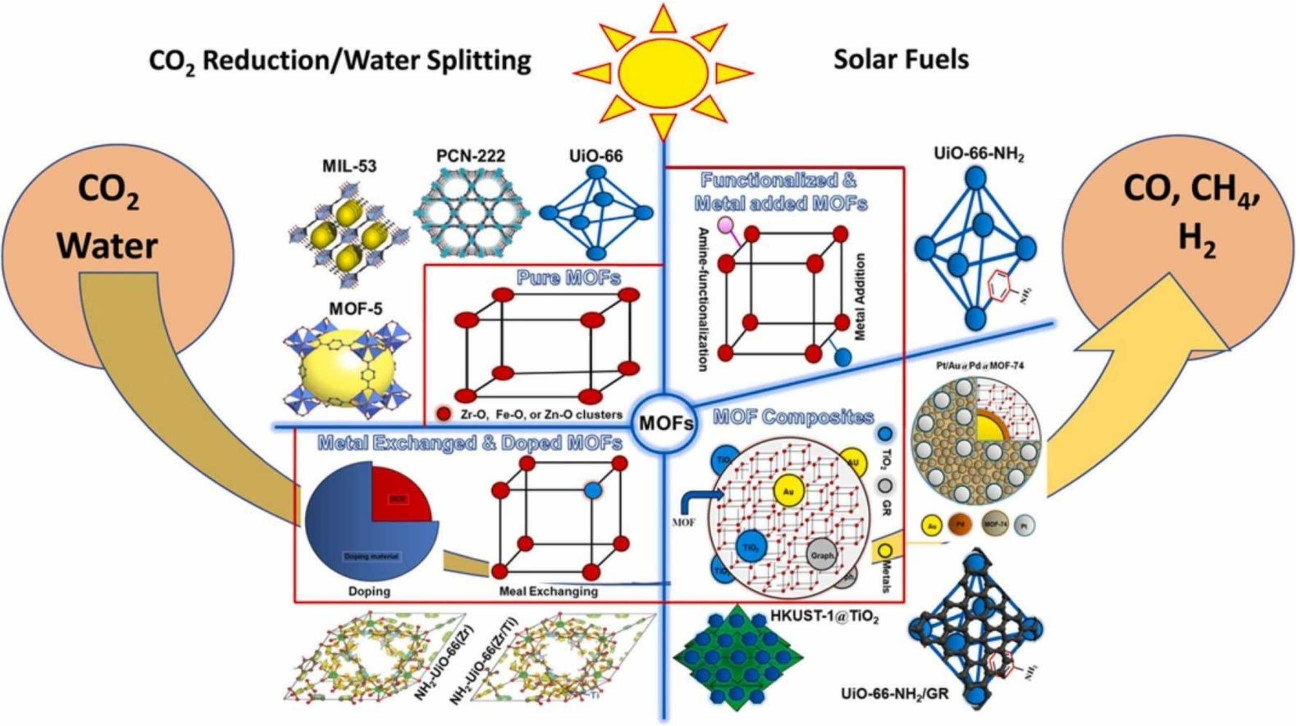
- Stabilization of complex anions in open-framework phosphate architectures (M = Mn^{3+}, Fe^{3+}, Co^{2+}, Cu^{2+}) etc.
- Potential for fluorine incorporation
- Multi-metallic combinations

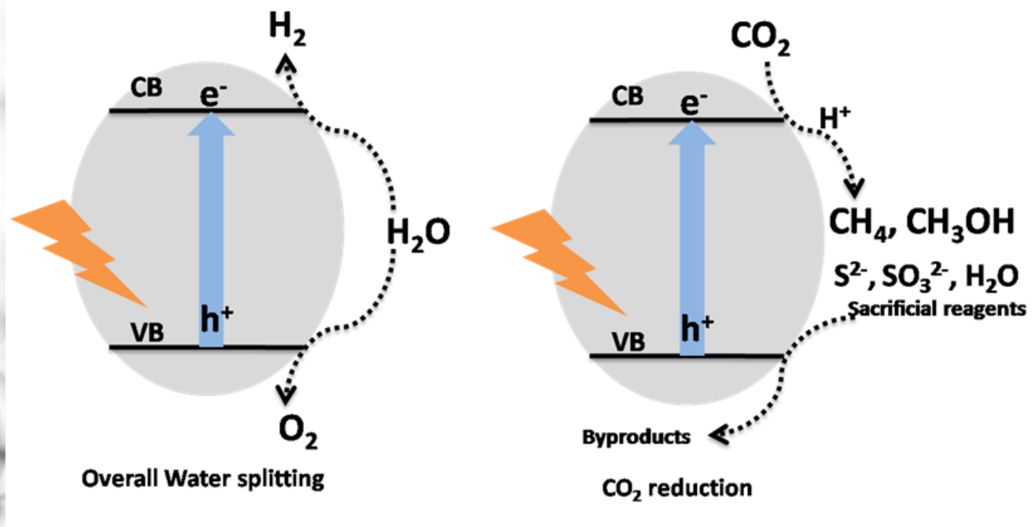
Metal Organic Frameworks

CO_2 reduction and H_2 production/water splitting

- **Atmospheric CO_2 and H_2O can be converted into renewable fuel and chemicals such as methane (CH_4), formic acid (HCOOH) and methanol (CH_3OH) using photocatalytic strategies under low temperature and atmospheric pressure without further polluting the environment**

- However, one of the major challenges in photocatalysis is the inefficient utilization of the solar spectrum, which is associated with their wide bandgap and lower photocatalytic efficiency due to the fast recombination of photogenerated electrons and holes

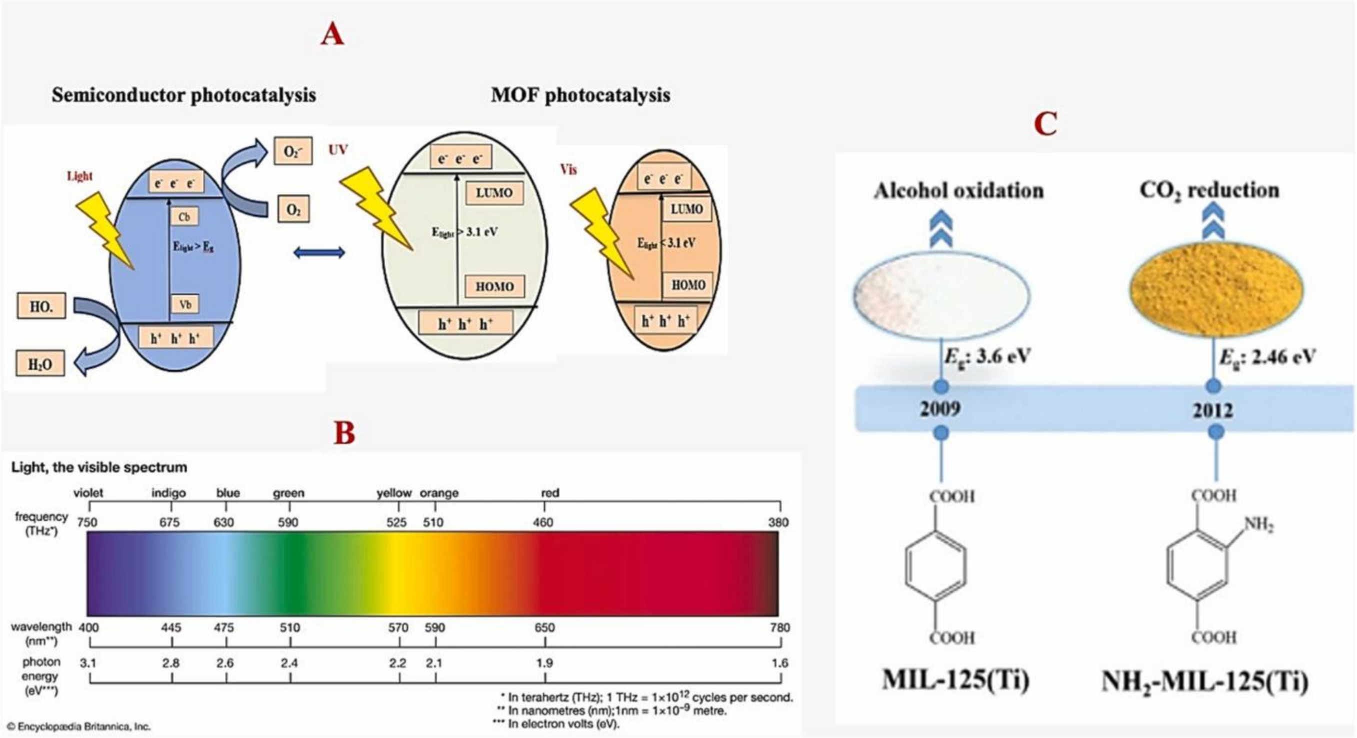


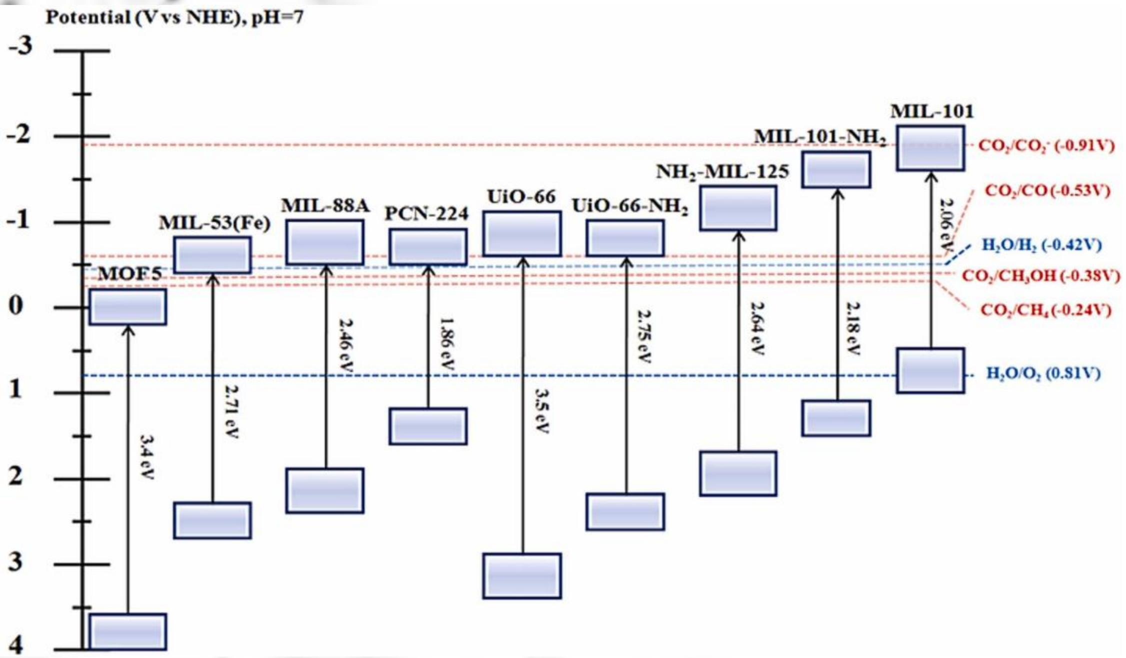


Metal Organic Frameworks

CO_2 reduction and H_2 production/water splitting

- MOFs are good candidates for application in heterogeneous photocatalytic due to their superior porosity and a well-ordered donor-acceptor interface suitable for effective electron-hole separation





Metal Organic Frameworks

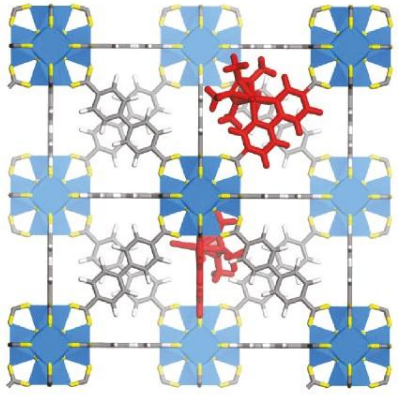
H_2 production

Current Status on Photolysis of Water using Porous Framework Materials

Examples that highlight the promise of MOFs as water oxidation photocatalysts include:

- A Zr-terephthalate based MOF has been shown to have a **quantum efficiency of 3.5%** (compared with rutile TiO_2 of 8%)
- A framework incorporated organometallic iridium species has shown promise for **water oxidation**, with heterogeneity allowing for recycling of the catalyst

- With a vast diversity of MOF structures, there is a vast untapped potential for hydrogen generation using MOF photocatalysts



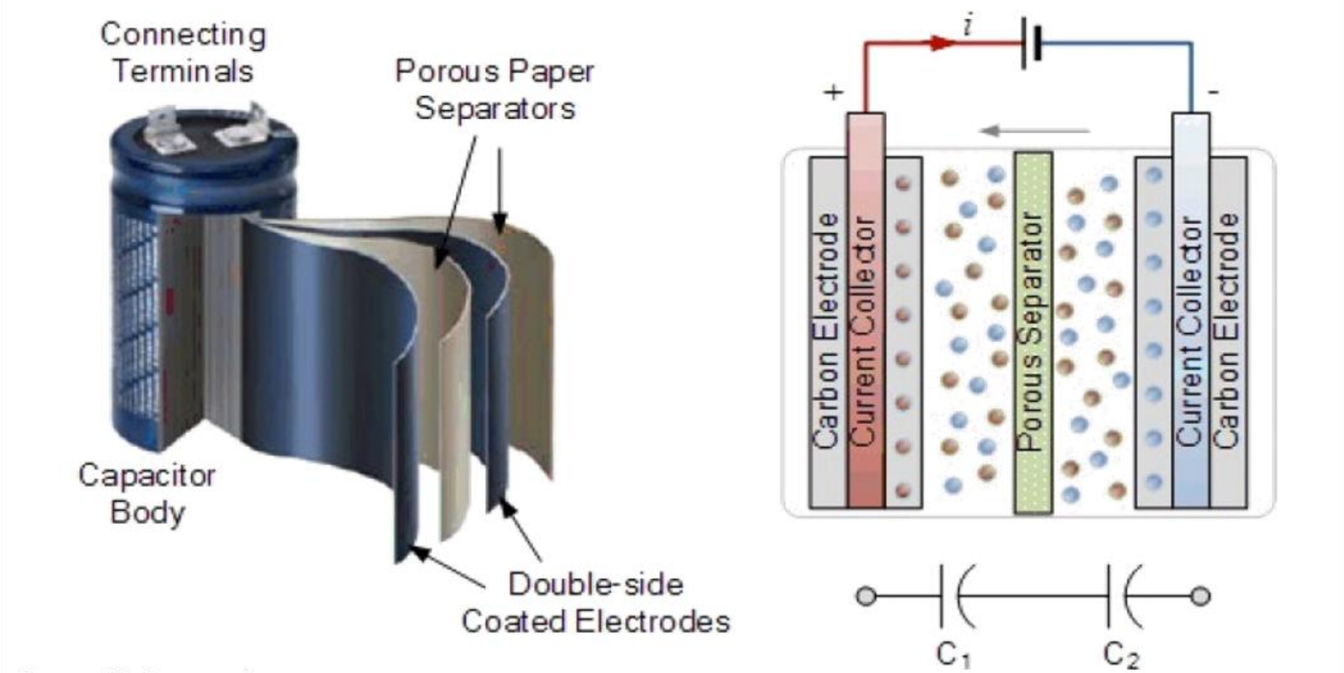
Metal Organic Frameworks

Supercapacitors

- Supercapacitors **are high-capacity energy storage devices that bridge the gap between conventional capacitors and rechargeable batteries by storing energy electrostatically**

- Metal–organic frameworks (MOFs) have attracted intensive attention for high-performance supercapacitors owing to their large specific surface area and tunable pore structure

EXHIBIT 2: Supercapacitor Construction

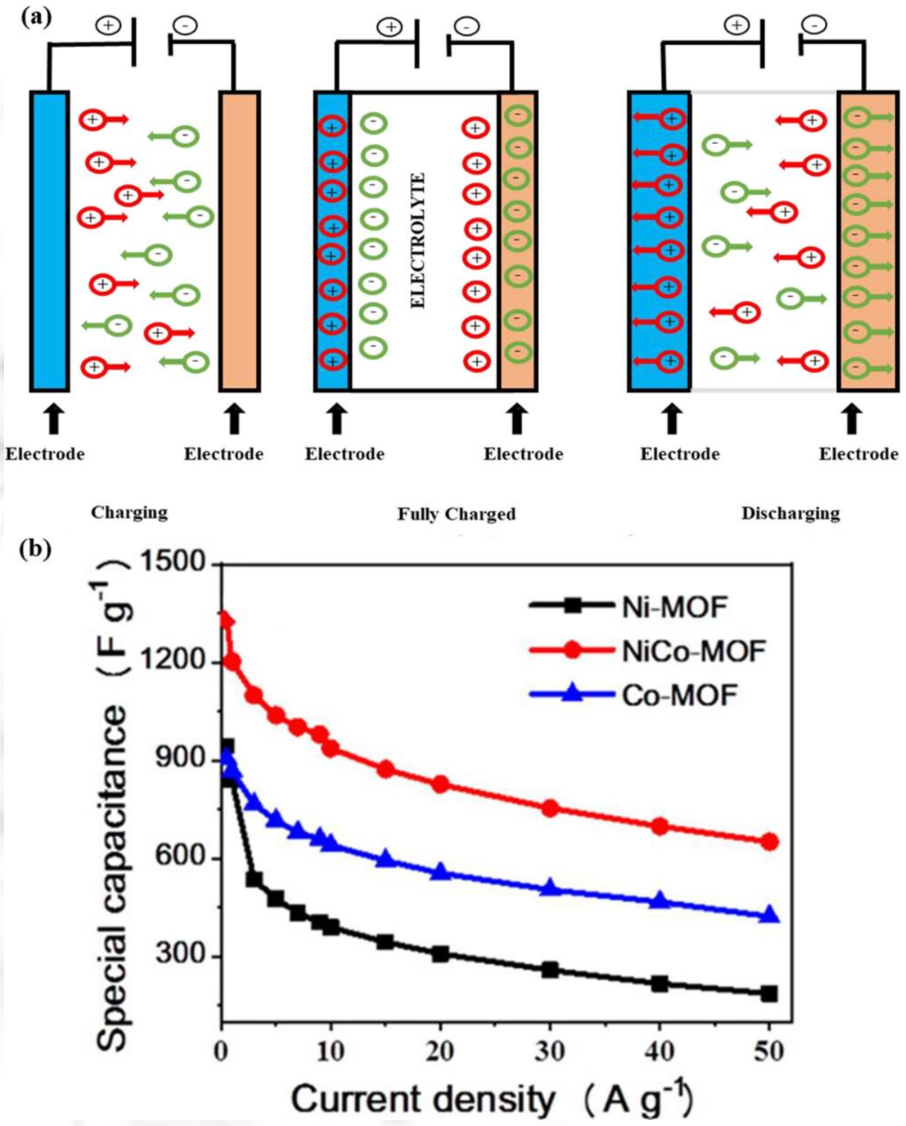


Source: ES Components

Metal Organic Frameworks

Supercapacitors

- **Ultrathin NiCo-MOF nanosheets fabricated by a facile ultrasonication at room temperature employed as a supercapacitor electrode material**
- The unique nanosheet-like structure of NiCo-MOF provides more electroactive sites and a shorter pathway for **electron transfer and electrolyte diffusion**, resulting in excellent electrochemical performance
- The results demonstrate a new method to fabricate ultrathin MOF nanosheets for high-performance supercapacitor electrode materials



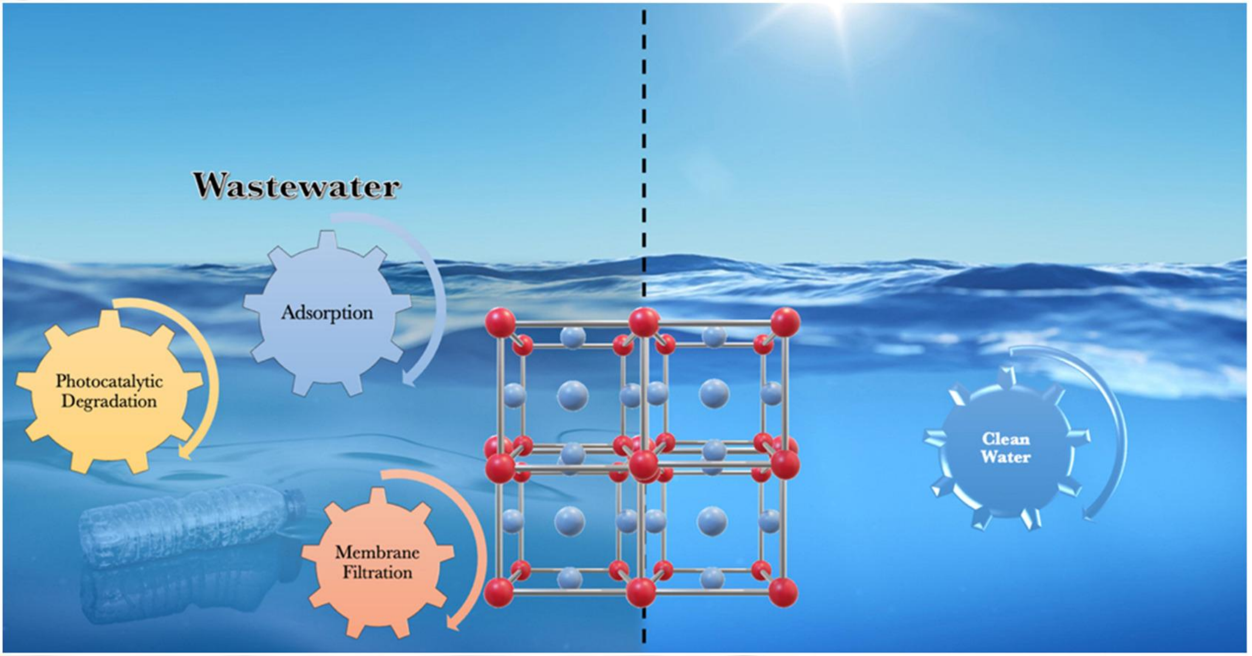
ACS Applied Energy Materials (2019), 2 (3), 2063-2071

Metal Organic Frameworks

Wastewater Treatment

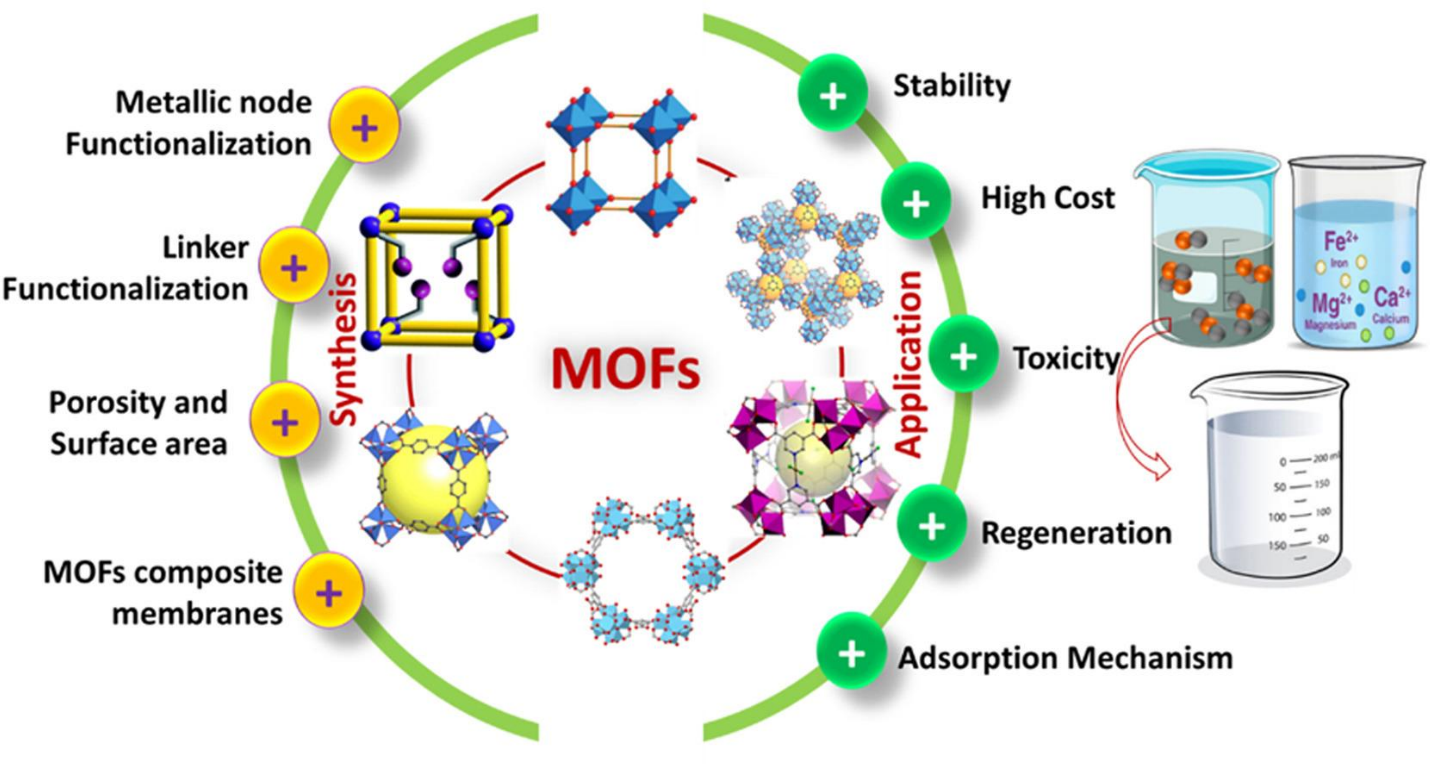
- **Wastewater treatment** is critically important for the existence of life on earth; however, this approach involves the **removal of toxic metal contaminants and organic pollutants, requiring efficient adsorbent materials**

- Within this agenda, metal-organic frameworks (MOFs) appear to be potential materials due to their unique properties as efficient adsorbents, effective photocatalysts, and reliable semi-permeable membranes



Metal Organic Frameworks

Wastewater Treatment

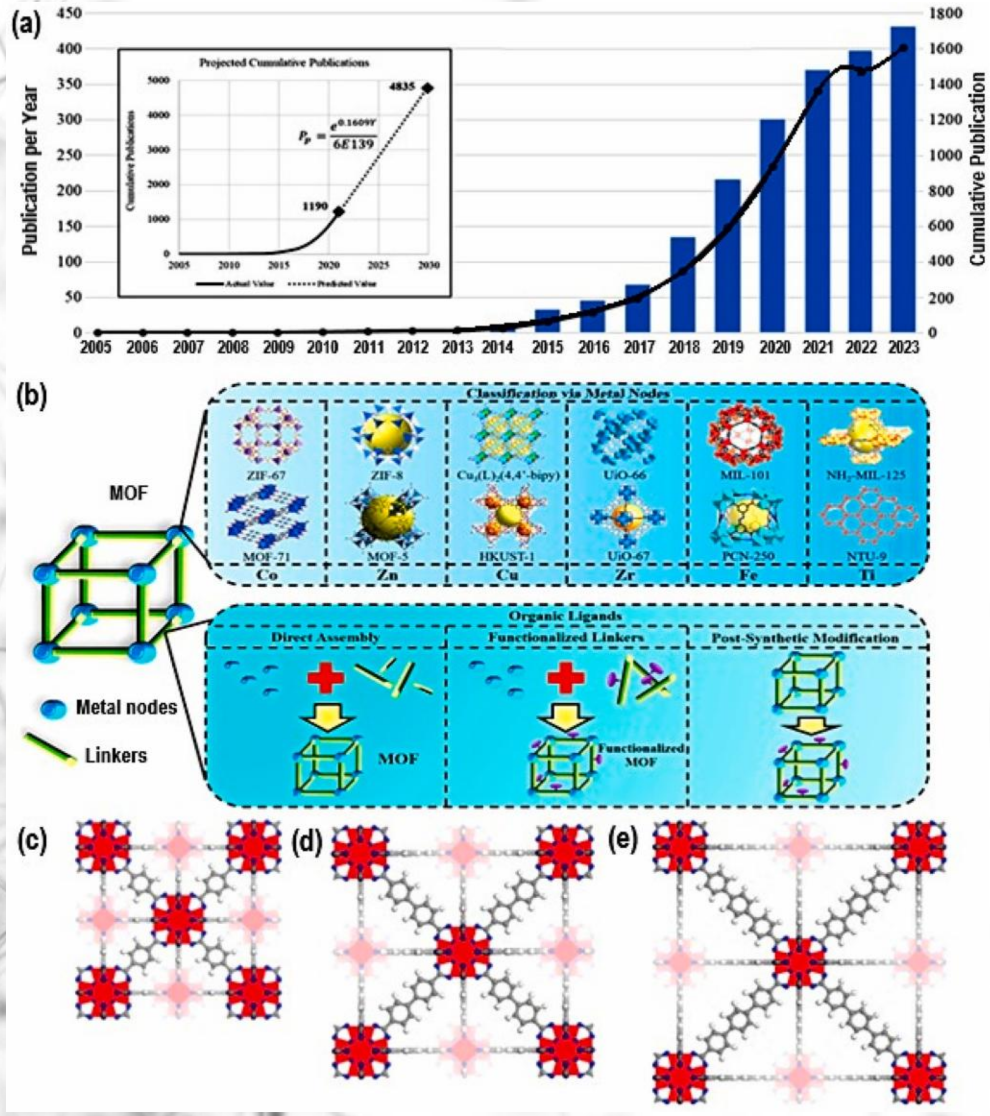


Chemosphere, 349, 140729, 2024

Metal Organic Frameworks

Wastewater Treatment

Publications in MOFs wastewater treatment

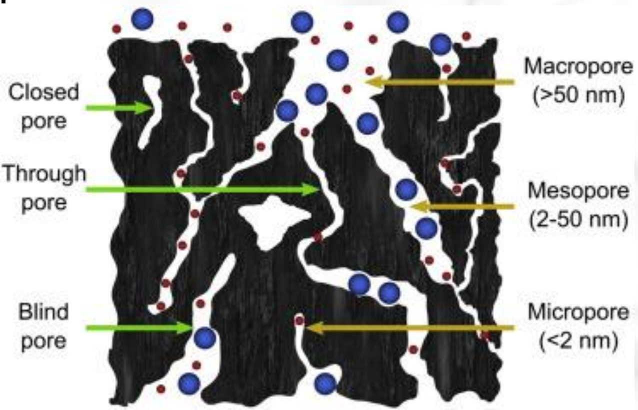


Chemosphere, 349, 140729, 2024

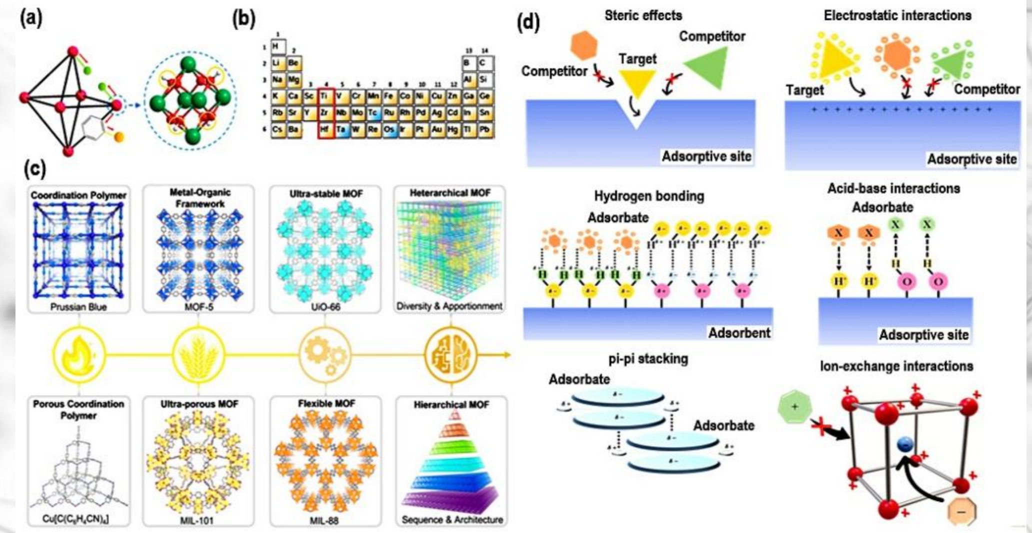
Metal Organic Frameworks

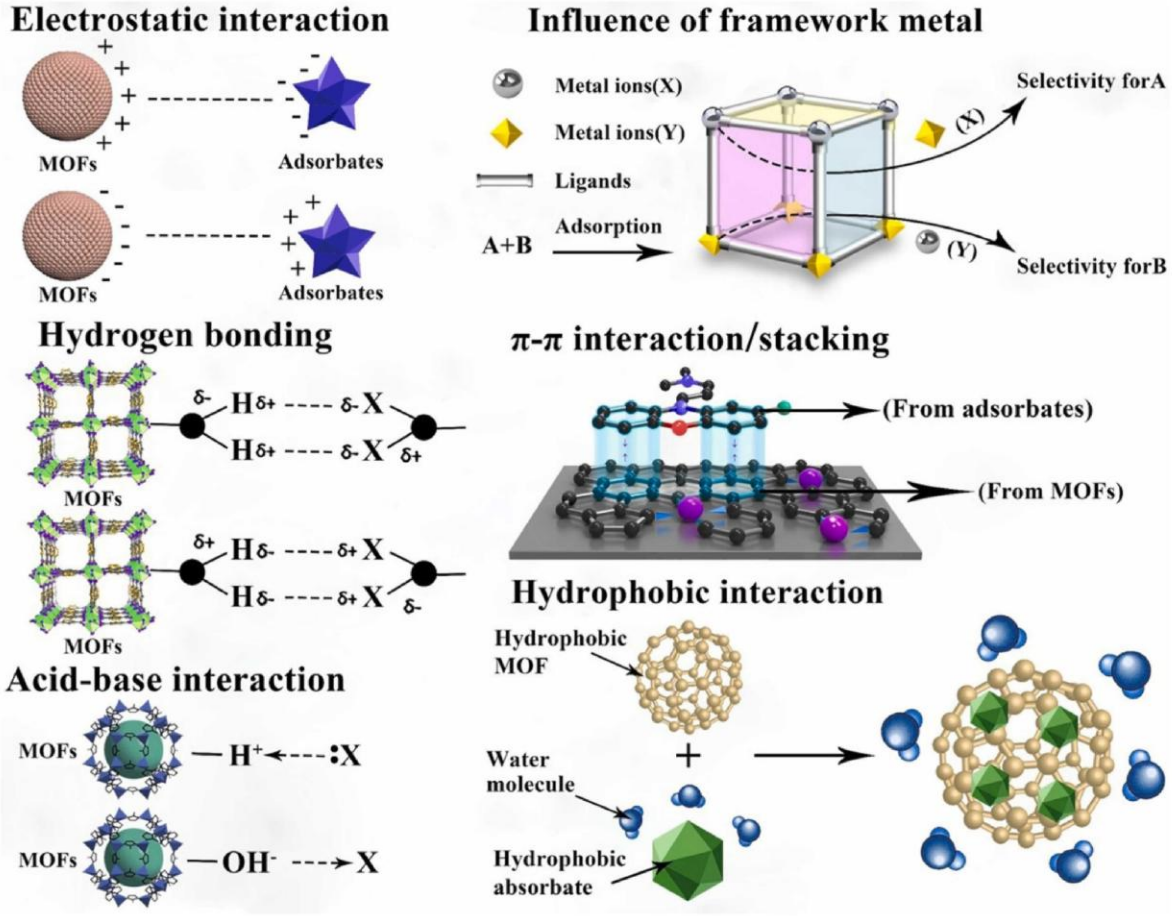
Wastewater Treatment

Physisorption



Chemisorption

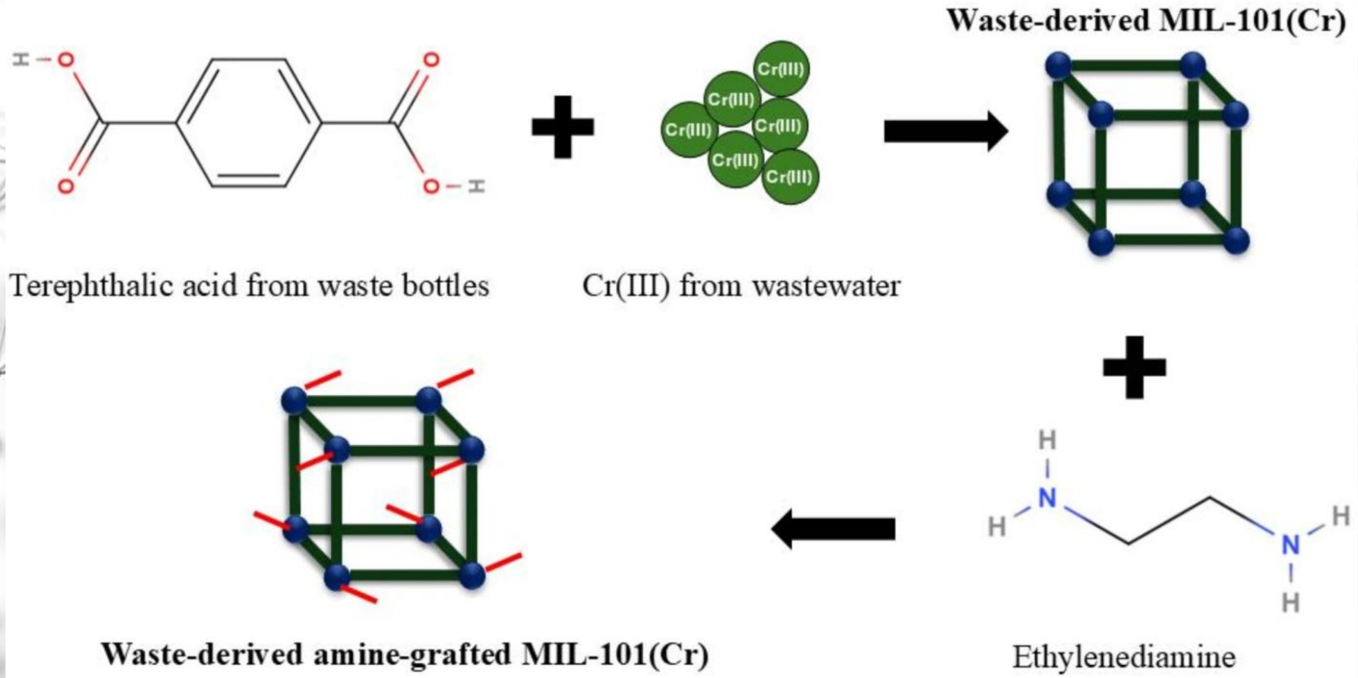


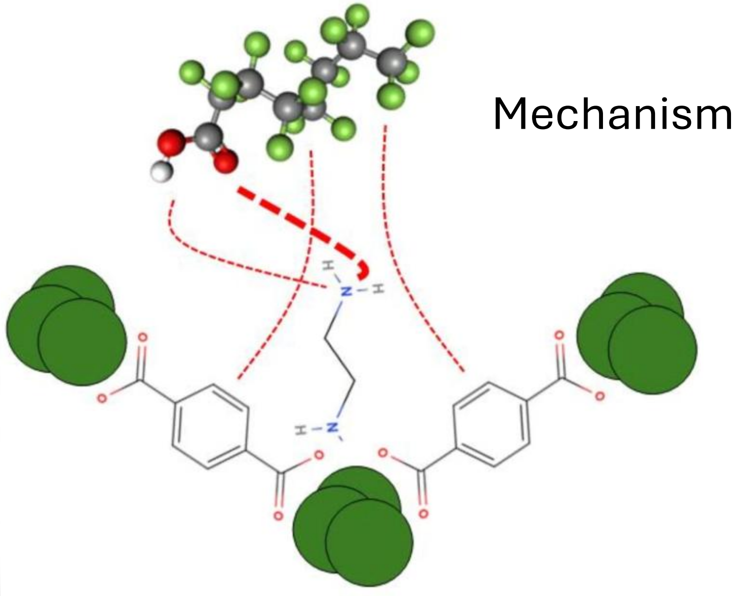


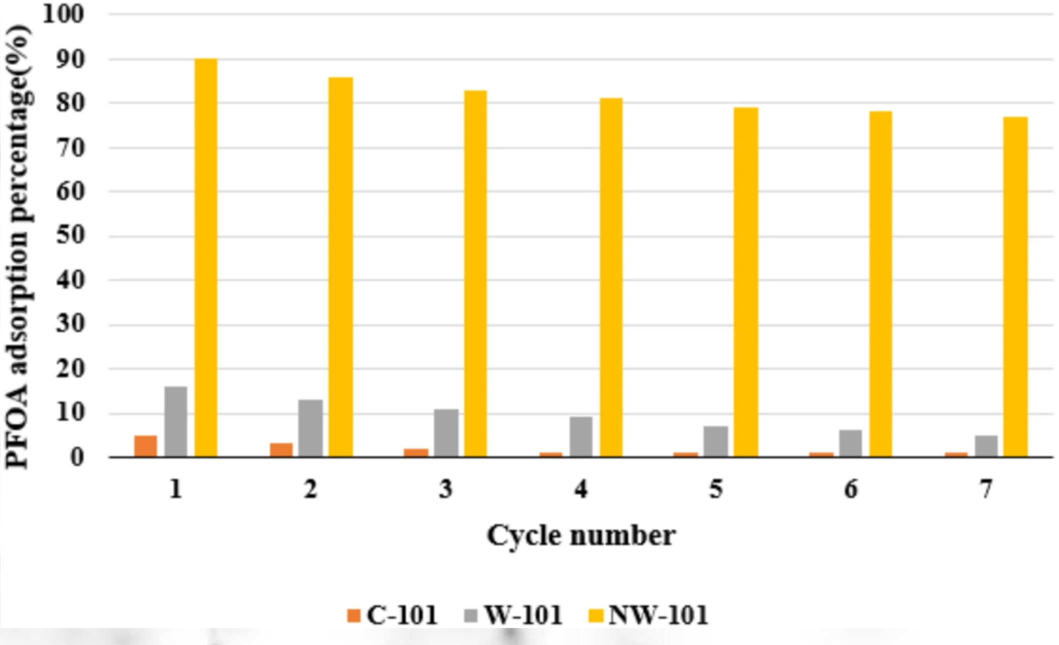
Chemosphere, 349, 140729, 2024

Metal Organic Frameworks

Wastewater Treatment



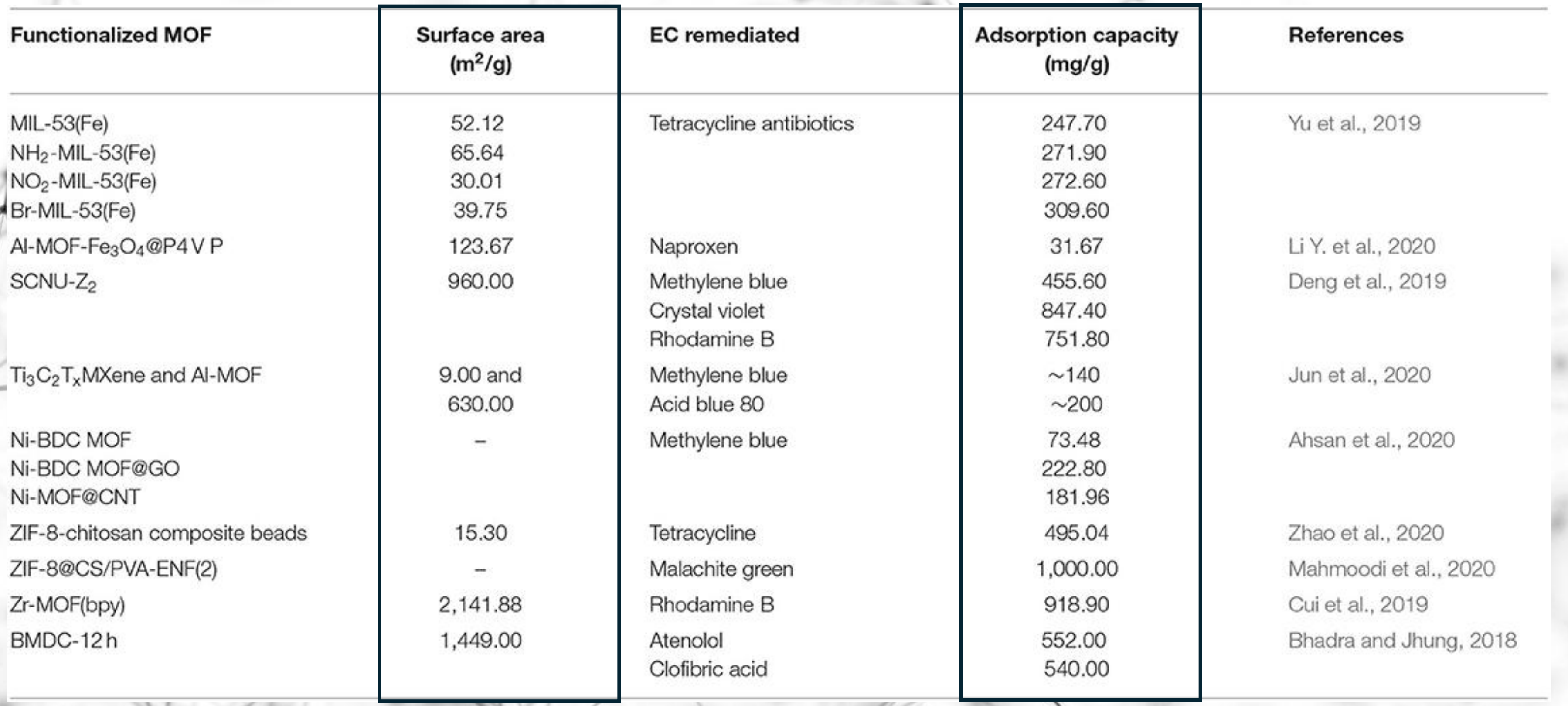

Mechanism



Ismail et al., Scientific Reports volume 15, Article number: 9439 (2025)

Metal Organic Frameworks

Wastewater Treatment



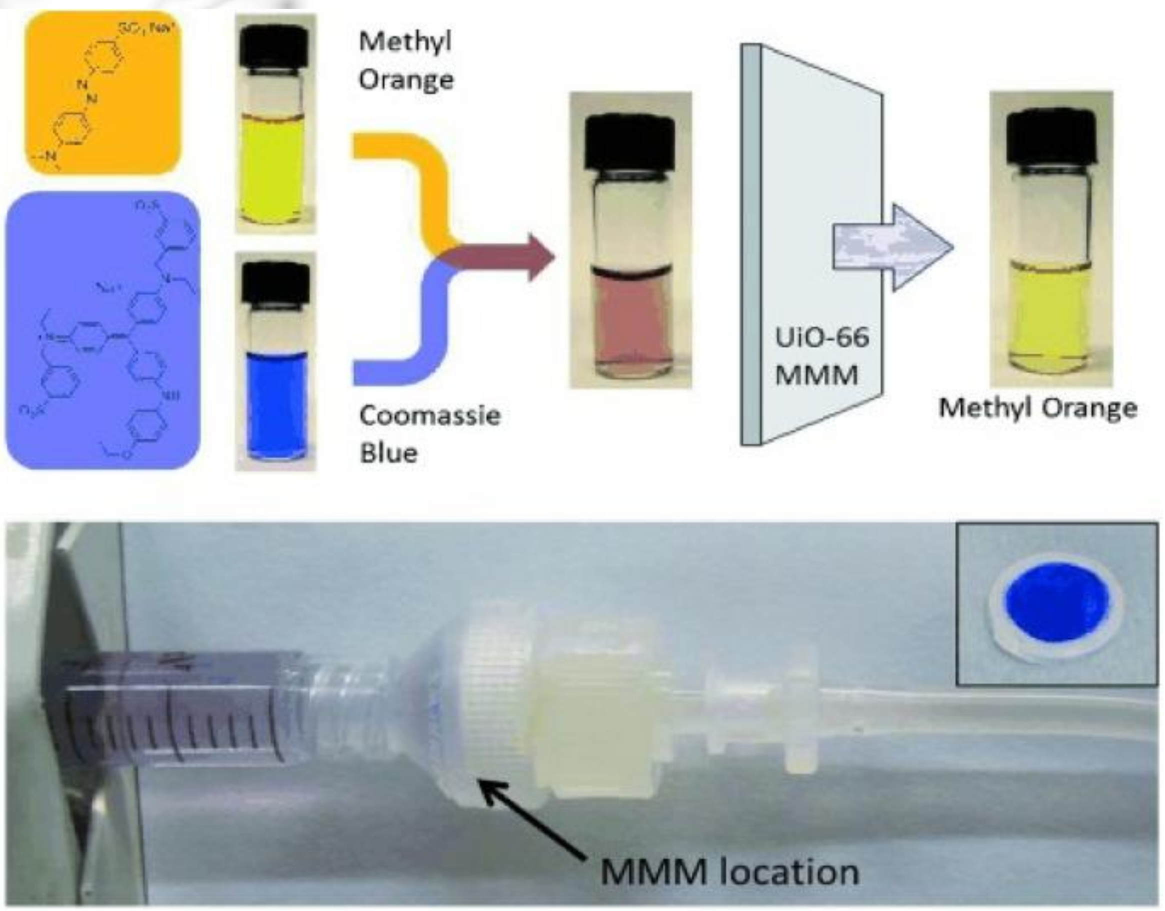
Functionalized MOF	Surface area (m^2/g)	EC remediated	Adsorption capacity (mg/g)	References
MIL-53(Fe) NH_2-MIL-53(Fe) NO_2-MIL-53(Fe) Br-MIL-53(Fe)	52.12 65.64 30.01 39.75	Tetracycline antibiotics	247.70 271.90 272.60 309.60	Yu et al., 2019
Al-MOF-Fe_3O_4@P4V P	123.67	Naproxen	31.67	Li Y. et al., 2020
SCNU-Z_2	960.00	Methylene blue Crystal violet Rhodamine B	455.60 847.40 751.80	Deng et al., 2019
$Ti_3C_2T_x$MXene and Al-MOF	9.00 and 630.00	Methylene blue Acid blue 80	~140 ~200	Jun et al., 2020
Ni-BDC MOF Ni-BDC MOF@GO Ni-MOF@CNT	–	Methylene blue	73.48 222.80 181.96	Ahsan et al., 2020
ZIF-8-chitosan composite beads	15.30	Tetracycline	495.04	Zhao et al., 2020
ZIF-8@CS/PVA-ENF(2)	–	Malachite green	1,000.00	Mahmoodi et al., 2020
Zr-MOF(bpy)	2,141.88	Rhodamine B	918.90	Cui et al., 2019
BMDC-12 h	1,449.00	Atenolol Clofibric acid	552.00 540.00	Bhadra and Jhung, 2018

Metal Organic Frameworks

Wastewater Treatment

- Six kinds of MOFs and PVDF powders, such as UiO-66, MIL-101 (Cr), MIL-101 (Fe), Cu-BTC, MIL-53 (Fe), ZIF-8, were blended into DMF according to the mass ratio of 2:1, and six large-scale doped MOFs/PVDF MMMs were prepared, extremely crystalline, porous, and adaptable MOFs in these MMMs can still undergo additional chemical alterations using postsynthetic modification (PSM) and postsynthetic exchange (PSE) procedures.

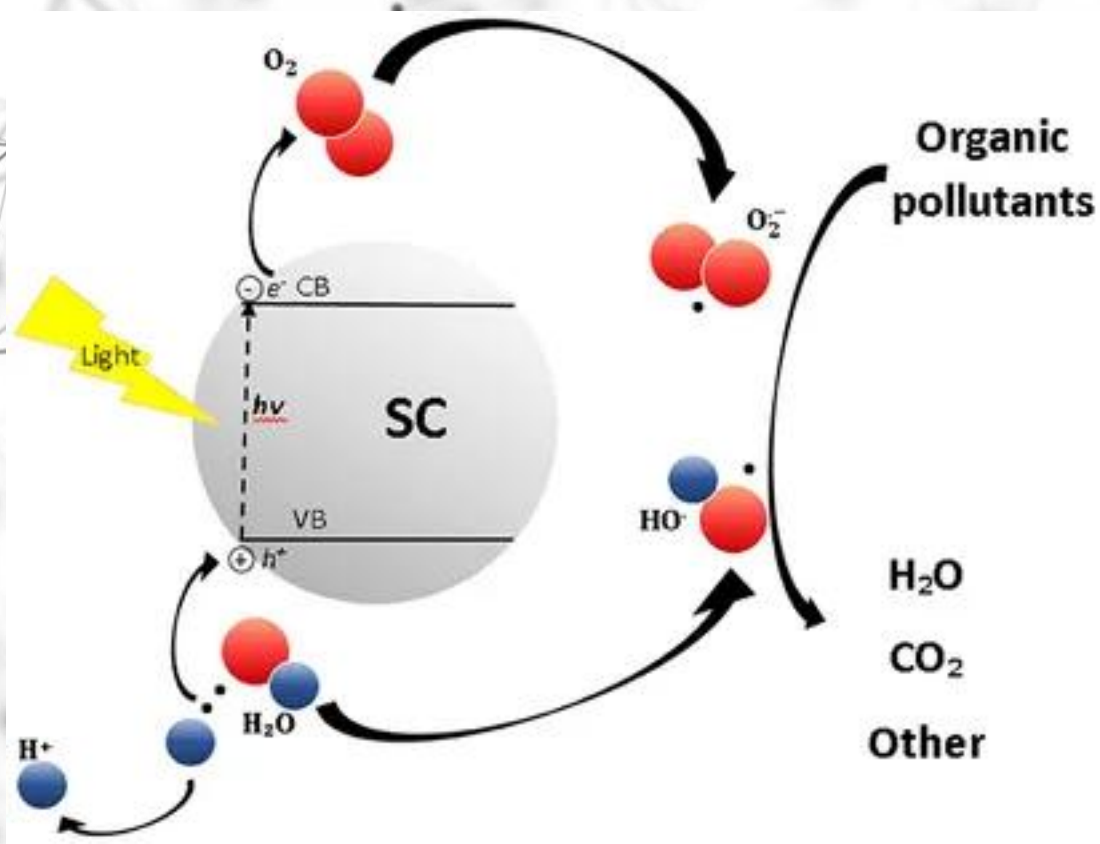
- It was discovered that UiO-66/PVDF can successfully remove 10 μM Coomassie brilliant blue R-250 from a mixed aqueous solution with methyl orange and entirely separate organic dye molecules in aqueous solution.

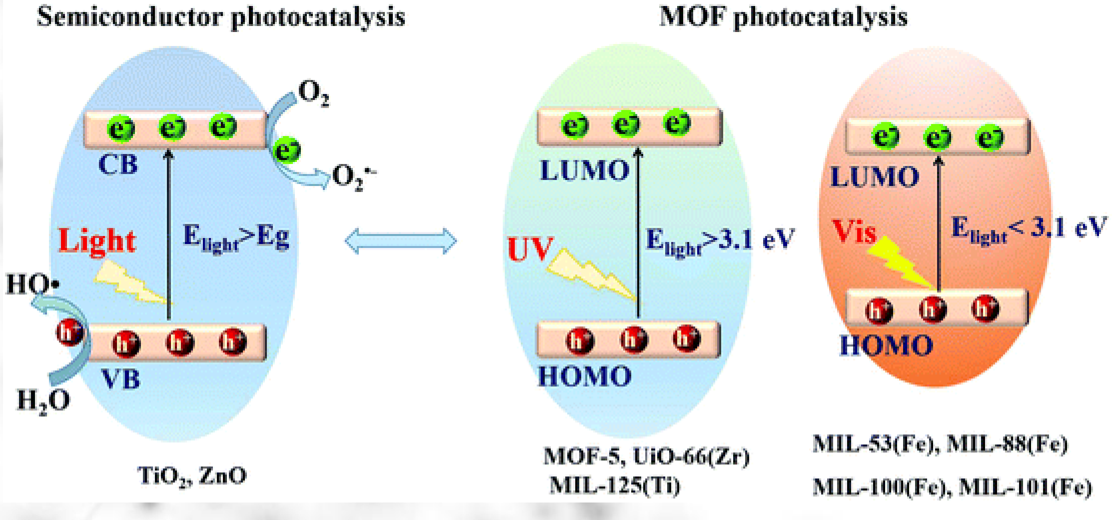


Metal Organic Frameworks

Wastewater Treatment

Photocatalysis



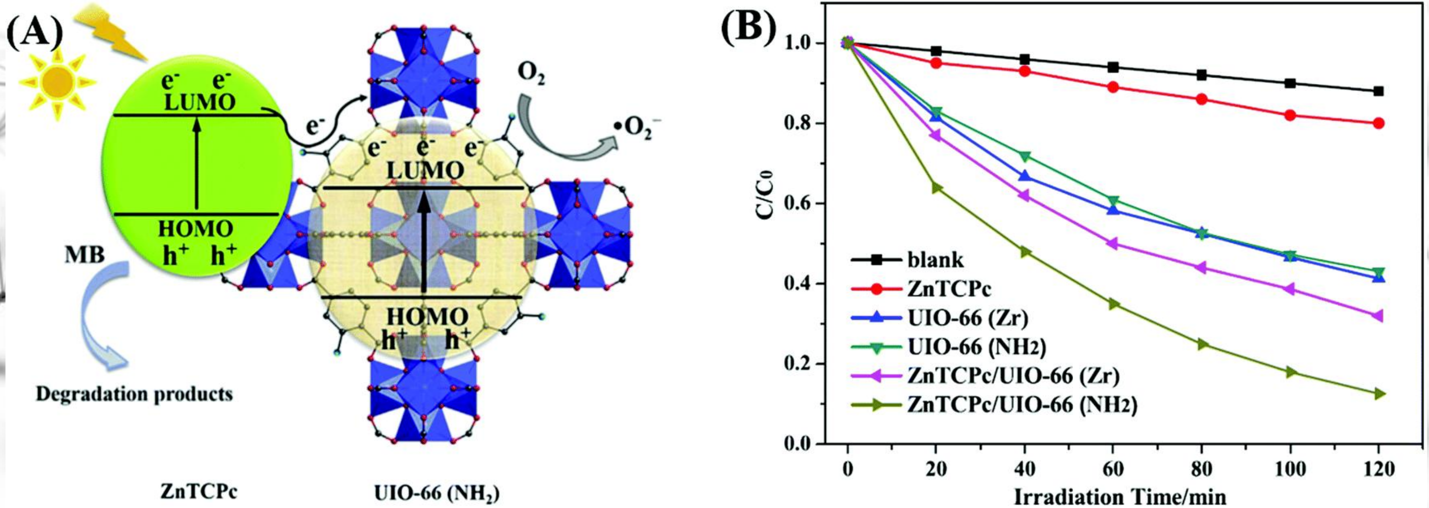


Wang et al., Inorg. Chem. Front., 2020, 7, 300–339

Metal Organic Frameworks

Wastewater Treatment

Photocatalysis



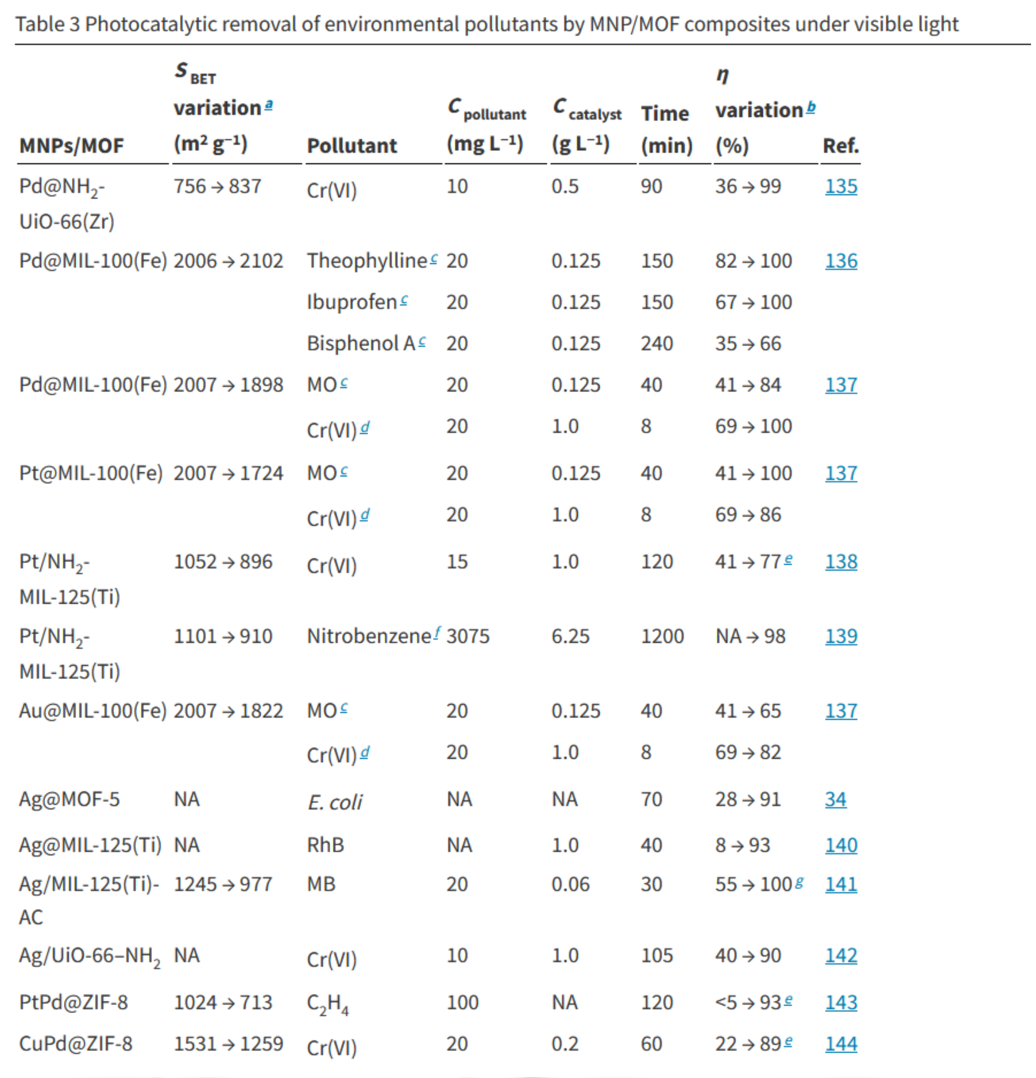


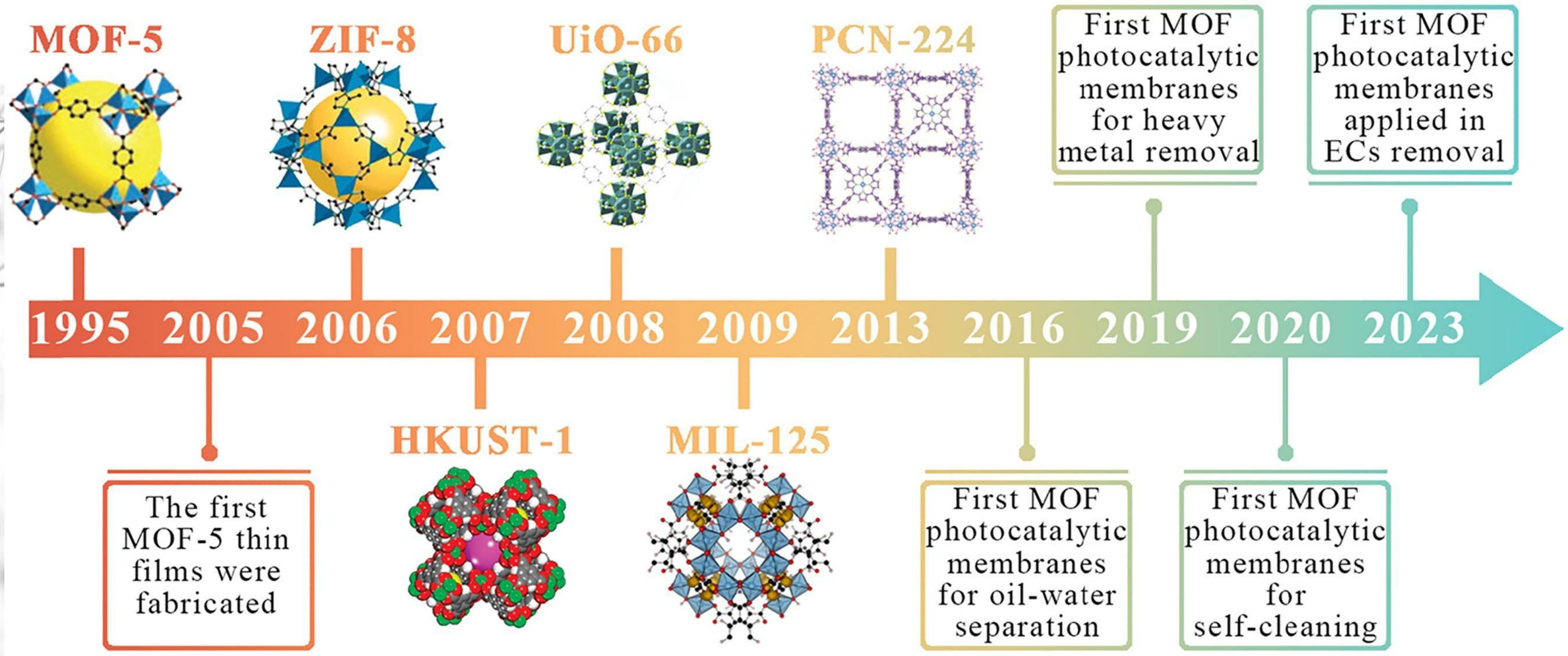
Table 3 Photocatalytic removal of environmental pollutants by MNP/MOF composites under visible light

MNPs/MOF	S_{BET} variation[a] ($m^2 g^{-1}$)	Pollutant	$C_{pollutant}$ ($mg L^{-1}$)	$C_{catalyst}$ ($g L^{-1}$)	Time (min)	η variation[b] (%)	Ref.
Pd@NH_2-UiO-66(Zr)	756 → 837	Cr(VI)	10	0.5	90	36 → 99	135
Pd@MIL-100(Fe)	2006 → 2102	Theophylline[c]	20	0.125	150	82 → 100	136
		Ibuprofen[c]	20	0.125	150	67 → 100	
		Bisphenol A[c]	20	0.125	240	35 → 66	
Pd@MIL-100(Fe)	2007 → 1898	MO[c]	20	0.125	40	41 → 84	137
		Cr(VI)[d]	20	1.0	8	69 → 100	
Pt@MIL-100(Fe)	2007 → 1724	MO[c]	20	0.125	40	41 → 100	137
		Cr(VI)[d]	20	1.0	8	69 → 86	
Pt/NH_2-MIL-125(Ti)	1052 → 896	Cr(VI)	15	1.0	120	41 → 77[e]	138
Pt/NH_2-MIL-125(Ti)	1101 → 910	Nitrobenzene[f]	3075	6.25	1200	NA → 98	139
Au@MIL-100(Fe)	2007 → 1822	MO[c]	20	0.125	40	41 → 65	137
		Cr(VI)[d]	20	1.0	8	69 → 82	
Ag@MOF-5	NA	*E. coli*	NA	NA	70	28 → 91	34
Ag@MIL-125(Ti)	NA	RhB	NA	1.0	40	8 → 93	140
Ag/MIL-125(Ti)-AC	1245 → 977	MB	20	0.06	30	55 → 100[g]	141
Ag/UiO-66–NH_2	NA	Cr(VI)	10	1.0	105	40 → 90	142
PtPd@ZIF-8	1024 → 713	C_2H_4	100	NA	120	<5 → 93[e]	143
CuPd@ZIF-8	1531 → 1259	Cr(VI)	20	0.2	60	22 → 89[e]	144

Metal Organic Frameworks

Wastewater Treatment

Photocatalysis/MOF membranes



Feng et al., Separation and Purification Technology 355 (2025) 129540

Metal Organic Frameworks

Wastewater Treatment

Photocatalysis/MOF membranes

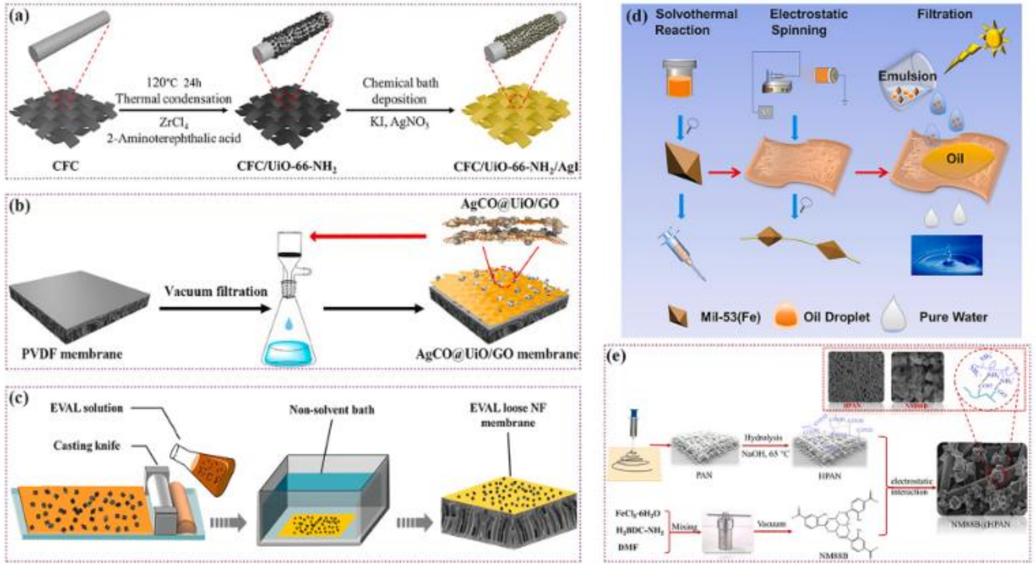


Fig. 6. Typical types of MOF based membrane preparation methods. (a) Crystalline growth [104], (b) vacuum filtration [120], (c) phase inversion [115], (d) electrostatic spinning [114], (e) Impregnation [117].

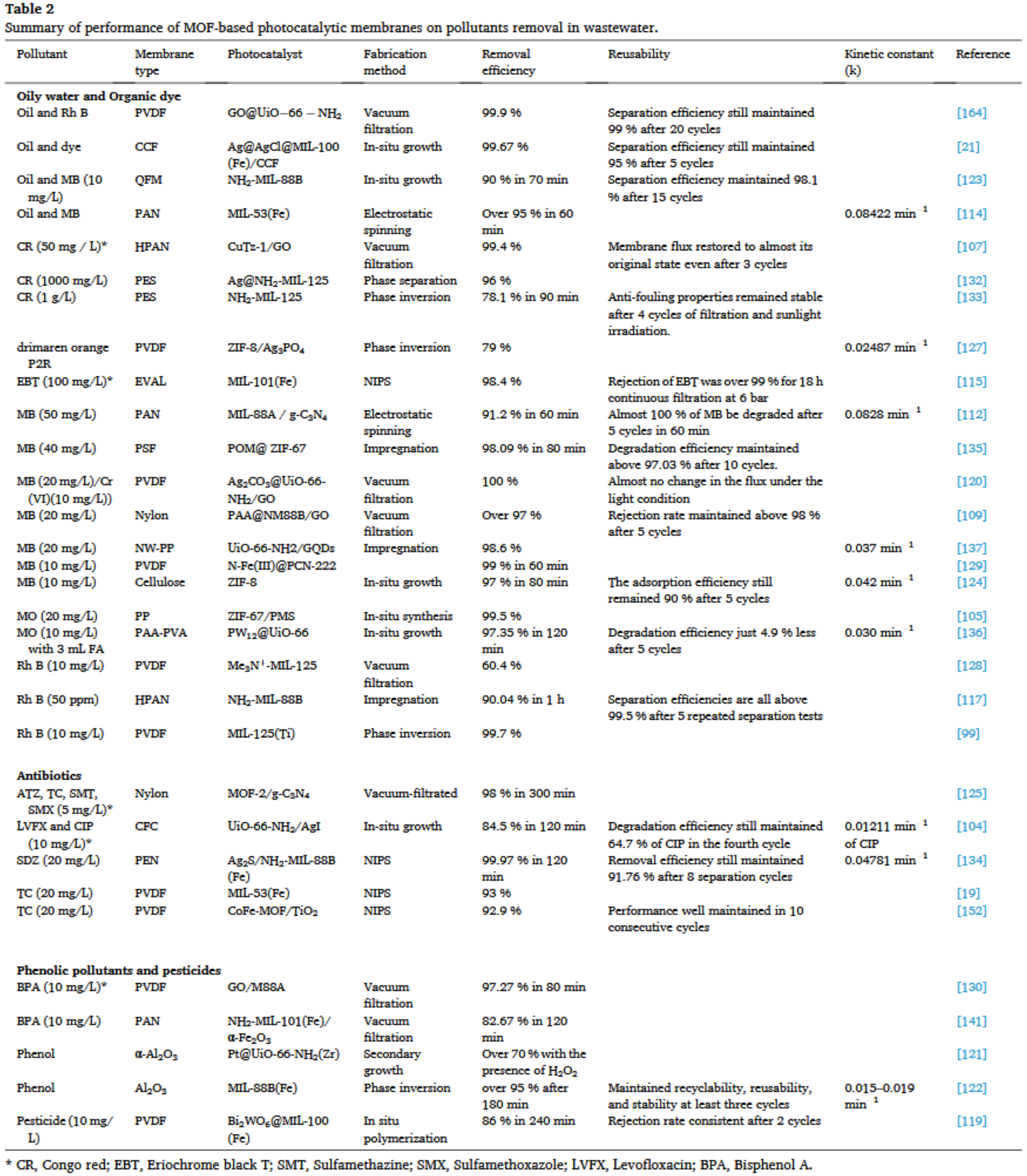


Table 2

Summary of performance of MOF-based photocatalytic membranes on pollutants removal in wastewater.

Pollutant	Membrane type	Photocatalyst	Fabrication method	Removal efficiency	Reusability	Kinetic constant (k)	Reference
Oily water and Organic dye							
Oil and Rh B	PVDF	GO@UiO−66 − NH_2	Vacuum filtration	99.9 %	Separation efficiency still maintained 99 % after 20 cycles		[164]
Oil and dye	CCF	Ag@AgCl@MIL-100 (Fe)/CCF	In-situ growth	99.67 %	Separation efficiency still maintained 95 % after 5 cycles		[21]
Oil and MB (10 mg/L)	QFM	NH_2-MIL-88B	In-situ growth	90 % in 70 min	Separation efficiency maintained 98.1 % after 15 cycles		[123]
Oil and MB	PAN	MIL-53(Fe)	Electrostatic spinning	Over 95 % in 60 min		0.08422 min^{-1}	[114]
CR (50 mg / L)*	HPAN	CuTz-1/GO	Vacuum filtration	99.4 %	Membrane flux restored to almost its original state even after 3 cycles		[107]
CR (1000 mg/L)	PES	Ag@NH_2-MIL-125	Phase separation	96 %			[132]
CR (1 g/L)	PES	NH_2-MIL-125	Phase inversion	78.1 % in 90 min	Anti-fouling properties remained stable after 4 cycles of filtration and sunlight irradiation.		[133]
drimaren orange P2R	PVDF	ZIF-8/Ag_3PO_4	Phase inversion	79 %		0.02487 min^{-1}	[127]
EBT (100 mg/L)*	EVAL	MIL-101(Fe)	NIPS	98.4 %	Rejection of EBT was over 99 % for 18 h continuous filtration at 6 bar		[115]
MB (50 mg/L)	PAN	MIL-88A / g-C_3N_4	Electrostatic spinning	91.2 % in 60 min	Almost 100 % of MB be degraded after 5 cycles in 60 min	0.0828 min^{-1}	[112]
MB (40 mg/L)	PSF	POM@ ZIF-67	Impregnation	98.09 % in 80 min	Degradation efficiency maintained above 97.03 % after 10 cycles.		[135]
MB (20 mg/L)/Cr (VI)(10 mg/L))	PVDF	Ag_2CO_3@UiO-66-NH_2/GO	Vacuum filtration	100 %	Almost no change in the flux under the light condition		[120]
MB (20 mg/L)	Nylon	PAA@NM88B/GO	Vacuum filtration	Over 97 %	Rejection rate maintained above 98 % after 5 cycles		[109]
MB (20 mg/L)	NW-PP	UiO-66-NH2/GQDs	Impregnation	98.6 %		0.037 min^{-1}	[137]
MB (10 mg/L)	PVDF	N-Fe(III)@PCN-222		99 % in 60 min			[129]
MB (10 mg/L)	Cellulose	ZIF-8	In-situ growth	97 % in 80 min	The adsorption efficiency still remained 90 % after 5 cycles	0.042 min^{-1}	[124]
MO (20 mg/L)	PP	ZIF-67/PMS	In-situ synthesis	99.5 %			[105]
MO (10 mg/L) with 3 mL FA	PAA-PVA	PW_{12}@UiO-66	In-situ growth	97.35 % in 120 min	Degradation efficiency just 4.9 % less after 5 cycles	0.030 min^{-1}	[136]
Rh B (10 mg/L)	PVDF	Me_3N^+-MIL-125	Vacuum filtration	60.4 %			[128]
Rh B (50 ppm)	HPAN	NH_2-MIL-88B	Impregnation	90.04 % in 1 h	Separation efficiencies are all above 99.5 % after 5 repeated separation tests		[117]
Rh B (10 mg/L)	PVDF	MIL-125(Ti)	Phase inversion	99.7 %			[99]
Antibiotics							
ATZ, TC, SMT, SMX (5 mg/L)*	Nylon	MOF-2/g-C_3N_4	Vacuum-filtrated	98 % in 300 min			[125]
LVFX and CIP (10 mg/L)*	CFC	UiO-66-NH_2/AgI	In-situ growth	84.5 % in 120 min	Degradation efficiency still maintained 64.7 % of CIP in the fourth cycle	0.01211 min^{-1} of CIP	[104]
SDZ (20 mg/L)	PEN	Ag_2S/NH_2-MIL-88B (Fe)	NIPS	99.97 % in 120 min	Removal efficiency still maintained 91.76 % after 8 separation cycles	0.04781 min^{-1}	[134]
TC (20 mg/L)	PVDF	MIL-53(Fe)	NIPS	93 %			[19]
TC (20 mg/L)	PVDF	CoFe-MOF/TiO_2	NIPS	92.9 %	Performance well maintained in 10 consecutive cycles		[152]
Phenolic pollutants and pesticides							
BPA (10 mg/L)*	PVDF	GO/M88A	Vacuum filtration	97.27 % in 80 min			[130]
BPA (10 mg/L)	PAN	NH_2-MIL-101(Fe)/ α-Fe_2O_3	Vacuum filtration	82.67 % in 120 min			[141]
Phenol	α-Al_2O_3	Pt@UiO-66-NH_2(Zr)	Secondary growth	Over 70 % with the presence of H_2O_2			[121]
Phenol	Al_2O_3	MIL-88B(Fe)	Phase inversion	over 95 % after 180 min	Maintained recyclability, reusability, and stability at least three cycles	0.015–0.019 min^{-1}	[122]
Pesticide (10 mg/ L)	PVDF	Bi_2WO_6@MIL-100 (Fe)	In situ polymerization	86 % in 240 min	Rejection rate consistent after 2 cycles		[119]

* CR, Congo red; EBT, Eriochrome black T; SMT, Sulfamethazine; SMX, Sulfamethoxazole; LVFX, Levofloxacin; BPA, Bisphenol A.

Feng et al., Separation and Purification Technology 355 (2025) 129540

Metal Organic Frameworks

Controlled release of fertilizers and nutritions

The Challenge

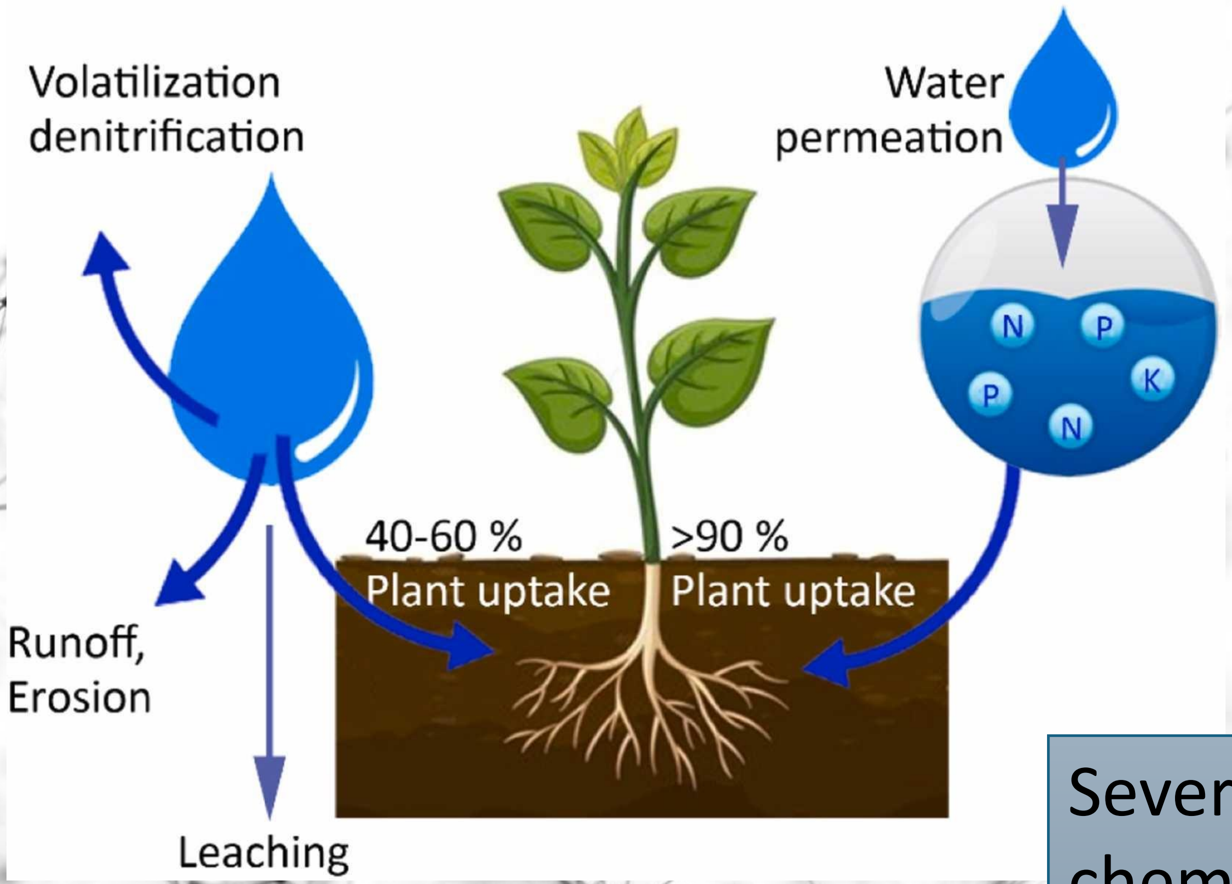
Over 90% of conventional fertilizers are lost due to volatilization or leaching.

Microplastic pollution from synthetic polymer coatings is degrading soil ecosystems.

Urgent need for biodegradable, efficient delivery systems to reduce waste and pollution.

Metal Organic Frameworks

Controlled release of fertilizers and nutritions



Challenges

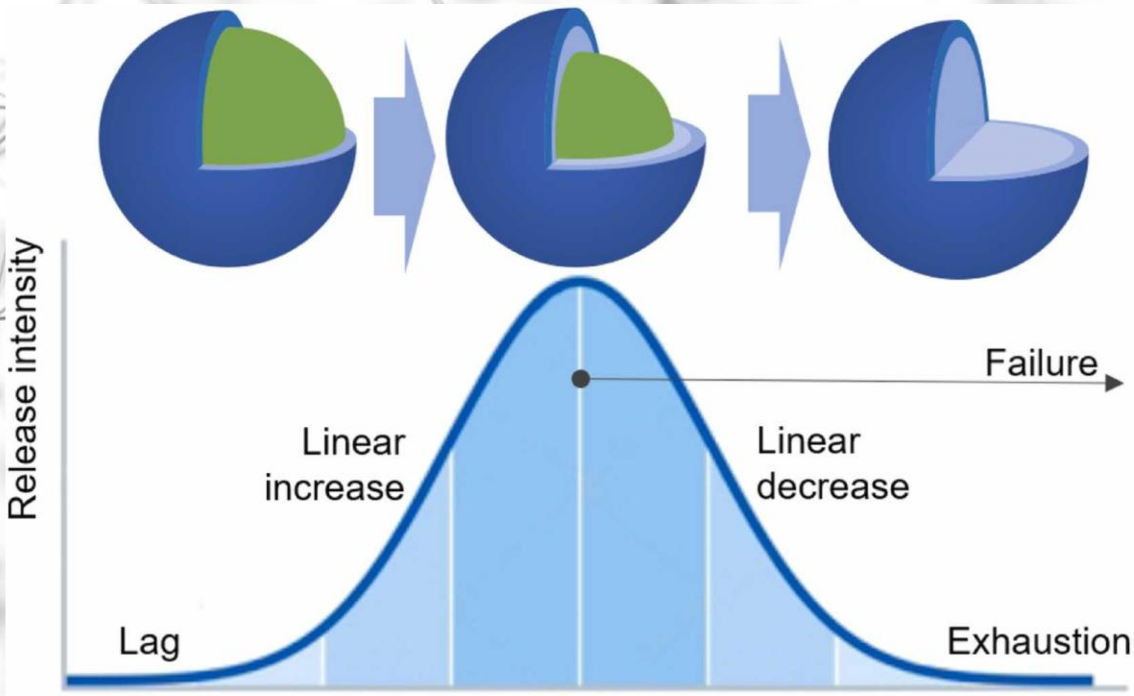
- Low Nutrient Use Efficiency (NUE)
- Environmental Pollution – Excess fertilizer application
- Variable Soil and Climatic Conditions – Differences in soil composition
- Increased Agricultural Demand and Sustainability Concerns

Several new technologies like plasmas, flow chemistry, Fe-based metal–organic framework (MOF), nanotechnologies, and microfluidic sensing have been developed

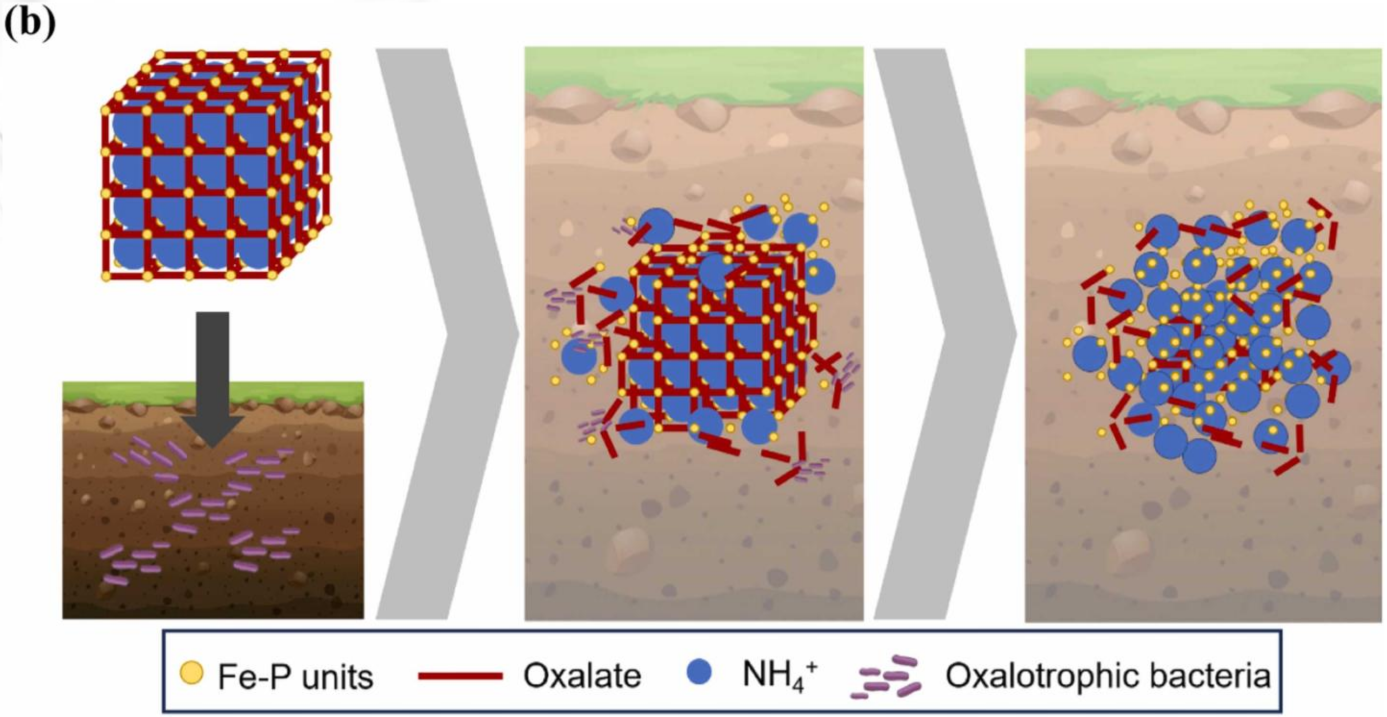
Metal Organic Frameworks

Controlled release of fertilizers and nutritions

Polymeric carriers



MOFs

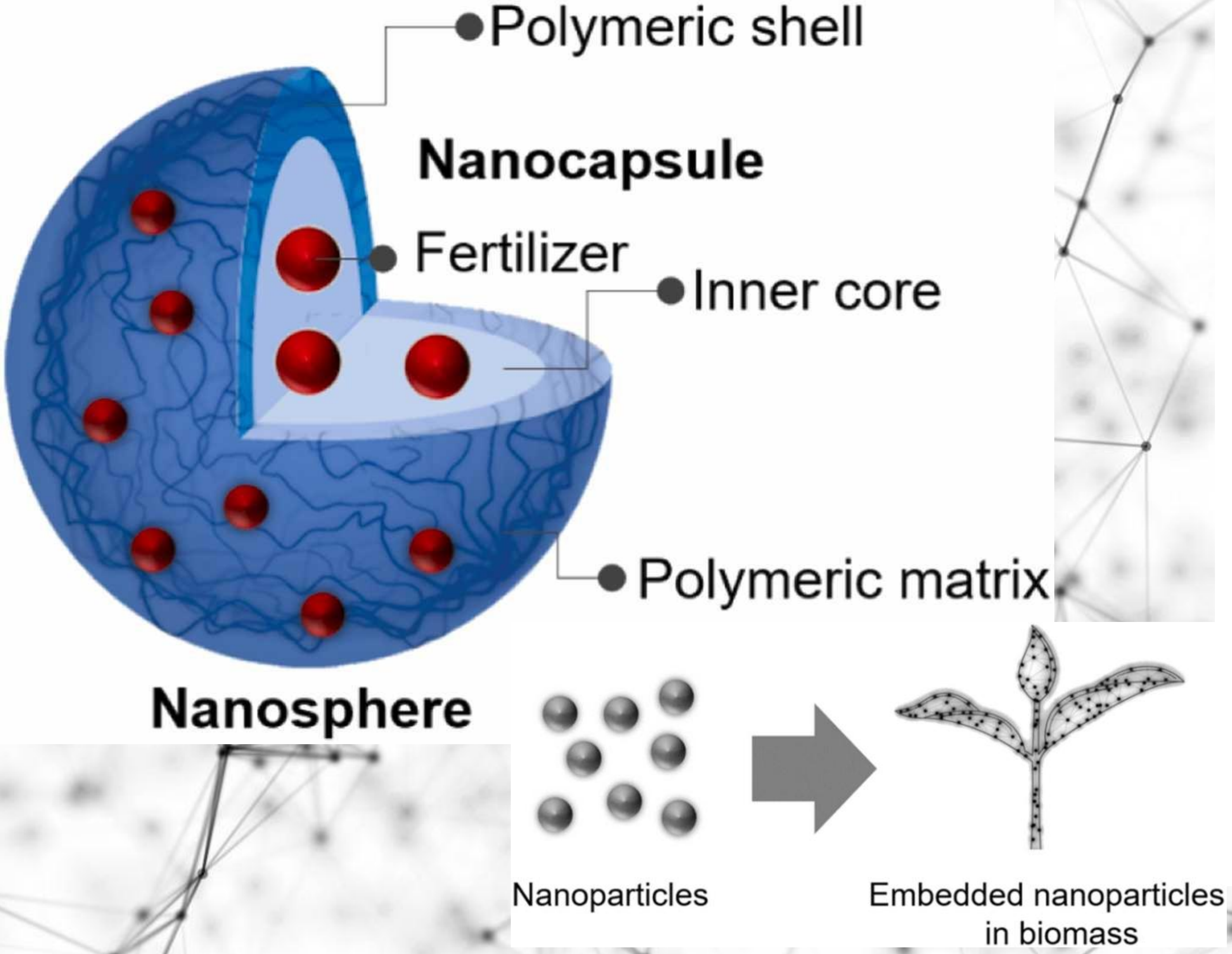


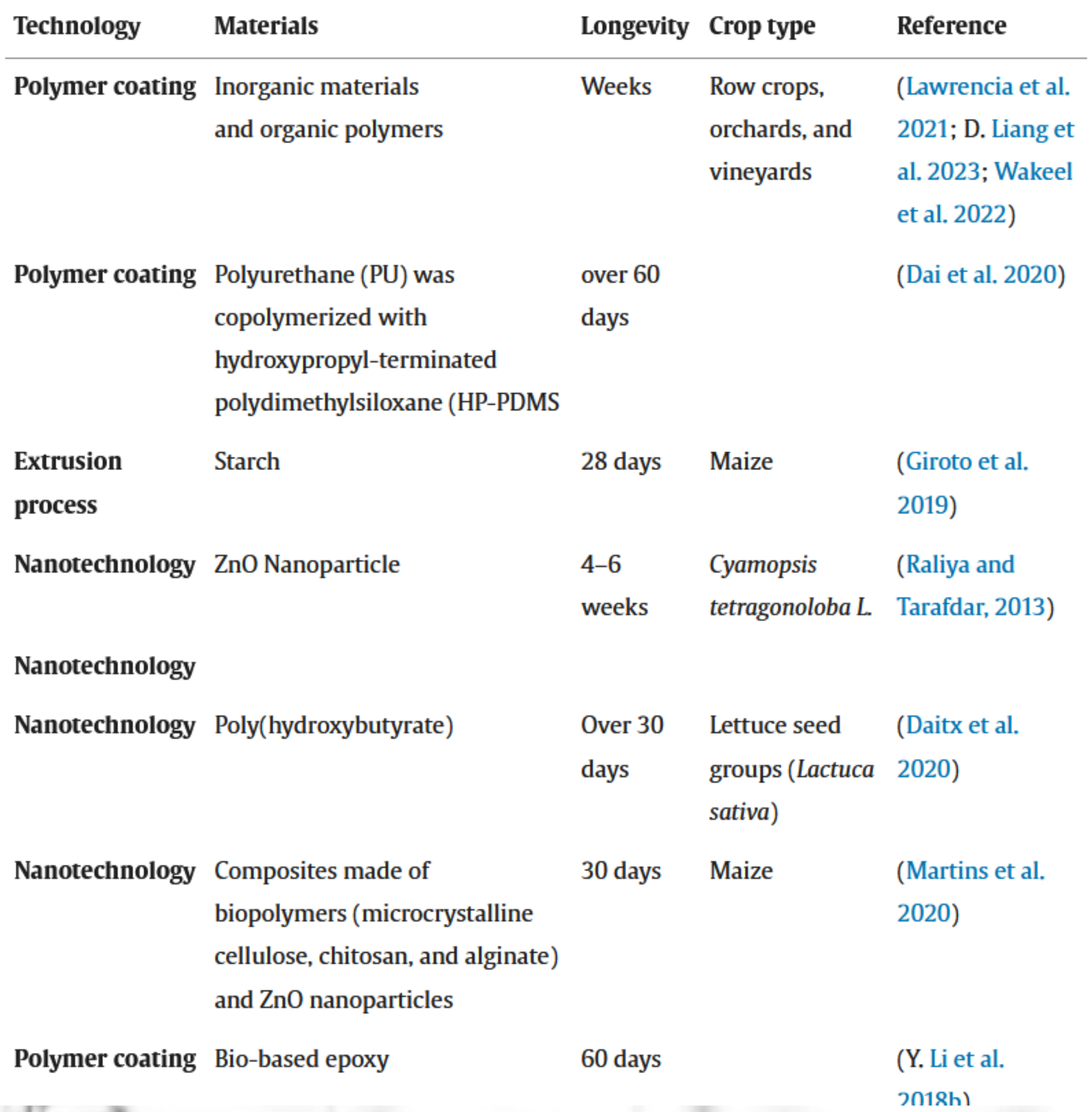
- Oxalate-phosphate amine-MOF with nitrogen, phosphorus, and iron nutrients, substantially improving wheat yield and nitrogen utilization efficiency in pot culture experiments
- 9.6 % enhancement after 96 h of treatment, in addition to chlorophyll content, protein and enzymes activities

Metal Organic Frameworks

Controlled release of fertilizers and nutritions

Polymeric nanocapsules

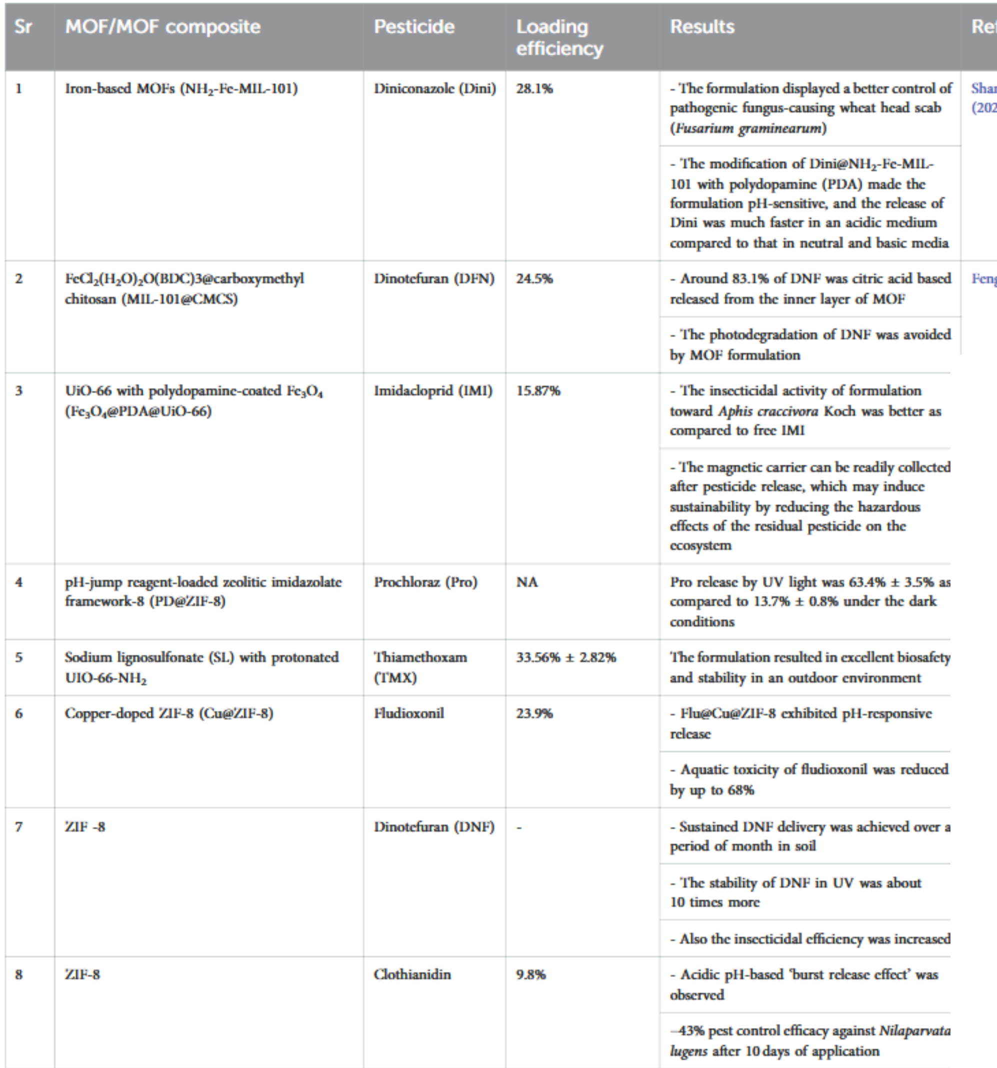




Technology	Materials	Longevity	Crop type	Reference
Polymer coating	Inorganic materials and organic polymers	Weeks	Row crops, orchards, and vineyards	(Lawrencia et al. 2021; D. Liang et al. 2023; Wakeel et al. 2022)
Polymer coating	Polyurethane (PU) was copolymerized with hydroxypropyl-terminated polydimethylsiloxane (HP-PDMS	over 60 days		(Dai et al. 2020)
Extrusion process	Starch	28 days	Maize	(Giroto et al. 2019)
Nanotechnology	ZnO Nanoparticle	4–6 weeks	*Cyamopsis tetragonoloba L.*	(Raliya and Tarafdar, 2013)
Nanotechnology				
Nanotechnology	Poly(hydroxybutyrate)	Over 30 days	Lettuce seed groups (*Lactuca sativa*)	(Daitx et al. 2020)
Nanotechnology	Composites made of biopolymers (microcrystalline cellulose, chitosan, and alginate) and ZnO nanoparticles	30 days	Maize	(Martins et al. 2020)
Polymer coating	Bio-based epoxy	60 days		(Y. Li et al. 2018b)

Metal Organic Frameworks

Controlled release of pesticides



Sr	MOF/MOF composite	Pesticide	Loading efficiency	Results	References
1	Iron-based MOFs (NH_2-Fe-MIL-101)	Diniconazole (Dini)	28.1%	- The formulation displayed a better control of pathogenic fungus-causing wheat head scab (*Fusarium graminearum*)	Shan et al. (2020b)
				- The modification of Dini@NH_2-Fe-MIL-101 with polydopamine (PDA) made the formulation pH-sensitive, and the release of Dini was much faster in an acidic medium compared to that in neutral and basic media	
2	$FeCl_2(H_2O)_2O(BDC)3$@carboxymethyl chitosan (MIL-101@CMCS)	Dinotefuran (DFN)	24.5%	- Around 83.1% of DNF was citric acid based released from the inner layer of MOF	Feng et al. (2020)
				- The photodegradation of DNF was avoided by MOF formulation	
3	UiO-66 with polydopamine-coated Fe_3O_4 (Fe_3O_4@PDA@UiO-66)	Imidacloprid (IMI)	15.87%	- The insecticidal activity of formulation toward *Aphis craccivora* Koch was better as compared to free IMI	
				- The magnetic carrier can be readily collected after pesticide release, which may induce sustainability by reducing the hazardous effects of the residual pesticide on the ecosystem	
4	pH-jump reagent-loaded zeolitic imidazolate framework-8 (PD@ZIF-8)	Prochloraz (Pro)	NA	Pro release by UV light was 63.4% ± 3.5% as compared to 13.7% ± 0.8% under the dark conditions	
5	Sodium lignosulfonate (SL) with protonated UIO-66-NH_2	Thiamethoxam (TMX)	33.56% ± 2.82%	The formulation resulted in excellent biosafety and stability in an outdoor environment	
6	Copper-doped ZIF-8 (Cu@ZIF-8)	Fludioxonil	23.9%	- Flu@Cu@ZIF-8 exhibited pH-responsive release	
				- Aquatic toxicity of fludioxonil was reduced by up to 68%	
7	ZIF -8	Dinotefuran (DNF)	-	- Sustained DNF delivery was achieved over a period of month in soil	
				- The stability of DNF in UV was about 10 times more	
				- Also the insecticidal efficiency was increased	
8	ZIF-8	Clothianidin	9.8%	- Acidic pH-based 'burst release effect' was observed	
				–43% pest control efficacy against *Nilaparvata lugens* after 10 days of application	

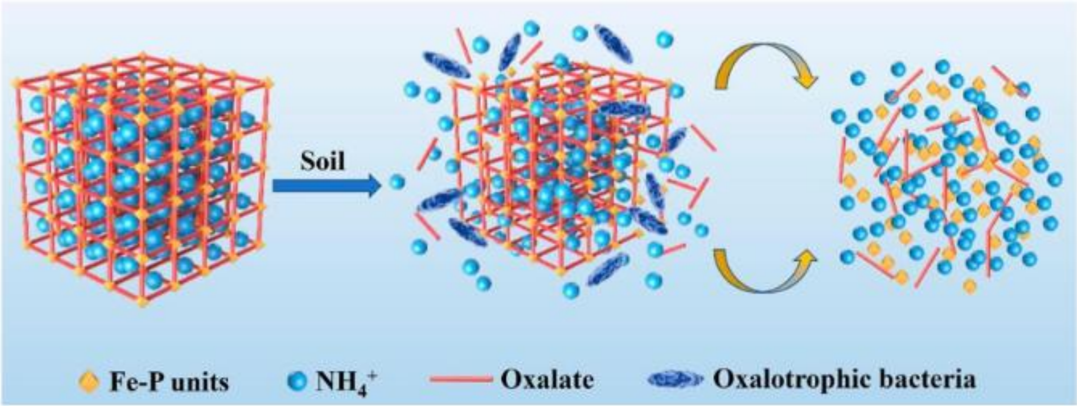
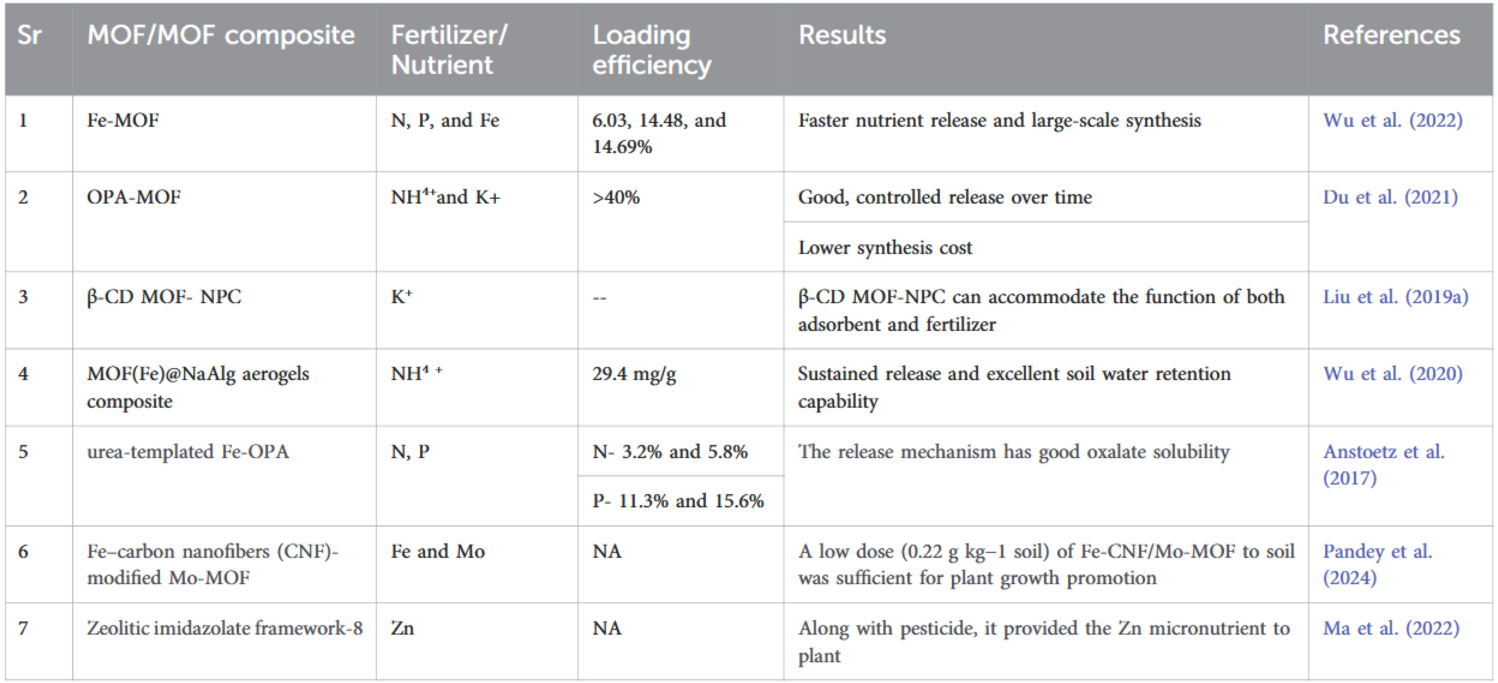


TABLE 2 List of MOF-based materials associated with the slow release of nutrients in agriculture.



Sr	MOF/MOF composite	Fertilizer/ Nutrient	Loading efficiency	Results	References
1	Fe-MOF	N, P, and Fe	6.03, 14.48, and 14.69%	Faster nutrient release and large-scale synthesis	Wu et al. (2022)
2	OPA-MOF	$NH^{4+}$and K+	>40%	Good, controlled release over time	Du et al. (2021)
				Lower synthesis cost	
3	β-CD MOF- NPC	K^+	--	β-CD MOF-NPC can accommodate the function of both adsorbent and fertilizer	Liu et al. (2019a)
4	MOF(Fe)@NaAlg aerogels composite	$NH^{4\ +}$	29.4 mg/g	Sustained release and excellent soil water retention capability	Wu et al. (2020)
5	urea-templated Fe-OPA	N, P	N- 3.2% and 5.8%	The release mechanism has good oxalate solubility	Anstoetz et al. (2017)
			P- 11.3% and 15.6%		
6	Fe–carbon nanofibers (CNF)-modified Mo-MOF	Fe and Mo	NA	A low dose (0.22 g kg−1 soil) of Fe-CNF/Mo-MOF to soil was sufficient for plant growth promotion	Pandey et al. (2024)
7	Zeolitic imidazolate framework-8	Zn	NA	Along with pesticide, it provided the Zn micronutrient to plant	Ma et al. (2022)

Metal Organic Frameworks

Controlled release of fertilizers and nutritions

Stimuli-responsive controlled release