HYDROGEN STORAGE IN METAL-ORGANIC FRAMEWORKS

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June 9, 2010

Project ID
ST049

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Overview

Timeline

Project start date: 5/1/2005
Project end date: 4/30/2010
Percent complete: 90%

Barriers

Barriers addressed

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

Budget

- ❑ Total project funding
  - DOE share: $1.71 M
- ❑ Funding received in FY09: $428 K

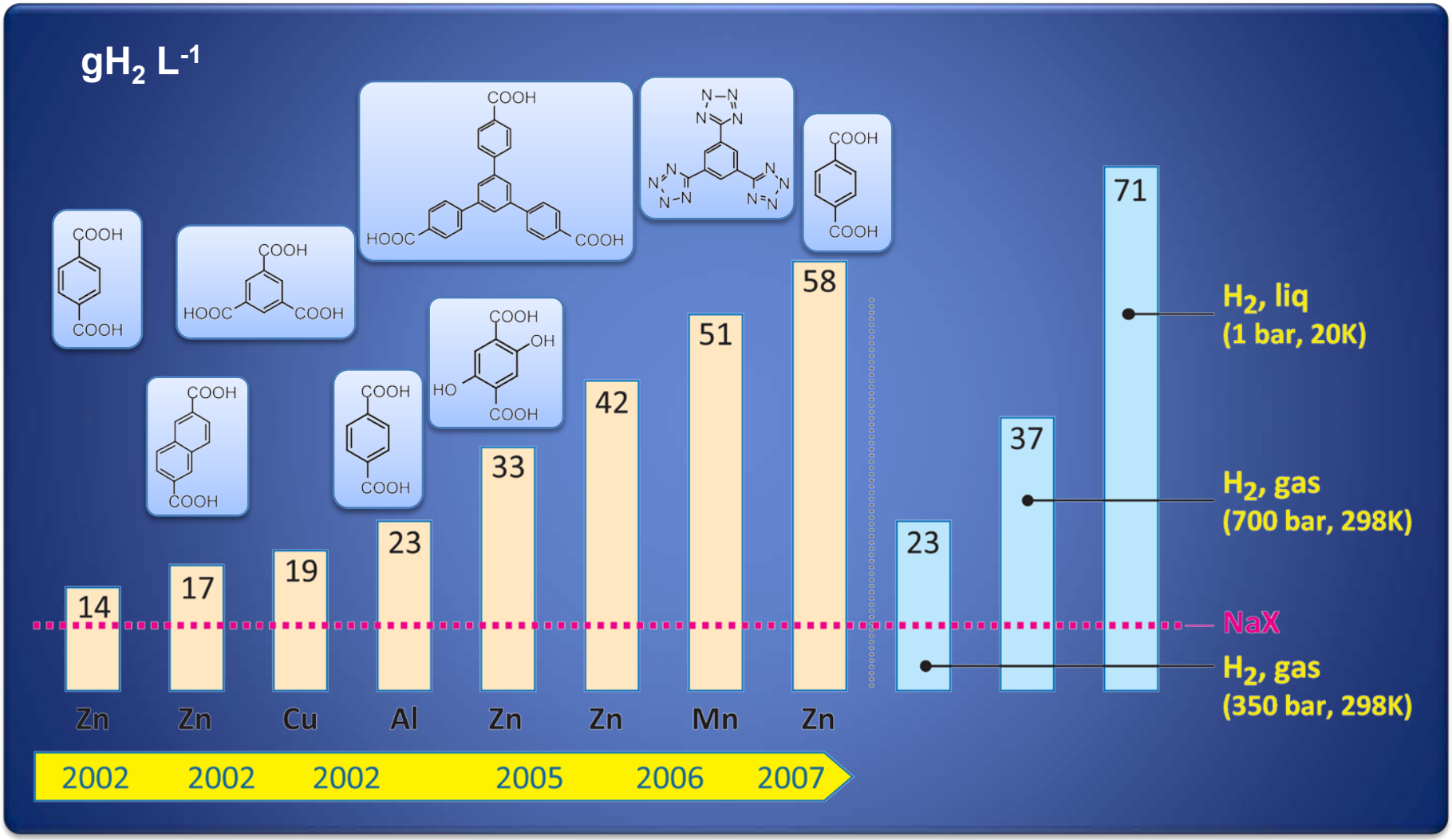
Collaborating Partners

- ❑ Randy Snurr (NW)
- ❑ Jeff Long (UC Berkley)
- ❑ Bill Goddard (Caltech)
- ❑ BASF

Important Aspects of MOF Chemistry

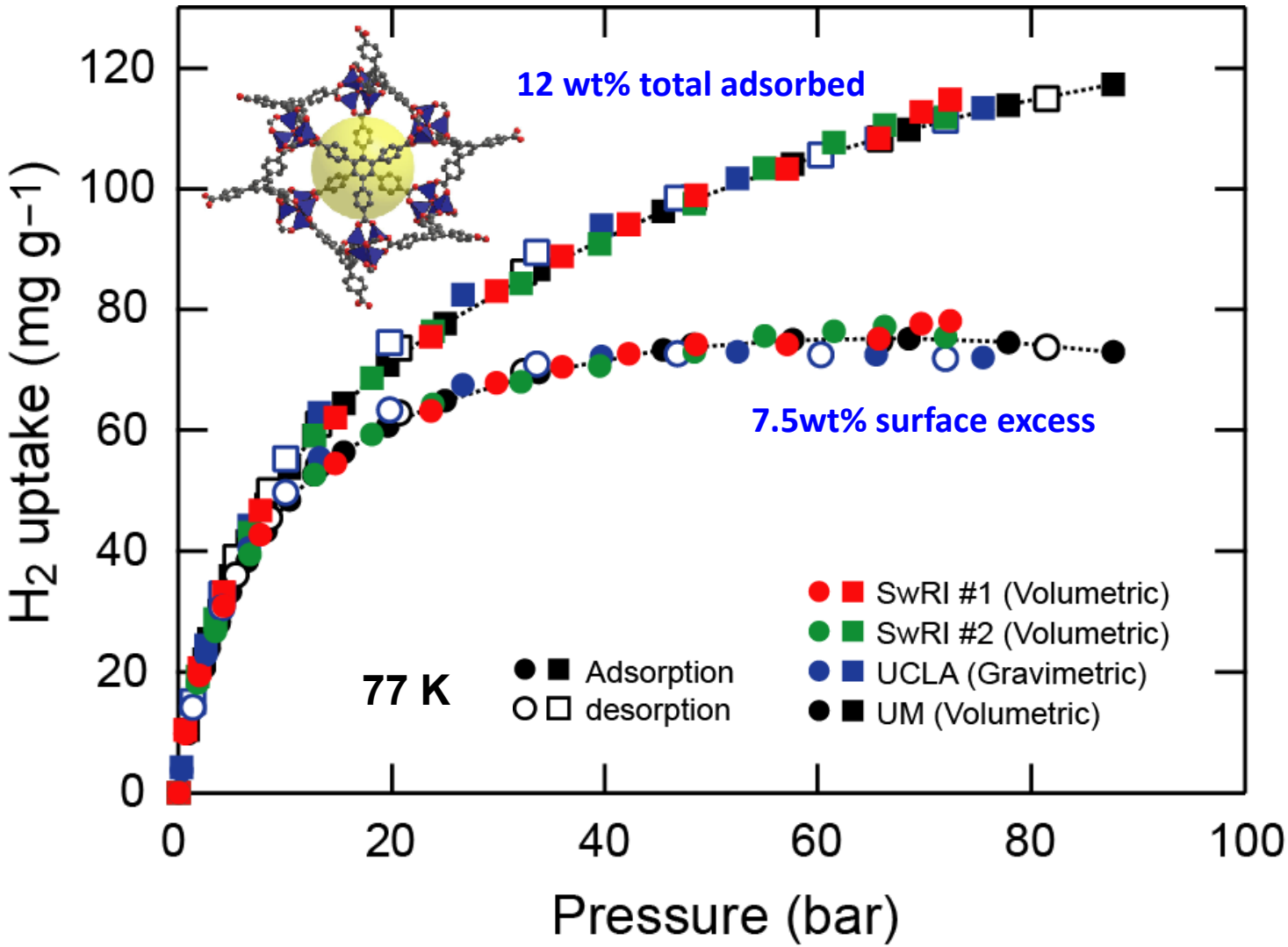
- Design of composition (metal centers and organic links). Synthesis and structural characterization is well worked out.
- Control of structure, topology, interpenetration and porosity.
- Formulation of hypothesis and testing of hypothesis is quite feasible. This leads to definitive conclusions and allows 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

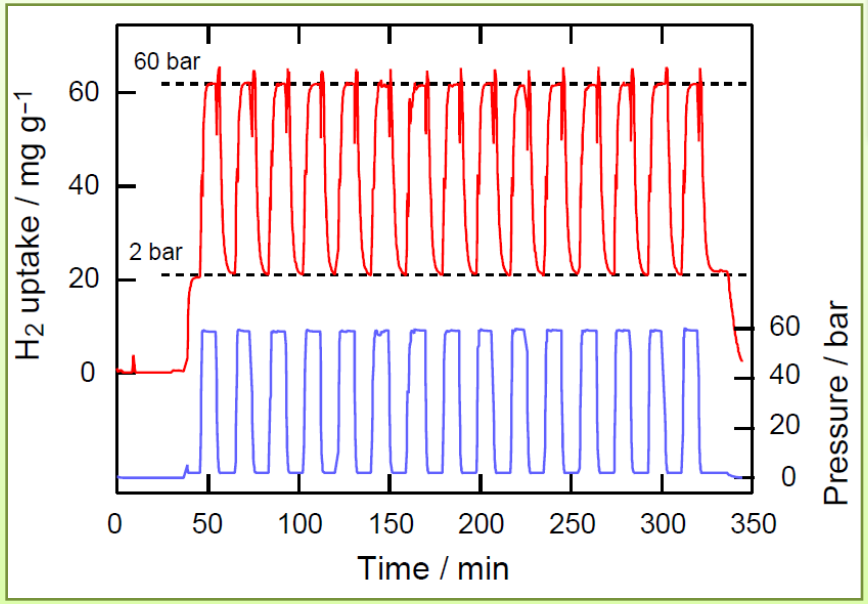
(volumetric and gravimetric measurements verified, shown using gravimetric scale)



Feasibility of MOFs for hydrogen storage

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)**

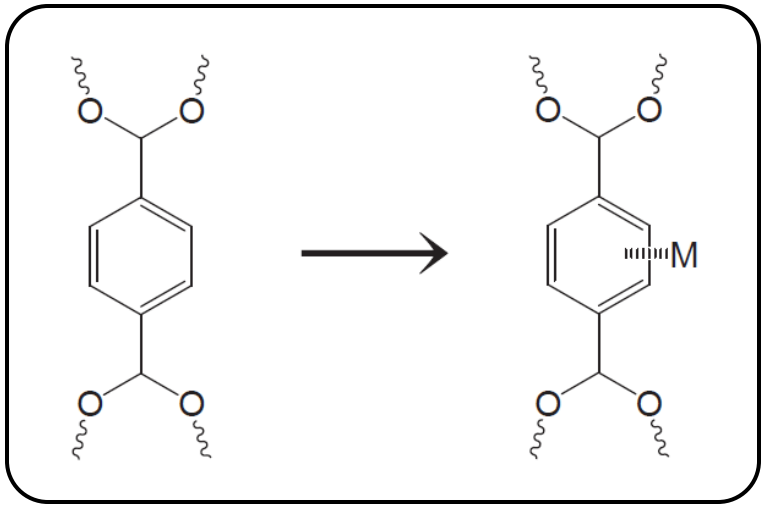
Objectives (FY09-10)

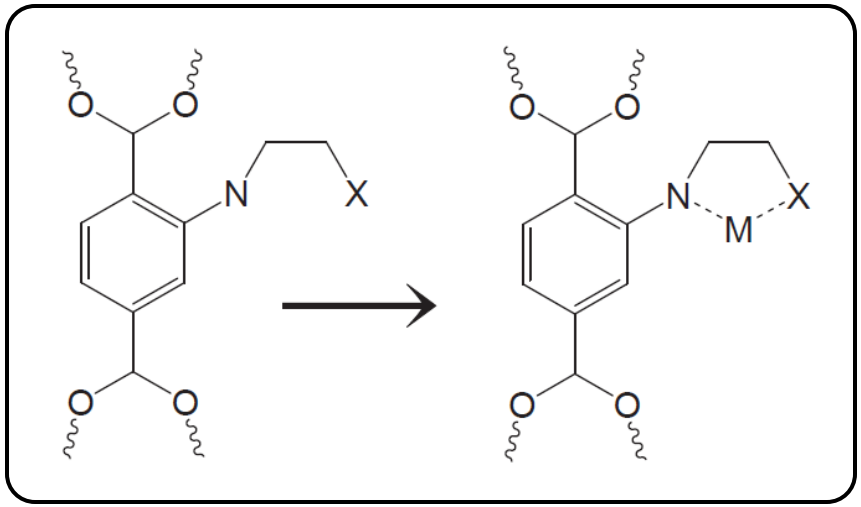
To increase hydrogen storage at room temperature

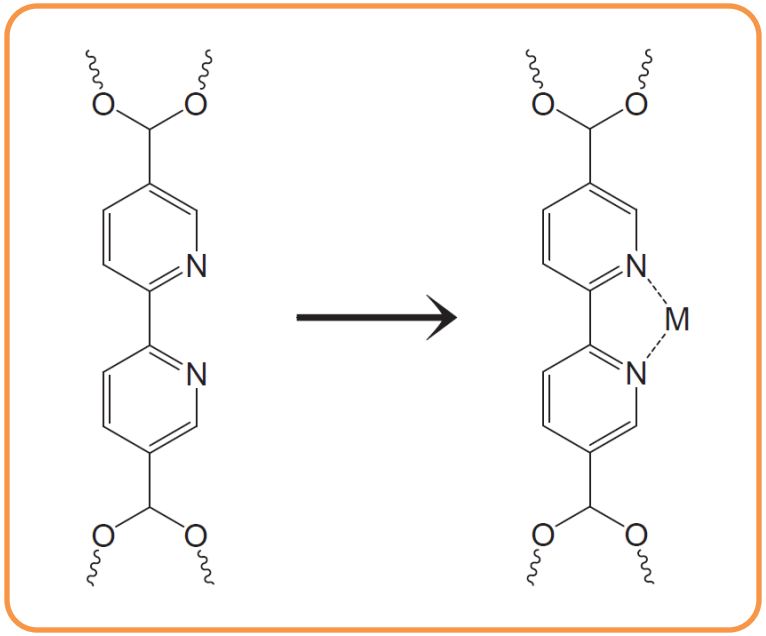
1. **Implementation of "*soft chemisorption*": design and preparation of new MOF with metal binding sites**
   - Impregnation of metals
   - Low-pressure measurements at various temperatures

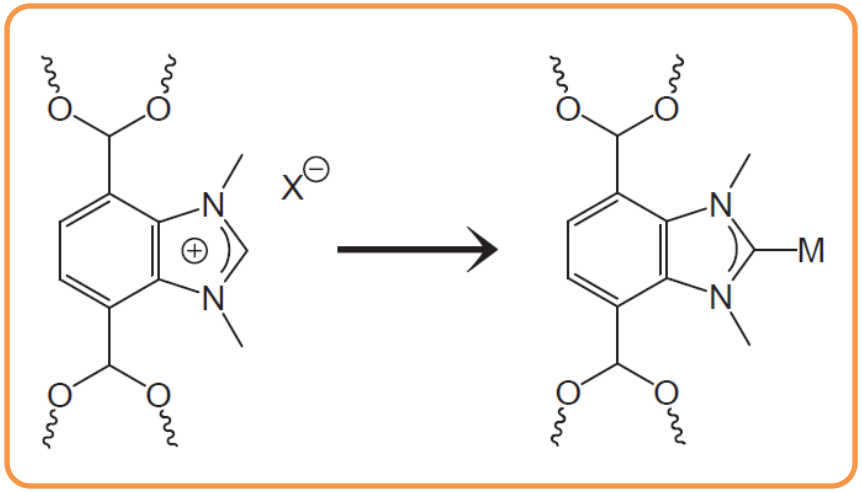
2. **Preparation of high-surface area MOFs**
   - Preparation of expanded organic link
   - High-throughput MOF synthesis
   - Activation of high-surface area MOFs

Possible routes for metal impregnation



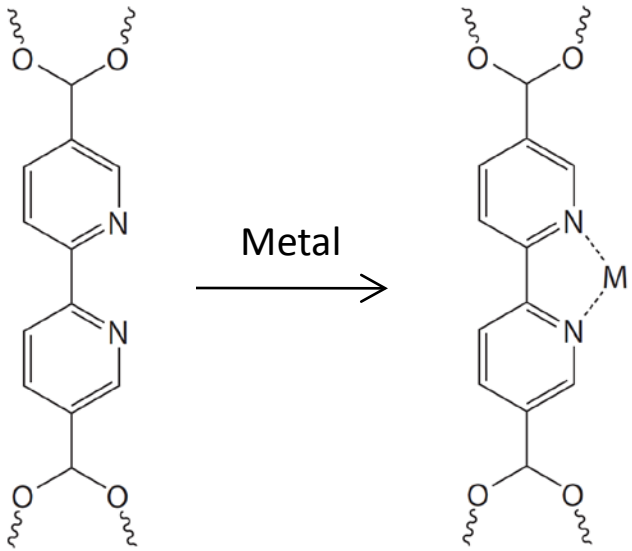


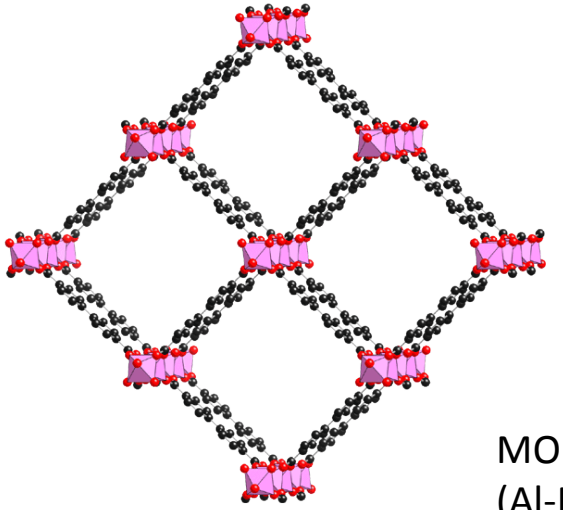




Control coordination number without losing exposed metal surface

MOFs with bipyridine link

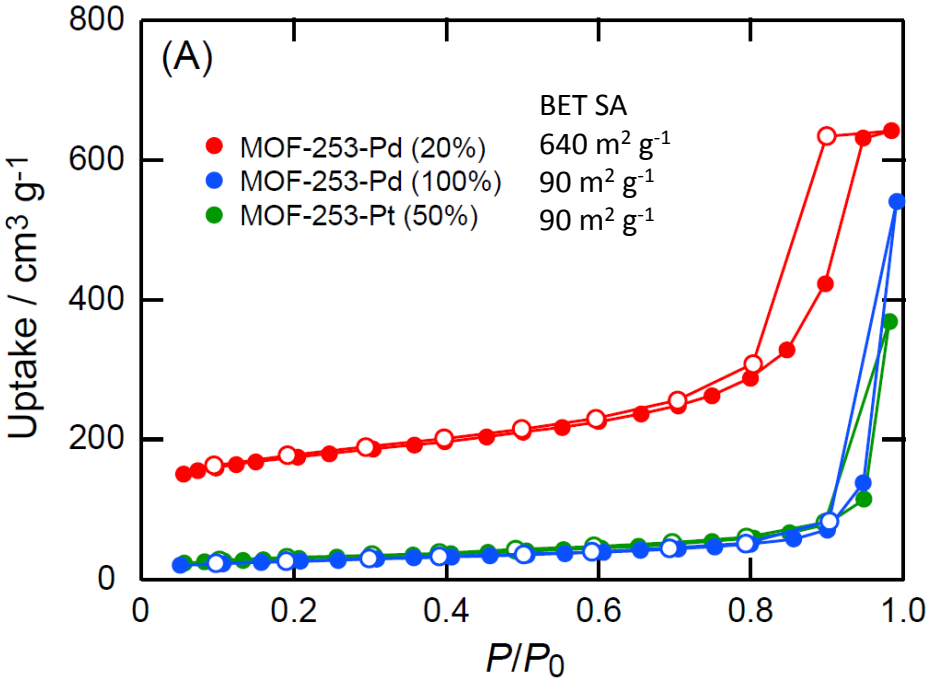


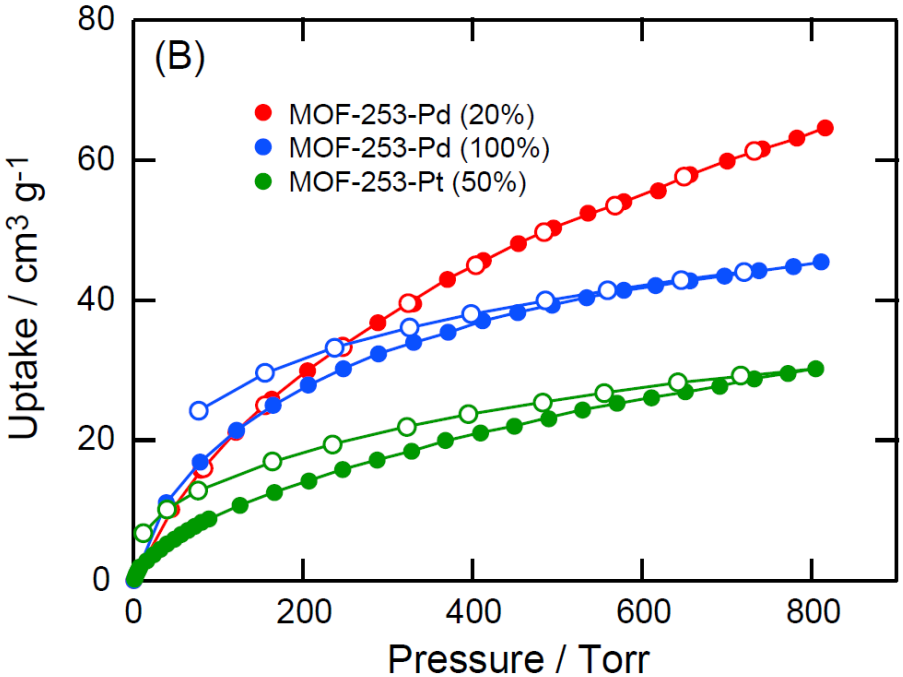


MOF-253
(Al-BPyDC)

- Does not form small molecules (e.g. $M(BPy)_3$)
- Higher stability compared to Zn-MOFs
- Simple synthetic procedure
- Prevention of metal exchange during the metal impregnation process

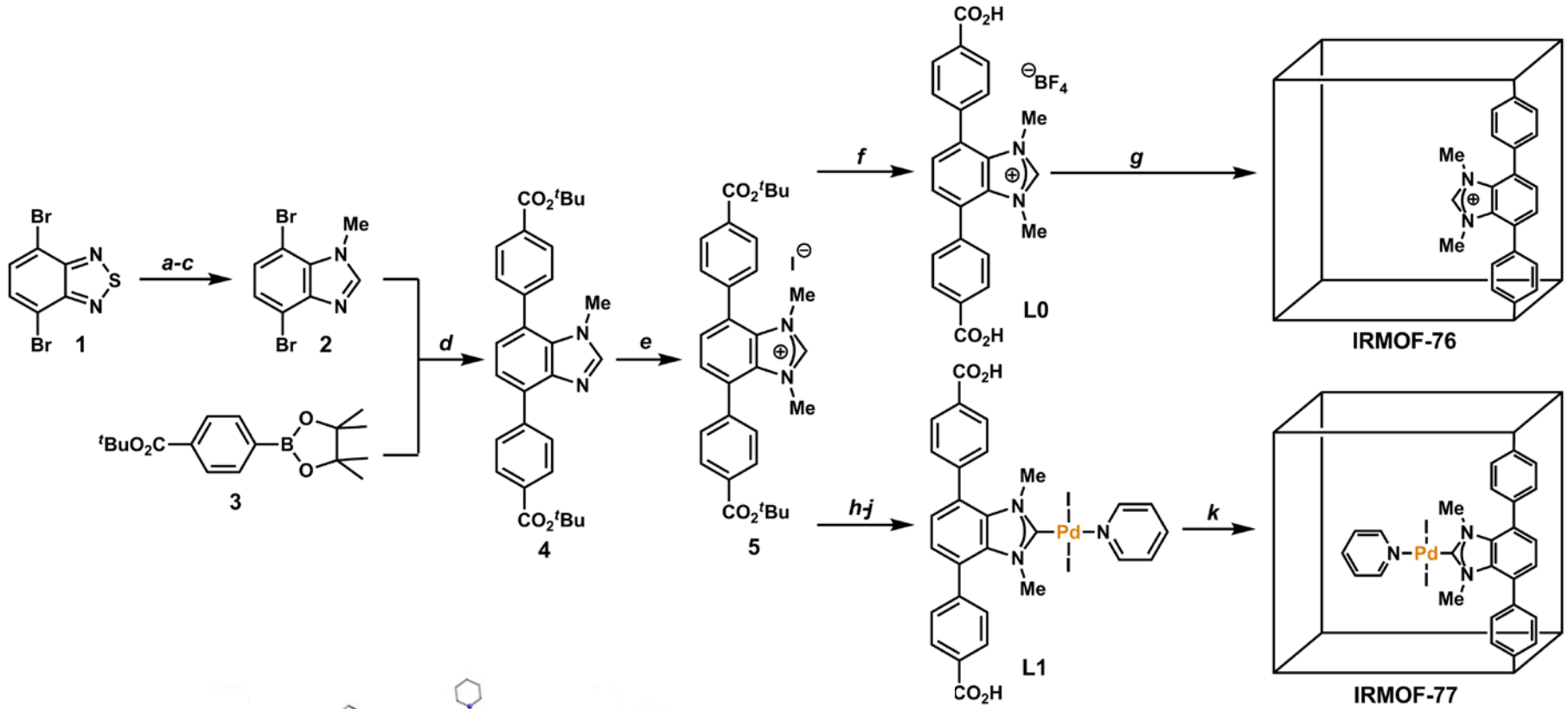
N_2 and H_2 isotherms for metalated MOF-253

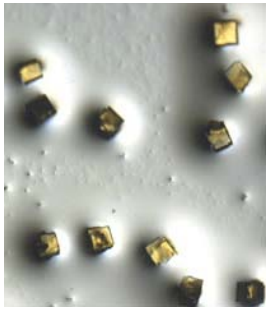


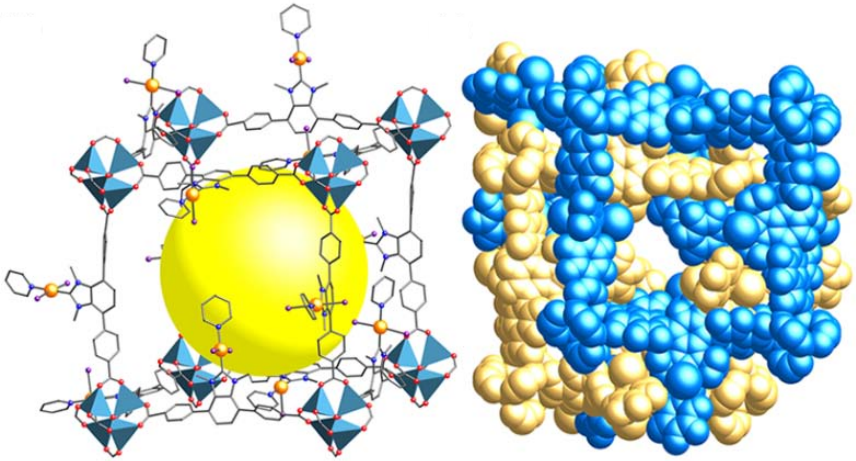


- Successive metalation was confirmed by K-edge extended X-ray absorption fine structure spectroscopy (EXAFS).
- Significant surface area decrement was observed in higher loading samples.
- It is not clear if the hysteresis is attributed to the strong interaction between metal and H_2.

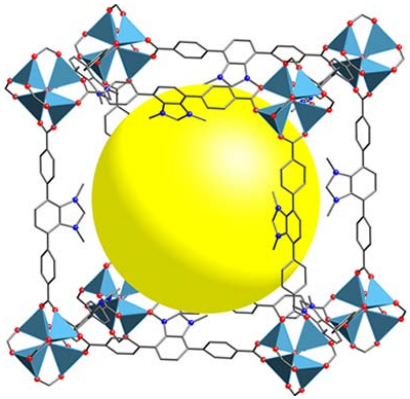
Preparation of IRMOF-76 and 77





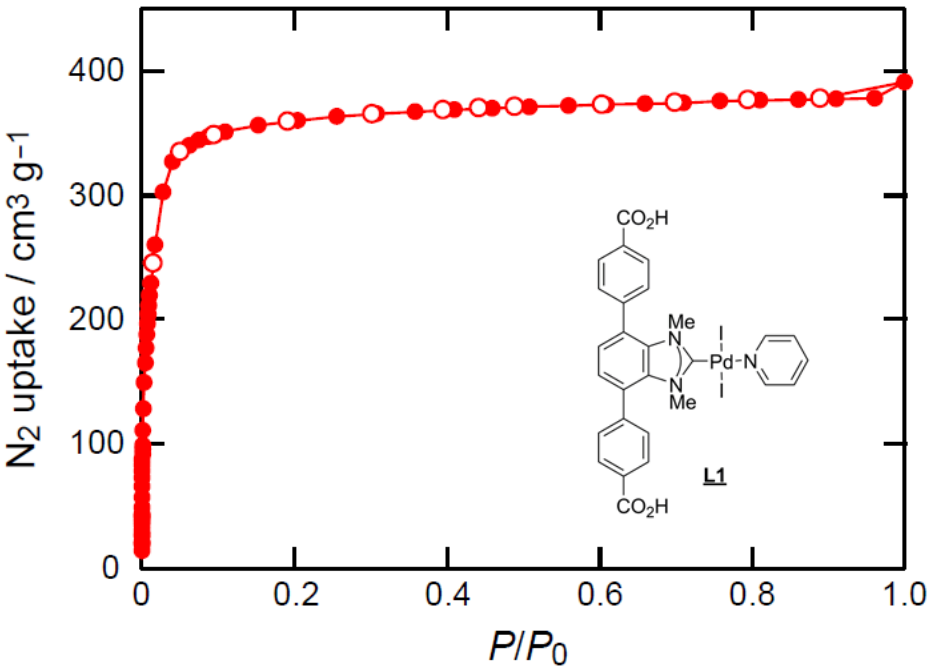


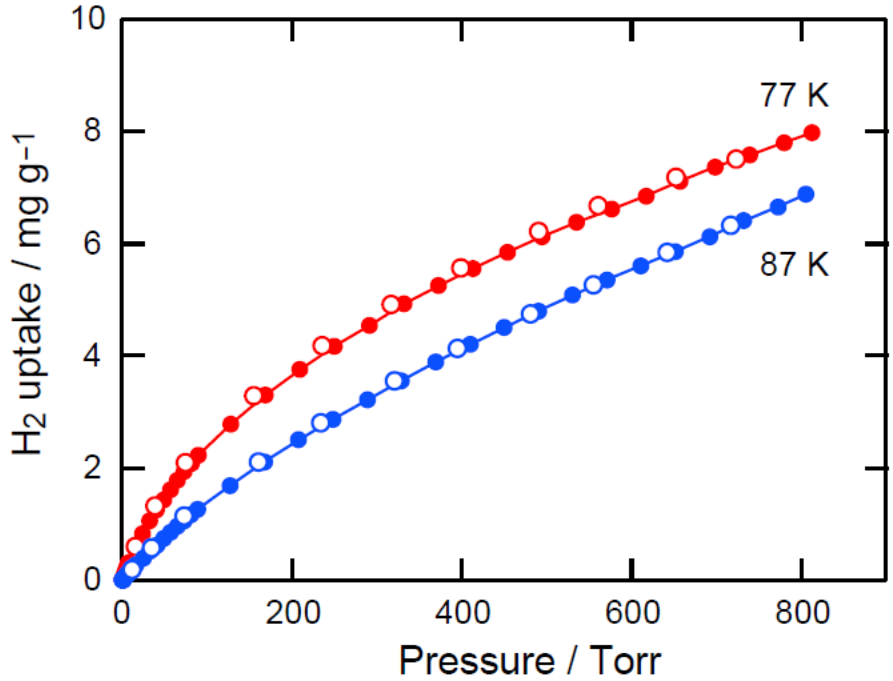
IRMOF-77 (interwoven)



IRMOF-76

N_2 and H_2 isotherms for IRMOF-77

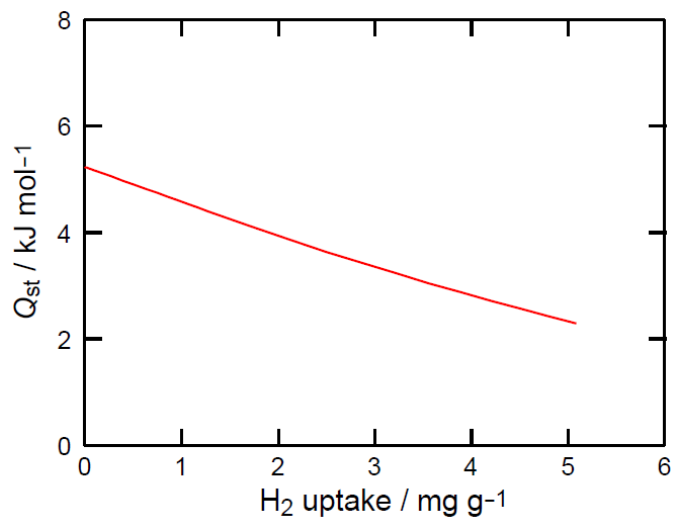




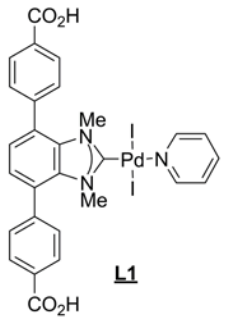
Surface area

BET	1590 $m^2\ g^{-1}$
Langmuir	1610 $m^2\ g^{-1}$

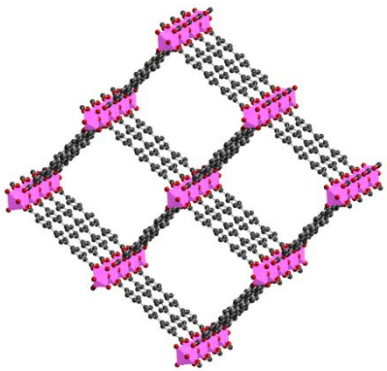
IRMOF-77 having a long linker was activated. Initial Q_{st} was estimated to be 5.2 kJ mol^{-1}

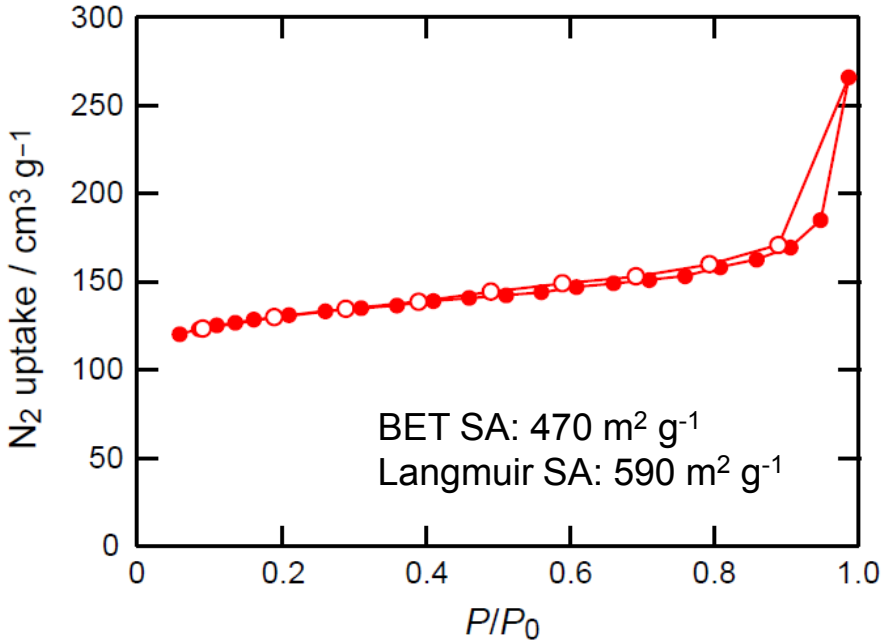


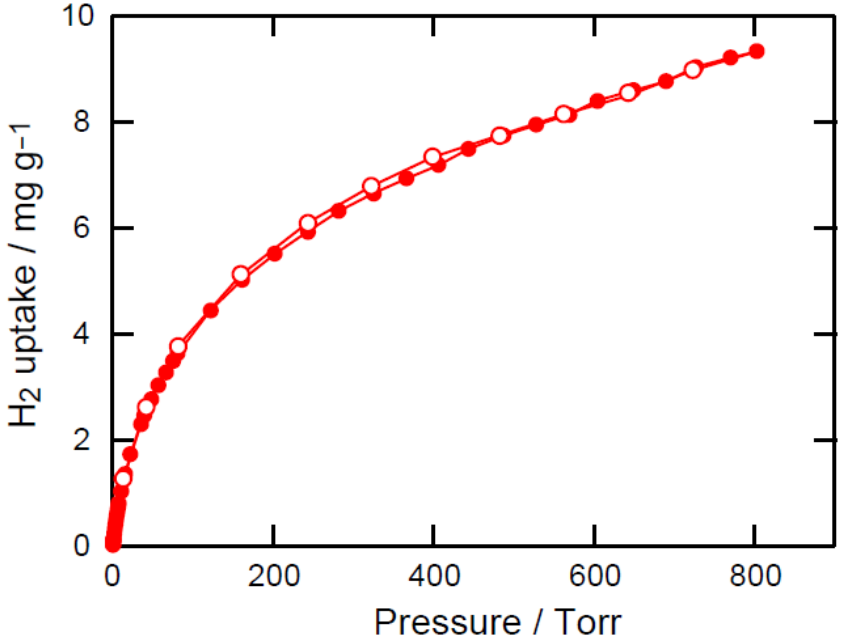
Preparation of MOF-353



+ $Al(NO_3)_3$ ⟶ MOF-353
Al(OH)(**L1**)

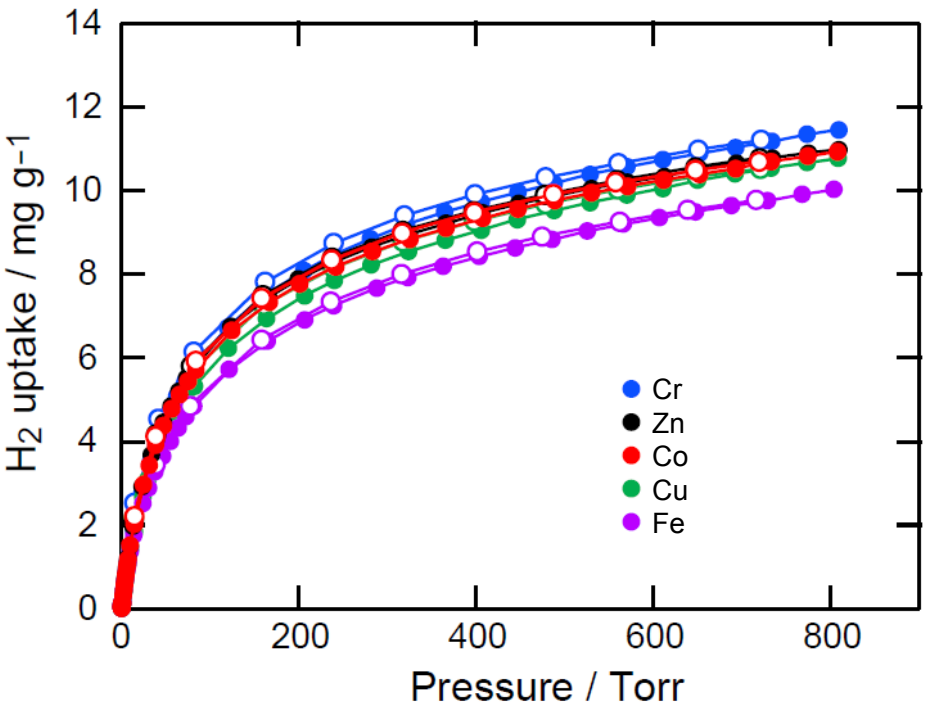


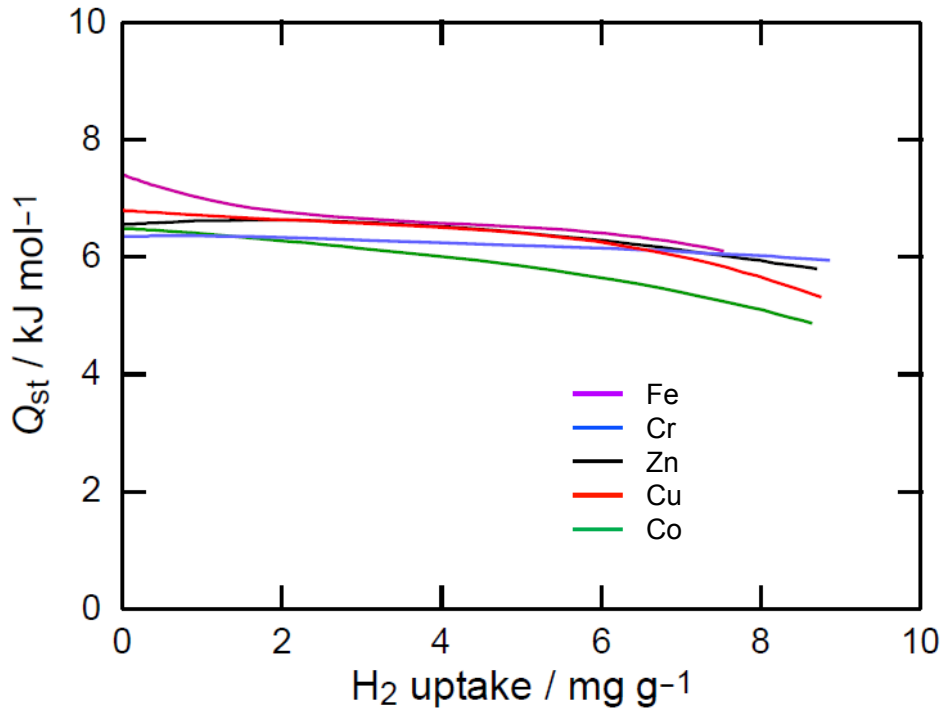




Better H_2 uptake behavior in the low pressure region compared to IRMOF-77.
When pyridine was removed, the surface area dropped.

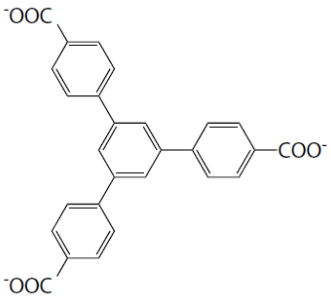
Metalated porphyrin MOFs



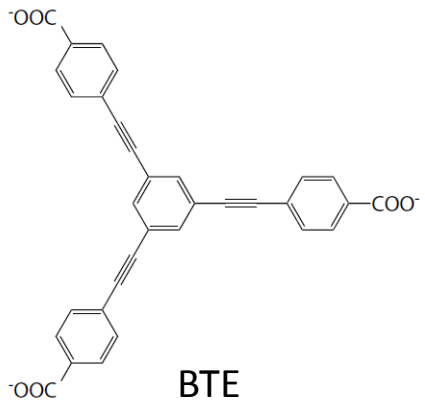


	BET area / m^2 g^{-1}	H_2 uptake / mg g^{-1}	Q_{st} / kJ mol^{-1}
MOF-130-Cr	370	11.3	6.3
MOF-130-Fe	490	9.8	7.4
MOF-130-Co	390	10.8	6.8
MOF-130-Cu	400	10.6	6.5
MOF-130-Zn	540	10.8	6.5

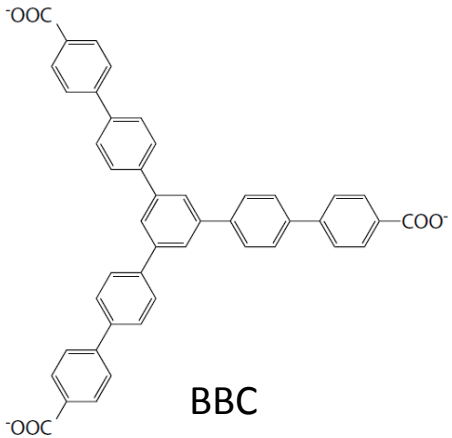
Isoreticular expansion



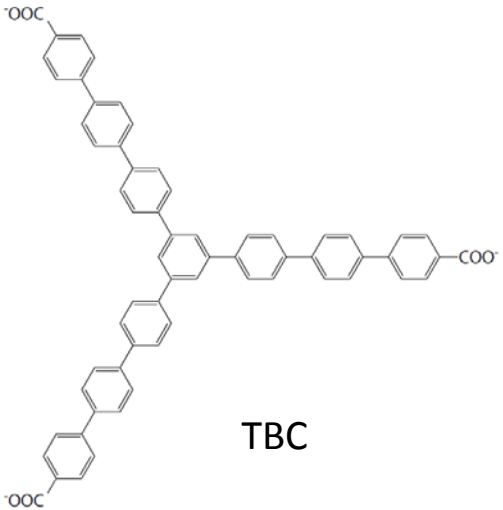
BTB



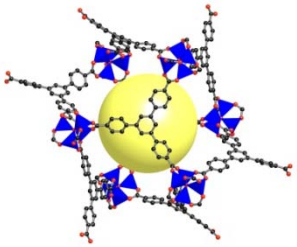
BTE



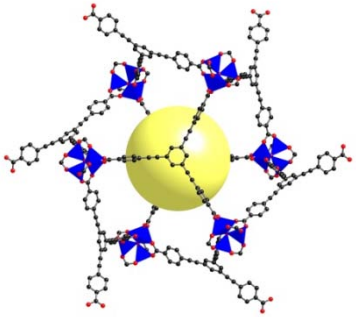
BBC



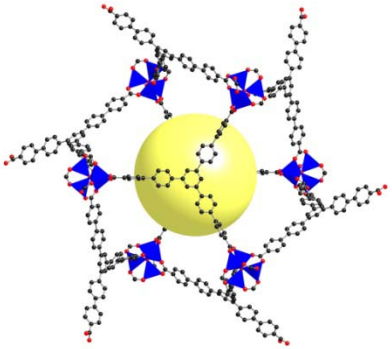
TBC



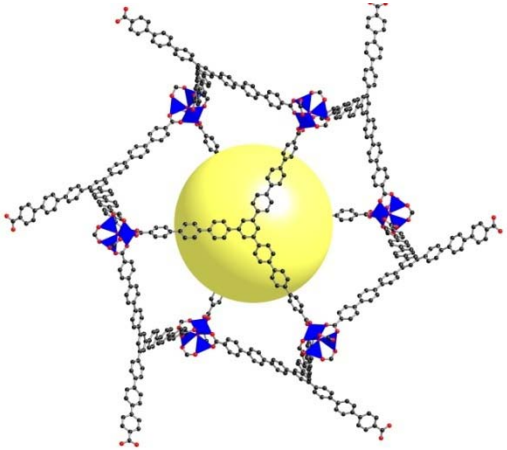
MOF-177



MOF-180



MOF-200



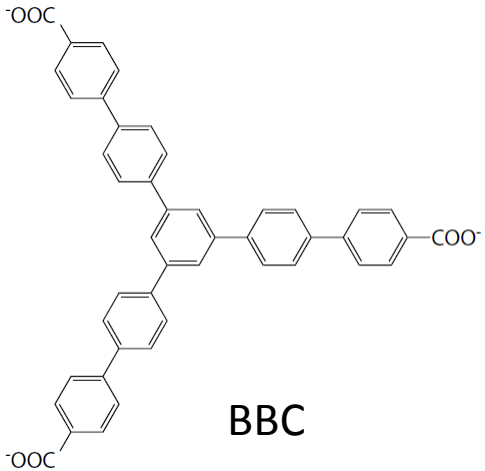
MOF-700

<u>High surface area and low density</u>

- Large gravimetric uptake (wt%)
- Poor volumetric uptake (g/L)

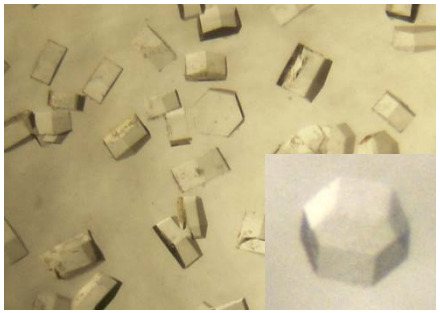
How many benzene rings can be inserted?

Synthesis of MOF-200

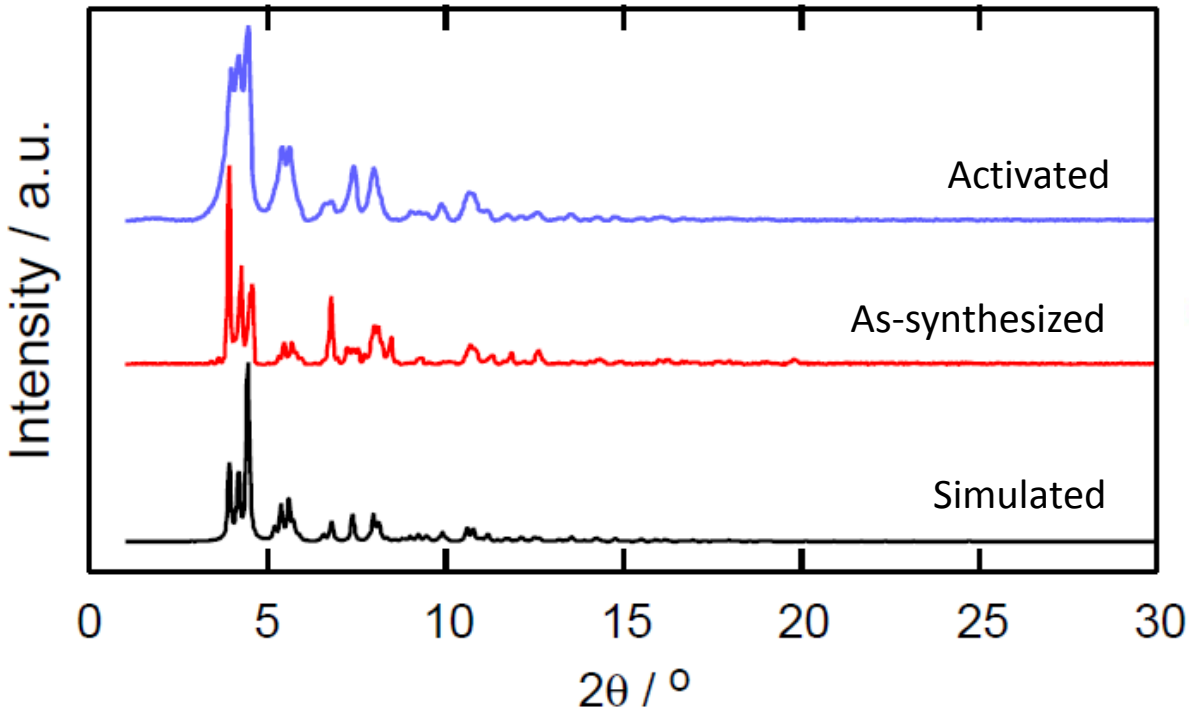


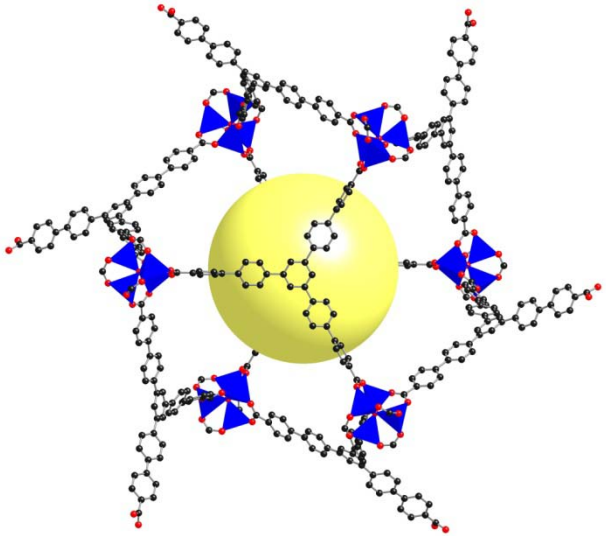
BBC

+ Zn^{2+} →



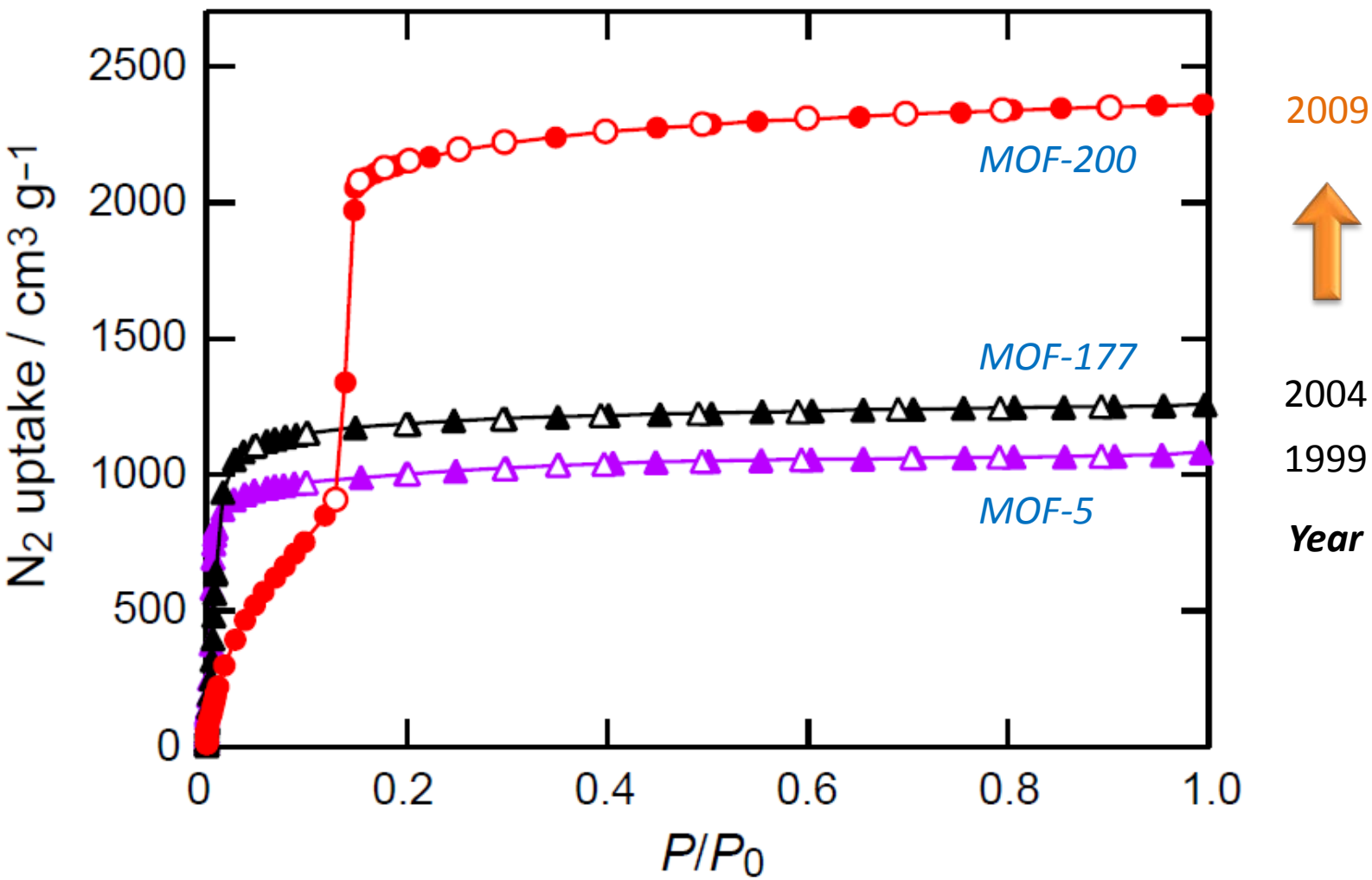
MOF-200 ($Zn_4O(BBC)_2$)





MOF-200 structure was maintained after removal of guest molecules.

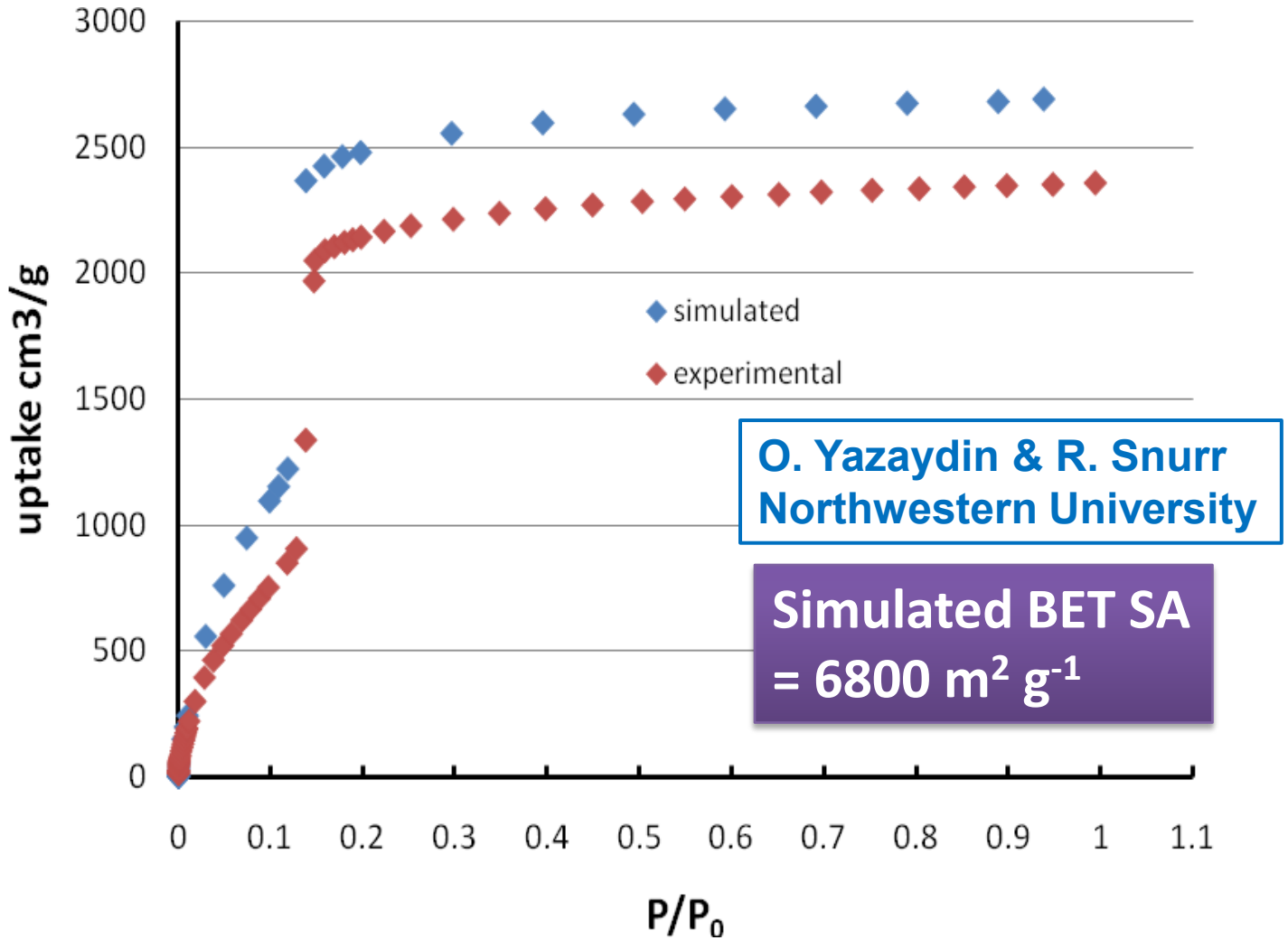
Low-pressure N_2 isotherms



BET surface area: 4530 $m^2\ g^{-1}$

Total pore volume: 3.59 $cm^3\ g^{-1}$ (the **largest** value among crystalline materials)

Simulated N_2 isotherm for MOF-200

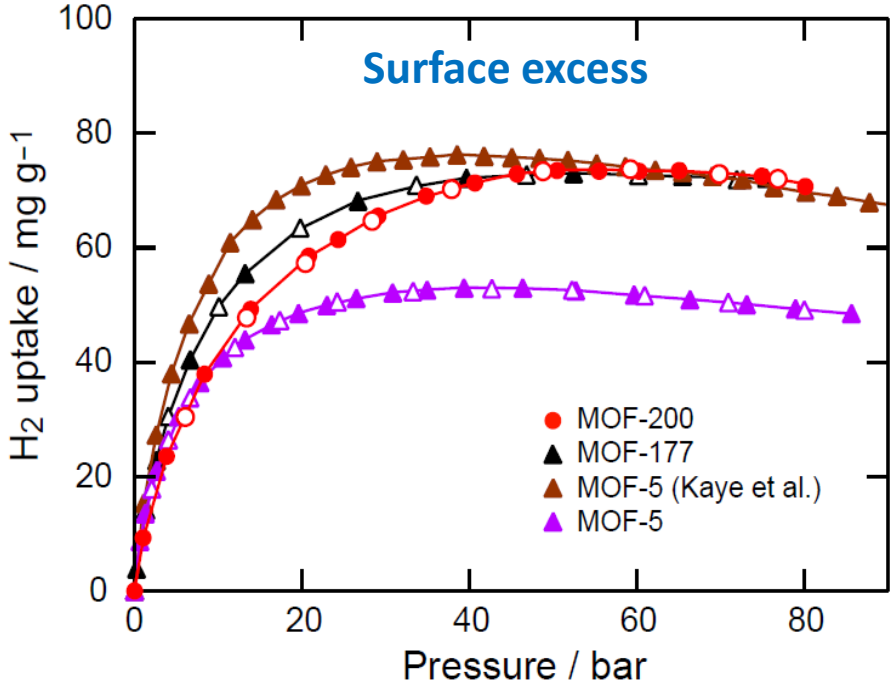


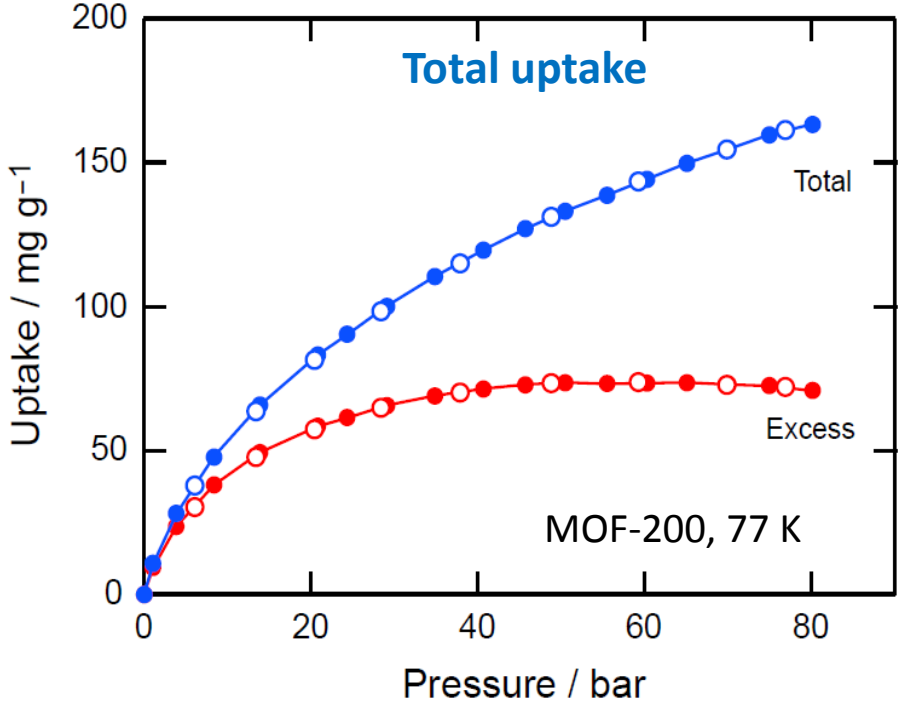
O. Yazaydin & R. Snurr
Northwestern University

Simulated BET SA = 6800 m^2 g^{-1}

Experimental data are well-reproduced by simulation calculations.

High-pressure H_2 isotherms at 77 K



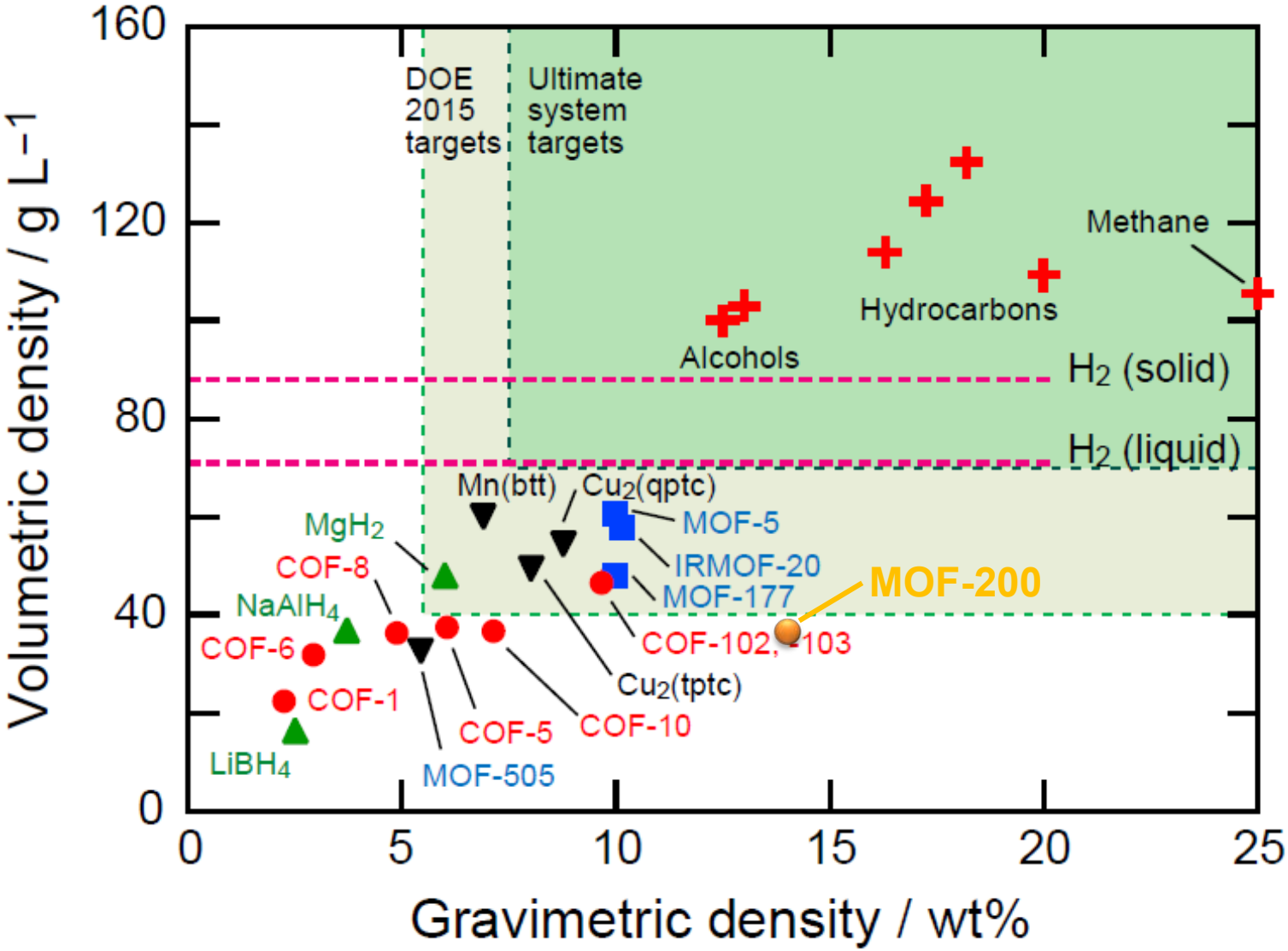


Porosity and H_2 uptake of MOFs at 77 K and 80 bar

	Density g/cm³	Void space %	BET SA m²/g	Excess mg/g	Total mg/g	Total g/L
Bulk H_2	n/a	n/a	n/a	n/a	n/a	26
MOF-200	0.22	90.1	4530	74	**163**	36
MOF-177	0.43	82.6	4500	73	116	50
MOF-5	0.59	79.8	3800	76	106	63
NOTT-112	0.50	79.8	3800	76	107	54
UMCM-2	0.40	84.2	5200	69	124	50

Stored hydrogen per mass and per volume

(only metal hydrides showing good recycling are included)



Gravimetric H_2 density in MOF-200 is approaching those of hydrocarbons.

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
- Synthesis and activation of ultra-high surface area MOFs

Technology transfer/collaborations: Active relationship with collaboration partners and BASF.

Proposed future research:

- Employ light weight metals to create strong binding sites.
- Material design based on theoretical prediction.

Current Group Members