DOE Hydrogen Program

HYDROGEN STORAGE IN METAL-ORGANIC FRAMEWORKS

Christian Doonan
for Omar M. Yaghi

Department of Chemistry
Center for Reticular Chemistry
UCLA

May 22, 2009

Project ID
st_33_doonan

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

Project start date: 5/1/2005
Project end date: 4/30/2010
Percent complete: 75%

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 FY08: $430 K
- ❑ Funding for FY09: $428 K

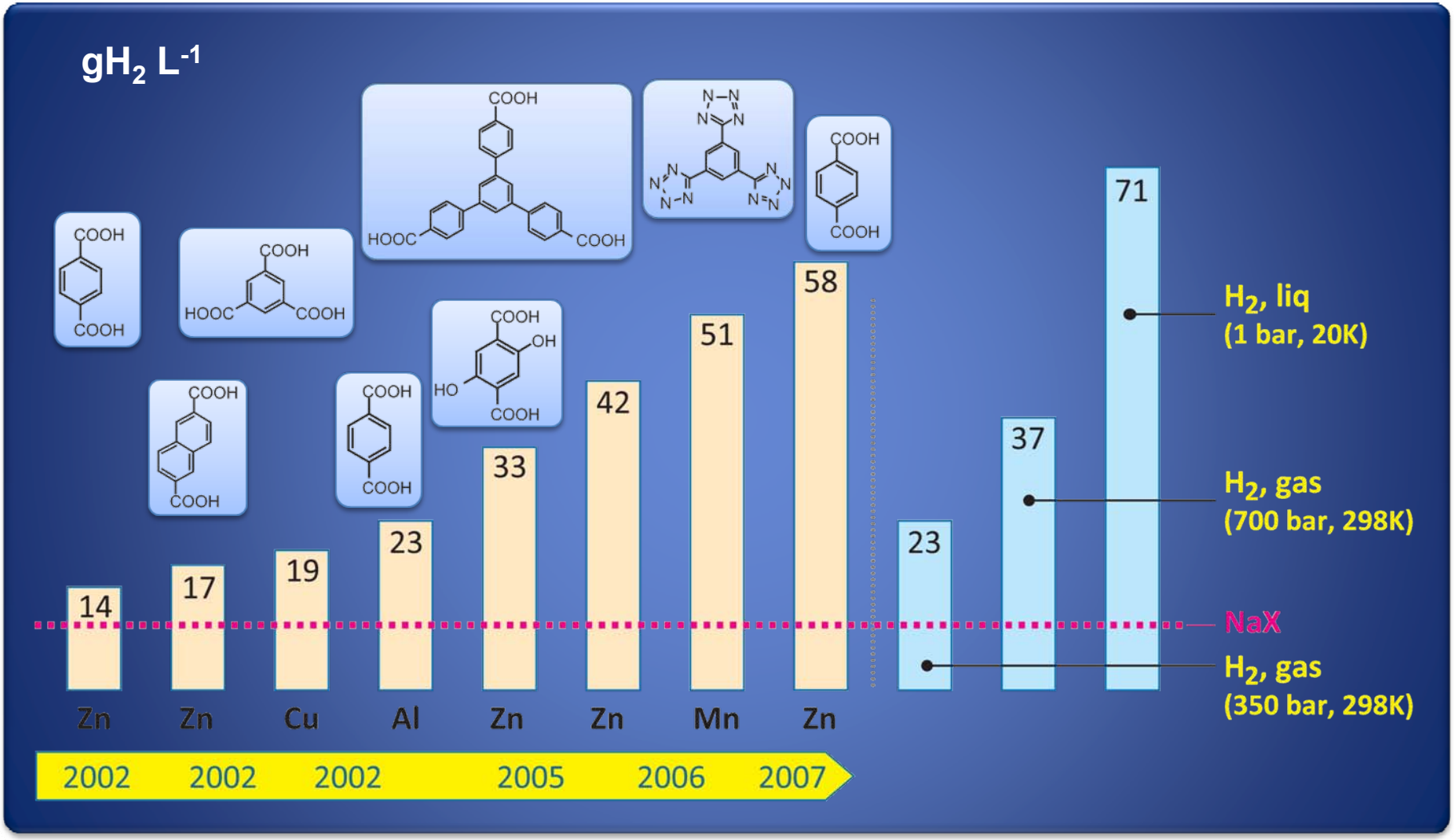
Collaborating Partners

- ❑ Bill Goddard (Caltech)
- ❑ Randy Snurr (NW)
- ❑ Joe Hupp (NW)
- ❑ Juergen Eckert (UCSB)
- ❑ BASF

Important Aspects of MOF Chemistry

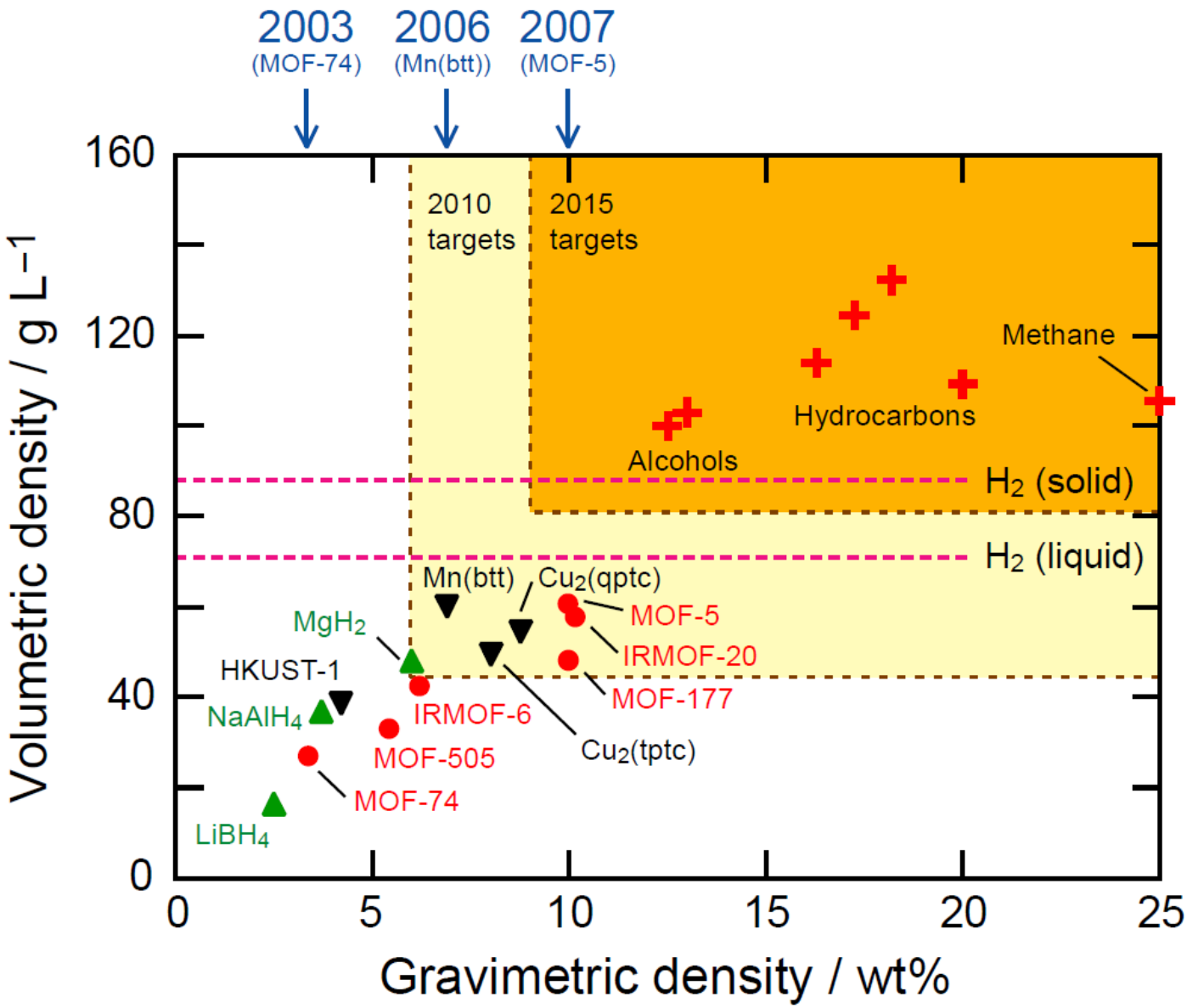
- Design of composition (metal centers and organic links). Synthesis and structural characterization is well worked out.
- Control of structure, topology, interpenetration and porosity.
- Formulation of hypothesis and testing of hypothesis is quite feasible. This leads to definitive conclusions and allows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

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



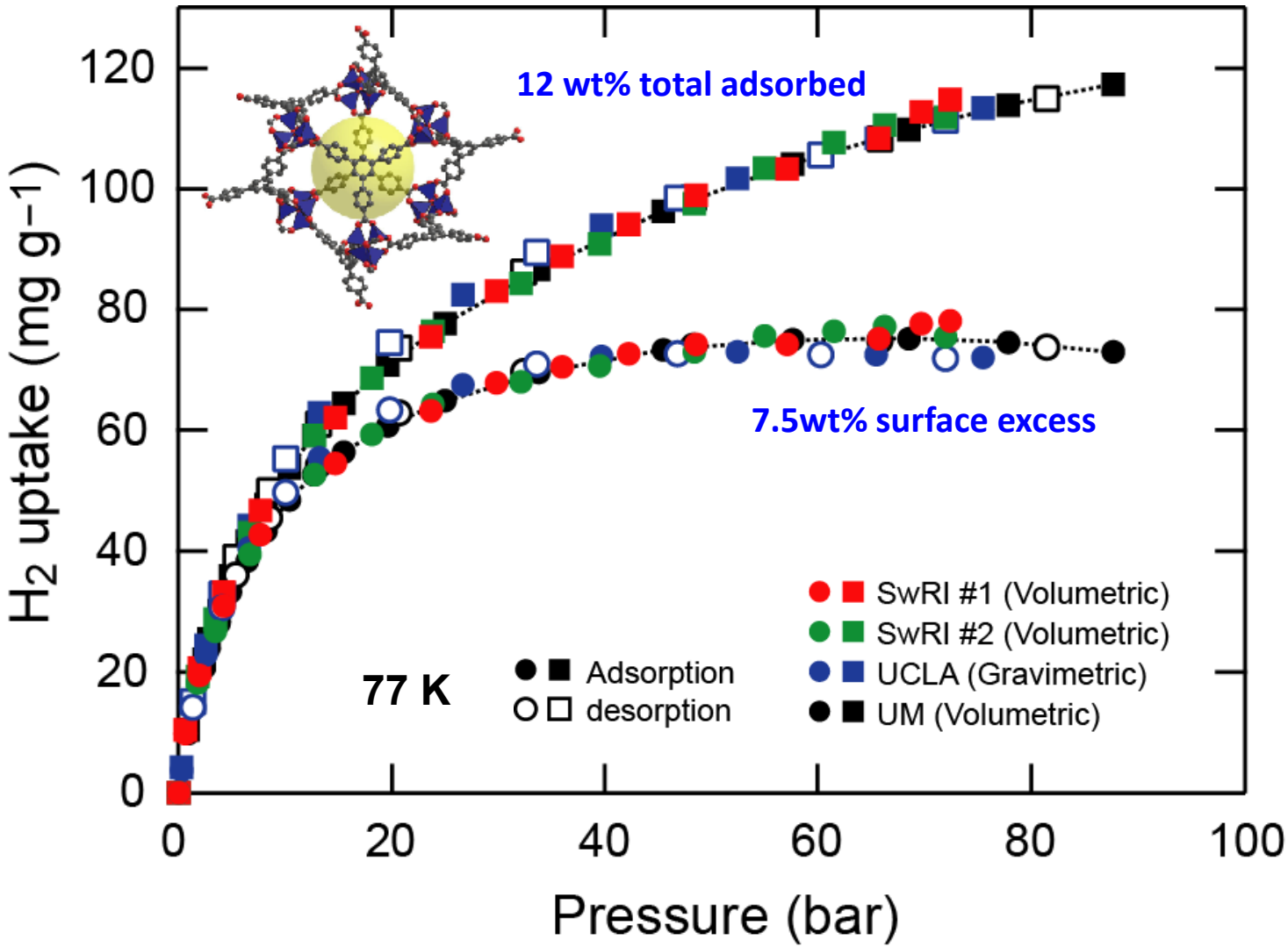
Stored hydrogen per mass and per volume

(only metal hydrides showing good recycling are included)



Independent Verification of MOF-177 Hydrogen Uptake Capacity

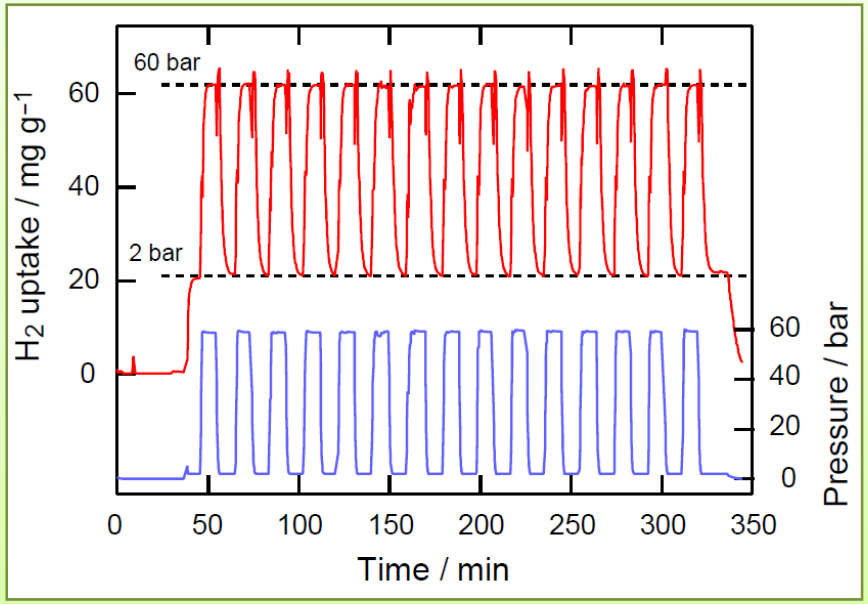
(volumetric and gravimetric measurements verified, shown using gravimetric scale)



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 (FY08-09)

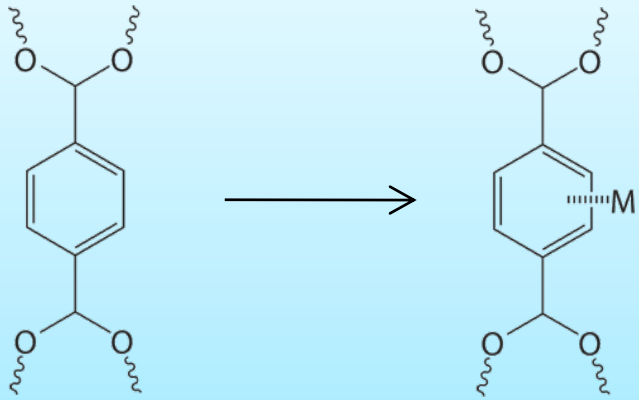
How to increase hydrogen storage at room temperature?

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

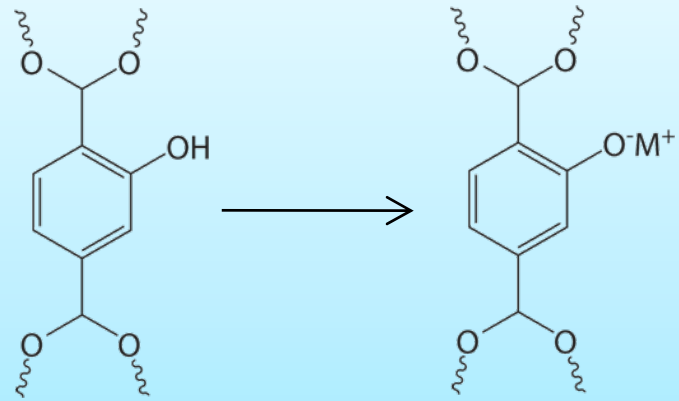
2. **Preparation of high-surface area MOFs for isoreticular covalent organic functionalization**
   - Preparation of expanded organic link
   - High-throughput MOF synthesis

3. **Coordination with theory**
   - Prediction of binding energy

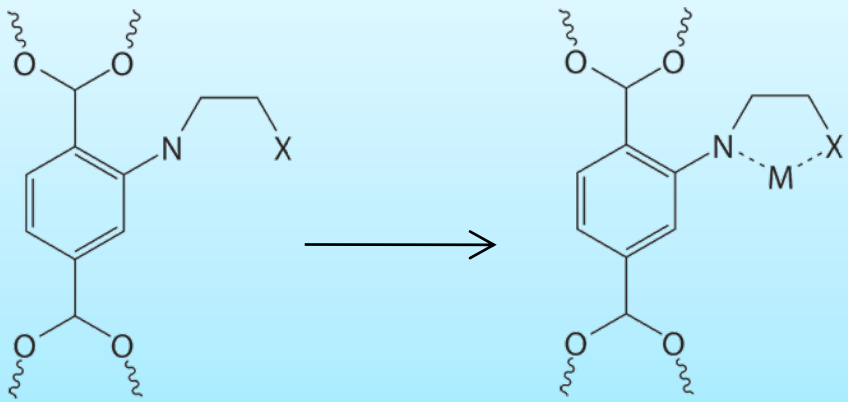
Strategy: Possible routes for metal impregnation



JACS **2007**, *129*, 8422

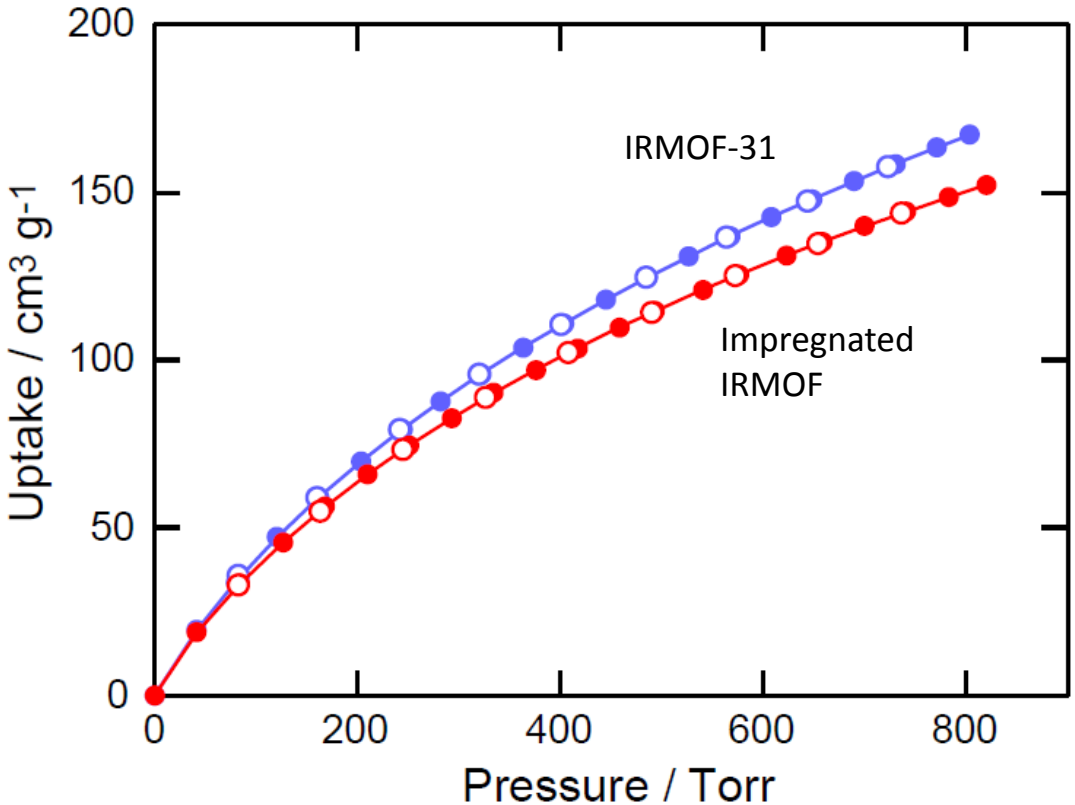


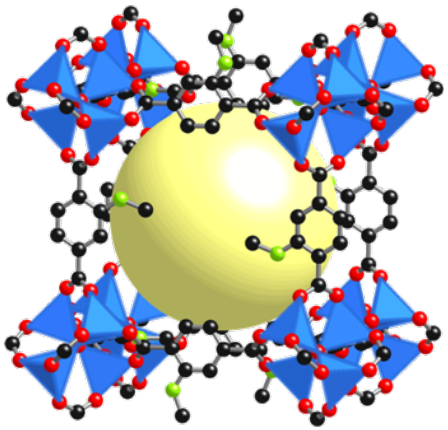
Nano Lett. **2008**, *8*, 1572



Control coordination number without losing exposed metal surface

Synthesis and Impregnation of IRMOF-31





IRMOF-31

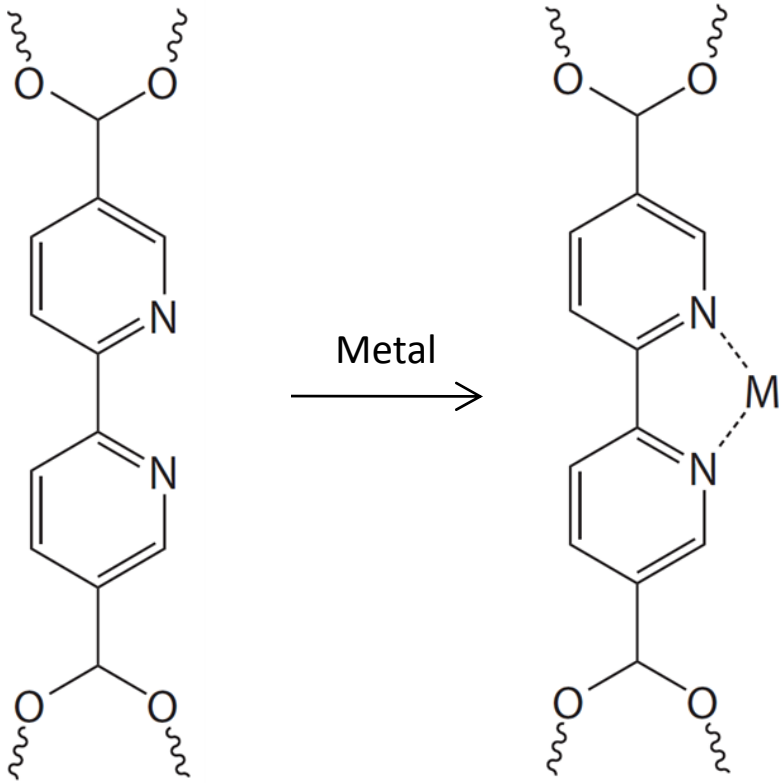
*t*BuK was mixed with IRMOF-31 in THF or ether under Ar atmosphere.

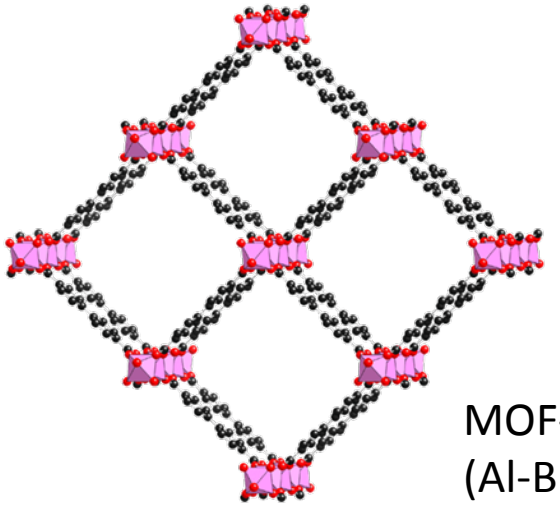
Other metal sources ($LiNH_2$, $LiAlH_4$, NaH, and KH) didn't show enough solubility in THF and ether

Initial slope (Henry's constant) is not improved.
→ Metal amount in the MOF is not enough to show clear difference.

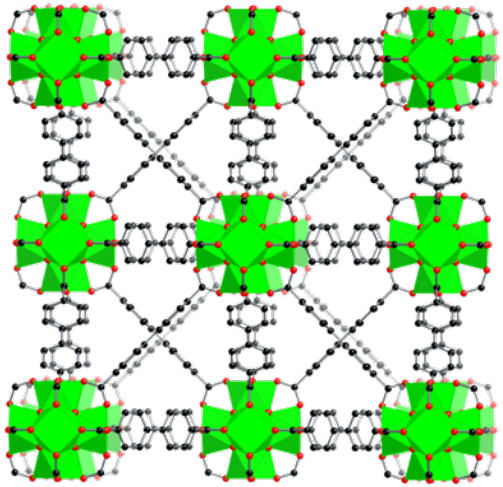
Low coordination number may not be a good way to immobilize metals.

MOFs with bipyridine link





MOF-253
(Al-BPyDC)

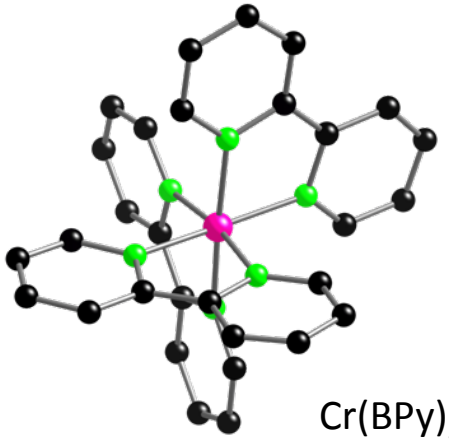


MOF-267 (Zr-BPyDC)

Preparation of Al or Zr-MOFs

Why?

Does not form small molecules (e.g. $M(BPy)_3$)

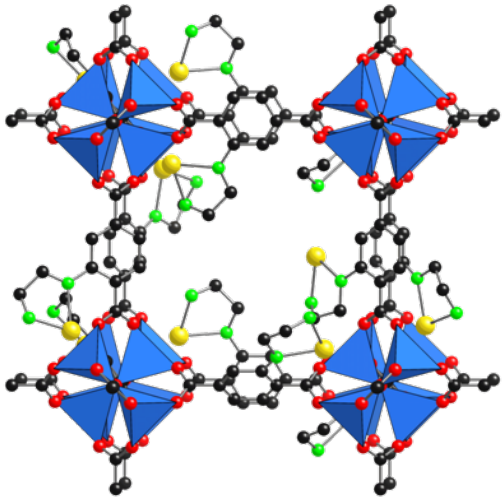


Higher stability compared to Zn-MOFs

- Stable in water

Simple synthetic procedure

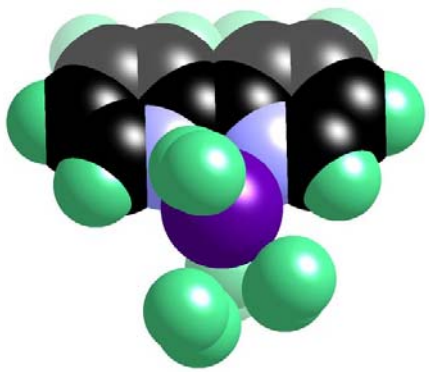
- Reflux in water
- Easy to scale-up



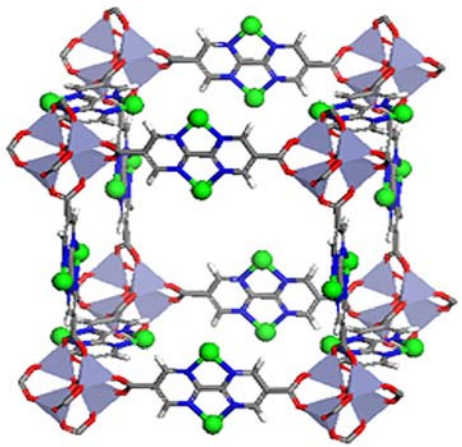
Prevention of metal exchange during the metal impregnation process

- Metal exchange to Zn was observed in IRMOF-3 system

Theoretical prediction of binding energy



$[(BPy)V^{2+}](H_2)_4$



Model system:
$[(BPyDC)M(CO)_4]^{2-}$

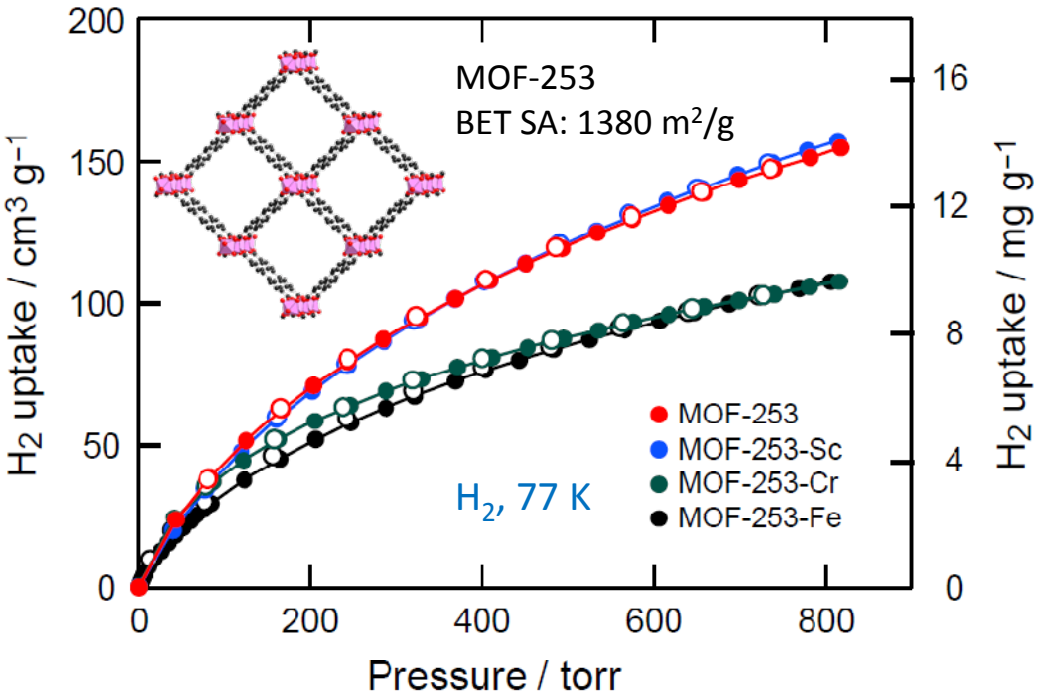
- M^{n+} = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn (n = 0, 1 and 2)
- DFT calculations

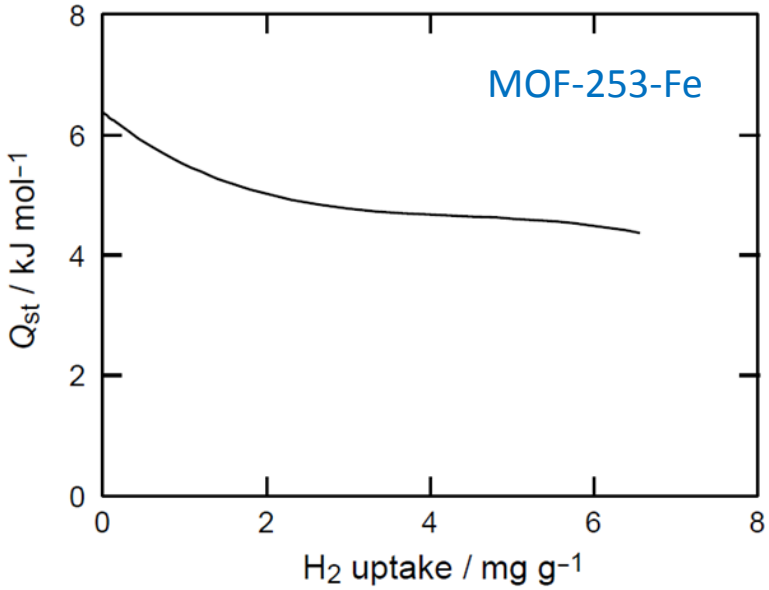
J. Mendoza-Cortés & W. Goddard (Caltech)

n = 0: Mn has stronger binding energy to BPyDC than its cohesive energy.
n = 1: Mn^+, Co^+, Ni^+, Cu^+, and Zn^+ have stronger binding energy to the ligand.
n = 2: All metals are favorable for formation of $(BPyDC)M^{2+}$ complexes.
Metal impregnated materials would be experimentally accessible.

Interaction between H_2 molecules and the $(BPyDC)M^{2+}$
$(BPyDC)M^{2+}(H_2)_4$ average H_2 binding energies per one H_2 molecule:
-24.6 kJ mol^{-1} for Zn^{2+} to -62.2 kJ mol^{-1} for V^{2+}
➔ These are ideal values for H_2 storage at room temperature.

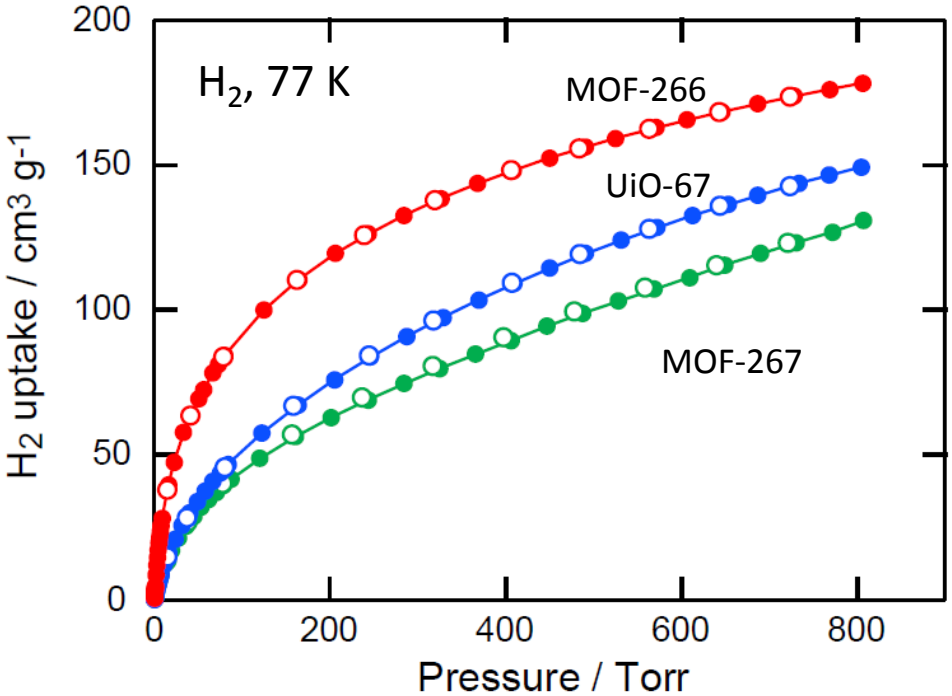
Metal impregnation in bipyridine-MOFs

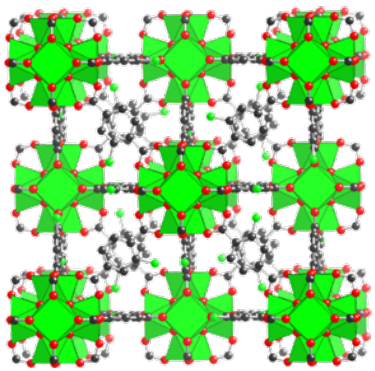




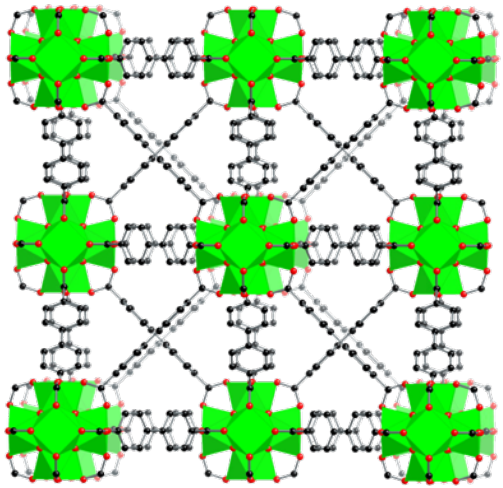
- Pristine MOF-253 was immersed in the solution containing Sc, Cr, and Fe ions.
- MOF-H_2 interaction does not seem to be improved. → Low metal loading (ICP)
- Bipyridine ring can rotate. → Rigid linker would be preferred.
- Other metals will be tested (e.g. Pt, Pd)

Synthesis of Zr-MOFs





MOF-266



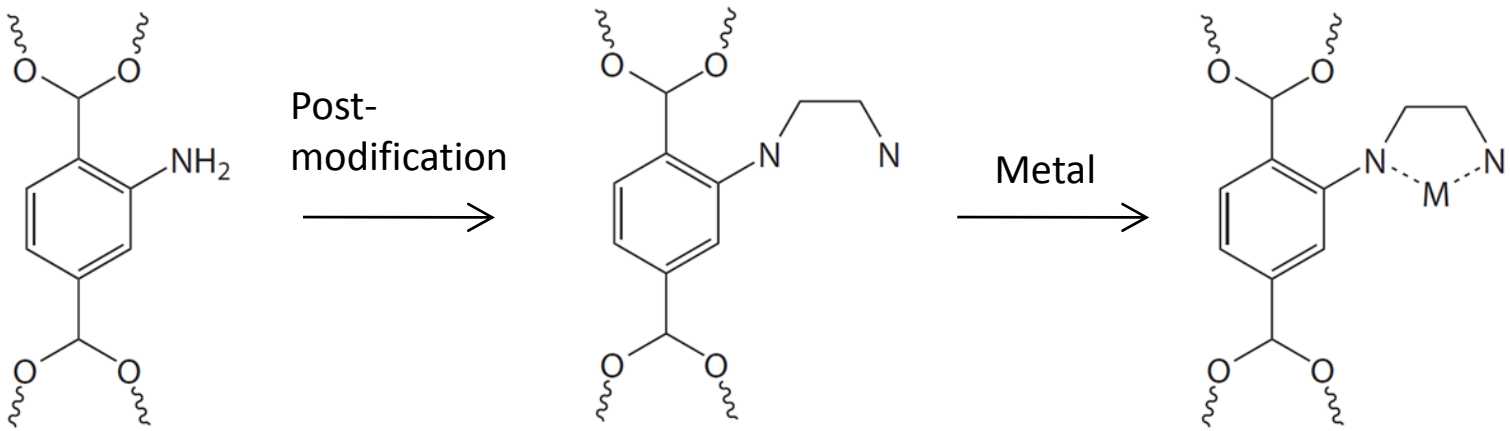
UiO-67

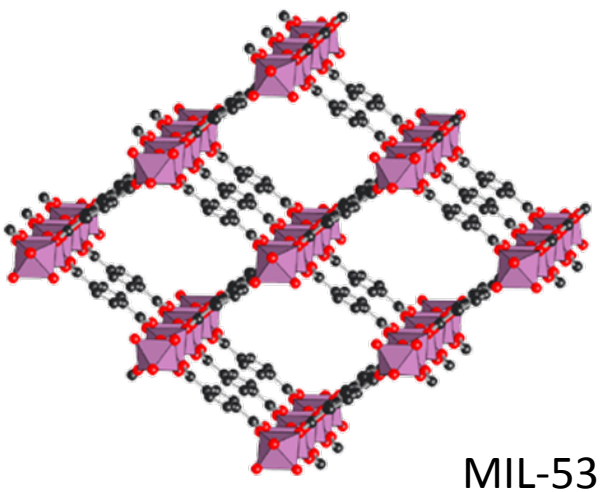
	BET surface area / m^2 g^{-1}	H_2 uptake at 77 K and 1 bar / mg g^{-1}
MOF-266 (Zr-NH_2-BDC)	1100	15
MOF-267 (Zr-BPyDC)	1550	11
UiO-67 (Zr-BPDC)*	1780	13

*Cavka *et al.*, *JACS*, **2008**, *130*, 13850.

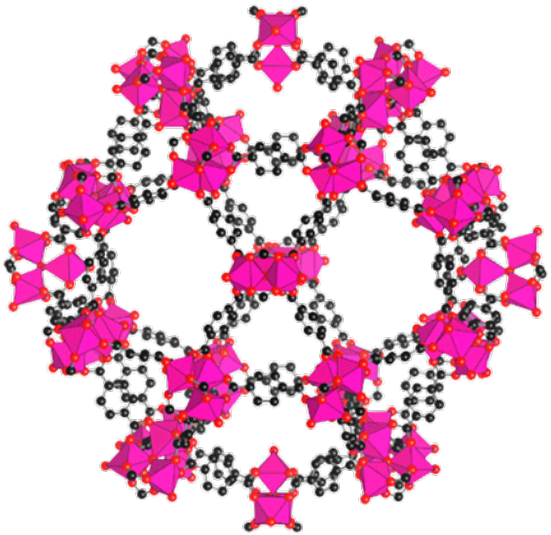
We will investigate metal-impregnated materials.

MOFs with ethylenediamine groups





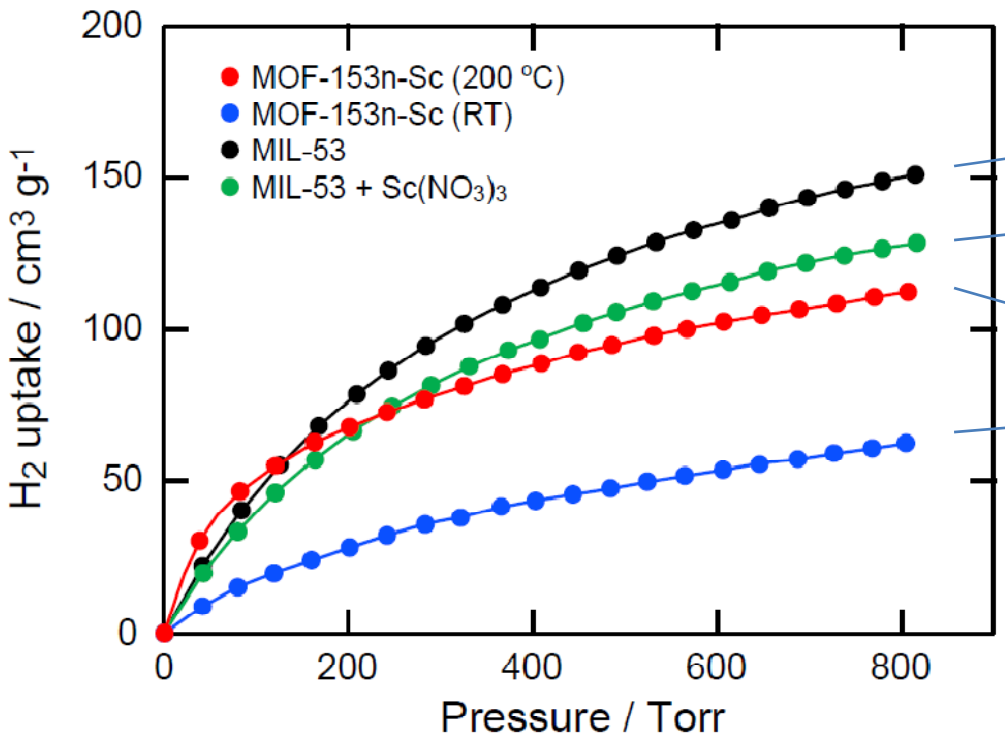
MIL-53



MIL-101

MIL-53 and MIL-101 analogues with ethylenediamine groups were prepared.

H_2 isotherms for MOF-153s



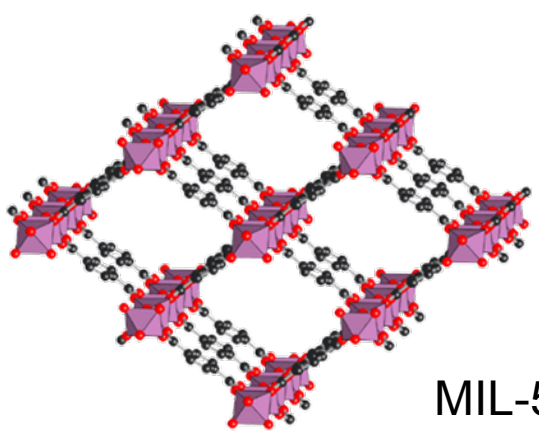
Functionalities

Pristine MIL-53

$Sc(NO_3)_3$

Ethylenediamine + Sc

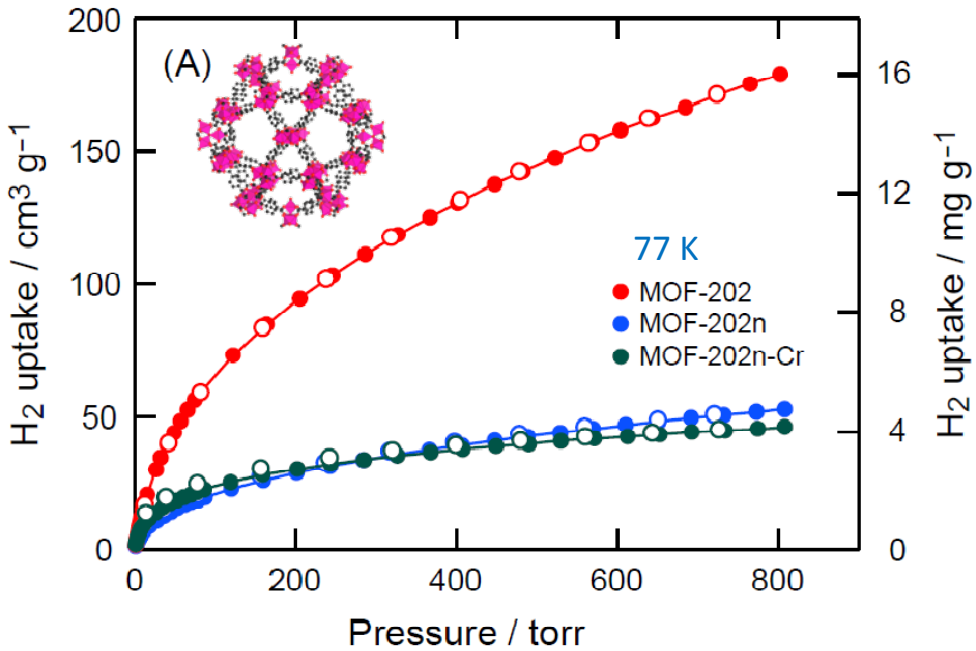
Ethylenediamine + Sc

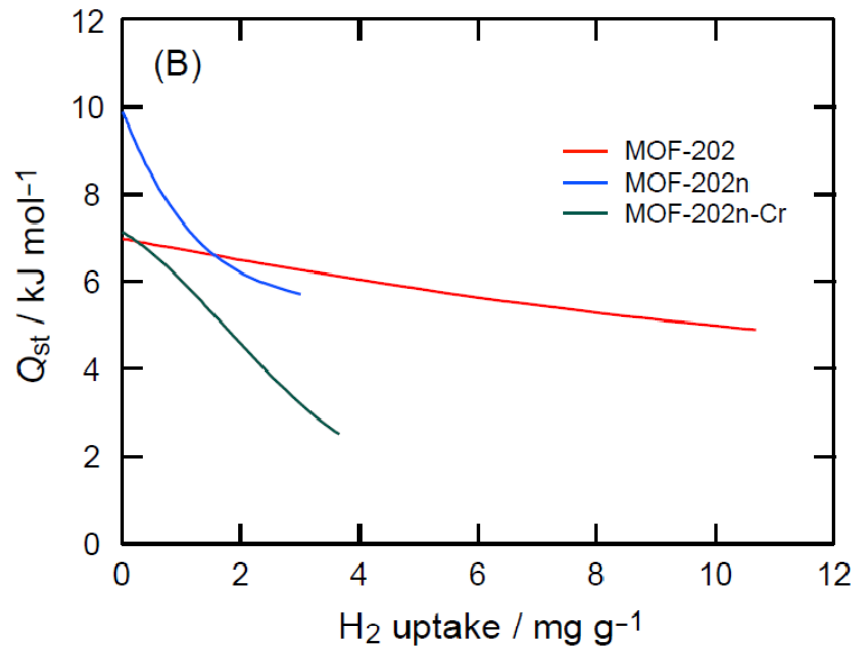


MIL-53

Although isoreticular metallation of MOFs showed smaller H_2 uptake, initial slope for MOF-153n-Sc can be better. However, no improvement was observed when Cr and V were used.

H_2 isotherms for MOF-202s

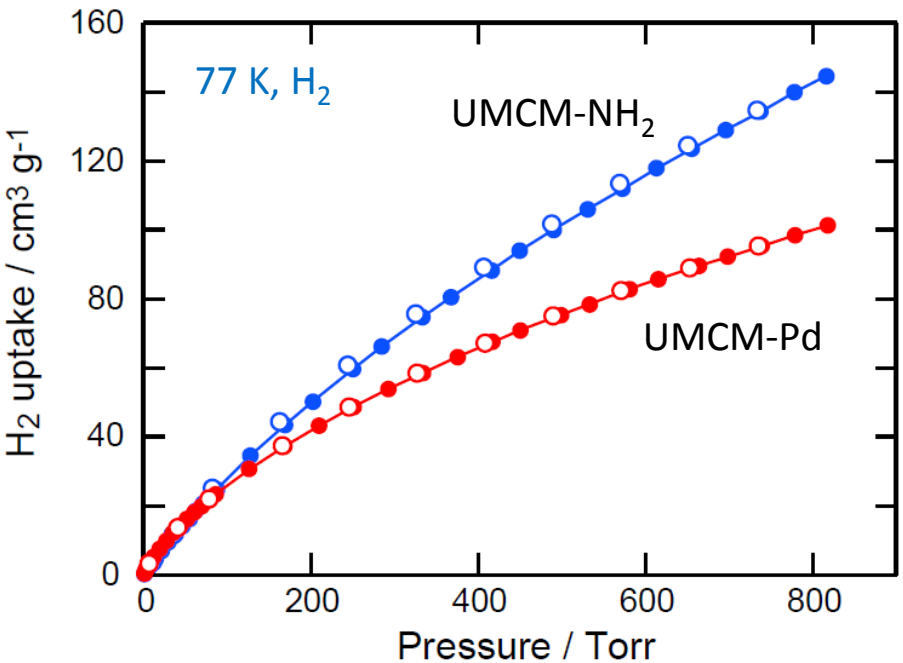


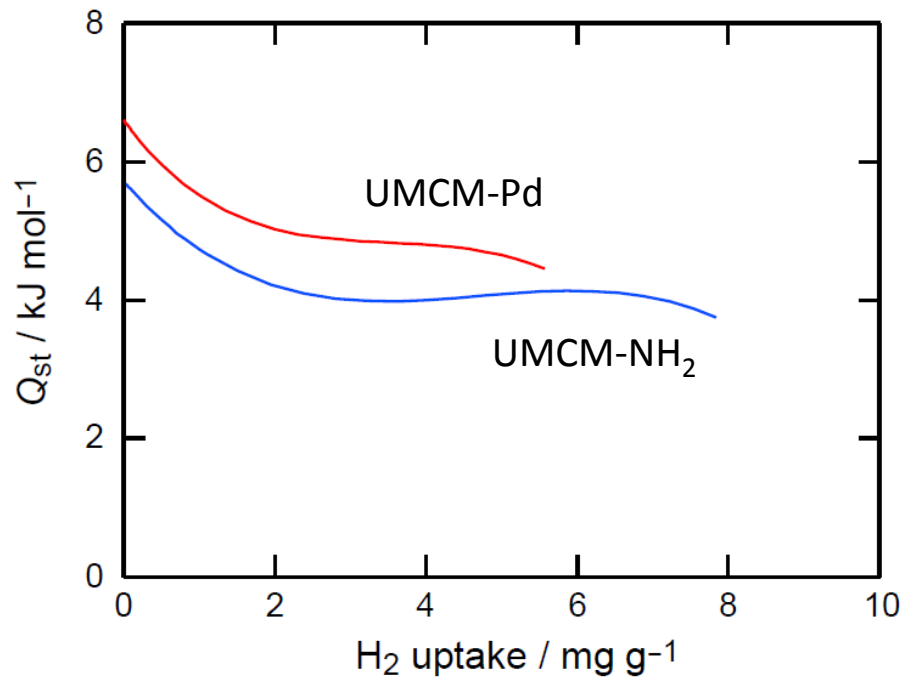


	Functionality	BET surface area / m^2 g^{-1}	H_2 uptake at 1 bar / mg g^{-1}	Q_{st} value / kJ mol^{-1}
MOF-202	NH_2	2000	16	7.0
MOF-202n	Ethylenediamine	525	4.6	9.9
MOF-202n-Cr	Ethylenediamine, Cr	200	4.1	7.1

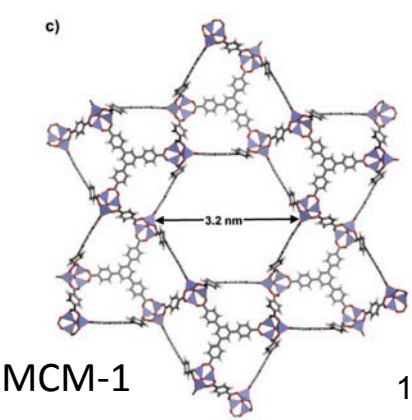
Due to the large decrease in surface area, it is difficult to see the effect of metal impregnation.

H_2 isotherms for UMCMs





Isoreticular covalent organic functionalization followed by metallation resulted in the initial Q_{st} value improving by 10%. Higher metal density is required for greater Q_{st} values.

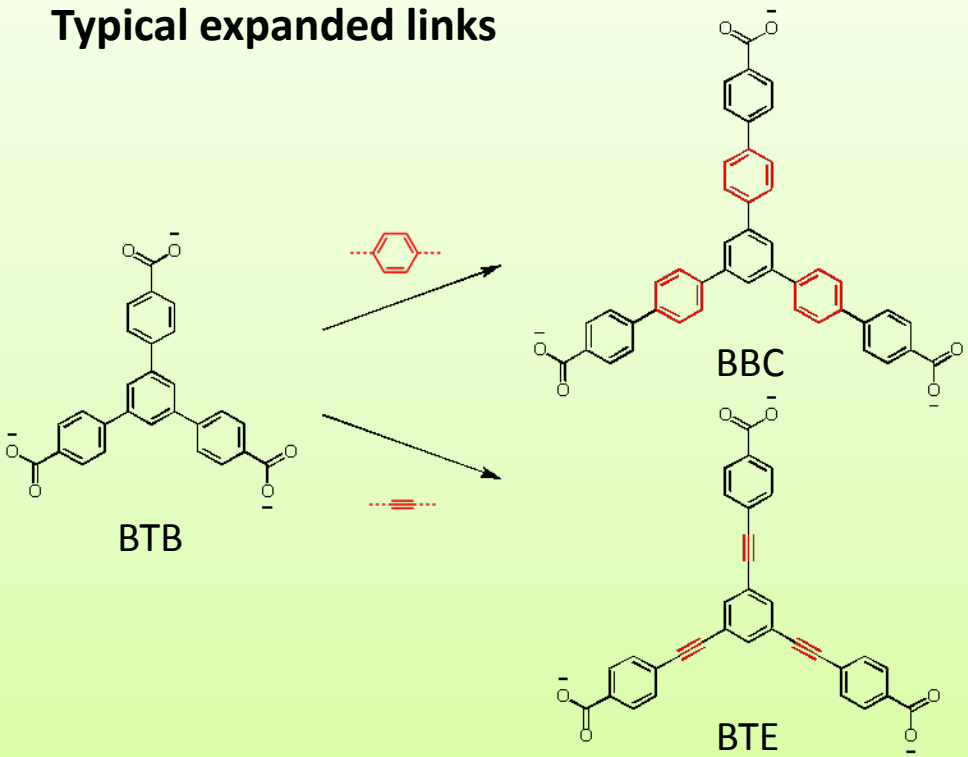


UMCM-1

Toward highly porous MOFs

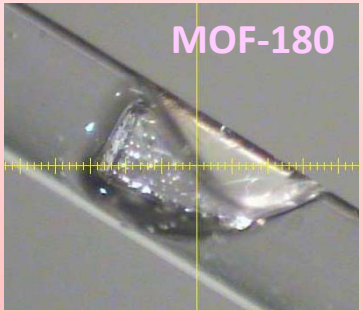
Surface area and pore volume of MOFs were decreased by the isoreticular-modification processes. Although meso-porosity is not preferable to store hydrogen at RT, larger pore size distribution should be important for isoreticular covalent organic functionalization and metallation.

Typical expanded links



New MOFs in hand

MOF-399
Cubic
a = 67.78 Å
d = 0.13 g cm^{-3}

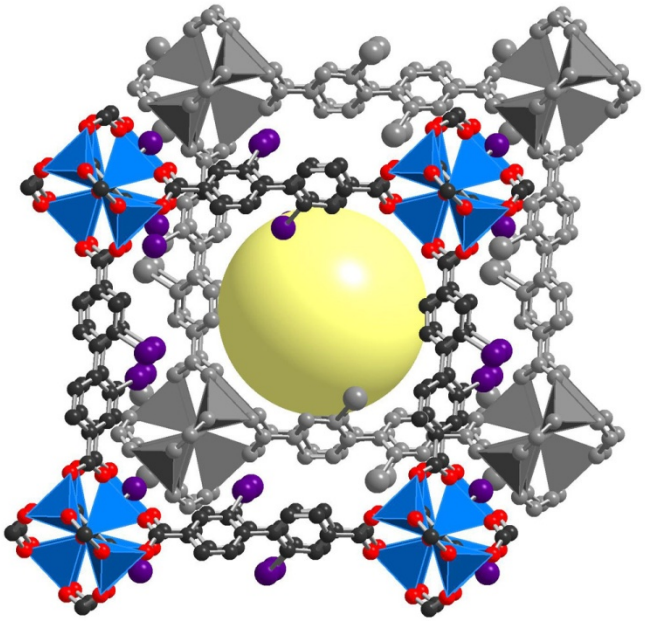


MOF-180
Trigonal
a = 46.04 Å
c = 37.22 Å
d = 0.25 g cm^{-3}

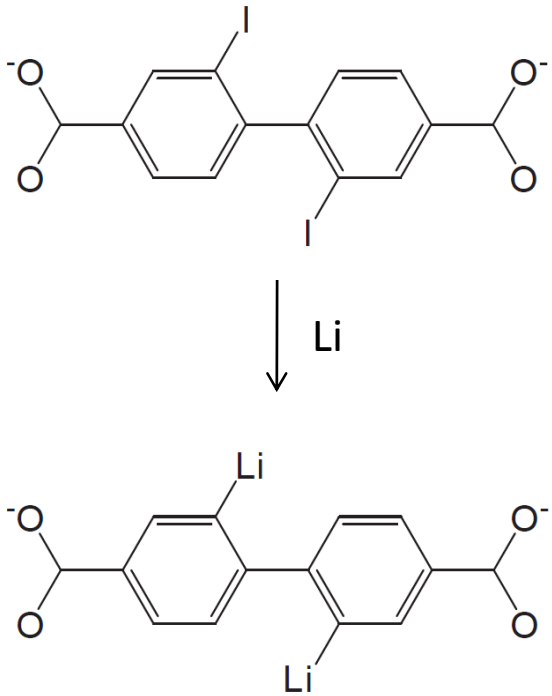
MOF-188
Cubic
a = 30.35 Å
d = 0.38 g cm^{-3}

Super critical CO_2 drying or freeze drying will be performed to survey optimized activation condition.

Approach 1: Post-synthesis modification of MOFs (e.g. potential halogen-lithium exchange)



IRMOF-19



IRMOF-19
d = 1.147 g cm^{-3}

Li-IRMOF-19
d = 0.676 g cm^{-3}

R-3*m*
a = 23.8130 Å, c = 31.0160 Å
V = 15231.6 Å^3

- MOF-5 type topology
- Doubly interpenetrated framework

If each Li in the link can capture 3 H_2 molecules, 4-5 wt% of H_2 uptake at RT is expected.

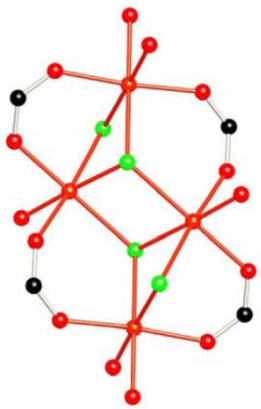
Approach 2: Use inorganic SBUs with transition metals Predicted to have higher adsorptive energy

Metal	Sc	Ti	V	Cr	Mn
E_b (kJ mol^{-1})	21.9	34.6	46.5	10.4	8.4
d (Å)	2.35	2.07	1.93	2.32	2.42

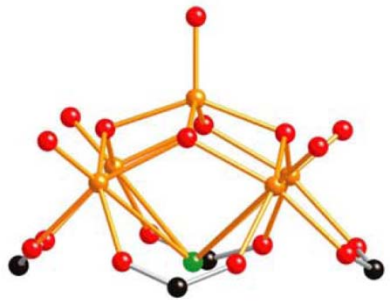
Sun *et al.*, *JACS* 2007

Reticular synthesis of novel materials combining all attributes deemed favorable to hydrogen storage

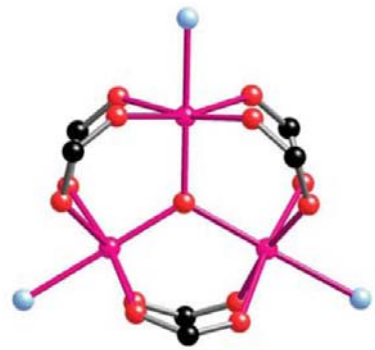
- Highly porous with little dead volume
- Smaller pore diameter (< 10 Å)
- Unsaturated metal surface
- Large density of strong binding sites



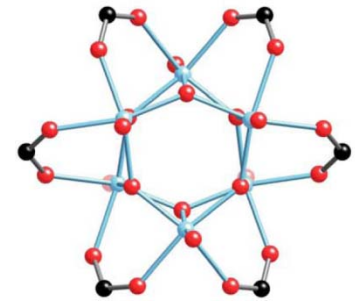
$V_4(CO_2)_4Cl_4(\mathbf{L})_6$



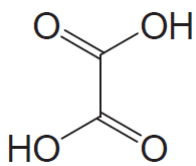
$V_5O_5(CO_2)_4Cl(\mathbf{L})_4$

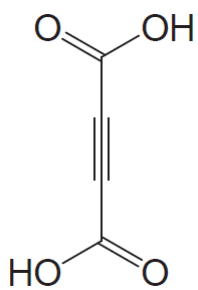


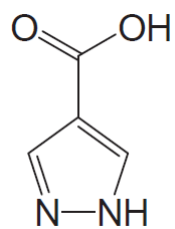
$M_3O(CO_2)_6(\mathbf{L})_3$
(M = V, Mn, Cr)

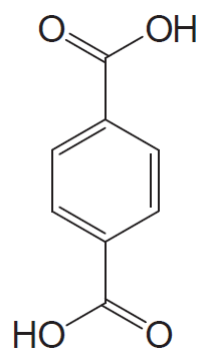


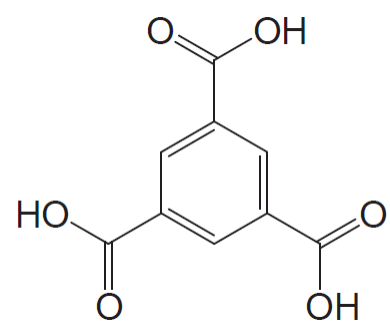
$Ti_6(CO_2)_6(\mathbf{L})_6$



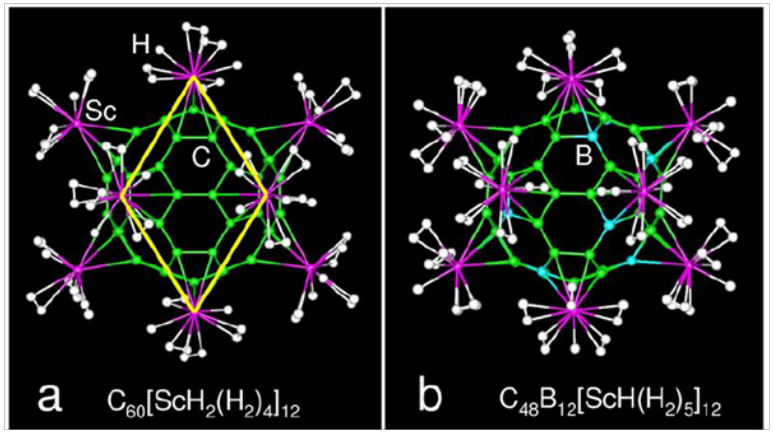








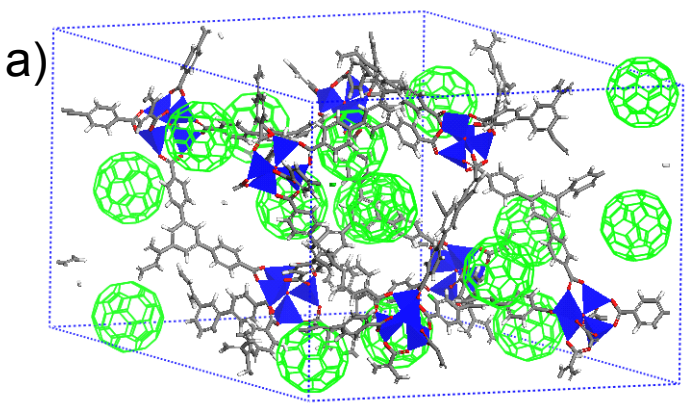
Approach 3: Impregnation of MOFs with organometallic buckyballs

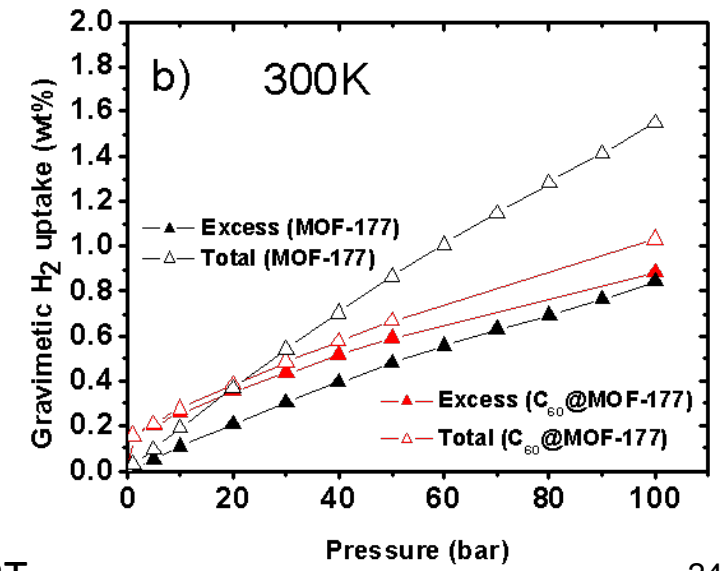


Zhao *et al.*, *PRL* **2005**, *94*, 155504.

MOF-177 or other high surface area MOFs can be hosts for organometallic C_{60}.

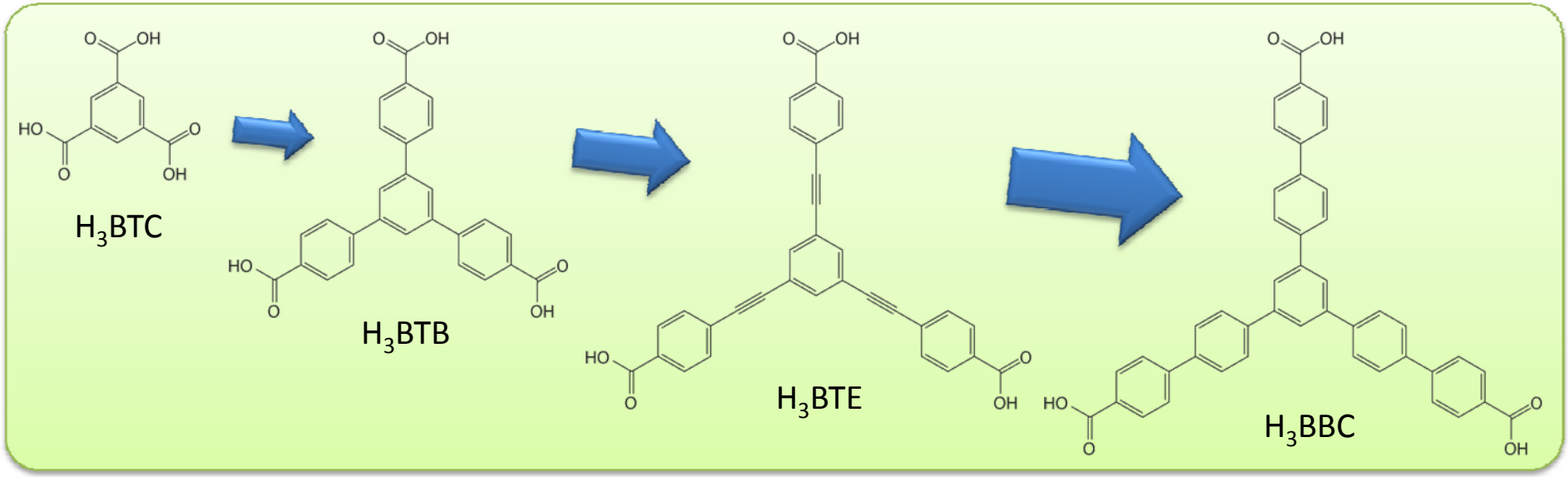
S. S. Han and W. Goddard (Caltech)

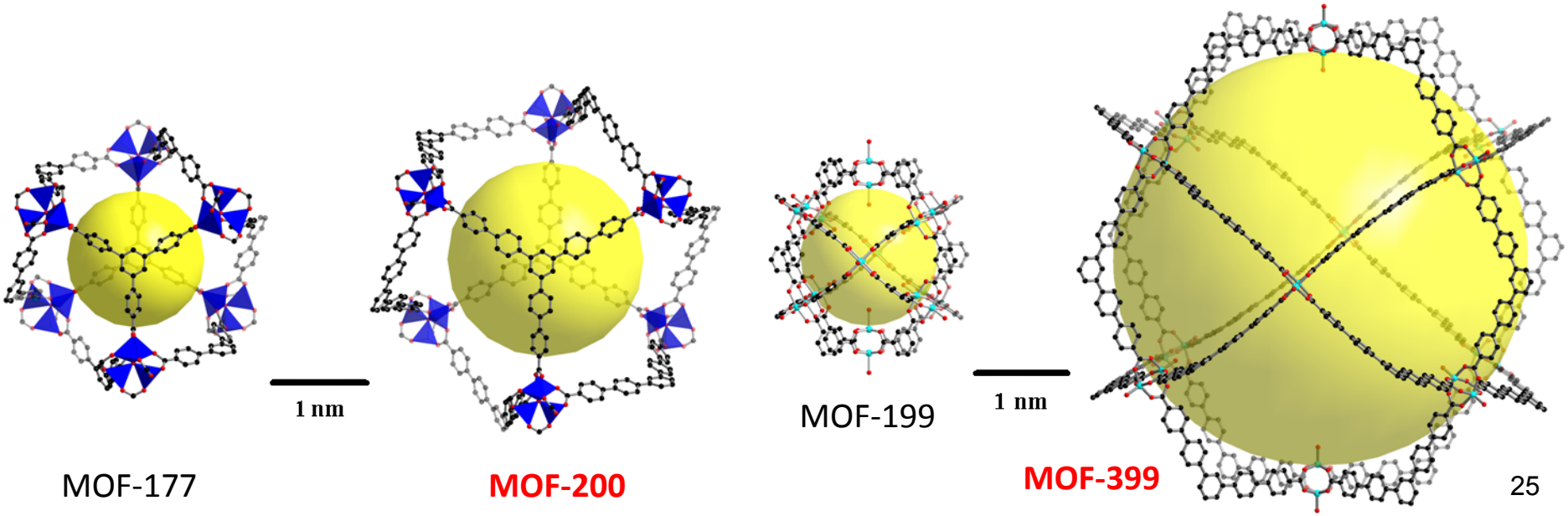




Structure of C_{60}-impregnated MOF-177 (a) and its predicted H_2 adsorption isotherms at 300 K (b).
C_{60} is not enough to improve H_2 uptake capacity at RT.

Approach 4: Isoreticular expansion





Summary

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

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 various functionalities
- Post synthesis modification of MOFs for metal impregnation
- High throughput synthesis for ultra-high surface area MOFs

Technology transfer/collaborations: Active relationship with collaboration partners and BASF. Began collaboration with Goddard theory group.

Proposed future research:

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

Current Group Members