HYDROGEN STORAGE IN METAL-ORGANIC FRAMEWORKS

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Progress report, May 07

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Project ST10

Overview

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

Budget
- Total project funding: DOE $1.6 M
- Funding received FY 05: $112 K
- Funding for FY 06: 150 K
- Funding for FY 07: 430 K

Barriers addressed

Technical barriers addressed:
- Improved gravimetric and volumetric density of hydrogen uptake
- Hydrogen capacity and fast kinetics at 77K
- Improved hydrogen binding energy
- Synthesis scale up of MOFs to cubic meters

Technical system targets by 2010:
- Gravimetric capacity: 6 wt% and 1.5 kWh/L; Volume capacity: 45gH/L; operating temperature: -30° to 45°C

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

Objectives and important directions

A. DESIGING POROSITY

1) **Increased binding energy**
2) **Increase surface area without increase of dead volume**
3) **Cycling and kinetics of hydrogen charge and discharge**
4) **Impact of open-metal sites on binding energy and uptake capacity**
5) **Impregnation with polymers and nano-particles of light metals**

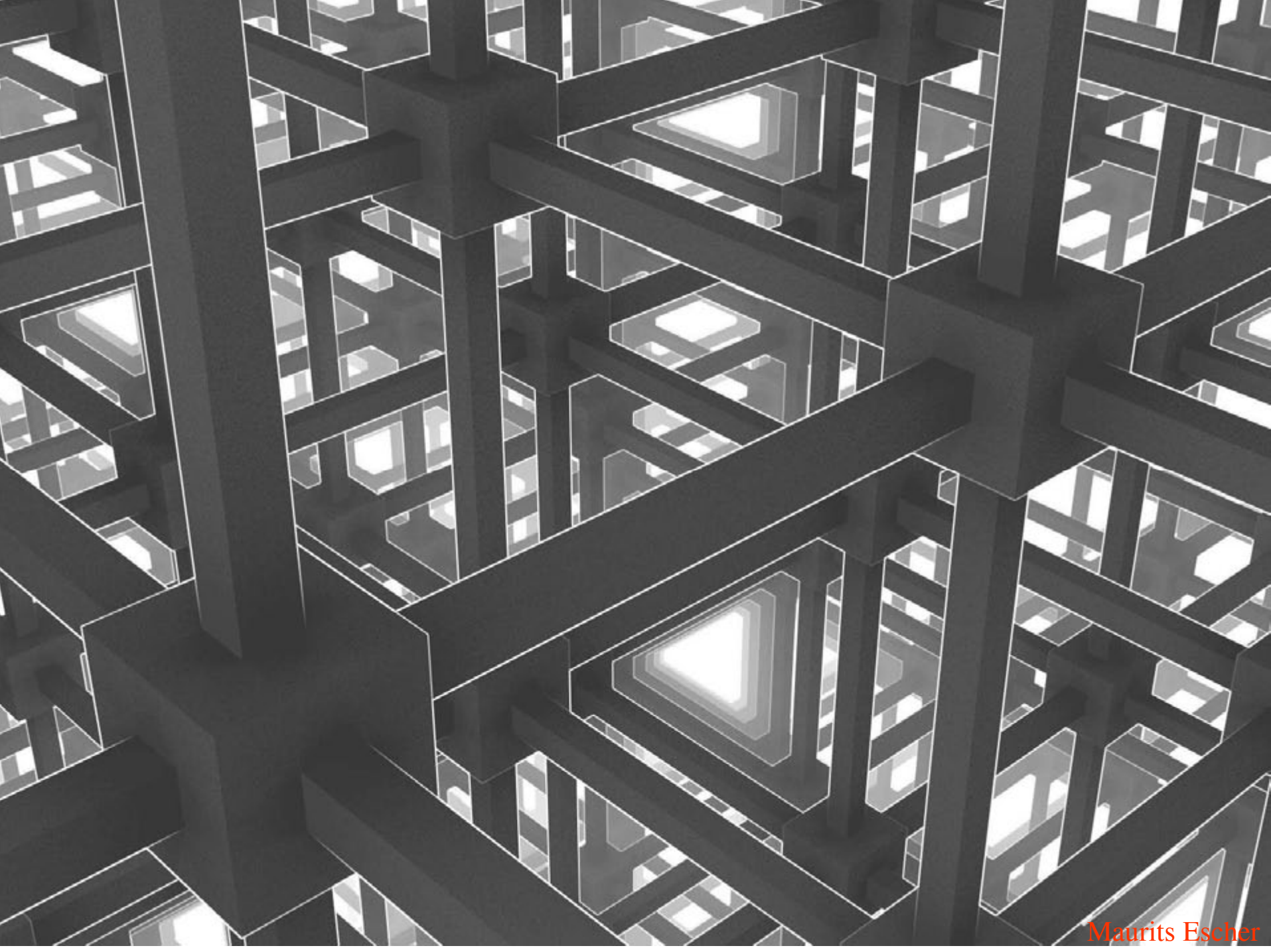
B. MOFs AS MOLECULAR FUEL TANKS

1) **Scale up of favored MOFs**
2) **Transfer of samples to DOE for independent verification of data**
3) **Establish a standard for hydrogen storage measurements**

Reticular chemistry *is concerned with linking of molecular building blocks (organic molecules, inorganic clusters, dendrimers, peptides, proteins,...) into predetermined structures in which such units are repeated and are held together by strong bonds.*

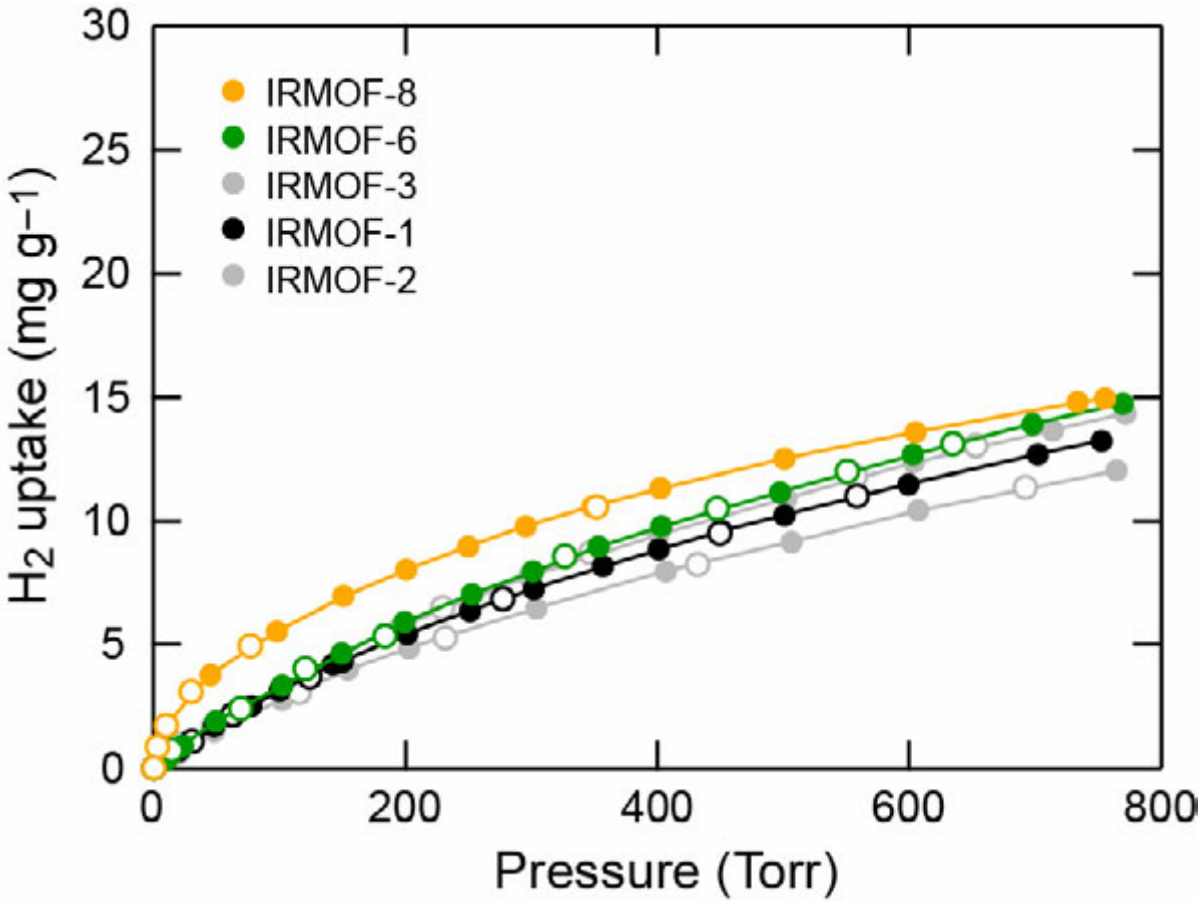
DESIGN OF POROSITY

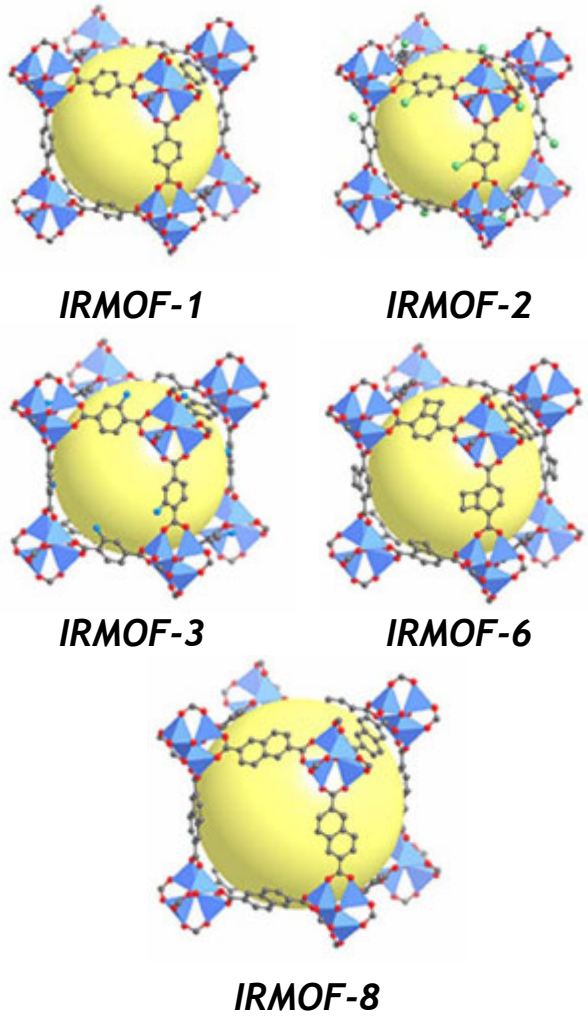
- Control of the organic link's functionality
- Variation in metal-oxide units' size and composition
- Control of pore-metrics
- Exposition of metal-sites within the pores
- Strategies for achieving high surface areas
- Control of dead volume


Maurits Escher

H_2 Adsorption in Non-Catenated MOFs

Functionality has little impact on uptake





H_2 Adsorption in Non-Catenated MOFs

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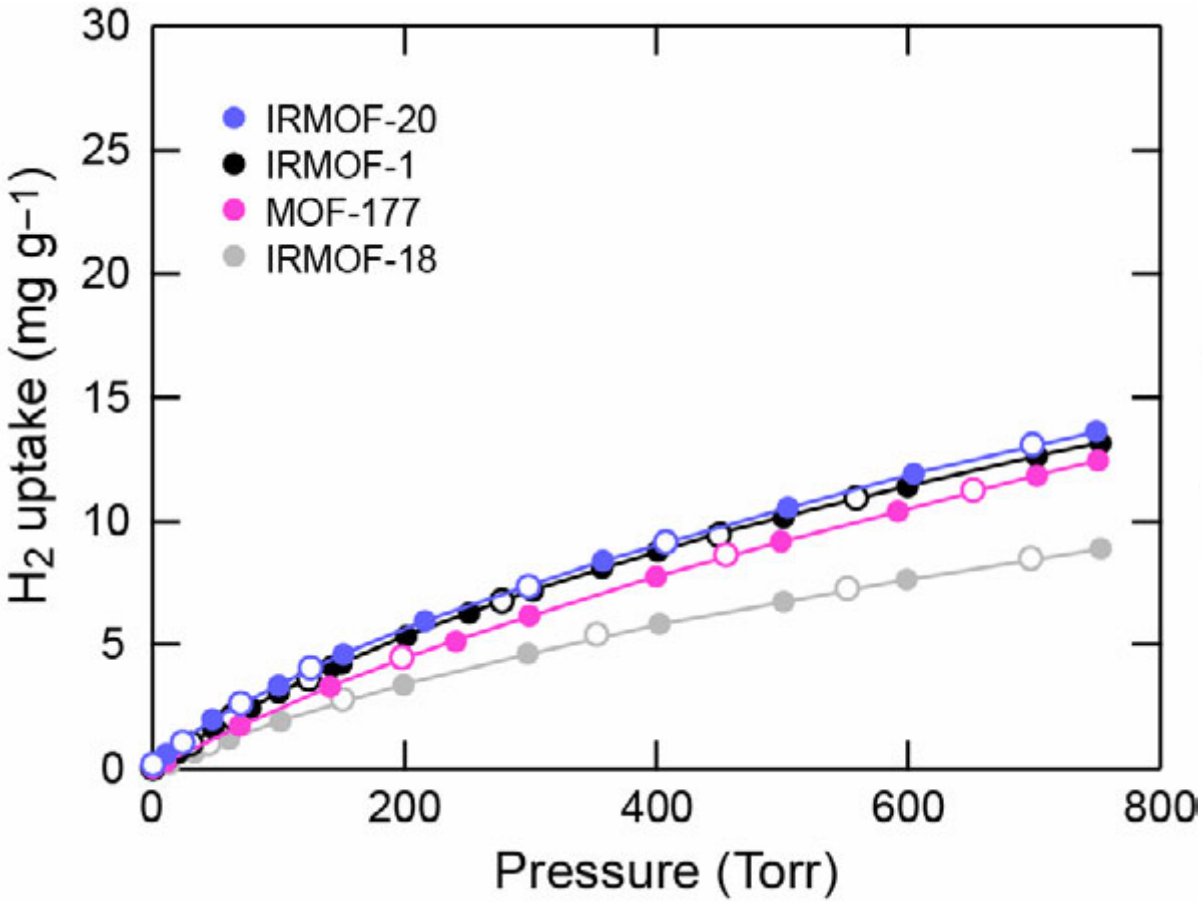

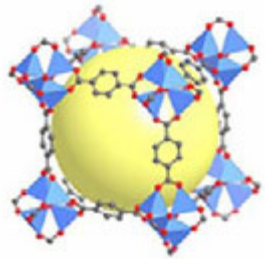

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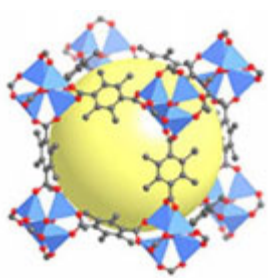

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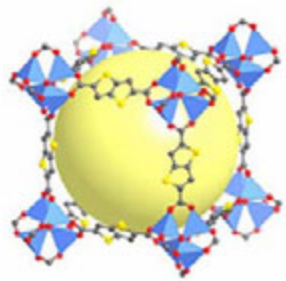

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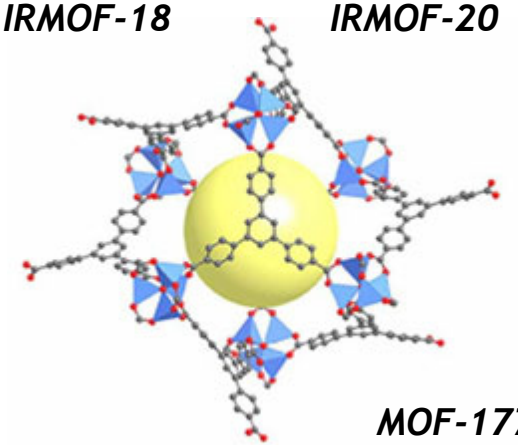
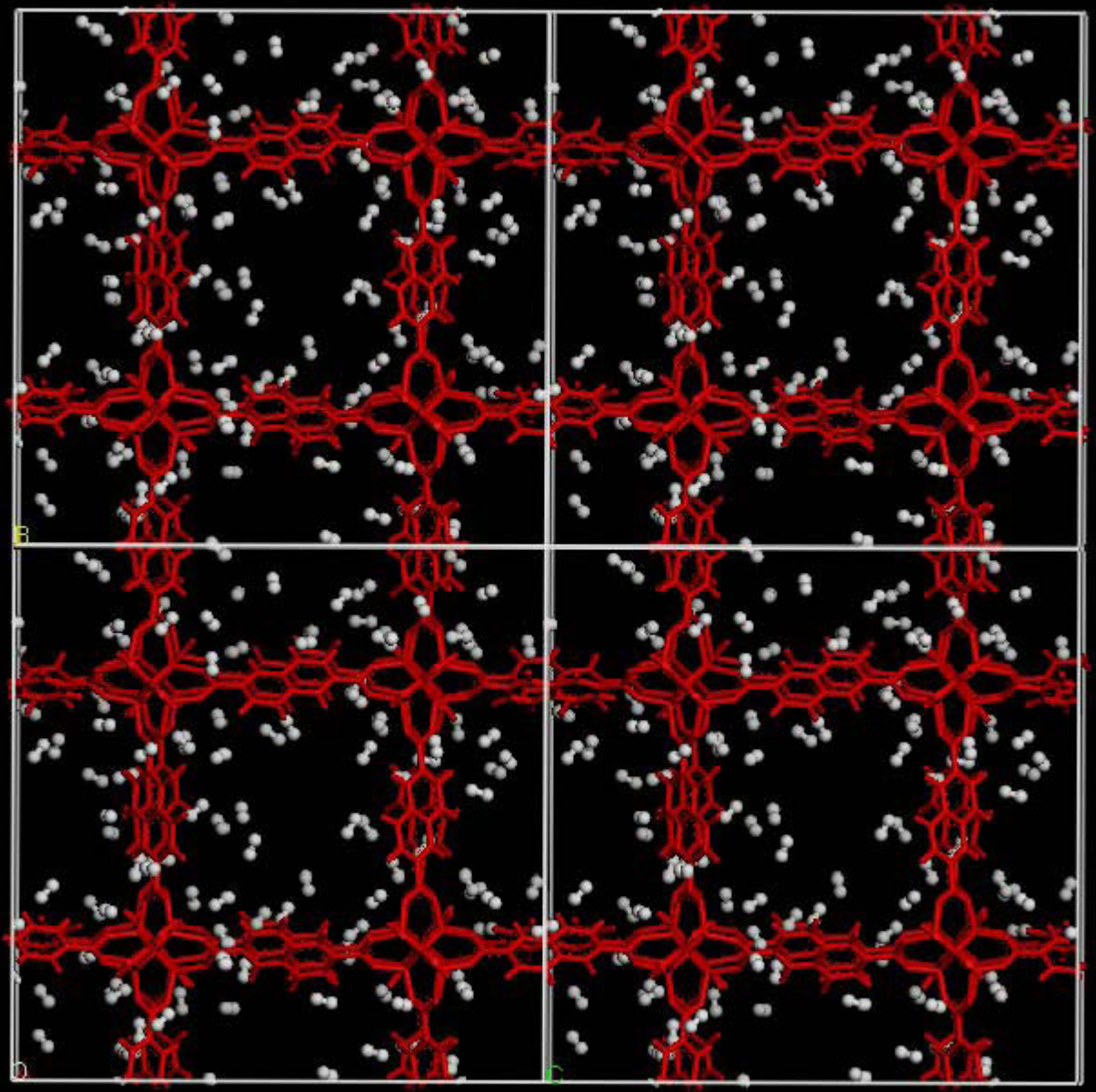


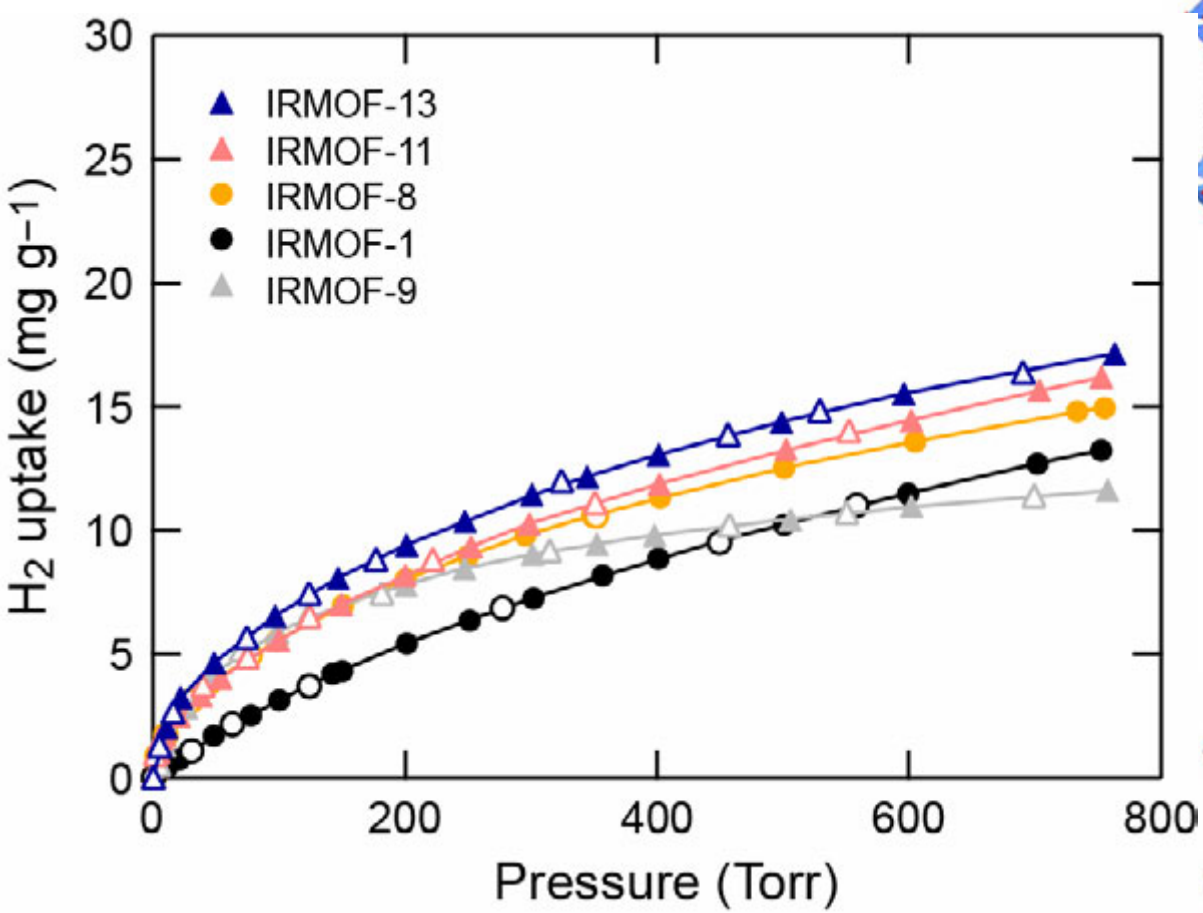
MOF-177

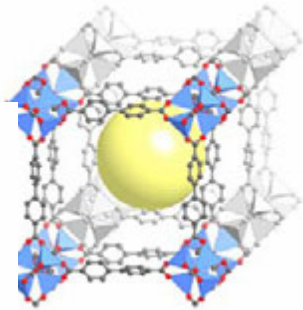
Unregistered



H_2 Adsorption in Catenated MOFs

Catenation increases uptake by 40% relative to non-catenated





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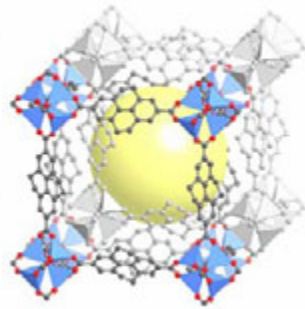

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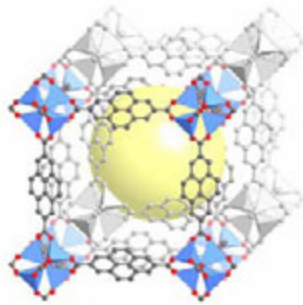

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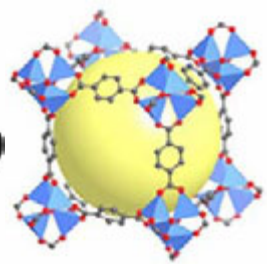

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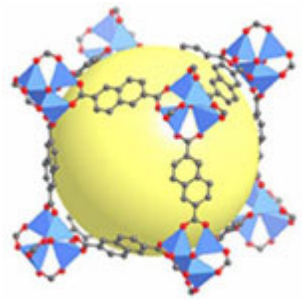
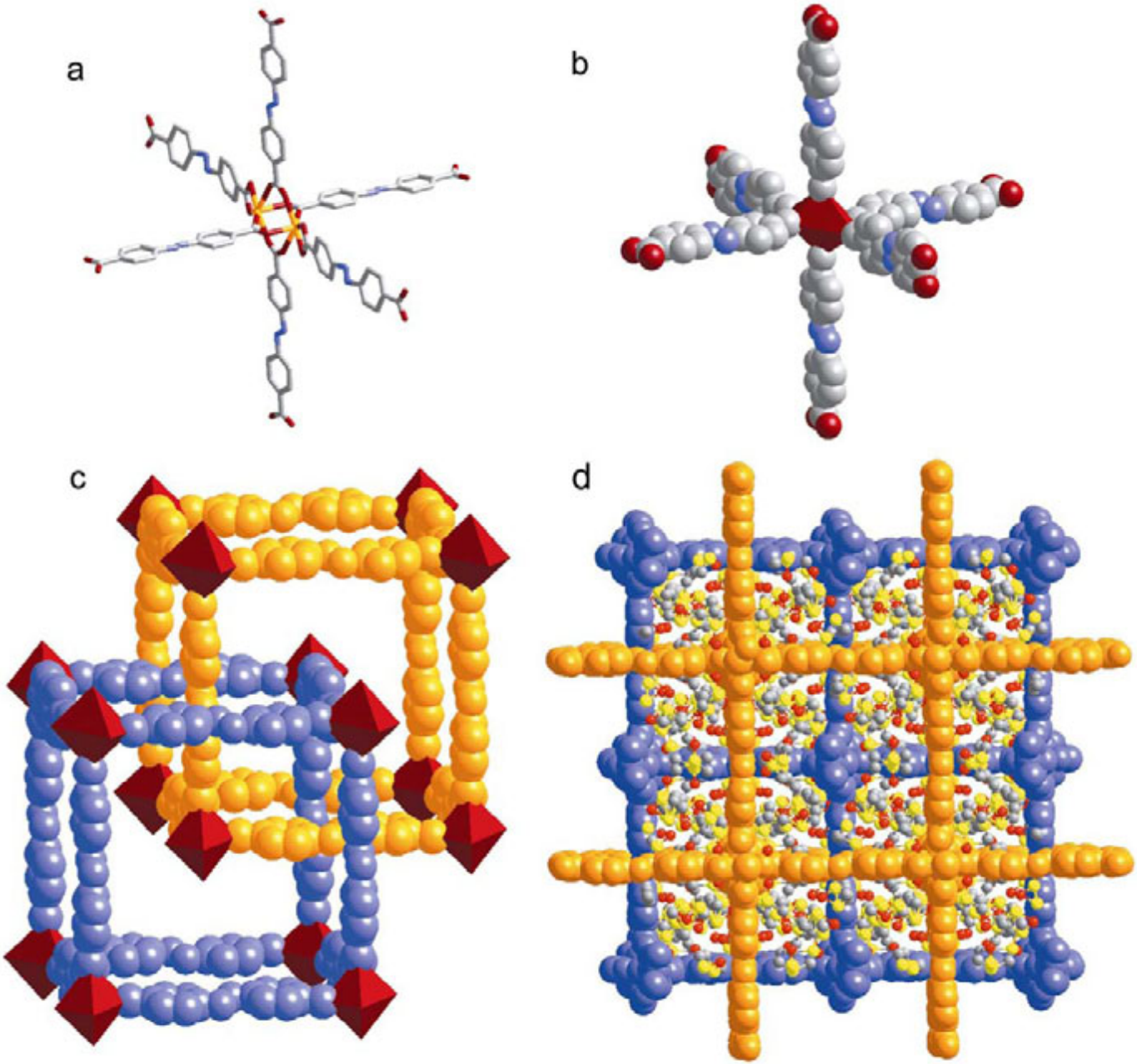


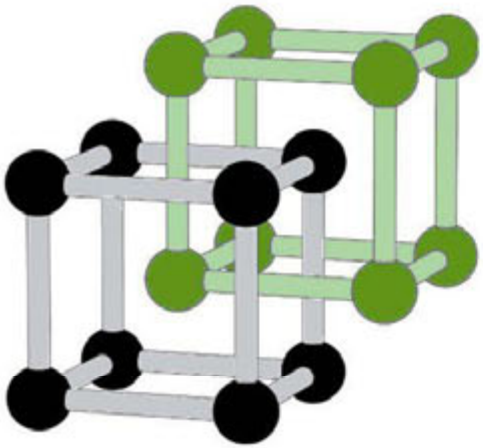
IRMOF-8

MOF-9: $Tb_2(ADB)_3[(CH_3)_2SO]_4 \cdot 16[(CH_3)_2SO]$



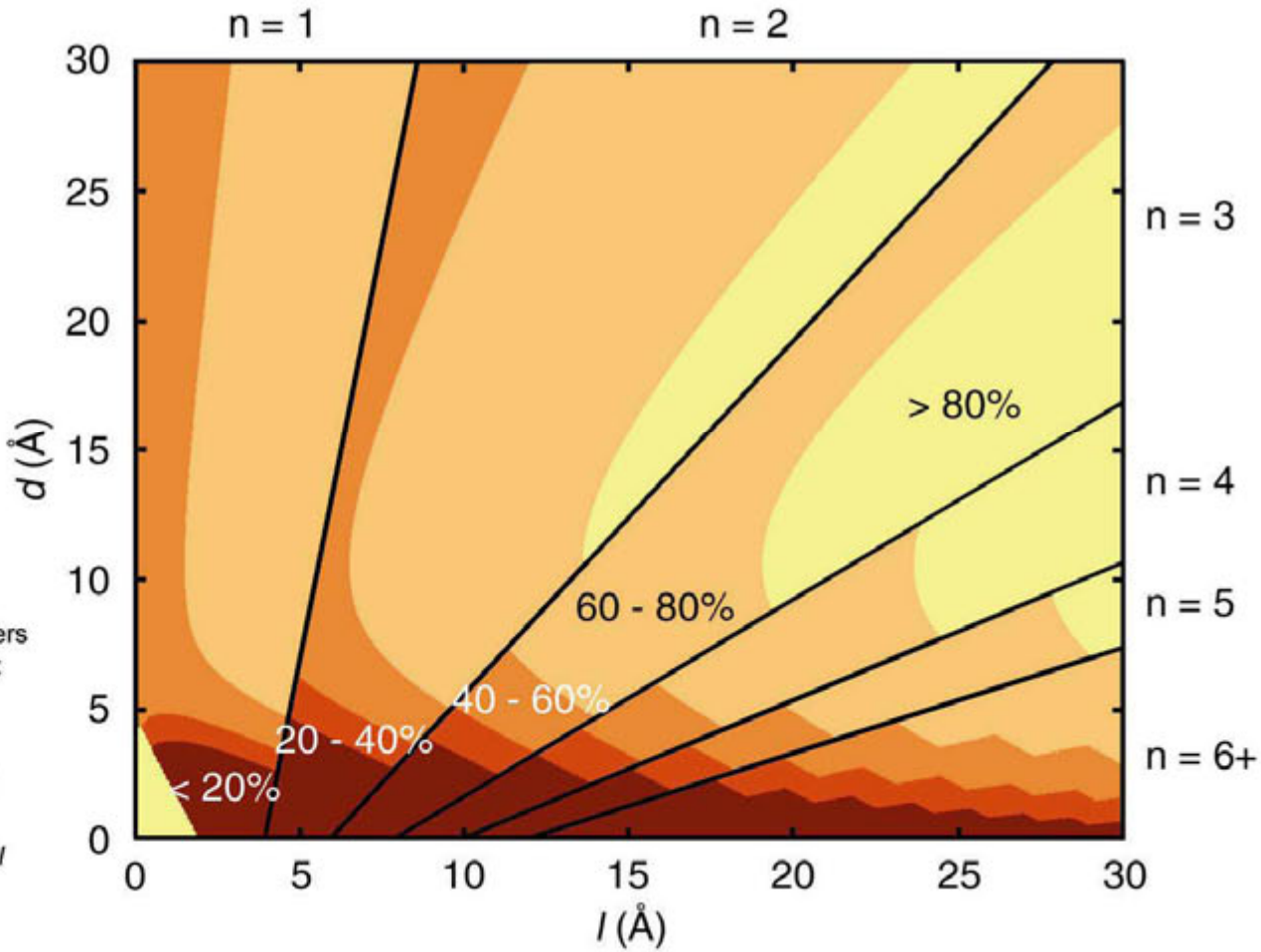
Reineke, T.M.; Eddaoudi, M.; Moler, D.; O'Keeffe, M.; Yaghi, O.M. *J. Amer. Chem. Soc.* **2000**, *122*, 4843.

Large Free Volume in Interpenetrating Networks: The role of Secondary Building Units

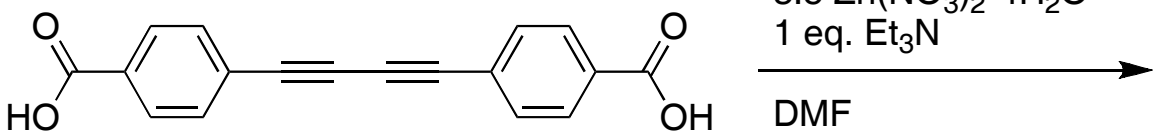


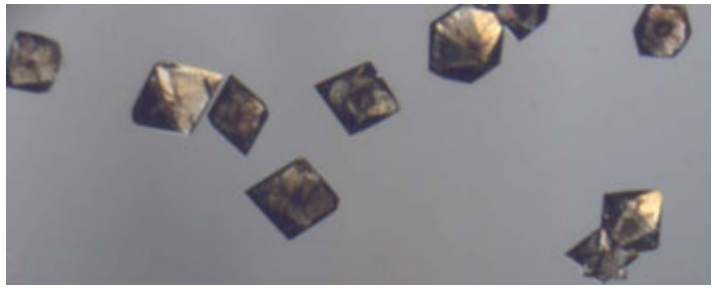
Cell edge: $a = d + l$
van der Waals Radius of SBU = $\delta / 2$
For n frameworks to interpenetrate with centers of the SBUs aligned along the body diagonal:
$n(d + \delta) \leq \sqrt{3}\, a$ thus $n \leq \sqrt{3}\,(d + l) / (d + \delta)$

Volume of the cell = $(d + l)^3$
Volume occupied by SBUs / cell = $n(\pi / 6)d^3$
Volume of the linkers / cell = $3n(\pi r^2)l$
Free Volume = $(d + l)^3 - (n(\pi / 6)d^3 + 3n(\pi r^2)l$



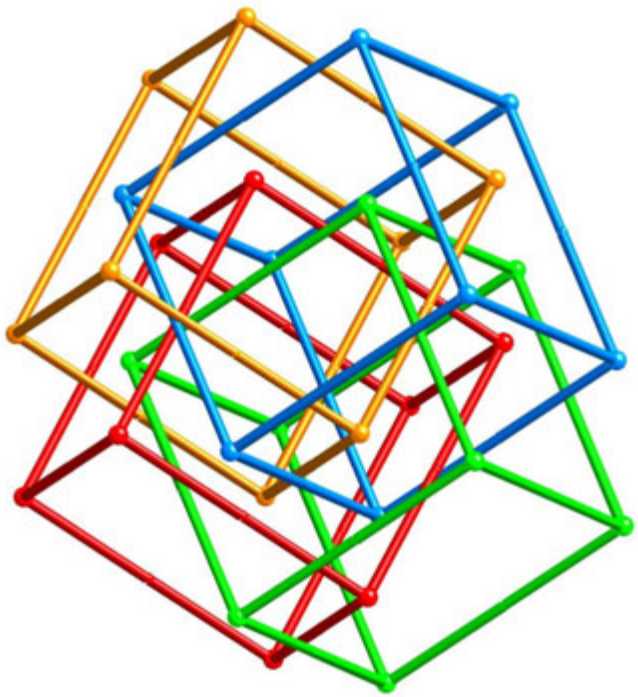
IRMOF-62: Design of highly catenated MOF with Pore size favored for hydrogen

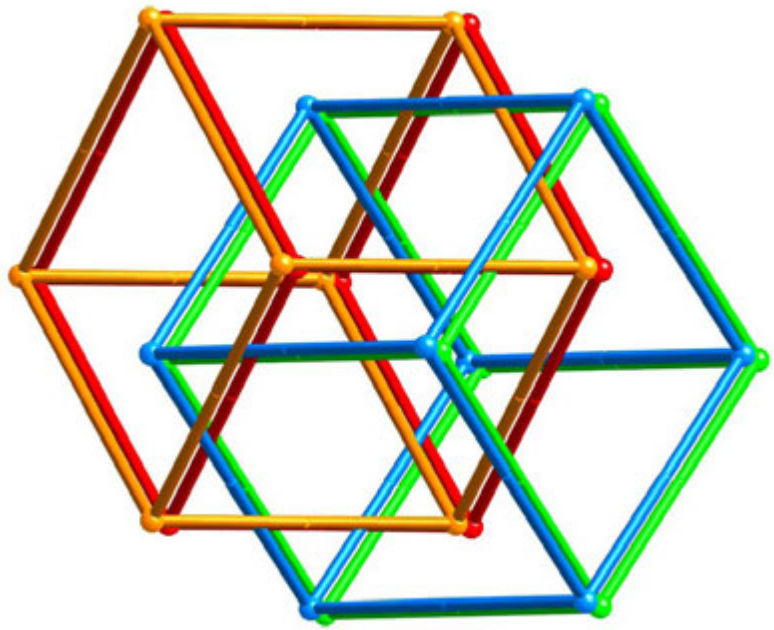




MOF-5 like framework
Quadra-interpenetrating
Small channel can be seen along crystallographic c-axis (5.2 Å in diameter)
Utilization of "edge" (diyne link)

$P3_212$
a = 31.114(1) Å, c = 39.280(3) Å
Cell Volume: 32931.2(2) $Å^3$
d = 0.691 g cm^{-3}

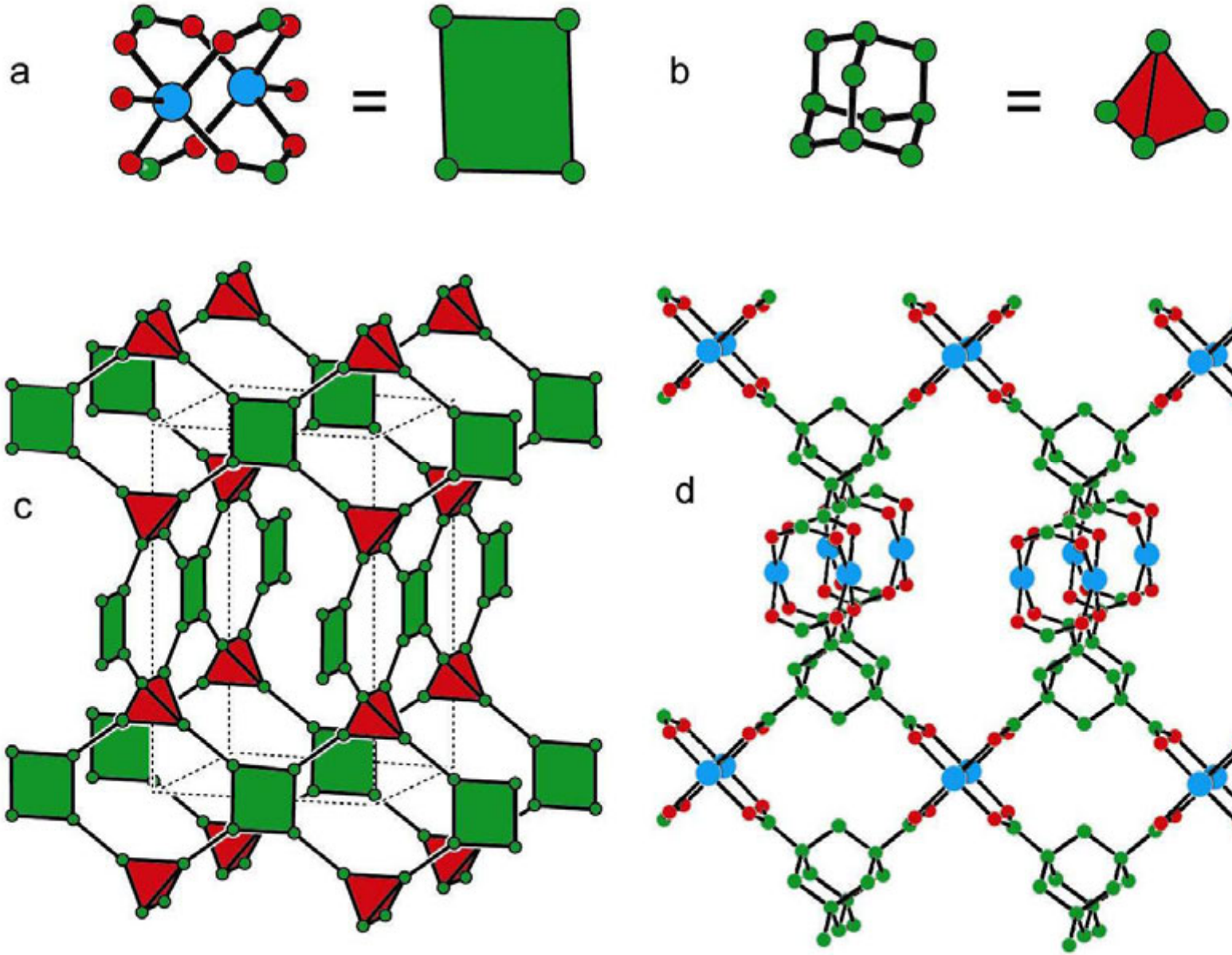


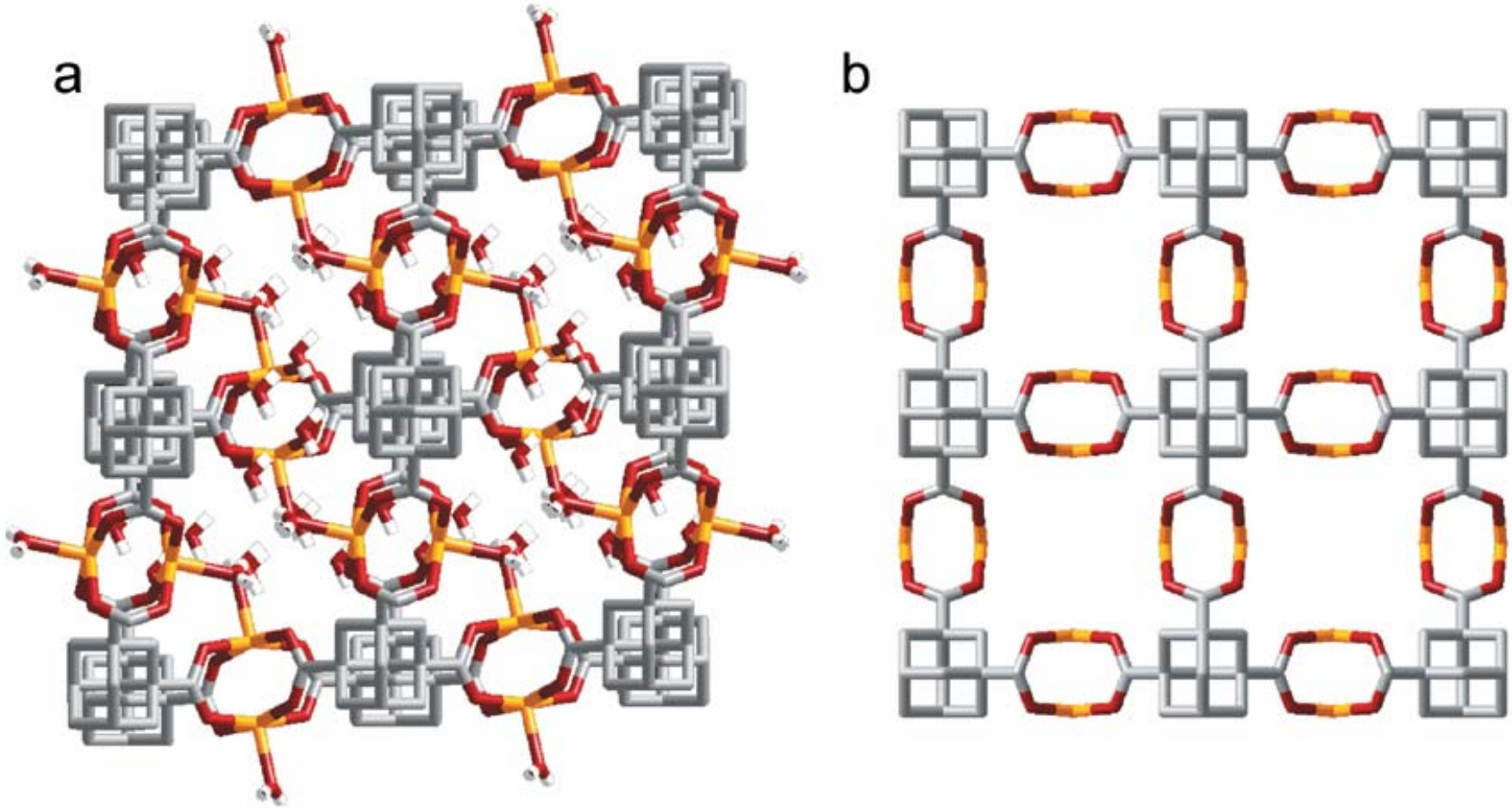


OPEN METAL SITES

- Design within MOF frameworks
- Impact on uptake capacity
- Impact on adsorption energy

MOFs with open metal sites

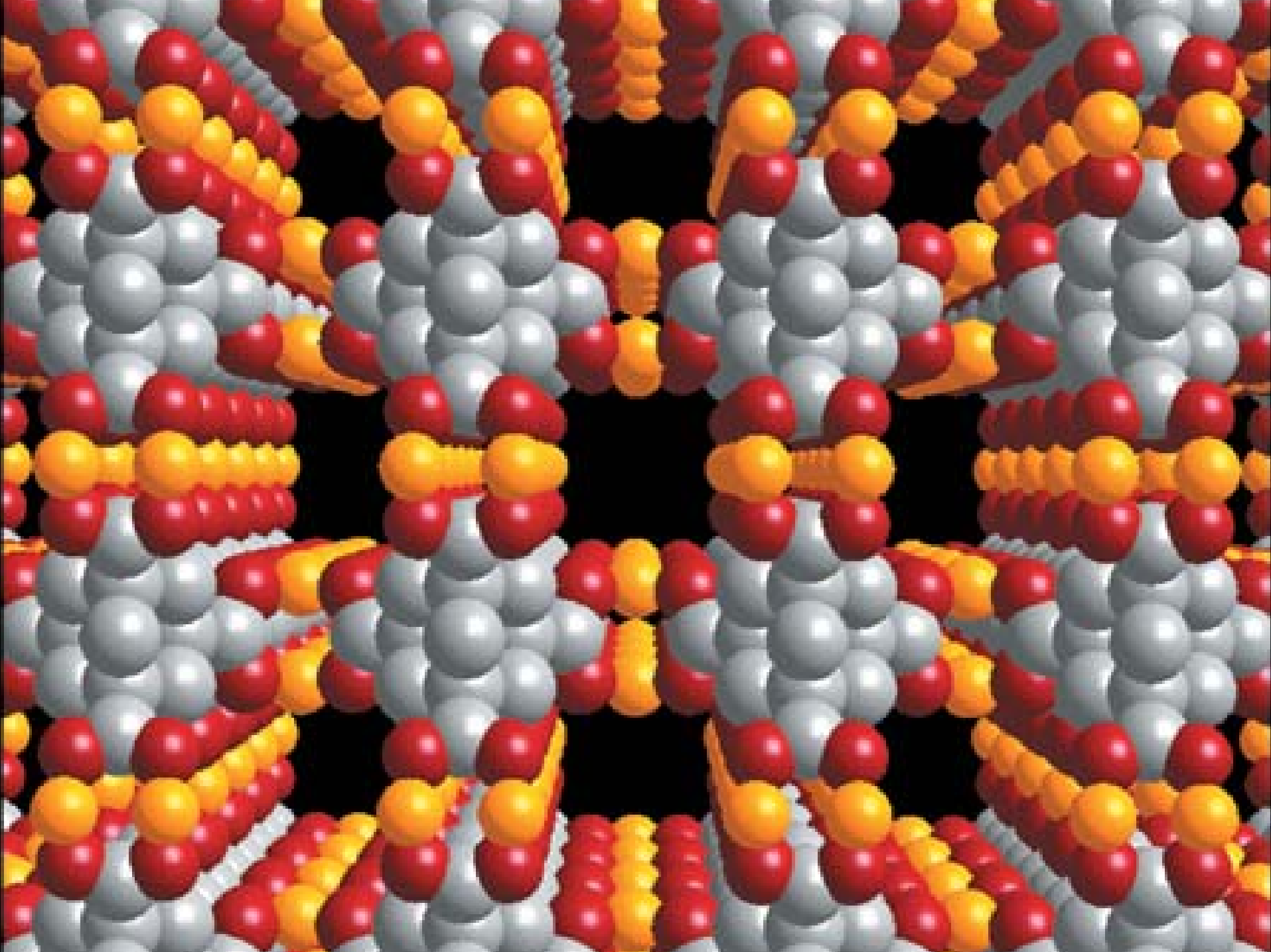




$Cu_2(ATC)\cdot 6H_2O$

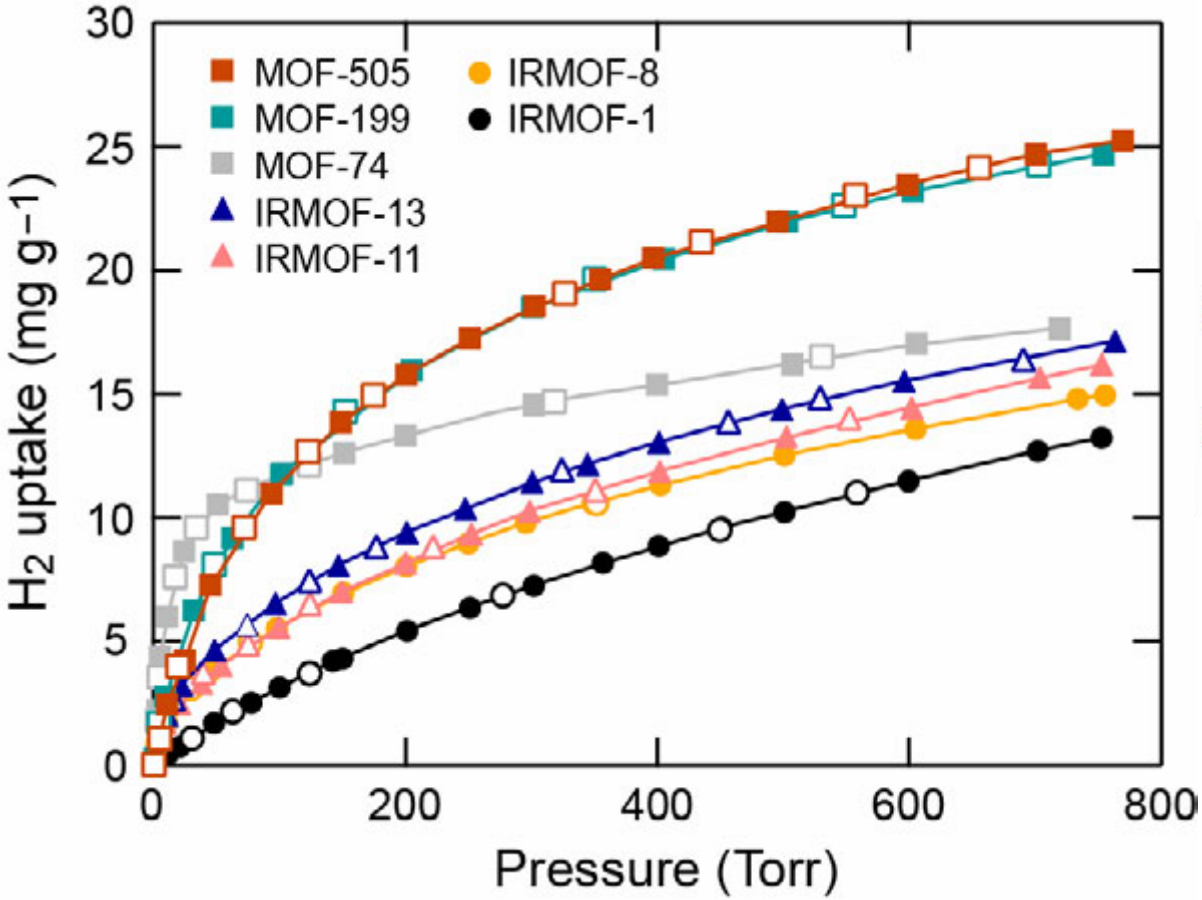
$Cu_2(ATC)$

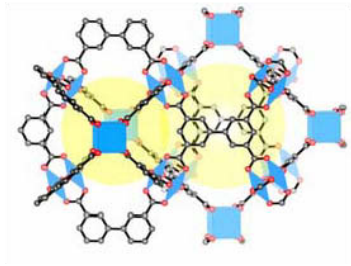
JACS 2001 (Banglin Chen)



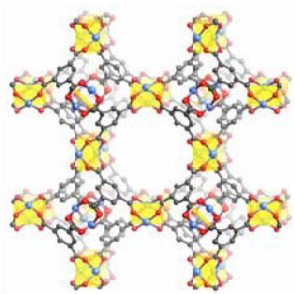
H_2 Uptake by MOFs with Open-Metal Sites

Open metal sites increase uptake by 70%

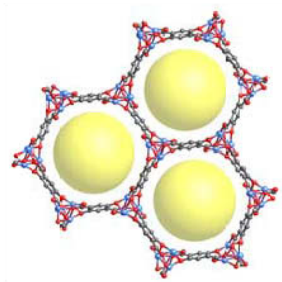




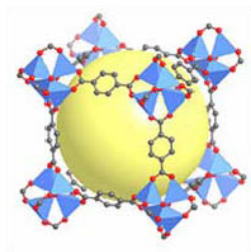
MOF-505



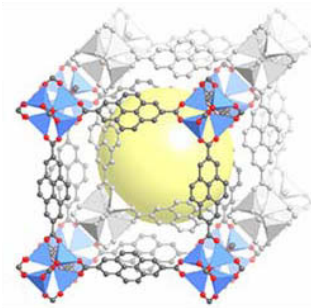
MOF-199



MOF-74



IRMOF-1

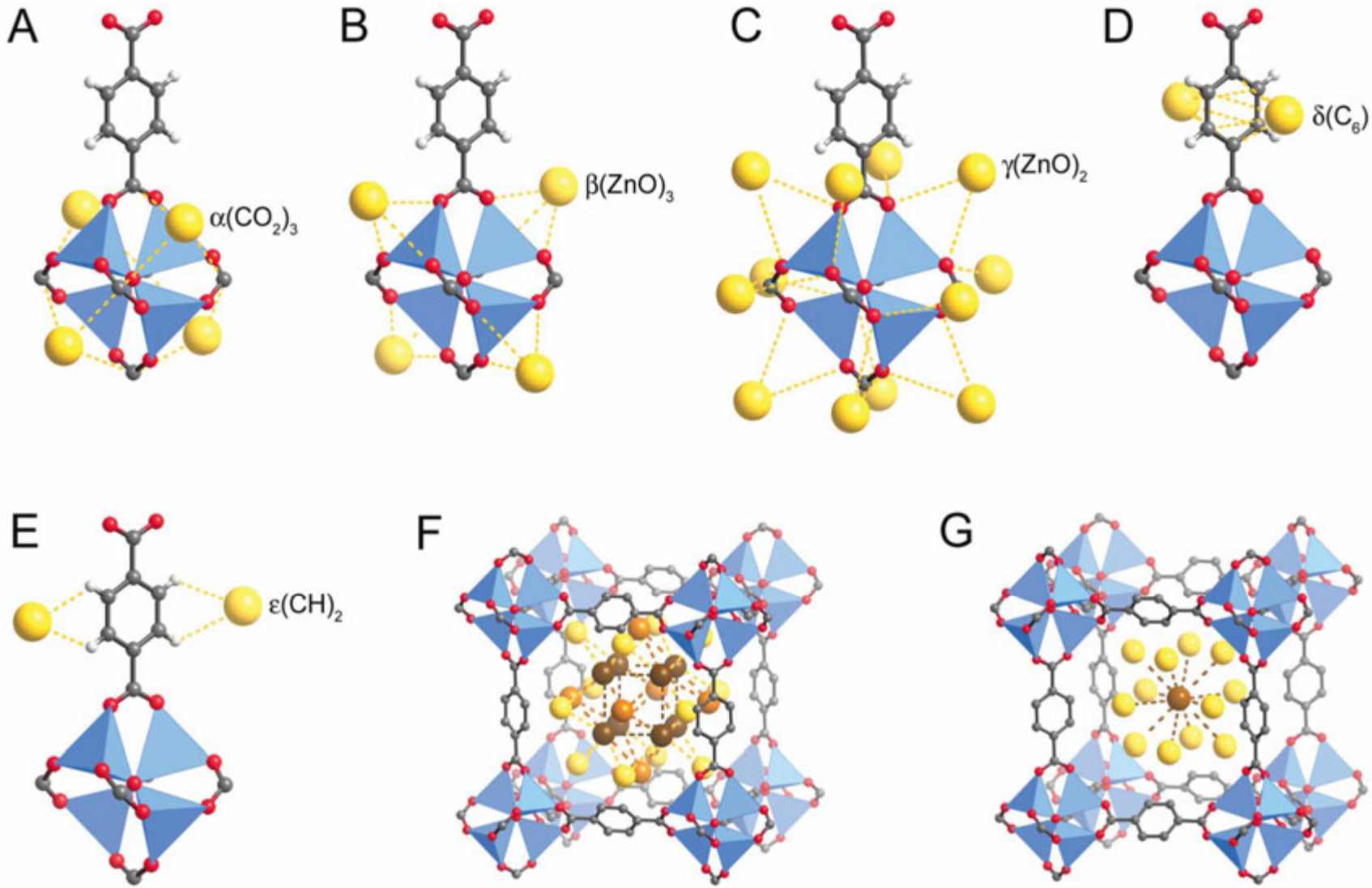


IRMOF-13

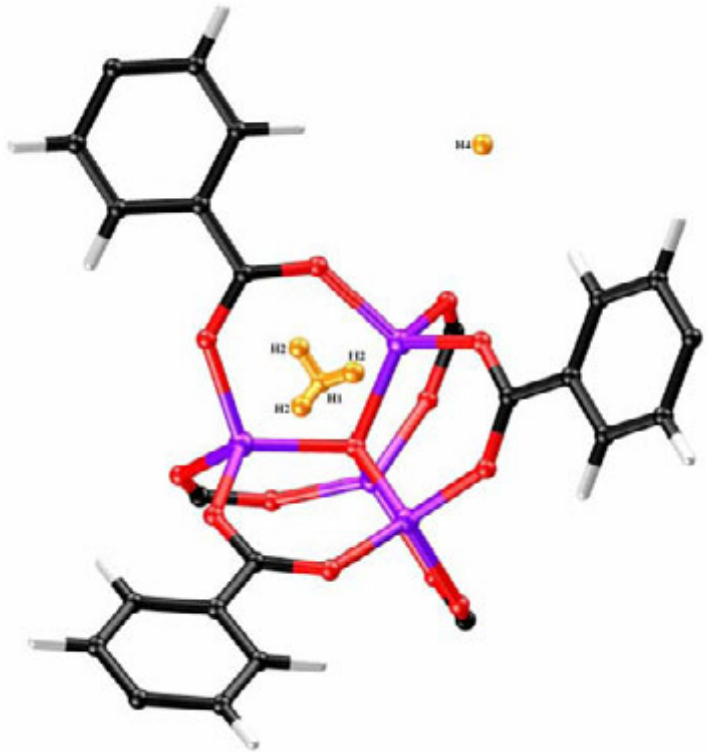
Hydrogen Adsorption Sites

- Inelastic neutron scattering (reported last review)
- X-ray single crystal structure on N_2 and Ar
- Single crystal neutron diffraction

Single crystal X-ray diffraction at 30 K for Ar guest



Single Crystal Neutron Diffraction



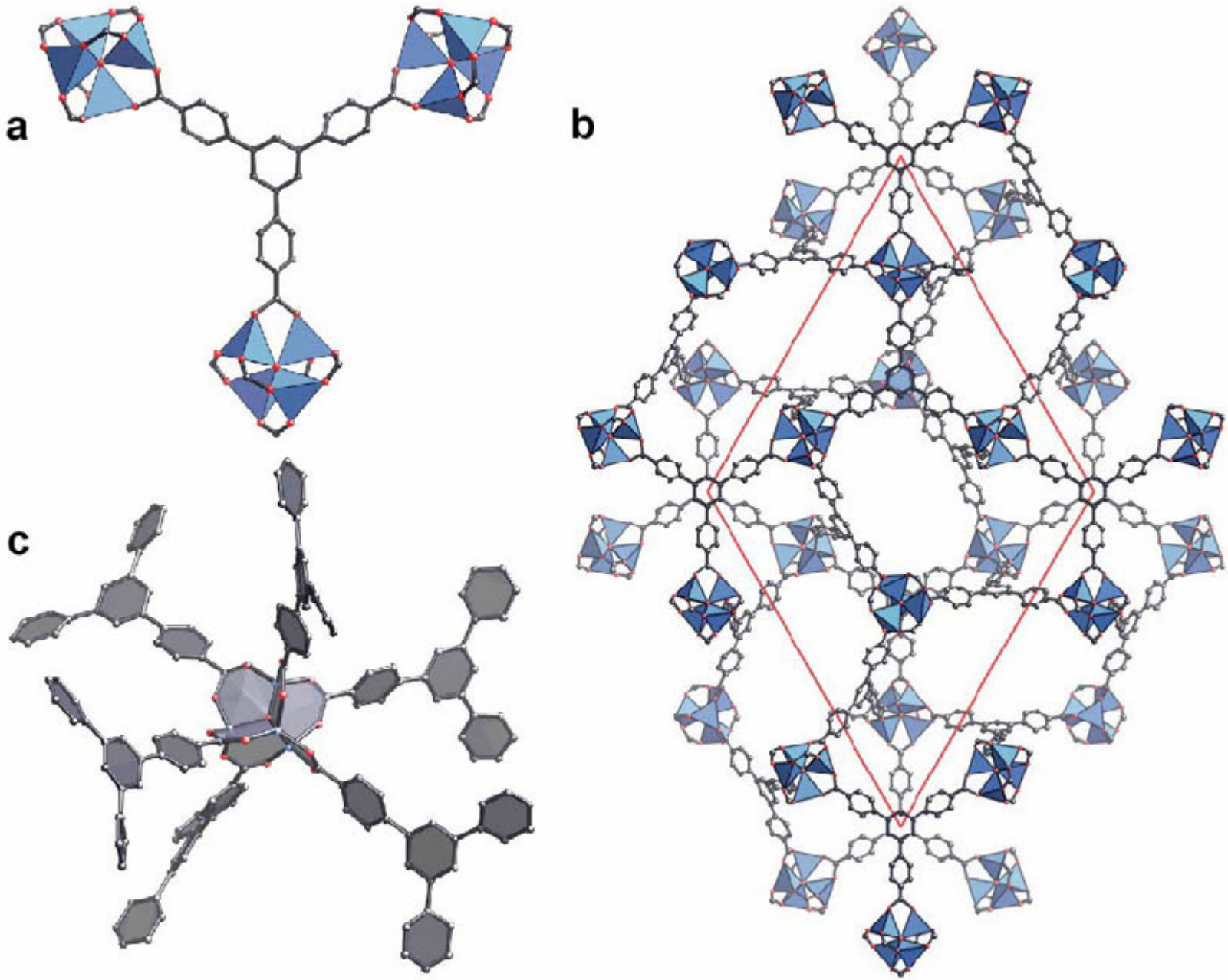
Data collected on VIVALDI (ILL) on 0.5 mm^3 crystal sealed under D_2

Appearance of D_2 on α**$(CO_2)_3$** site at 50 K, additional D_2 appears on β**$(ZnO)_3$** at 5 K

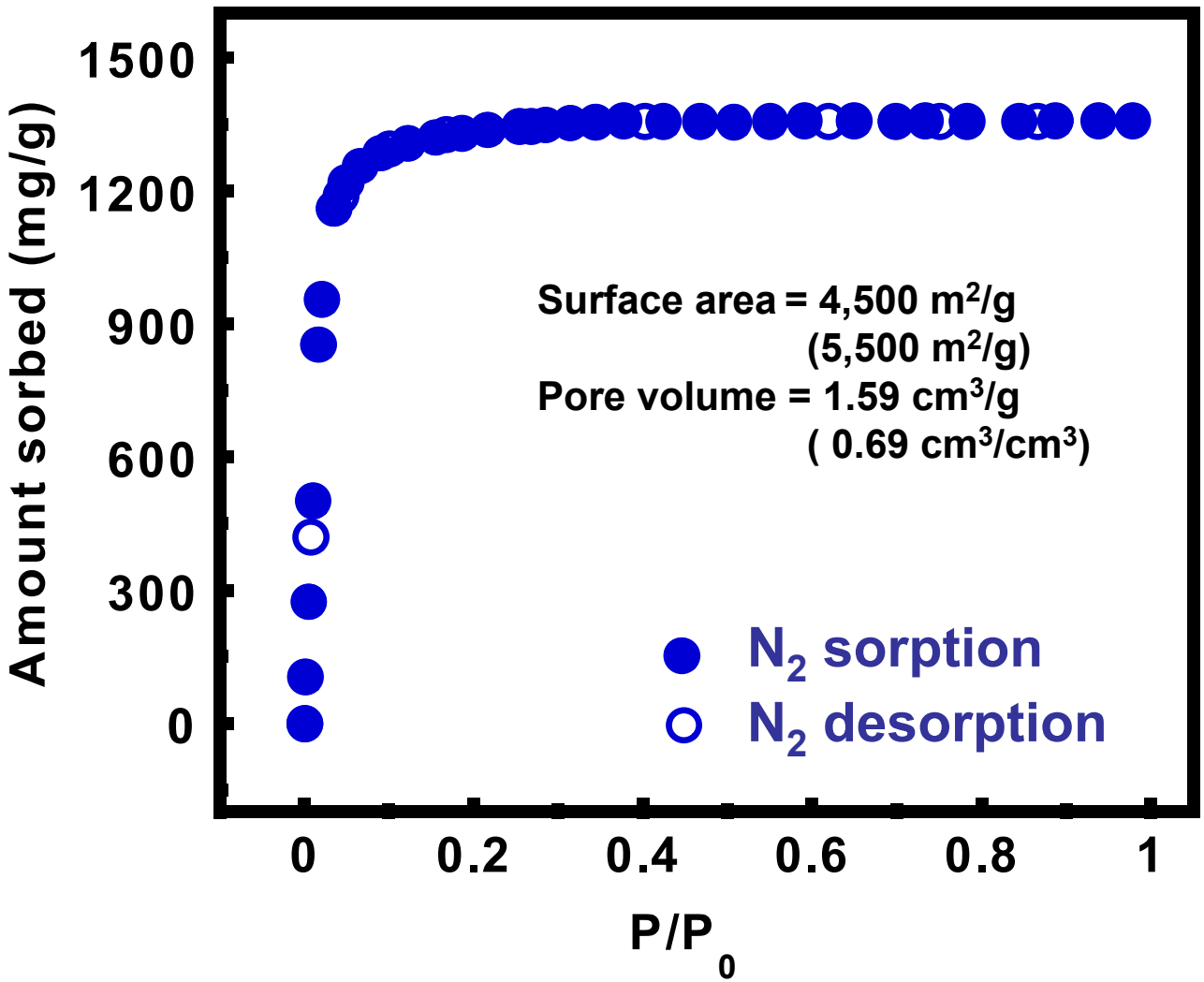
J. Howard and O. Yaghi , Chem. Commun. 2006

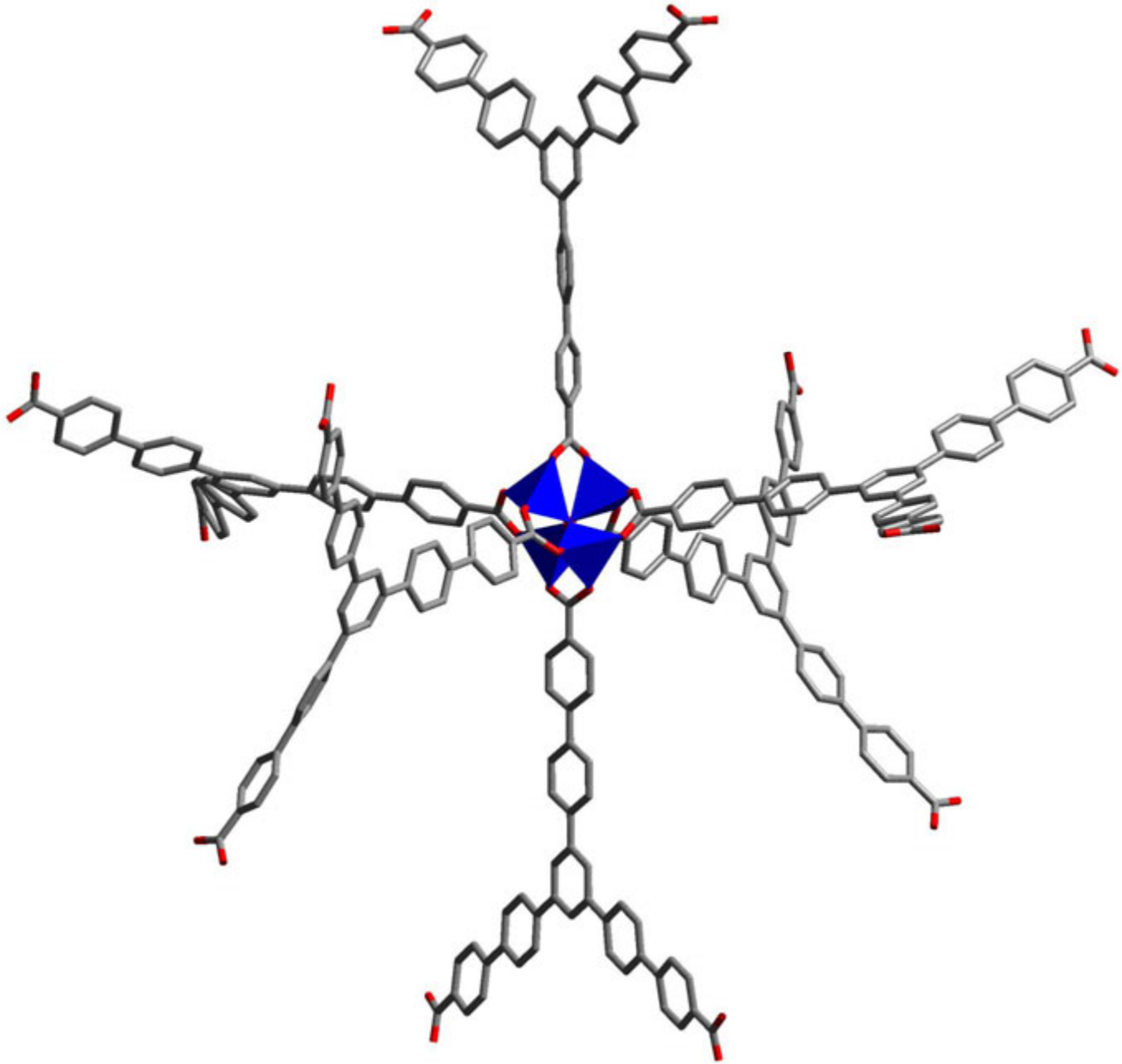
Relationship of surface area to hydrogen uptake and reversibility of uptake

- Design of surfaces replete with adsorption sites
- Can high surface area and reduced dead volume (*i.e.* good volumetric capacity) be achieved in one material?
- Uptake capacities of MOFs under high pressure conditions and 77K
- 4. Reversibility of uptake

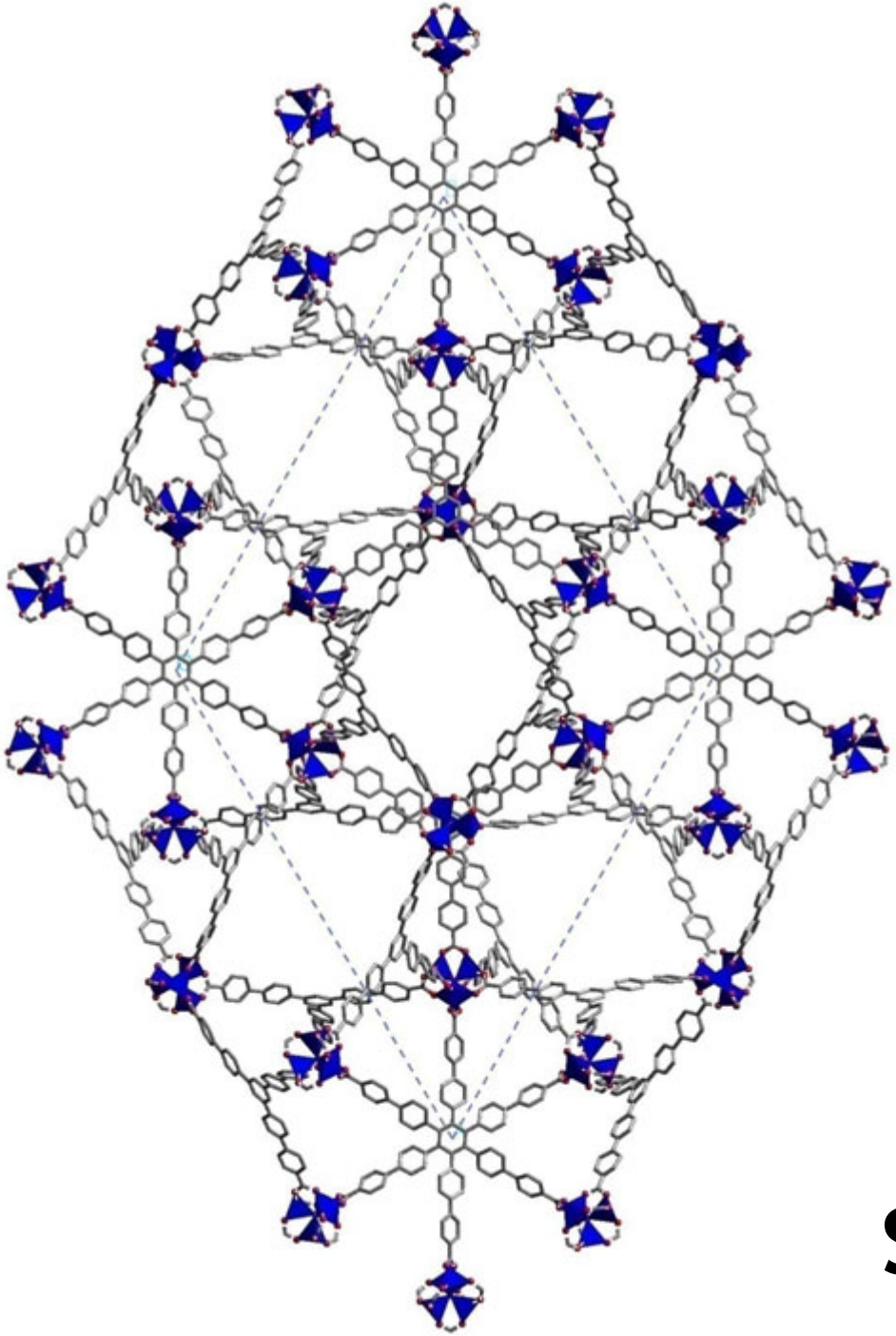

a
b
c

N_2 adsorption isotherm for $Zn_4O(BTB)_2$





$Zn_4O(BBC)_2$



MOF-200:

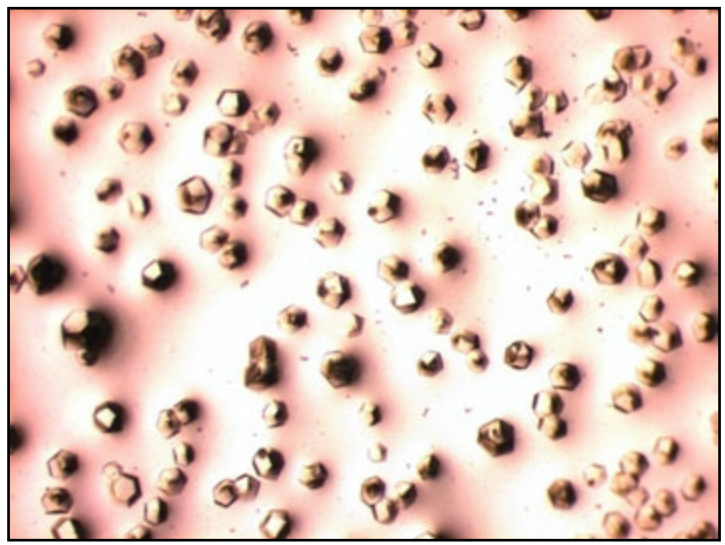
$Zn_4O(BBC)_2$

Trigonal, P-3

a = b = 51.45 Å

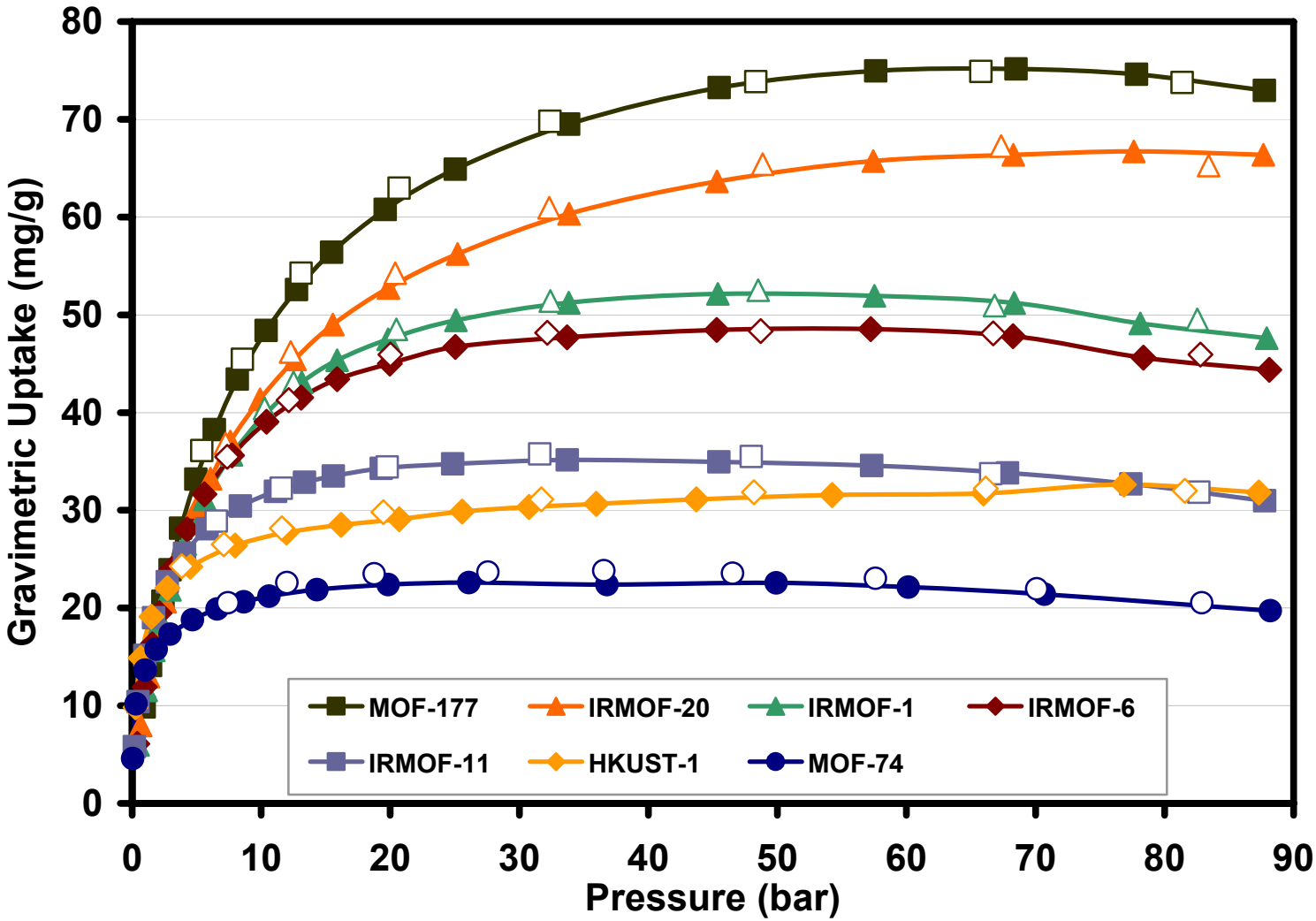
c = 41.80 Å

V = 95,822.1 $Å^3$

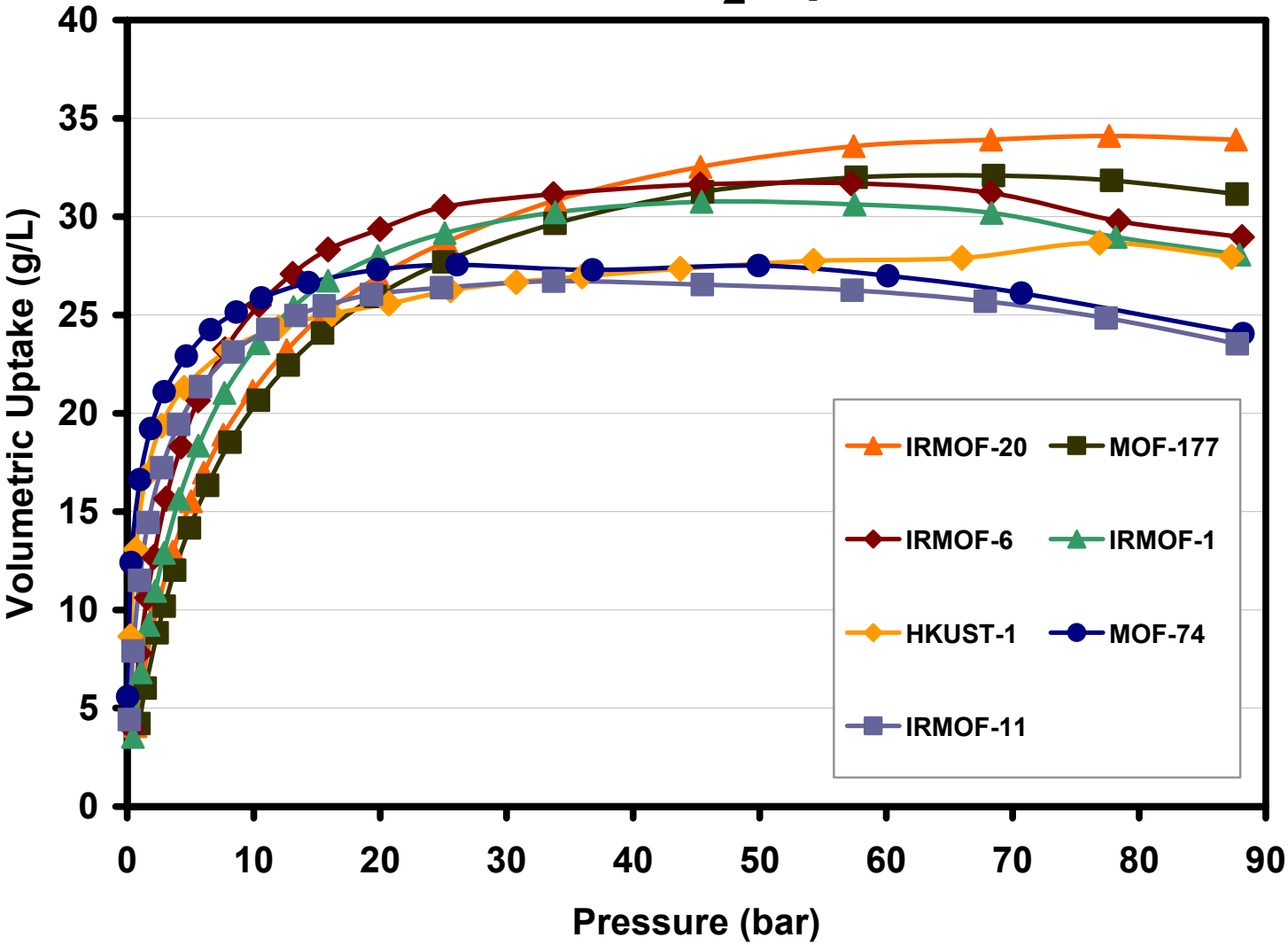


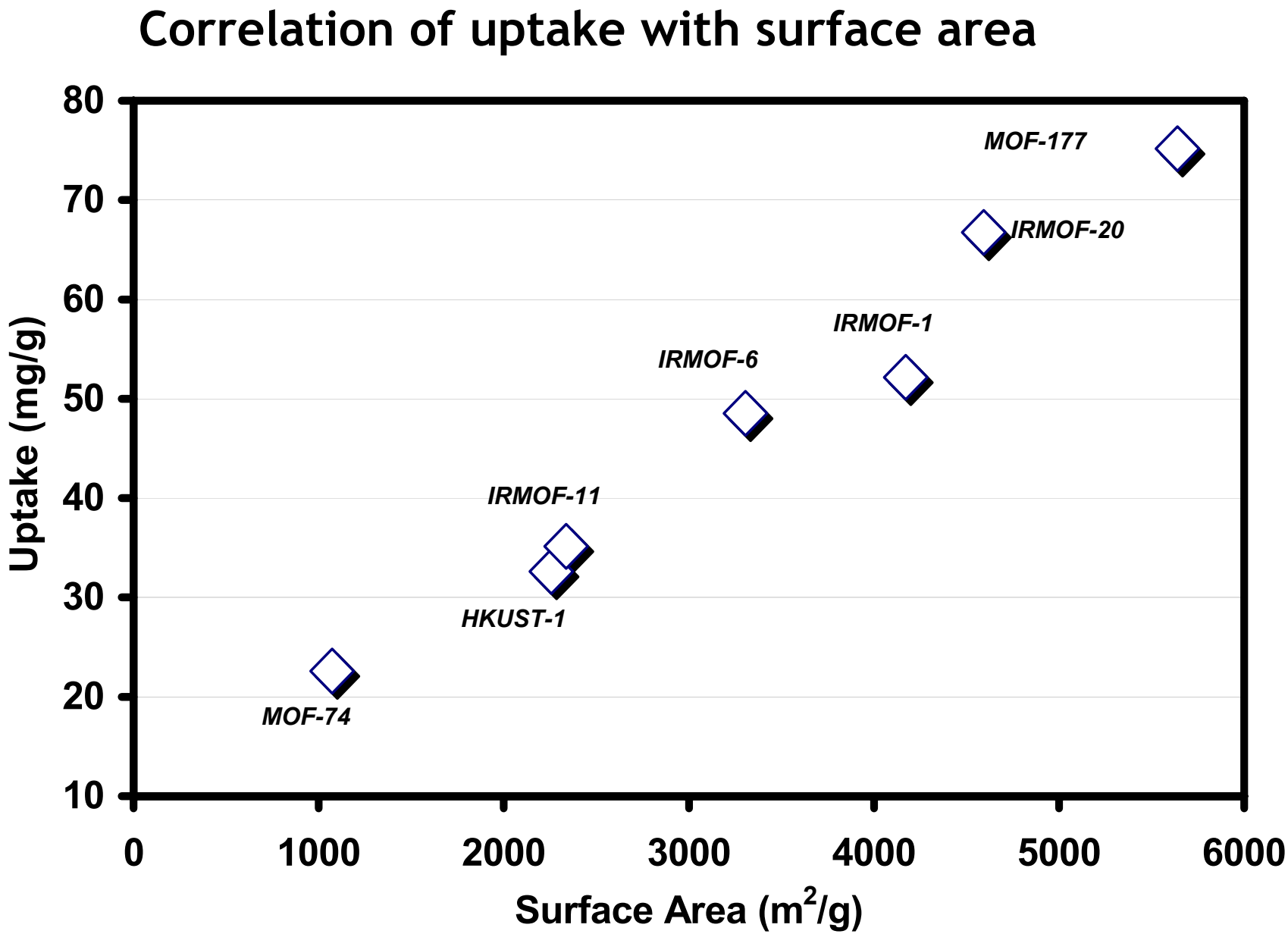
S.A. = ‘8,000’ m^2/g

7.5 wt % Hydrogen uptake at 77K



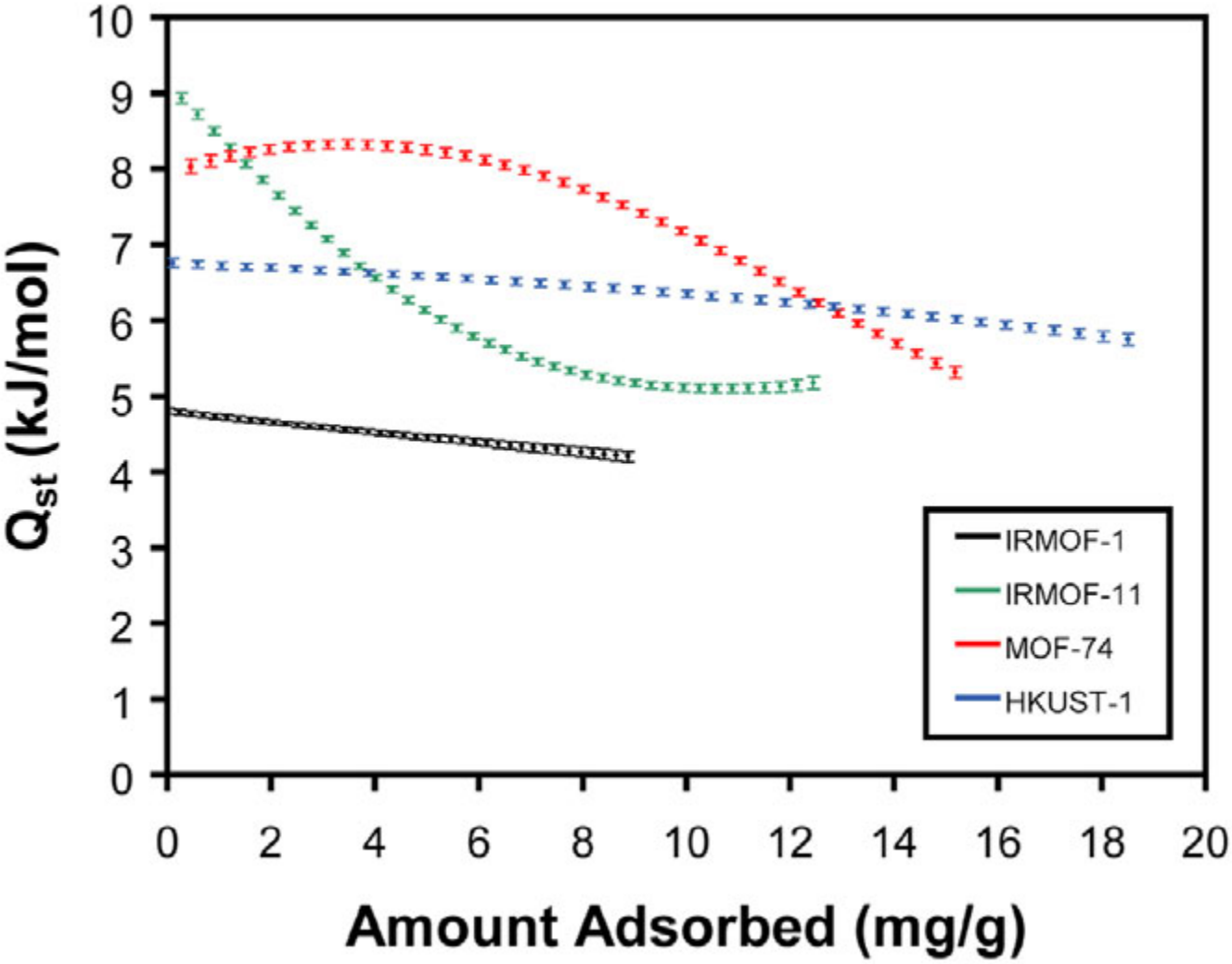
MOF volumetric H_2 uptake at 77 K

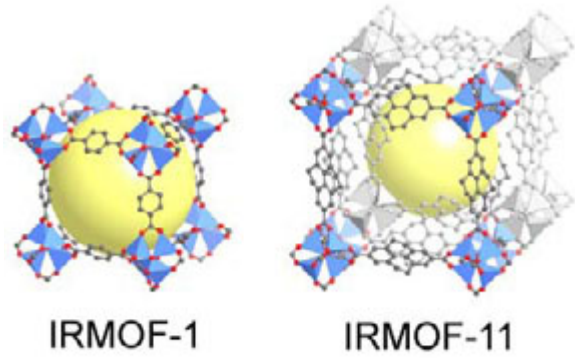


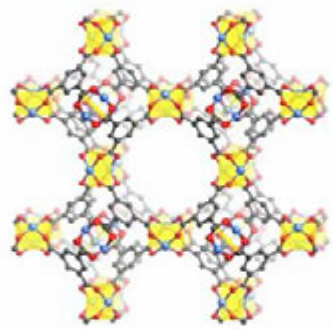

Correlation of uptake with surface area
Uptake (mg/g)
Surface Area (m2/g)
80
70
60
50
40
30
20
10
0
1000
2000
3000
4000
5000
6000
MOF-177
IRMOF-20
IRMOF-1
IRMOF-6
IRMOF-11
HKUST-1
MOF-74

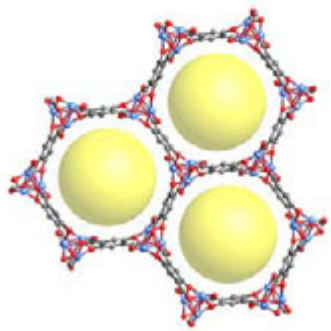
Isosteric Heats of Adsorption

MOFs combining open metal sites with 7-8 Angstroms pore size are most favored



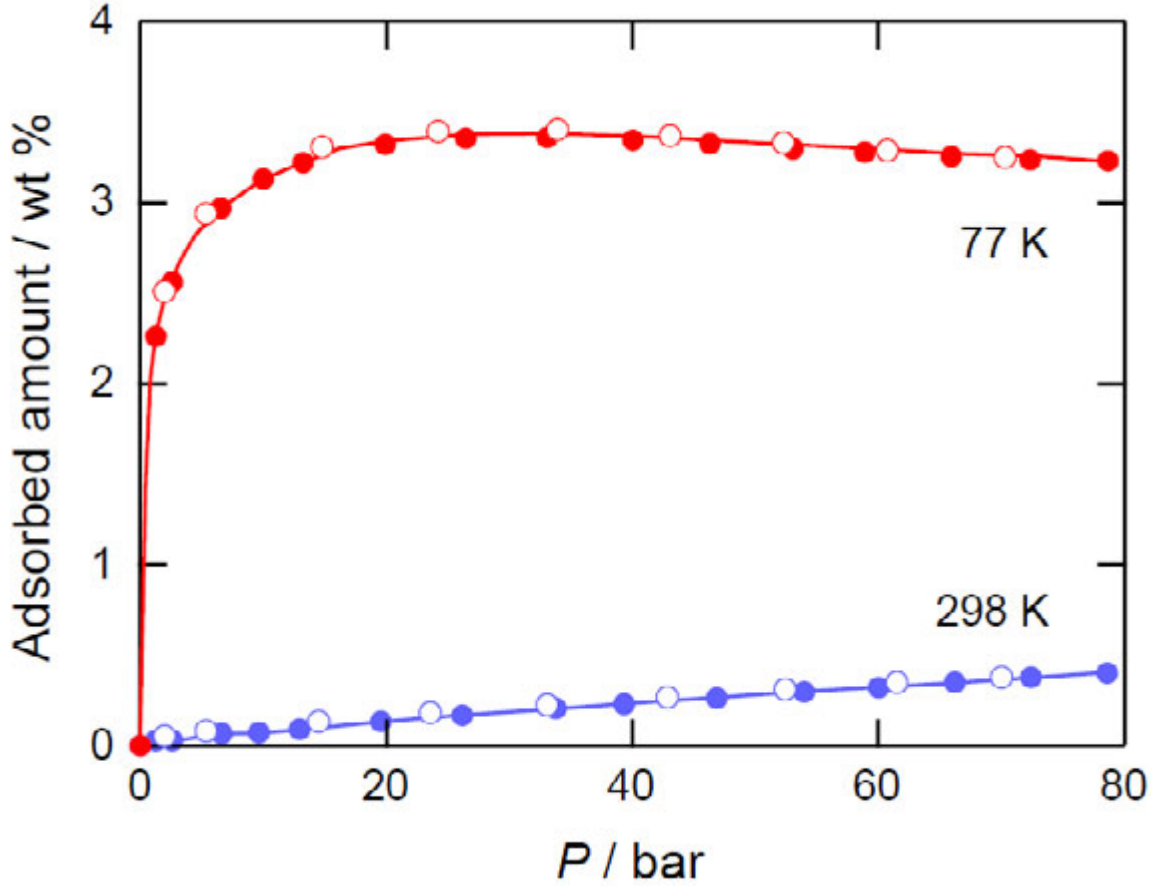






H_2 Adsorption (high-P)

Poor room temperature uptake



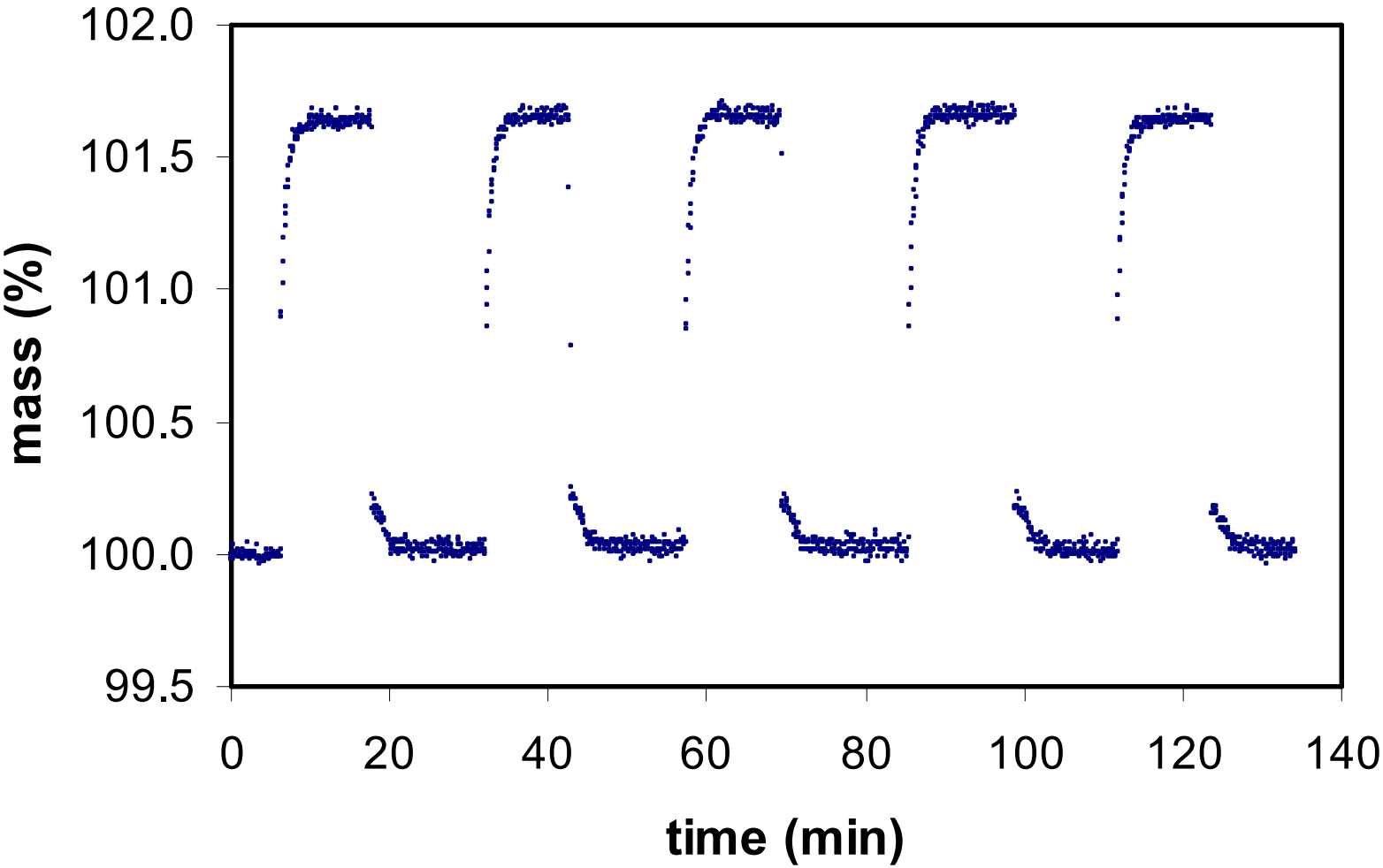
d = 0.884

	wt%	mg/g	mmol/g	cc/g	cc/cc	g/L
77 K	3.3	33	16.5	370	327	29.2
298 K	0.4	4	2	45	40	3.5

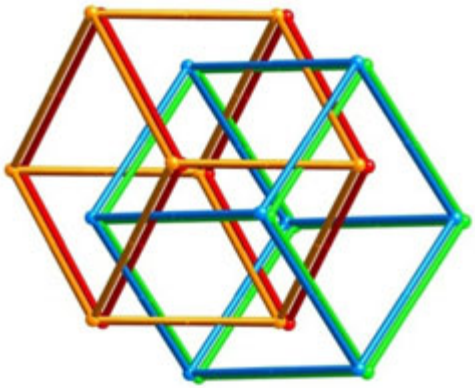
Kinetic Profile of Uptake and Release of hydrogen

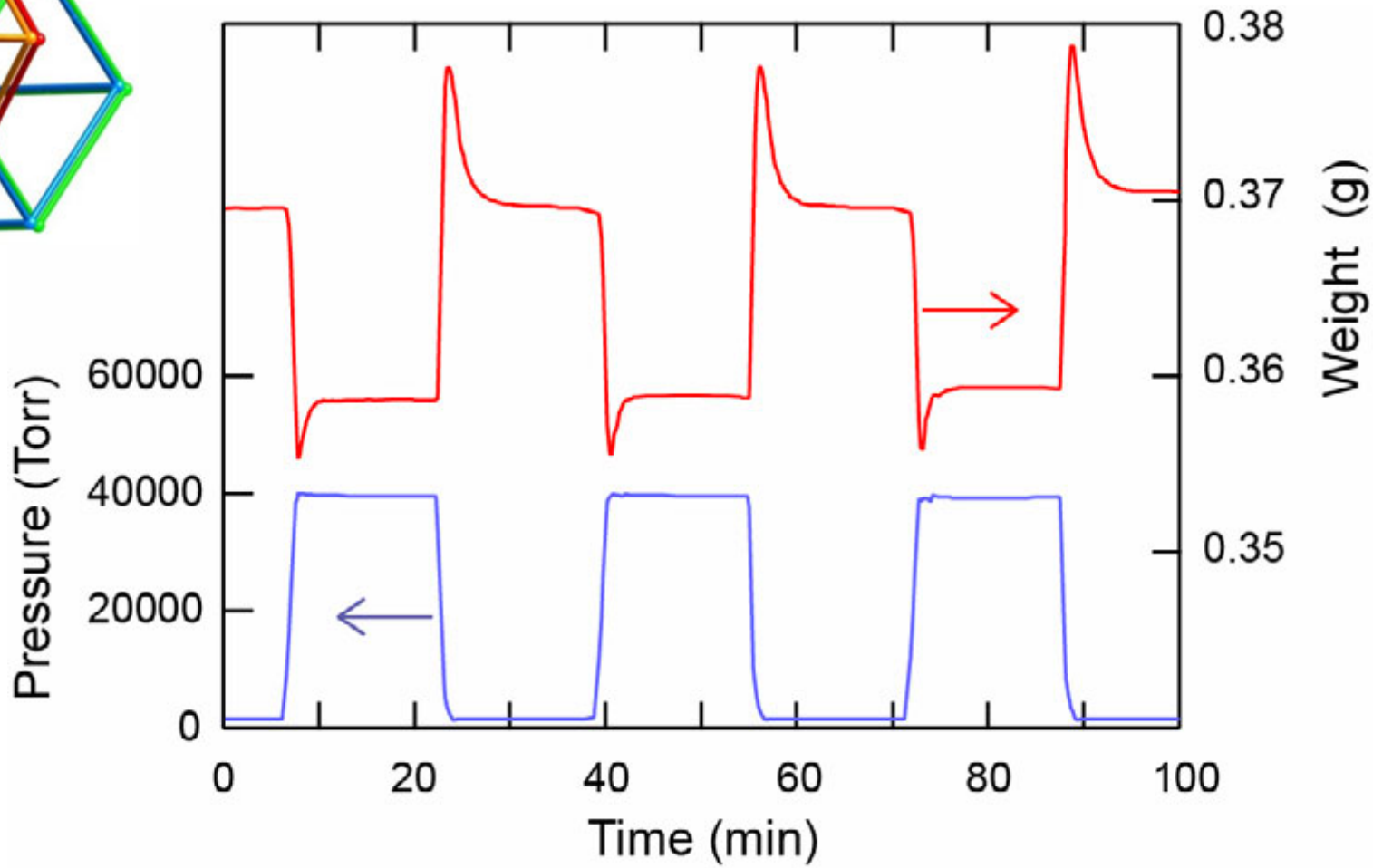
(Fueling Time)

Completely Reversible Charge/Discharge of Hydrogen Adsorption in IRMOF-11 Fueling time 2.5 minutes



Typical IRMOF-62 kinetic profile (Fueling time 2 minutes)

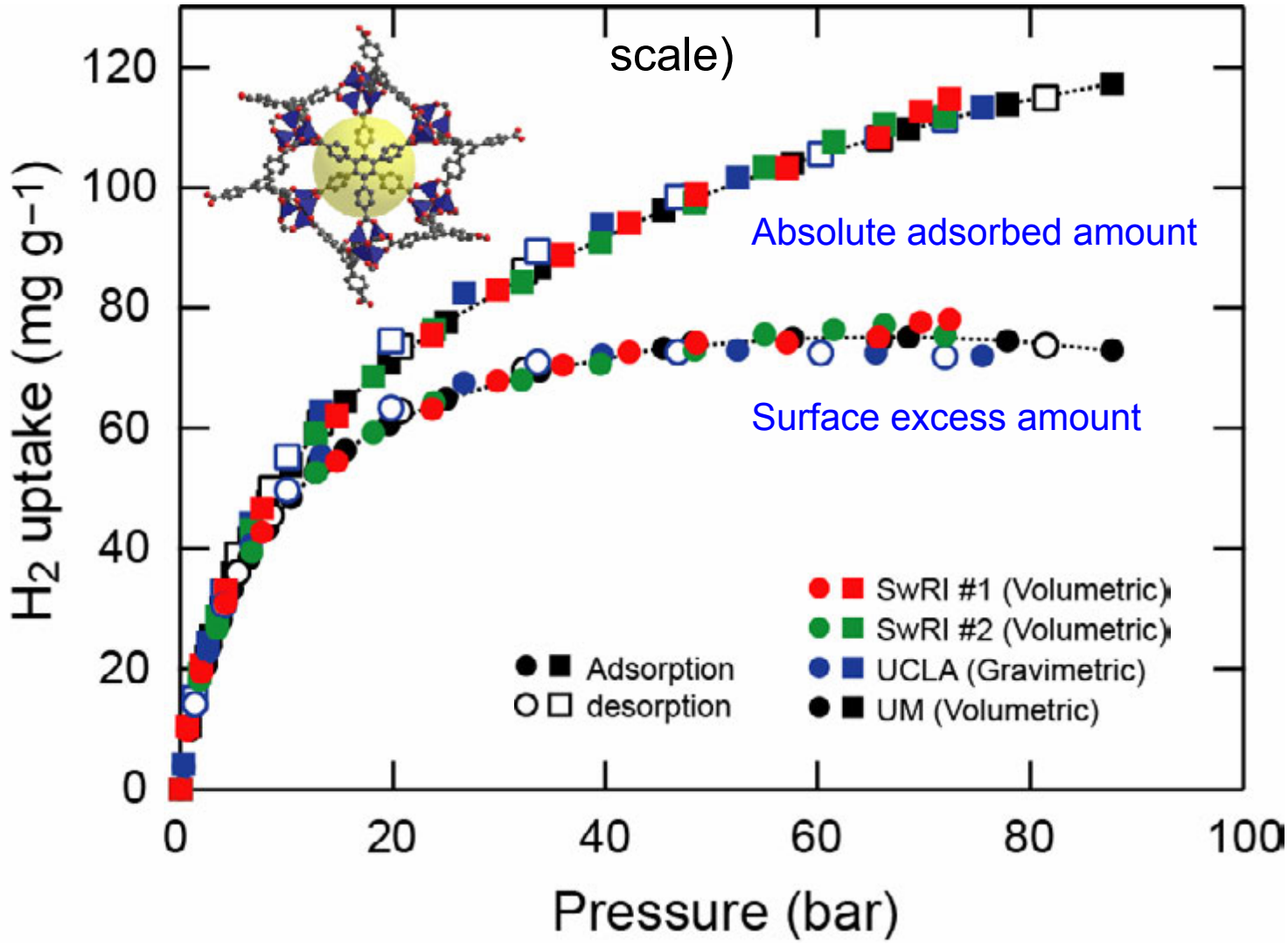




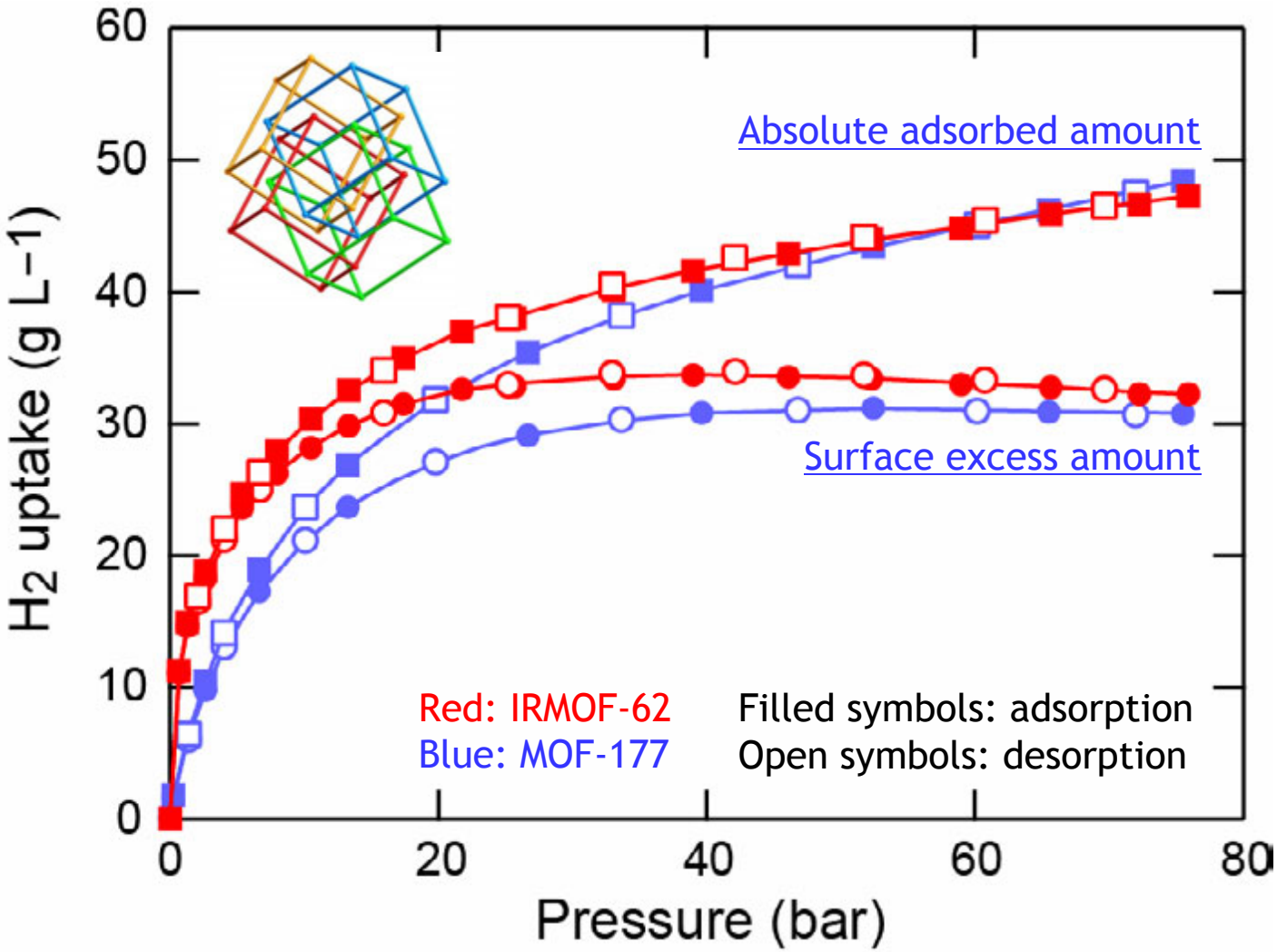
Blue: applied pressure, red: weight change (without buoyancy correction)

Independent Verification of MOF-177 Hydrogen Uptake Capacity

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



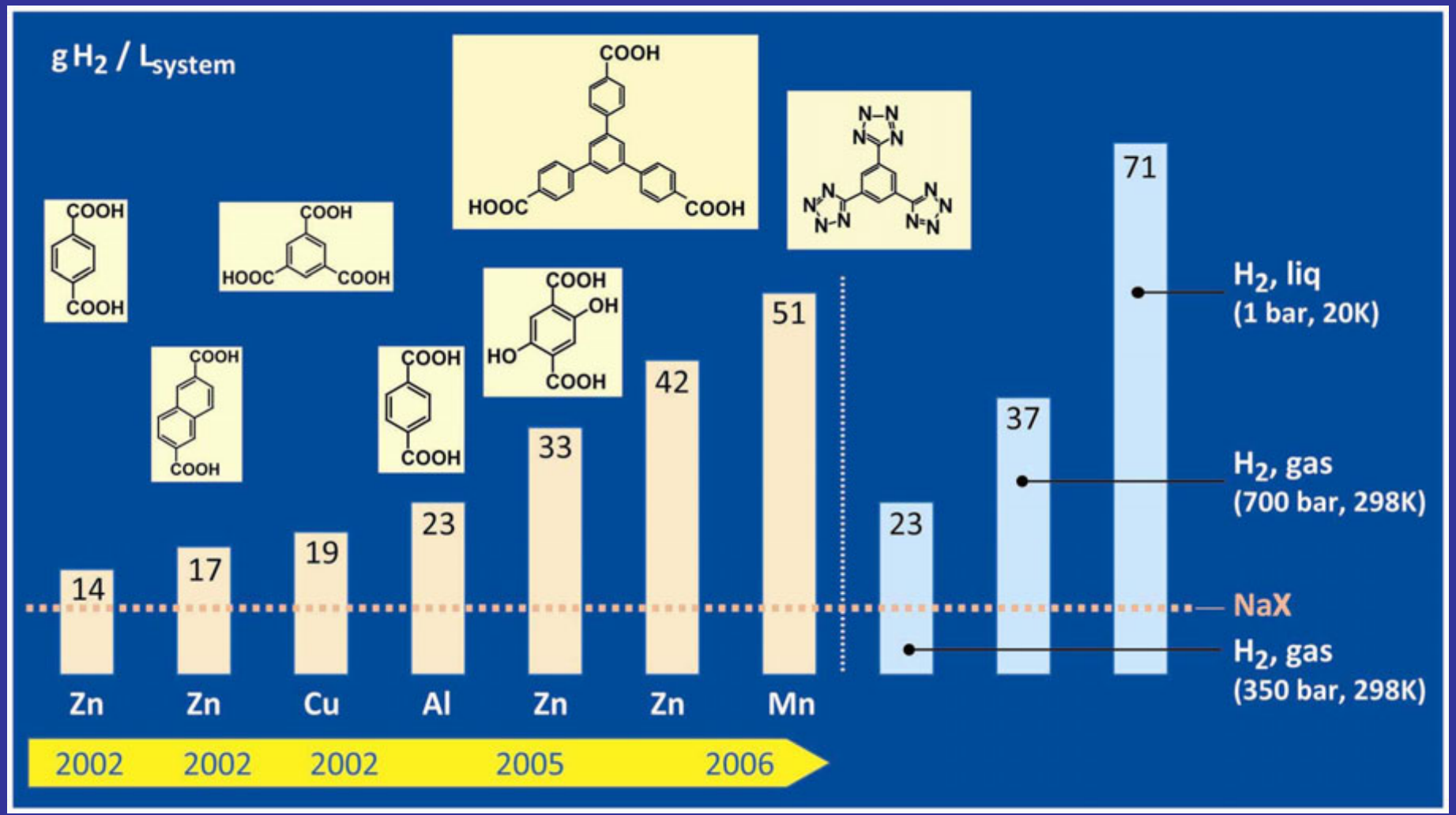
Volumetric H_2 uptake for IRMOF-62



IRMOF-62 Surface area: 2650 m^2/g, Pore volume: 0.95 cm^3/g

MOF

Hydrogen Storage Capacities (50 bar, 77K)



Nanocubes as molecular fuel tanks
BASOCUBES

Strategies for increasing adsorption energy

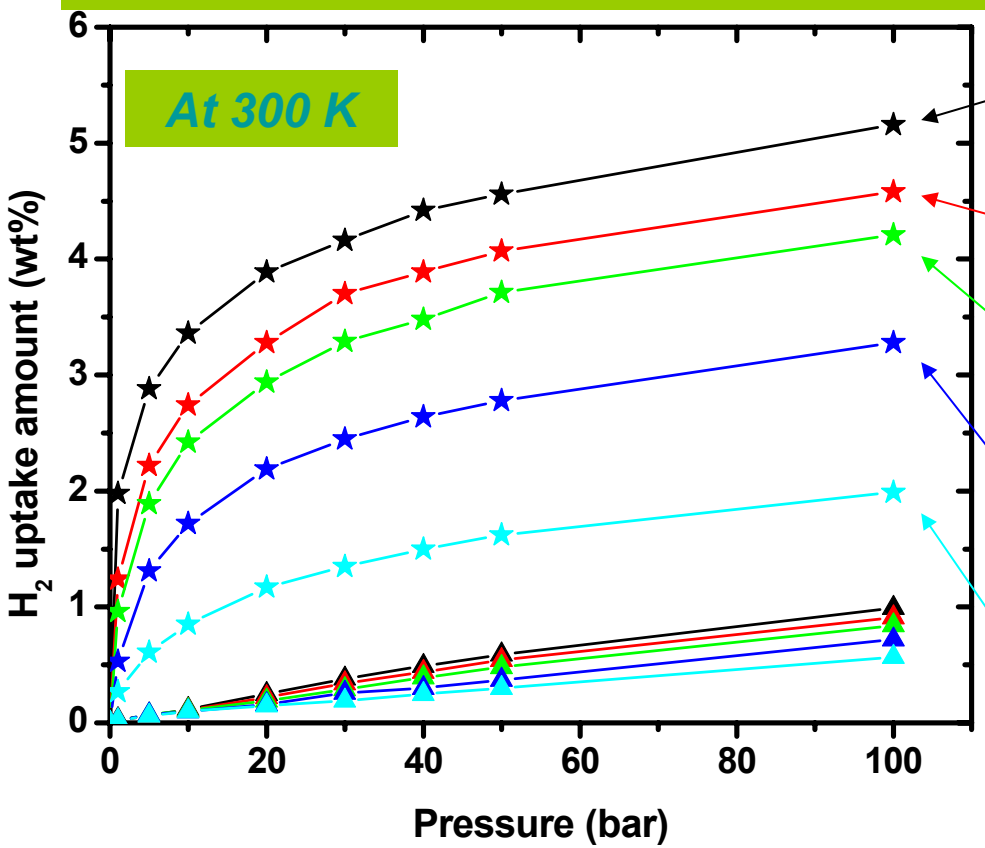
- Coordination with theory (Prof. Bill Goddard, Caltech)
- Impregnation strategies: (a) polar polymers, (b) clusters of lights metals, and organo-metallic complexes
- Design of soft chemi-sorption within the pores: Proximal Lewis acid-Lewis base sites

Strategy 1:

Binding Li to six membered rings

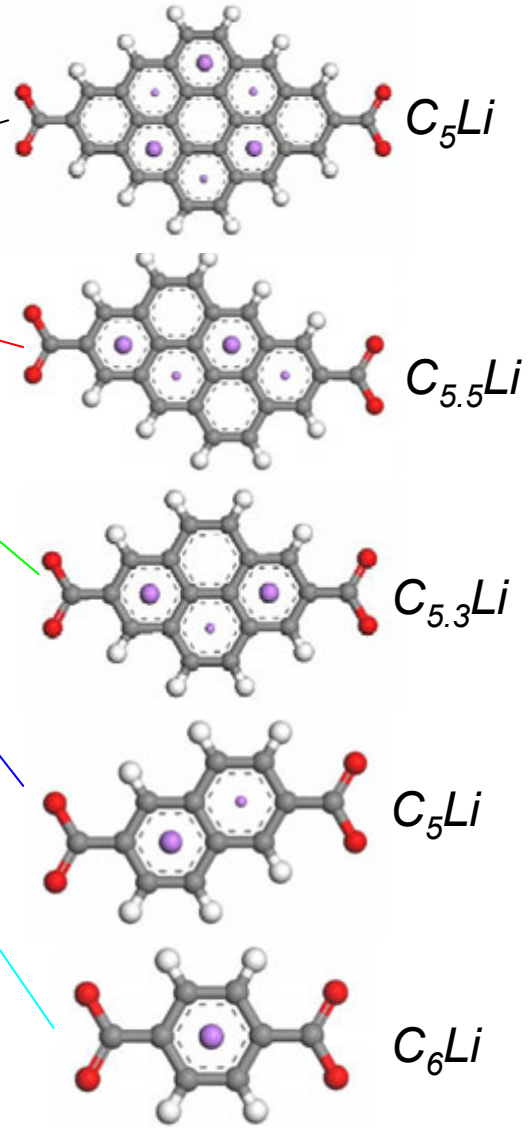
High room temperature hydrogen uptake (5%wt) in Li-doped Zn-MOF systems

Predictions (Han and Goddard, Caltech)



Triangle: pure MOFs, Star: Li-doped MOFs

Cyan: MOF6, Blue: MOF10, Green: MOF16, Red: MOF22, Black: MOF30

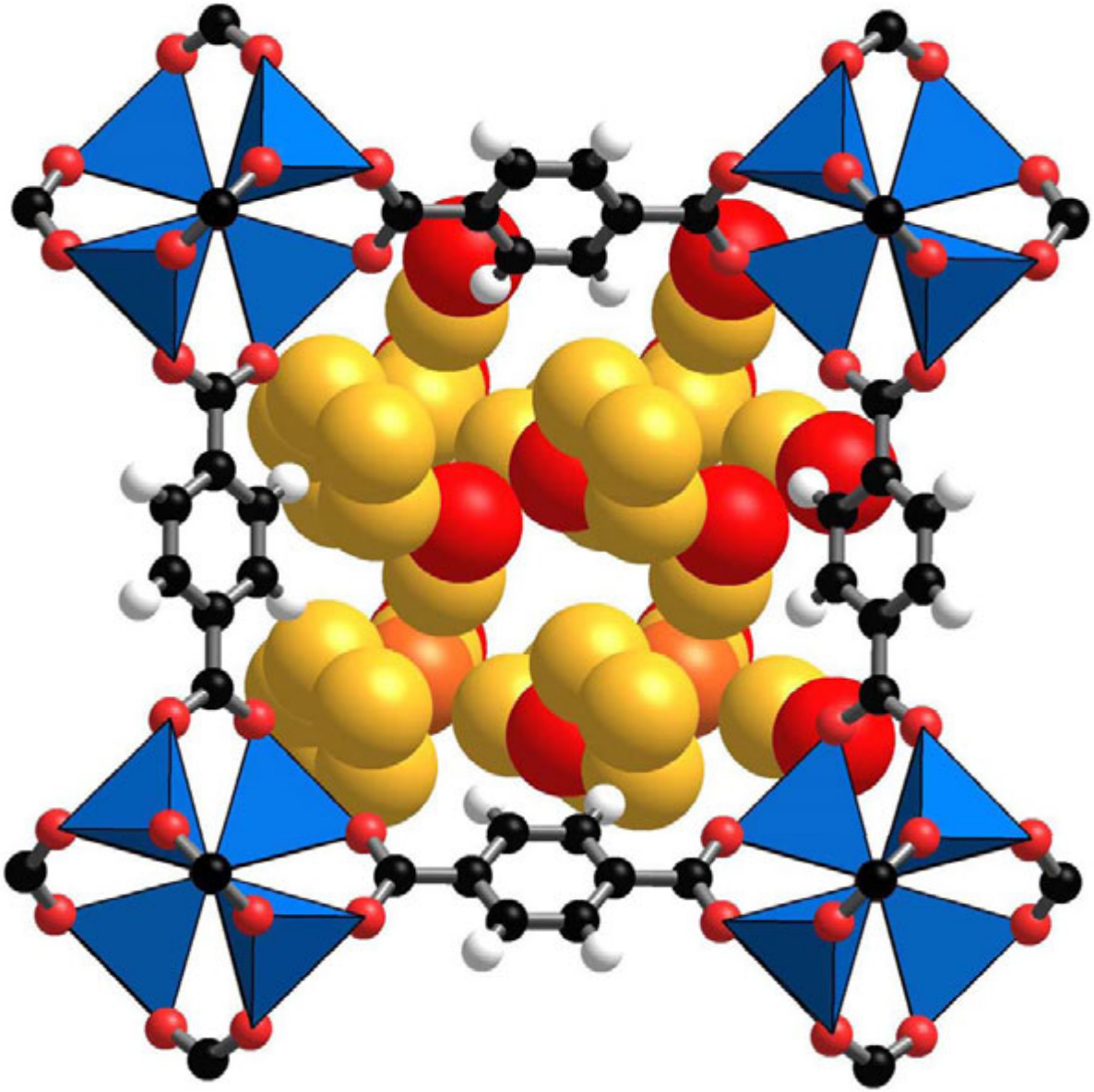


Strategy 2A:

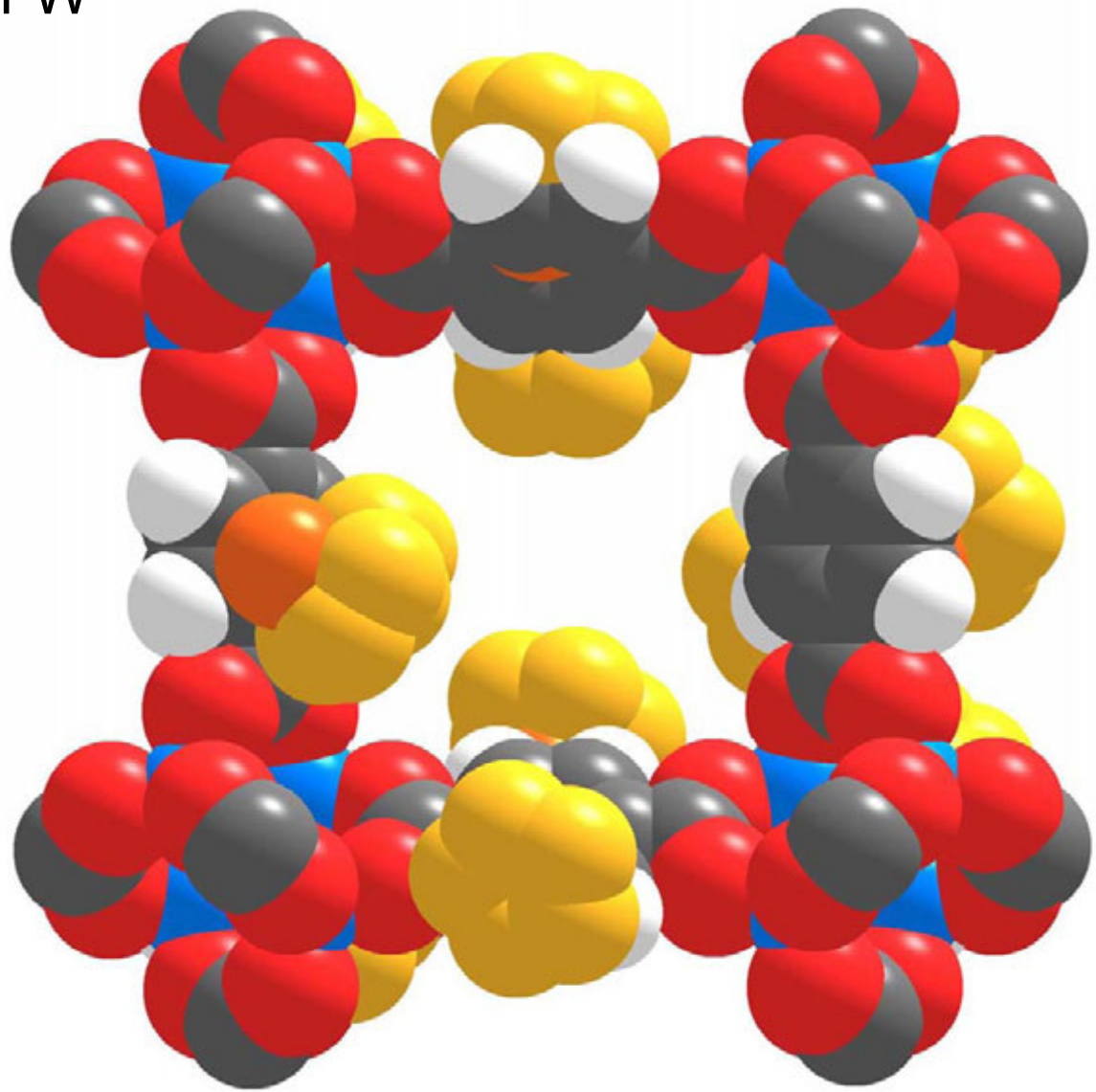
Impregnation with metal complexes having open metal sites

Proof of Concept

Successful Impregnation of CpW(CO)3 in M



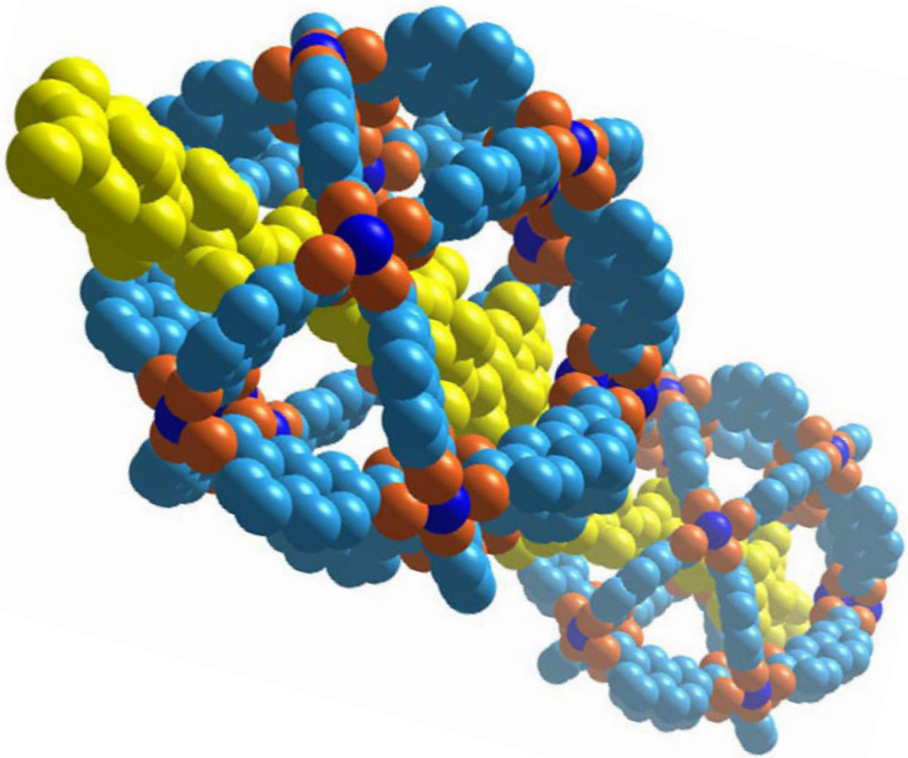
Carbonyl groups can be removed by heating under vacuum, leaving behind open metal sites of W

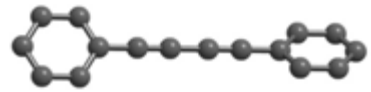


Strategy 2B:

Impregnation with polymers containing conjugation

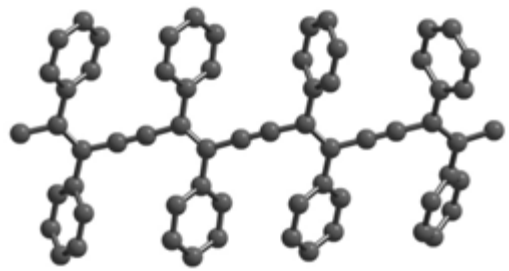
Polymer impregnation MOF-177



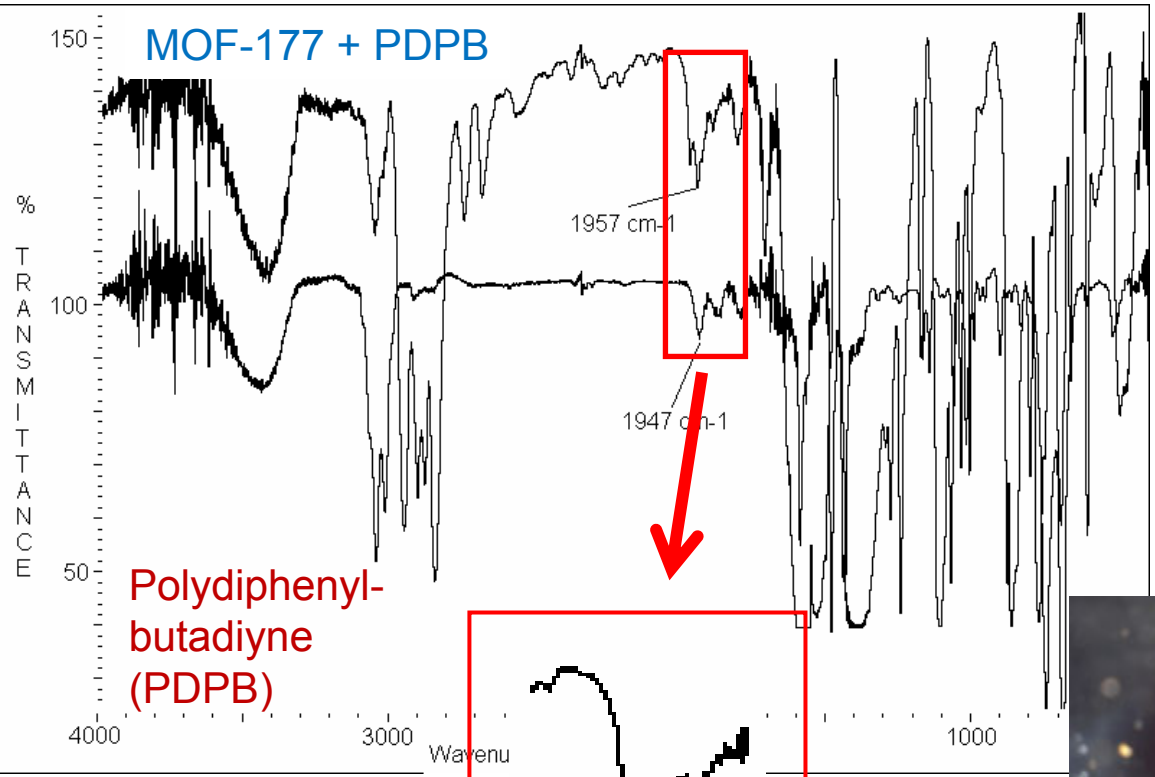


1,4-Diphenylbutadiyne

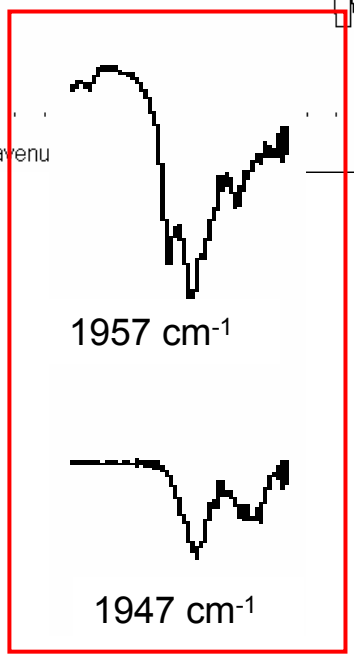
Polymerization of monomer in MOF-177



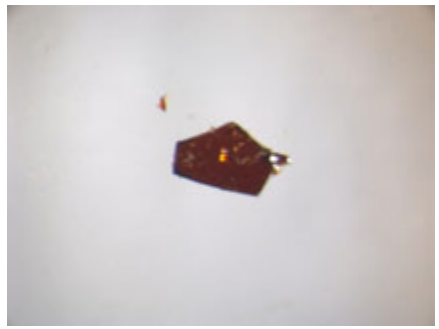
Impregnation



Polydiphenyl-butadiyne (PDPB)



C≡C stretching



A

Sliced face

B

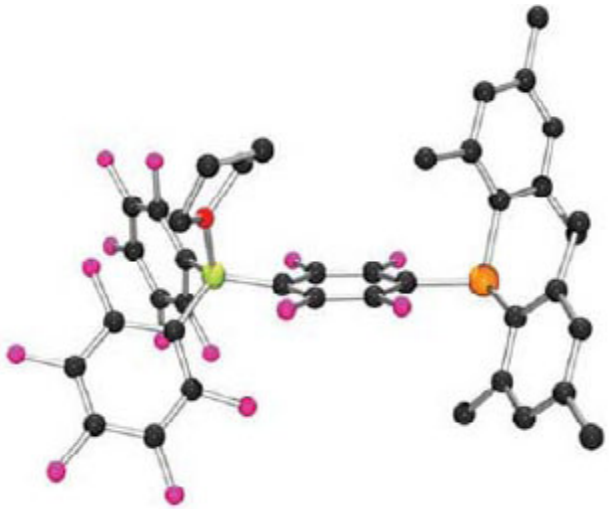
C

A. Single crystal of PDPB
B. MOF-177 + PDPB
C. Sliced MOF-177 + PDPB

Strategy 3:

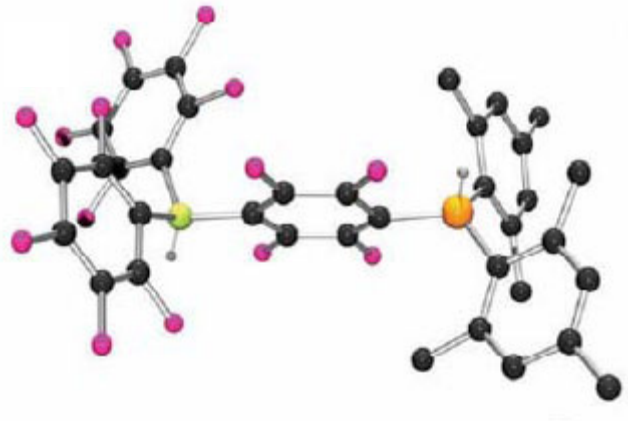
Chemisorption *douce*

Fully Reversible Splitting of H_2



$+H_2$

$- H_2$

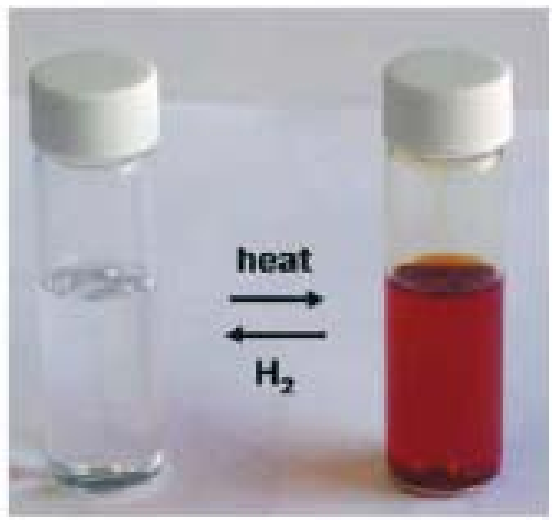


3

Reversible, Metal-Free Hydrogen Activation

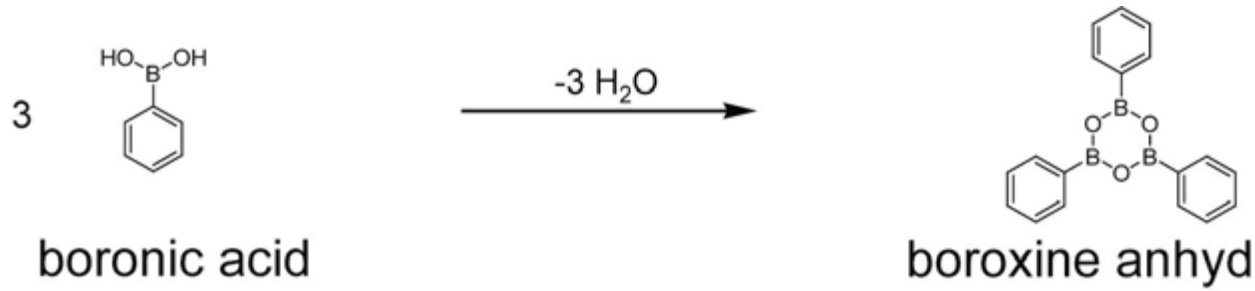
Gregory C. Welch, Ronan R. San Juan, Jason D. Masuda, Douglas W. Stephan*

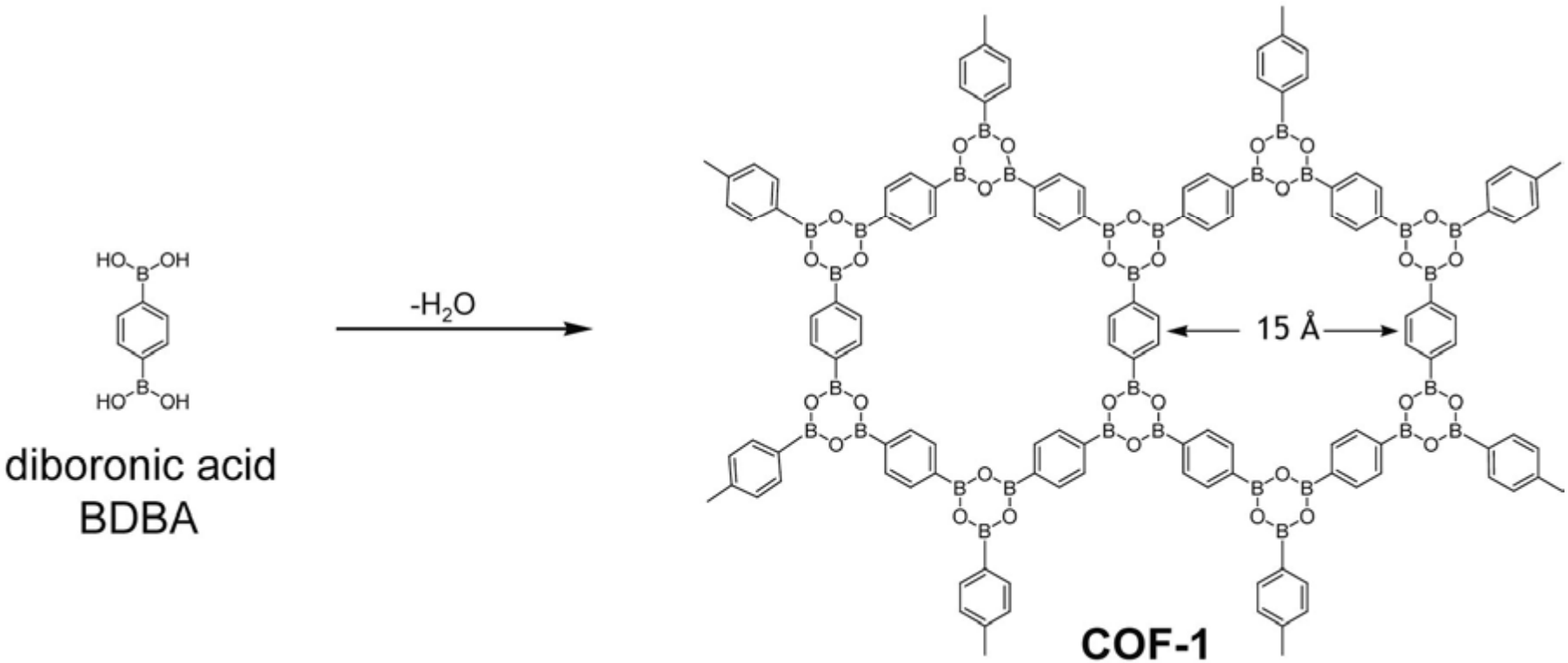
17 NOVEMBER 2006 VOL 314 SCIENCE 1126

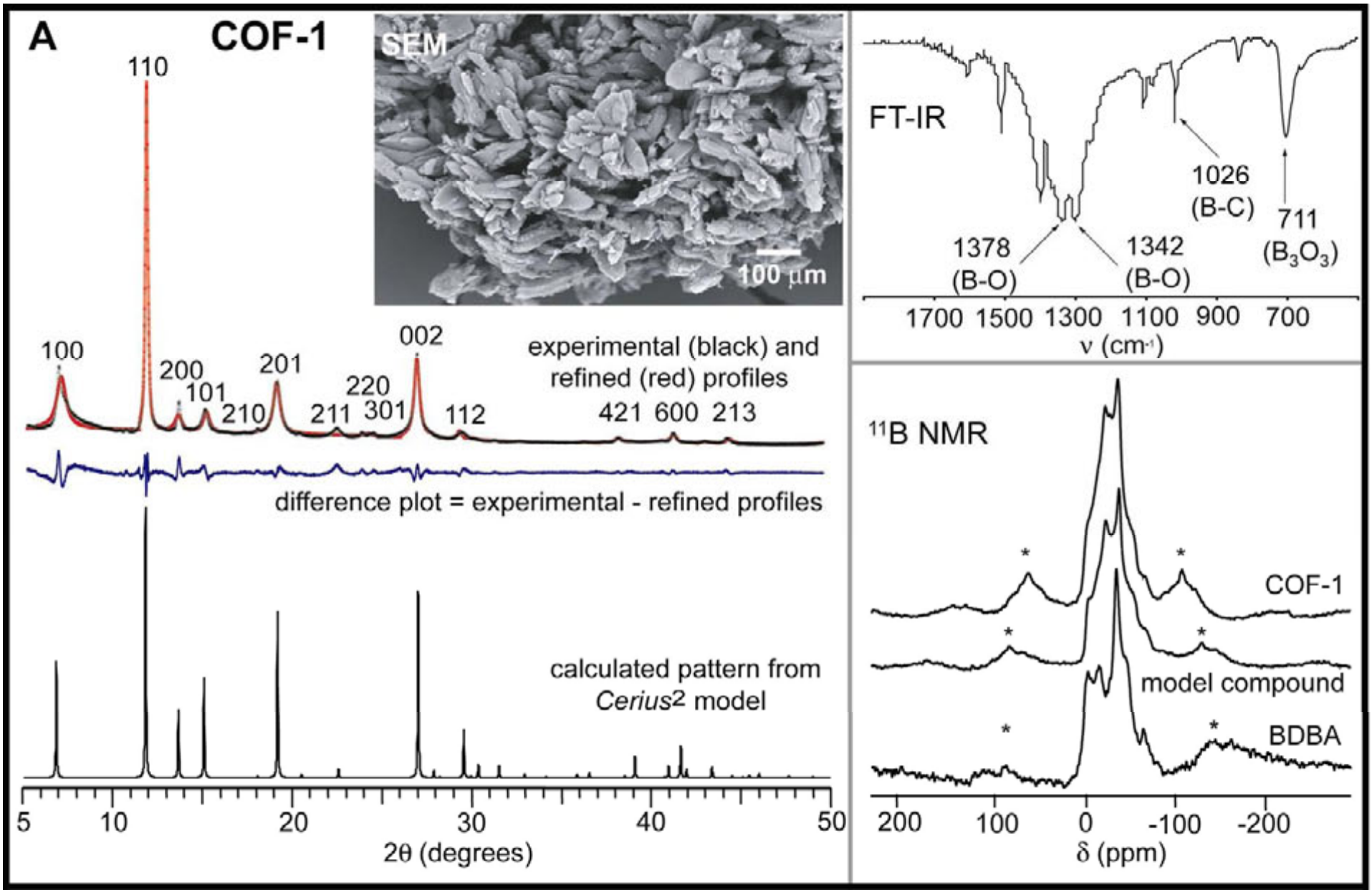


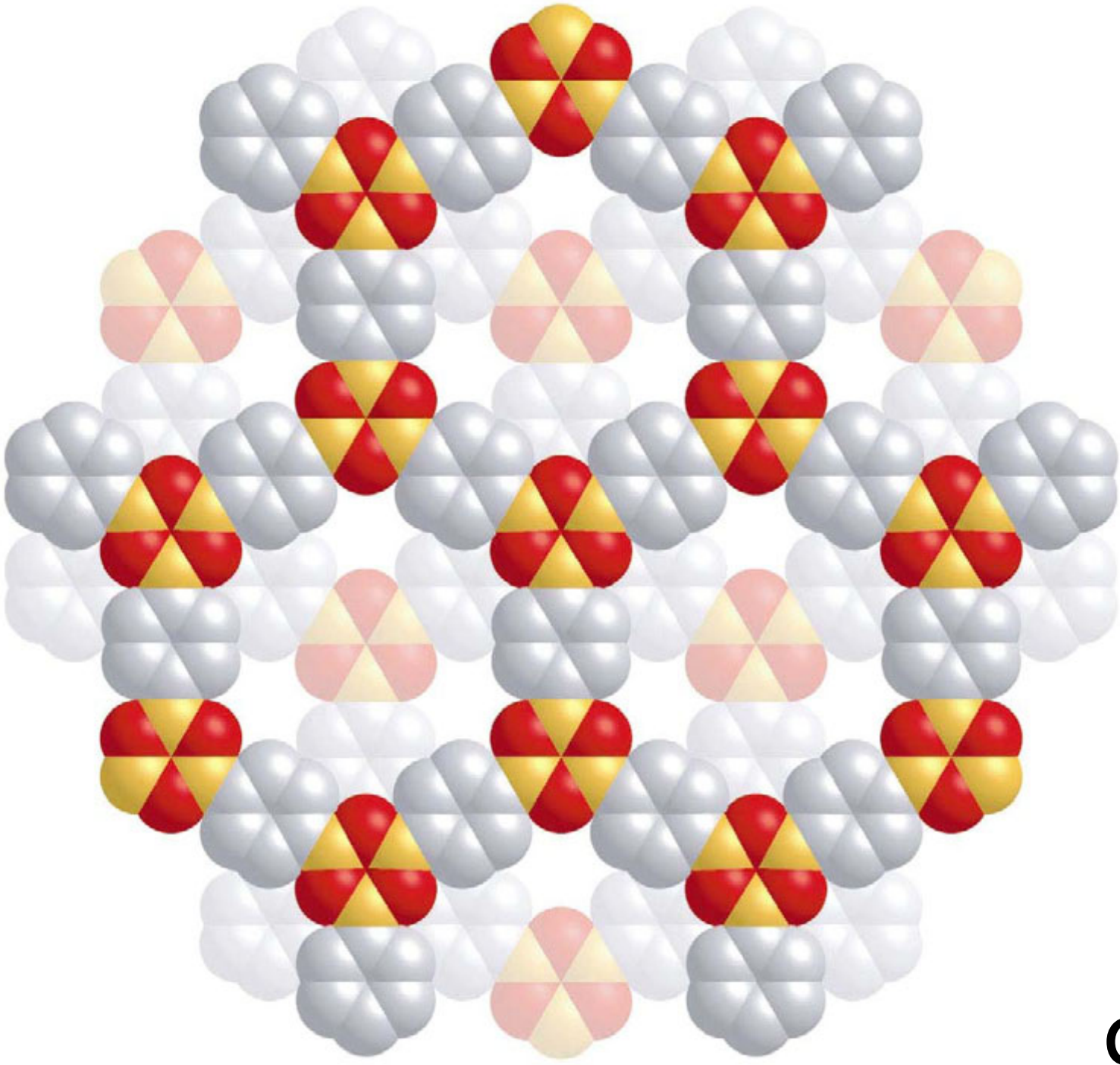
Heating to >100° C quantitatively reverses H_2 dissociation with change in color.

Covalent Organic Frameworks (COFs)

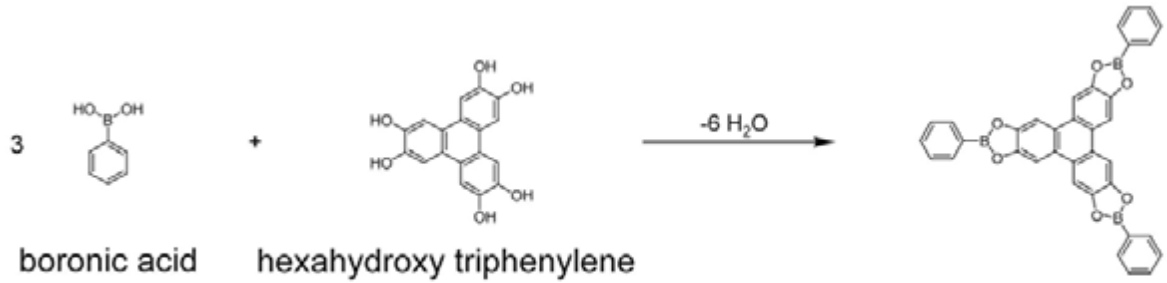


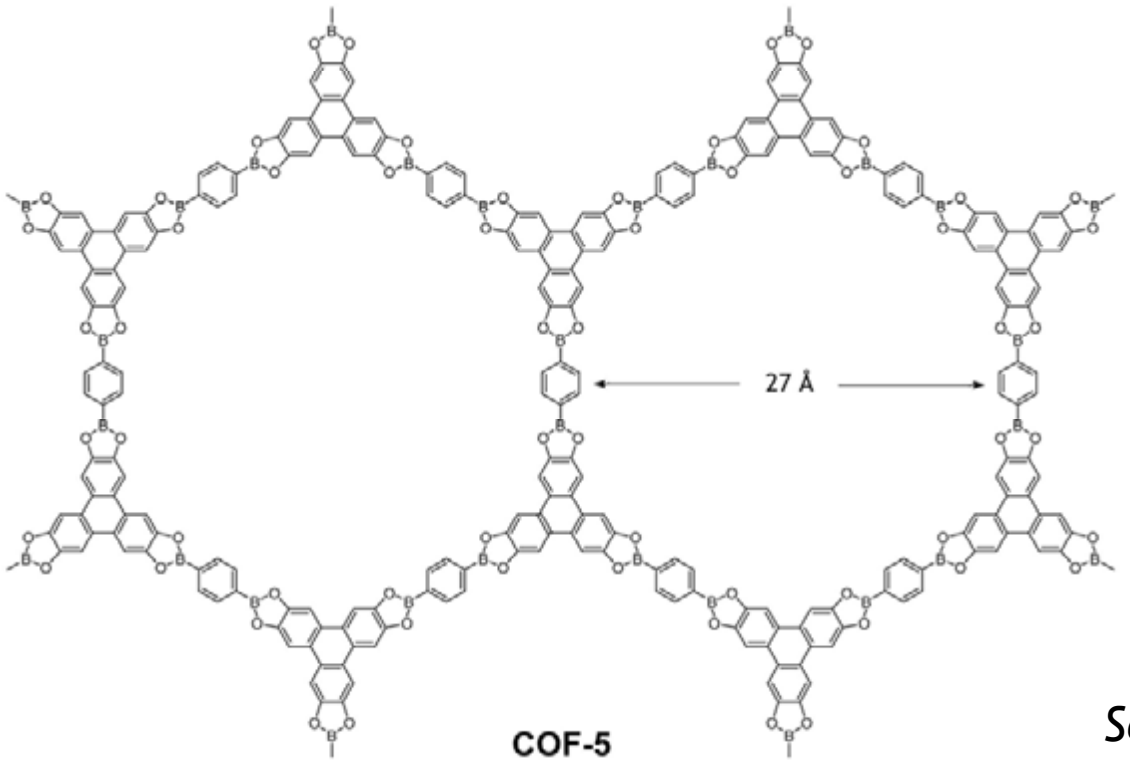



A
COF-1
110
100
200
101
210
201
211
220
301
002
112
421 600 213
experimental (black) and
refined (red) profiles
difference plot = experimental - refined profiles
calculated pattern from
Cerius2 model
5
10
20
30
40
50
2θ (degrees)
SEM
100 μm
FT-IR
1026
(B-C)
711
(B3O3)
1378
(B-O)
1342
(B-O)
1700 1500 1300 1100 900 700
ν (cm-1)
11B NMR
COF-1
model compound
BDBA
200
100
0
-100
-200
δ (ppm)

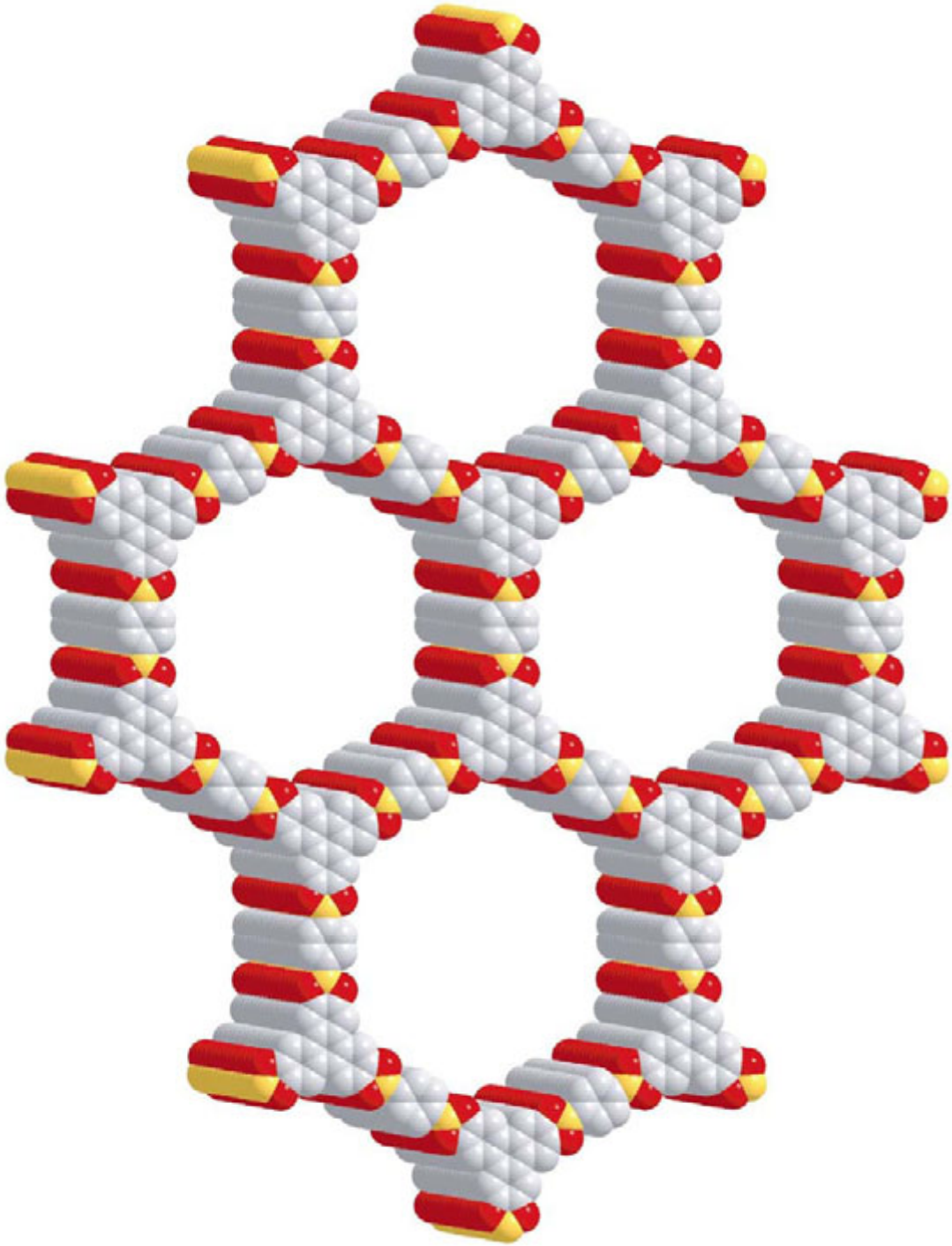


COF-1

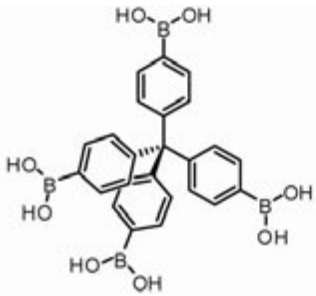


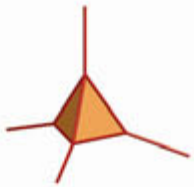


Science 2005

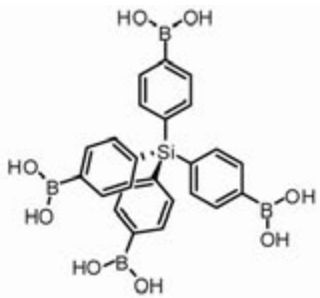


COF-5

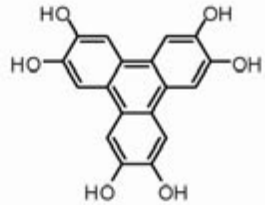




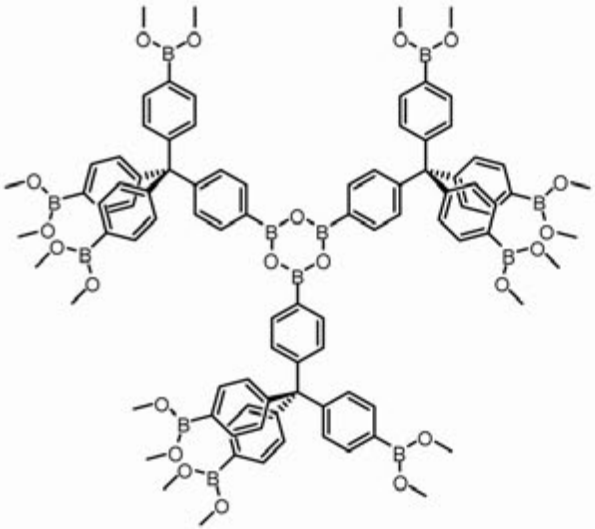
A: TBPM



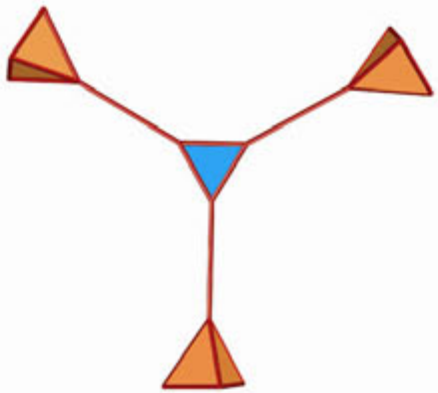
B: TBPS

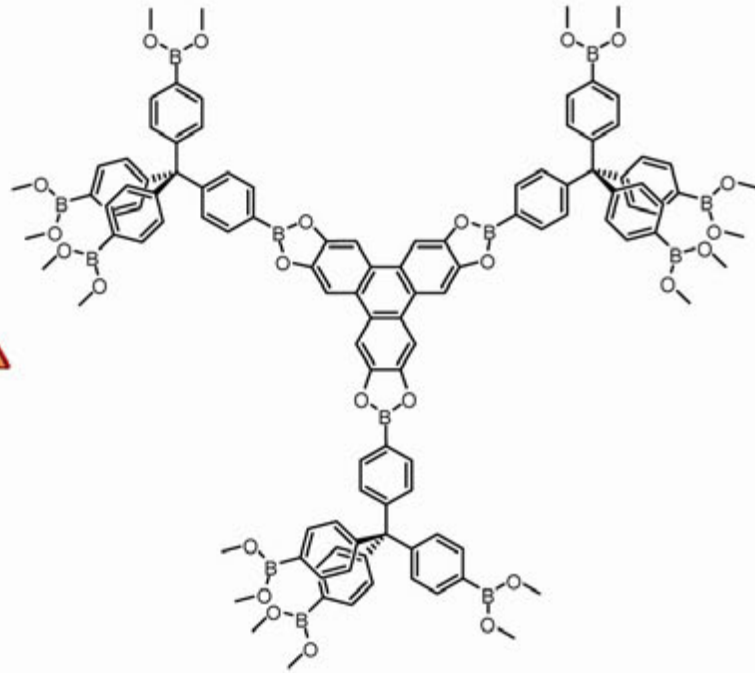


C: HHTP

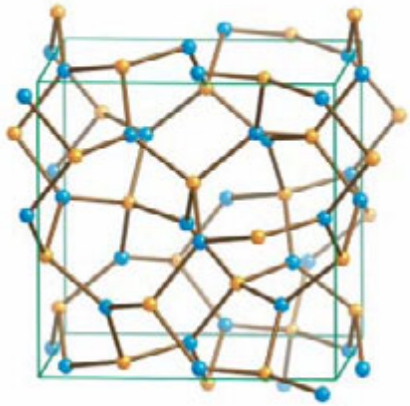


D: B_3O_3 ring

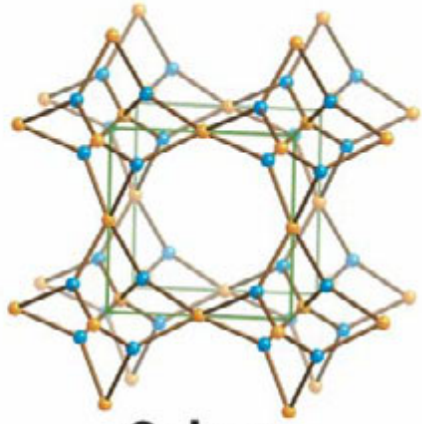




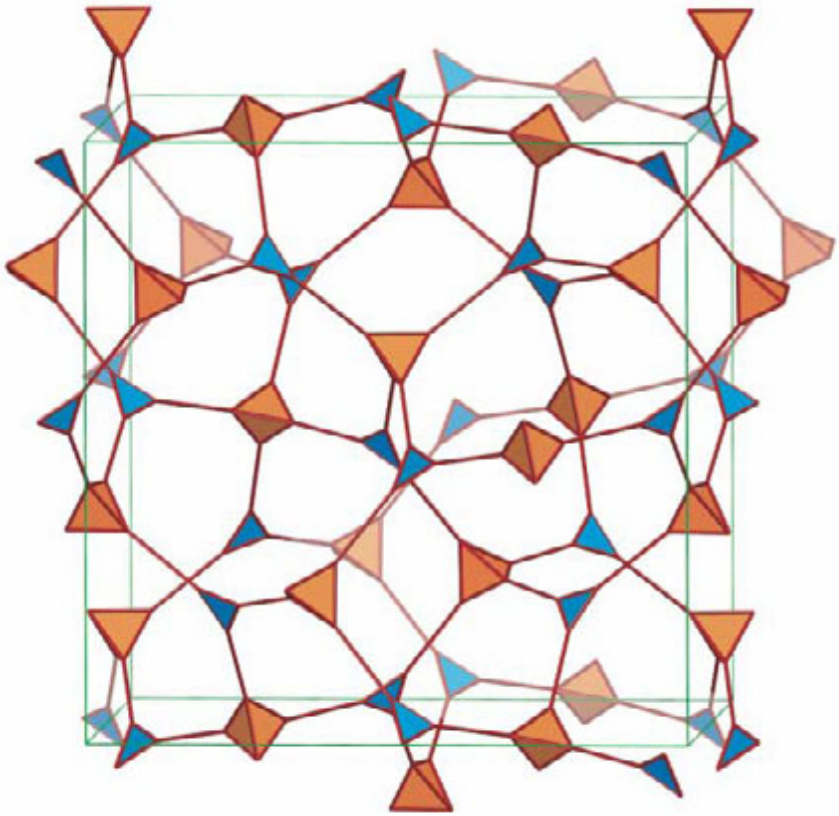
E: C_2O_2B ring



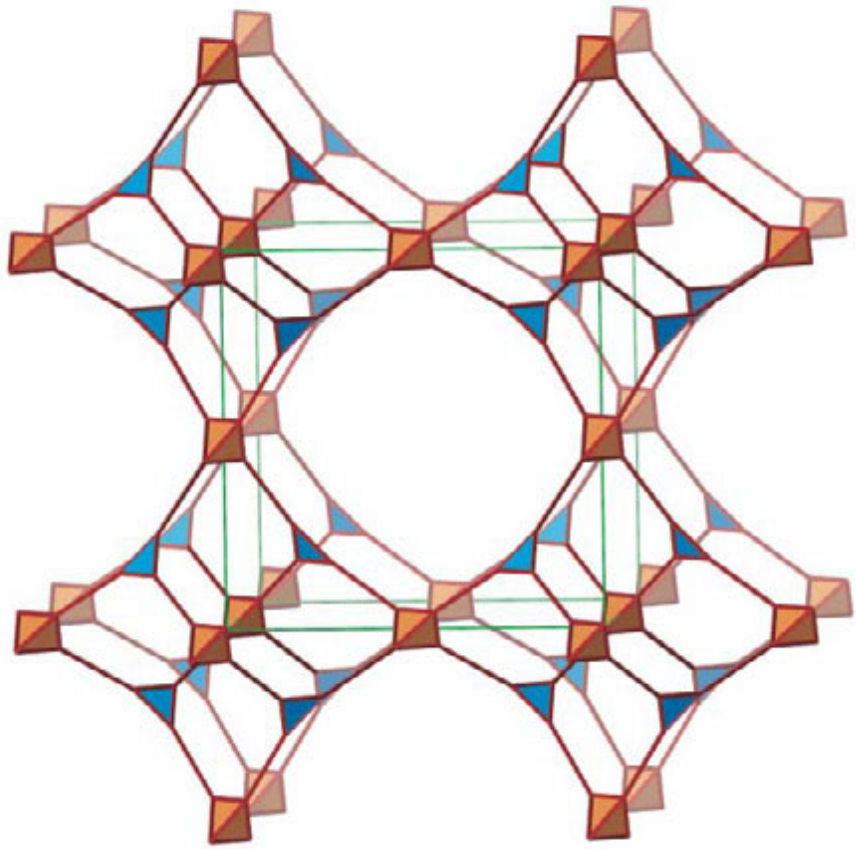
F: **ctn**



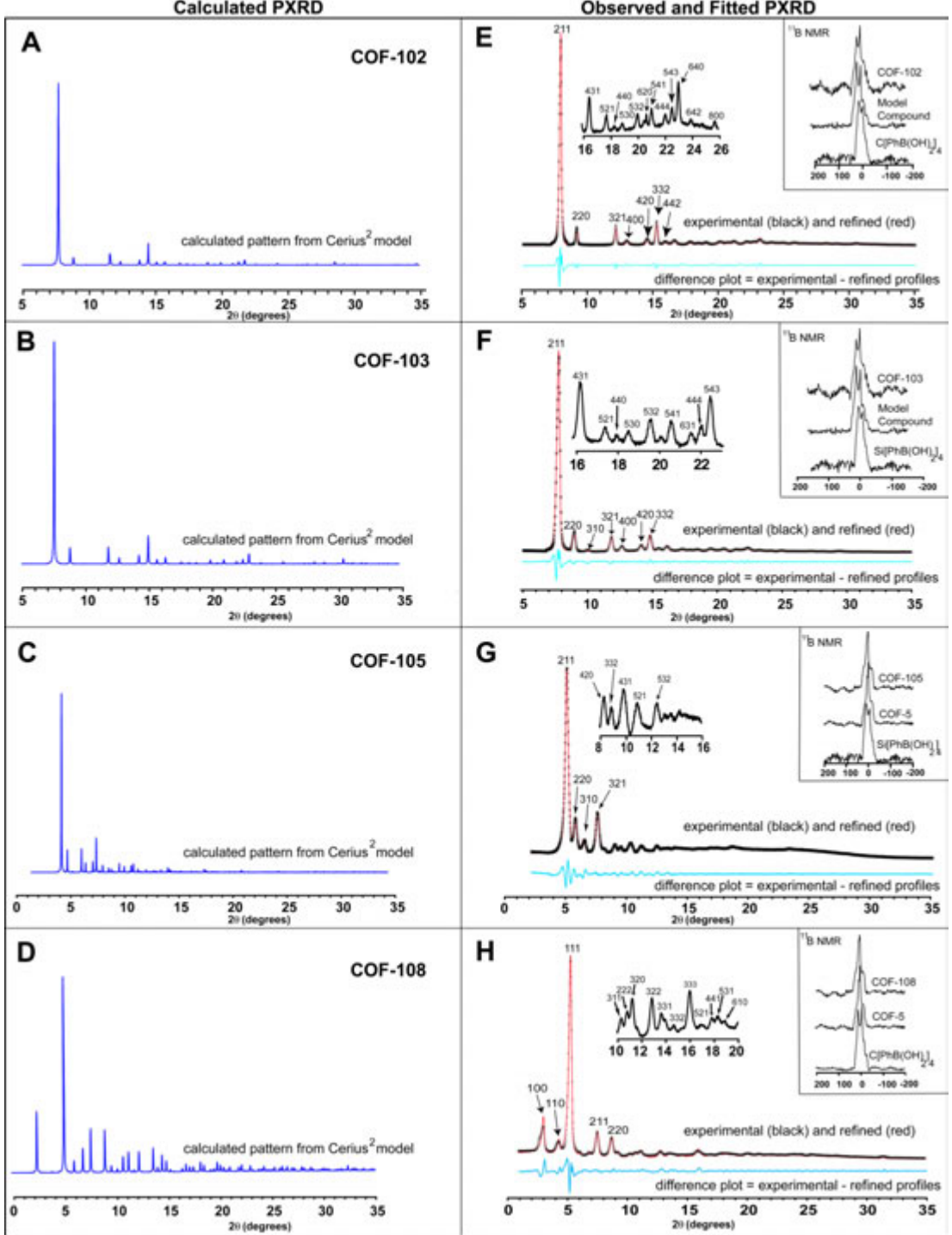
G: **bor**

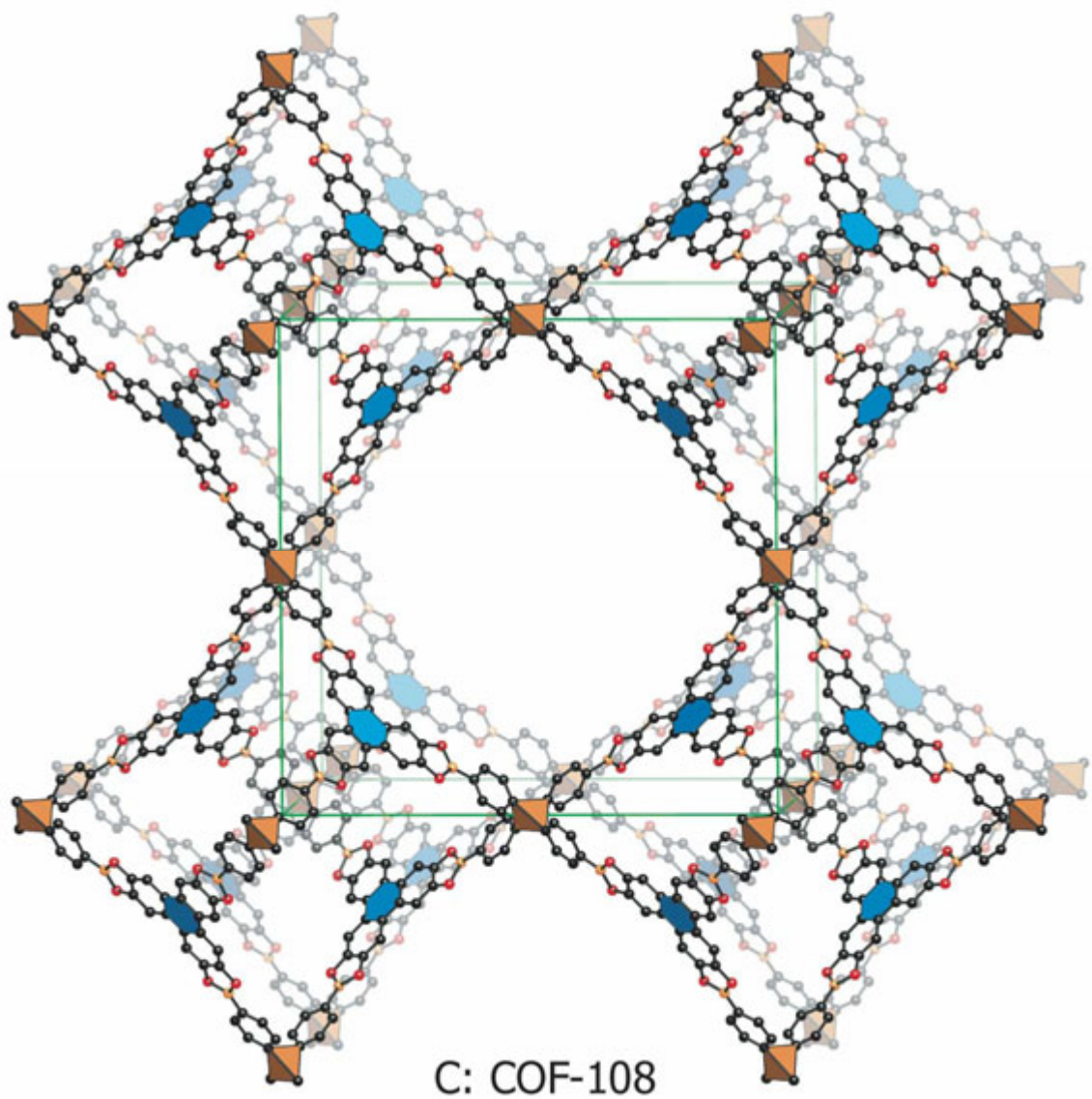


H



I


Calculated PXRD
Observed and Fitted PXRD
A
COF-102
calculated pattern from Cerius2 model
B
COF-103
calculated pattern from Cerius2 model
C
COF-105
calculated pattern from Cerius2 model
D
COF-108
calculated pattern from Cerius2 model
2θ (degrees)
E
F
G
H
experimental (black) and refined (red)
difference plot = experimental - refined profiles
11B NMR
COF-102
Model Compound
C[PhB(OH)2]4
COF-103
Si[PhB(OH)2]4
COF-105
COF-5
Si[PhB(OH)2]4
COF-108
COF-5
C[PhB(OH)2]4



COF-108: Density = 0.17 g/cm^3
Surface area = 4,700 m^2/g

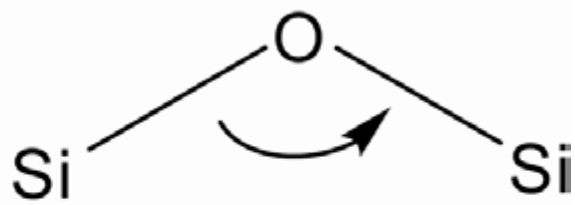
Science 2007

It’s all in the angle (145°)

M - IM - M

1

145°

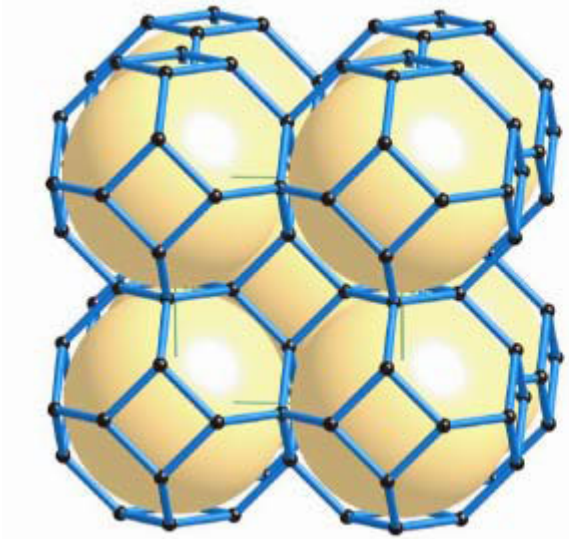


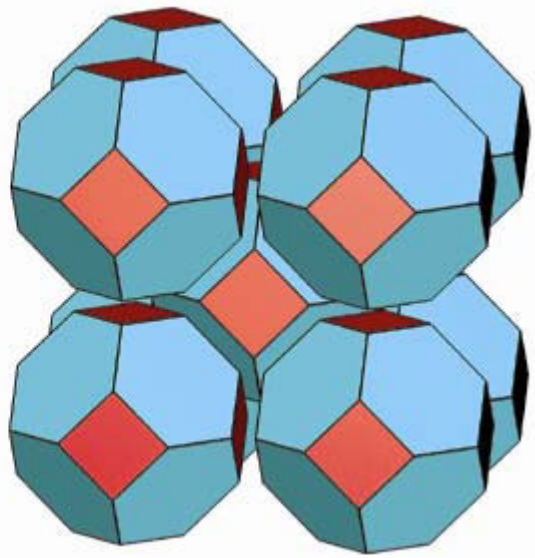
Si - O - Si

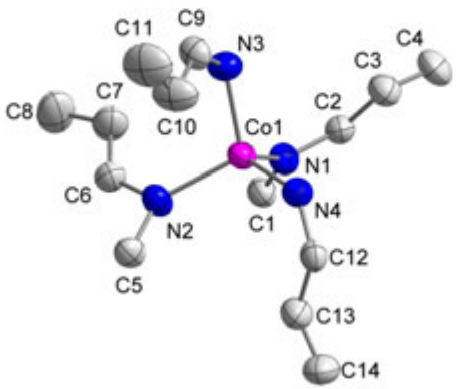
2

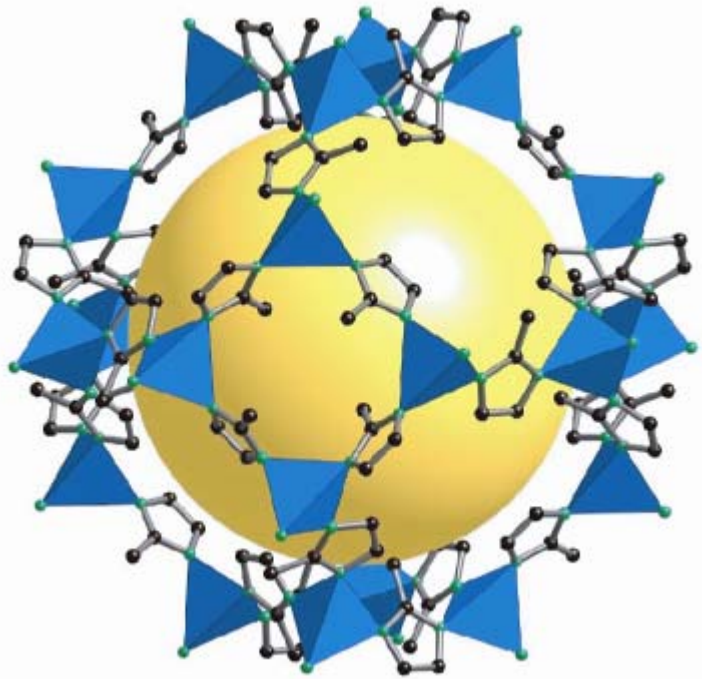
145°

ZIF-8 sod

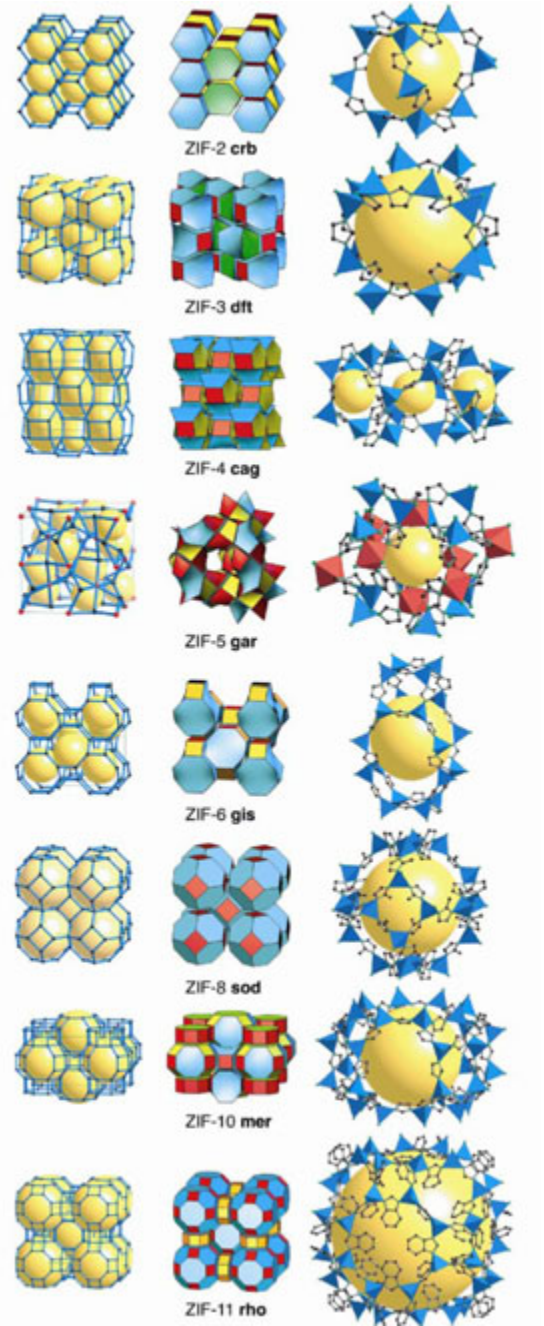


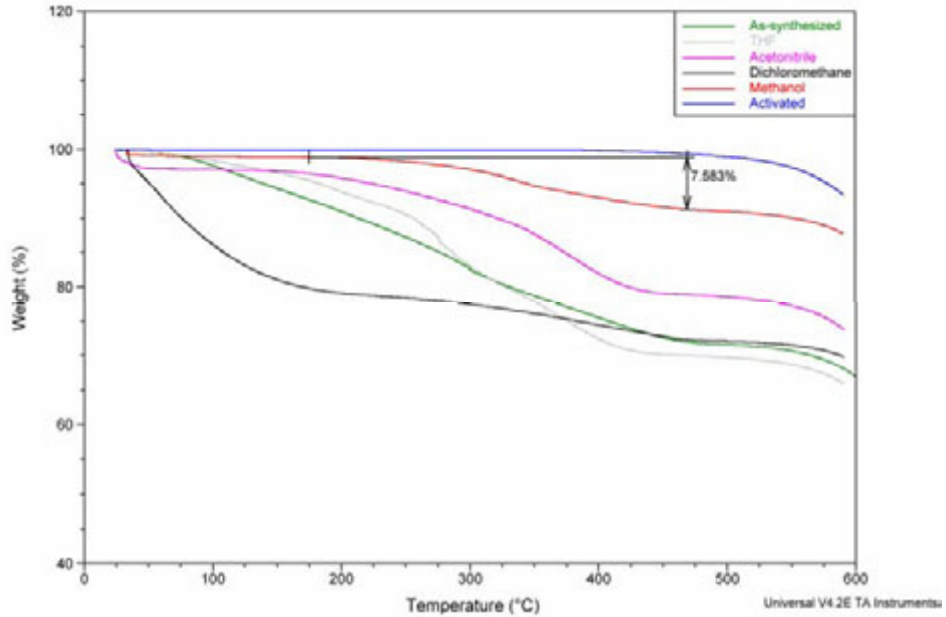


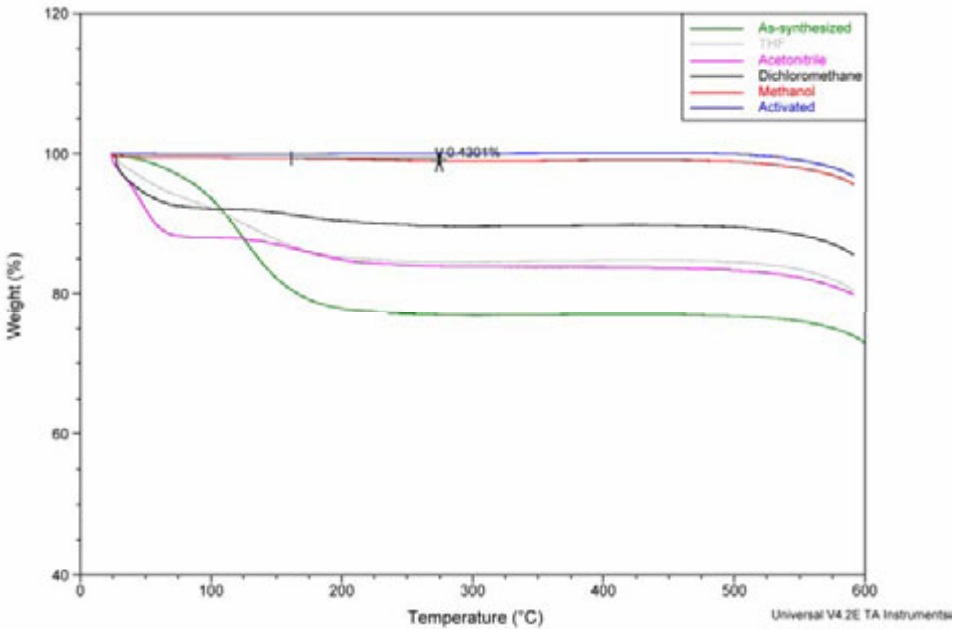




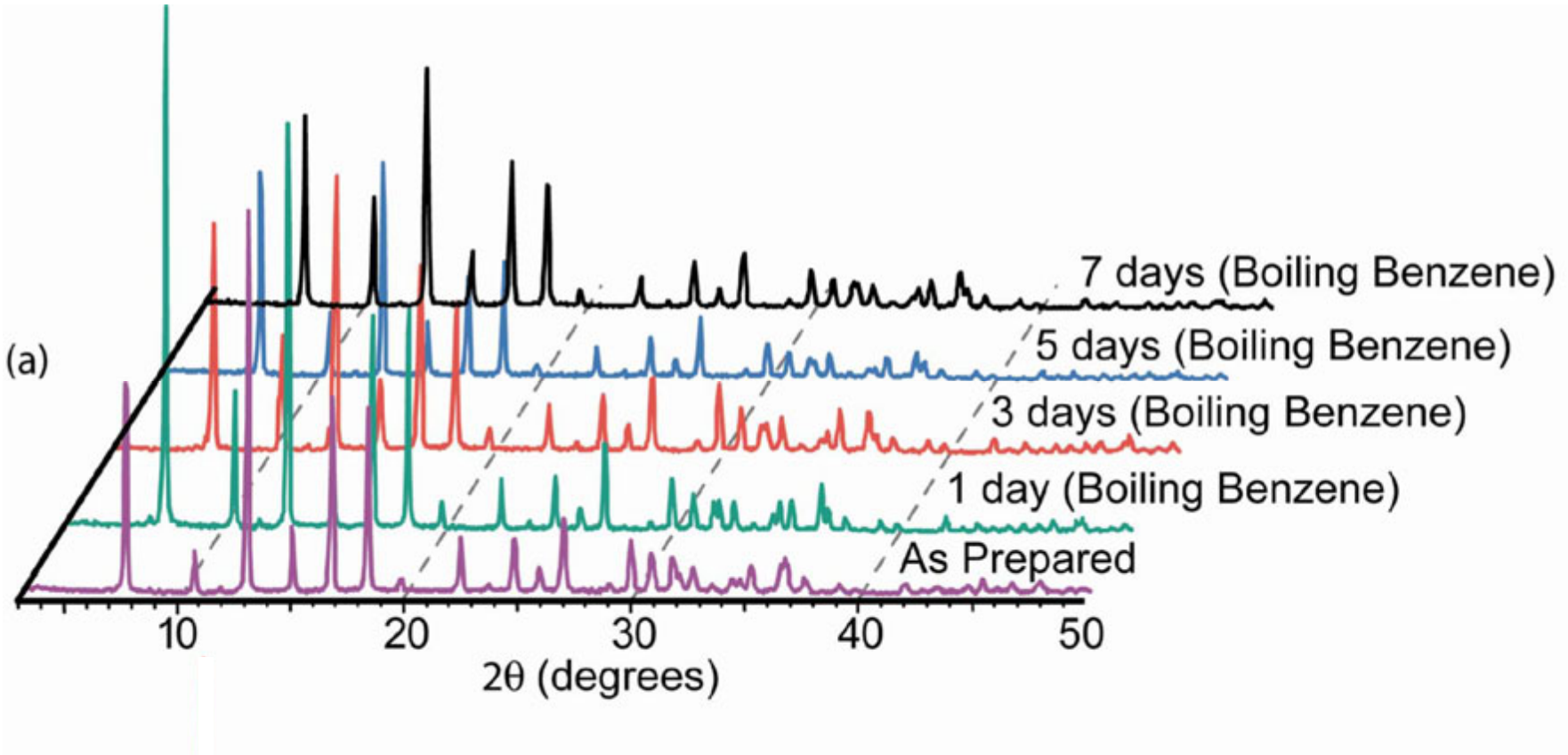
Thermal stability of ZIFs

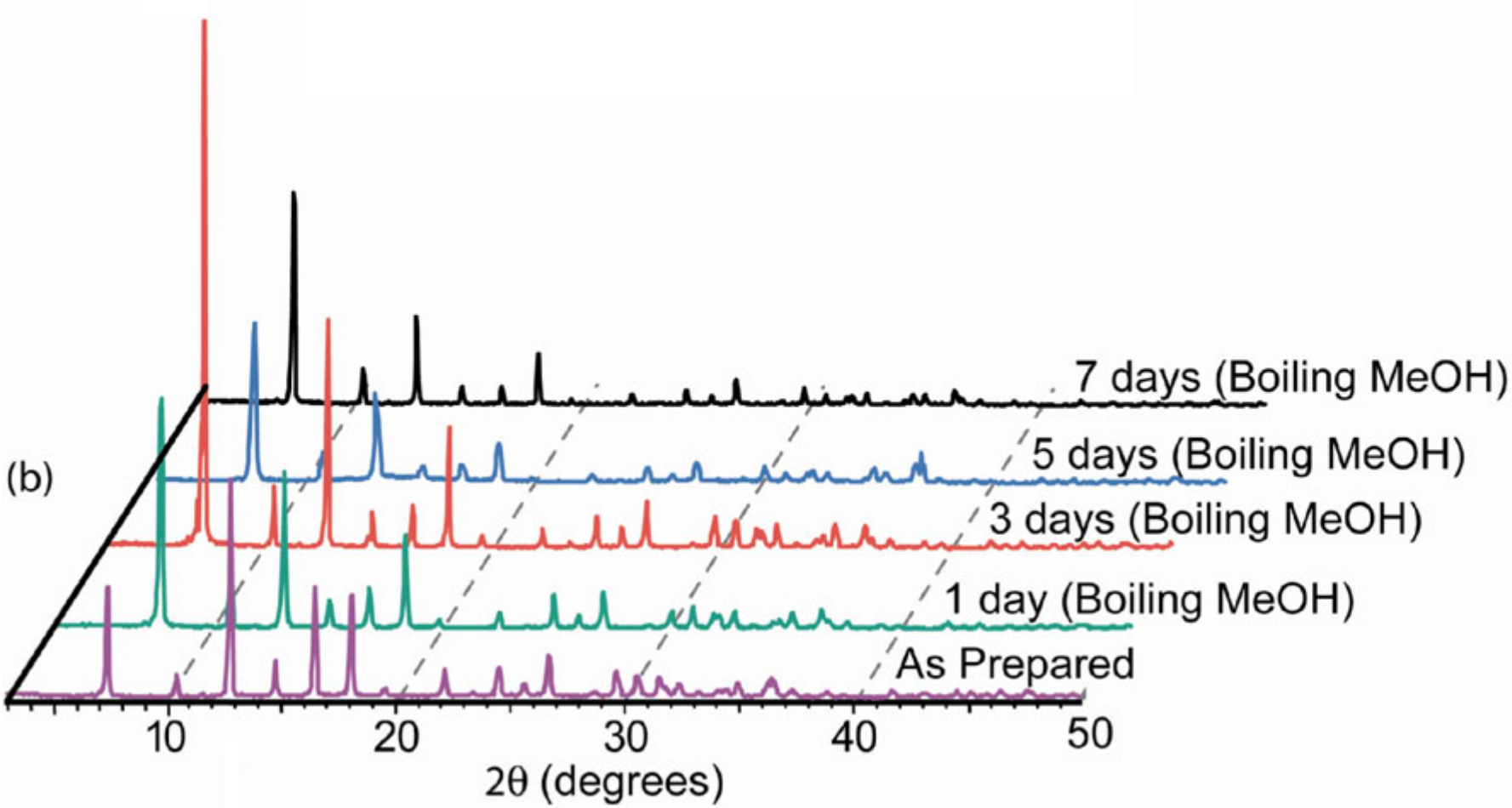


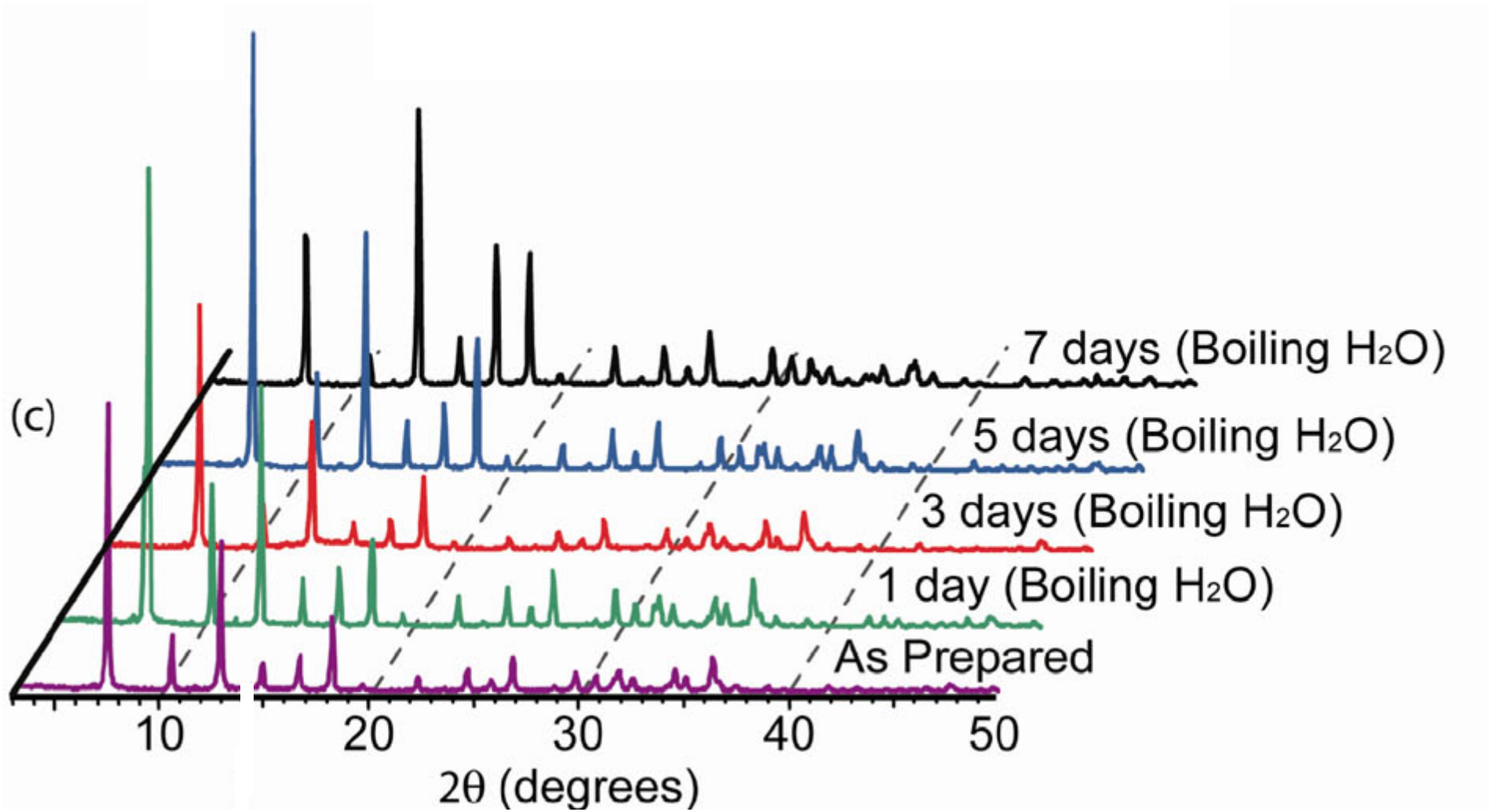


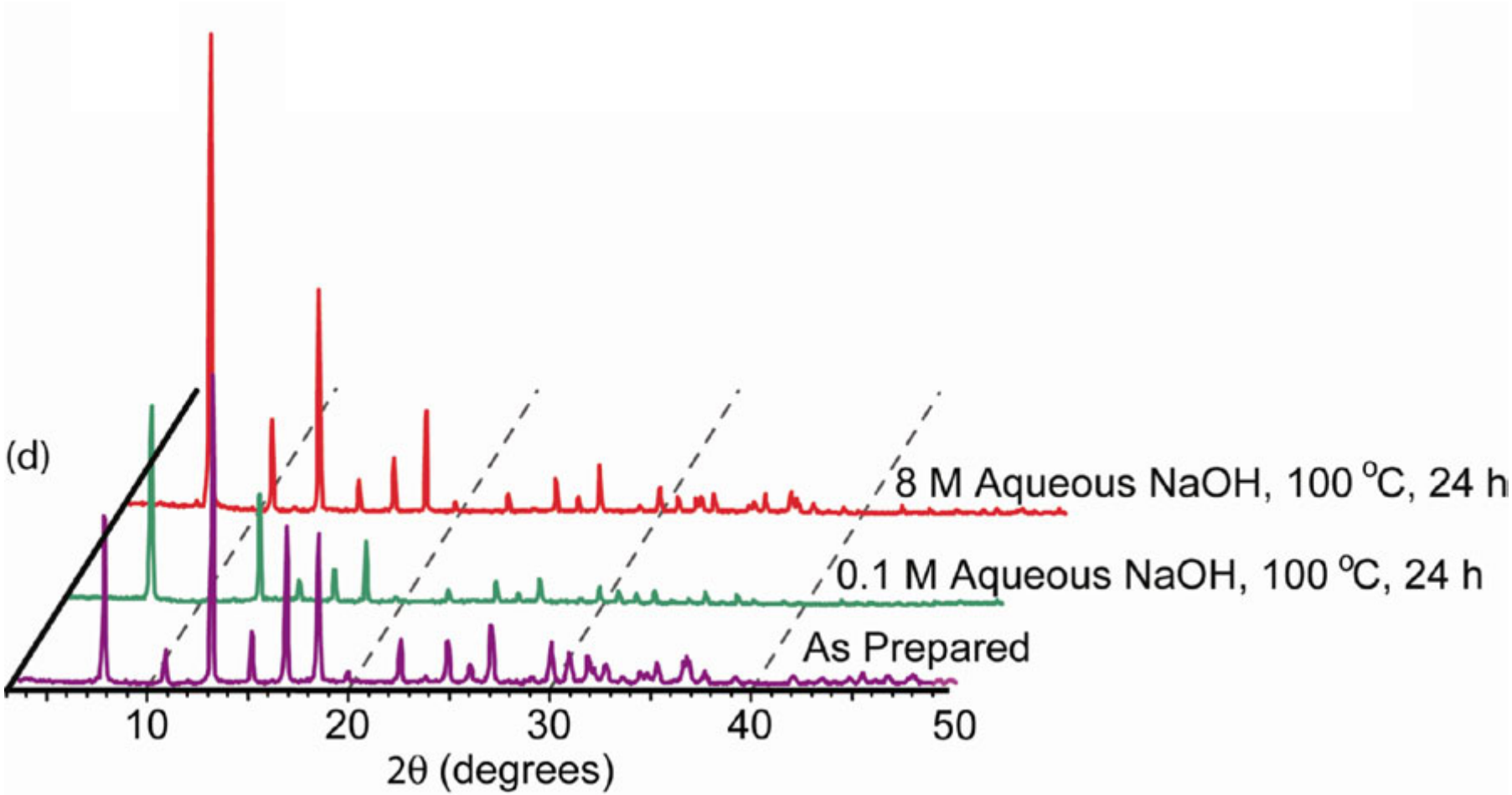


Chemical stability of ZIF-8

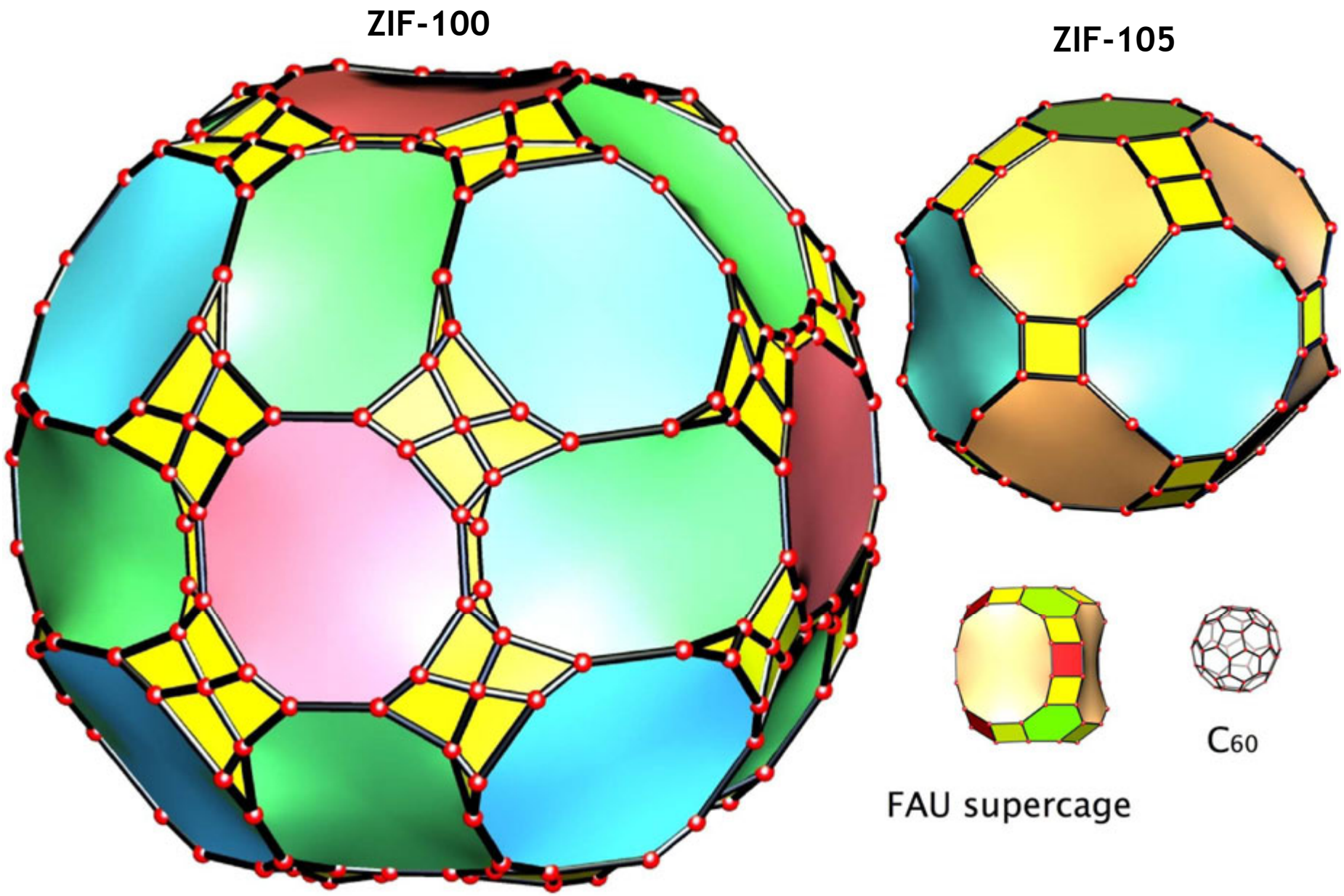



(b)
7 days (Boiling MeOH)
5 days (Boiling MeOH)
3 days (Boiling MeOH)
1 day (Boiling MeOH)
As Prepared
10
20
30
40
50
2θ (degrees)


(c)
7 days (Boiling H2O)
5 days (Boiling H2O)
3 days (Boiling H2O)
1 day (Boiling H2O)
As Prepared
10
20
30
40
50
2θ (degrees)



K. S. Park, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, ***Proc. Nat. Acad. Sci. USA,* 2006*, 103,* 10186-10191.**



Trigonal Zn metal site next to Z-F bond both pointing to the center of pore

PROGRESS

1.Tuning porosity lead to tripling of hydrogen uptake in MOFs (excess 7.5% wt, absolute 12% wt)
2.The 35 grams H2/L achieved in MOF-177, clearly indicates that dead volume is none issue for MOFs
3.MOFs exhibit fast kinetics (1-3 minutes for charging and discharging)
4.MOF materials porosity and uptake are stable to charge/discharge cycling
5.Cubic meter scale of useful MOFs is now developed by BASF

FUTURE WORK

1. Higher adsorption energy by:
   (a) Design of Lewis-acid and Lewis-base sites
   (b) Doping with Li and impregnation with early T.M. complexes
   (c) Acetylene MOFs for high surface areas and stronger binding of hydrogen
2. Application of high throughput and characterization methods to search for specific structures
3. Testing new materials :
   (a) Zeolite imidazolate Frameworks (ZIFs)
   (b) Covalent organic frameworks (COFs)

Current Group Members

Thanks for putting up with Professor

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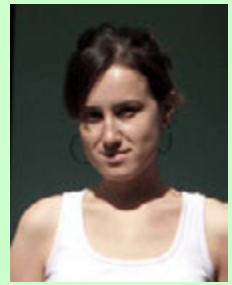
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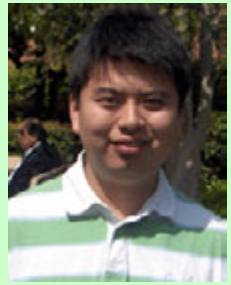
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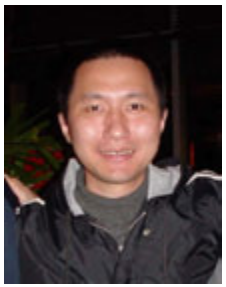
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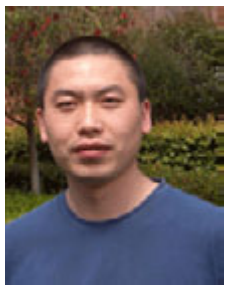
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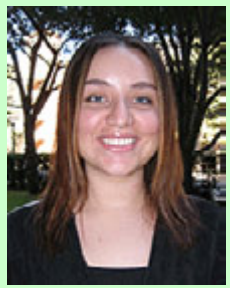
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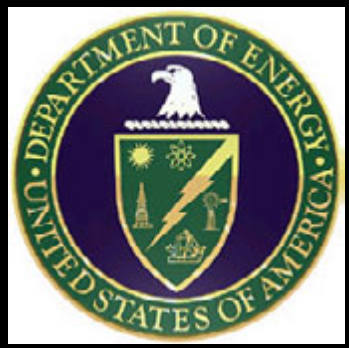
CENTER FOR RETICULAR CHEMISTRY

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