Hydrogen storage in Metal-Organic Frameworks

Omar M. Yaghi

Department of Chemistry and Biochemistry
California NanoSystems Institute
University of California-Los Angeles

May 16-19, 2006

No confidential information in this presentation

Project ID #:ST22

Overview

Timeline
Project start date: 5/1/2005
Project end date: 4/30/2009

Budget
Total project funding: DOE $1.6 M
UCLA: $0.40 M
Funding received FY 05: $112 K
Funding for FY 06: 50 K

Barriers addressed
Technical barriers addressed:
Improved volumetric density of hydrogen uptake
Hydrogen capacity and reversibility at 77K
Efficiency of synthesis and uptake recovery

Technical targets by 2010:
Gravimetric capacity: 6.5%; Volume capacity: 4.5%; operating temperature: -30° to 45°C

Partners (depends on funding)
Juergen Eckert (UCSB)
Joe Hupp (NW)
Randy Snurr (NW)

Objectives

Develop strategies for achieving MOFs that have increased uptake at higher temperature

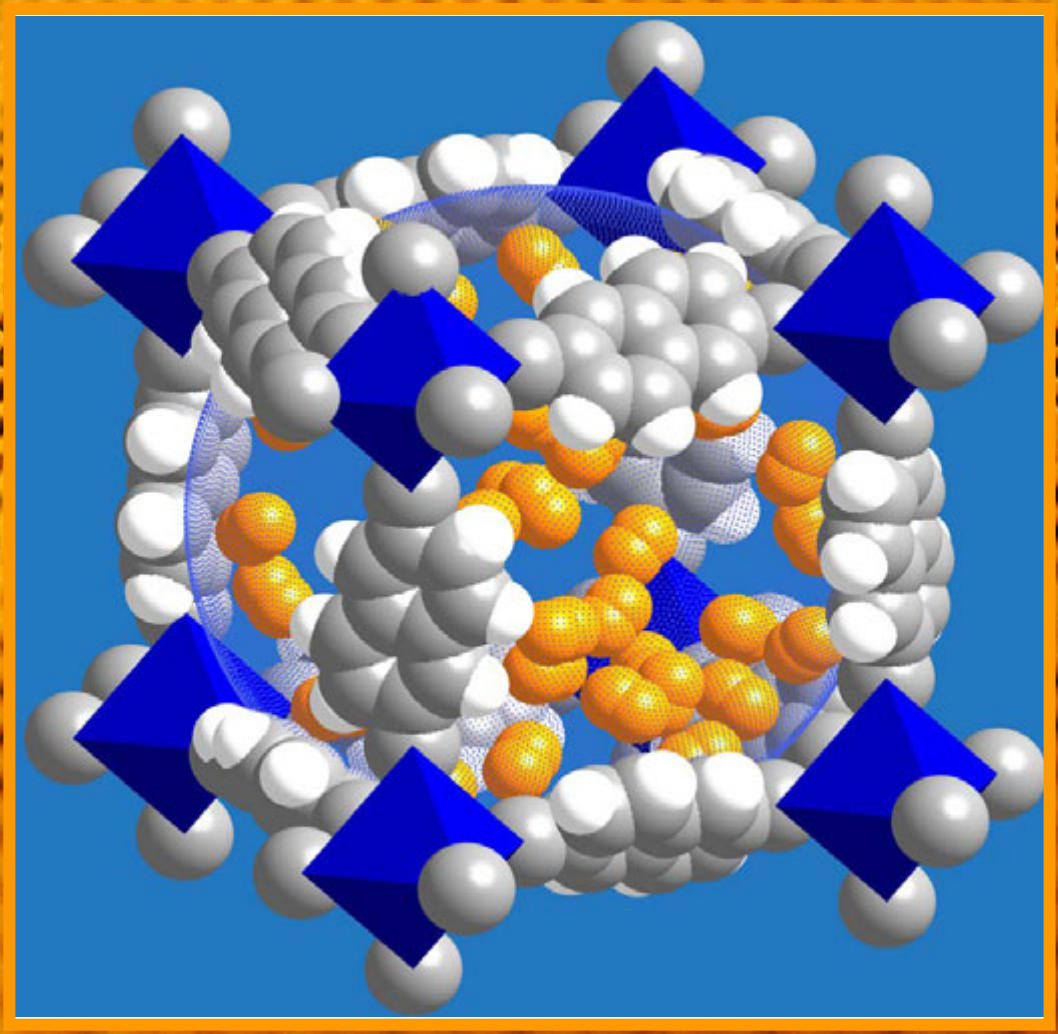
1. MOFs with high surface areas that combine molecular features for enhancing the adsorption energy of hydrogen to MOFs
   - Utilize new concepts for increased surface areas
   - Implement strategies for higher adsorption energy
   - Develop strategies for increased hydrogen density in MOFs

2. Employ MOFs in hydrogen storage systems
   - Scale up of favored MOFs
   - Transfer of samples to DOE for independent verification of data

Design and Approach

1. Introduction of metal-open sites within the pores
2. Impregnation using metal particles and molecular metal-oxide
3. Prepare and test composite MOF/polymer blends
4. Prepare and test mixtures of MOF materials
5. Introduction of light metals in the frameworks

Compacting Hydrogen in MOFs for storage and transport



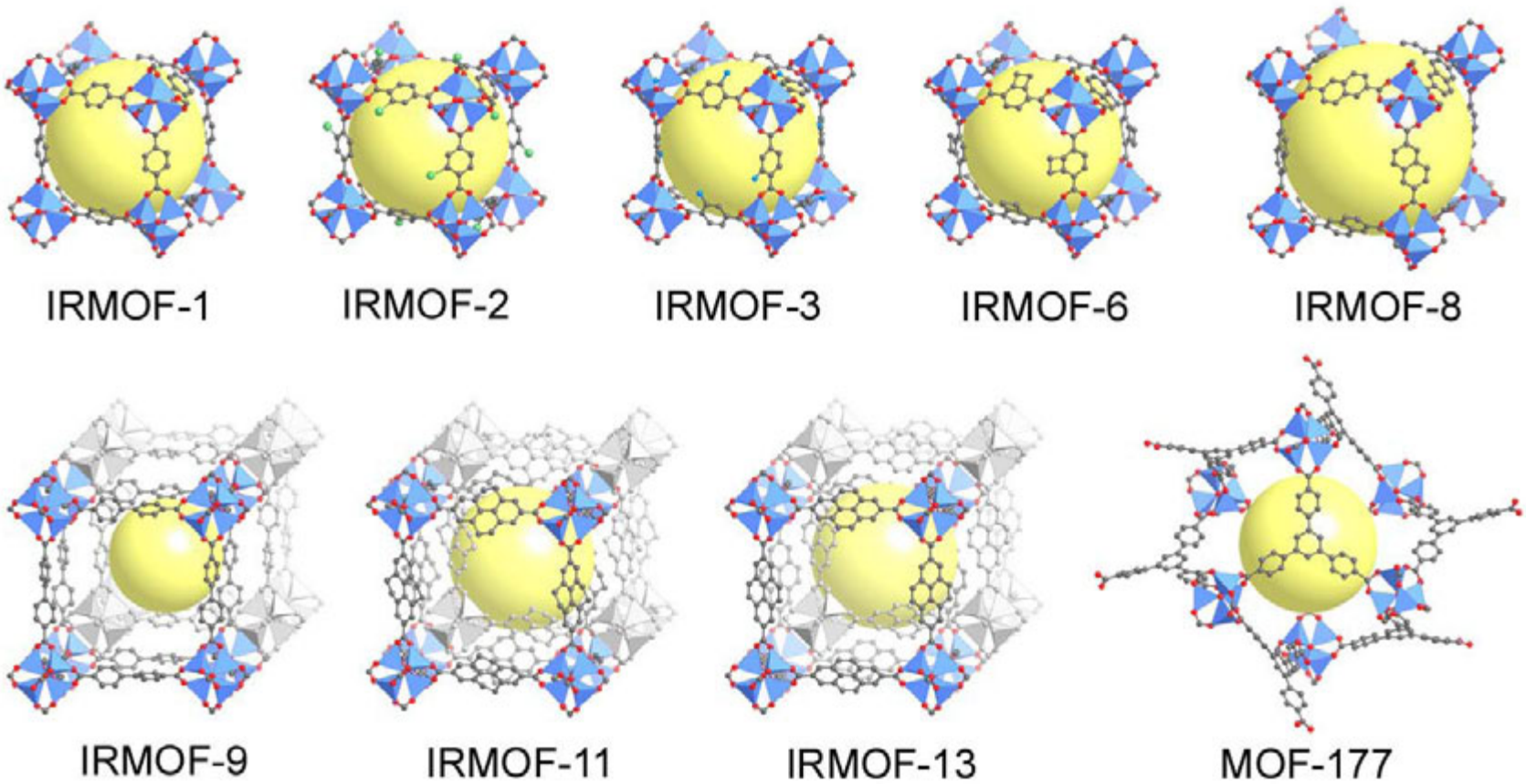
Hydrogen Sorption in MOFs

- Low temperature/low pressure adsorption
- Identification of adsorption sites, and their steric and electronic nature
- Low temperature/high pressure adsorption
- Relationship of uptake to porosity

MOFs based on $Zn_4O(O_2C\text{-})_6$

Isoreticular Metal-Organic Frameworks (IRMOFs)

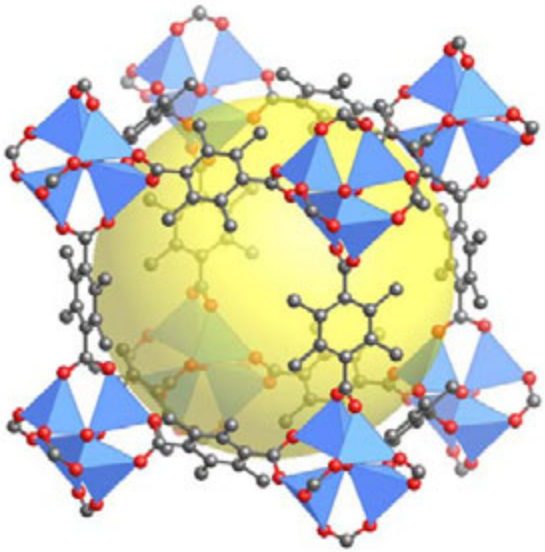
a series of materials having the same underlying topology and (typically) constructed from the same secondary building units



M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi, *Science,* **2002,** *295*, 469.

H. K. Chae, D. Y. Siberio-Perez, J. Kim, Y-B. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe, O.M. Yaghi, *Nature*, **2004**, *427*, 523.

MOFs based on $Zn_4O(O_2C\text{-})_6$: new IRMOF-18



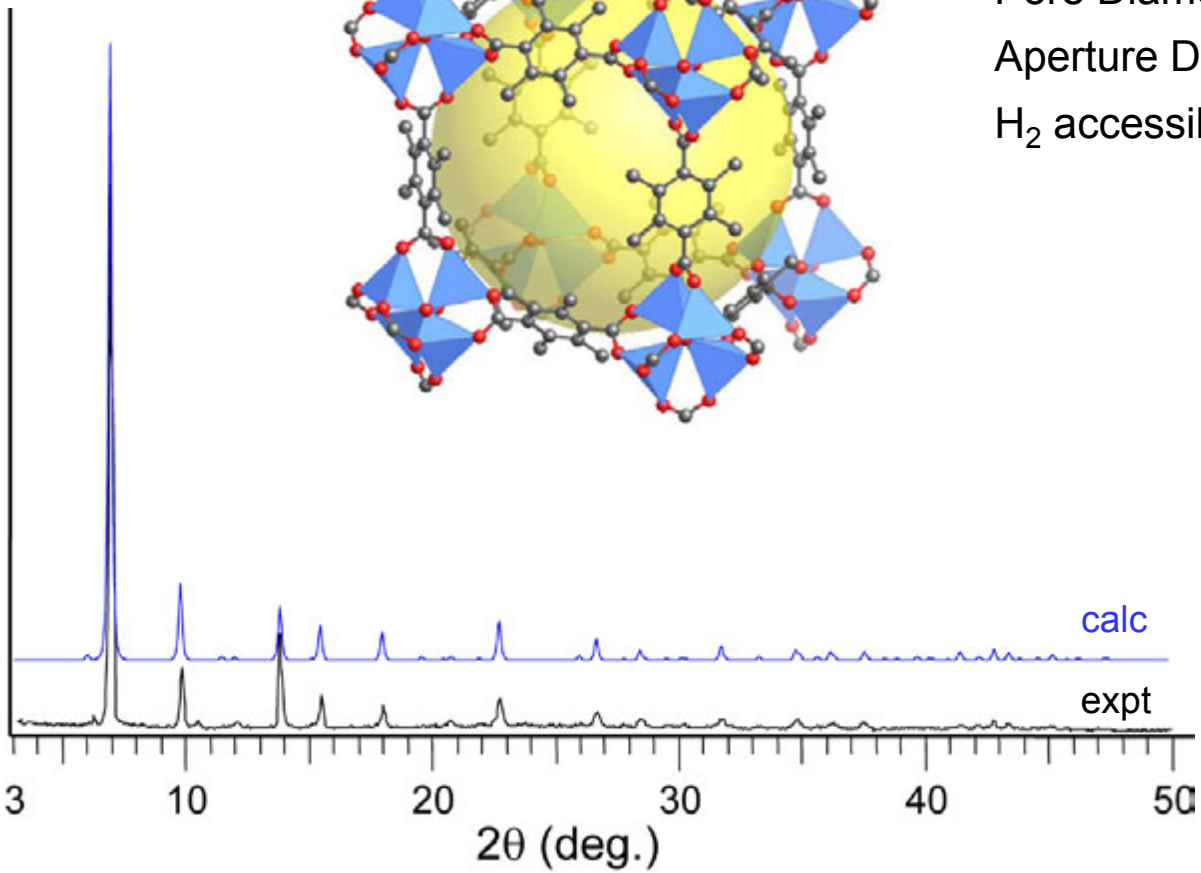
Empirical Formula: $C_{36}H_{36}O_{13}Zn_4$

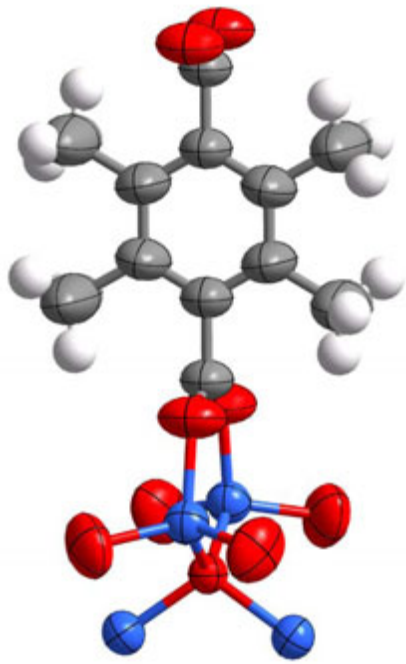
Crystal Data: $Fm\bar{3}m$, a = 25.6135(7) Å

Pore Diameters: 13.8, 9.2 Å

Aperture Diameter: 5.4 Å

H_2 accessible volume: 44 %





J. L. C. Rowsell, A. R. Millward, K. S. Park, O.M. Yaghi, *JACS,* **2004,** *126*, 5666.

MOFs based on $Zn_4O(O_2C\text{-})_6$: new IRMOF-20

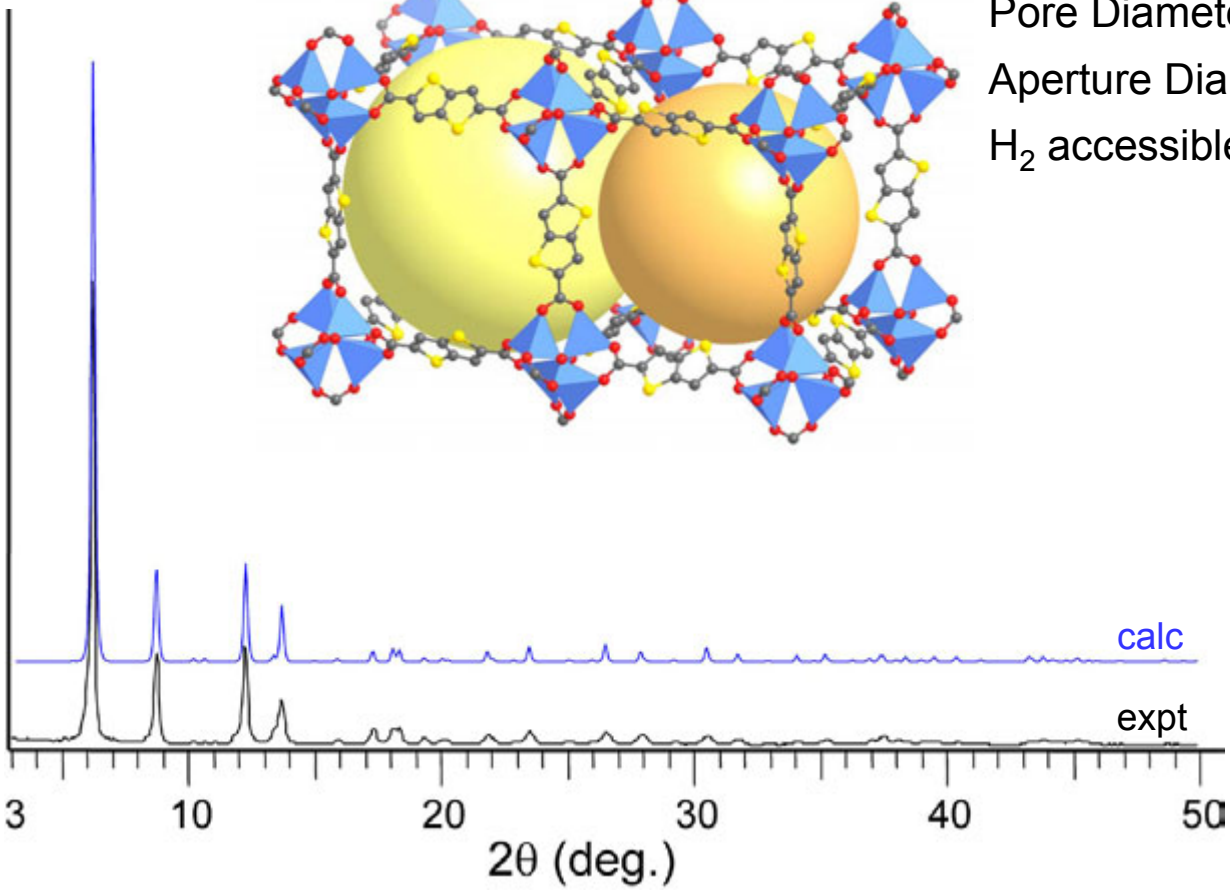
Empirical Formula: $C_{24}H_6O_{13}S_6Zn_4$

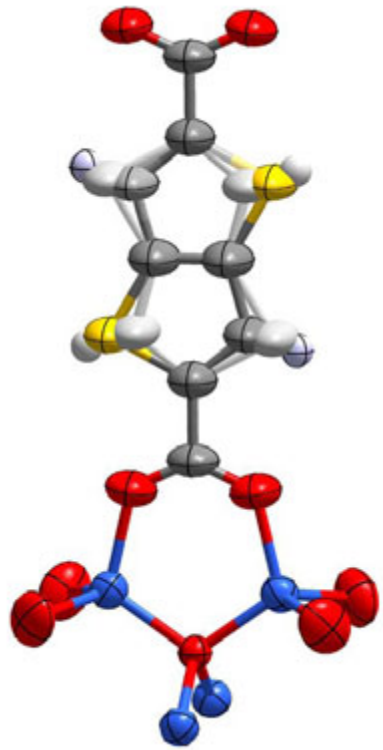
Crystal Data: $Fm\bar{3}m$, a = 29.186(2) Å

Pore Diameters: 17.2, 14.3 Å

Aperture Diameter: 9.6 Å

H_2 accessible volume: 66 %





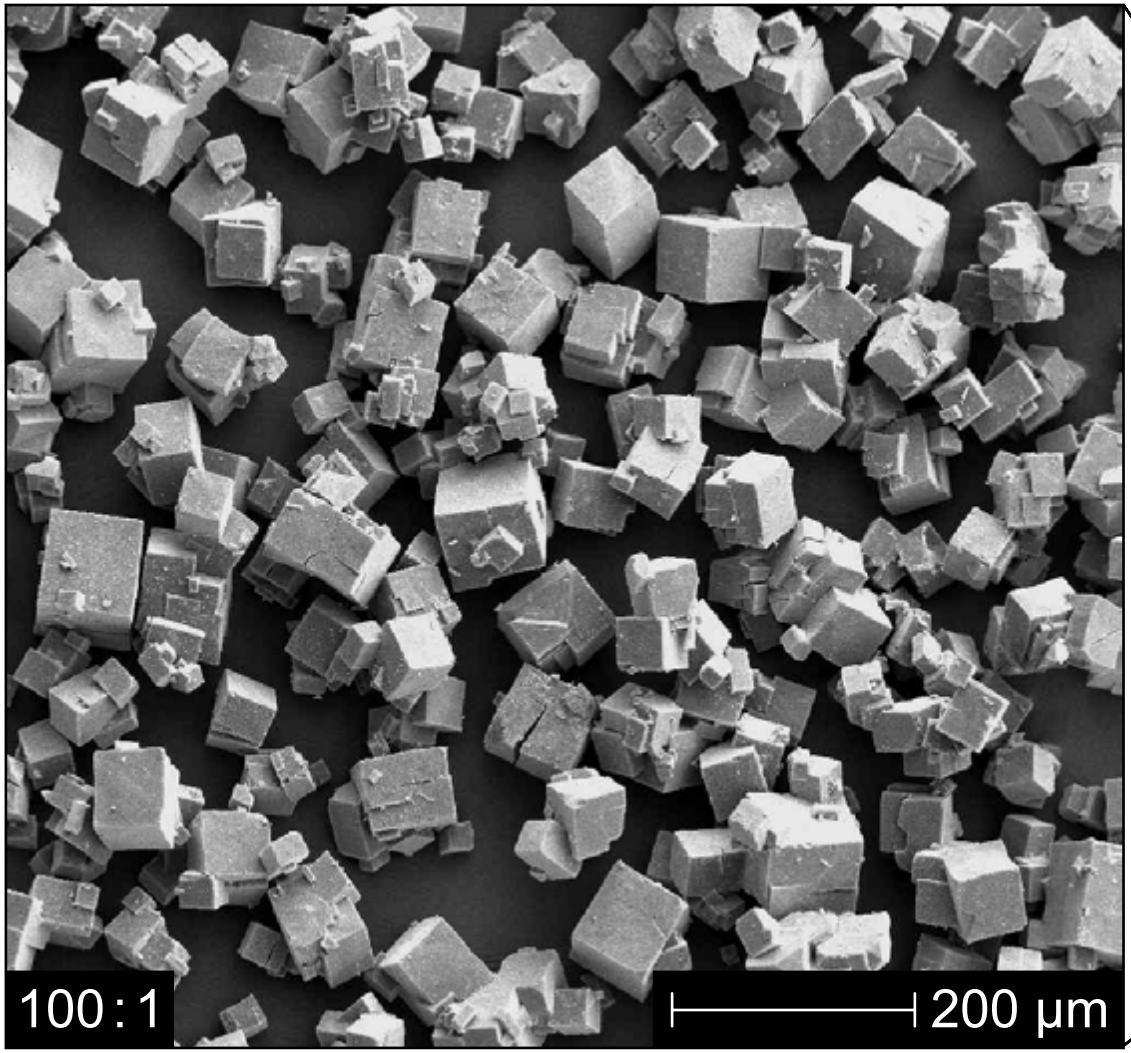
MOFs based on $Zn_4O(O_2C\text{-})_6$: Synthesis

$$4\ Zn^{2+} + 3\ H_2L + H_2O \xrightarrow[\text{amide solvent}]{\Delta} Zn_4O(L)_3\cdot(solv)_x$$

Material	$[Zn^{2+}]$ (m*M*)	[L] (m*M*)	M / L	solvent	conditions
IRMOF-1	100	45	2.2	DEF	100°C, 18 h
IRMOF-2	60	15	4	DEF	100°C, 40 h
IRMOF-3	100	40	2.5	DEF	100°C, 18 h
IRMOF-6	100	50	2	DEF	100°C, 18 h
IRMOF-9	70	12	5.8	DMF	100°C, 18 h
IRMOF-11	100	17	5.9	DEF	100°C, 18 h
IRMOF-13	25	3.5	7.1	DMF	70°C, 40 h
MOF-177	70	7	10	DMF	70°C, 40 h

- optimized conditions determined empirically at 20 mL scale, increased to 1 L
- yields typically 70 -100%

Manufacturing process for MOF-5

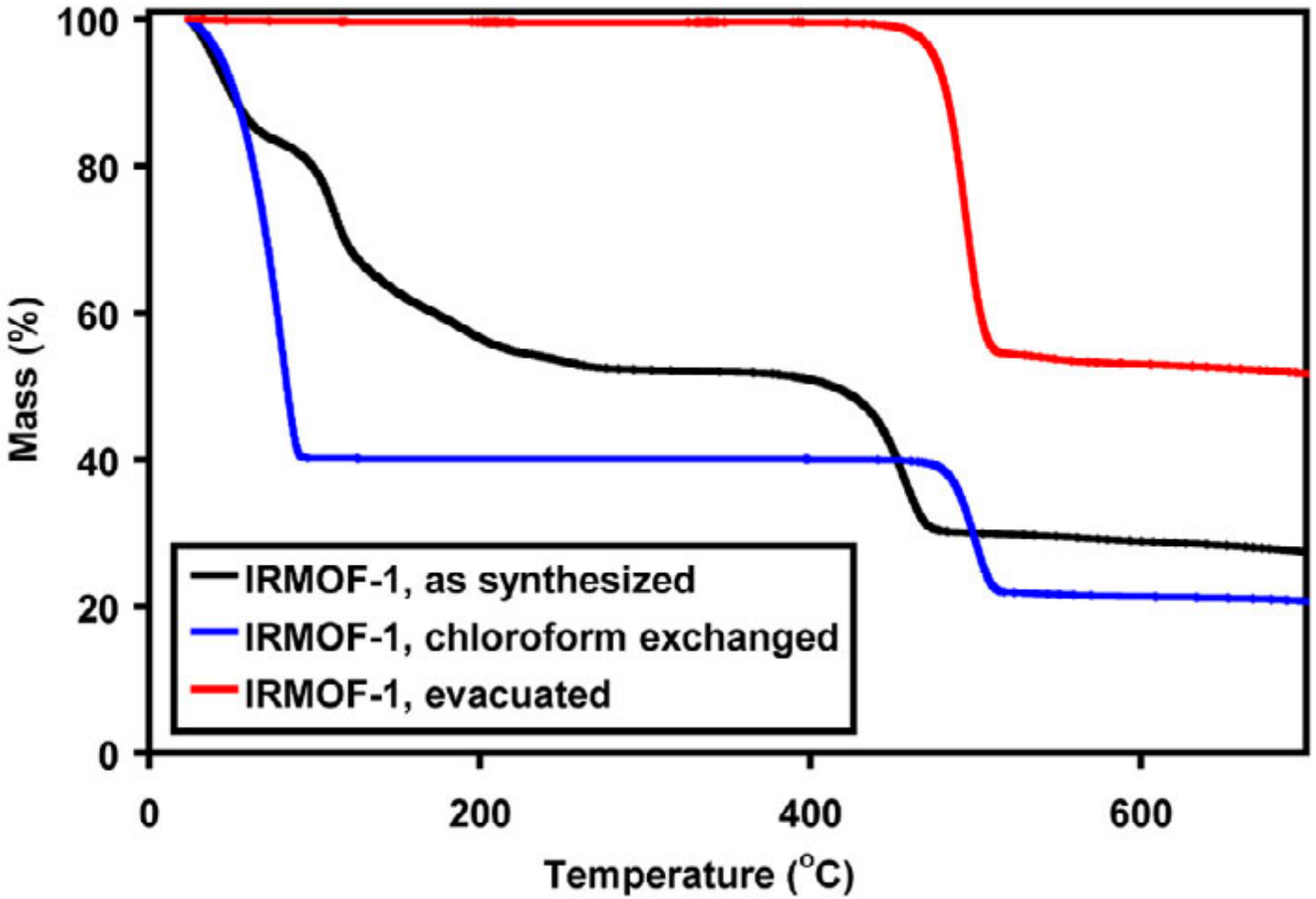


H_2-Storage in MOFs Pilot Production IRMOF-8 (m^3-Scale)**(BASF, Dr. U. Müller)**

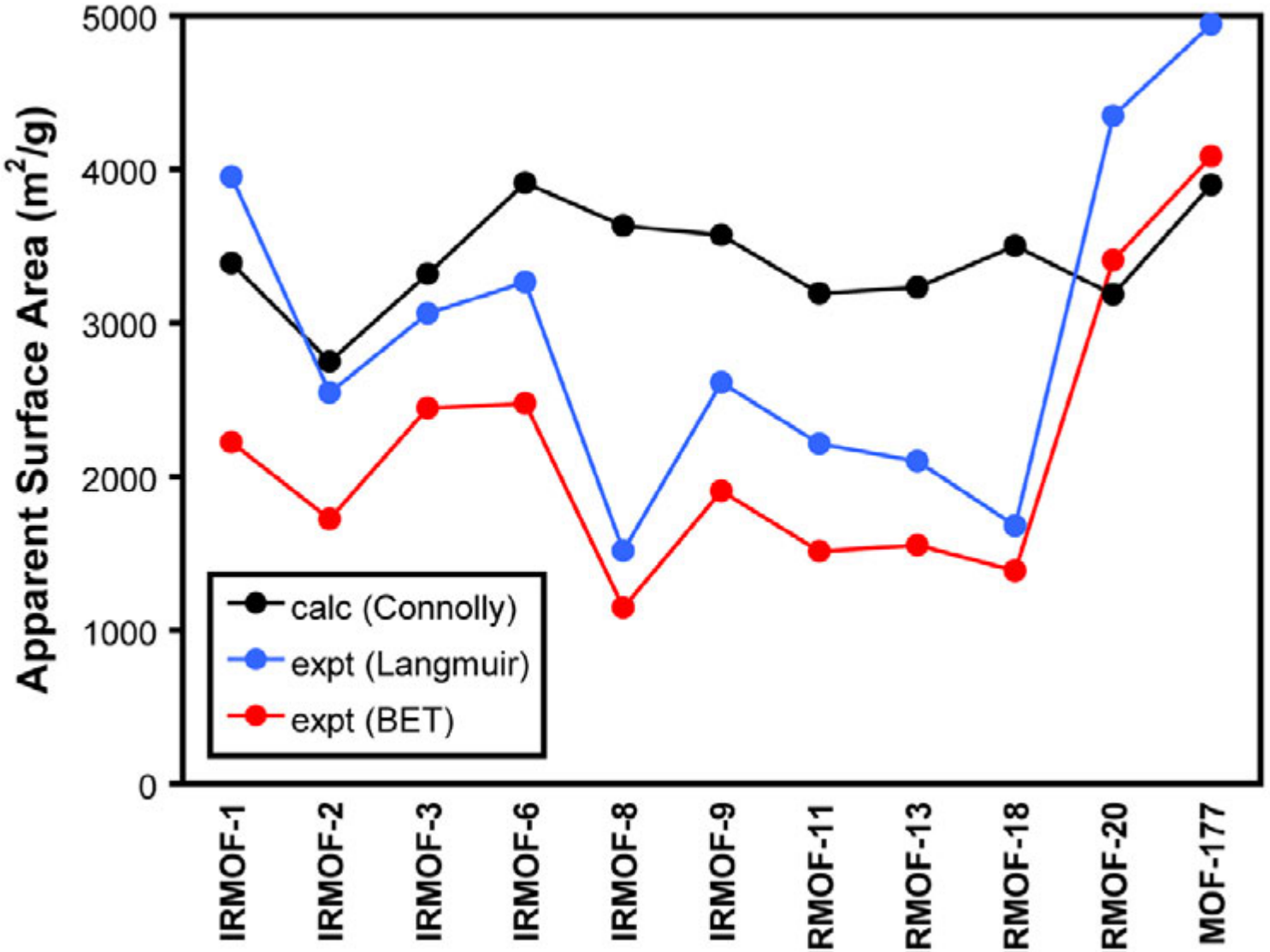
Semi-technical scale using ´state-of-art´manufacturing methods

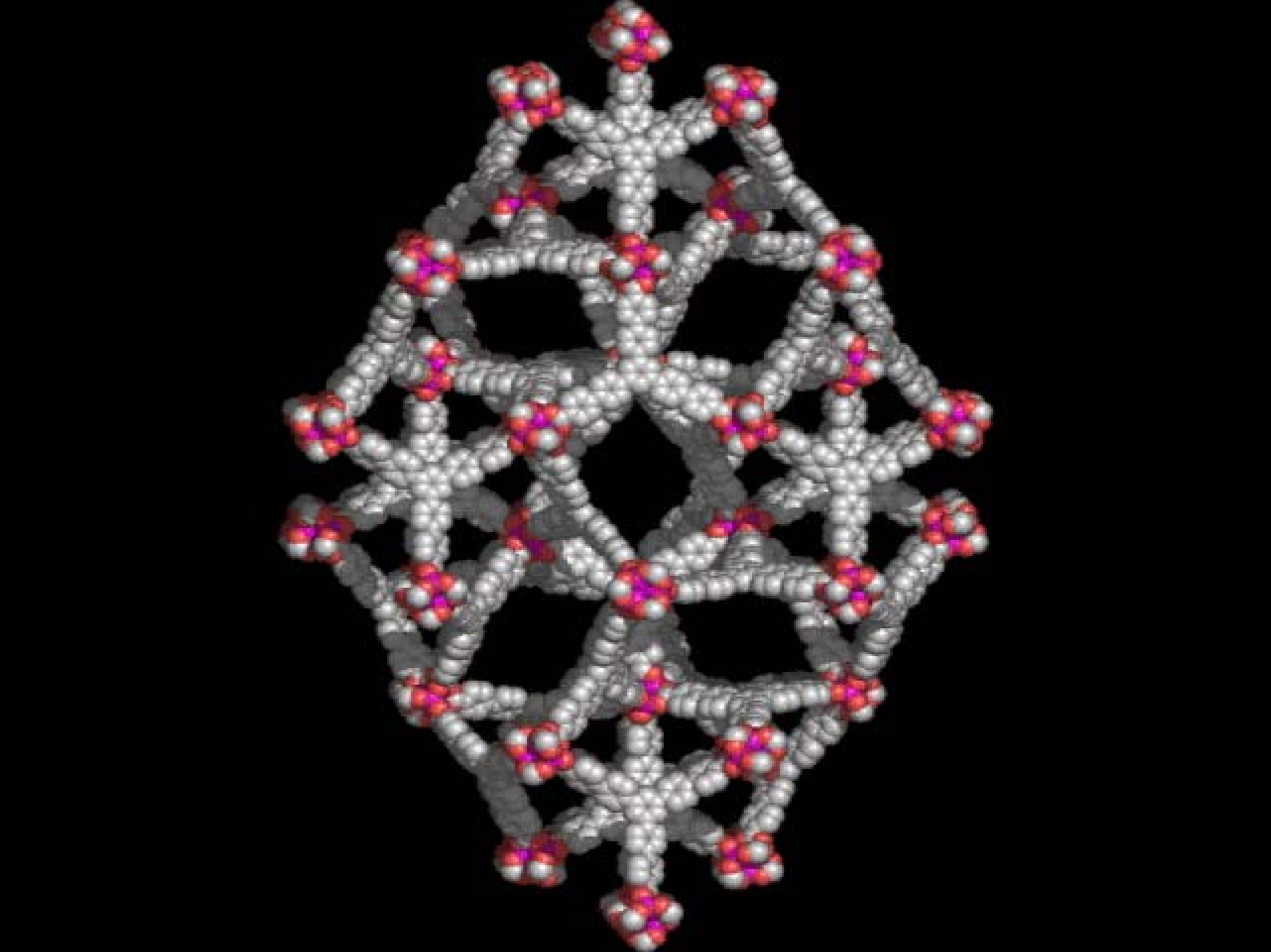
MOFs based on $Zn_4O(O_2C\text{-})_6$: Activation

$$Zn_4O(L)_3\cdot(solv)_x \xrightarrow[CHCl_3]{25^oC,\ 48\ hr} \xrightarrow{\text{evacuate}} Zn_4O(L)_3$$

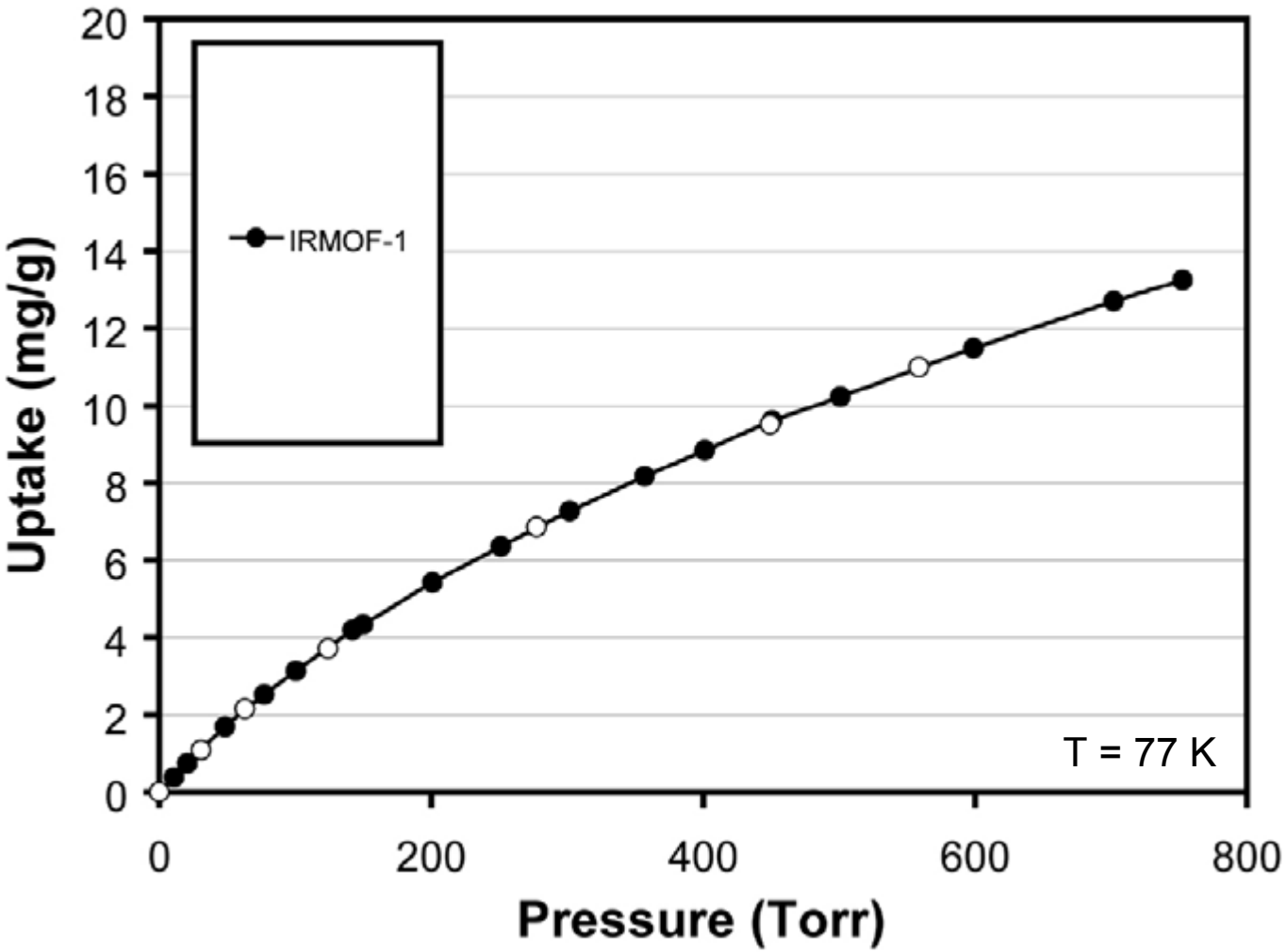


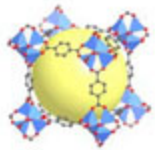
MOFs based on $Zn_4O(O_2C\text{-})_6$: N_2 Adsorption



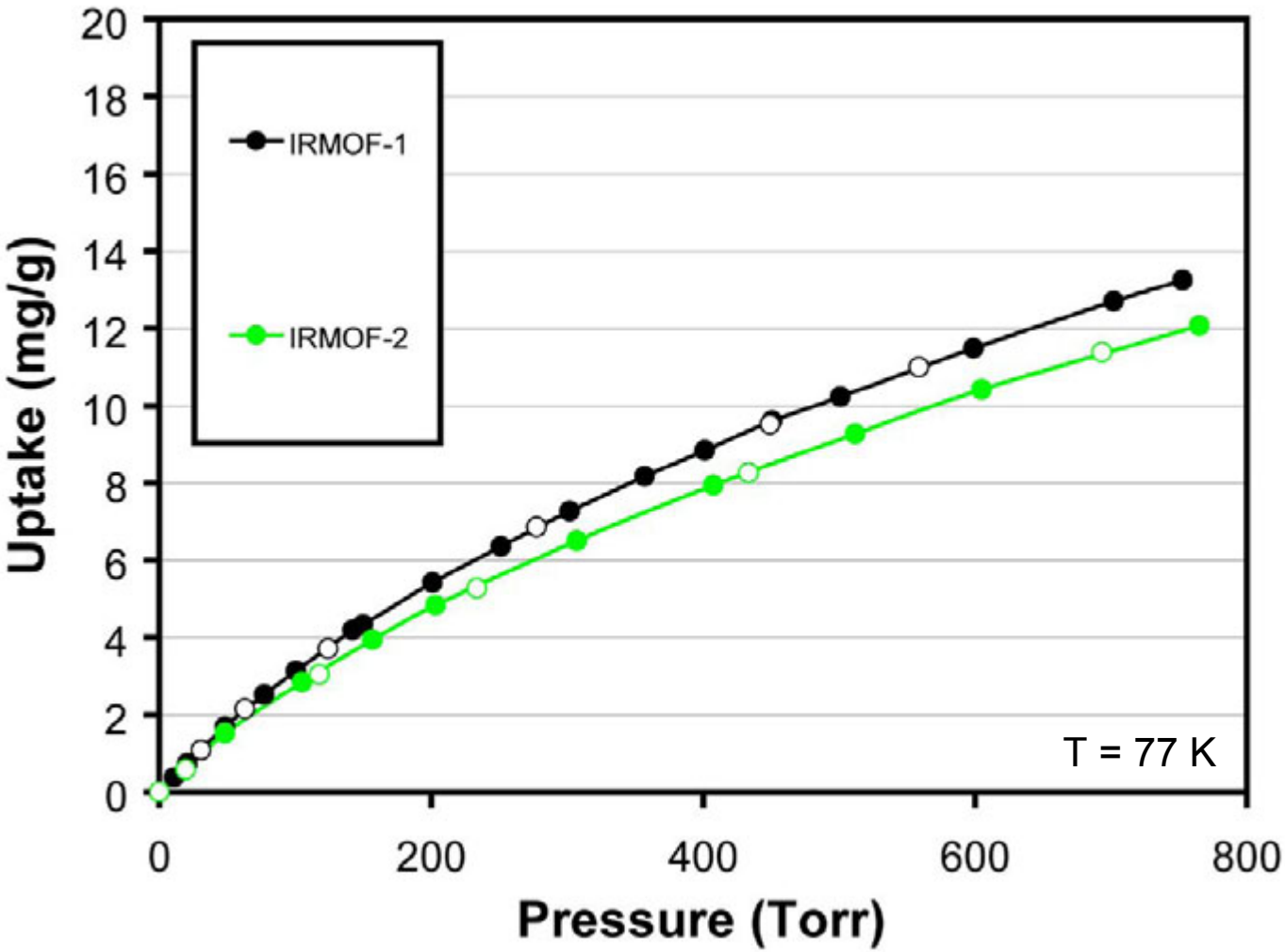


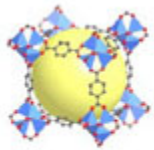
H_2 Adsorption in Non-Catenated MOFs

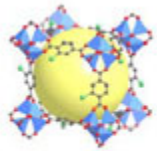




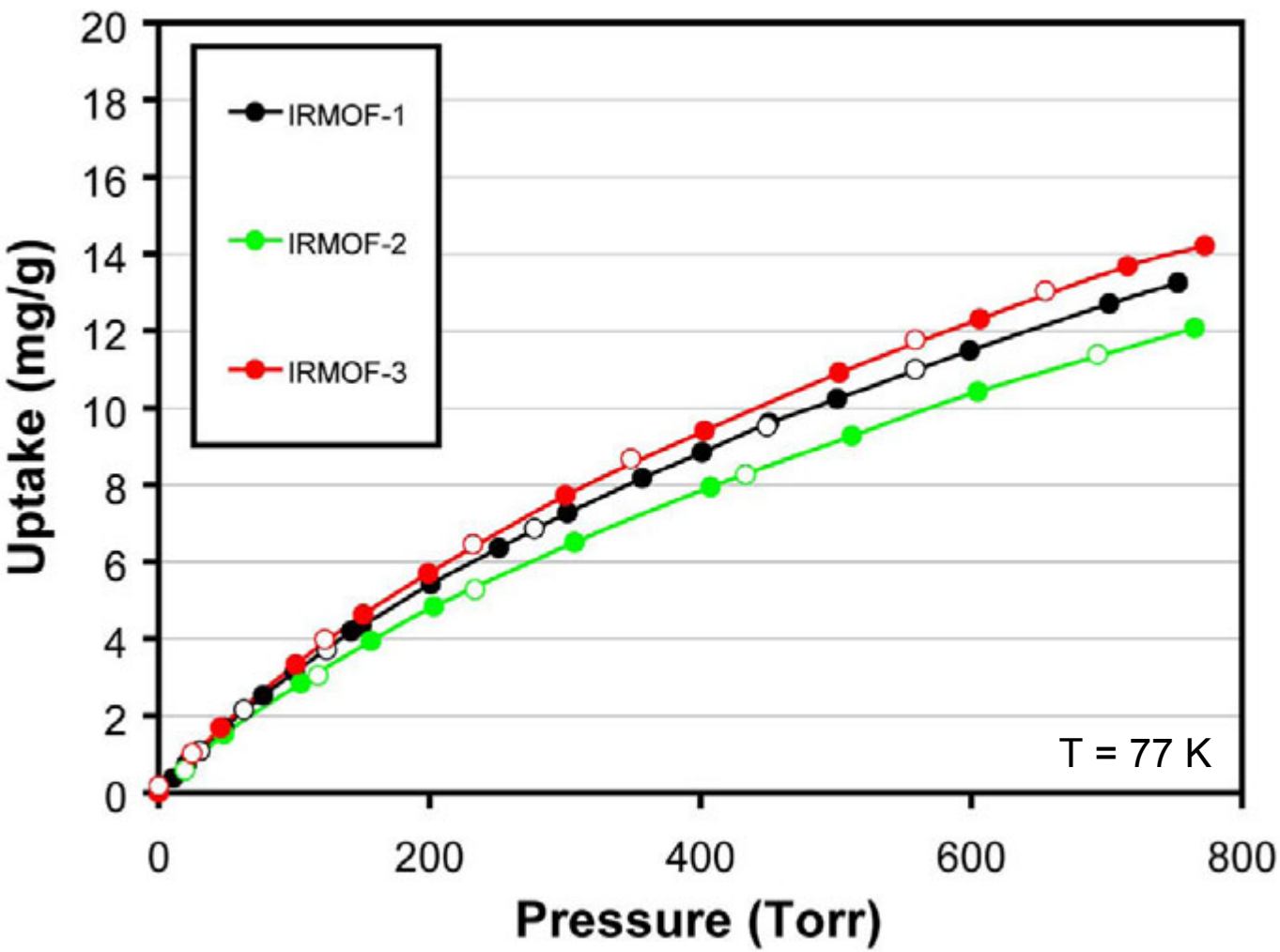
H_2 Adsorption in Non-Catenated MOFs

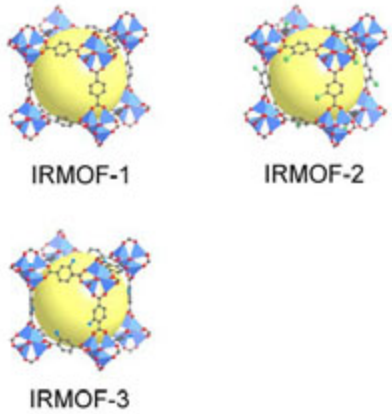



IRMOF-1

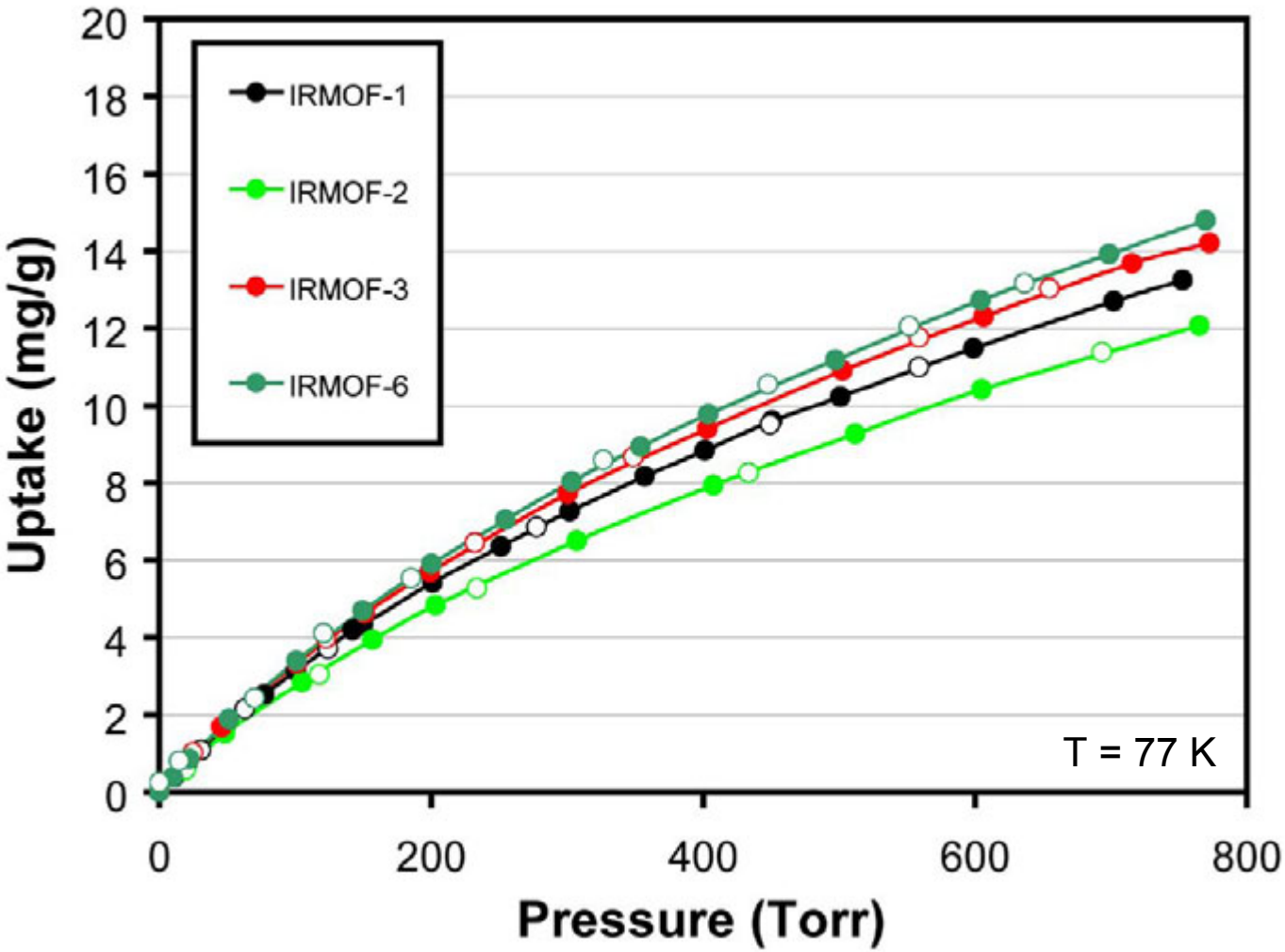

IRMOF-2

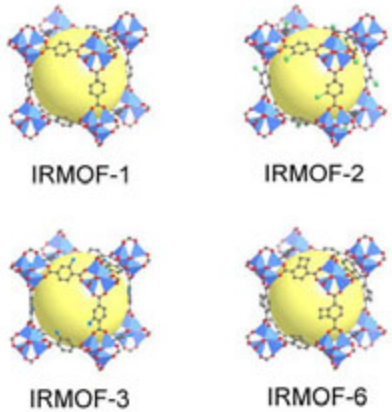
H_2 Adsorption in Non-Catenated MOFs



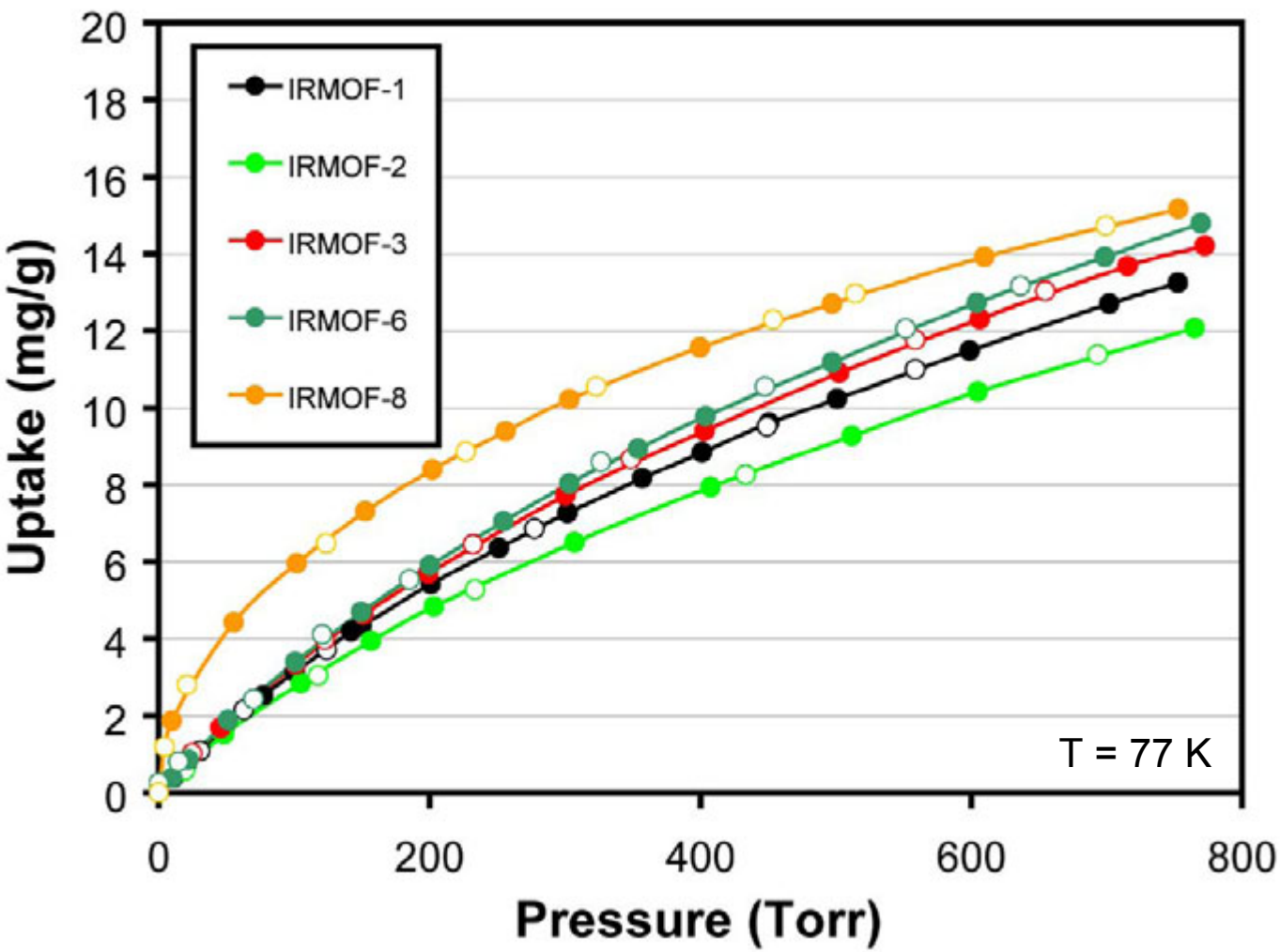


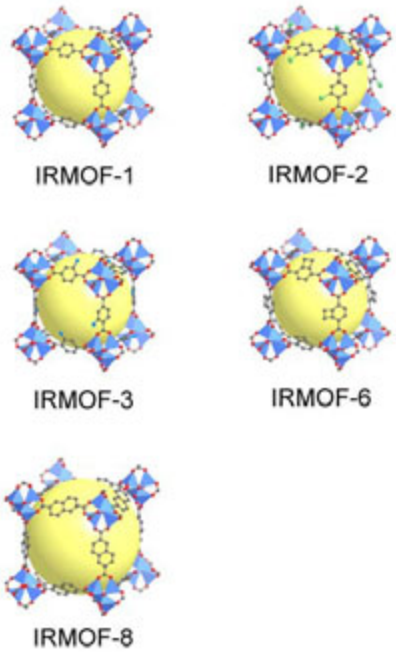
H_2 Adsorption in Non-Catenated MOFs



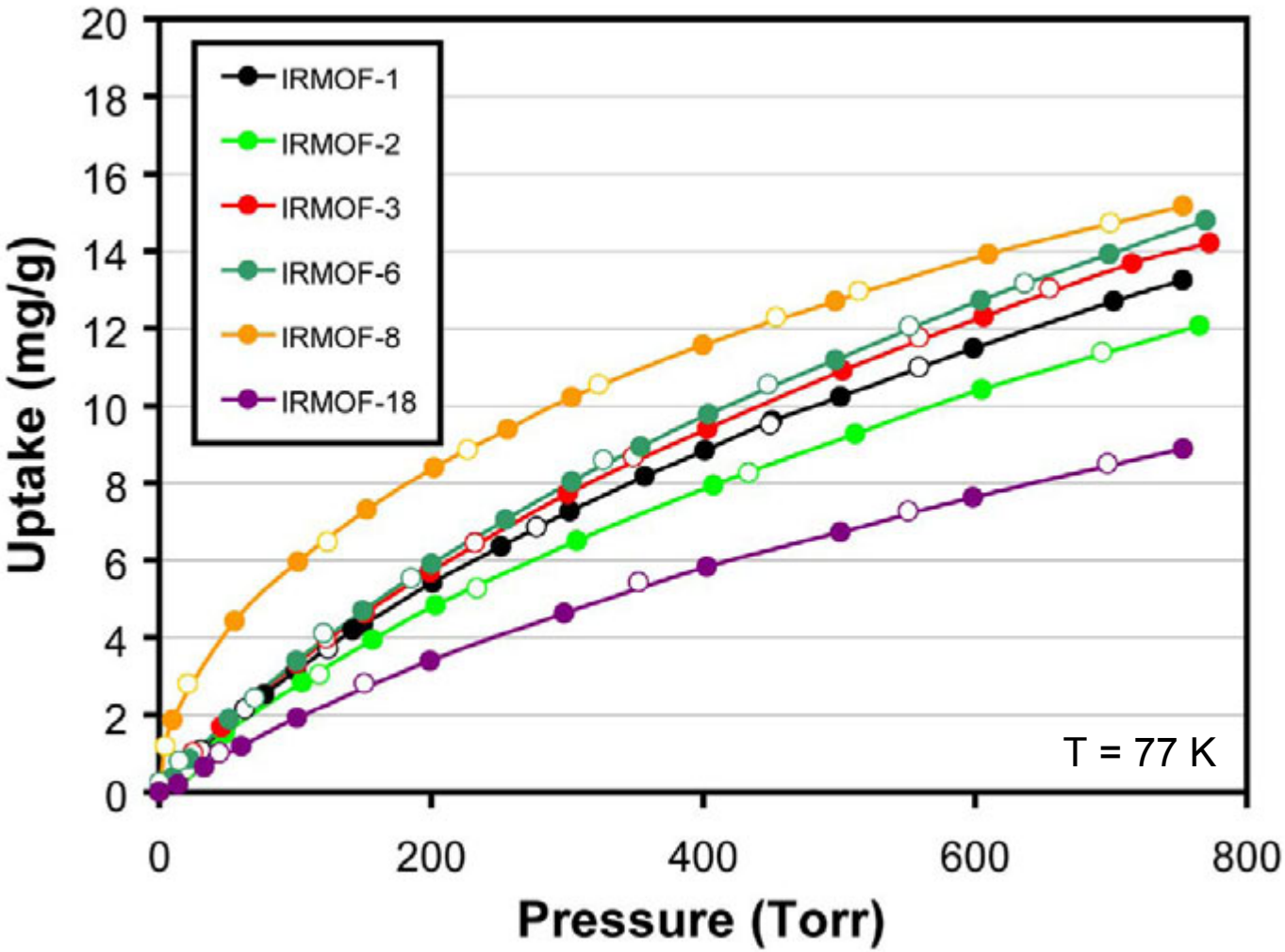


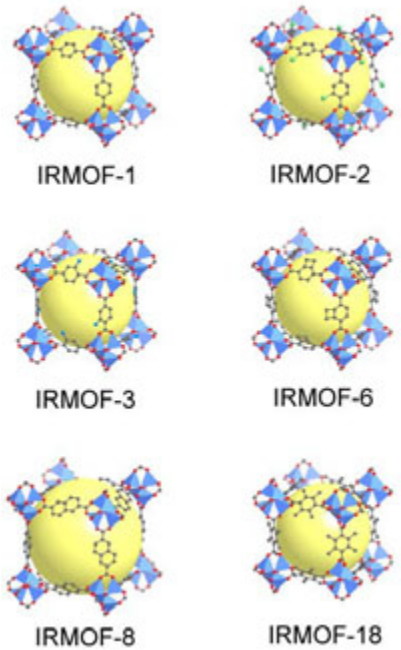
H_2 Adsorption in Non-Catenated MOFs



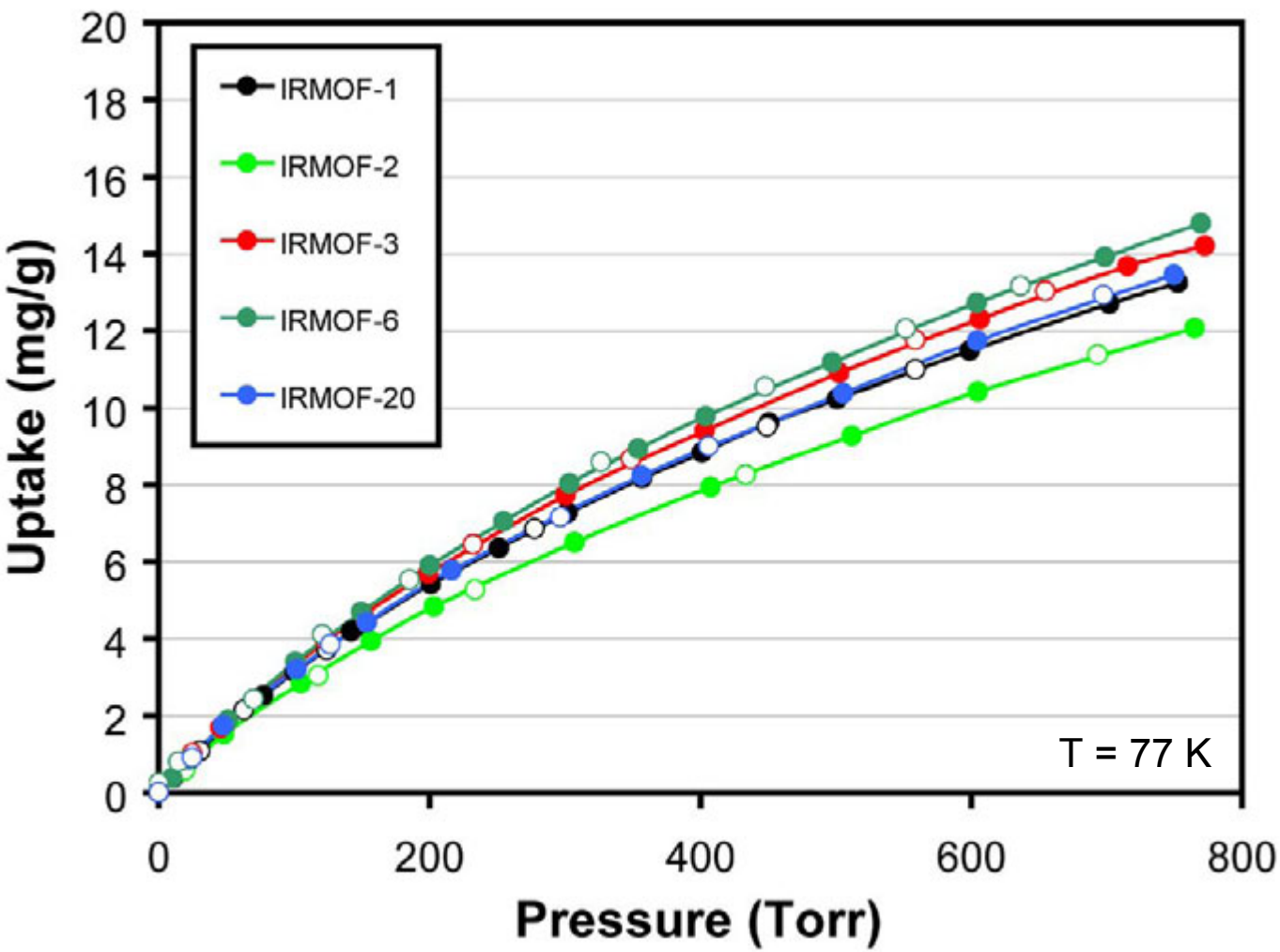


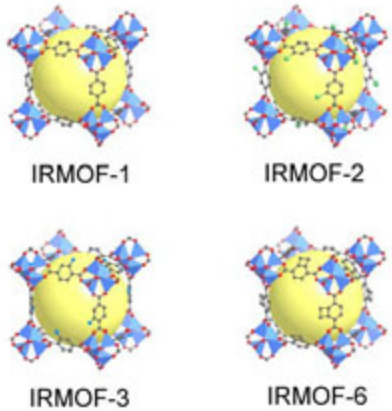
H_2 Adsorption in Non-Catenated MOFs

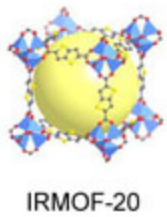




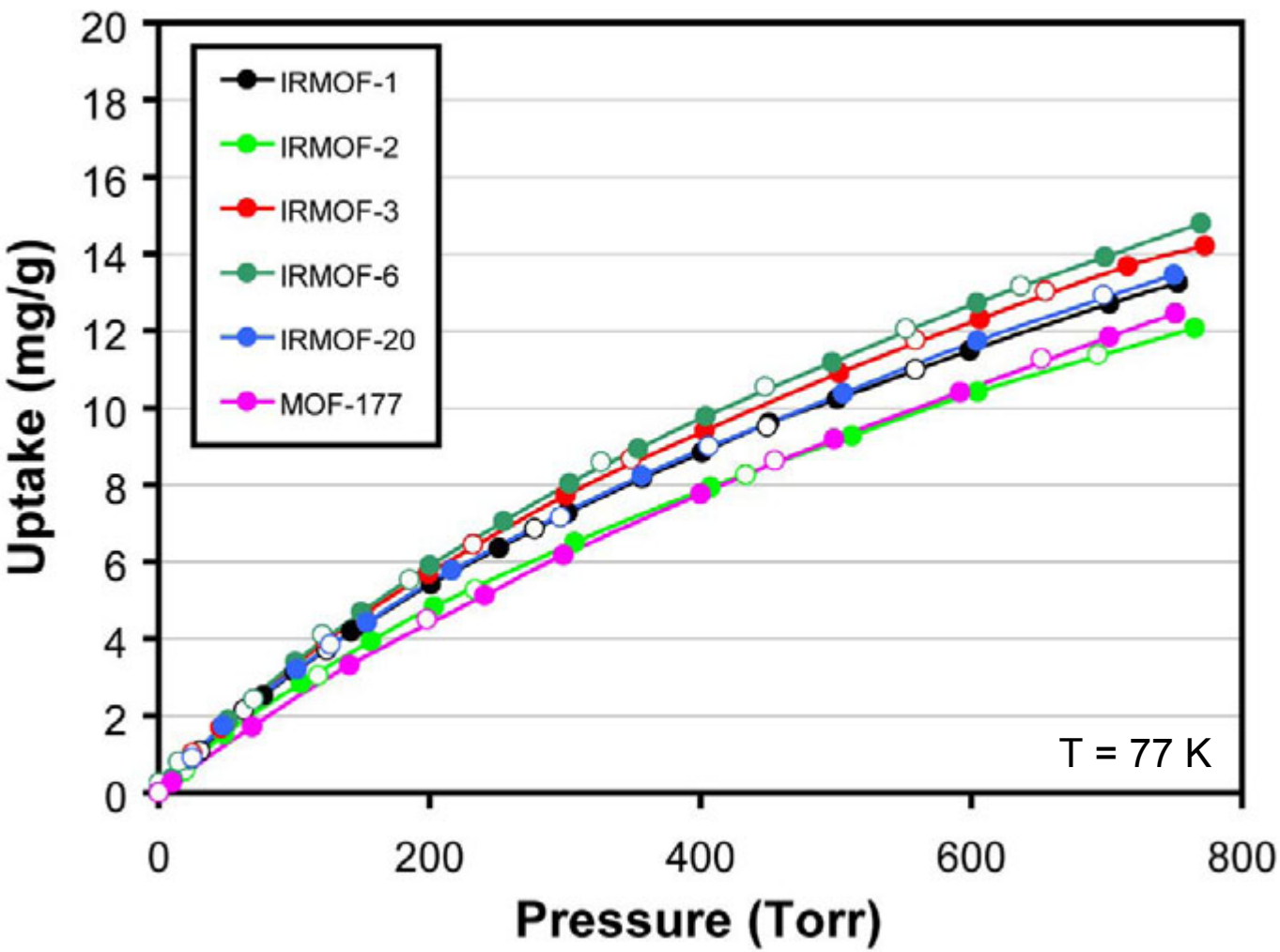
H_2 Adsorption in Non-Catenated MOFs

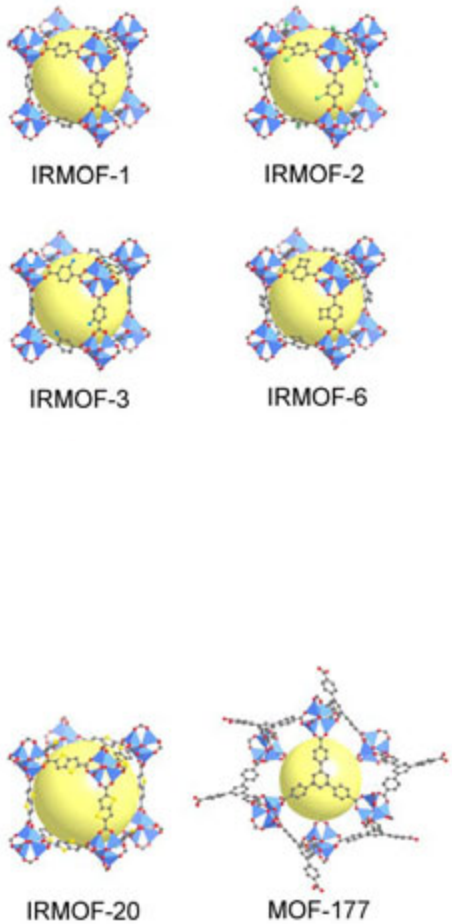




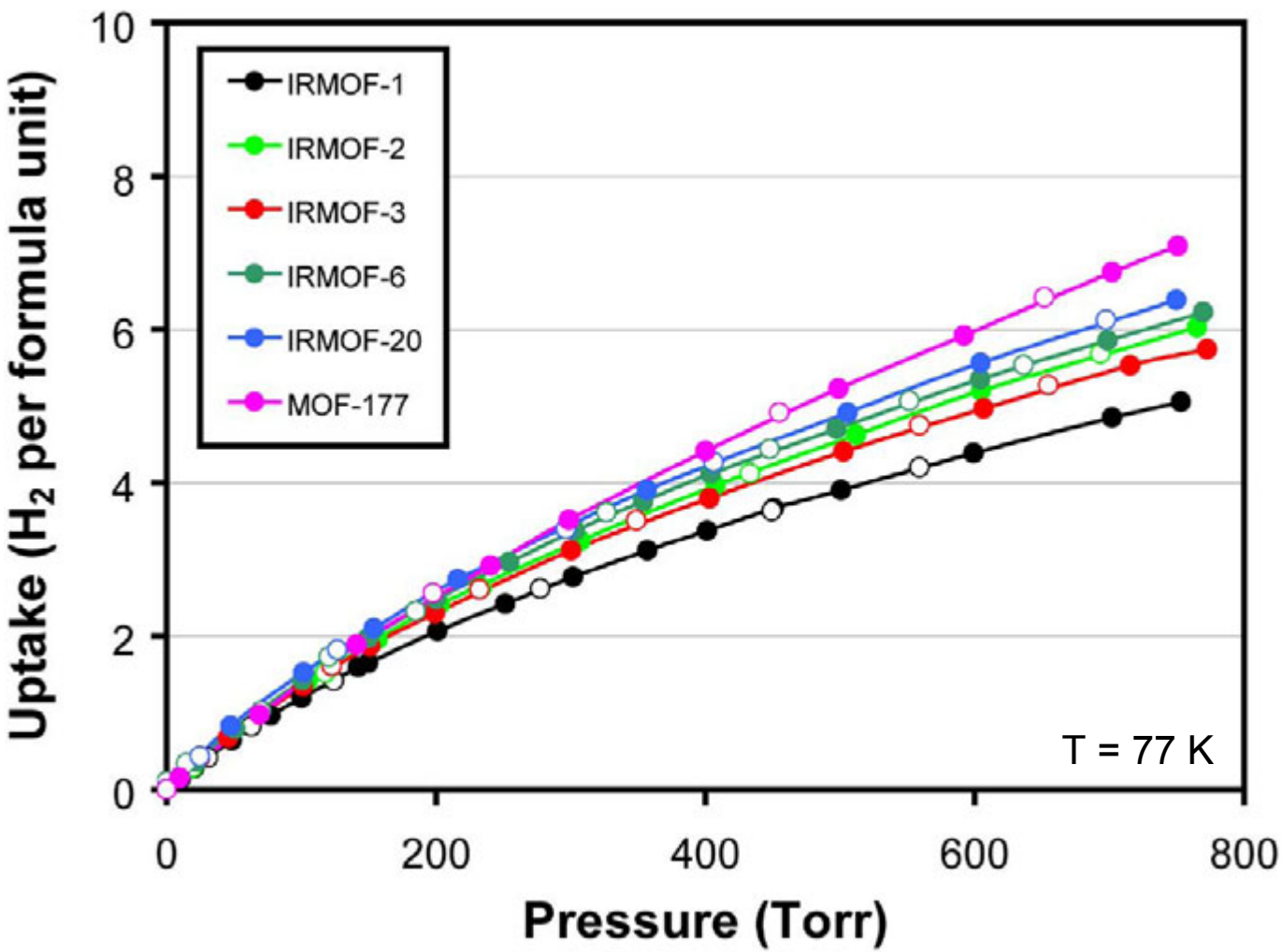


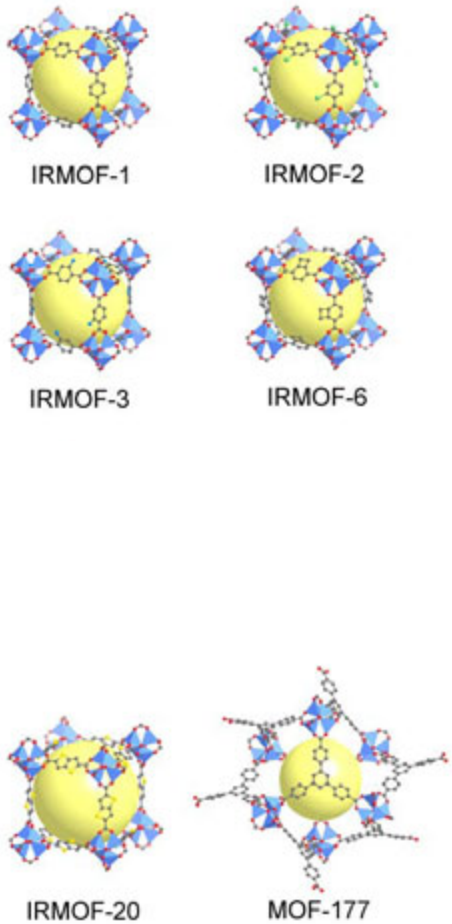
H_2 Adsorption in Non-Catenated MOFs



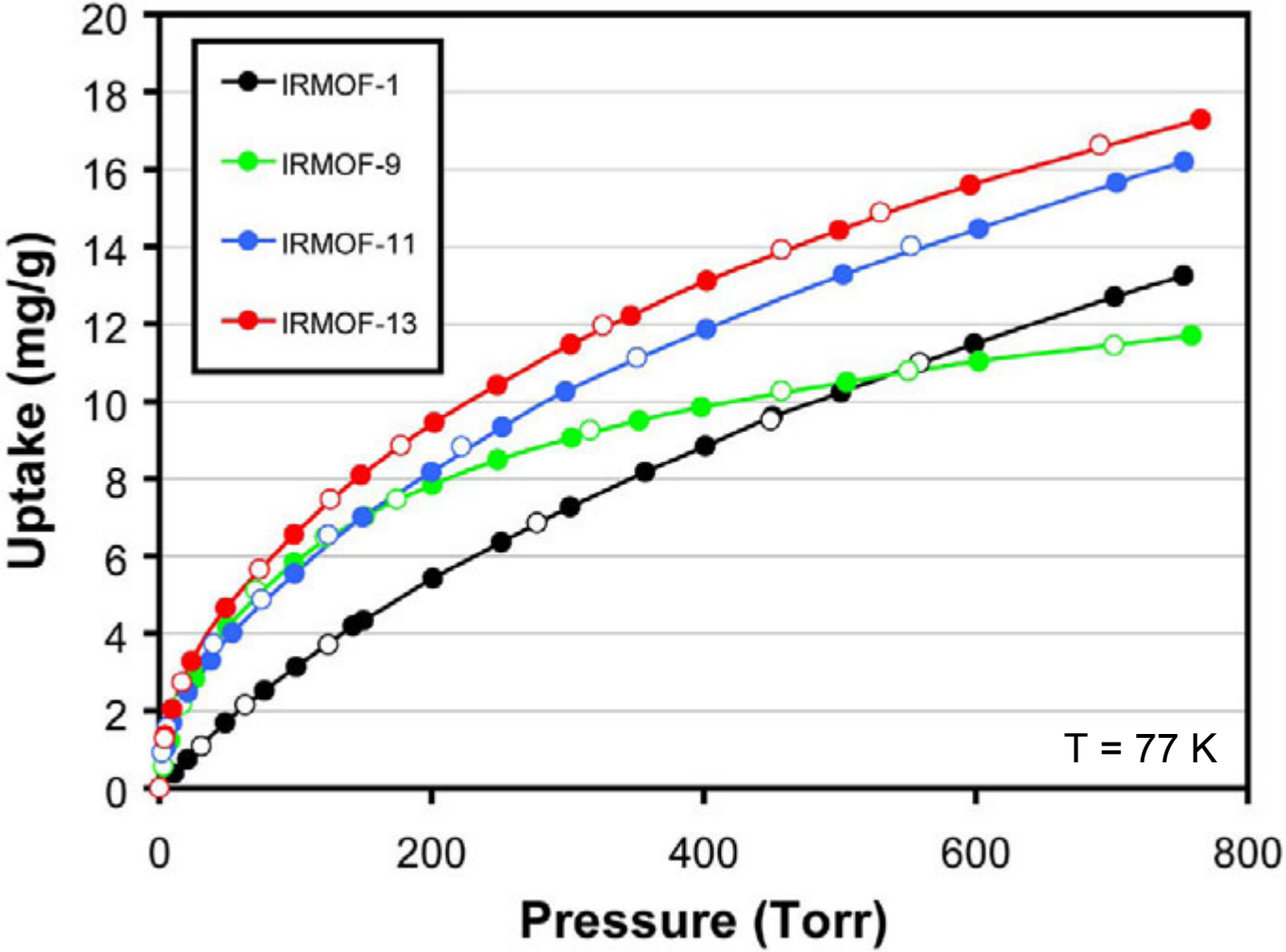


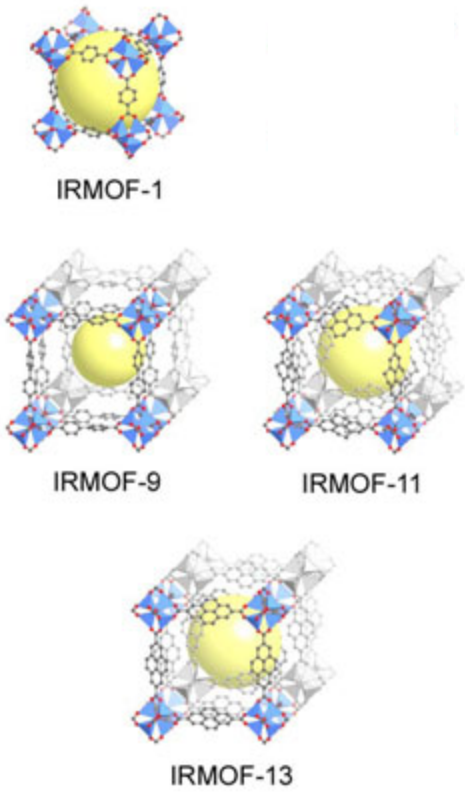
H_2 Adsorption in Non-Catenated MOFs



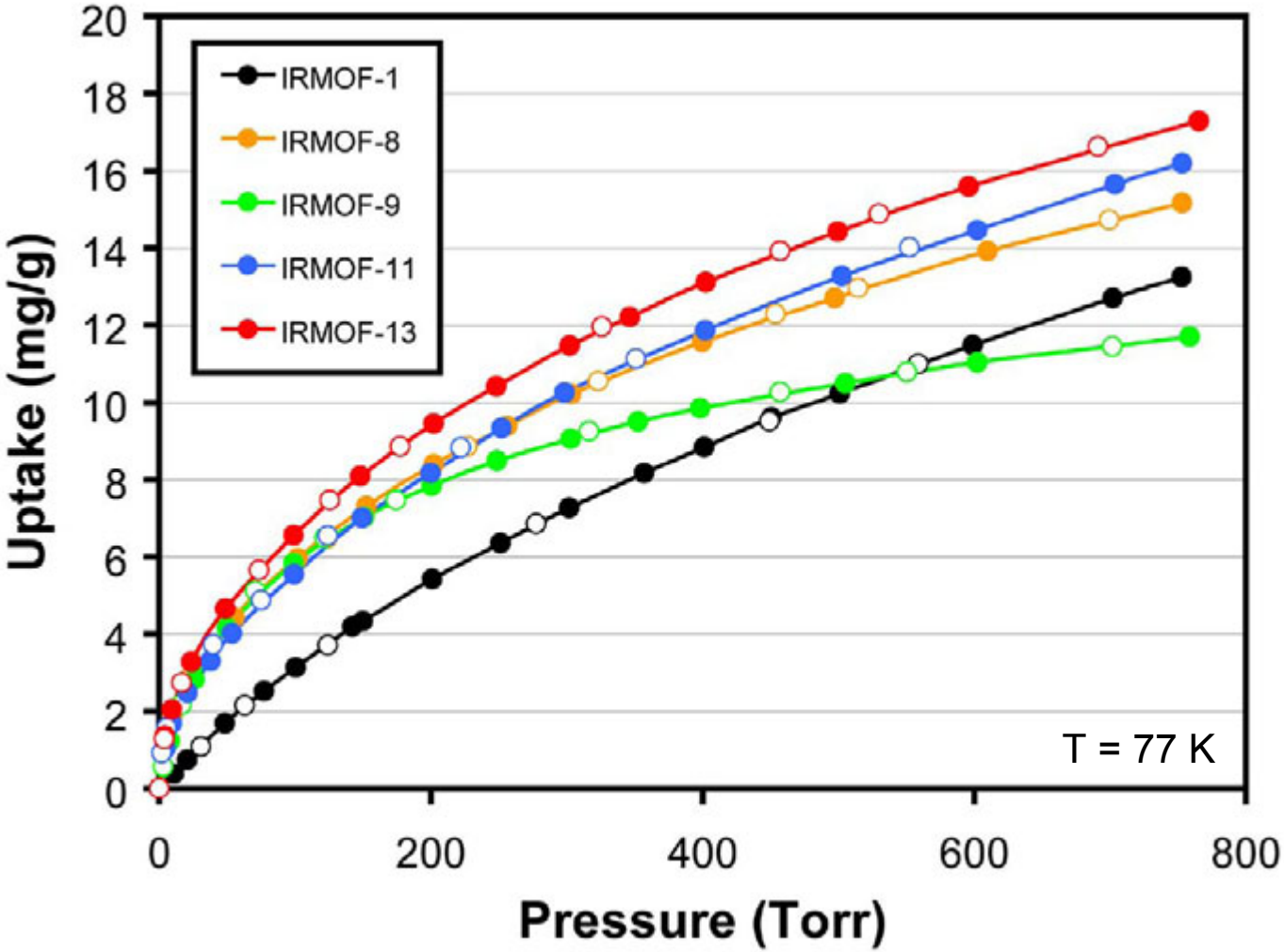


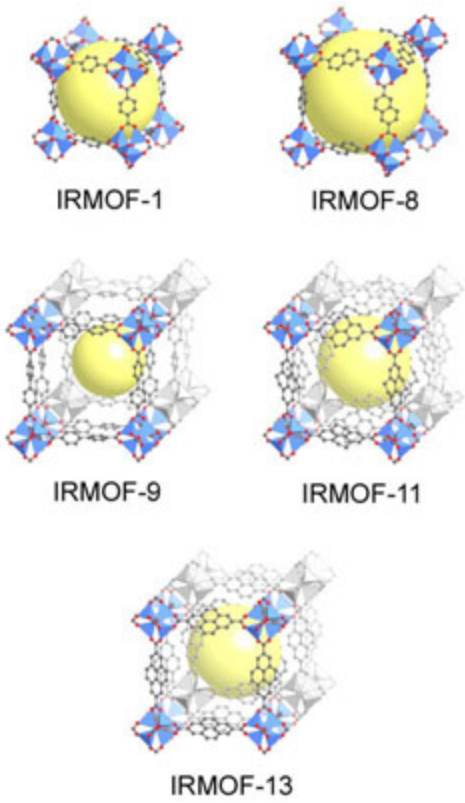
H_2 Adsorption in Catenated MOFs



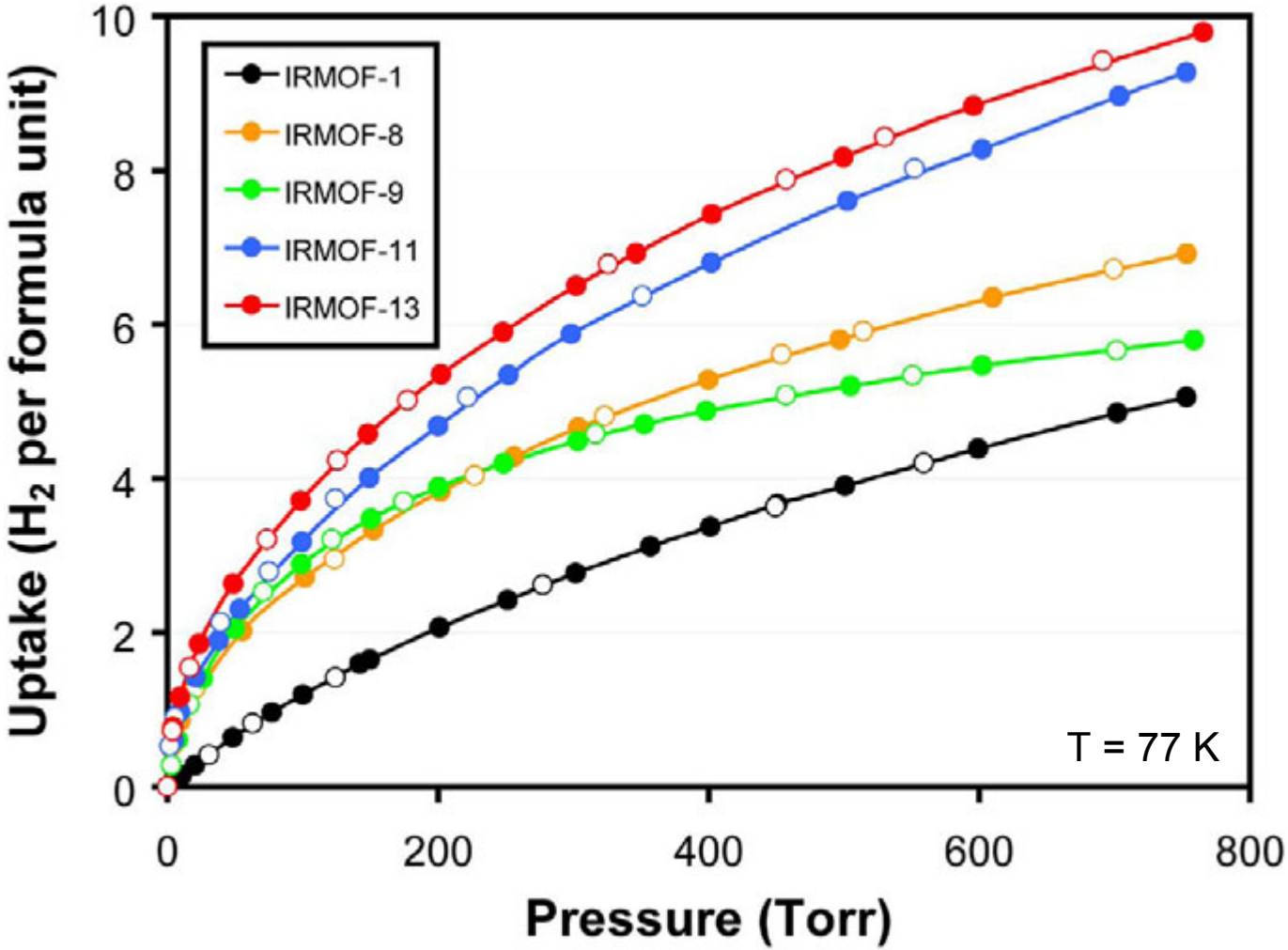


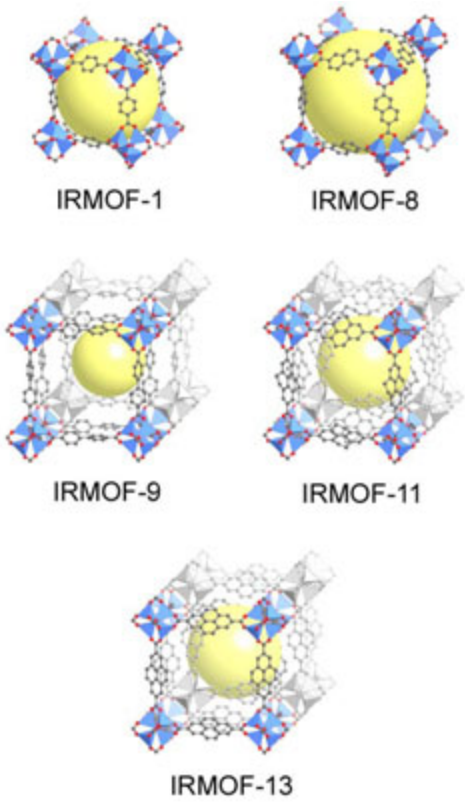
H_2 Adsorption in Catenated MOFs



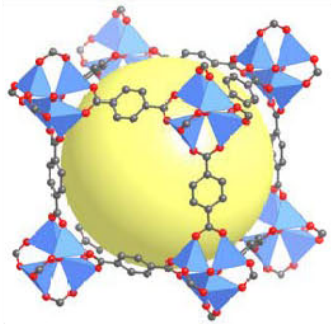


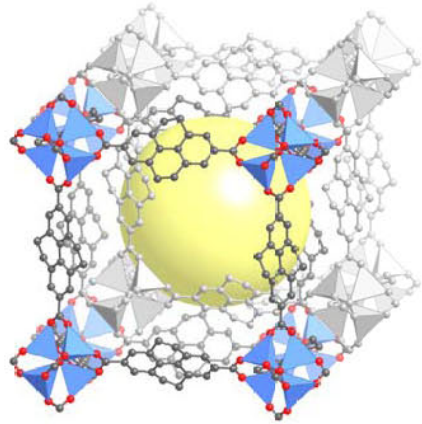
H_2 Adsorption in Catenated MOFs

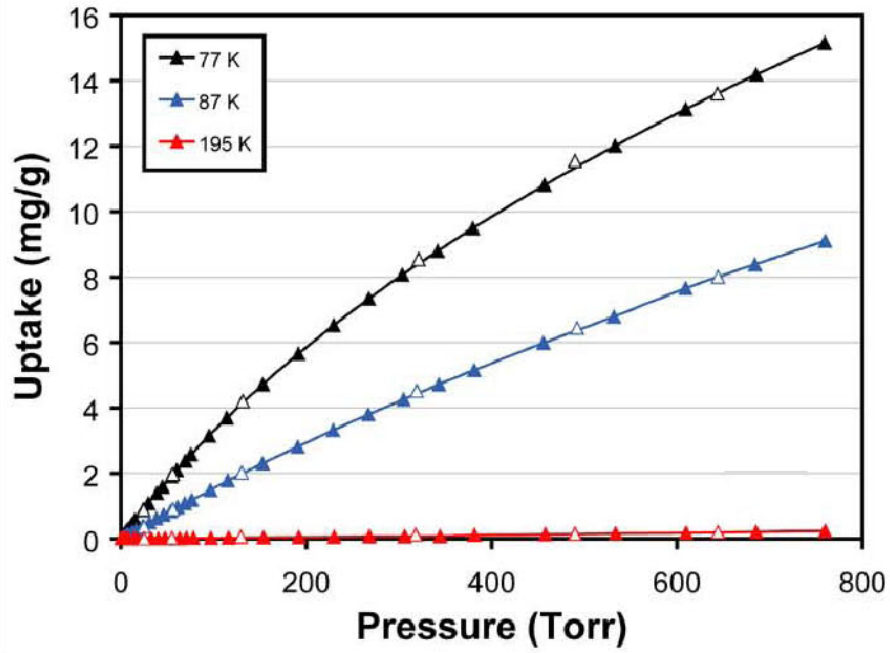


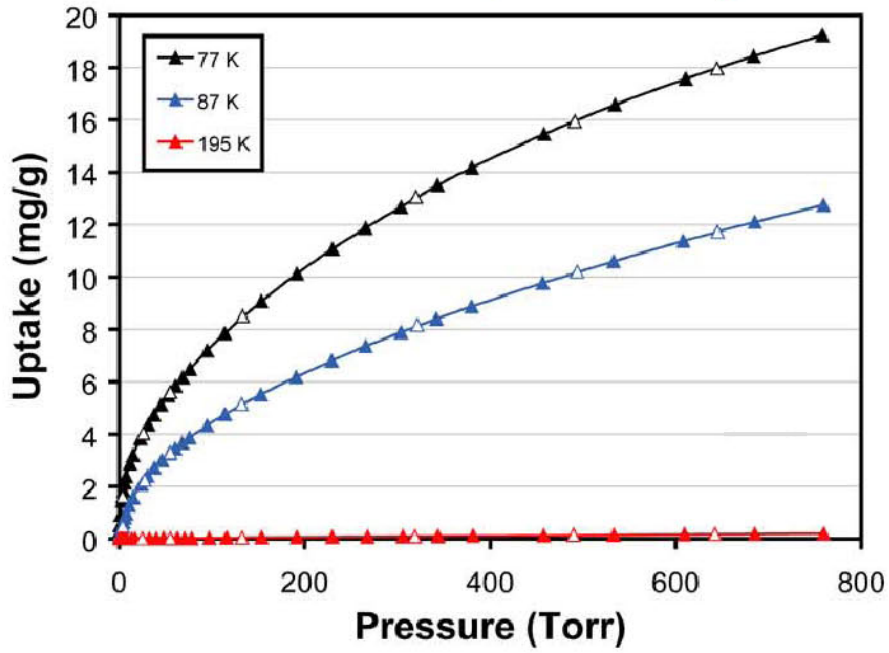


T Dependence of H_2 Uptake: IRMOF-1 and -11



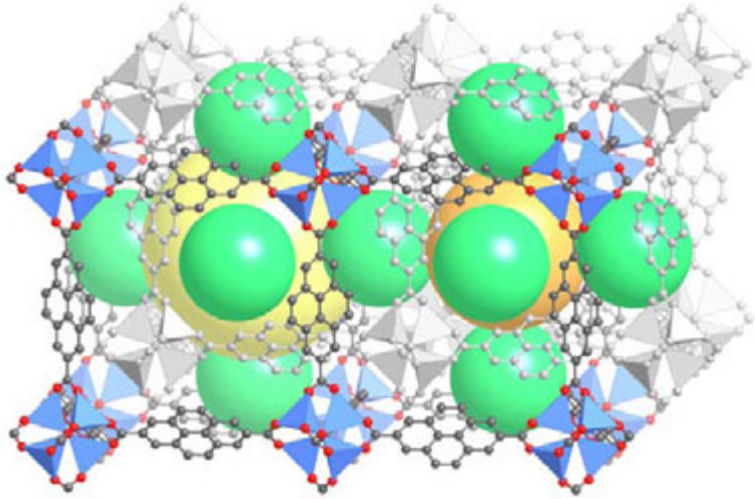


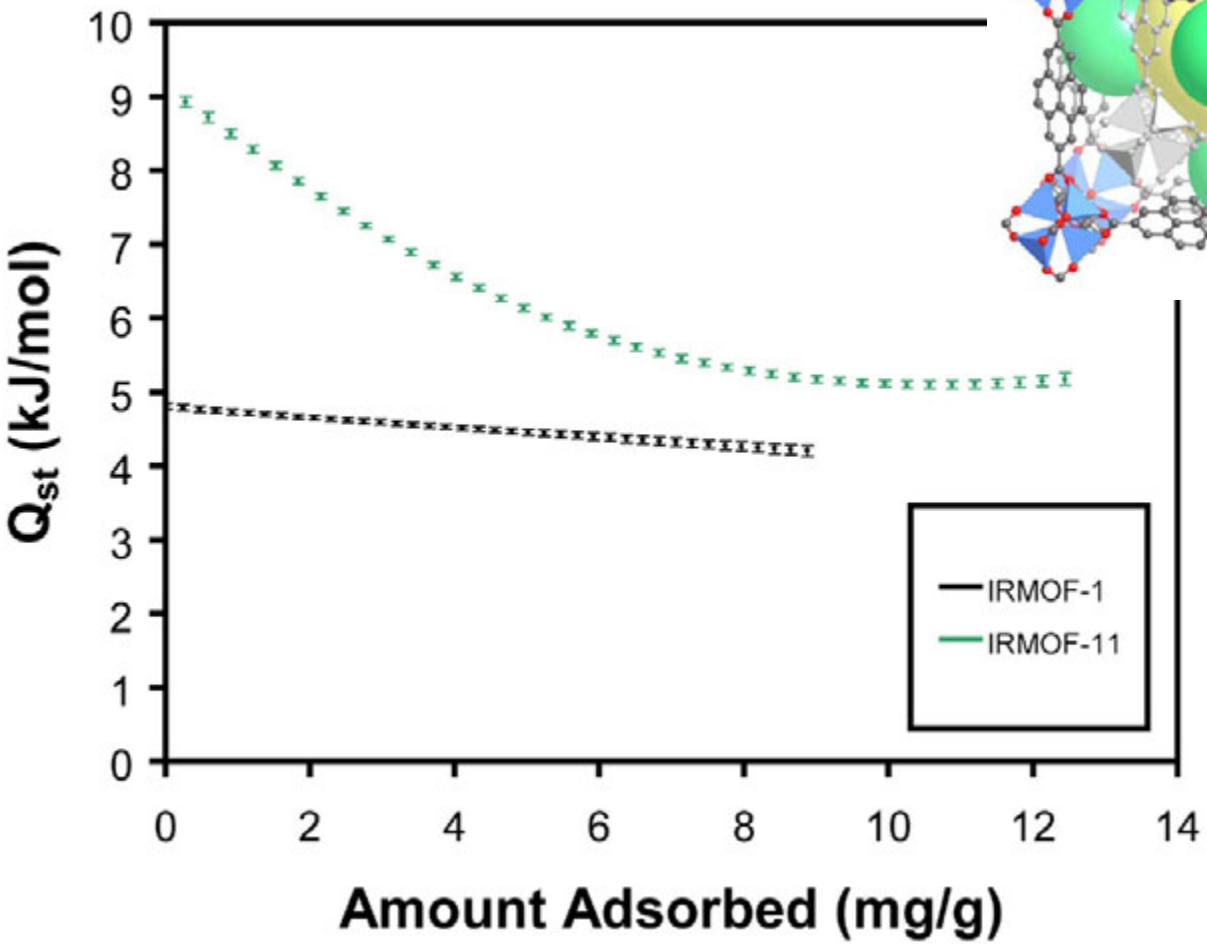




Isosteric Heats of Adsorption

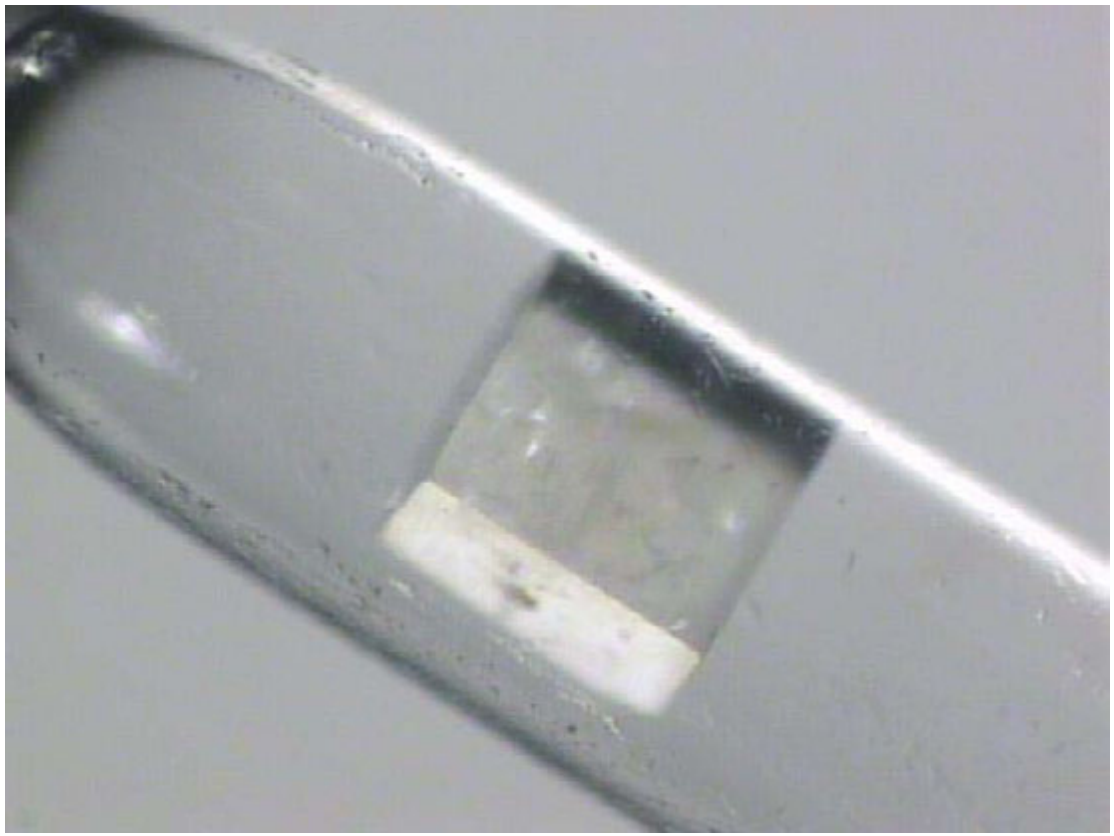
- values extracted by fitting isotherms with virial-type expansions





- pore constriction results in overlap of the attractive surface potential

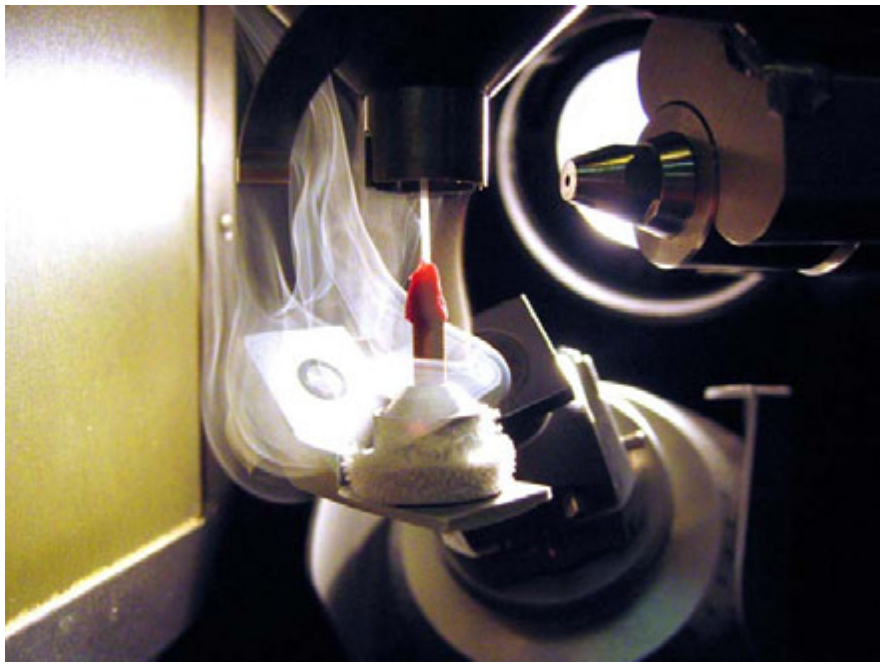
Evacuated Single Crystals of IRMOF-1



- solvent-free crystals maintain diffraction quality under vacuum or an atmosphere of gas

Low Temperature Single Crystal X-ray Diffraction

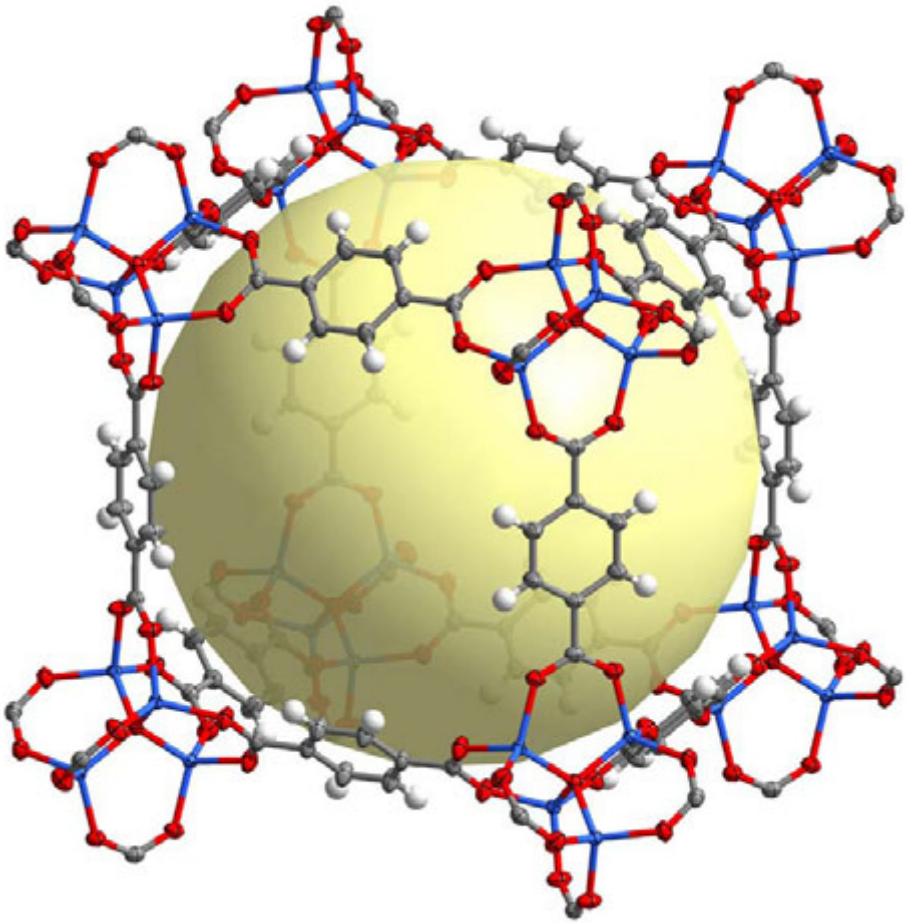
- Helix cryostat (University of Durham, UK) provides temperature control to 30 K

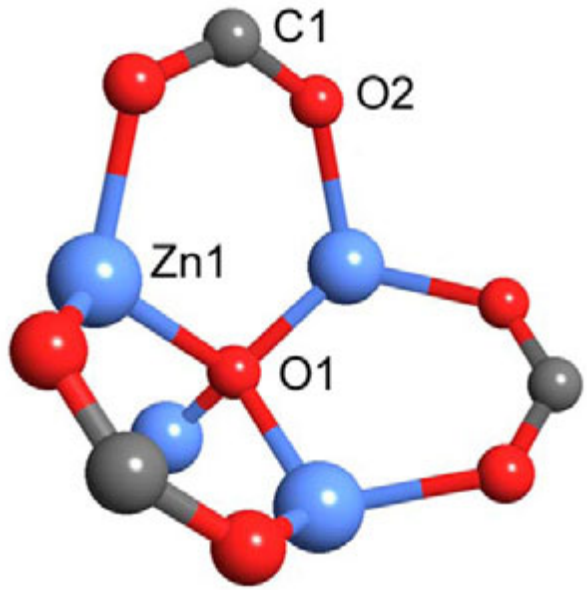


Refinement of evacuated framework at 30 K:

Empirical Formula	$Zn_4O_{13}C_{24}H_{12}$
Crystal Size	0.43 x 0.43 x 0.30 mm
Space Group	$Fm\bar{3}m$
Cell parameter	a = 25.894(4) Å
Calculated density	0.589 g/cm^3
θ range (for $Mo_{K\alpha}$)	2.61 to 29.56^o
Total Reflections	16341
Data / restraints / parameters	1258 / 0 / 28
R indices [I>2s(I)]	R_1 = 0.0199, wR_2 = 0.0542
R indices (all data)	R_1 = 0.0211, wR_2 = 0.0550
GOF on F^2	1.121
Largest diff. peak/hole	+0.419 / -0.227 e-/Å^3

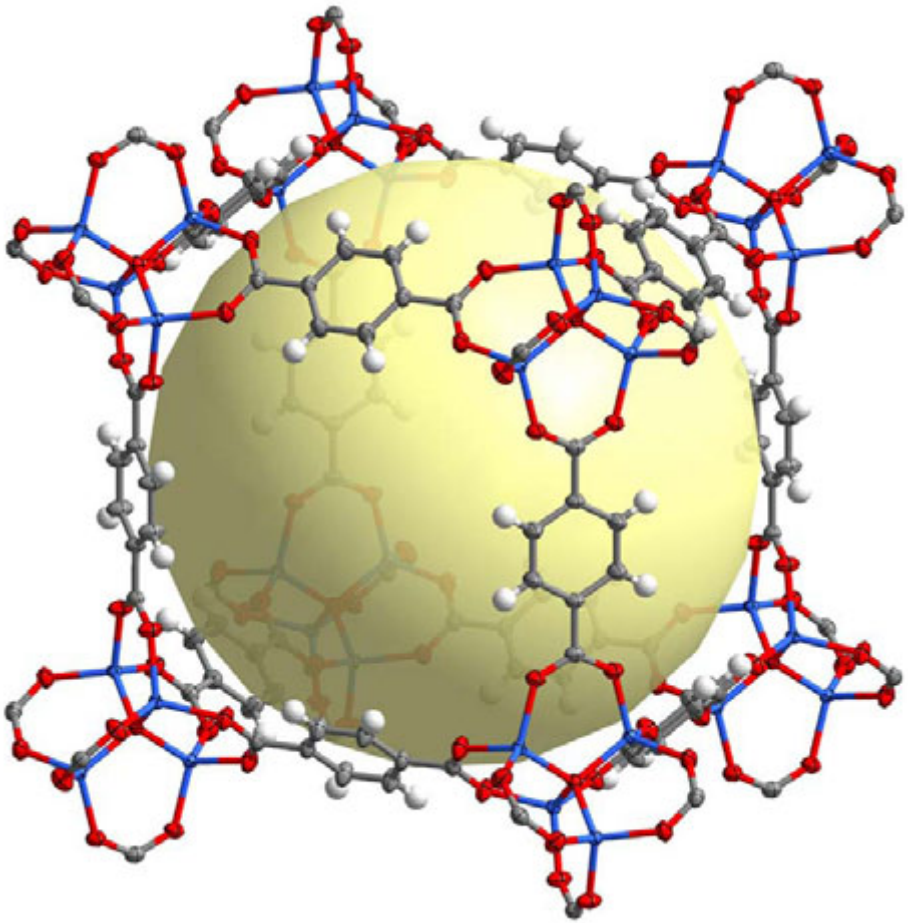
Crystallographic Identification of Primary Adsorption Sites of IRMOF-1

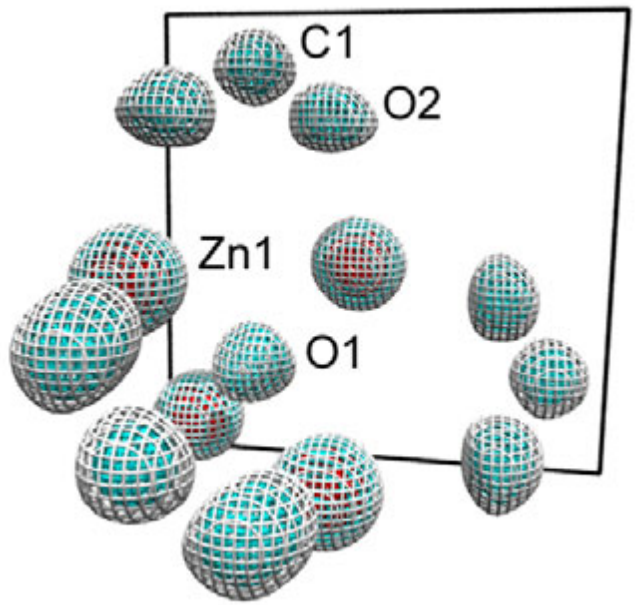




J.L.C. Rowsell, E.C. Spencer, J. Eckert, J.A.K. Howard, O.M. Yaghi, *Science* **2005**, *309*, 1350.

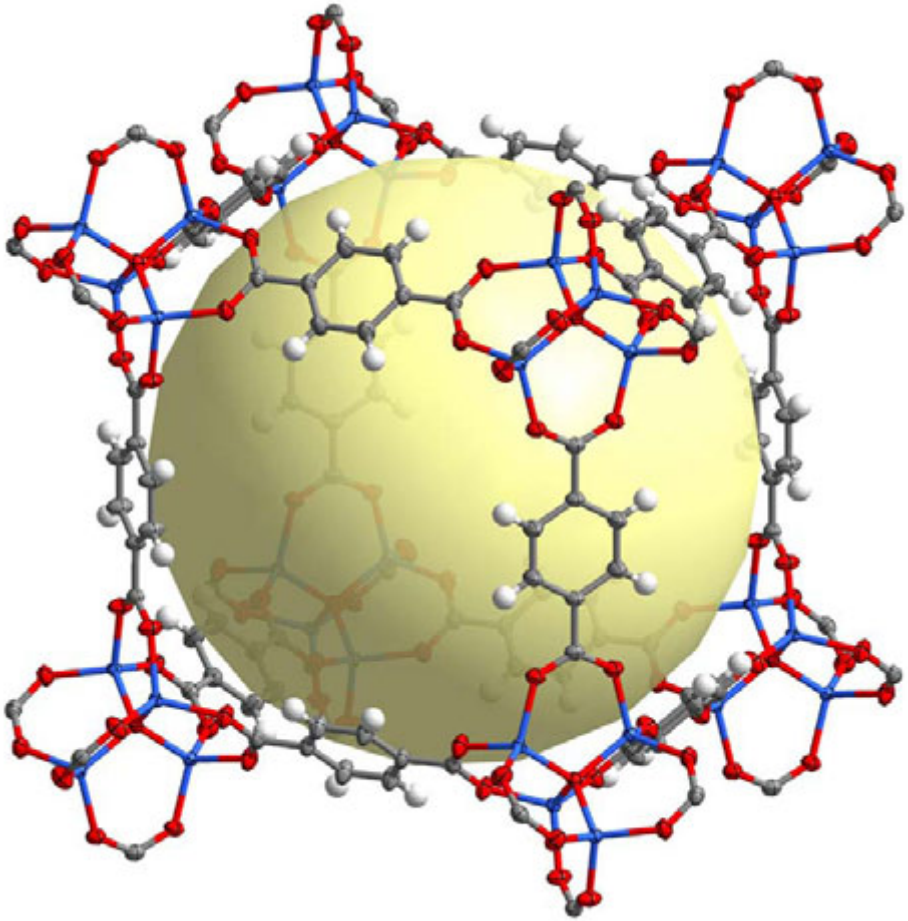
Crystallographic Identification of Primary Adsorption Sites of IRMOF-1

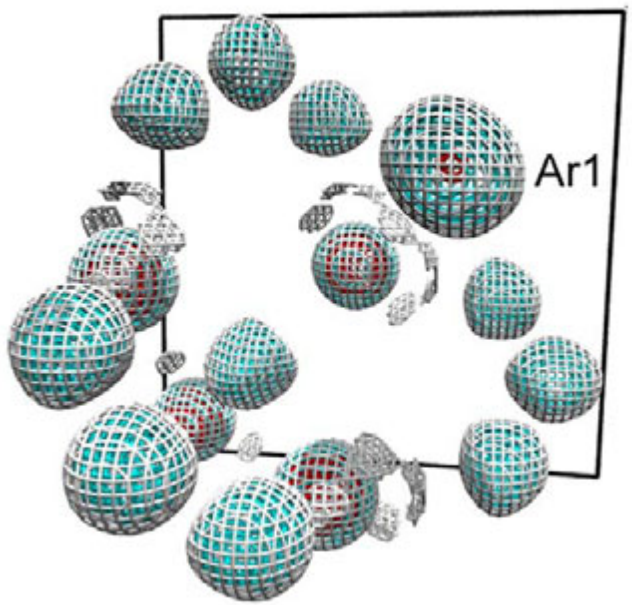




J.L.C. Rowsell, E.C. Spencer, J. Eckert, J.A.K. Howard, O.M. Yaghi, *Science* **2005**, *309*, 1350.

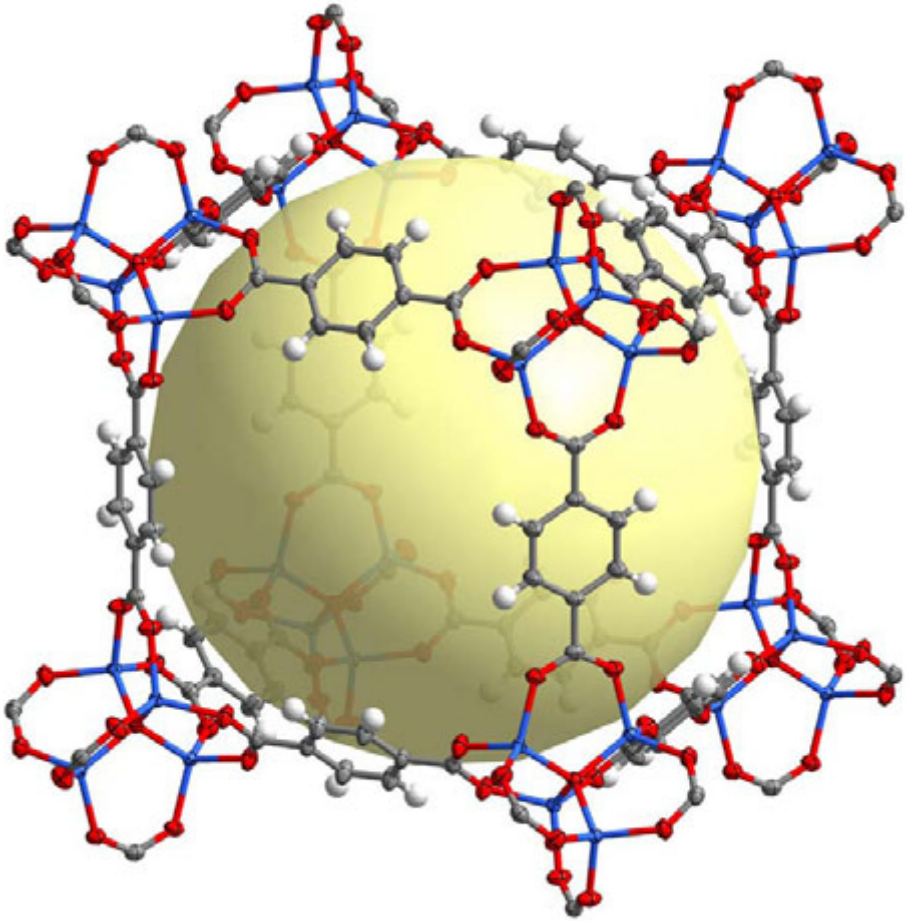
Crystallographic Identification of Primary Adsorption Sites of IRMOF-1

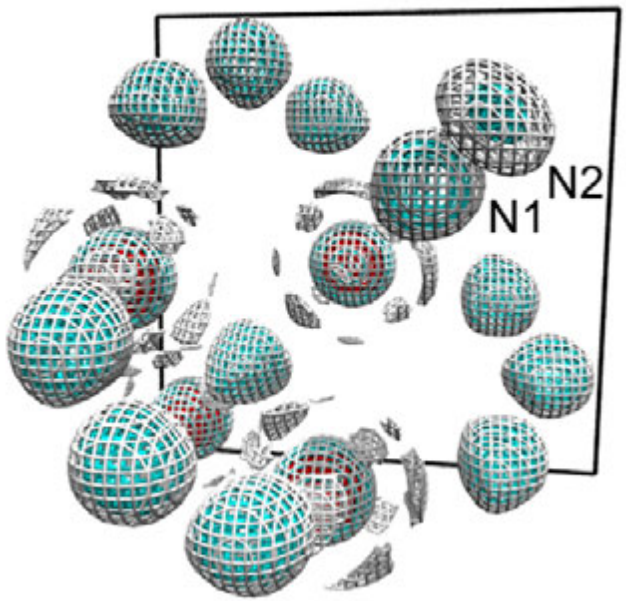




J.L.C. Rowsell, E.C. Spencer, J. Eckert, J.A.K. Howard, O.M. Yaghi, *Science* **2005**, *309*, 1350.

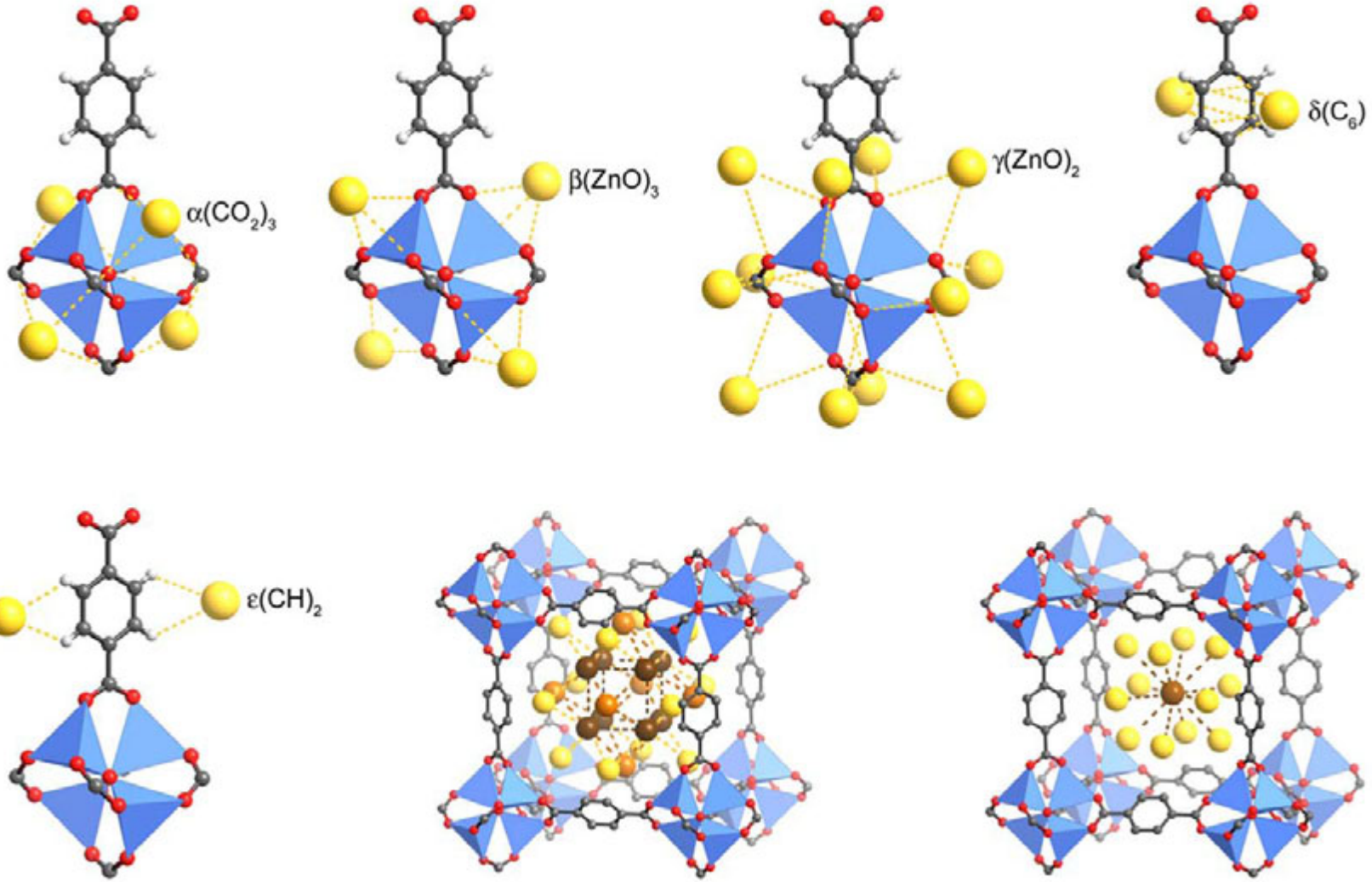
Crystallographic Identification of Primary Adsorption Sites of IRMOF-1



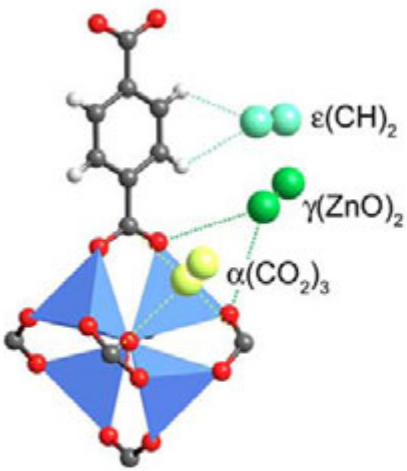


J.L.C. Rowsell, E.C. Spencer, J. Eckert, J.A.K. Howard, O.M. Yaghi, *Science* **2005**, *309*, 1350.

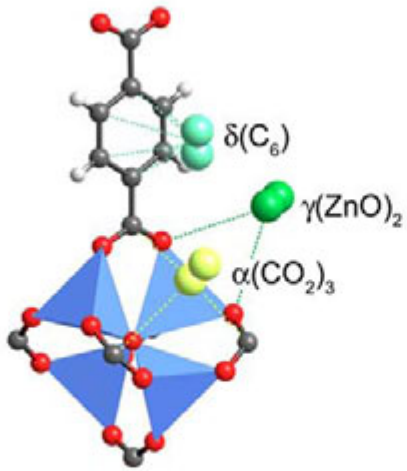
Eight Independent Adsorption Sites



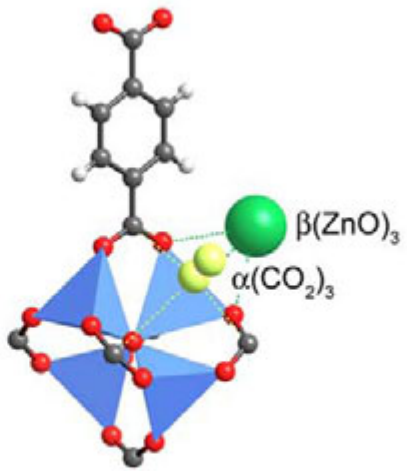
Thermal Dependence of N_2 Adsorption



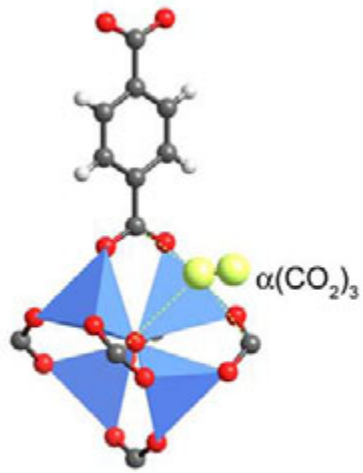
30 K



50 K

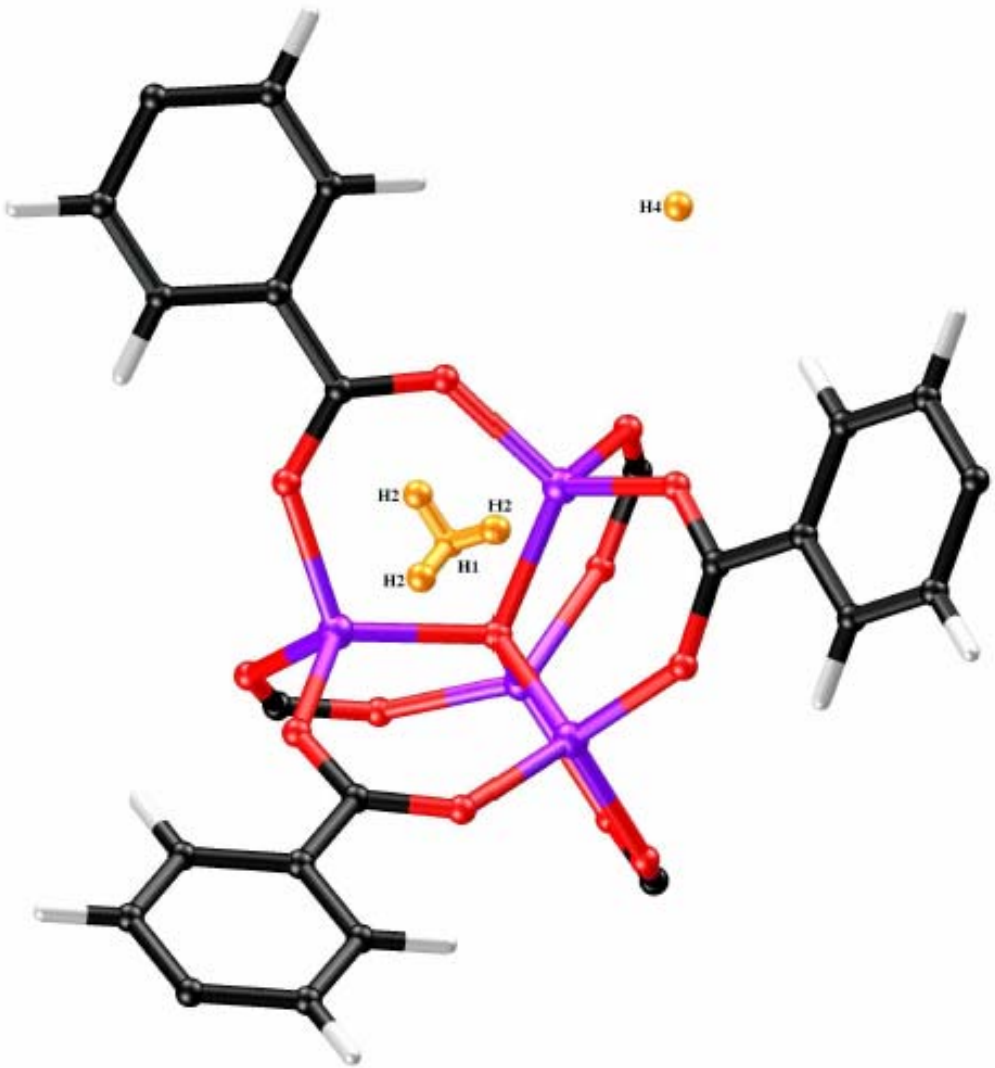


90 K



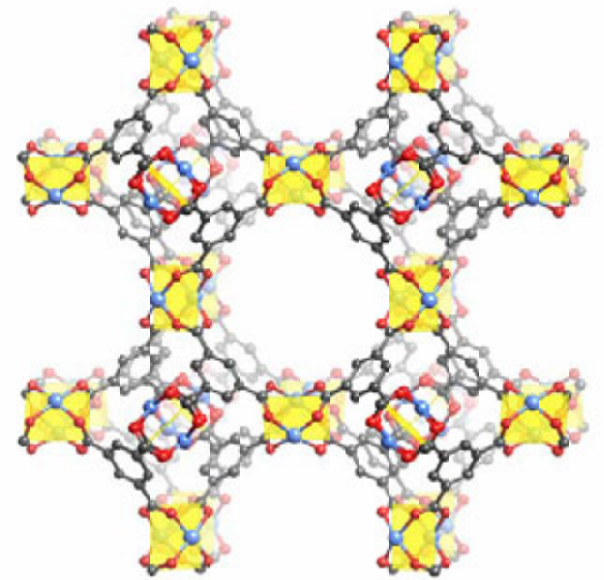
120 K

Single Crystal Neutron Diffraction



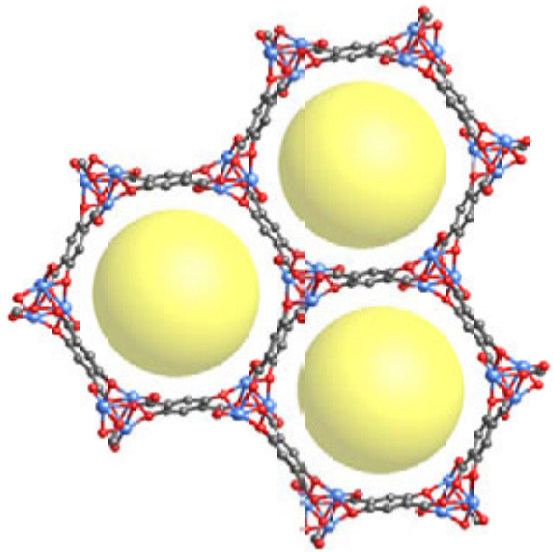
- data collected on VIVALDI (ILL) on ~$(0.5\ mm)^3$ crystal sealed under H_2
- appearance of H_2 on α**$(CO_2)_3$** site at 50 K, additional H_2 appears on β**$(ZnO)_3$** at 5 K

Porous Materials with Unsaturated Metal Centers



HKUST-1, $Cu_2(BTC)_{4/3}$

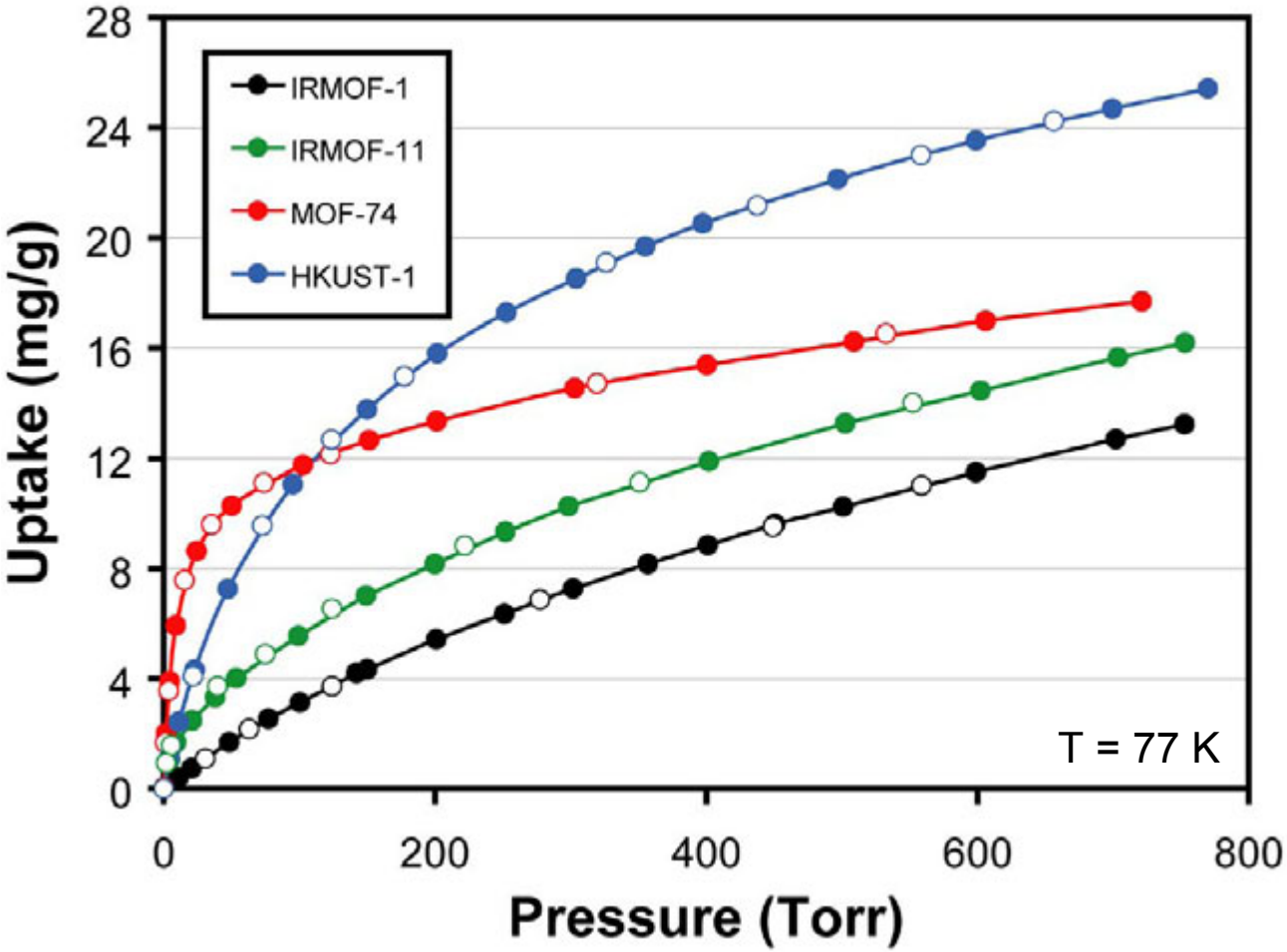
A_{Lang}	2175 m^2/g
A_{BET}	1507 m^2/g
V_p	66%

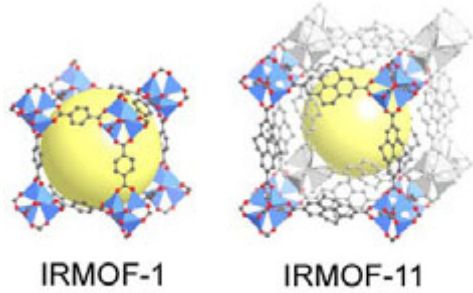


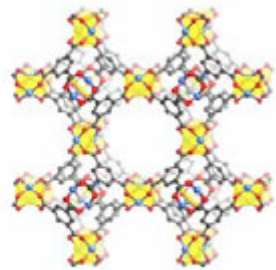
MOF-74, $Zn_2(dhBDC)$

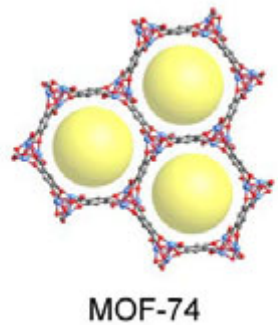
A_{Lang}	1132 m^2/g
A_{BET}	783 m^2/g
V_p	48%

H_2 Uptake at 77 K, 1 atm

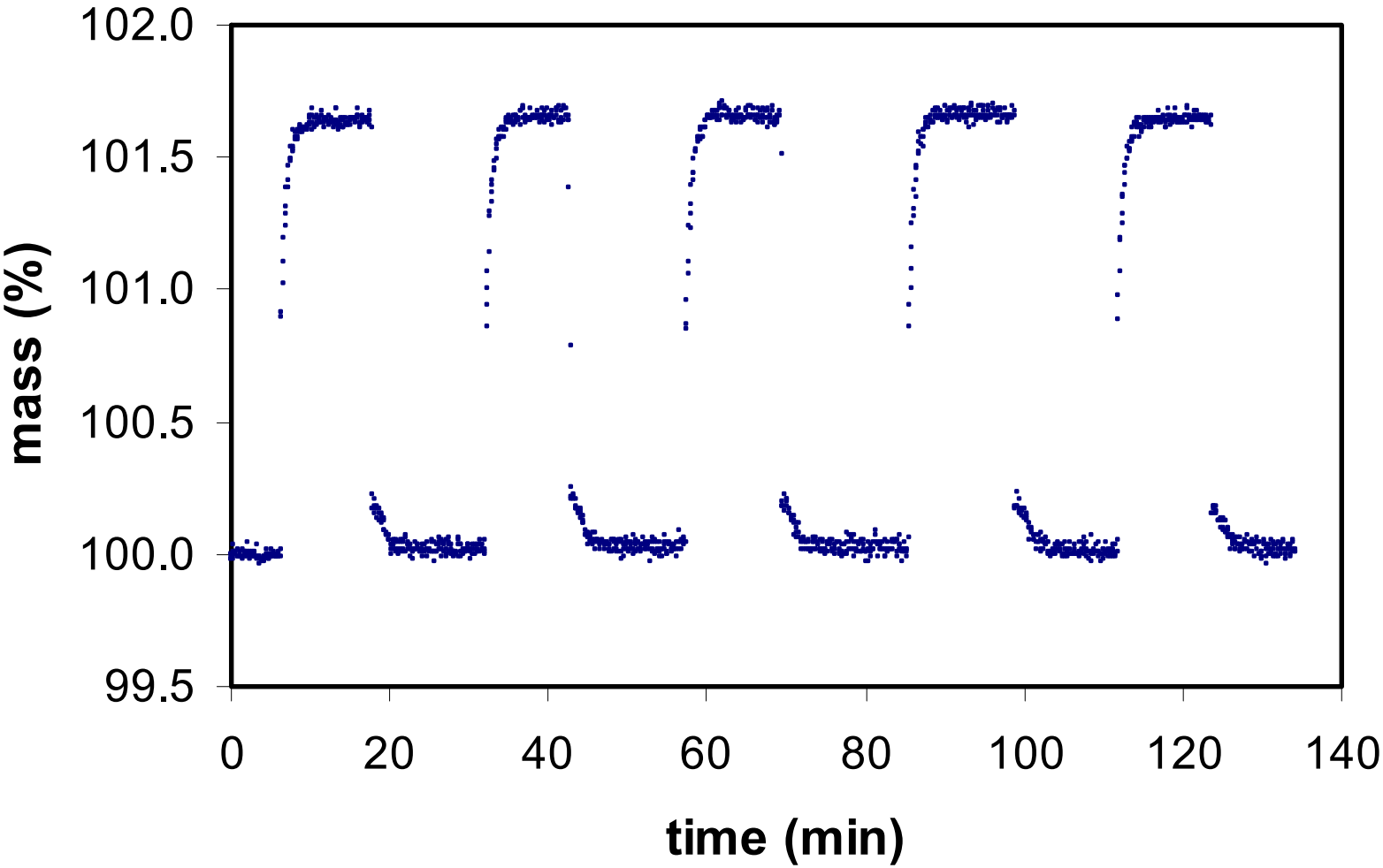




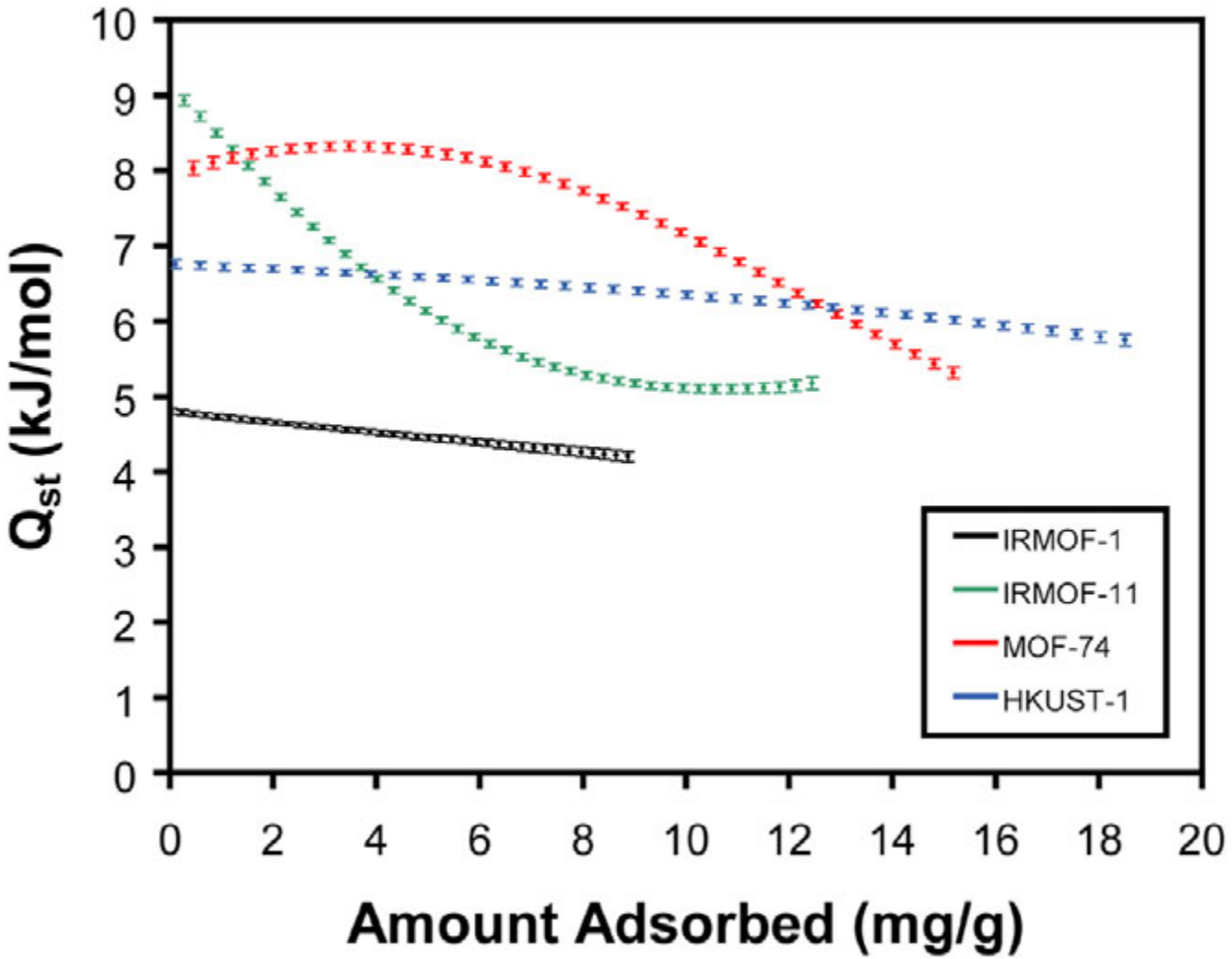


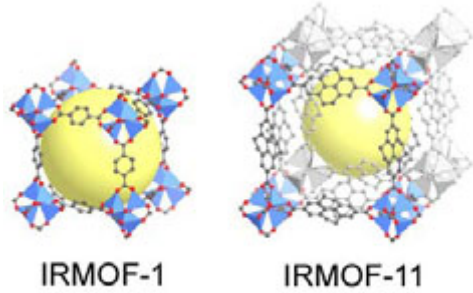


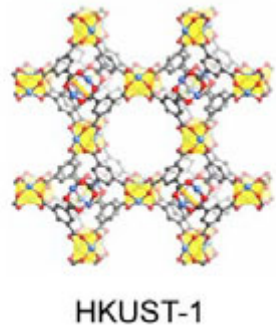
Reversibility of hydrogen sorption in IRMOF-11

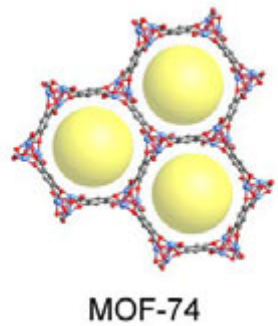


Isosteric Heats of Adsorption

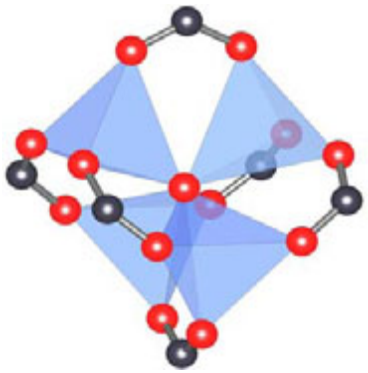




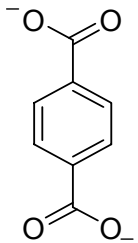




a)



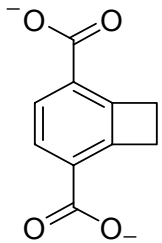
$Zn_4O(CO_2)_6$



BDC

IRMOF-1

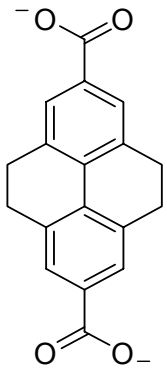
4,170



CBBDC

IRMOF-6

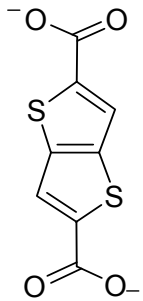
3,300



HPDC

IRMOF-11

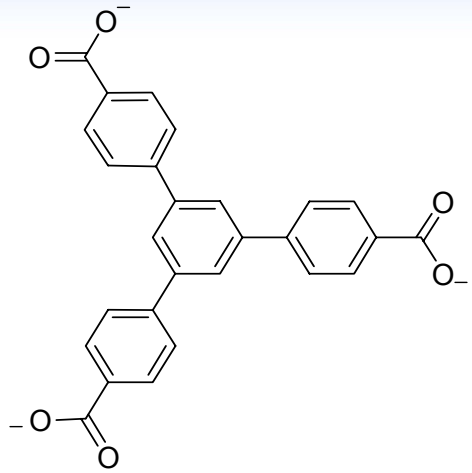
2,340



TTDC

IRMOF-20

4,590

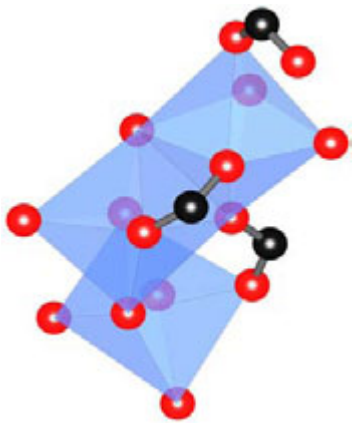


BTB

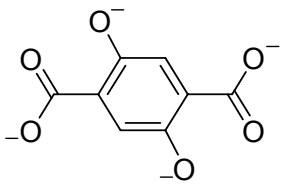
MOF-177

5,640

b)



$Zn_3[(O)_3(CO_2)_3]_\infty$

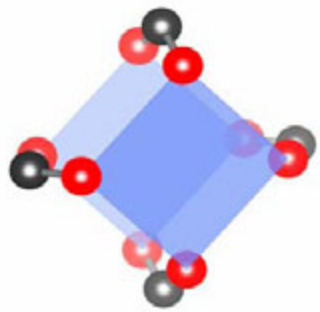


DHBDC

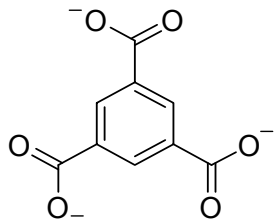
MOF-74

1,070

c)



$Cu_2(CO_2)_4$



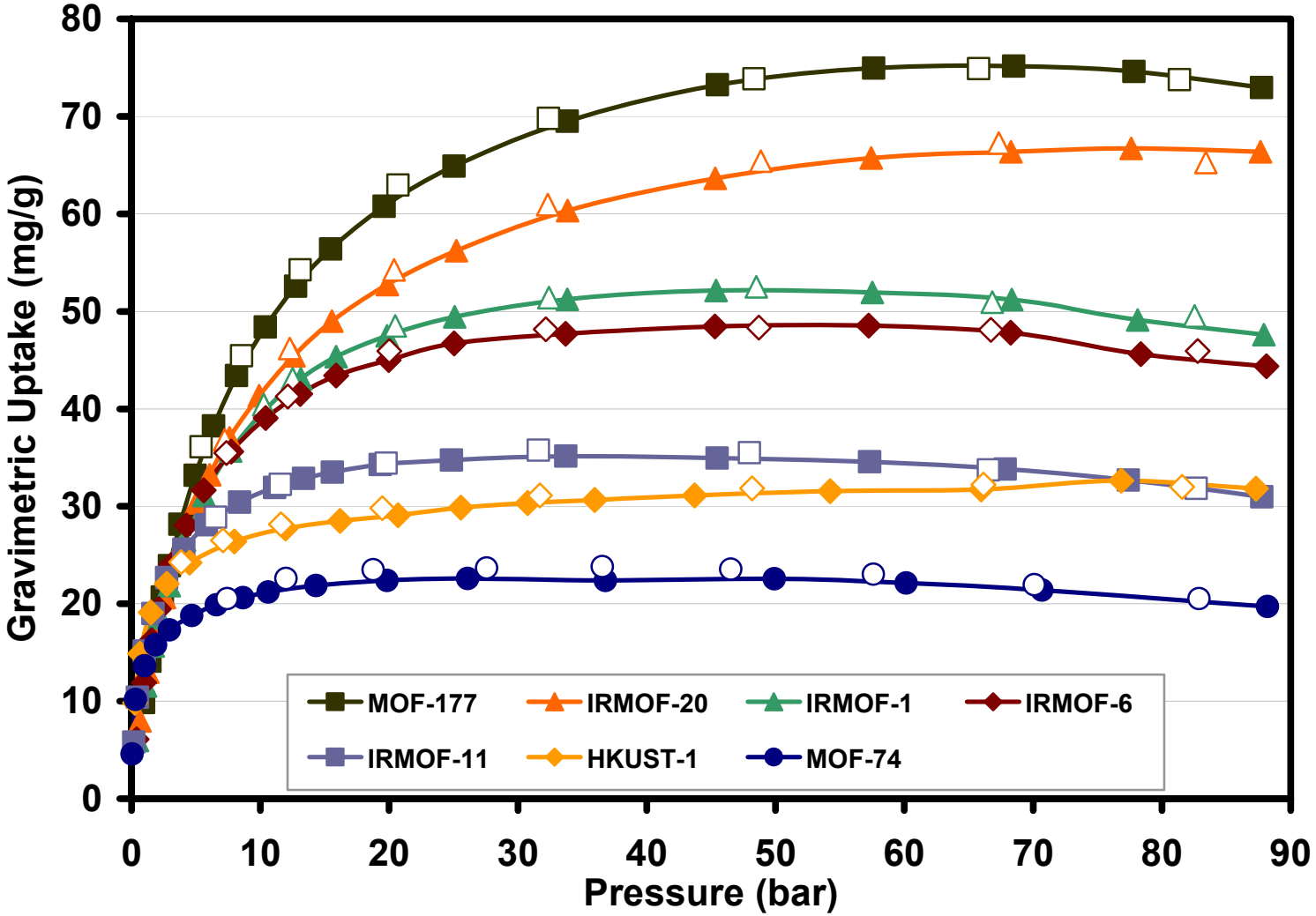
BTC

HKUST-1

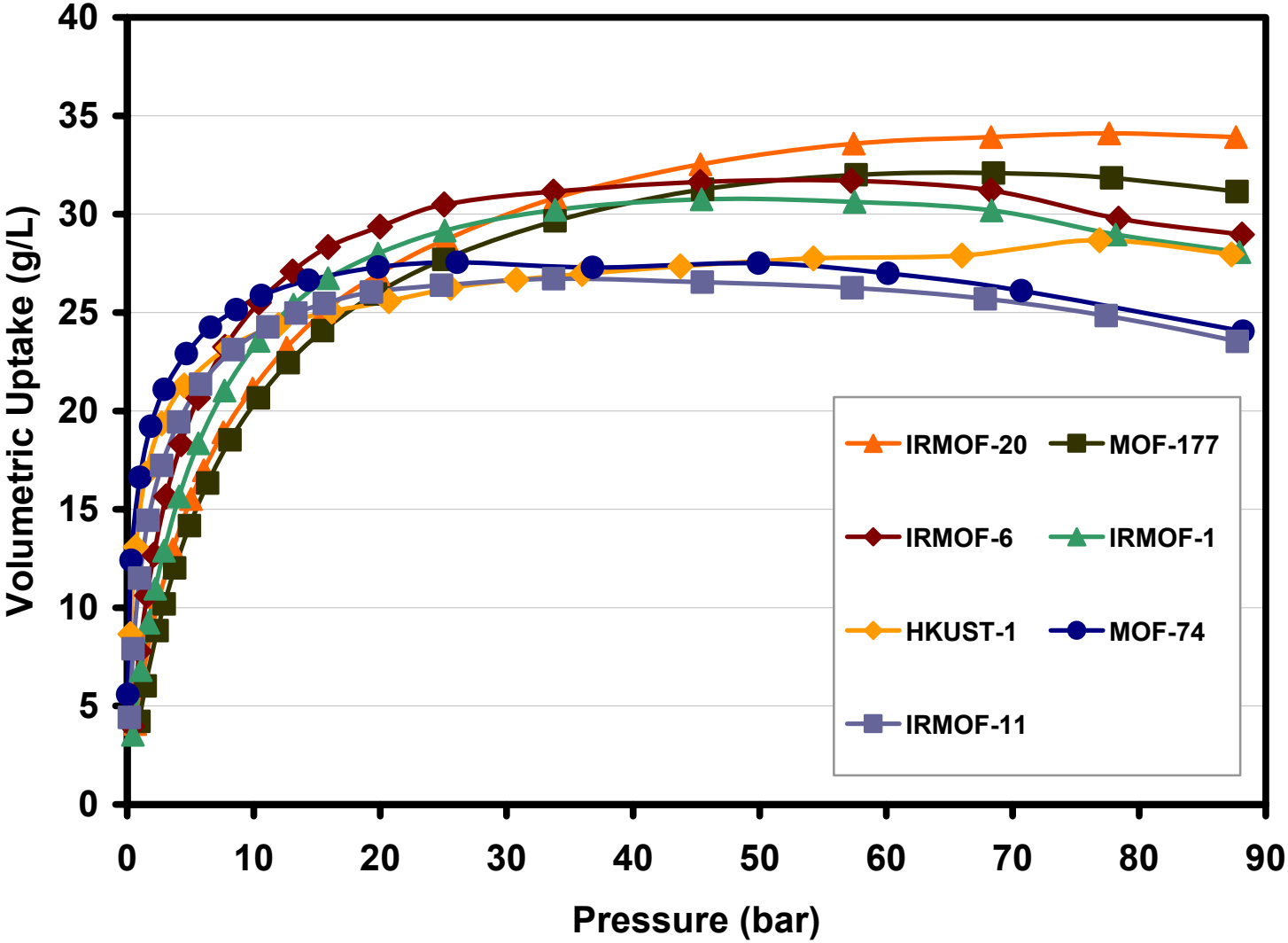
2,260

Hydrogen uptake at 77 K

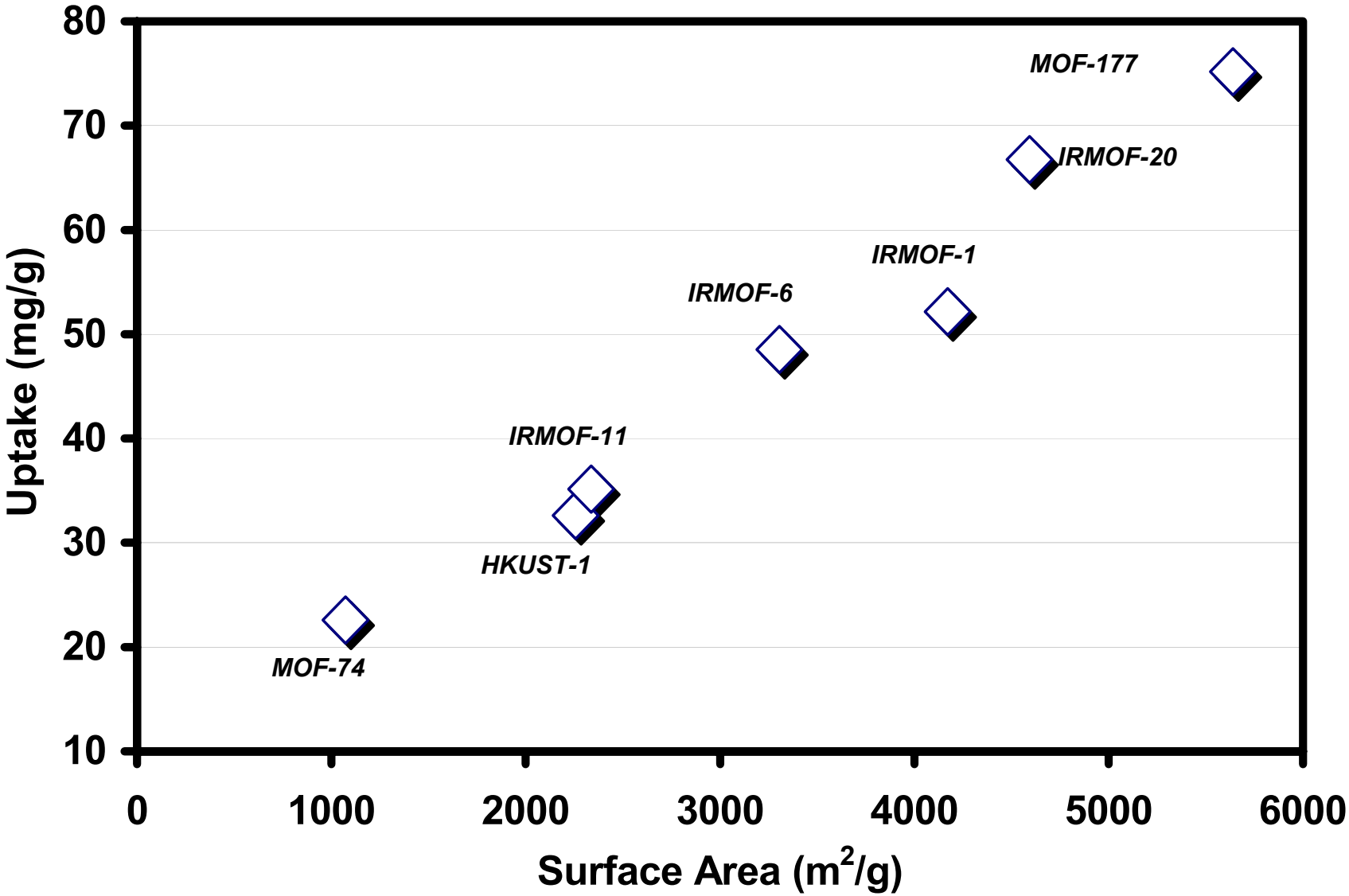
(30% more hydrogen in a vessel containing MOFs)



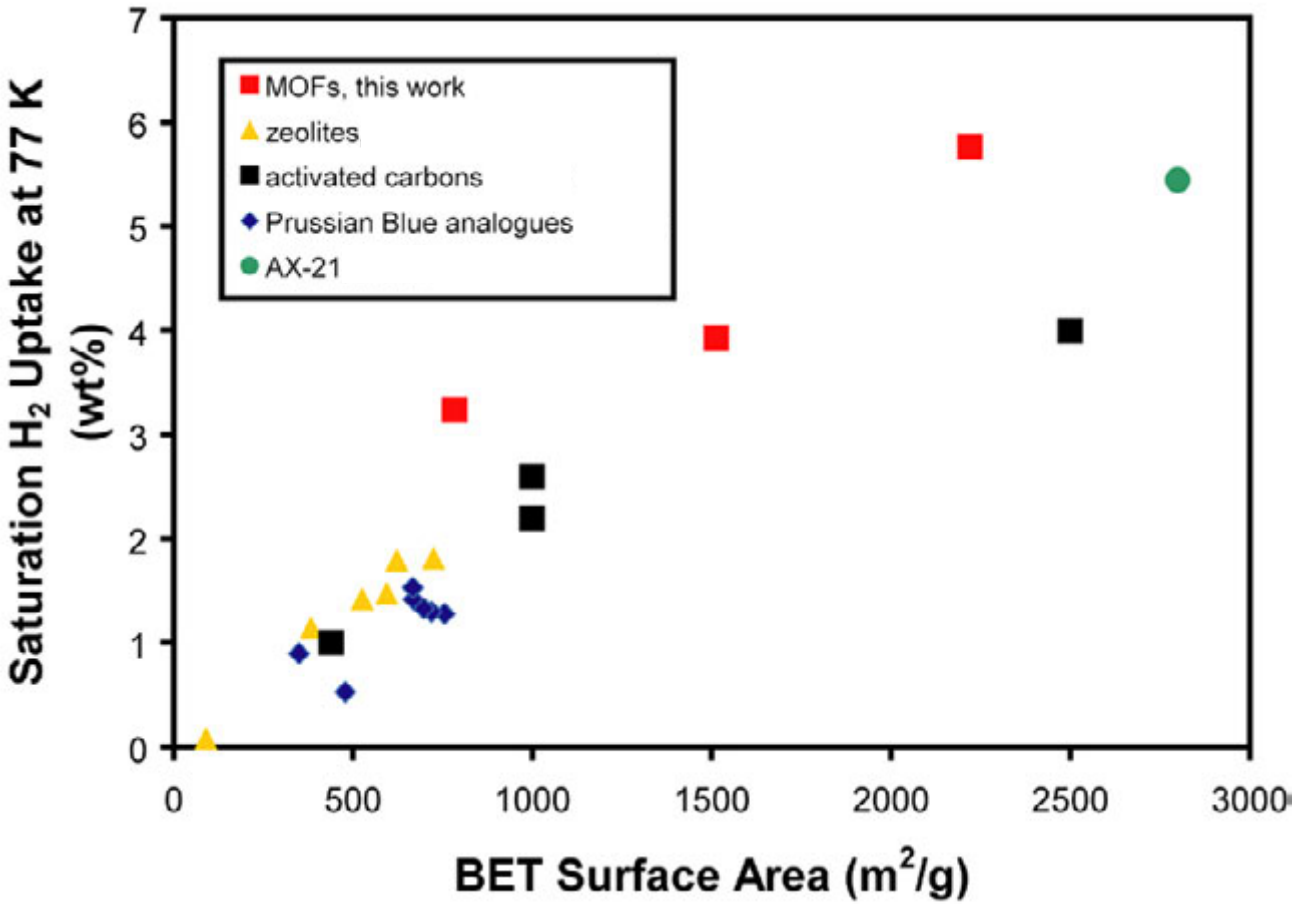
Volumetric uptake at 77 K



Correlation of uptake with surface area



Correlation with N_2 Adsorption Data



Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

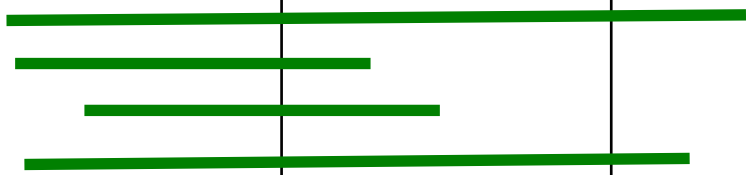
- High exposure to H_2 gas with possibility of personal injury due to decreased oxygen content in the atmosphere.
- High concentrations of H_2 may pose a fire or explosion in and around instrumentation.

Safety Plan setup at UCLA

Our approach to deal with this hazard:

- Dedicated a single laboratory for all H_2 experiments.
- Installed active ventilation snorklesfrom laboratory hoods to all instrumentation consuming/releasing H_2.
- Installed atmospheric H_2 detector (% level detection) outfitted with an alarm in the dedicated laboratory.

Future Work

Task	2006	2007	2008
1. High surface area MOFs Synthesize MOFs Expose metal sites Impregnate MOFs with metal clusters, metal oxides and polymers			
2. Hydrogen uptake studies Measure adsorption energy Measure uptake in real-life conditions			
3. Characterization and testing and scale up of favorable MOFs			
4. Submit samples to DOE			

Acknowledgments

Jesse Rowsell
Adrien Cote
Jun Yang
Kyosung Park
Ni Zheng
Antek Wong-Foy
Adam Matzger

Funding
DOE BES and Hydrogen FreedomCAR programs
NSF
BASF
Toyota
GM