Reticular Chemistry and Hydrogen Storage in MOFs

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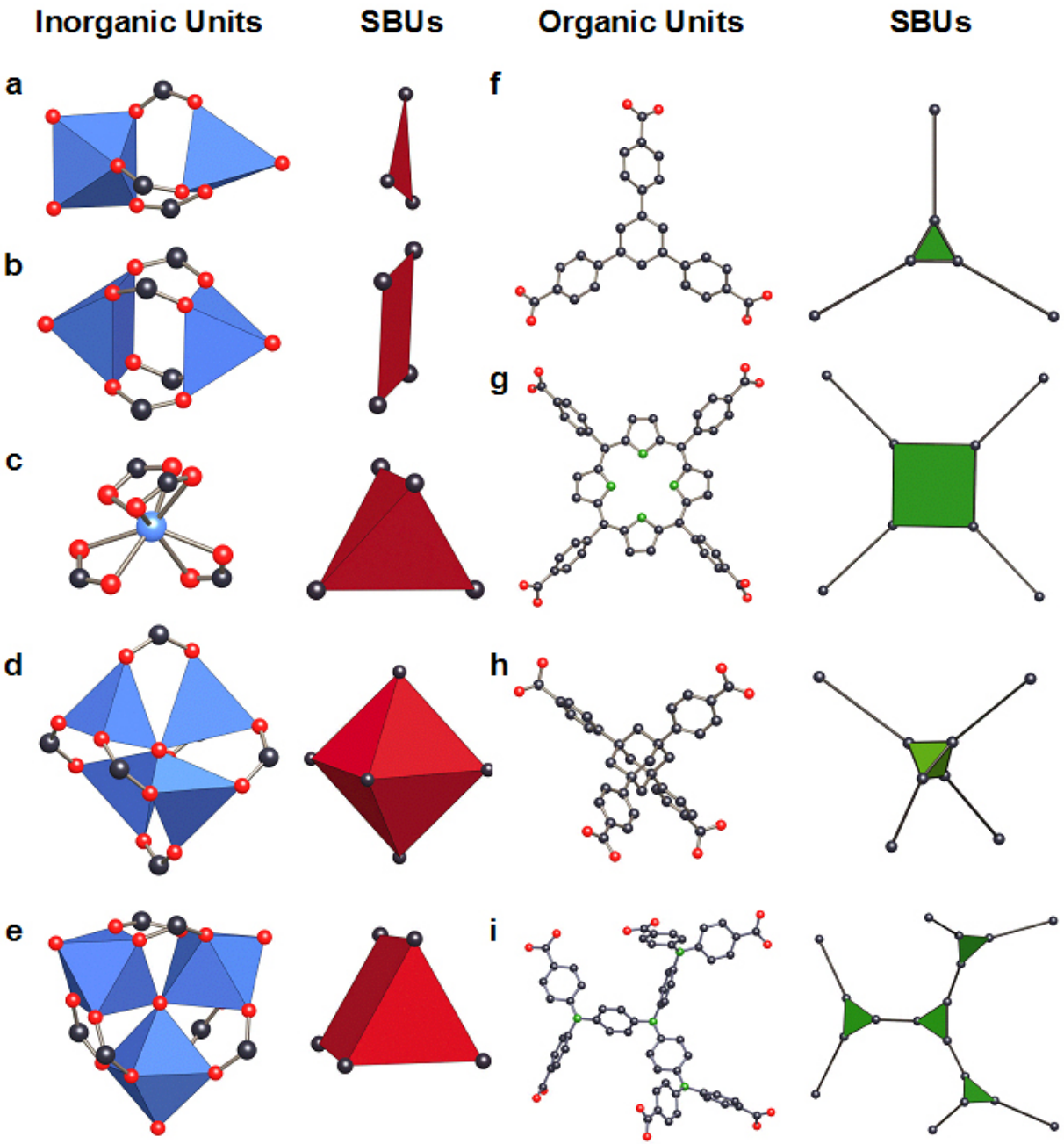
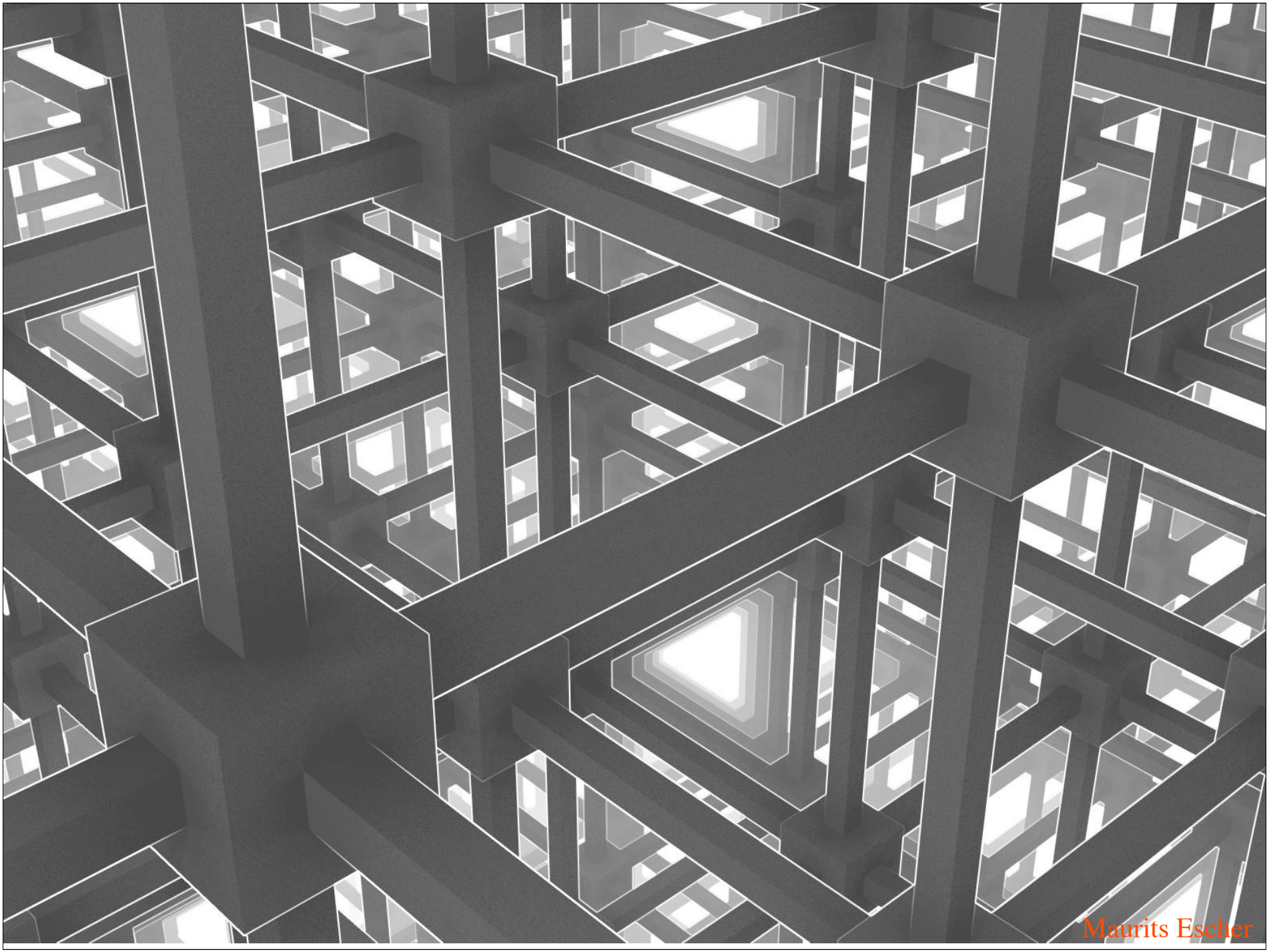
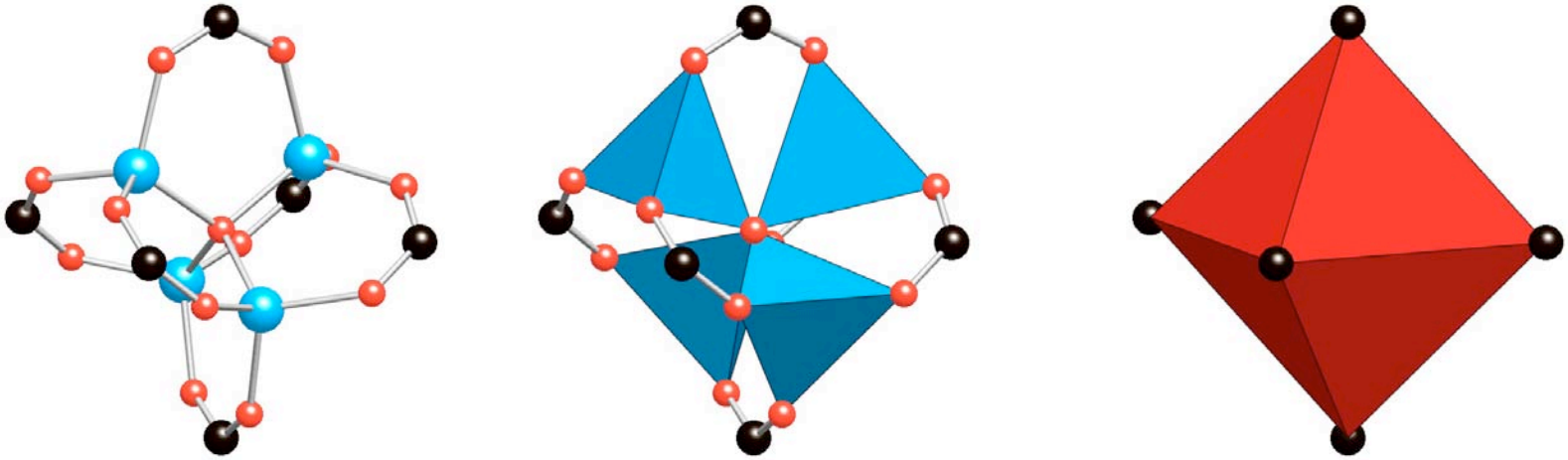
Reticular chemistry *is concerned with linking of molecular building blocks (organic molecules, inorganic clusters, dendrimers, peptides, proteins,...) into predetermined structures in which such units are repeated and are held together by strong bonds.*



Nature 2003

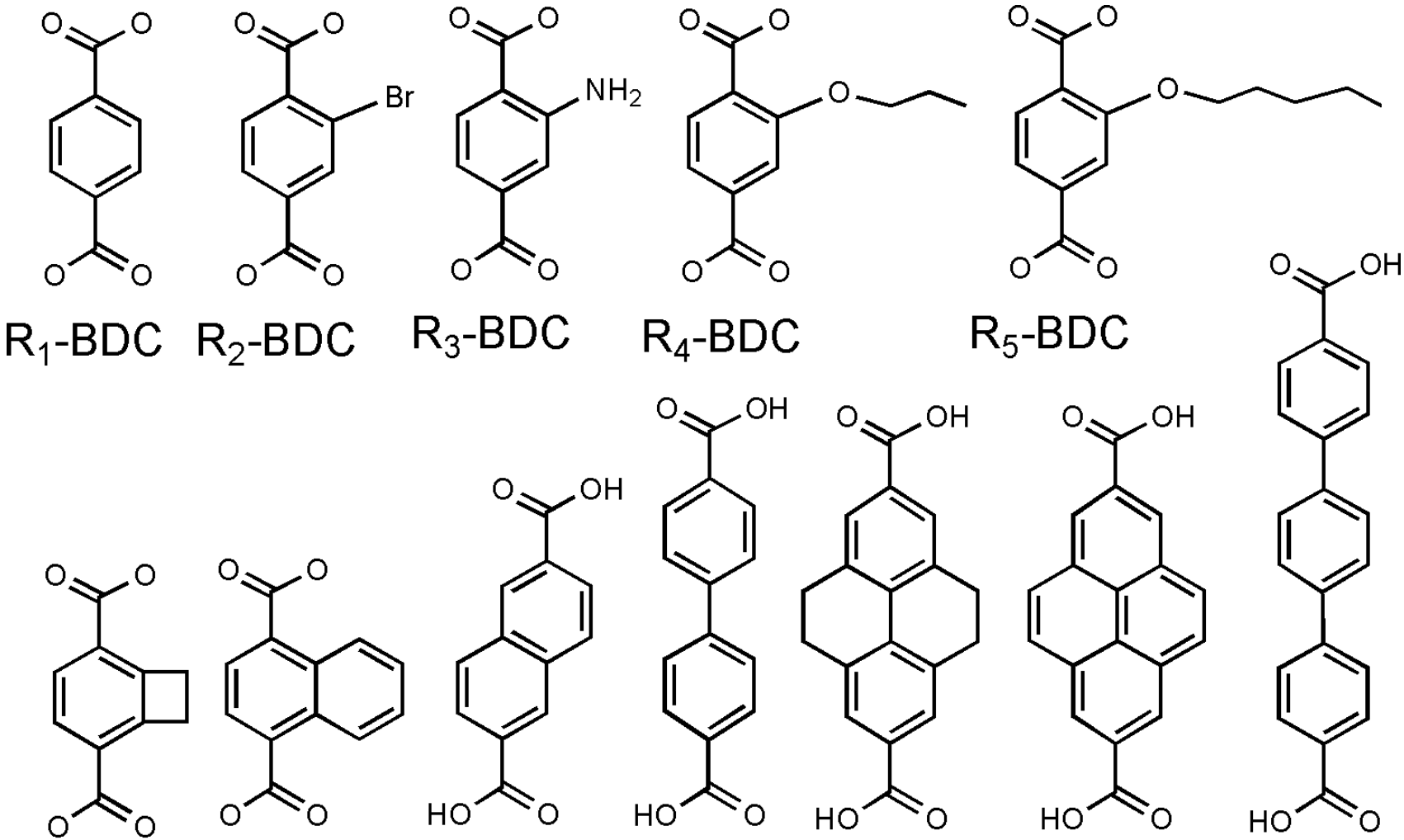

Maurits Escher

Basic Zinc Acetate

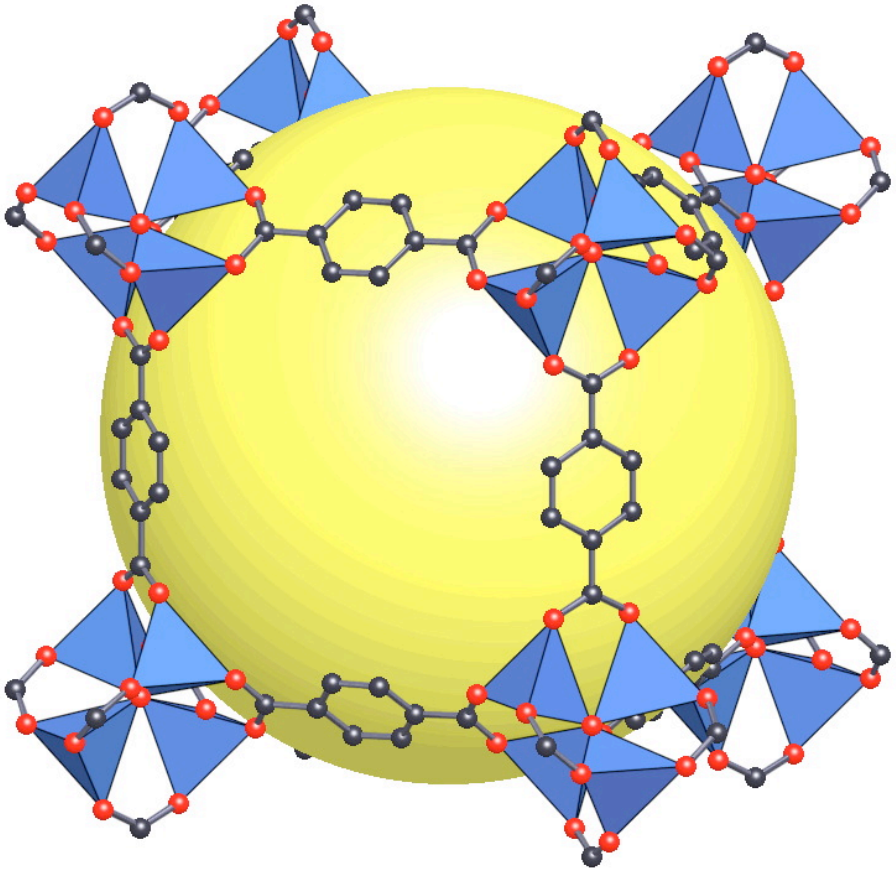


red, O; blue, Zn; black, C

Linkers “struts”

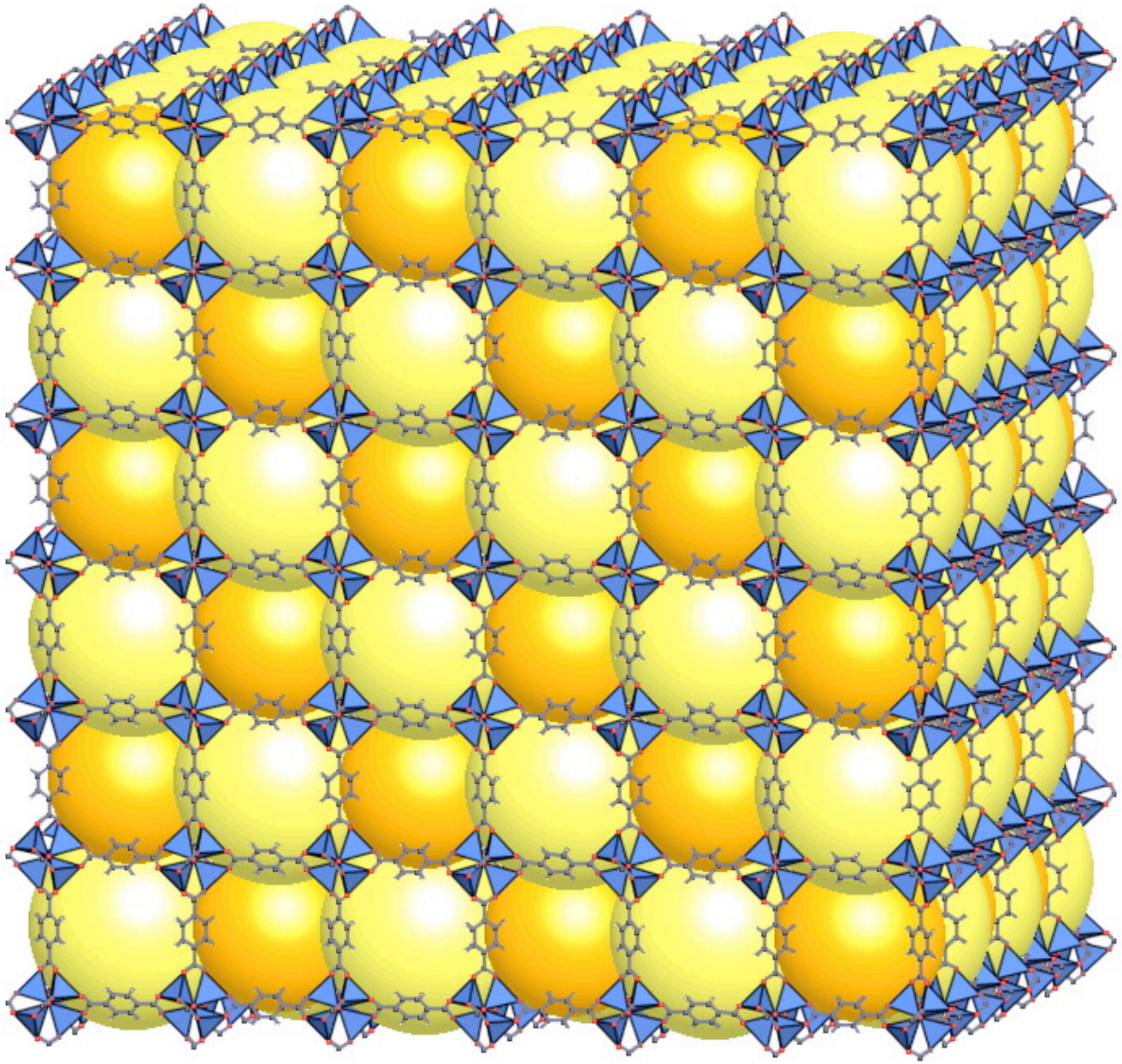


$$H_2BDC + Zn(NO_3)_2 \cdot 4H_2O \xrightarrow{DEF\ (12mL)} Zn_4O(BDC)_3 \cdot (DEF)_7$$

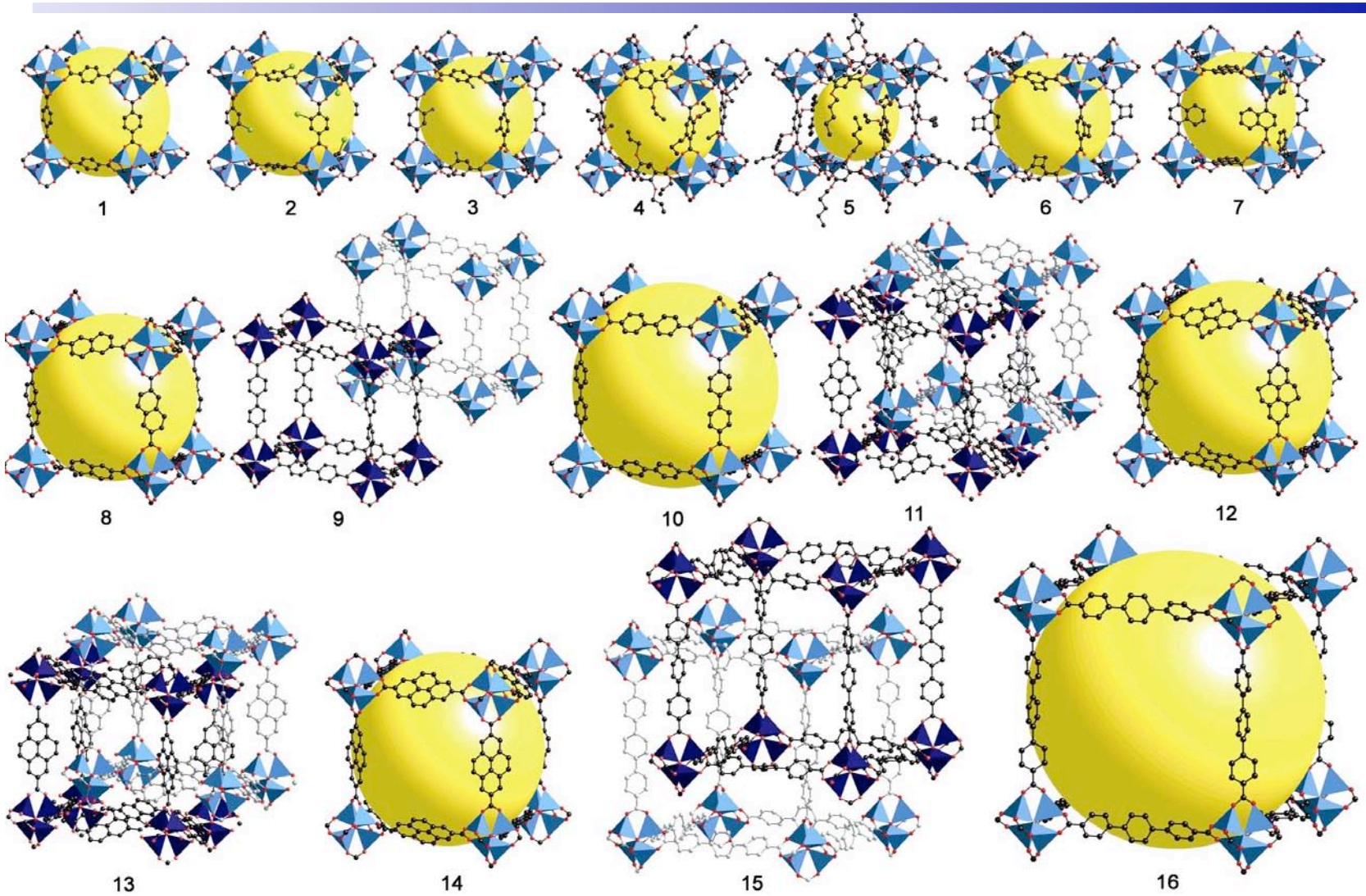


$Zn_4O(O_2C\text{-}C_6H_4\text{-}CO_2)_3$: MOF-5

H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi. *Nature* (1999) *402*, 276-279



Systematic design of functionality and metrics



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

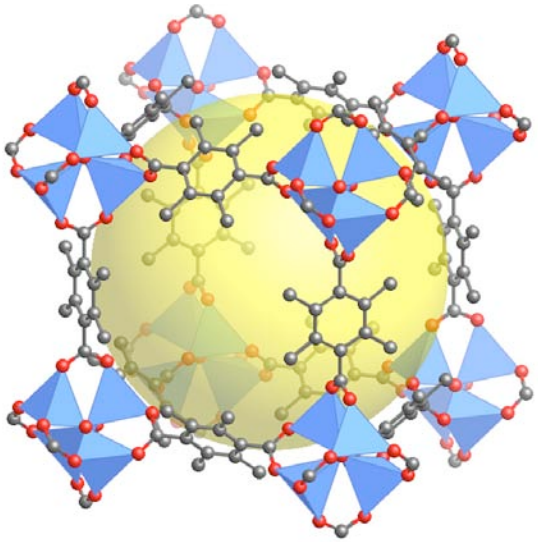
Empirical Formula: $C_{36}H_{36}O_{13}Zn_4$

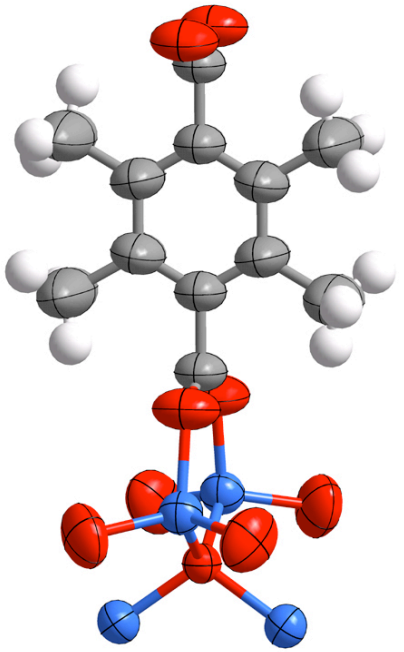
Crystal Data: $Fm\bar{3}m$, a = 25.6135(7) Å

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

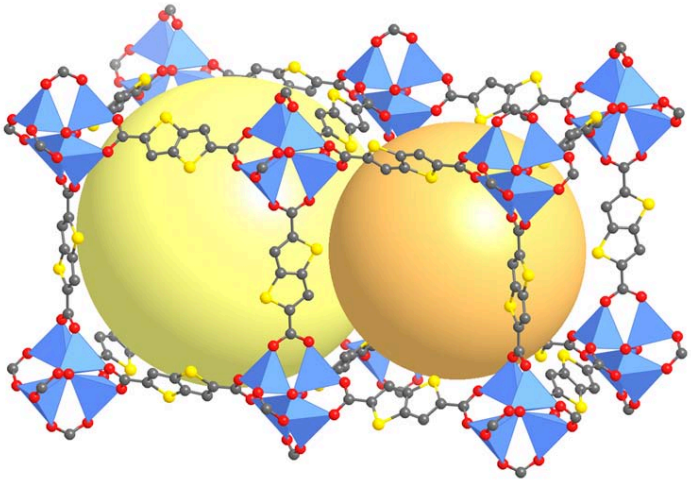
Empirical Formula: $C_{24}H_6O_{13}S_6Zn_4$

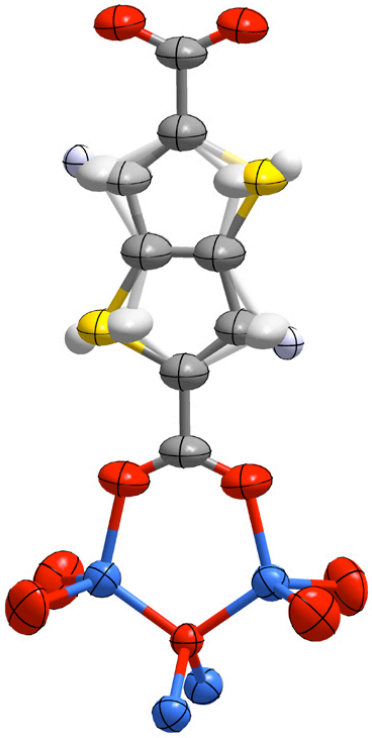
Crystal Data: $Fm\bar{3}m$, a = 29.186(2) Å

Pore Diameters: 17.2, 14.3 Å

Aperture Diameter: 9.6 Å

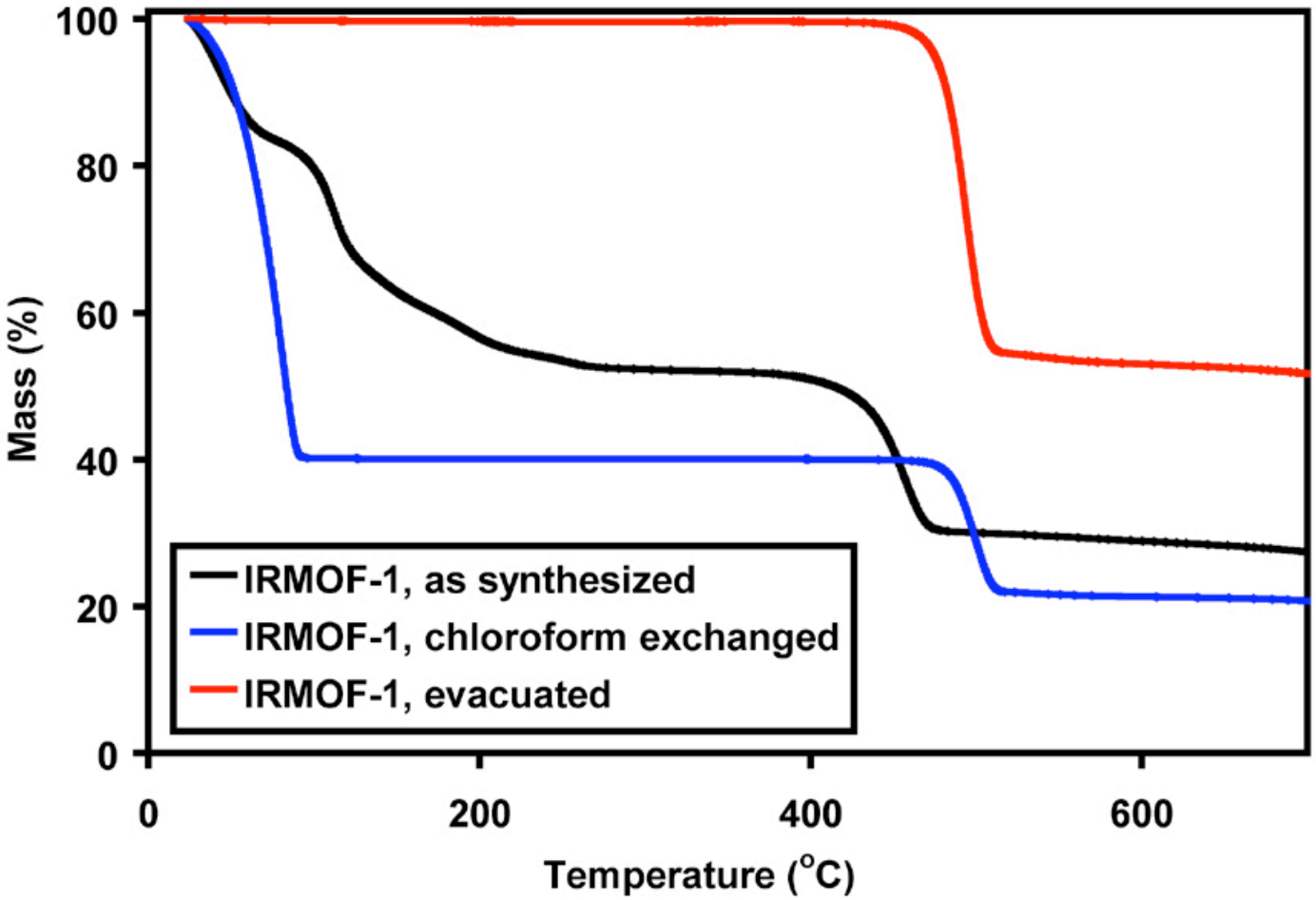
H_2 accessible volume: 66 %

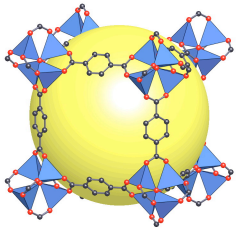




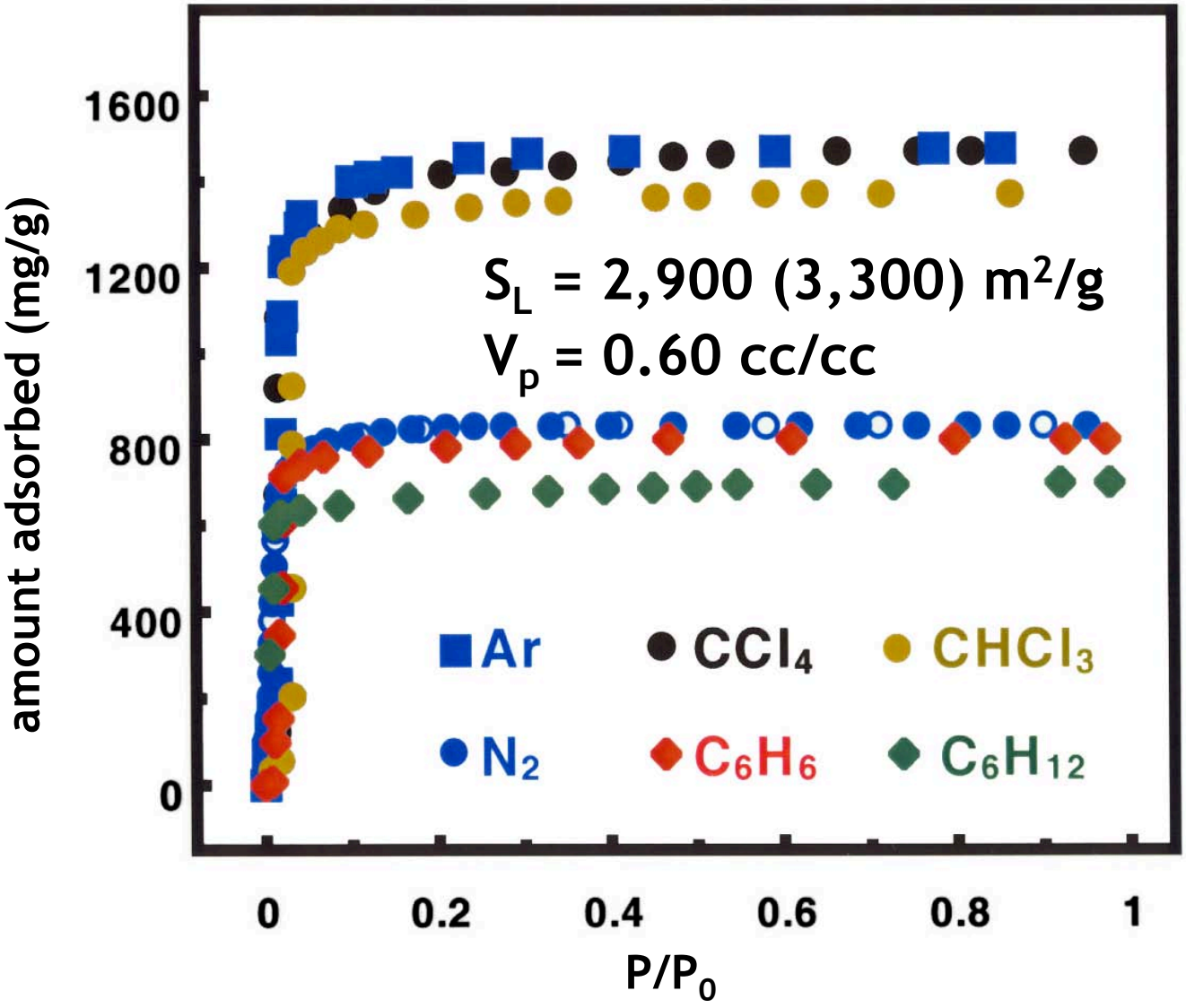
MOFs based on $Zn_4O(O_2C\text{-})_6$: Activation

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





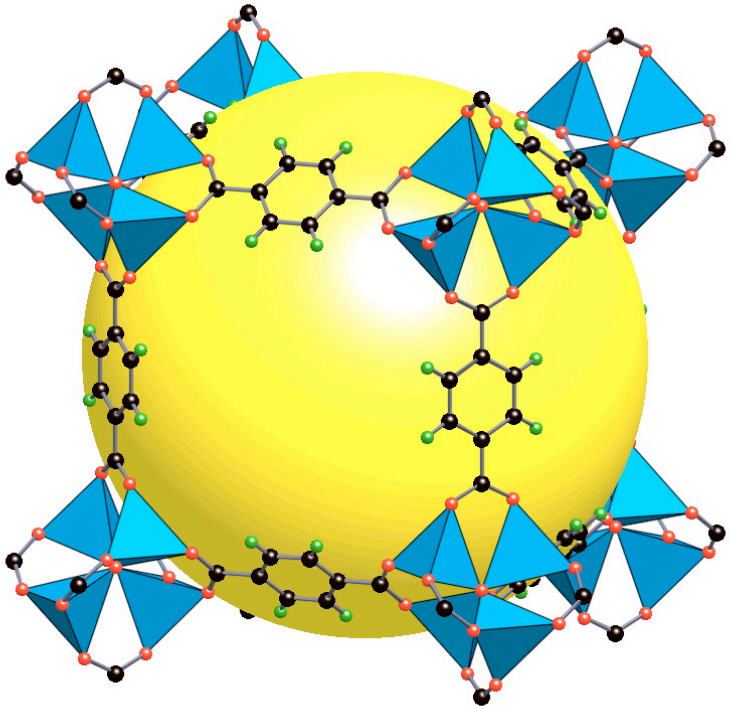
Porosity of MOF-5



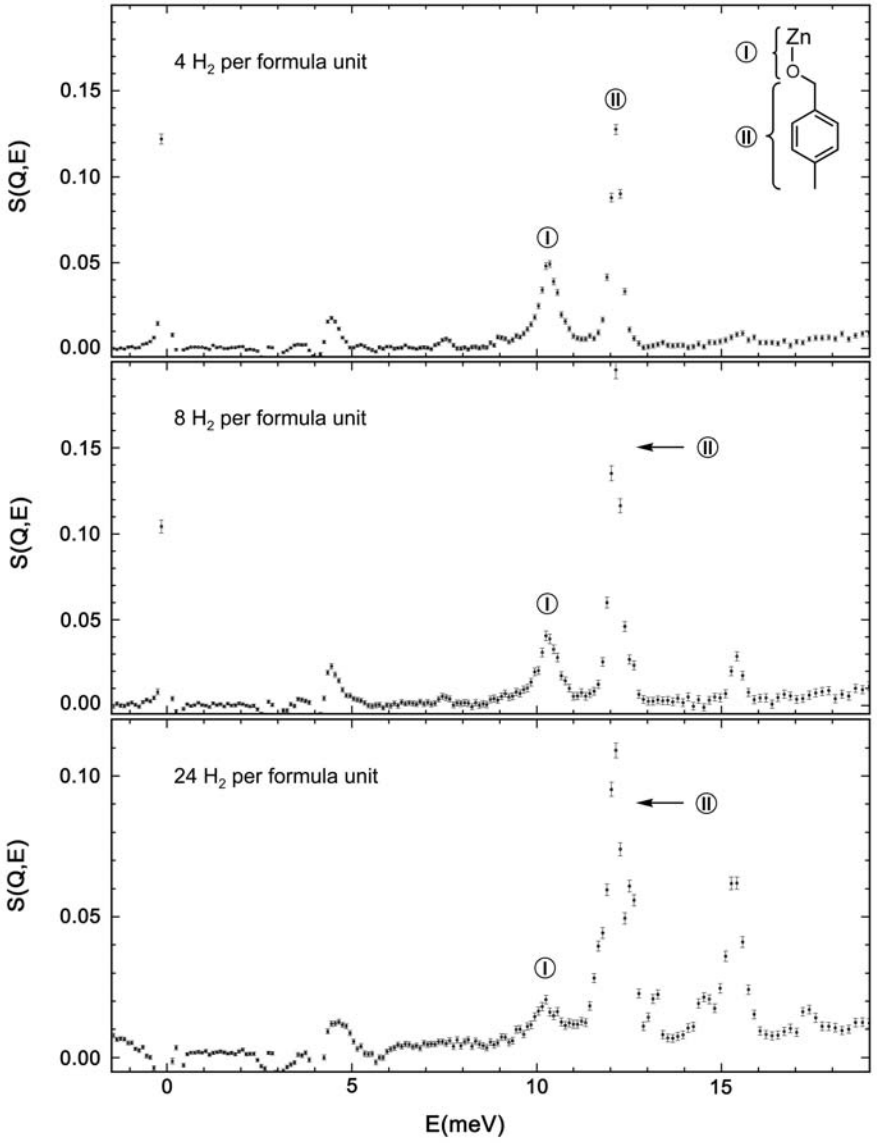
Comparison of Crystallographic Data for MOF-5

MOF-5	Crystal System	Lattice Parameters	Space Group	Maximum peak in Final Diff. Map	R value
As-synthesized Crystal	Cubic	a = 25.6690 Å	$Fm\bar{3}m$	1.56 $e^-/Å^3$	R = 0.11 R*w* = 0.32
Desolvated Crystal (*in air*)	Cubic	a = 25.8849 Å	$Fm\bar{3}m$	0.25 $e^-/Å^3$	R = 0.023 R*w* = 0.026
Desolvated Crystal (*in vacuo*)	Cubic	a = 25.8556 Å	$Fm\bar{3}m$	0.20 $e^-/Å^3$	R = 0.019 R*w* = 0.024
Desolvated Crystal (*300°C/24h*)	Cubic	a = 25.8496 Å	$Fm\bar{3}m$	(Maintain Single Crystal)	

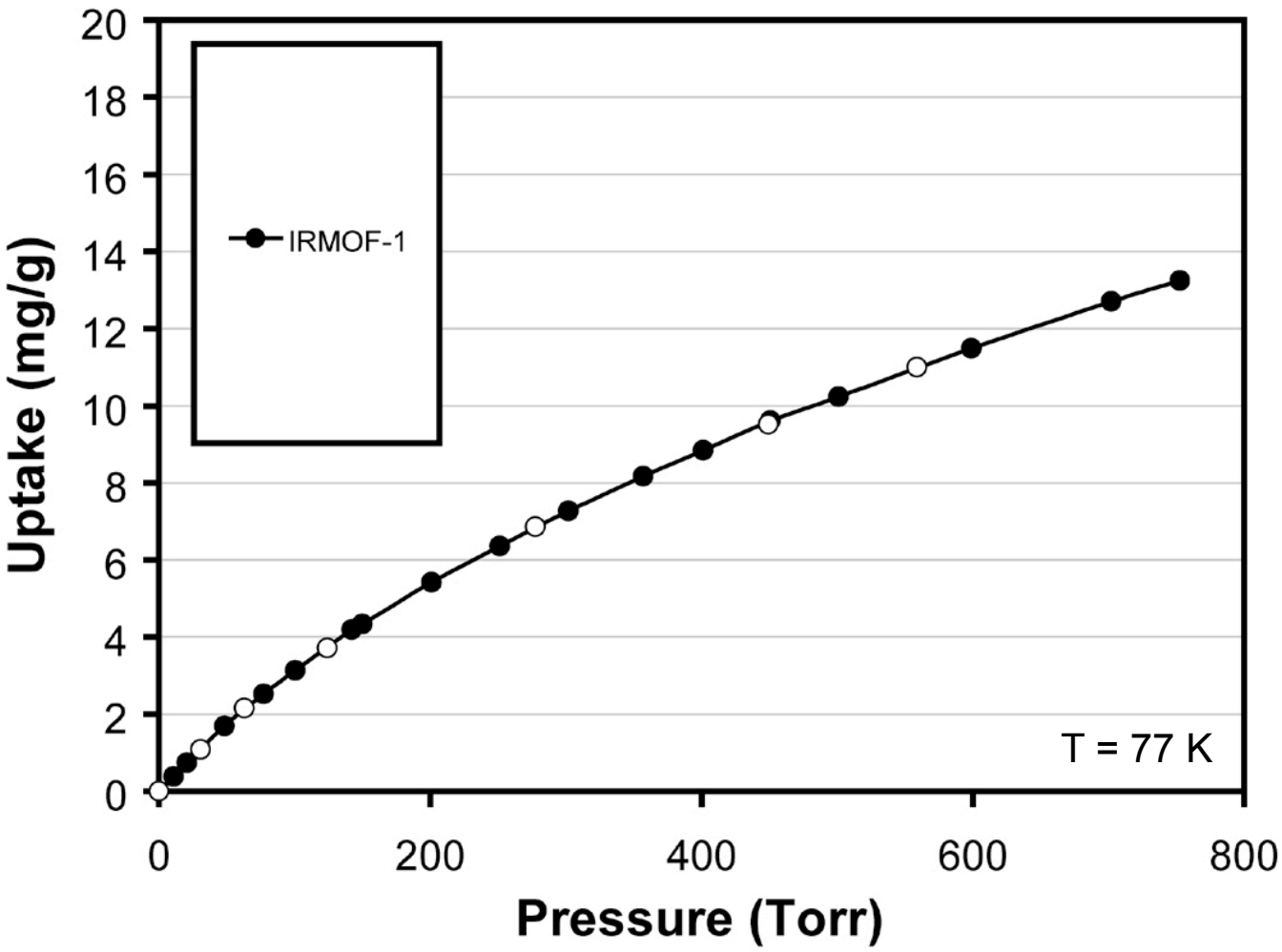
Inelastic neutron scattering experiments on MOF-5

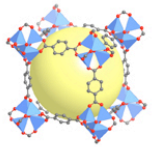


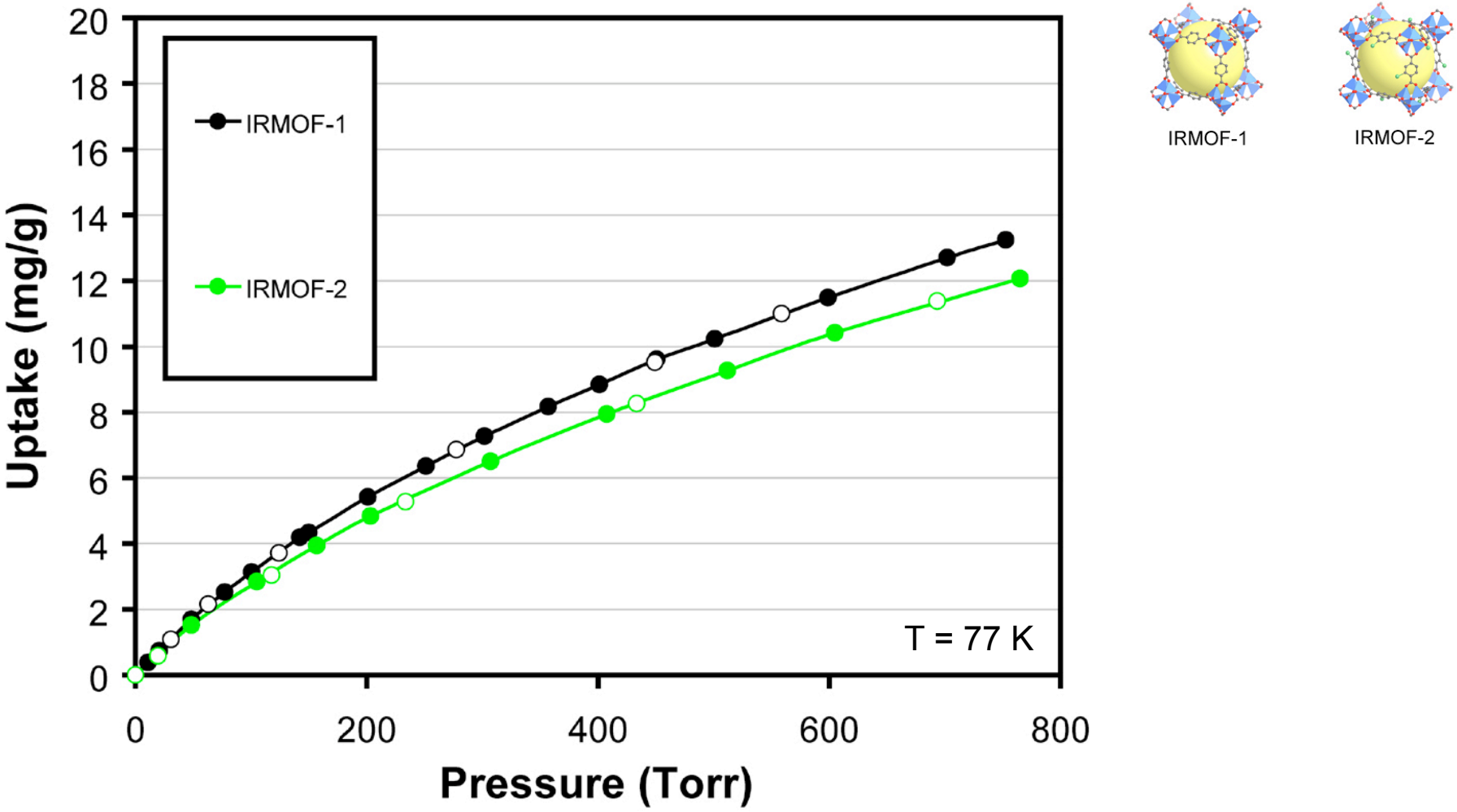
Rosi, Eckert and Yaghi *Science*, **300**, 1127, (2003)

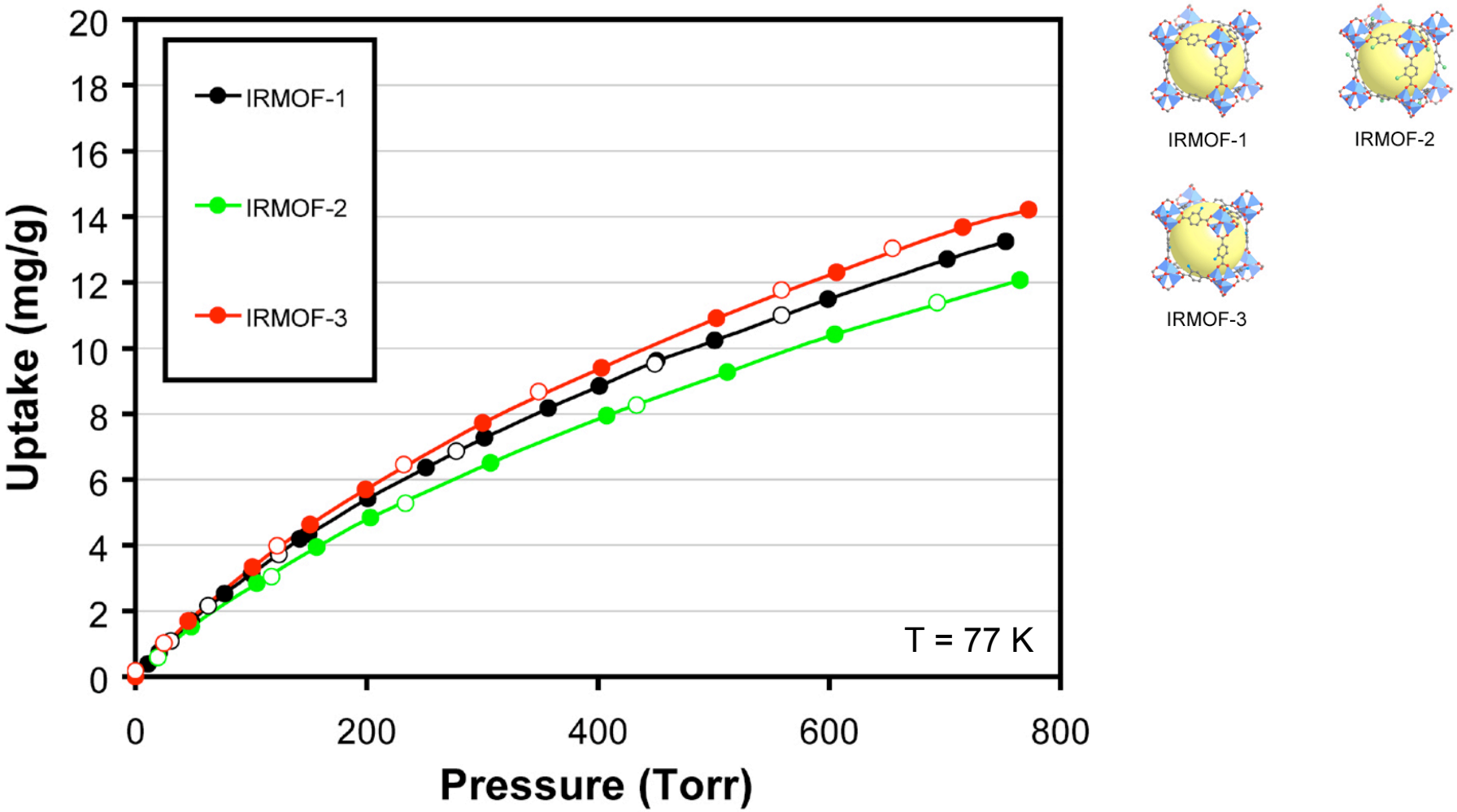


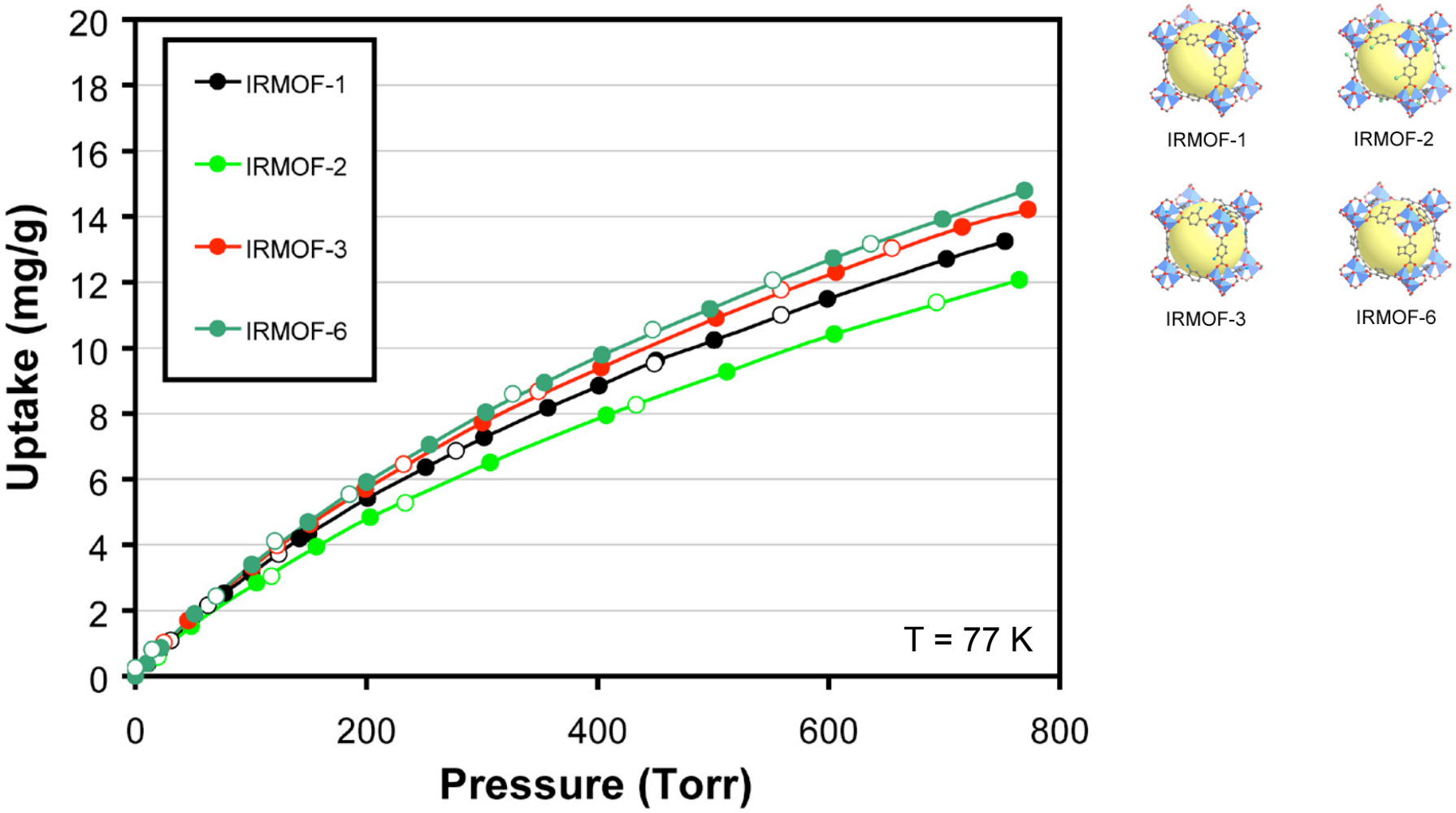
H_2 Adsorption in Non-Catenated MOFs

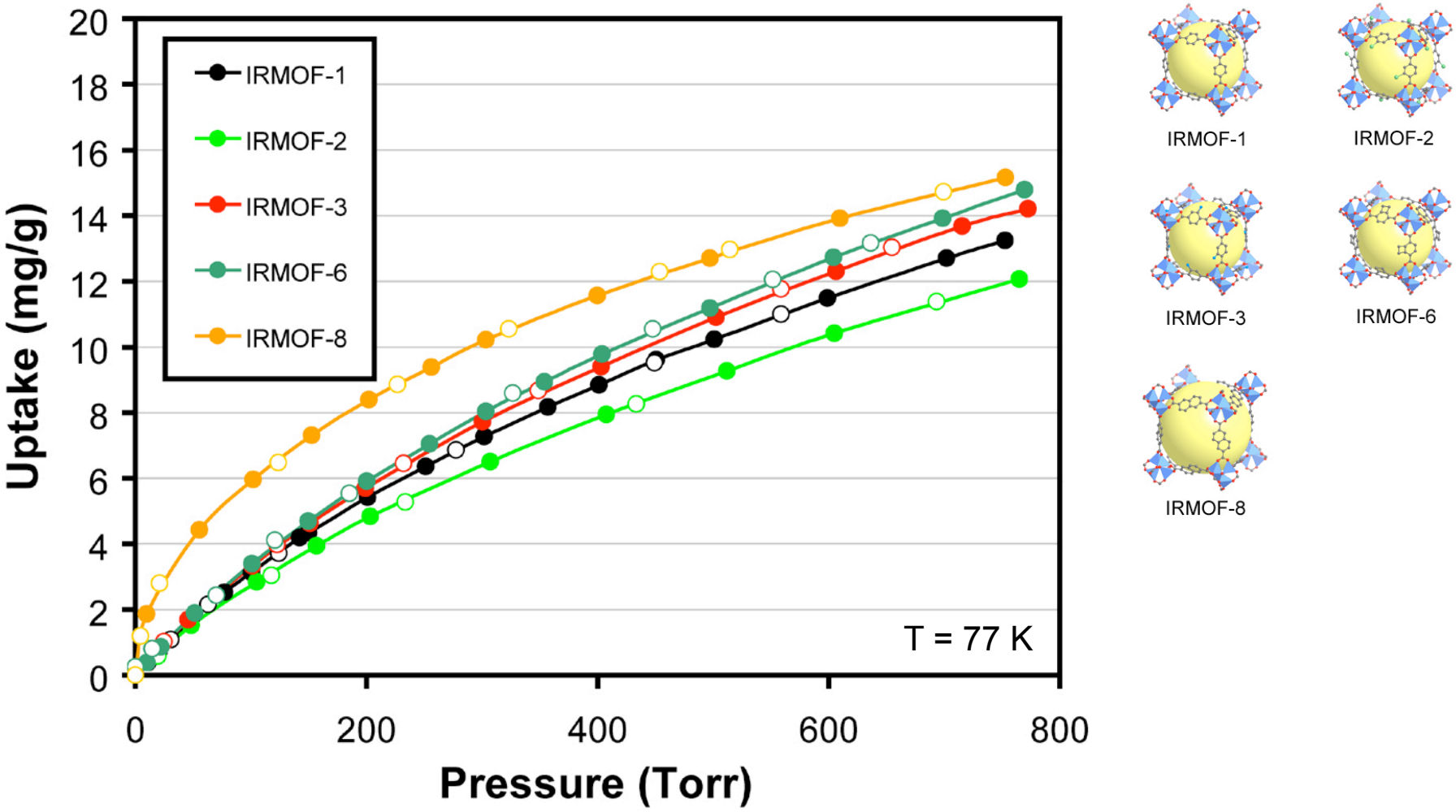


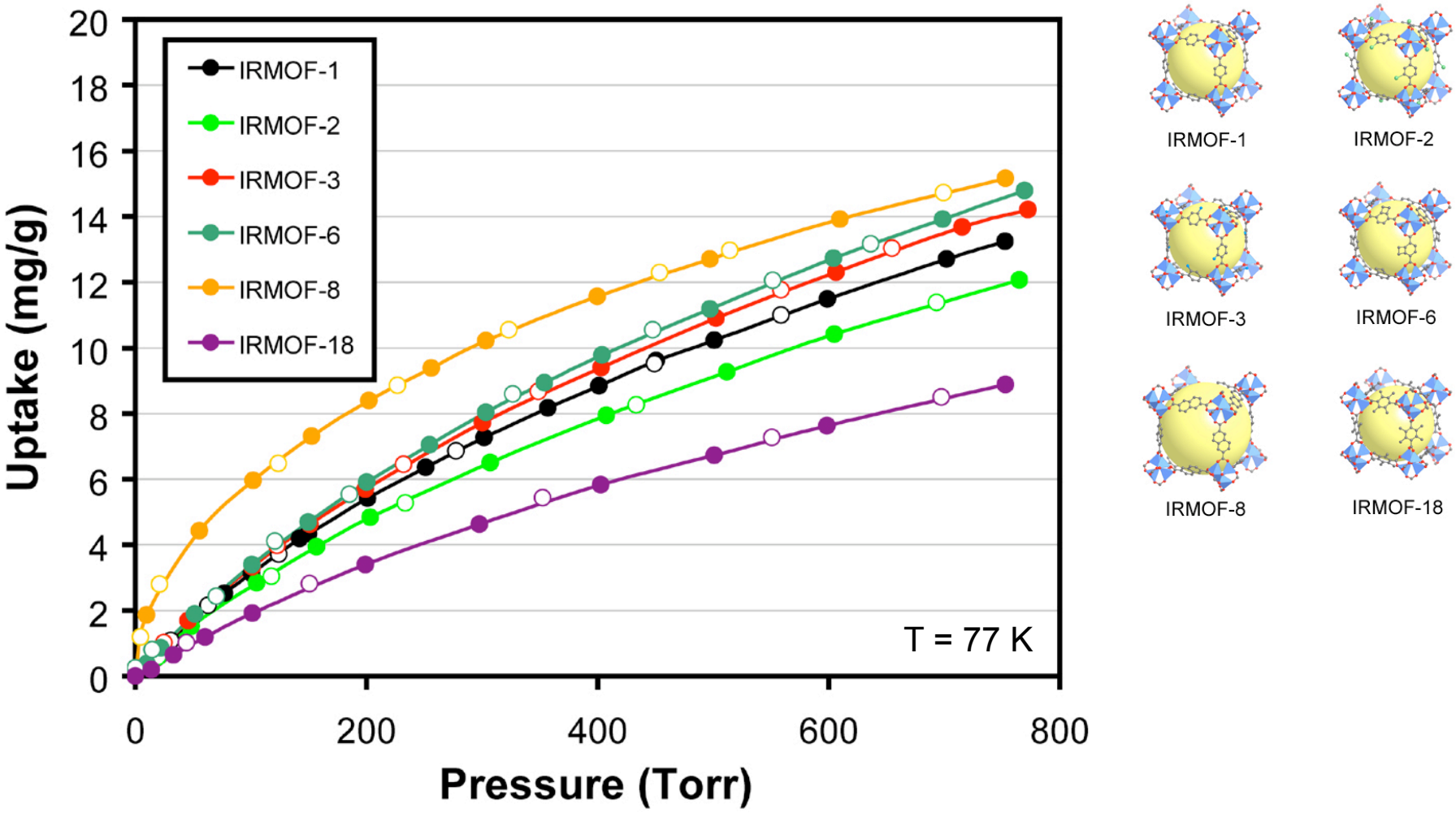

IRMOF-1

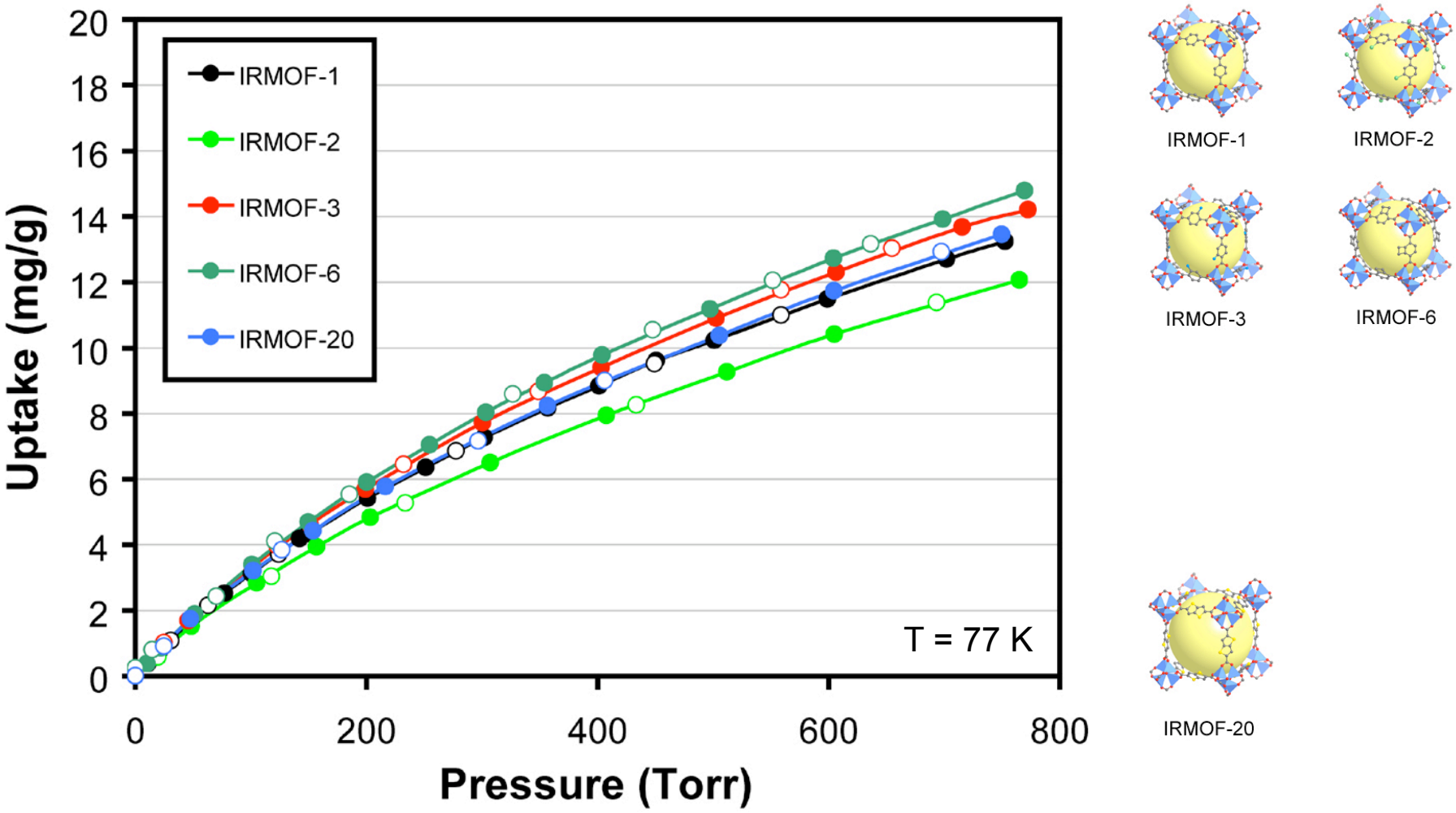

IRMOF-1
IRMOF-2
Uptake (mg/g)
Pressure (Torr)
T = 77 K
0
2
4
6
8
10
12
14
16
18
20
0
200
400
600
800

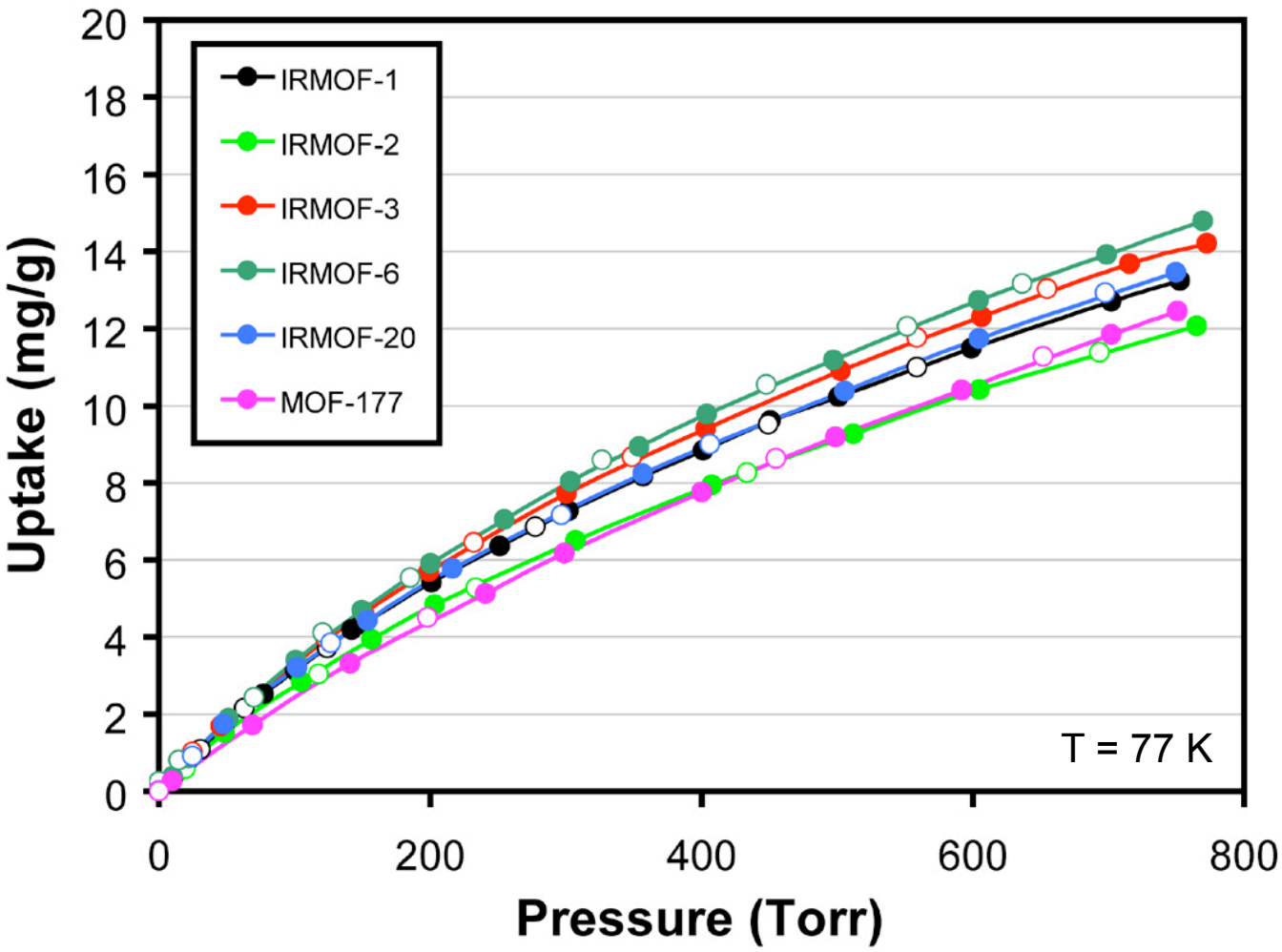

IRMOF-1
IRMOF-2
IRMOF-3
Uptake (mg/g)
Pressure (Torr)
T = 77 K
0
2
4
6
8
10
12
14
16
18
20
0
200
400
600
800
IRMOF-1
IRMOF-2
IRMOF-3

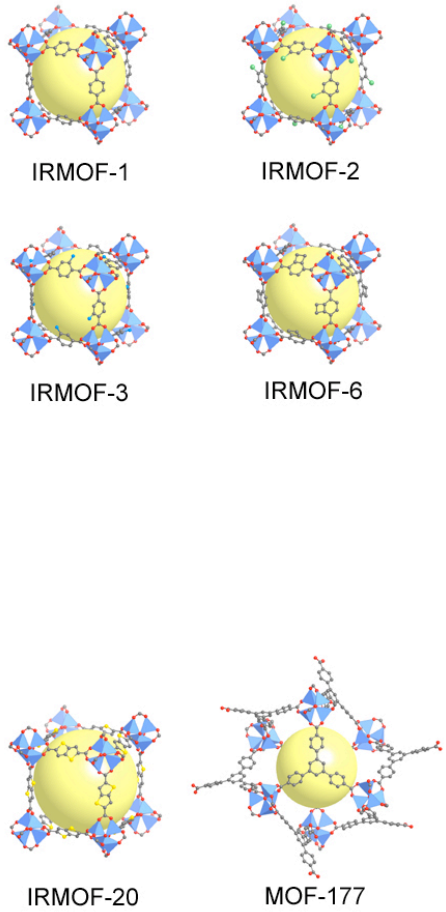

Uptake (mg/g)
Pressure (Torr)
IRMOF-1
IRMOF-2
IRMOF-3
IRMOF-6
T = 77 K
0
2
4
6
8
10
12
14
16
18
20
0
200
400
600
800
IRMOF-1
IRMOF-2
IRMOF-3
IRMOF-6

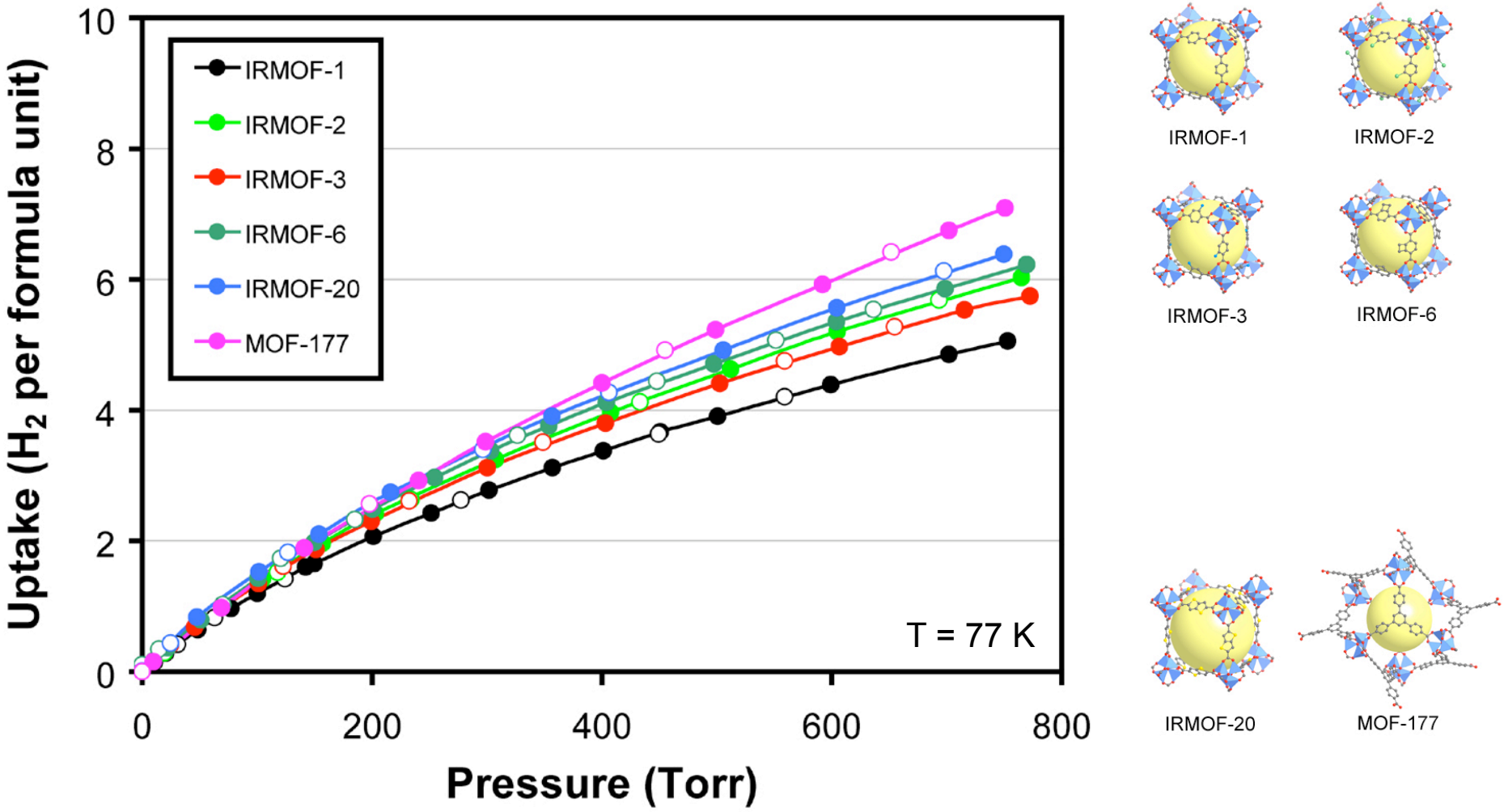

IRMOF-1
IRMOF-2
IRMOF-3
IRMOF-6
IRMOF-8
Uptake (mg/g)
Pressure (Torr)
T = 77 K
0
2
4
6
8
10
12
14
16
18
20
0
200
400
600
800
IRMOF-1
IRMOF-2
IRMOF-3
IRMOF-6
IRMOF-8


IRMOF-1
IRMOF-2
IRMOF-3
IRMOF-6
IRMOF-8
IRMOF-18
T = 77 K
Uptake (mg/g)
Pressure (Torr)
0
2
4
6
8
10
12
14
16
18
20
0
200
400
600
800

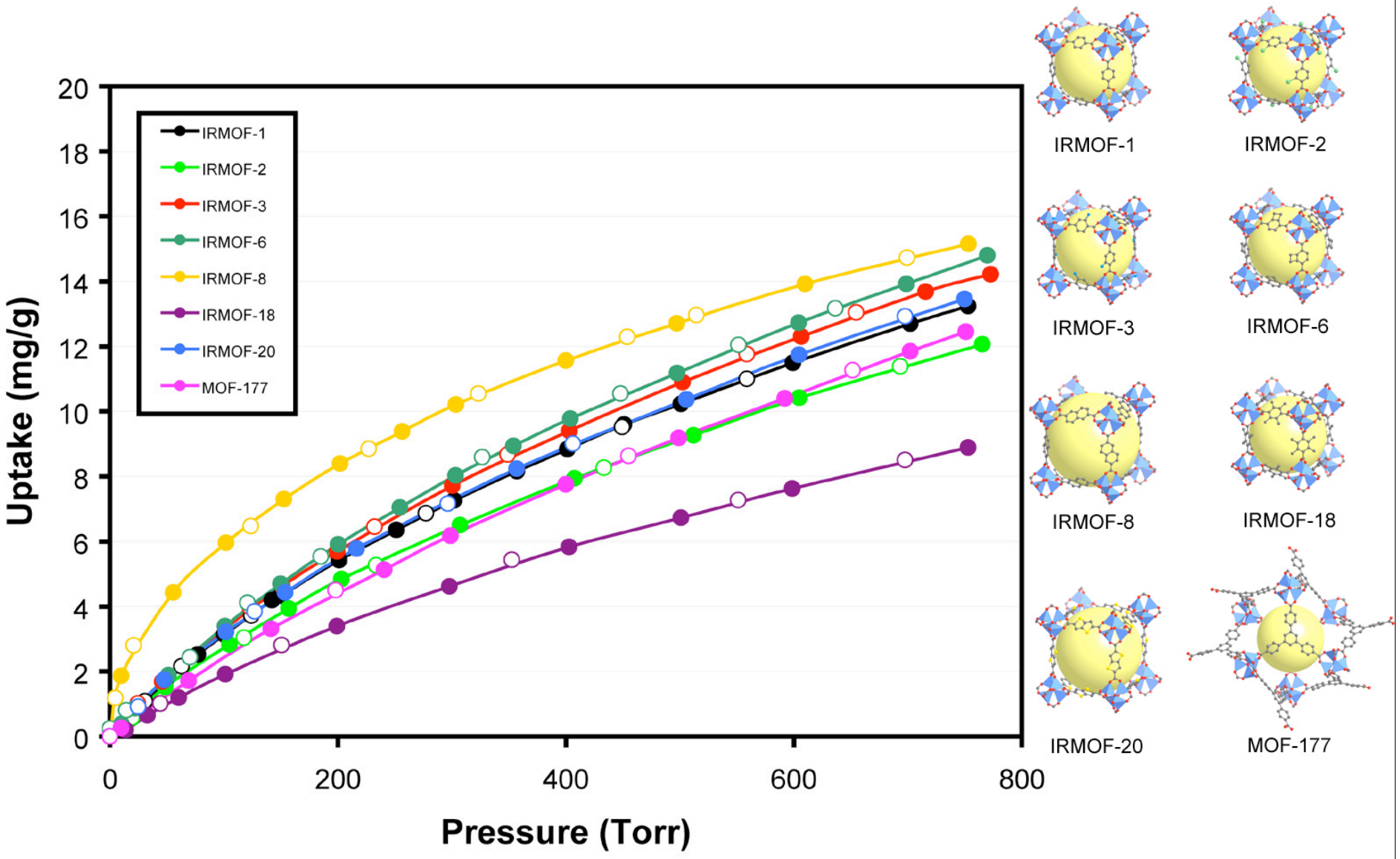

Uptake (mg/g)
Pressure (Torr)
IRMOF-1
IRMOF-2
IRMOF-3
IRMOF-6
IRMOF-20
T = 77 K
0
2
4
6
8
10
12
14
16
18
20
0
200
400
600
800
IRMOF-1
IRMOF-2
IRMOF-3
IRMOF-6
IRMOF-20


IRMOF-1
IRMOF-2
IRMOF-3
IRMOF-20
MOF-177
T = 77 K
Uptake (mg/g)
Pressure (Torr)
0
2
4
6
8
10
12
14
16
18
20
0
200
400
600
800

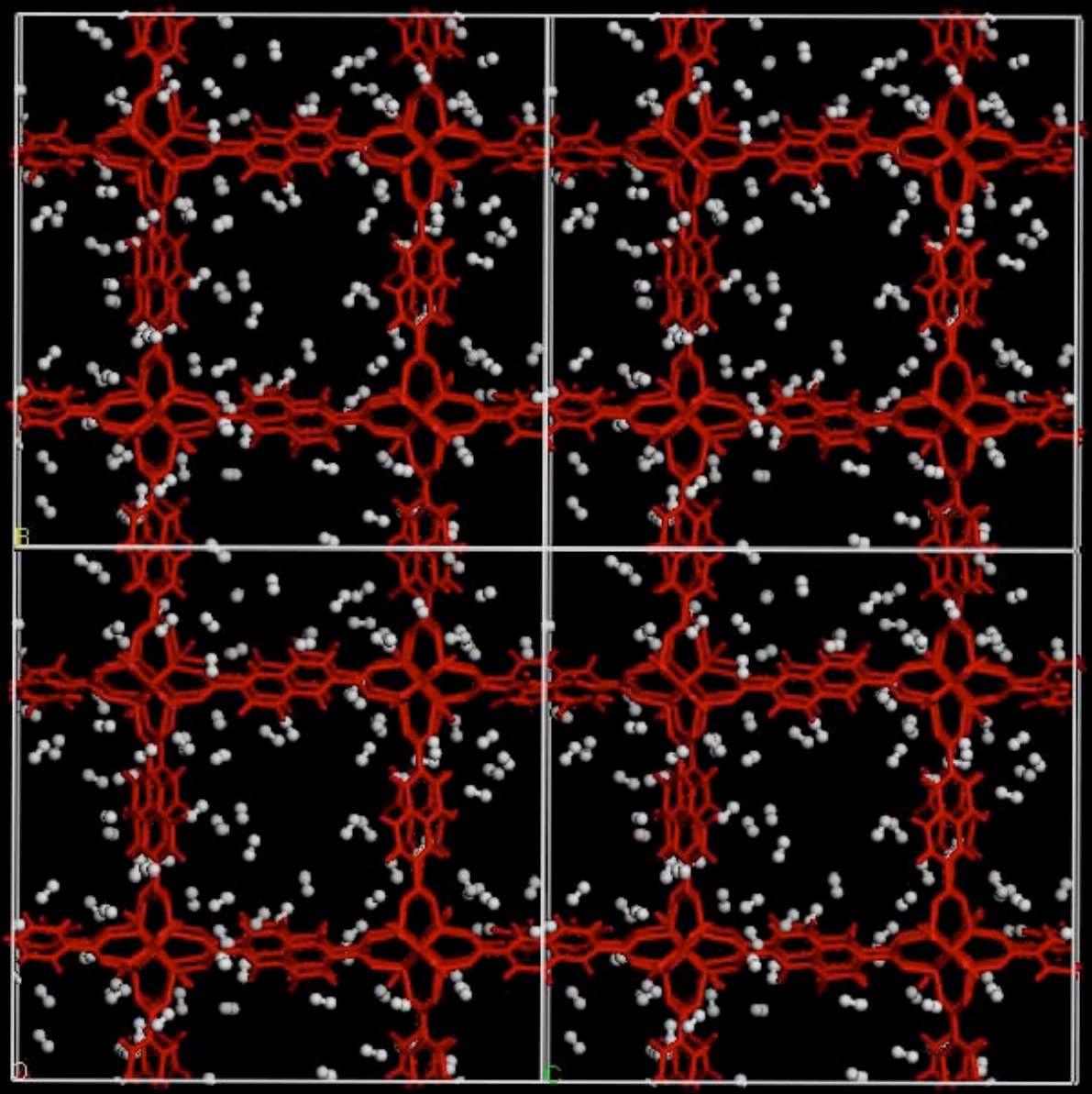

IRMOF-1
IRMOF-2
IRMOF-3
IRMOF-6
IRMOF-20
MOF-177


Uptake (H_2 per formula unit)
Pressure (Torr)
IRMOF-1
IRMOF-2
IRMOF-3
IRMOF-6
IRMOF-20
MOF-177
T = 77 K
0
2
4
6
8
10
0
200
400
600
800
IRMOF-1
IRMOF-2
IRMOF-3
IRMOF-6
IRMOF-20
MOF-177

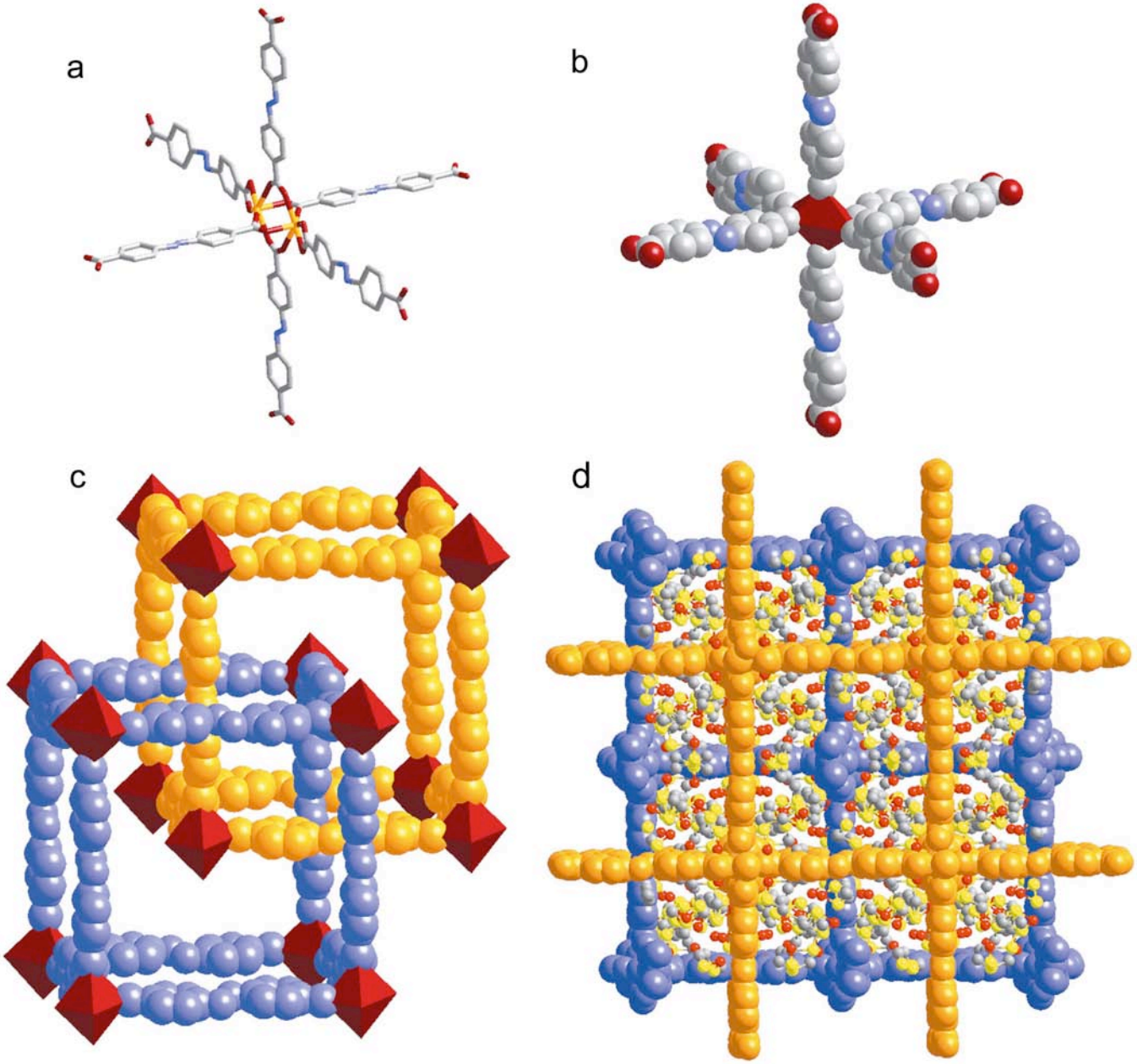
H_2 Adsorption in Non-Catenated MOFs



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

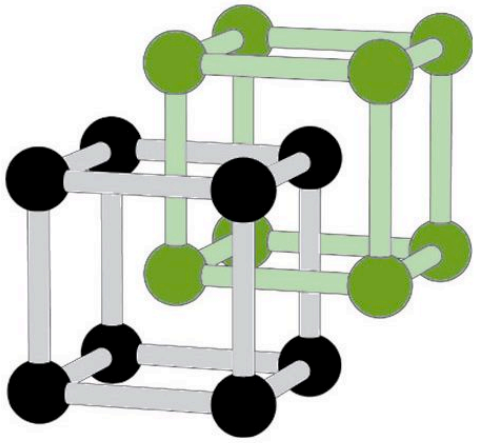


MOF-9: $Tb_2(ADB)_3[(CH_3)_2SO]_4 \cdot 16[(CH_3)_2SO]$



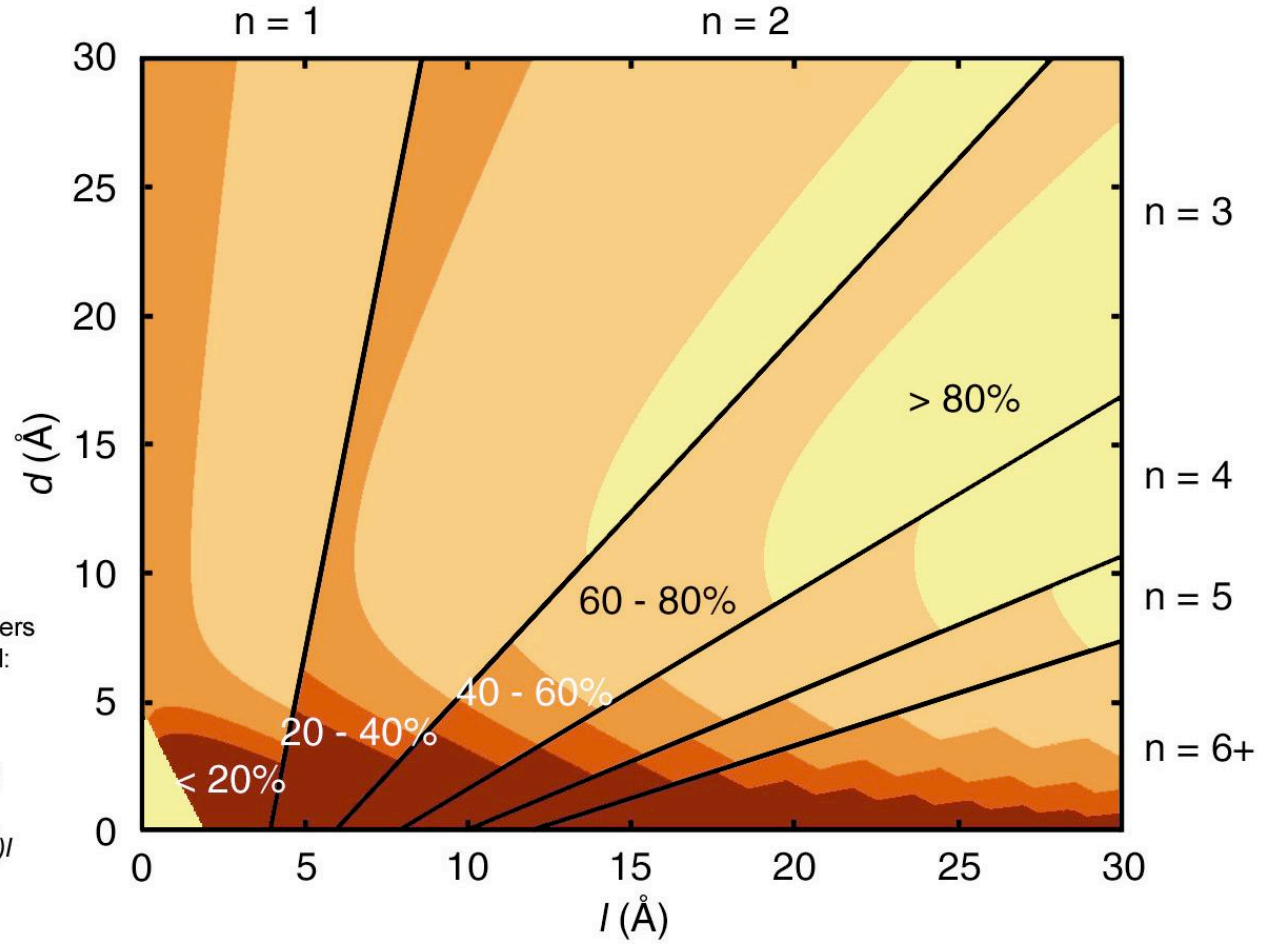
Reineke, T.M.; Eddaoudi, M.; Moler, D.; O'Keeffe, M.; Yaghi, O.M. *J. Amer. Chem. Soc.* **2000,** *122,* 4843.

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

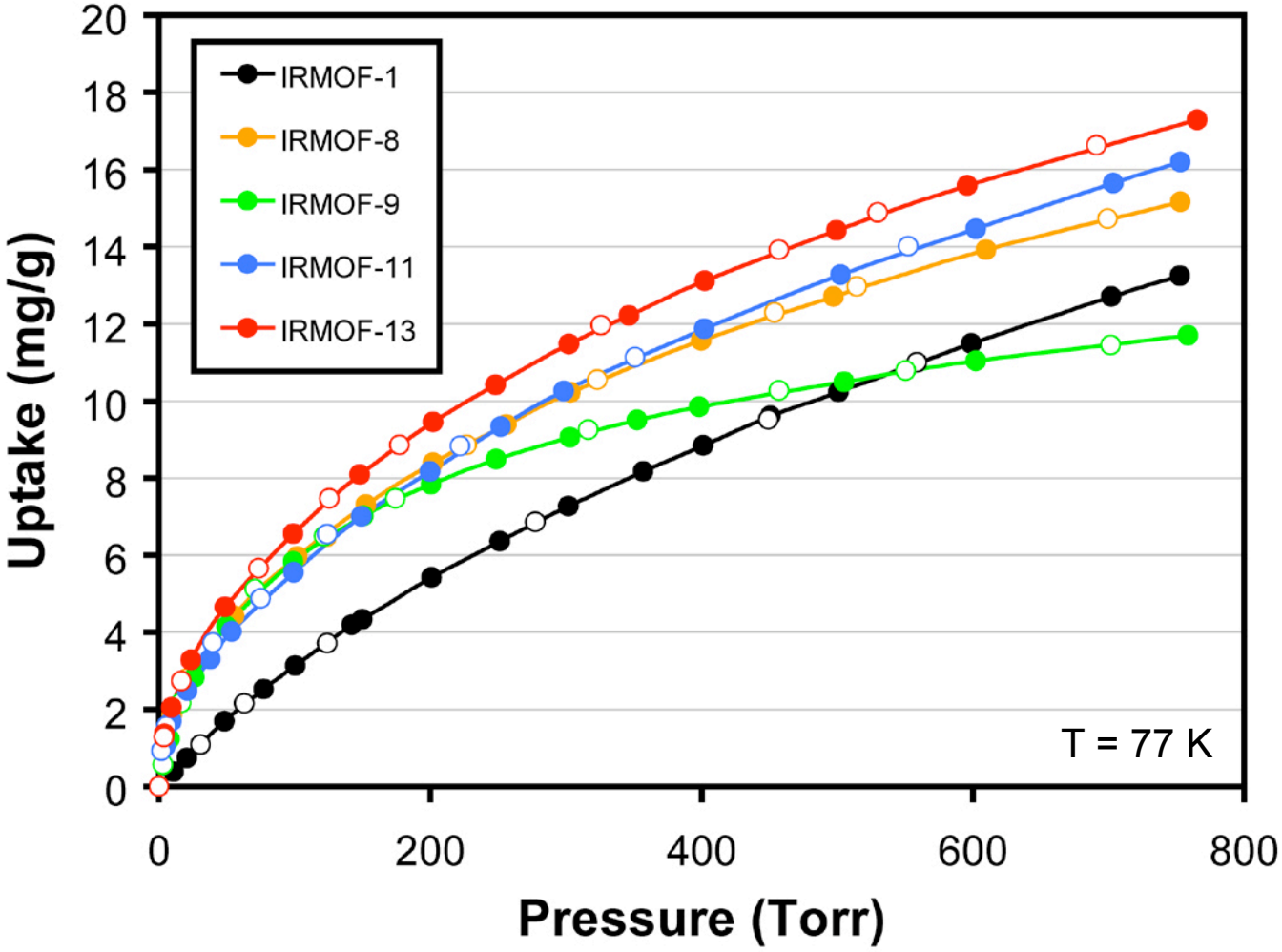


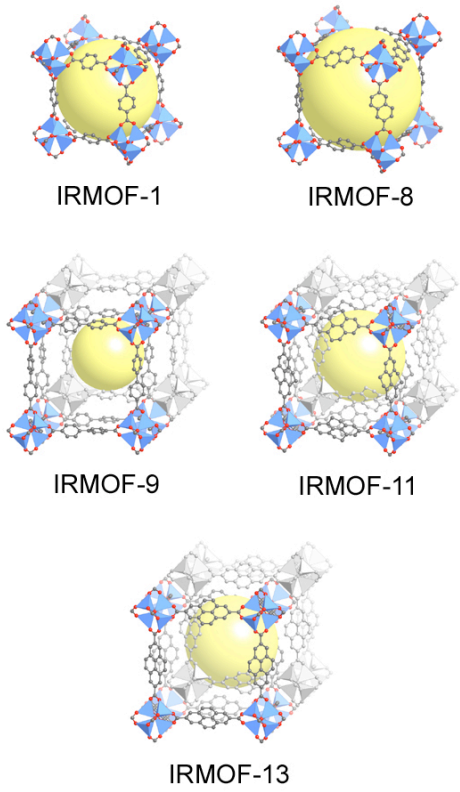
Cell edge: $a = d + l$
van der Waals Radius of SBU = $\delta / 2$
For n frameworks to interpenetrate with centers of the SBUs aligned along the body diagonal:
$n(d + \delta) \leq \sqrt{3}\, a$ thus $n \leq \sqrt{3}\,(d + l) / (d + \delta)$

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 = $(d + l)^3 - (n(\pi / 6)d^3 + 3n(\pi r^2)l$

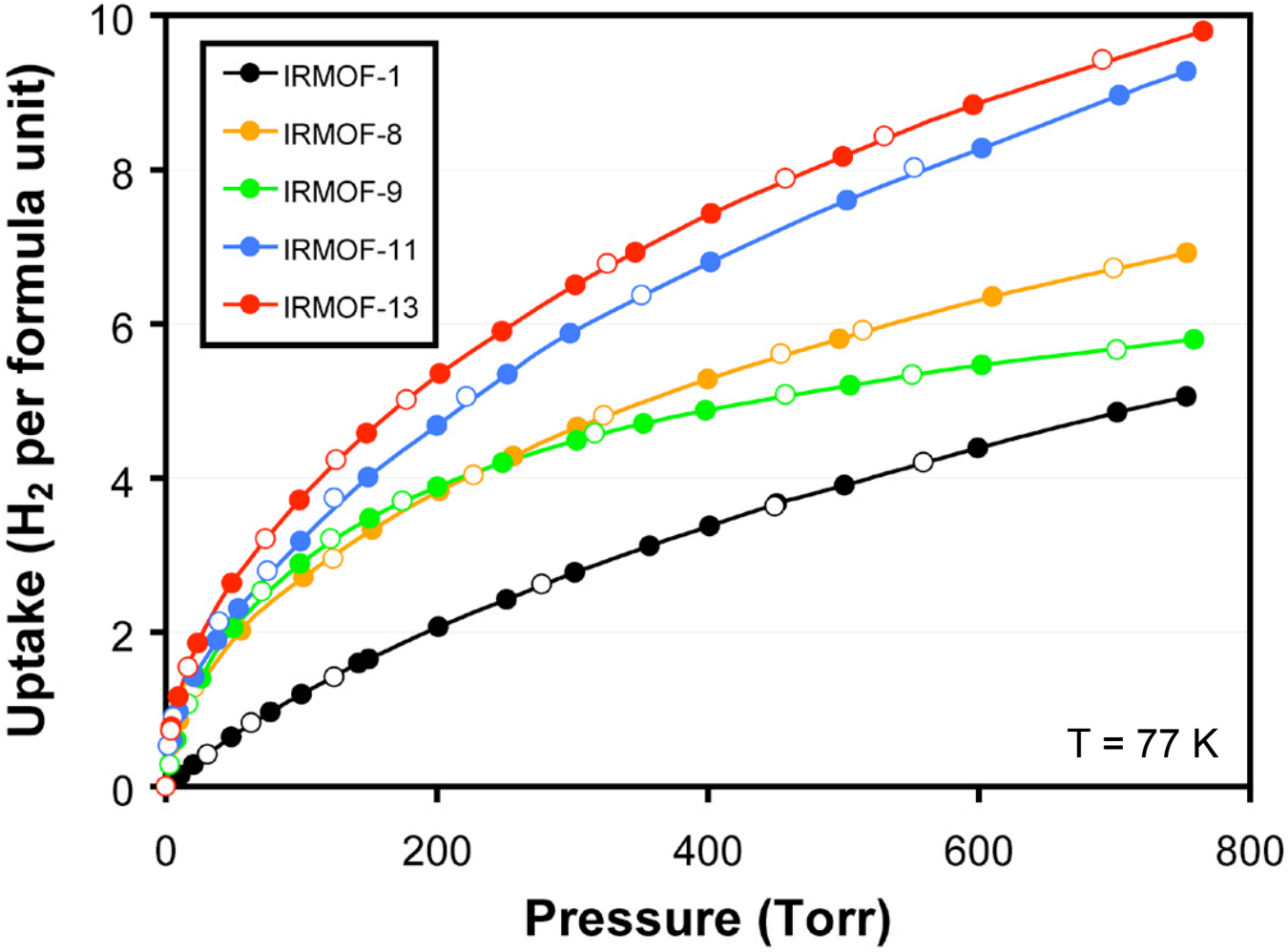


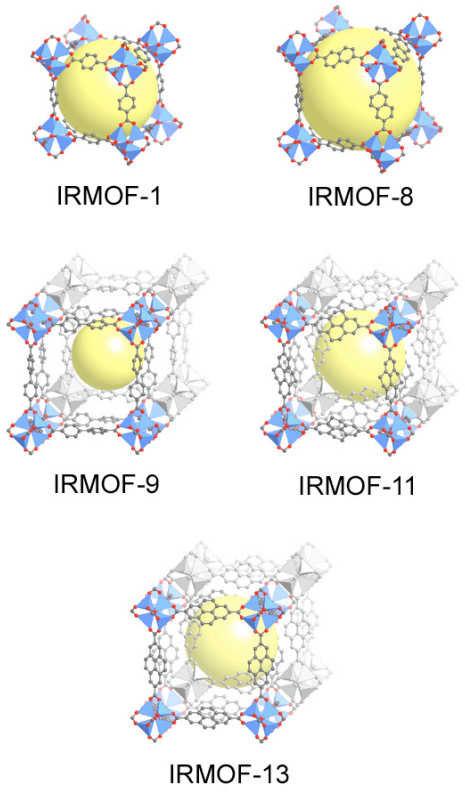
H_2 Adsorption in Catenated MOFs



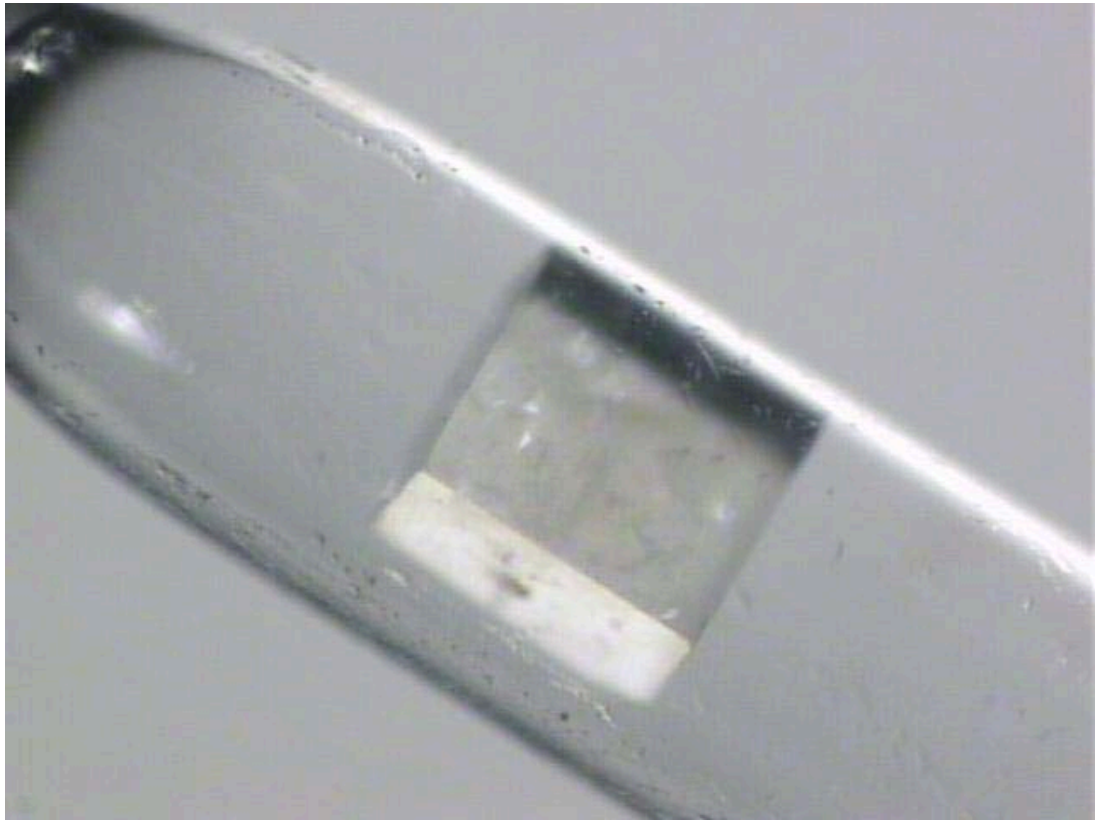


H_2 Adsorption in Catenated MOFs





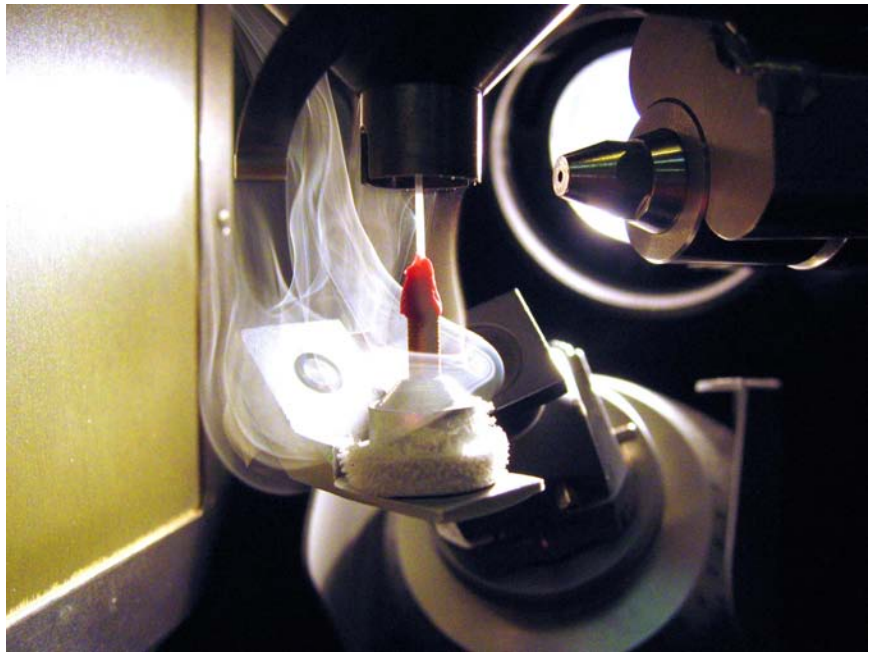
Evacuated Single Crystals of IRMOF-1



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

Low Temperature Single Crystal X-ray Diffraction

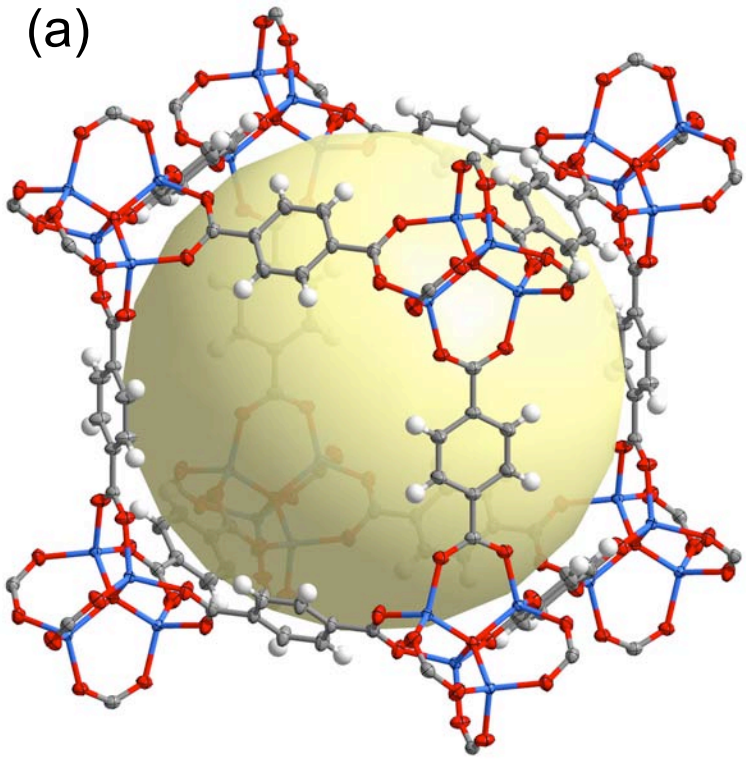
- Helix cryostat (University of Durham, UK) provides temperature control to 30 K



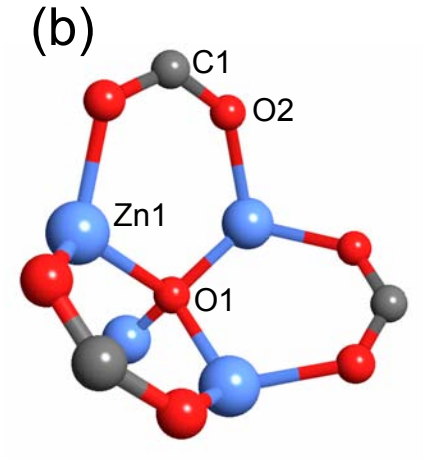
Refinement of evacuated framework at 30 K:

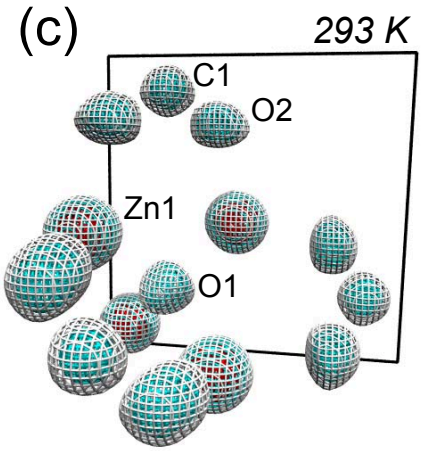
Empirical Formula	$Zn_4O_{13}C_{24}H_{12}$
Crystal Size	0.43 x 0.43 x 0.30 mm
Space Group	$Fm\bar{3}m$
Cell parameter	a = 25.894(4) Å
Calculated density	0.589 g/cm^3
θ range (for $Mo_{K\alpha}$)	2.61 to 29.56^o
Total Reflections	16341
Data / restraints / parameters	1258 / 0 / 28
R indices [I>2s(I)]	R_1 = 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

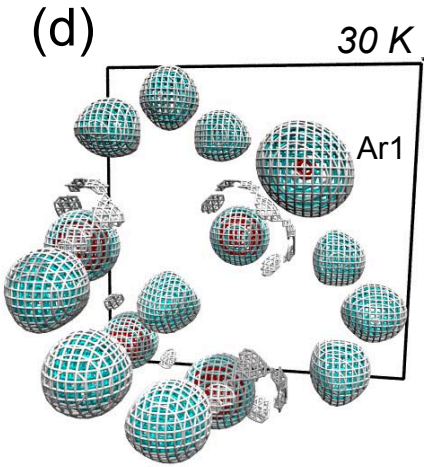
Crystallographic identification of gas (Ar, and N_2 Guests) adsorption sites in MOF-5

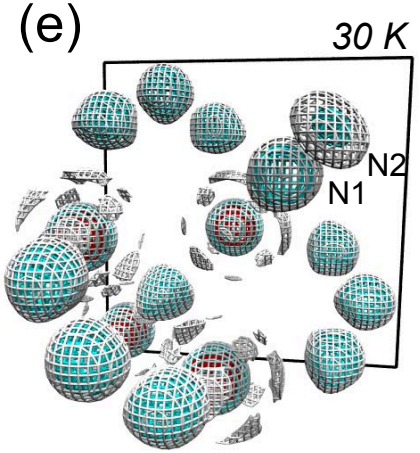


ORTEP (90% ellipsoids) $Zn_4O(BDC)_3$, *30 K*



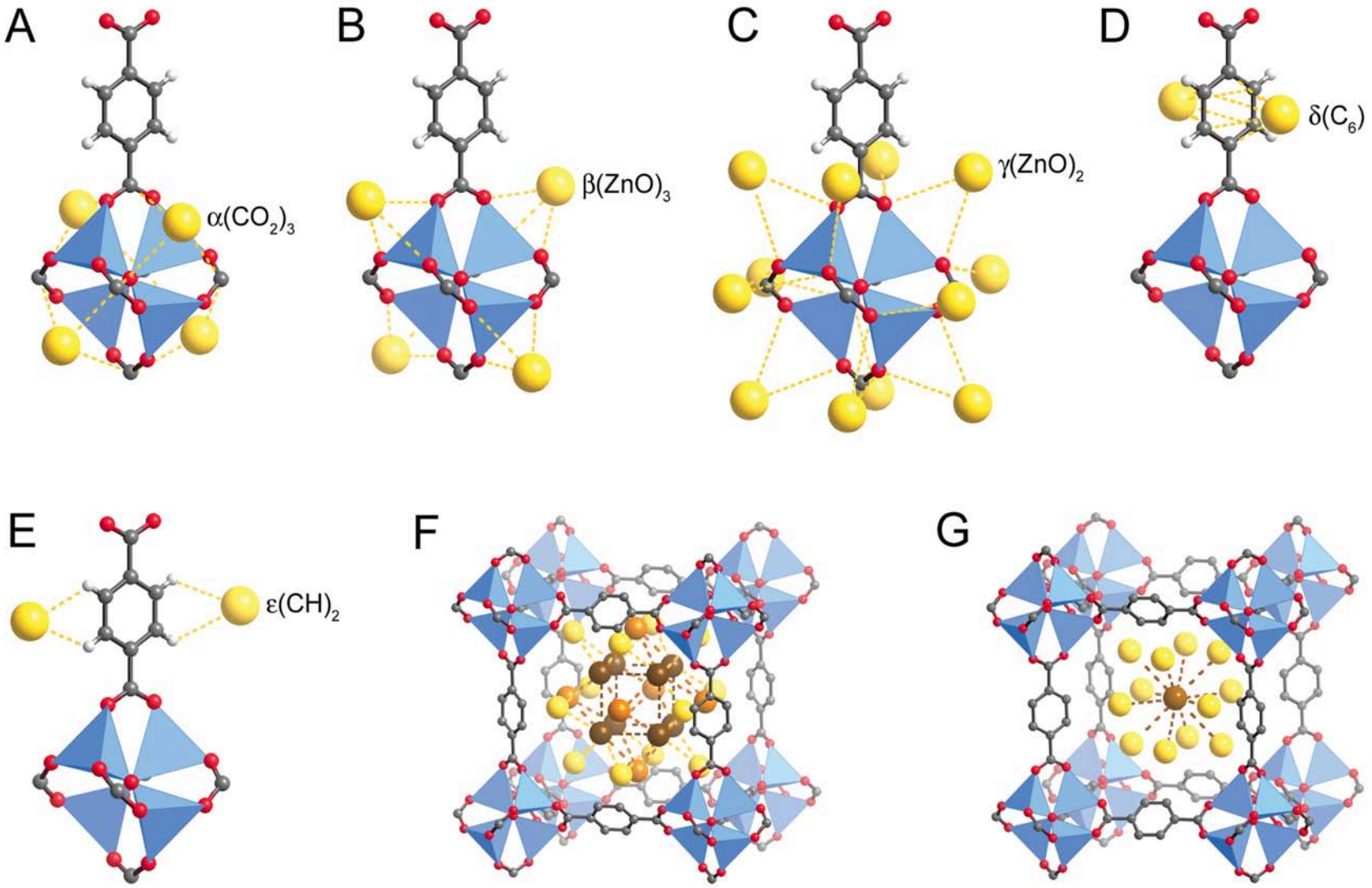




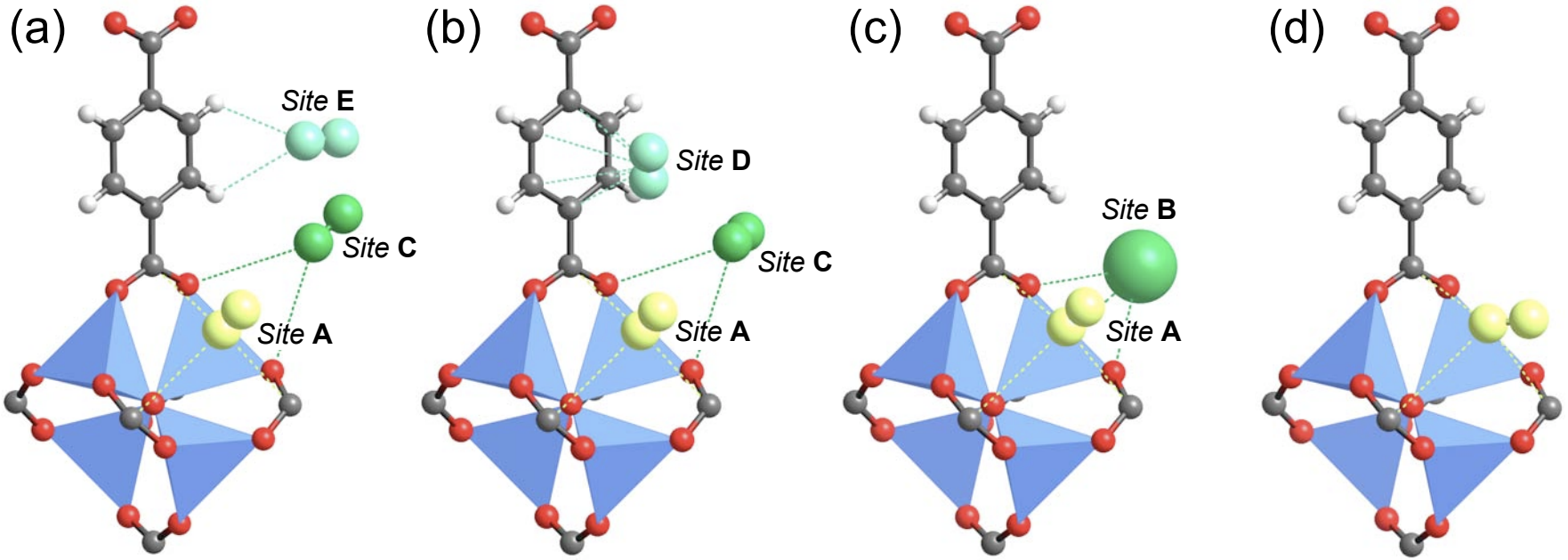


Science 2005

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

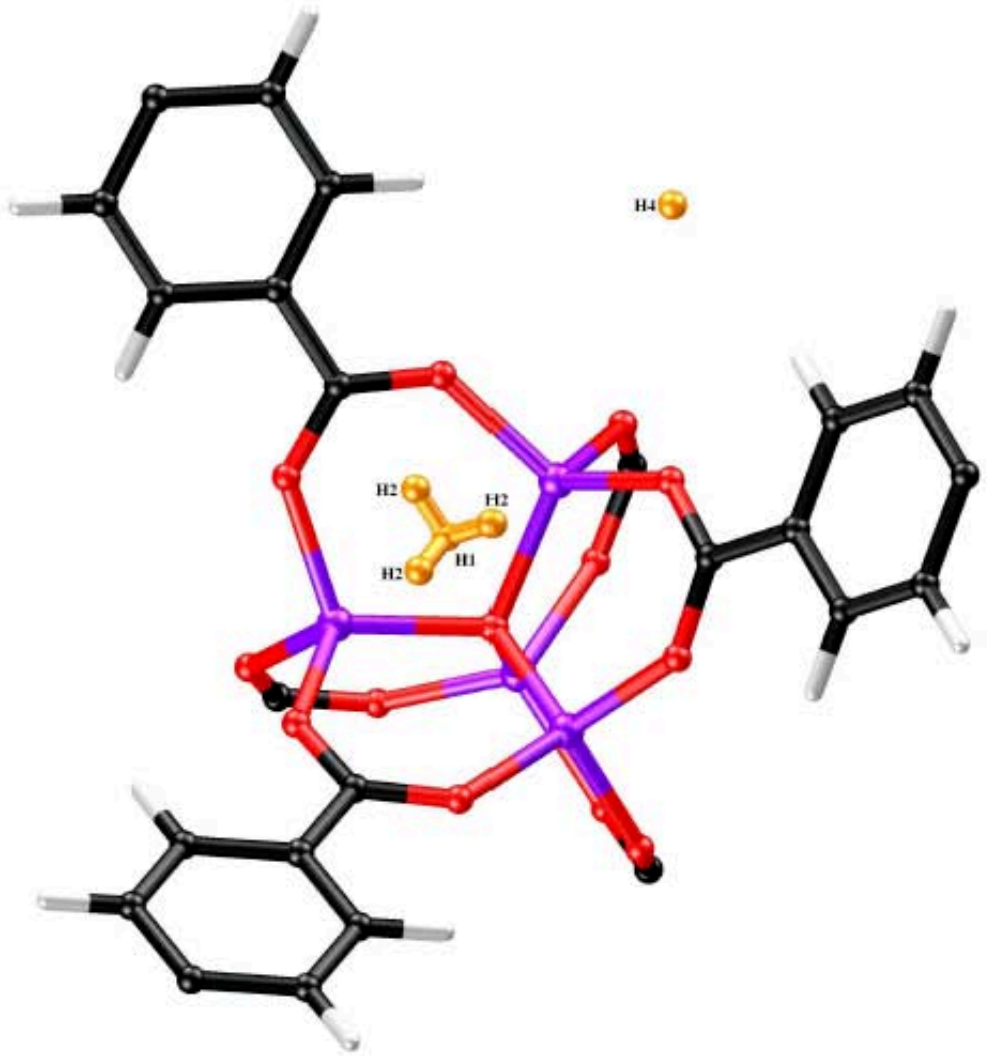


Single crystal X-ray diffraction for N_2 guests

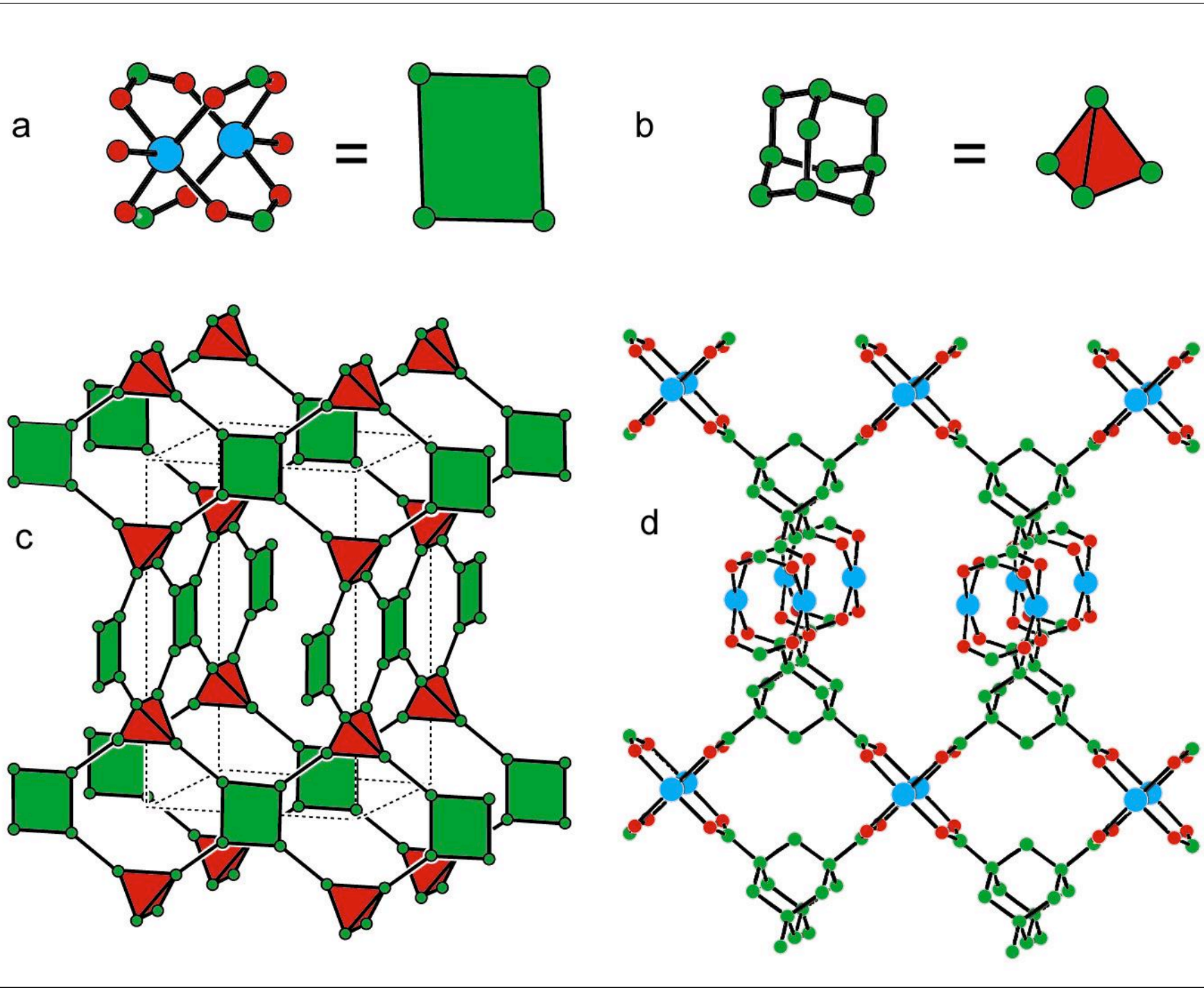


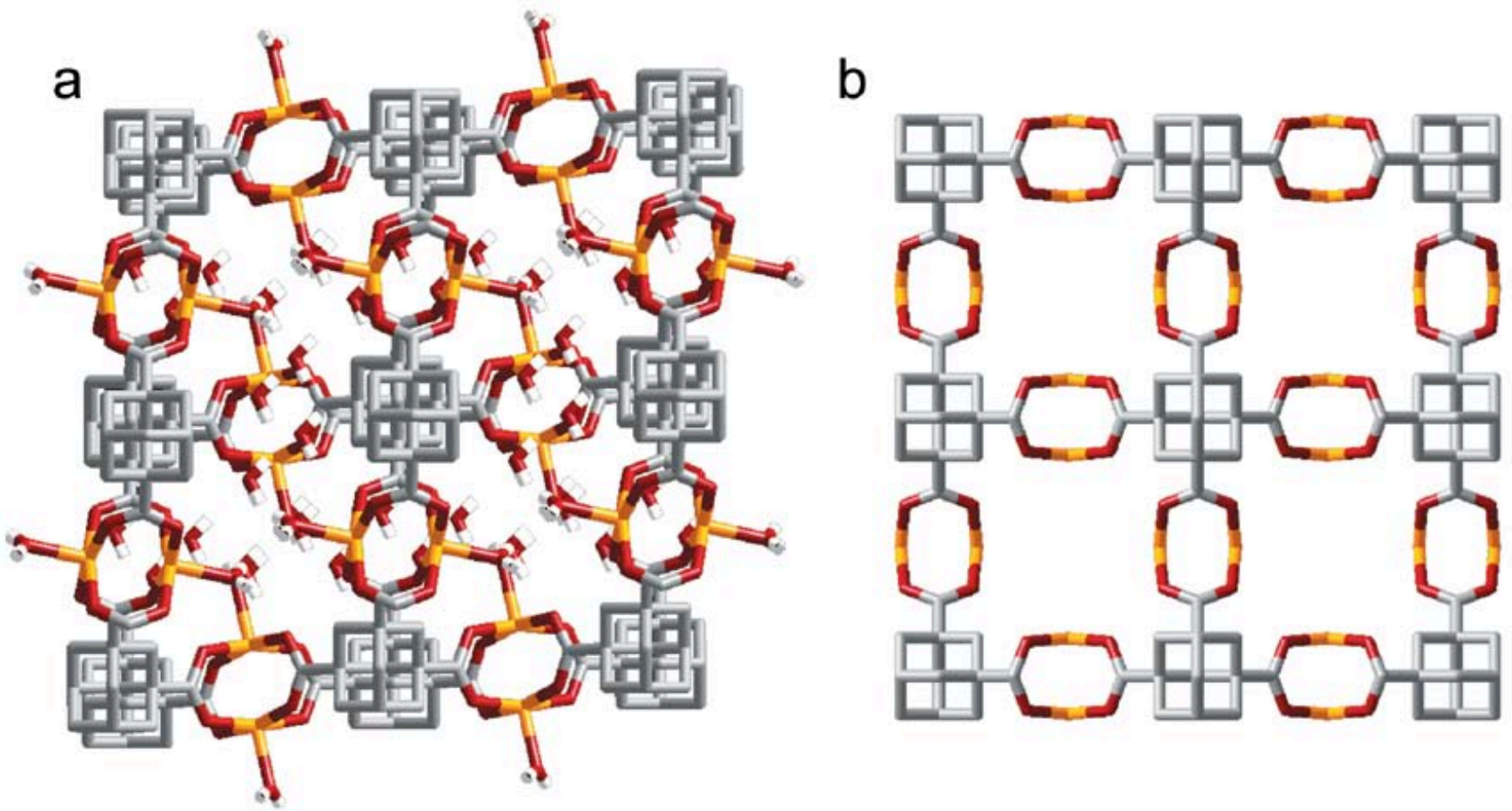
30 K ***50 K*** ***90 K*** ***120 K***

Single Crystal Neutron Diffraction



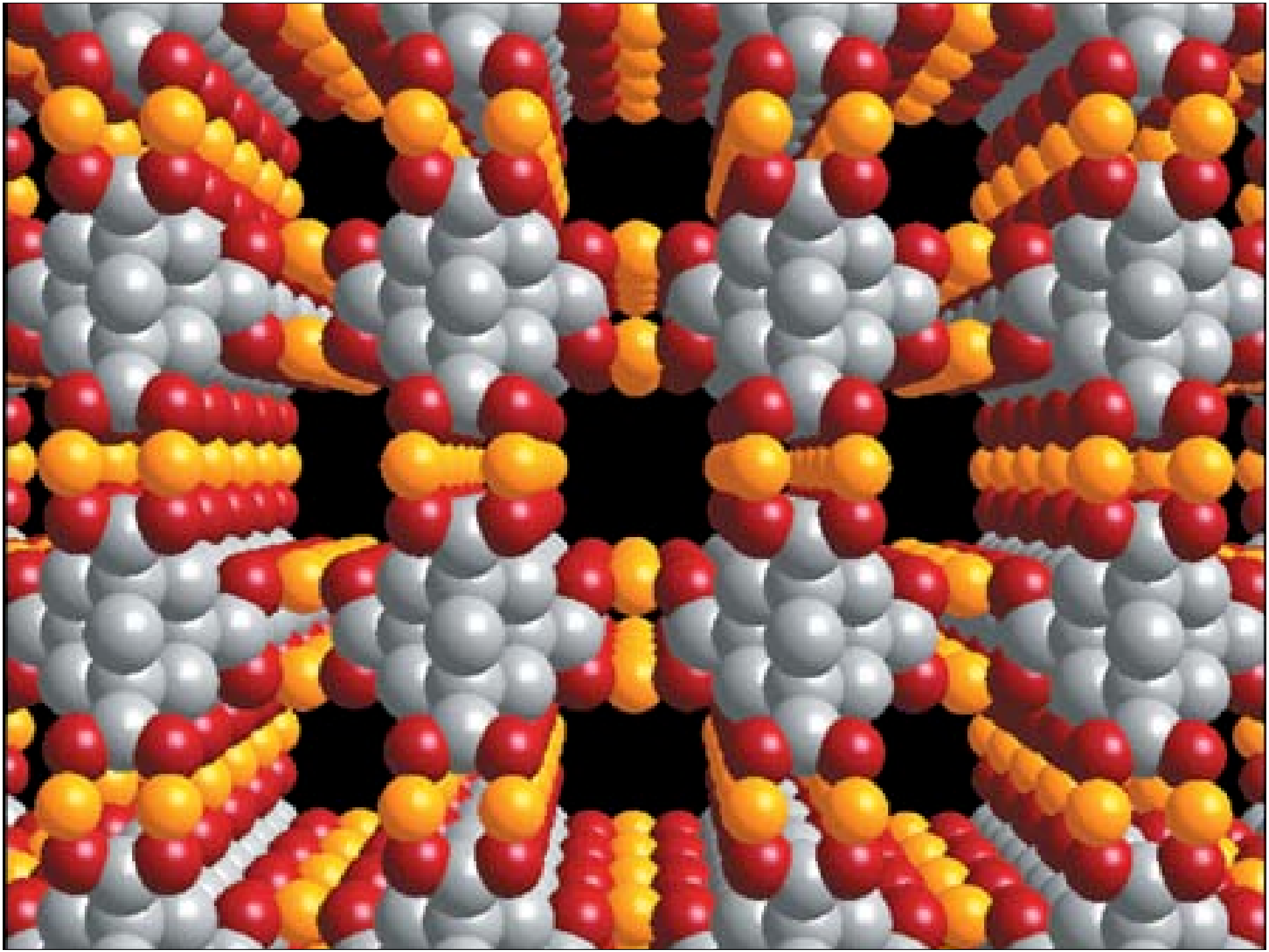
- data collected on VIVALDI (ILL) on ~$(0.5\ mm)^3$ crystal sealed under H_2
- appearance of H_2 on α $\mathbf{(CO_2)_3}$ site at 50 K, additional H_2 appears on β $\mathbf{(ZnO)_3}$ at 5 K


a
=
b
=
c
d

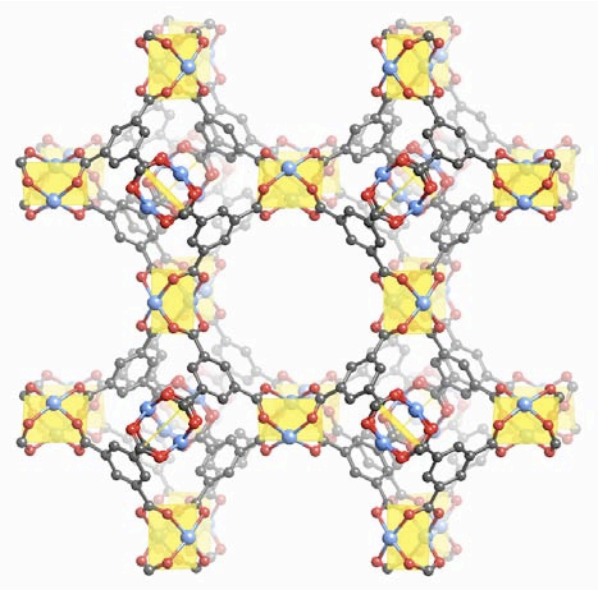


$Cu_2(ATC)\cdot 6H_2O$ $Cu_2(ATC)$

JACS 2001 (Banglin Chen)

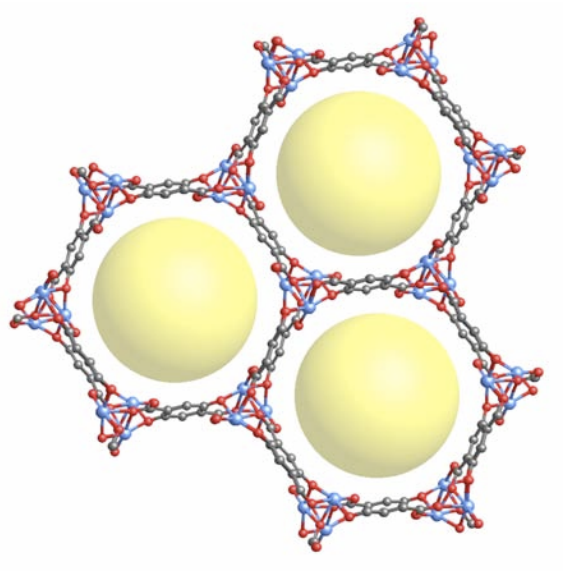


MOFs with open metal sites



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

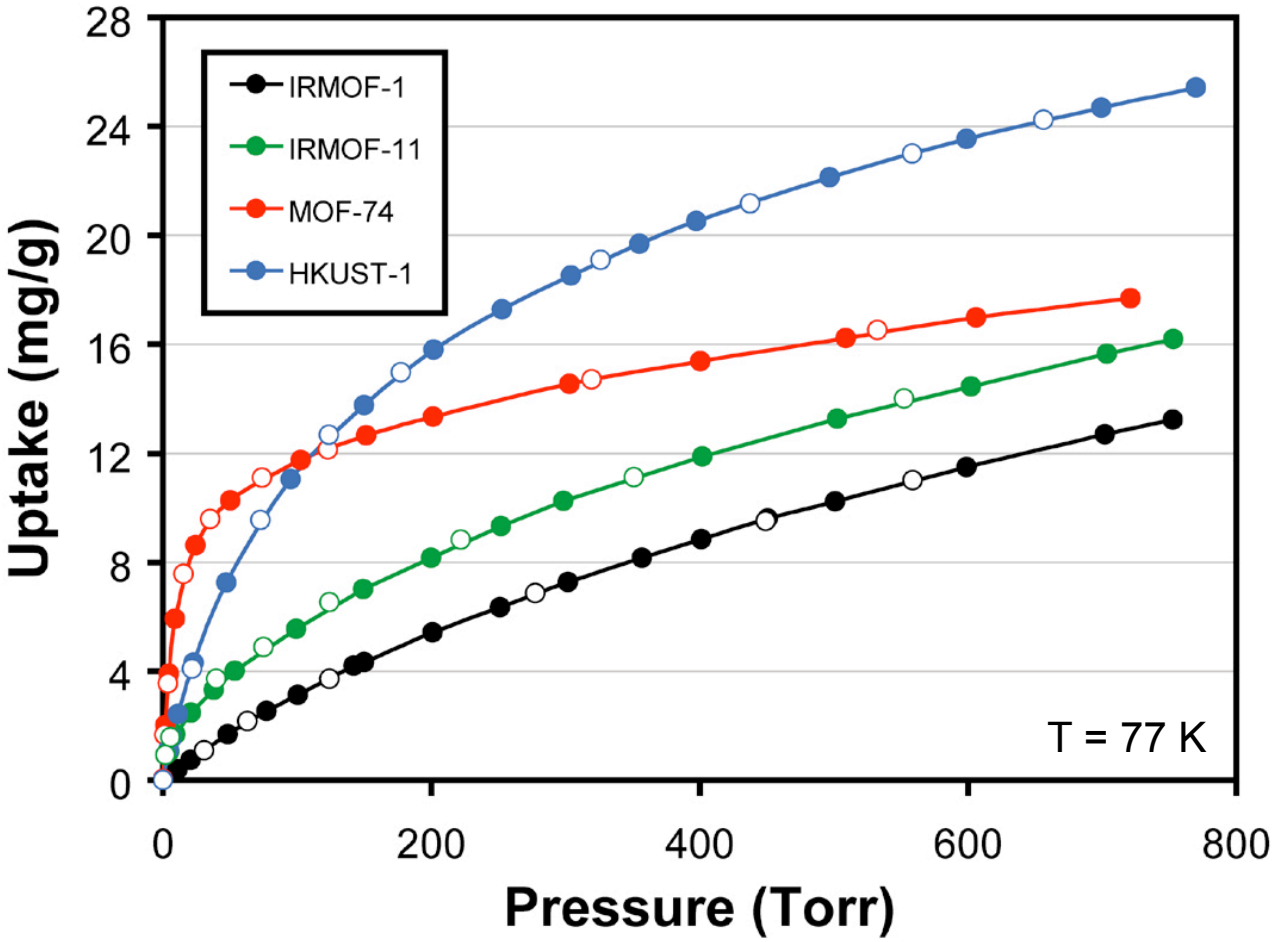
A_{Lang} 2175 m^2/g
A_{BET} 1507 m^2/g
V_p 66%

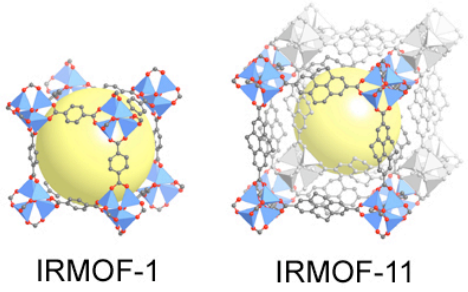


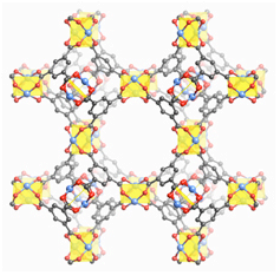
MOF-74, $Zn_2(dhBDC)$

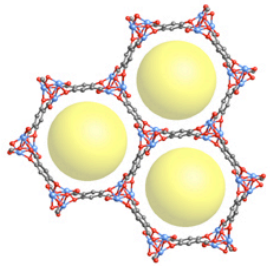
A_{Lang} 1132 m^2/g
A_{BET} 783 m^2/g
V_p 48%

H_2 Uptake for MOFs with Open-Metal Sites

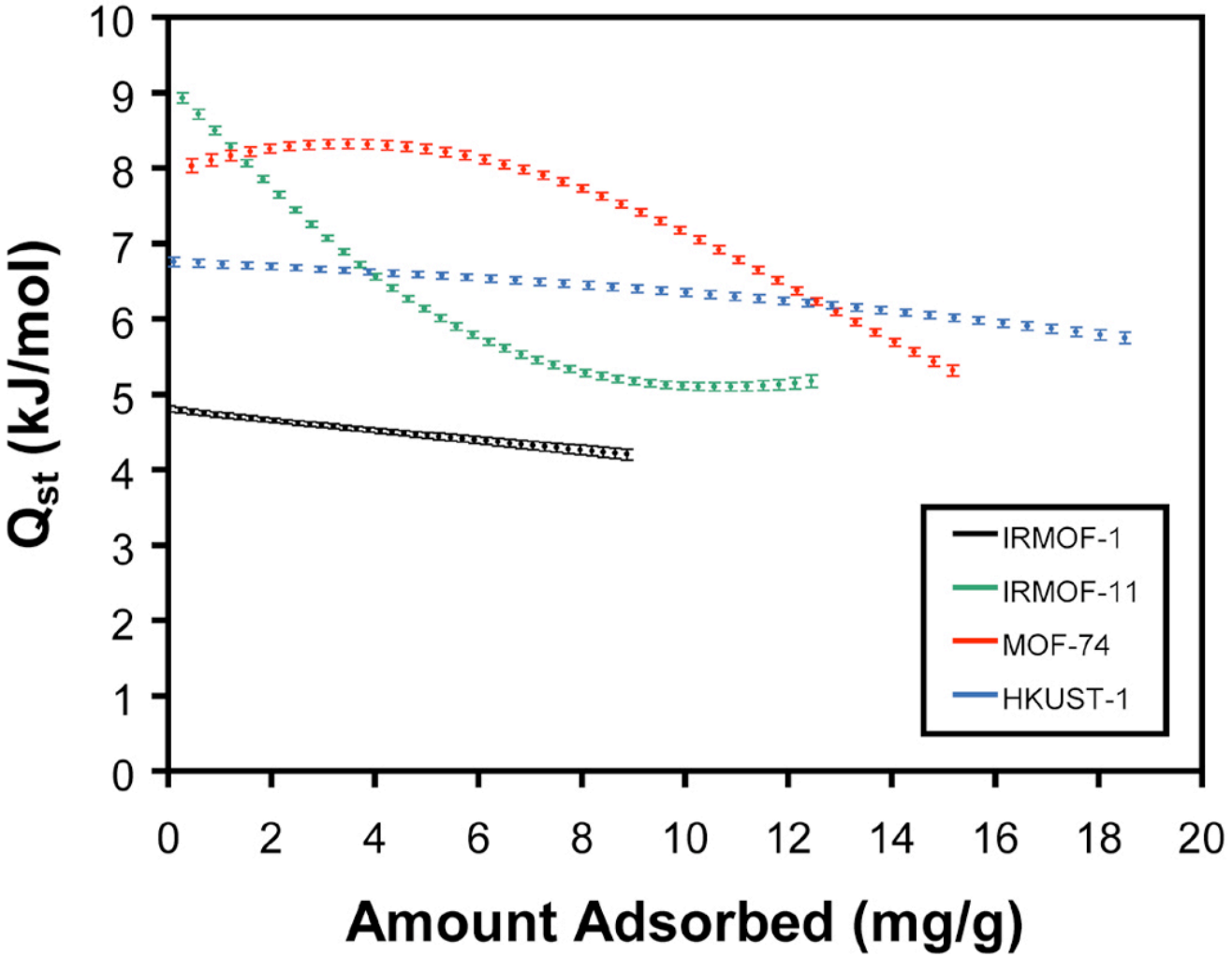


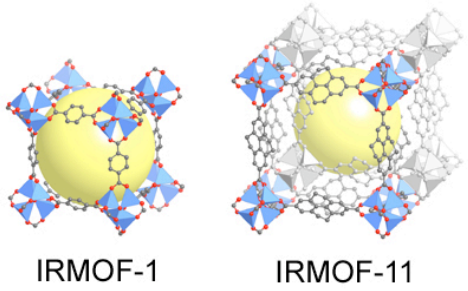




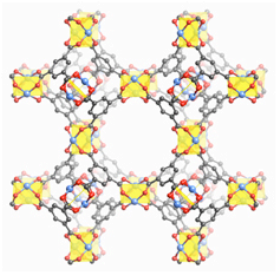


Isosteric Heats of Adsorption

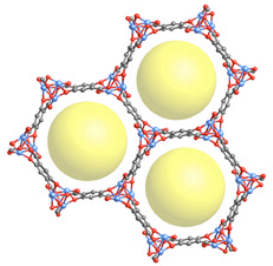




IRMOF-1 IRMOF-11

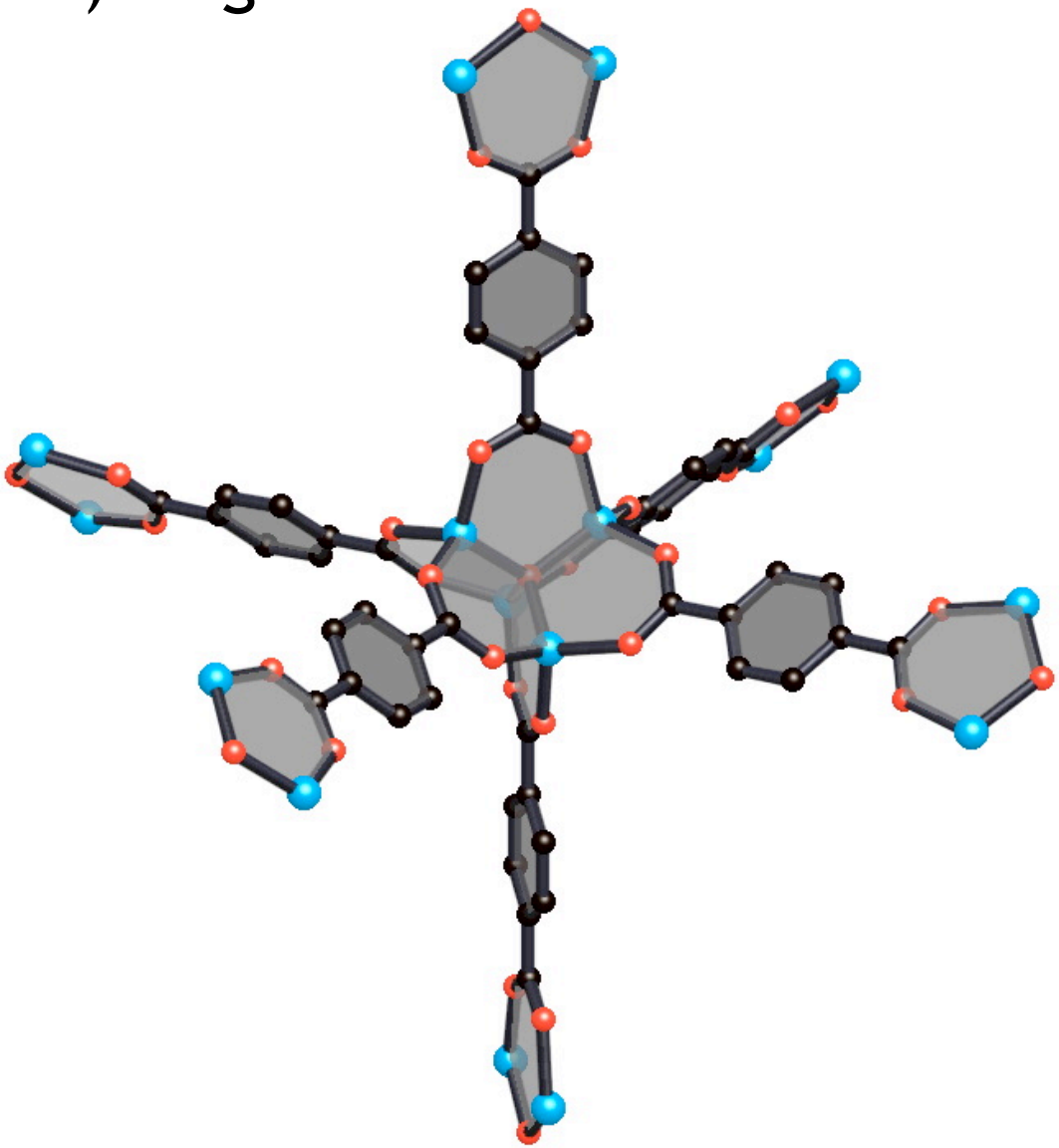


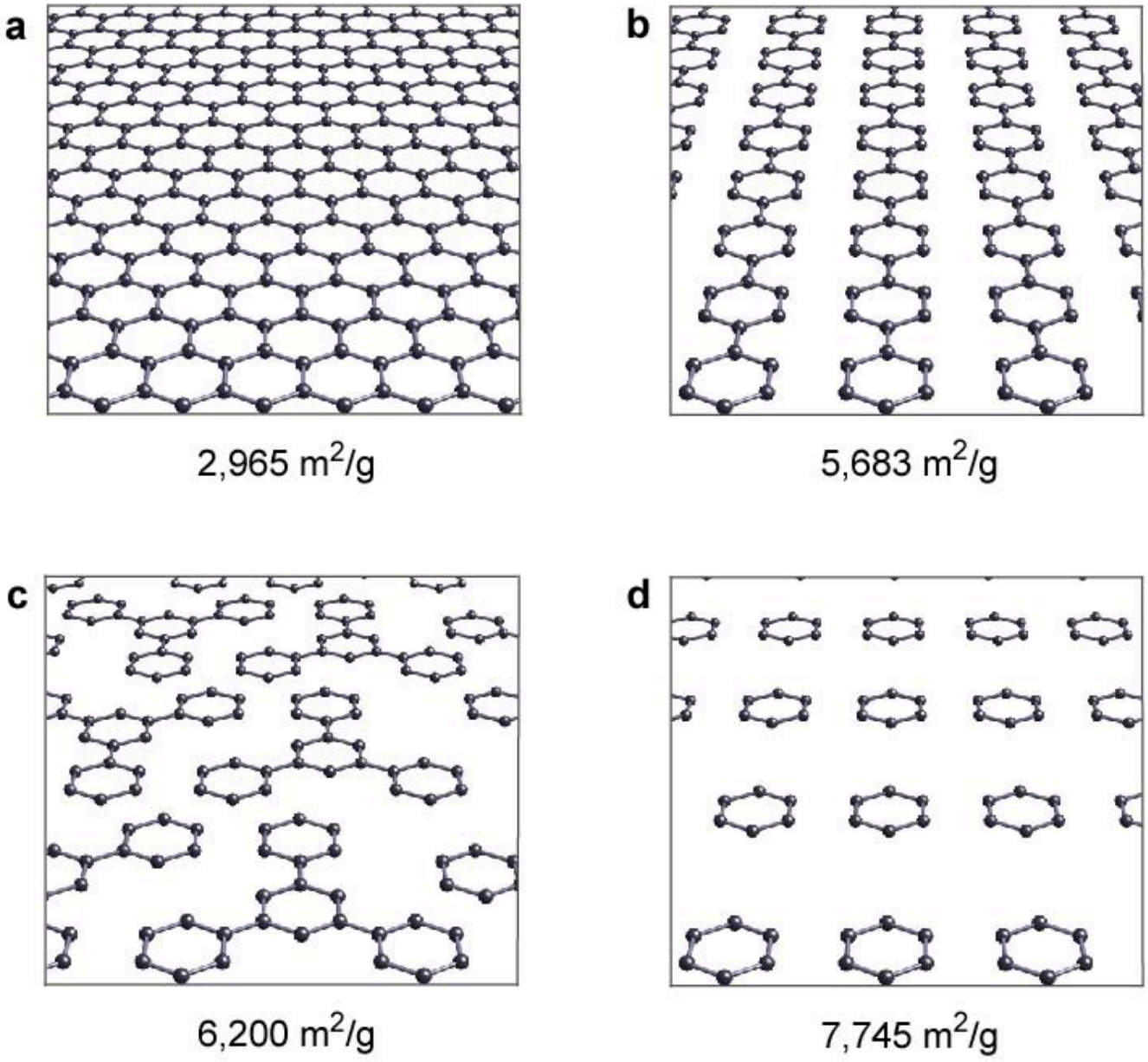
HKUST-1



MOF-74

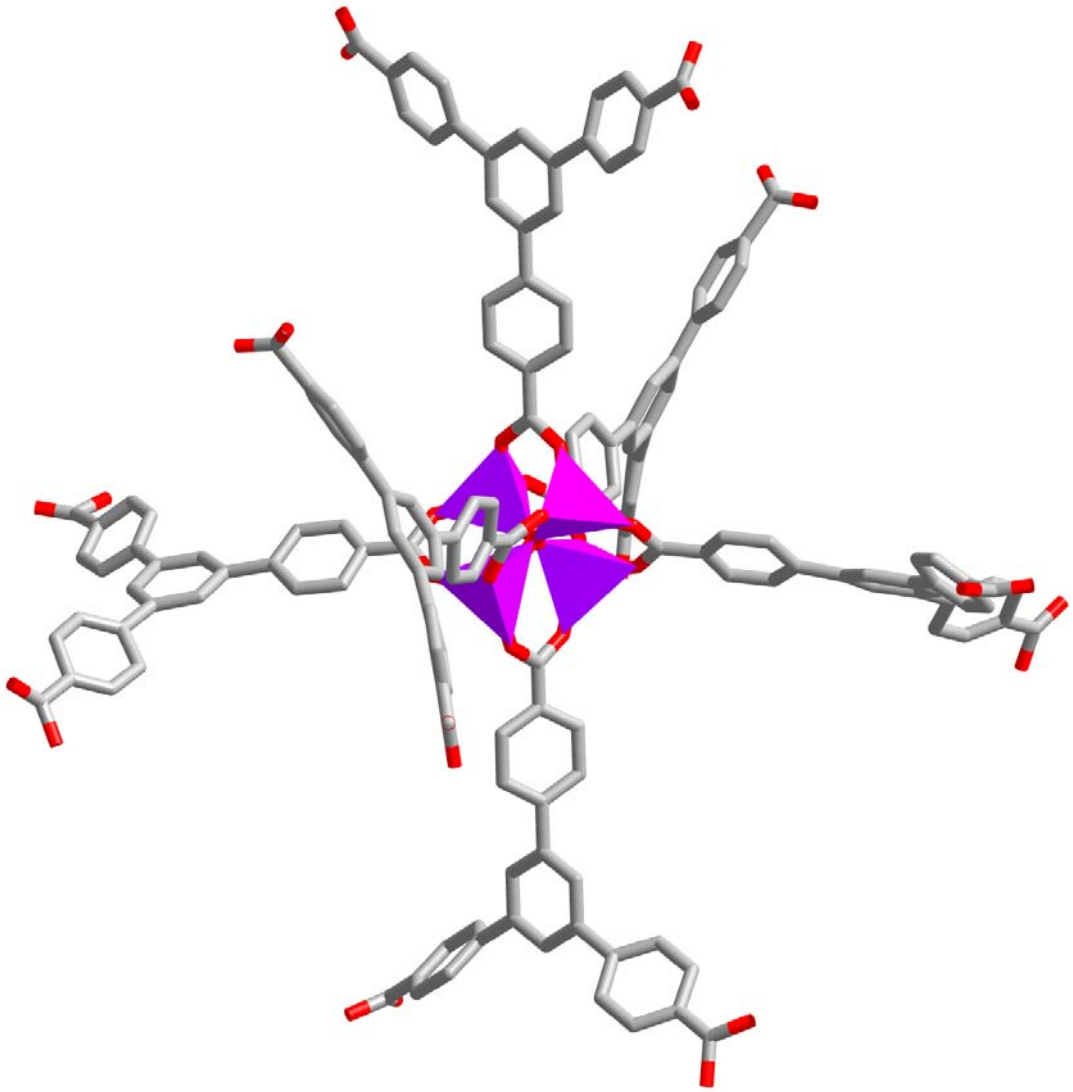
MOF-5 is entirely composed of 6-membered (polarized) rings

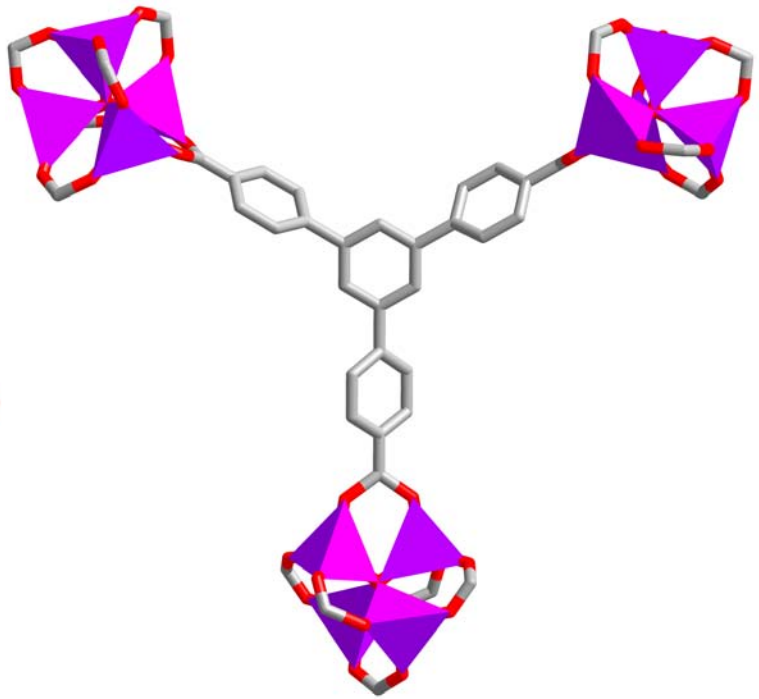




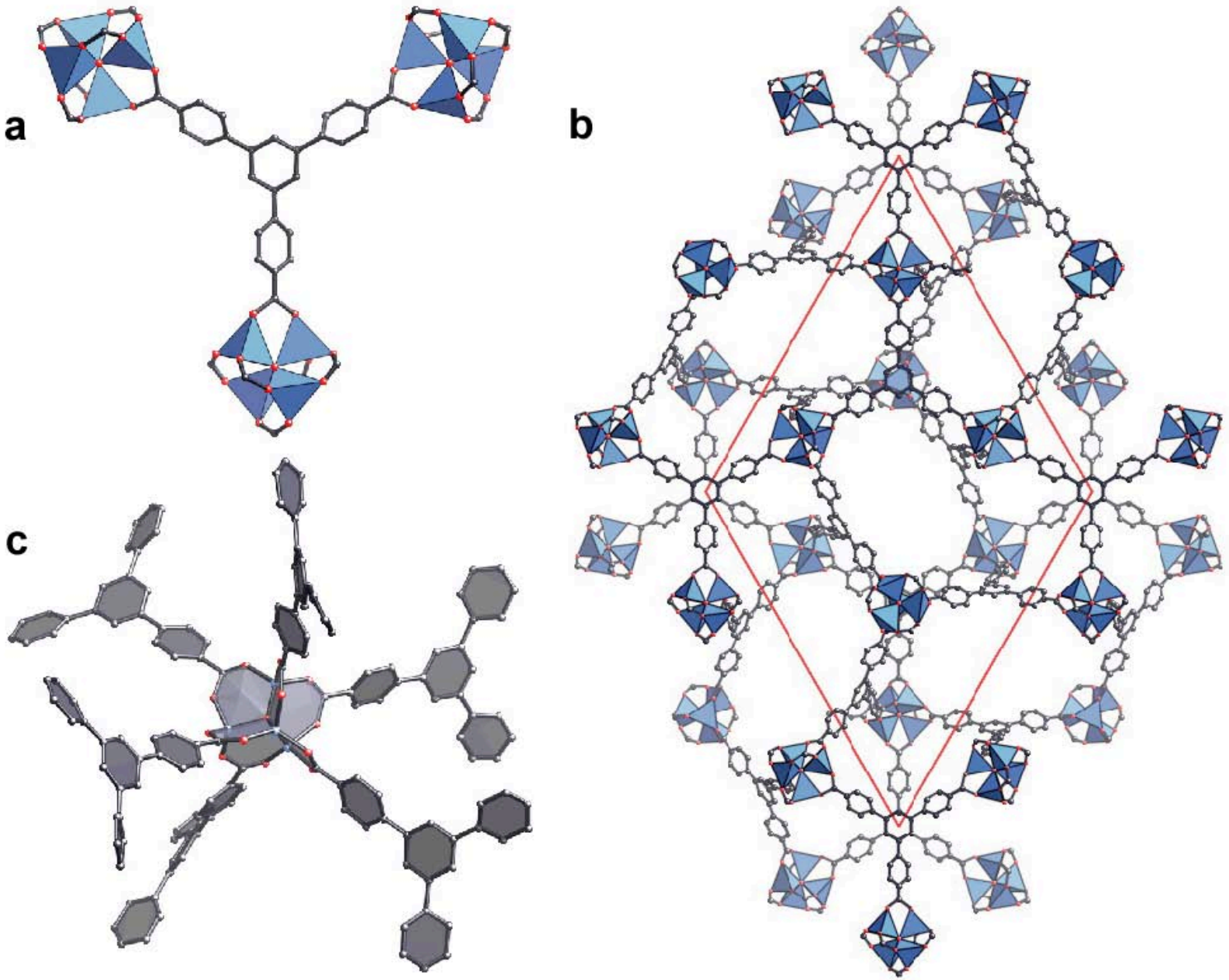
Calculated surface areas

$Zn_4O(BTB)_2 \bullet (DEF)_{15}$

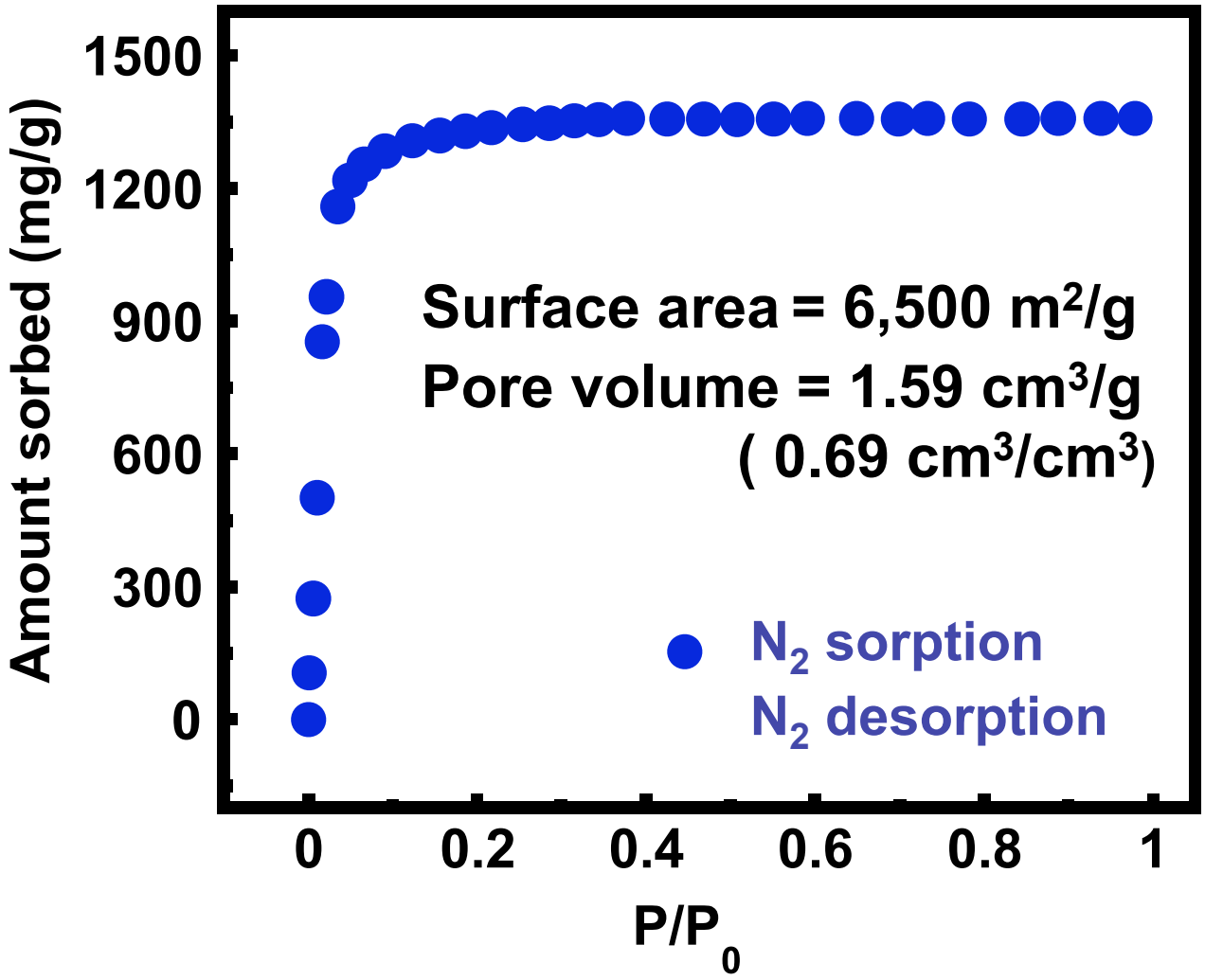




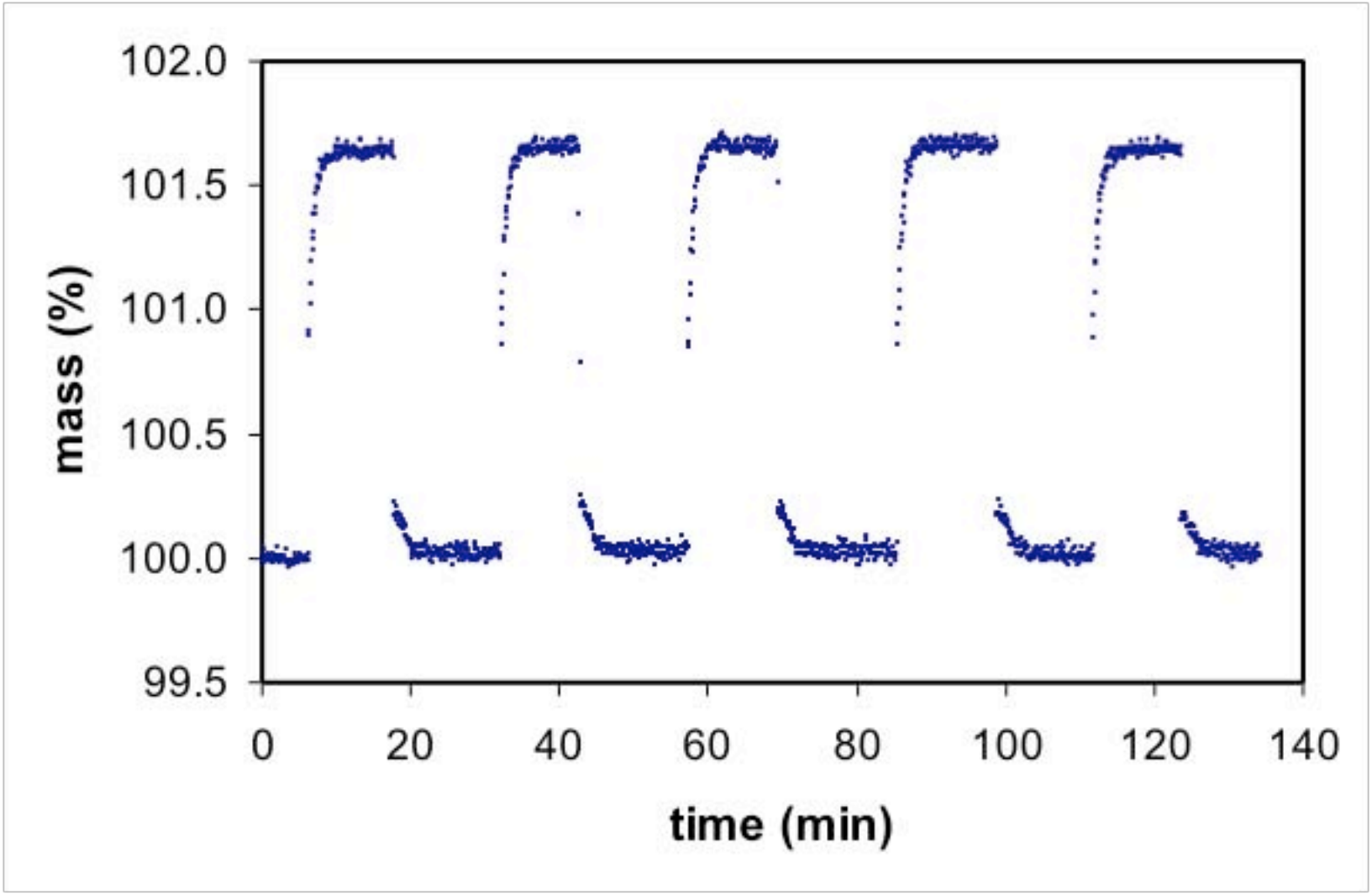
Nature 2004


a
b
c

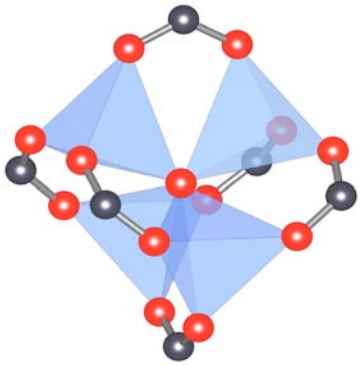
N_2 adsorption isotherm for $Zn_4O(BTB)_2$



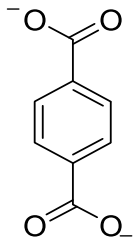
Reversibility of hydrogen sorption in IRMOF-11



a)



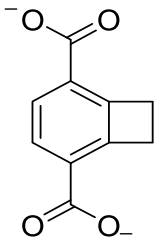
$Zn_4O(CO_2)_6$



BDC

IRMOF-1

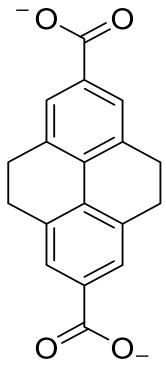
4,170



CBBDC

IRMOF-6

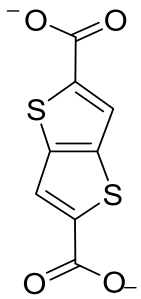
3,300



HPDC

IRMOF-11

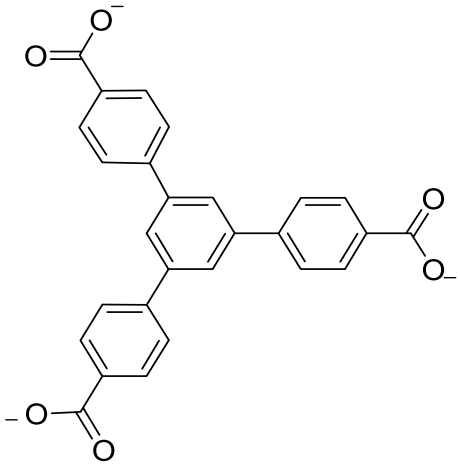
2,340



TTDC

IRMOF-20

4,590

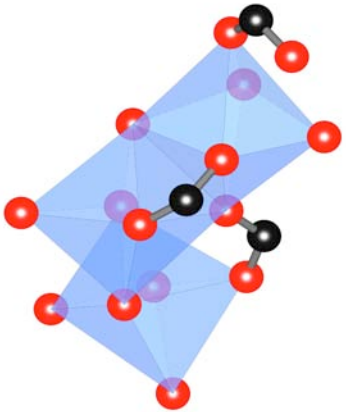


BTB

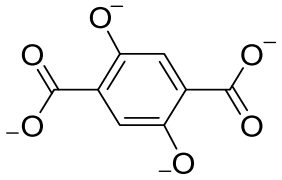
MOF-177

5,640

b)



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

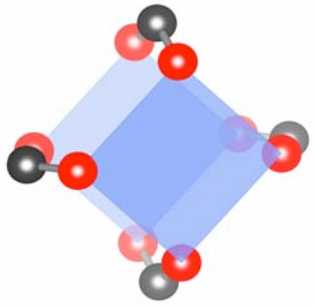


DHBDC

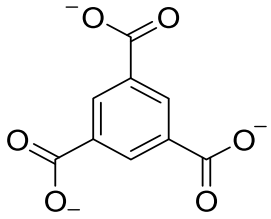
MOF-74

1,070

c)



$Cu_2(CO_2)_4$



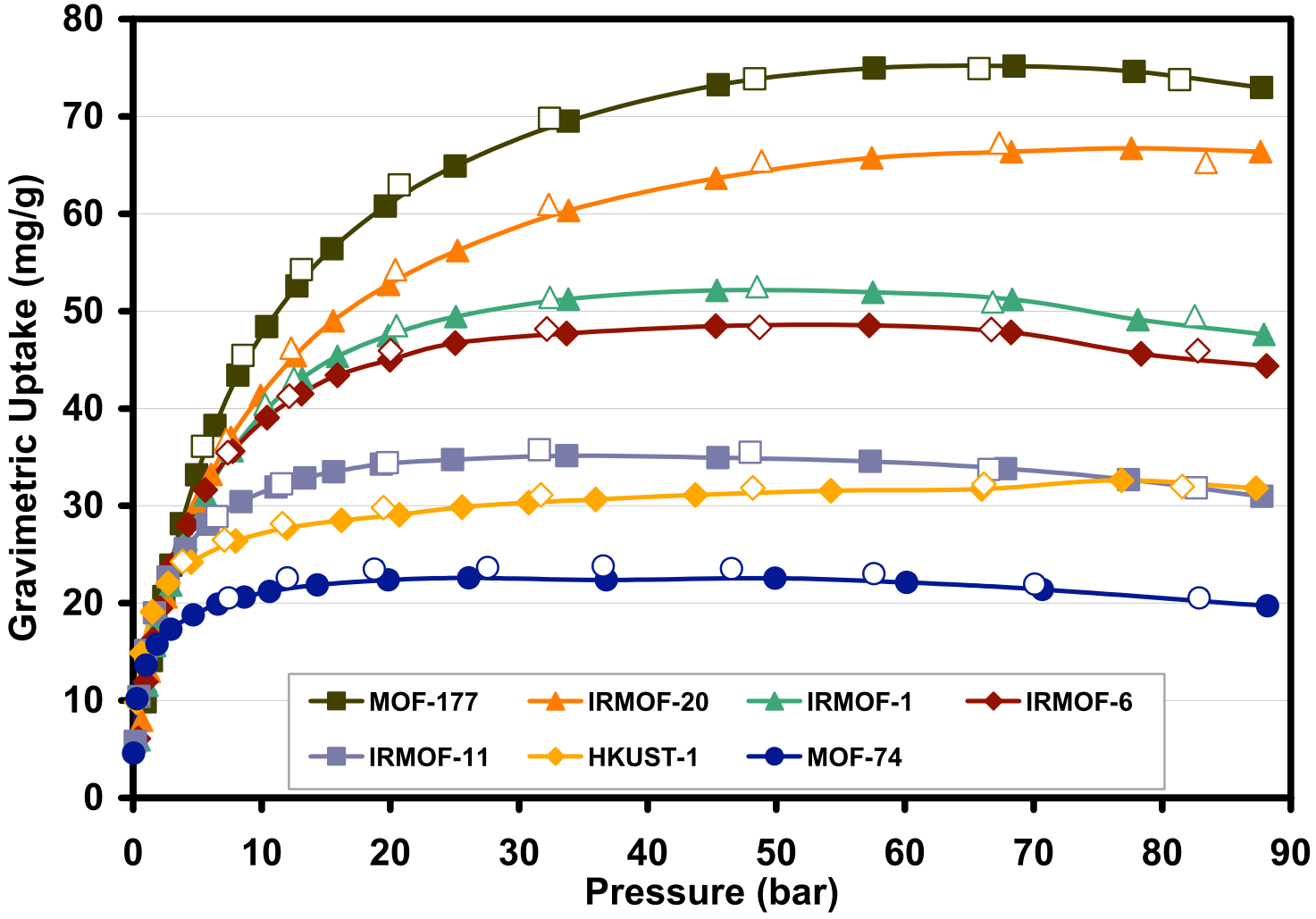
BTC

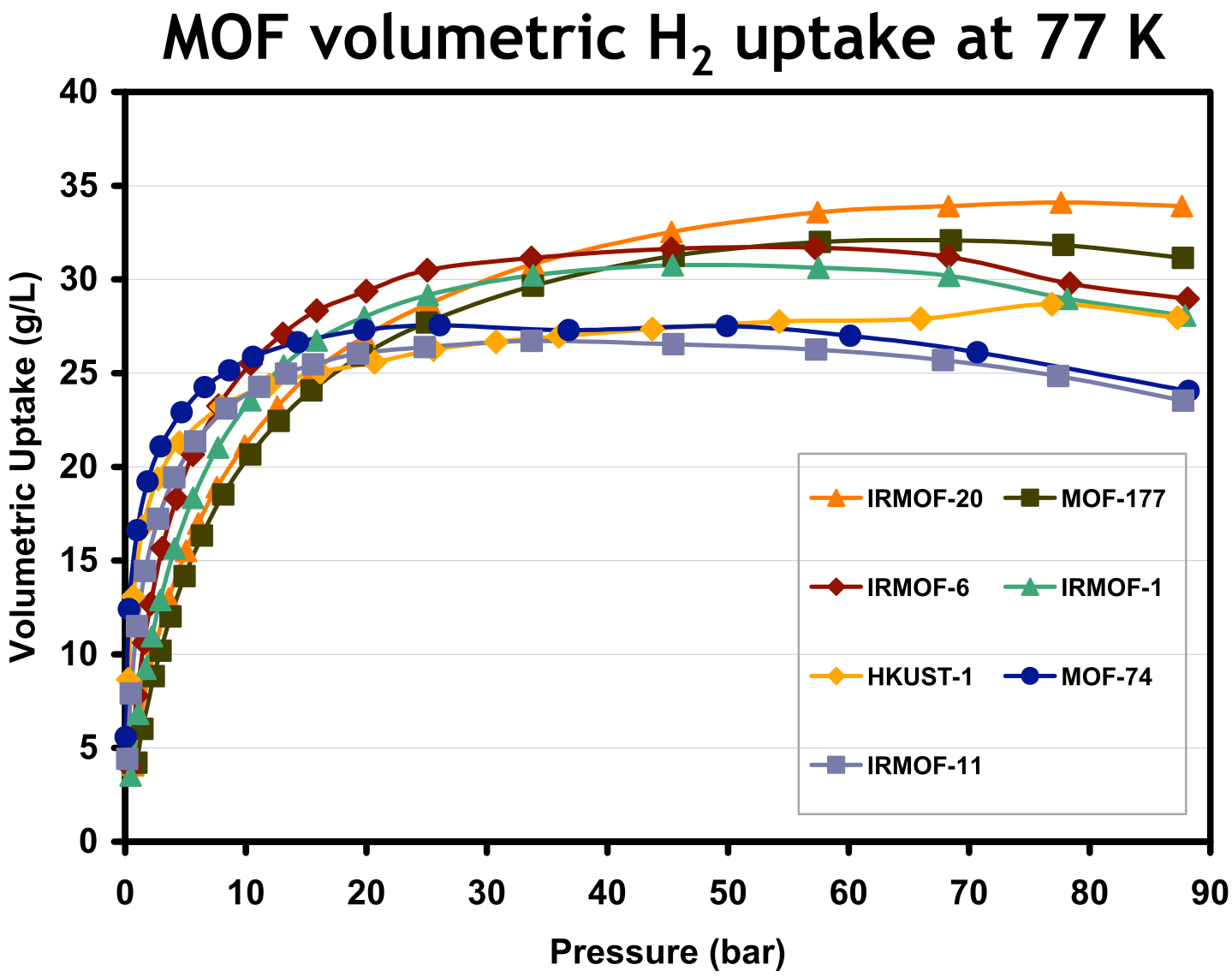
HKUST-1

2,260

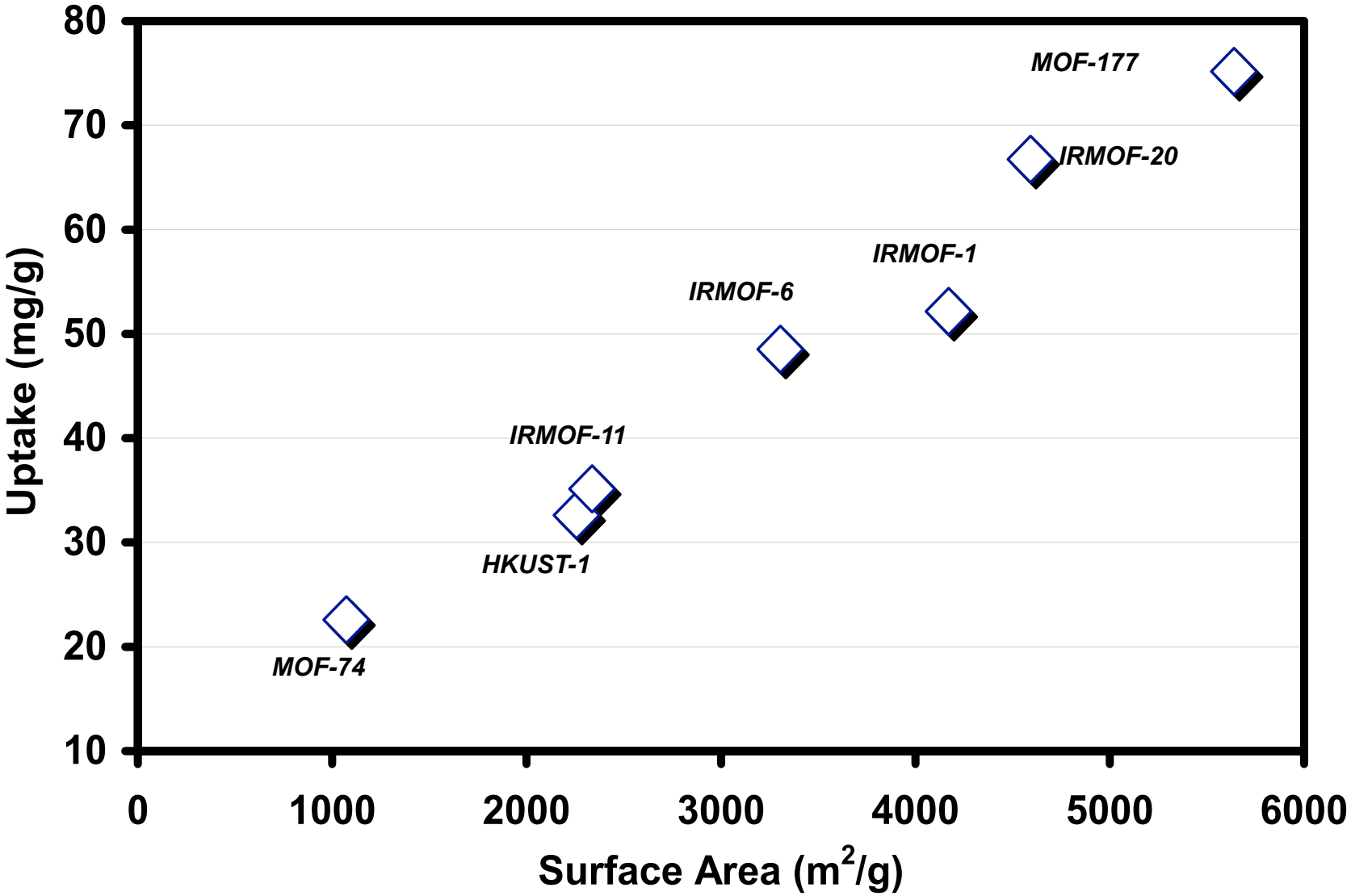
7.5 wt % Hydrogen uptake at 77K

(30 % more Hydrogen in a tank filled with MOF)

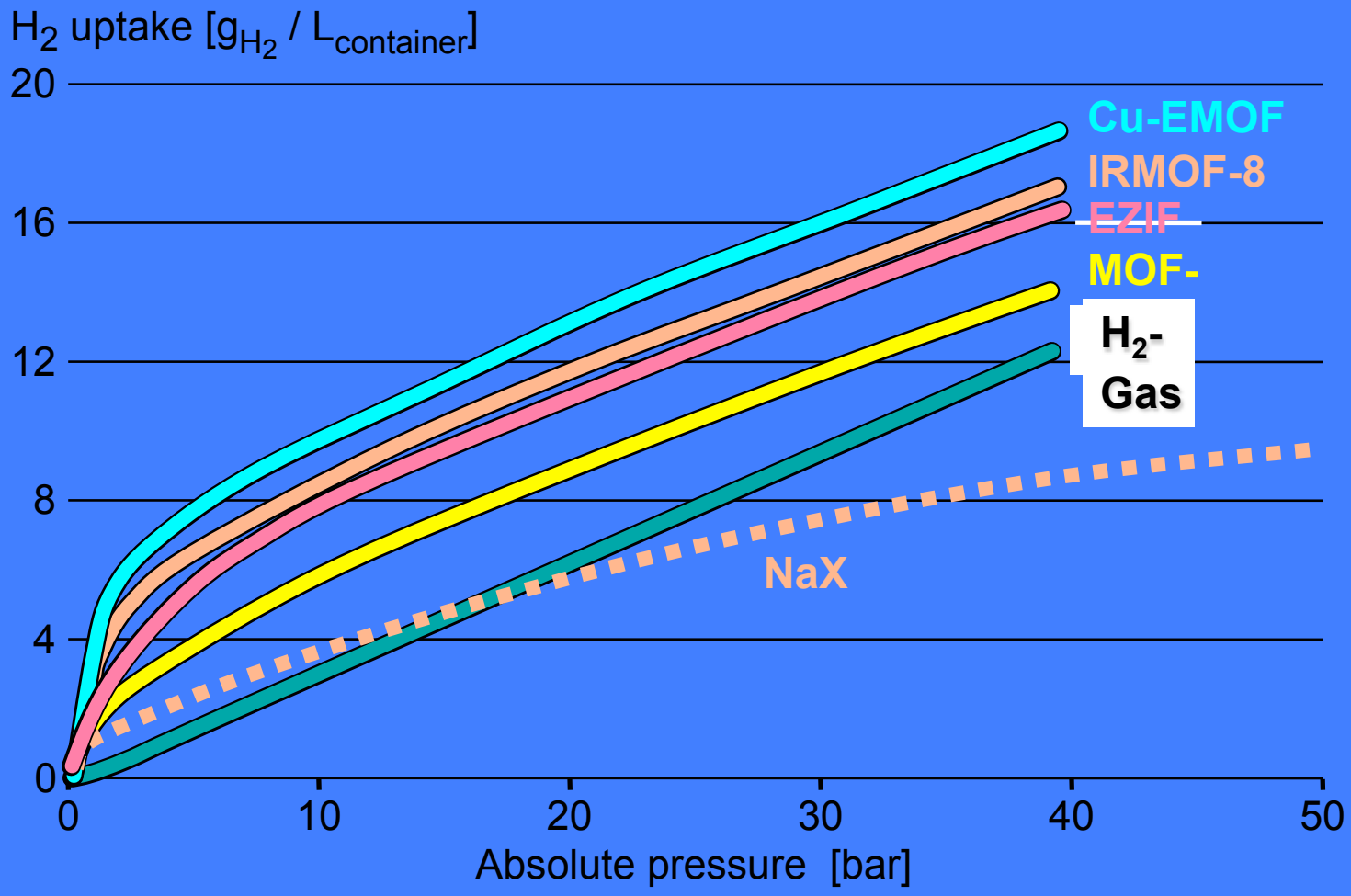



MOF volumetric H2 uptake at 77 K
Volumetric Uptake (g/L)
Pressure (bar)
0
5
10
15
20
25
30
35
40
0
10
20
30
40
50
60
70
80
90
IRMOF-20
MOF-177
IRMOF-6
IRMOF-1
HKUST-1
MOF-74
IRMOF-11

Correlation of uptake with surface area

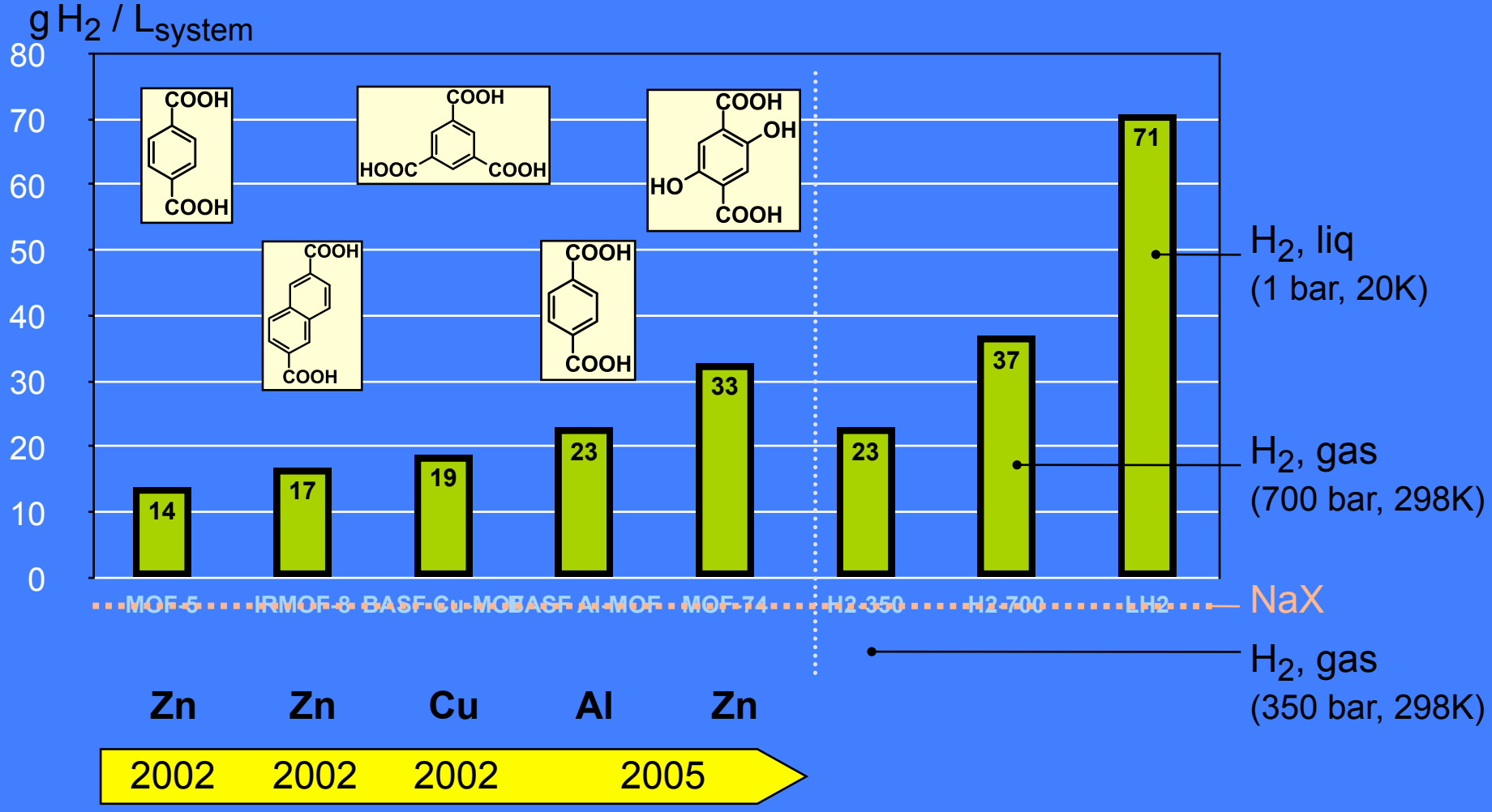


H_2-Prototype Results
Measurements: T = 77 K



MOF

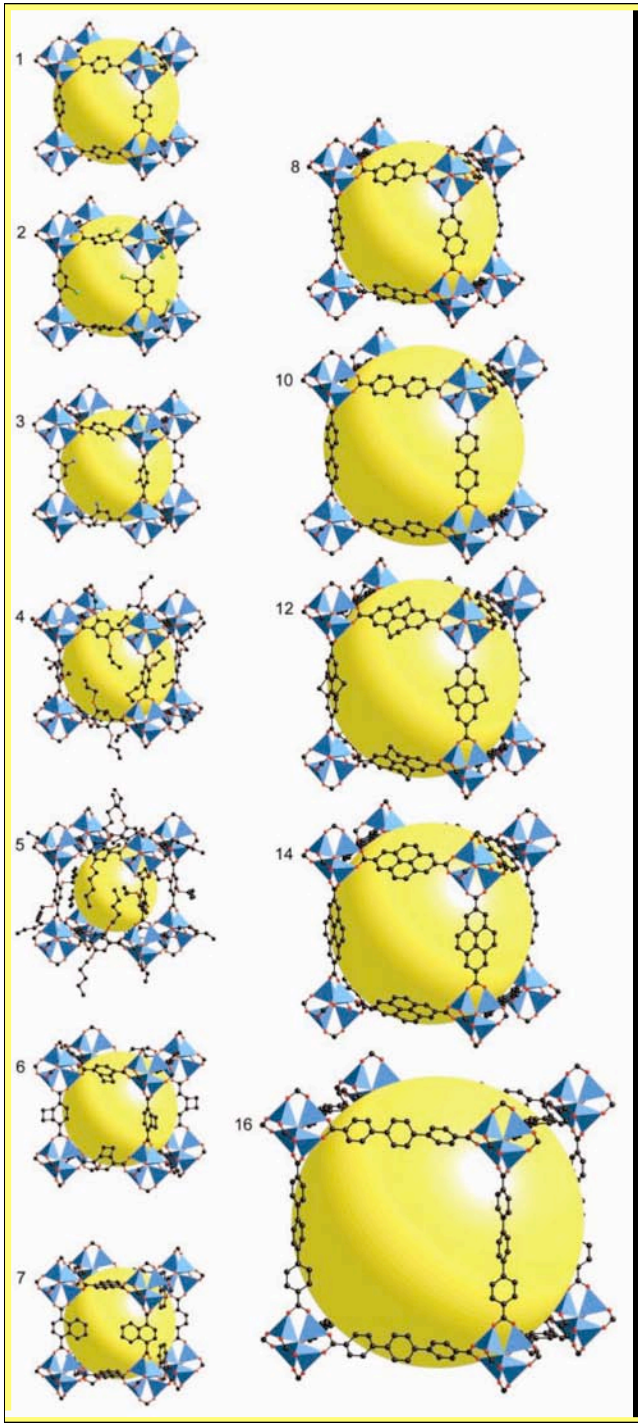
Hydrogen Storage Capacities (50 bar, 77K)



Advanced Synthesis

Scale up 250 kg MOF-5/batch – Semi-technical

J. Mater. Chem., 2006, 16, 626 – 636.



Metal-Organic Frameworks (MOFs)

1. Their structure, composition and function are achieved by design
2. Their synthesis is simple and scalable using inexpensive starting materials
3. A conceptual framework and a system of taxonomy and grammar now exists for their design
4. Over 2,200 MOFs have been reported: the fastest growing field in chemistry
5. The basic science of MOFs is now developed all the way to applications (catalysis, hydrogen and methane gas storage, highly selective sensors…)

Nothing in this world is good or bad, but thinking makes it so

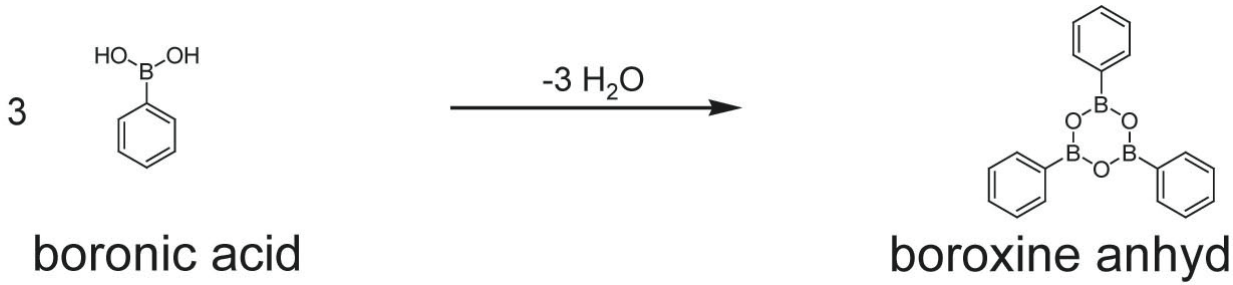
—William Shakespeare

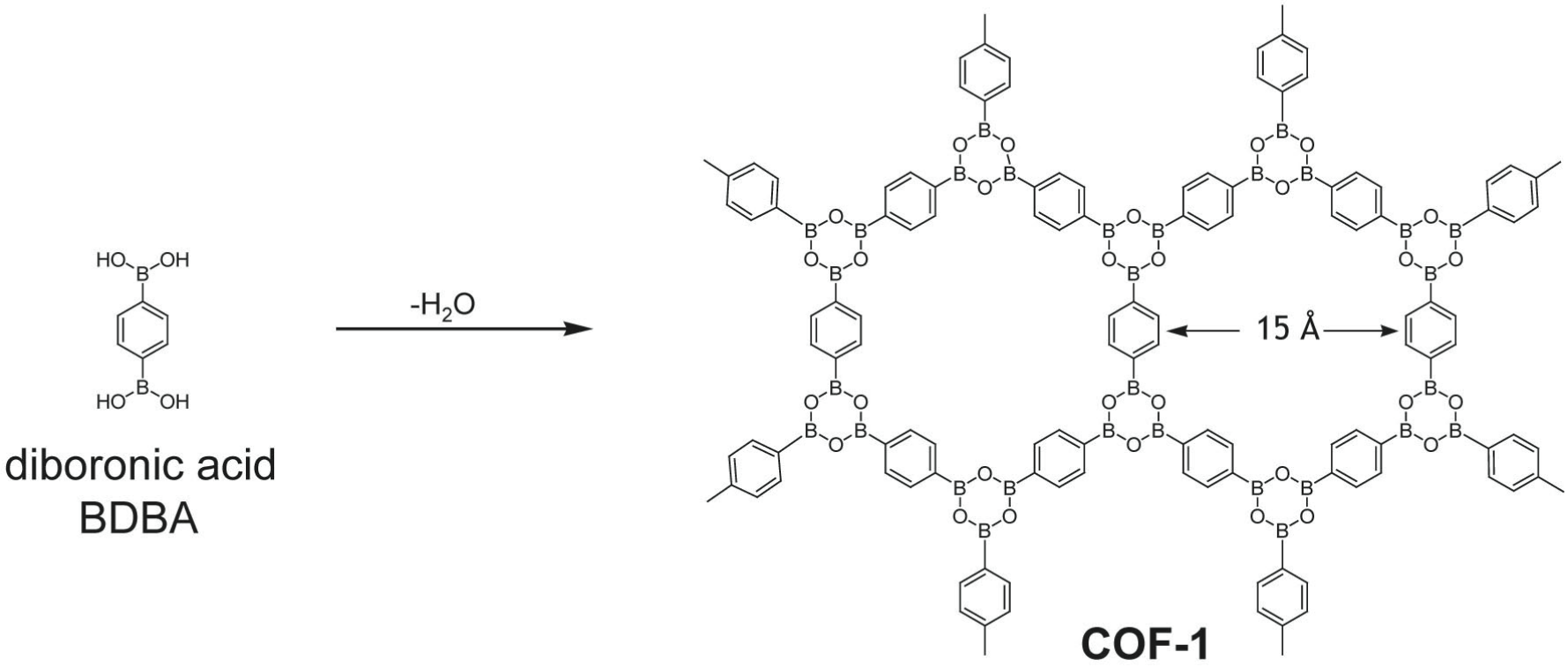
Conventional wisdom:

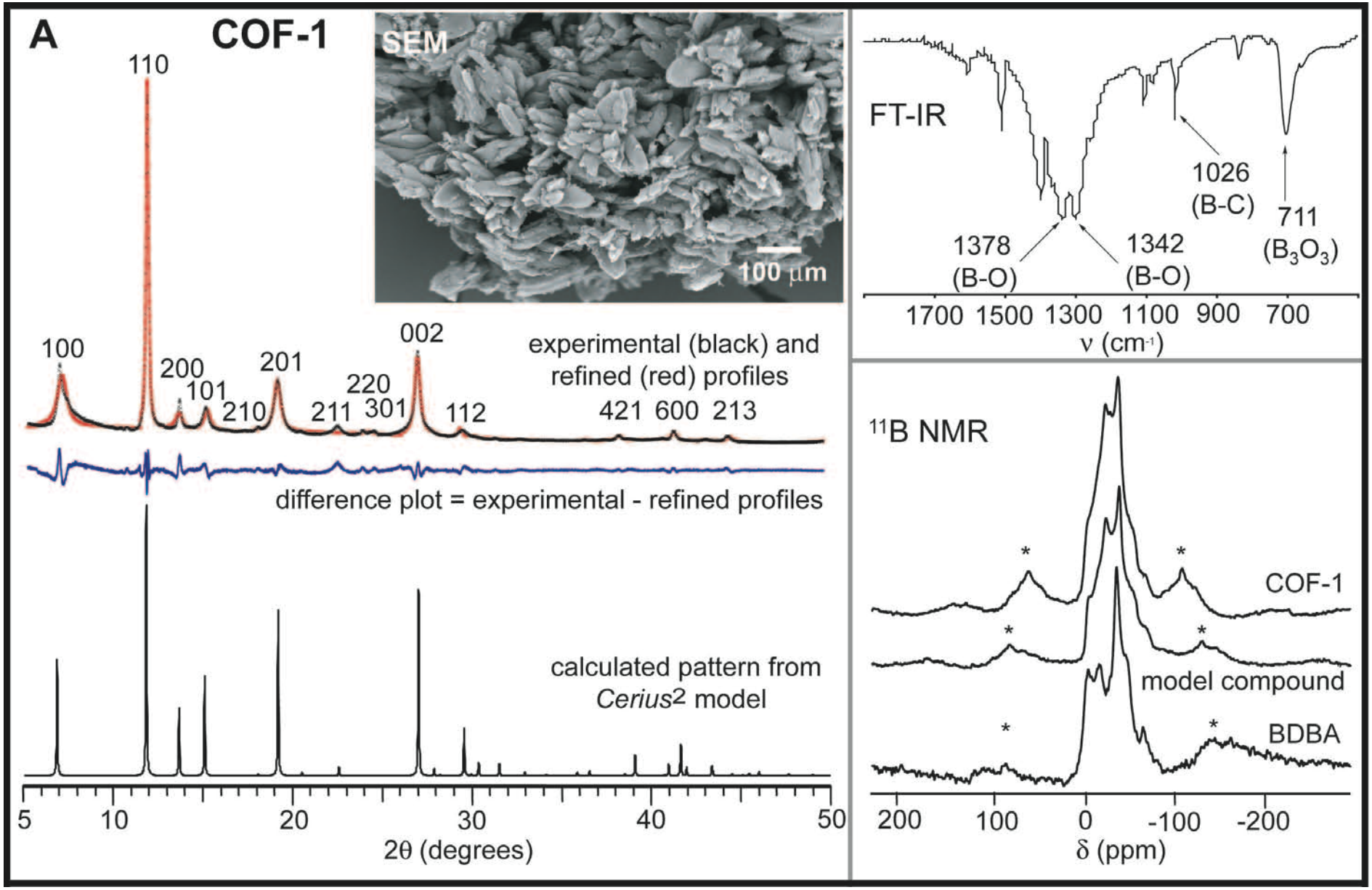
It is easy to obtain crystals of materials when the building blocks are linked by weak bonds; harder when linked by M-L bonds; and of course nearly impossible when linked by strong covalent bonds (C-C, C-O, C-N, B-C, B-O,…)

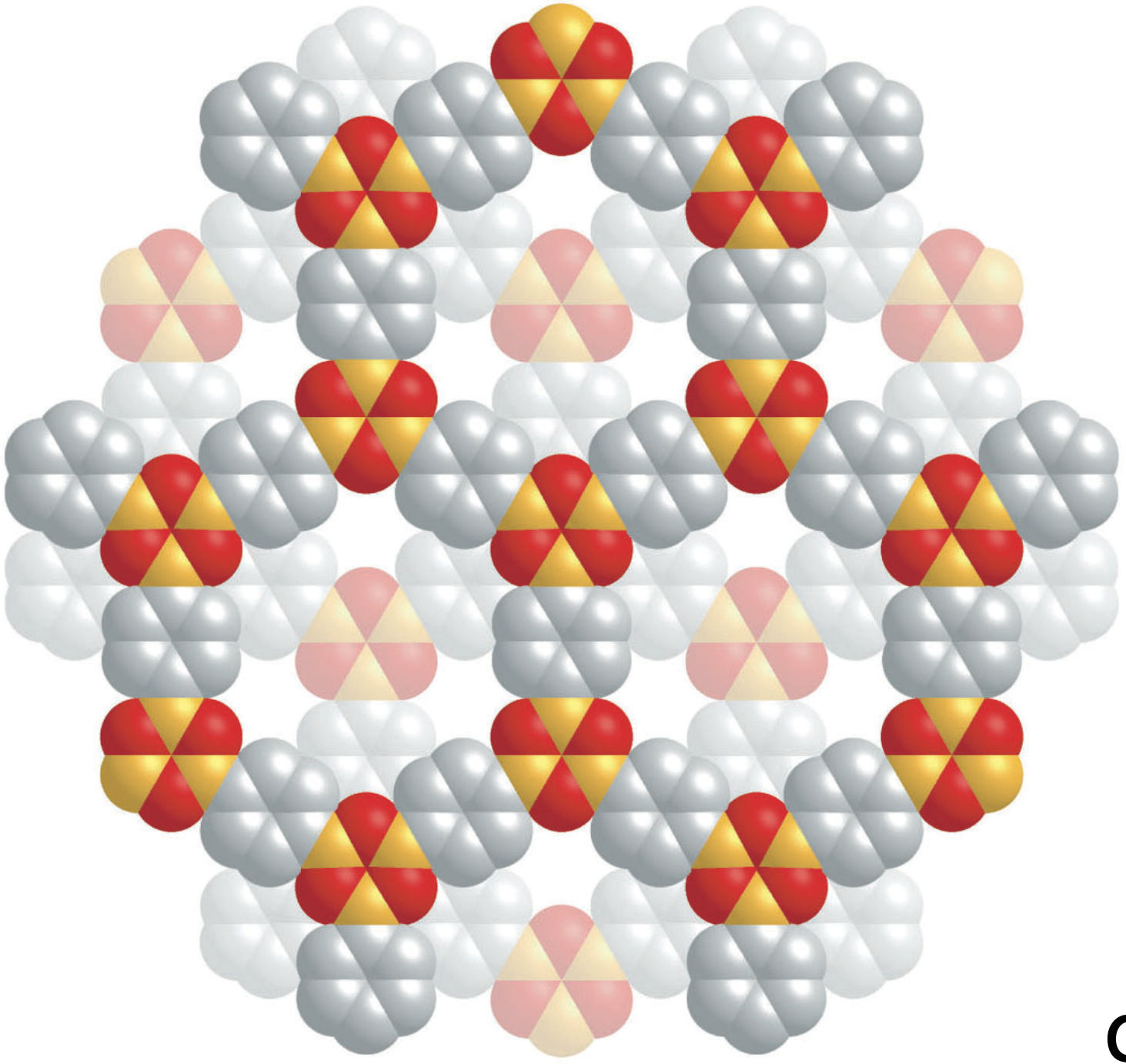
Dr. Adrien Côté

Covalent Organic Frameworks (COFs)

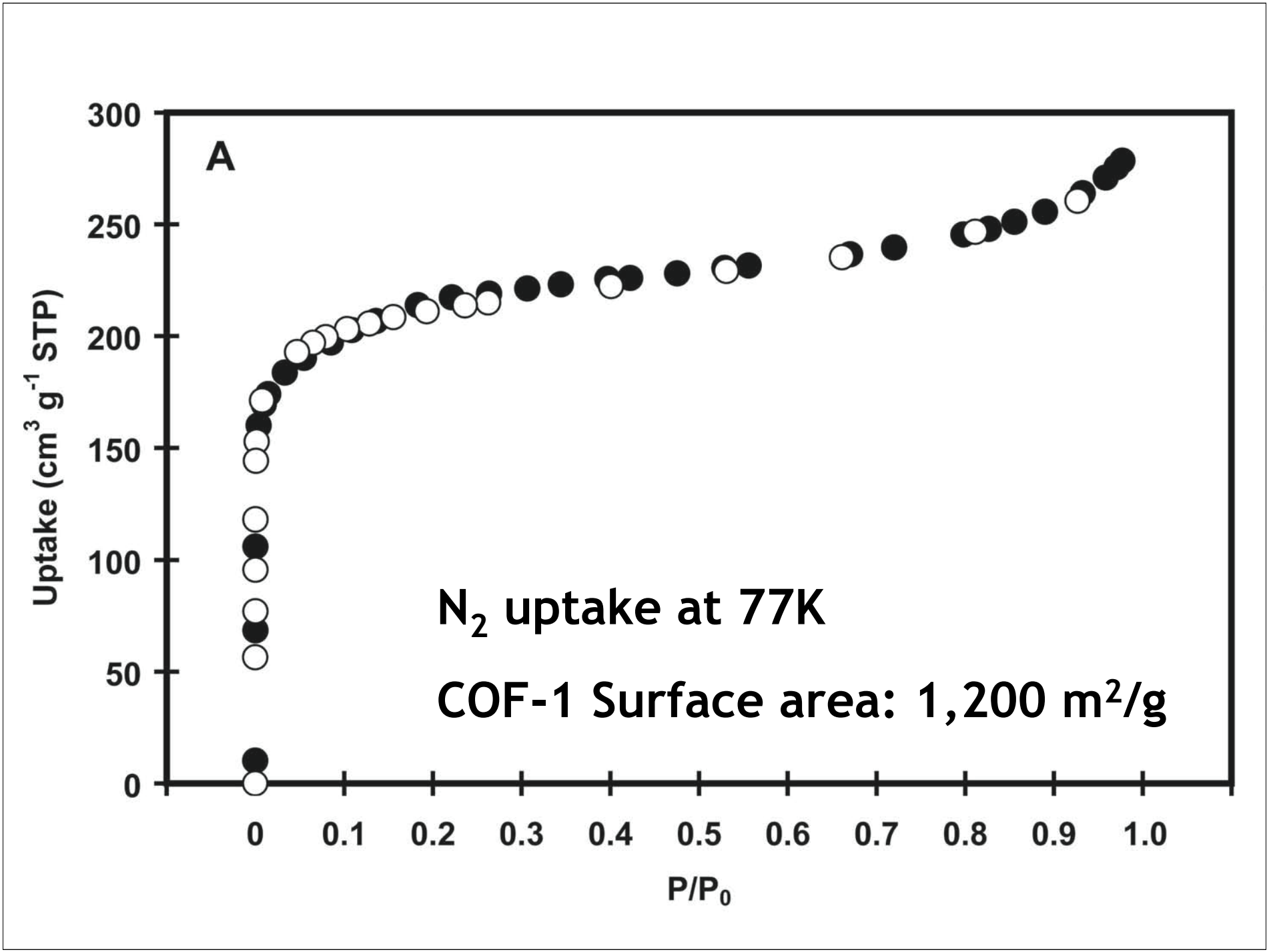


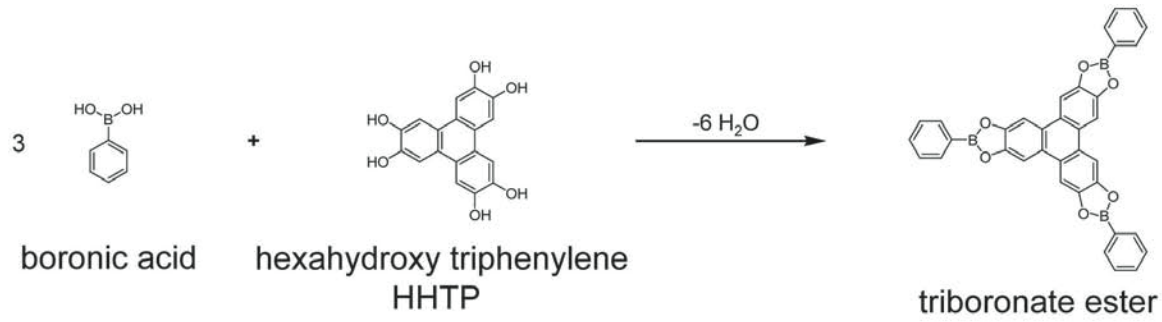


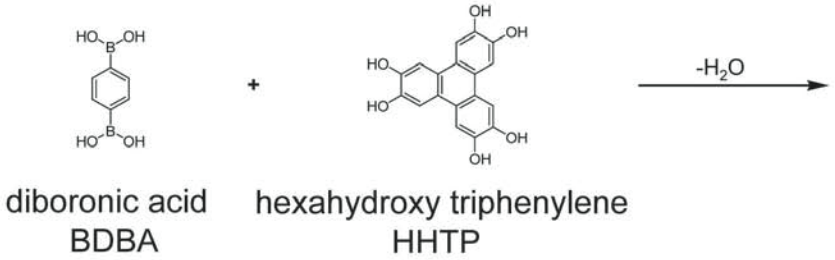

A
COF-1
SEM
100 μm
110
100
200
101
210
201
211
220
301
002
112
421 600 213
experimental (black) and
refined (red) profiles
difference plot = experimental - refined profiles
calculated pattern from
Cerius2 model
5
10
20
30
40
50
2θ (degrees)
FT-IR
1026
(B-C)
711
(B3O3)
1378
(B-O)
1342
(B-O)
1700 1500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

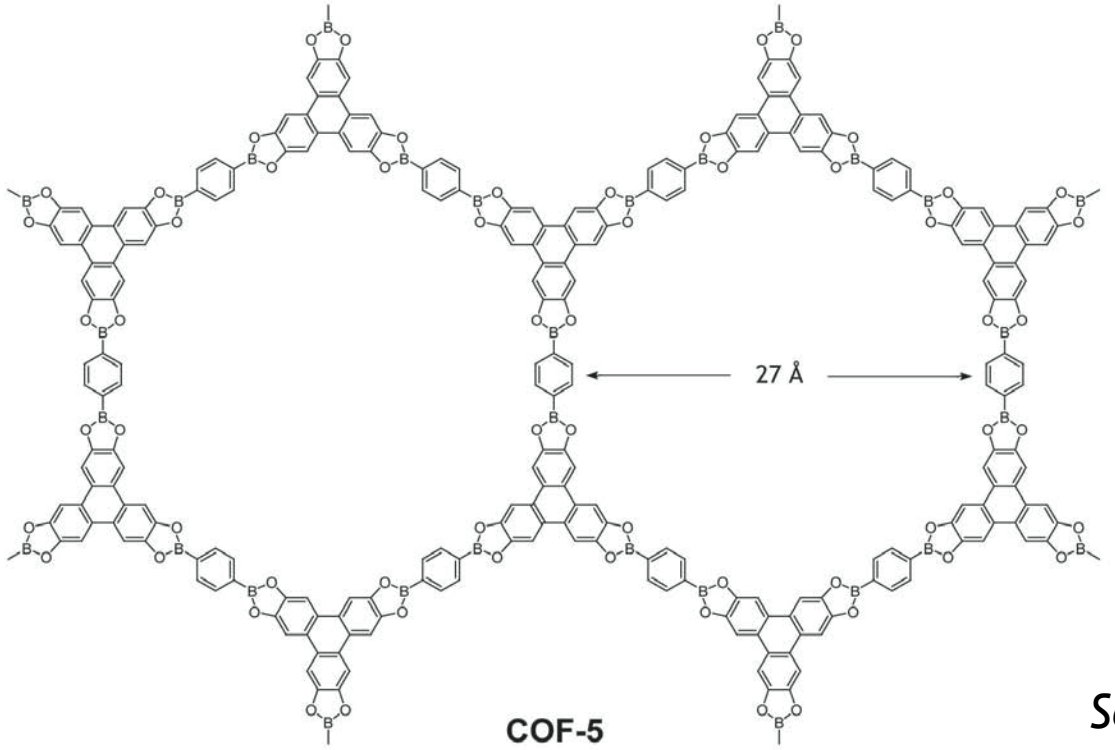


COF-1

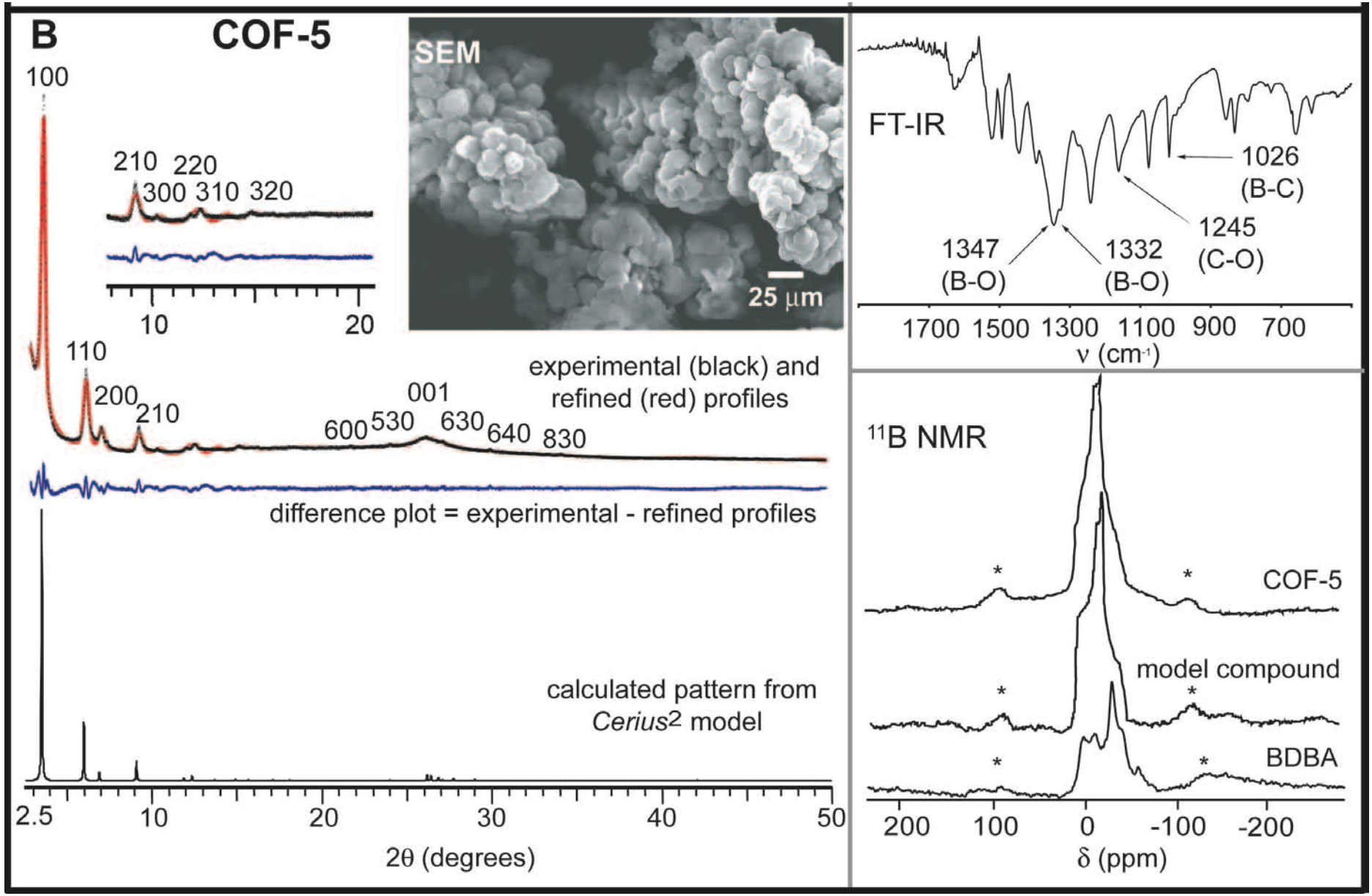

A
300
250
200
150
100
50
0
Uptake (cm3 g-1 STP)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
P/P0
N2 uptake at 77K
COF-1 Surface area: 1,200 m2/g

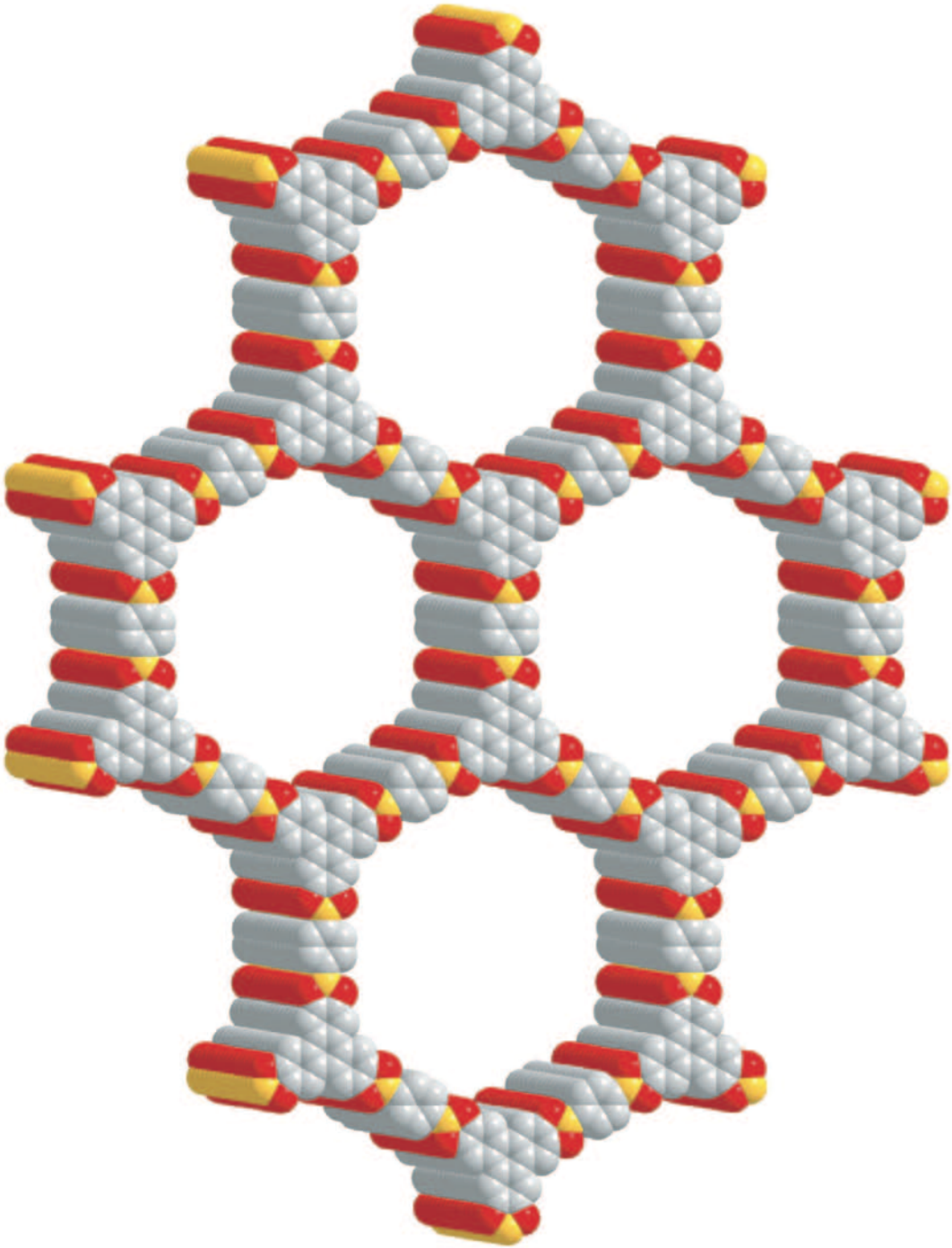




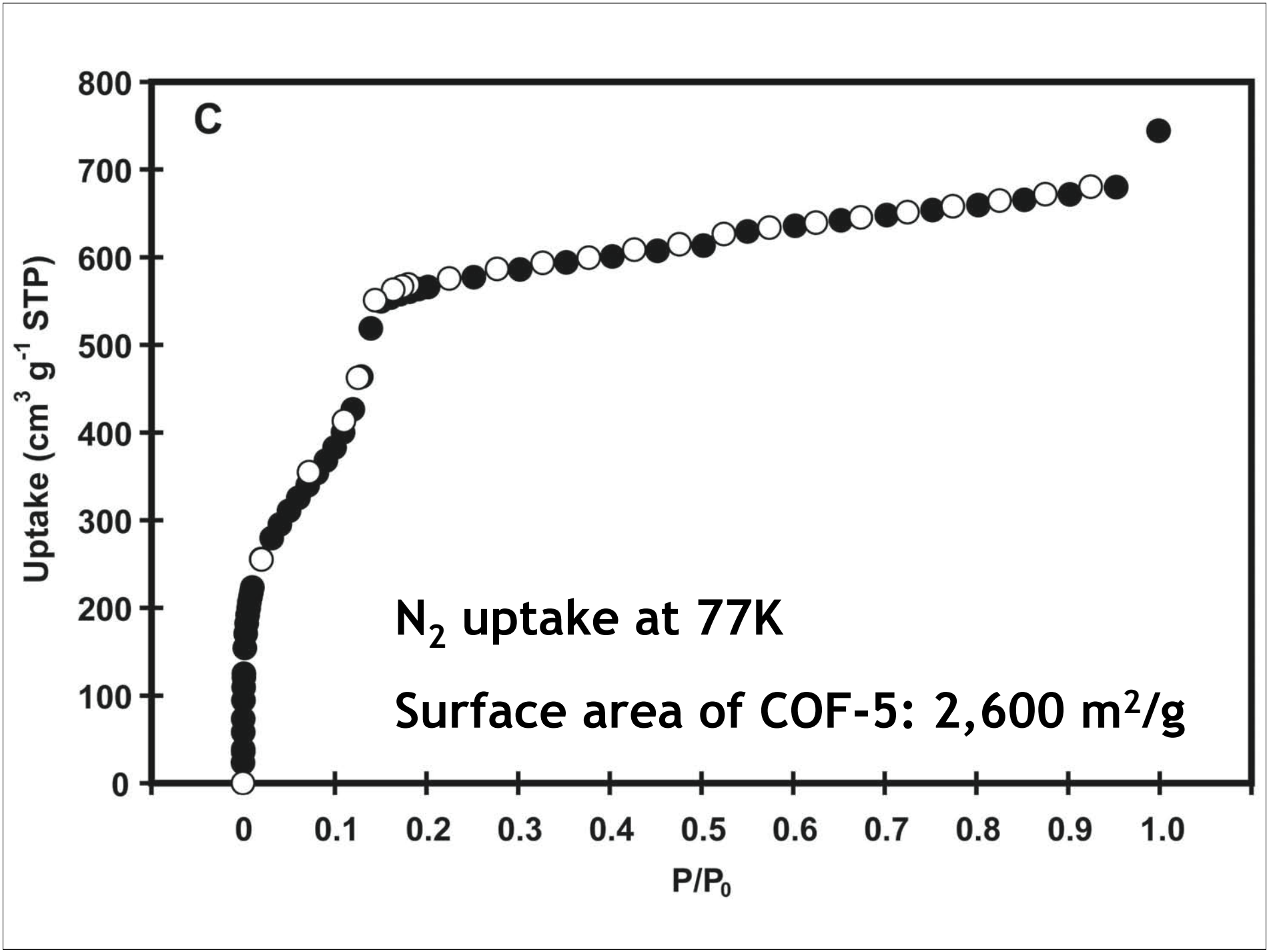


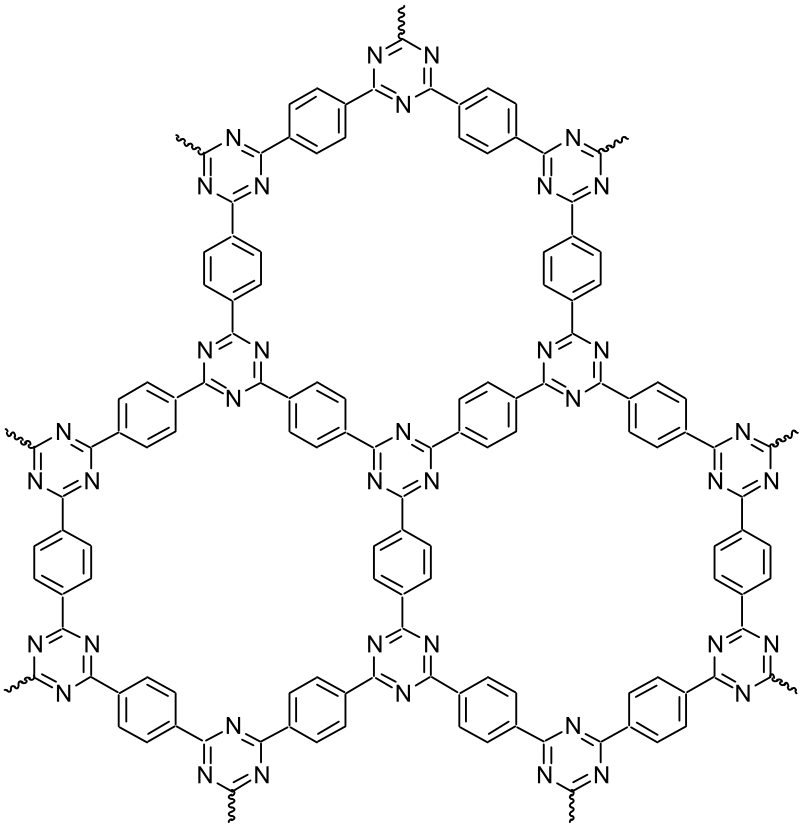
Science 2005

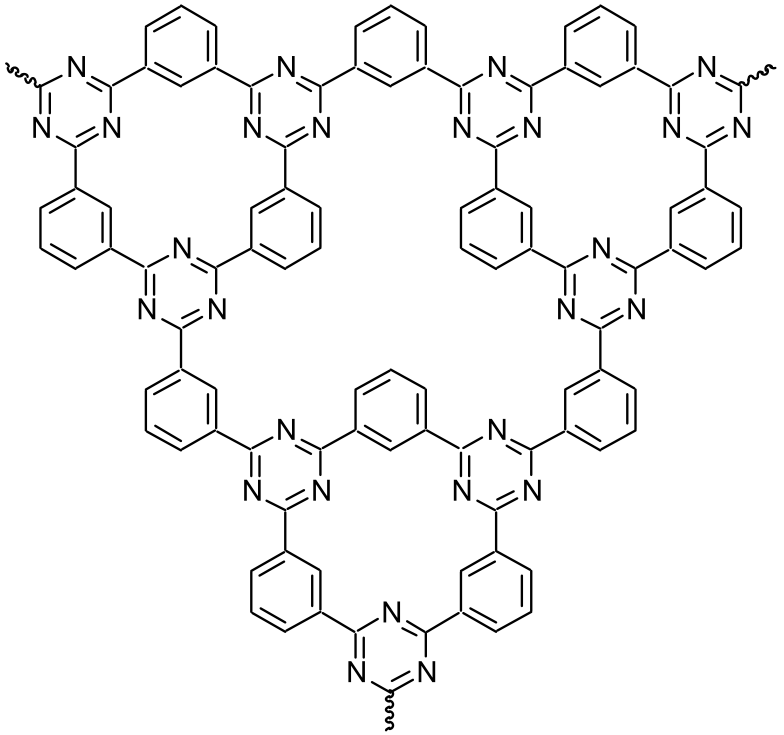

B
COF-5
100
210
220
300
310
320
10
20
110
200
210
600
530
001
630
640
830
experimental (black) and
refined (red) profiles
difference plot = experimental - refined profiles
calculated pattern from
Cerius2 model
2.5
10
20
30
40
50
2θ (degrees)
SEM
25 μm
FT-IR
1026
(B-C)
1245
(C-O)
1347
(B-O)
1332
(B-O)
1700 1500 1300 1100 900 700
ν (cm-1)
11B NMR
COF-5
model compound
BDBA
200
100
0
-100
-200
δ (ppm)

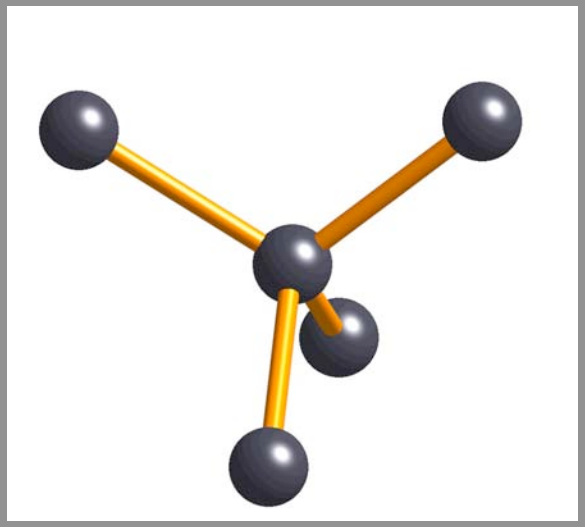


COF-5


C
800
700
600
500
400
300
200
100
0
Uptake (cm3 g-1 STP)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
P/P0
N2 uptake at 77K
Surface area of COF-5: 2,600 m2/g



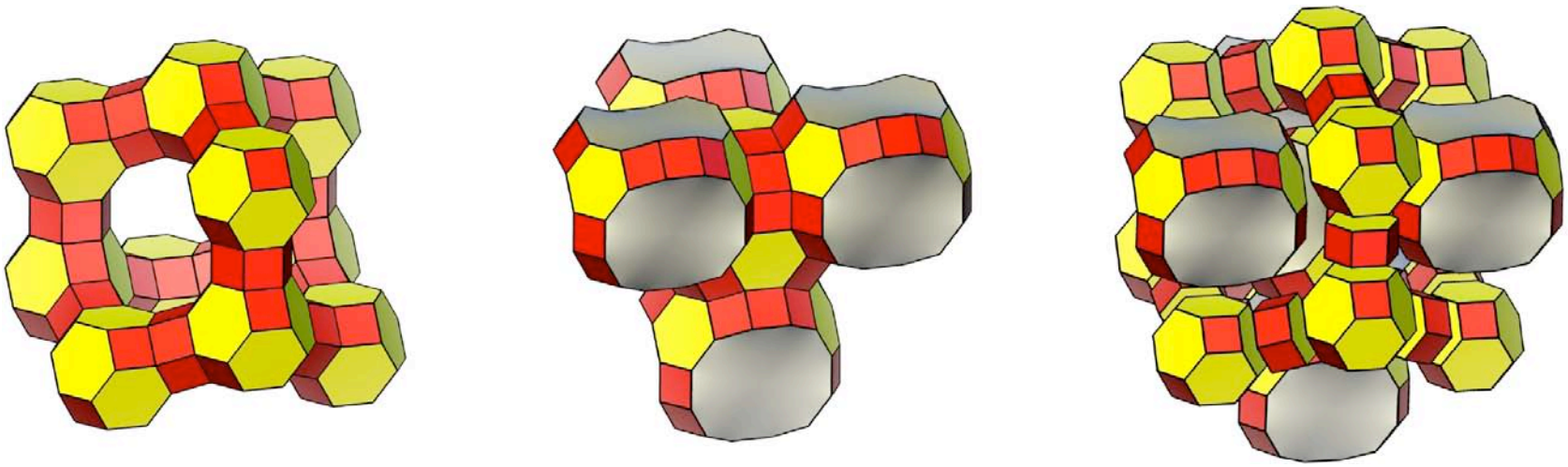




Why 4-coordinated tetrahedral nets?

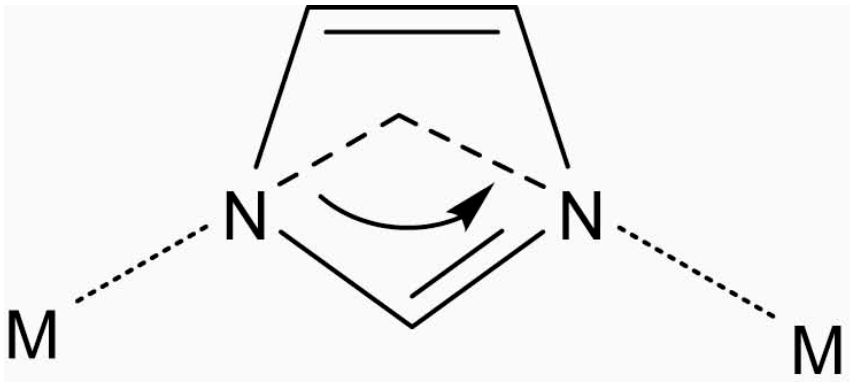
1. **Most important materials on earth: ice and feldspar**
2. **Zeolites: a global economy of US$ 350 G**

Faujasite **fau**



Tetrahedral nets of aluminosilicates

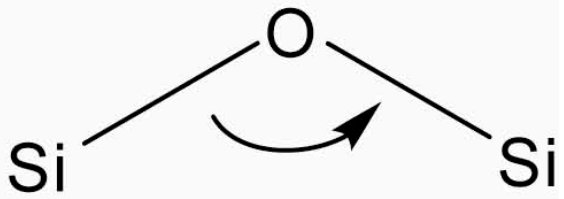
It’s all in the angle (145°)



M - IM - M

1

145°

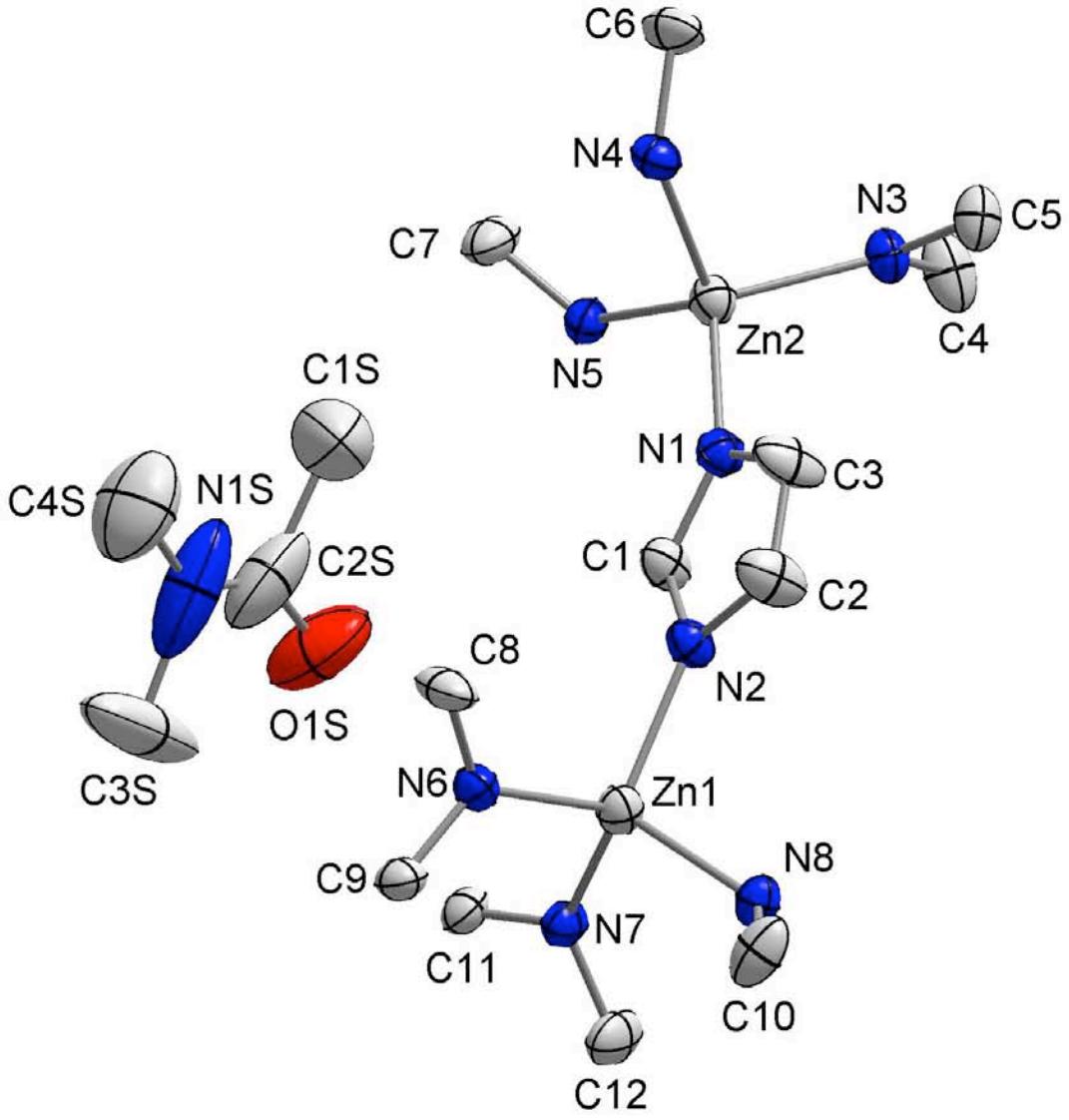


Si - O - Si

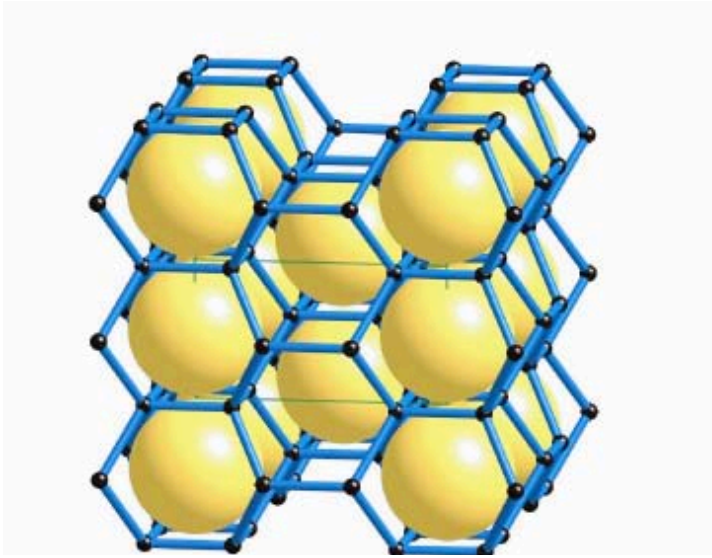
2

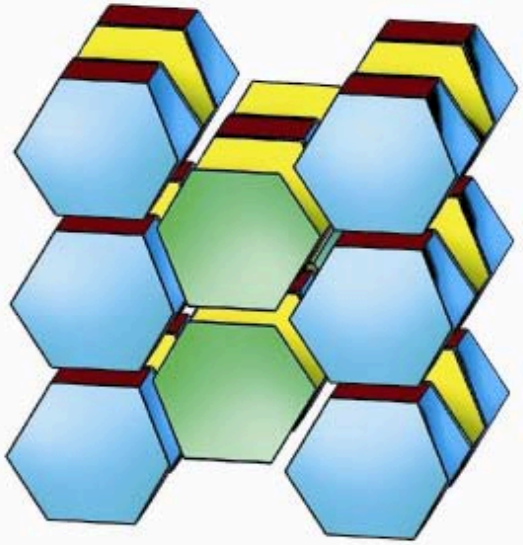
145°

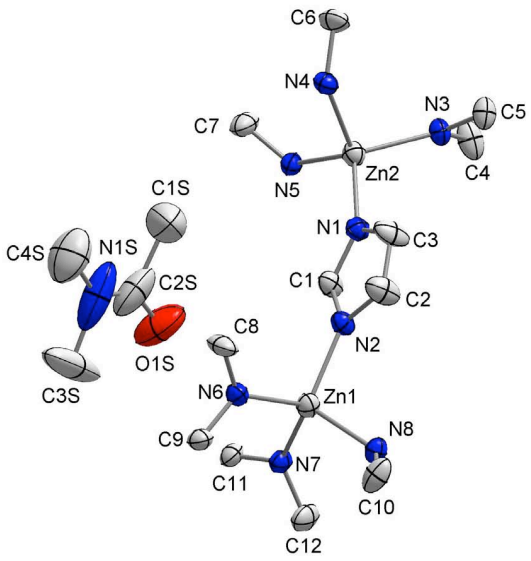
Kyosung Park

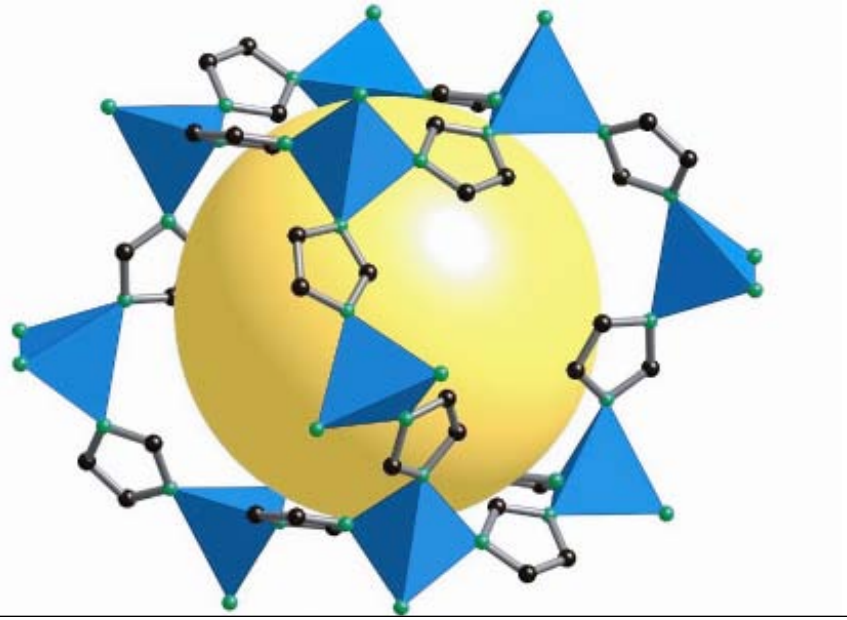

C6
N4
N3
C5
C7
N5
Zn2
C4
C1S
N1
C3
C4S
N1S
C1
C2S
C2
C8
N2
O1S
C3S
N6
Zn1
N8
C9
N7
C11
C10
C12

ZIF-2 crb

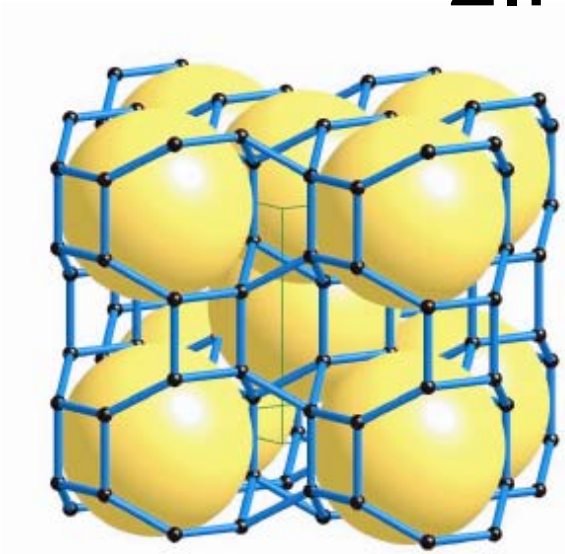


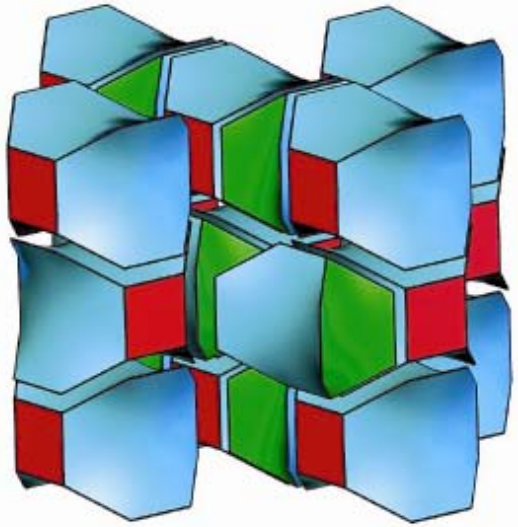


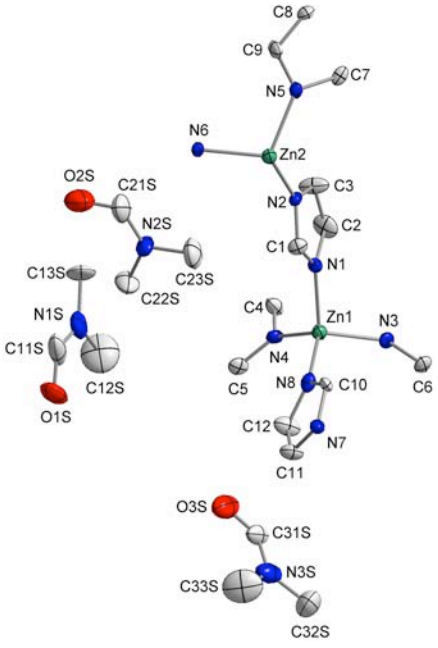

C6
N4
N3
C5
C7
Zn2
C4
N5
C1S
N1
C3
C4S
N1S
C2S
C1
C2
C8
N2
O1S
C3S
N6
Zn1
N8
C9
N7
C11
C10
C12

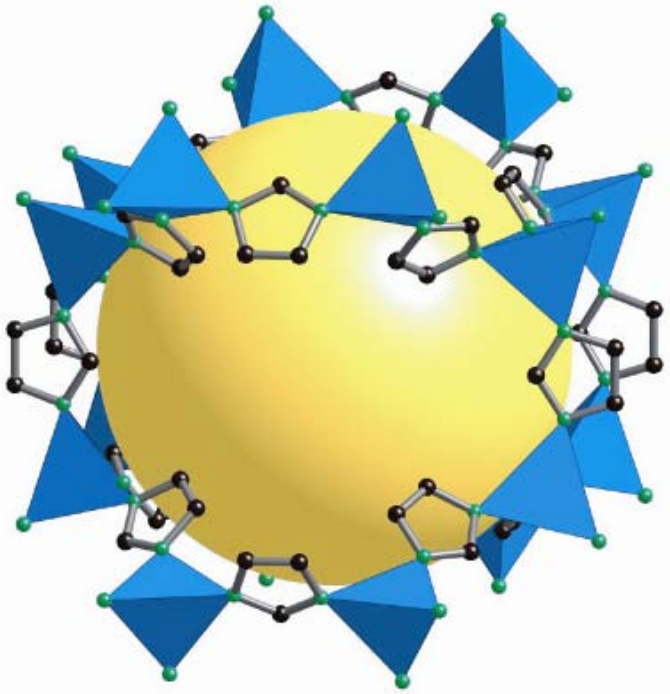


ZIF-3 dft

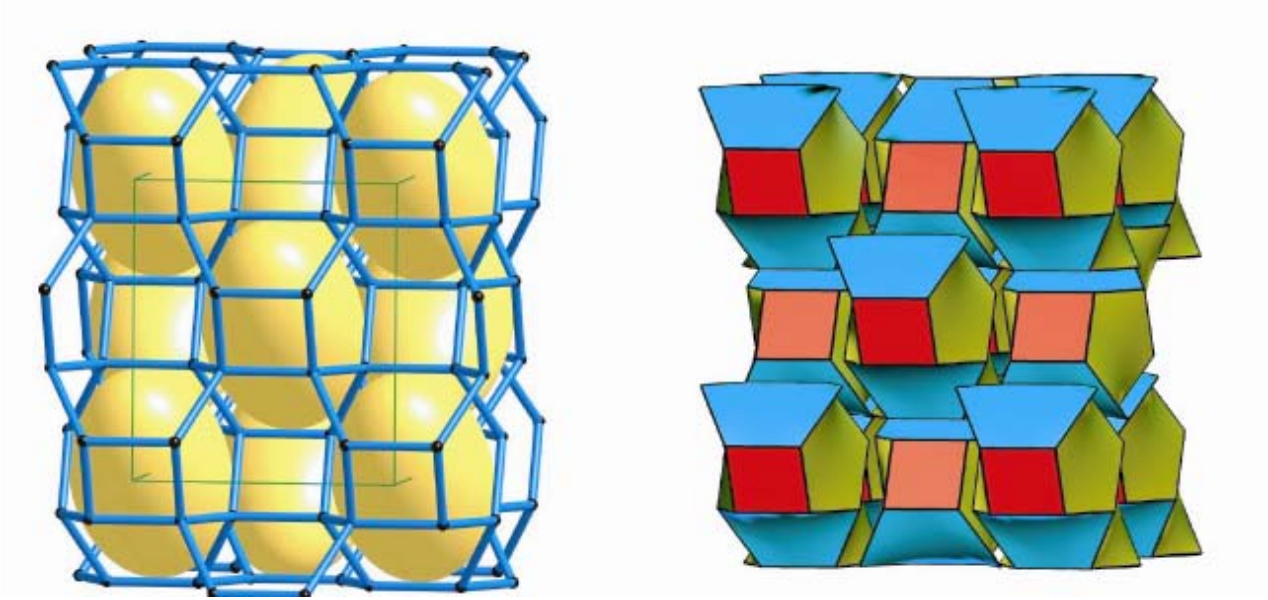


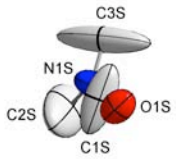


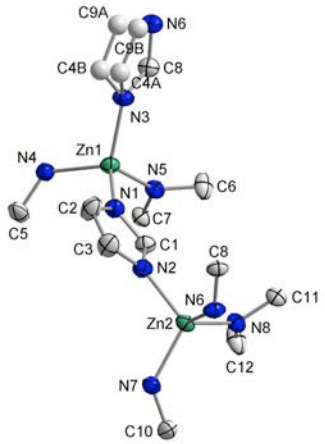

C8
C9
N5
C7
N6
Zn2
O2S
C21S
C3
N2
N2S
C2
C1
C13S
C23S
N1
C22S
C4
Zn1
N3
N1S
C11S
N4
C12S
C5
N8
C10
C6
O1S
C12
N7
C11
O3S
C31S
N3S
C33S
C32S

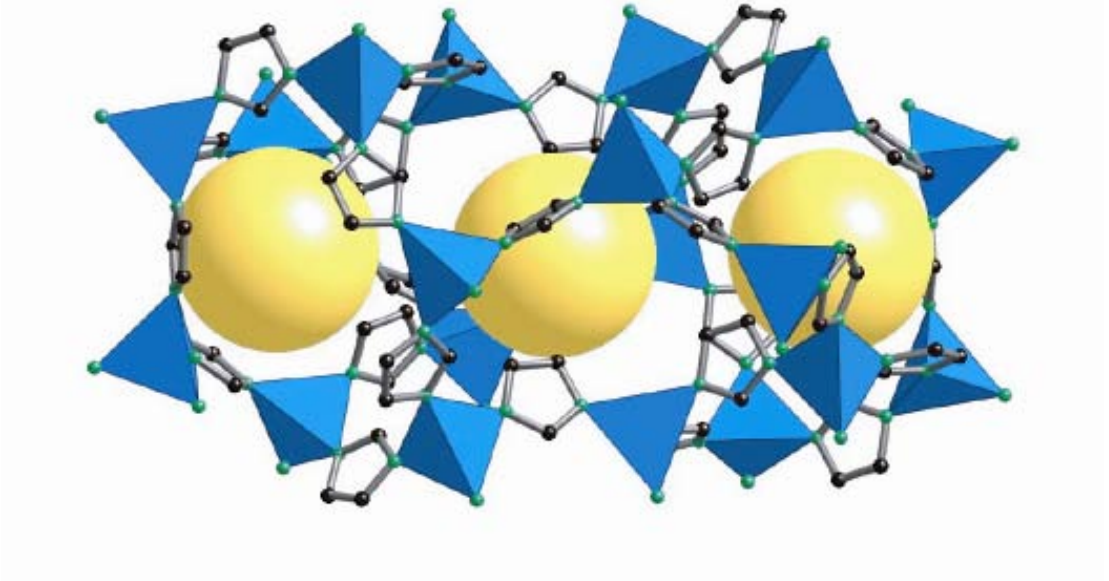


ZIF-4 cag

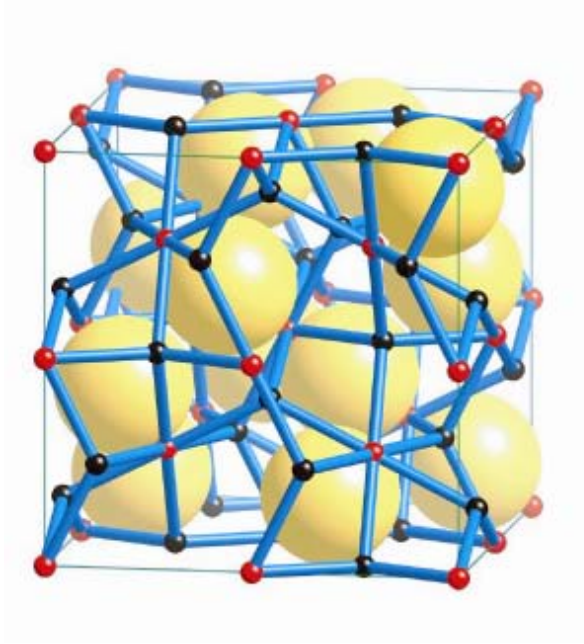


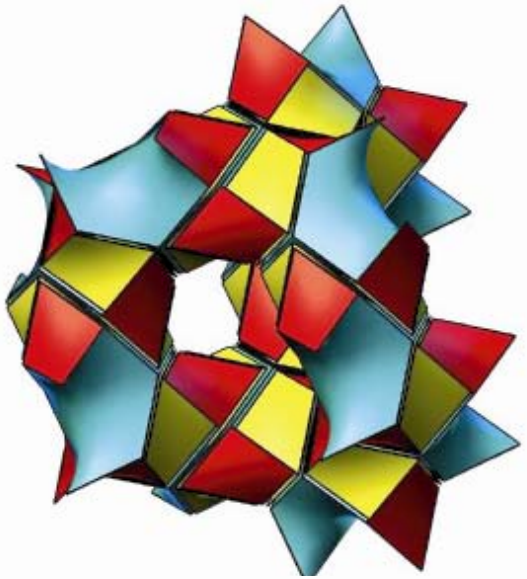

C3S
N1S
C2S
O1S
C1S

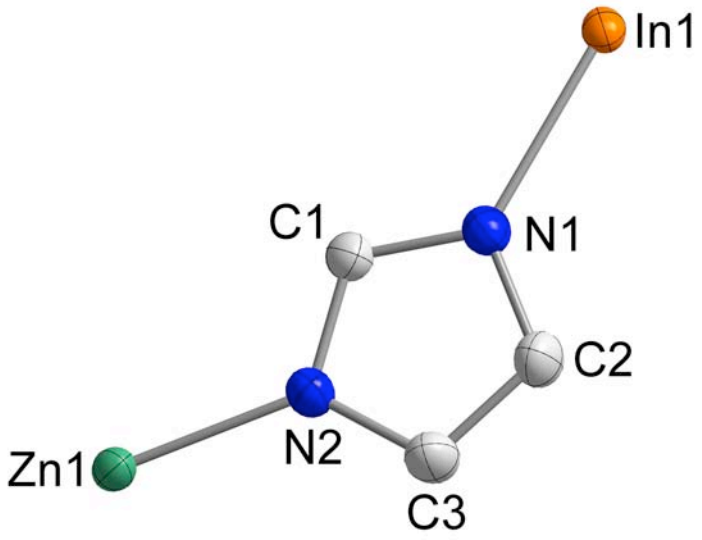

C9A
N6
C9B
C4B
C8
C4A
N3
N4
Zn1
N5
C6
N1
C2
C7
C5
C3
C1
C8
N2
N6
C11
Zn2
N8
C12
N7
C10

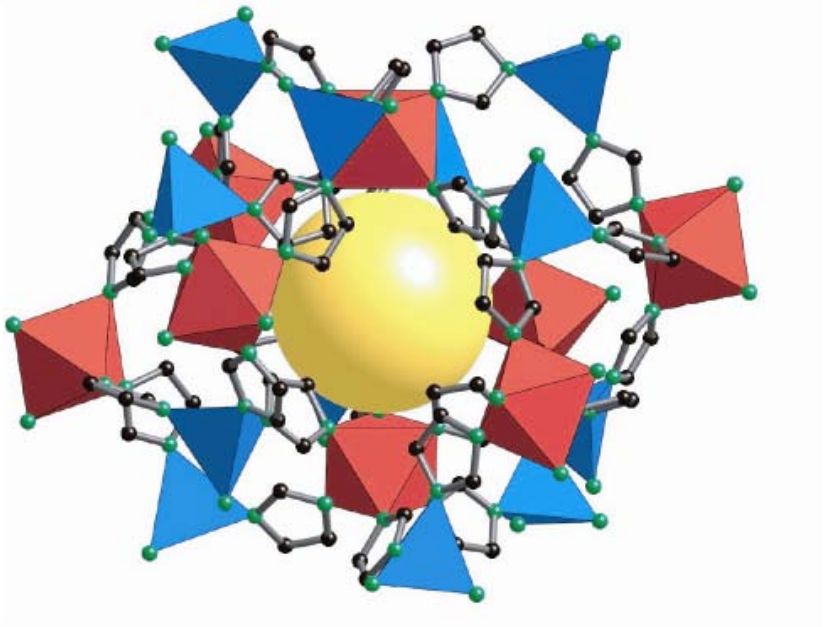


ZIF-5 gar

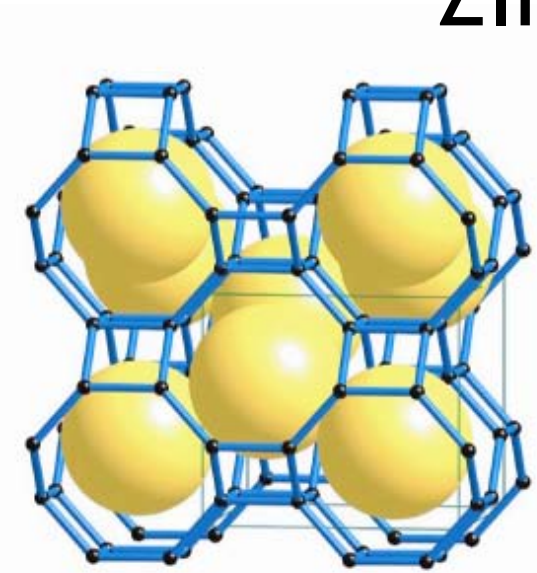


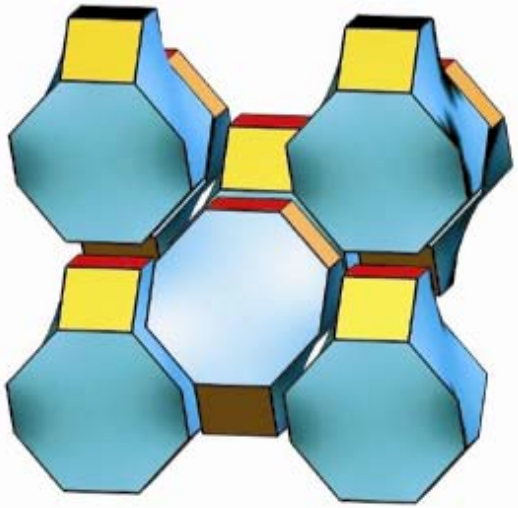


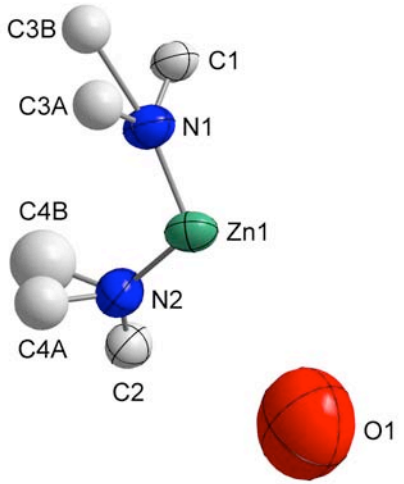


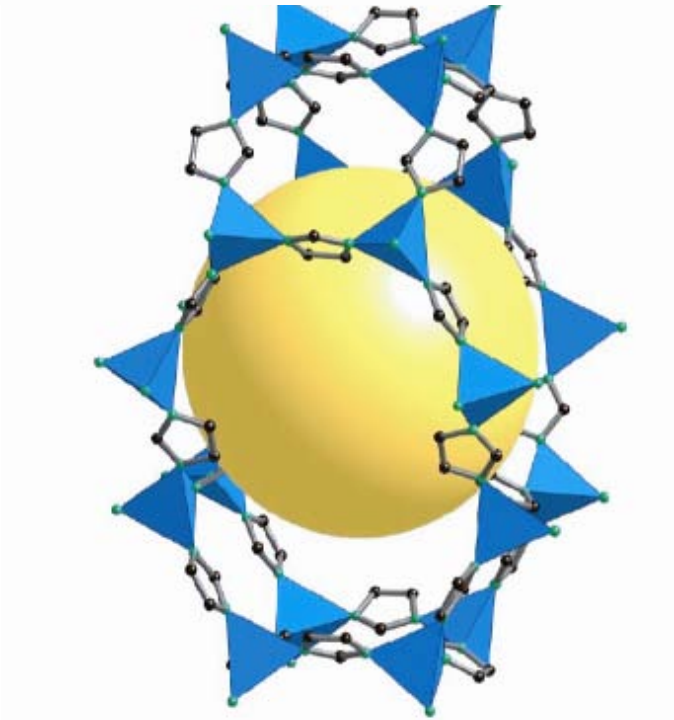


ZIF-6 gis

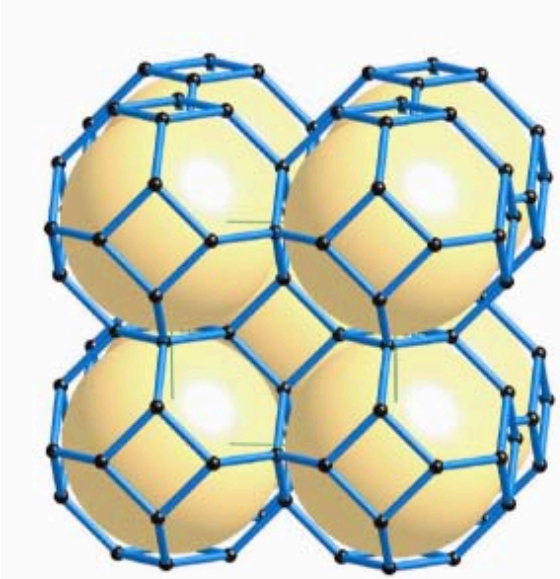


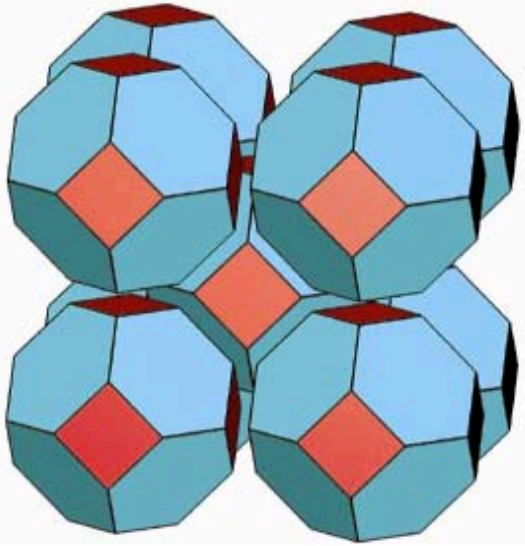


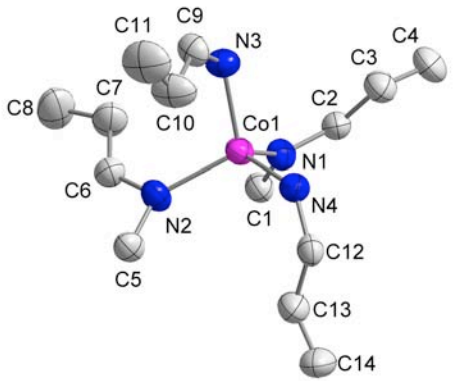


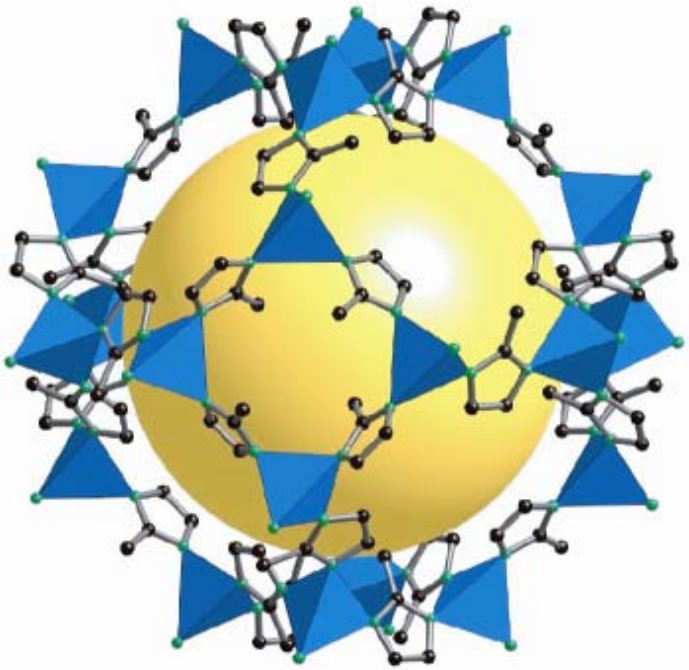


ZIF-8 sod

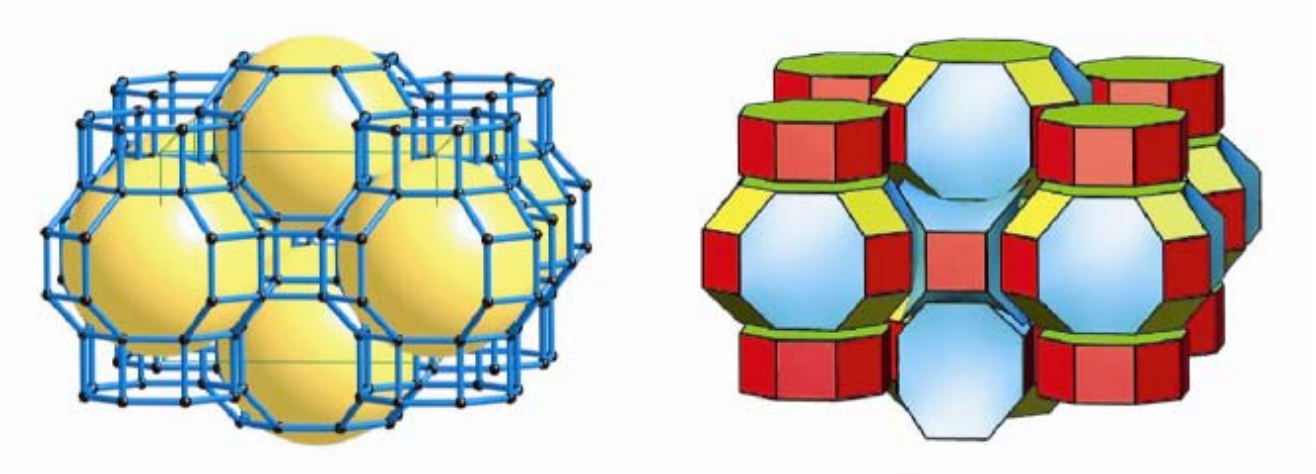


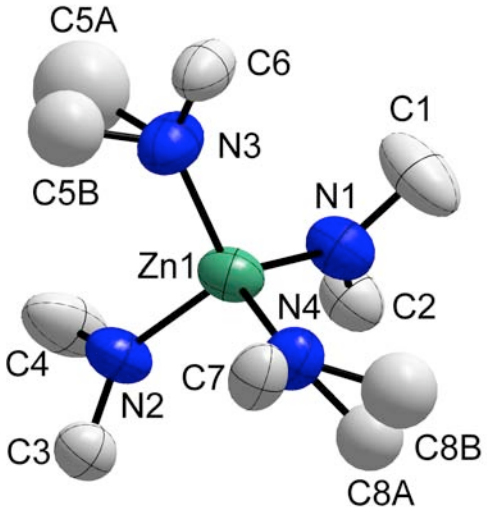


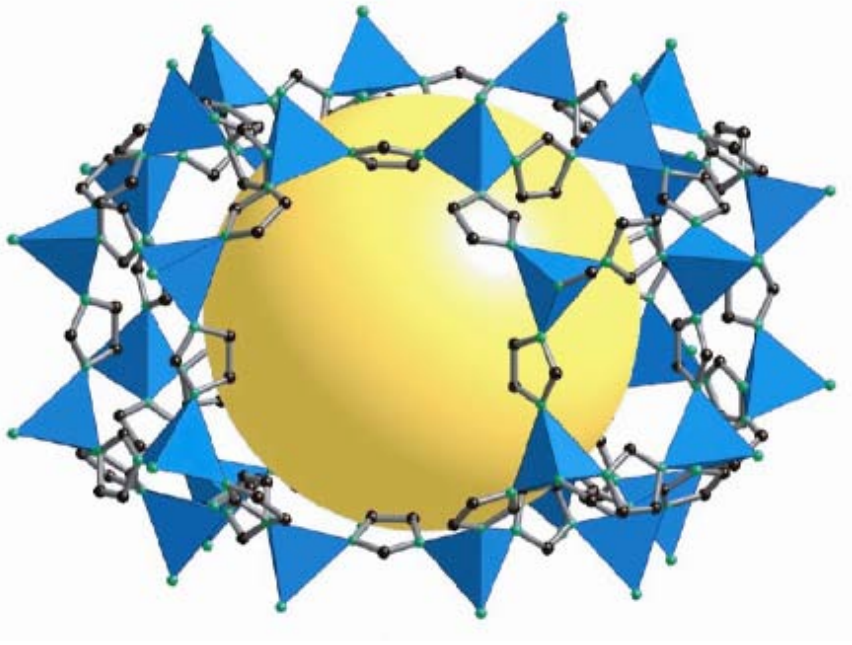




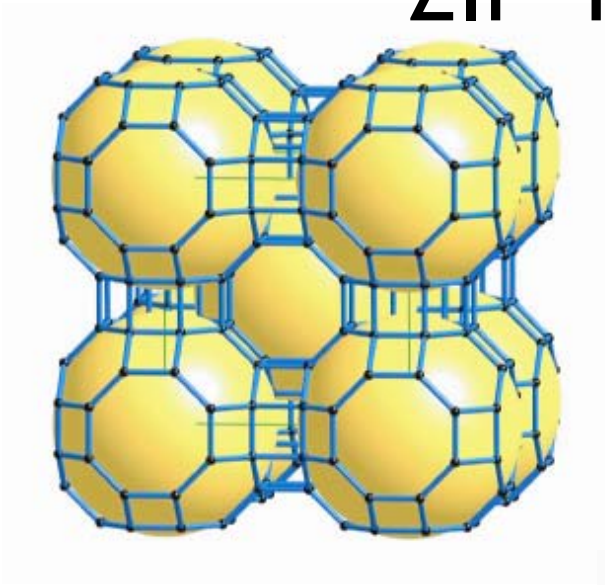
ZIF-10 mer

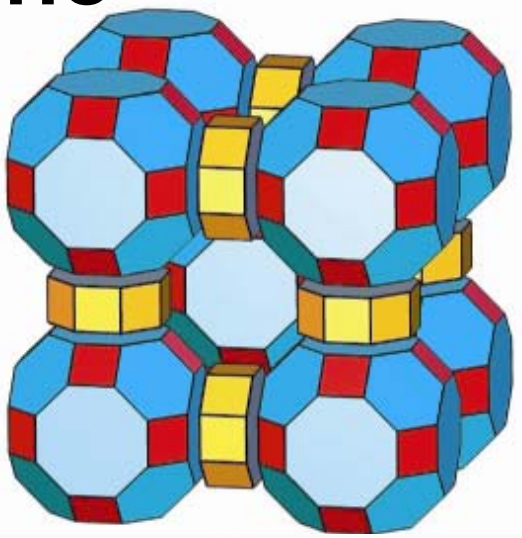


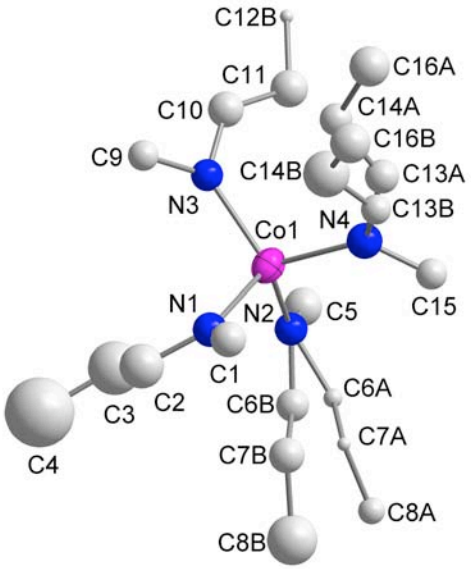


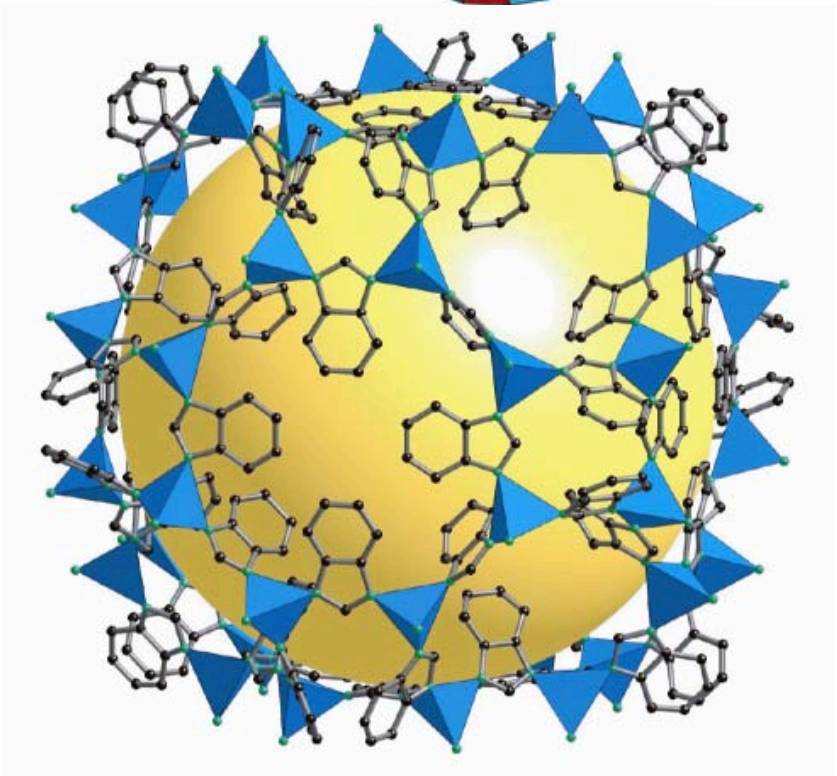


ZIF-11 rho

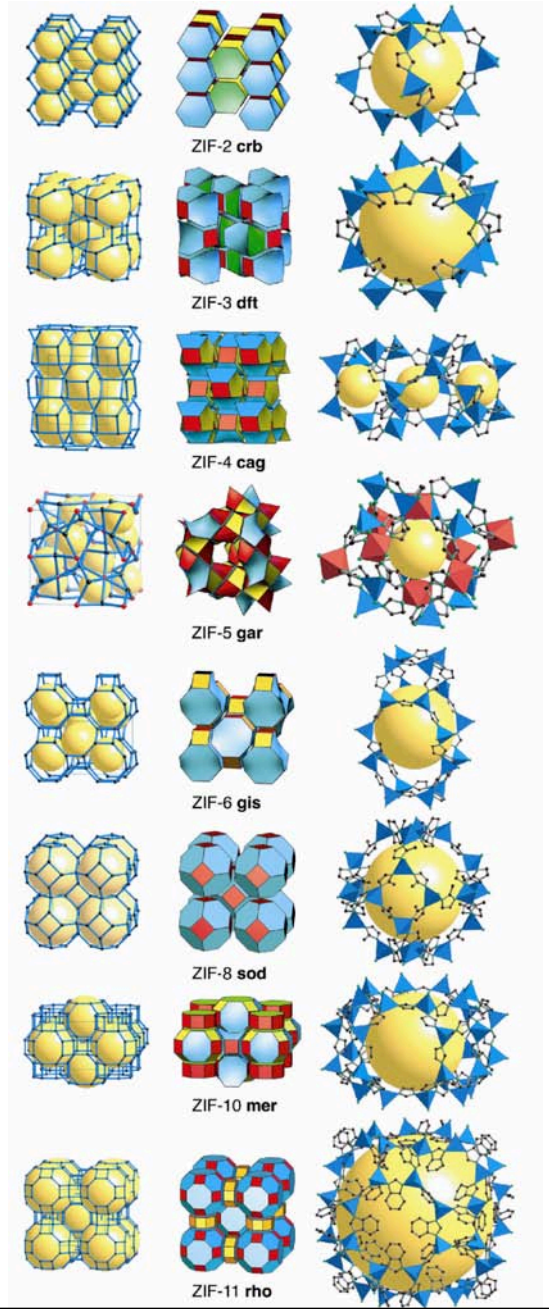


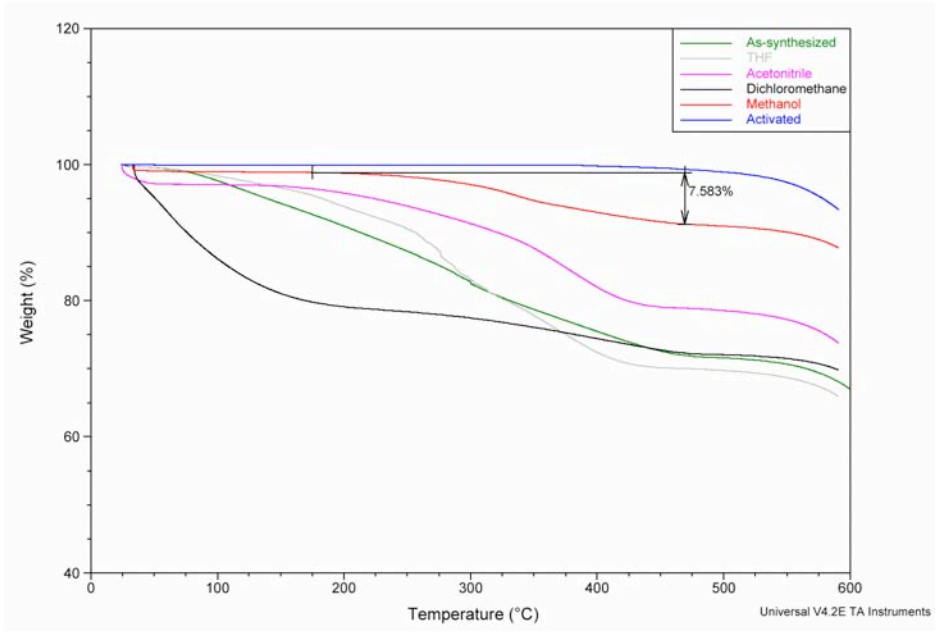


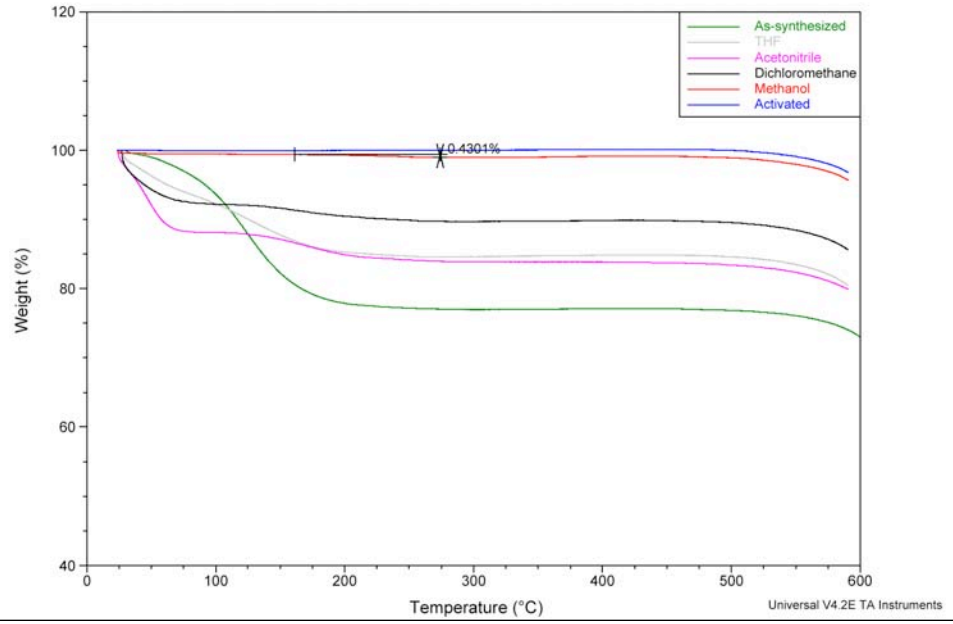

C12B
C11
C10
C9
N3
C14B
C16A
C14A
C16B
C13A
C13B
N4
Co1
C15
N1
N2
C5
C1
C2
C3
C4
C6A
C6B
C7A
C7B
C8A
C8B



Thermal stability of ZIFs

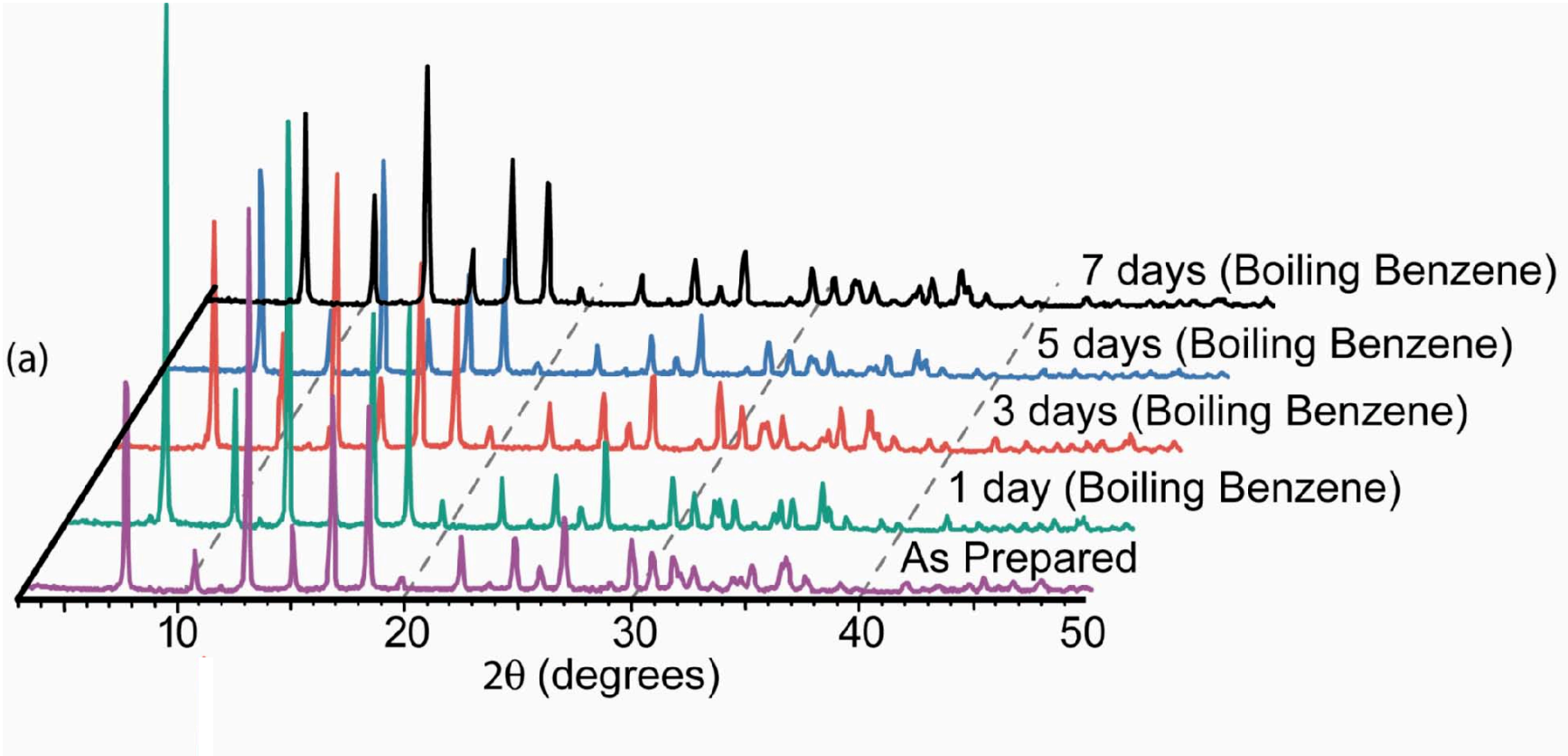


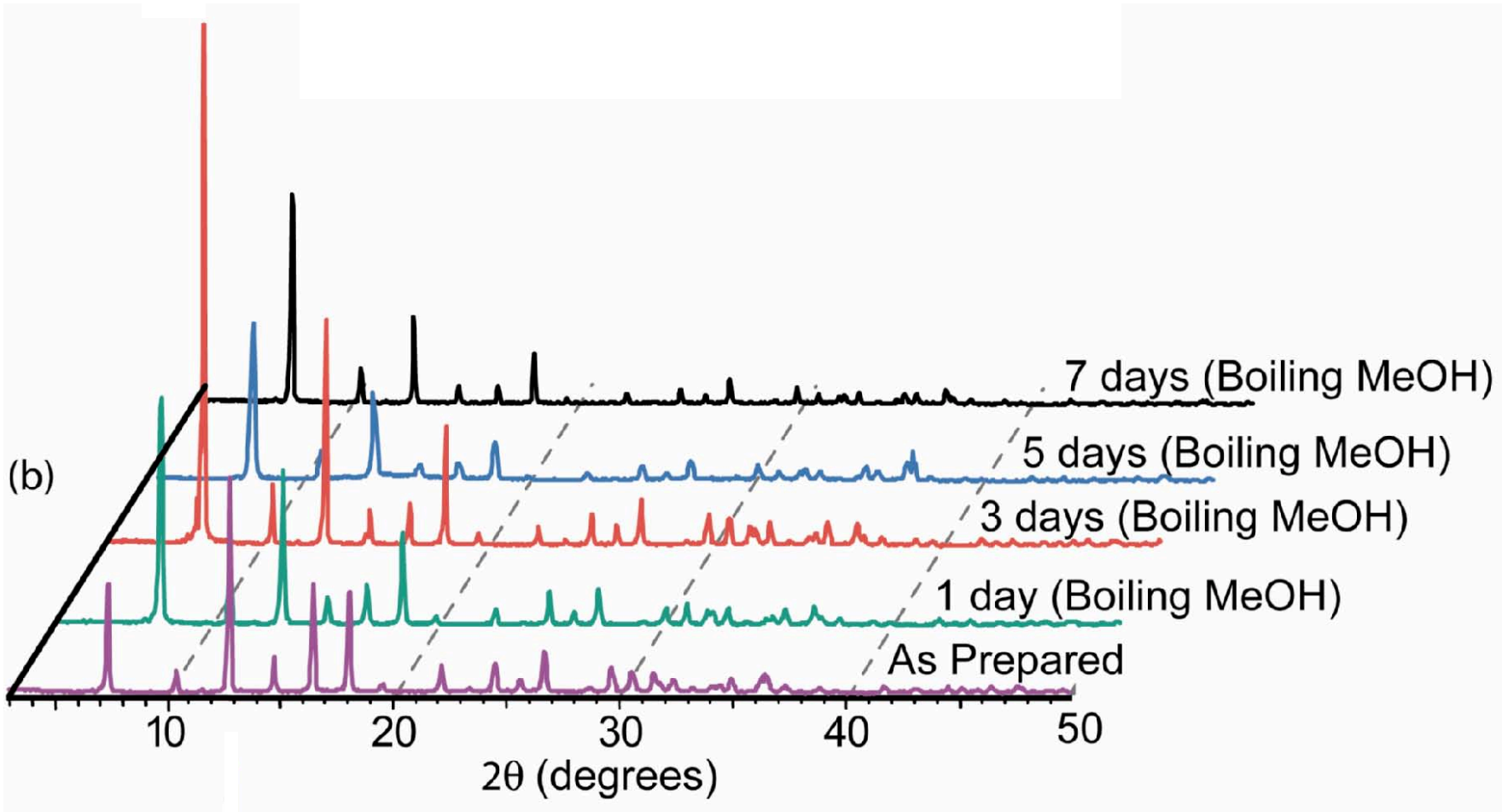


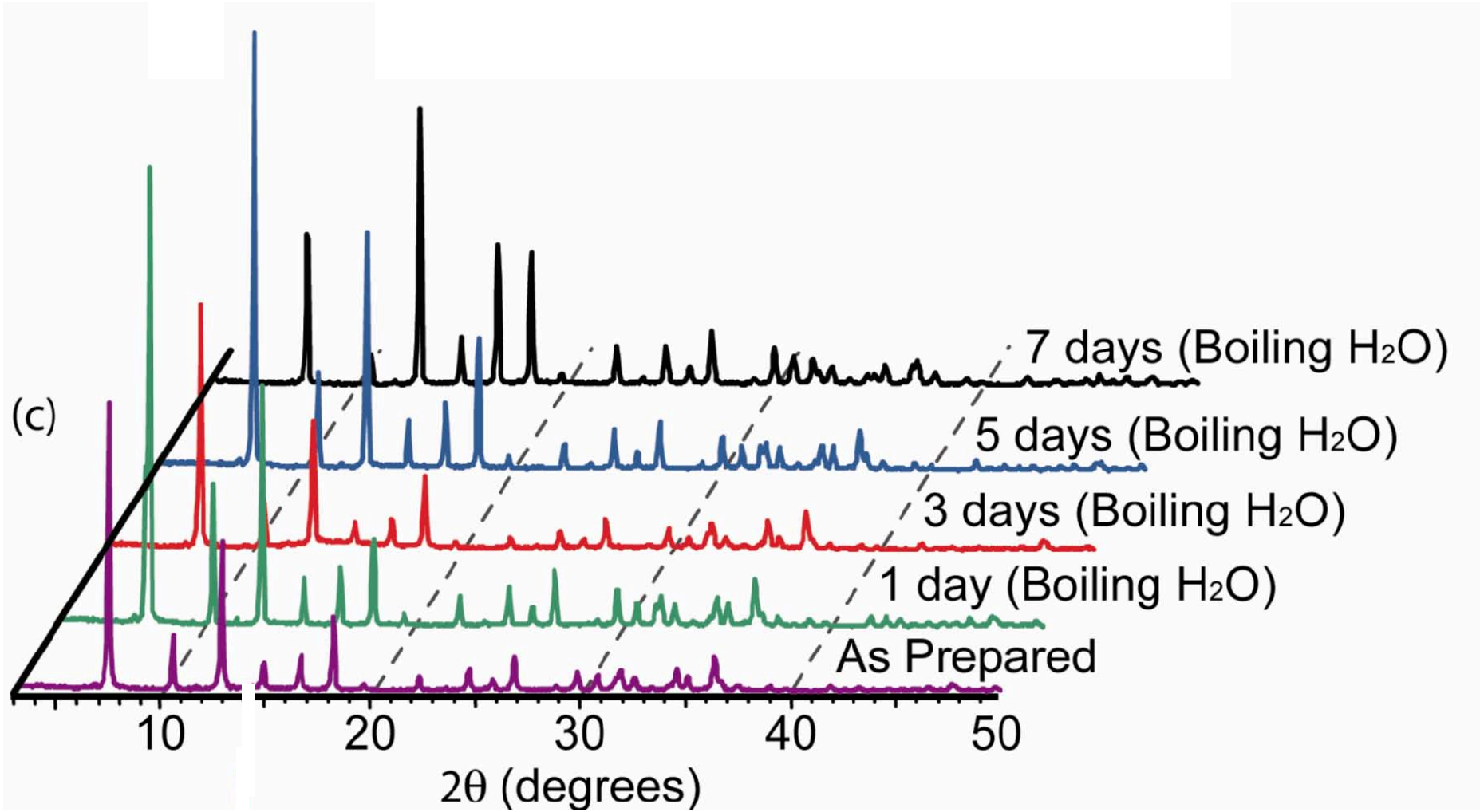


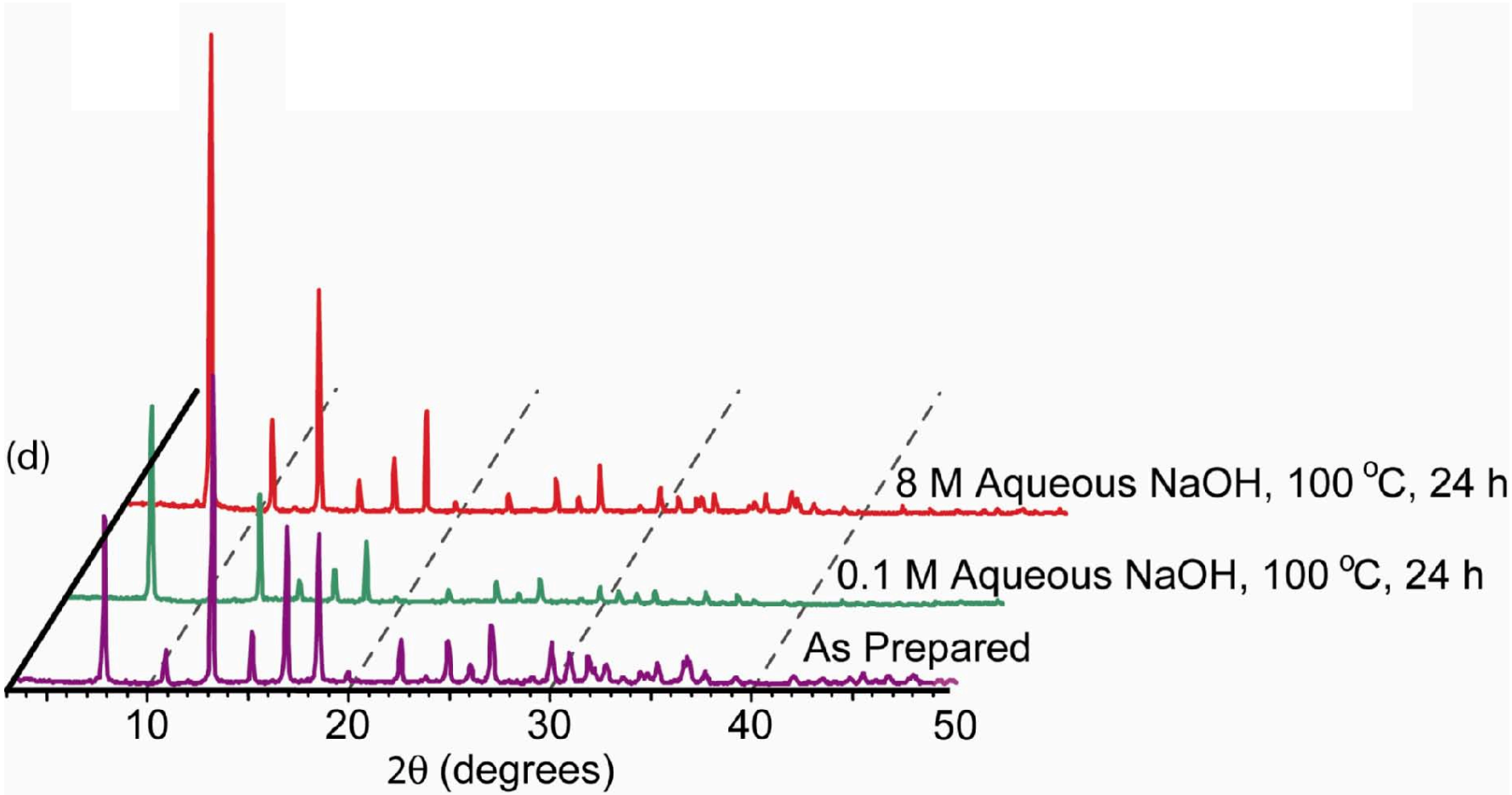
ZIF-*n*	composition	net	zeolite	T/*V*, nm^{-3}	*d*, Å	*N*
ZIF-1	$Zn(IM)_2$	**crb**	BCT	3.64	6.94	12
ZIF-2	$Zn(IM)_2$	**crb**	BCT	2.80	6.00	12
ZIF-3	$Zn(IM)_2$	**dft**	DFT	2.66	8.02	16
ZIF-4	$Zn(IM)_2$	**cag**	-	3.68	2.04	20
ZIF-5	$In_2Zn_3(IM)_{12}$	**gar**	-	3.80	3.03	20
ZIF-6	$Zn(IM)_2$	**gis**	GIS	2.31	8.80	20
ZIF-7	$Zn(PhIM)_2$	**sod**	SOD	2.50	4.31	24
ZIF-8	$Zn(MeIM)_2$	**sod**	SOD	2.47	11.60	24
ZIF-9	$Co(PhIM)_2$	**sod**	SOD	2.51	4.31	24
ZIF-10	$Zn(IM)_2$	**mer**	MER	2.25	12.12	24
ZIF-11	$Zn(PhIM)_2$	**rho**	RHO	2.01	14.64	48
ZIF-12	$Co(PhIM)_2$	**rho**	RHO	2.01	14.64	48

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)

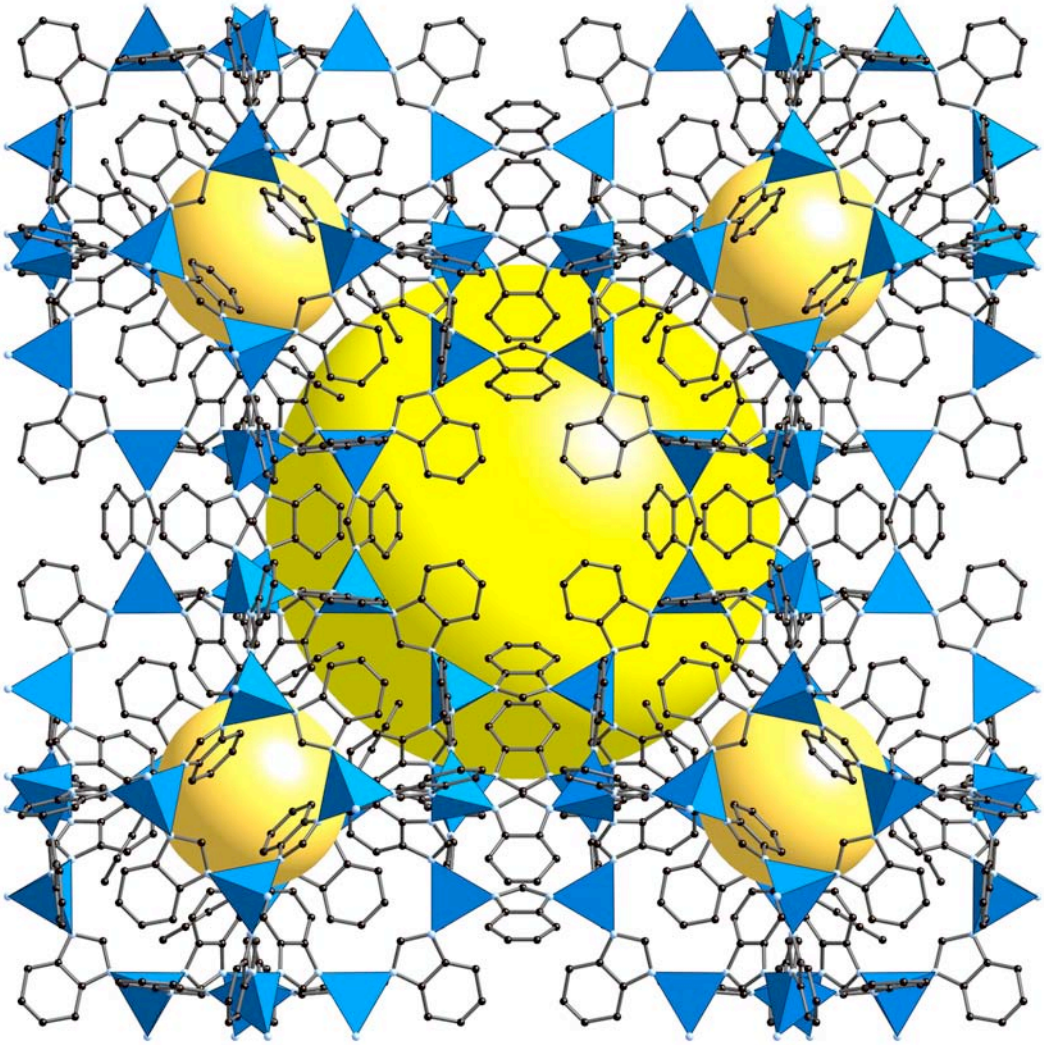

(c)
7 days (Boiling H2O)
5 days (Boiling H2O)
3 days (Boiling H2O)
1 day (Boiling H2O)
As Prepared
10
20
30
40
50
2θ (degrees)

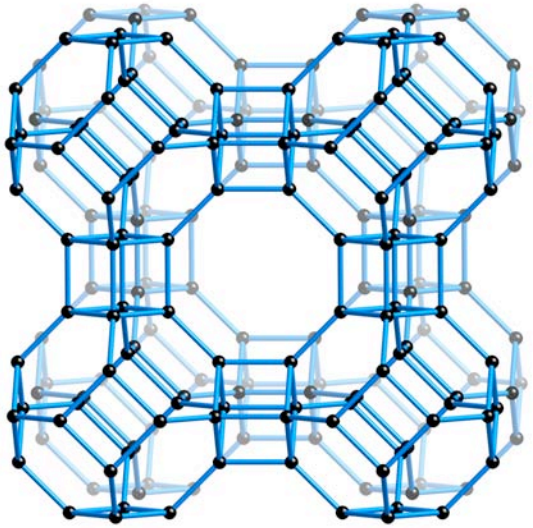


K. S. Park, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, ***Proc. Nat. Acad. Sci. USA,* 2006*, 103,* 10186-10191.**

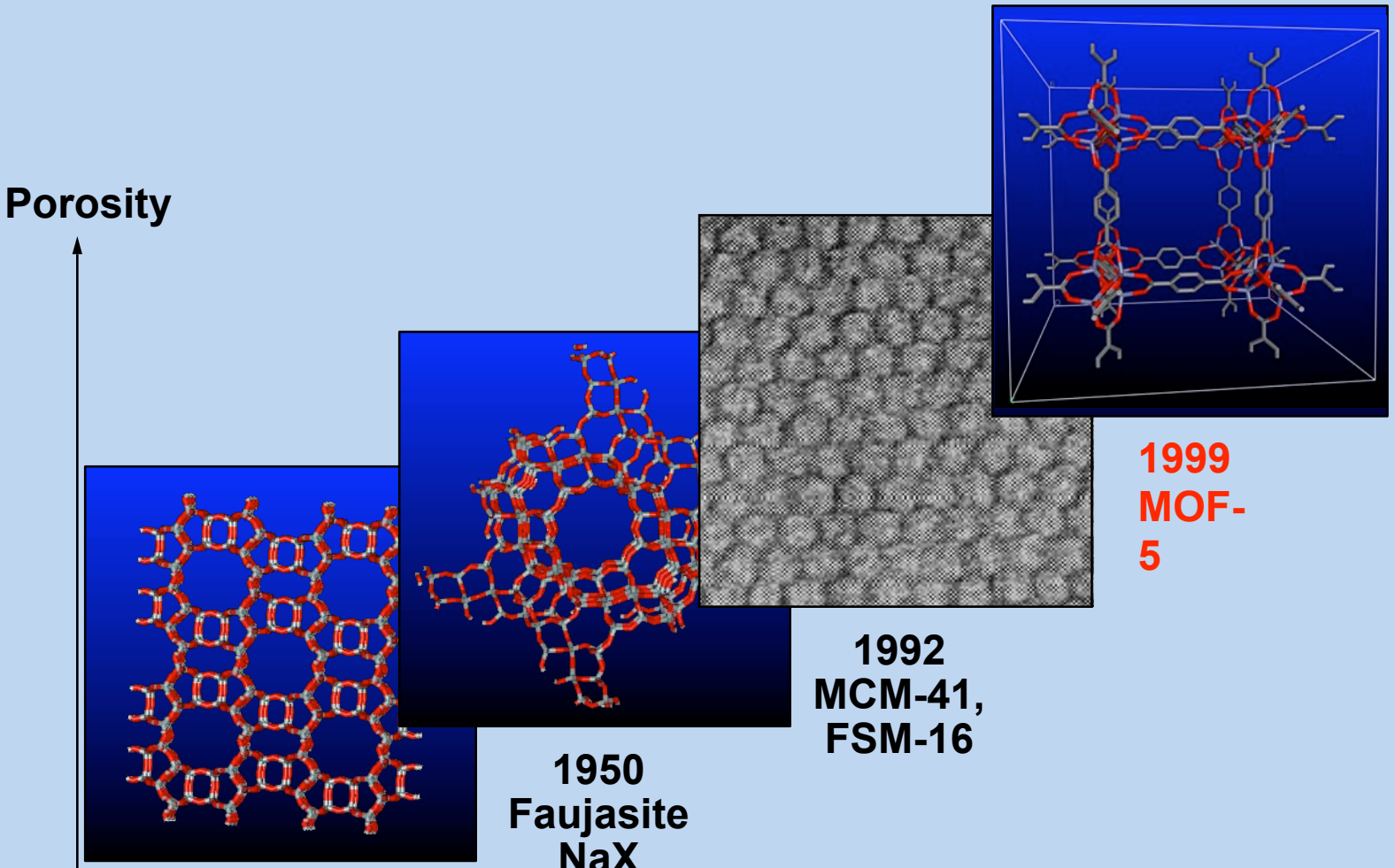
Dr. Hideki Hayashi

ZIF-20 LTA





Classes of Porous Materials

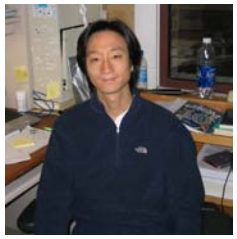


What are the chances of reaching the DOE targets for hydrogen storage?

What are the chances of reaching the DOE targets for hydrogen storage?

1. *Pipeline of new materials*
2. *Crystalline materials that are fully characterized*
3. *Materials in which the building units can be varied 'nearly at will'*
4. *Air stable, robust and beautiful*

Acknowledgments to Group Members



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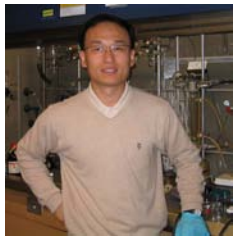

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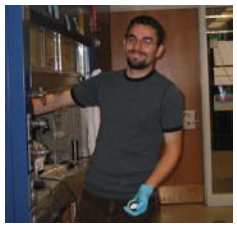

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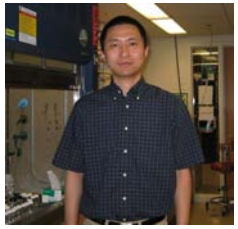

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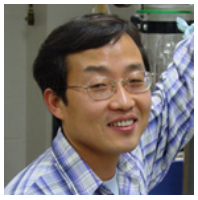

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