Metal–Organic Frameworks: From Structure to Function

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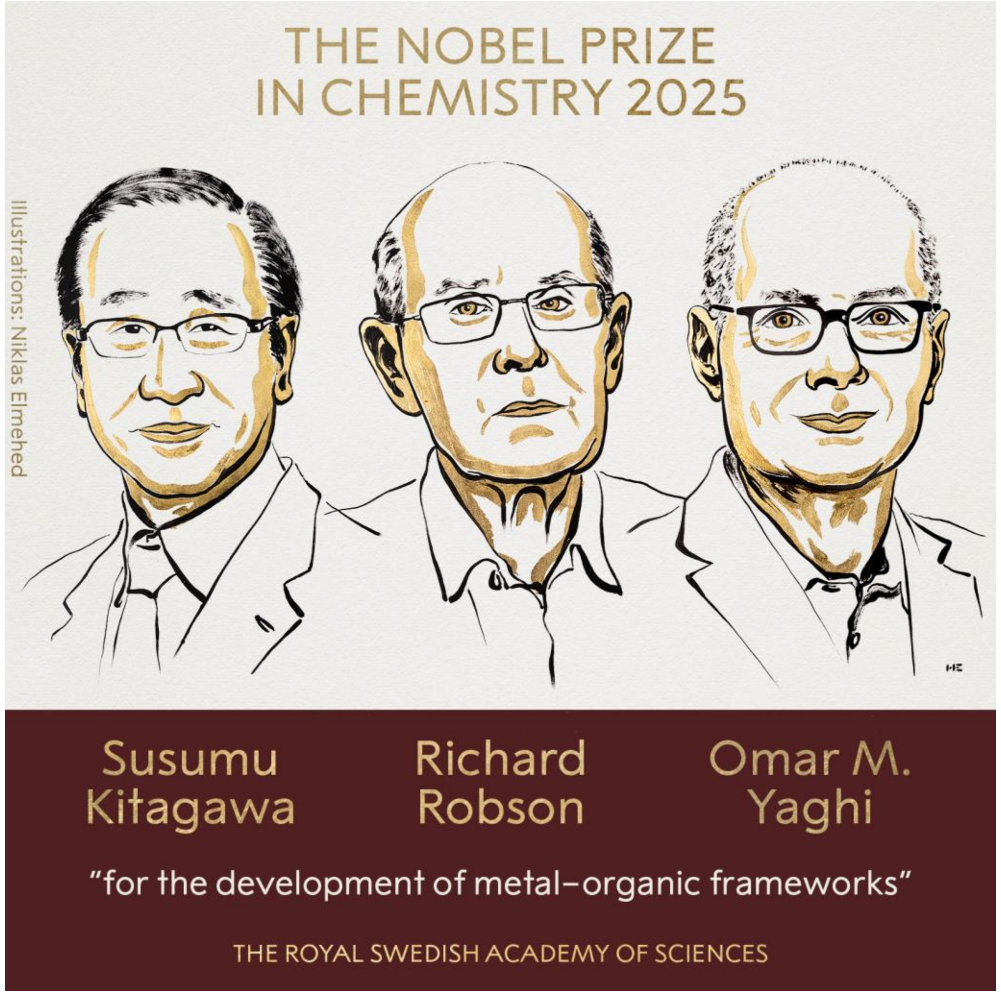
UNIVERSITY OF LIVERPOOL

MOFs won the Nobel Prize in Chemistry!



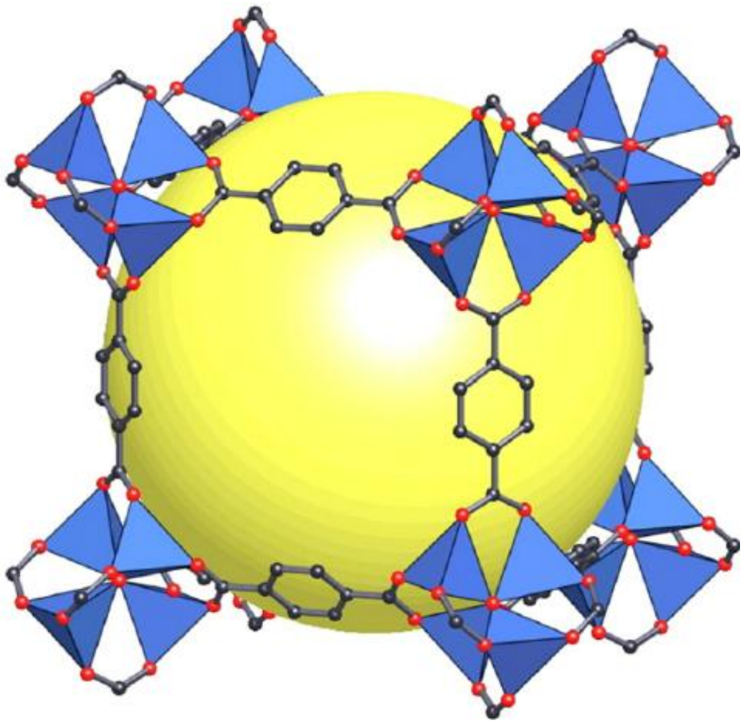
Metal–organic frameworks (MOFs)

- Metal–organic frameworks (MOFs) are network solids which consist of metal ions or clusters connected to organic linkers

- Scope to modulate their properties via:
    - Metal centres
    - Linker
    - Defect formation

- Their cage-like structure typically leads to a void space within the framework known as a 'pore'

- This porosity leads to high surface areas



MOF-5 (IRMOF-1)
$Zn_4O(BDC)_3$
Zn centres with
1,4-benzenedicarboxylate (BDC) linkers

H. Li et al., *Nature*, 1999, **402**, 276-279.

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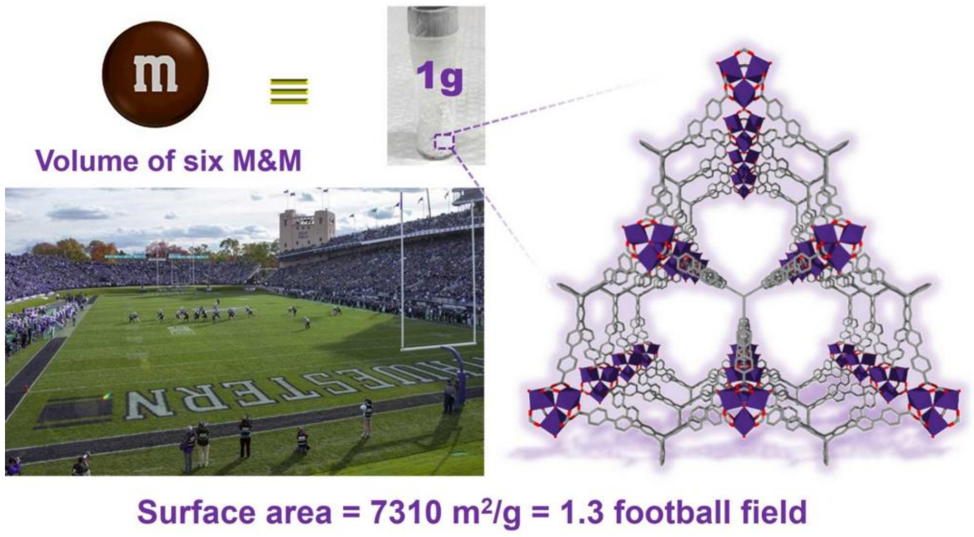
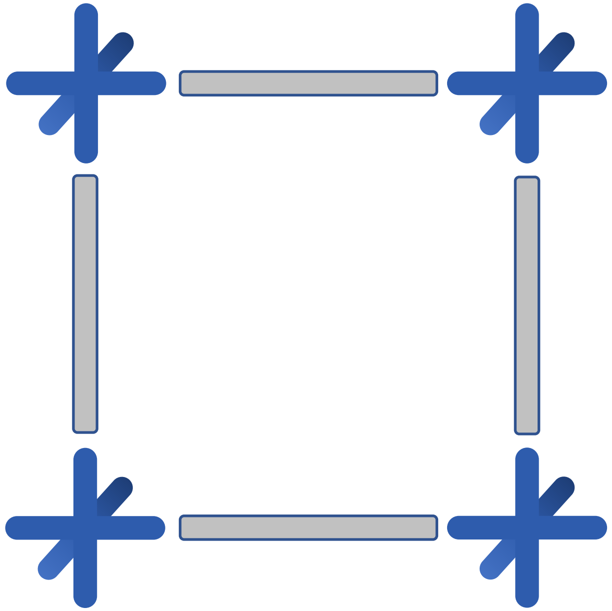
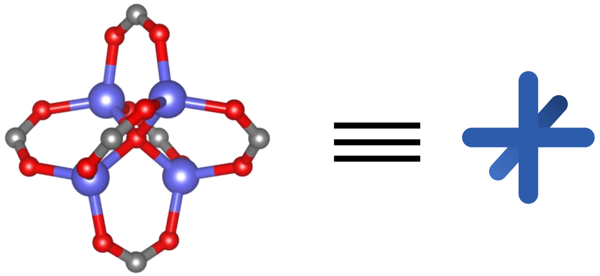


1g of MOF can have a greater surface area than a football field!

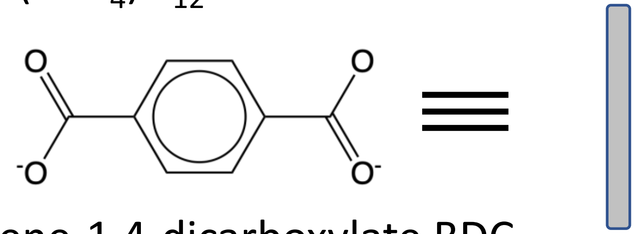
Metal–organic frameworks (MOFs)

- Framework is formed by polydentate ligands (organic linkers) coordinating to metal centres
- Carboxylate linkers are most common, but various functionalities, such as imidazolates are possible
- SBUs – small, well-defined clusters of metal ions that act as repeating nodes in the structure





$(OZn_4)O_{12}$ cluster



Benzene-1,4-dicarboxylate BDC

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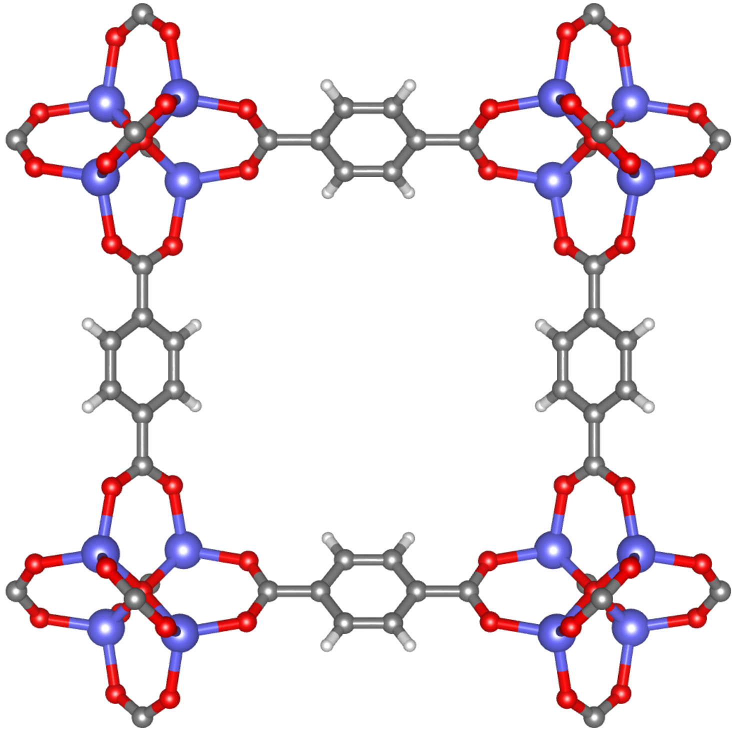
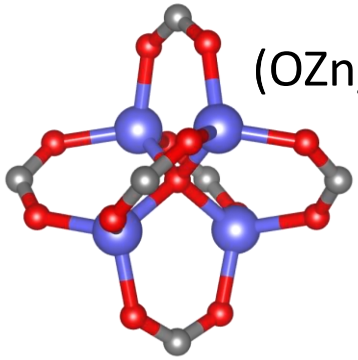
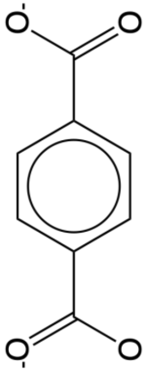




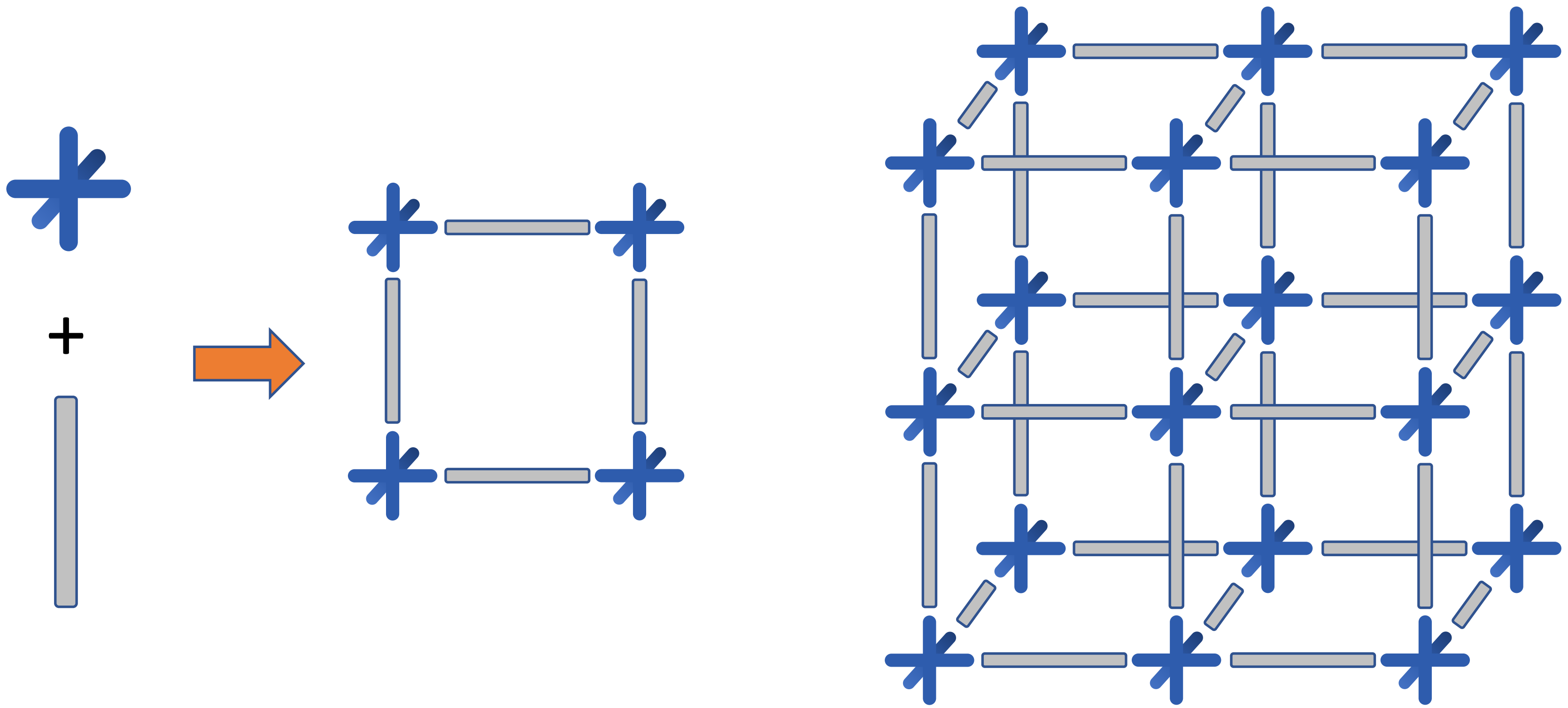
$(OZn_4)O_{12}$ cluster



BDC

SBUs

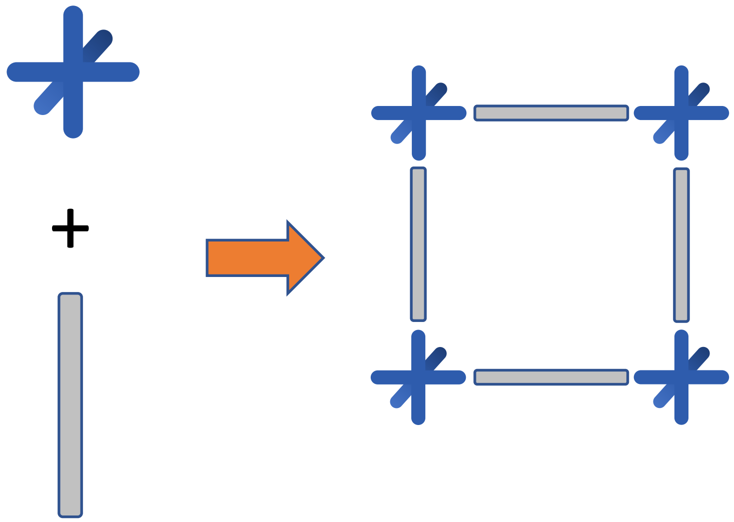
Reticular chemistry

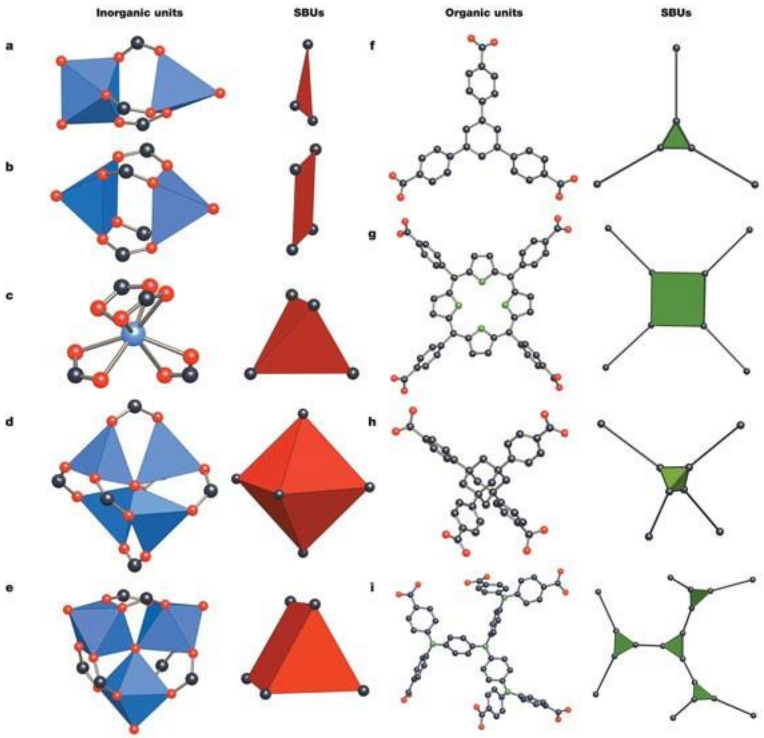


- Chemical components form nodes and linkers in a network
- The geometrical diversity of metal ion and clusters combines with synthetic diversity of organic linkers
- Enables ‘controlled’ assembly of extended architectures

O. M. Yaghi et al., *Nature*, 2003, **423**, 705-714.

Reticular chemistry





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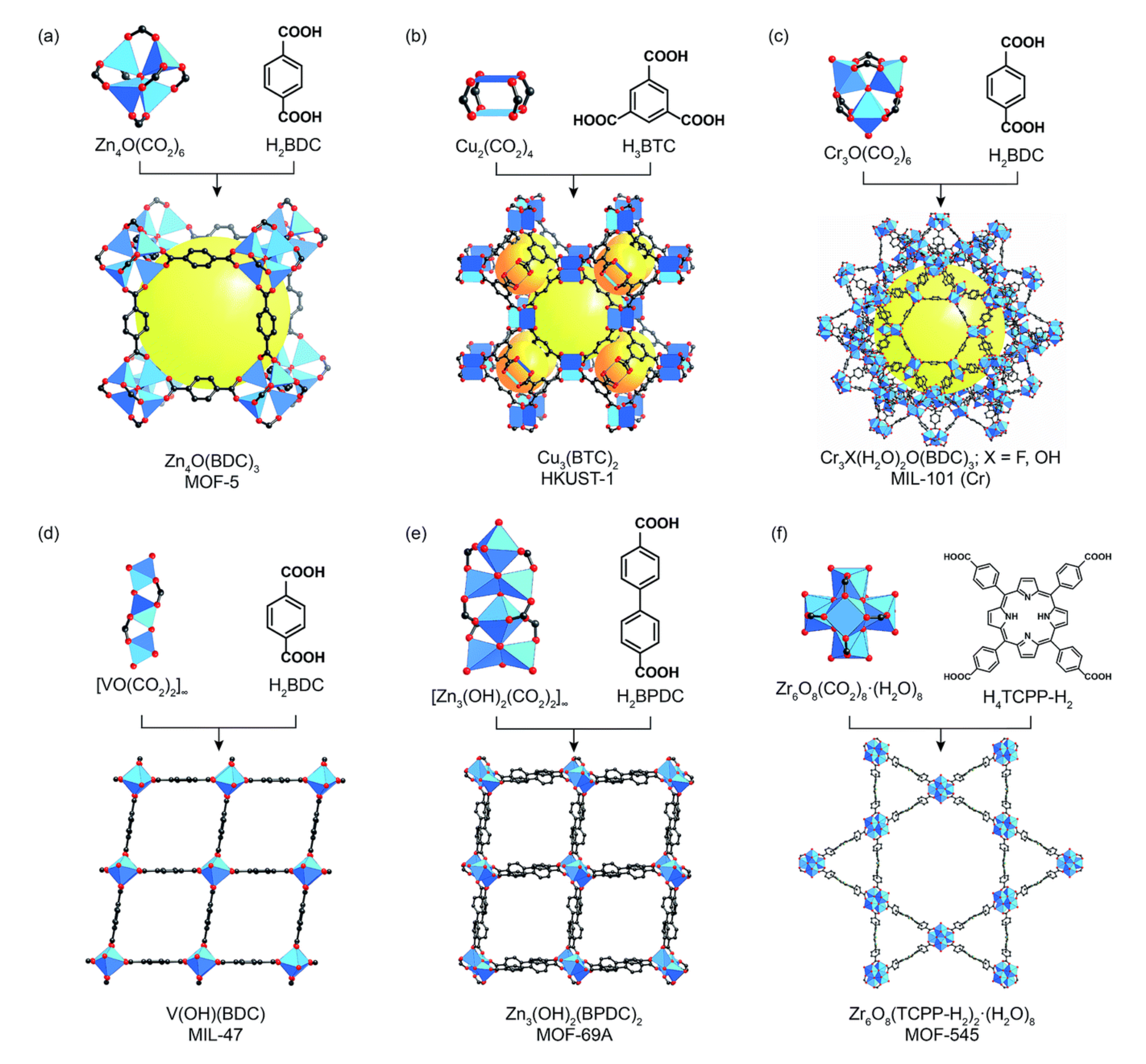
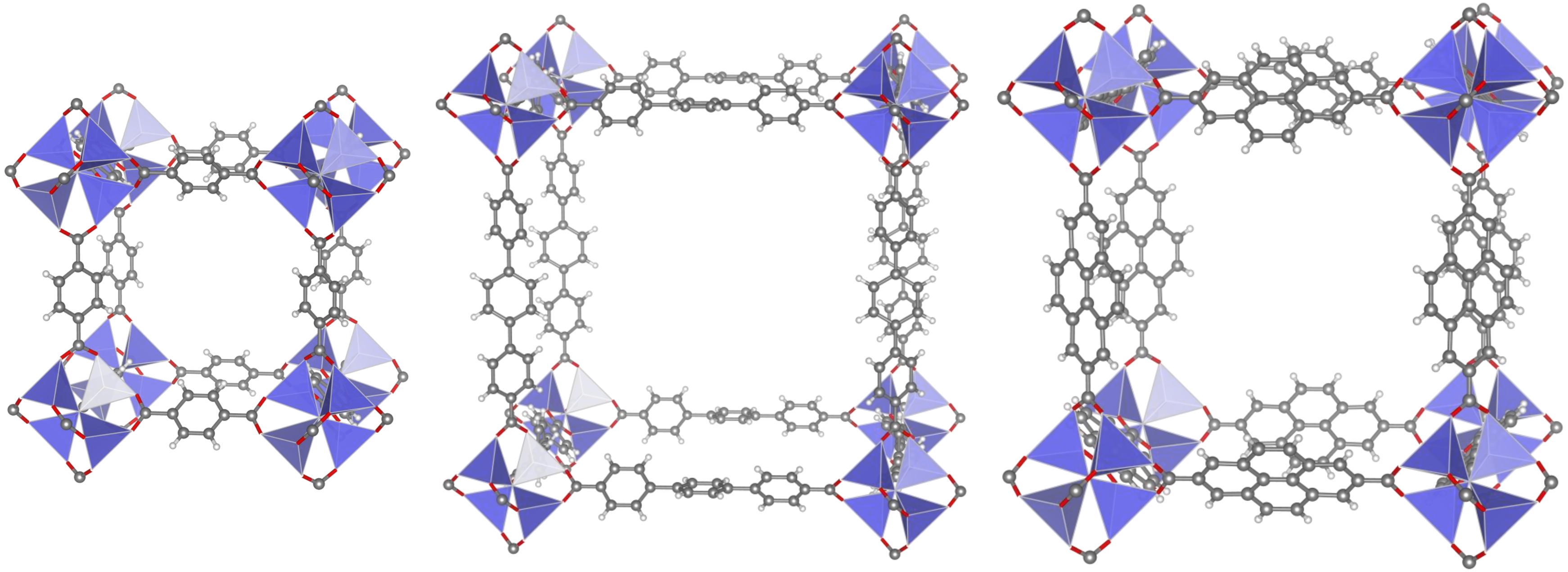


B. Rungtaweevoranit et al., *Faraday Discuss*, 2017, **201**, 9-45.

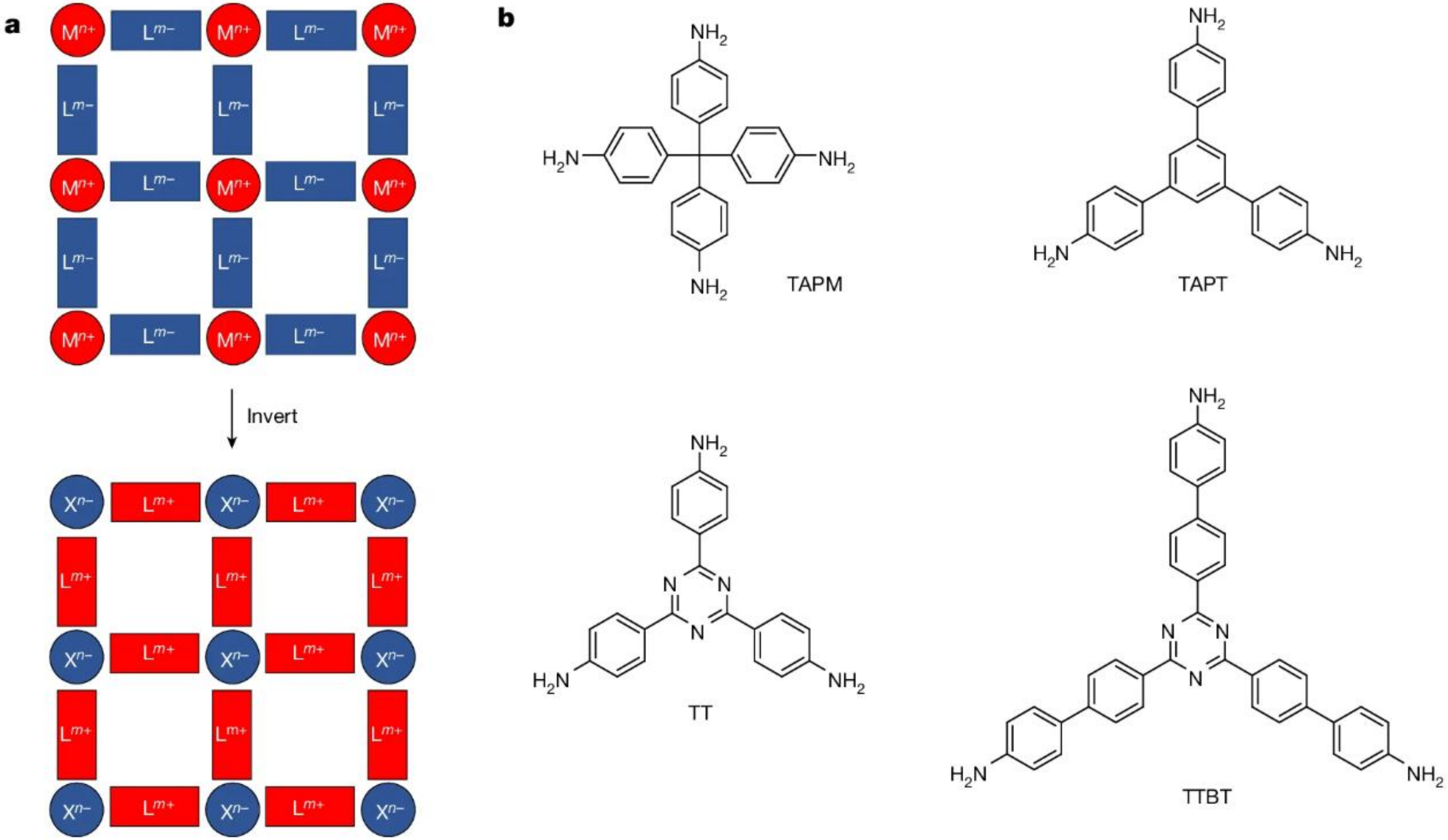
Crystal engineering: Isoreticular MOFs



- For some families of MOFs it is possible to change the organic linker and maintain the same framework type
- Relatively strong metal-linker interactions are conserved, but the linker can be swapped
- Modulates the pore size and chemical environment of guests

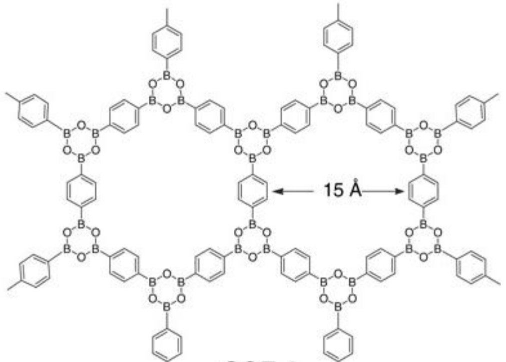
Porous isoreticular non-metal organic frameworks

Andy Cooper

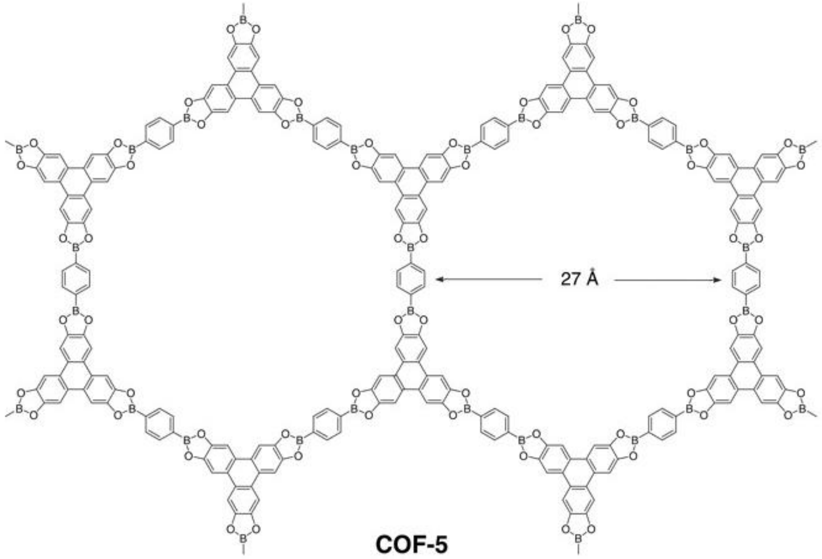


M. O'Shaughnessy et al., *Nature*, 2024, **630**, 102-108.

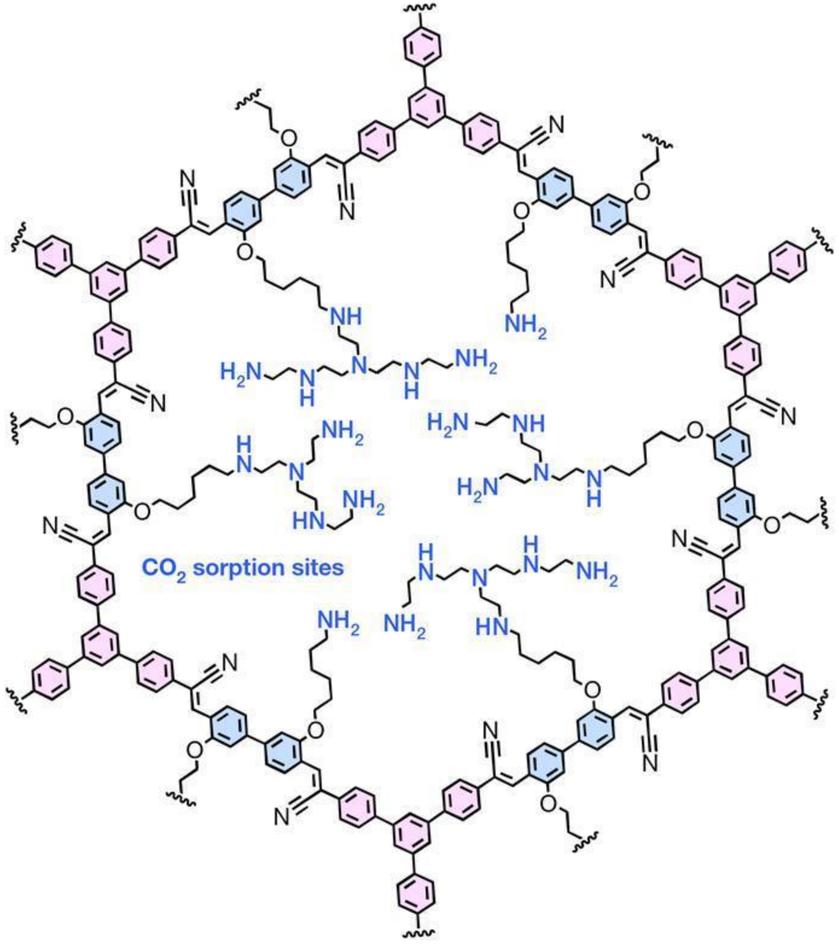
Covalent organic frameworks (COFs)



COF-1



COF-5

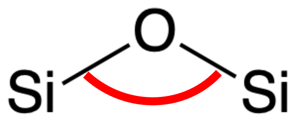


COF-999
[(TCPB)$_2$(BPDA-NH$_2$)$_3$(C$_2$H$_5$N)$_n$]$_{olefin}$

A. P. Côté et al., *Science*, 2005, **310**, 1166-1170.

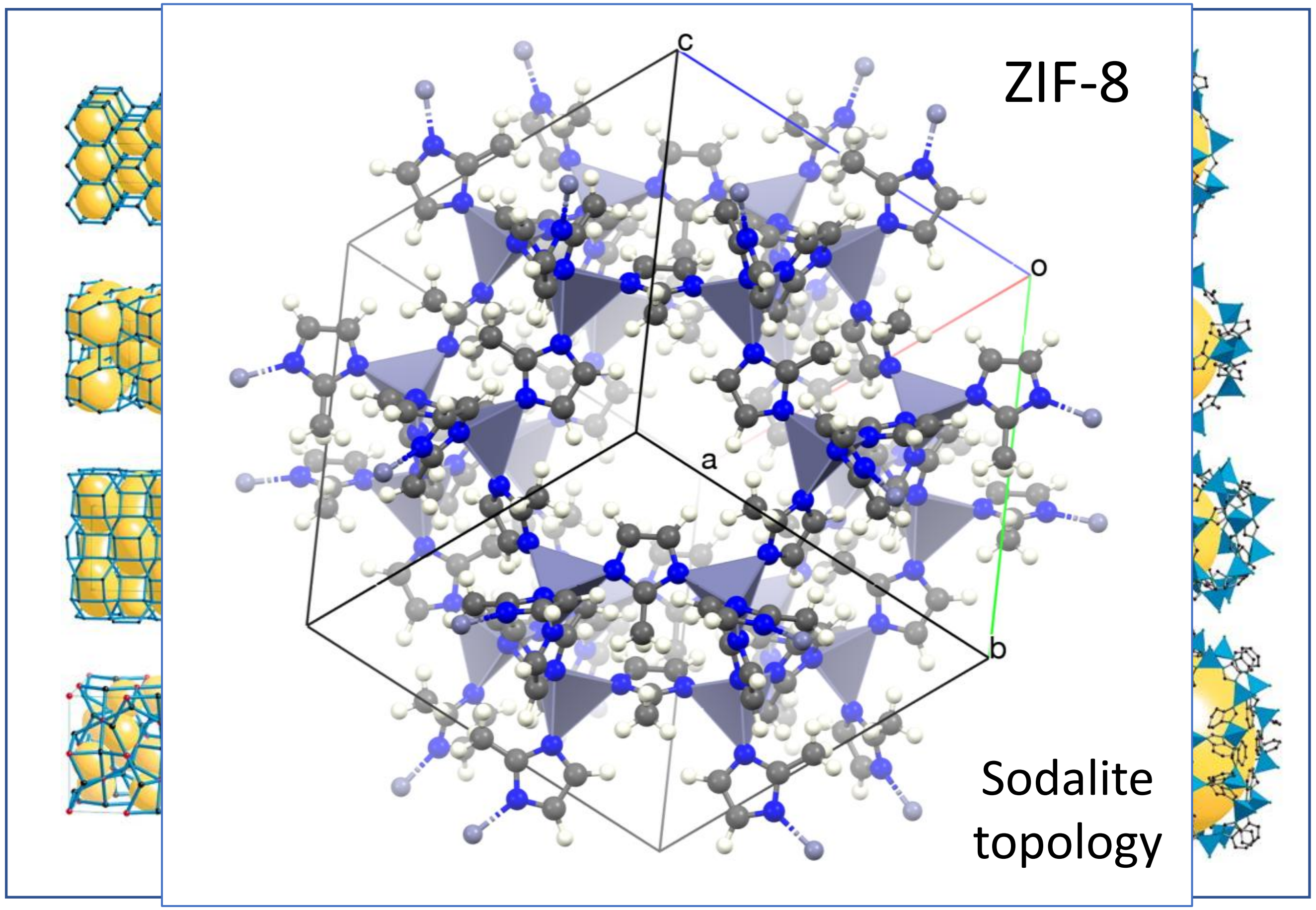
Z. Zhou et al., *Nature*, 2024, **635**, 96-101.

Zeolitic imidazolate frameworks (ZIFs)

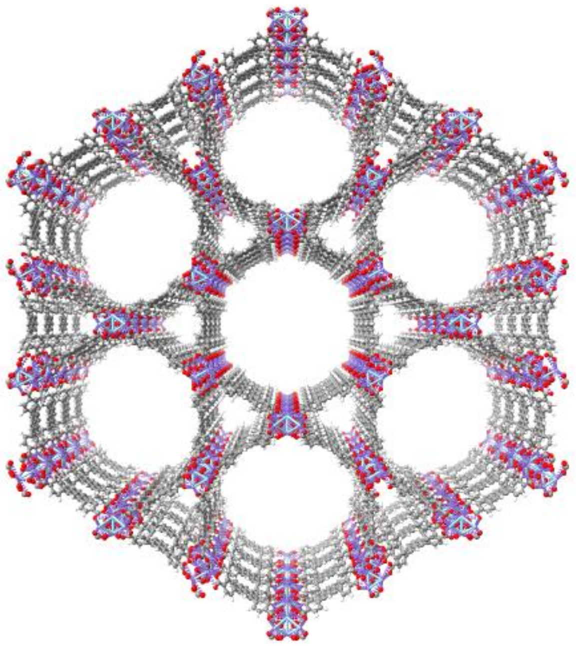


∠ Si–O–Si ≈ 145°

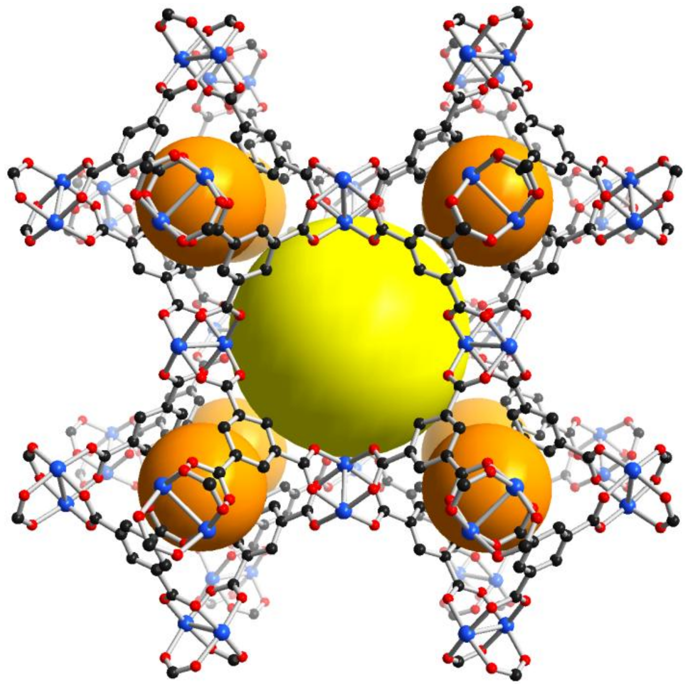
∠ M–Im–M ≈ 145°



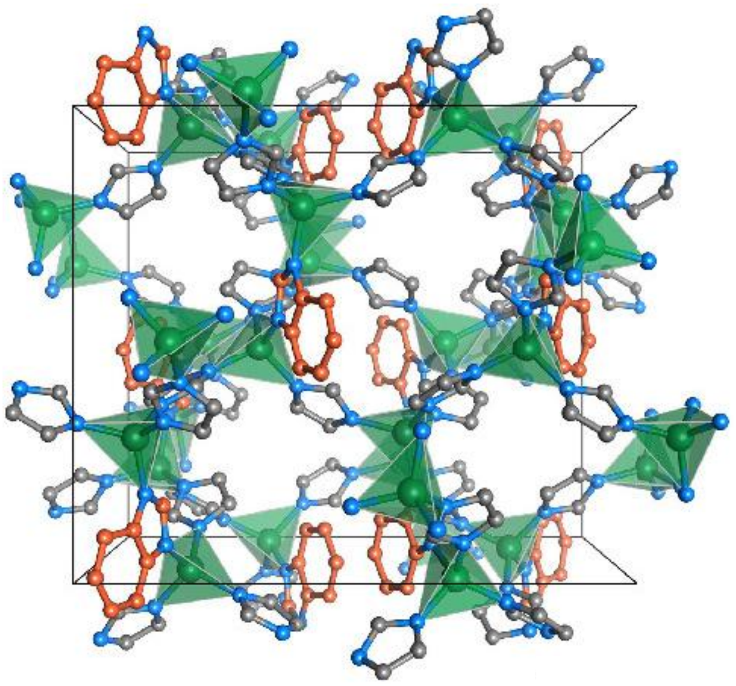
Some common MOFs



NU-1000
Zirconium-based
(yellow)

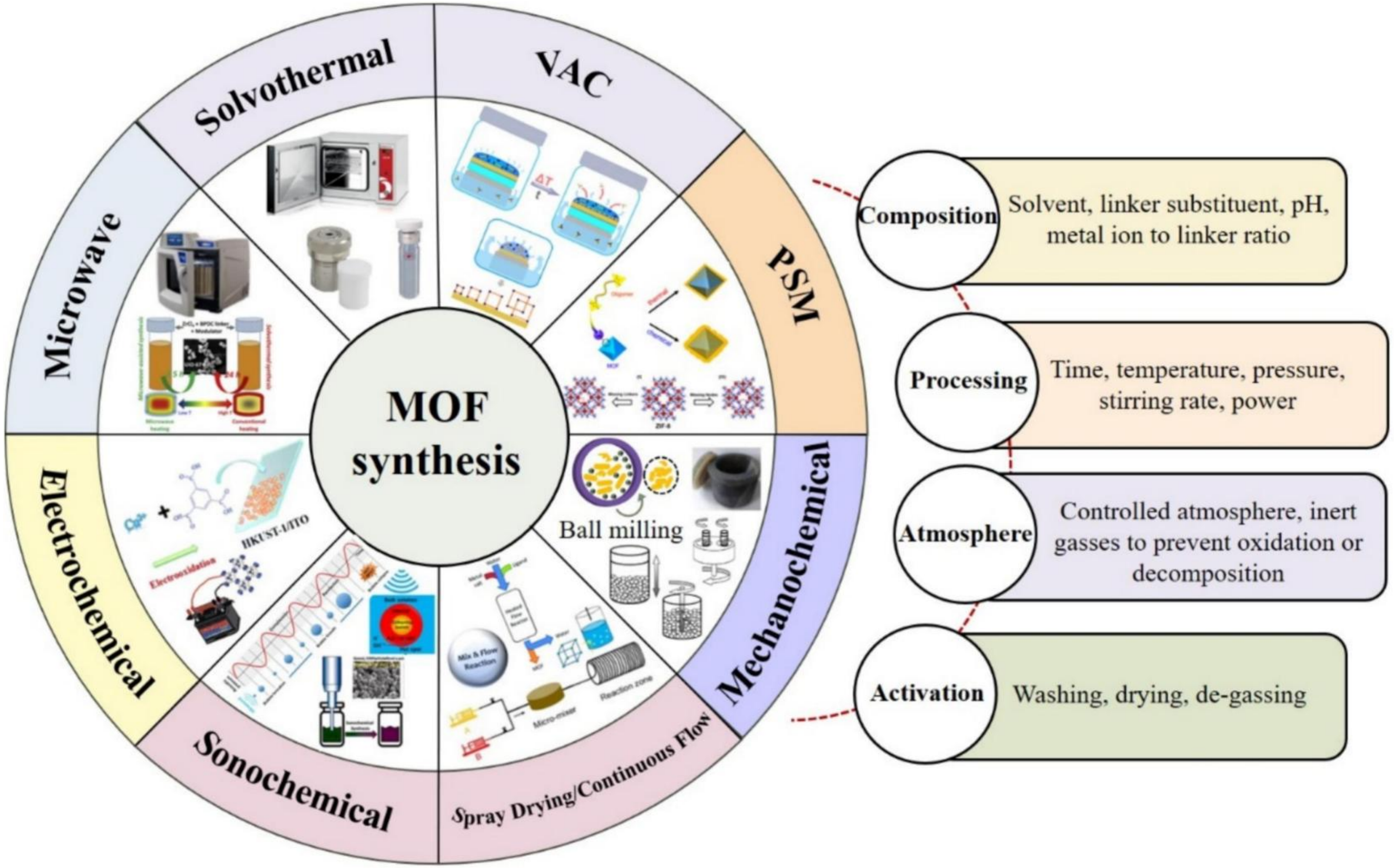


HKUST-1
Copper-based
(blue)



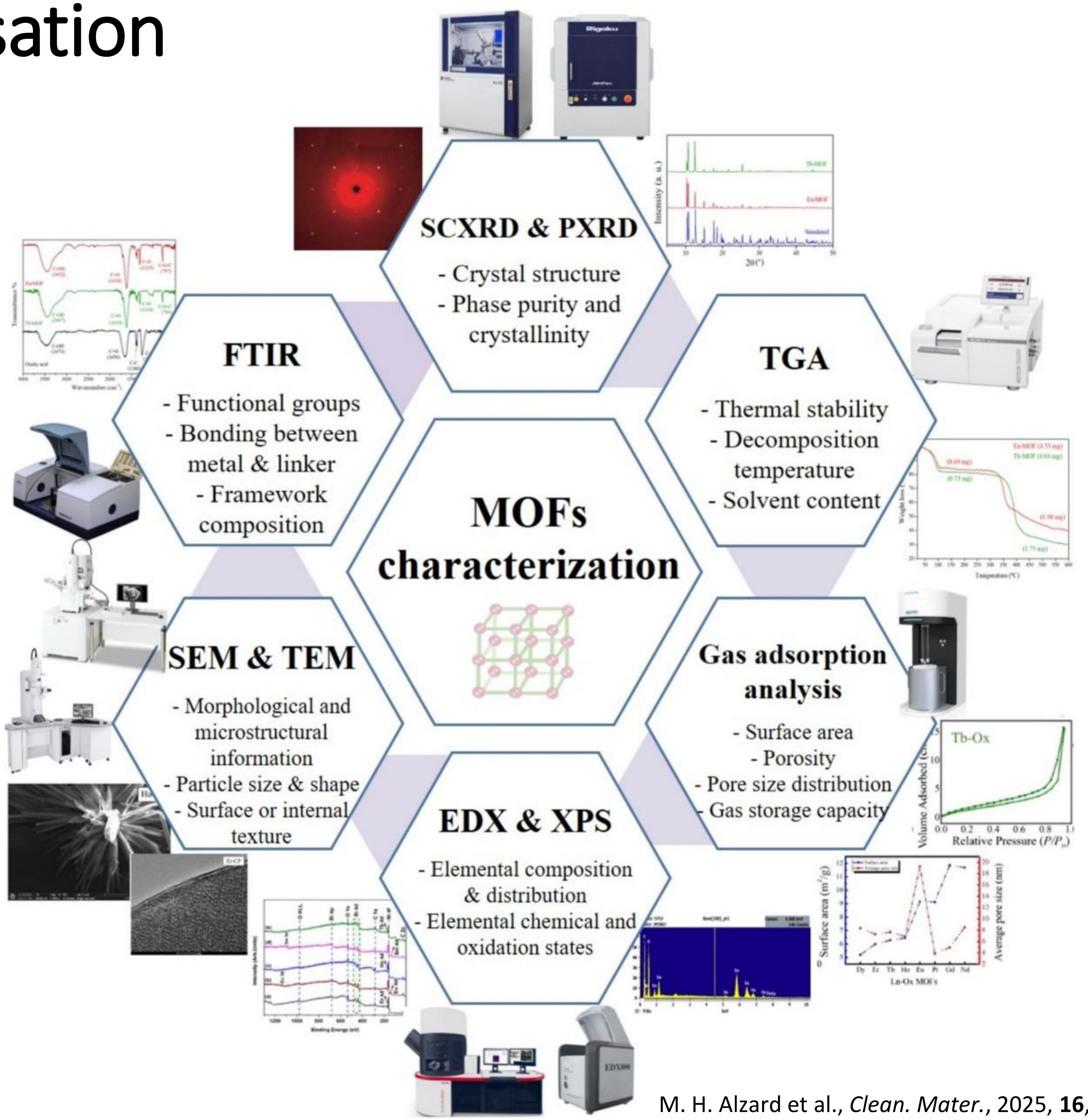
ZIF-62 (Zn/Co)
Zinc or cobalt-based
(colourless or purple)

MOF synthesis



M. H. Alzard et al., *Clean. Mater.*, 2025, **16**, 100314.

MOF characterisation



M. H. Alzard et al., *Clean. Mater.*, 2025, **16**, 100314.

Tuning MOF properties

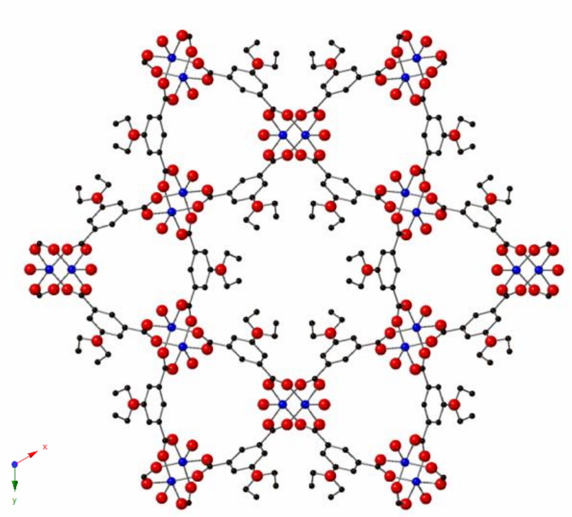
- **Metal centres**
  - Structure type – change coordination
  - Catalytic properties, *e.g.*, open metal sites

- **Organic linker**
  - Essentially endless possibilities
  - Structure type – change denticity
  - Maintain structure type – change pore dimensions (IRMOFs)
  - Chemical environment in pores – hydrophobicity, catalytic, polarity, specific chemical functionalities

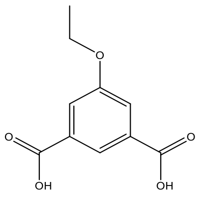
- **Synthesis and post-synthetic modifications**

- **Defect engineering**

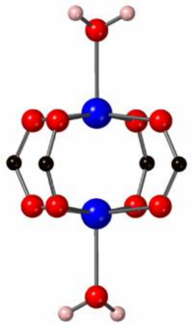
Water stability in copper MOFs



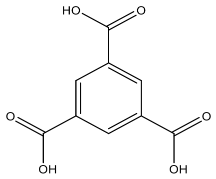
STAM-17-OEt



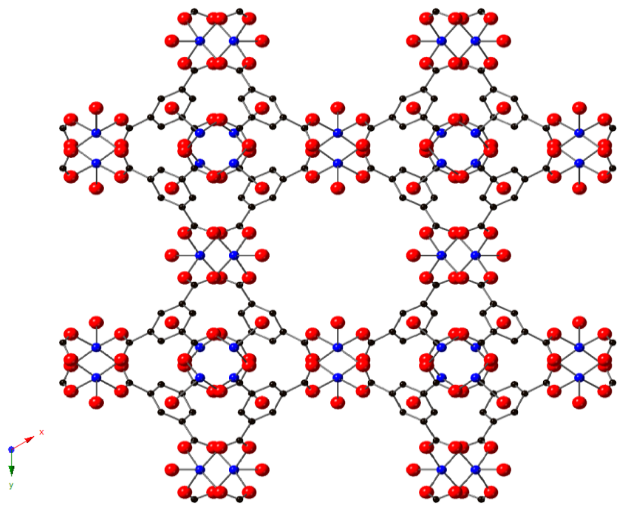
5-ethoxy isophthalic acid



Copper paddlewheel



Trimesic acid



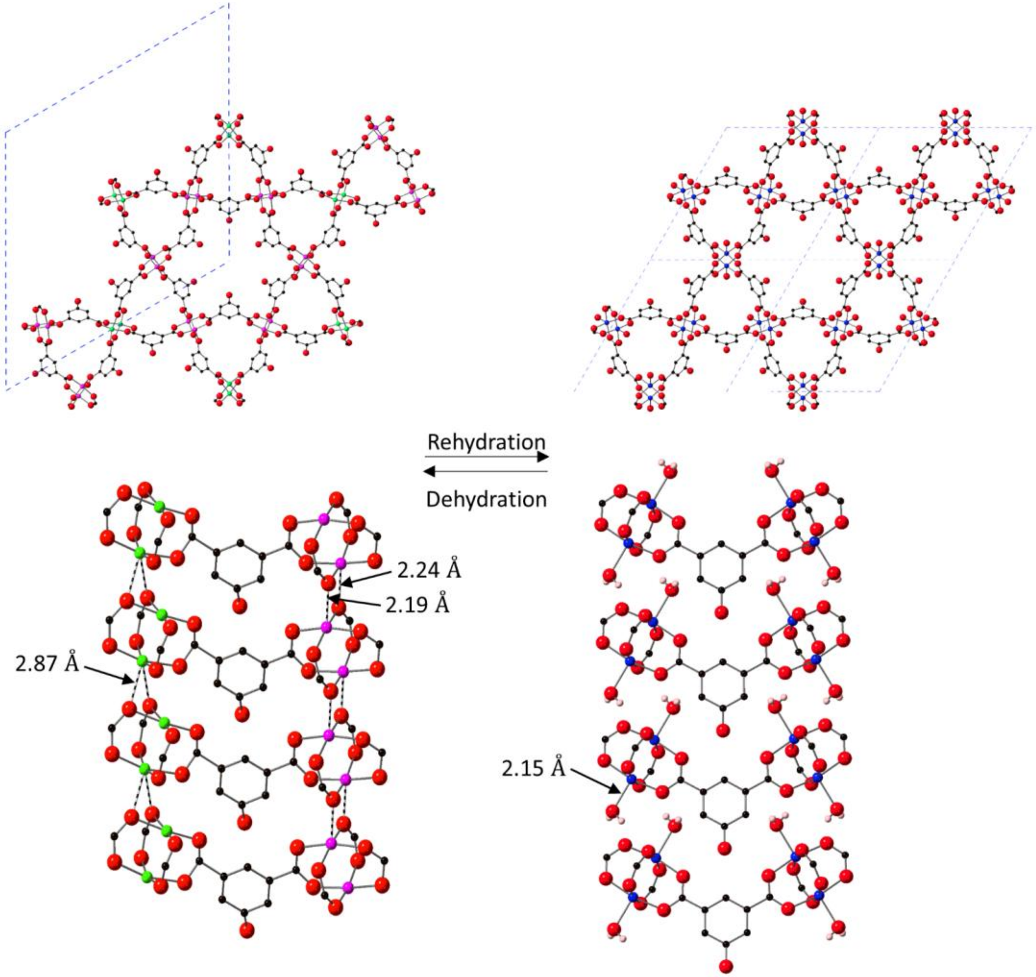
HKUST-1

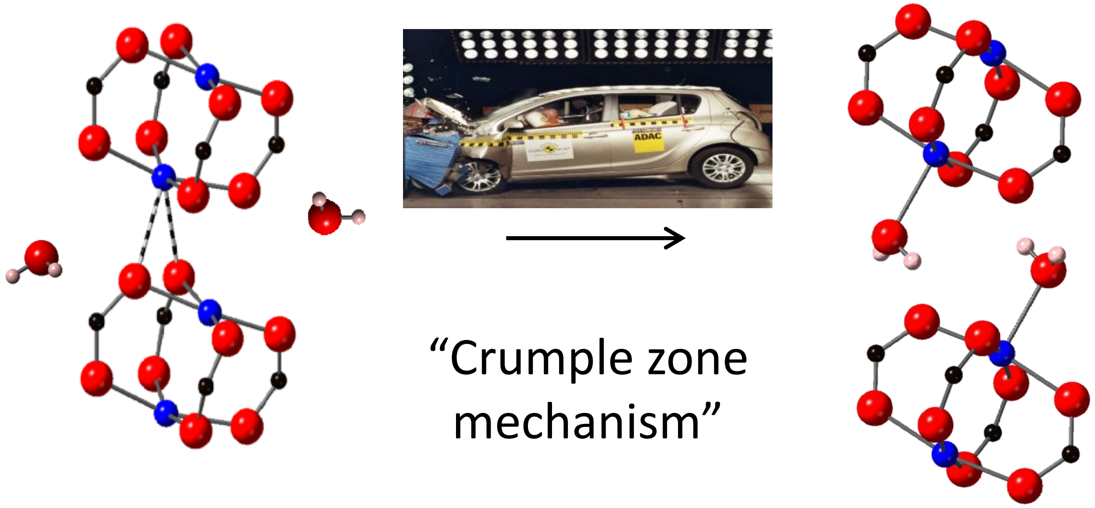
- Copper paddlewheel dimer units present in both structures.
- Similarities in syntheses and structures allow the comparison of properties.
- HKUST-1 is affected by long-term water instability, is STAM-17-OEt similarly affected?

L. N. McHugh et al., *Nat. Chem.*, 2018, **10**, 1096-1102.

S. S-Y. Chui et al., *Science*, 1999, **283**, 1148-1150.

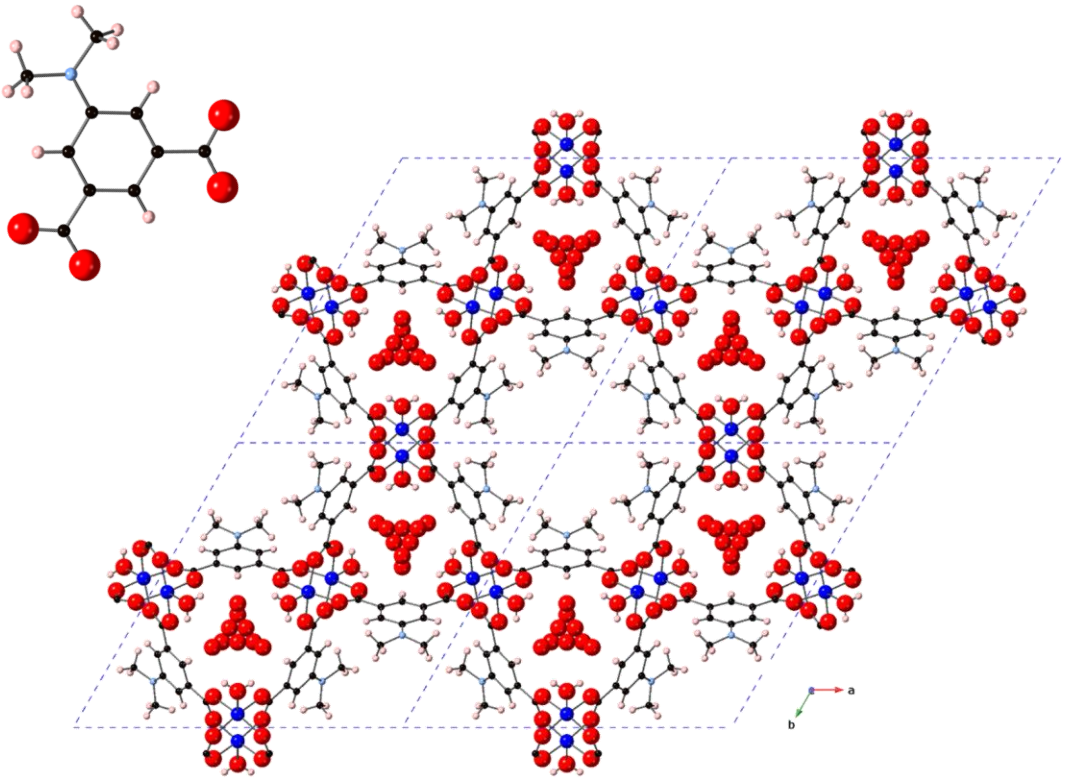
Hemilability in copper MOFs

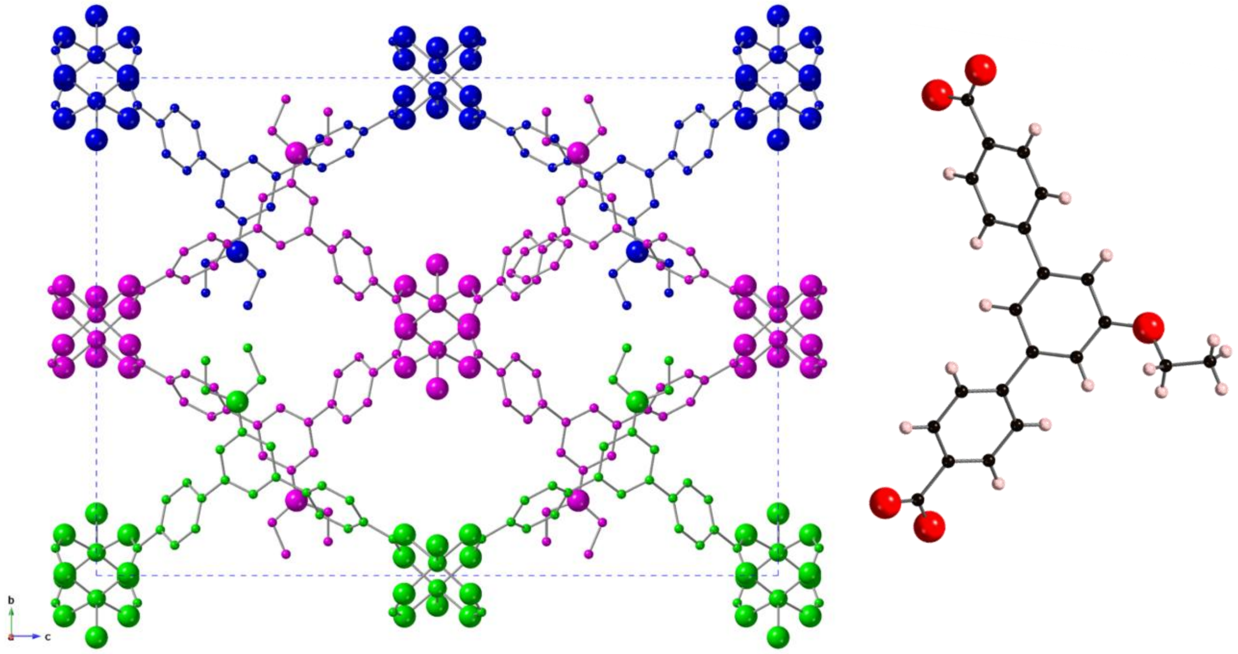




L. N. McHugh et al., *Nat. Chem.*, 2018, **10**, 1096-1102.

Structural variations

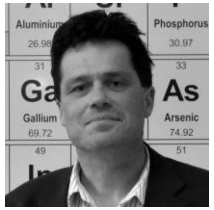




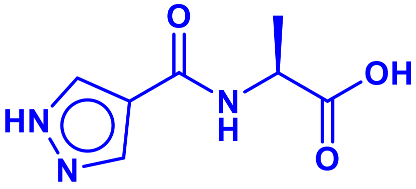
L. N. McHugh et al., *CrystEngComm*, 2019, **21**, 5387-5391.

L. N. McHugh et al., *Cryst. Growth. Des.*, 2020, **20**, 39-42.

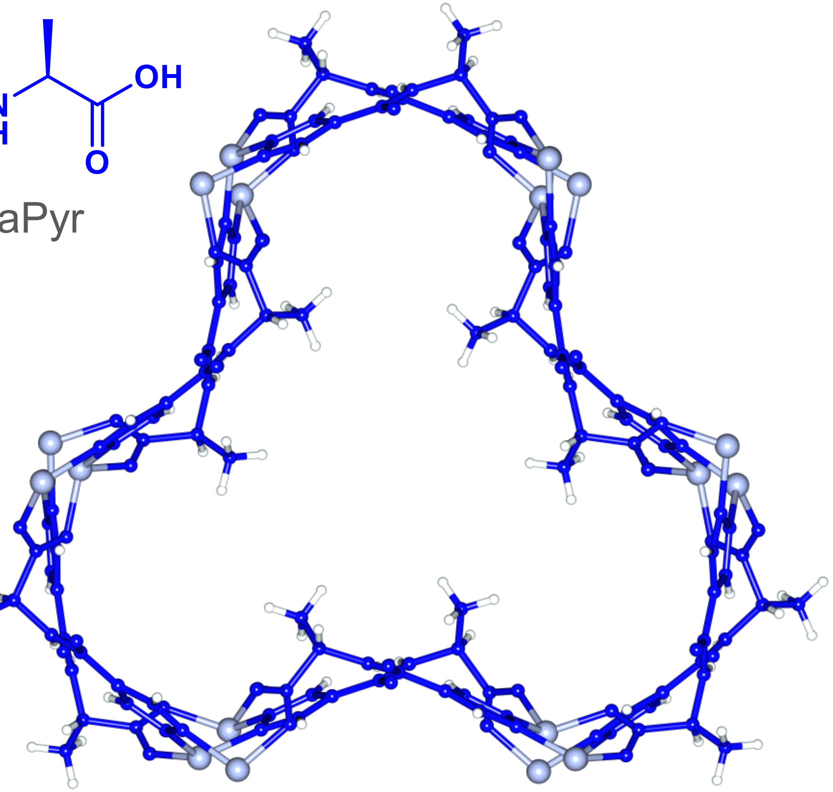
Ordered sidechains of flexible MOFs



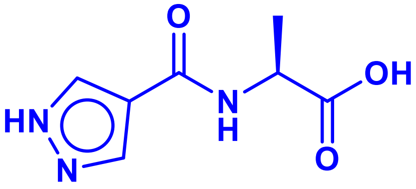
Matt Rosseinsky



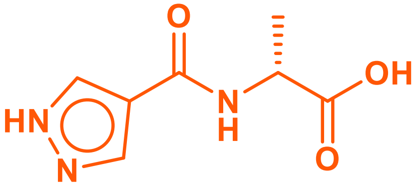
L-H_2AlaPyr



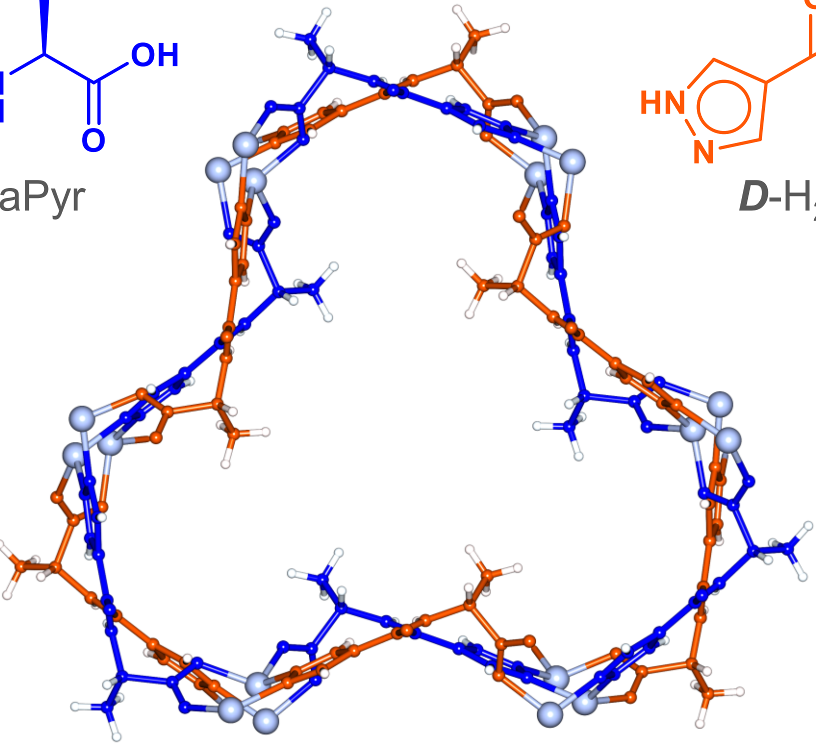
[Zn_2(*L*-AlaPyr)$_2$]



L-H_2AlaPyr



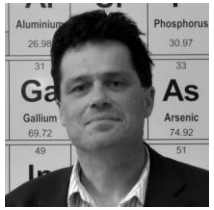
D-H_2AlaPyr



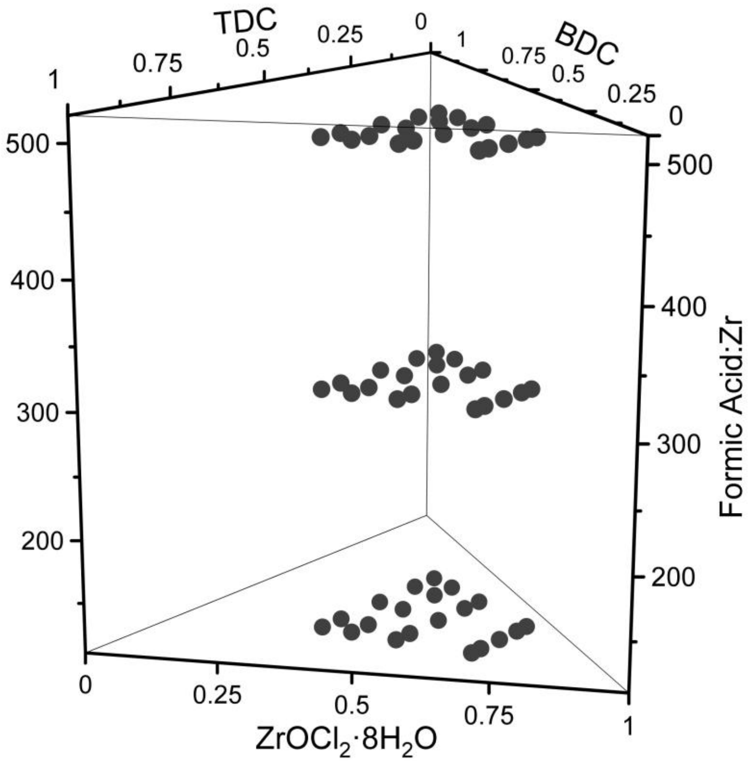
[Zn_2(*L*-AlaPyr)(*D*-AlaPyr)]

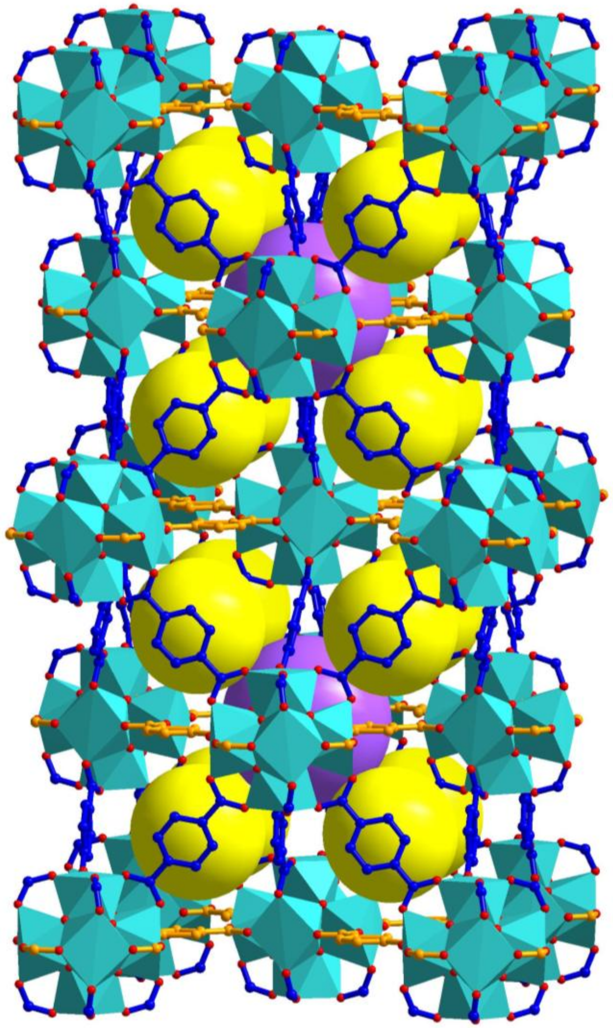
D. Markad et al., *Angew. Chem. Int. Ed.*, 2024, **63**, e202411960.

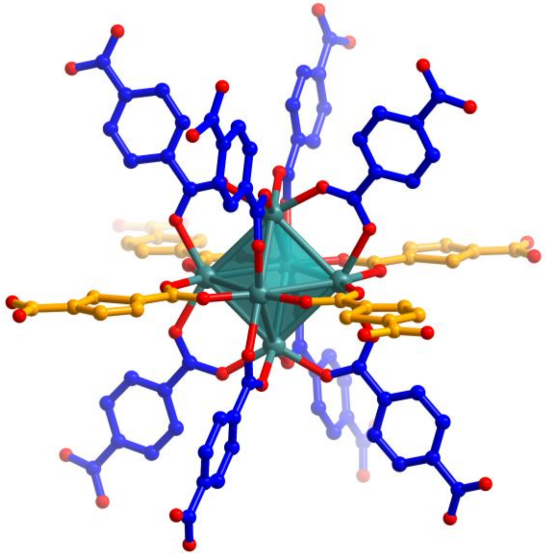
Ordered straight and bent linkers on Zirconium MOFs

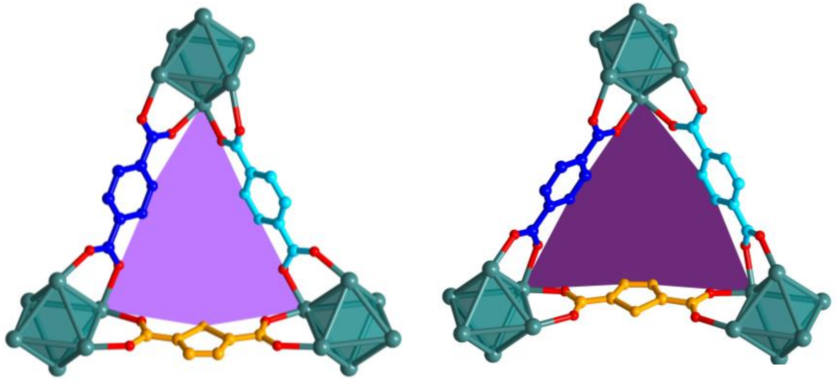


Matt Rosseinsky



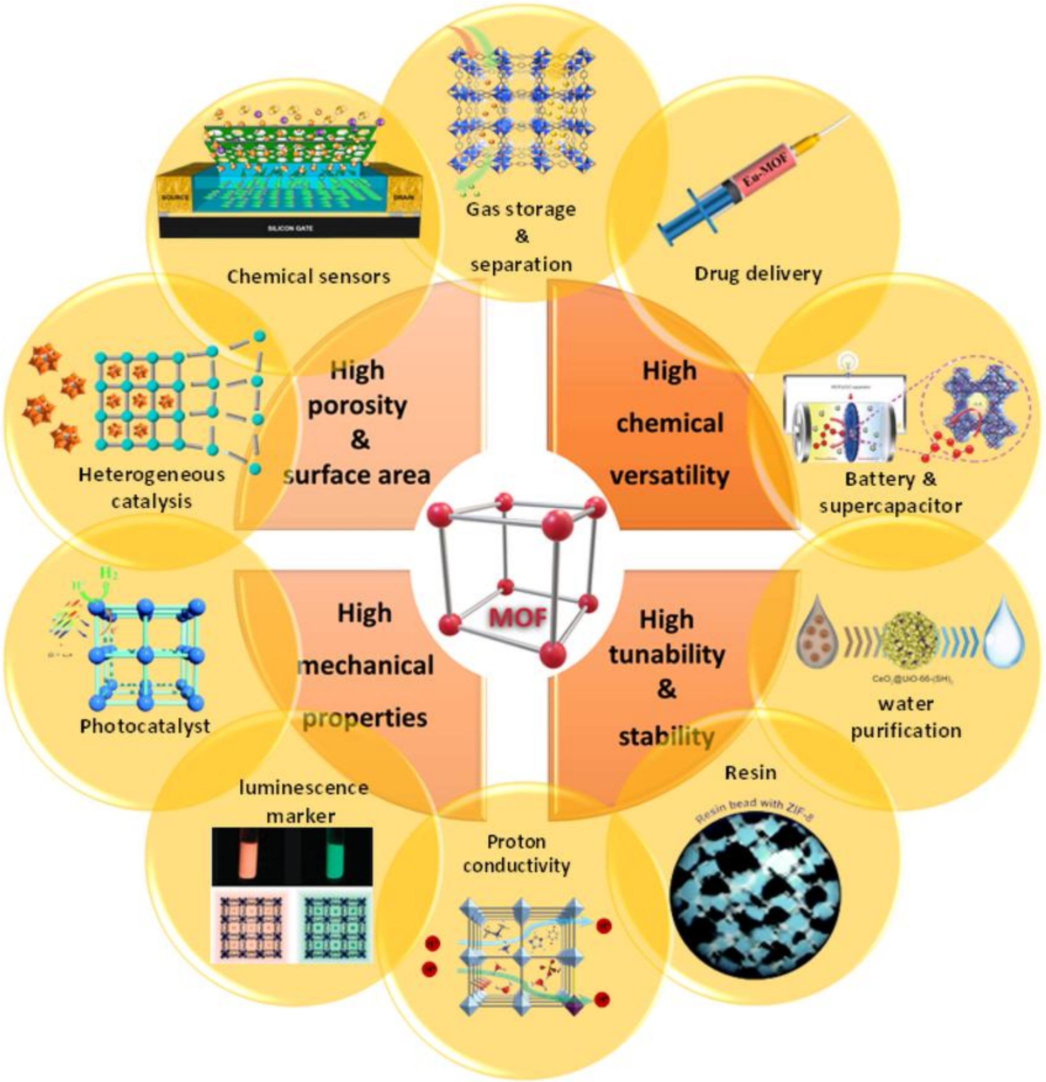






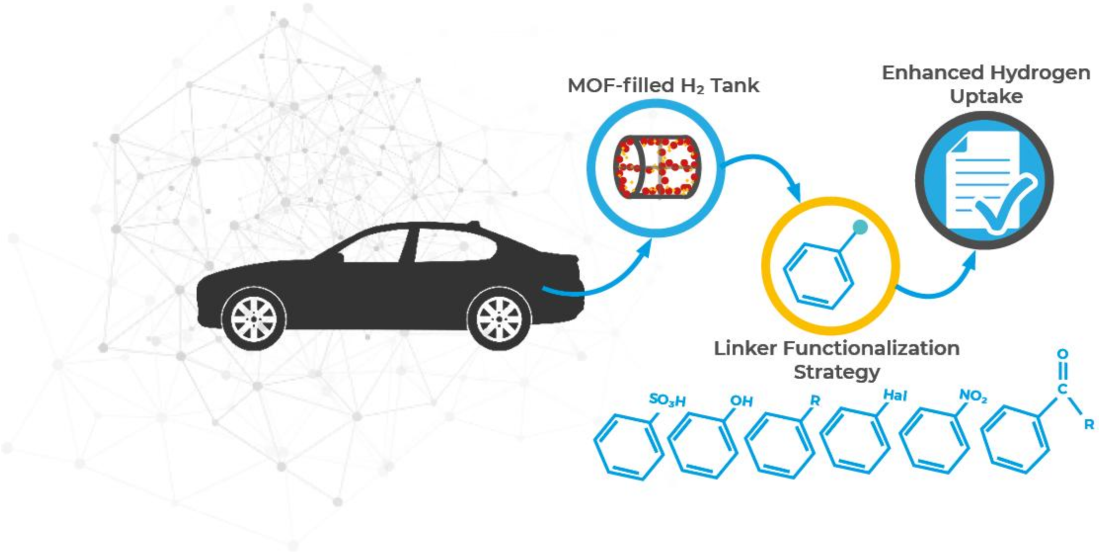
G. S. G. Farmer et al., *J. Am. Chem. Soc.*, 2025, **147**, 27586-27598.

General applications of MOFs



Zahra Ahrestani et al., *RSC Adv.*, 2023, **13** , 10273-10307.

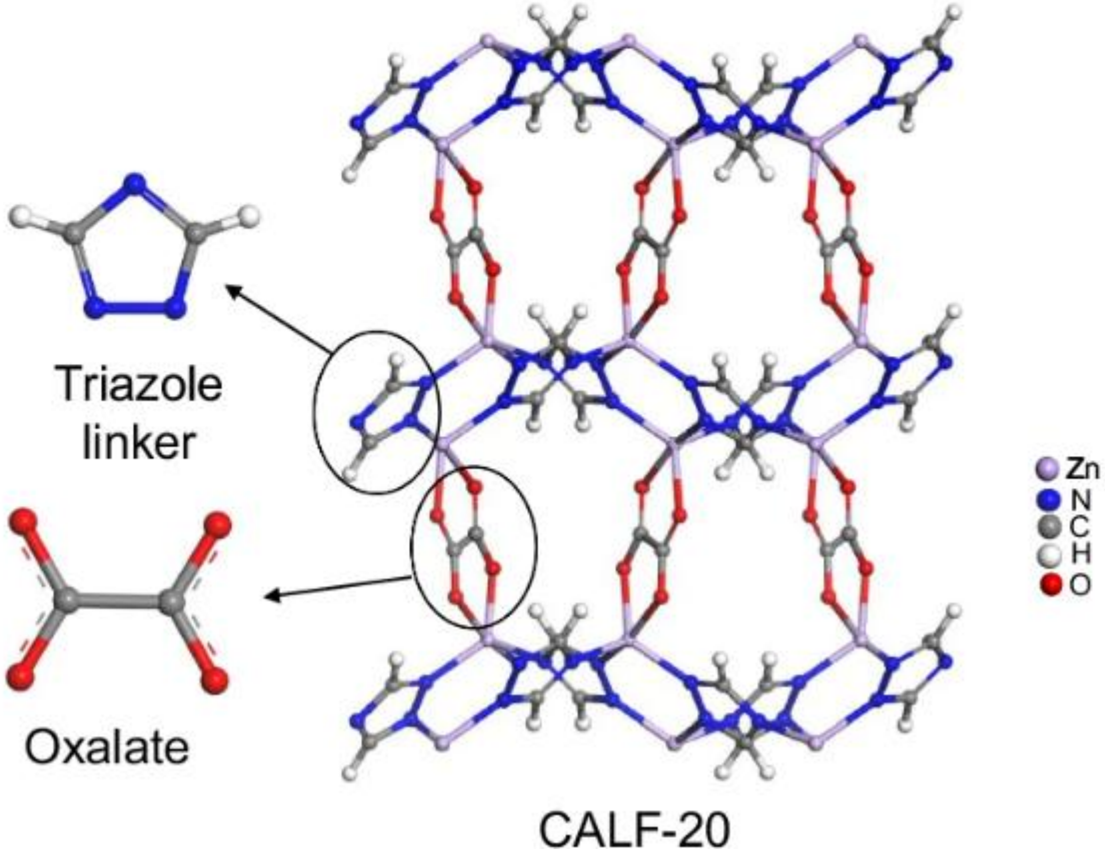
Adsorptive applications of MOFs

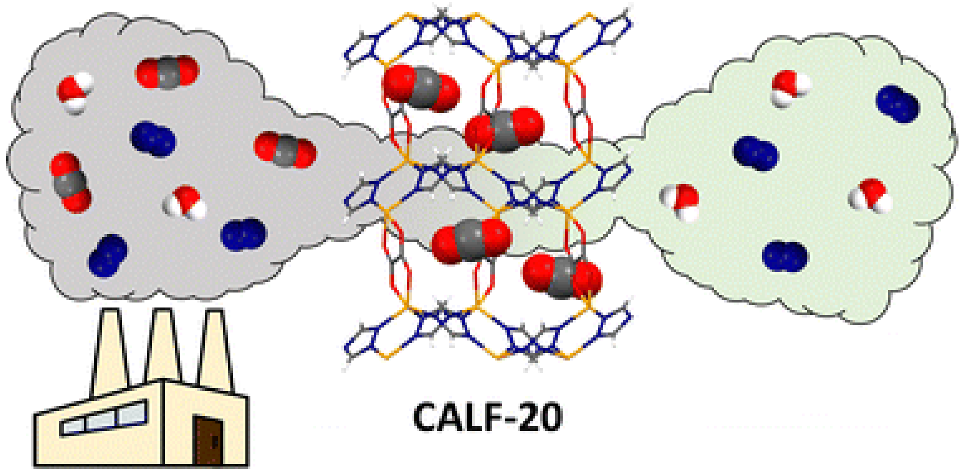


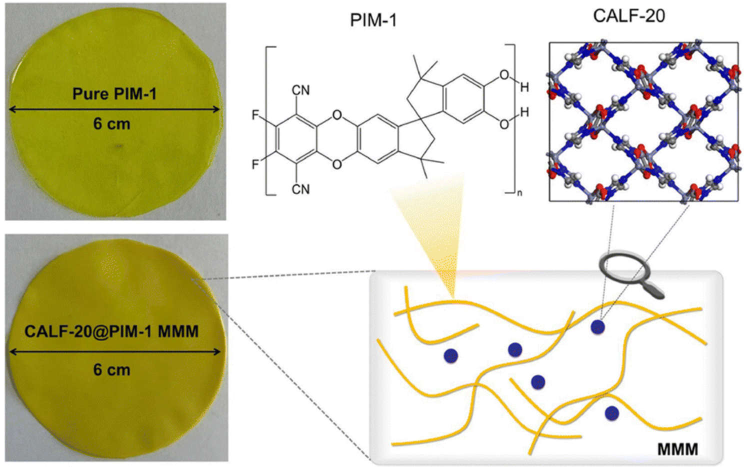
Vehicular fuel storage

Prevention of fruit over-ripening

Carbon dioxide capture



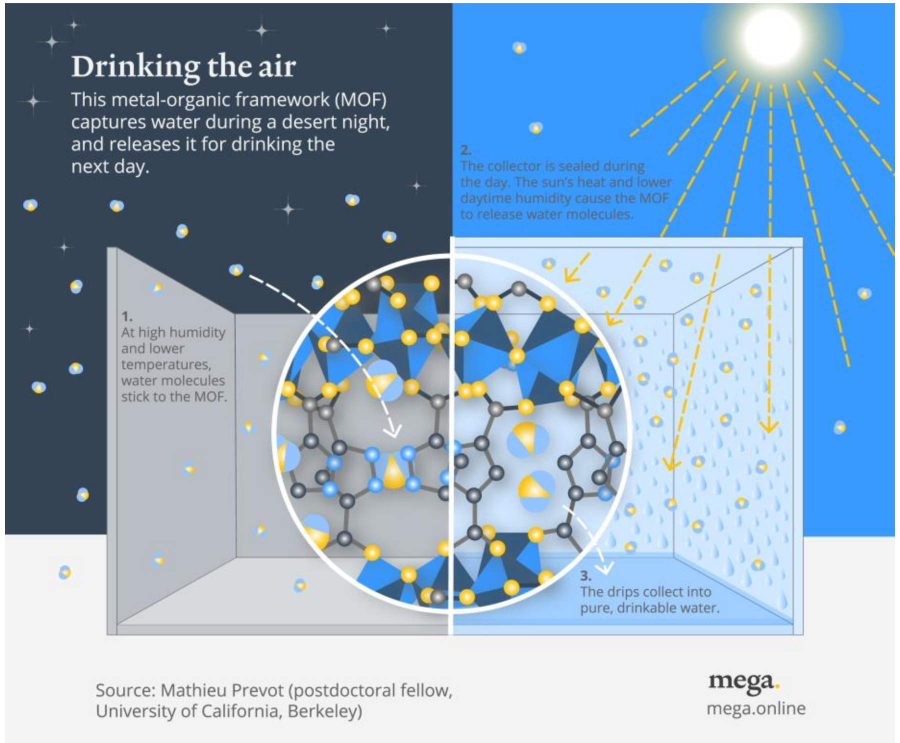




J-B. Lin et al., *Science*, 2021, **374**, 1464-1469.

H. Zhang et al., *CCST*, 2021, **13**, 100276.

Water harvesting



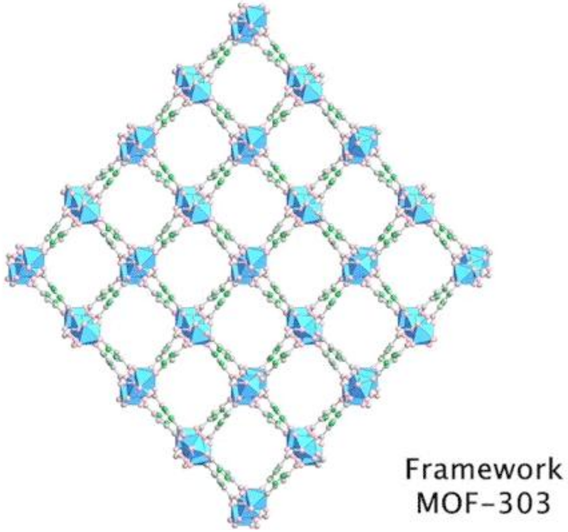
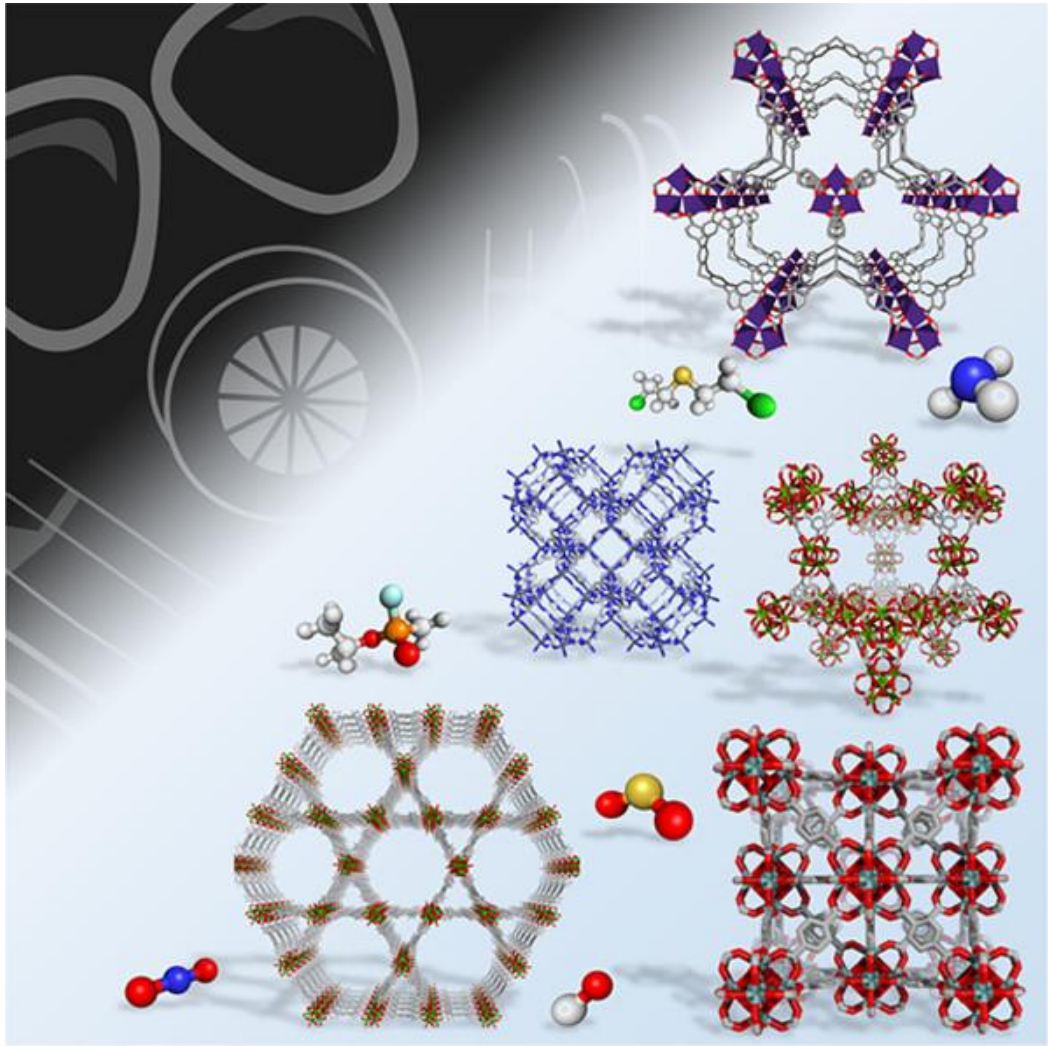


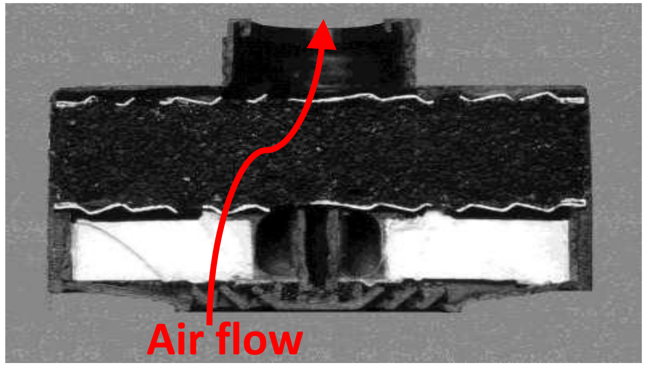
Image source: Lawrence Berkeley National Lab

W. Song, Z. Zheng, A. H. Alawadhi and O. M. Yaghi, *Nat. Water*, 2023, **1**, 626-634.

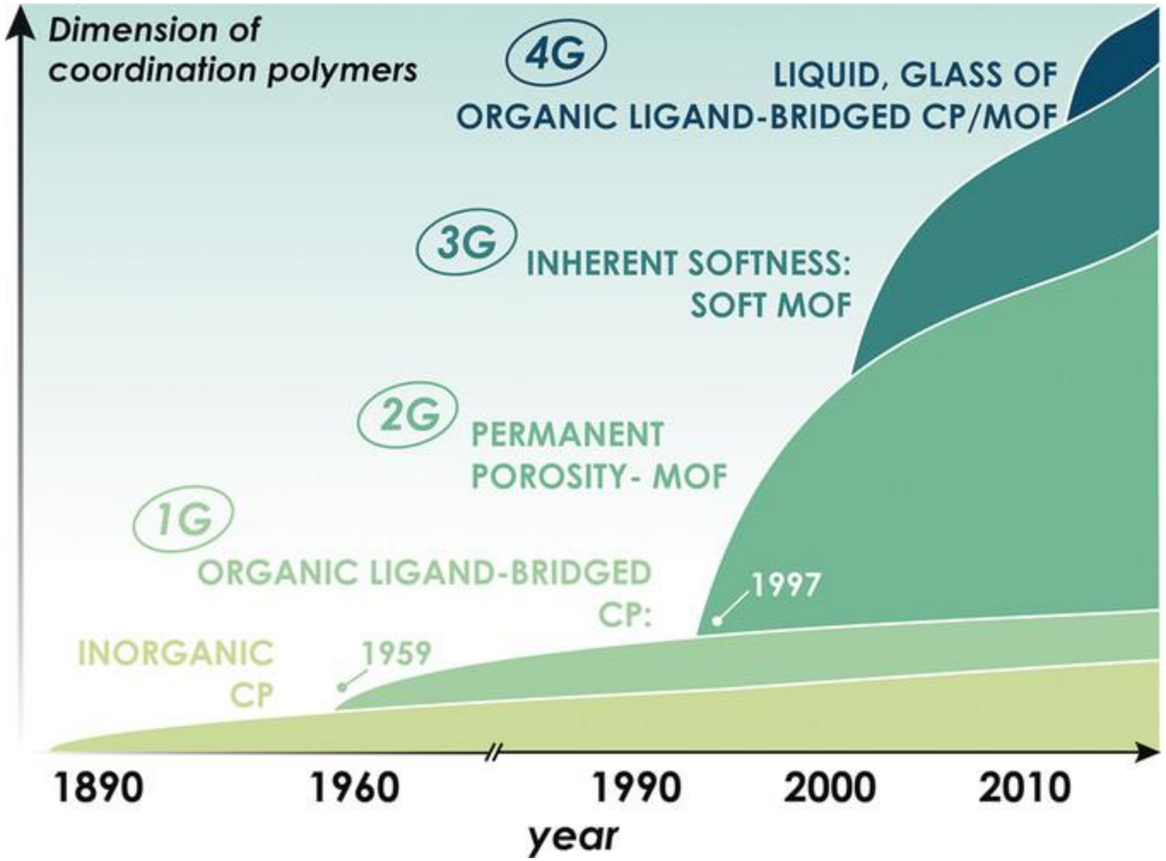
Toxic gas adsorption

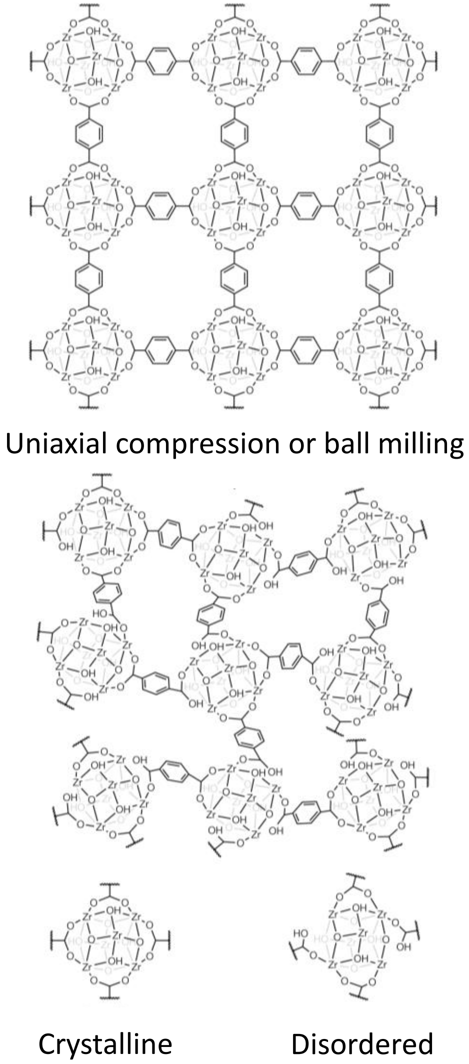


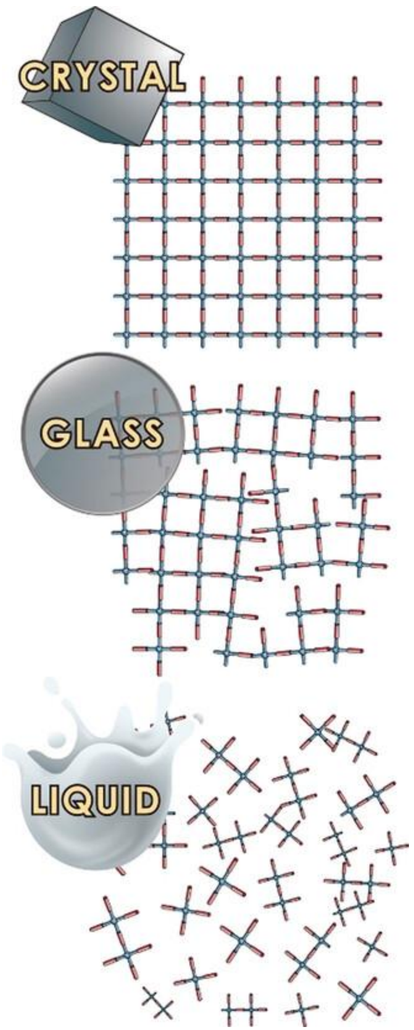
T. Islamoglu et al., *Chem. Rev.*, 2020, **120**, 8130-8160.



The changing state of MOFs

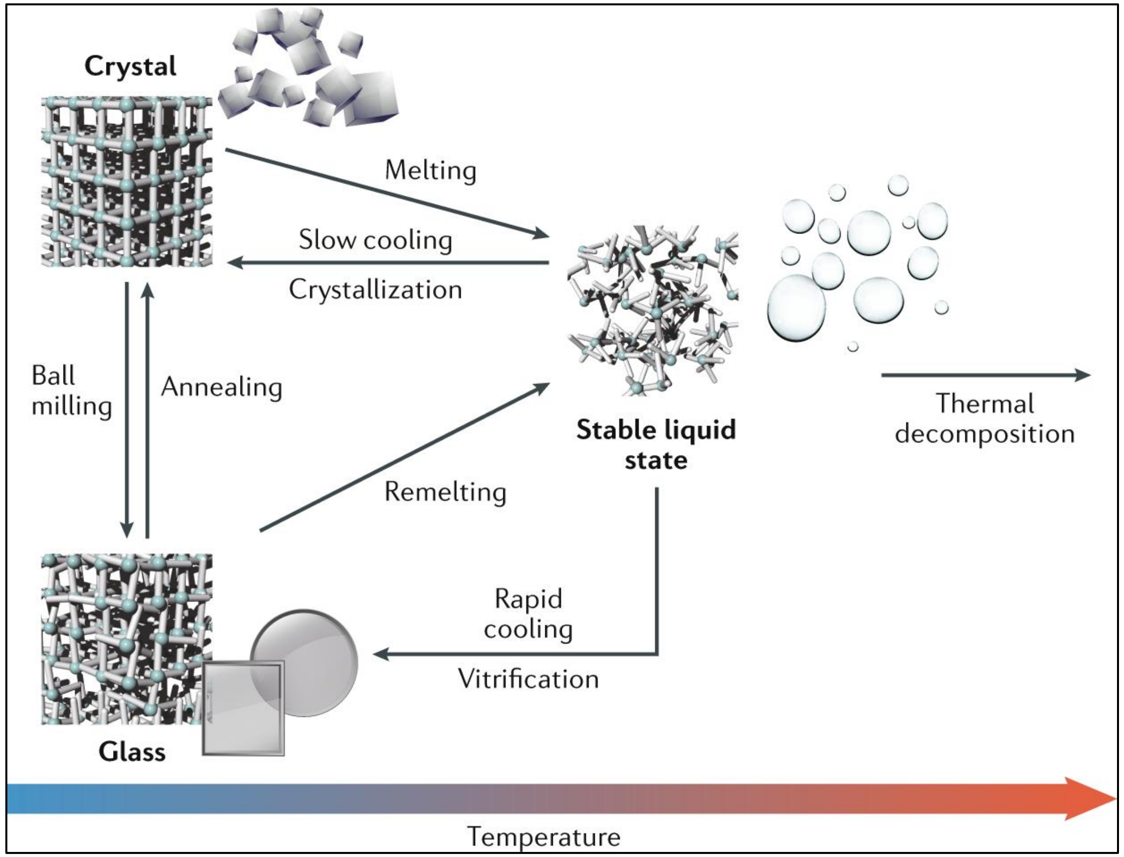


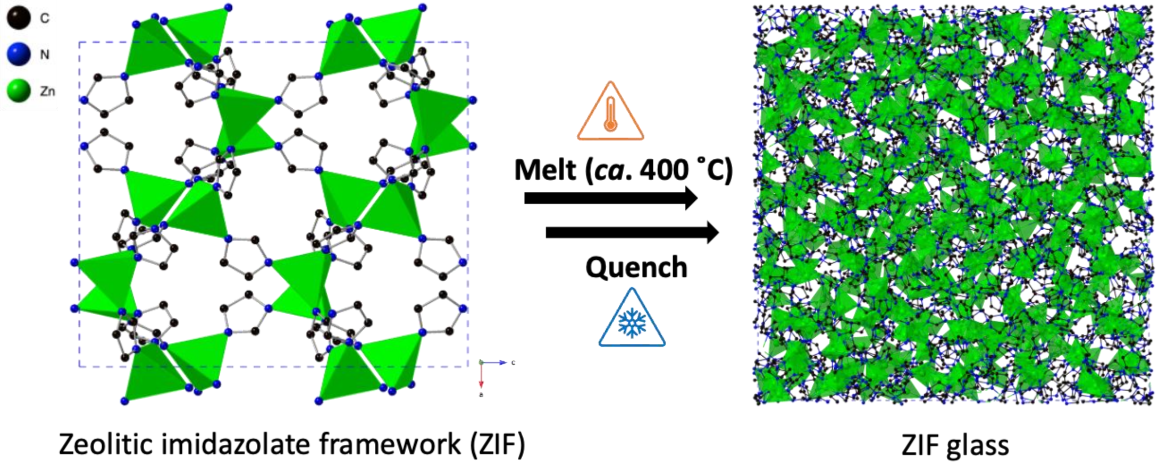




S. Horike et al., *Angew. Chem. Int. Ed.*, 2020, **59**, 6652-6664.

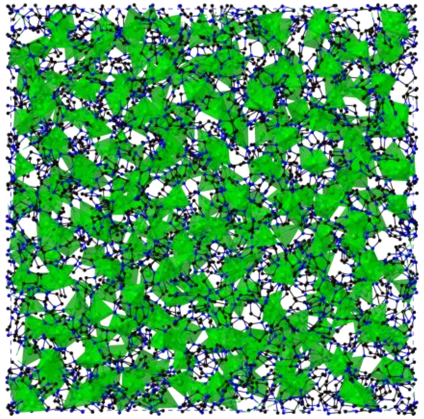
MOF glasses



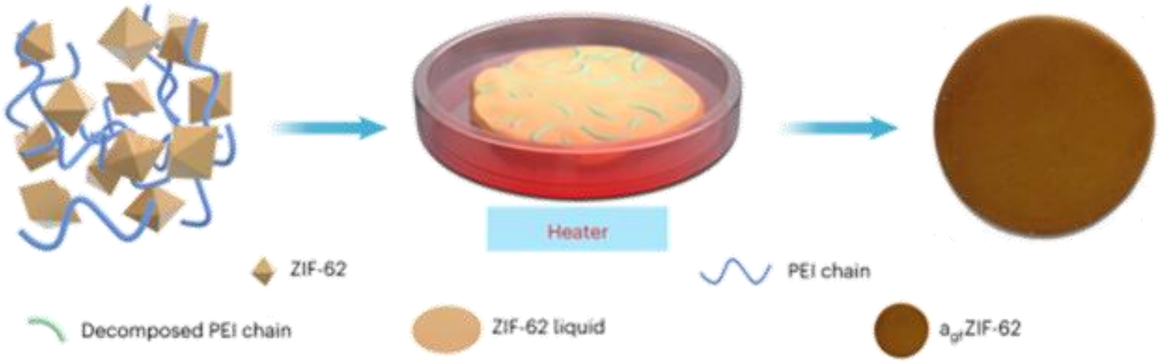


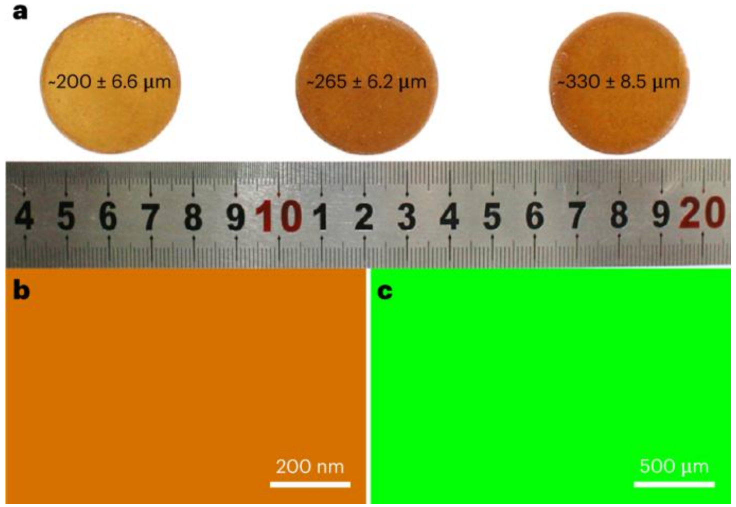
T. D. Bennett and S. Horike, *Nat. Rev. Mater.*, 2018, **3**, 431-440.

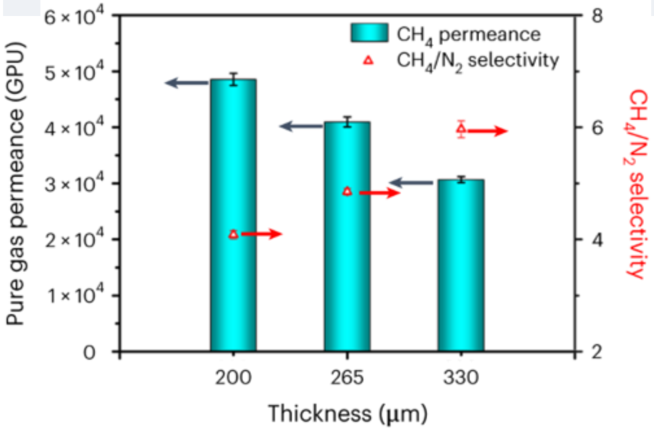
Membrane materials in chemical separations

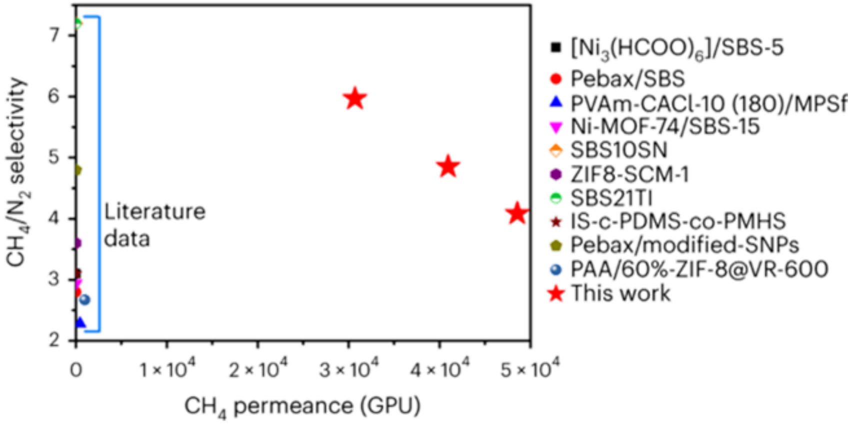


ZIF glass



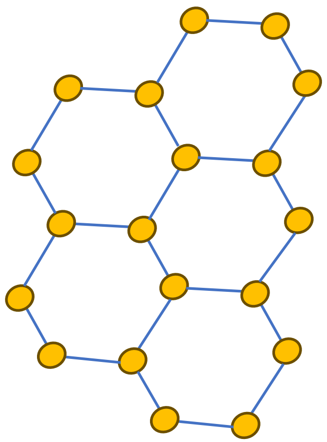


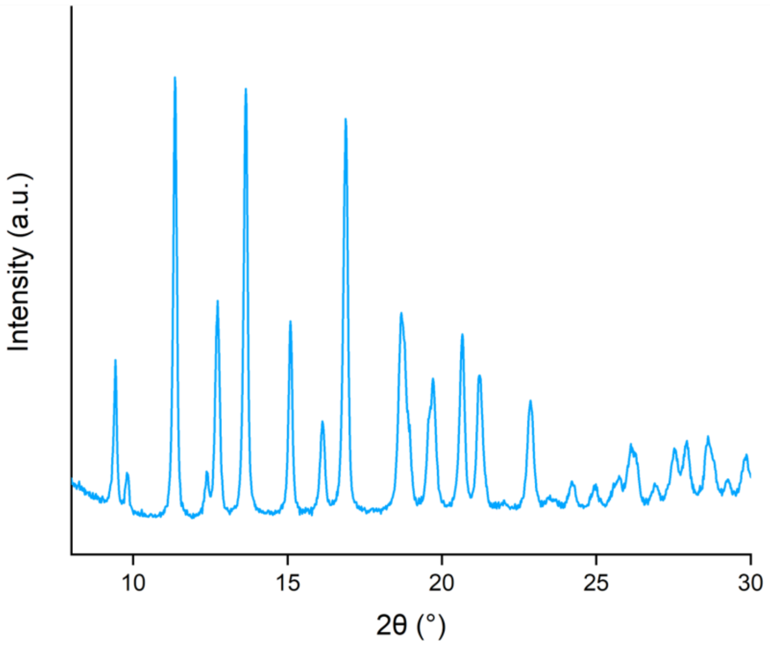




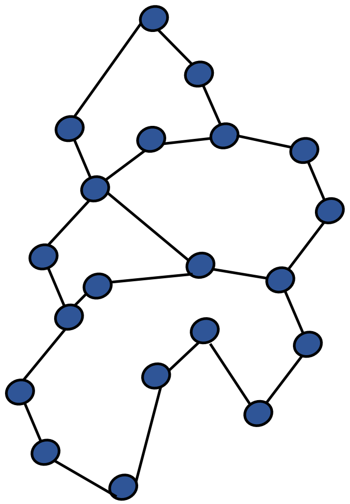
Z. Yang[‡], Y. Belmabkhout[‡], L. N. McHugh[‡] et al., *Nat. Mater.*, 2023, **22**, 888-894.

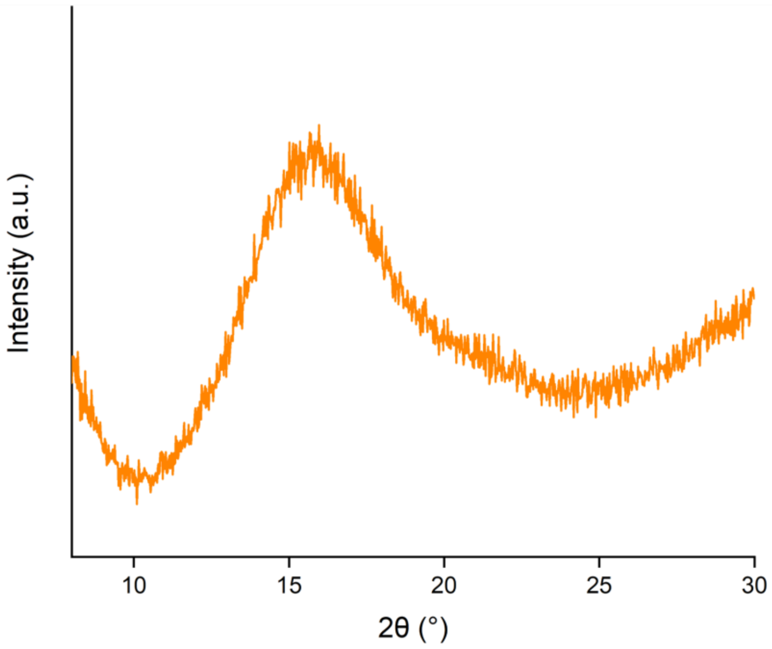
Crystalline v non-crystalline





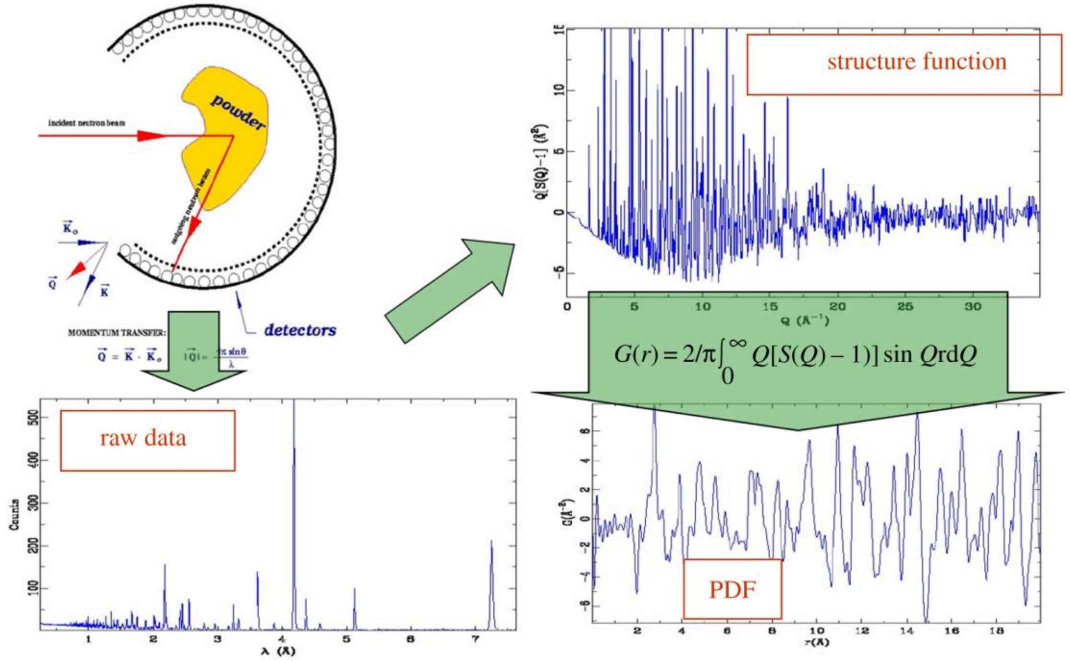
Crystalline





Non-crystalline

Total scattering and pair distribution function



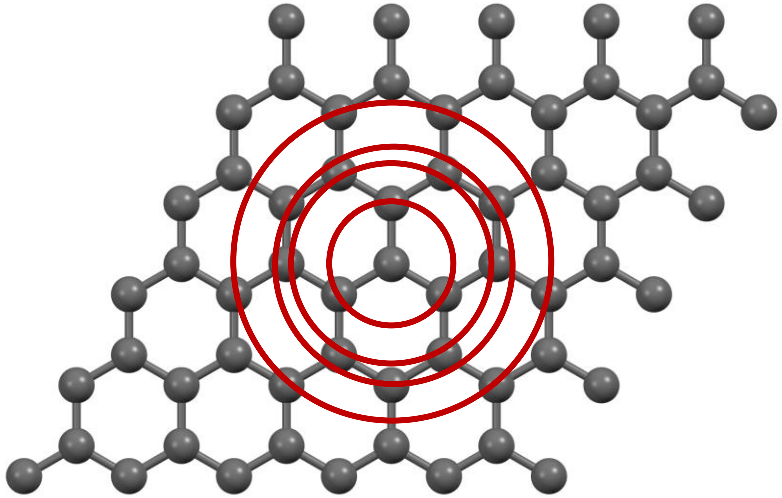
- **Total scattering** (Bragg + diffuse) experiments are similar to normal diffraction experiments.
- **Diffuse scattering provides information on the short-range structure of materials.**
- Total scattering can even be used for amorphous solids, liquids and glasses.

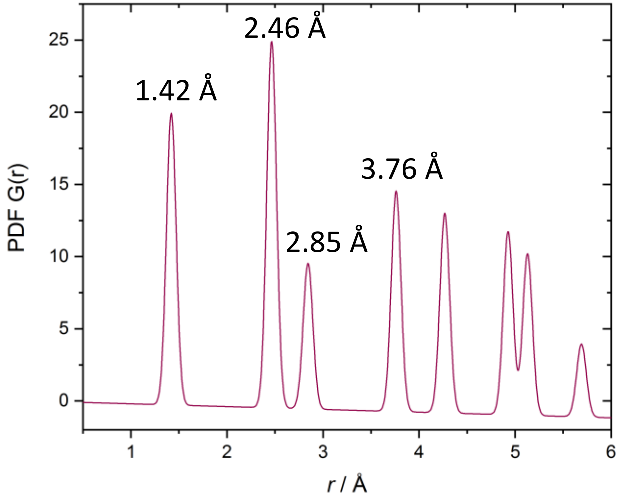
- For disordered crystalline materials, it helps characterise the periodic structure **and** the deviations from long-range order.

S. J. L. Billinge, *Phil. Trans. R. Soc. A.*, 2019, **377**, 20180413.

Pair distribution function (PDF)

- Total scattering is mathematically related to the PDF *via* Fourier transform (like the reciprocal and direct lattices)



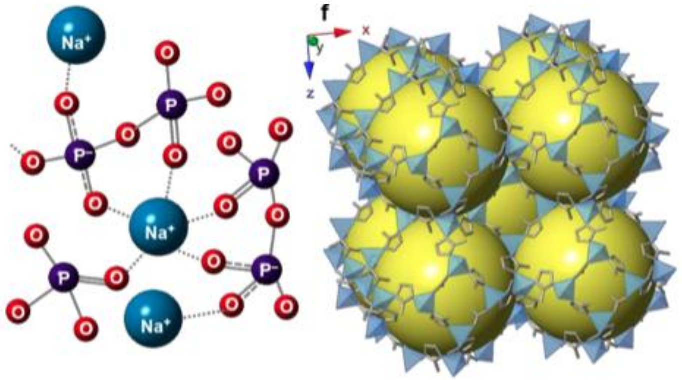


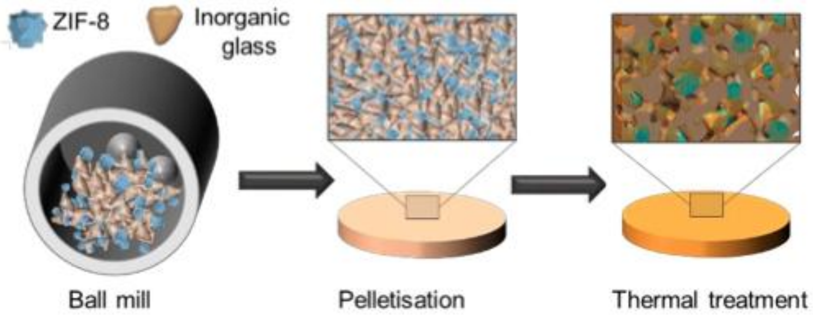
- Peak positions give interatomic separations
- Area provides information about coordination number

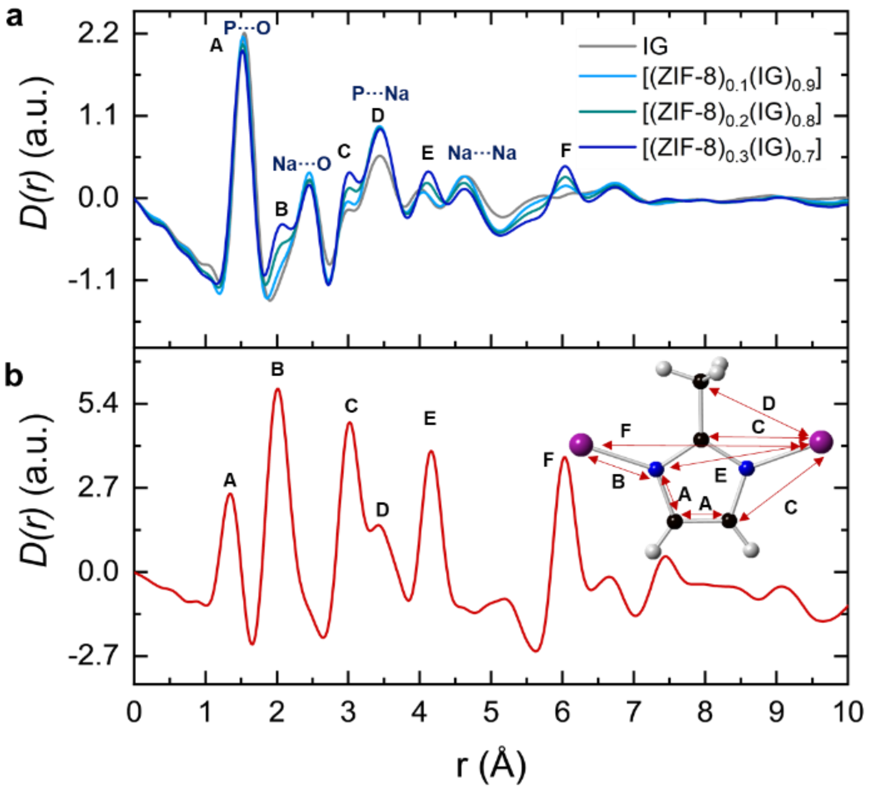
S. J. L. Billinge, *Phil. Trans. R. Soc. A.*, 2019, **377**, 20180413.

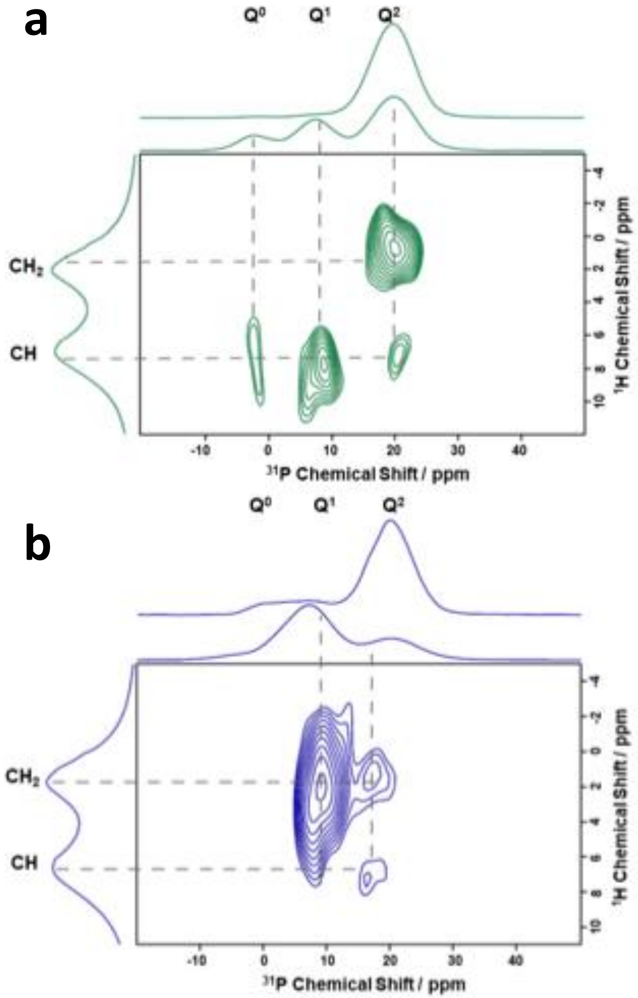
Interfaces in MOF crystal-glass composites

Frédéric Blanc









C. Castillo-Blas et al., *J. Am. Chem. Soc.*, 2023, **145**, 22913-22924.

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Summary

- MOFs are framework materials made from metal ions or clusters linked by organic ligands, forming porous 3D networks with exceptionally high surface areas.

- Their structure, pore size, and functionality can be precisely tuned by selecting different metals and linkers, allowing for tailored chemical and physical properties.

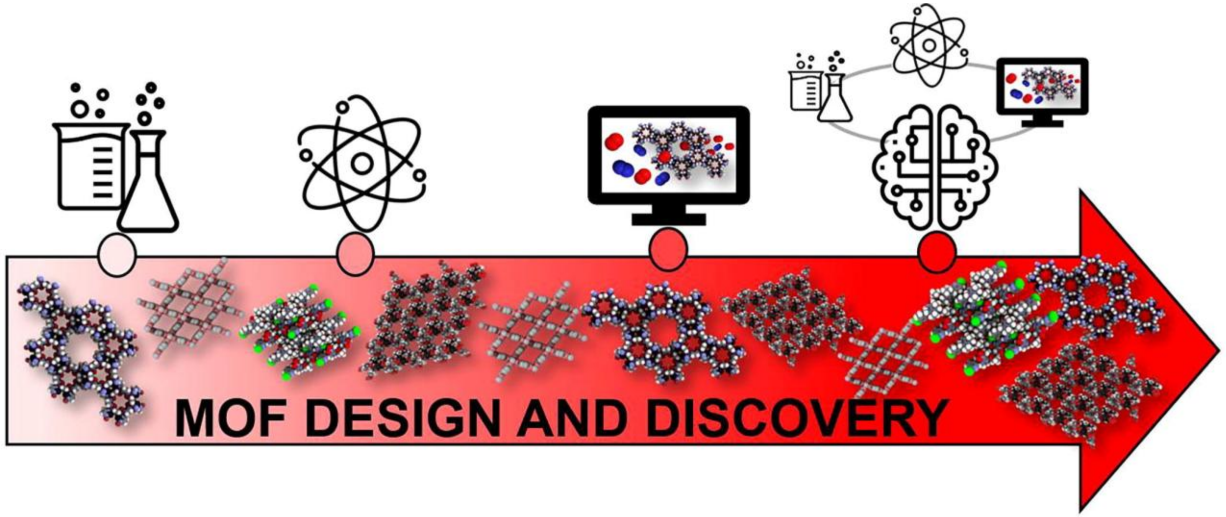
- MOFs have wide-ranging uses, including gas storage, separation, catalysis, drug delivery, and sensing – driven by their tuneable porosity and reactivity.

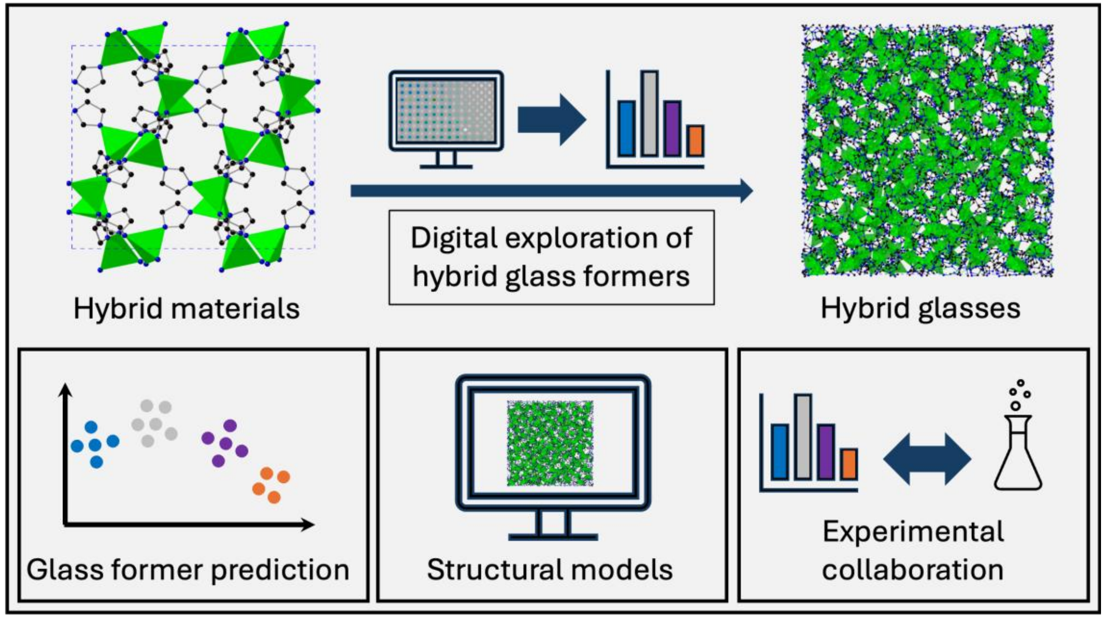
✓ Advantages: large surface areas, tuneability, and versatility.

x Challenges: stability (especially in moisture/heat), scalability, and cost of synthesis.

Future perspectives: digital discovery

- Digital materials chemistry goes hand in hand with experimental materials chemistry
- AI and machine learning is driving MOF commercialisation with interest from several start-ups and large companies





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Thanks for listening!
Questions?

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