DOE Hydrogen Program

HYDROGEN STORAGE IN METAL-ORGANIC FRAMEWORKS

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Project ID
ST049

Overview

Timeline

Project start date: 5/2/2005
Project end date: 4/30/2011
Percent complete: 95%

Barriers

Barriers addressed

- ❑ Improved gravimetric and volumetric density of hydrogen uptake
- ❑ Improved hydrogen binding energy
- ❑ Synthetic scale up of MOFs to cubic meters

Budget

- ❑ Total project funding
  - DOE share: $1.71 M
  - Contractor share: $0.50 M

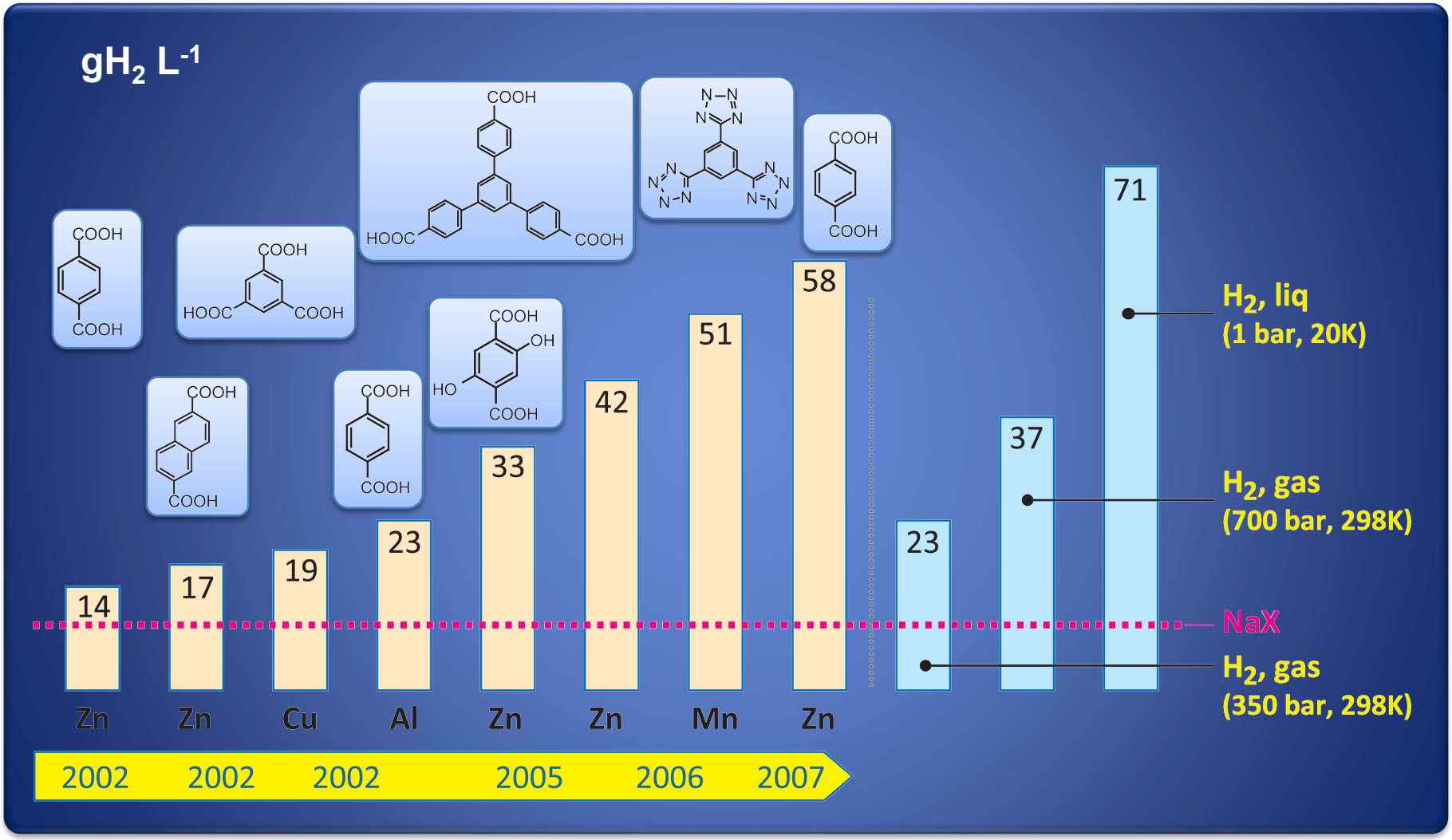
Collaborating Partners

- ❑ Bill Goddard (Caltech)
- ❑ Fraser Stoddart (NW)
- ❑ Randy Snurr (NW)
- ❑ Jaheon Kim (Soongsil University)
- ❑ BASF

Important Aspects of MOF Chemistry

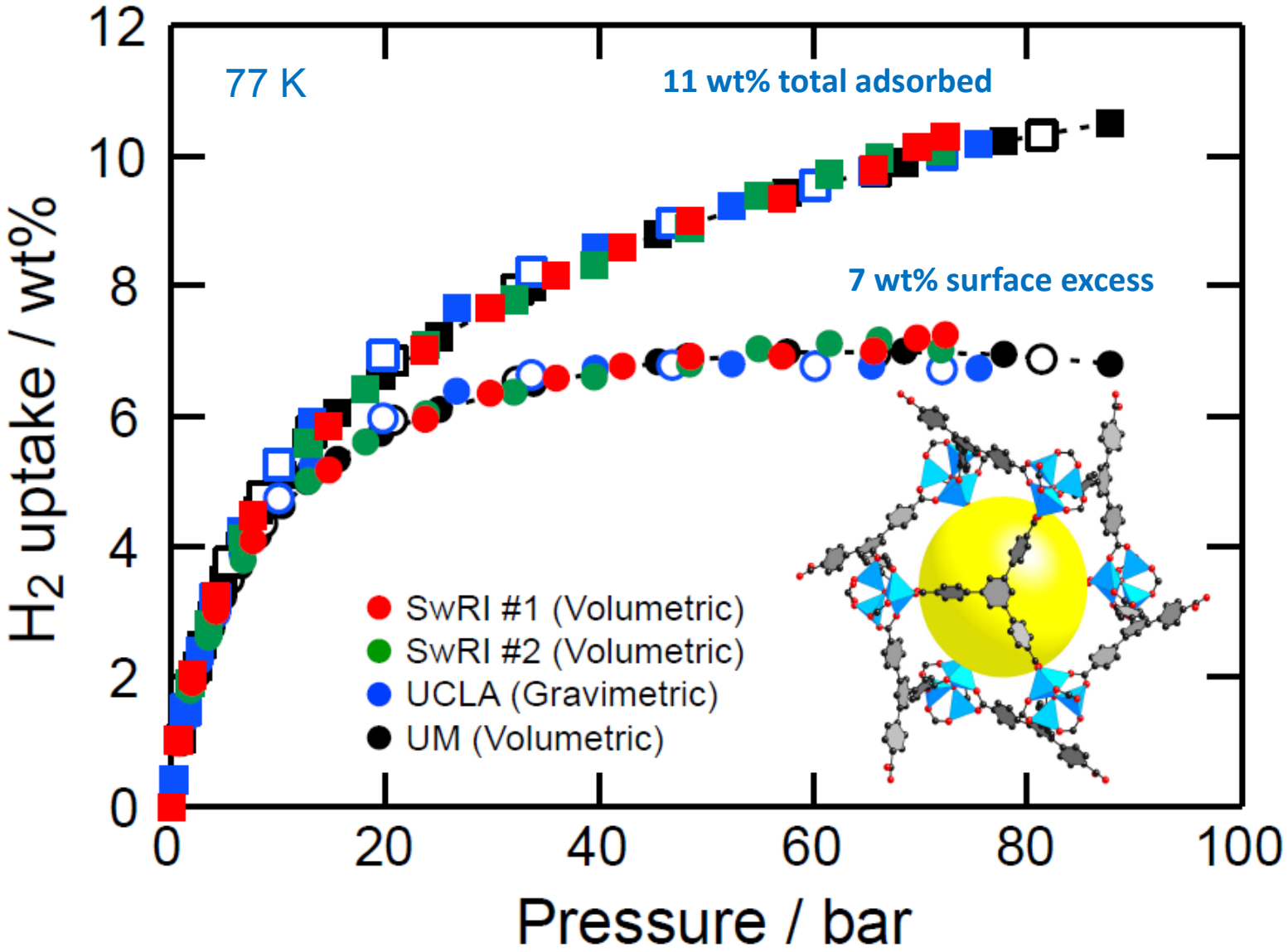
- Design of composition (metal centers and organic linkers). Synthesis and structural characterization is well worked out.
- Control of structure, topology, interpenetration and porosity.
- Formulation of hypotheses and testing of hypotheses is quite feasible. This leads to definitive conclusions and allows for rapid identification of important parameters which impact hydrogen uptake.

MOF: Hydrogen Storage Capacities (50 bar, 77 K)



Independent Verification of MOF-177 Hydrogen Uptake Capacity

(volumetric and gravimetric measurements verified, shown using gravimetric scale)



Feasibility of MOFs for hydrogen storage


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Image

1 of 1

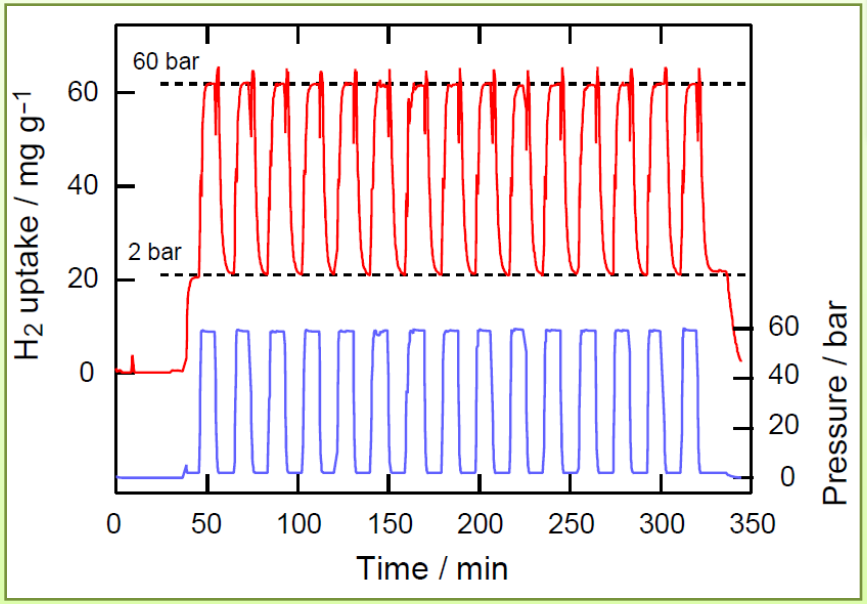
686859 Aldrich — 1,3,5-Tris(4-carboxyphenyl)benzene
≥98%, ≤20 wt. % solvent

Price and Availability
Click For Pricing and Availability

Synonyms:	4,4',4",-Benzene-1,3,5-triyl-tris(benzoic acid)
CAS Number:	50446-44-1
Empirical Formula (Hill Notation):	$C_{27}H_{18}O_6$
Molecular Weight:	438.43
MDL number:	MFCD10000888

Inexpensive organic links

Scale-Up and Shaping at BASF



- **Excellent durability**
- **Fast H_2 charge rate (< 3 min)**
- **4 wt% of H_2 delivery (2-60 bar at 77 K)**

Objectives (FY10-11)

Last year:

1. Impregnated metals as strong binding sites

→ Metalated materials show larger binding energy, while significant surface area drop was observed.

2. Isoreticular expansion of the framework

→ High surface area MOF (MOF-200) was prepared, but H_2 density per volume should be increased.

This year:

1. Expand the framework with keeping strong H_2 binding sites

- Design new porphyrin MOF to increase the storage space
- Expand Mg-MOF-74; high Q_{st} and BET surface area to achieve high H_2 density at RT.

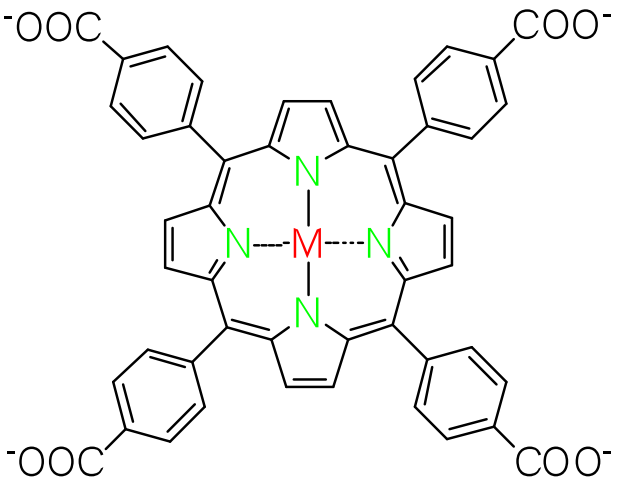
2. Preparation of ultrahigh-surface area MOFs

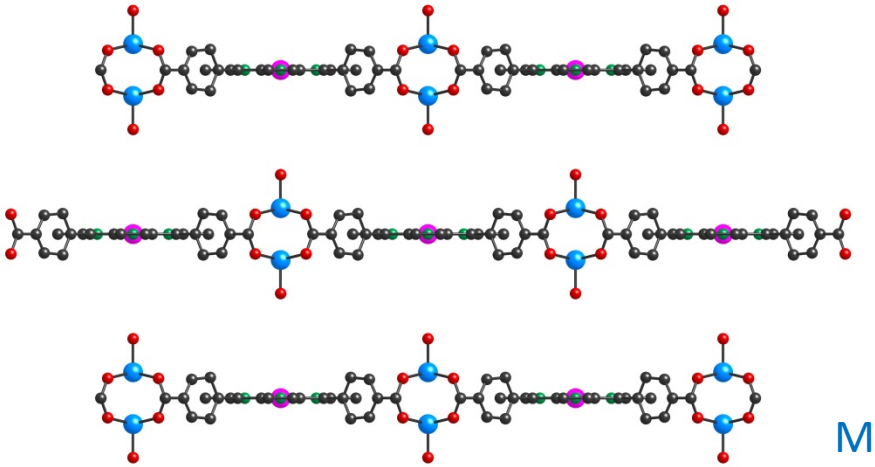
- Large storage space, but minimize dead space (*i.e.* high BET surface area)
- Evaluate RT H_2 storage capacity by new high-surface area MOFs

3. Large scale synthesis and metalation of MOF-253

- Optimize the synthetic condition

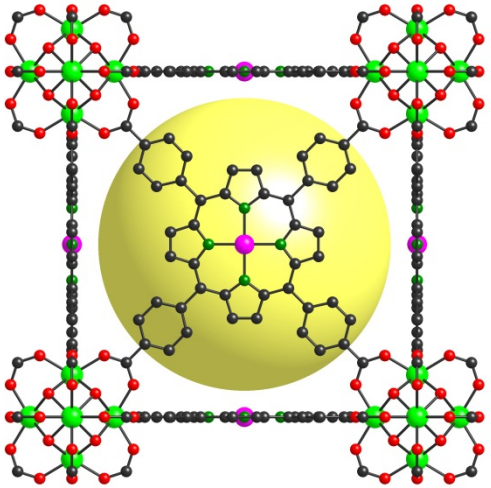
Design of highly porous porphyrin MOFs

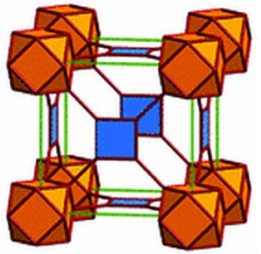




MOF-122

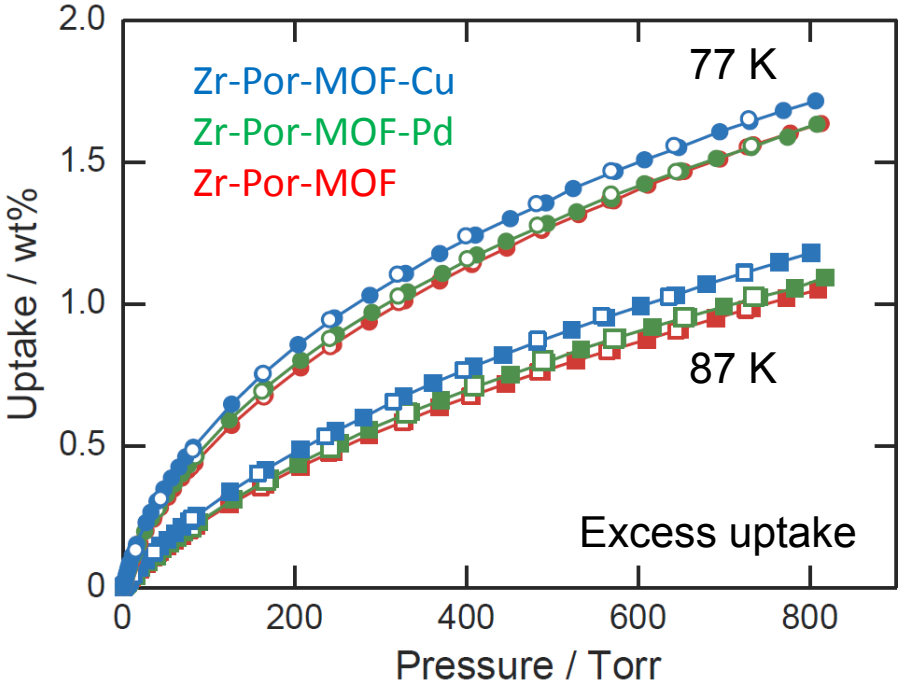
- Limited accessible space because of the layered structure (BET ≈ 500 m^2/g)
- 3D structure with large storage space is required for better H_2 storage capacity
- Use $Zr_6O_4(OH)_4(CO_2)_{12}$ unit
  - Chemically stable
  - **ftw** net can be formed

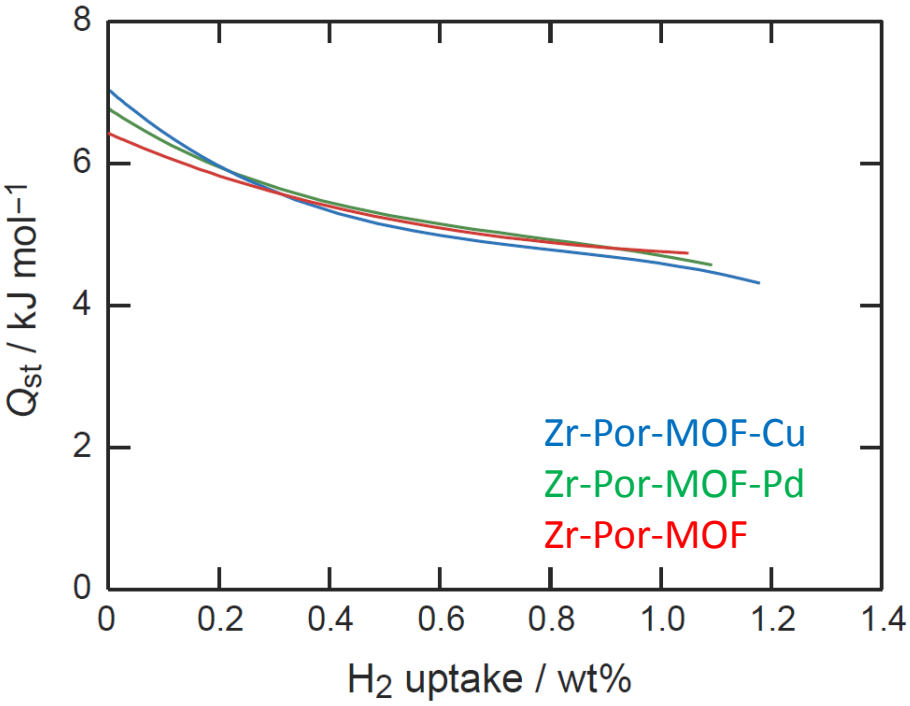




ftw net

H_2 uptake of metalated porphyrin MOFs

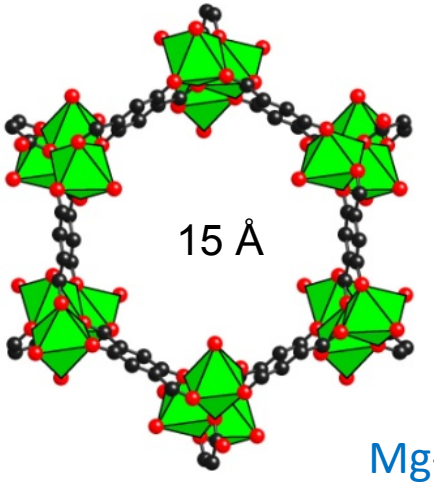


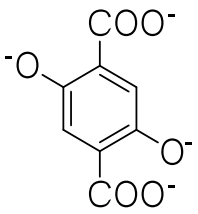


	BET SA (m^2/g)	Langmuir SA (m^2/g)	Pore volume (cm^3/g)	Uptake at 1 bar and 77 K (wt%)	Uptake at 1 bar and 87 K (wt%)	Initial Q_{st} (kJ/mol)
Zr-Por-MOF	2100	2390	0.80	1.6	1.0	6.4
Zr-Por-MOF-Cu	1850	2270	0.75	1.7	1.1	7.0
Zr-Por-MOF-Pd	1700	2310	0.79	1.6	1.0	6.8

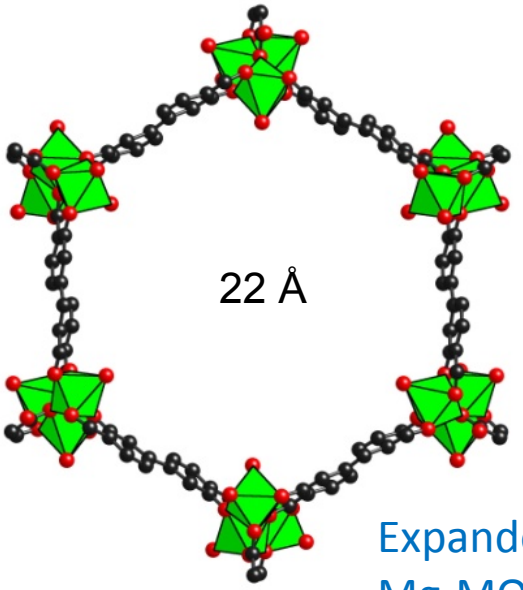
- High BET surface areas were observed by all Zr-Por-MOFs.
- H_2 uptakes by Zr-Por-MOFs at 1 bar and 77 K are higher than that of MOF-177.
- Metalated MOFs show better H_2 uptake and higher initial Q_{st}.

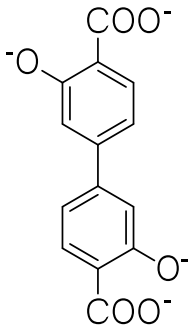
Isoreticular expansion of Mg-MOF-74



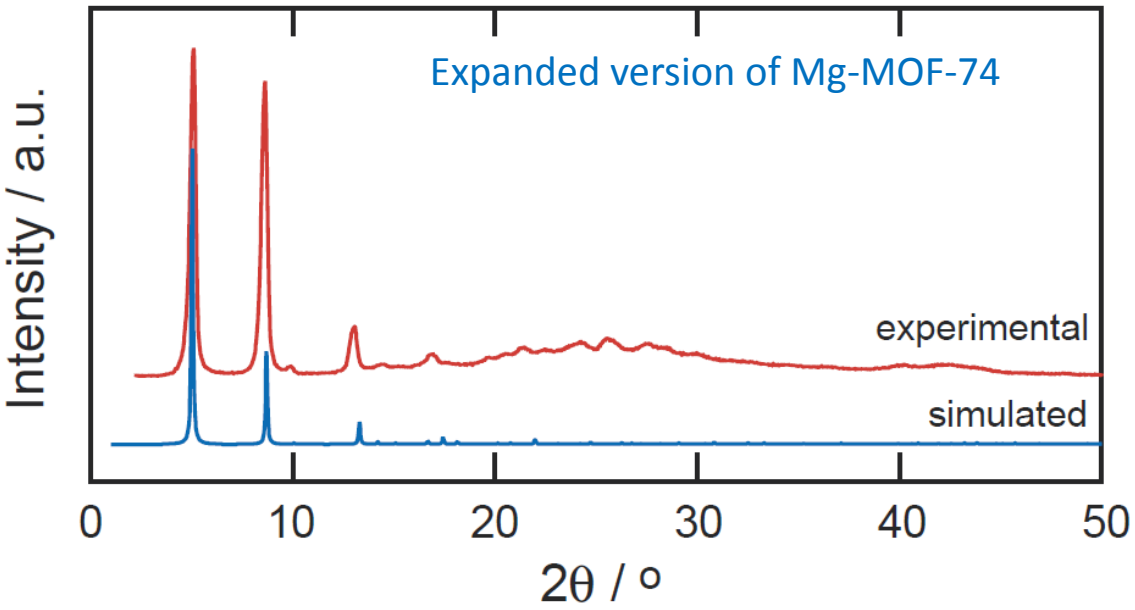


Mg-MOF-74





Expanded version of Mg-MOF-74

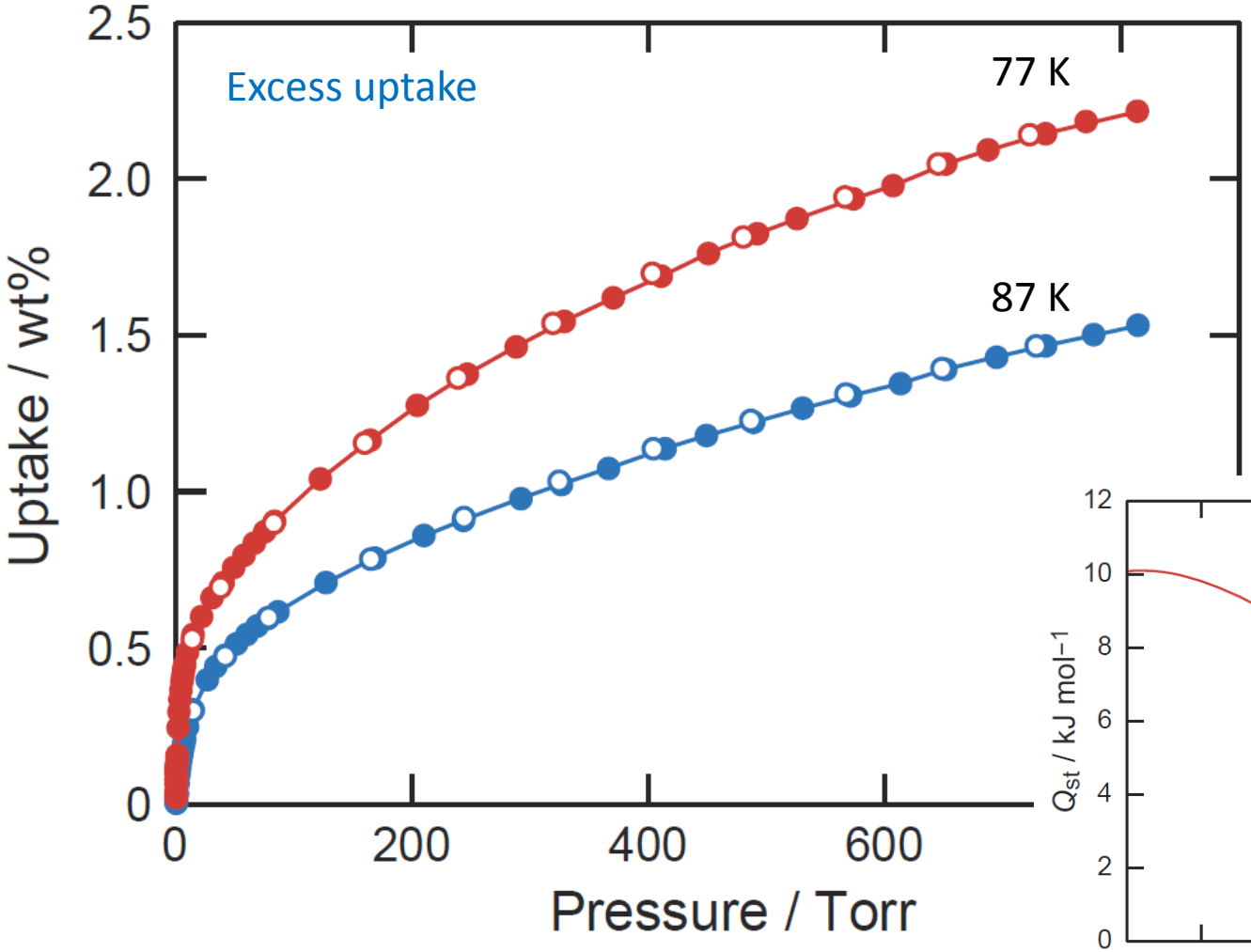


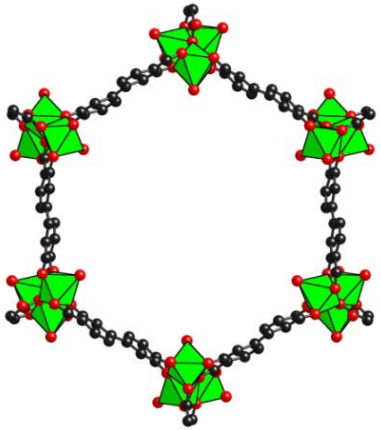
Advantages

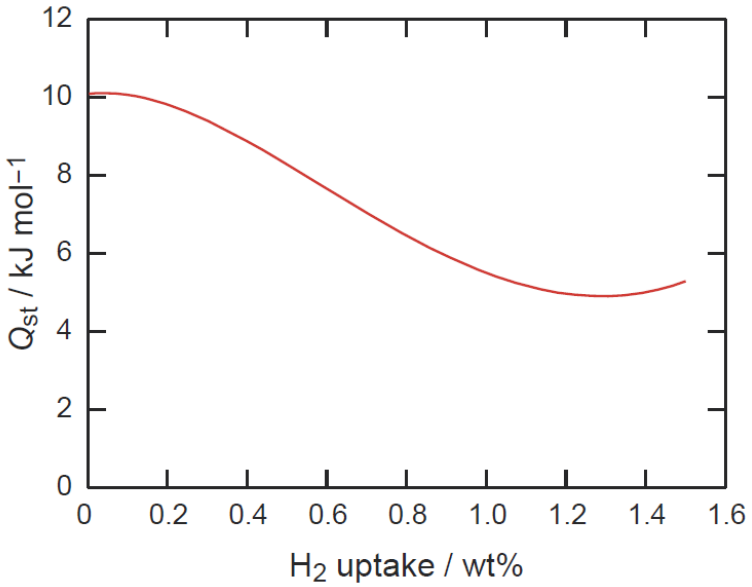
- ❑ High surface area and large pore volume
- ❑ Strong interaction between MOF and H_2

In collaboration with Prof. Stoddart group (Northwestern)

Low-pressure H_2 isotherms

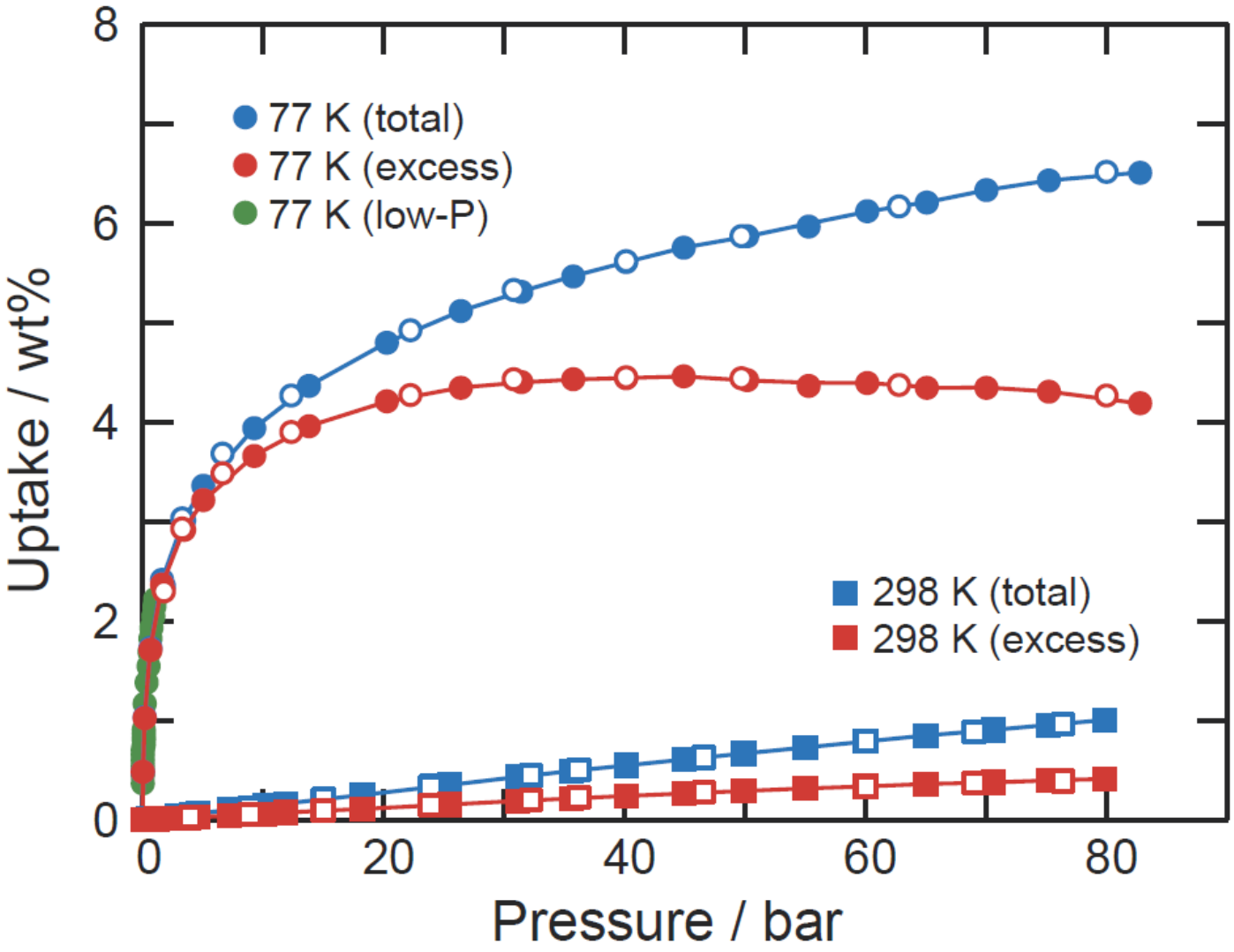


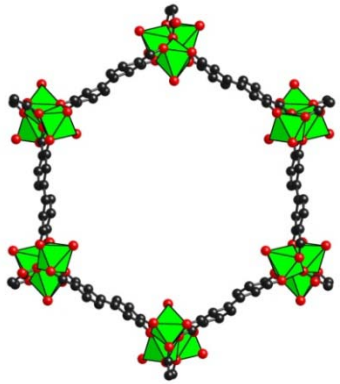




- 2.2 wt% H_2 uptake at 1 bar and 77 K
- High initial Q_{st} (10.1 kJ/mol)

High-pressure H_2 isotherms

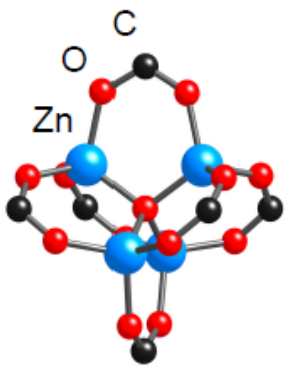




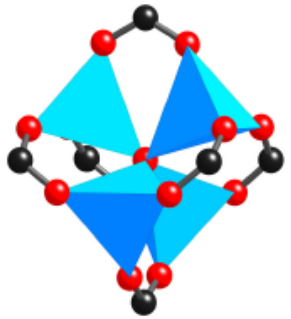
- 6.5 wt% (43 g/L) at 77 K and 80 bar
- 1.0 wt% (6.3 g/L) at 298 K and 80 bar

Expansion of frameworks (mixed link system)

How to avoid interpenetration?

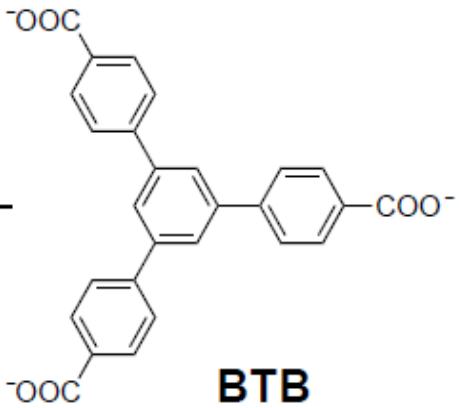


III



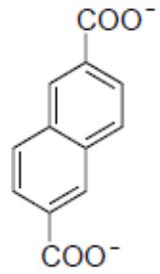
$Zn_4O(CO_2)_6$

+



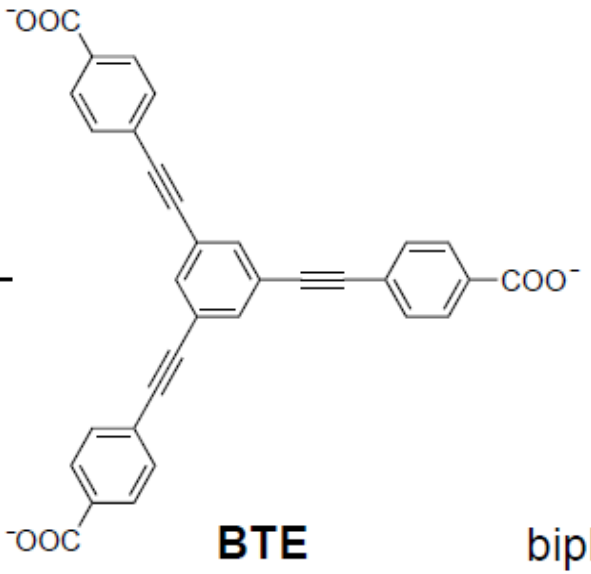
BTB

+



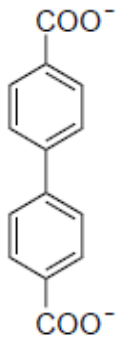
2,6-naphthalendicarboxylate (**NDC**)

→ MOF-205



BTE

+

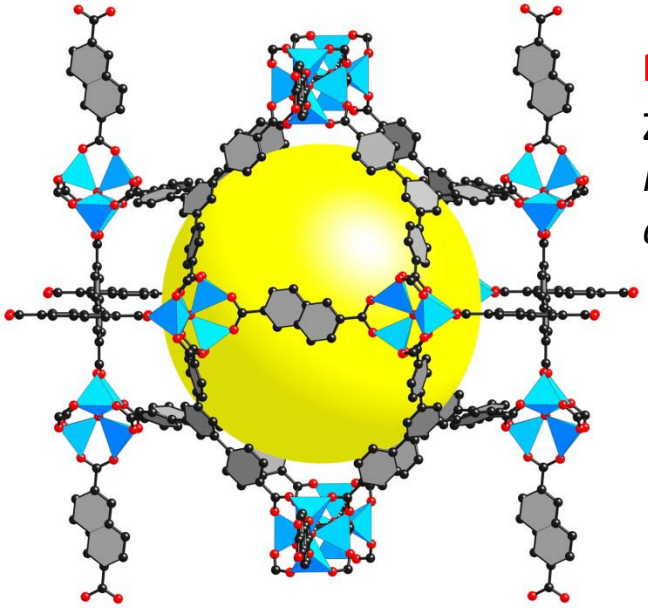


biphenyl-4,4'-dicarboxylate (**BPDC**)

→ MOF-210

In collaboration with Prof. Kim (Soongsil University, Korea)

Synthesis of MOF-205 and 210



MOF-205

$Zn_4O(BTB)_{4/3}(NDC)$

Pm-3*n*

a = 30.353(4) Å

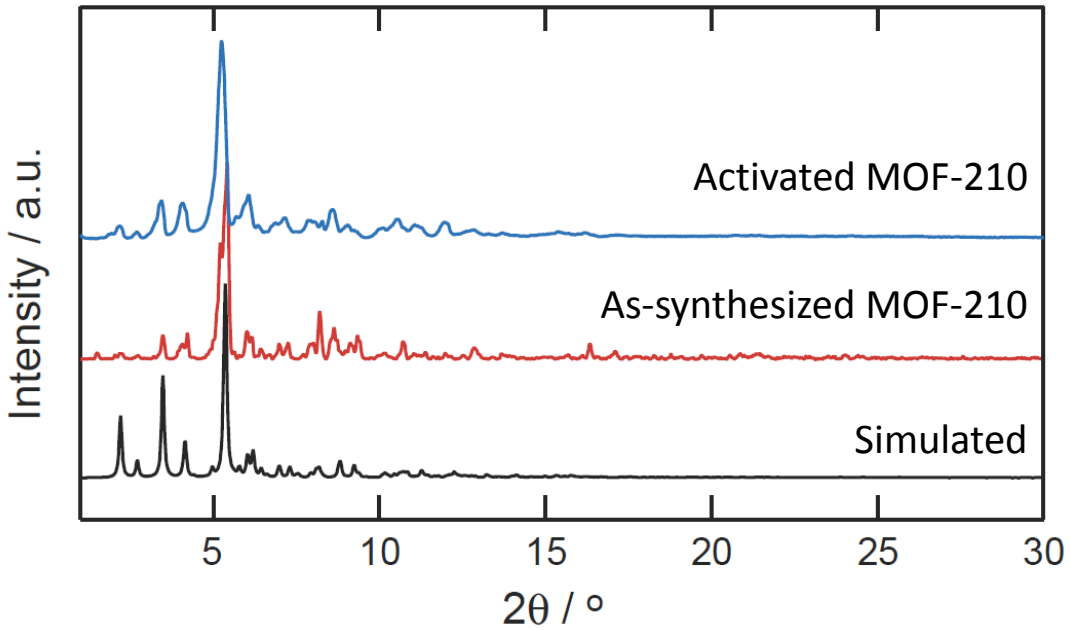
MOF-210

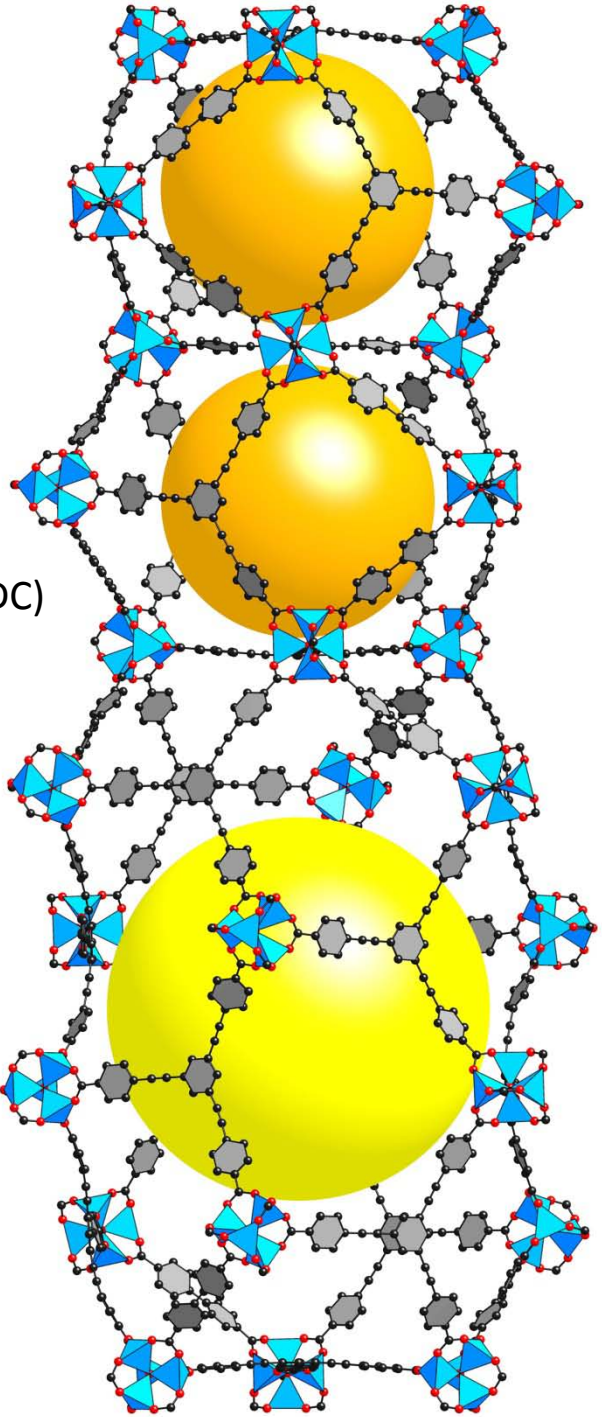
$Zn_4O(BTE)_{4/3}(BPDC)$

R-3

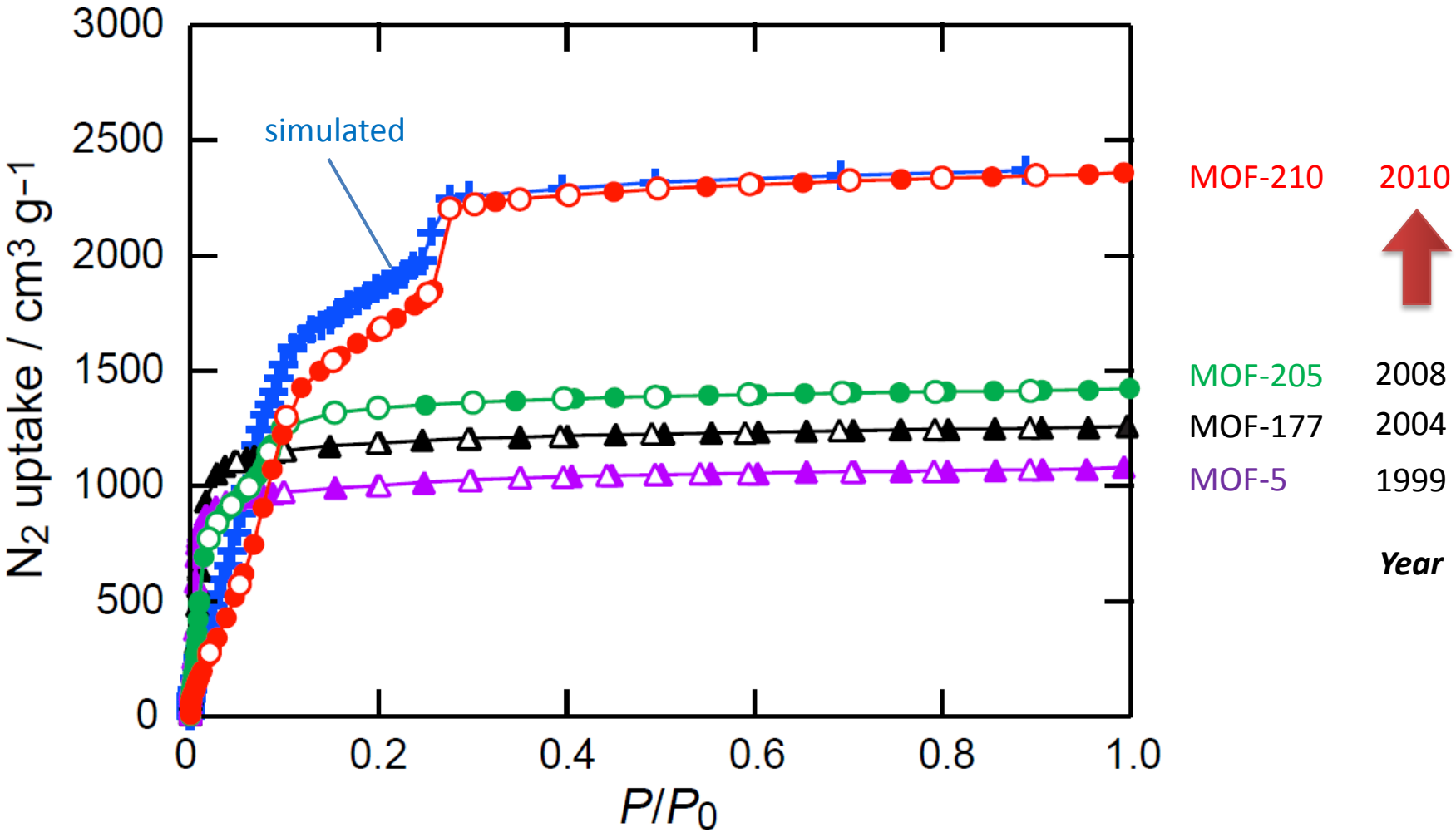
a = 50.745(1) Å

c = 194.256(5) Å





Low-pressure N_2 isotherms

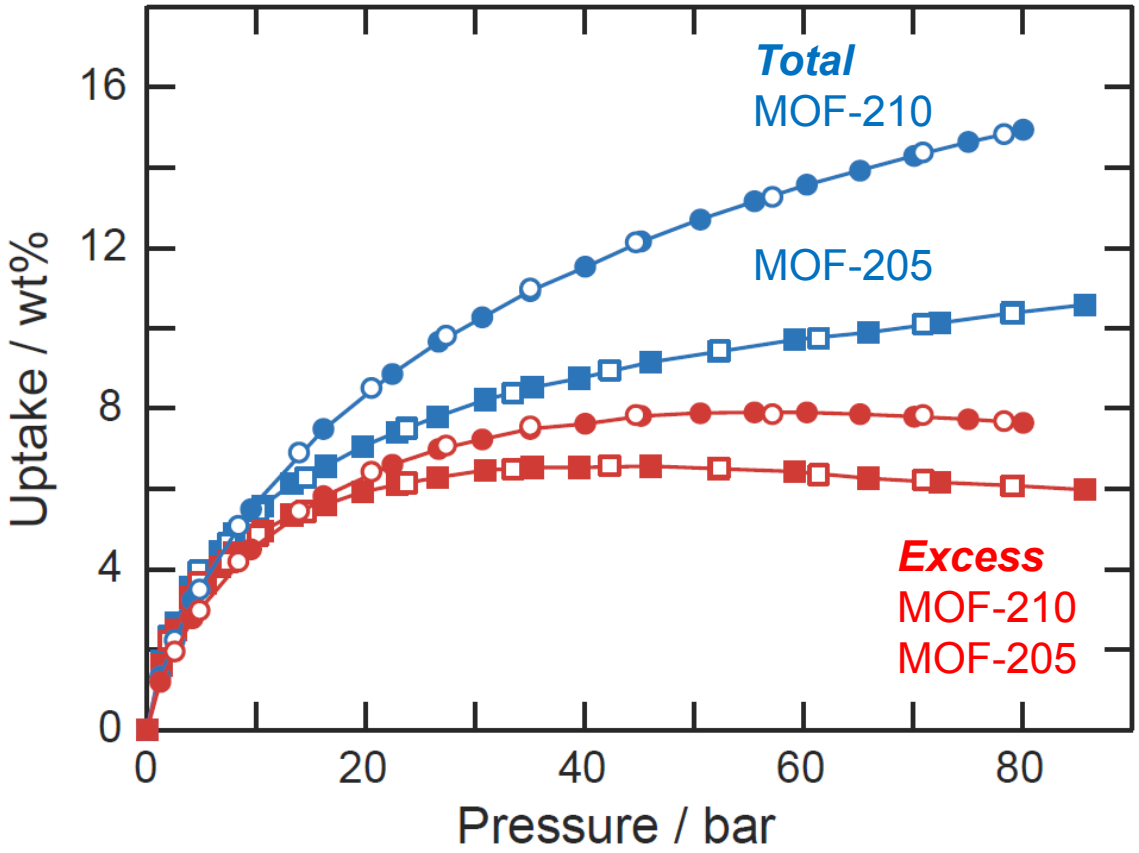


- BET surface area: 6240 $m^2\ g^{-1}$ (the **highest** surface area)
- Total pore volume: 3.60 $cm^3\ g^{-1}$ (the **largest** value among crystalline materials)

In collaboration with O. Yazaydin & R. Snurr (Northwestern University)

High-pressure H_2 isotherms

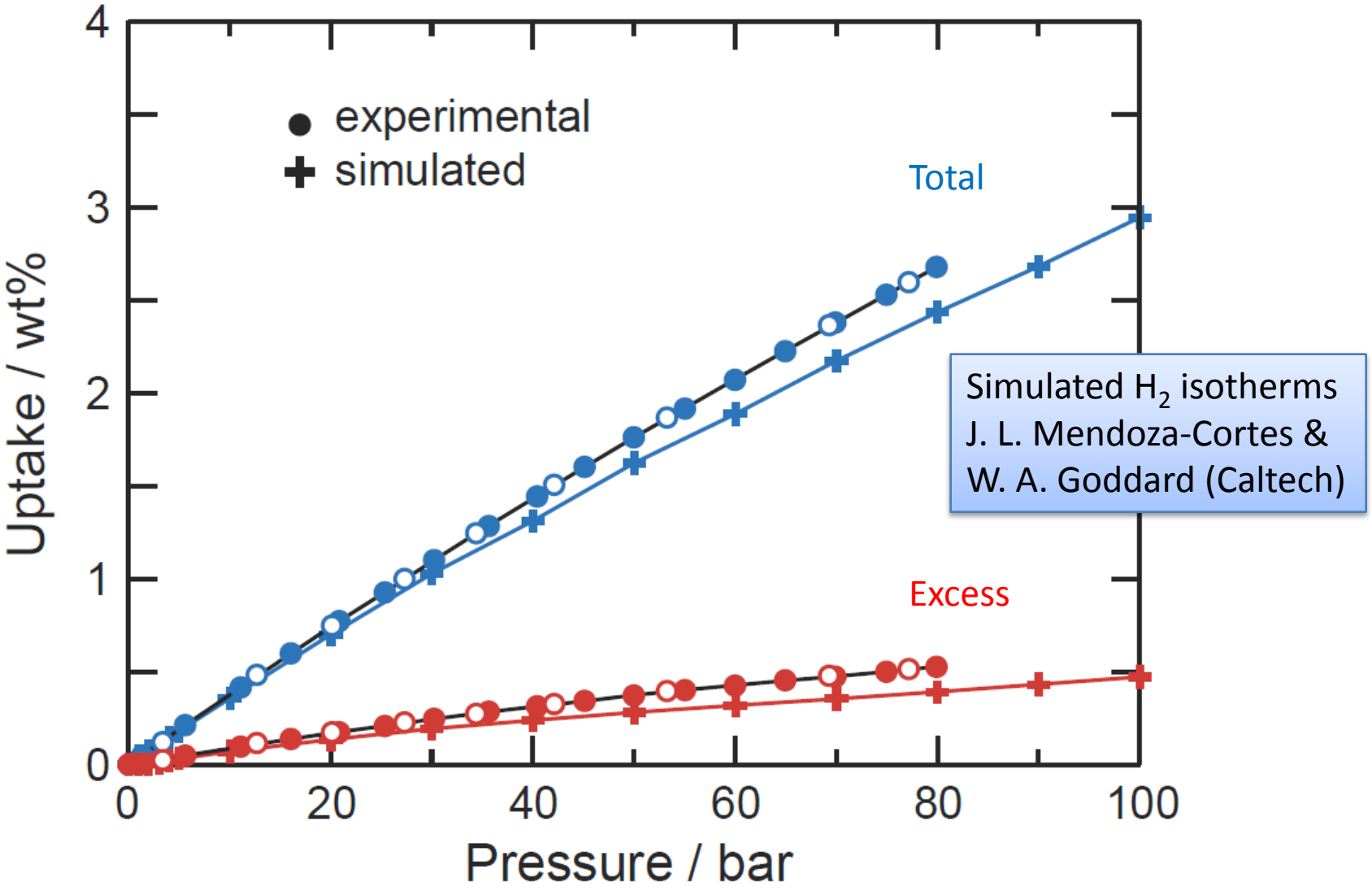
H_2 uptake capacity of MOF-210 was confirmed by BASF.



Porosity and H_2 uptake of MOFs at 77 K and 80 bar

	Density (g/cm^3)	Void space (%)	BET SA (m_2/g)	Excess (wt%)	Total (wt%)	Total (g/L)
Bulk H_2	n/a	n/a	n/a	n/a	n/a	26
MOF-5	0.59	79	3800	7.1	9.6	63
MOF-177	0.43	83	4500	6.8	10.4	50
MOF-200	0.22	90	4530	6.9	14.0	36
MOF-205	0.38	85	4460	6.5	10.7	46
MOF-210	0.25	89	6240	7.9	15.0	44
UMCM-2	0.4	83	5200	6.5	11.0	50
NU-100	0.29	87	6143	9.0	14.1	41

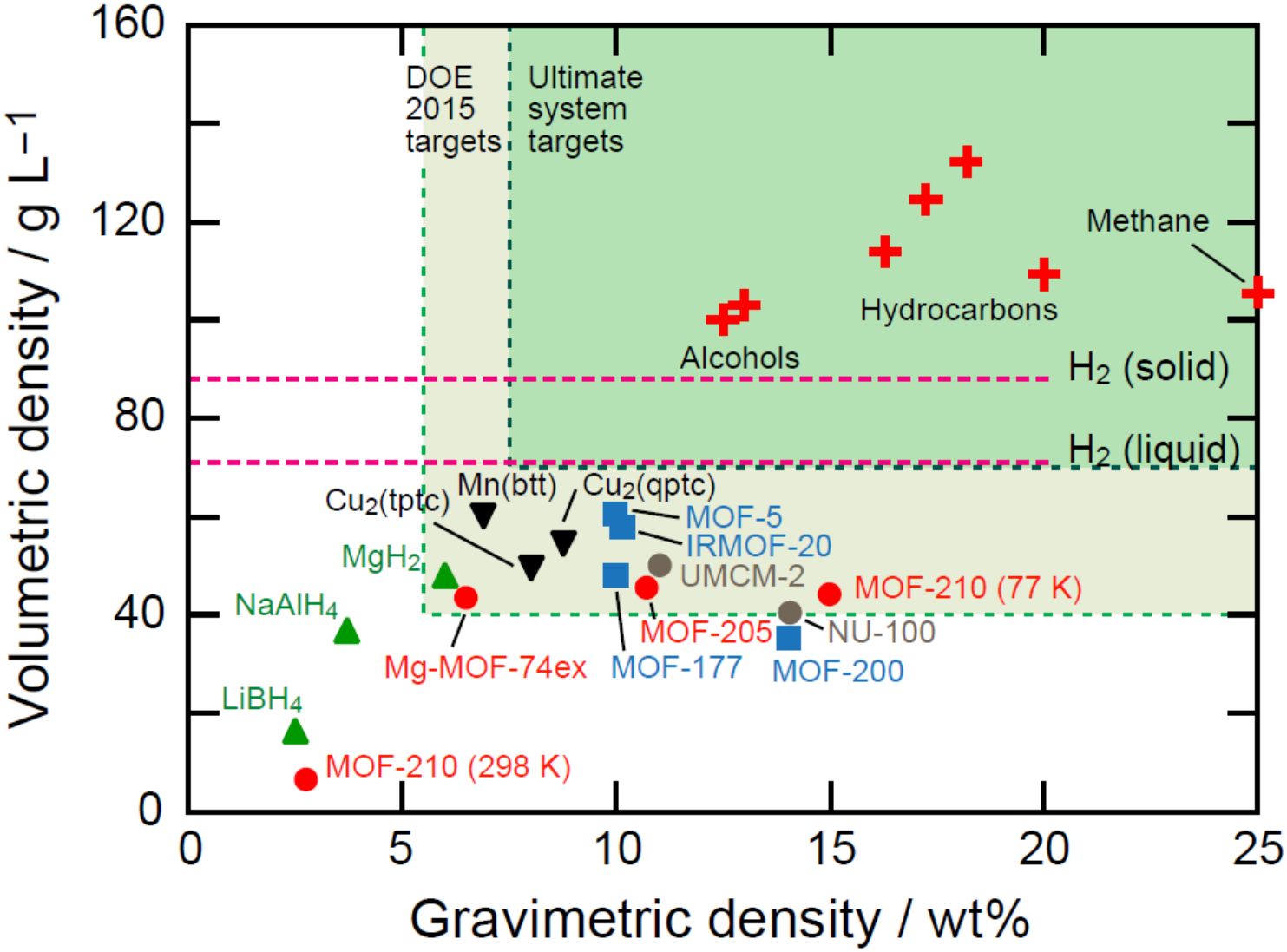
H_2 isotherm of MOF-210 at 298 K



- **2.7 wt% (total) uptake at 298 K and 80 bar**
- Experimental data are close to predicted values

Stored hydrogen per mass and per volume

(only metal hydrides showing good recycling are included)

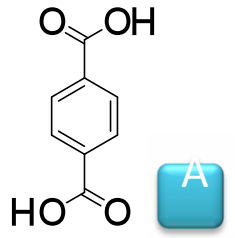


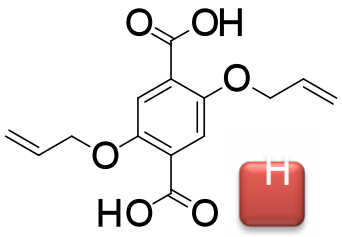
Gravimetric H_2 density in MOF-210 is approaching those of hydrocarbons.

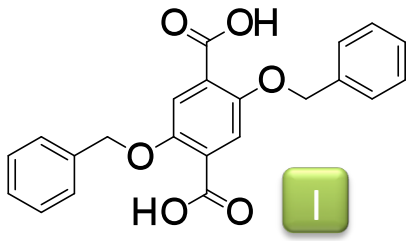
What's next?

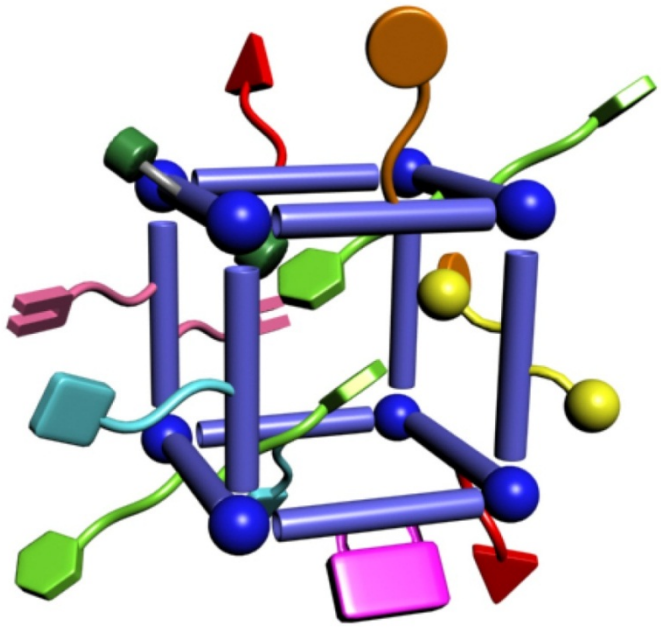
How to increase volumetric H_2 uptakes by MOFs?

- Multi-variate MOF (MTV-MOF) can improve the storage capacity.
- Various organic functionalities and metals will be incorporated/impregnated in the frameworks.

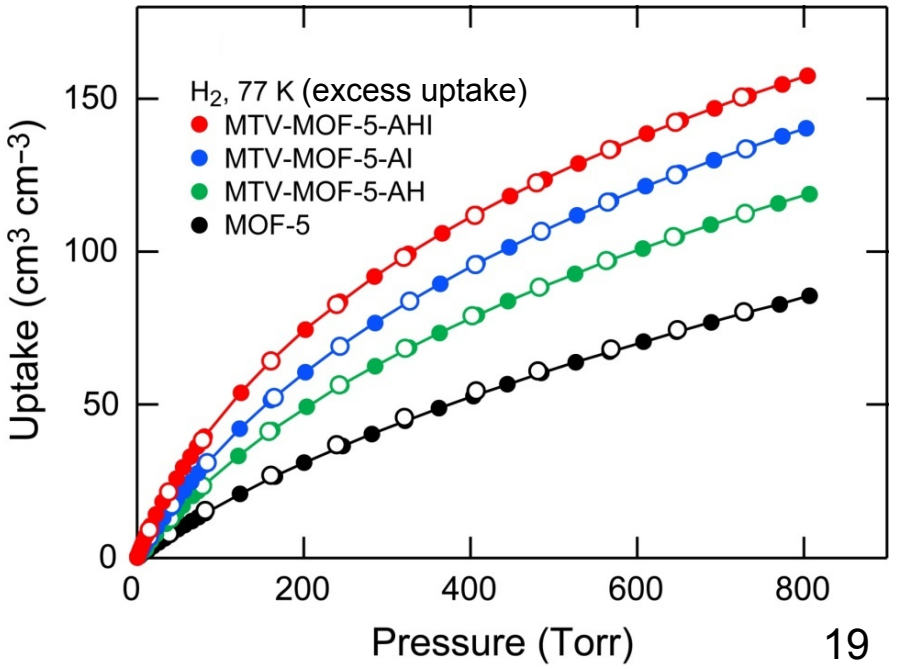








MTV-MOF-5 structure
with eight different functionalities



Summary

Relevance: For room temperature hydrogen storage, a systematic survey was pursued experimentally.

Approach: Aim at increasing strong binding sites for maximum hydrogen uptake capacity without losing pore volume.

Technical accomplishments and progress:

- Preparation of novel MOFs with metals
- Highest BET surface area among porous solids
- 15 and 2.7 wt% H_2 uptake by MOF-210 at 77 K and RT
- Characterization of metalated MOF-253

Technology transfer/collaborations: Active relationship with collaboration partners (theory, organic synthesis, and material design) and BASF (verification of H_2 uptake).

Proposed future research:

- Employ metals to create strong binding sites.
- Utilize the MTV concept for improved volumetric H_2 uptake.