Metall-organische Netzwerke --
Metal-Organic Frameworks (MOFs)

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Was sind Metall-organische Netzwerke / Metal-Organic Frameworks (MOFs):

1. Was sind MOFs – ein Beispiel – ZIF-8
2. Vergleich mit anderen porösen Materialien
3. Synthese und Anwendungen

Berliner Blau Koordinationsnetzwerk
- aber kein MOF

Berliner Blau (Prussian Blue)

Eisen(III)-hexacyanidoferrat(II)

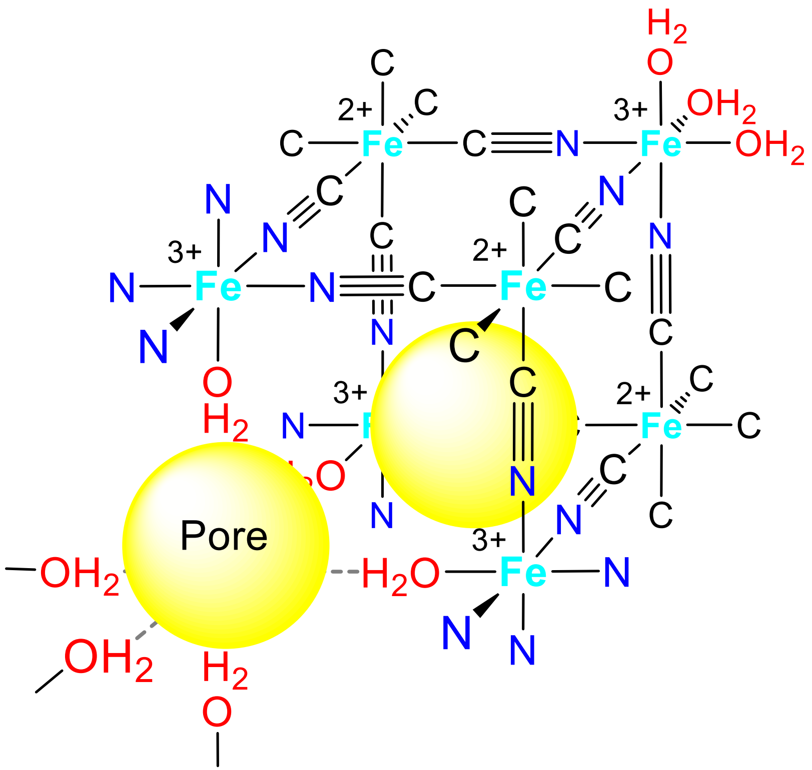
"$\{Fe_4[Fe(CN)_6]_3\}_\infty$"

dreidimensionales Gitter / Netzwerk

Cyanid, CN^- Brücken

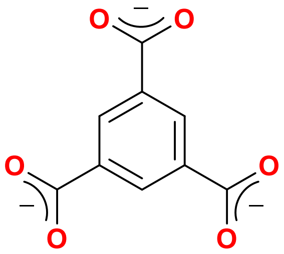
- porös

- keine organischen Liganden

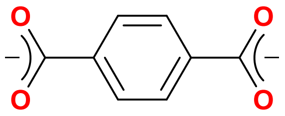


Metal-Organic Frameworks (MOFs)
– typische Liganden

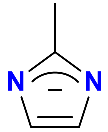
Linker



Benzol-1,3,5-tricarboxylat,
Trimesat, BTC



Benzol-1,4-dicarboxylat,
Terephthalat, BDC



2-Methyl-
imidazolat,
MeIm

Metal-Organic Frameworks (MOFs)
– Beispiel

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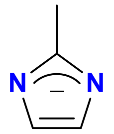

2-Methyl-
imidazolat
+
Zn^{2+}

Metal-Organic Frameworks (MOFs)
– Beispiel

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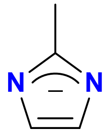

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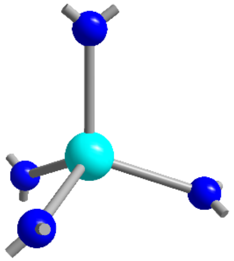
+
Zn^{2+}



Metal-Organic Frameworks (MOFs) – Beispiel

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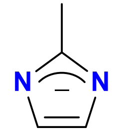

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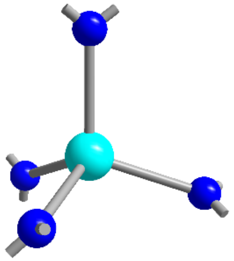
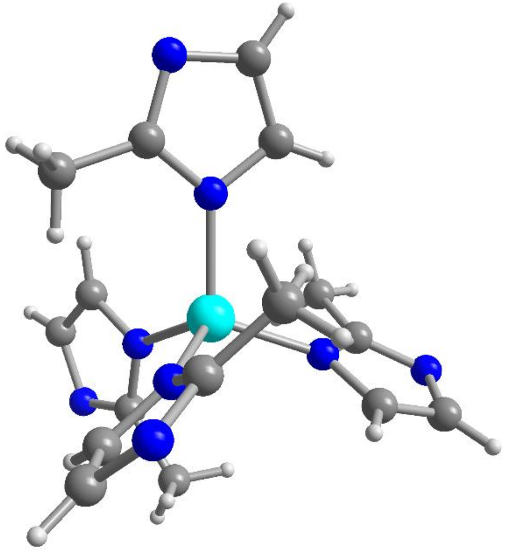
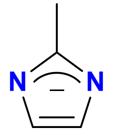




Metal-Organic Frameworks (MOFs)
– Beispiel

Linker



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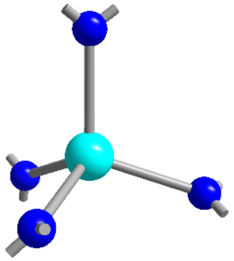
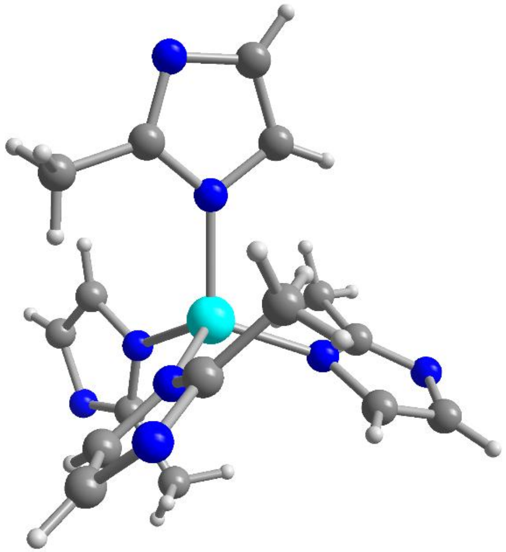
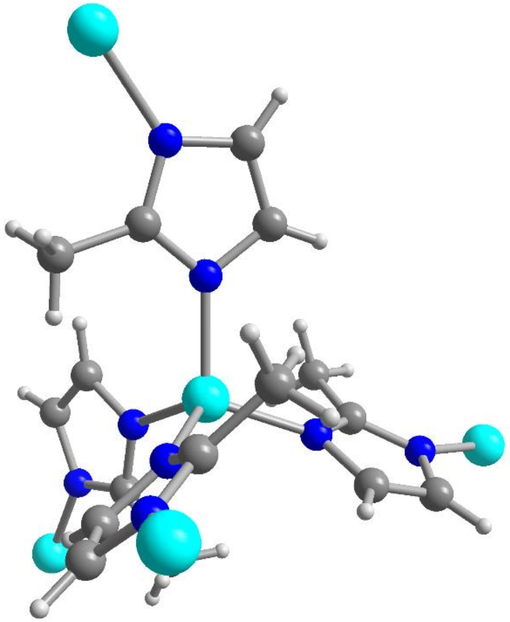
imidazolat
+
Zn^{2+}

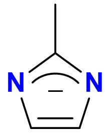






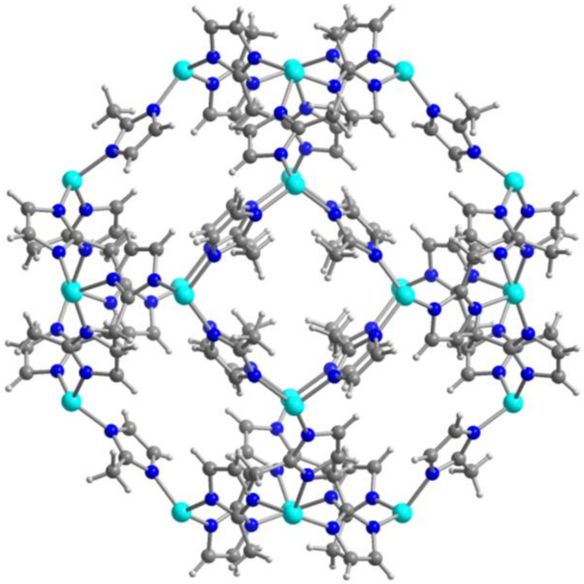
Metal-Organic Frameworks (MOFs) – Beispiel

Linker



2-Methyl-imidazolat
+
Zn^{2+}

3D Netzwerk



Acronym ZIF-8

Metal-Organic Frameworks (MOFs)
– Beispiel

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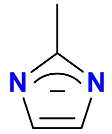
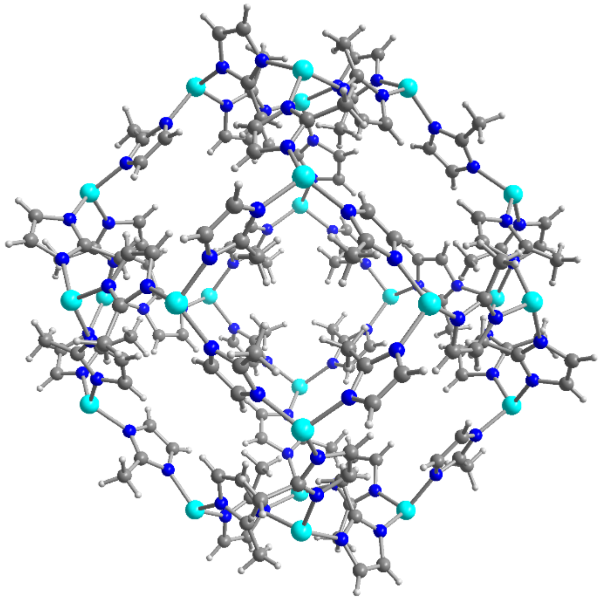
HEINRICH HEINE UNIVERSITÄT DÜSSELDORF

Linker



2-Methyl-
imidazolat
+
Zn^{2+}

3D Netzwerk



Acronym ZIF-8

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– Beispiel

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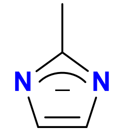

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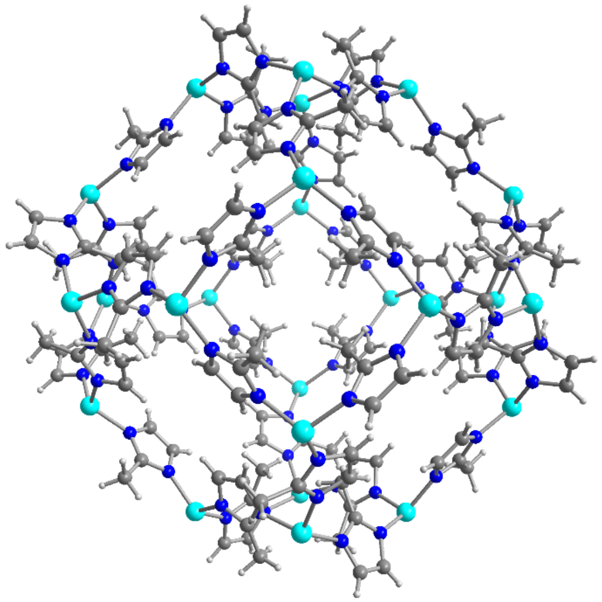

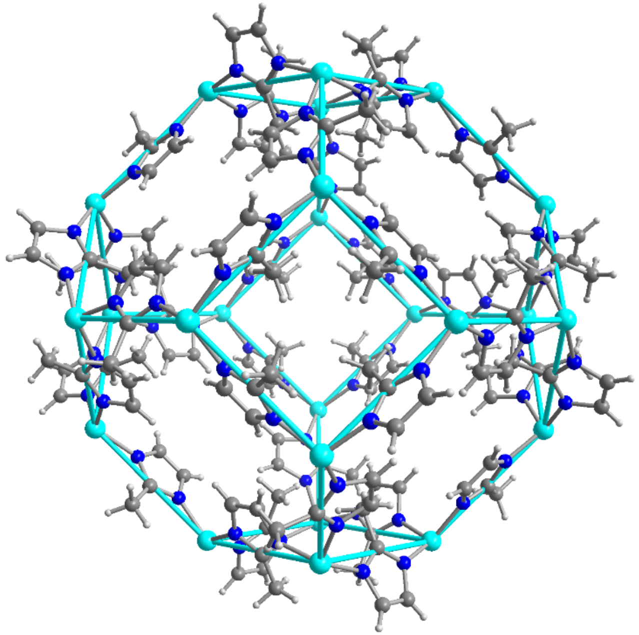

Acronym ZIF-8

Metal-Organic Frameworks (MOFs)
– Beispiel

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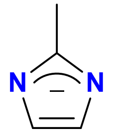

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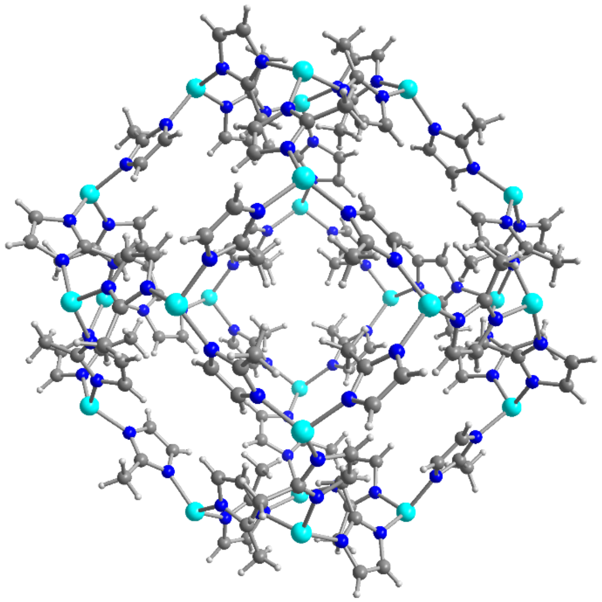
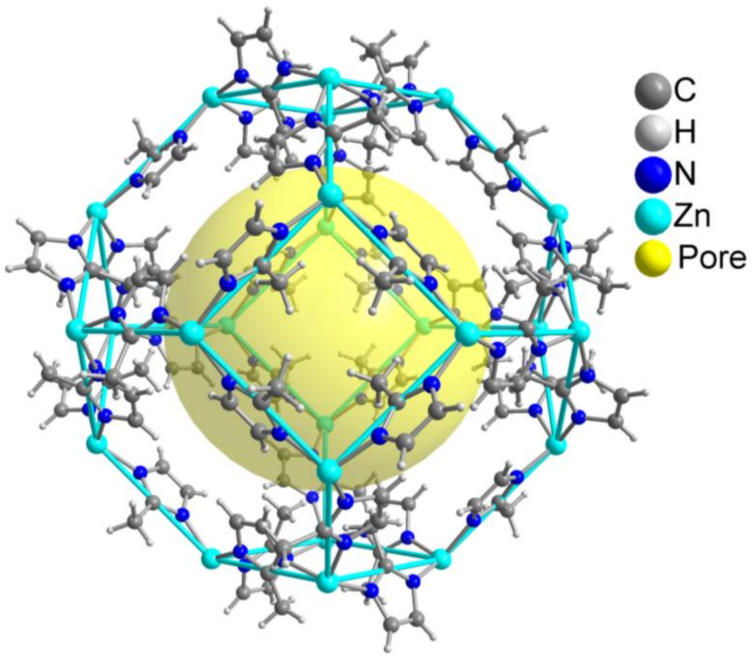
3D Netzwerk





Acronym ZIF-8

Metal-Organic Frameworks (MOFs) – Beispiel

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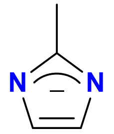
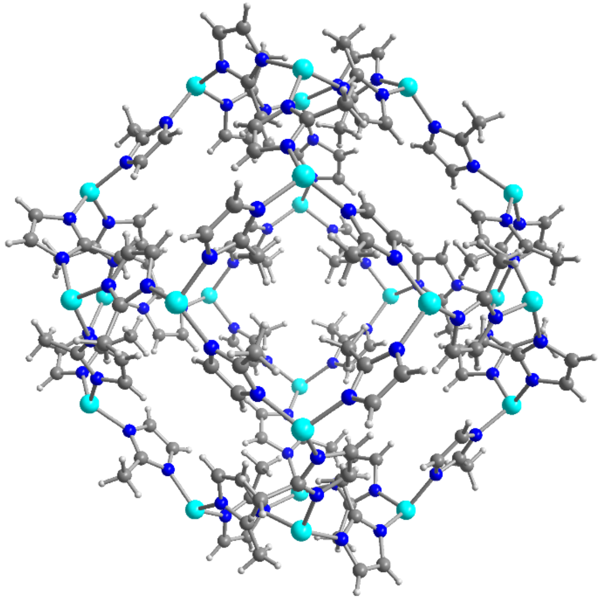


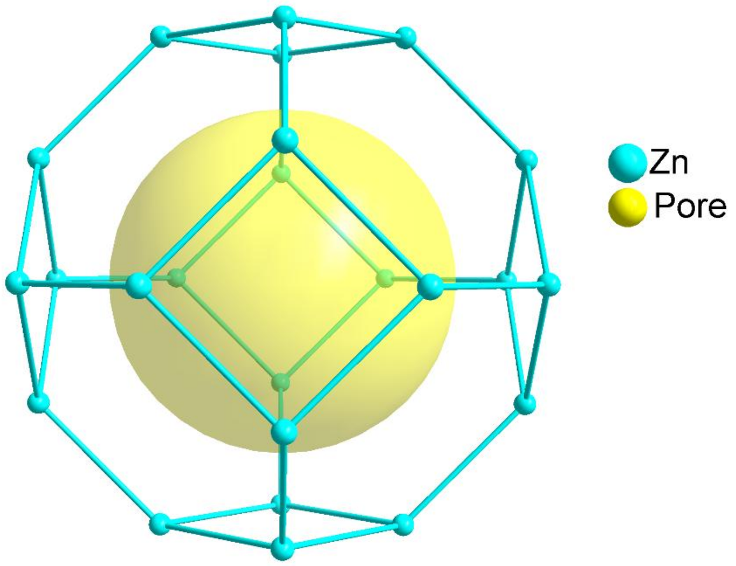
2-Methyl-imidazolat

+

Zn^{2+}

3D Netzwerk





Acronym ZIF-8

Metal-Organic Frameworks (MOFs)
– Beispiel

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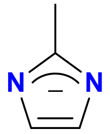

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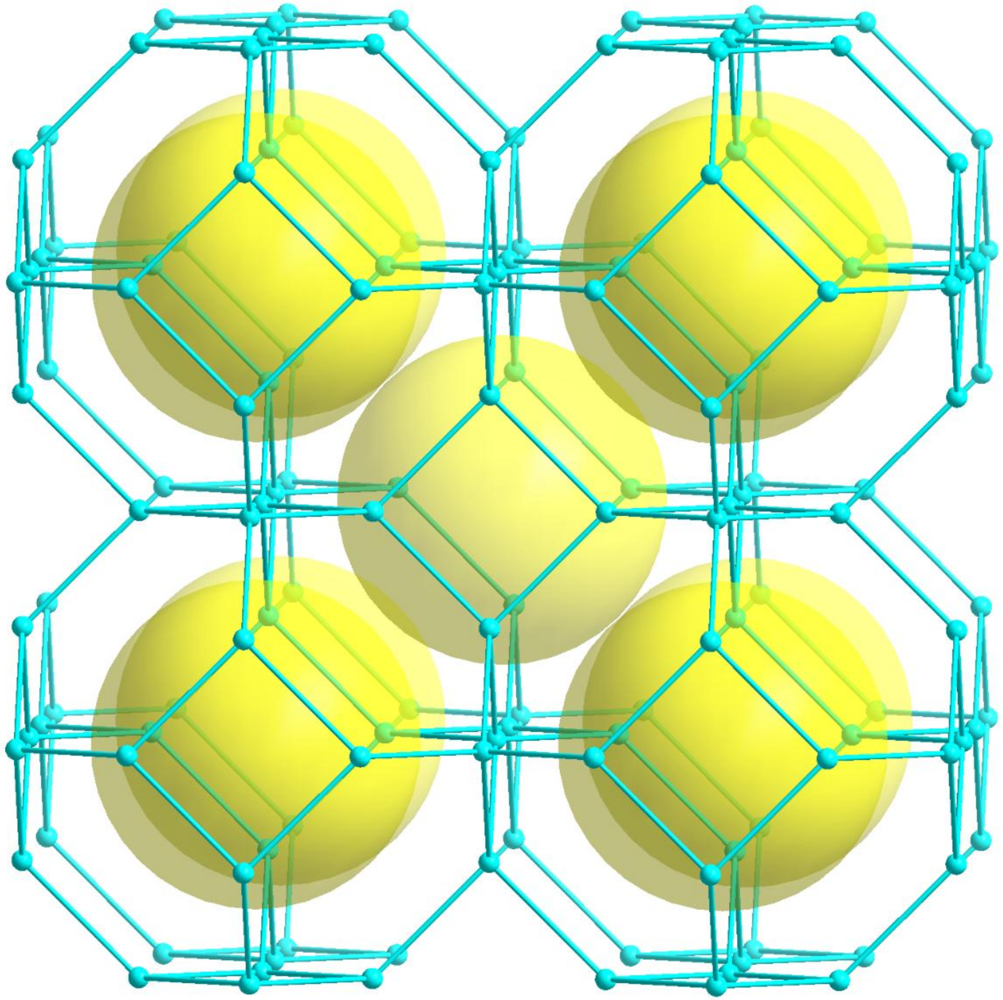
imidazolat
+
Zn^{2+}

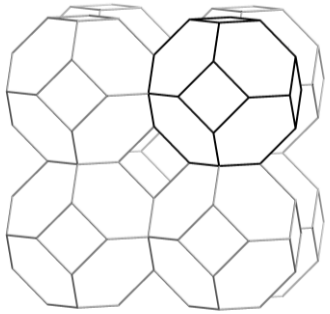
3D Netzwerk



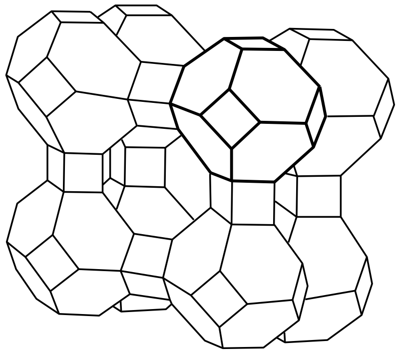
Acronym ZIF-8

ZIF = zeolitic imidazolate framework

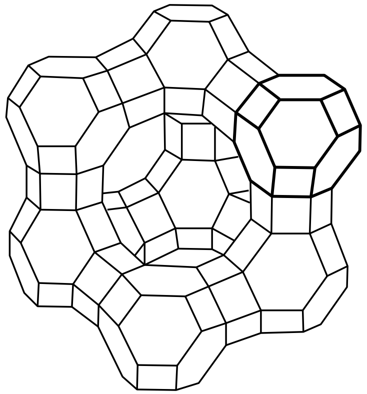
natürliche Zeolithe:



Sodalith

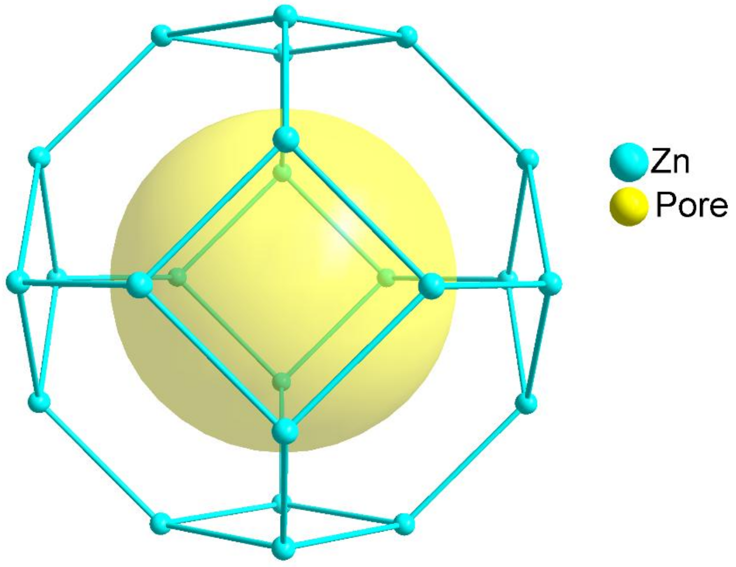


Zeolith A



(c) Faujasit

β-Käfig



Was sind Metall-organische Netzwerke / Metal-Organic Frameworks (MOFs):

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1. Was sind MOFs – ein Beispiel – ZIF-8

2. Vergleich mit anderen porösen Materialien

3. Synthese und Anwendungen

Poröse Materialien

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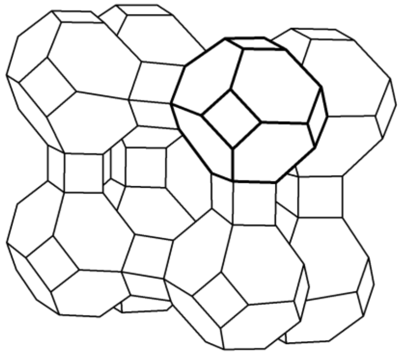
	identical pores	design
anorganisch:		
Zeolithe,	✓	✗
Silica Gel,	✗	✗
mesoporöse Silica	✗	✗
		= rather limited

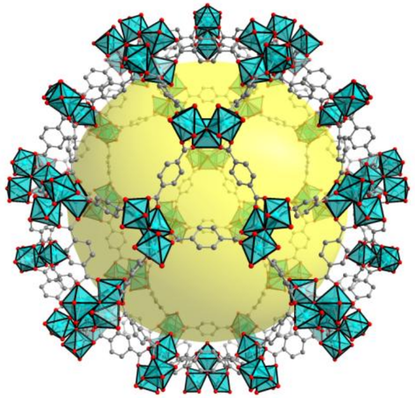


hygroskopisch

Trockenmittel

anorganisch-organisch Hybride:

Metal-Organic Frameworks, MOFs
- definierte, identische Poren ✓
- maßschneiderbare Eigenschaften durch organische Linker ✓



Mikro- bis Mesoporen

organisch:

Aktivkohle	✗	✗
poröse organische Polymere	✓	✓

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Poröse Materialien
spezifische Oberfläche (BET) pro Gramm

anorganisch:
Zeolithes,
Silica Gel,
mesoporöses Silica ~1000 m^2/g

Metal-Organic Frameworks, MOFs

~2000-4000 m^2/g

organisch:
Aktivkohle
~1000 m^2/g

Was sind Metall-organische Netzwerke / Metal-Organic Frameworks (MOFs):

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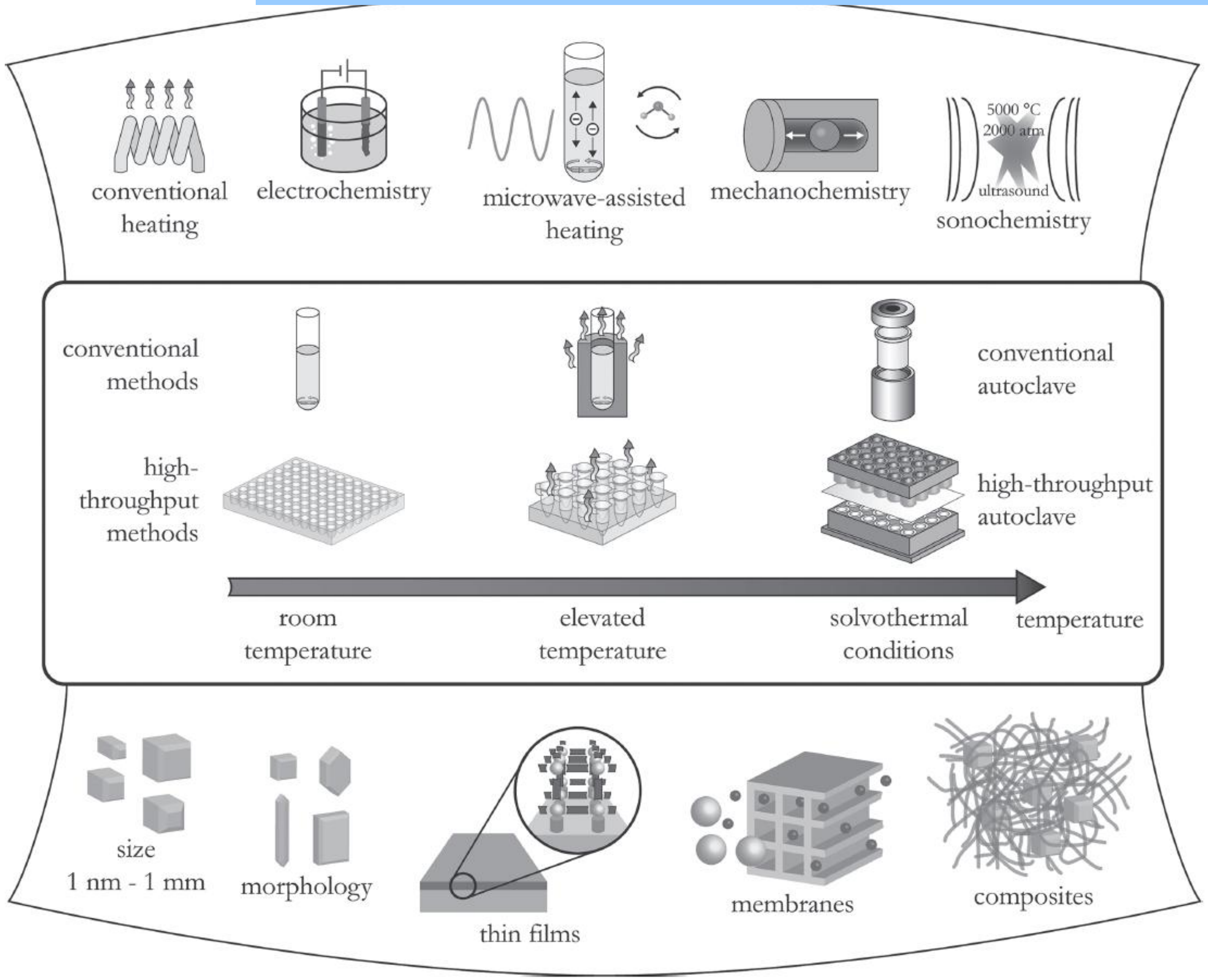
1. Was sind MOFs – ein Beispiel – ZIF-8

2. Vergleich mit anderen porösen Materialien

3. Synthese und Anwendungen

Overview of synthesis methods, possible reaction temperatures, and final reaction products in MOF synthesis



- different synthesis methods that have been applied in the last 20 years:

-- room temperature synthesis,
-- conventional electric (CE) heating,
-- microwave (MW) heating,
-- electrochemistry (EC),
-- mechanochemistry (MC), and
-- ultrasonic (US) methods

-- conventional step-by-step methods
-- high-throughput methods

N. Stock, S. Biswas, *Chem. Rev.* **2012**, *112*, 933–969.

MOF synthesis
- synthesis methods over years

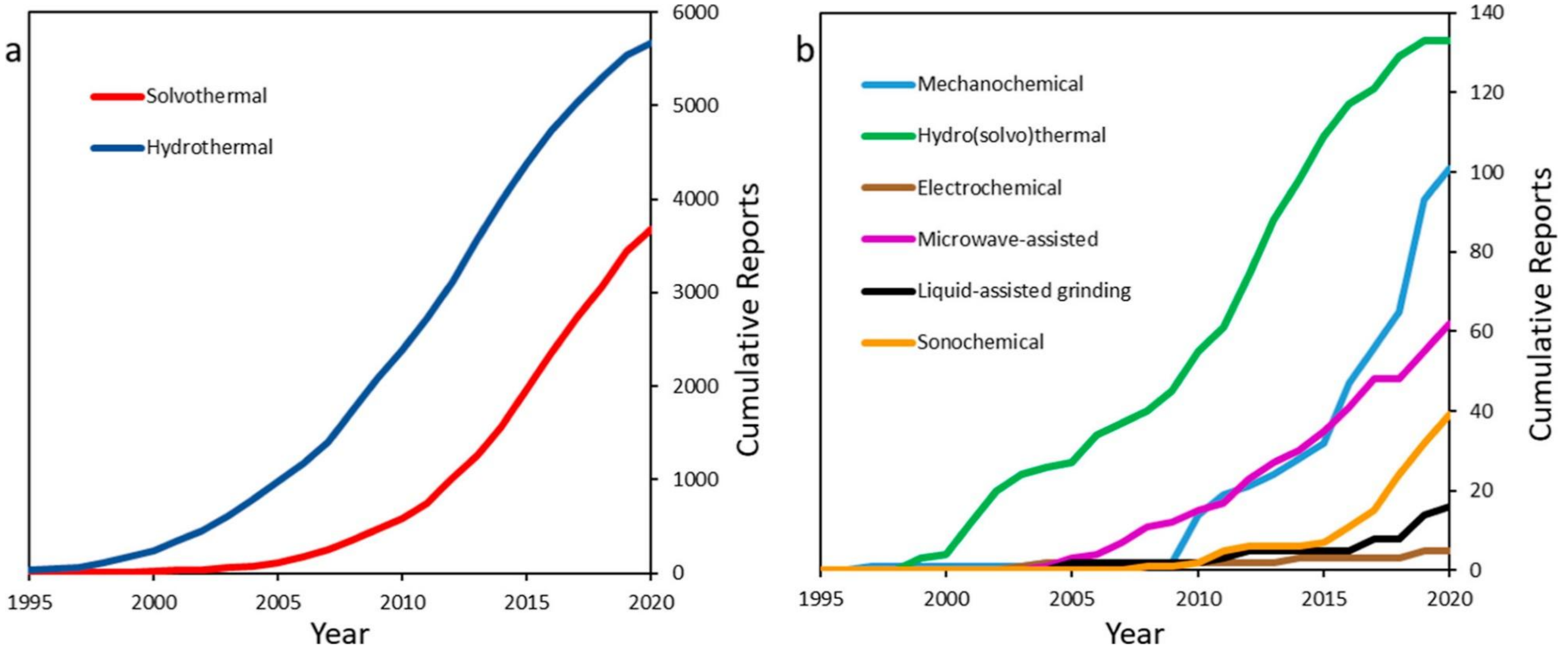
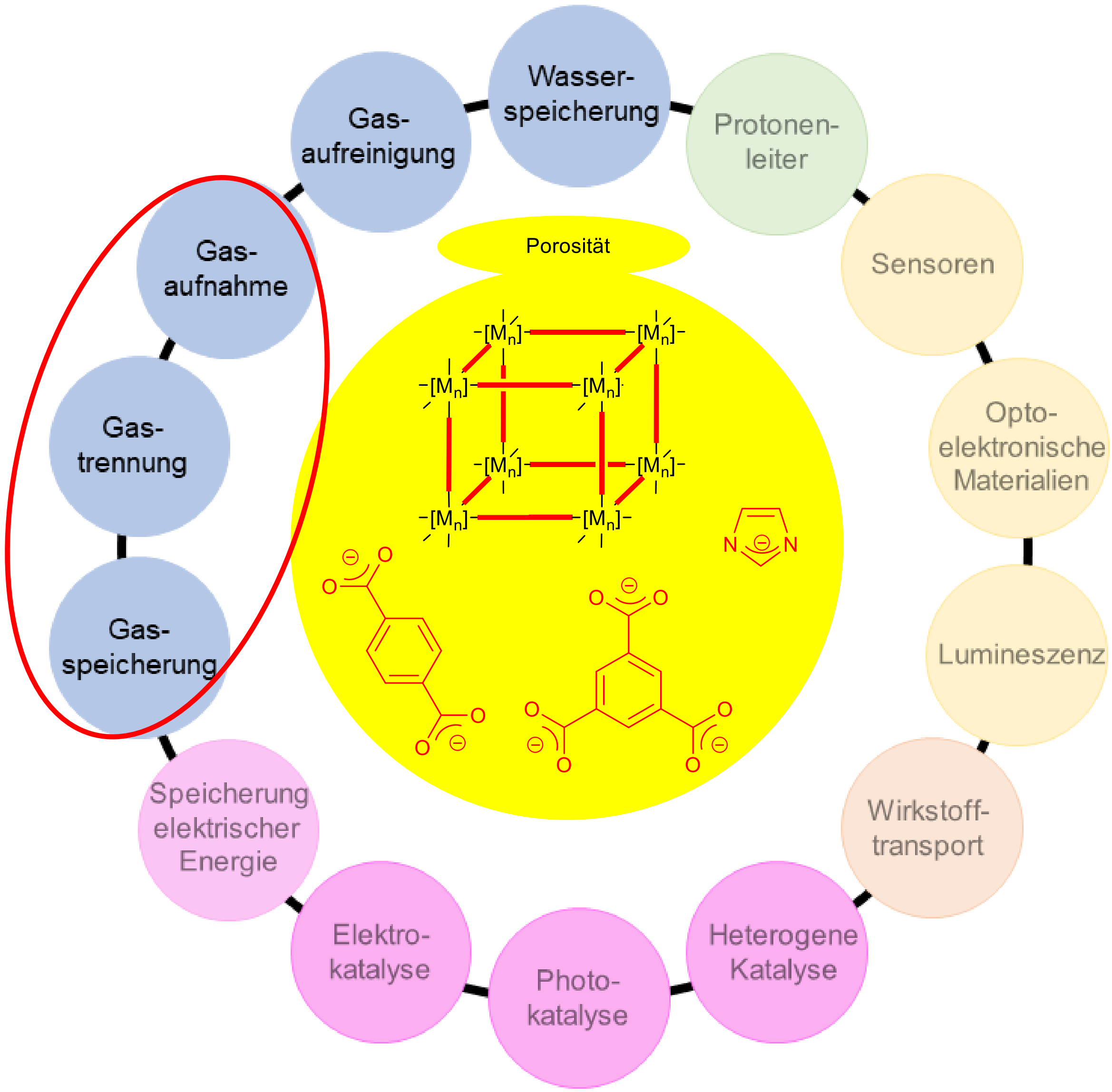


Figure 5. (a) Cumulative sum of the two main MOF synthesis methods from 1995 to 2020. (b) Cumulative sum of alternative and emerging synthesis methods showing periods where these techniques were first introduced for MOF synthesis.

L. T. Glasby et al. Chem. Mater. **2023**, 35, 4510−4524.
https://doi.org/10.1021/acs.chemmater.3c00788

Metal-Organic Frameworks (MOFs):
Anwendungsorientierte Eigenschaften



Metal-Organic Frameworks (MOFs):
Zahl der Publikationen pro Jahr

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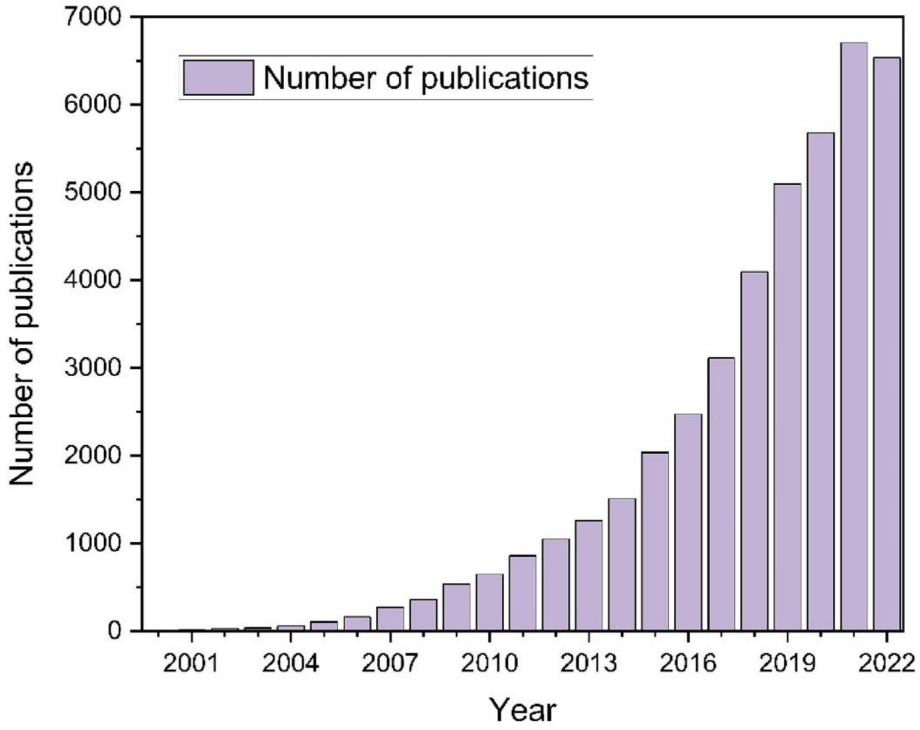

P. Wisniewska et al., Chem. Eng. J. **2023**, 471, 144400. https://doi.org/10.1016/j.cej.2023.144400

PrometheanParticles™

Nanomaterials **reimagined**

Metal-organic Frameworks (MOFs) as industrial scale, cost-effective adsorbents for Carbon Capture and Storage (CCS) Applications

Promethean believes that MOFs represent a viable carbon capture technology based on their CO_2 uptake performance, selectivity, cost, versatility, and energy efficiency.

March 2022

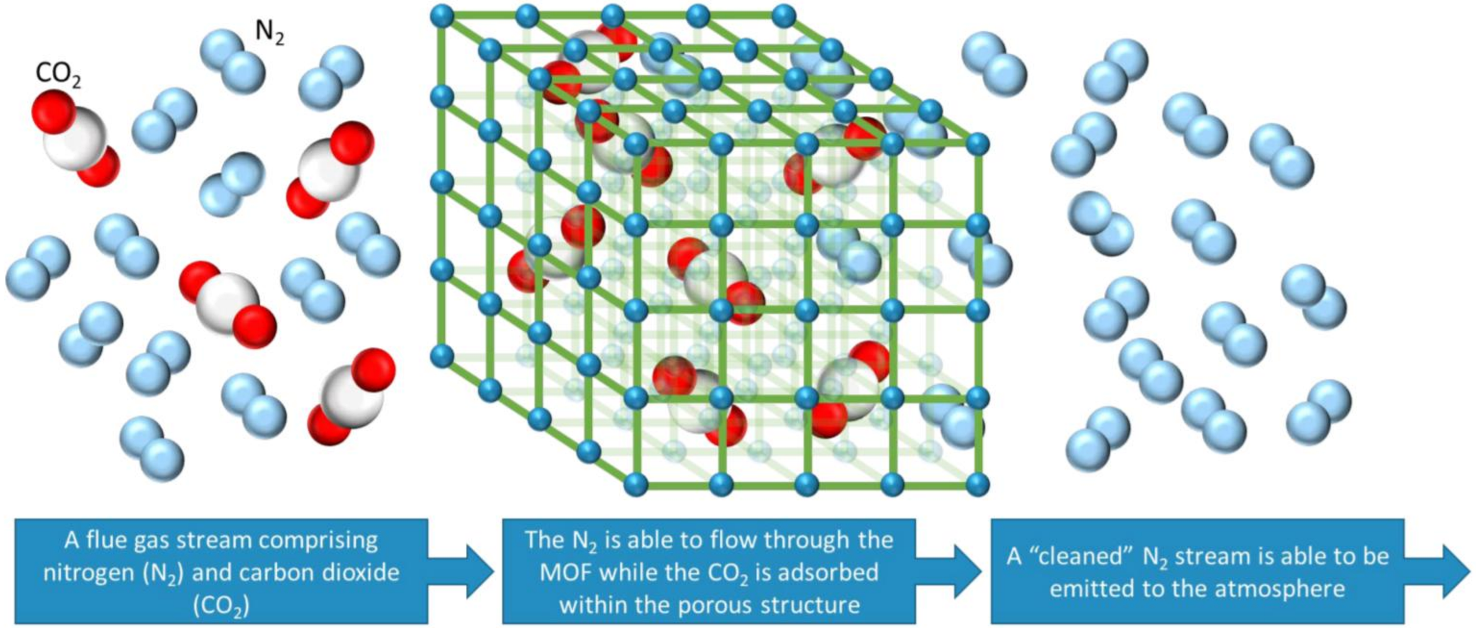

Figure 11: Schematic representation of CO_2 being selectively trapped within the MOF 'cage' structure

https://prometheanparticles.co.uk/
https://decarbonisationtechnology.com/article/175/metal-organic-frameworks-for-carbon-capture

Presse-Mitteilung P327/23e
October 10, 2023

BASF
We create chemistry

News Release

P327/23e
Oktober 10, 2023

BASF becomes first company to successfully produce metal-organic frameworks on a commercial scale for carbon capture

- **Production scale-up of MOF successfully completed for Canadian technology provider Svante Technologies Inc.**
- **MOFs will be applied in Svante's own carbon capture technology**
- **BASF has capacity to produce customized MOFs at multiple sites**

BASF is the first company to produce metal-organic frameworks (MOFs) on a production scale of several hundred tons per year. MOFs are highly crystalline structures with nanometer-sized pores and a large surface area. This structure offers a high capacity for the storage of carbon dioxide (CO_2), the dehumidification of air for room climate control, and the adsorption of the greenhouse gas methane. BASF has developed expertise on the scale-up and production of MOFs, can tailor MOFs to customers' needs and specifications, and today has the capacity to produce customized MOFs for various applications and industries.

A first project has now been successfully completed for Canadian carbon capture and removal solutions provider Svante Technologies Inc. (Svante). The interdisciplinary BASF team of researchers, scale-up experts and engineers worked collaboratively on the scale-up by converting the Svante lab recipe into a safe plant procedure for large scale production. The MOFs produced will be used as solid sorbents for carbon capture projects. The collaboration with Svante will help to significantly reduce carbon emissions in various industrial sectors including hydrogen, pulp and paper, cement, steel, aluminum and chemicals.

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Svante
(https://www.svanteinc.com/)

https://www.svanteinc.com/press-releases/svante-secures-commercial-supply-of-mof-advanced-sorbent-materials-with-basf-for-carbon-capture-market/

Svante Secures Commercial Supply of MOF

Advanced Sorbent Materials with BASF for Carbon Capture Market

October 10, 2023

VANCOUVER, BC, CA

Svante announced today that it has entered into an arm's length Commercial Supply Agreement with BASF to scale up its proprietary sorbent material, Calgary Framework 20 (CALF-20), used in Svante's carbon capture process. This metal-organic framework (MOF) sorbent can capture up to 95% of carbon dioxide (CO_2) emitted from industrial sources, such as cement and blue hydrogen plants, using rapid solid adsorption and low-pressure steam.

Svante has pioneered carbon capture and removal technology using structured adsorbent beds, known as "filters". The company is the most advanced industry player in the use of solid sorbents for carbon capture, with the world's first commercially available MOF nanomaterial filter manufacturing facility in Vancouver, BC. This commercial supply agreement with BASF will unlock the next phase of Svante's growth, scaling carbon capture filter manufacturing up to multi-million-tonne capacity and implementing hundreds of large-scale carbon capture and storage (CCS) facilities by 2030.

BASF commercially produces metal-organic frameworks for CO_2 capture in world first

IChemE

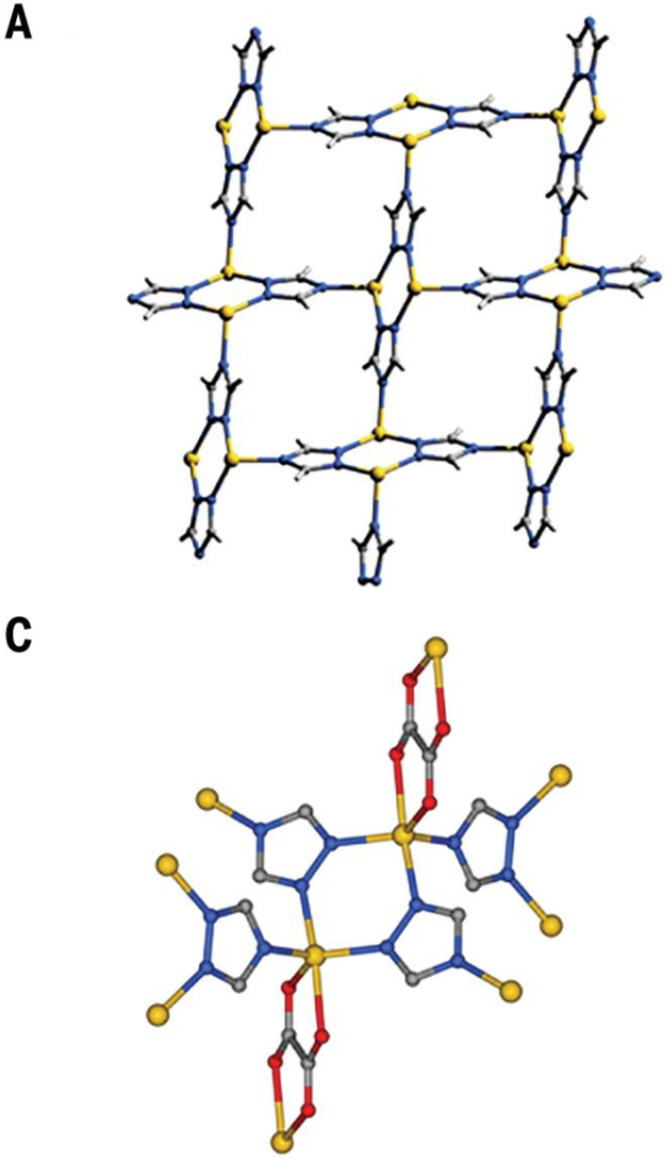
The Chemical Engineer, Industry, 3rd November 2023
https://www.thechemicalengineer.com/news/basf-commercially-produces-metal-organic-frameworks-for-co2-capture-in-world-first/

BASF claims to be the first company to produce metal-organic frameworks at a scale of several hundred tons per year, after completing a scaleup project on behalf of CO_2 capture and removal company Svante Technologies.

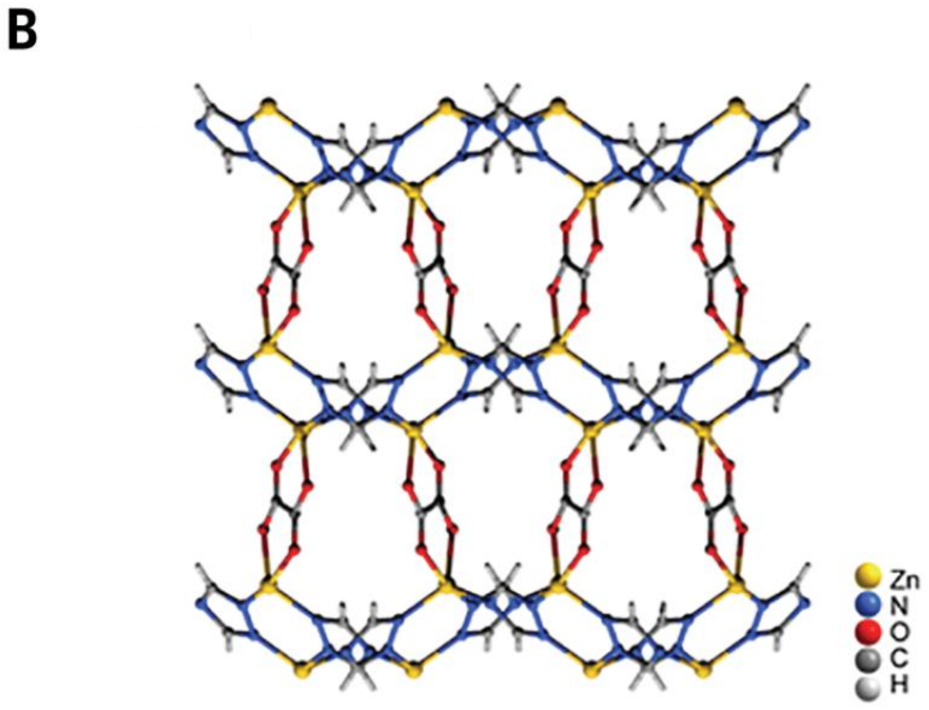
Metal-organic frameworks, or MOFs, are highly crystalline, porous materials with nanometre-sized pores and large internal surface areas. Their structures make them useful for applications such as carbon capture, adsorption of greenhouse gas methane, and dehumidification of air for room climate control. Until now, large-scale production of the materials at low cost has been a barrier for use in the gas separation industry.

BASF has expertise in the production and scaleup of MOFs and for the past two years has been collaborating with Svante to scale up the technology company's proprietary sorbent material, Calgary Framework 20 (CALF-20). The MOF sorbent can capture up to 95% of CO_2 emitted from industrial sources.

Metal-Organic Frameworks (MOFs):
CALF-20



Zn-triazolat-oxalat



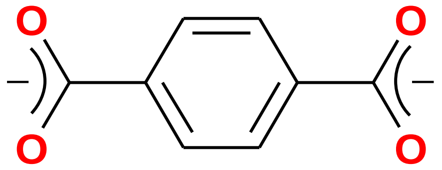
- physisorbiert CO_2 mit hoher Kapazität
- selektiv für CO_2 gegenüber H_2O und N_2
- stabil über >450 000 Dampfzyklen
- stabil gegenüber sauren Gasen

Lin et al., Science 374, 1464–1469 (2021). DOI: 10.1126/science.abi7281

Ende

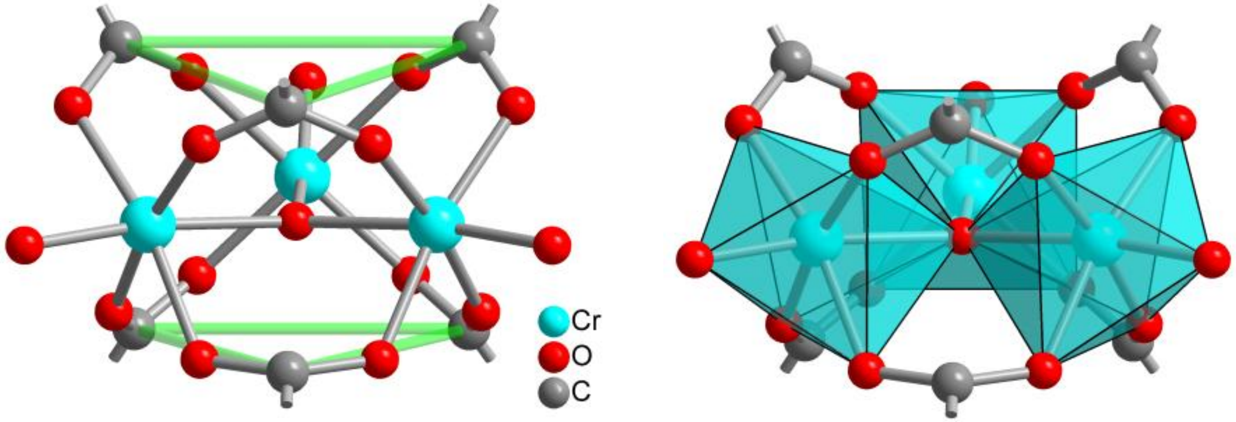
Danke für die Aufmerksamkeit

MIL example:
3D-$[Cr_3(O)(bdc)_3(F,OH)(H_2O)_2]\cdot{\sim}25H_2O$ or MIL-101(M)



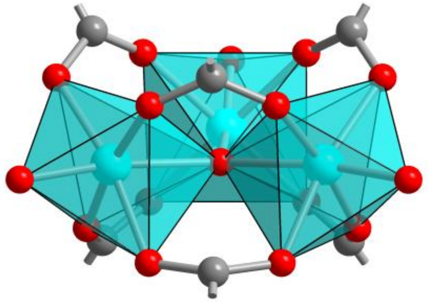
benzene-1,4-dicarboxylate,
terephthalate, bdc

+ $\{Cr_3(\mu_3\text{-}O)(F)(H_2O)_2\}$

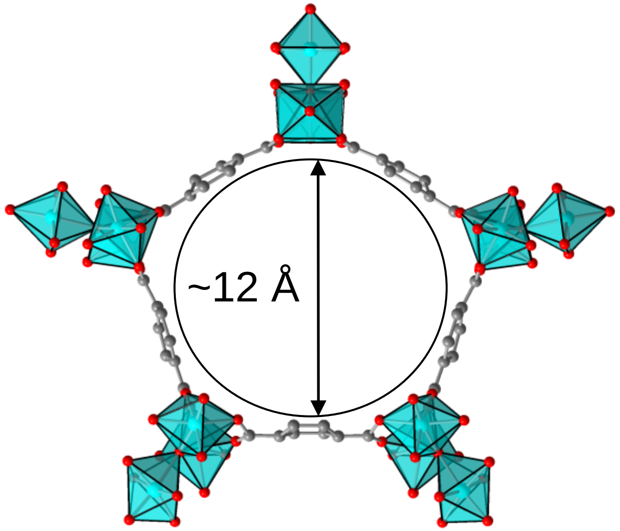


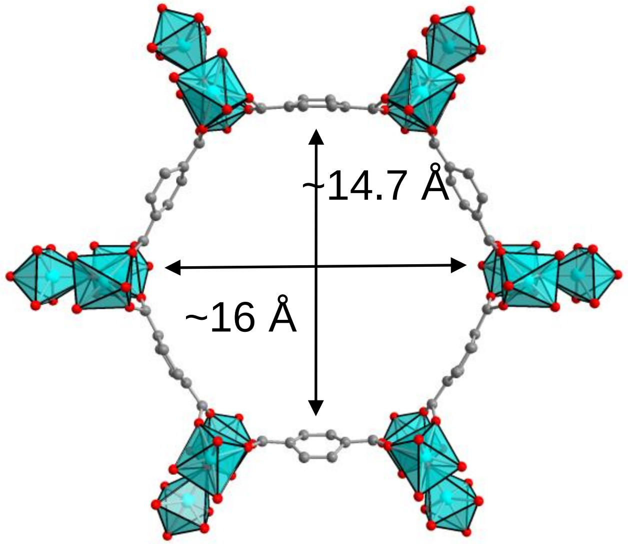
G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S Surble and I. Margiolaki, Science **2005**, *309*, 2040–2042.

MIL example:
3D-$[Cr_3(O)(bdc)_3(F,OH)(H_2O)_2]\cdot{\sim}25H_2O$ or MIL-101



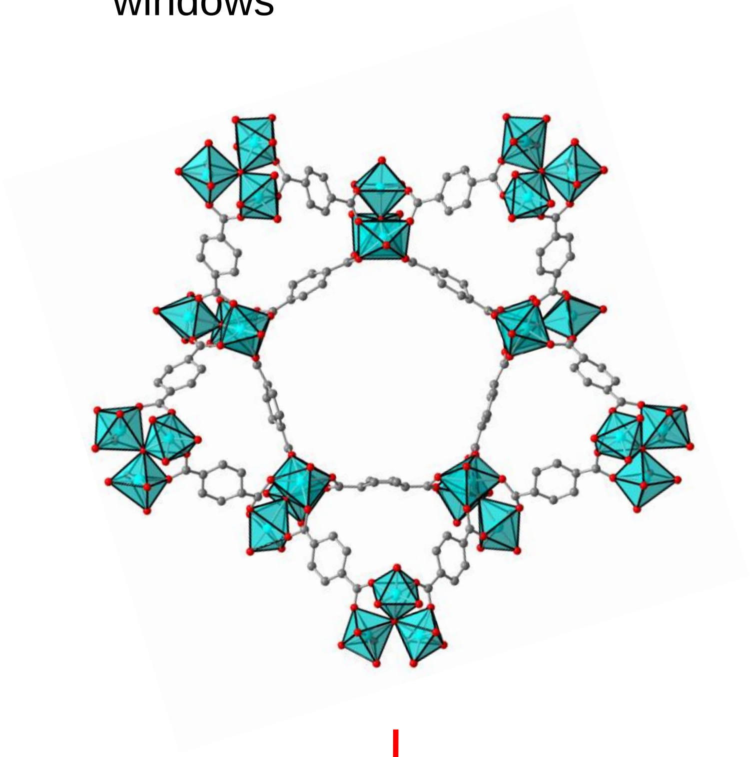
→ pentagonal windows and hexagonal windows as largest windows in cages:



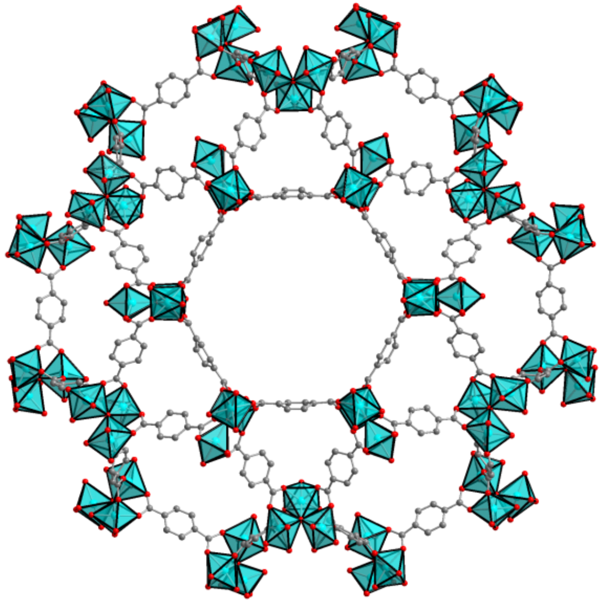


MIL example:
3D-$[Cr_3(O)(bdc)_3(F,OH)(H_2O)_2]\cdot{\sim}25H_2O$ or MIL-101

pentagonal + trigonal windows

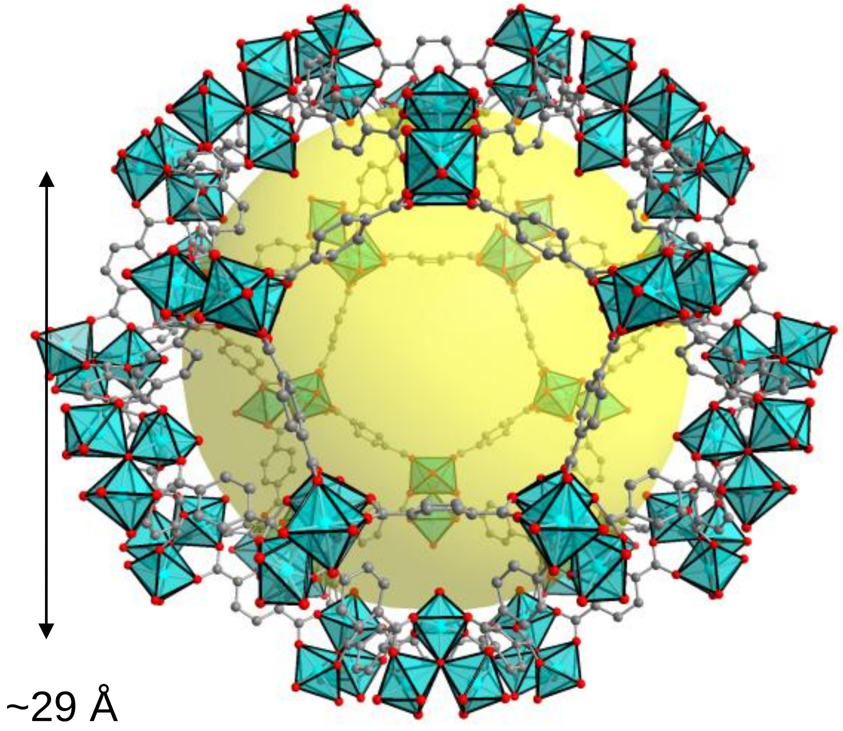


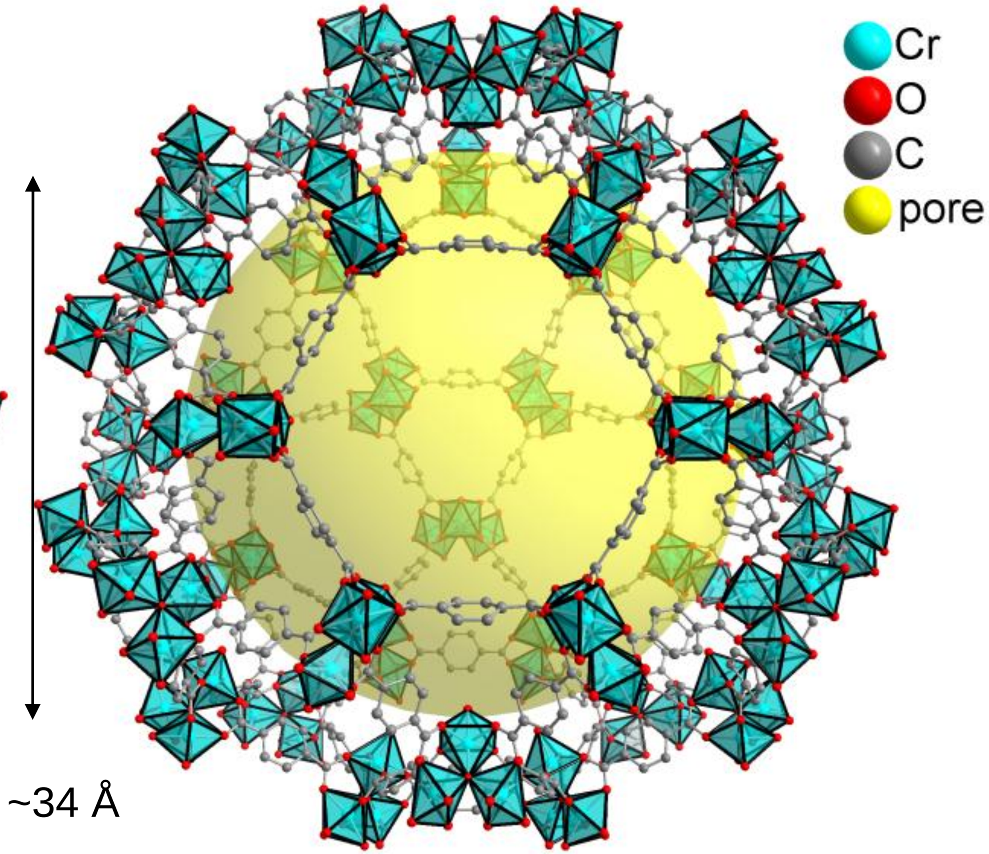
hexgonal + pentagonal + trigonal windows



MIL example:
3D-$[Cr_3(O)(bdc)_3(F,OH)(H_2O)_2]\cdot{\sim}25H_2O$ or MIL-101

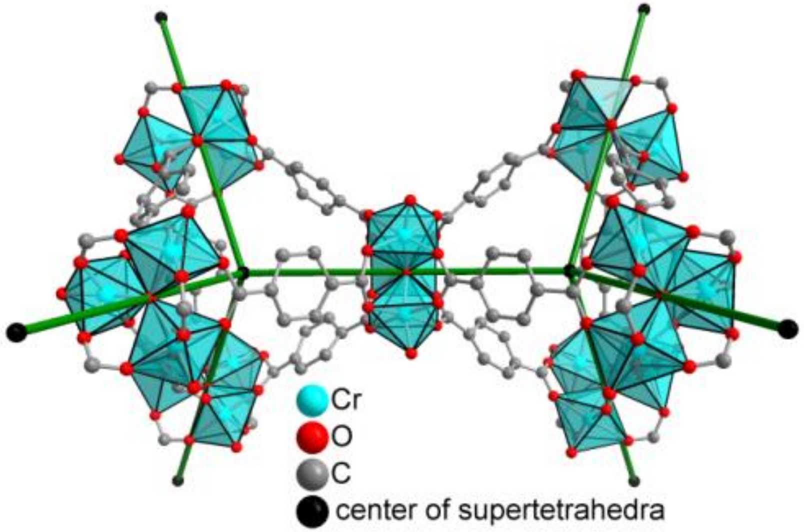
mesoporous cages:





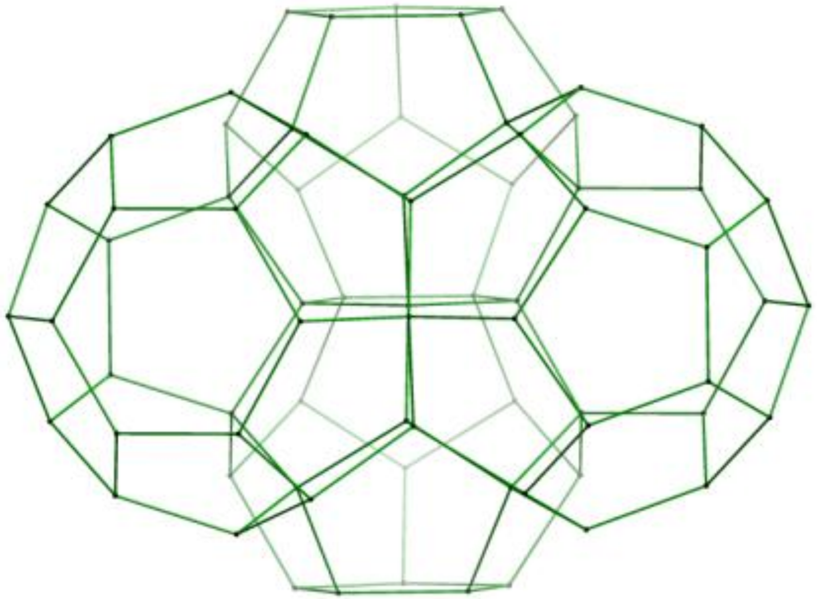
Building blocks for MIL-101, $[Cr_3(O)(BDC)_3(F,OH)(H_2O)_2]\cdot{\sim}25H_2O$. The benzene-1,4-dicarboxylate ligands bridge between trinuclear $\{Cr_3O\}$ building units. The largest aperture windows of the mesoporous cages which build up the MTN zeolite network are pentagonal and hexagonal rings. The yellow spheres in the mesoporous cages with diameter of 29 or 34 Å, respectively, take into account the van-der-Waals radii of the framework walls (water-guest molecules are not shown). The different objects are not drawn to scale

MIL example: 3D-$[Cr_3(O)(bdc)_3(F,OH)(H_2O)_2]\cdot{\sim}25H_2O$ or MIL-101



The vertex-sharing supertetrahedra

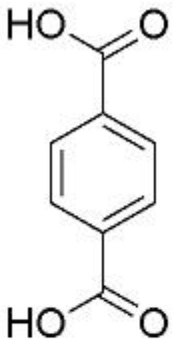
and MTN zeolite topology from two types of mesoporous cages with pentagonal and hexagonal windows

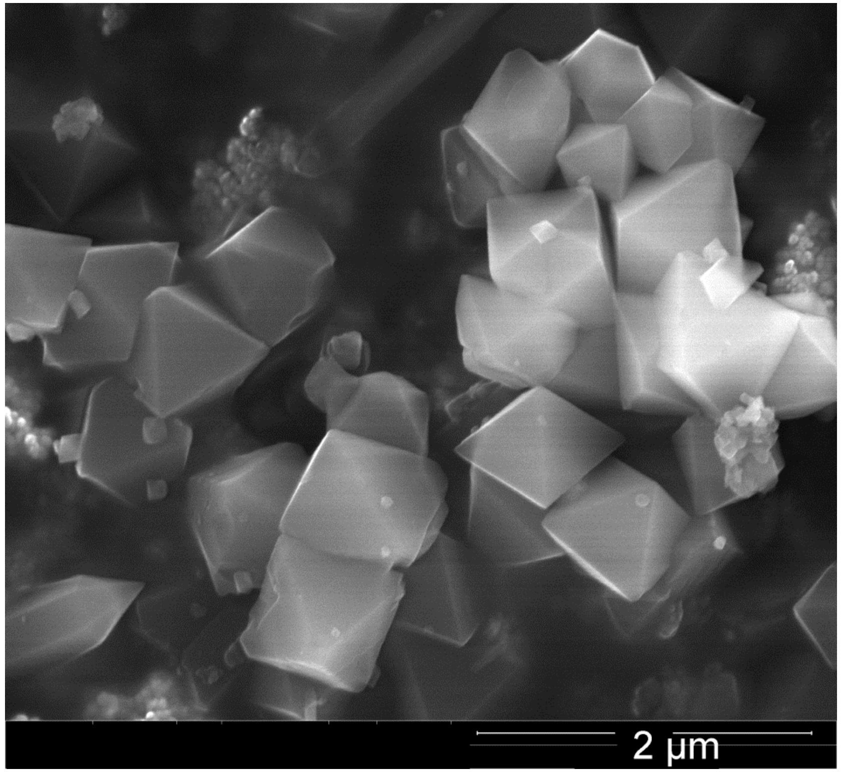


BET surface ~4000 m^2/g

G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S Surble and I. Margiolaki, Science **2005**, *309*, 2040–2042.

MIL example:
3D-$[Cr_3(O)(bdc)_3(F,OH)(H_2O)_2]\cdot{\sim}25H_2O$ or MIL-101

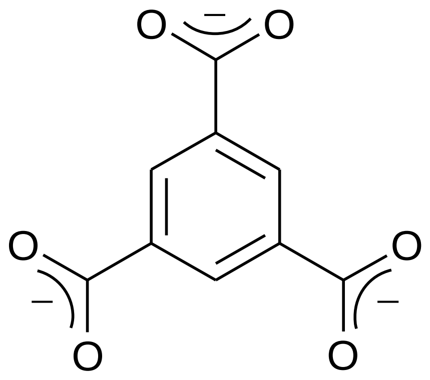




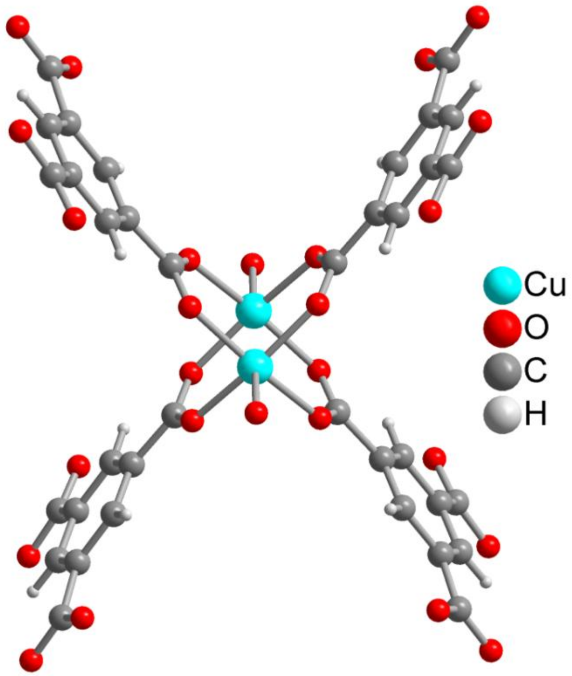
Tanh: (MIL101-je_17_01modif.tif)

MOF example:
3D-[$Cu_3(btc)_2(H_2O)_3$] (also called HKUST-1 or Cu-btc)

HKUST = Hongkong University of Science and Technology



benzene-1,3,5-tricarboxylate,
trimesate
btc



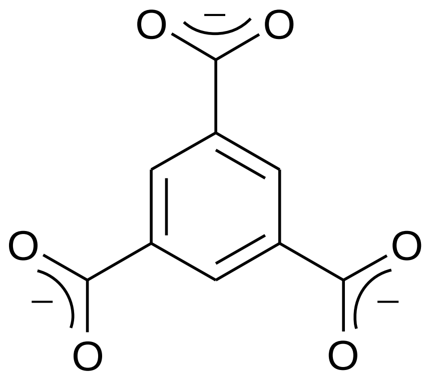
One of the most studied MOFs is copper trimesate, (“HKUST-1”) because of easy formation, high porosity and known properties associated with this compound.

3D-[$Cu_3(btc)_2(H_2O)_3$] (also called HKUST-1 or Cu-btc) is one of the first 3-dimensional porous coordination polymers that has been studied intensively. It contains {Cu_2} units coordinated by four carboxylate groups in the well-known paddle-wheel structure of copper acetate.

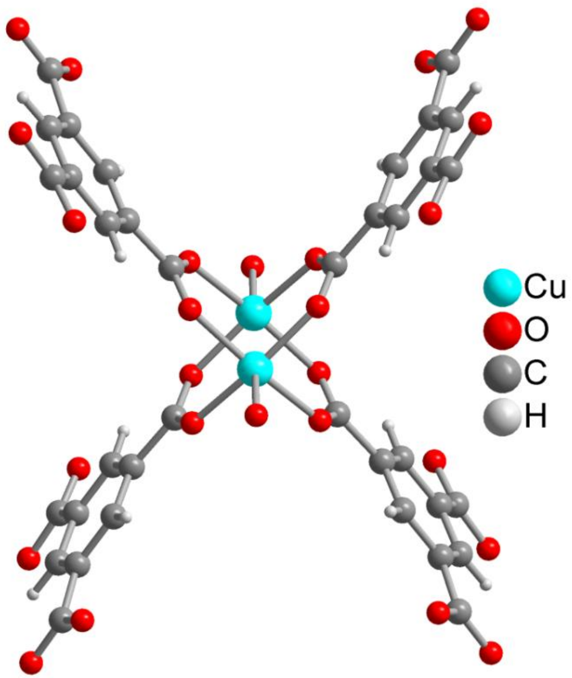
S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, 283, 1148-1150.

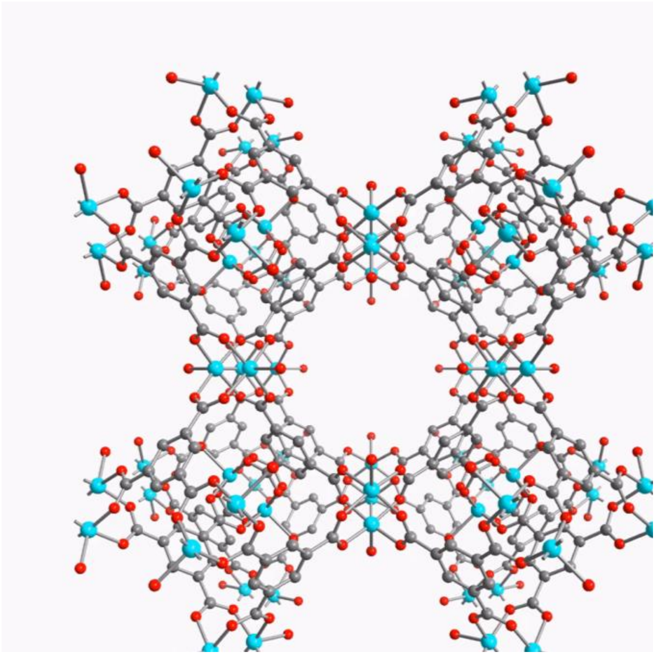
MOF example:
3D-$[Cu_3(btc)_2(H_2O)_3]$ (also called HKUST-1 or Cu-btc)

HKUST = Hongkong University of Science and Technology



benzene-1,3,5-tricarboxylate,
trimesate
btc

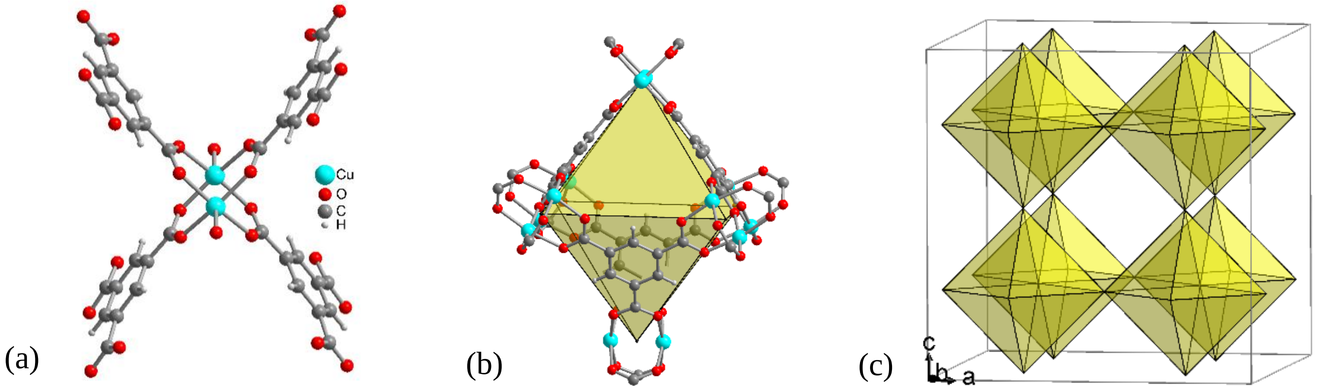




$\{Cu_2(btc)_4\}$ building unit and two views of the packing diagram with the cubic unit cell of 3D-$[Cu_3(btc)_2(H_2O)_3]\cdot{\sim}10H_2O$ (HKUST-1, a = 26.34 Å) to illustrate the zeolite analogy of this highly symmetric and porous framework. The disordered water molecules in the pores are not shown, nor are the H atoms on the aqua ligands and on carbon in the packing diagrams. The different objects are not drawn to scale.

S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, 283, 1148-1150.

MOF example:
3D-[$Cu_3(btc)_2(H_2O)_3$] (also called HKUST-1 or Cu-btc)

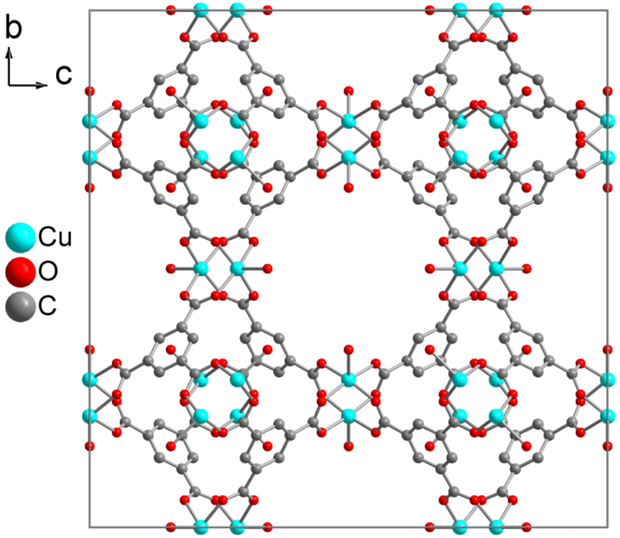


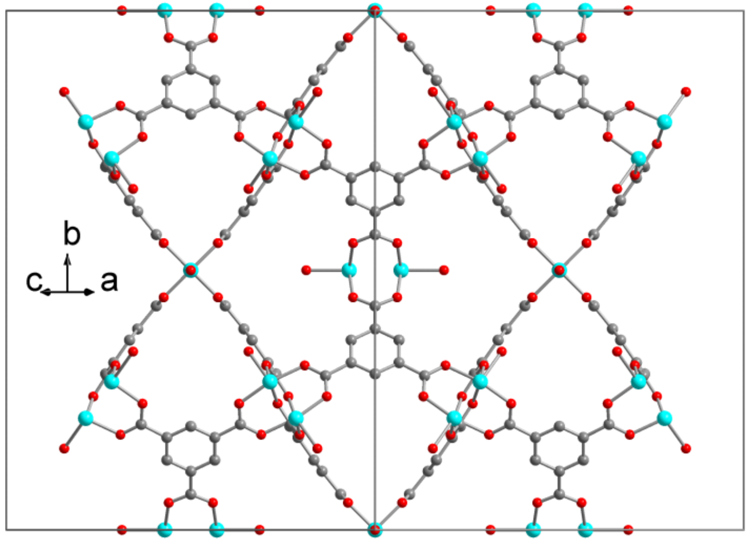
(a) $\{Cu_2(btc)_4\}$ "paddle-wheel" unit in Cu-btc (HKUST-1).

(b) The $\{Cu\}_2$ dumbbells sit at the corners of an octahedron. Four btc ligands each span opposite four of the eight faces of the octahedron.

(c) These octahedra form a porous 3D network via vertex linkage. The network is traversed by channels along the *a*, *b*, and *c* axis. The specific surface area is ~1300 m^2/g.

MOF example:
3D-[$Cu_3(btc)_2(H_2O)_3$] (also called HKUST-1 or Cu-btc)



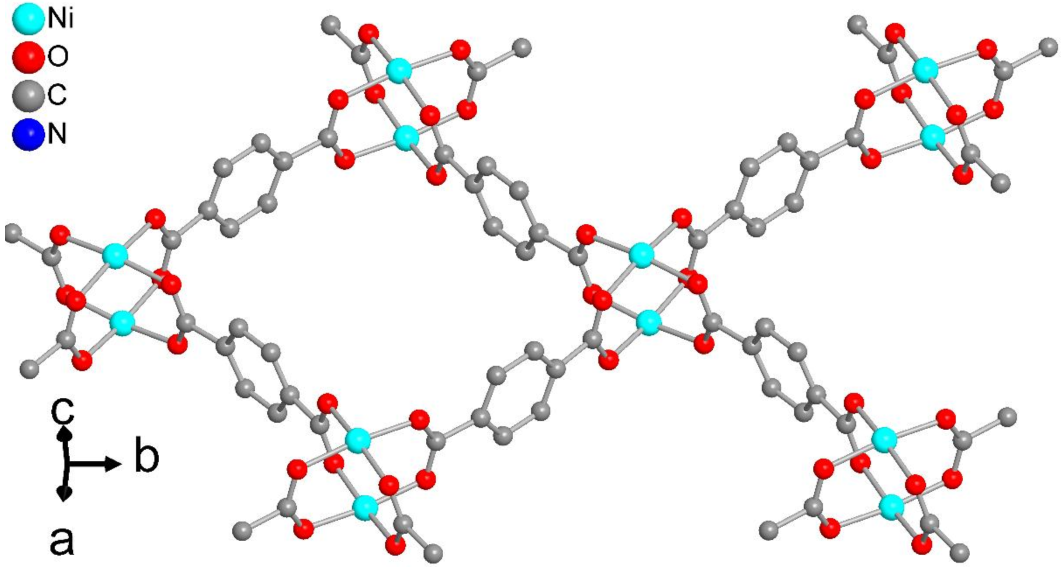


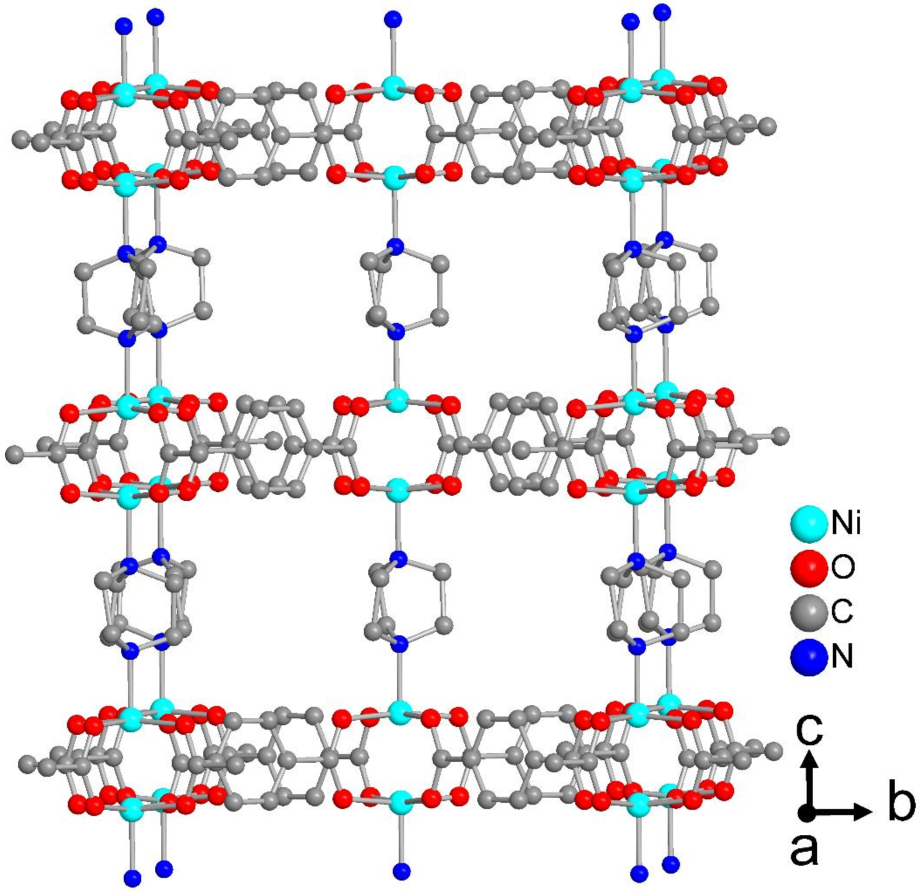
The 3D-coordination polymer [$Cu_3(btc)_2(H_2O)_3$] crystallizes with formation of a highly porous cubic structure with a complicated 3D network of channels. Along the *a*-axis there are large square channels of 9x9 Å (btc = benzene-1,3,5-tricarboxylate).

Cu-btc is stable up to 240 °C. Both the water of crystallization and the aqua ligands coordinating the copper atoms can be removed thermally without loss of the structural integrity and exchanged by pyridine ligands.
BET surface S_{BET} = 1500 m²/g

S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, 283, 1148-1150.

MOF example:
3D-[Ni/Zn/Cu_2(bdc)$_2$(DABCO)], DMOF-Ni/Zn/Cu



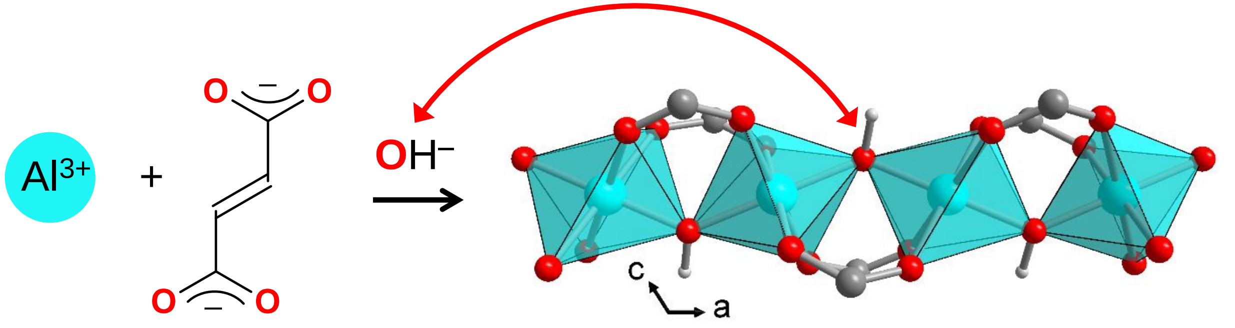


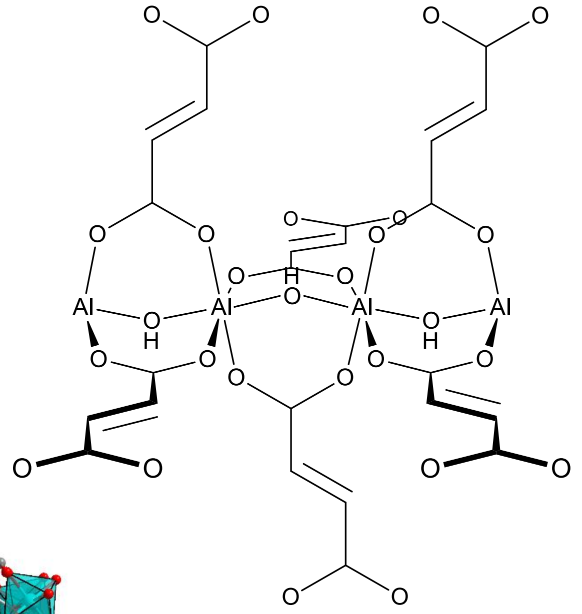
DMOF-Ni: P. Maniam, N. Stock, Investigation of Porous Ni-Based Metal–Organic Frameworks Containing Paddle-Wheel Type Inorganic Building Units via High-Throughput Methods. *Inorg. Chem.* **2011**, *50*, 5085-5097. https://doi.org/10.1021/ic200381f, CCDC 802892

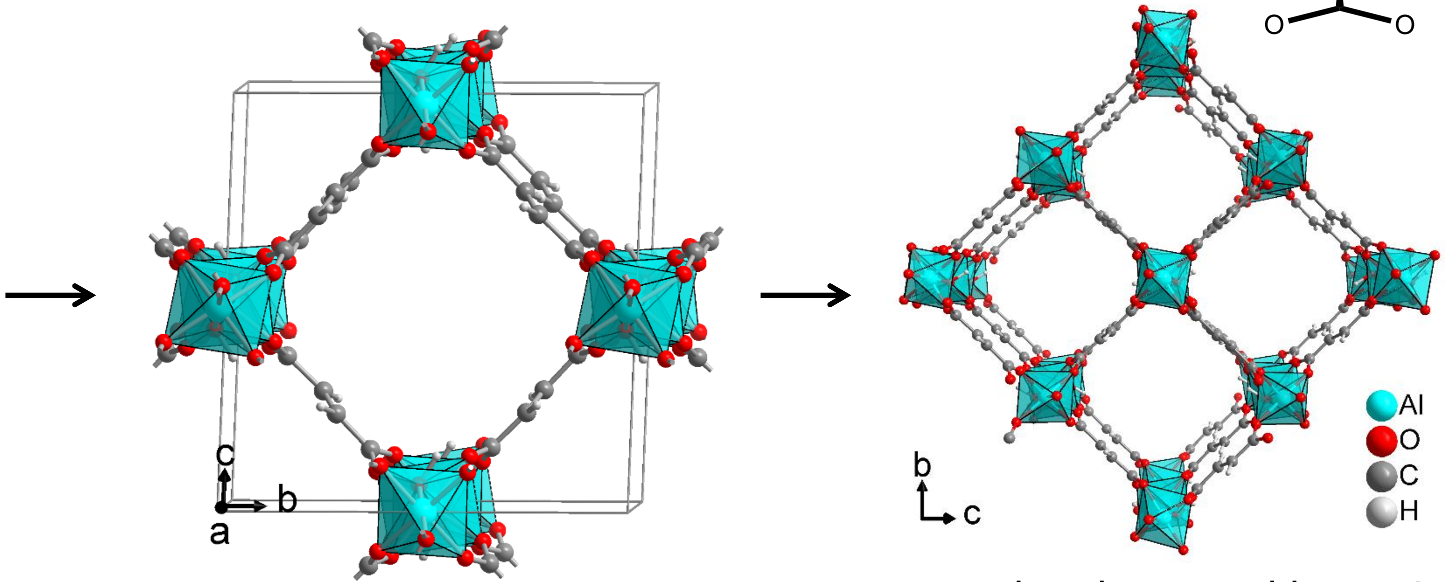
DMOF-Cu: R. Matsuda, W. Kosaka, R. Kitaura, Y. Kubota, M. Takata, S. Kitagawa, Microporous Structures Having Phenylene Fin: Significance of Substituent Groups for Rotational Linkers in Coordination Polymers. *Microporous Mesoporous Mater.* **2014**, *189*, 83-90. https://doi.org/10.1016/j.micromeso.2013.10.029, CCDC 260859

MOF example:
3D-[Al(OH)(O_2C-CH=CH-CO_2)], aluminium fumarate

(no MIL but similar structure to MIL-53)







Patented and reported by BASF SE: Basolite™ A520

Structure: E. Alvarez, N. Guillou, C. Martineau, B.t Bueken, B. Van de Voorde, C. Le Guillouzer, P. Fabry, F. Nouar, F. Taulelle, D. de Vos, J.-S. Chang, K. H. Cho, N. Ramsahye, T. Devic, M. Daturi, G. Maurin, C. Serre, *Angew. Chem. Int. Ed.* **2015**, *54*, 3664-3668