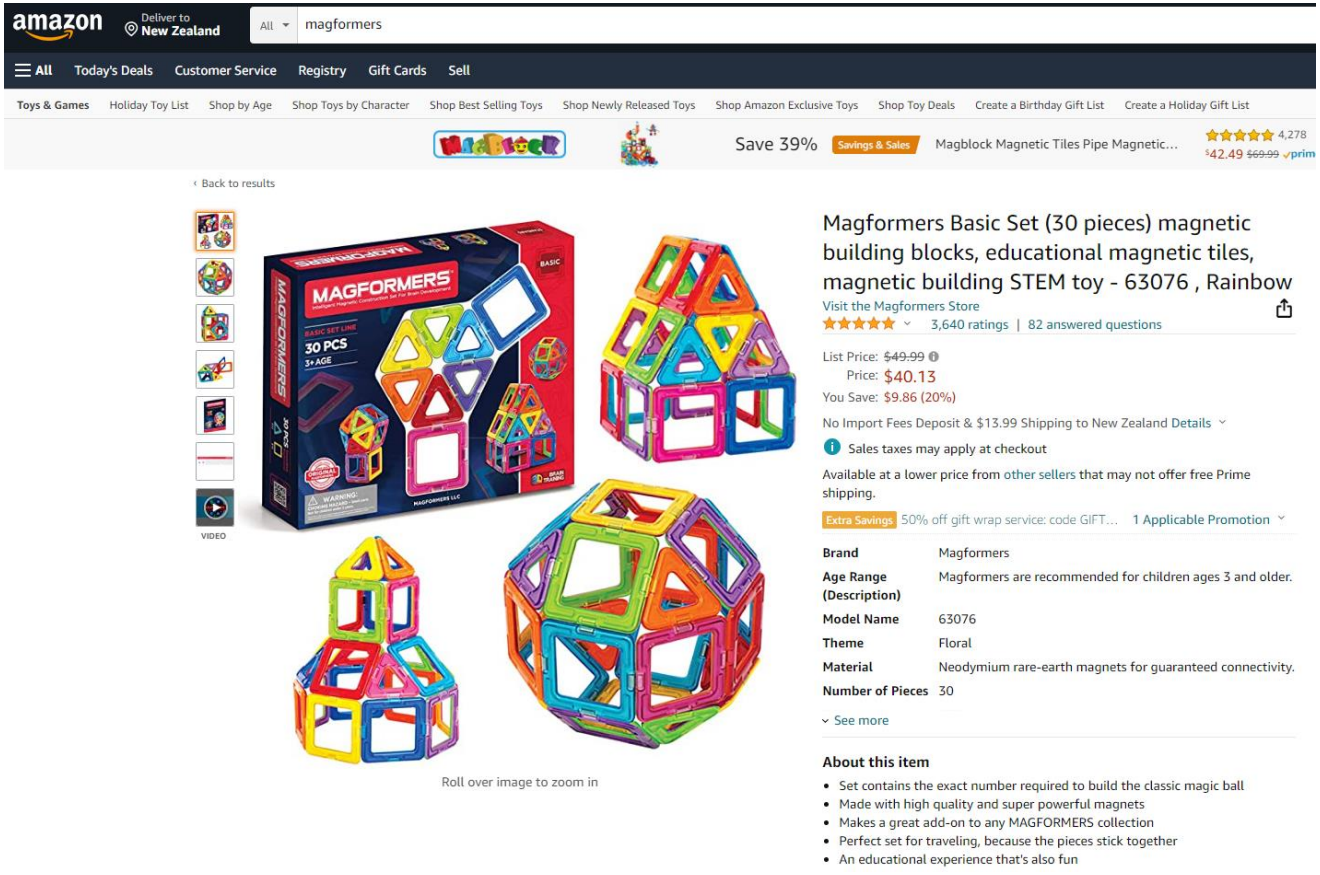
Magforming Chemistry:
From Methane Capture to Hydrogen Storage

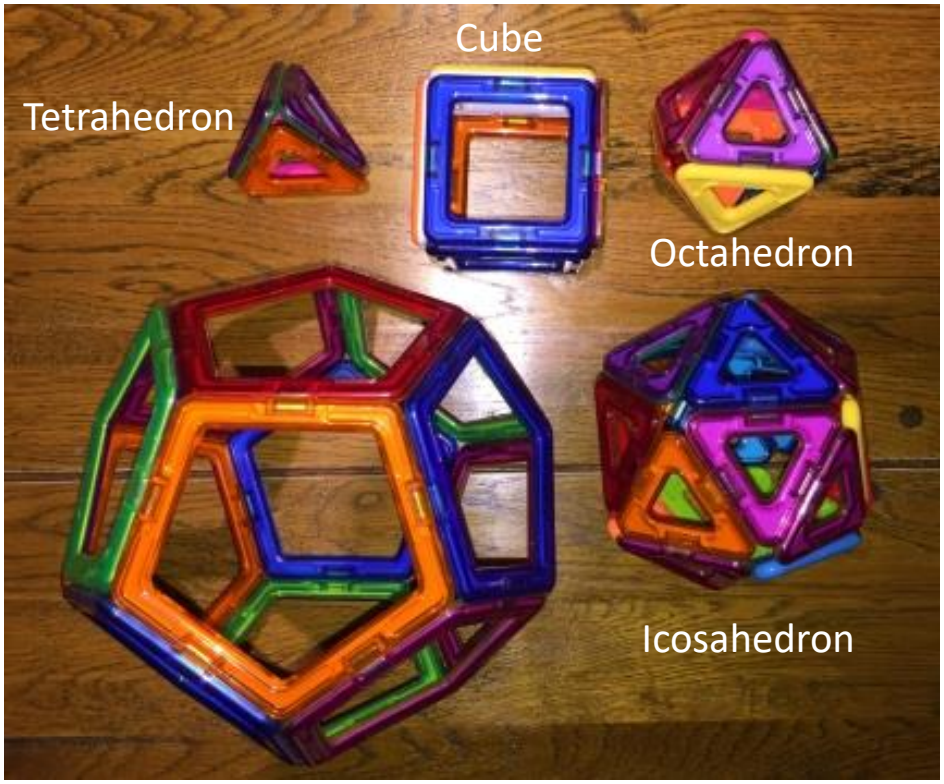
Lujia (Luke) Liu, Lecturer in Inorganic Chemistry

Nelson, 7 December 2022

As A Magnetochemist…

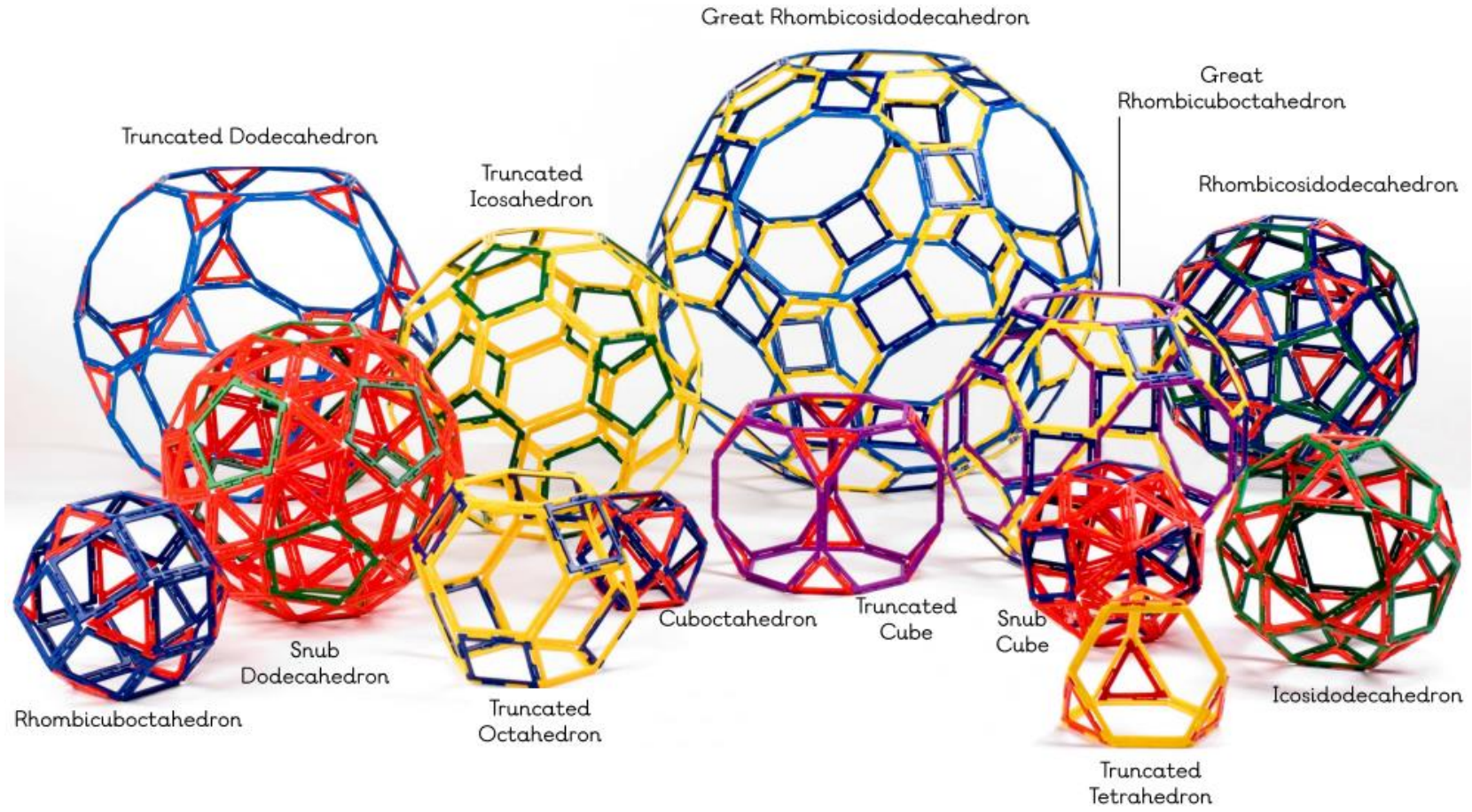


Magforming Polyhedrons

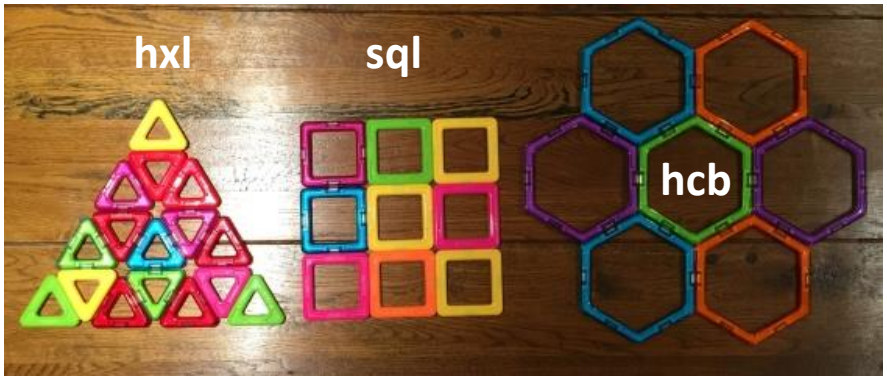


Dodecahedron

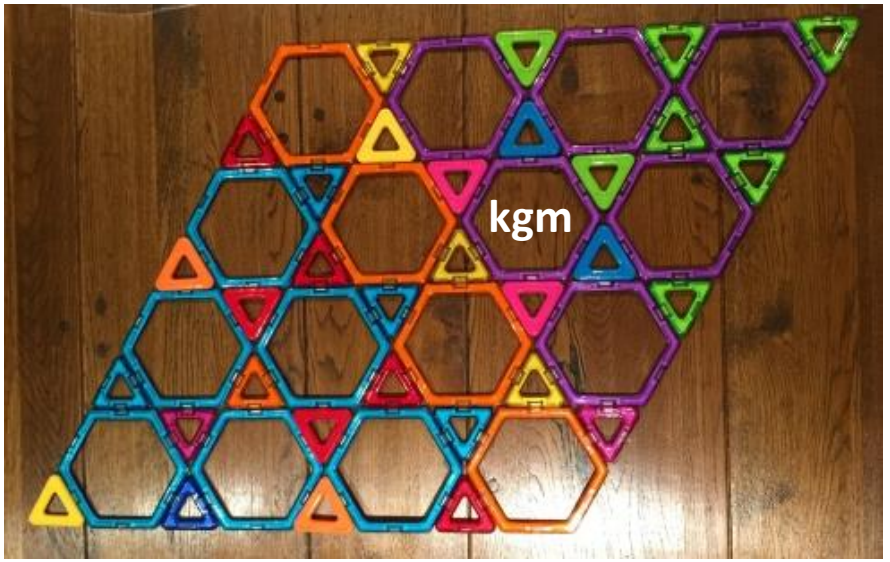
Magforming Polyhedrons



Magforming 2D Lattices



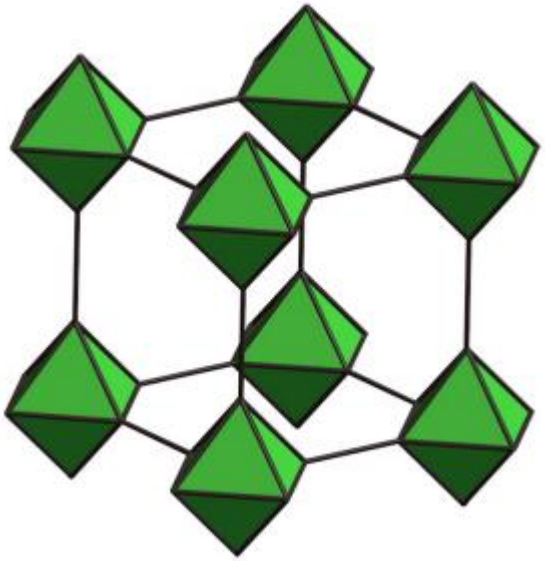
hexagonal square honeycomb

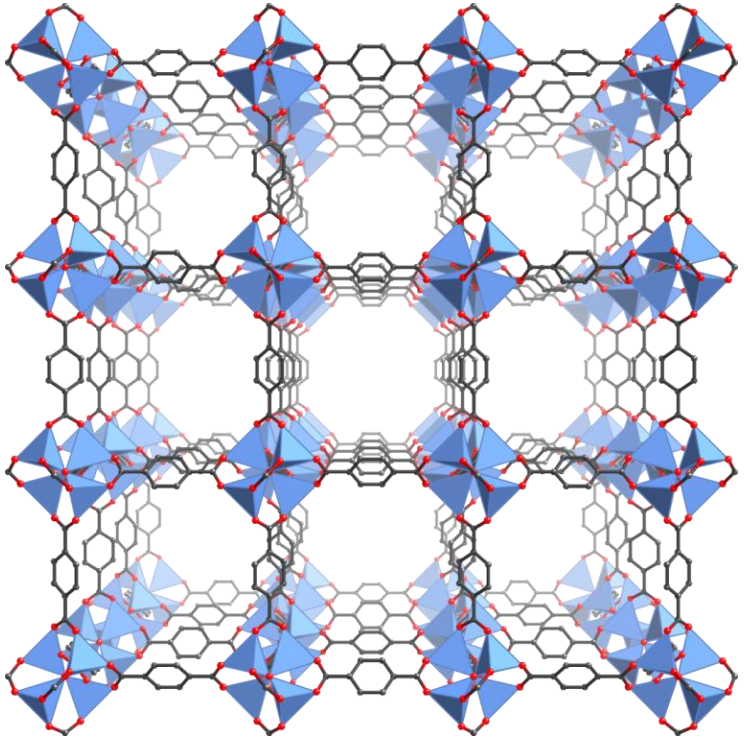


kagome

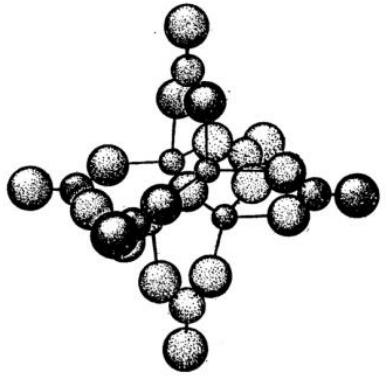
Magforming 3D Lattices

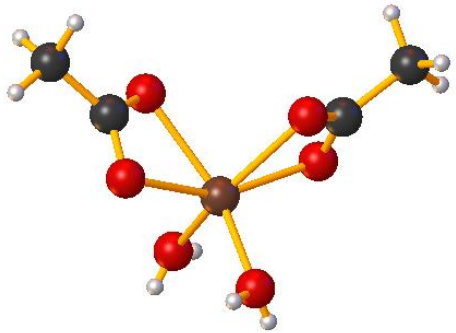
Linking octahedron to form **pcu** (primitive cubic) network

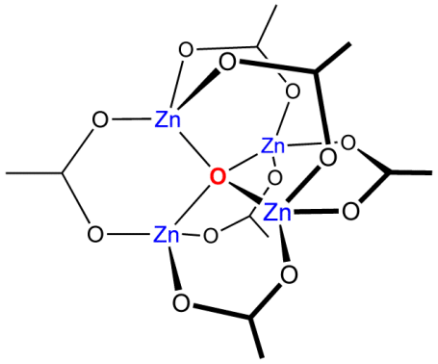




Octahedron Chemical Building Block







Sublimation

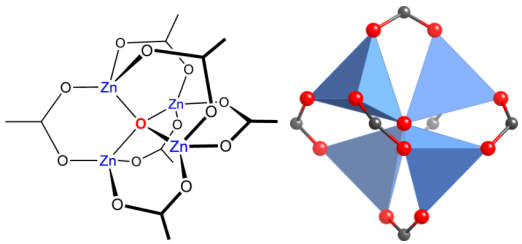
$Zn(CH_3COO)_2(H_2O)_2$

$Zn_4O(CH_3COO)_6$

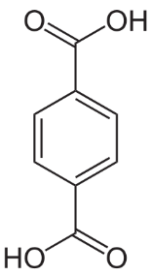
H. Koyama & Y. Saito; The Crystal Structure of Zinc Oxyacetate, $Zn_4O(CH_3COO)_6$. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 112-114.

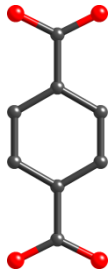
Metal-Organic Framework-5 (MOF-5)

III + III ⟶

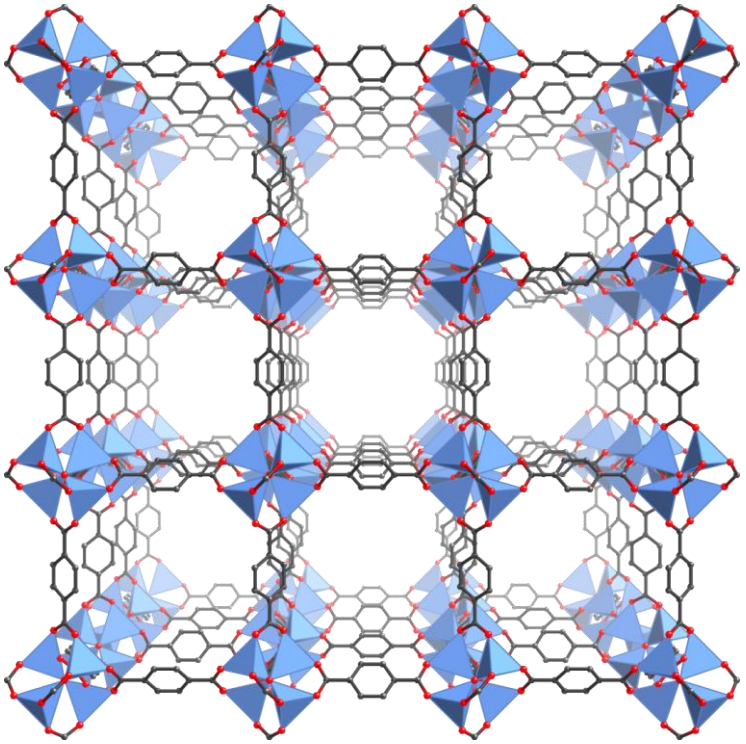


$Zn_4O(CO_2\text{-}R)_6$ cluster





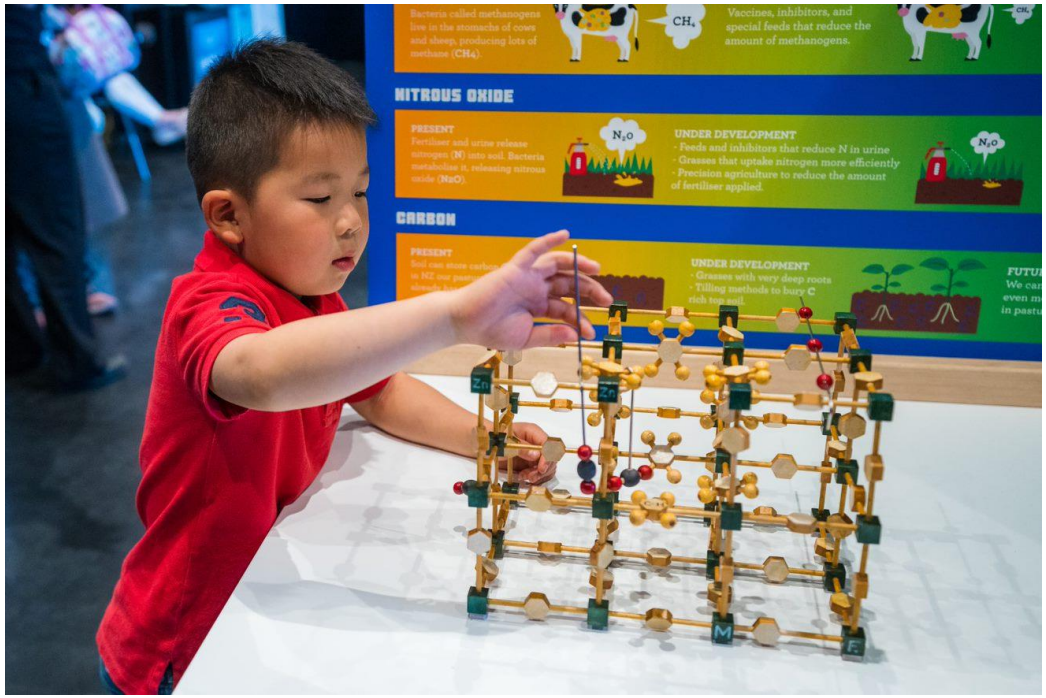
Terephthalic acid
H_2BDC



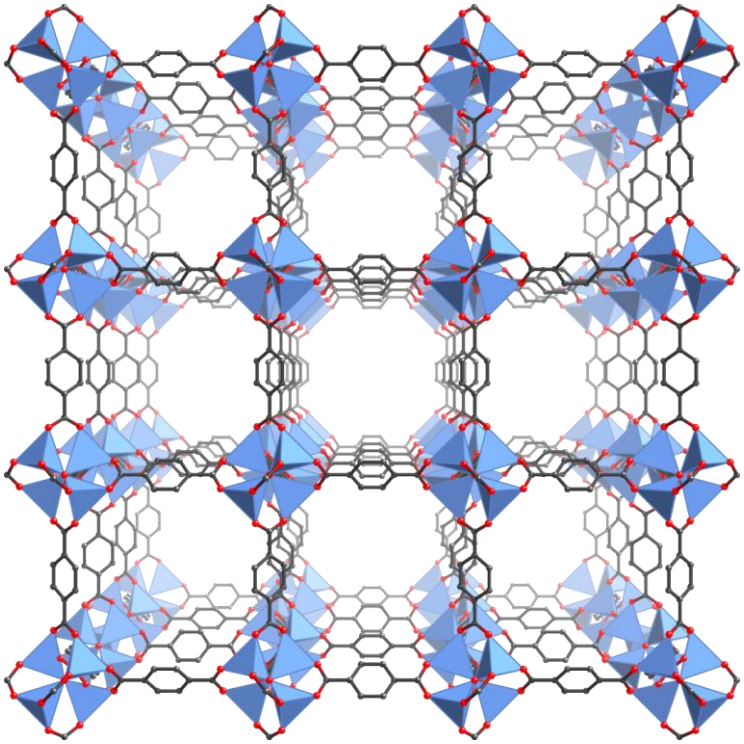
MOF-5 $[Zn_4O(BDC)_3]$
Surface Area = 3500 m^2/g

H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature*, **1999**, *402*, 276-279.

Metal-Organic Framework-5 (MOF-5)



MOF-5 Model at Otago Museum
(Te Papa also has a MOF-5 model)



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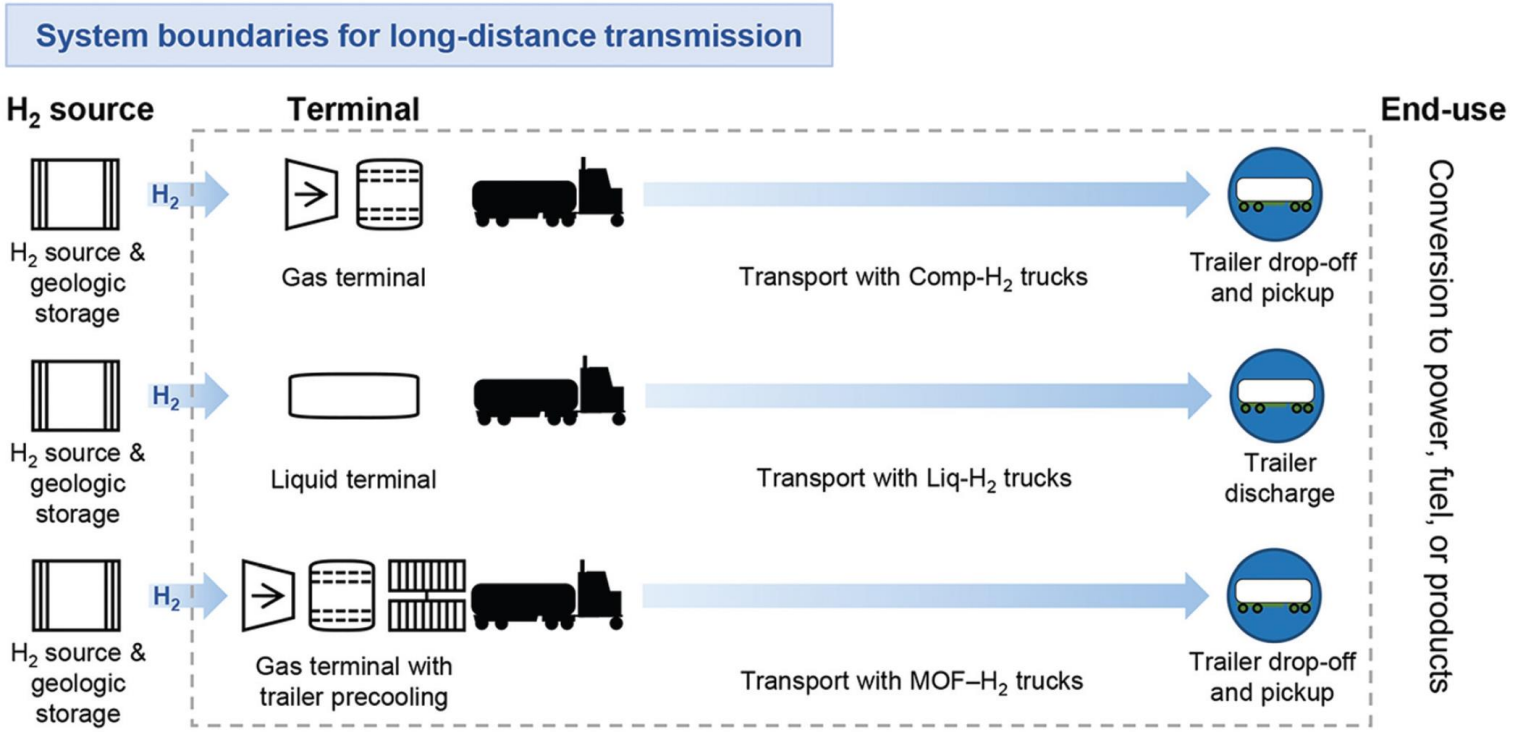
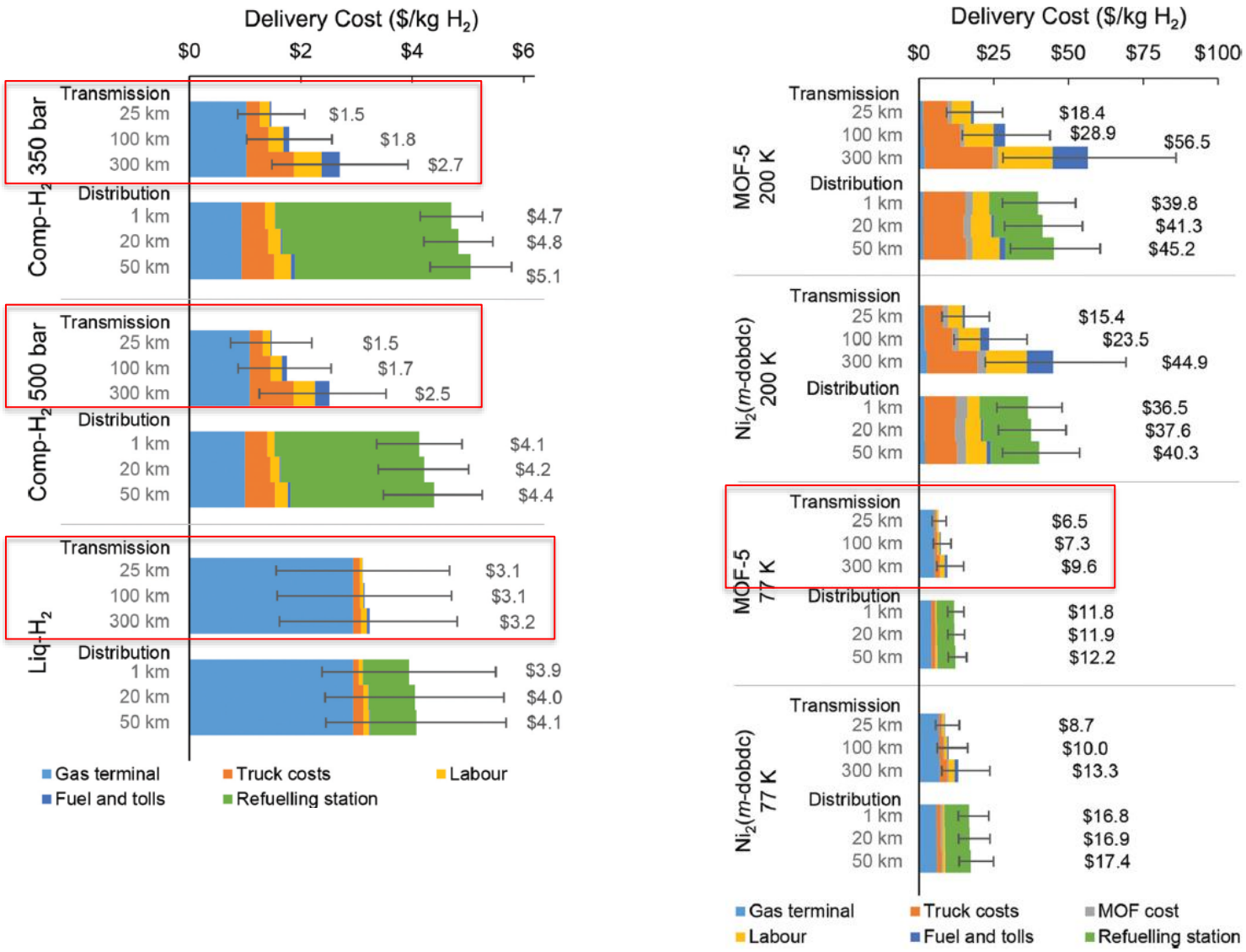
MOF-5 for Hydrogen Storage

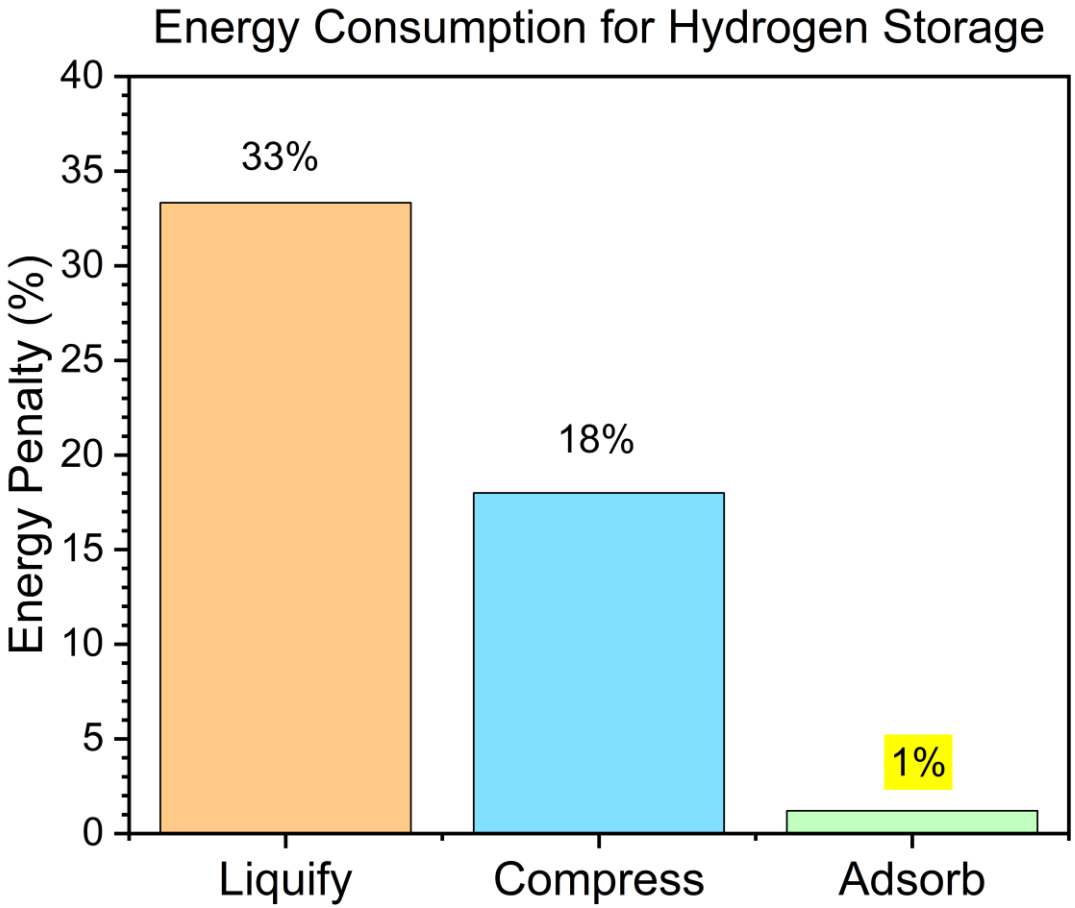


Yaghi and co-workers, *Science* **2003**, *300*, 1127.
Matzger and co-workers, *Nat. Commun.,* **2019**, *10*, 1568.
Breunig, Long and co-workers, *Energy Environ. Sci.*, **2021**, *14*, 1083.

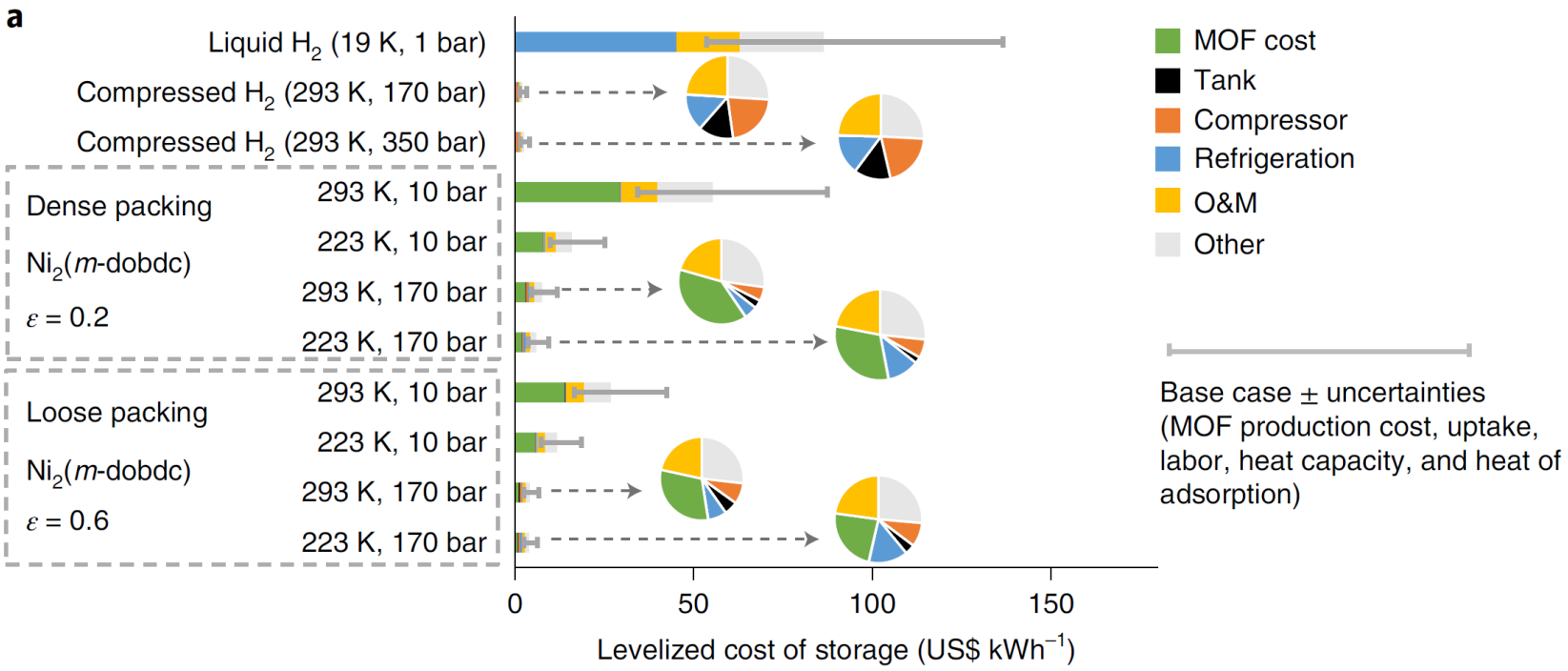


Breunig, Long and co-workers, *Energy Environ. Sci.*, **2021**, *14*, 1083.

Why MOFs for Hydrogen Storage?



Hydrogen Storage MOFs for Back-up Power Supply



Breunig, Long and co-workers, *Nature Energy*, **2022**, *7*, 448.

Further Cost Reduction?

- Increase Materials Durability
- Increase Storage Capacity

How?

Methane Emissions

Methane is 25× more potent greenhouse gas than CO_2 (100-year span).

Methane emissions' contribution to global warming:

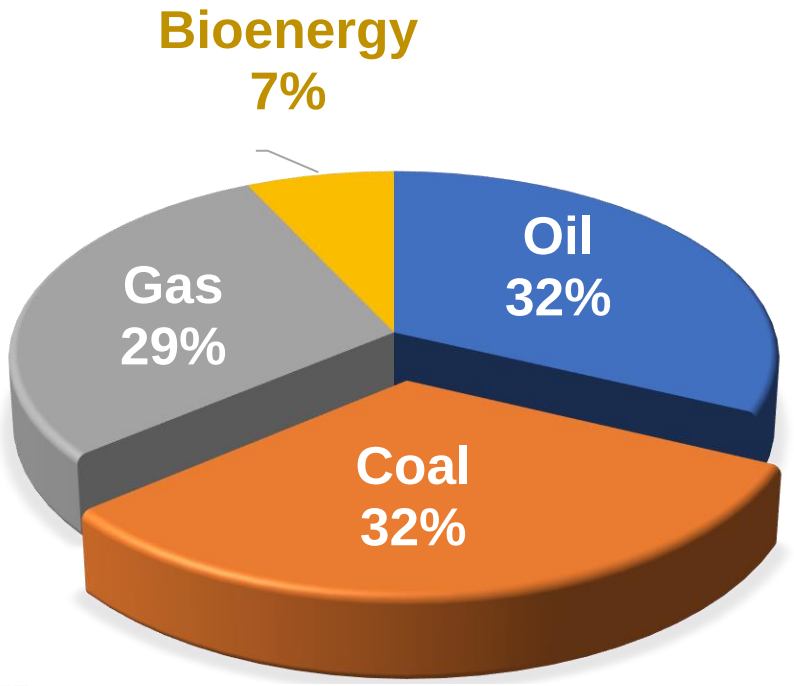
20% -- US Environment Protection Agency

30% -- International Energy Agency

The **energy sector** is responsible for 38% of human-activity-related emissions, second only to agriculture (40%).

International Energy Agency, *Global Methane Tracker,* **2022**

Methane Emissions by The Energy Sector

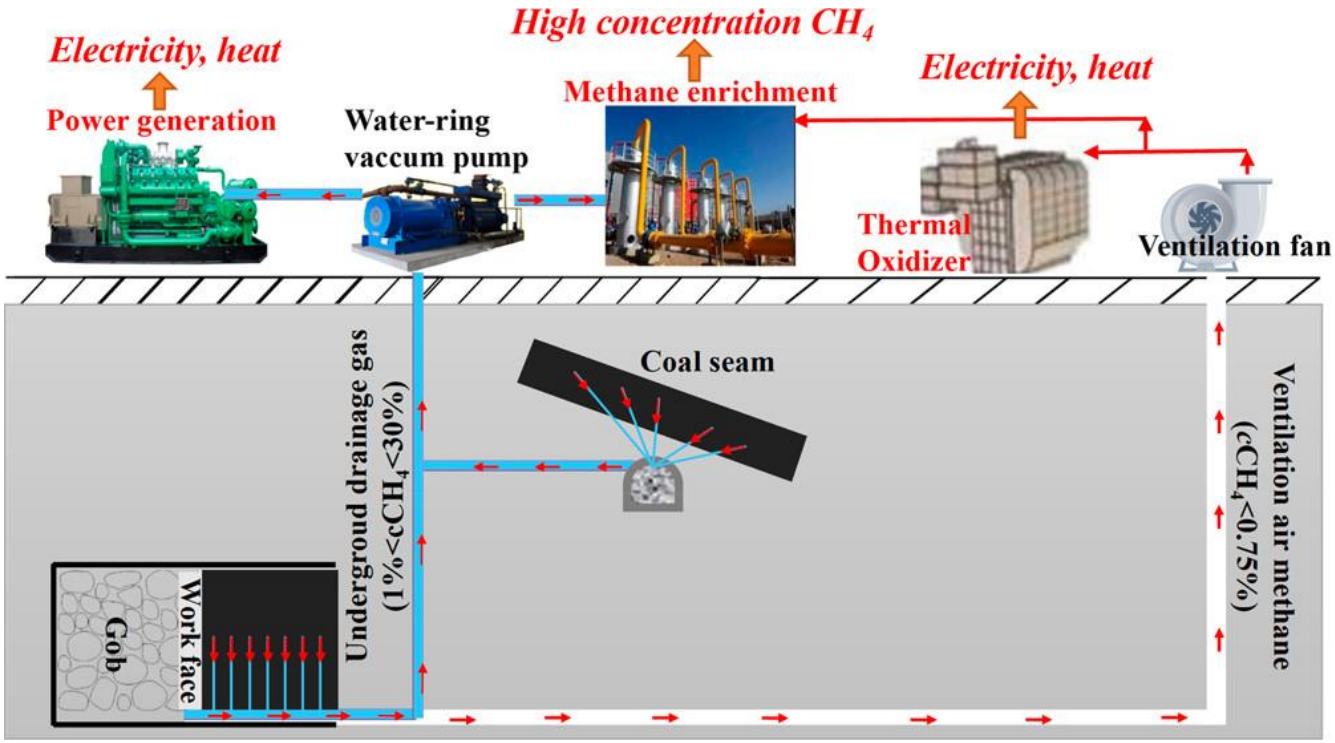


Flaring

Explosion limit: 5 – 15 % in air

International Energy Agency, *Global Methane Tracker,* **2022**

Coal Mine Methane Capture



- Drainage gas (methane > 6%) utilisation rate reached 45% in China (2020).
- Capturing ventilation air methane (methane < 0.75%) remains a challenge.

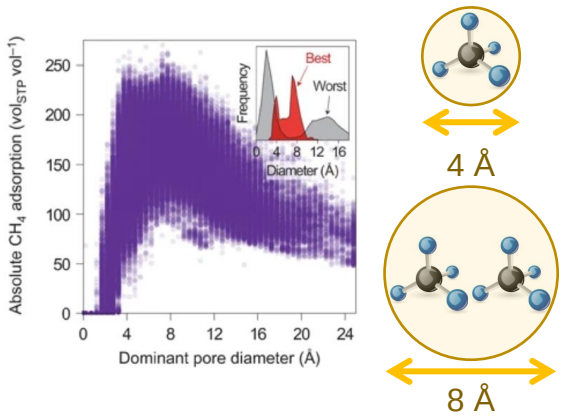
Fubao Zhou *et. al*, *Energy & Fuels* **2021**, 35, 15398.

Design Principles for Methane Capture Materials

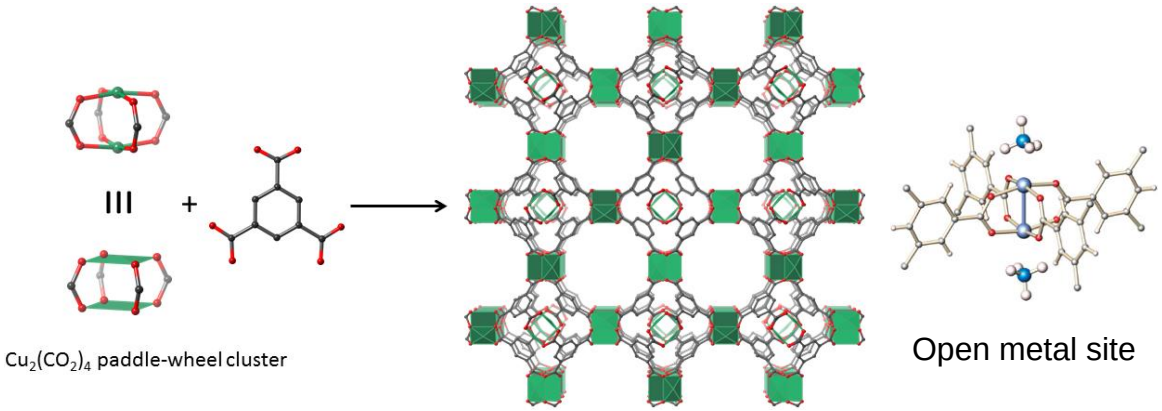
Selective for CH_4 over other gases in the air (mostly N_2)

Gas	Kinetic Diameter (Å)	Polarisability (Å^3)
CH_4	3.80	2.6
N_2	3.64	1.4

Simulations over 137,000 hypothetical MOFs



MOFs with open metal sites show higher CH_4/N_2 selectivity



R. Q. Snurr and co-workers, *Nature Chem.* **2011**, *4*, 83.
I. D. Williams and co-workers, *Science* **1999**, *283*, 1148.
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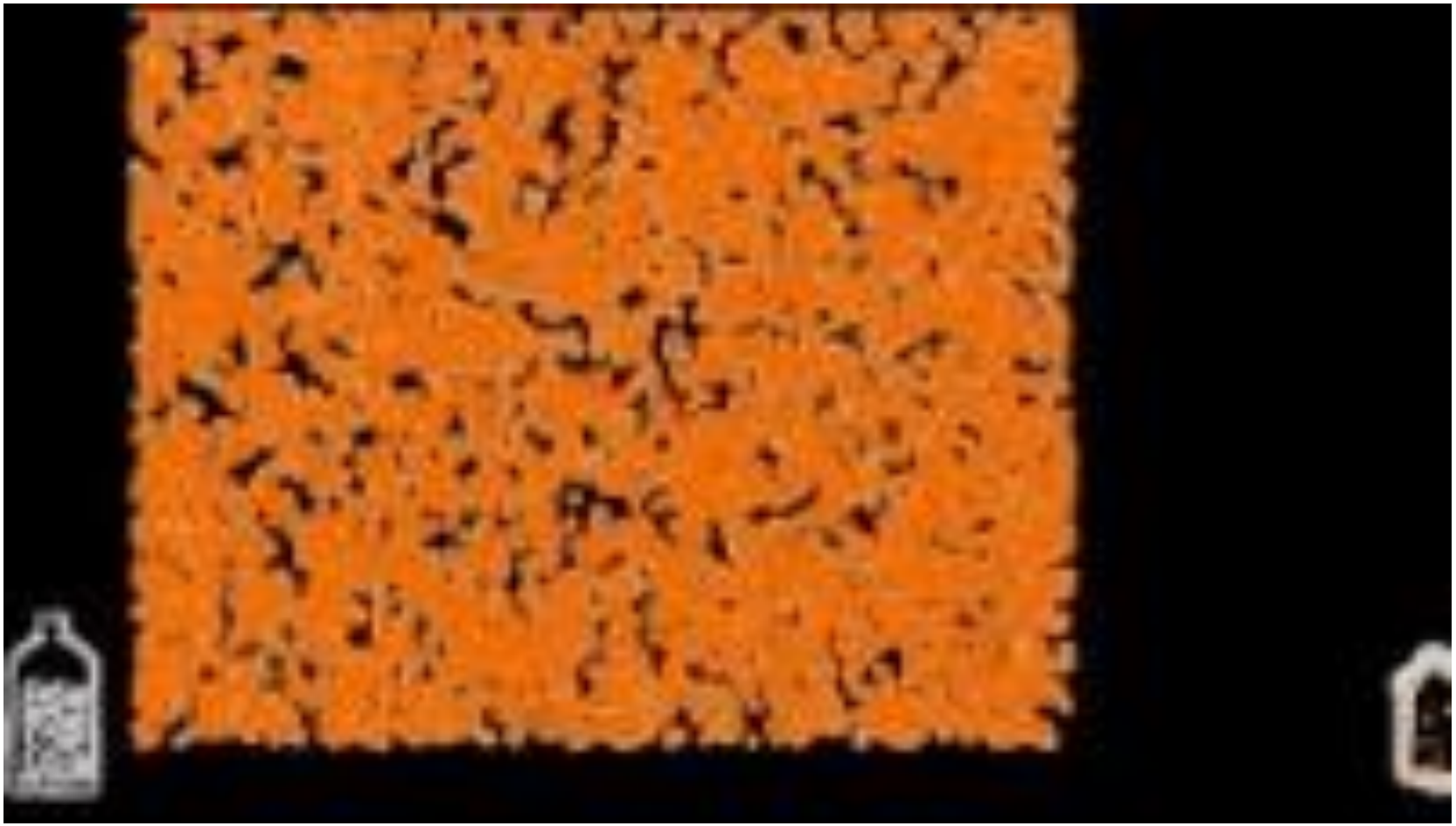

https://www.youtube.com/watch?v=bVVvTH_d4hI

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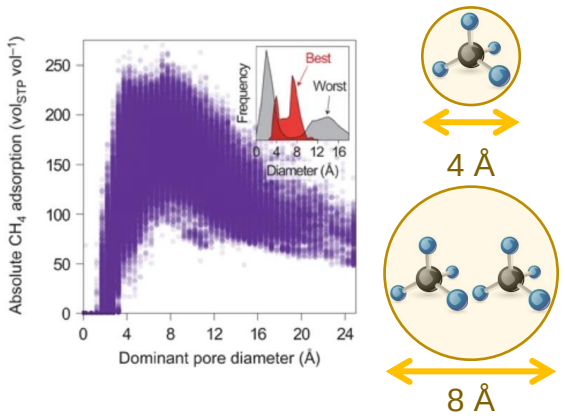

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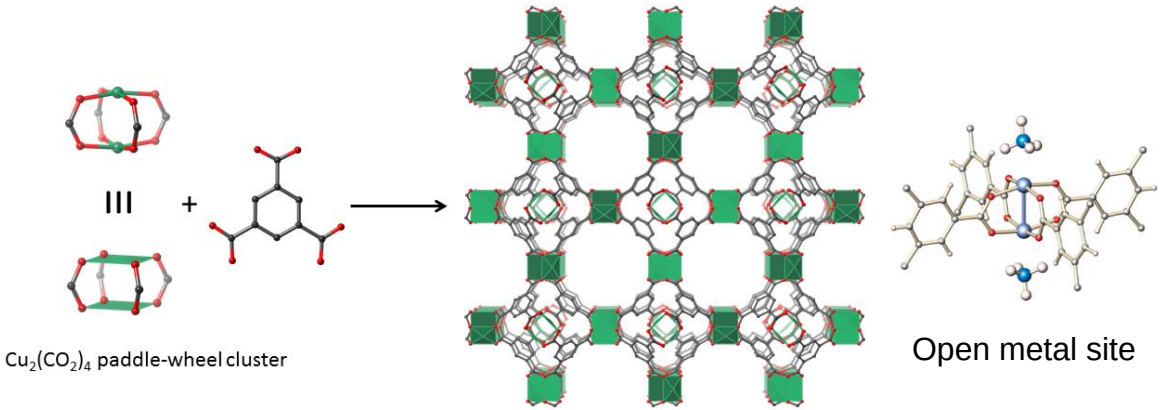

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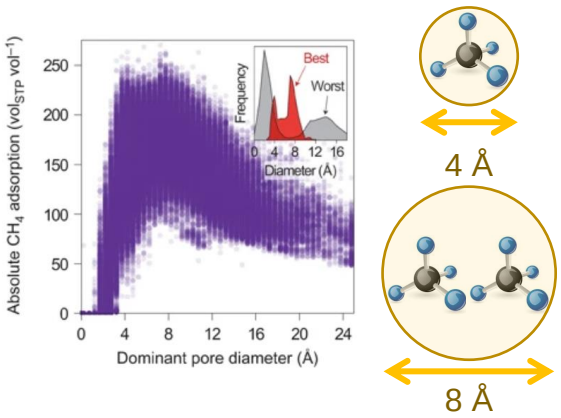

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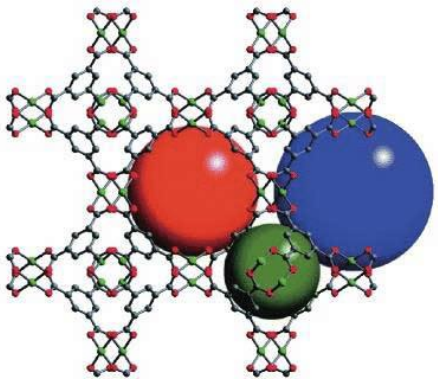
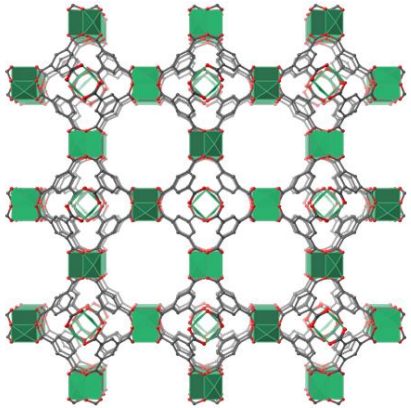
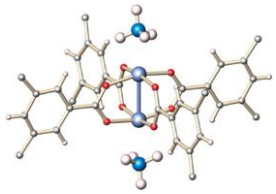


5 Å, 11 Å, 13 Å



HKUST-1



Open metal site

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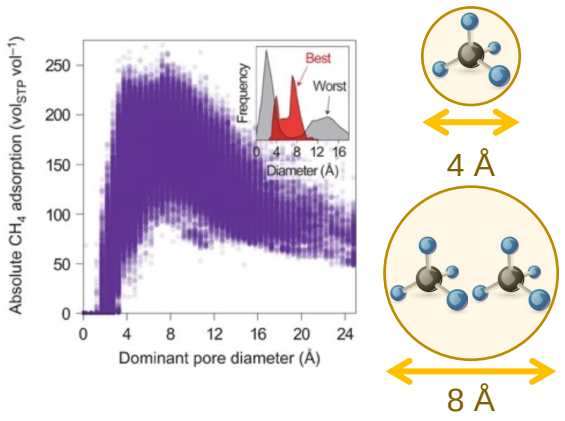

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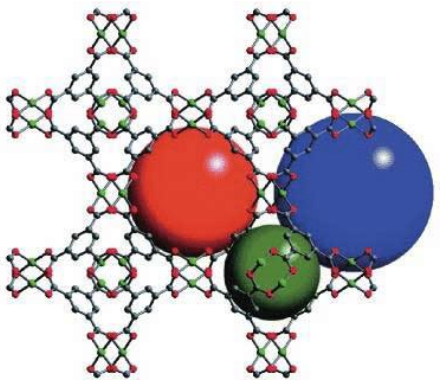

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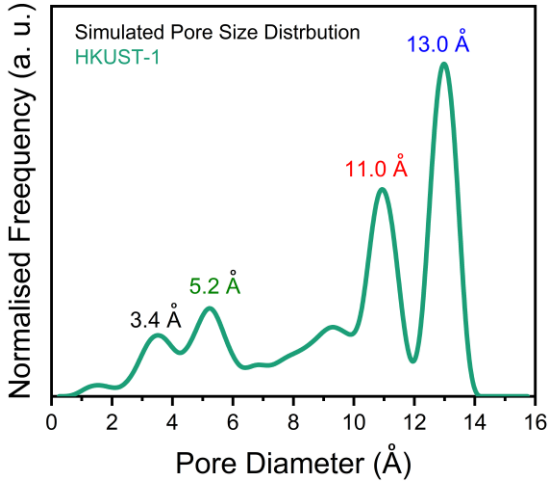

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Our Goal

Design a material with **both** open metal sites and optimal pore sizes

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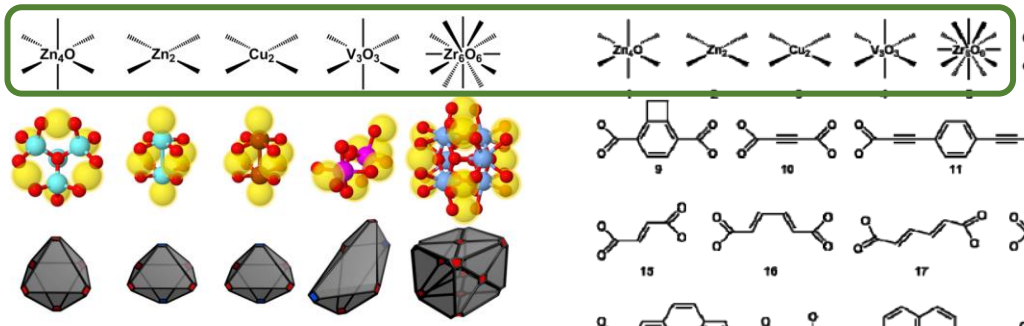
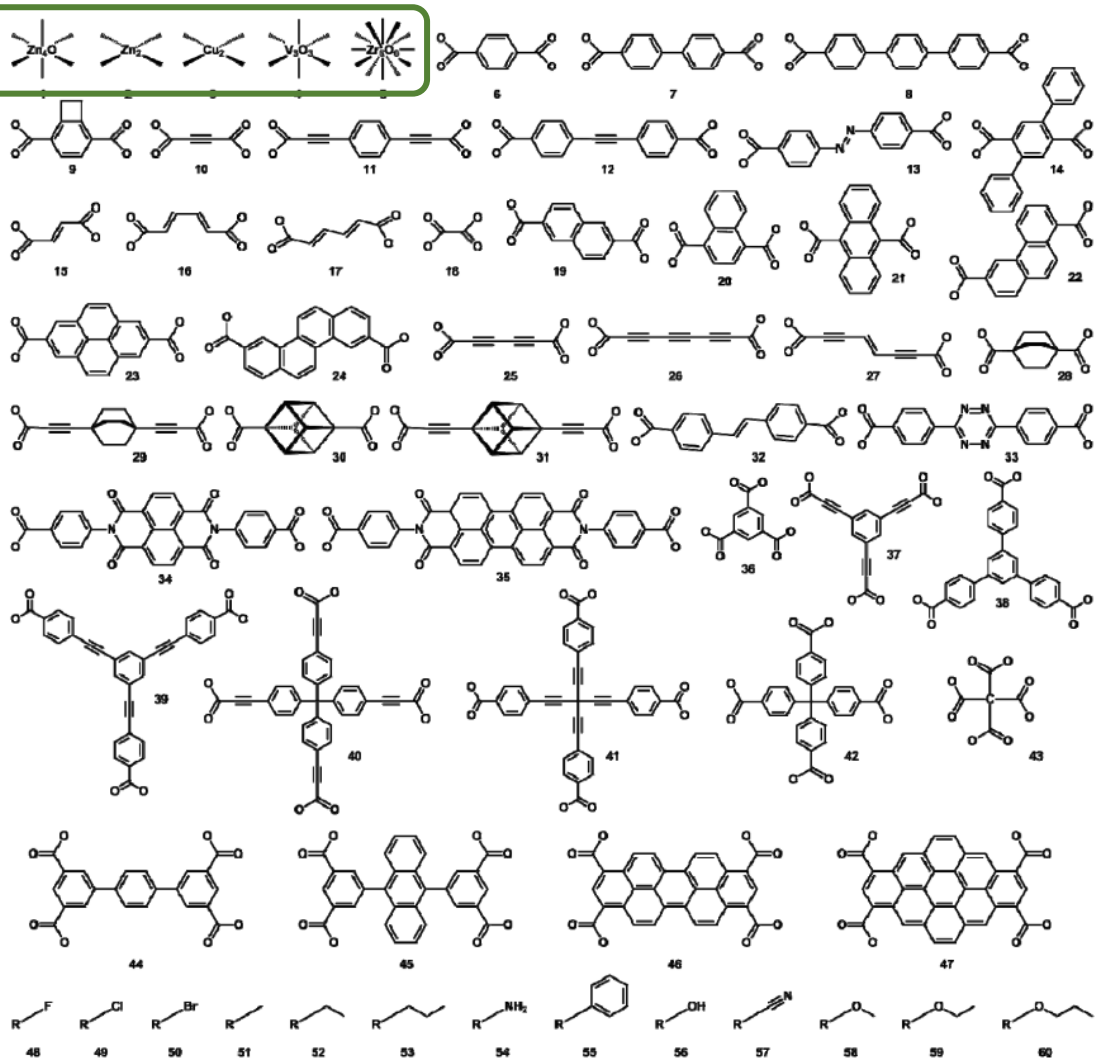
Design materials with **both** open metal site and optimal pore size





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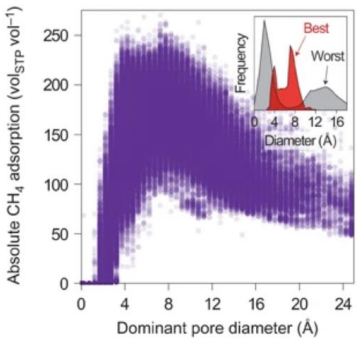

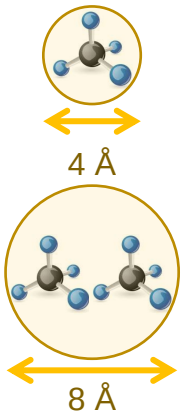

R. Q. Snurr and co-workers, *Nature Chem.* **2011**, *4*, 83.

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Design a material with **both** open metal sites and optimal pore sizes

Building unit 2 \ Building unit 1	2-c Linear	3-c Triangle	4-c Square	4-c **tet**	6-c Hexagon	6-c **oct**
3-c Triangle	**srs**	bwt, **pyo**, srs-b, ths-b	**fjh**, fmj, gee, iab, yac, yao	asn, **ept**, ofp	**cys**, dnf*	anh, **ant**, apo, brk, cep*, cml, czz, eea, qom, rtl, tsx, zzz
4-c Square	**nbo**, lvt, rhr	**pto**, tbo	cev, cdl, cdm, cdn, cds, cdz, **mot**, muo, qdl, qzd, ssd, sse, ssf, sst	**pts**	**nts**	myd, **ybh**
4-c **tet**	**dia**, lcs, qtz, sod	**bor**, ctn	fgl, mog, pds, **pth**, pti, ptr, ptt	bnl, byl, cag, cbt, coe, crb, fel, icm, kea, **lon**, pcl, qtz-b, sca, tpd, ucn	–	alw, bix, **cor**, ing, spl, toc
6-c Hexagon	**hxg**	**cys**, dnf	**she**	–	**hxg-b**	–
6-c **oct**	**pcu**, bcs, crs, reo	**pyr**, spn	**soc**	**gar**, iac, ibd, toc	–	**pcu-b**, bcs-b
6-c **trp**	**lcy**, acs	ceq, dag, fmz, hwx, moo, sab, **sit**, ydq	**stp**	fsi, hea, **tpt**	**htp**	**nia**

Building unit 2 \ Building unit 1	2-c Linear	3-c Triangle	4-c Square	4-c **tet**	6-c Hexagon	6-c **oct**
8-c **cub**	**bcu**	**the**	**scu**, csq, sqc	**flu**	–	**ocu**
12-c **cuo**	**fcu**	**sky**	**ftw**	**edc**	–	–
12-c **ico**	–	–	–	**ith**	–	–
12-c **hpr**	–	**aea**	**shp**	–	–	–
12-c **tte**	–	**ttt**	–	–	**mgc**	–
24-c **tro**	–	–	–	**twf**	–	–

O. M. Yaghi and co-workers, *Sci. Adv.* **2018**, *4*, eaat9180.

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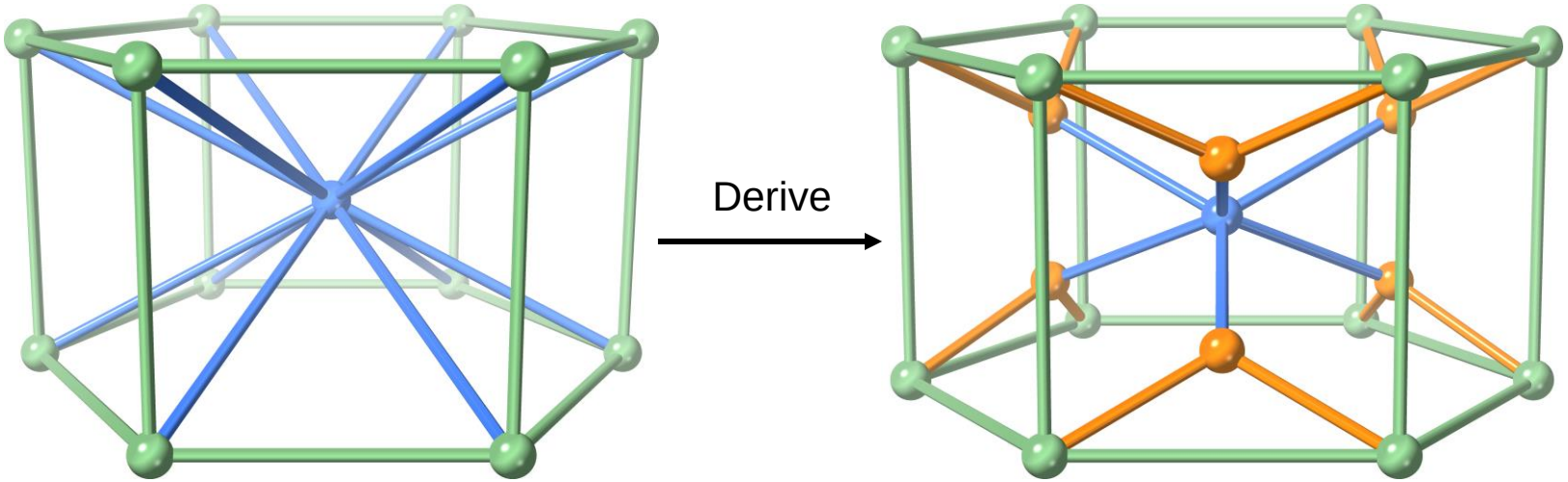
Design a material with **both** open metal sites and optimal pore sizes

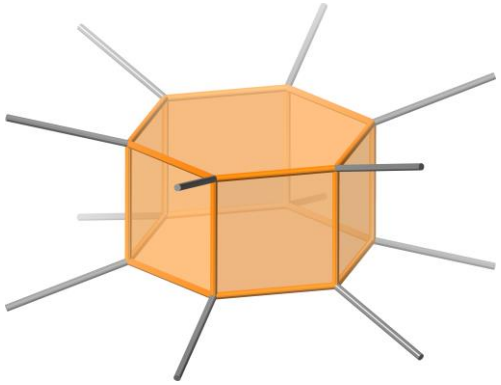
Building unit 2 \ Building unit 1	2-c Linear	3-c Triangle	4-c Square	4-c **tet**	6-c Hexagon	6-c **oct**
3-c Triangle	**srs**	bwt, **pyo**, srs-b, ths-b	**fjh**, fmj, gee, iab, yac, yao	asn, **ept**, ofp	**cys**, dnf*	anh, **ant**, apo, brk, cep*, cml, czz, eea, qom, rtl, tsx, zzz
4-c Square	**nbo**, lvt, rhr	**pto**, tbo	cev, cdl, cdm, cdn, cds, cdz, **mot**, muo, qdl, qzd, ssd, sse, ssf, sst	**pts**	**nts**	myd, **ybh**
4-c **tet**	**dia**, lcs, qtz, sod	**bor**, ctn	fgl, mog, pds, **pth**, pti, ptr, ptt	bnl, byl, cag, cbt, coe, crb, fel, icm, kea, **lon**, pcl, qtz-b, sca, tpd, ucn	–	alw, bix, **cor**, ing, spl, toc
6-c Hexagon	**hxg**	**cys**, dnf	**she**	–	**hxg-b**	–
6-c **oct**	**pcu**, bcs, crs, reo	**pyr**, spn	**soc**	**gar**, iac, ibd, toc	–	**pcu-b**, bcs-b
6-c **trp**	**lcy**, acs	ceq, dag, fmz, hwx, moo, sab, **sit**, ydq	**stp**	fsi, hea, **tpt**	**htp**	**nia**

Building unit 2 \ Building unit 1	2-c Linear	3-c Triangle	4-c Square	4-c **tet**	6-c Hexagon	6-c **oct**
8-c **cub**	**bcu**	**the**	**scu**, csq, sqc	**flu**	–	**ocu**
12-c **cuo**	**fcu**	**sky**	**ftw**	**edc**	–	–
12-c **ico**	–	–	–	**ith**	–	–
12-c **hpr**	–	**aea**	**shp**	–	–	–
12-c **tte**	–	**ttt**	–	–	**mgc**	–
24-c **tro**	–	–	–	**twf**	–	–

O. M. Yaghi and co-workers, *Sci. Adv.* **2018**, *4*, eaat9180.

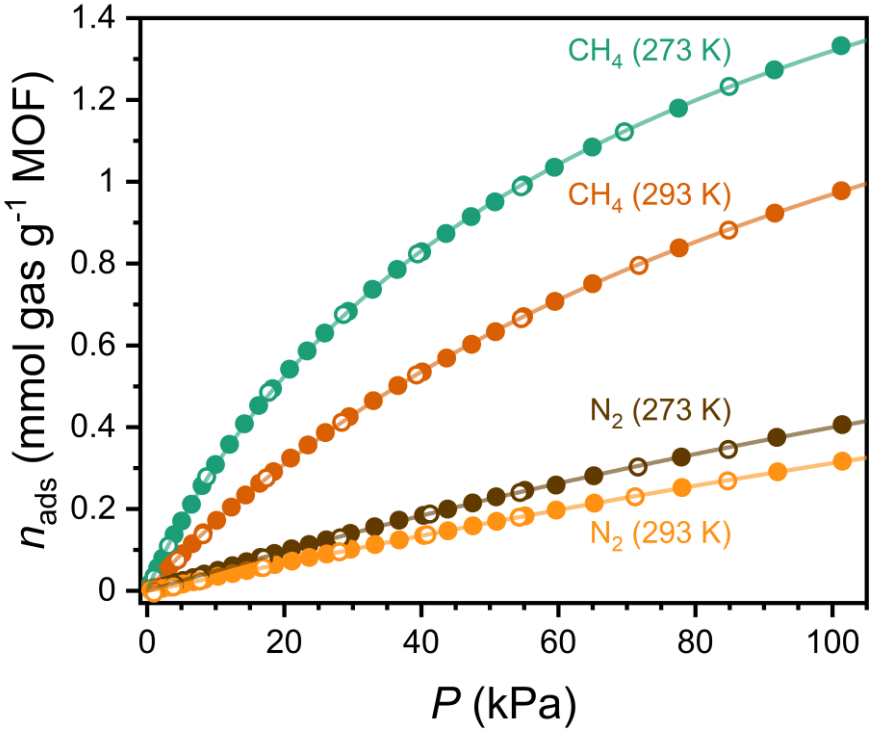
Deriving The 12-c Building Block



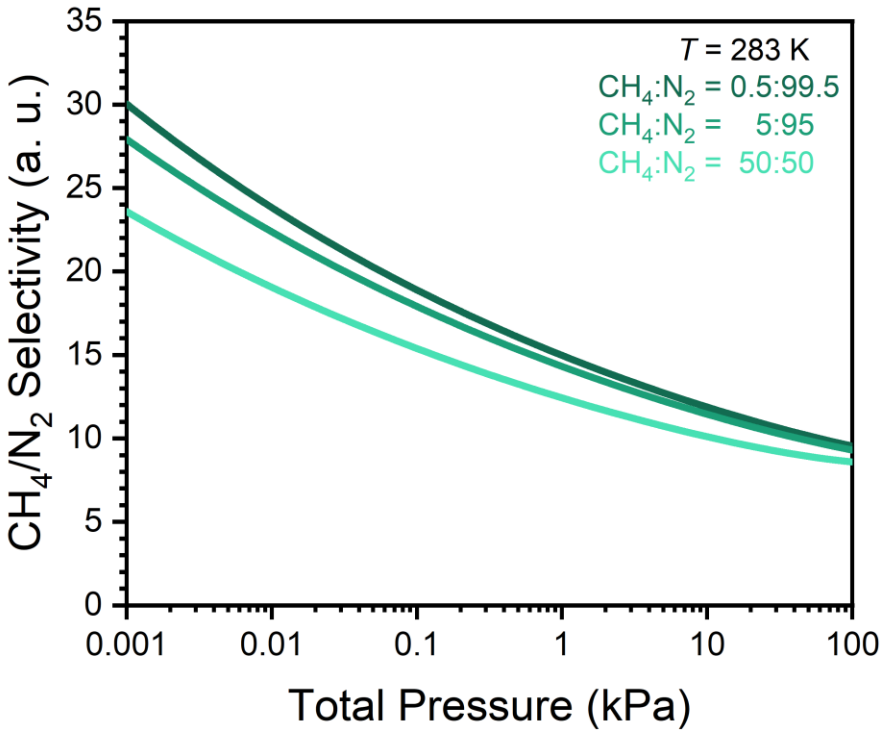


Methane Capture Performance

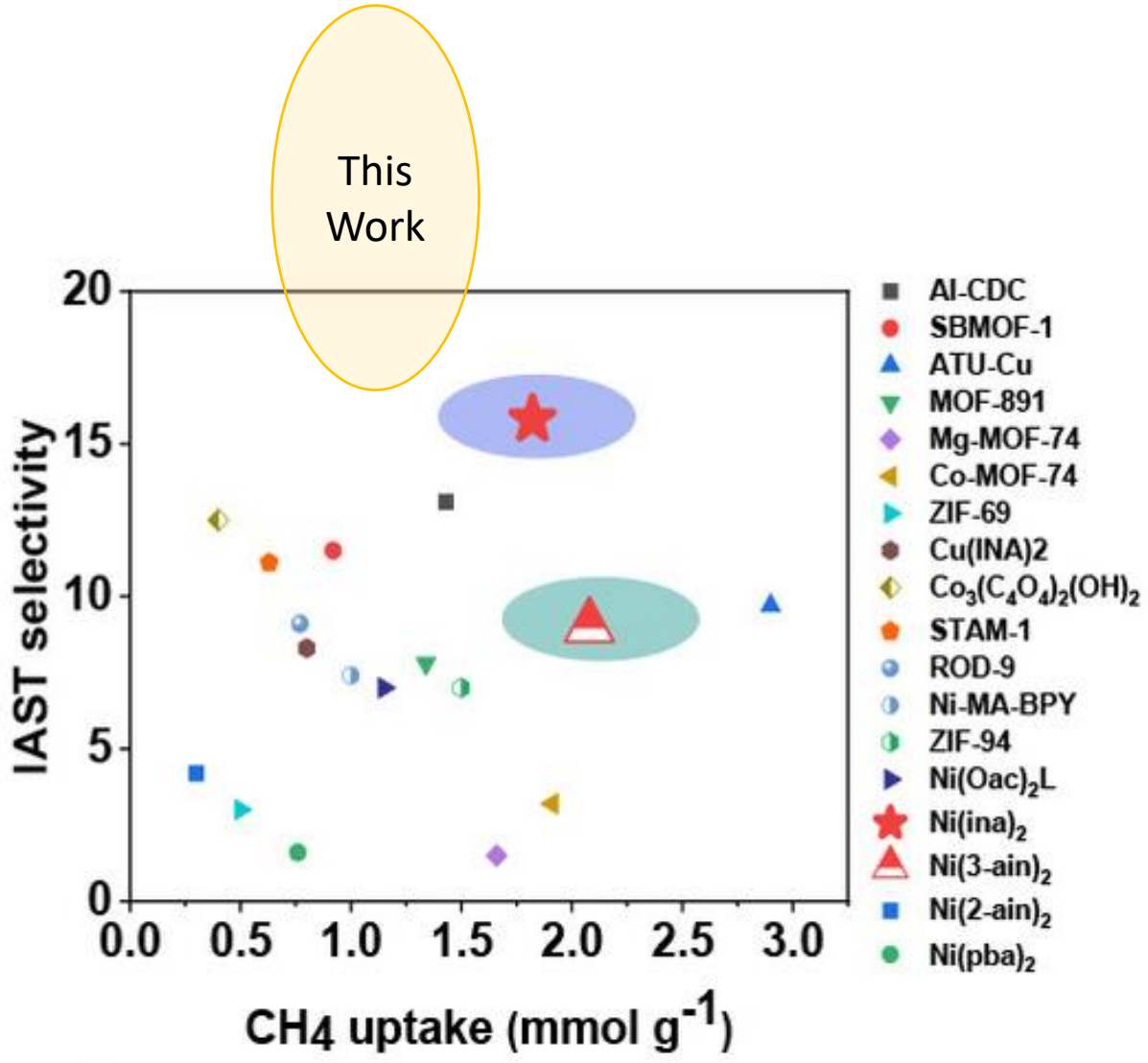
Adsorption isotherms



CH$_4$/N$_2$ Selectivity



CH_4/N_2 Selectivity Comparison



Qing-Yuan Yang and co-workers, *Angew. Chem. Int. Ed.* **2022**, *61*, e202201017.

Further Cost Reduction for Hydrogen Storage?

- Increase Materials Durability
- Increase Storage Capacity

How?

Further Cost Reduction for Hydrogen Storage?

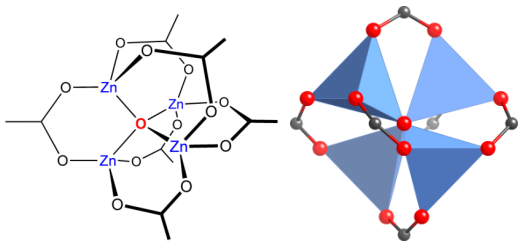
- Increase Materials Durability
- Increase Storage Capacity

How?

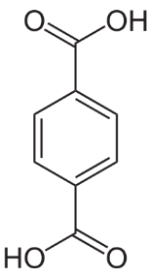
- Increase Materials Durability – Stronger Bonds
- Increase Storage Capacity – Higher Surface Area

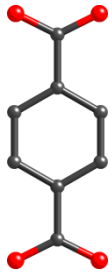
Metal-Organic Framework-5 (MOF-5)

III + III ⟶

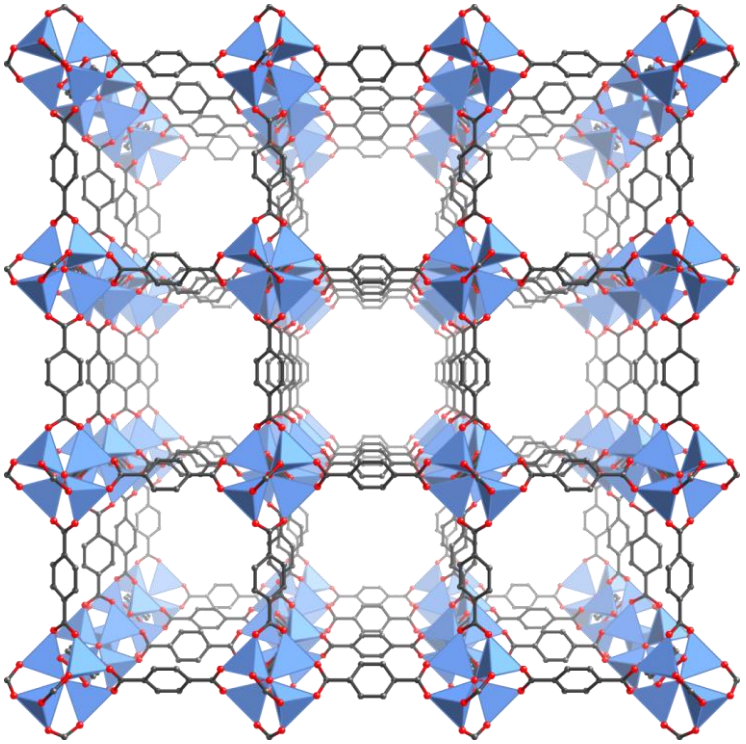


$Zn_4O(CO_2\text{-}R)_6$ cluster





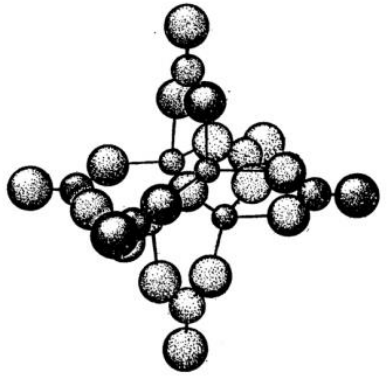
Terephthalic acid
H_2BDC

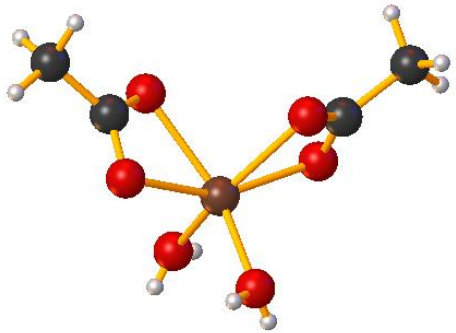


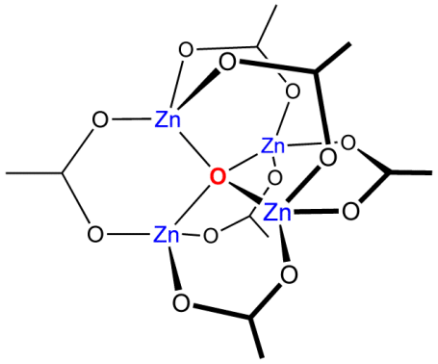
MOF-5 $[Zn_4O(BDC)_3]$
Surface Area = 3500 m^2/g

H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature*, **1999**, *402*, 276-279.

Octahedron Chemical Building Block







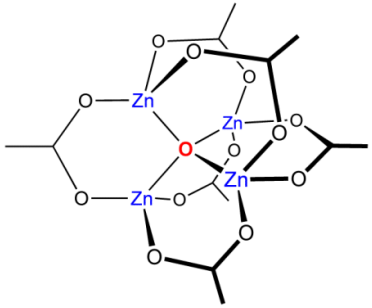
Sublimation

$Zn(CH_3COO)_2(H_2O)_2$

$Zn_4O(CH_3COO)_6$

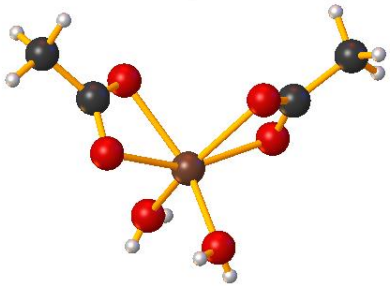
H. Koyama & Y. Saito; The Crystal Structure of Zinc Oxyacetate, $Zn_4O(CH_3COO)_6$. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 112-114.

From Weaker Coordination Bonds to Stronger Covalent Bonds

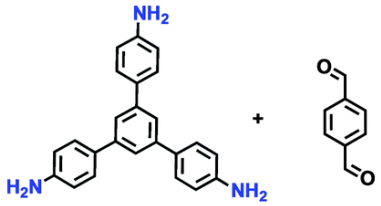


$Zn_4O(CH_3COO)_6$

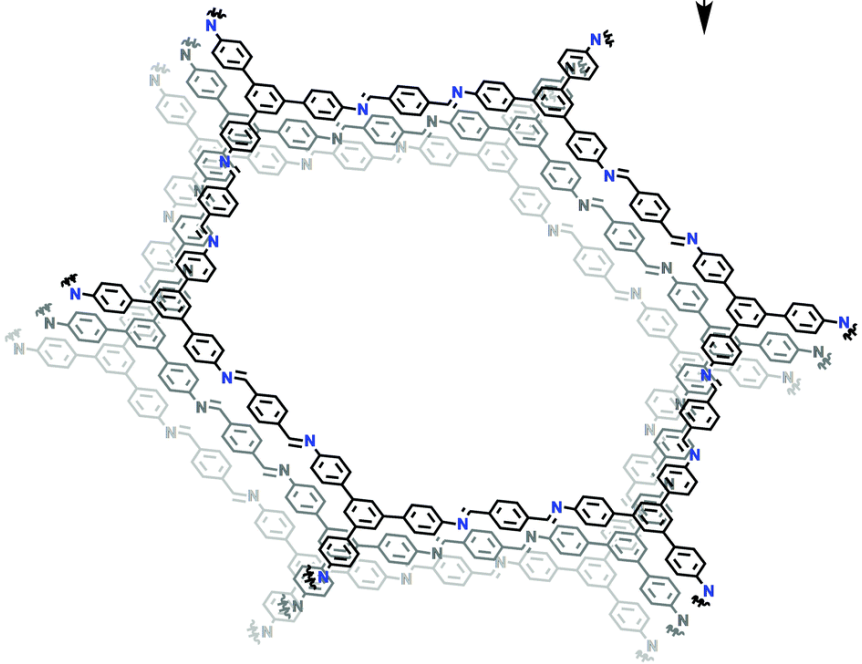
> 30%
Relative Humidity



$Zn(CH_3COO)_2(H_2O)_2$

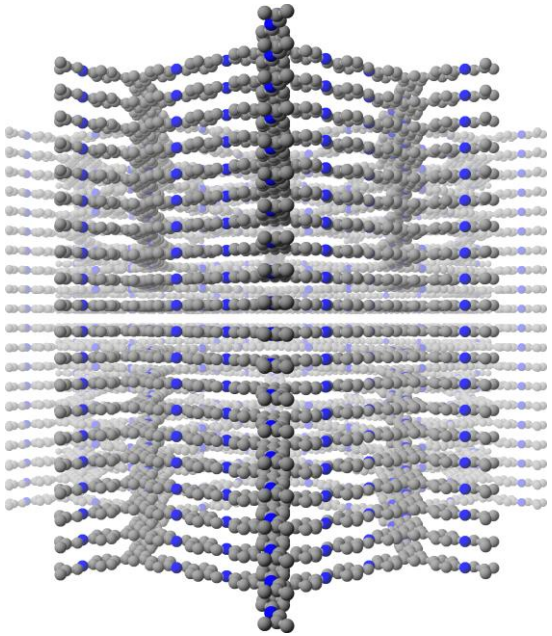


TAPB PDA

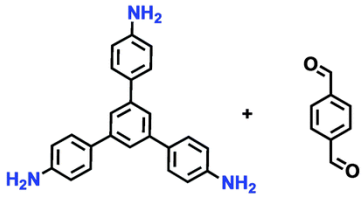


Covalent organic frameworks (COFs)

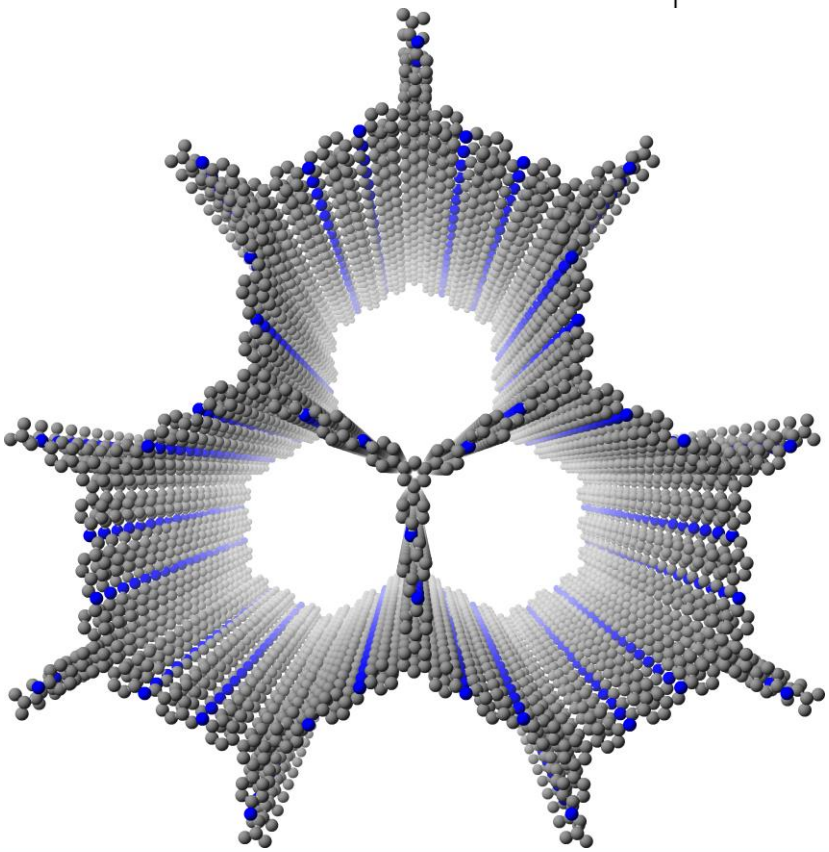
Covalent organic frameworks



honeycomb



TAPB PDA



Further Cost Reduction for Hydrogen Storage?

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How?

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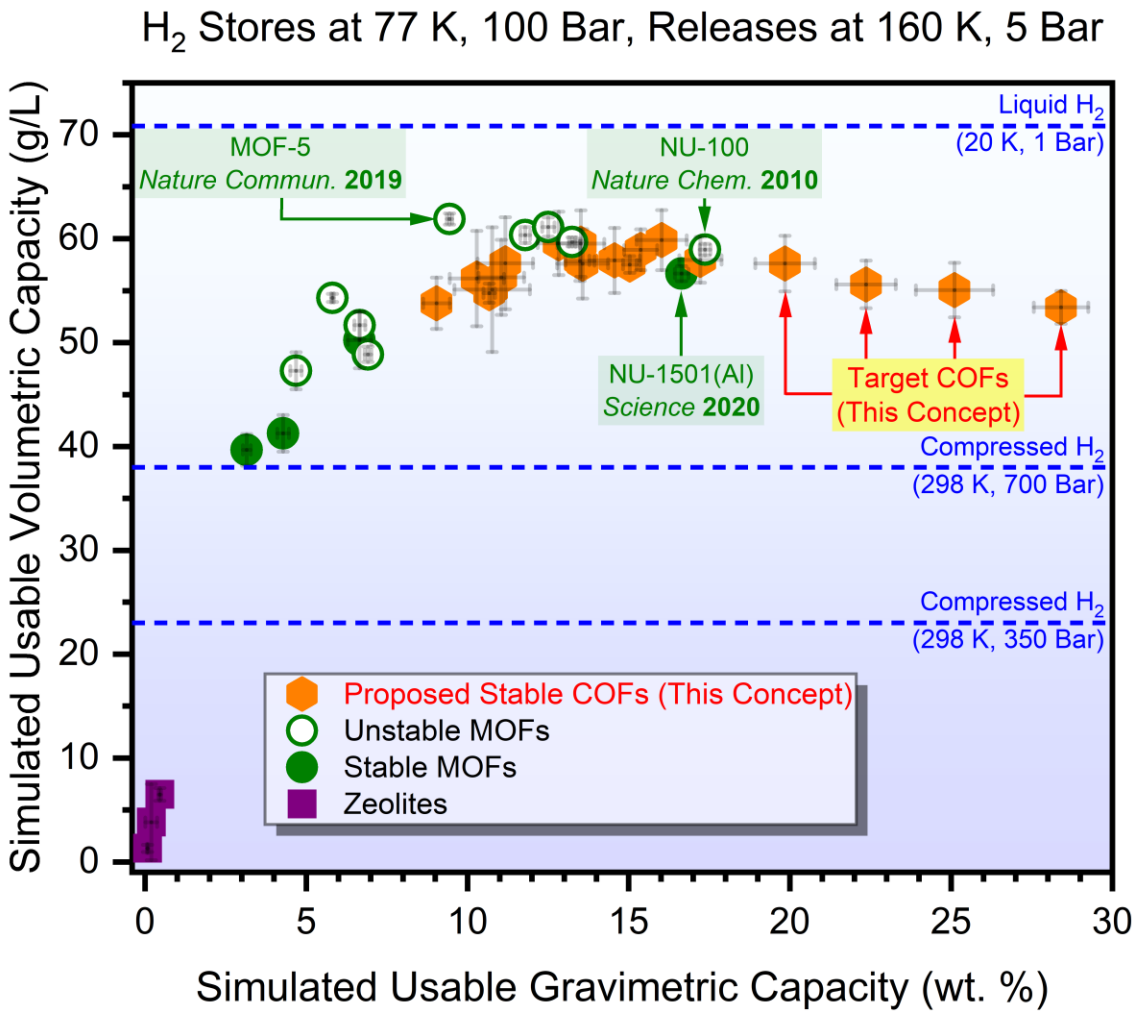
Vastly Underexplored Geometries

Building unit 2 \ Building unit 1	2-c Linear	3-c Triangle	4-c Square	4-c **tet**	6-c Hexagon	6-c **oct**
3-c Triangle	**srs**	bwt, **pyo**, srs-b, ths-b	**fjh**, fmj, gee, iab, yac, yao	asn, **ept**, ofp	**cys**, dnf*	anh, **ant**, apo, brk, cep*, cml, czz, eea, qom, rtl, tsx, zzz
4-c Square	**nbo**, lvt, rhr	**pto**, tbo	cev, cdl, cdm, cdn, cds, cdz, **mot**, muo, qdl, qzd, ssd, sse, ssf, sst	**pts**	**nts**	myd, **ybh**
4-c **tet**	**dia**, lcs, qtz, sod	**bor**, ctn	fgl, mog, pds, **pth**, pti, ptr, ptt	bnl, byl, cag, cbt, coe, crb, fel, icm, kea, **lon**, pcl, qtz-b, sca, tpd, ucn	–	alw, bix, **cor**, ing, spl, toc
6-c Hexagon	**hxg**	**cys**, dnf	**she**	–	**hxg-b**	–
6-c **oct**	**pcu**, bcs, crs, reo	**pyr**, spn	**soc**	**gar**, iac, ibd, toc	–	**pcu-b**, bcs-b
6-c **trp**	**lcy**, acs	ceq, dag, fmz, hwx, moo, sab, **sit**, ydq	**stp**	fsi, hea, **tpt**	**htp**	**nia**

Building unit 2 \ Building unit 1	2-c Linear	3-c Triangle	4-c Square	4-c **tet**	6-c Hexagon	6-c **oct**
8-c **cub**	**bcu**	**the**	**scu**, csq, sqc	**flu**	–	**ocu**
12-c **cuo**	**fcu**	**sky**	**ftw**	**edc**	–	–
12-c **ico**	–	–	–	**ith**	–	–
12-c **hpr**	–	**aea**	**shp**	–	–	–
12-c **tte**	–	**ttt**	–	–	**mgc**	–
24-c **tro**	–	–	–	**twf**	–	–

O. M. Yaghi and co-workers, *Sci. Adv.* **2018**, *4*, eaat9180.

Computational Screening



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