

HYDROGEN STORAGE IN METAL-ORGANIC FRAMEWORKS

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May 11, 2011

Project ID
ST049

Overview

Timeline

Project start date: 5/2/2005

Project end date: 4/30/2011

Percent complete: 95%

Budget

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

Barriers

Barriers addressed

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

Collaborating Partners

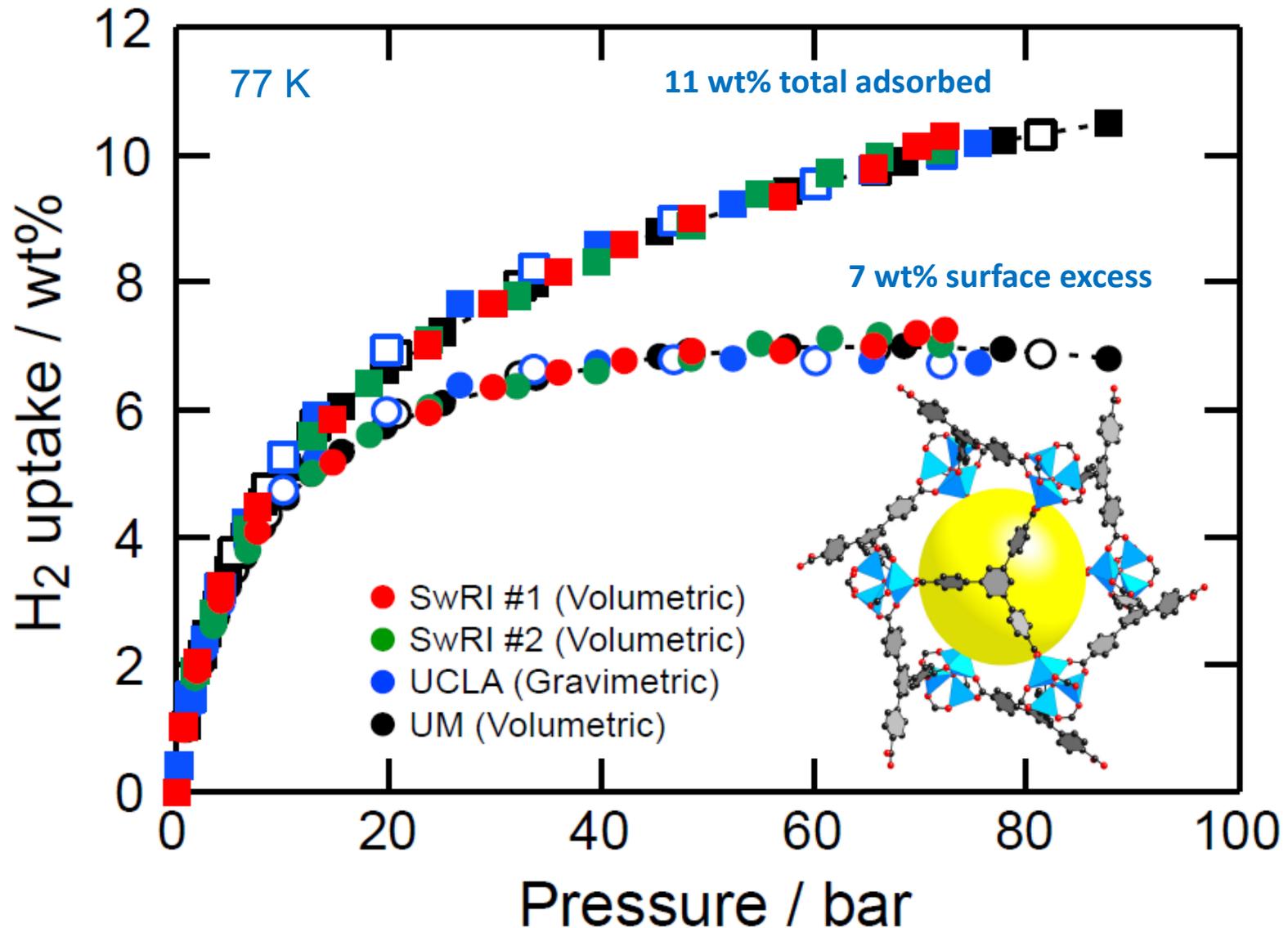
- Bill Goddard (Caltech)
- Fraser Stoddart (NW)
- Randy Snurr (NW)
- Jaheon Kim (Soongsil University)
- BASF

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.

Independent Verification of MOF-177 Hydrogen Uptake Capacity

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



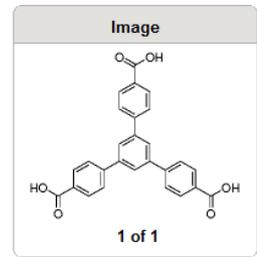
Feasibility of MOFs for hydrogen storage

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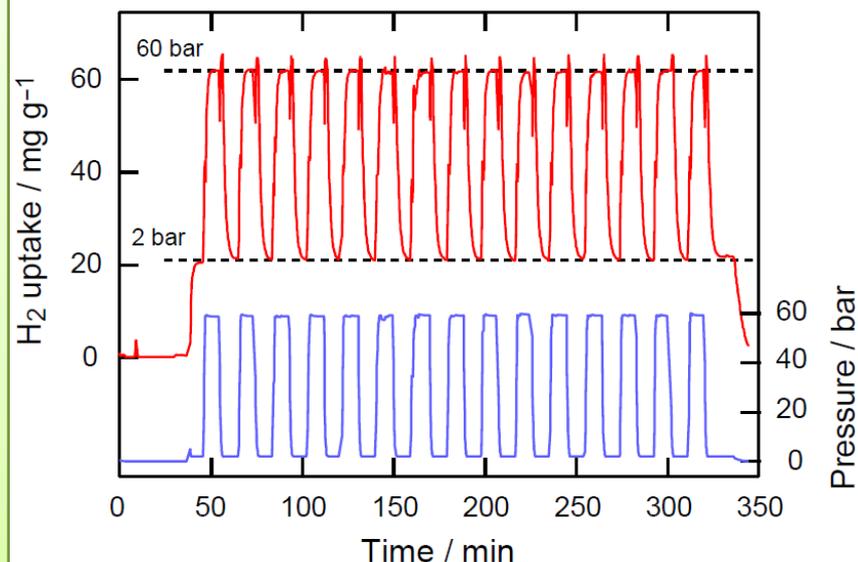
686859 **1,3,5-Tris(4-carboxyphenyl)benzene**
Aldrich $\geq 98\%$, ≤ 20 wt. % solvent

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 H₂ charge rate (< 3 min)
- 4 wt% of H₂ delivery (2-60 bar at 77 K)

Objectives (FY10-11)

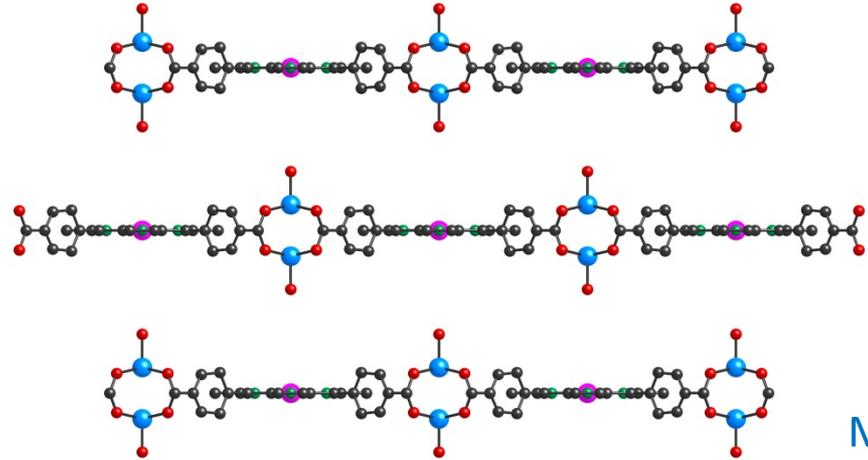
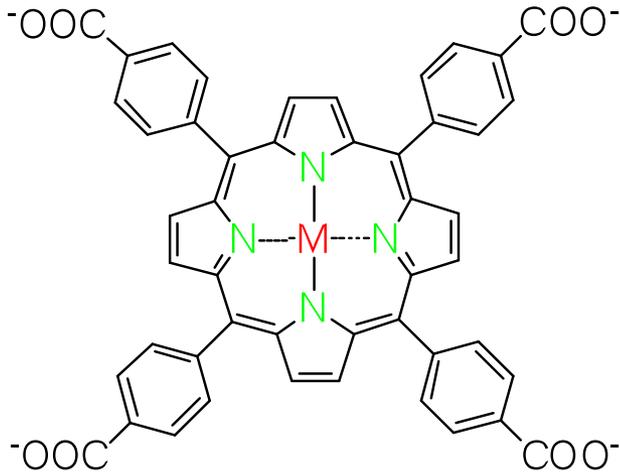
Last year:

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 H₂ density per volume should be increased.

This year:

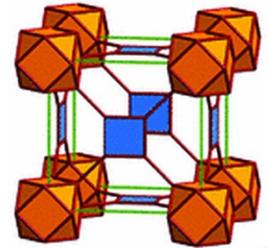
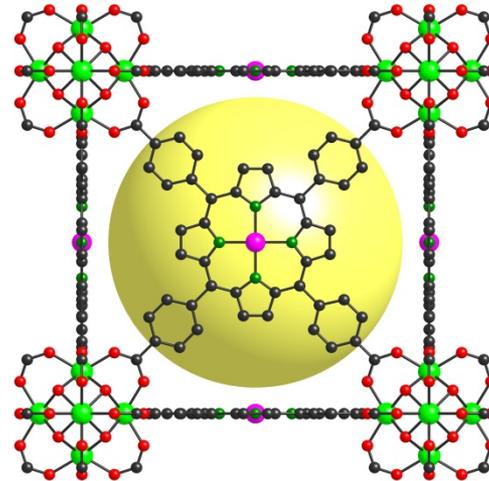
- 1. Expand the framework with keeping strong H₂ binding sites**
 - Design new porphyrin MOF to increase the storage space
 - Expand Mg-MOF-74; high Q_{st} and BET surface area to achieve high H₂ density at RT.
- 2. Preparation of ultrahigh-surface area MOFs**
 - Large storage space, but minimize dead space (*i.e.* high BET surface area)
 - Evaluate RT H₂ 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



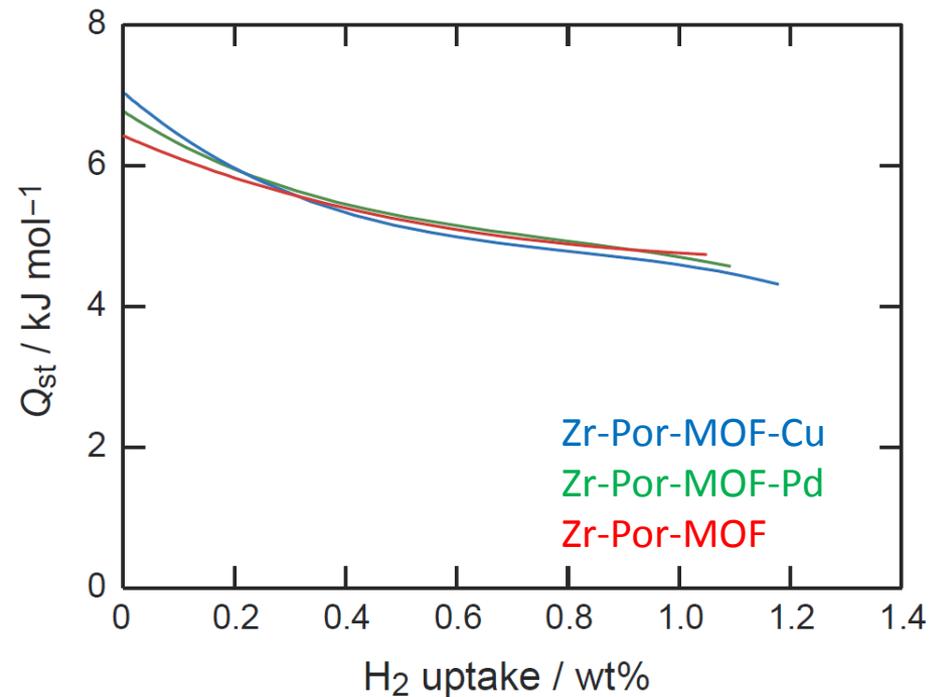
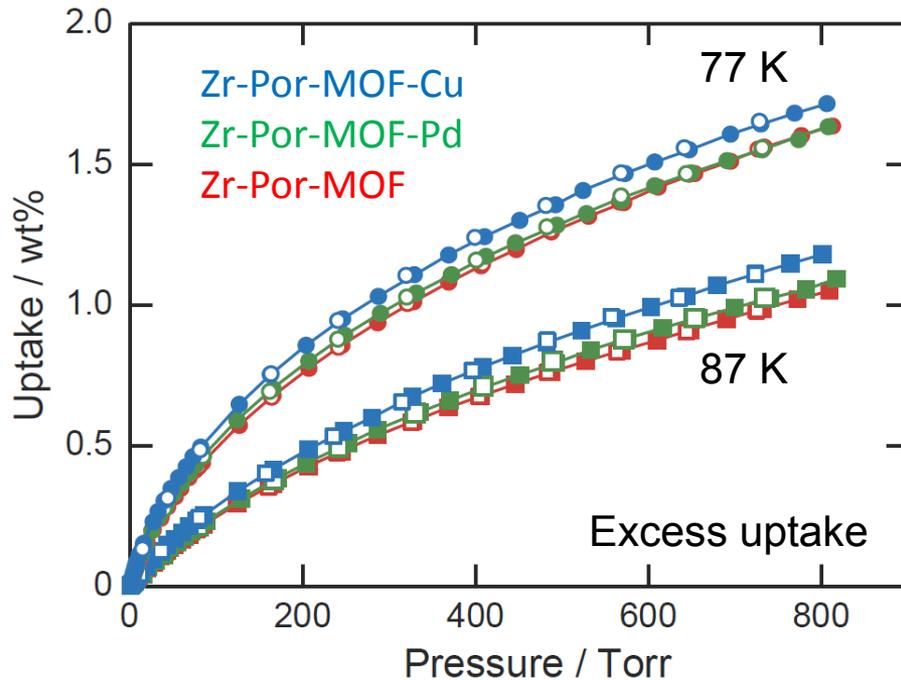
MOF-122

- ❑ Limited accessible space because of the layered structure (BET \approx 500 m²/g)
- ❑ 3D structure with large storage space is required for better H₂ storage capacity
- ❑ Use Zr₆O₄(OH)₄(CO₂)₁₂ unit
 - Chemically stable
 - **ftw** net can be formed



ftw net

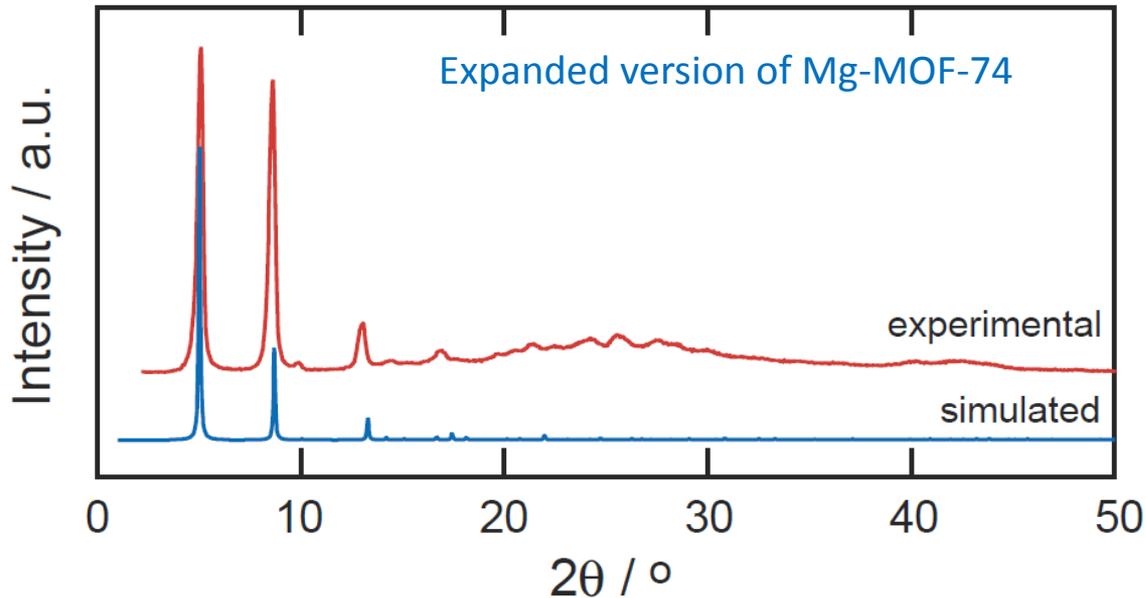
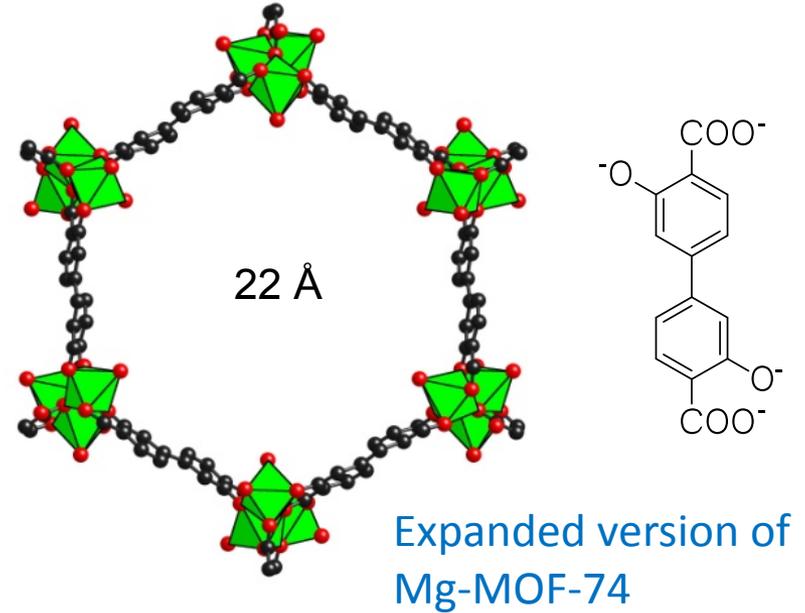
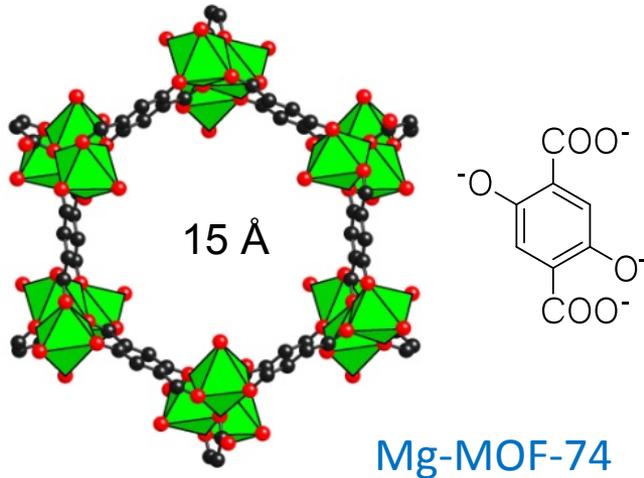
H₂ uptake of metalated porphyrin MOFs



	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.
- H₂ uptakes by Zr-Por-MOFs at 1 bar and 77 K are higher than that of MOF-177.
- Metalated MOFs show better H₂ uptake and higher initial Q_{st}.

Isorecticular expansion of Mg-MOF-74

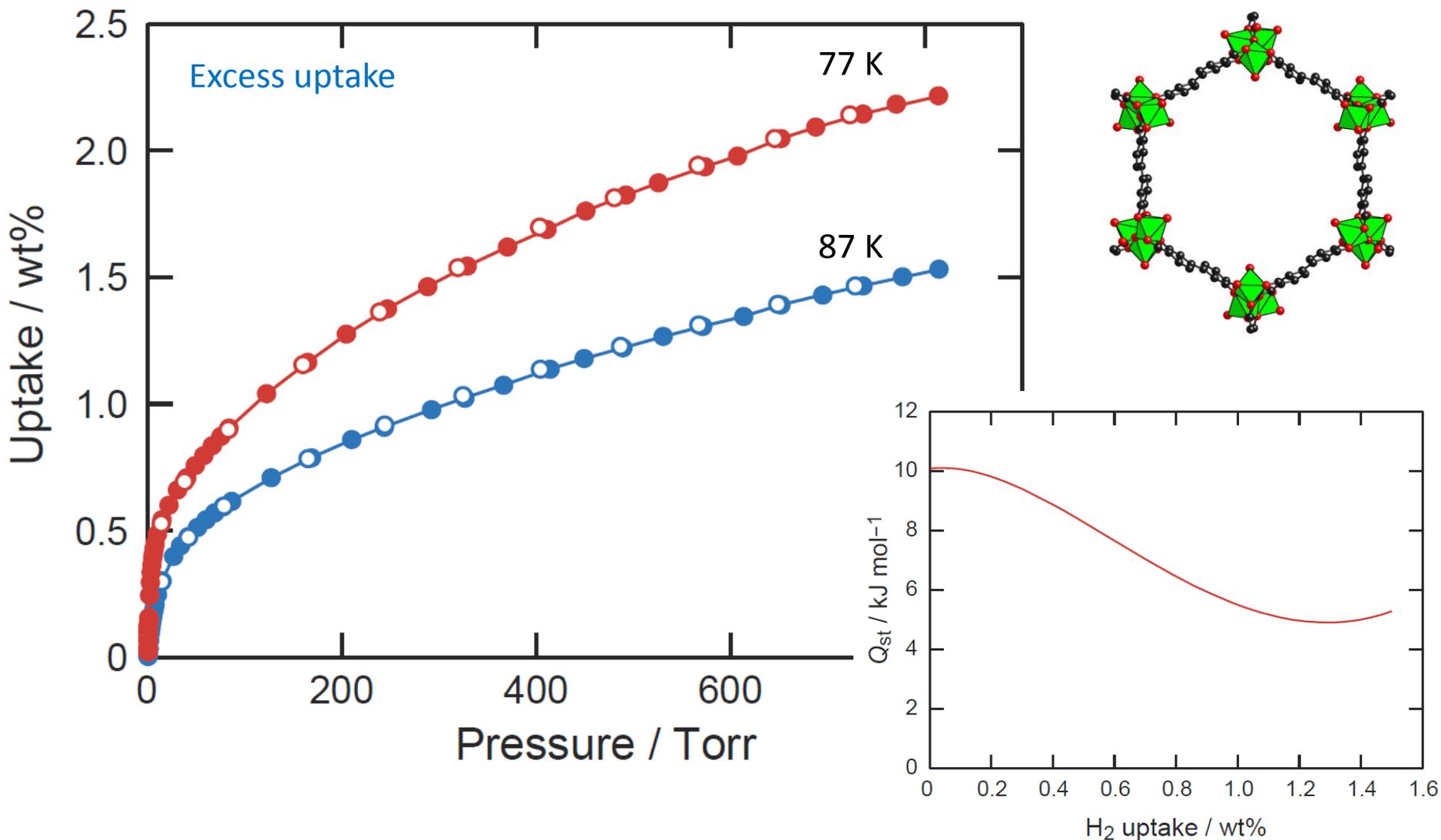


Advantages

- High surface area and large pore volume
- Strong interaction between MOF and H₂

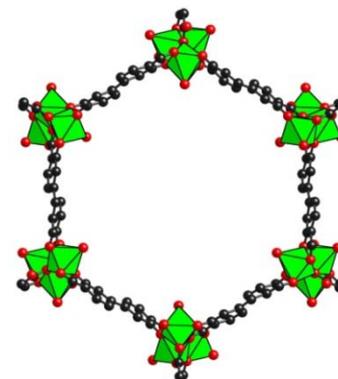
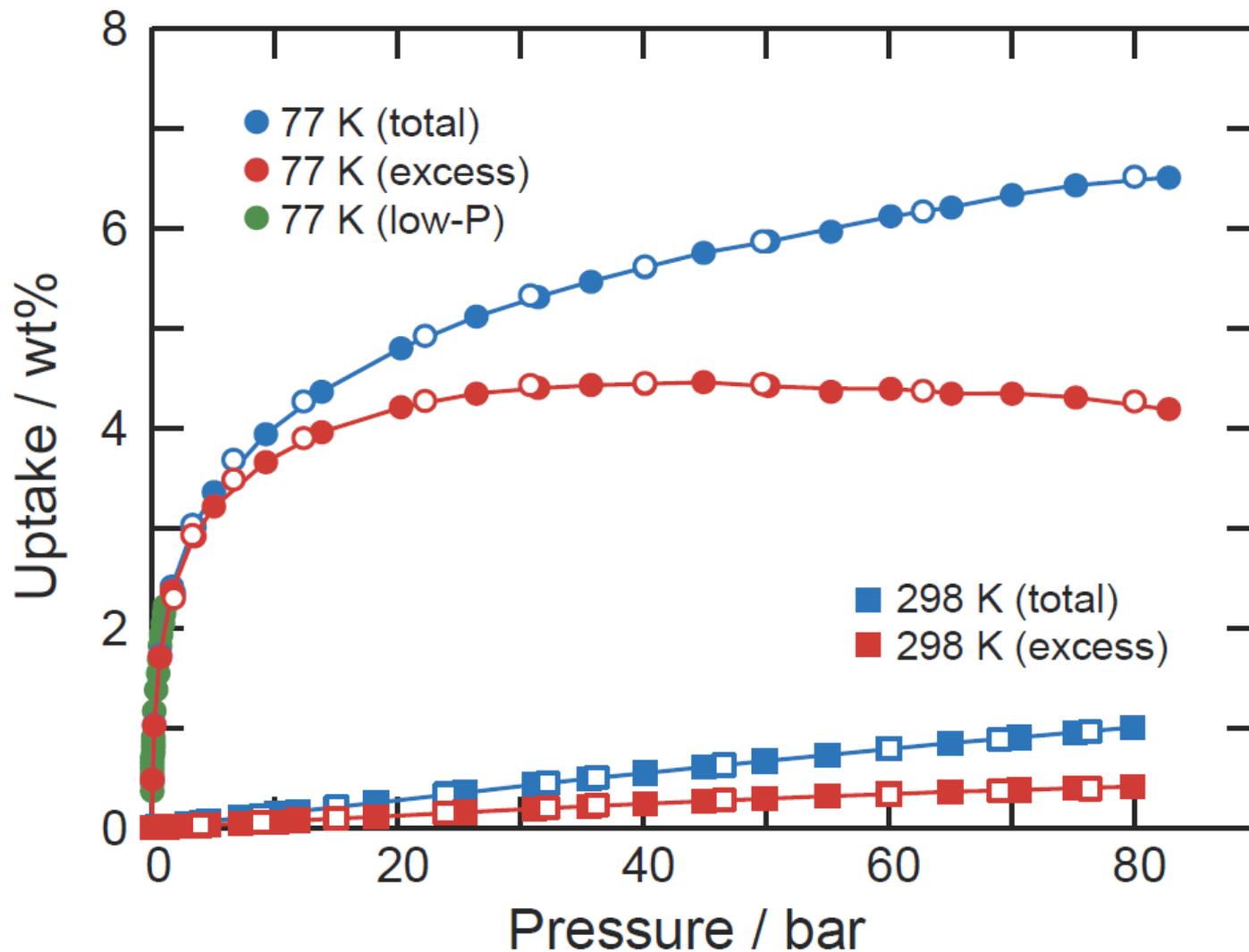
In collaboration with Prof. Stoddart group (Northwestern)

Low-pressure H₂ isotherms



- 2.2 wt% H₂ uptake at 1 bar and 77 K
- High initial Q_{st} (10.1 kJ/mol)

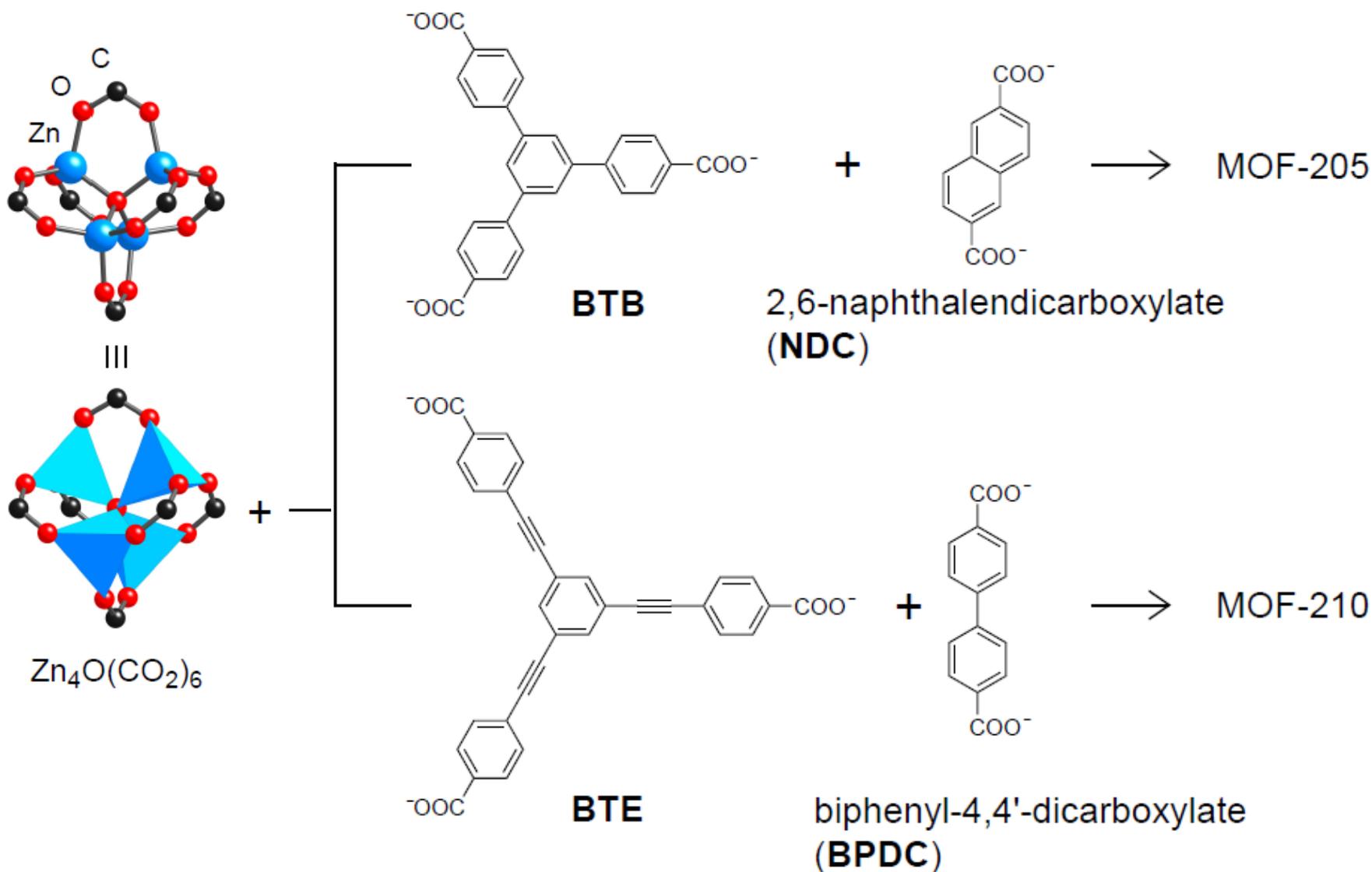
High-pressure H₂ isotherms



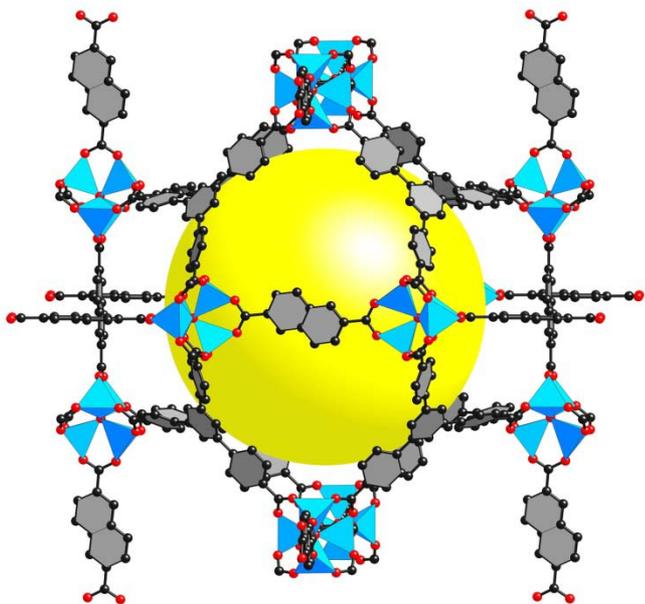
- 6.5 wt% (43 g/L) at 77 K and 80 bar
- 1.0 wt% (6.3 g/L) at 298 K and 80 bar

Expansion of frameworks (mixed link system)

How to avoid interpenetration?



Synthesis of MOF-205 and 210



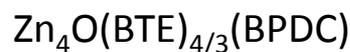
MOF-205



Pm-3n

$a = 30.353(4) \text{ \AA}$

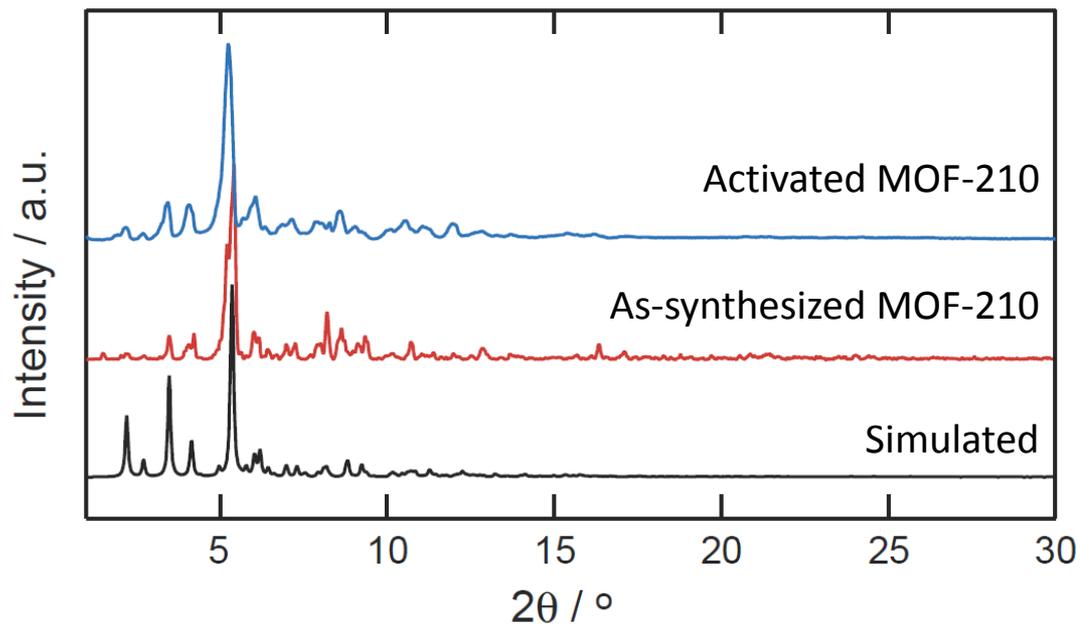
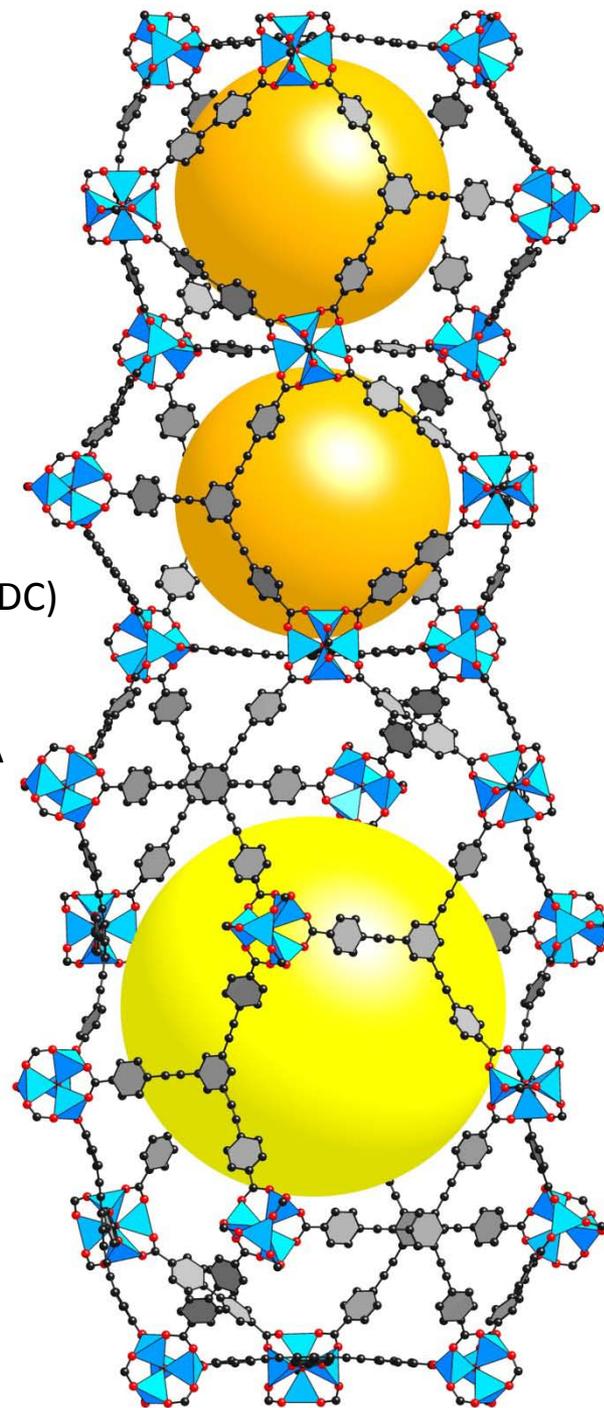
MOF-210



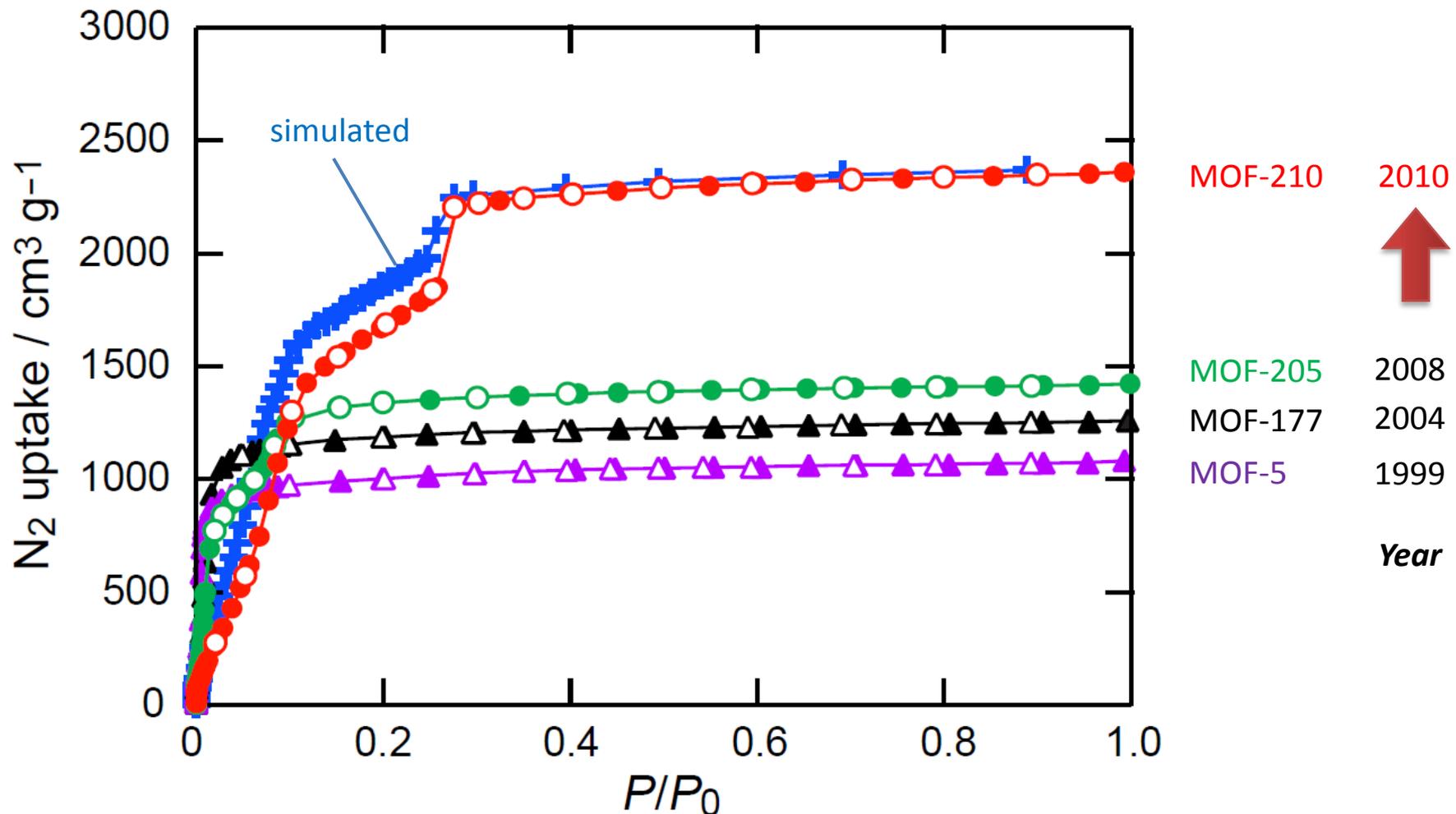
R-3

$a = 50.745(1) \text{ \AA}$

$c = 194.256(5) \text{ \AA}$



Low-pressure N₂ isotherms



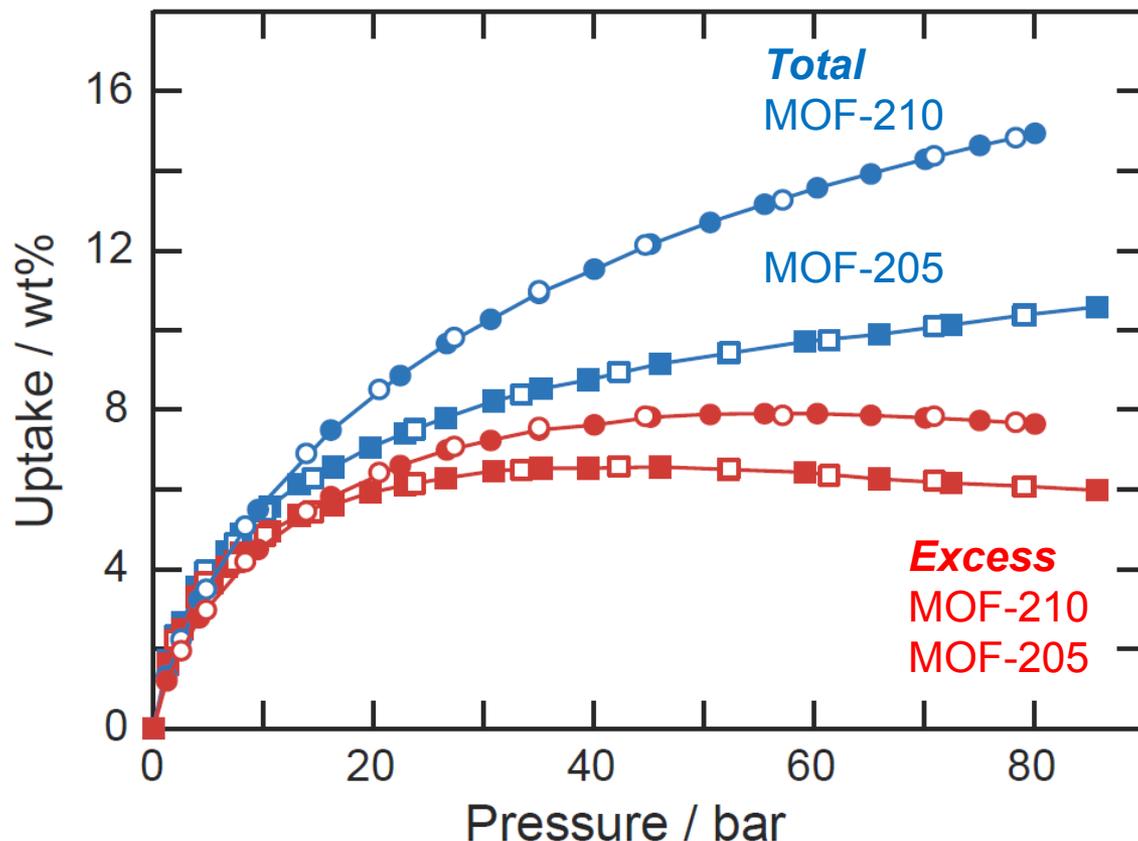
- BET surface area: 6240 m² g⁻¹ (the **highest** surface area)
- Total pore volume: 3.60 cm³ g⁻¹ (the **largest** value among crystalline materials)

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

High-pressure H₂ isotherms

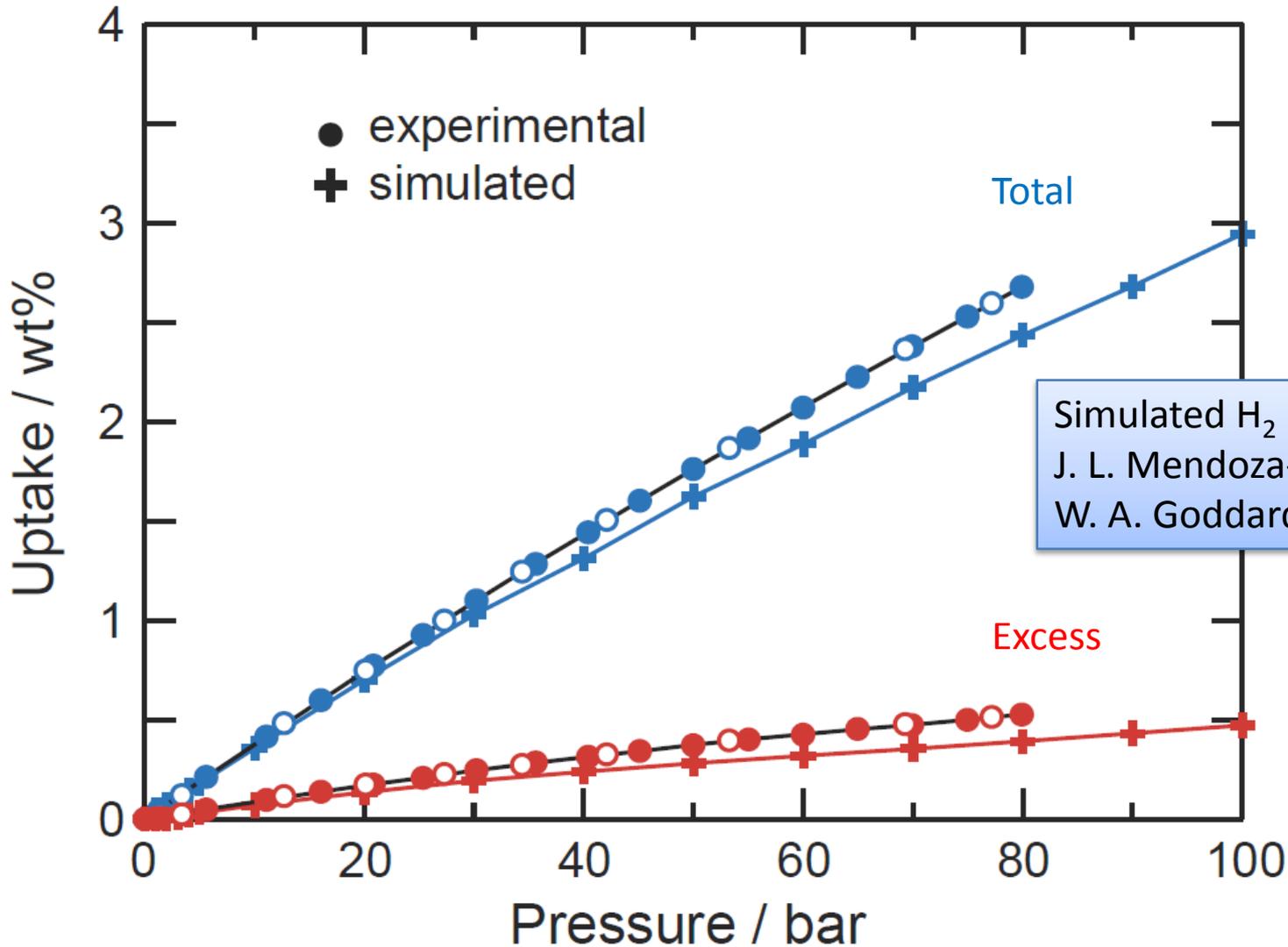
H₂ uptake capacity of MOF-210 was confirmed by BASF.

Porosity and H₂ 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

H₂ isotherm of MOF-210 at 298 K

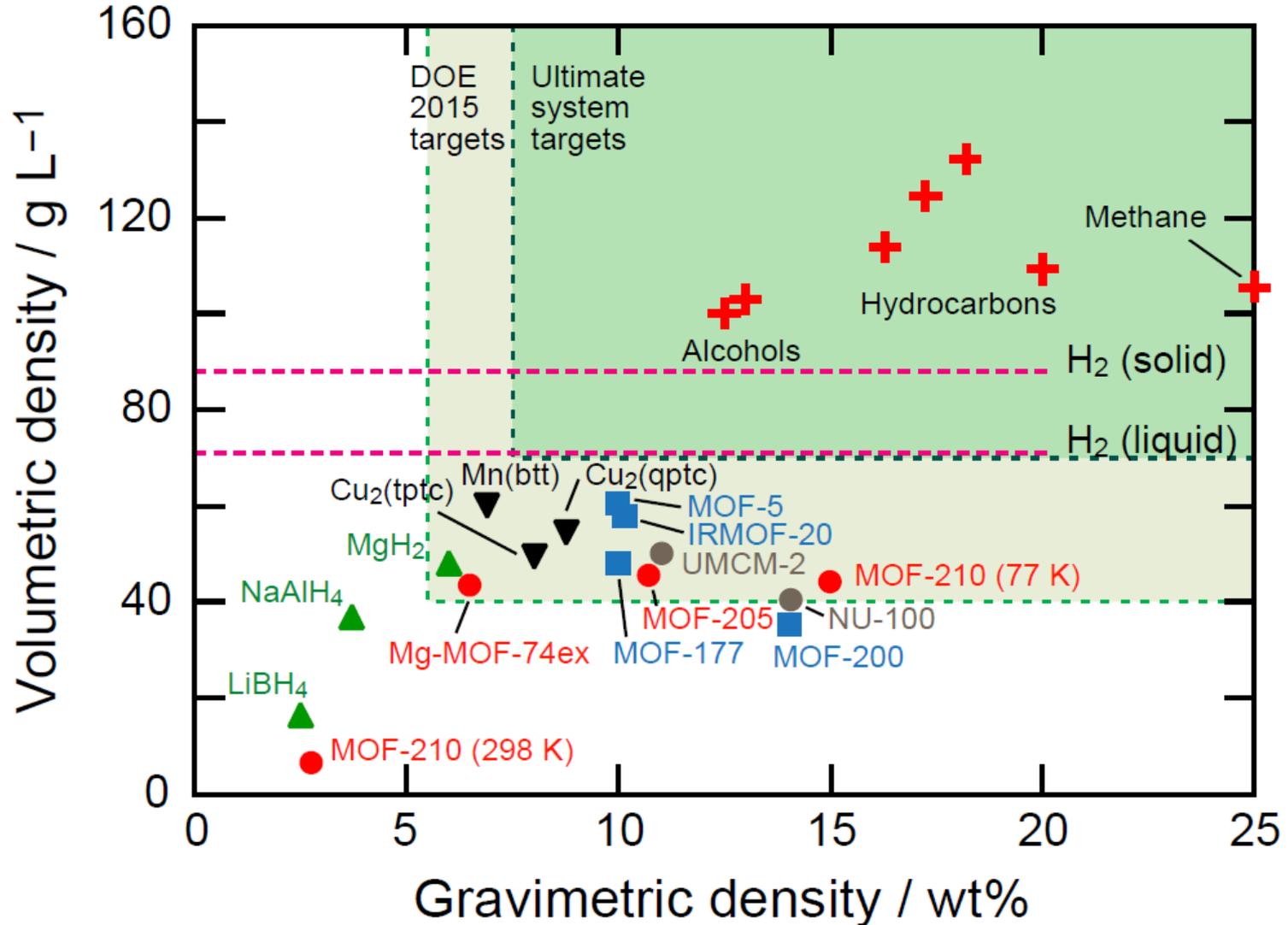


□ 2.7 wt% (total) uptake at 298 K and 80 bar

□ Experimental data are close to predicted values

Stored hydrogen per mass and per volume

(only metal hydrides showing good recycling are included)

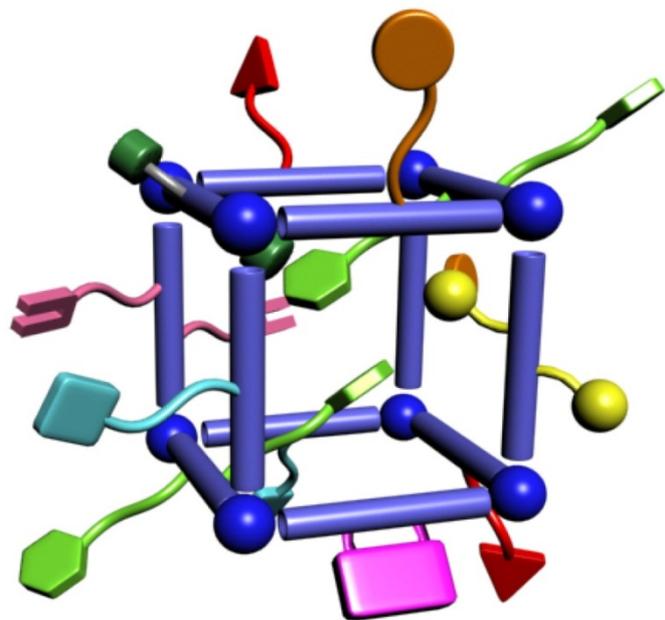


Gravimetric H₂ density in MOF-210 is approaching those of hydrocarbons.

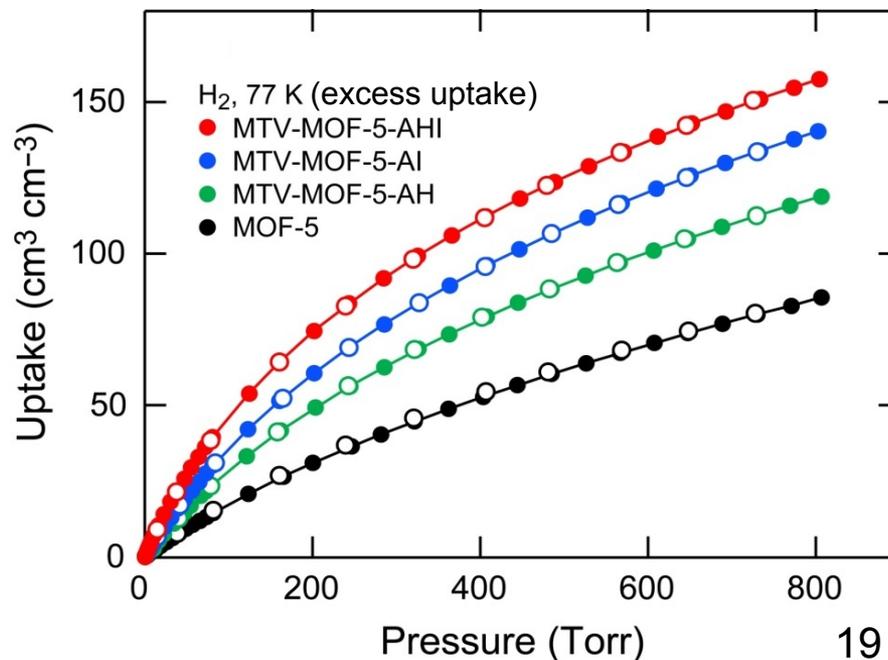
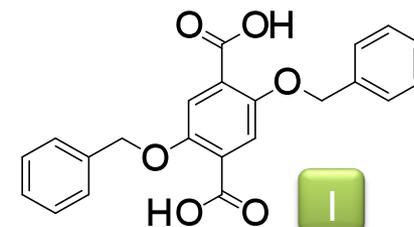
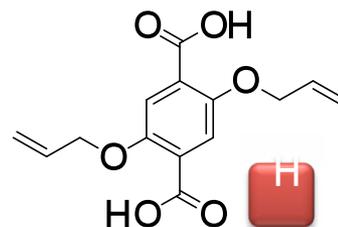
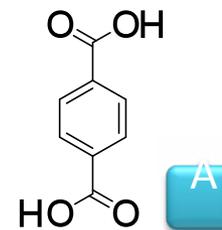
What's next?

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% H₂ 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 H₂ uptake).

Proposed future research:

- Employ metals to create strong binding sites.
- Utilize the MTV concept for improved volumetric H₂ uptake.