# Hydrogen storage in Metal-Organic Frameworks

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*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

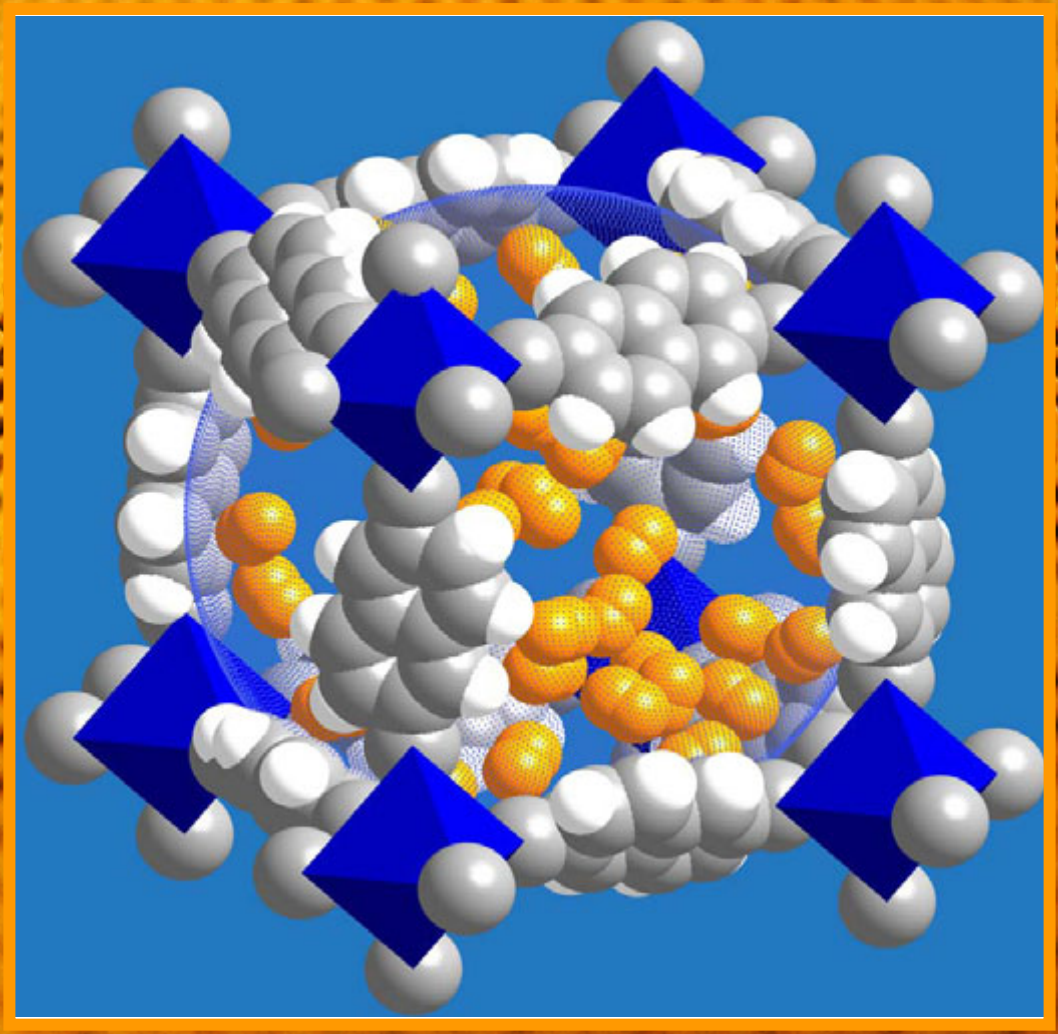
1. MOFs with high surface areas that combine molecular features for enhancing the adsorption energy of hydrogen to MOFs
   - Utilize new concepts for increased surface areas
   - Implement strategies for higher adsorption energy
   - Develop strategies for increased hydrogen density in MOFs

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



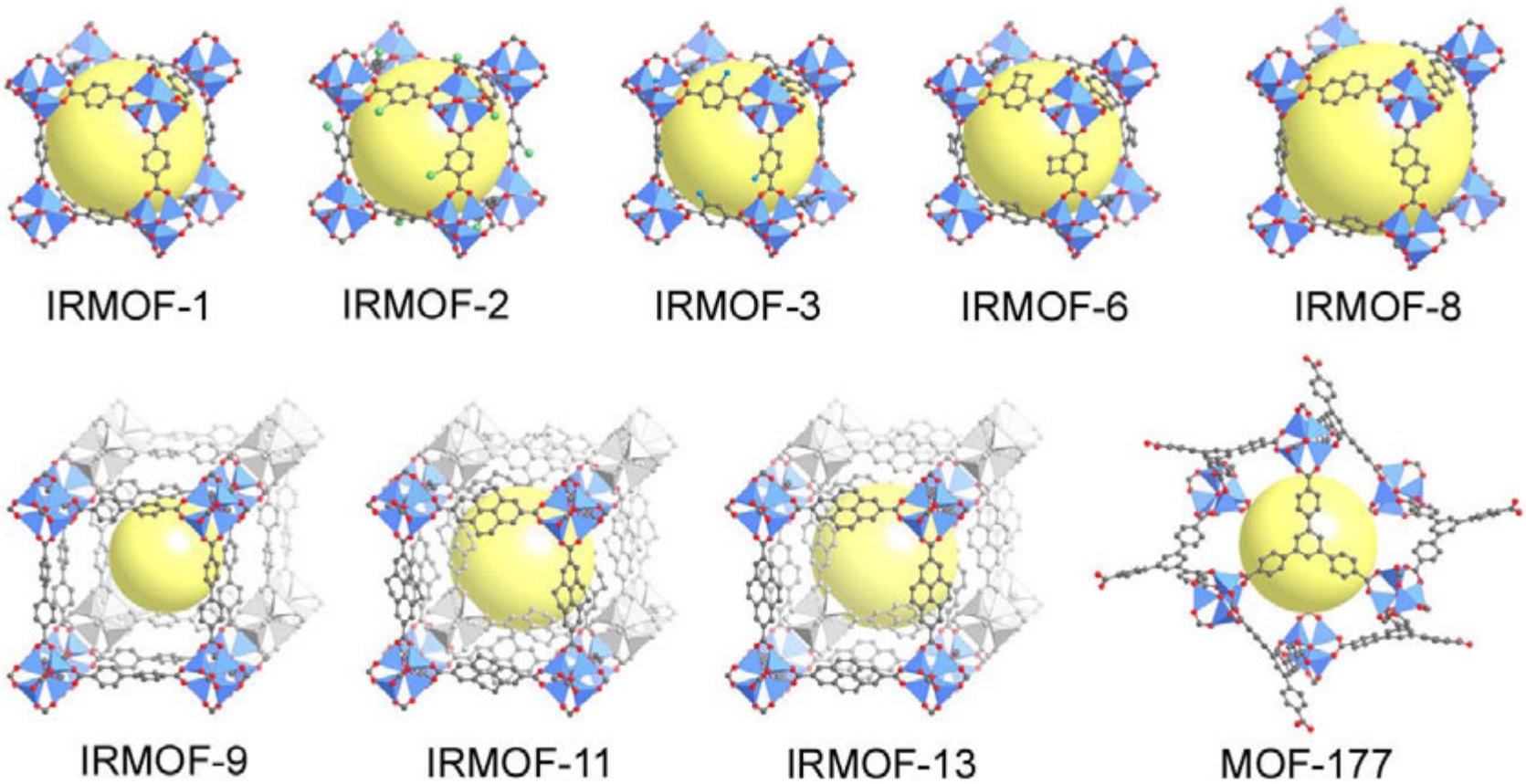
# Hydrogen Sorption in MOFs

- 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)**

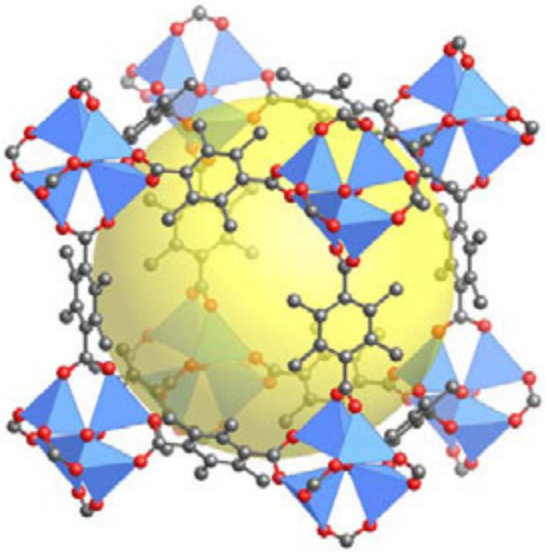
a series of materials having the same underlying topology and (typically) constructed from the same secondary building units




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



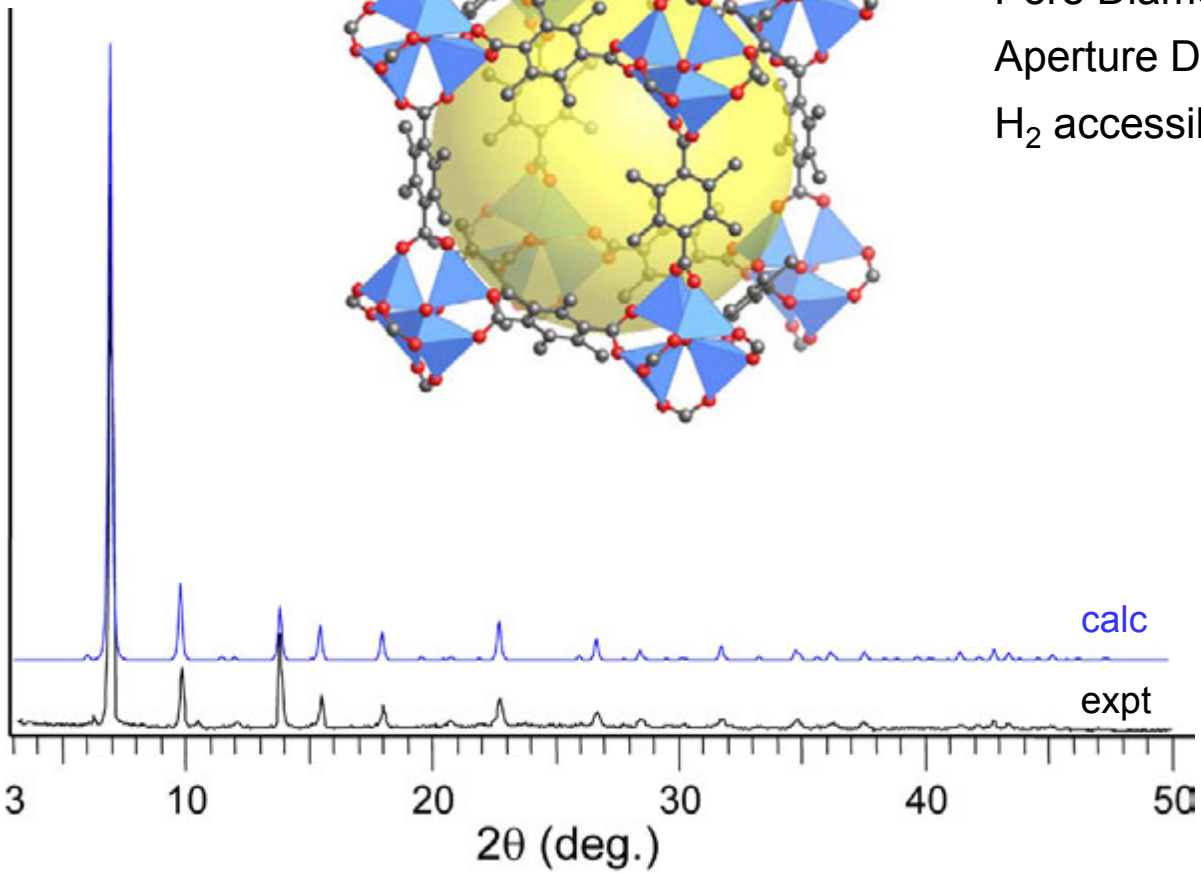
Empirical Formula: $C_{36}H_{36}O_{13}Zn_4$

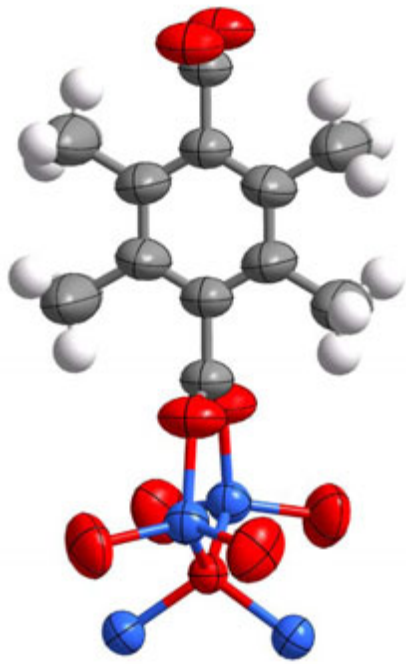
Crystal Data: $Fm\bar{3}m$, $a$ = 25.6135(7) Å

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



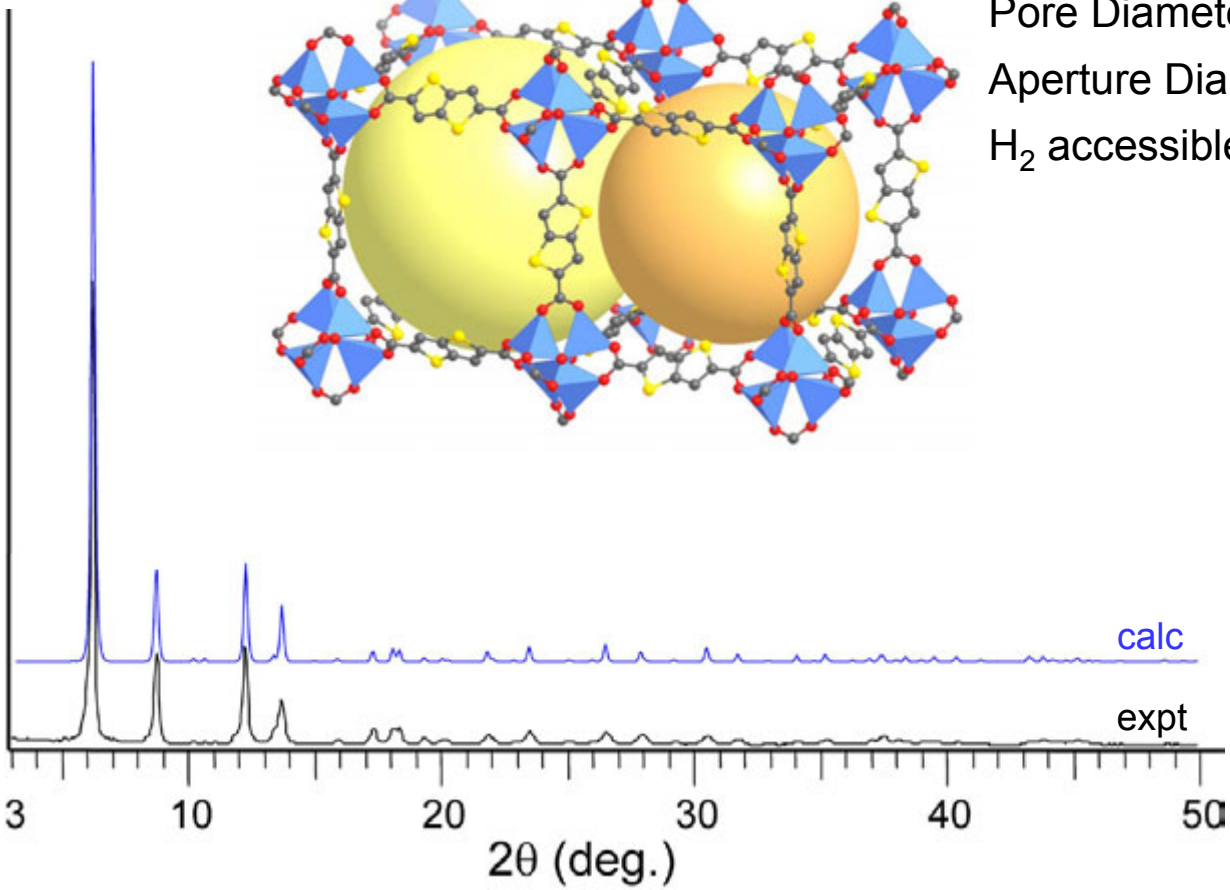
Empirical Formula: $C_{24}H_6O_{13}S_6Zn_4$

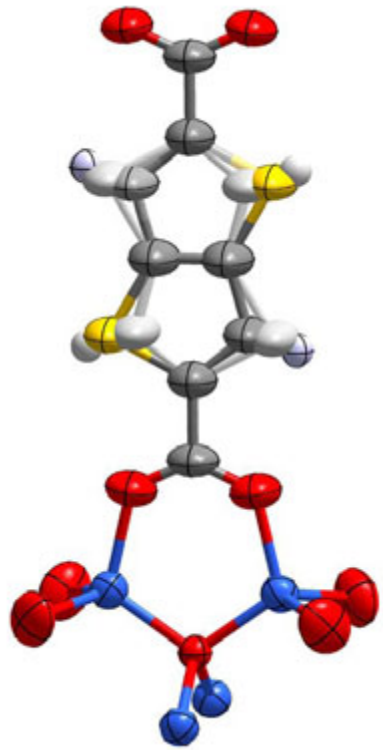
Crystal Data: $Fm\bar{3}m$, $a$ = 29.186(2) Å

Pore Diameters: 17.2, 14.3 Å

Aperture Diameter: 9.6 Å

$H_2$ accessible volume: 66 %



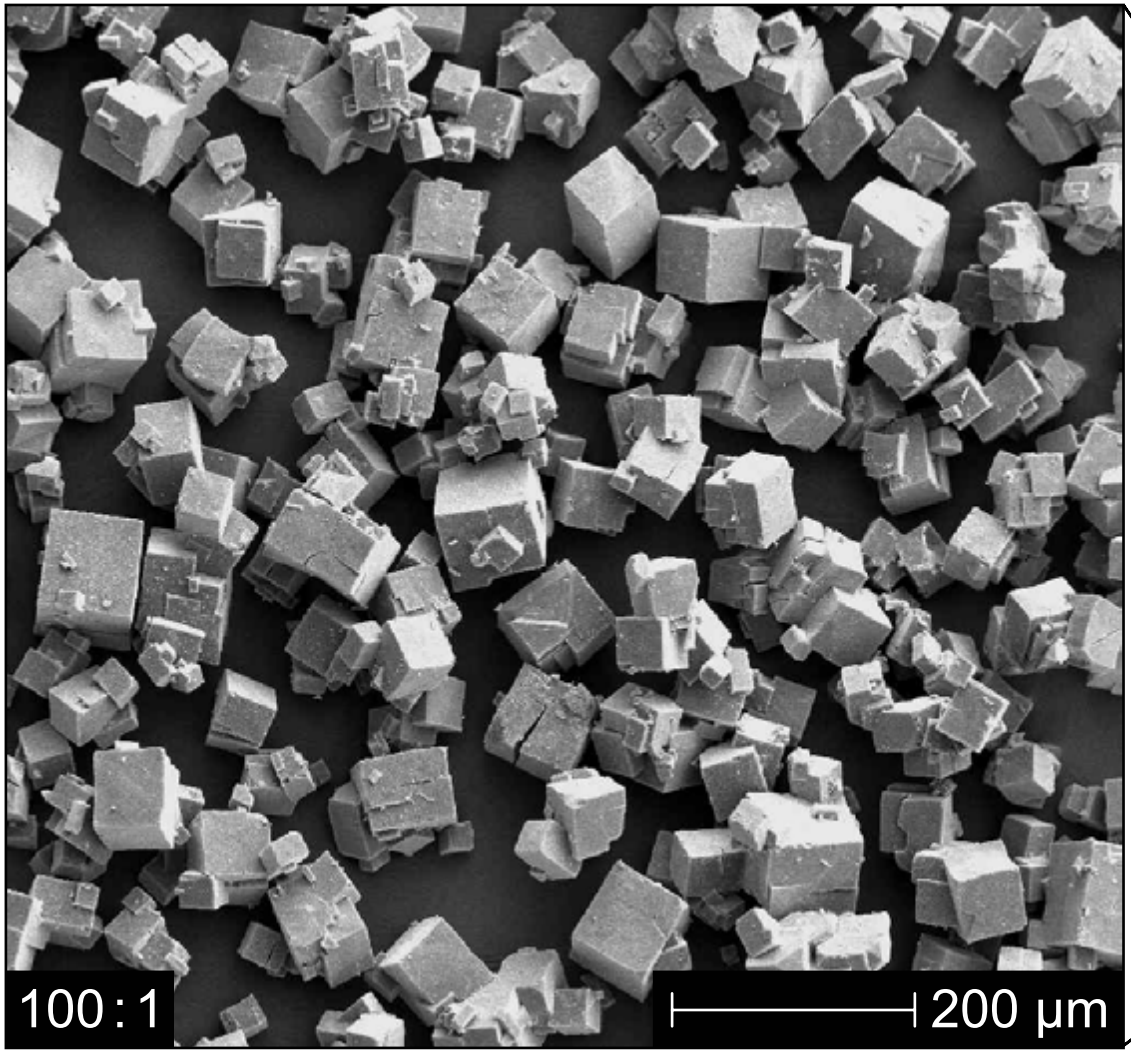
# *MOFs based on $Zn_4O(O_2C\text{-})_6$: Synthesis*

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

| 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*

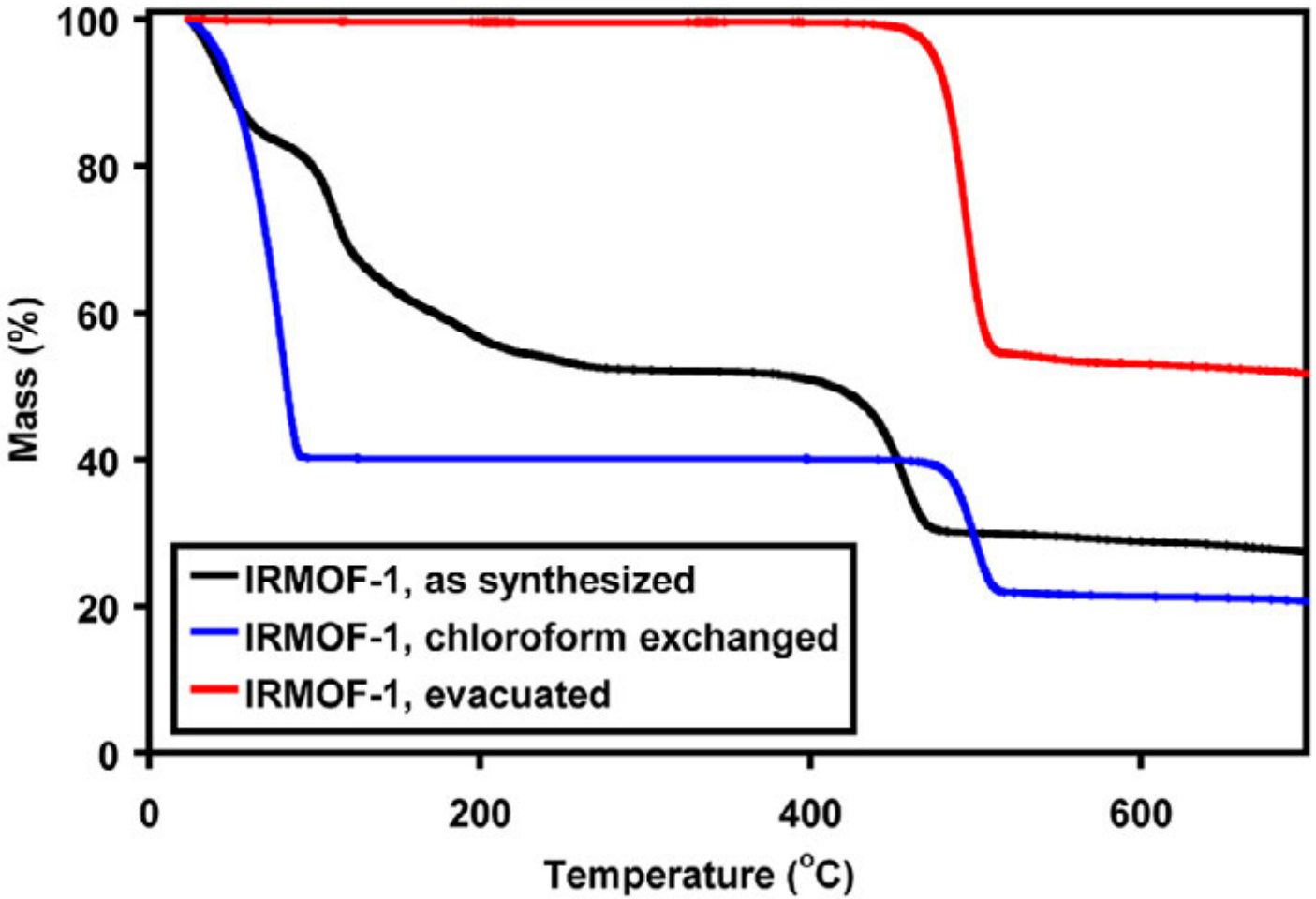


# $H_2$-Storage in MOFs Pilot Production IRMOF-8 ($m^3$-Scale)**(BASF, Dr. U. Müller)**

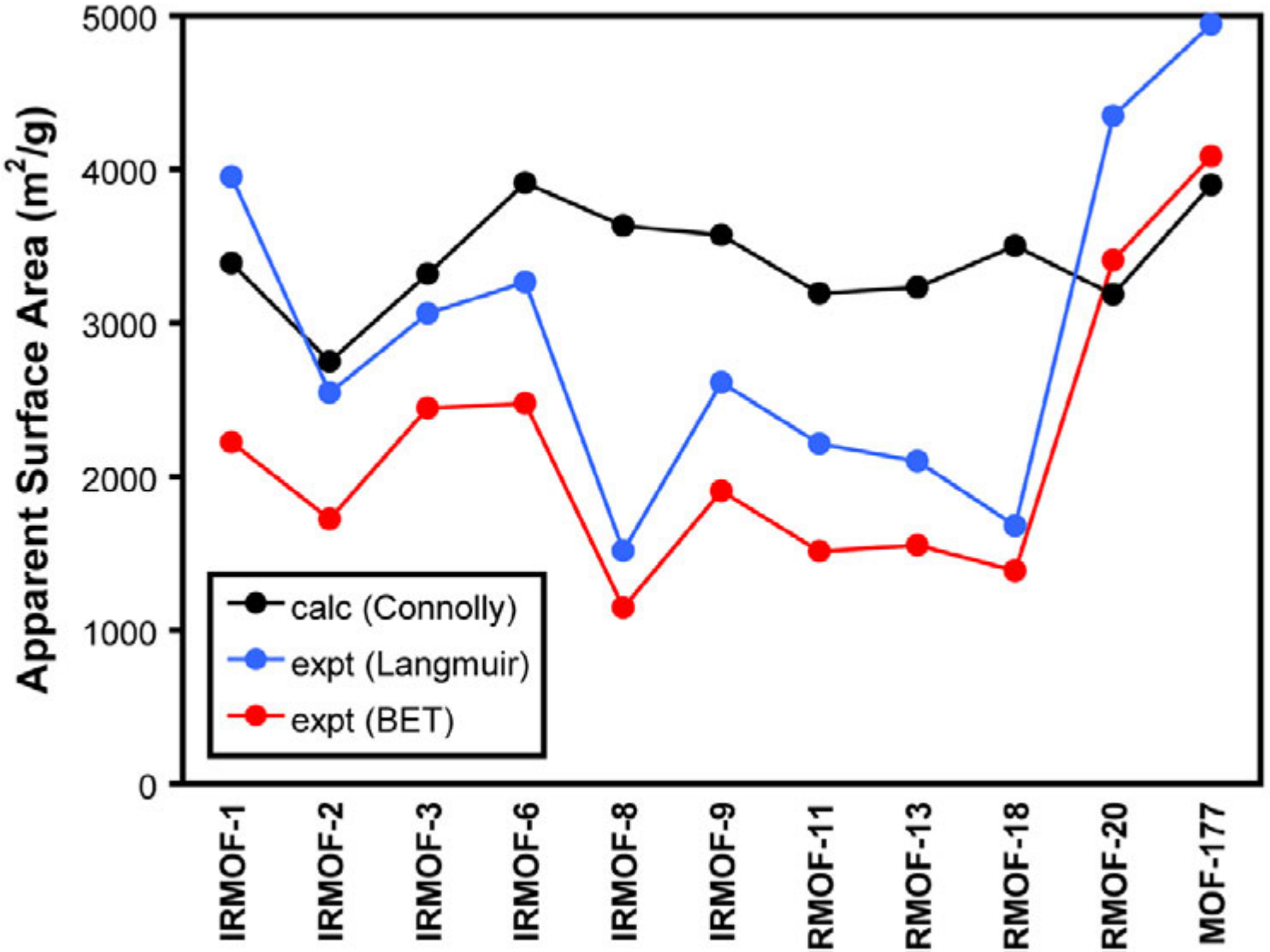
Semi-technical scale using ´state-of-art´manufacturing methods

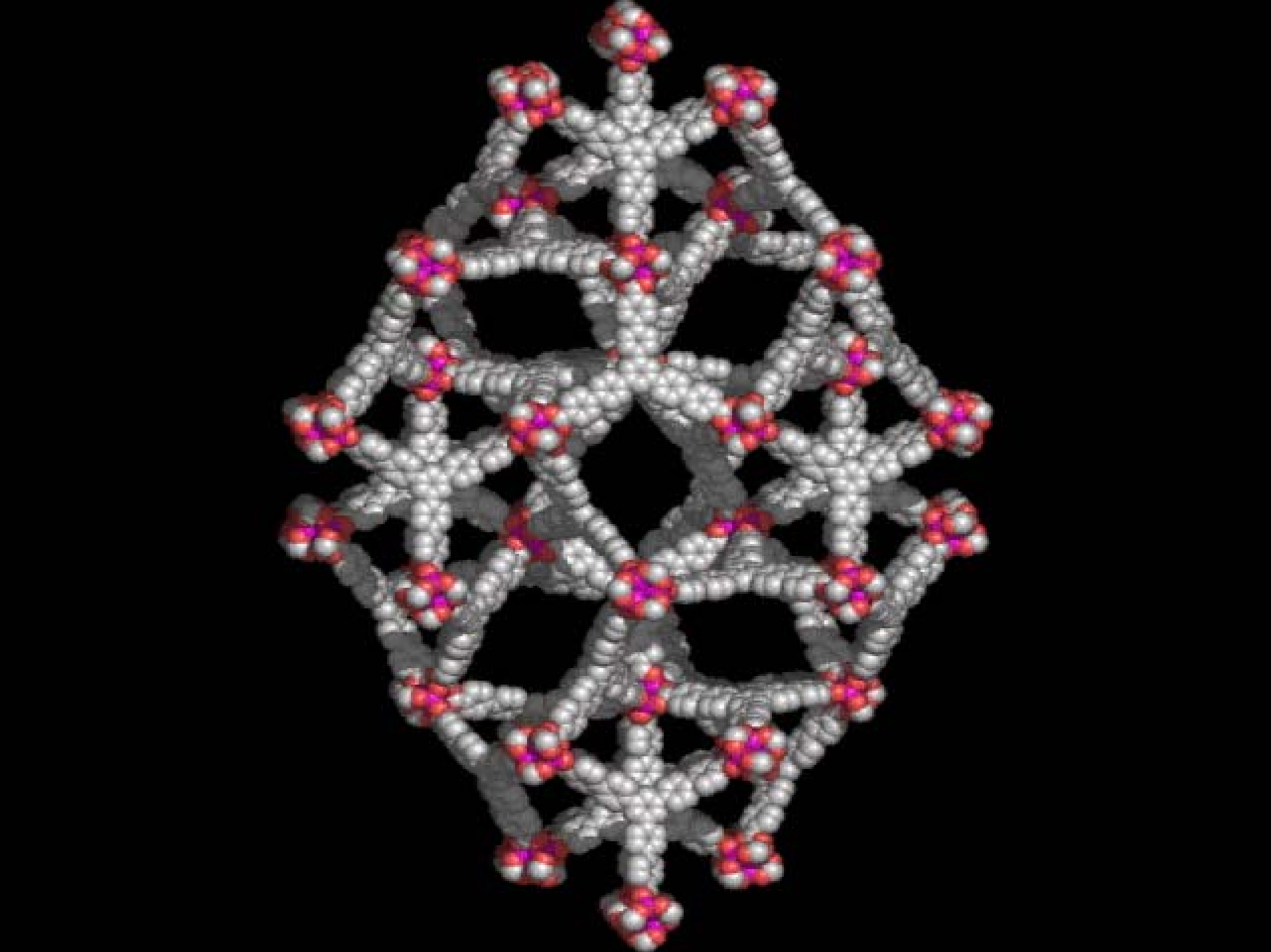
# MOFs based on $Zn_4O(O_2C\text{-})_6$: Activation

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

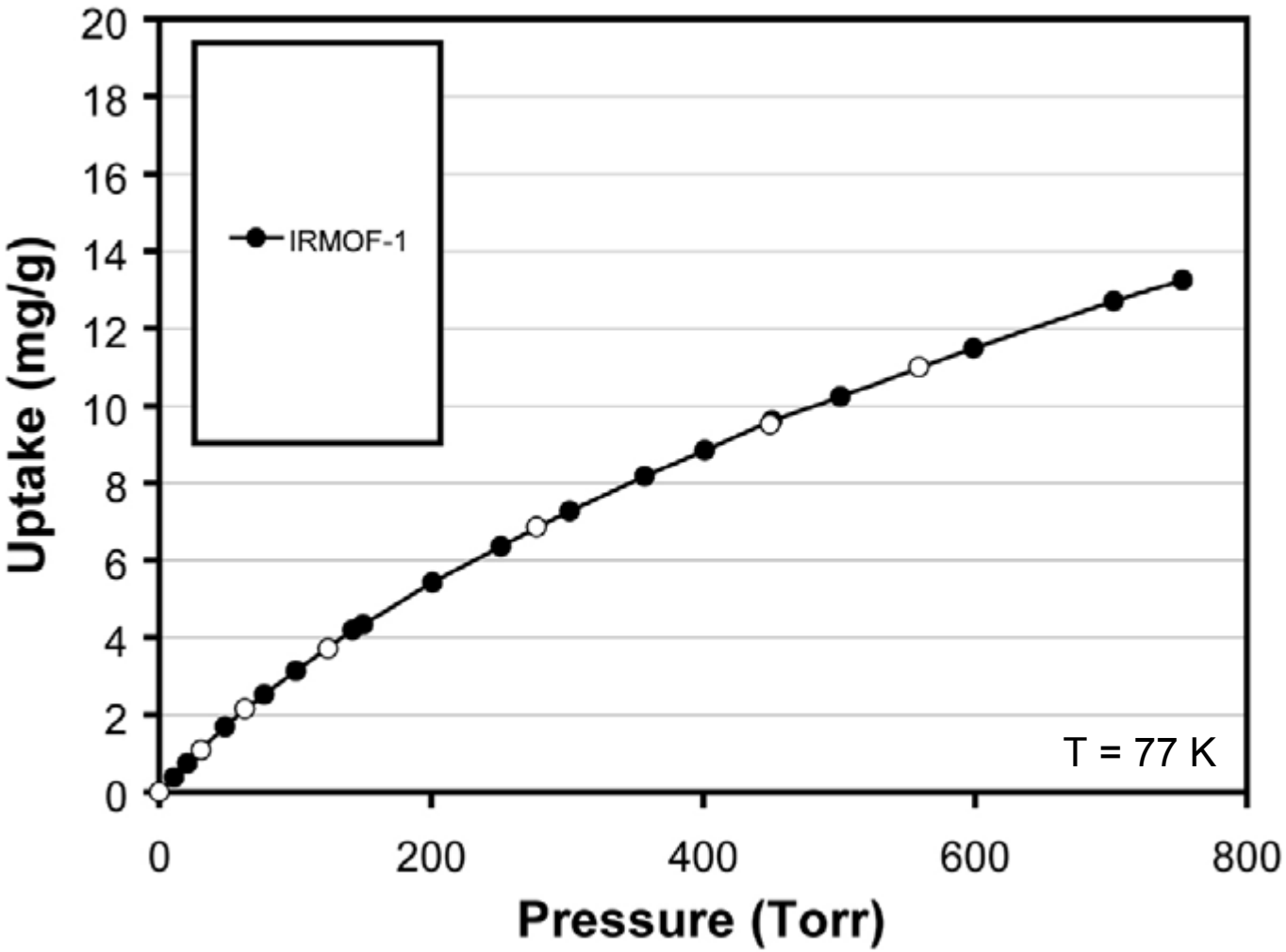


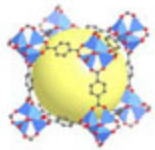
# MOFs based on $Zn_4O(O_2C\text{-})_6$: $N_2$ Adsorption





# $H_2$ Adsorption in Non-Catenated MOFs



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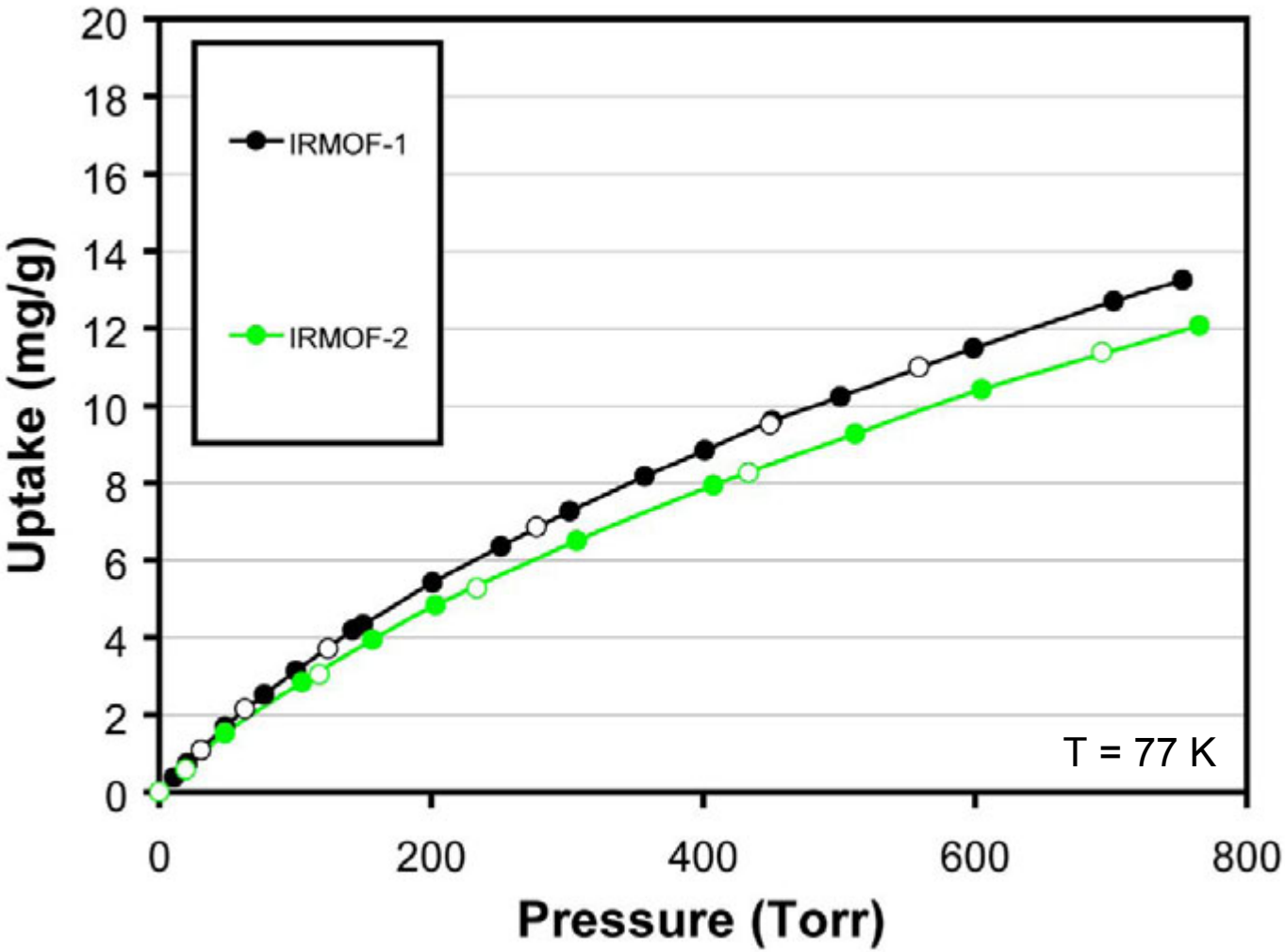
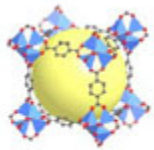
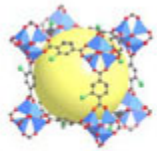
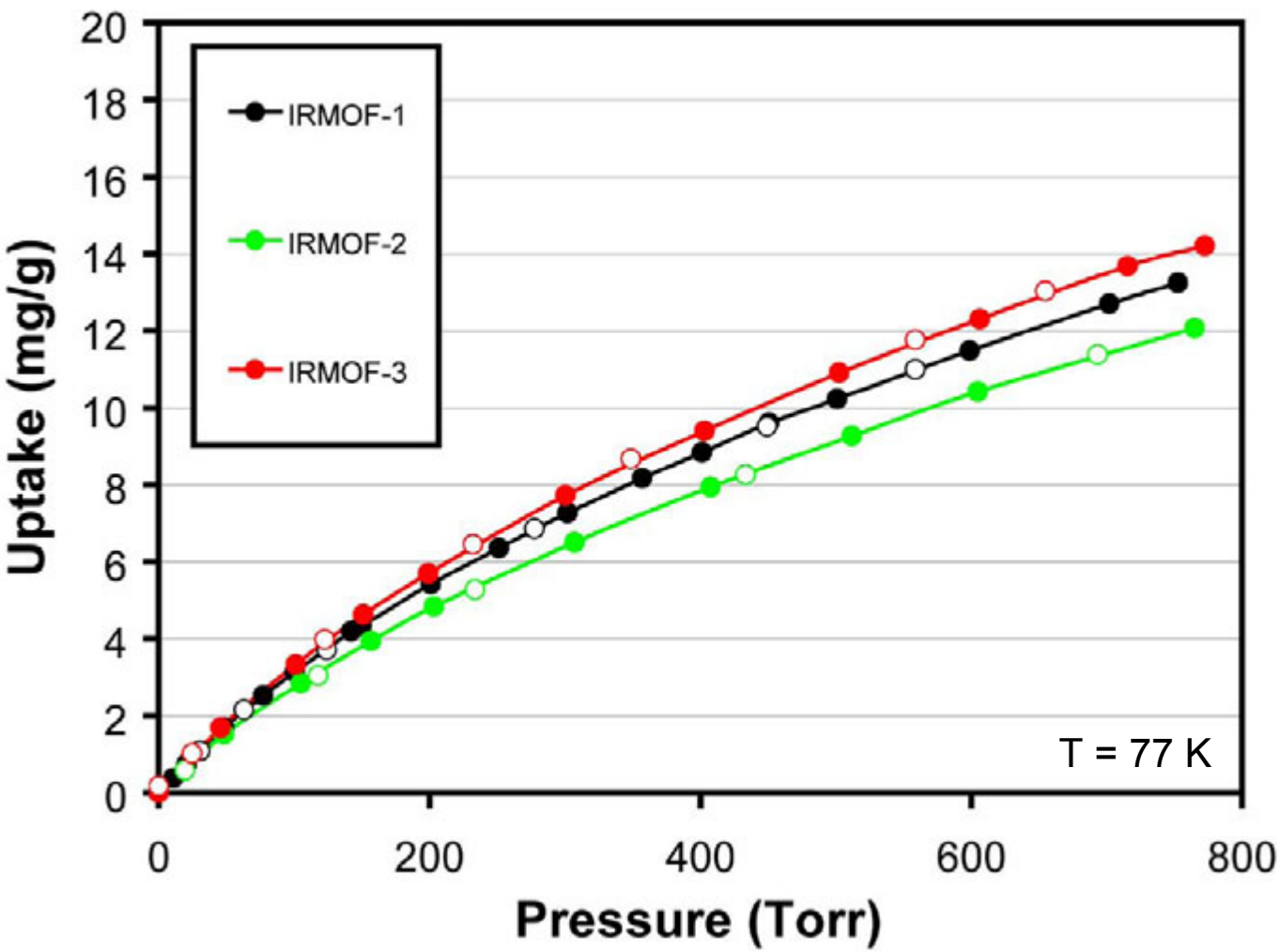
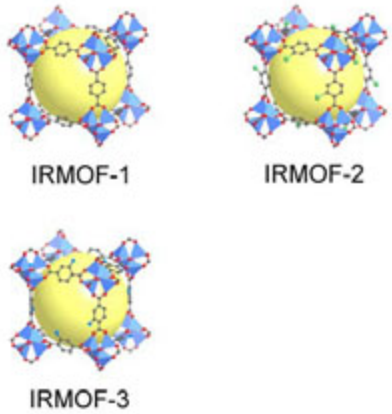




IRMOF-1


IRMOF-2

# $H_2$ Adsorption in Non-Catenated MOFs



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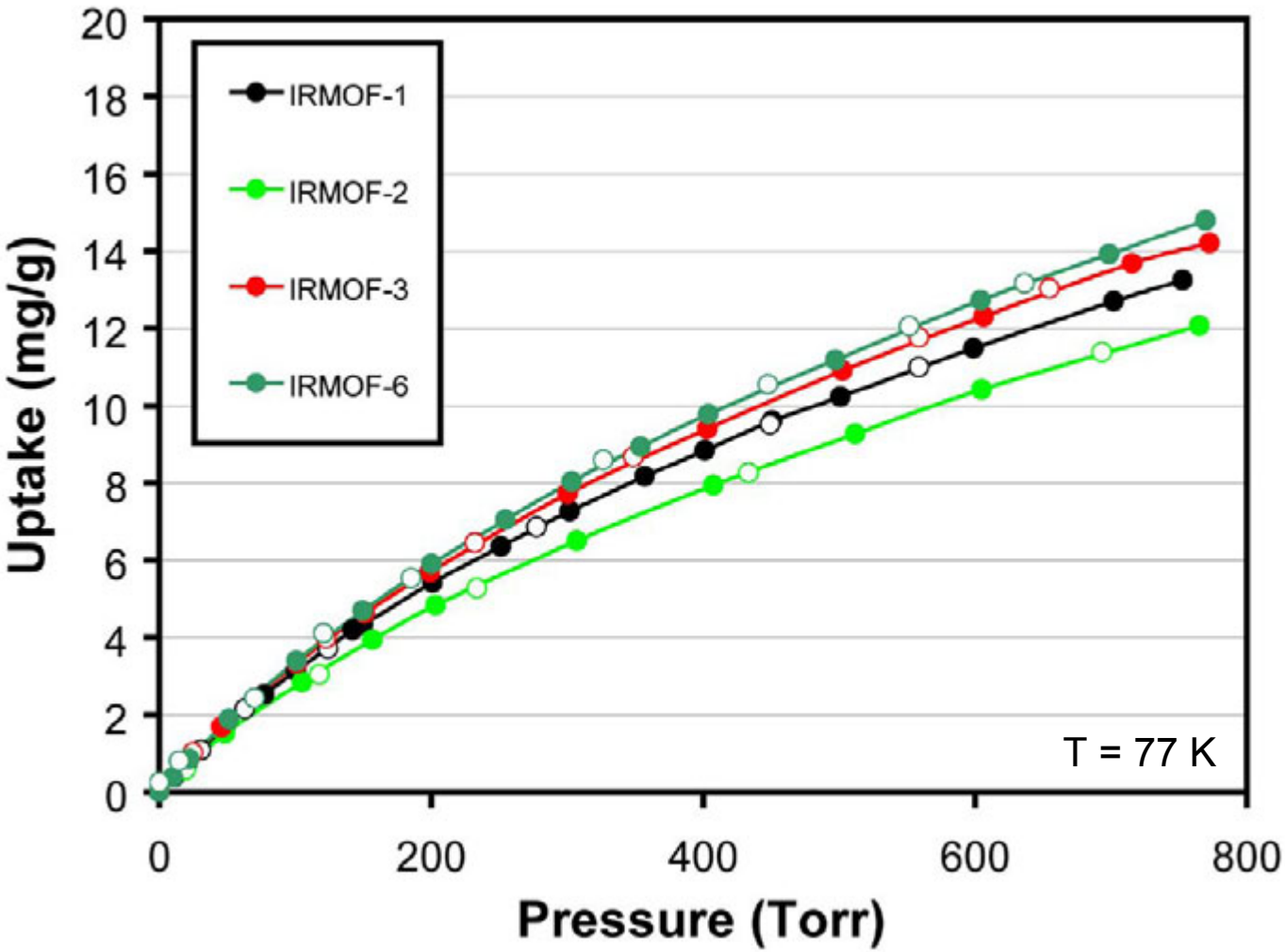


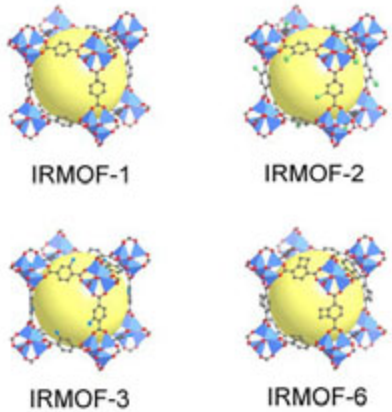

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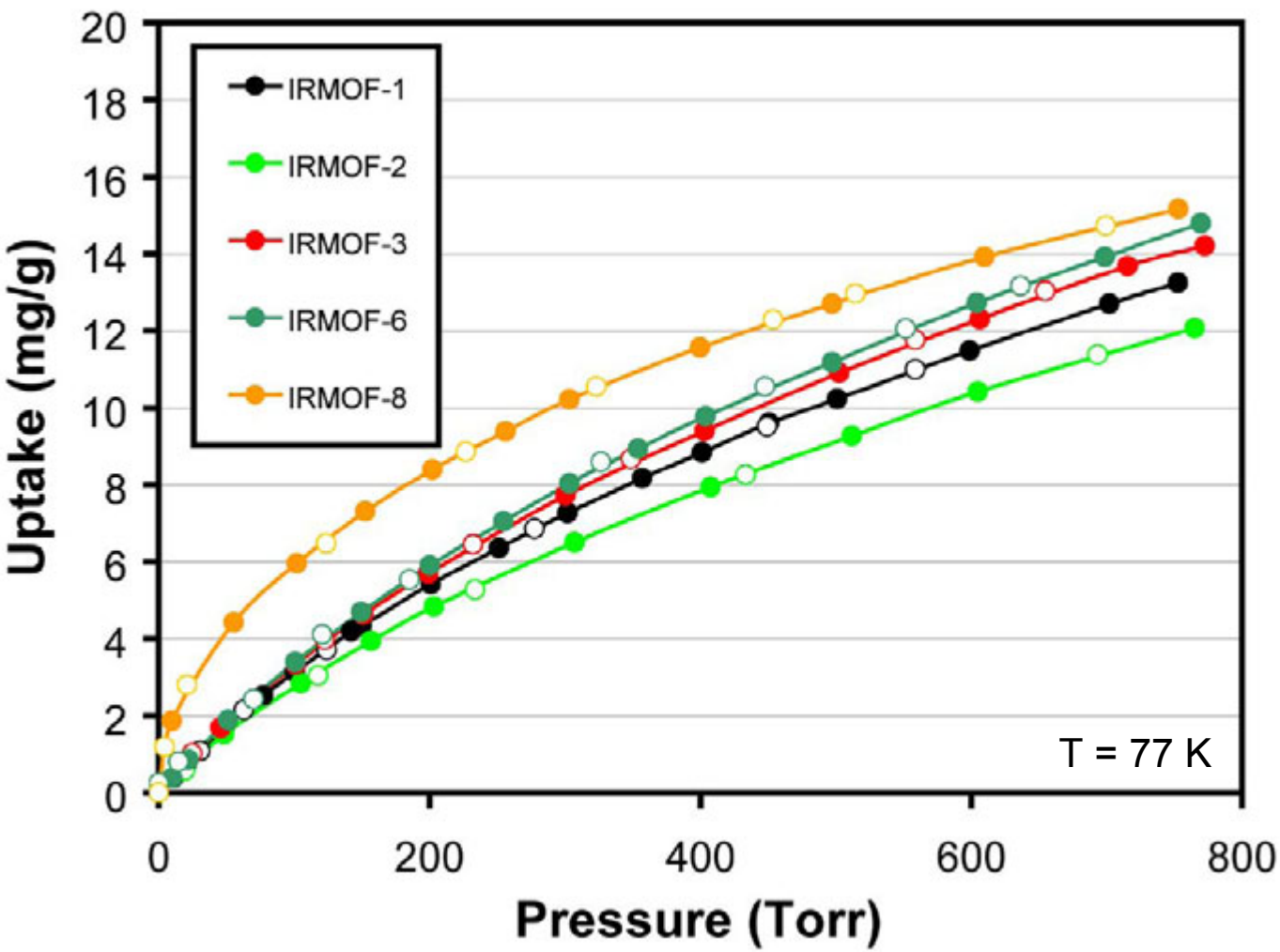


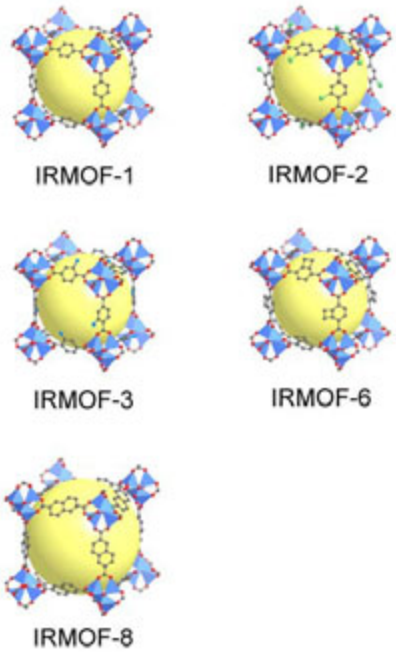

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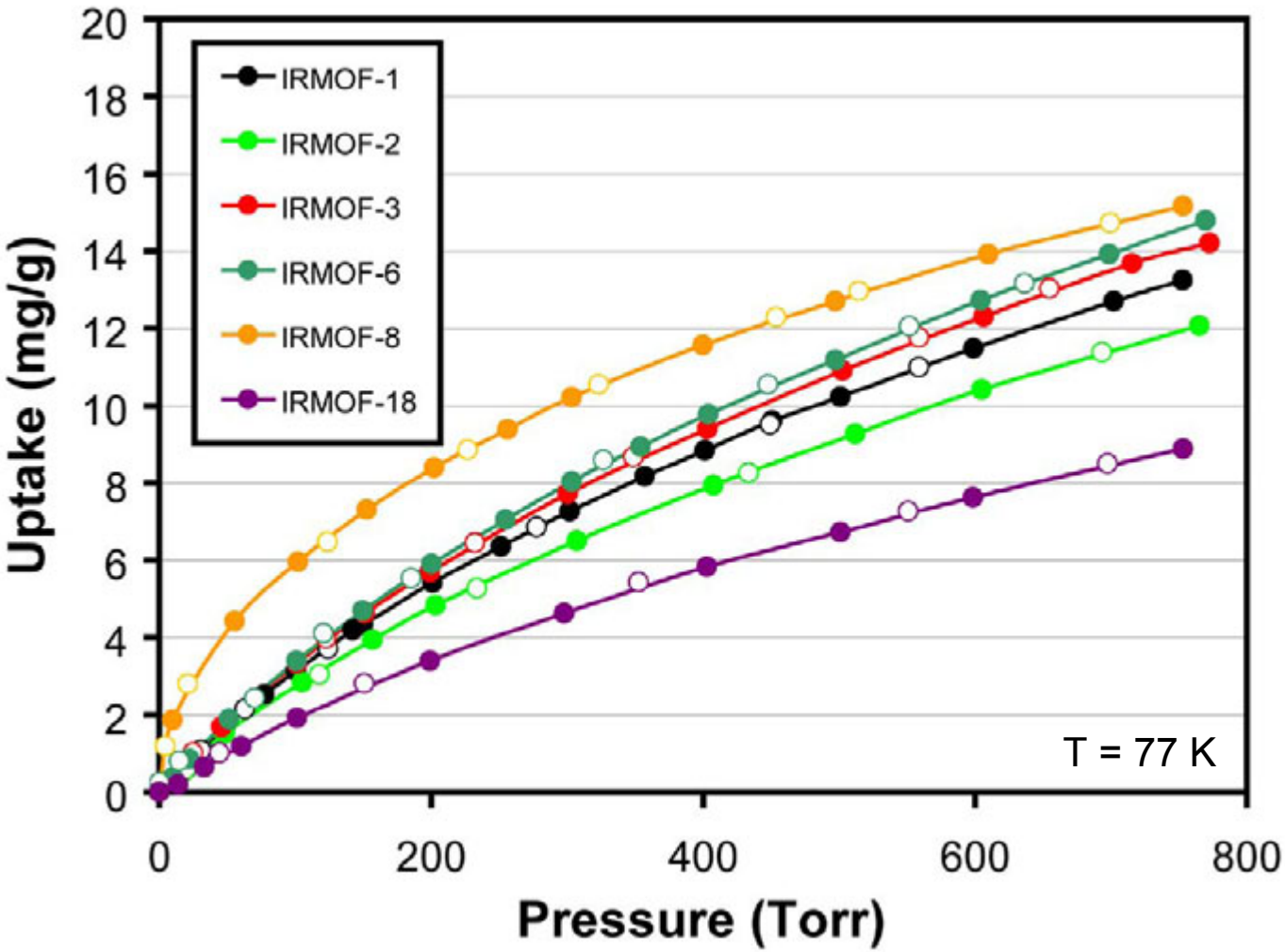


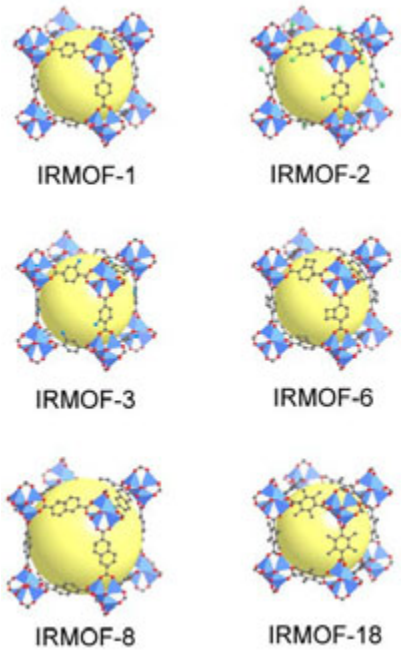

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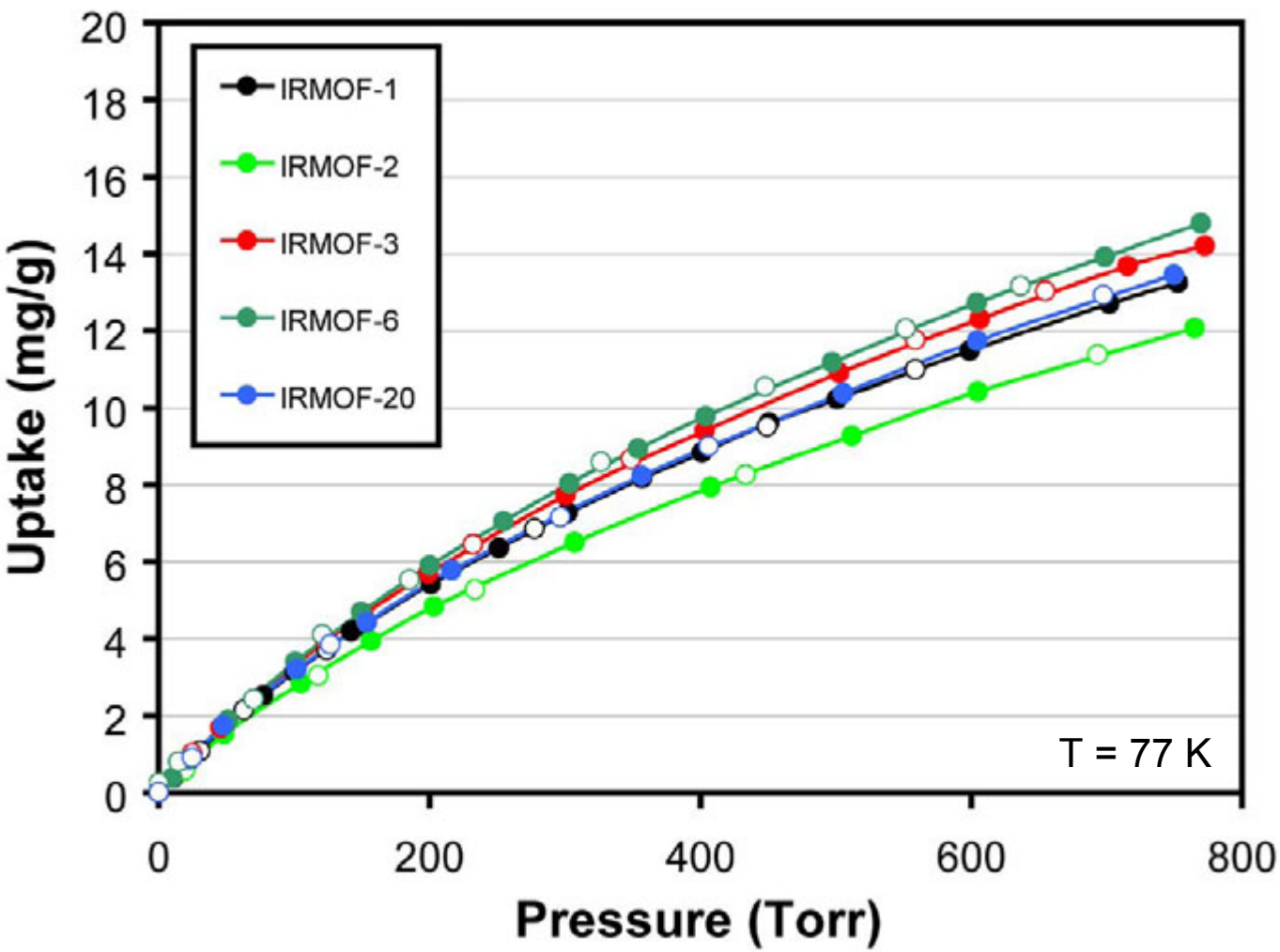


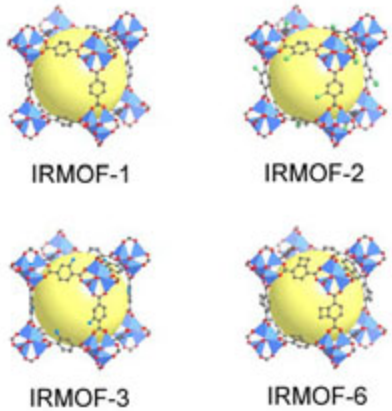


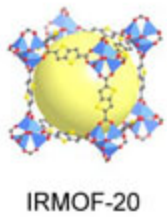

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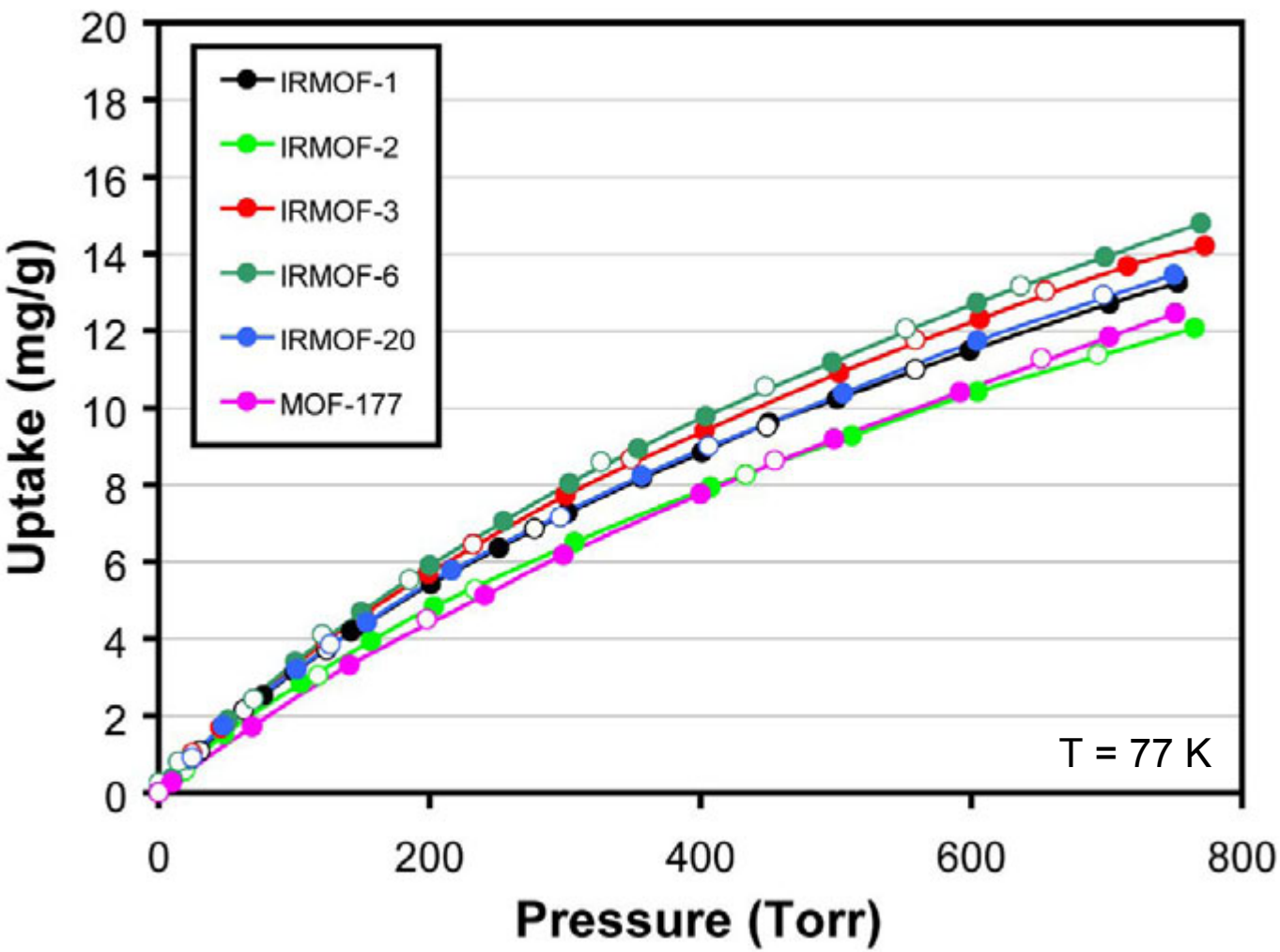


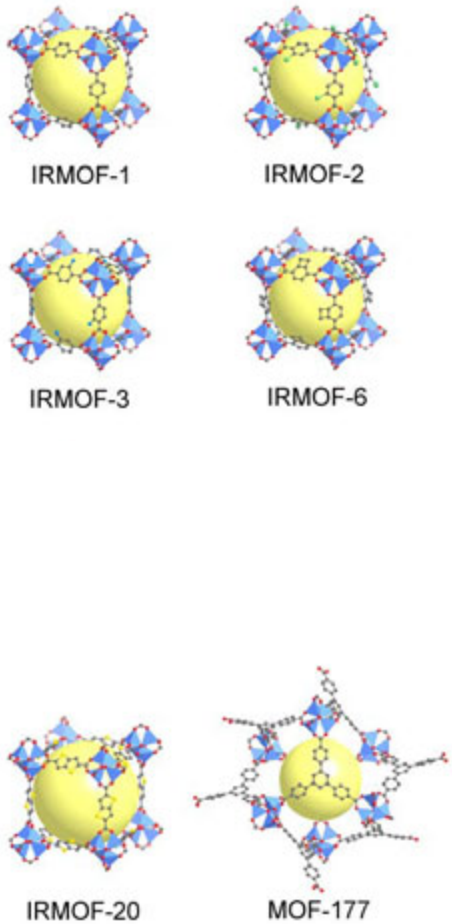

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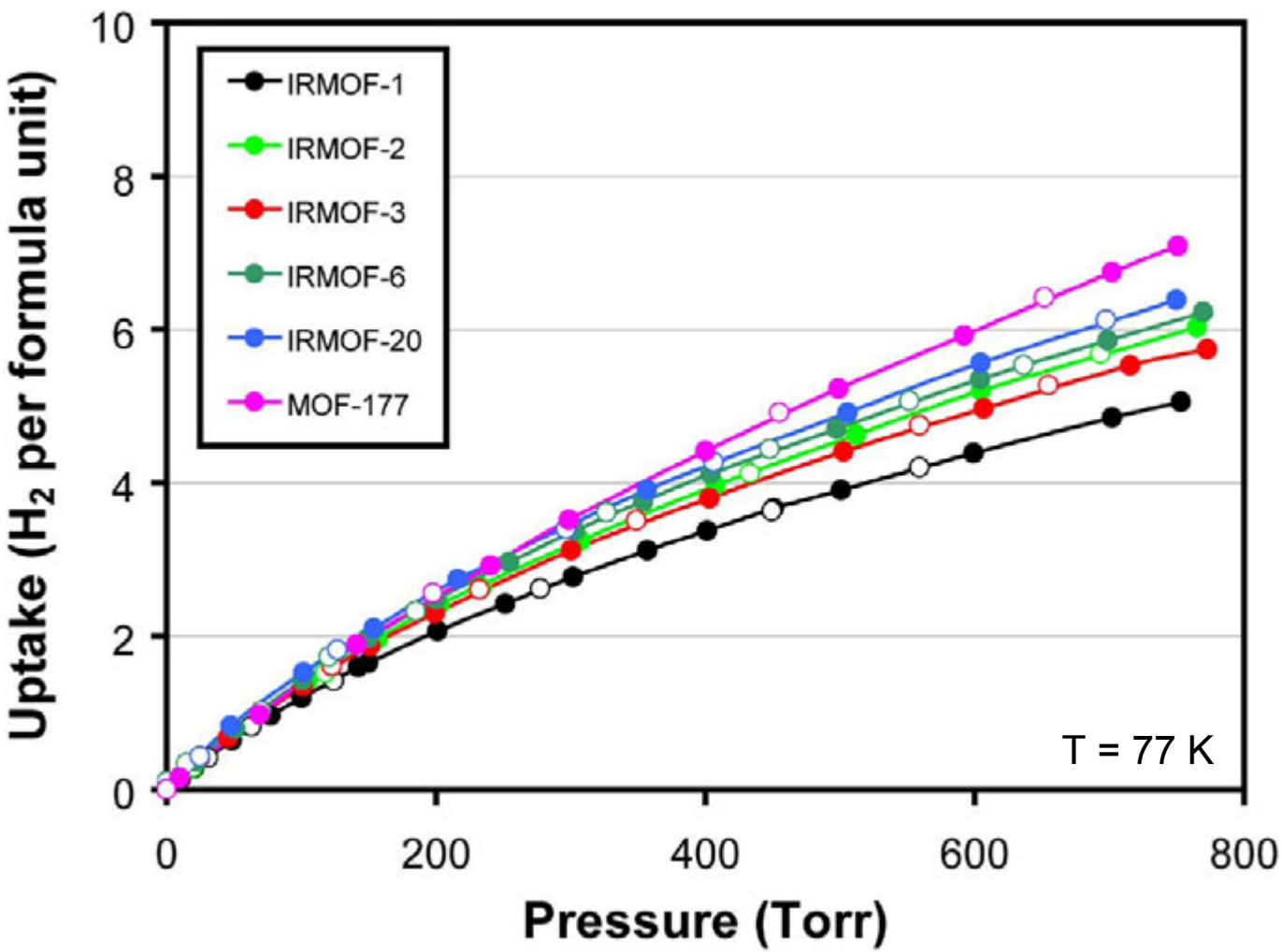
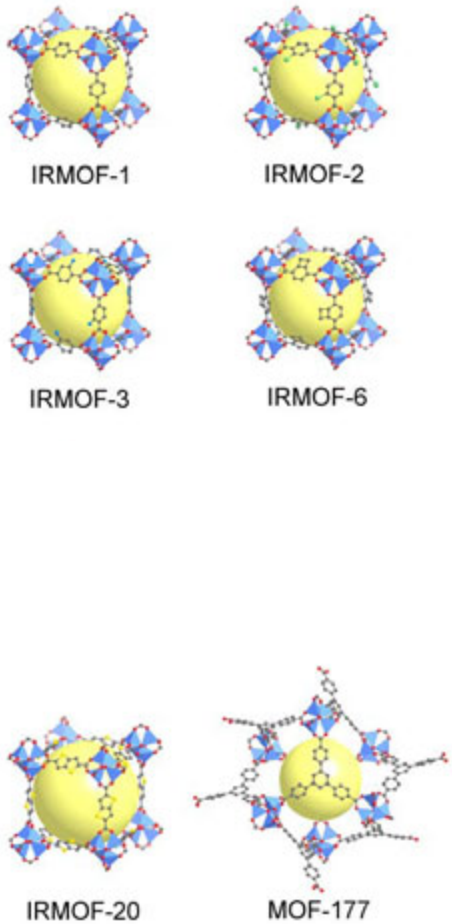
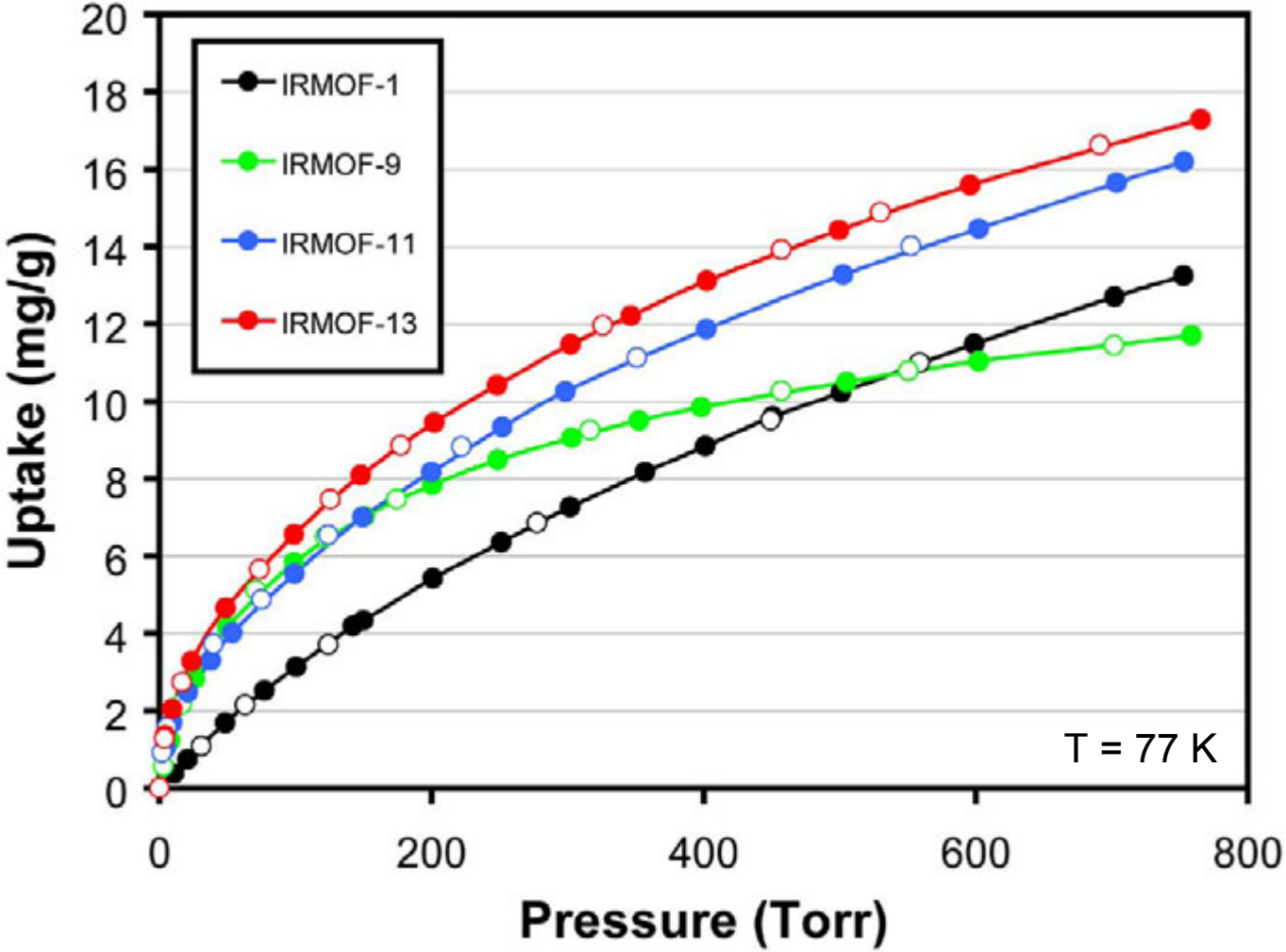
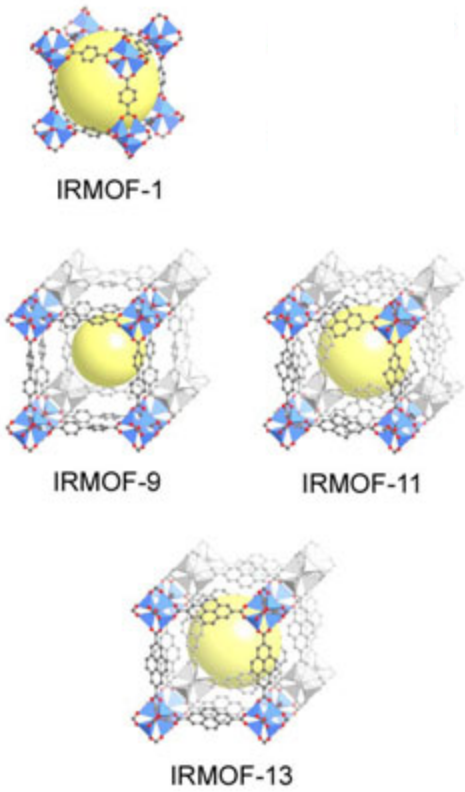


# $H_2$ Adsorption in Catenated MOFs



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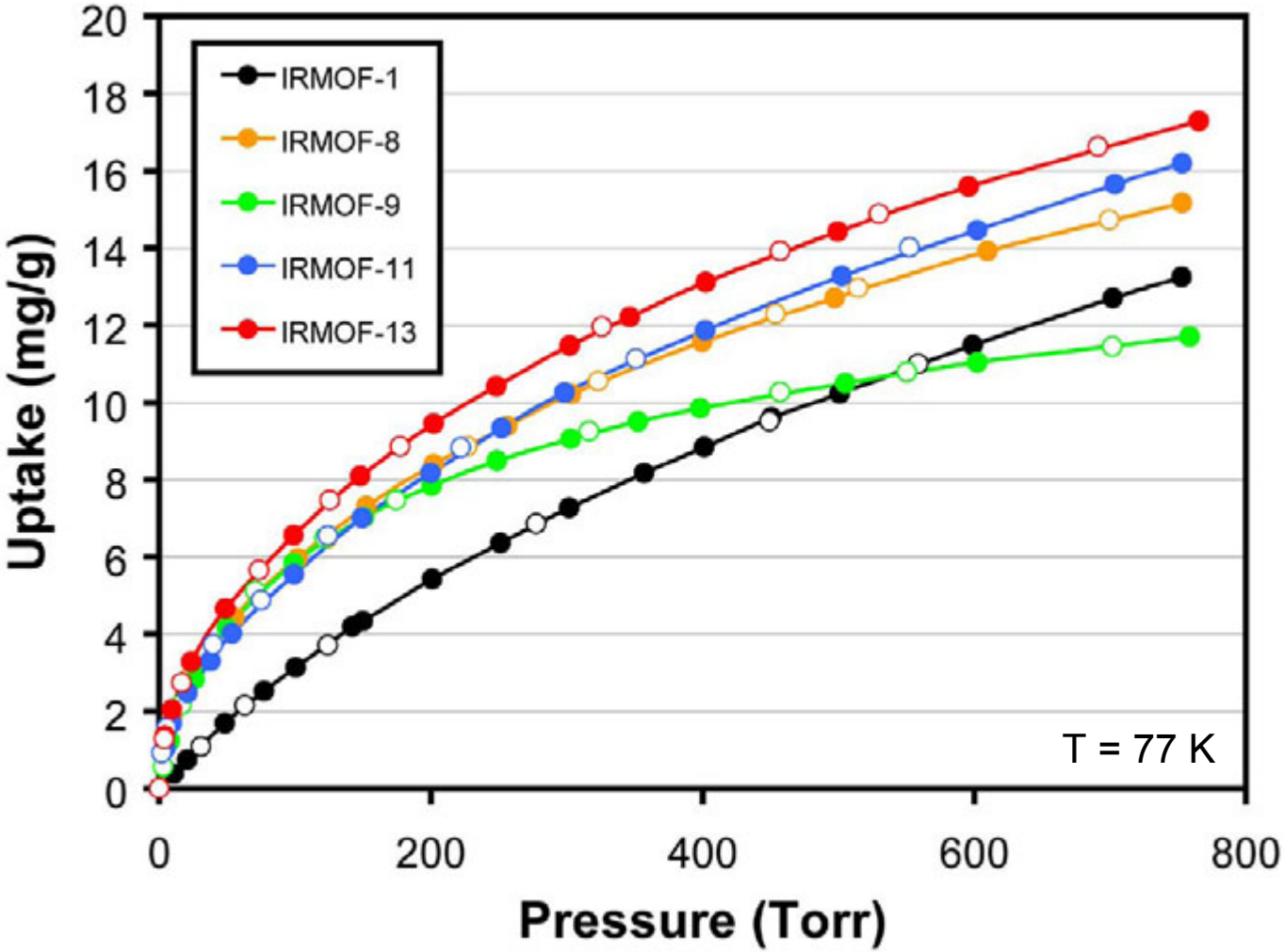


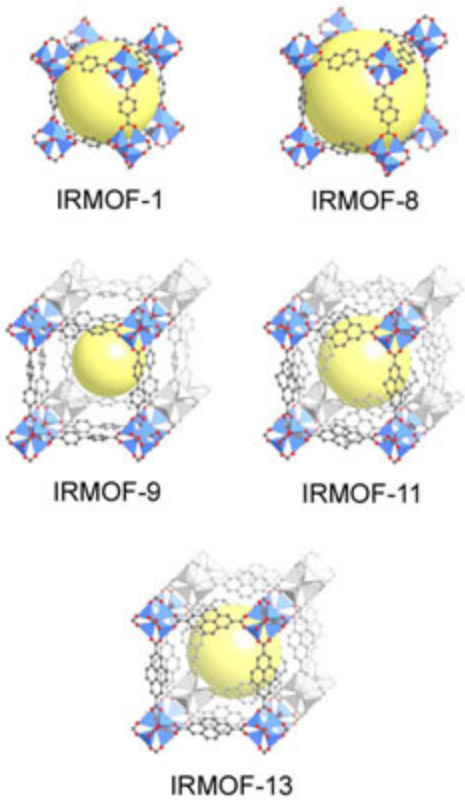

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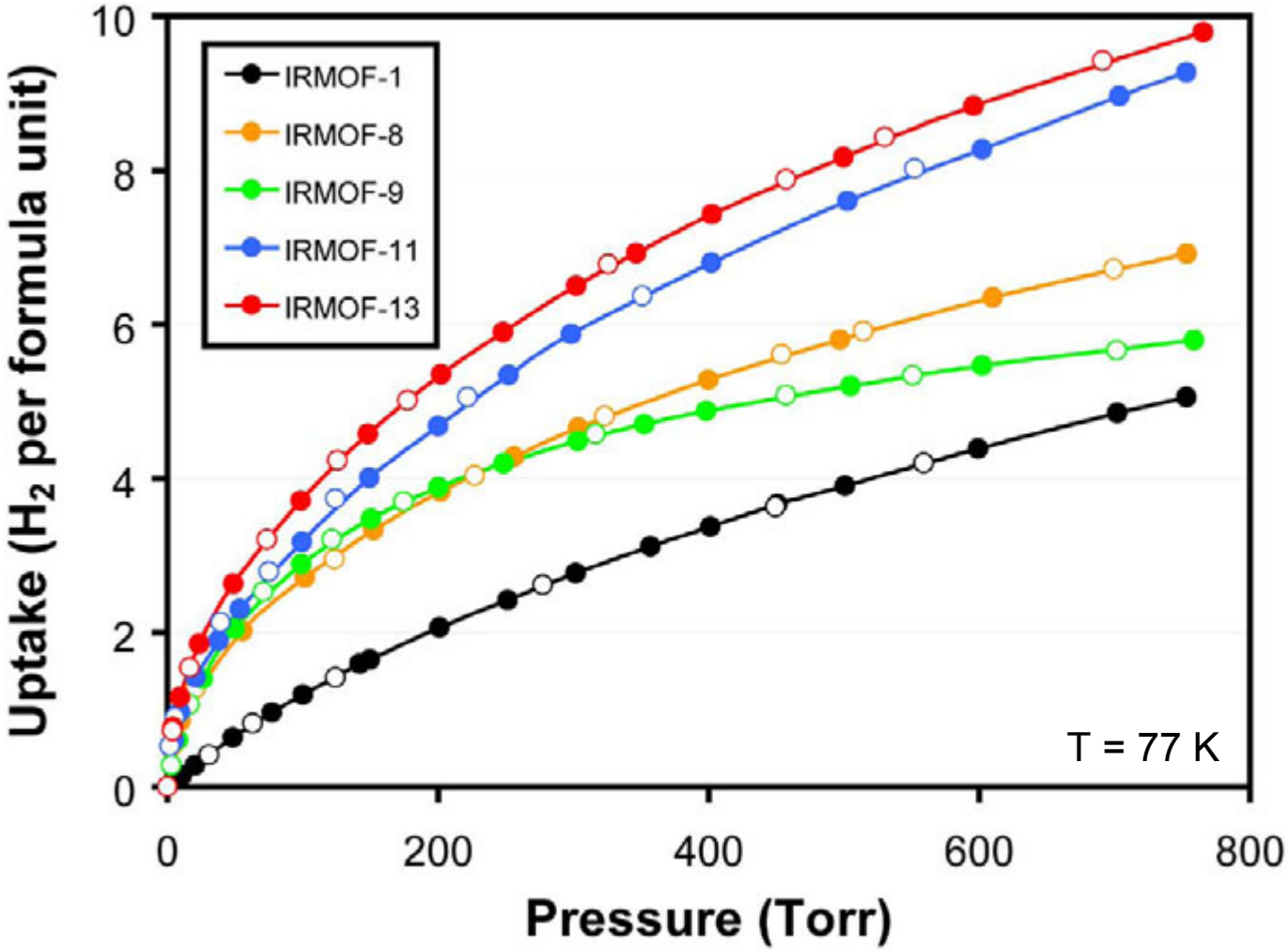
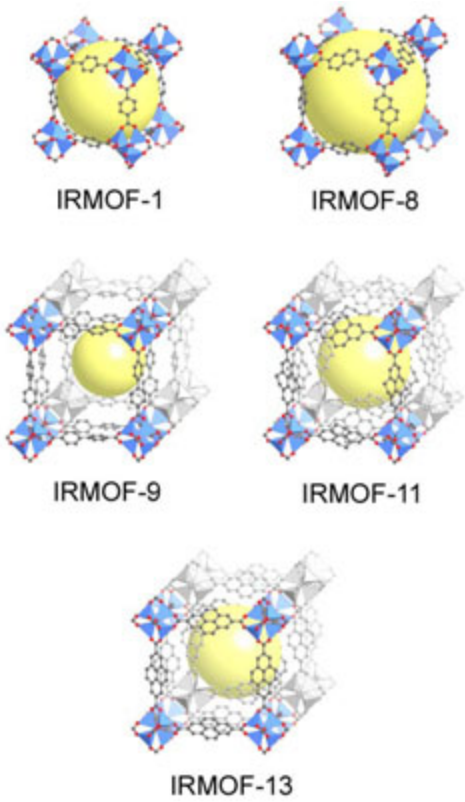
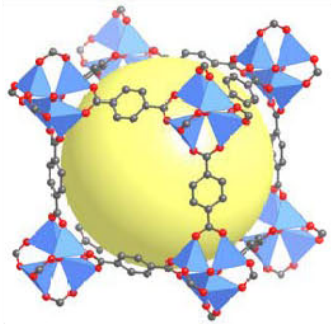
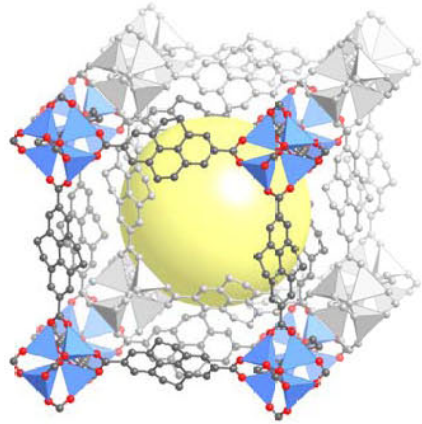
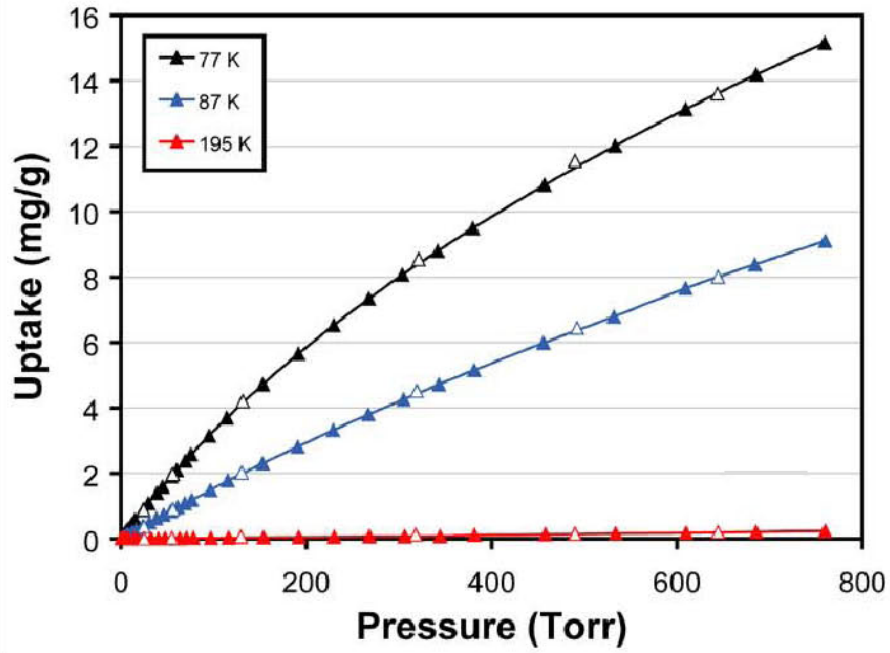


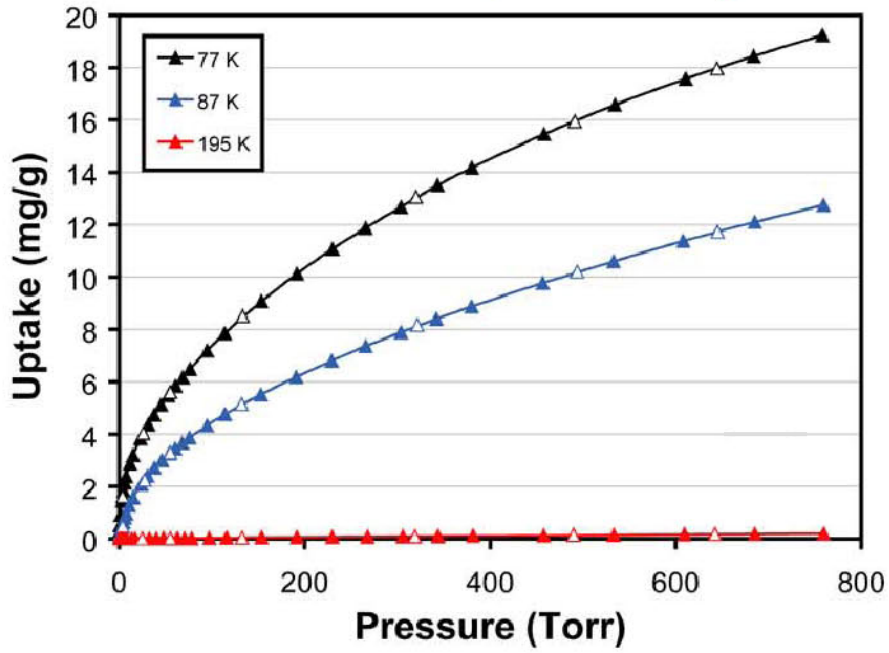



# T Dependence of $H_2$ Uptake: IRMOF-1 and -11



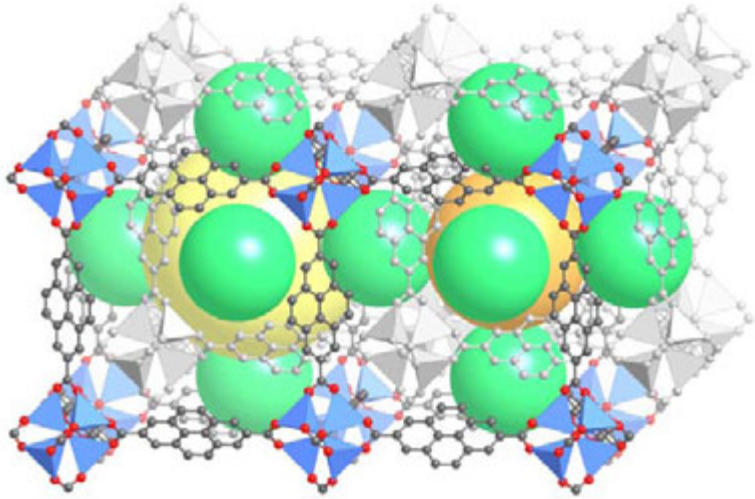


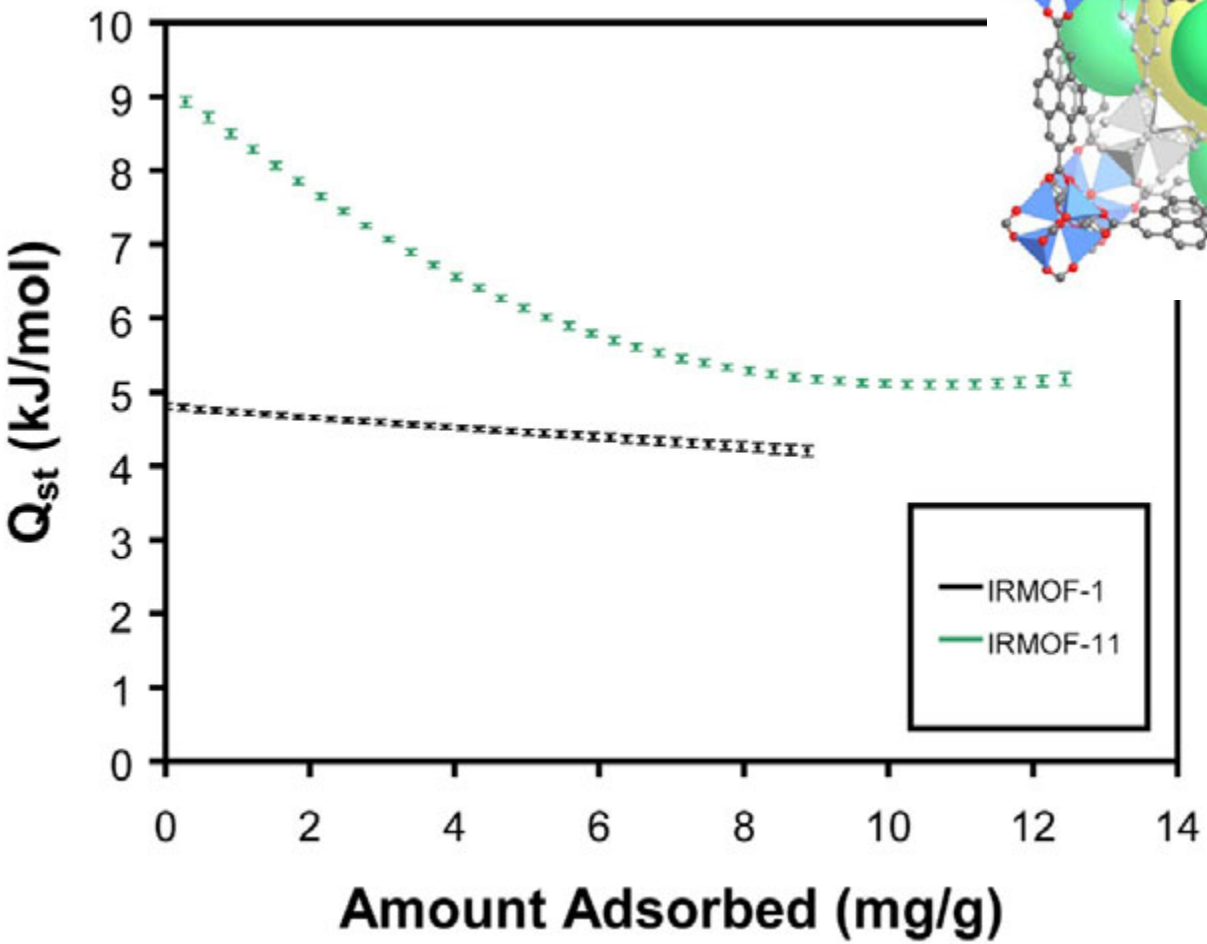


# *Isosteric Heats of Adsorption*

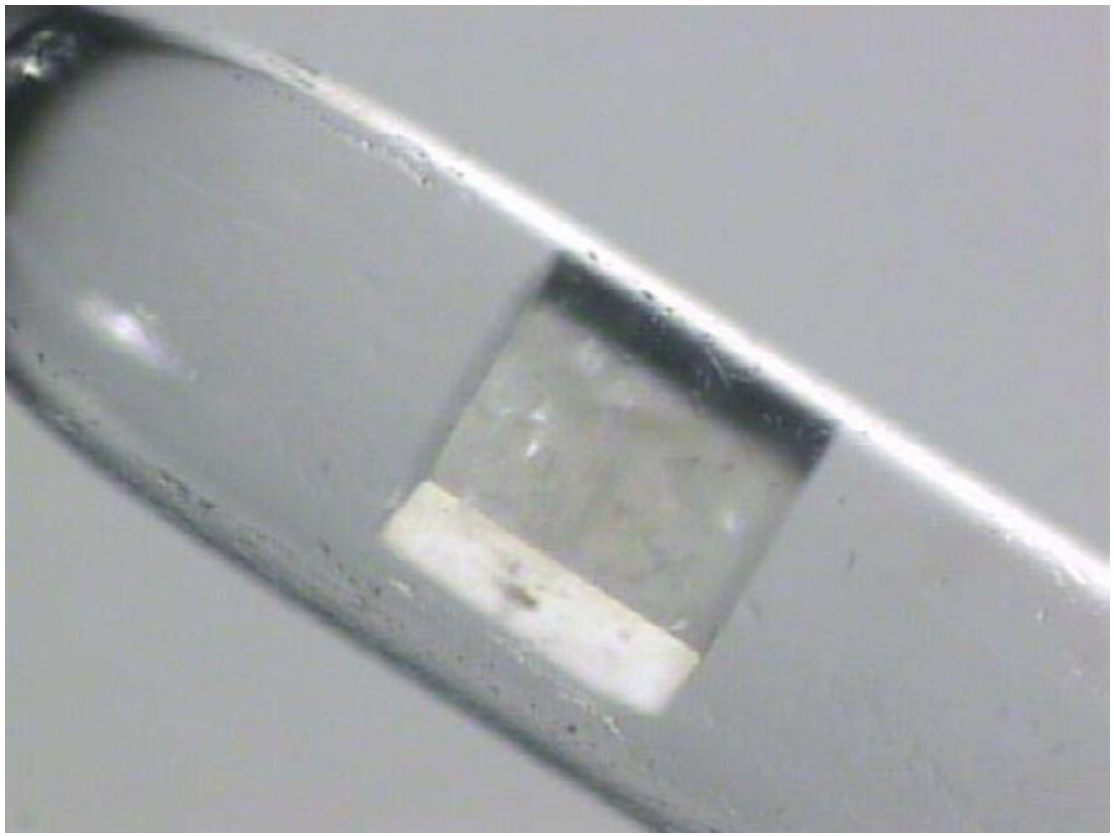
- values extracted by fitting isotherms with virial-type expansions






- pore constriction results in overlap of the attractive surface potential

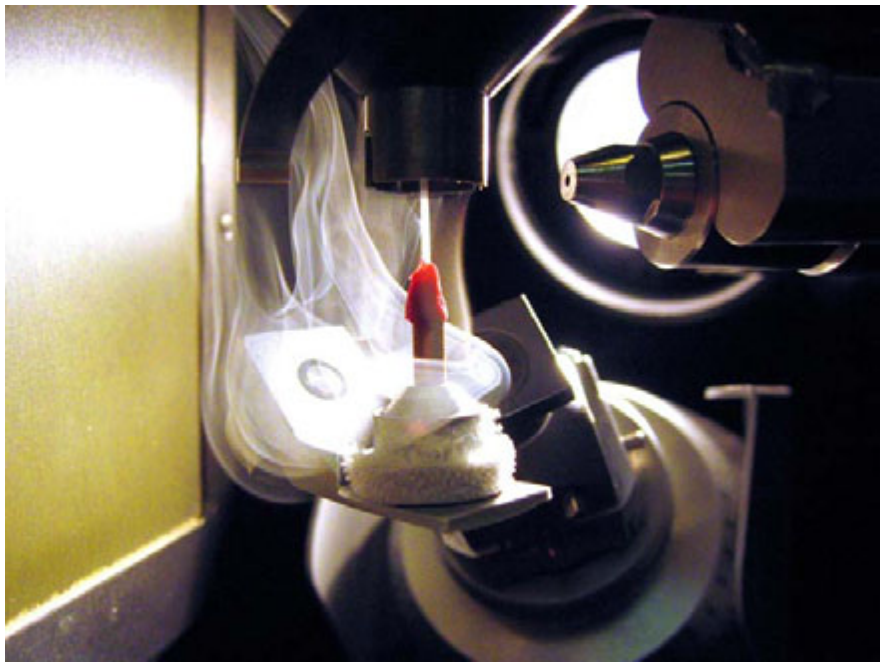
# *Evacuated Single Crystals of IRMOF-1*



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

# *Low Temperature Single Crystal X-ray Diffraction*

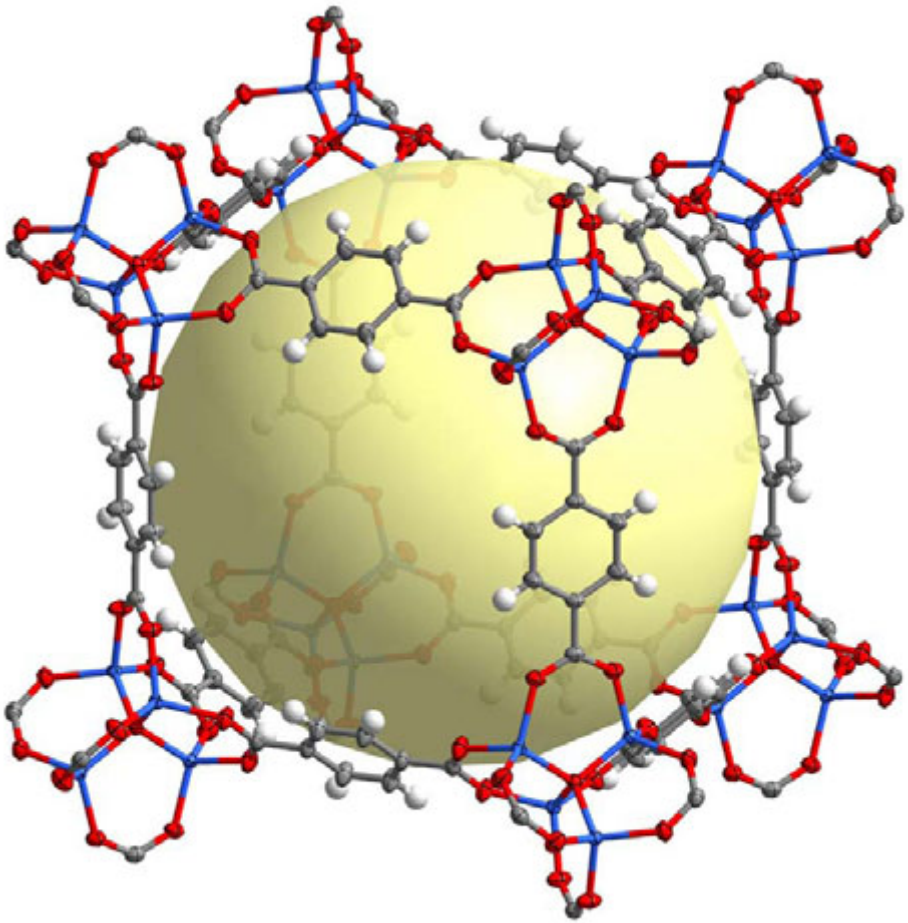
- Helix cryostat (University of Durham, UK) provides temperature control to 30 K

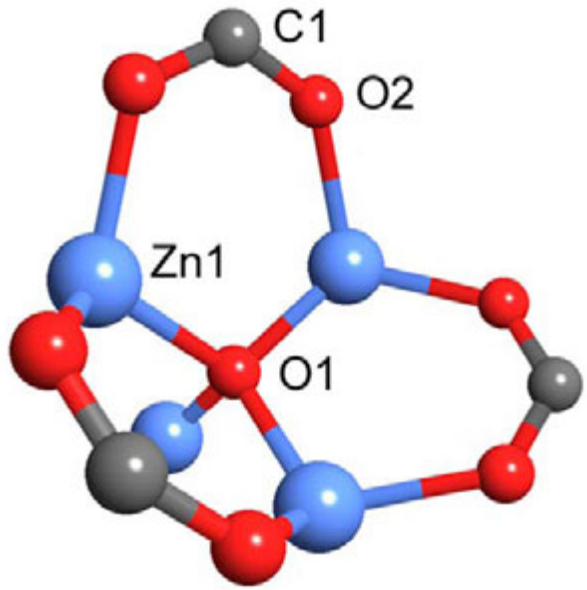


Refinement of evacuated framework at 30 K:

| | |
|---|---|
| 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$^3$ |
| $\theta$ 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.

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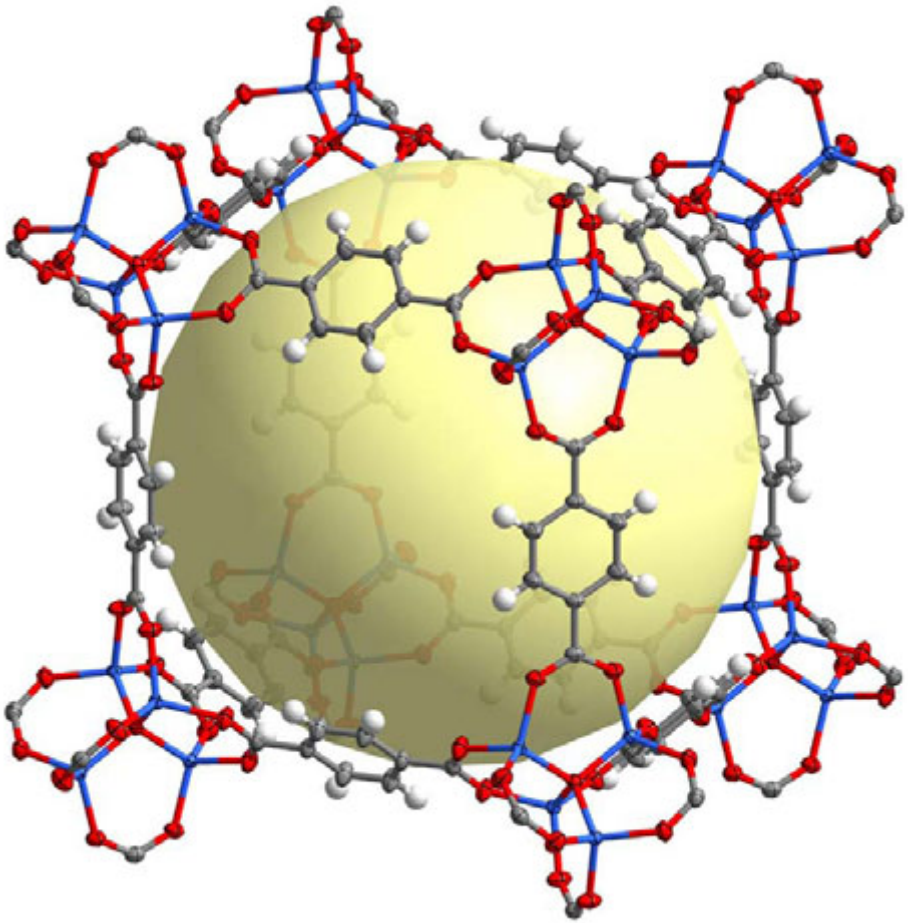

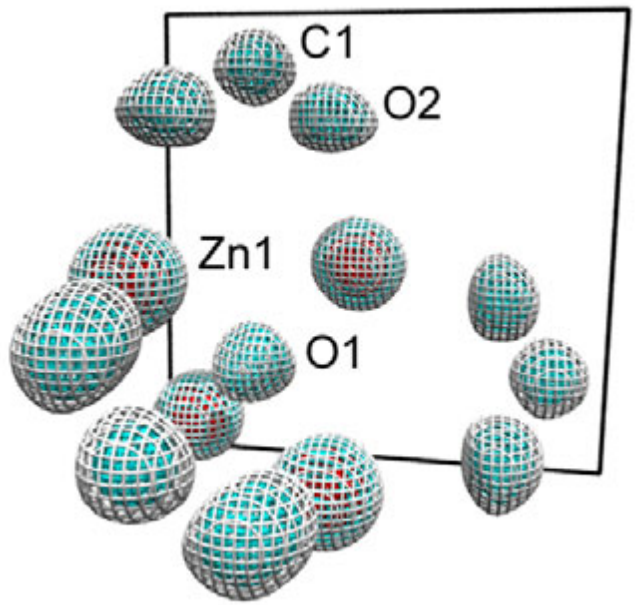


J.L.C. Rowsell, E.C. Spencer, J. Eckert, J.A.K. Howard, O.M. Yaghi, *Science* **2005**, *309*, 1350.

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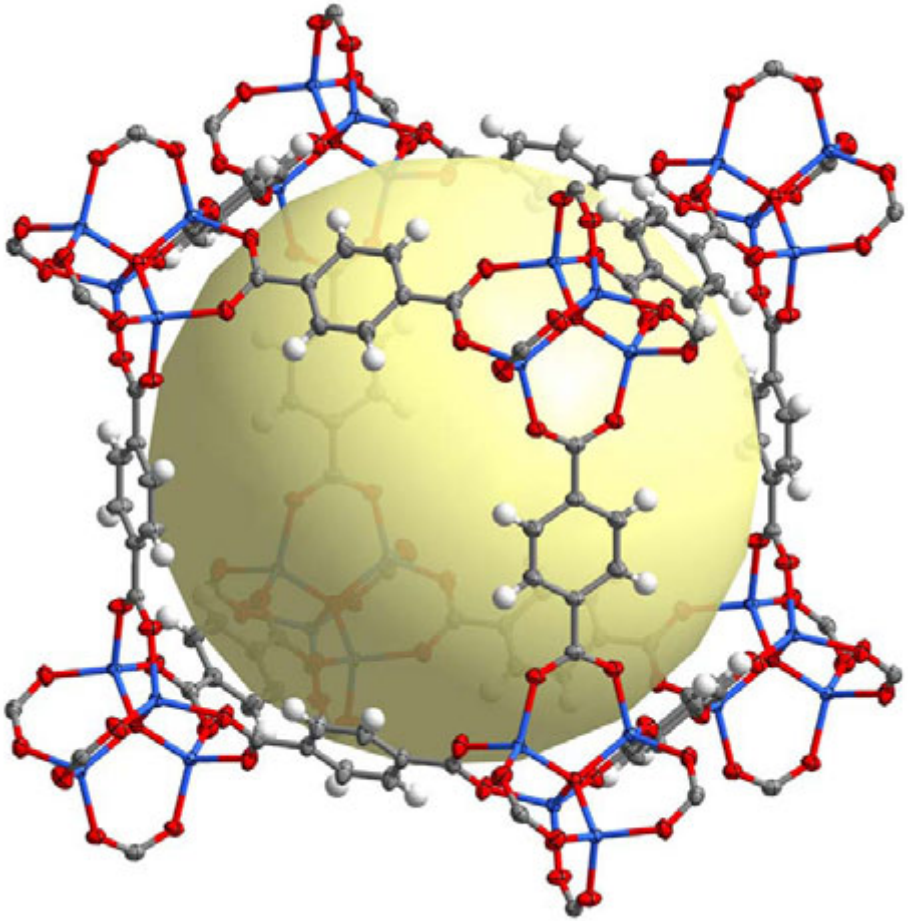

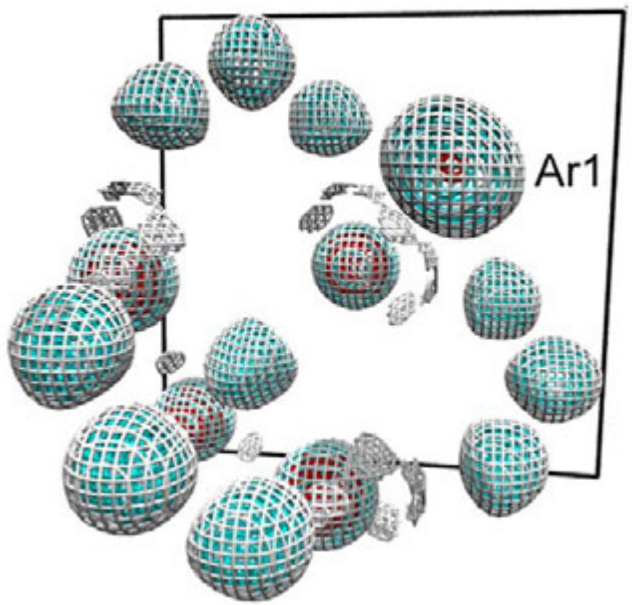


J.L.C. Rowsell, E.C. Spencer, J. Eckert, J.A.K. Howard, O.M. Yaghi, *Science* **2005**, *309*, 1350.

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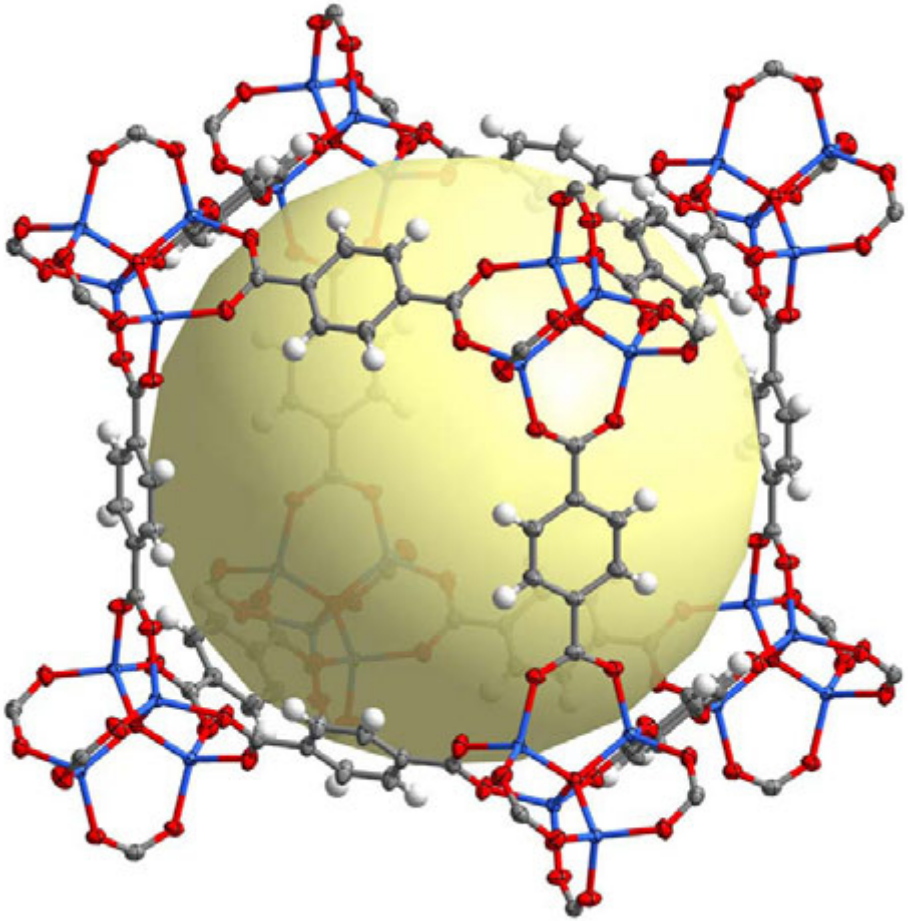
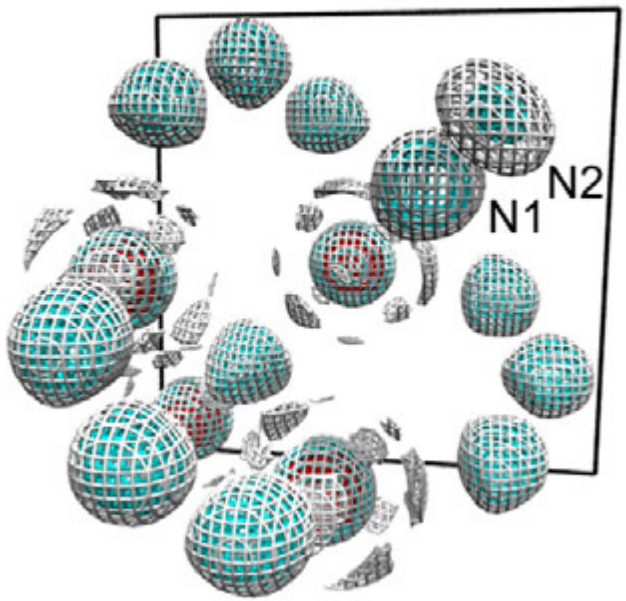
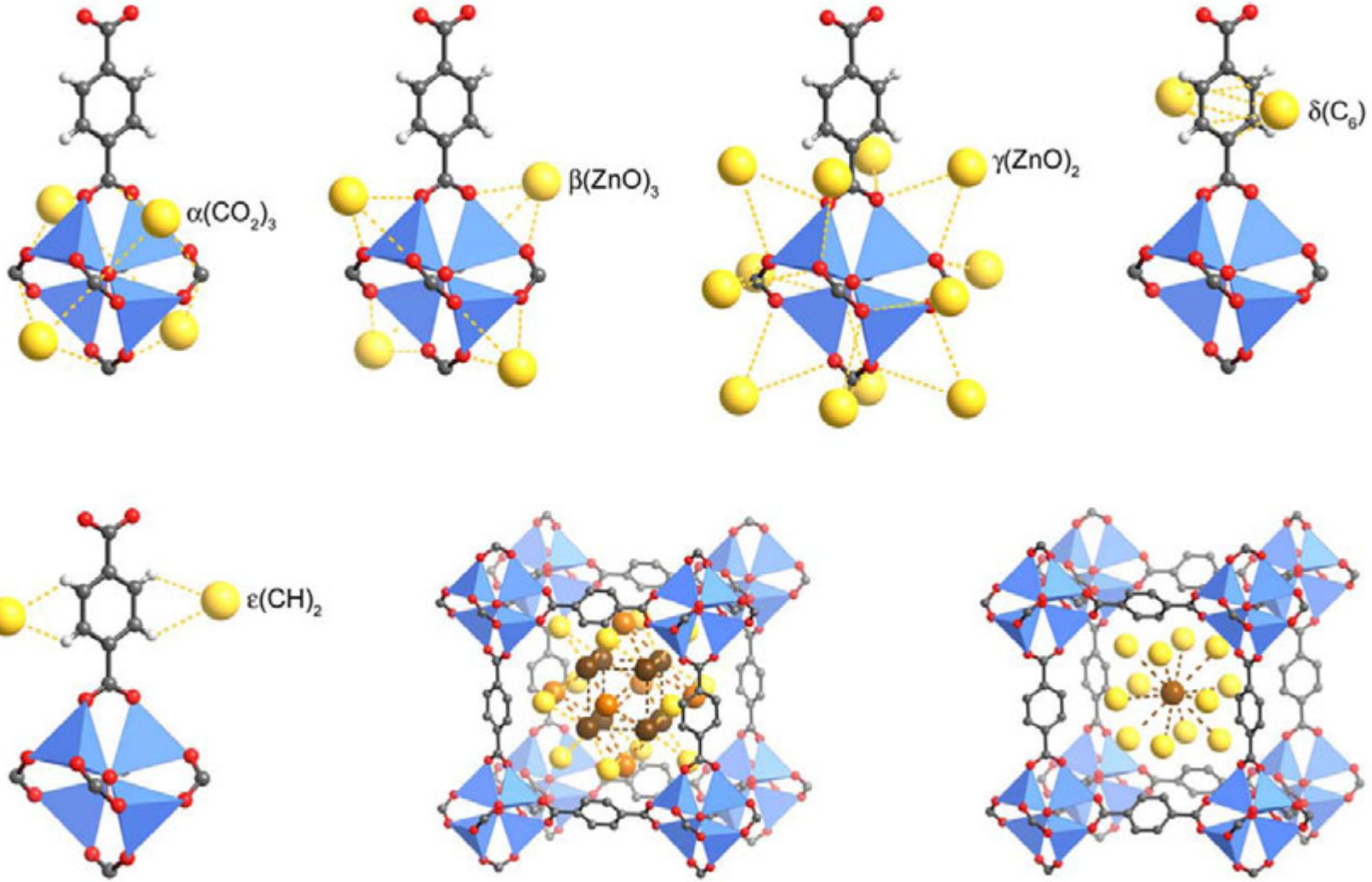


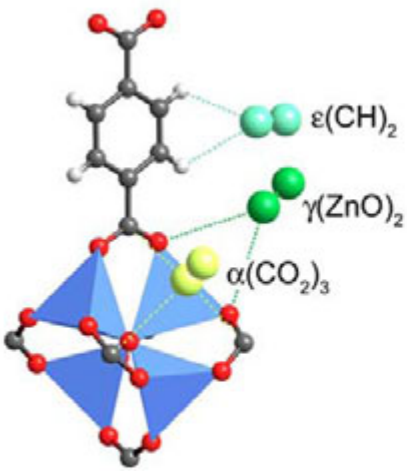



J.L.C. Rowsell, E.C. Spencer, J. Eckert, J.A.K. Howard, O.M. Yaghi, *Science* **2005**, *309*, 1350.

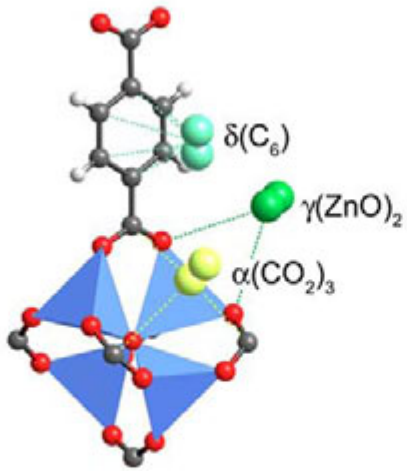
# *Eight Independent Adsorption Sites*



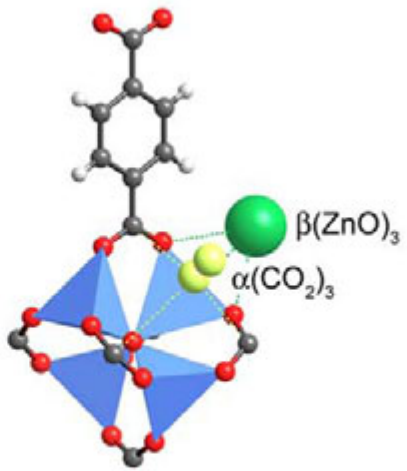
# *Thermal Dependence of $N_2$ Adsorption*



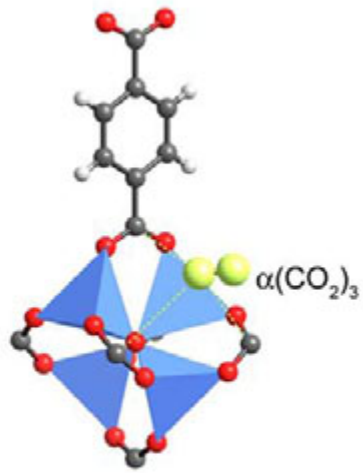

*30 K*




*50 K*

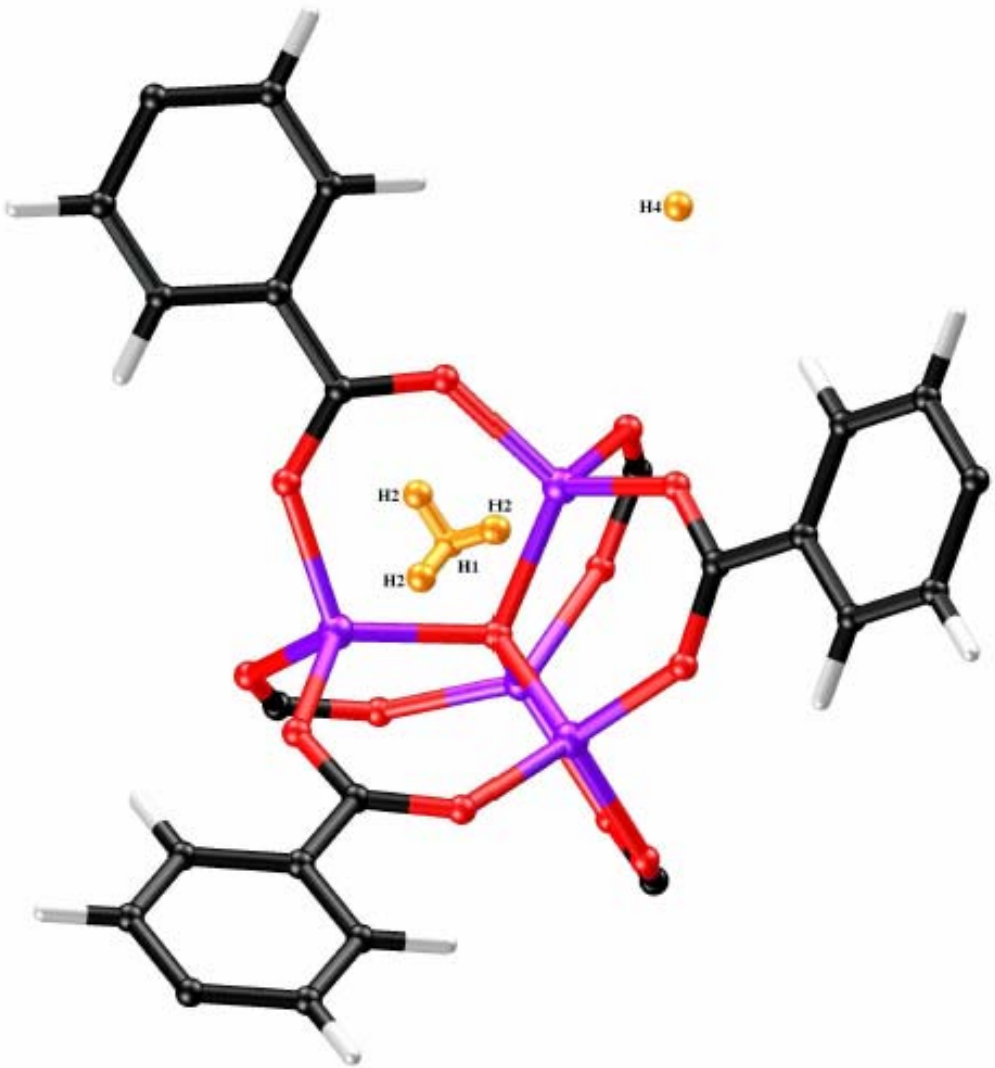



*90 K*



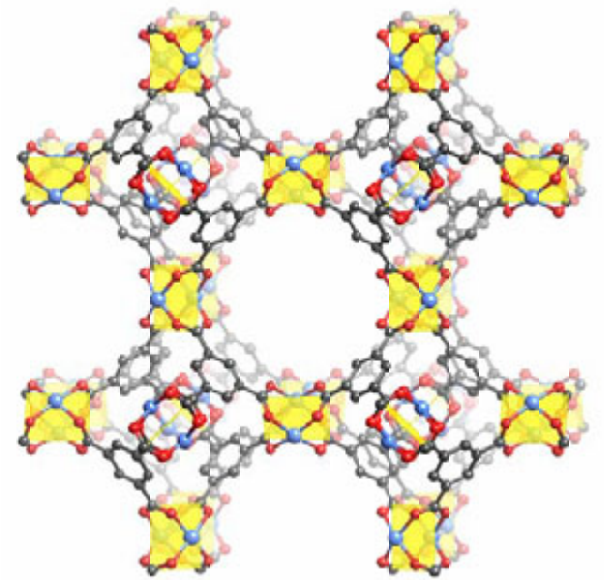

*120 K*

# *Single Crystal Neutron Diffraction*



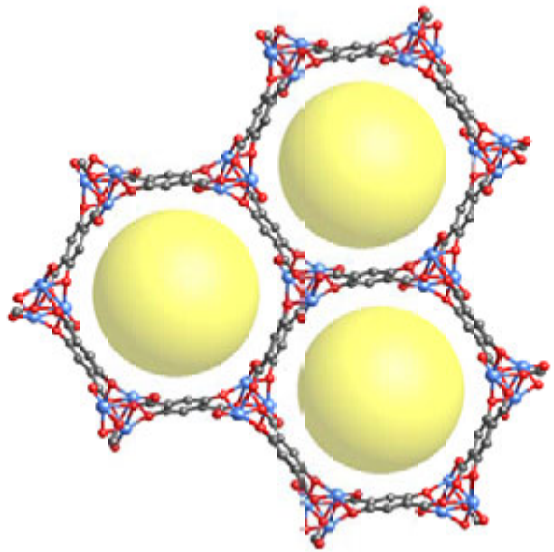

- data collected on VIVALDI (ILL) on ~$(0.5\ mm)^3$ crystal sealed under $H_2$
- appearance of $H_2$ on $\alpha$**$(CO_2)_3$** site at 50 K, additional $H_2$ appears on $\beta$**$(ZnO)_3$** at 5 K

# *Porous Materials with Unsaturated Metal Centers*



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

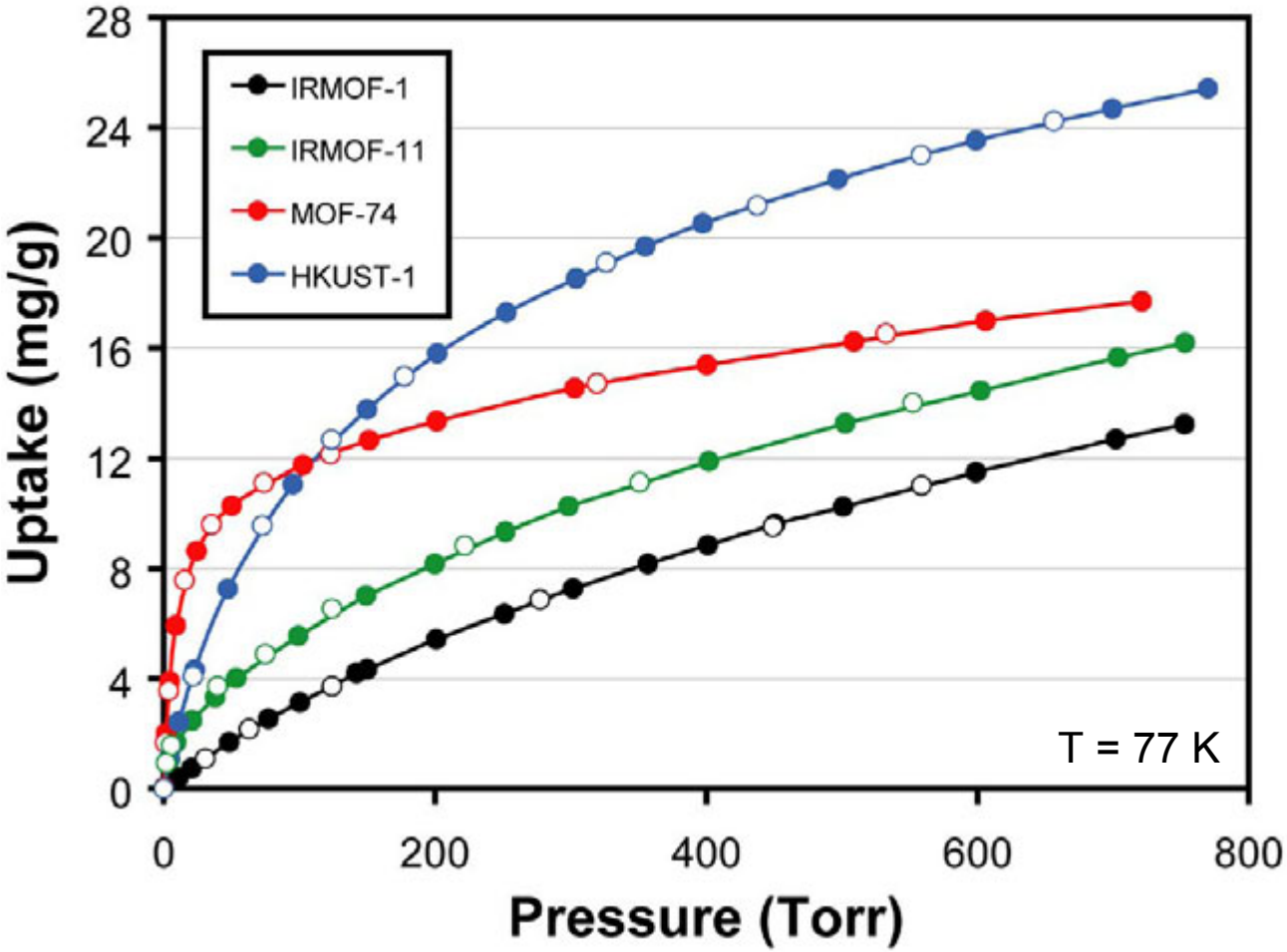
| | |
|---|---|
| $A_{Lang}$ | 2175 $m^2/g$ |
| $A_{BET}$ | 1507 $m^2/g$ |
| $V_p$ | 66% |

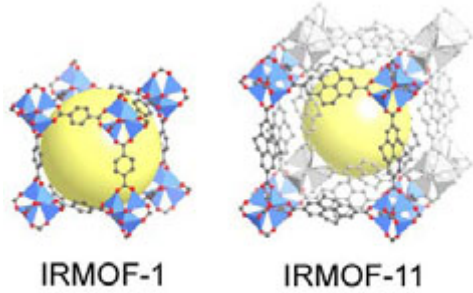


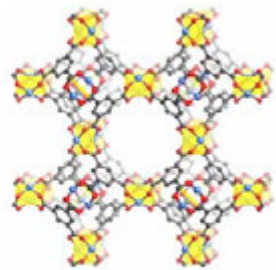
**MOF-74**, $Zn_2(dhBDC)$

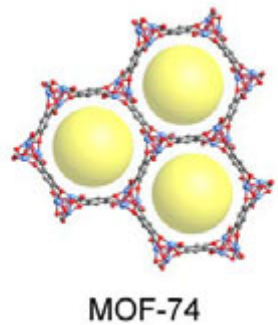
| | |
|---|---|
| $A_{Lang}$ | 1132 $m^2/g$ |
| $A_{BET}$ | 783 $m^2/g$ |
| $V_p$ | 48% |

# $H_2$ Uptake at 77 K, 1 atm

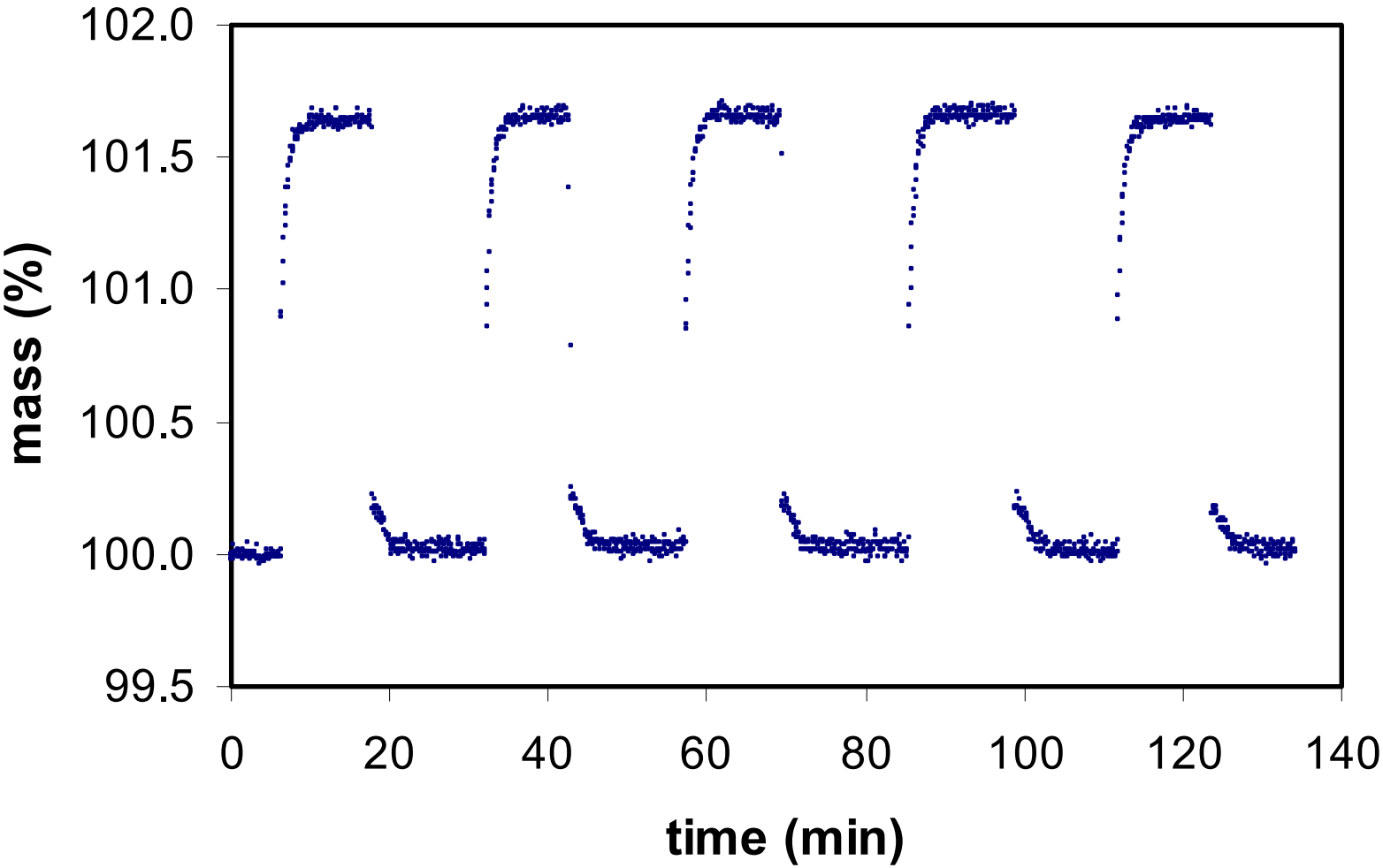


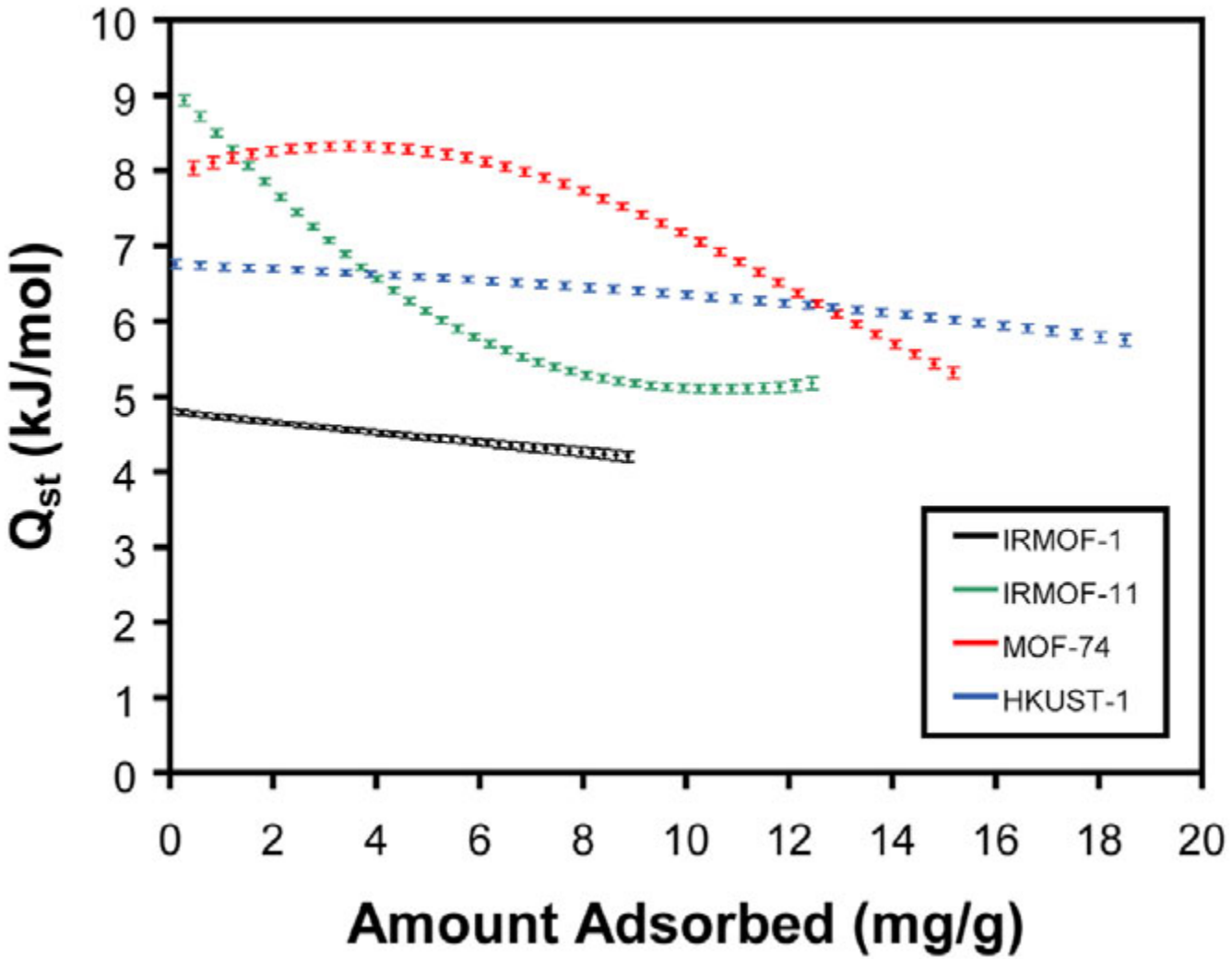



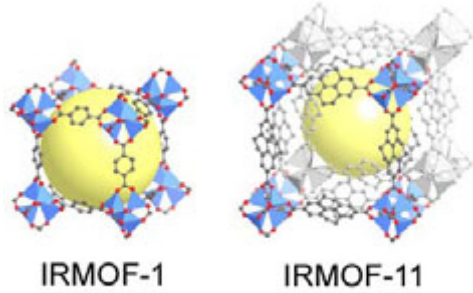



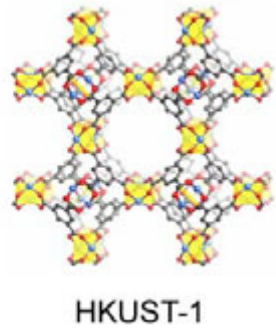
# *Reversibility of hydrogen sorption in IRMOF-11*

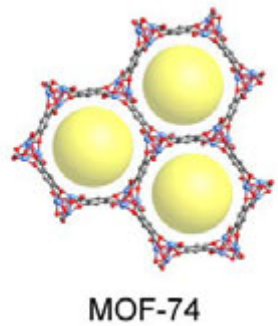


# *Isosteric Heats of Adsorption*

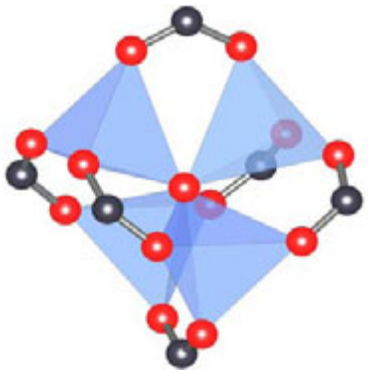


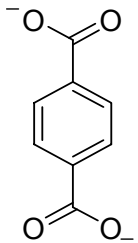



a)



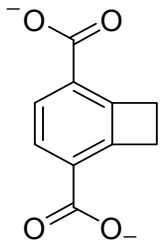
$Zn_4O(CO_2)_6$



**BDC**

*IRMOF-1*

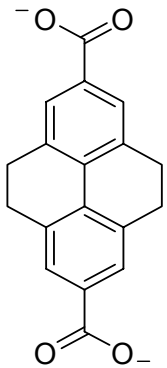
4,170



**CBBDC**

*IRMOF-6*

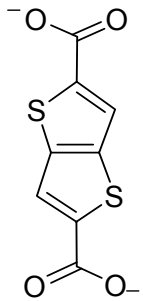
3,300



**HPDC**

*IRMOF-11*

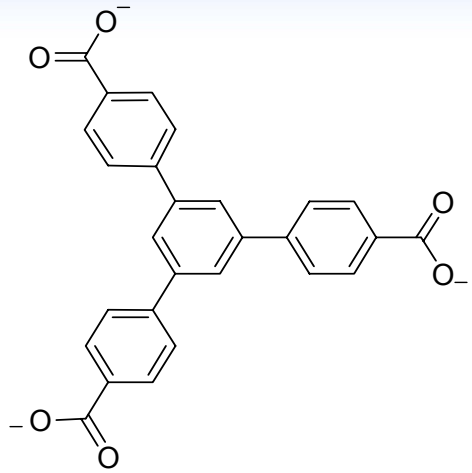
2,340



**TTDC**

*IRMOF-20*

4,590

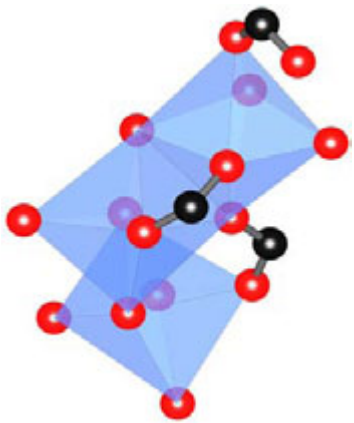


**BTB**

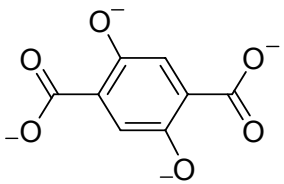
*MOF-177*

5,640

b)



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

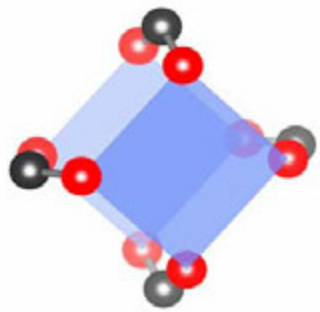


**DHBDC**

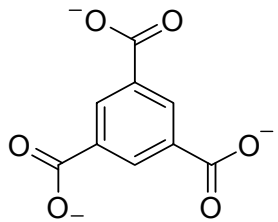
*MOF-74*

1,070

c)



$Cu_2(CO_2)_4$



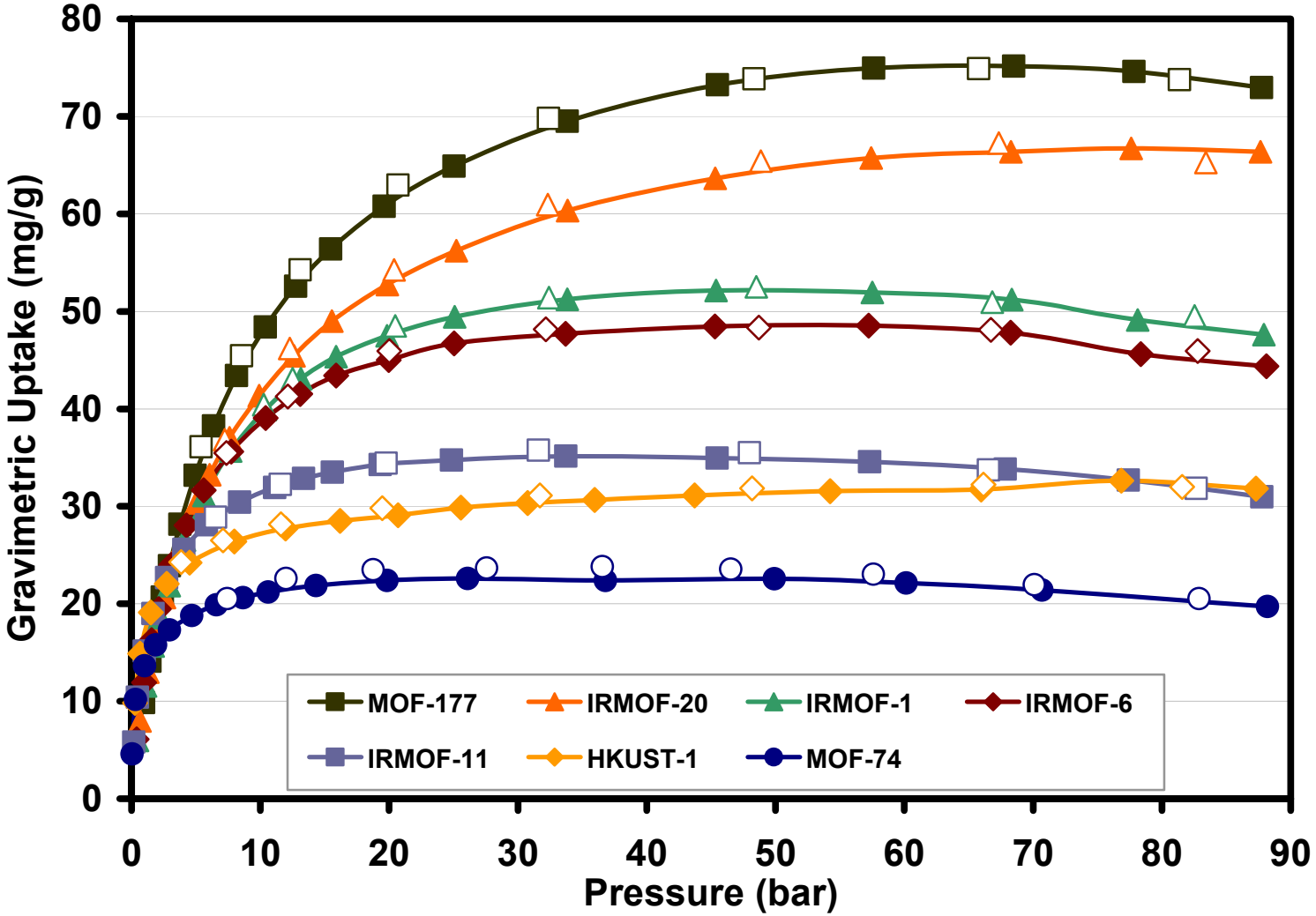
**BTC**

*HKUST-1*

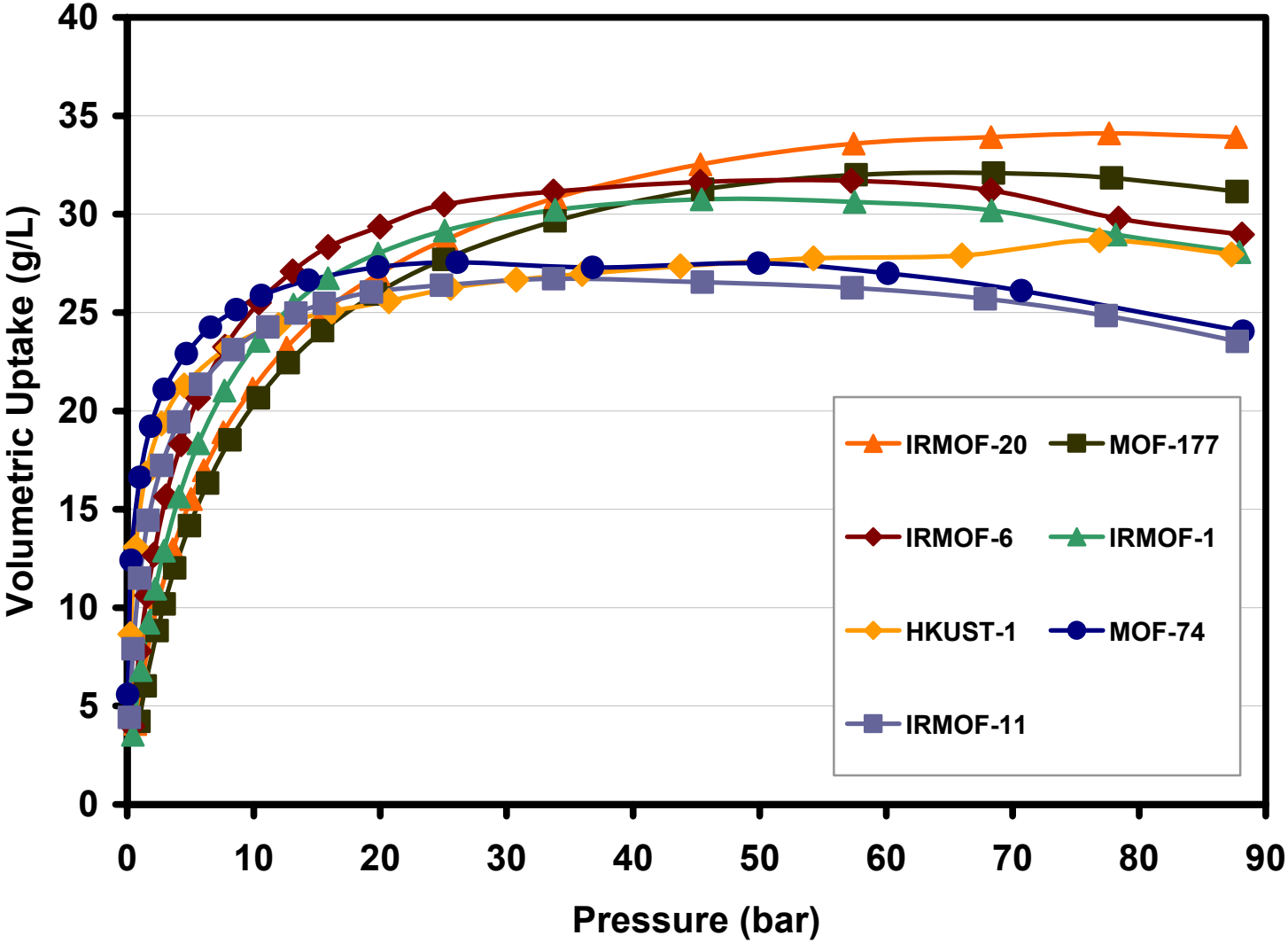
2,260

# Hydrogen uptake at 77 K

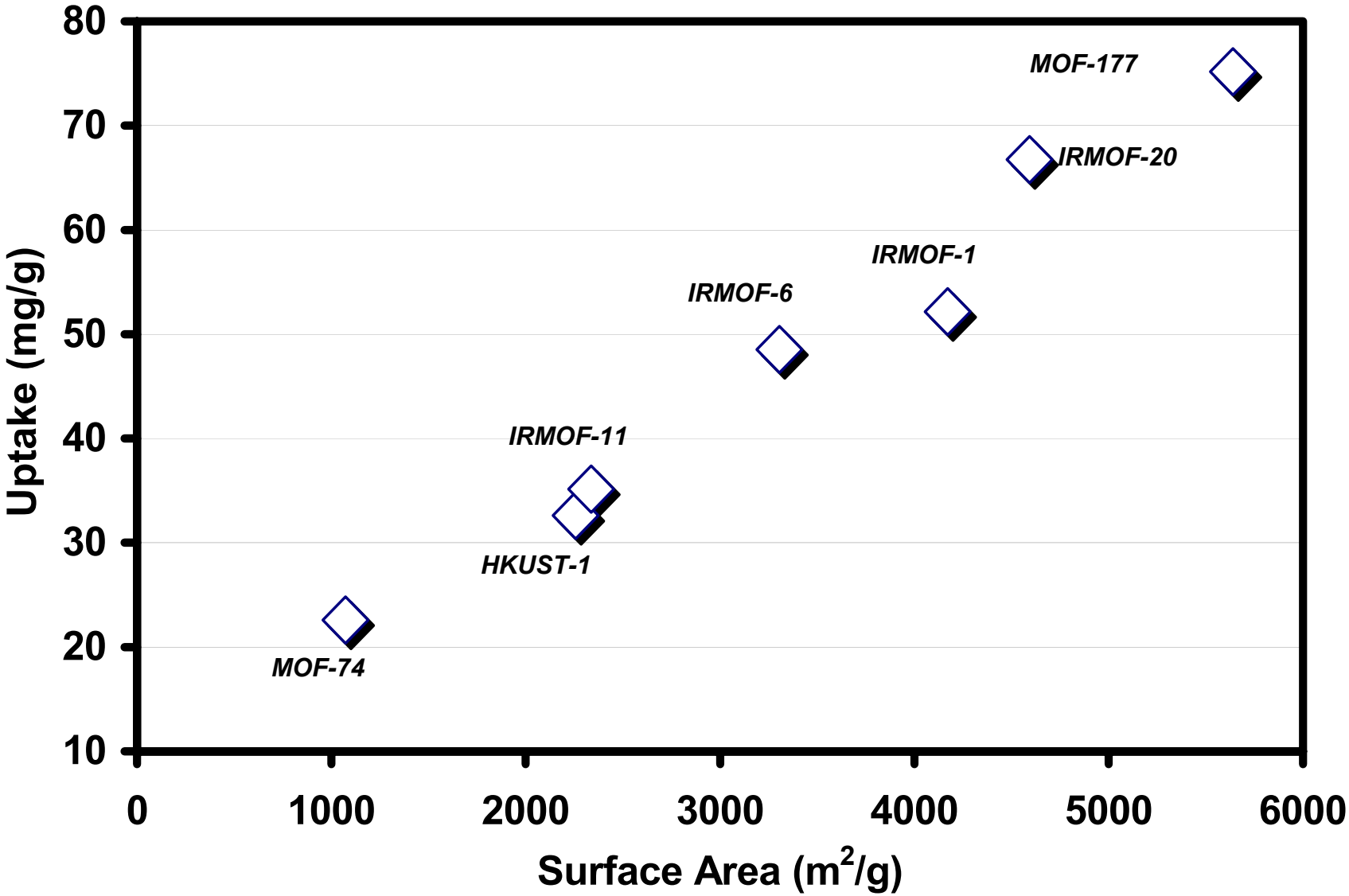
(30% more hydrogen in a vessel containing MOFs)



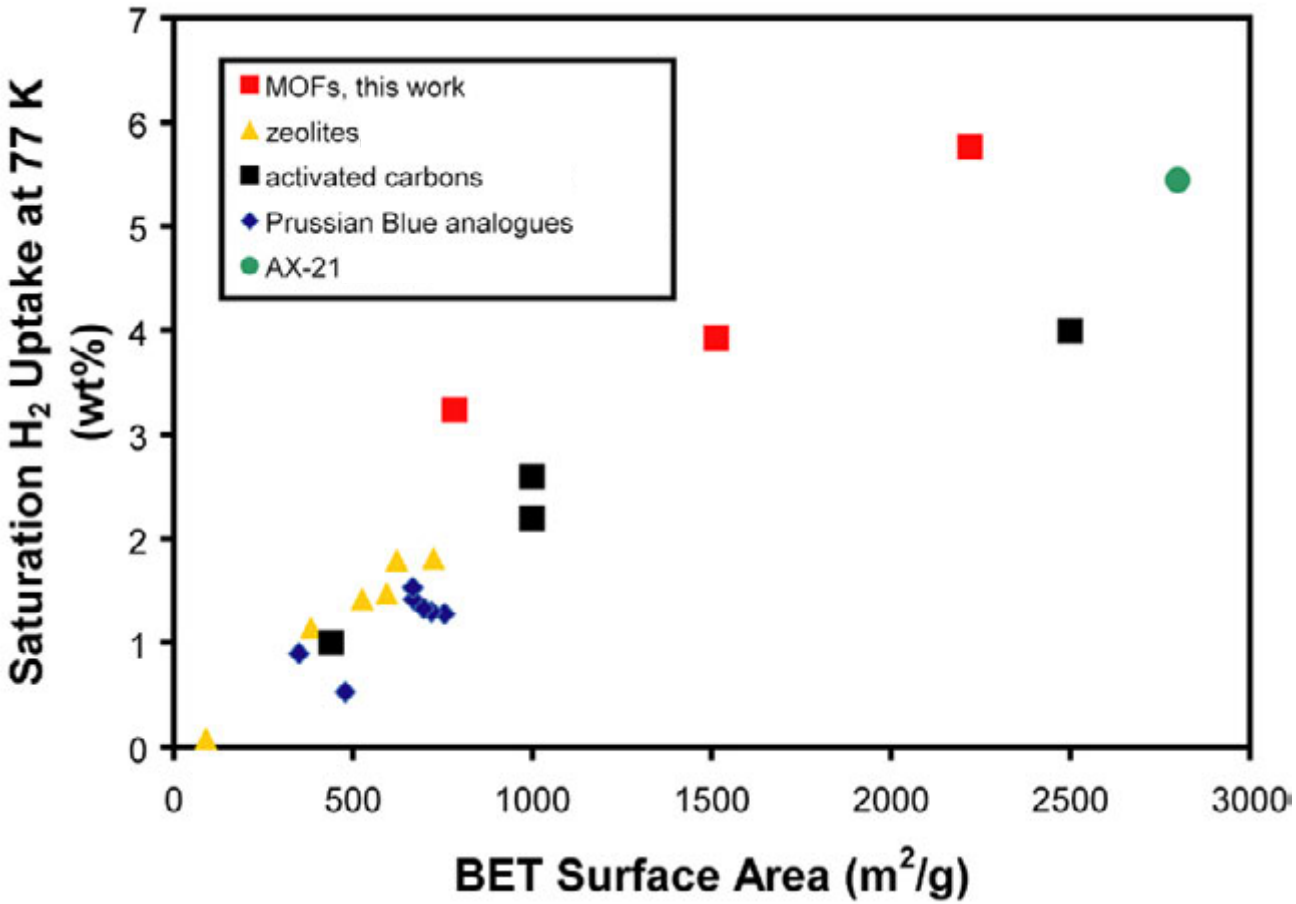
# Volumetric uptake at 77 K



# Correlation of uptake with surface area



# *Correlation with $N_2$ Adsorption Data*



## Hydrogen Safety

*The most significant hydrogen hazard associated with this project is:*

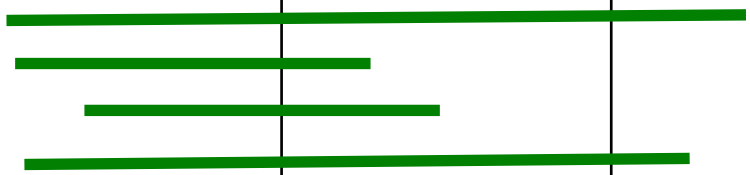
- High exposure to $H_2$ gas with possibility of personal injury due to decreased oxygen content in the atmosphere.
- High concentrations of $H_2$ may pose a fire or explosion in and around instrumentation.

# 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<br>Synthesize MOFs<br>Expose metal sites<br>Impregnate MOFs with metal clusters, metal oxides and polymers |  | | |
| 2. Hydrogen uptake studies<br>Measure adsorption energy<br>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**
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**Antek Wong-Foy**
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**BASF**
**Toyota**
**GM**