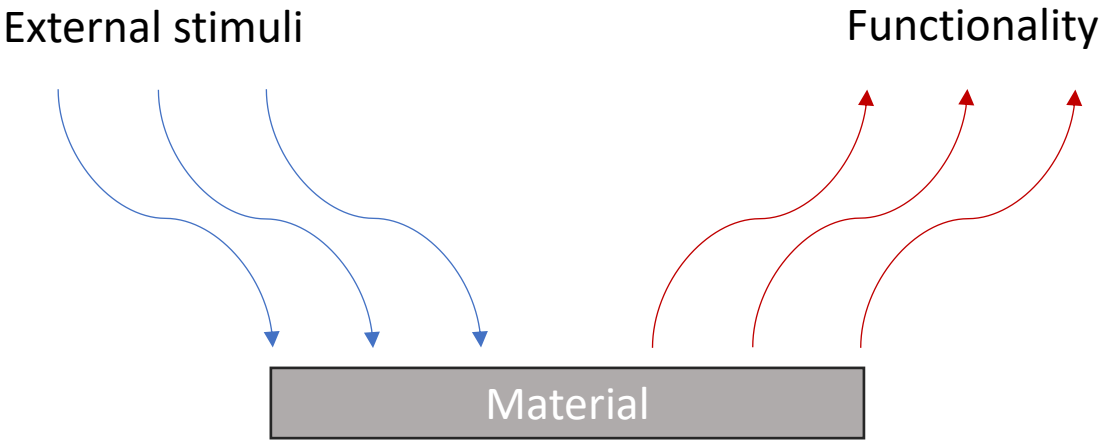
Responsive Functional Materials

Assist.-Prof. Dr. Heidi A. Schwartz

Photoactive Hybrid Materials

Universität Innsbruck



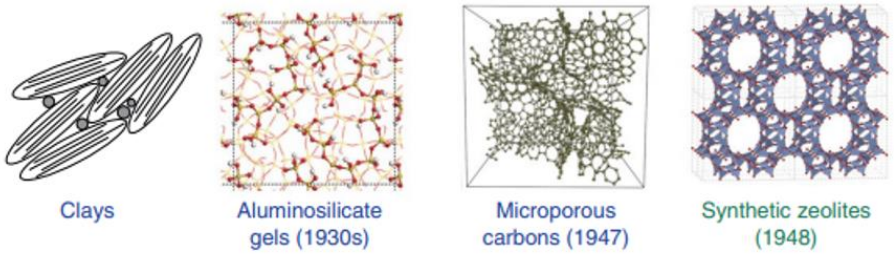
https://www.uibk.ac.at/en/aatc/ag-schwartz/

heidi.schwartz@uibk.ac.at

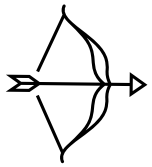
L01.063

Outline for today´s lecture

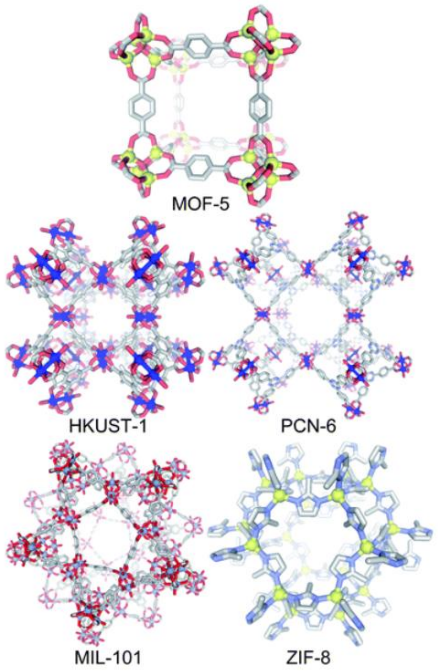
1. Short conclusion of last lecture



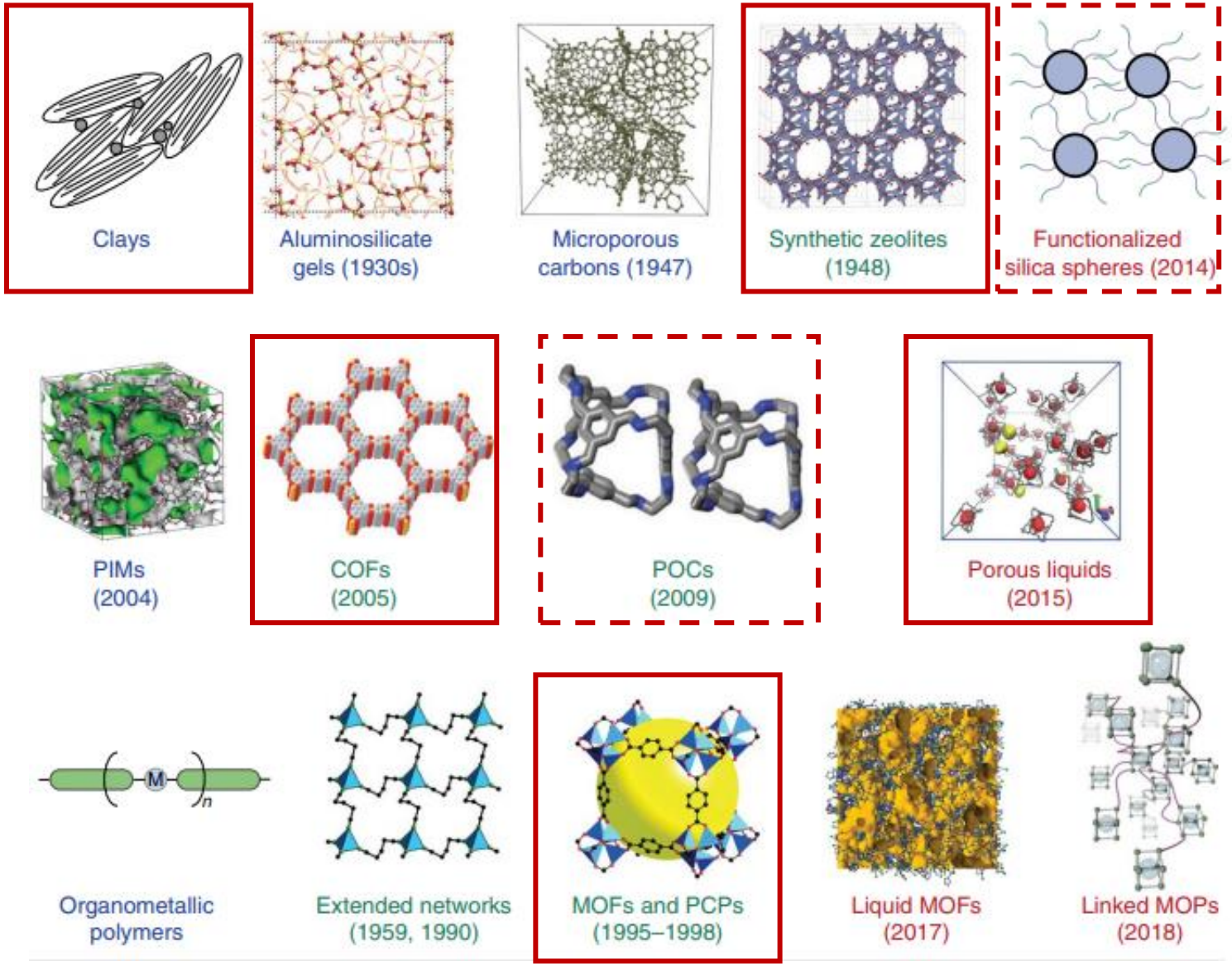
2. Learning objectives



- Porous liquids, MOFs – History, Properties, Synthesis



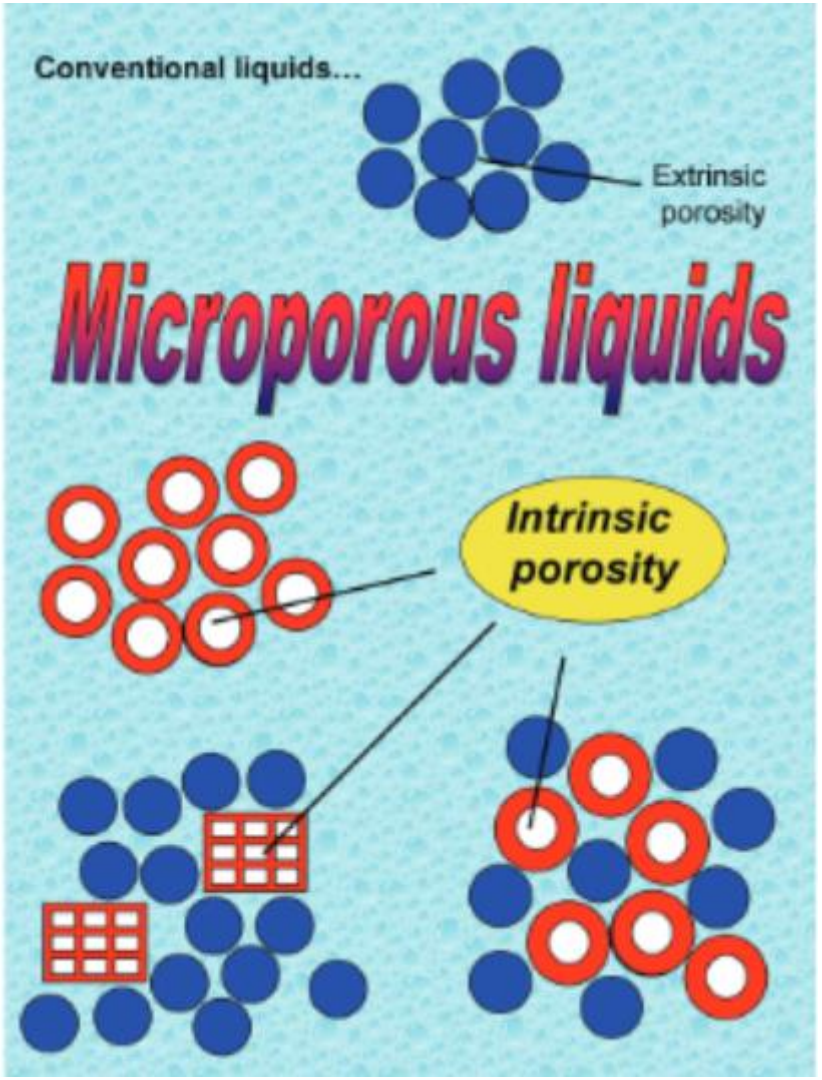
- Next time: Responsive Materials



Porous materials

Porous liquids - Characteristics

Concept firstly described by Stuart and co-workers in 2007:
“In contrast to the small, transient cavities that exist between the molecules of any liquid (here called “extrinsic” porosity), we suggest that a truly microporous liquid could exist if it had empty pores *within* the molecules of the liquid (“intrinsic” porosity).”



Porous Liquids - O'Reilly - 2007 - Chemistry – A European Journal - Wiley Online Library (8th March, 2025)
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White Board

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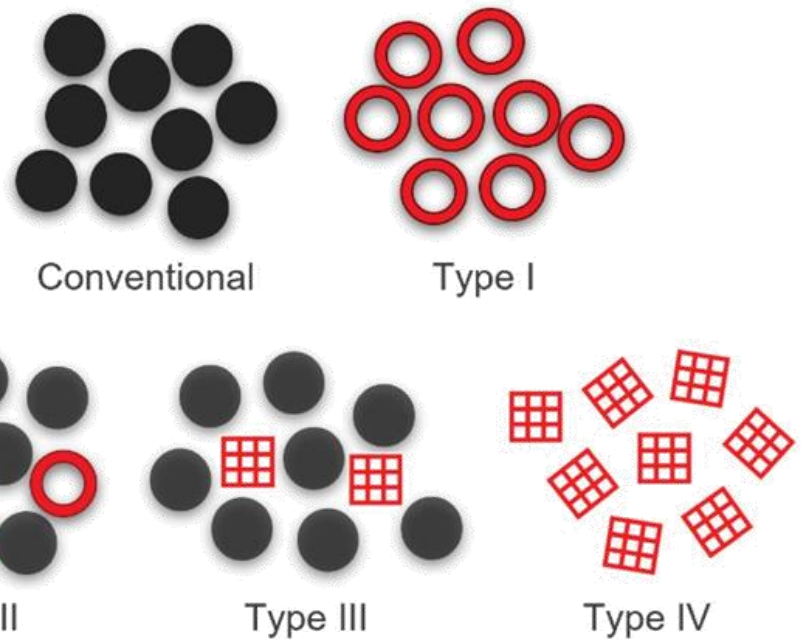

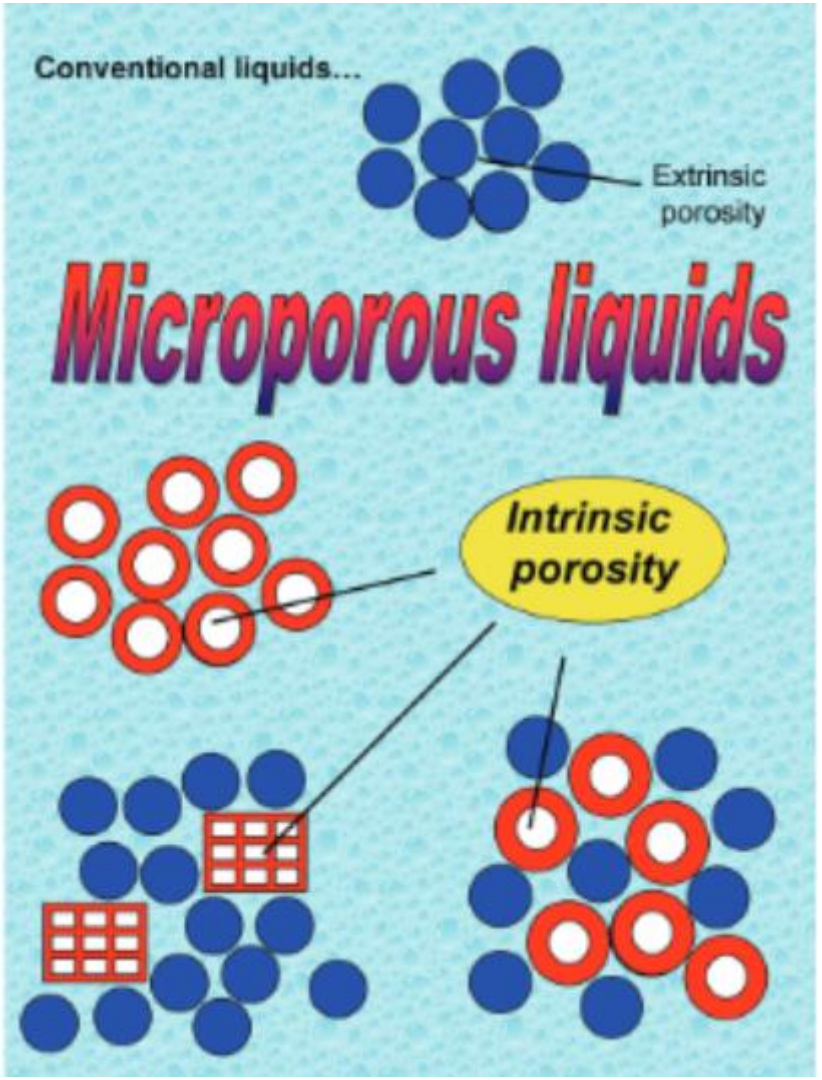

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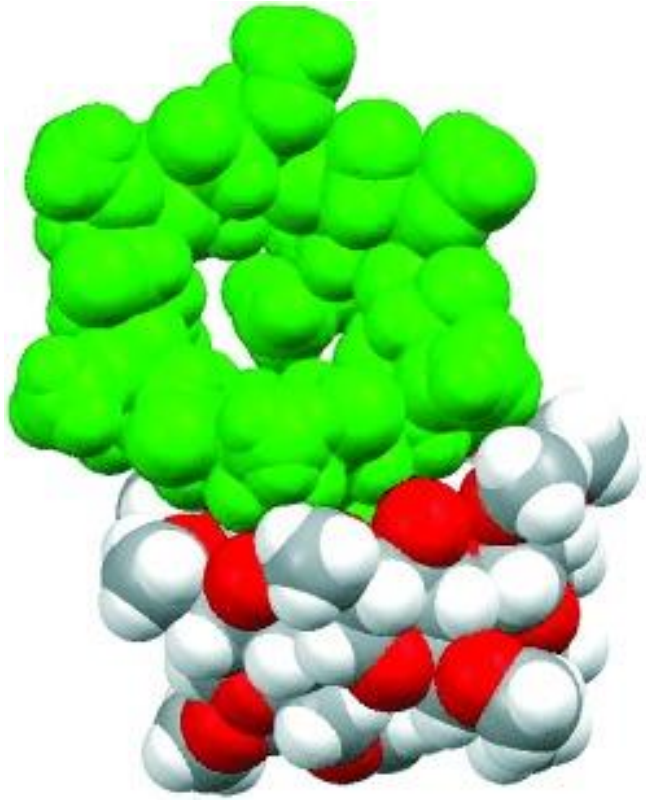
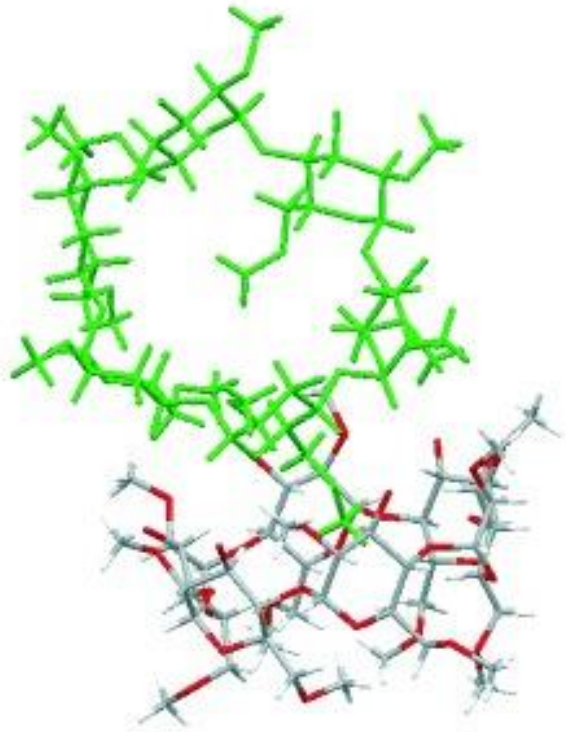
Porous liquids – Type I

Porous liquids: Relatively new class of materials, which exhibits accessible and permanent porosity of a porous solid, and simultaneously fluid properties like a liquid.





Structure of permethyl *β*-cyclodextrin (CD)

In the crystalline state in the absence of included guests, the cavities of permethyl-*β*-CD are largely filled in both an inter- and intramolecular fashion, with an OCH_3 substituent of one CD (green) occupying the cavity of another, and a twisted conformation of one sugar residue. It suggests that cavities may effectively be filled in the pure liquid state.

A POC – porous organic cage!

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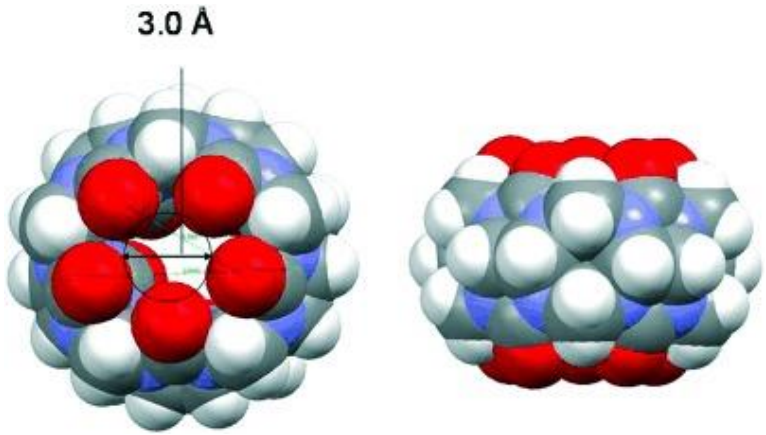
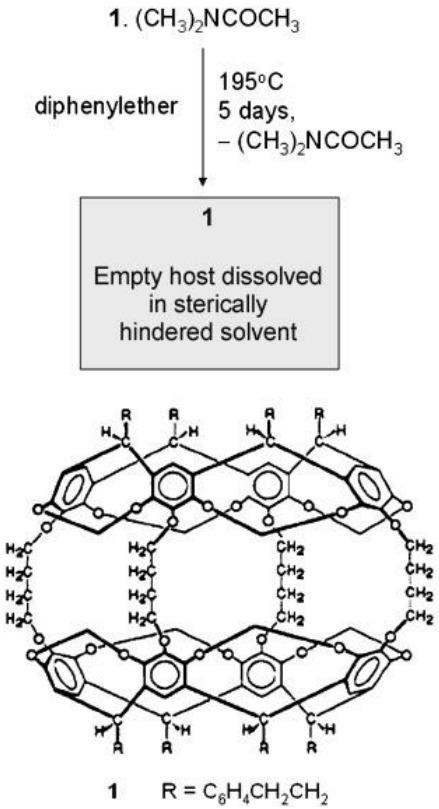
Porous liquids – Type II

Porous liquids: Relatively new class of materials, which exhibits accessible and permanent porosity of a porous solid, and simultaneously fluid properties like a liquid.





Structures of the cucurbituril CB adapted from the single-crystal structure of the trihydrate with water molecules removed to give an impression of the empty host, and dimensions of the portal indicated.

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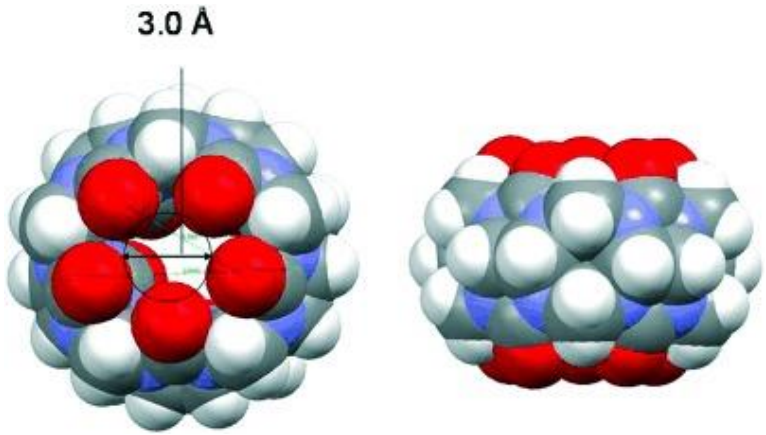
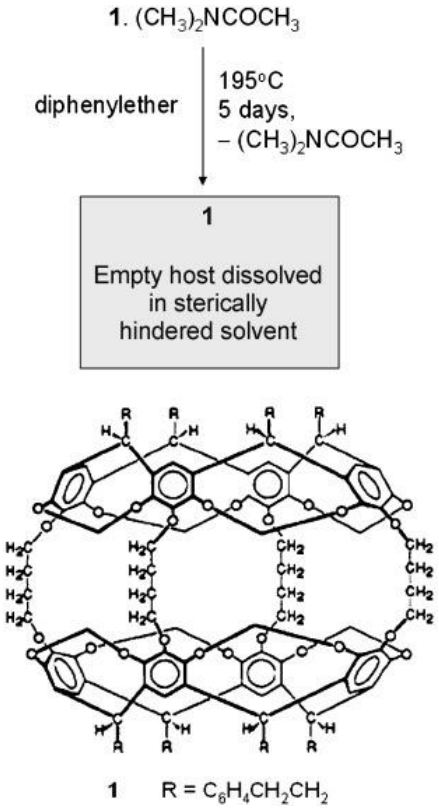
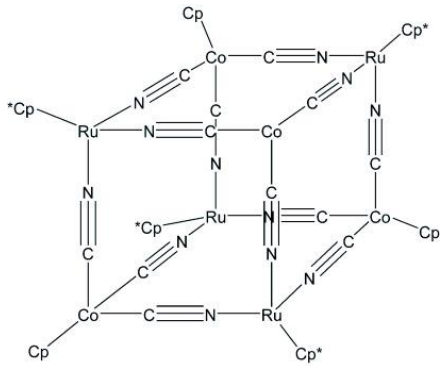
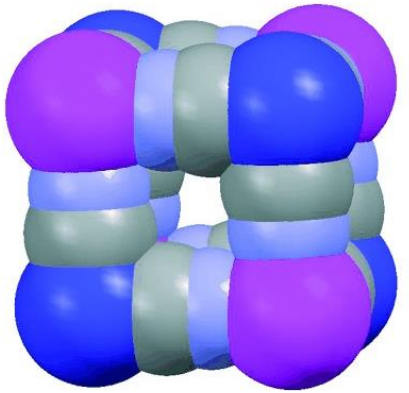




Structures of the cucurbituril CB adapted from the single-crystal structure of the trihydrate with water molecules removed to give an impression of the empty host, and dimensions of the portal indicated.

Empty cyano-bridged metallocubes that are rigid, have small access windows, have internal cavities which are capable of including guests or being empty, and which are soluble in a range of solvents.





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Porous liquids – Type III

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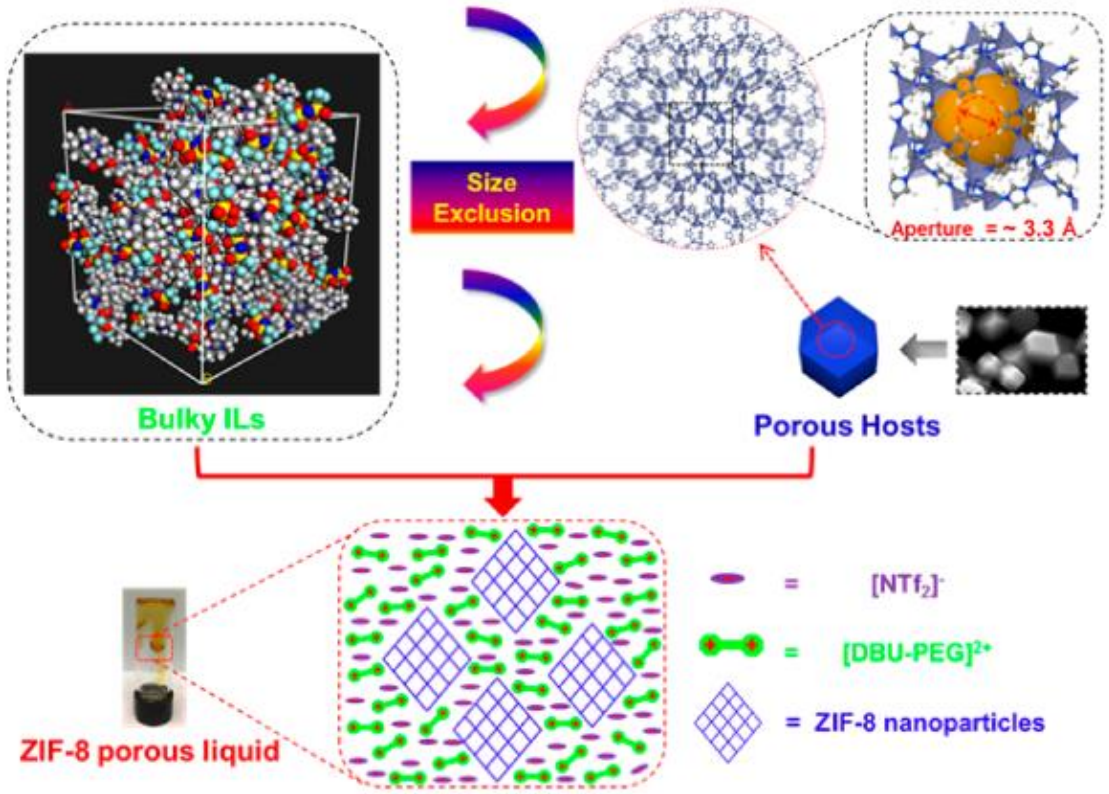
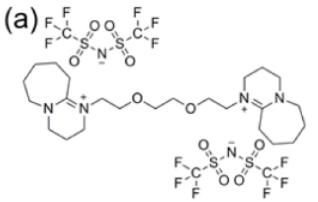


Strategy

Type 3 porous liquids based on rational coupling of microporous framework nanoparticles as porous hosts with a bulky ionic liquid as the fluid media:

ZIF-8 and ZSM-5 as porous material

[DBU-PEG] [NTf_2] as ionic liquid and liquid medium

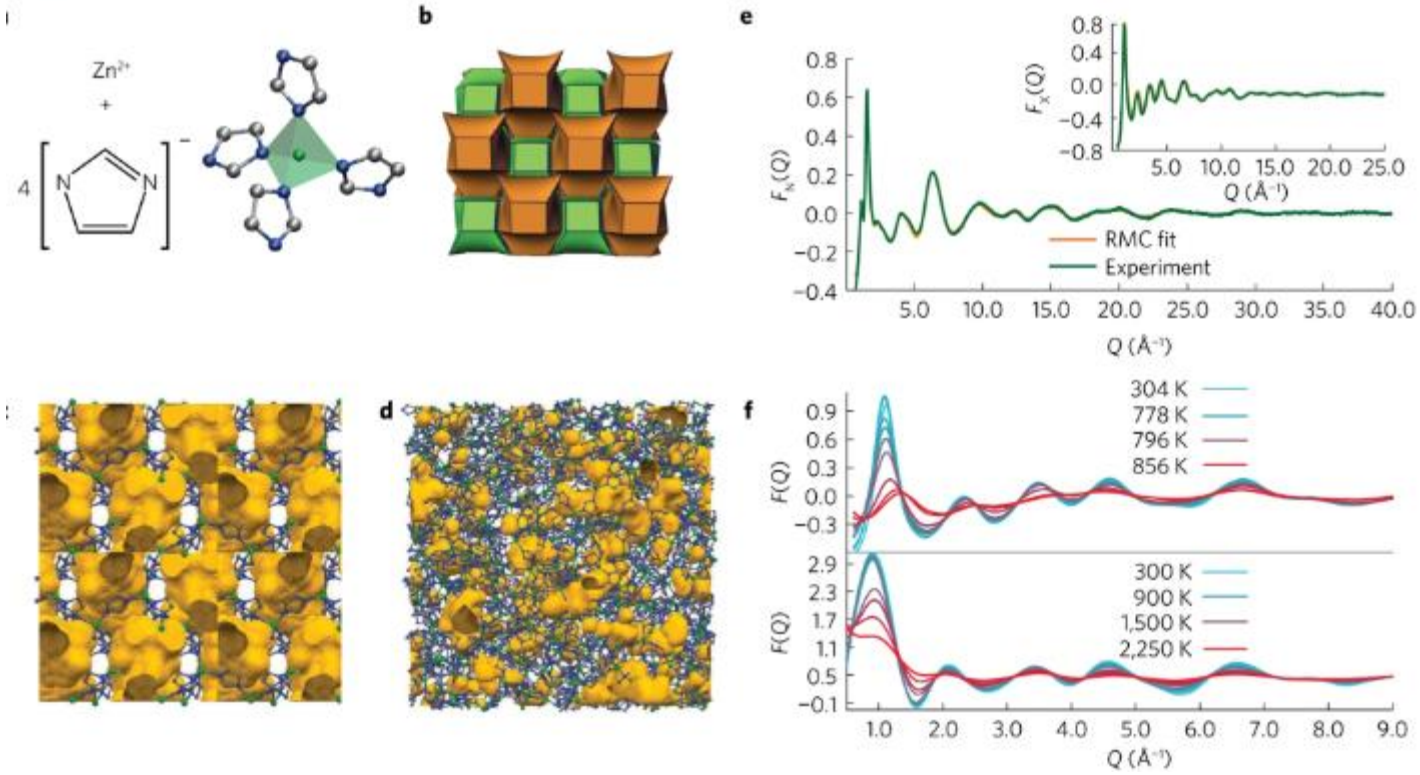


New Class of Type III Porous Liquids: A Promising Platform for Rational Adjustment of Gas Sorption Behavior | ACS Applied Materials & Interfaces (8th March, 2025)

Porous liquids – the future is looking emptier - Chemical Science (RSC Publishing) (7th March, 2025)

Porous liquids – Type IV

In 2017, Coudert, Bennett and co-workers reported the structure of a liquid MOF, ZIF-4, which melted at 865 K, with computational modelling indicating that some of the porosity of the parent framework structure was maintained on melting to form a liquid

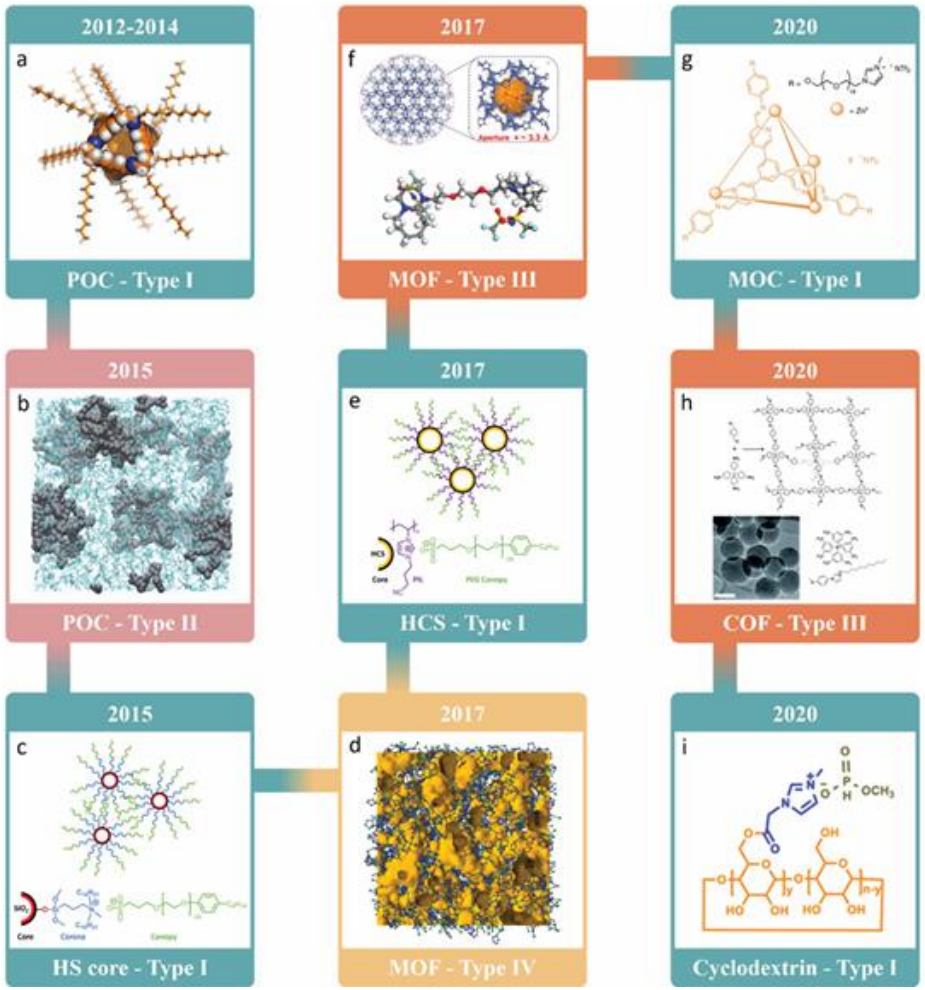


The authors:

"we introduce the general term 'MOF liquid', for a liquid formed from the melting of a MOF, due to the retention of chemical configuration and coordinative bonding modes between the solid and liquid phases. Importantly, we show the retention of porosity in the liquid state, with a pore volume larger than in the glass state, making liquid ZIF-4 a rare example of an intrinsically porous liquid, enabling a compromise between the selectivity of crystalline MOFs and diffusivity of amorphous membranes."

Liquid metal–organic frameworks | Nature Materials (8th March, 2025)
Porous liquids – the future is looking emptier - Chemical Science (RSC Publishing) (7th March, 2025)

Porous liquids – Historical overview



POC – Porous Organic Cage

HS – Hollow Silica (spheres)

MOF – Metal Organic Framework

HCS – Hollow Carbon Spheres

MOC – Metal-Organic Cage

COF – Covalent Organic Framework

Note: IL widely used as liquid medium especially for type II

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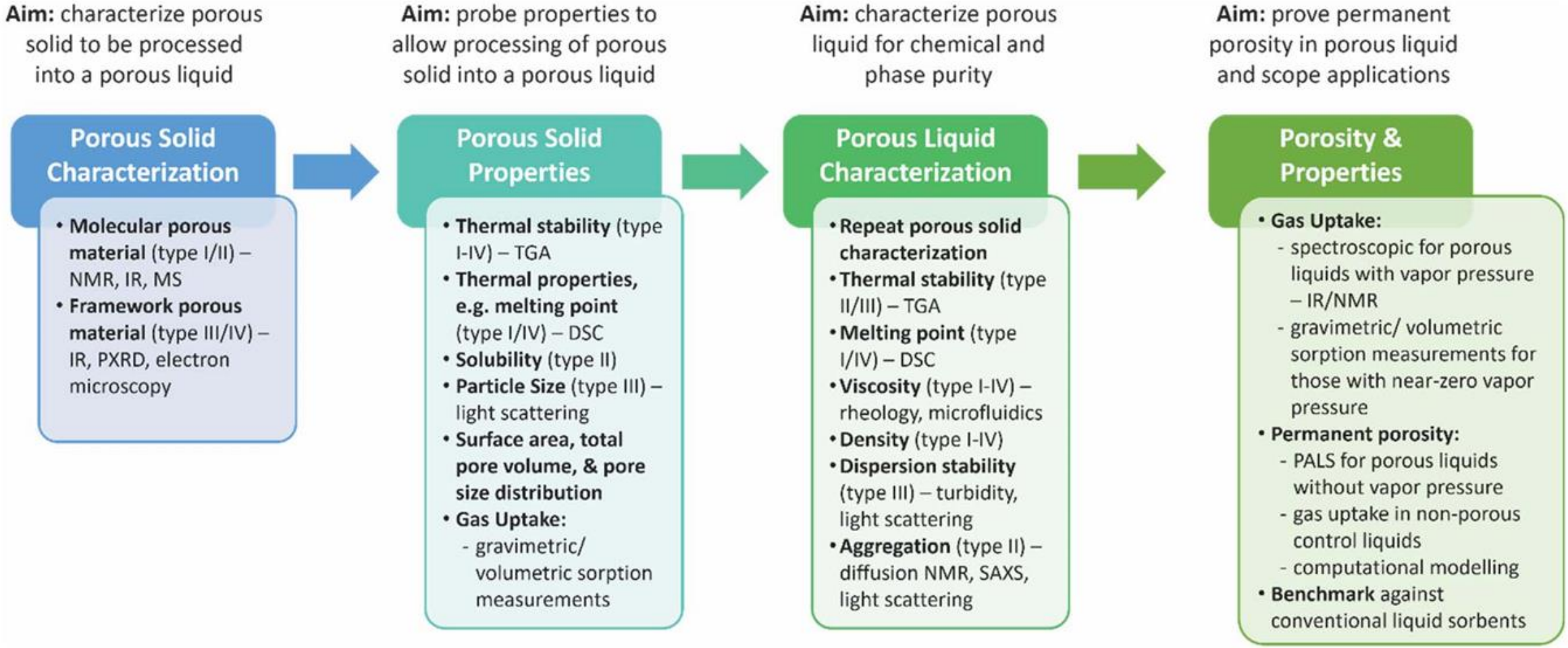
Characterization of porous liquids



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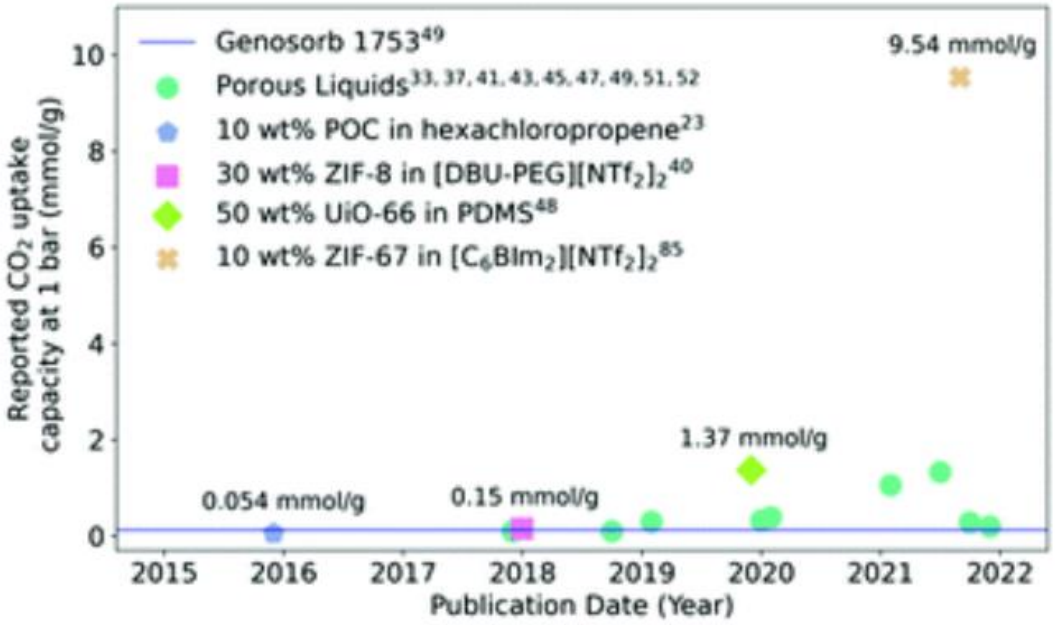
Applications of porous liquids

Gas uptake and selective gas separation

e.g., based on the potential for porous liquids to be an alternative liquid absorbent for carbon capture, the uptake of CO_2 has been reported for a large number of these systems



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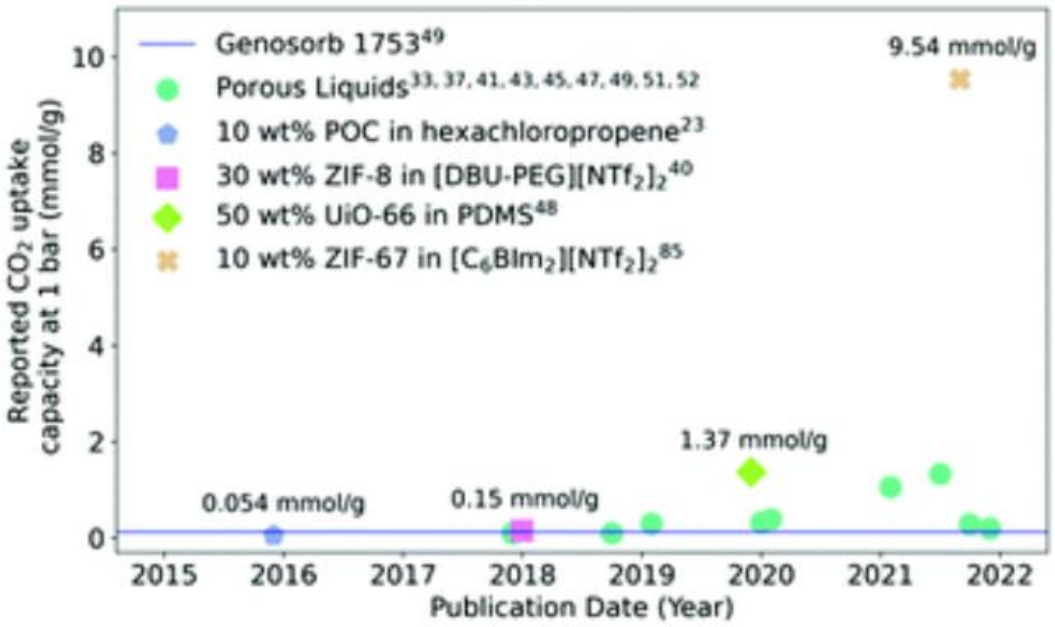

Carbon Capture & Sequestration/Utilization

- adaptation of HS nanorod porous liquids can be combined with carbonic anhydrase, a metalloenzyme effective for converting CO_2 to $CaCO_3$, as a material for CCS
- enhancing CCU through use of PL: addition of ZIF-8 to a catalytic IL not only increased the CO_2 uptake, but also its catalysis with epoxides to form cyclic carbonates, as well as increasing the overall yield

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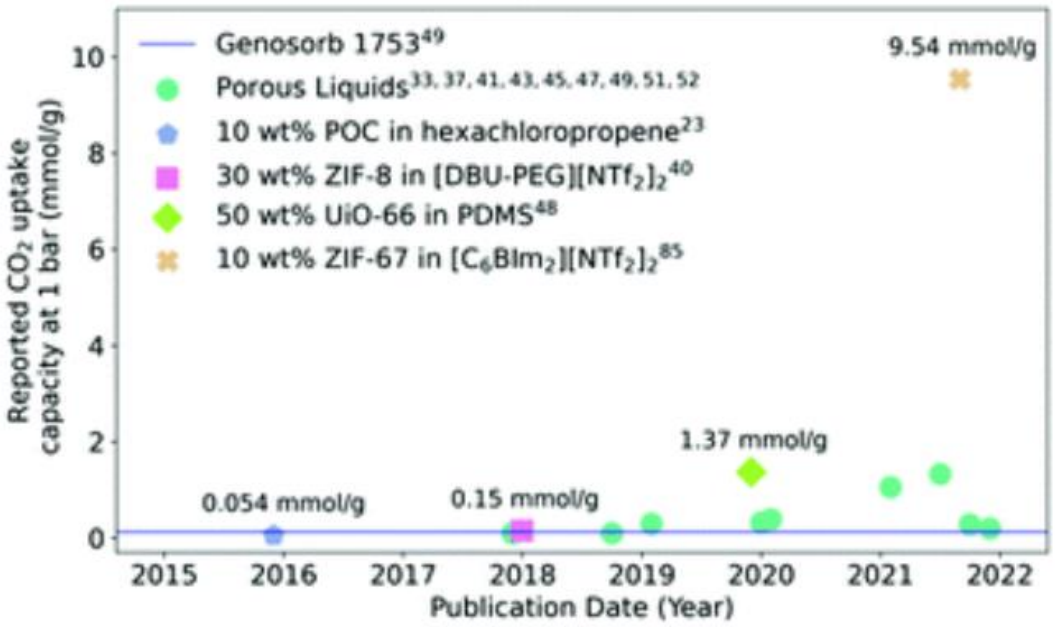

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Molecular separation of non-gaseous molecules

Absorption of volatile organic compounds

Introduction of catalytic compounds

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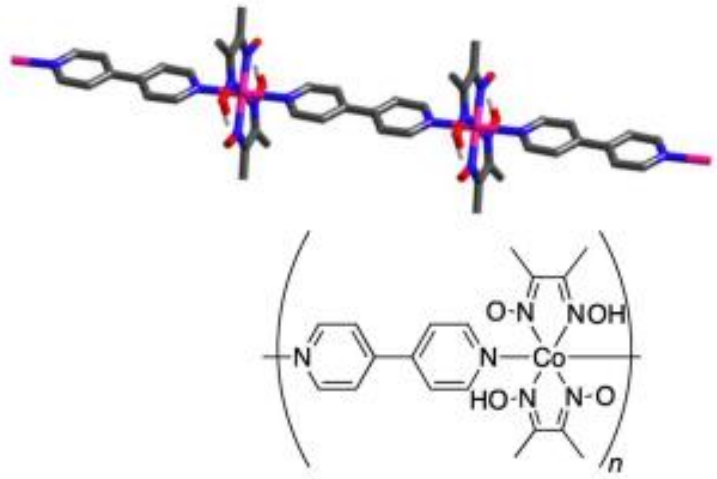
Combining organic and inorganic parts

IUPAC definition **Coordination polymer**:

A coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions.



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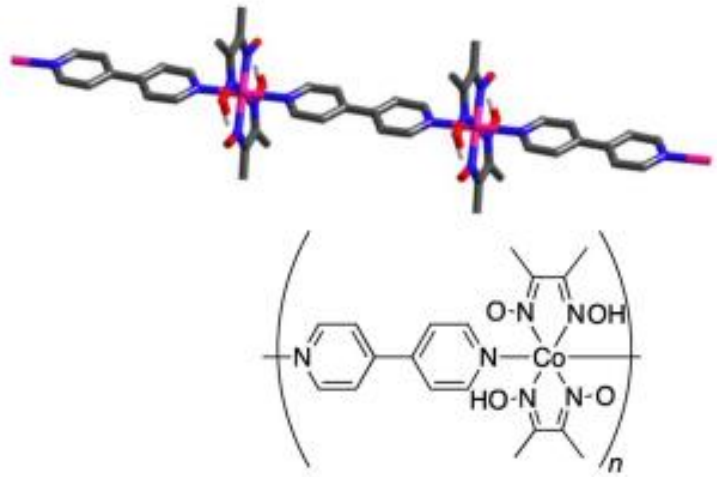
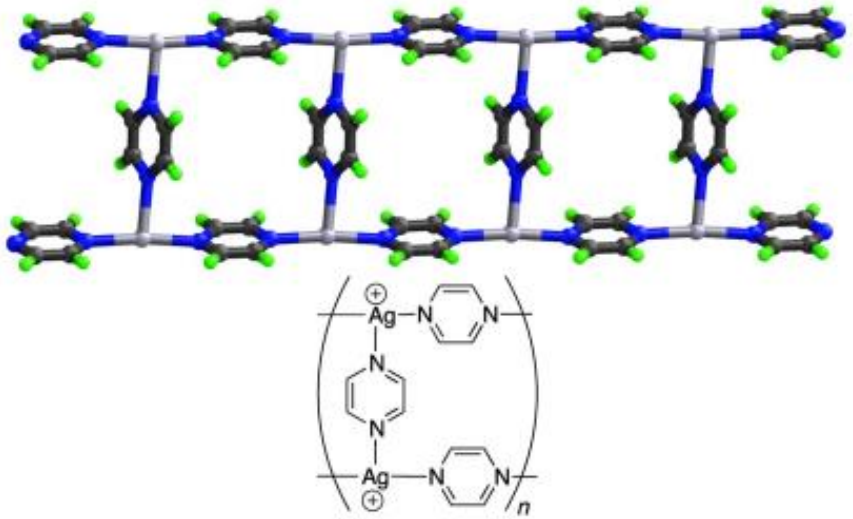


IUPAC definition **Coordination network**:

A coordination compound extending, through repeating coordination entities, in 1 dimension, but with cross-links between two or more individual chains, loops, or spiro-links, or a coordination compound extending through repeating coordination entities in 2 or 3 dimensions.



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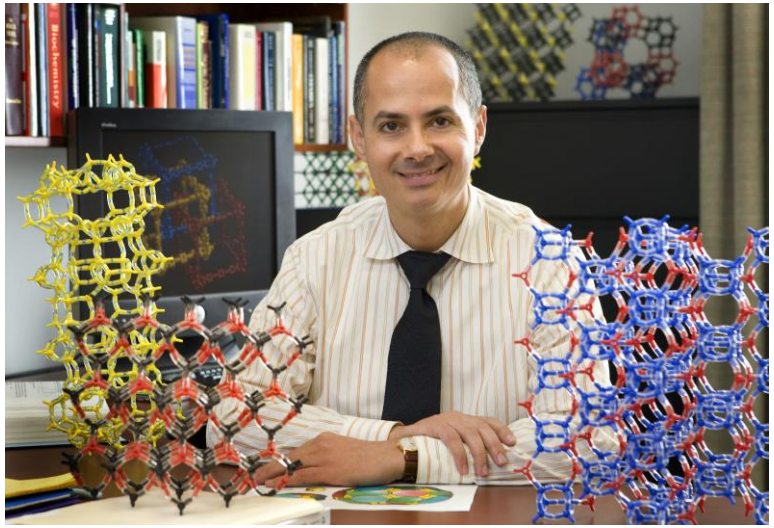
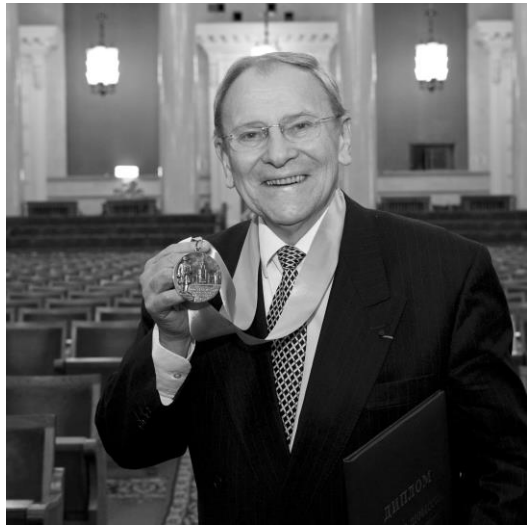
The fathers of MOF chemistry



O. M. Yaghi, breakthrough publication 1999 with MOF-5.



G. Ferey, construction of MIL-MOFs.

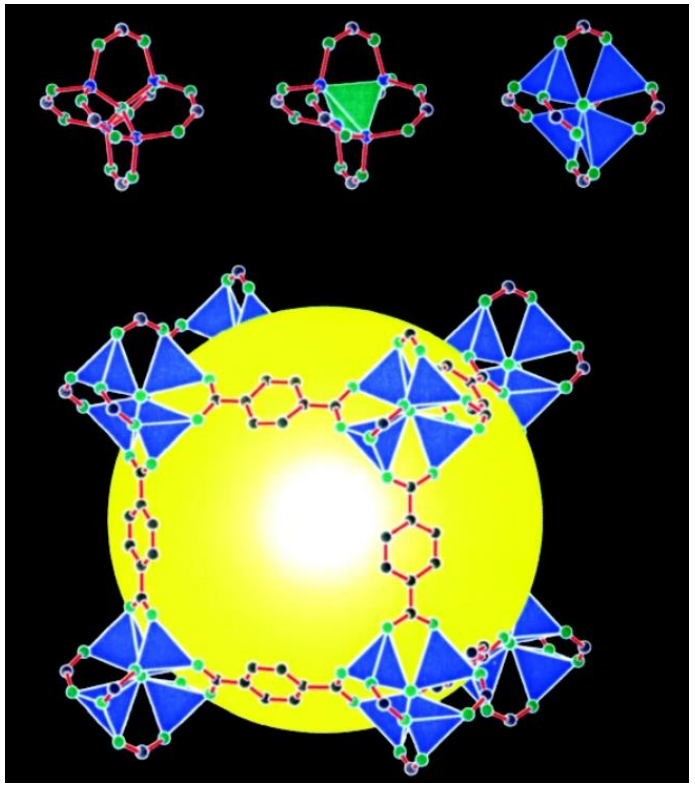
S. Kitagawa, introduction of functionality

Significantly shaped the research field of MOFs and their continuous evolving regarding applications and functionality.

MOF-5 – the beginning of emptiness

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

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



Tetranuclear supertetrahedral cluster motif
Sphere diameter: 18.5 Å

Design and synthesis of an exceptionally stable and highly porous metal-organic framework | Nature
(14th March, 2025)

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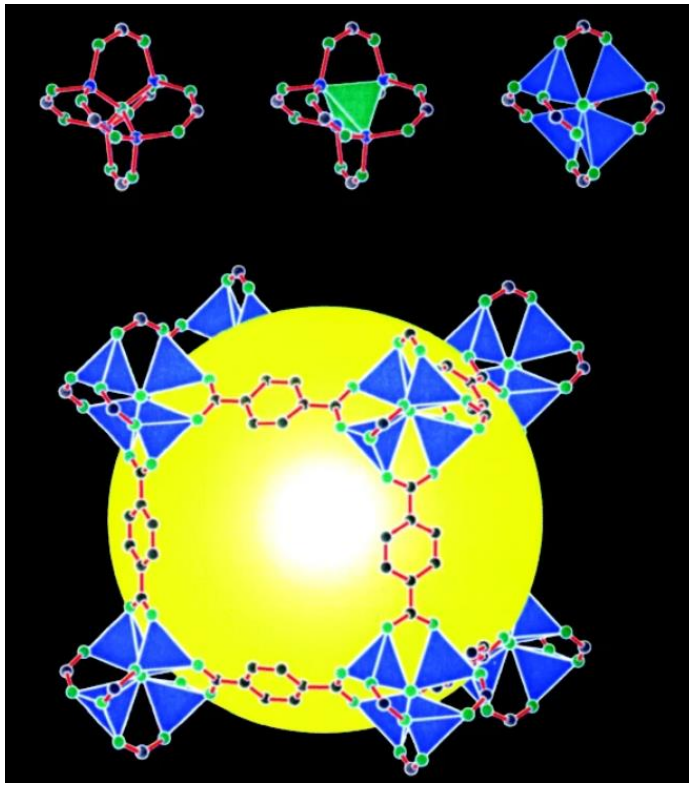

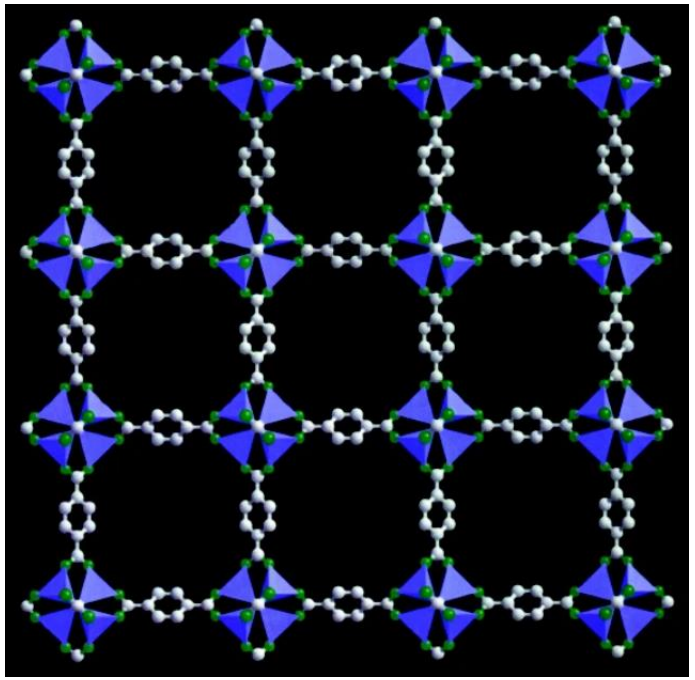

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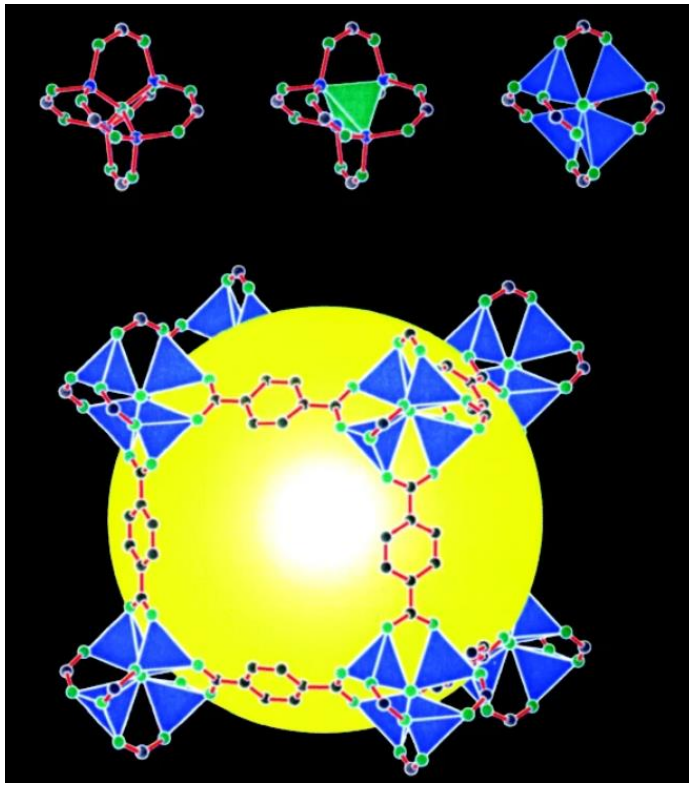
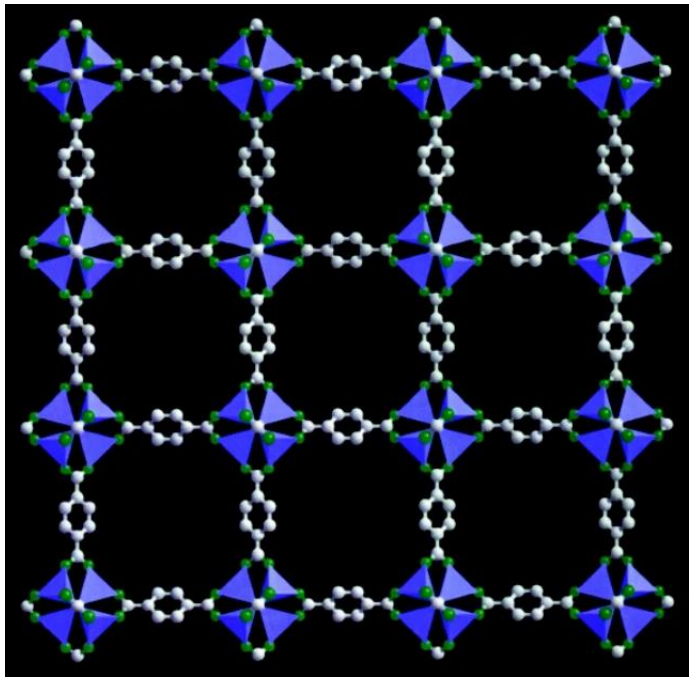
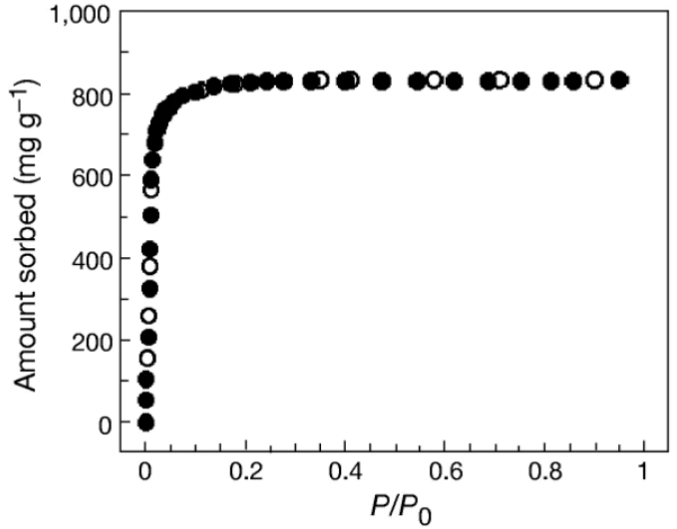




Tetranuclear supertetrahedral cluster motif
Sphere diameter: 18.5 Å

- framework atoms only take small fraction of available space in crystal: free volume!
- 55-61% available for guest molecules
- BET measurements: surface area was estimated at 2900 m^2/g

Figure 3: Nitrogen gas sorption isotherm at 78?K for MOF-5 (filled circles, sorption; open circles desorption).



P/P_0 is the ratio of gas pressure (P) to saturation pressure (P_0), with P_0 = 746?torr.

[Design and synthesis of an exceptionally stable and highly porous metal-organic framework | Nature](#)
(14th March, 2025)

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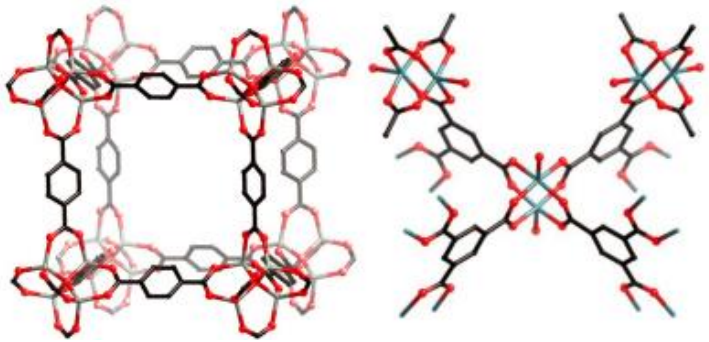
Combining organic and inorganic parts - MOFs

IUPAC definition **Metal-Organic Framework**:

A metal-organic framework, abbreviated to MOF, is a coordination network with organic ligands containing potential voids.



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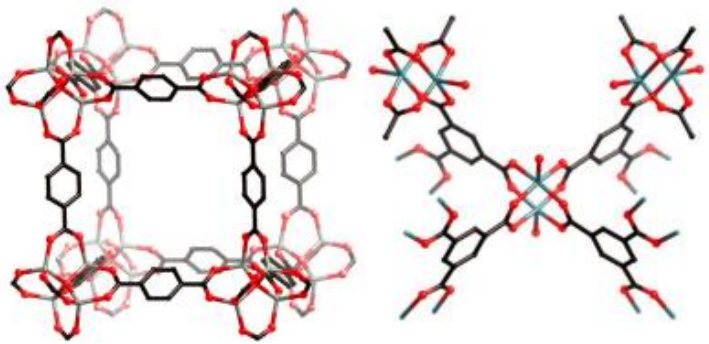

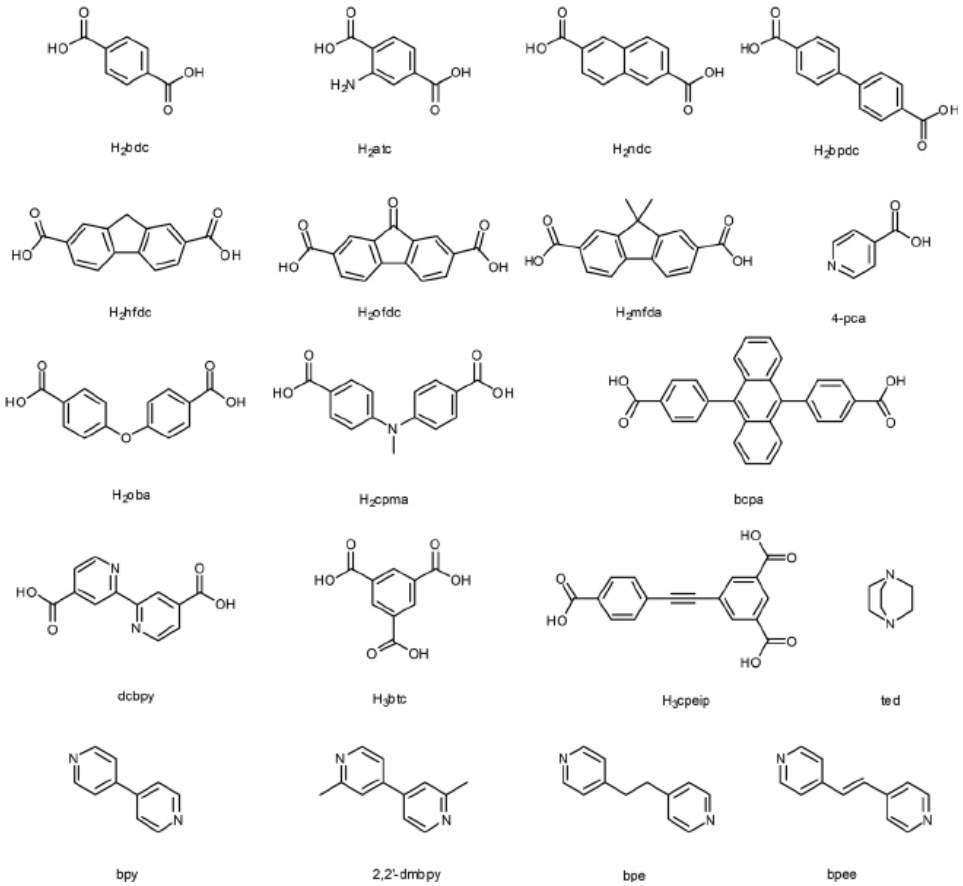

Infinite list of organic linker molecules.

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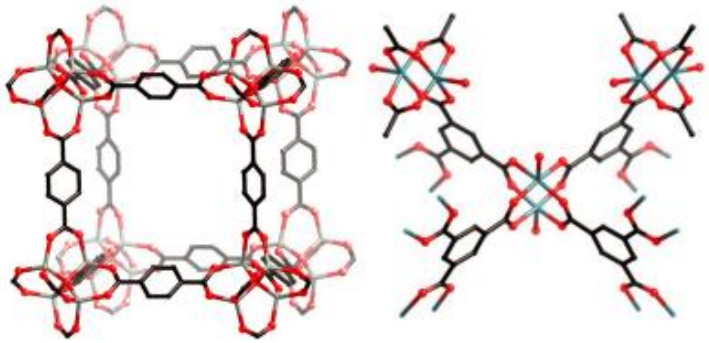
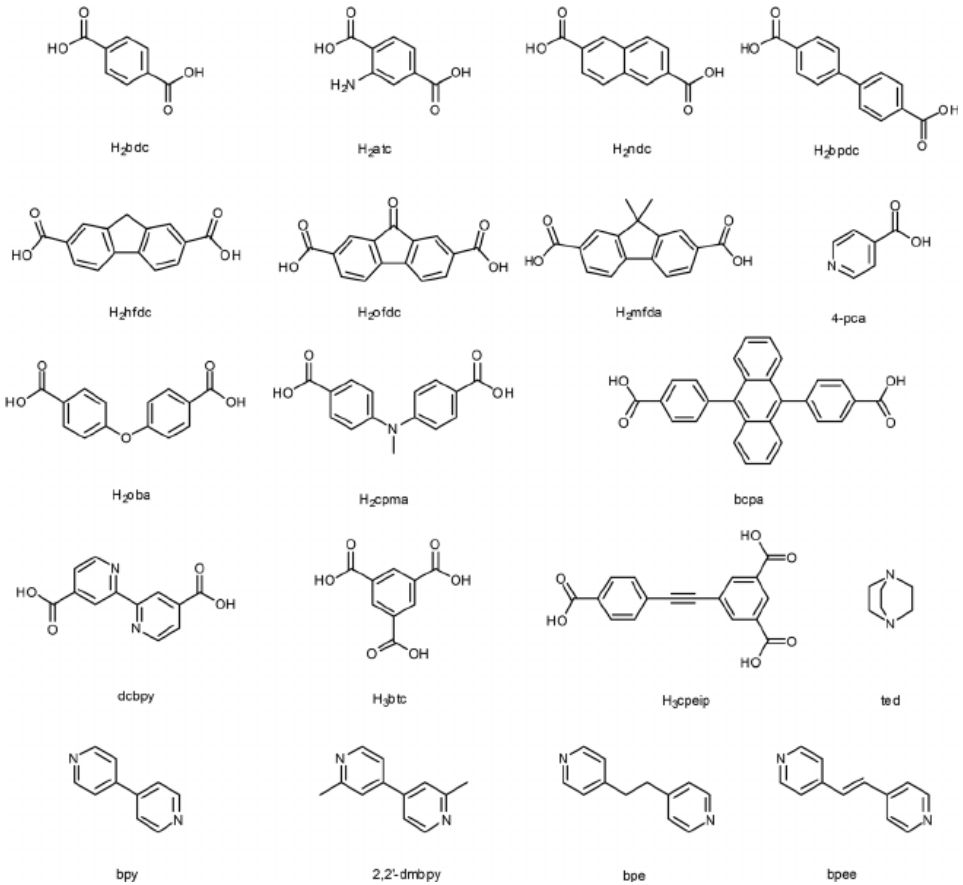


Inorganic node *e.g.*, metals, metal-ions, metal-oxo-clusters.



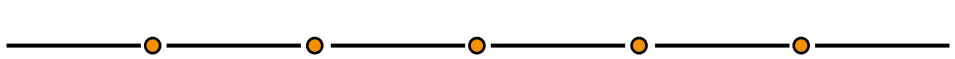
Infinite list of organic linker molecules.

In simple terms: combination of metal-salt and any at least bifunctional organic molecule gives a MOF!

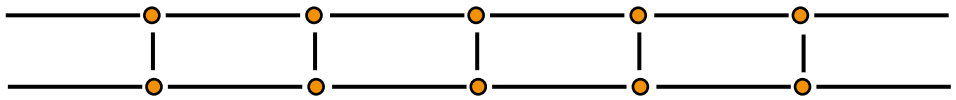
S. R. Batten et al., *J. Pure Appl. Chem* **2013**, *85* (8), 1715–1724.
D. Banerjee et al., *Dalton Trans.* **2014**, *43*, 10668-10685.

Systematic structure assembly

1 D



Linear chain



Ladder

Metal ions: nodes

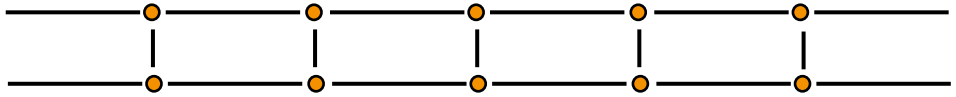
Multifunctional ligands: connectors

B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101* (6), 1629–1658.

Systematic structure assembly

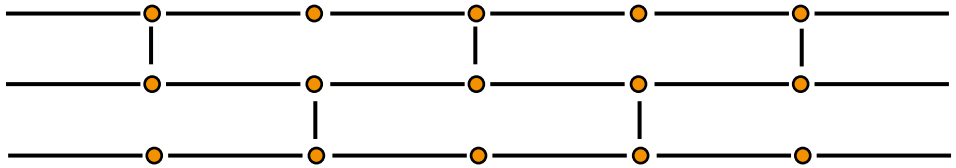
1 D

Linear chain

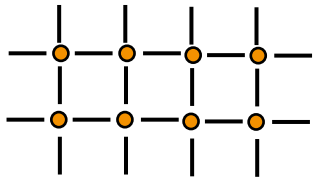


Ladder

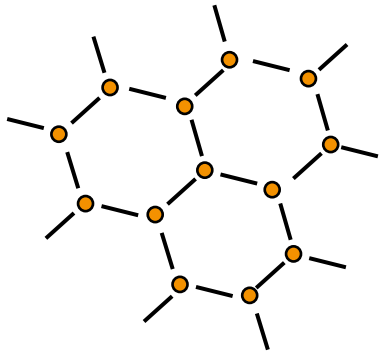
2D



Brick



Square Grid



Honeycomb

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Multifunctional ligands: connectors

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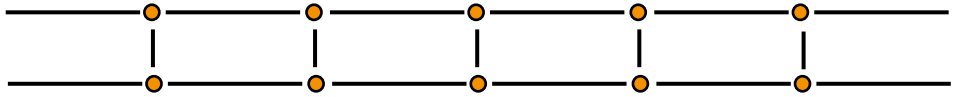
Systematic structure assembly

1 D

Linear chain



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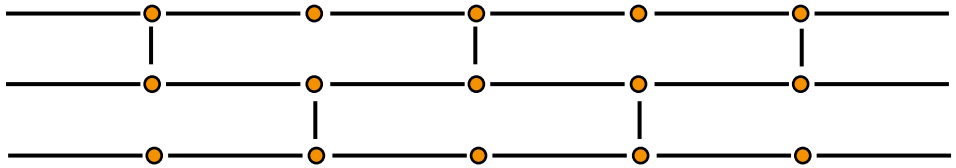

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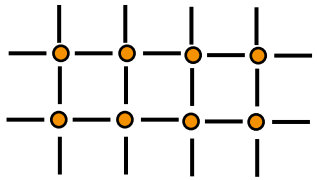

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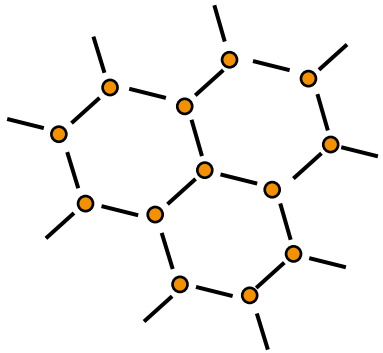
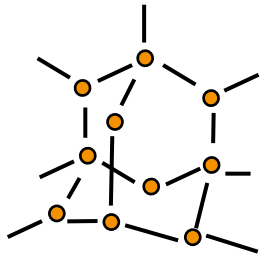
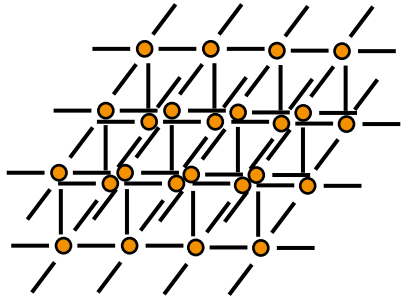


Honeycomb

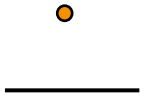
3D



Diamondoid



Octahedral



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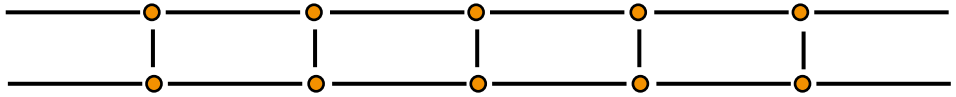
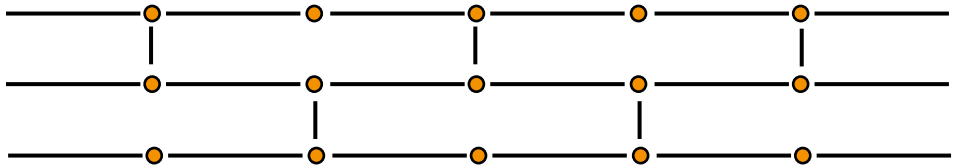
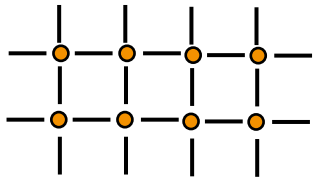


Ladder

2D



Brick



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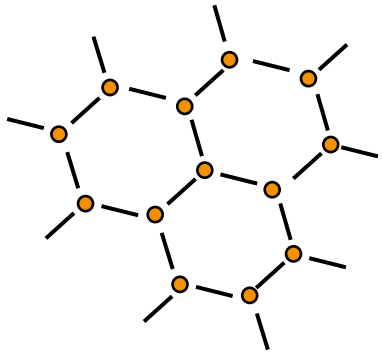
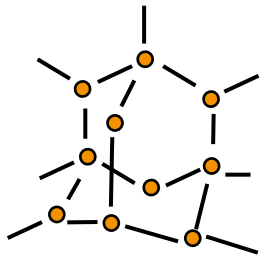


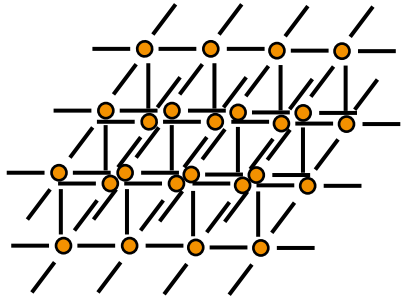
Honeycomb

Crystal engineering.

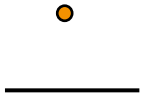
3D



Diamondoid



Octahedral



Metal ions: nodes

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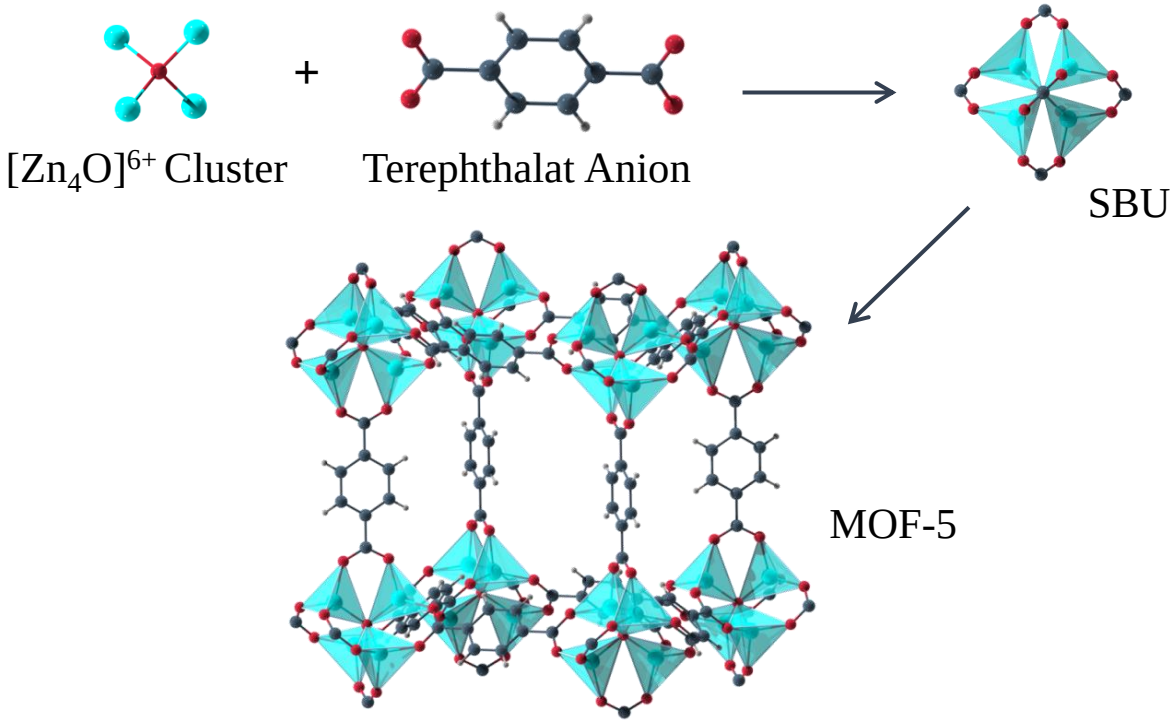
Construction of a MOF - General

Metal-node and shape of linker molecule direct the structure of the SBU and of the MOF scaffold.



O. M. Yaghi et al., *Nature* **2003**, *423*, 705-714.
H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276.

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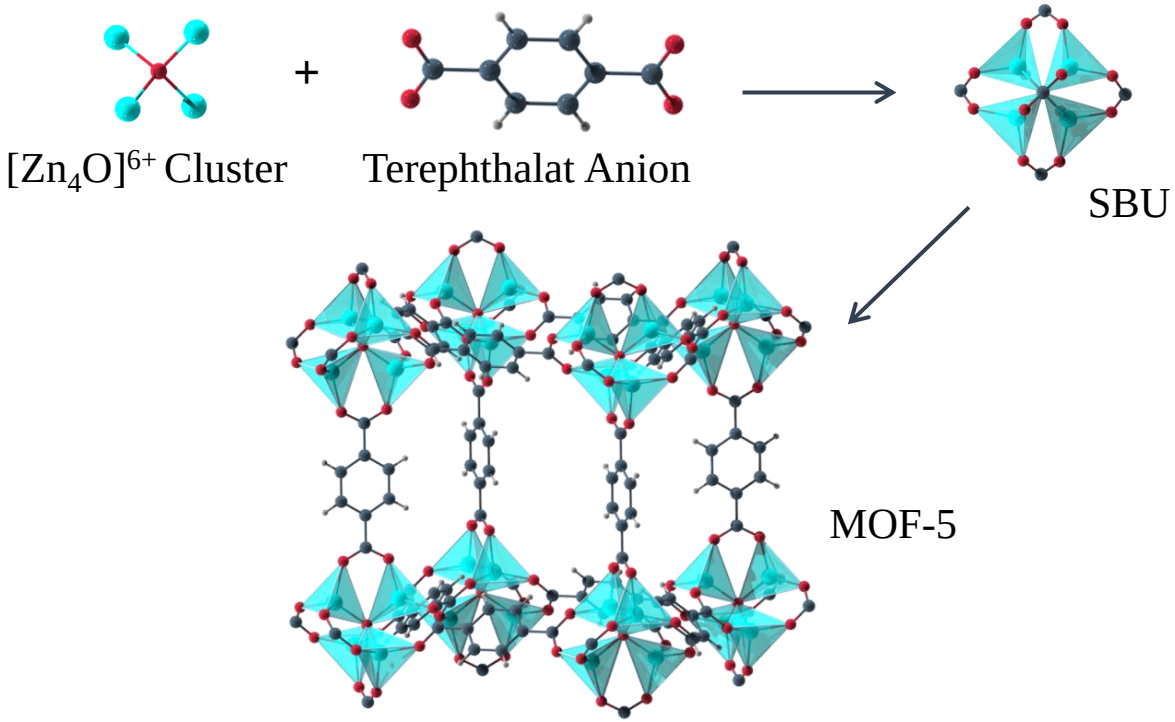

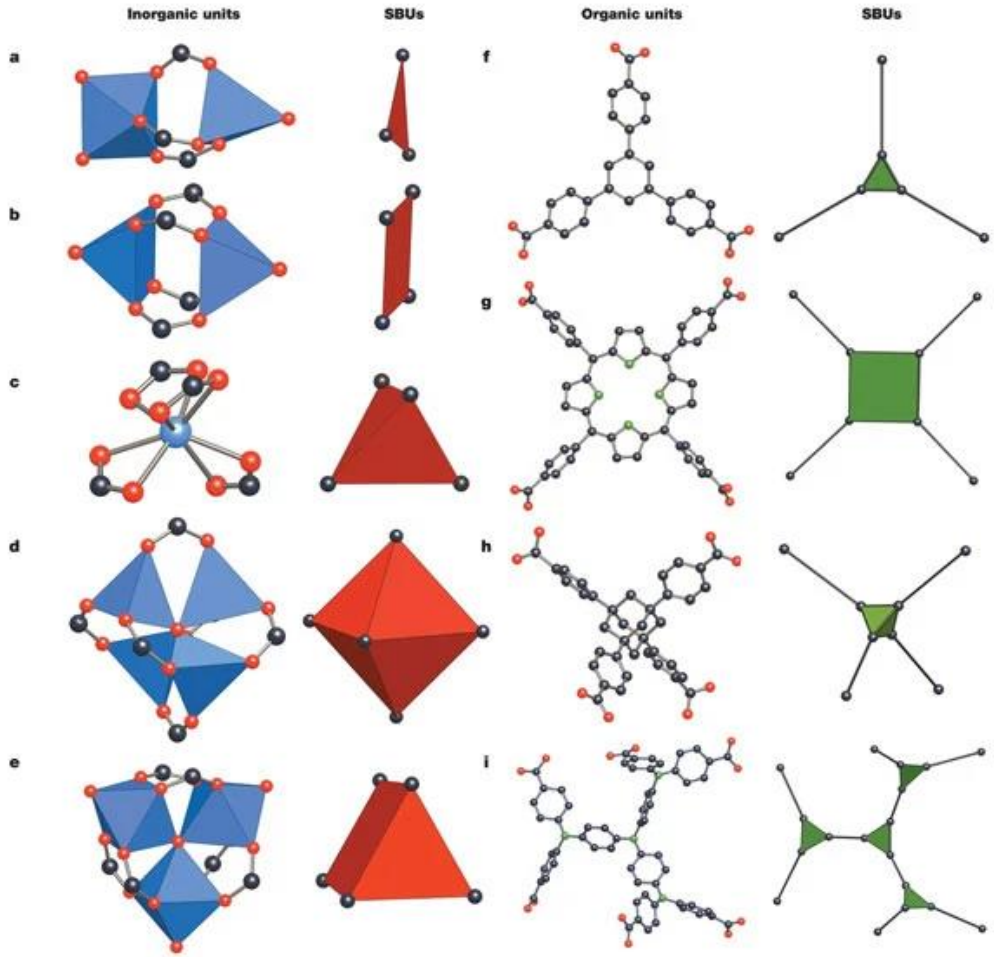

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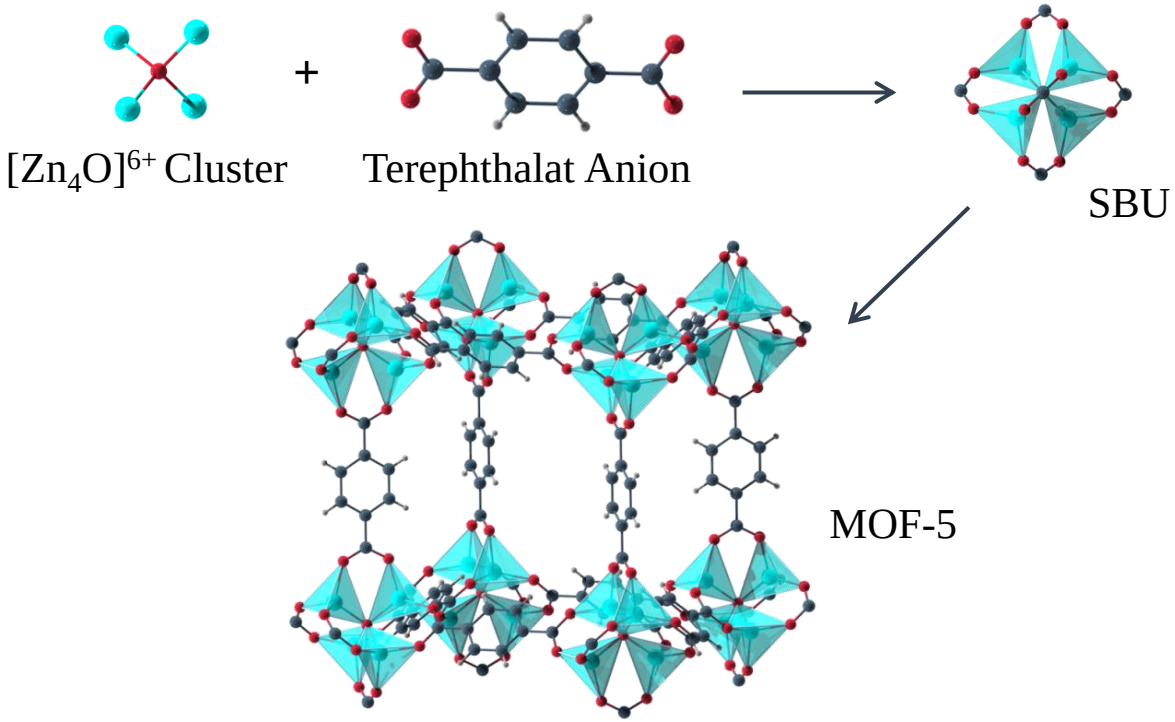

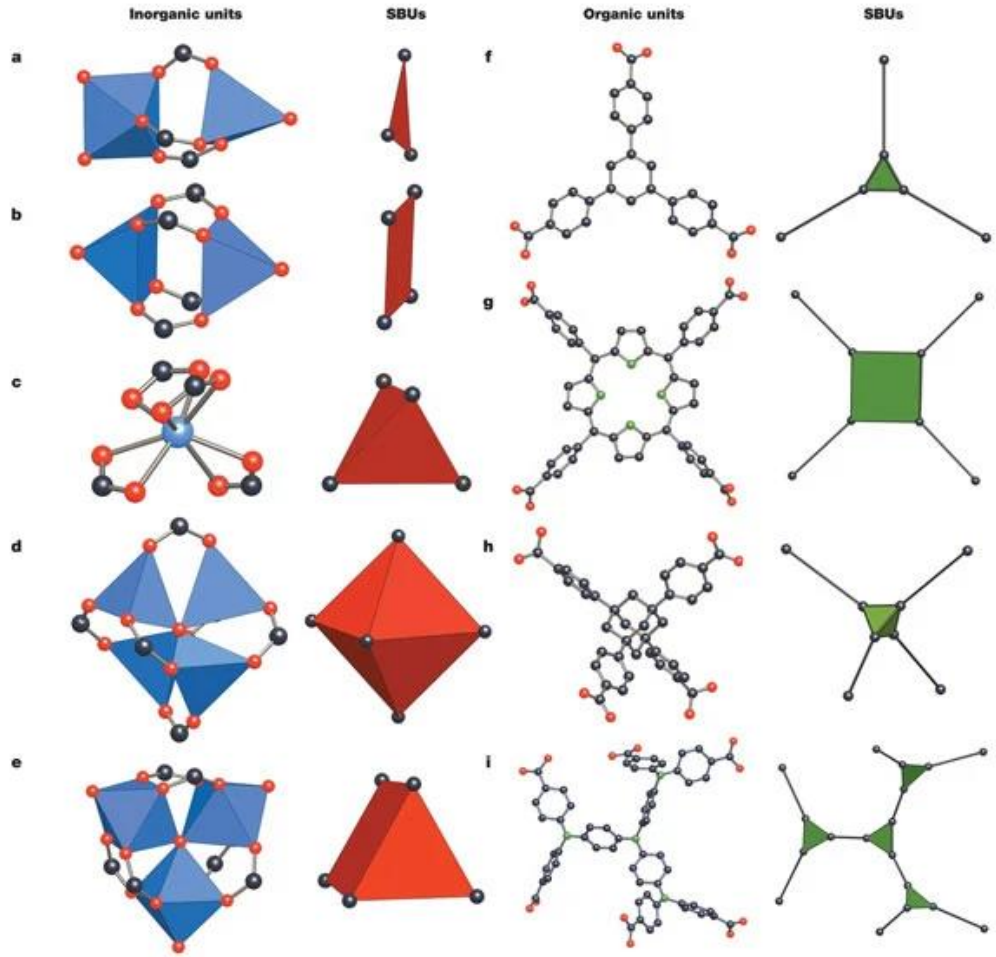

Large variety of possible linkers and SBUs: infinite possibilities to construct MOFs.

O. M. Yaghi et al., *Nature* **2003**, *423*, 705-714.
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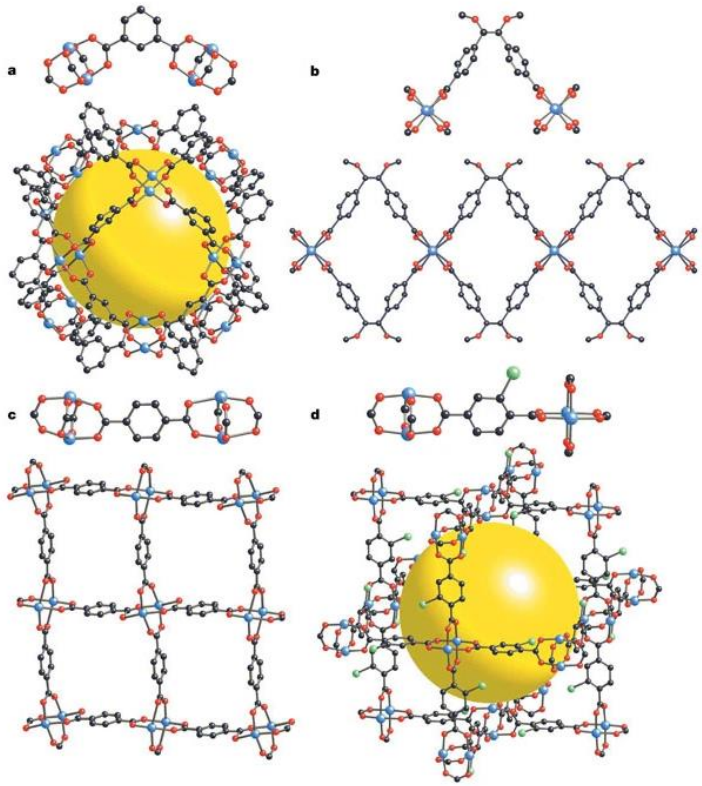
Structural diversity- controlling porosity

Metal-node and shape of linker molecule direct the structure of the SBU and of the MOF scaffold.



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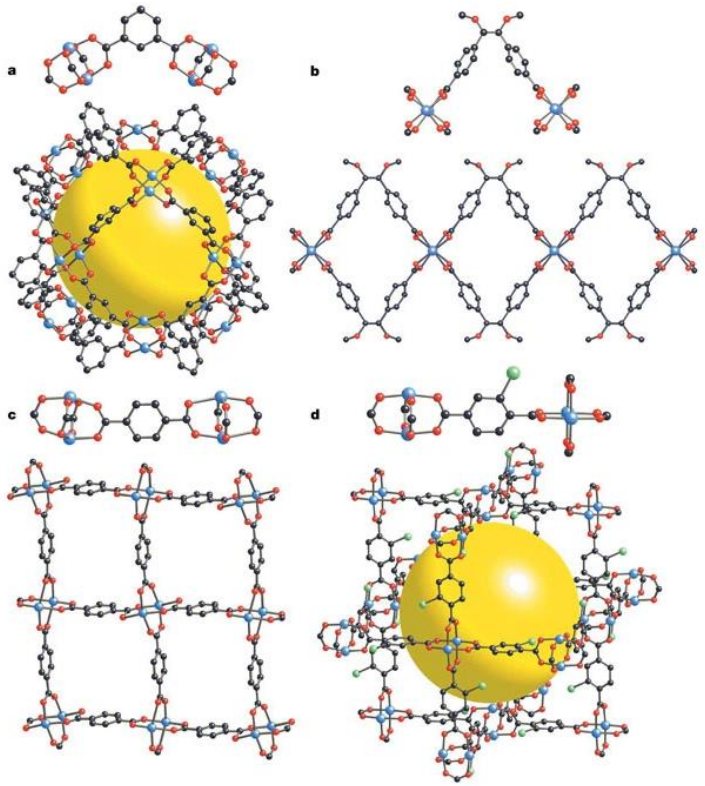

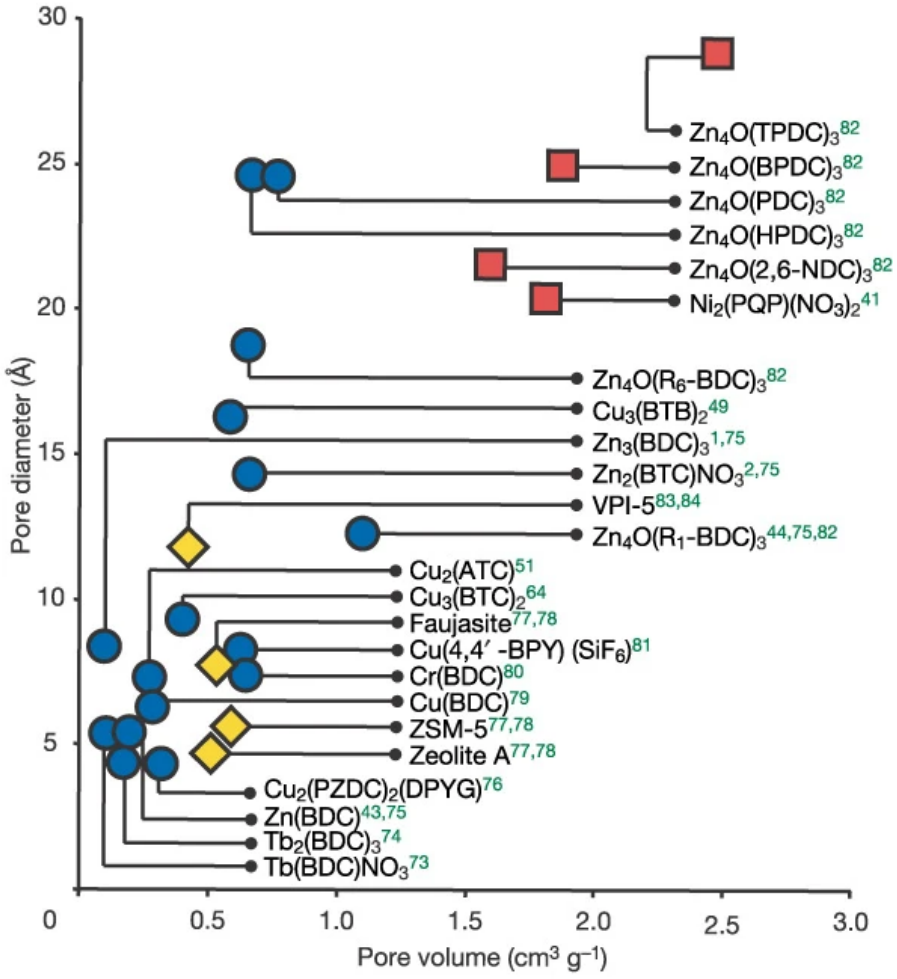

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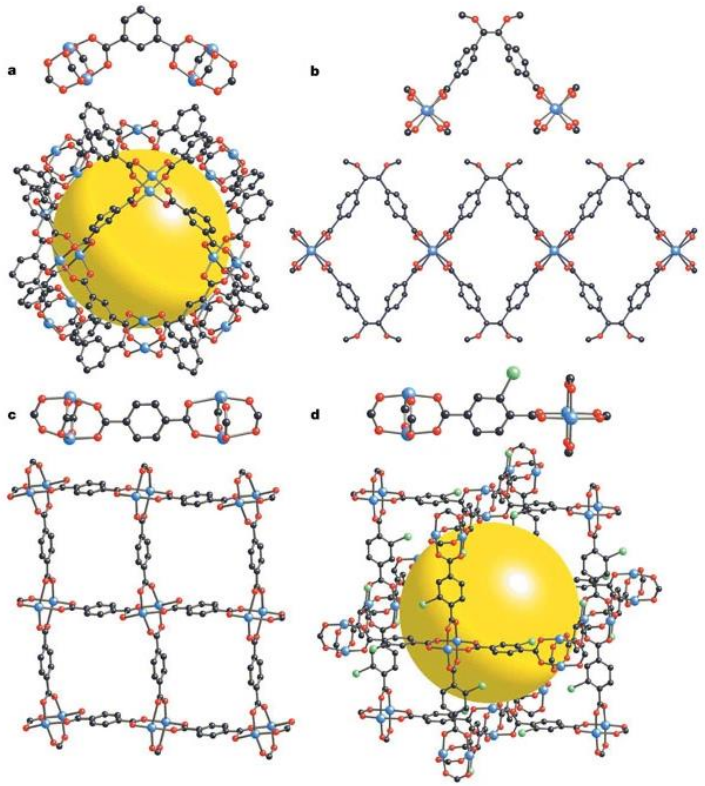
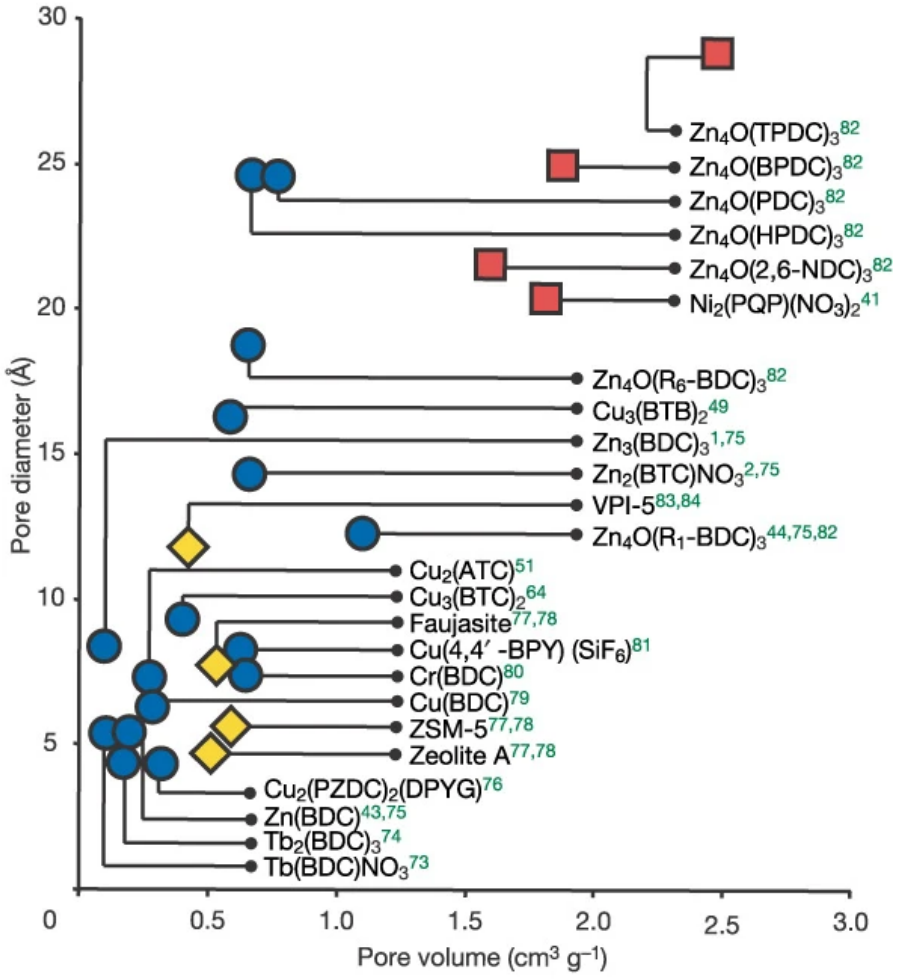


MOFs are exceptionally porous with pore diameters and volumes, which exceed most zeolites.

MOFs can be systema-tically functionalized and therefore modified for targeted applications.



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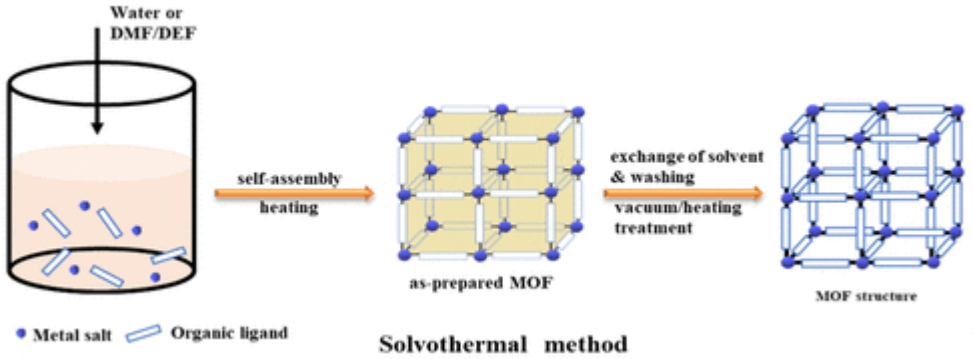
Many ways lead to MOFs - Syntheses



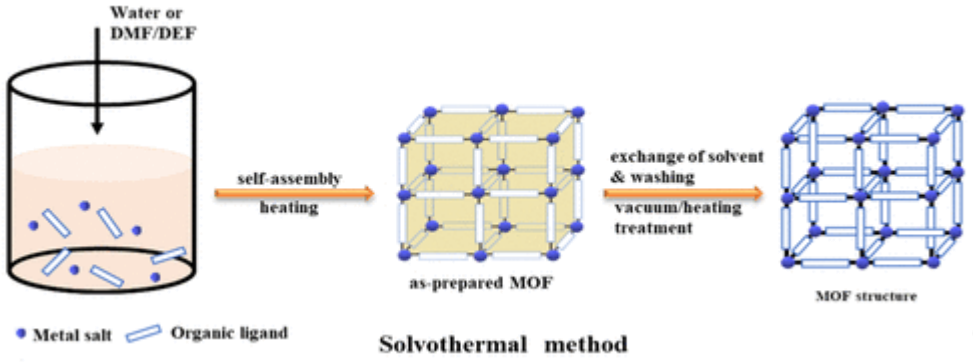
Solvothermal
Energy: thermal
Time: 48-96 h
Temperature 353-453 K

Metal salt
+
Ligand
+
(Solvent)

Review on Metal–Organic Framework Classification, Synthetic Approaches, and Influencing Factors: Applications in Energy, Drug Delivery, and Wastewater Treatment | ACS Omega (11th March, 2025)

White Board

Many ways lead to MOFs - Syntheses



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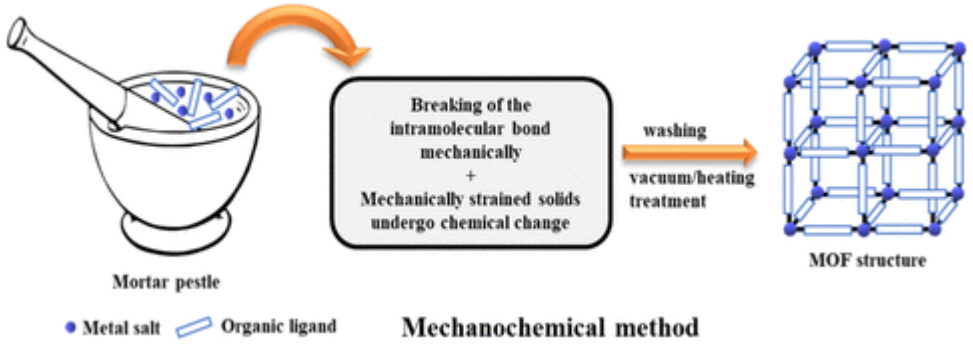

Mechanochemical
Energy: mechanic
Time: 30 mins – 2 h
Temperature 298 K

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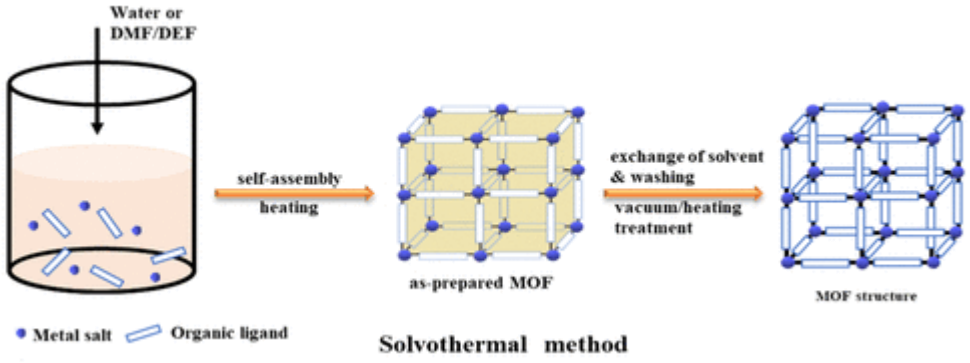

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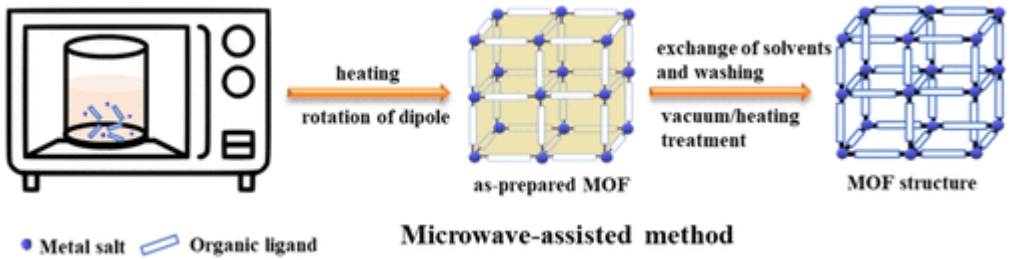
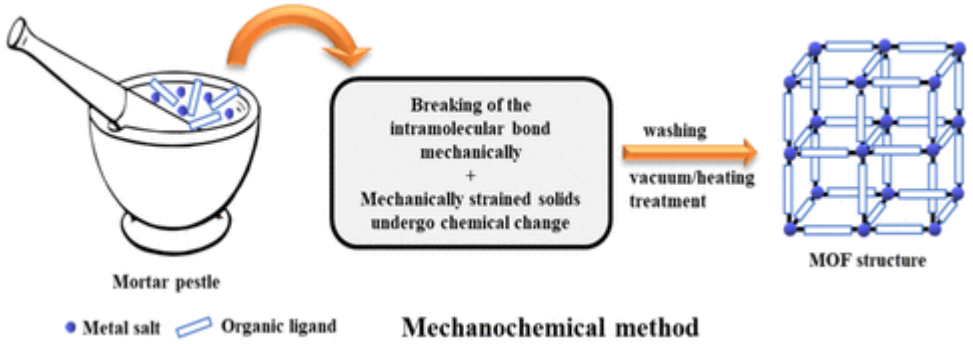


Microwave
Energy: microwave rays
Time: 4 mins – 4 h
Temperature 303-373 K

Metal salt
+
Ligand
+
(Solvent)



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Energy: mechanic
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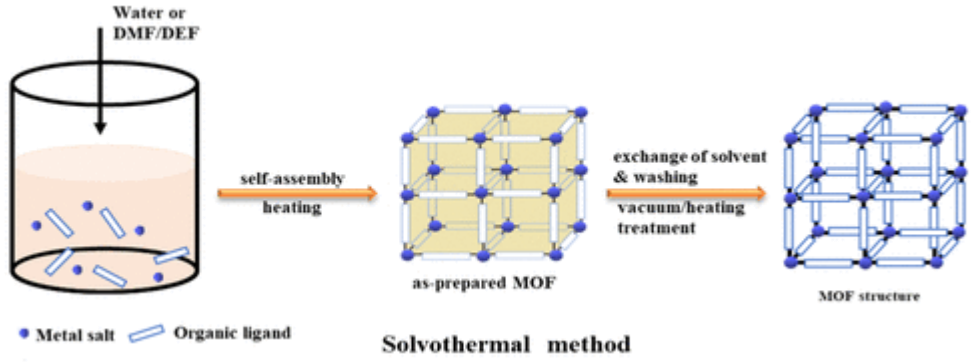

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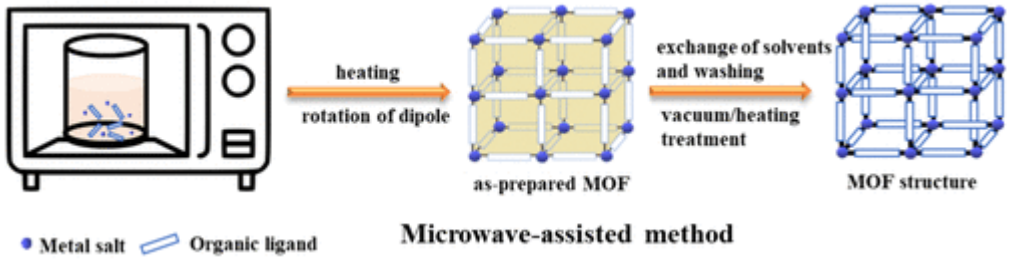

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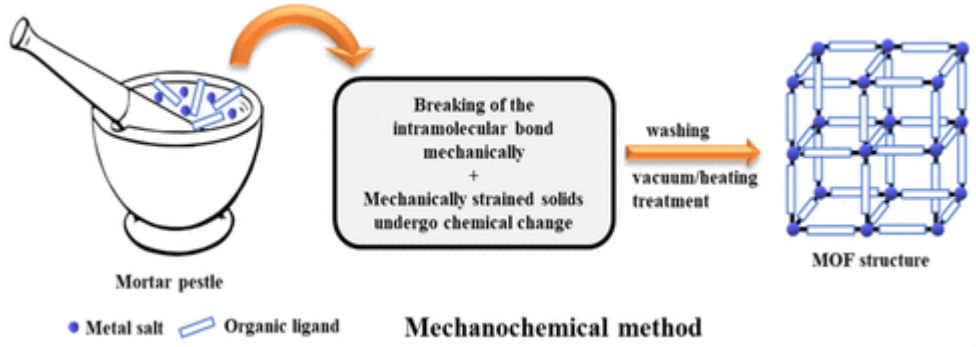

Mechanochemical
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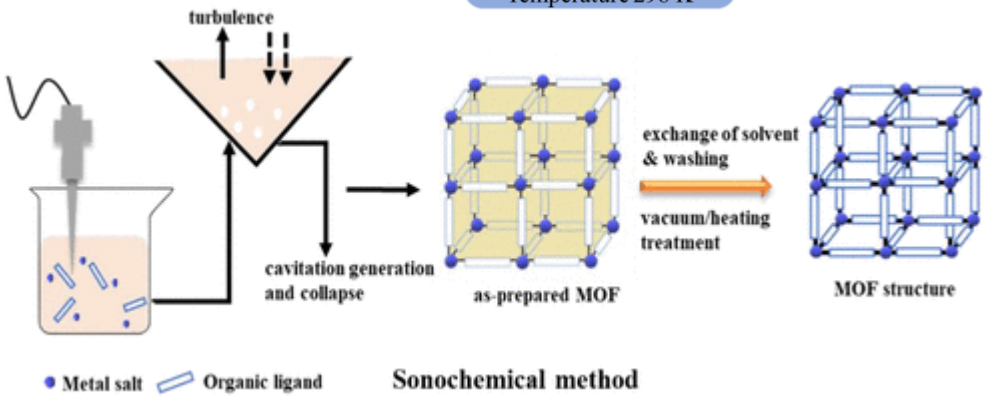
Temperature 298 K



Sonochemical
Energy: ultrasonic rays
Time: 30-180 mins
Temperature 273-313 K

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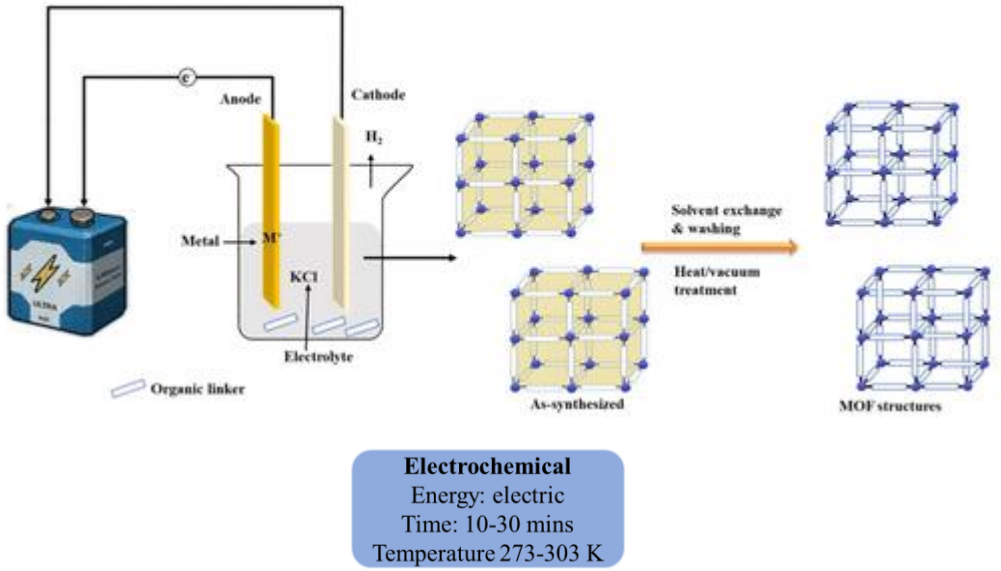

- Stirring synthesis
- Evaporation of solvent
- …

Synthesis method, reaction conditions and starting materials direct structure and therewith the resulting properties!

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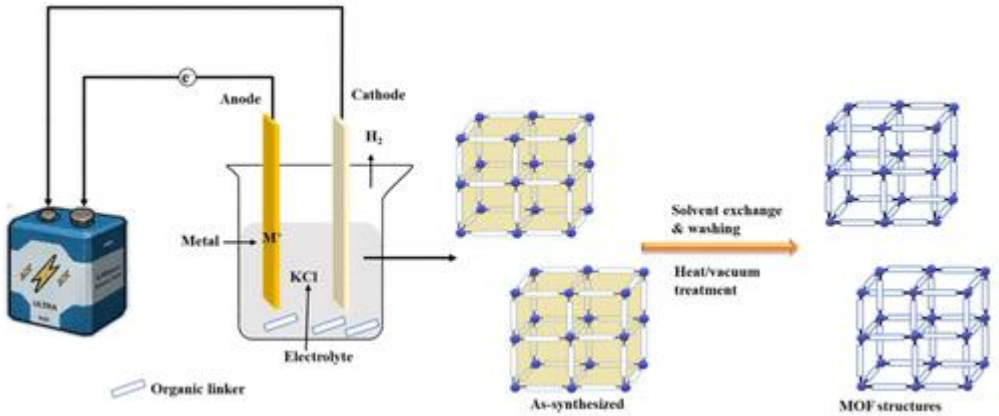
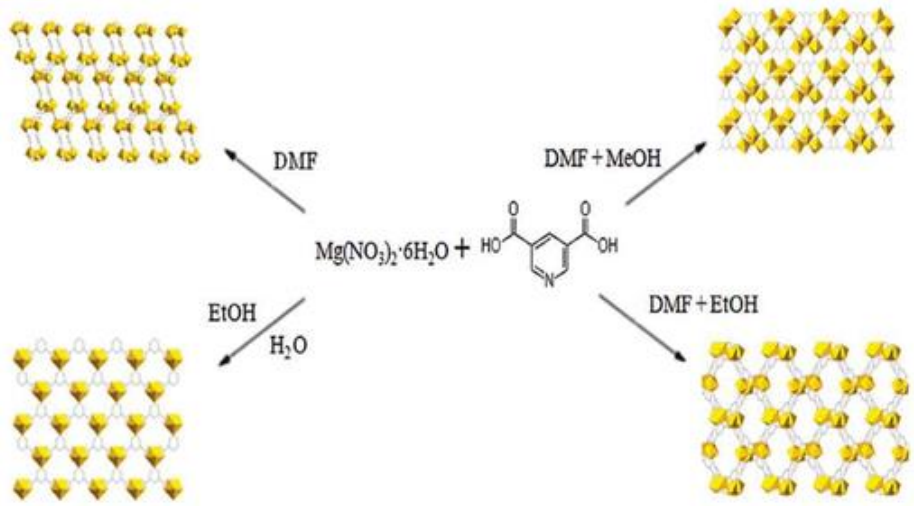


Electrochemical
Energy: electric
Time: 10-30 mins
Temperature 273-303 K

- Stirring synthesis
- Evaporation of solvent
- …

Synthesis method, reaction conditions and starting materials direct structure and therewith the resulting properties!



"The solvent plays a significant part in the synthesis of MOFs and also in morphology determination of the MOFs. Solvents are coordinated through metal ions as a structure-directing agent. In view of this, solvents with a polar nature and higher boiling points are widely used in MOF synthesis."

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Questions?