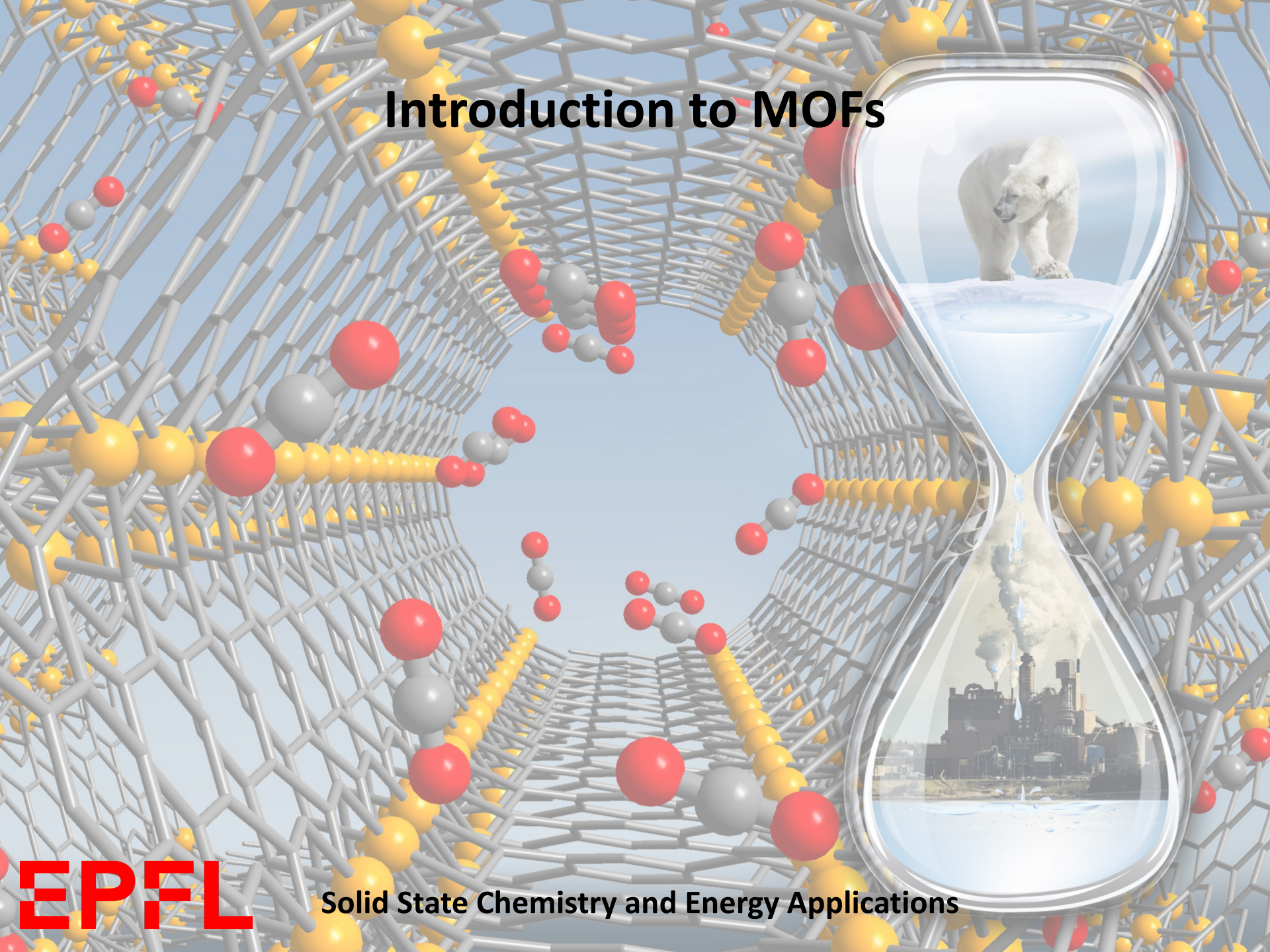
Introduction to MOFs

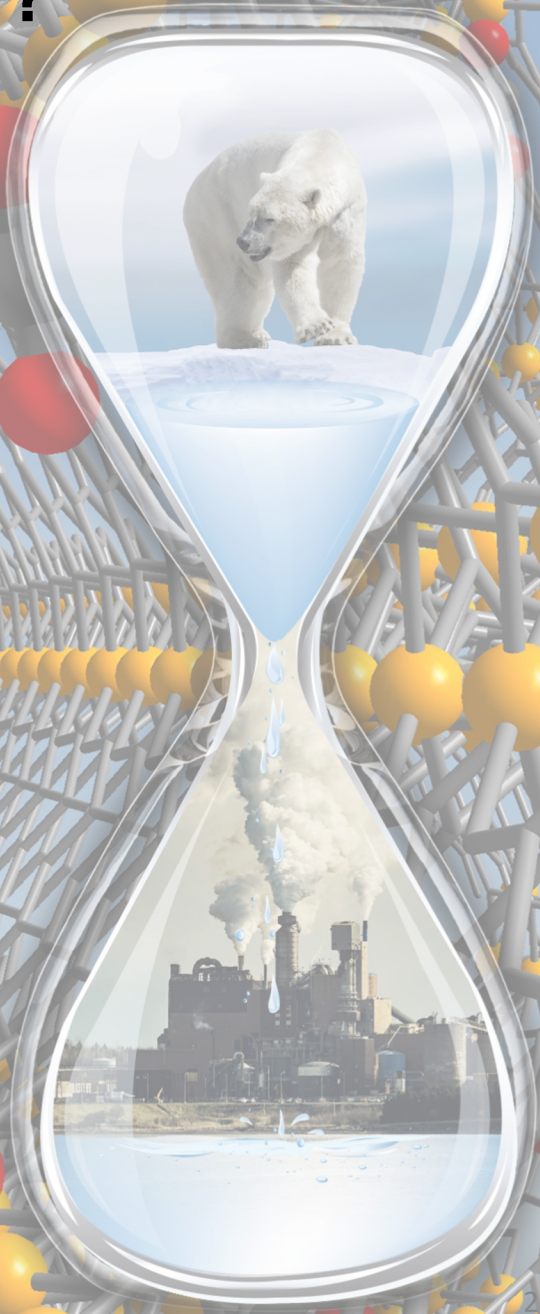


EPFL

Solid State Chemistry and Energy Applications

What will we cover?

- Classes of Porous Materials
- MOFs and why they are Special
- Synthesis
- Building Blocks
- Most well-known Frameworks
- Post-synthetic Modification

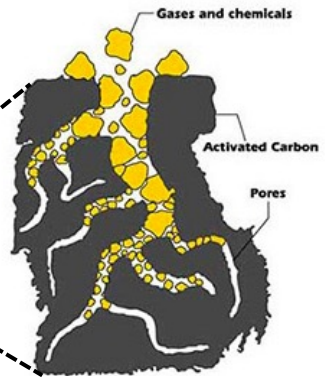


EPFL

History of porous materials

Activated Carbon

Heat



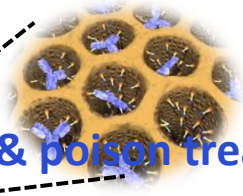
1500 BC – medicinal use

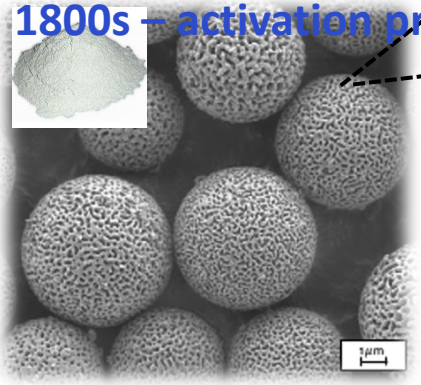
400 BC – water treatment

1776 – water decoloration

1800s – activation process & poison treatment

Porous Silica

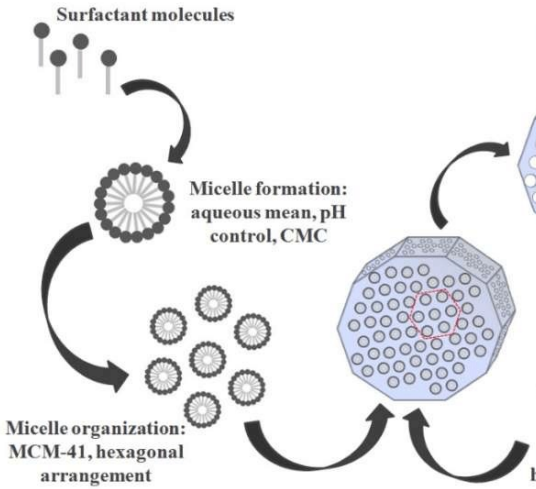




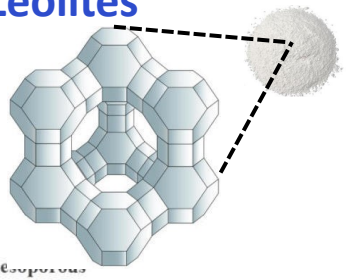
1970s – first patent

1997– wave of reports

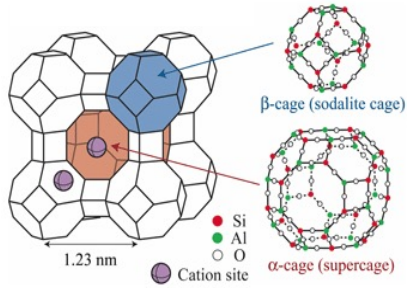
4.6 - 30 nm pore size



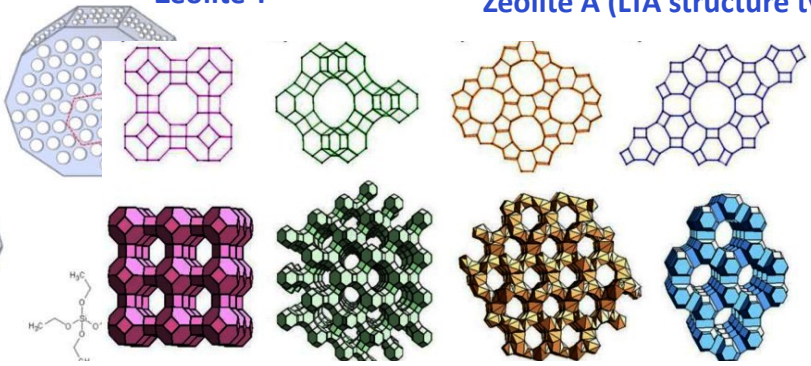
Zeolites



Zeolite Y



Zeolite A (LTA structure type)



zeolite A (4.2 Å) zeolite Y (7.4 Å) Zeolite L (7.1 Å) ZSM-5 (5.6 Å)

1765 – boiling stone, 1862 – synthesis

1950 – Union Carbide – sol gel synthesis

https://atlascarbonllc.com/ac/history/Lite

O.D. Velev et all, *Nature* **389**, 447-448

C.T. Kresge et all, *Nature* **359,** 710-712

Sigmund M. Csicery, *Zeolites*, **4,** 202-213

Veronique Van Speybroek, *Chem. Soc. Rev.* **44**, 7044-7111

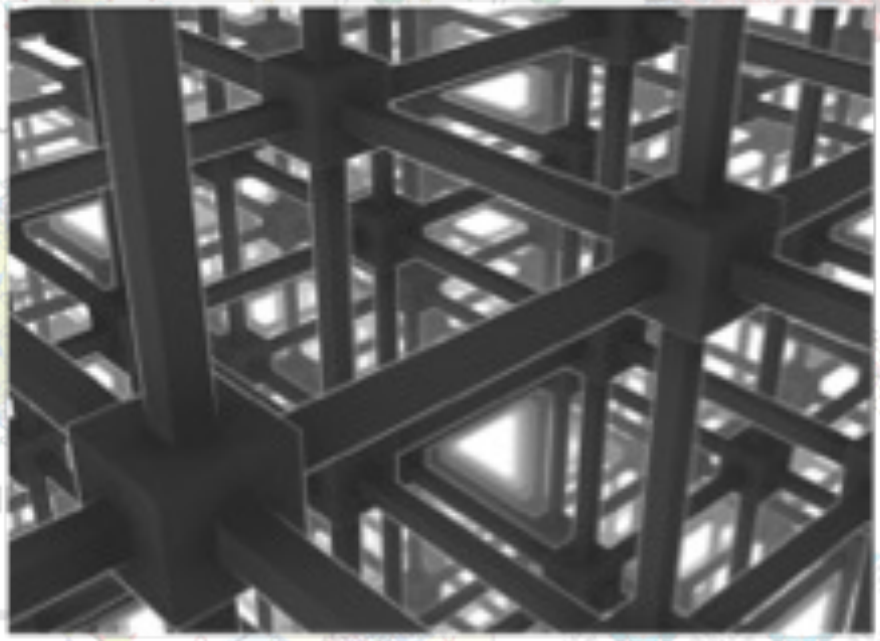
Microporous <2nm. **Mesoporous 2-50nm** **Macroporous > 50 nm**

What is a MOF?

MOFs offer a modular design and unprecedented chemical tunability!

Metal-ions or metal-ion clusters

Organic ligands



3-D MOF Structure

MOFs

What are they?

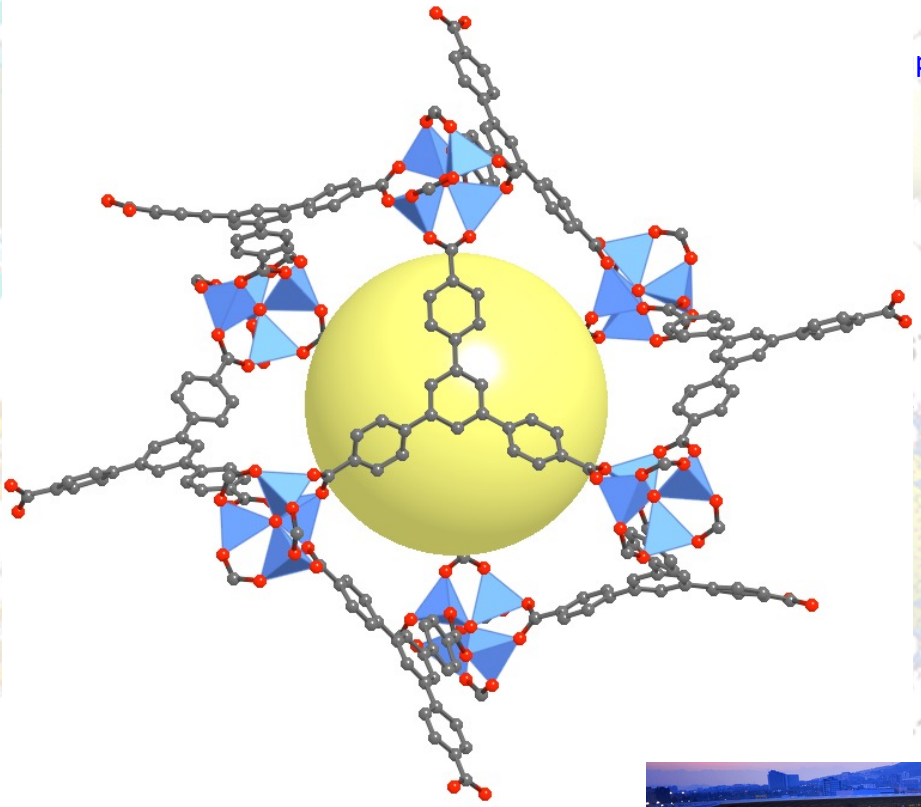
Why are they special?

How are they made?

How can you increase stability?

What can they be used for?

Why are MOFs special?



MOF Properties:

Nano sized channels that connect in 1-, 2-, and 3- Dimensions

High Surface Areas

Chemically Tunable
-Tunable Pore size and shape
-Tunable Properties

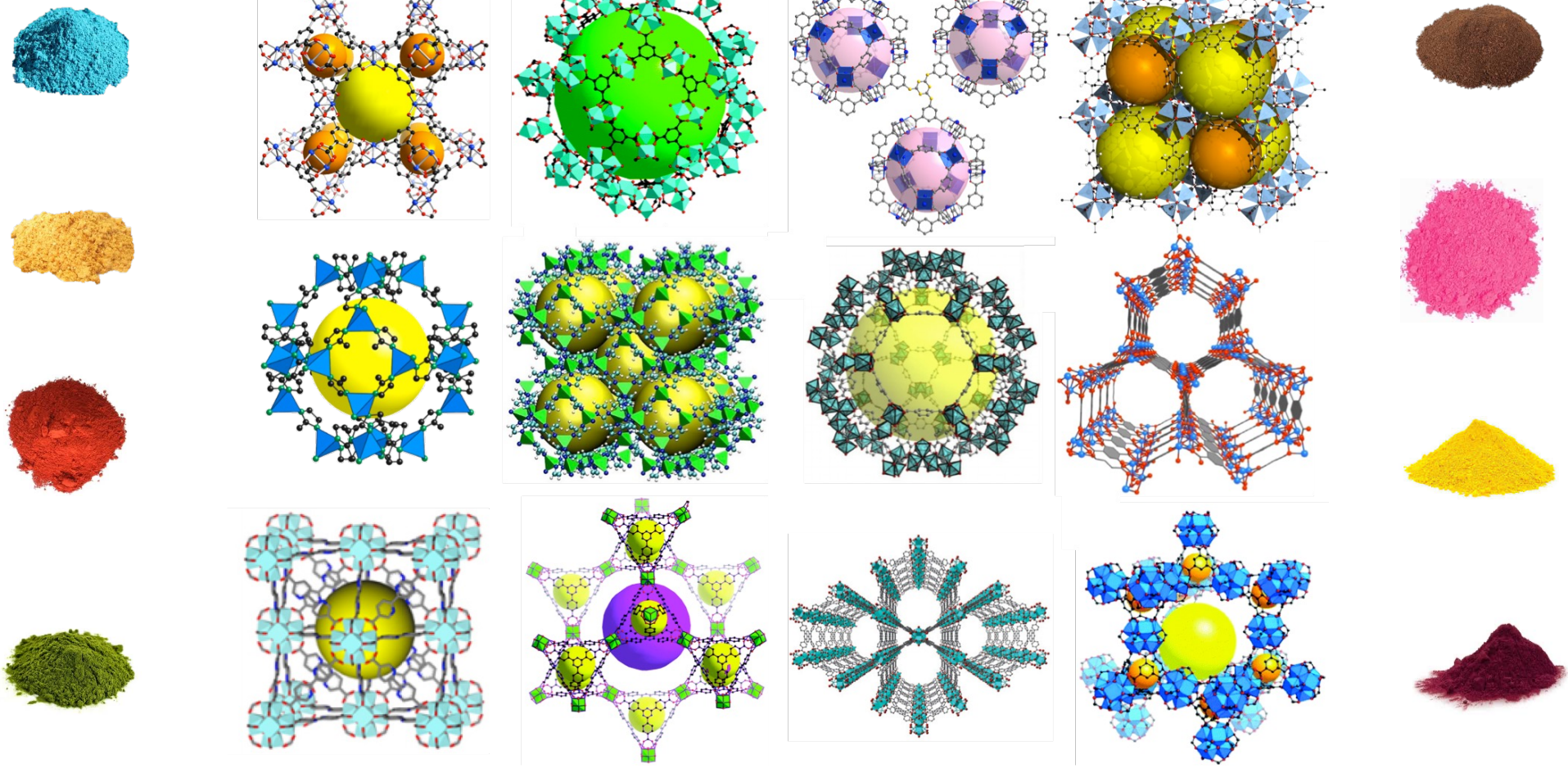
Pore sizes 0.5 – 10 nm

Li, et al, *Nature* 1999, 402, 276.
Rosi, et al *Science*. 2003, 300(5622), 1127.
Farha, et al *J. Am. Chem. Soc.*,2012,134(36), 15016.

Surface areas up to 7800 m^2/g, a world record = 1 football field

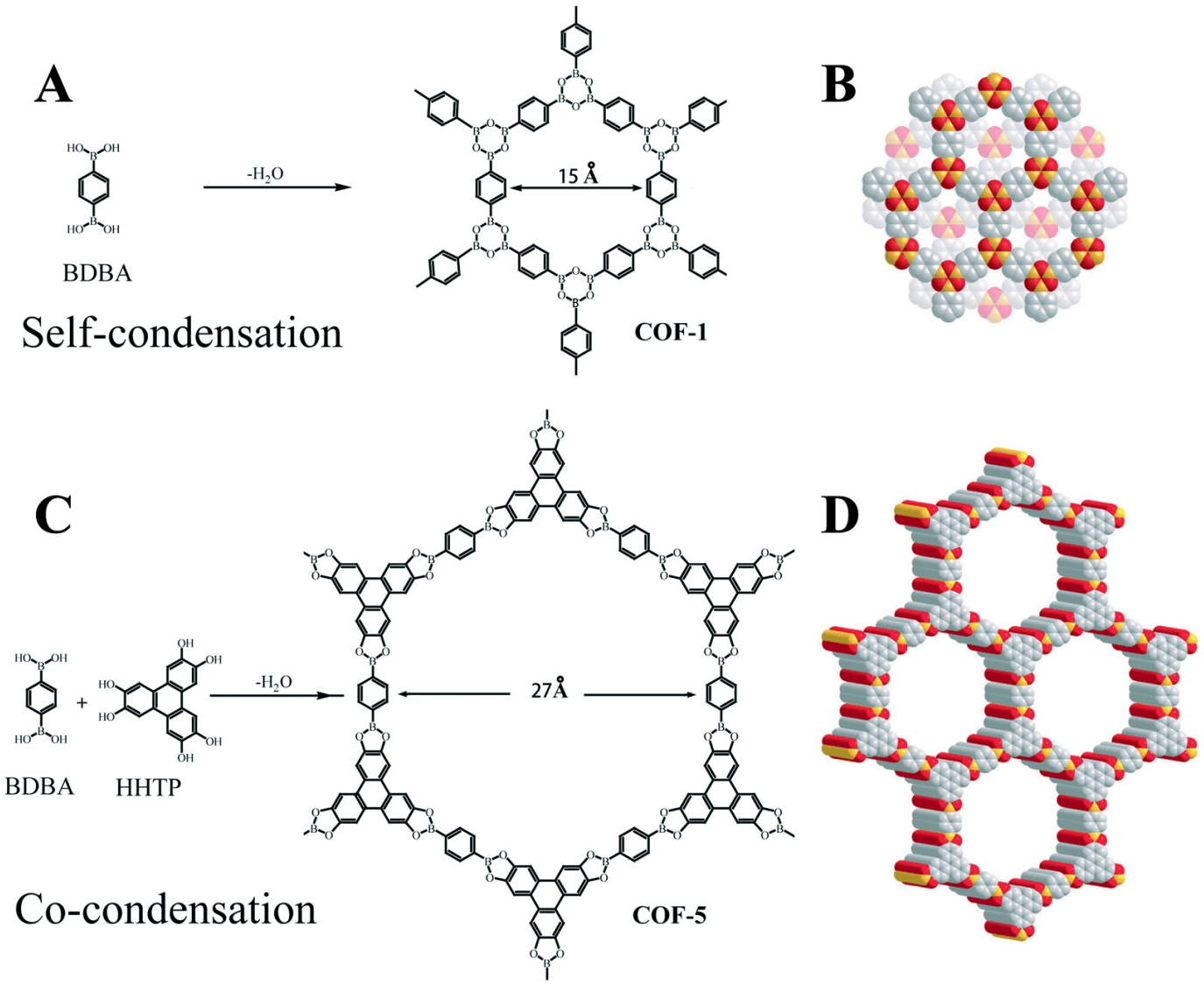
Metal-Organic Frameworks

"Reticular chemistry, the chemistry of linking molecular building blocks by strong bonds to make crystalline open frameworks, has significantly expanded the scope of chemical compounds and the useful materials"



Yaghi and Li, "Hydrothermal synthesis of a metal-organic framework containing large rectangular channels" *J. Am. Chem. Soc.* 1995, 117, 10401.

Covalent-Organic Frameworks



CrystEngComm, 2018, **20**, 1613-1634

General Synthesis

- **Conventional Hydrothermal or Solvothermal Synthesis**

RT-250°C

RT-120°C

T<220°C

T>220°C

Alternatives:

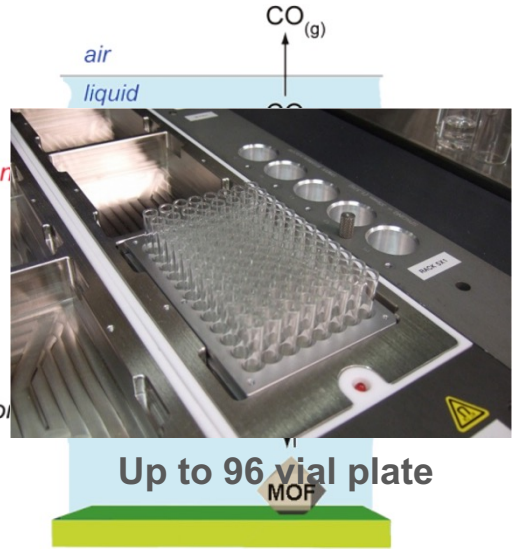
- **Ionothermal**
  - **Low-Vapor pressure**
  - **Templating effect**

- **Microwave**
  - **Shorter reaction times (minutes)**
  - **More uniform heating profiles**
  - **Different reaction kinetics**

High Throughput Methodologies:

- **Reproducibility**
- **Explore multi parameter space**

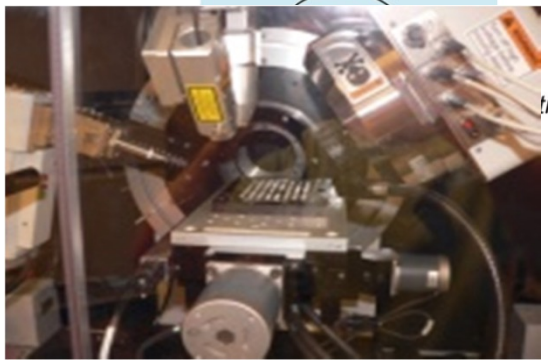
Solid and liquid dispensing



Up to 96 vial plate

Scale-up

- **Spray Drying (8.4 g / hr)**
- **Ball milling**
- **Continuous Flow (up to 20 g / hr)**
- **Microwave Synthesis**
- **Batch reactors**

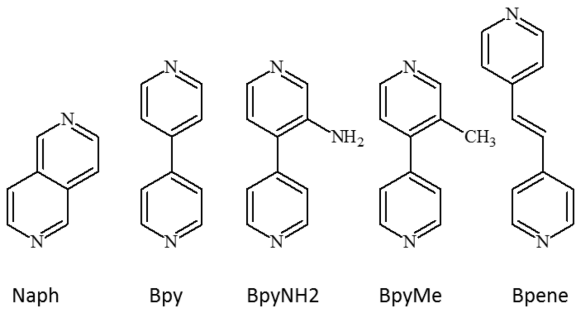


High-throughput PXRD

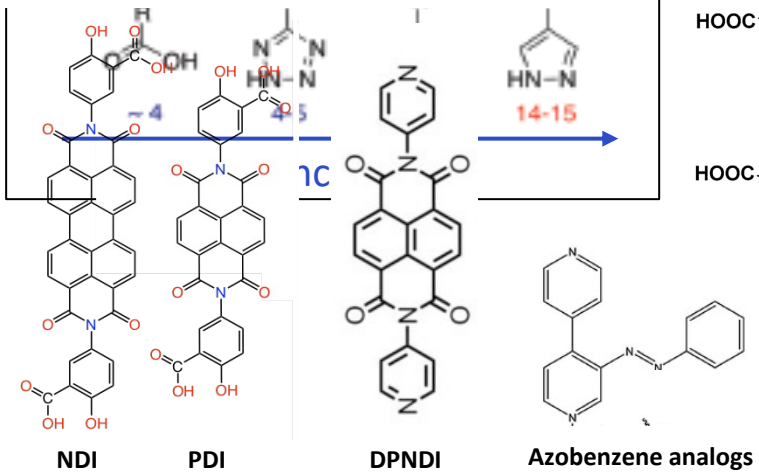
Soc., **2011**, *133*, 12926.

Ligands

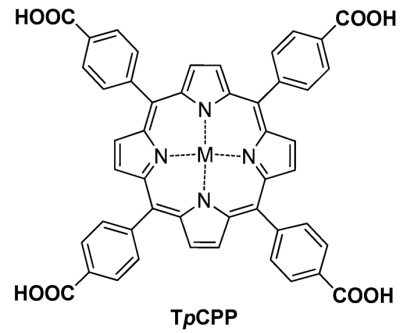
First generation linkers

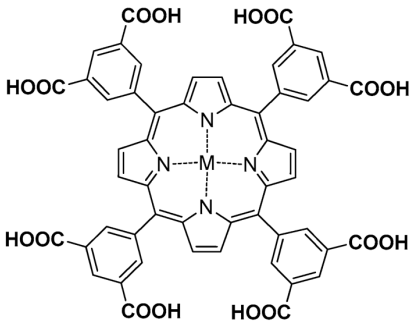


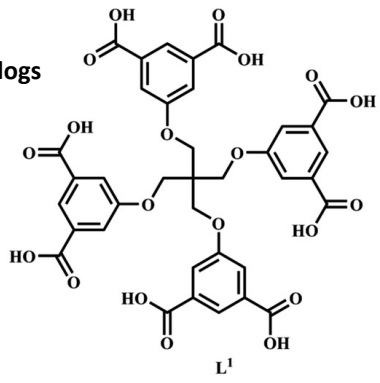
Impart specific functionality



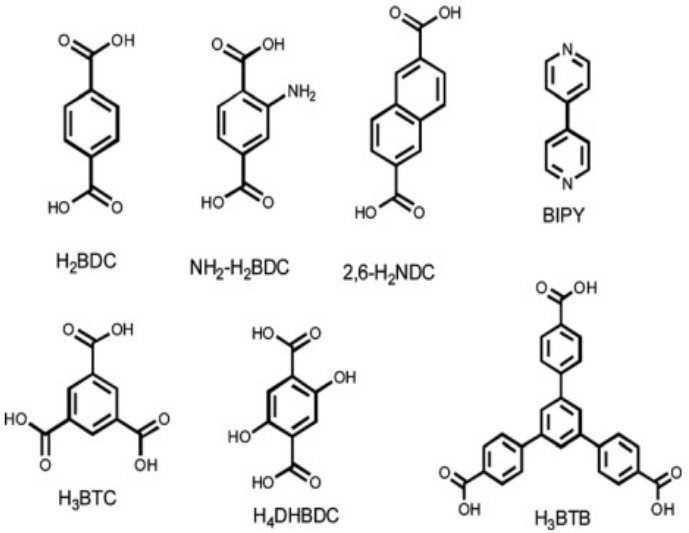
Porphyrin linkers



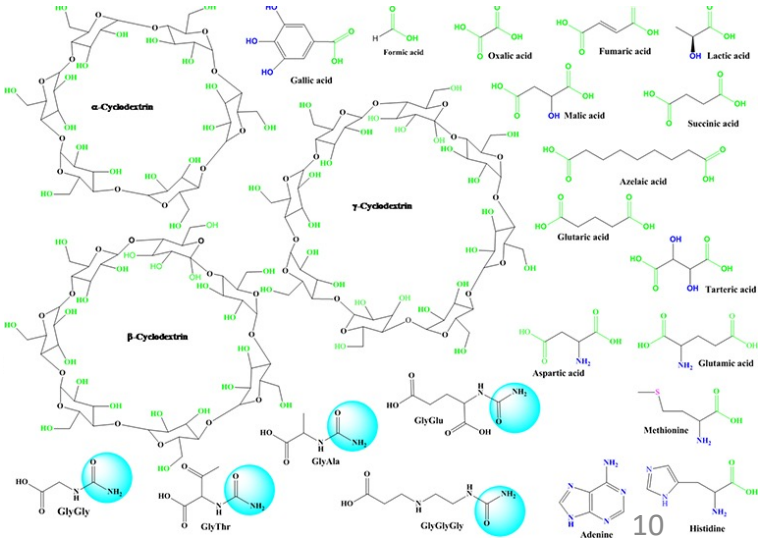




Most Common Linkers



Other BioMOFs



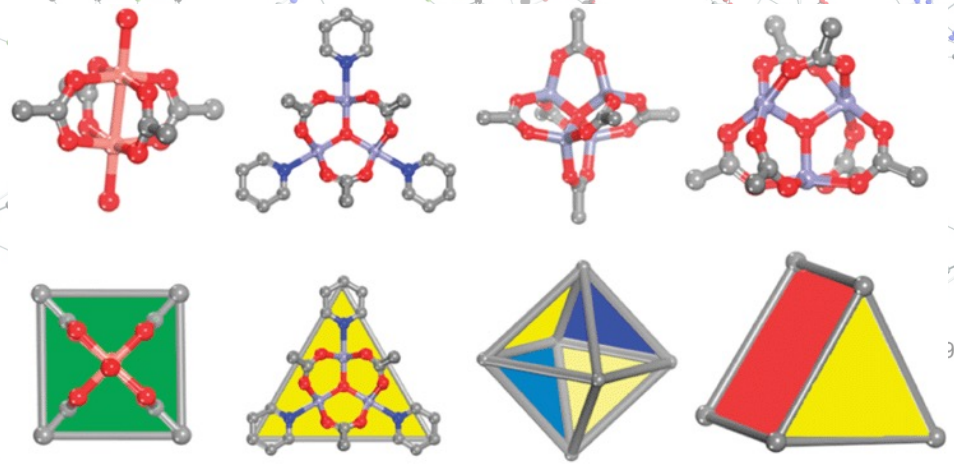
AlKabbi et al, Chem, 2016, **1**, 186.

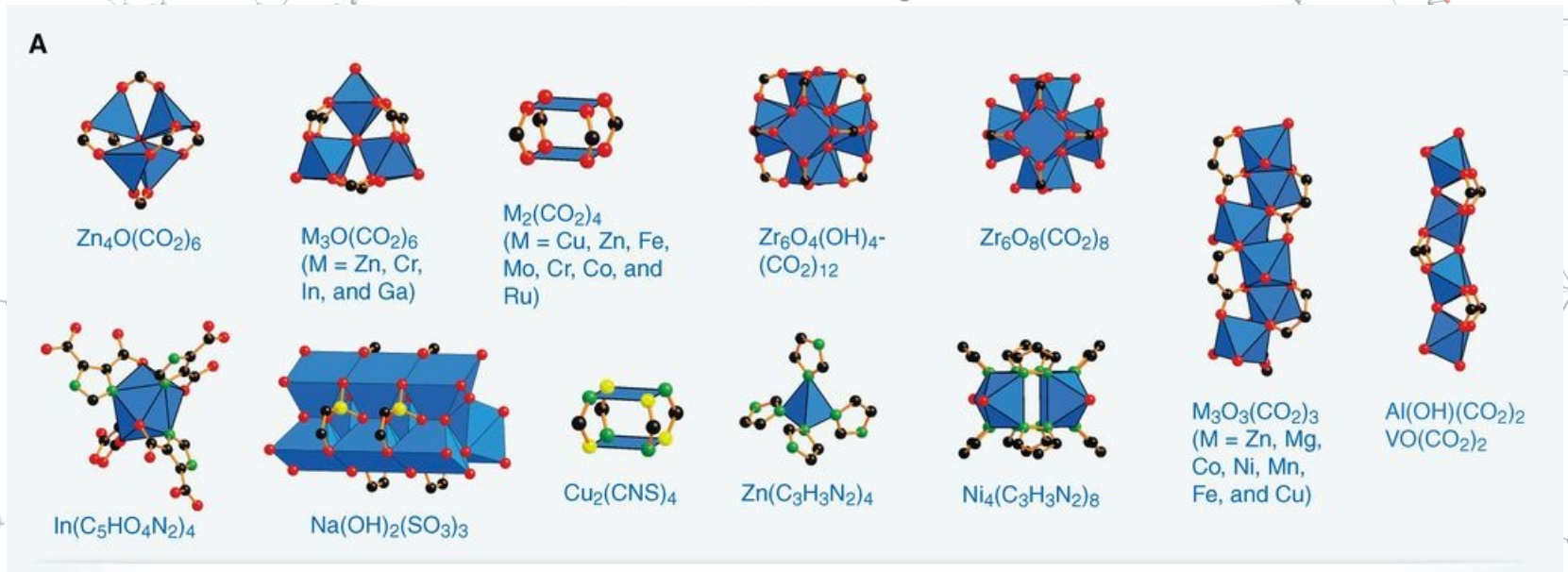
Dong-Ying Du et all, *Chem. Soc. Rev.* **43,** 4615-4632

Kristina Konstas et all, *J. Mater. Chem.* **22,** 16698

SBUs

Most Common SBUs

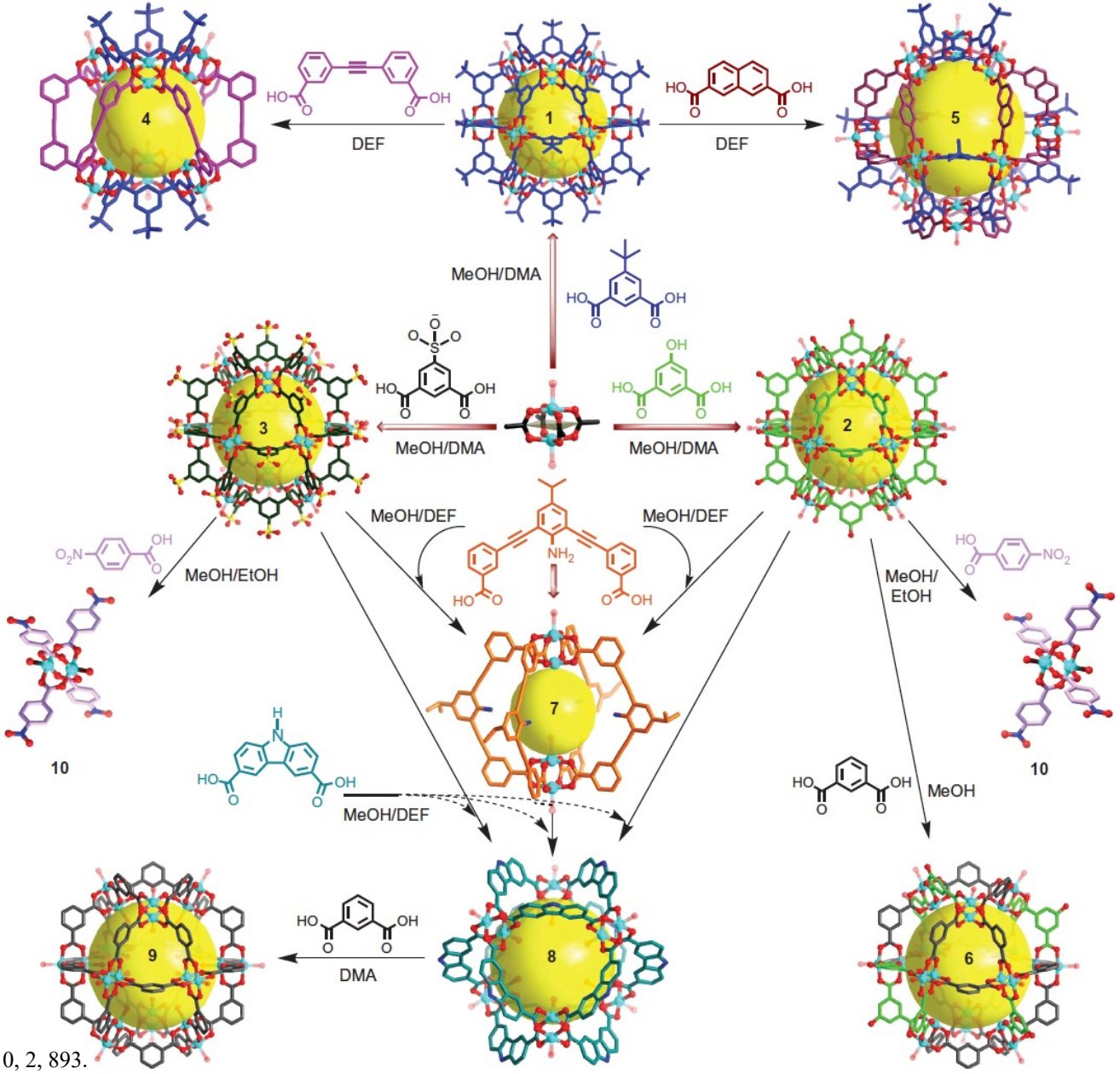




Tranchemontagne et al. *Chem.Soc.Rev.*, 2009, 38, 1257.

Hiroyasu Furukawa et al., *Science*, 341 120444.

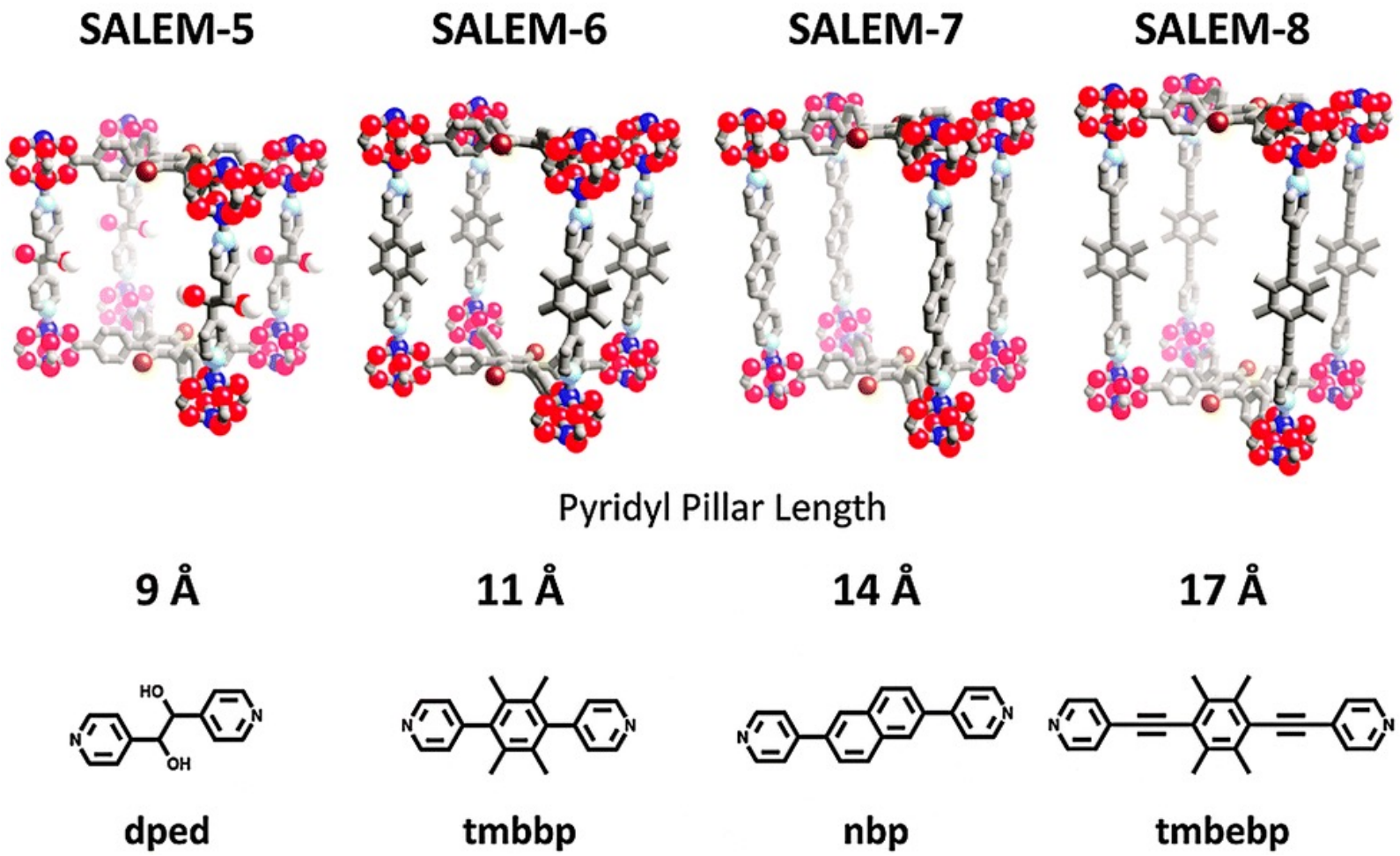
Metal-organic Polyhedra



Li, Zhu, *Nature Chemistry*, 2010, 2, 893.

Most common structures

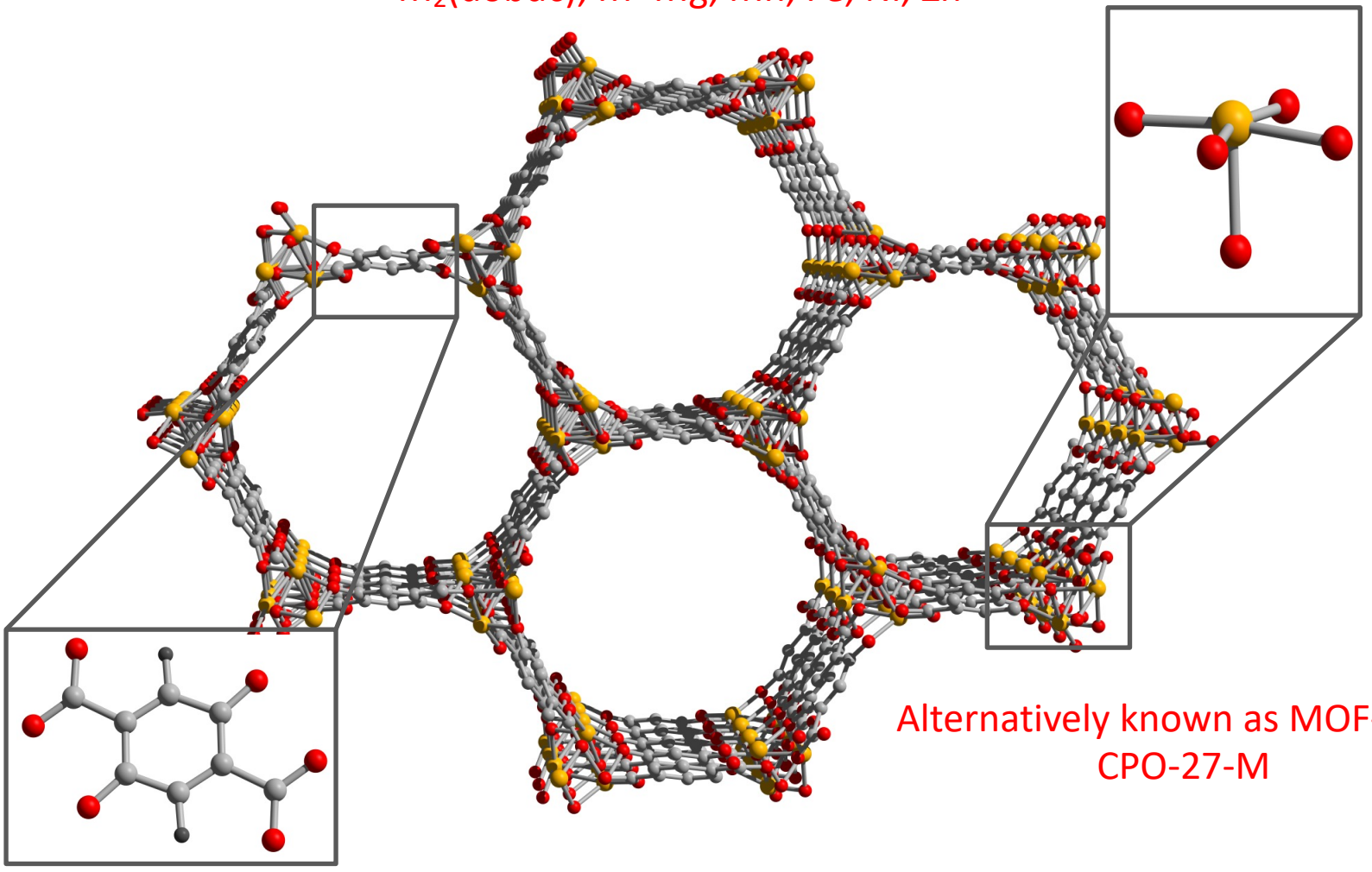
Bipyridine based MOFs



Christoph Janiak et al, *New J. Chem*, **34,** 2366-2388
Pravas Deria et al, *Chem. Soc. Rev.,* **43**, 5896

MOF-74 structure

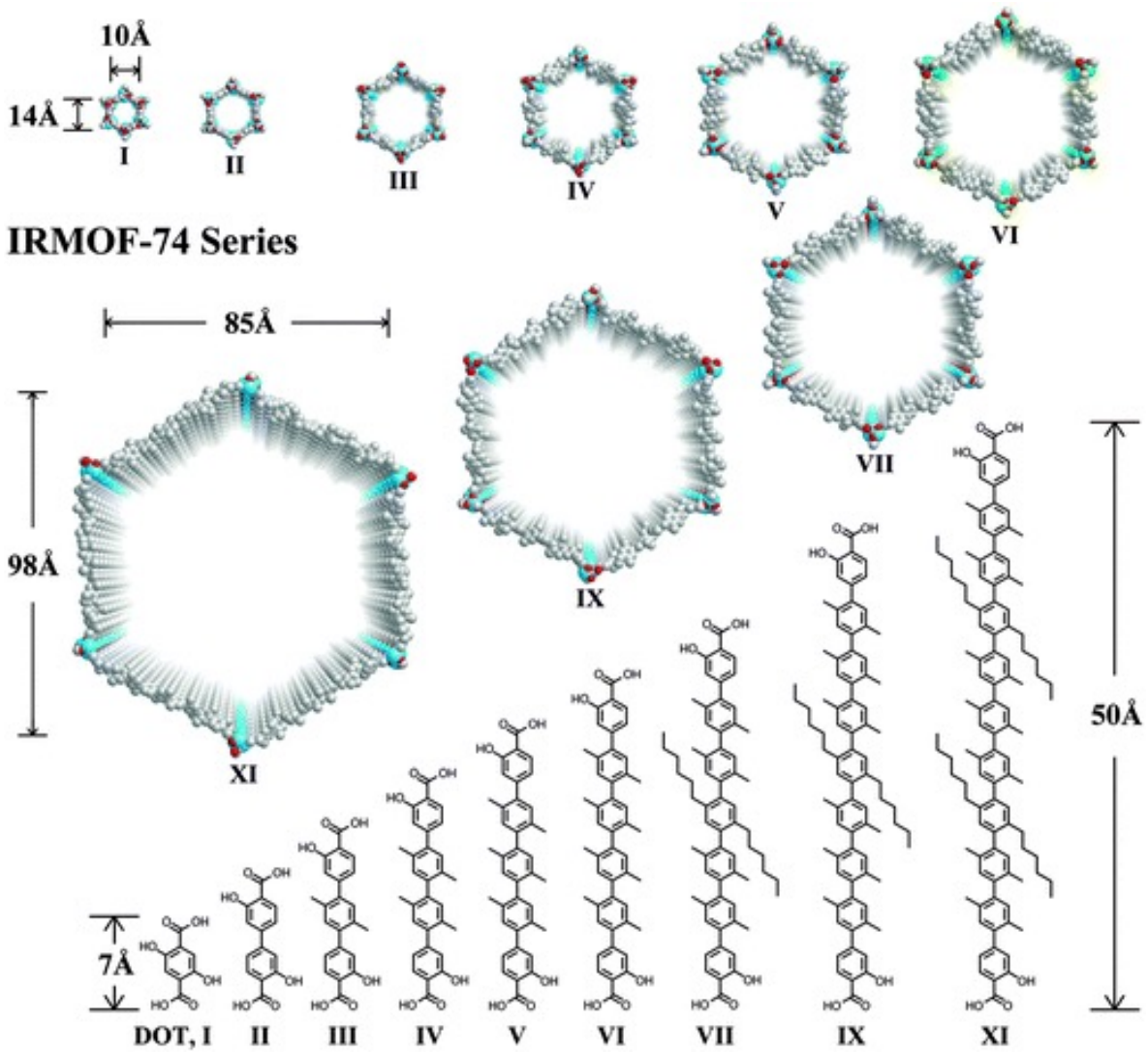
M_2(dobdc), M=Mg, Mn, Fe, Ni, Zn



Alternatively known as MOF-74 or CPO-27-M

Rosi, Kim, Eddaoudi, Chen, O'Keeffe, Yaghi, *J. Am. Chem. Soc*., **2005**, *127*, 1504.
Dietzel, Morita, Blom, Fjellvåg, *Angew. Chem., Int. Ed*., **2005**, *44*, 6354.

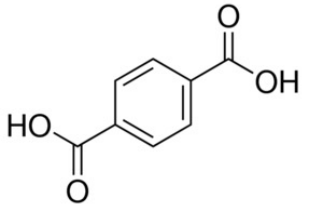
Ligands



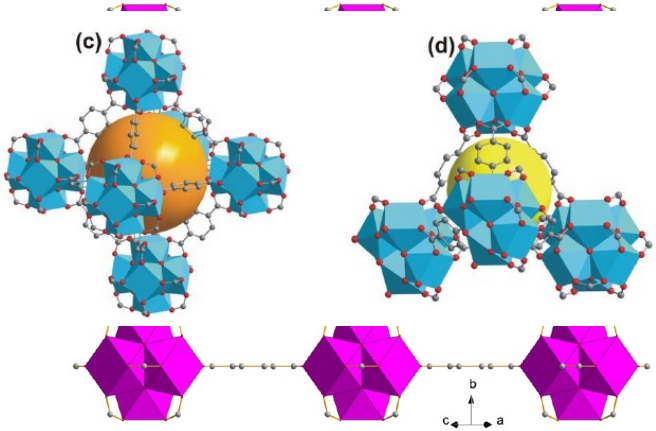
Deng et al. Science 336, (6084) 1018.

UIO-66 and analogs

UiO-66 (Universitetet i Oslo)



Zr^{4+} or Hf^{4+}



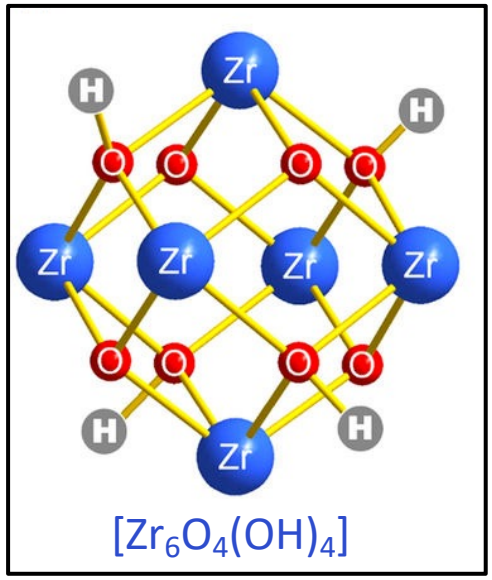
UIO-66

Crystal system: ?

Space group: *Fm*-3*m*

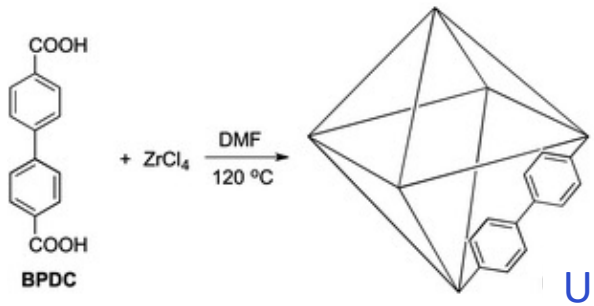
a = 20.7465 Å

V = 8929.65 Å^3

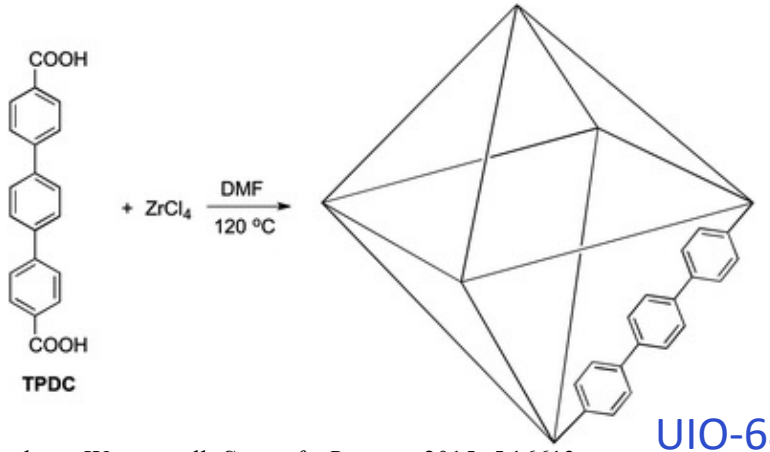


$[Zr_6O_4(OH)_4]$

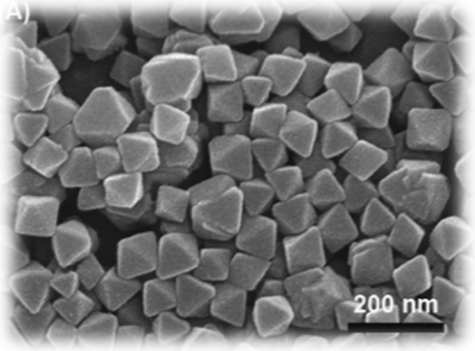
$-2H2O = Zr_6O_6(CO_2)_{12}$



UIO-67



UIO-68



Special Attributes

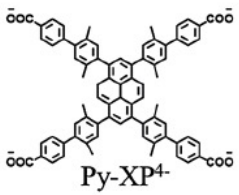
- Cheap (based on Zr4+ and terephthalic acid)
- High porosity
- High thermal stability
- High stability to hydrolysis
- Easy to synthesize
- Extremely versatile

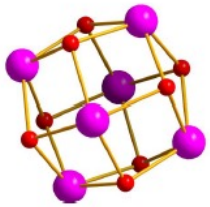
Chenghong Wang et all, *Scientific Reports*, 2015, ***5*** 16613

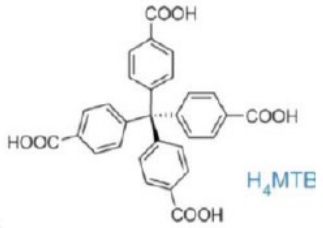
Sergio J. Garibay et all, *Chem. Commun.* 2010, **46,** 7700-7702

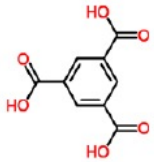
Min Kim et all, *CrystEngComm,* **14**, 4096-4104

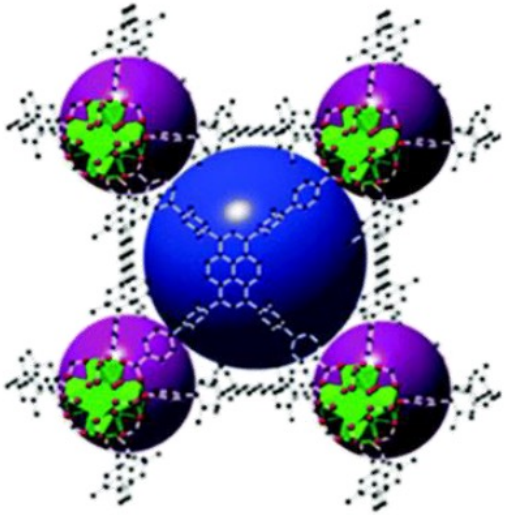
UIO-66 analogs



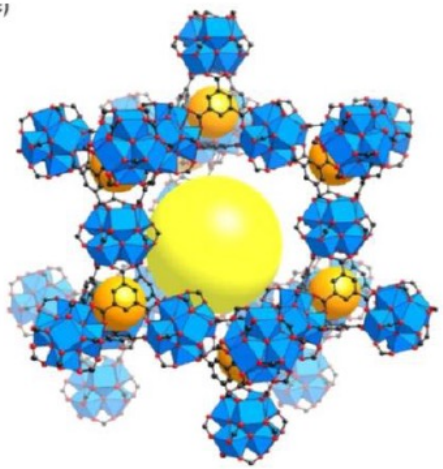




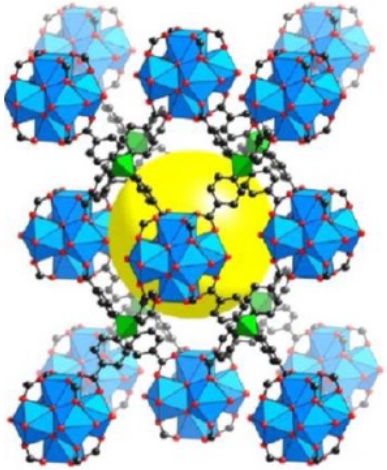




NU-1101



MOF-808

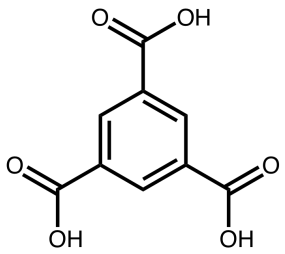


MOF-812

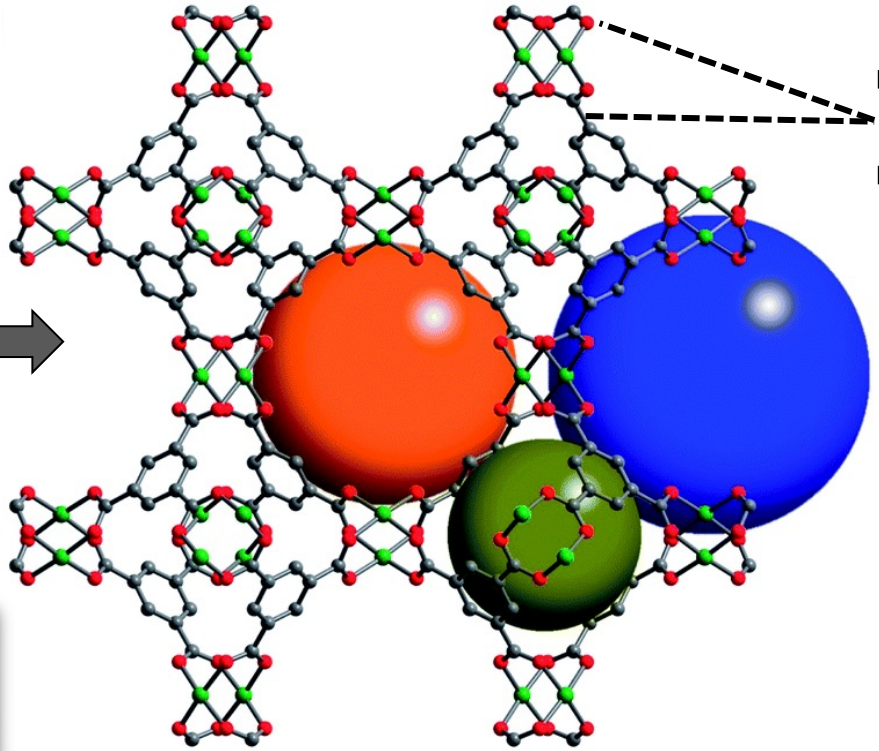
Furukawa, et al *J. Am. Chem. Soc.*, **2014**, 136, 4369.

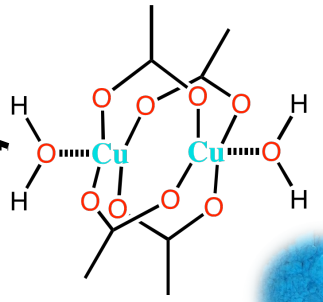
HKUST-1, Cu-BTC, Basolite C300

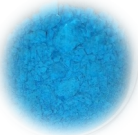
HKUST-1 (Hong Kong University of Science and Technology)



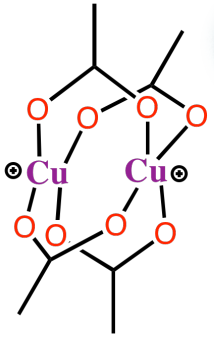
Cu^{2+}

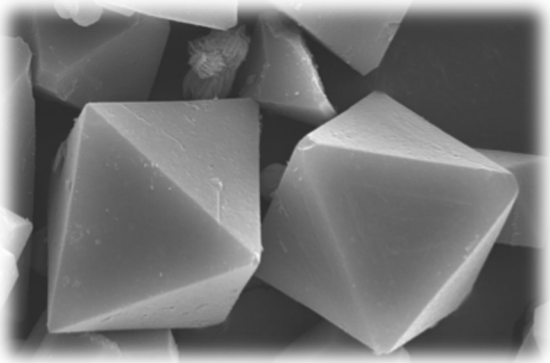






Δ → H_2O





M = Cr, Fe, Ni, Cu, Mo

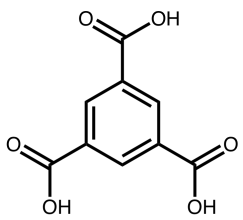
Fm3m $a = 26.2243(5)$

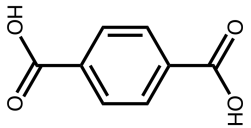
Williams et all, *Science,* **283,** 1148-1150

Gregory W. Peterson et all, *Ind. Eng. Chem. Res.,* **54**, 3626-3633

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

MIL-100 (Fe-BTC) and MIL-101 (Fe-BDC)



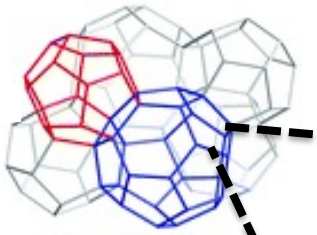


M^{3+}

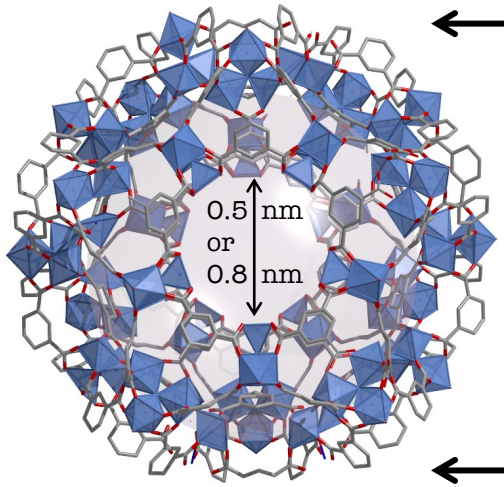
Δ

M = Fe, Al, Cr

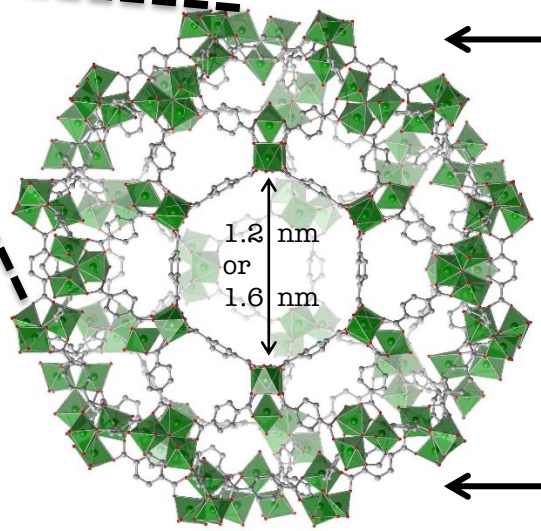
H_2O or DMF



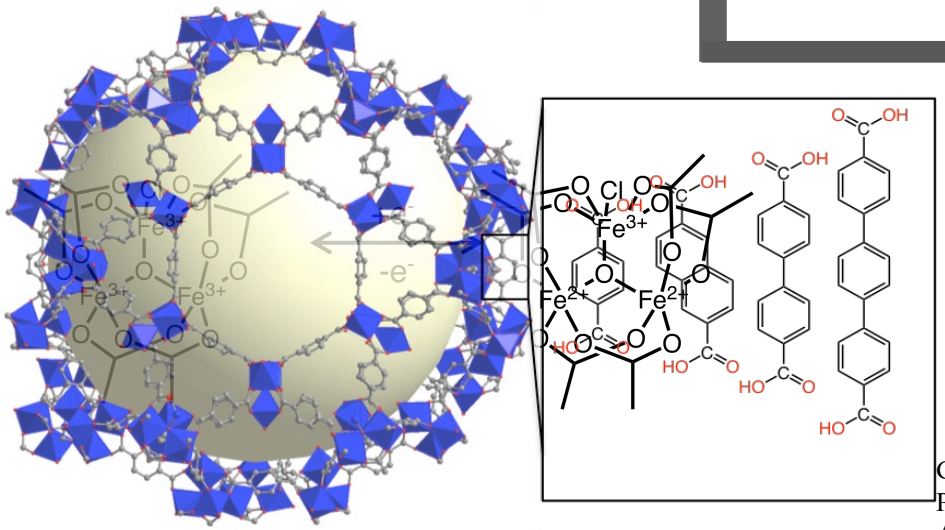
MTN Topology



2.5 nm
&
2.9 nm



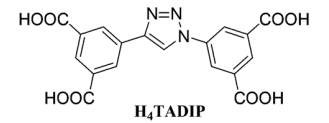
2.9 nm
&
3.4 nm



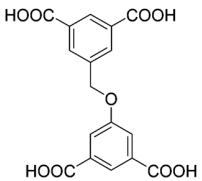
Gerald Ferey et all, *Science*, **309,** 2040-2042
Patricia Horcajada et all, *Chem. Commun. 2820-2822*
Amarajothu Dhakshinamoorthy et all, *ACS Catal.*, **2**, 2060-2065

Tetracarboxylates

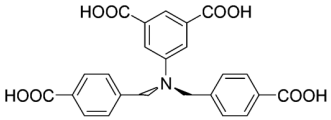
Tetracarboxylates



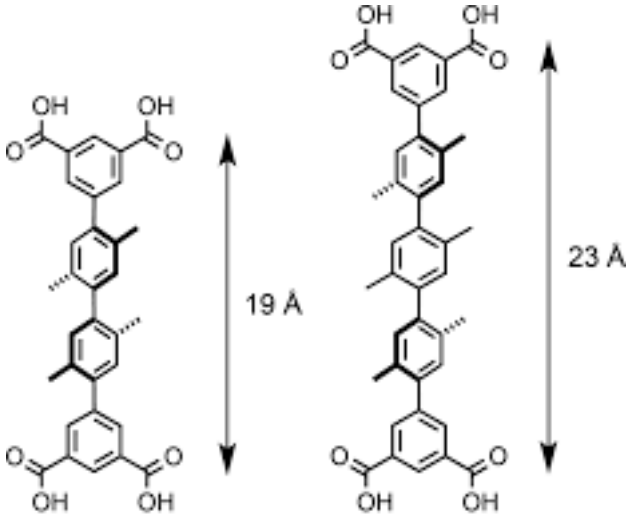
H_4TADIP



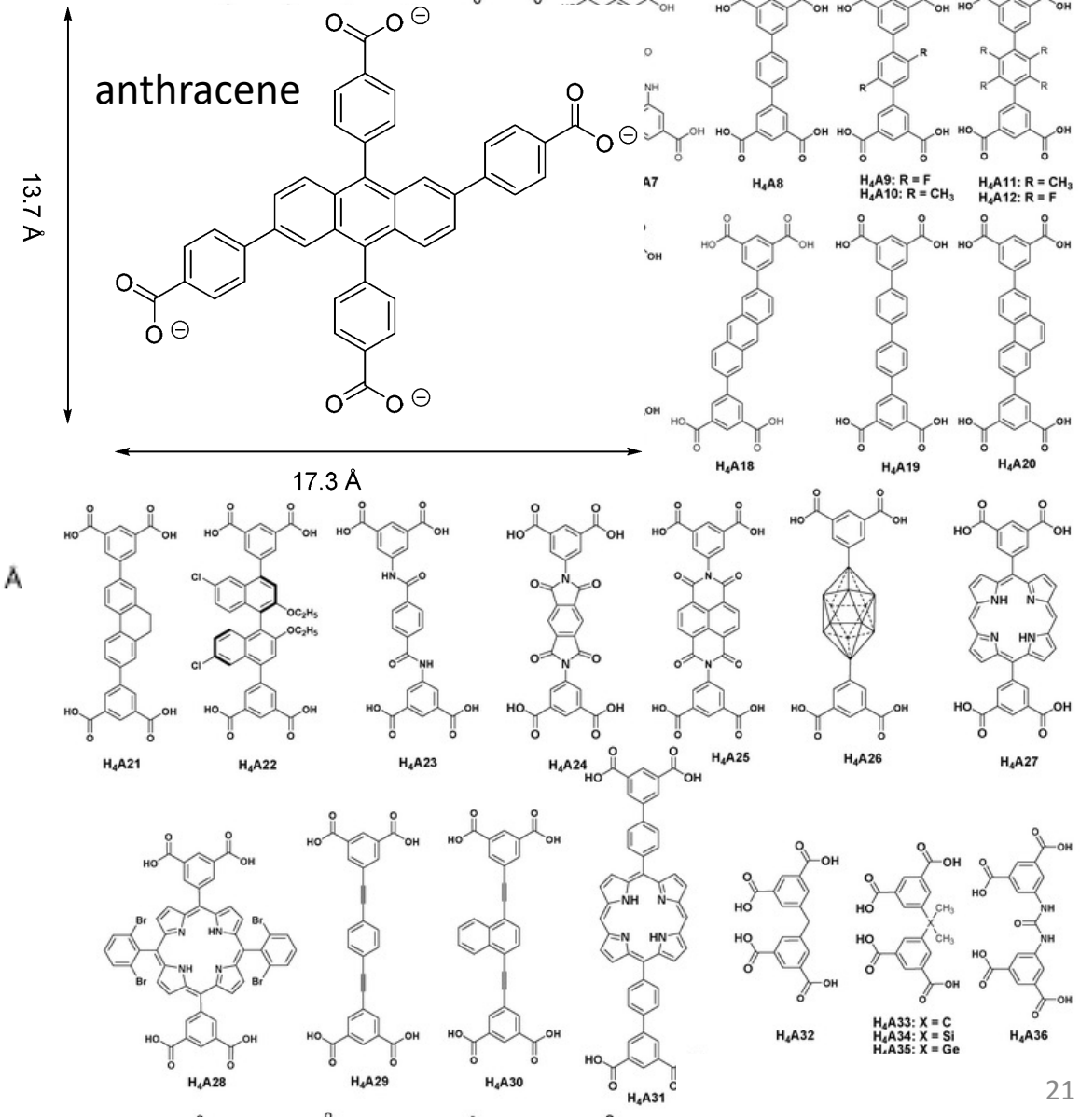
H_4DBIP



$H_4BCBAIP$



H_4L^{IV} H_4L^{V}

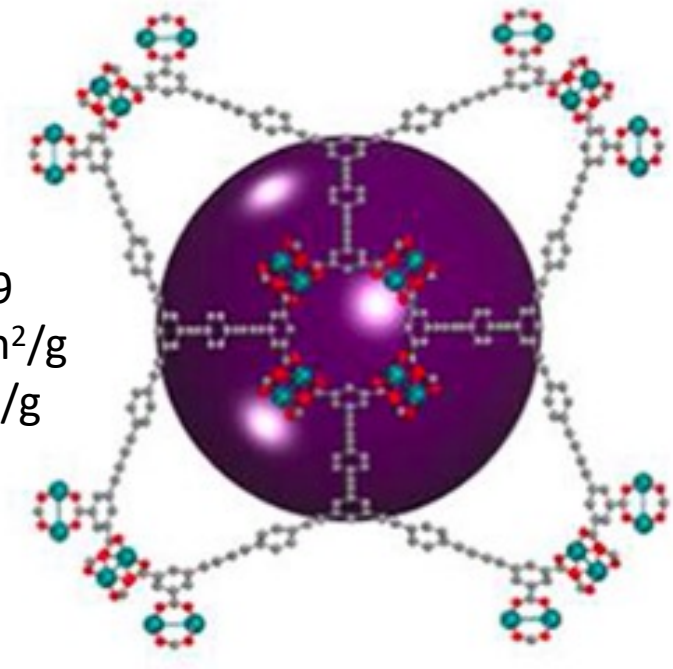


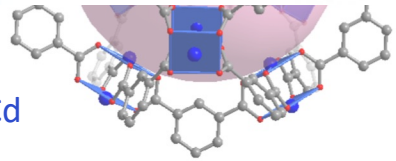
Yong yan et all, *J. Am. Chem.* Soc, **138,** 3371-3381
Libo Sun et all, *Inorg. Chem. Front.*, **1,** 478
A. V. Vinogradov, *Dalton Trans.*, **45,** 7244
Hong-Mei Zhang et all, *CrystEngComm,* **17,** *3181*
Wen-Jing Yu et all, CrystEngComm, **15**, 7732

Hexacarbolyates

M-TDPAT framework

NU-109
7010 m^2/g
3.75 cc/g

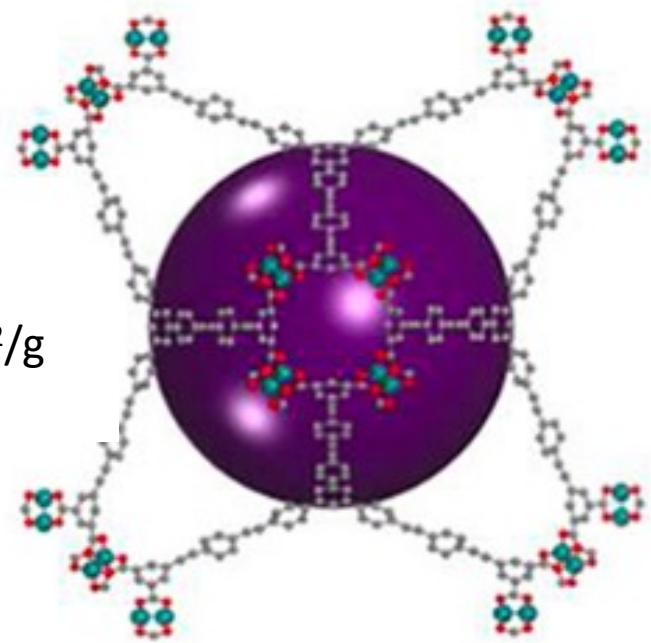


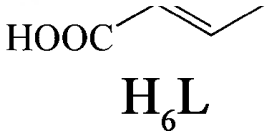


Open M^{2+} site
M = Co, Ni, Cu, Zn, and Cd

2000 m^2/g

NU-110
7140 m^2/g
4.4 cc/g





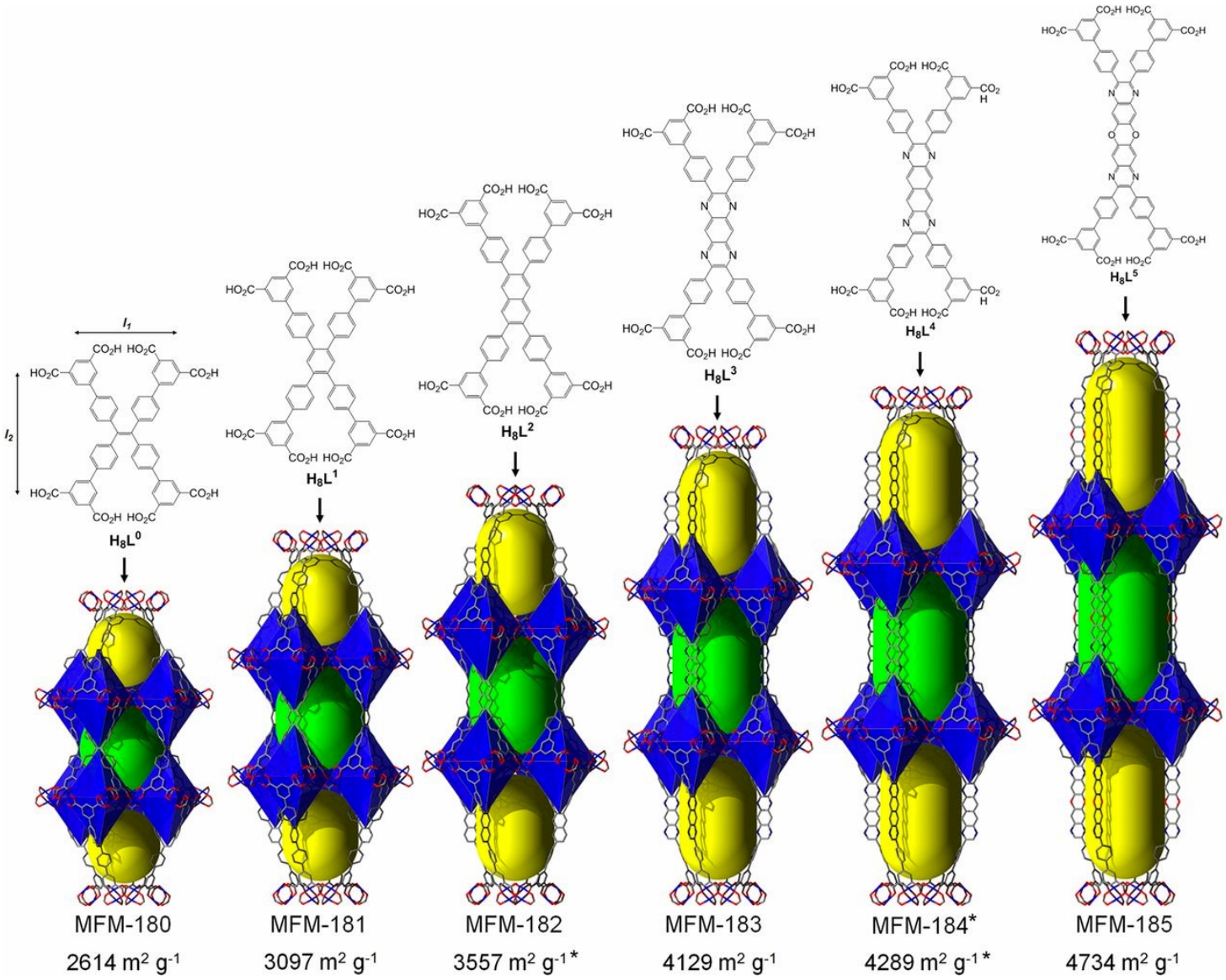
H_6L

NU-100

Farha, et al *Nature Chemistry*,2010, 2, 944

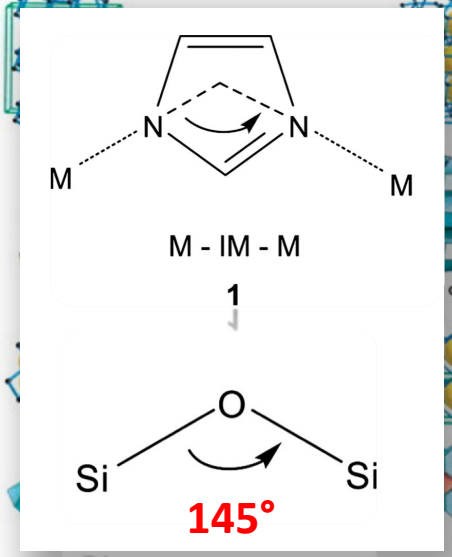
Hauhan Wu et al, *J. Phys. Chem. C,* **116**, 16609-16618
Baiyan Li et al, *Angew. Chem. Int. Ed.,* **51**, 1412-1415

octacarboxylates



Florian Moreau et al, *PNAS,* 2017, **114**, 3056-3061

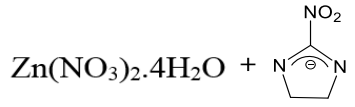
Zeolitic imidazolate Frameworks

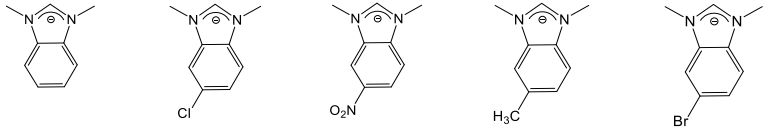


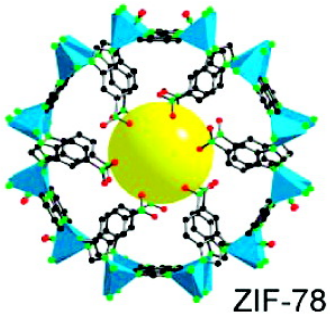
ZIF-4
ZIF-62
ZIF-69
ZIF-68
ZIF-70
cag
gme
ZIF-73
ZIF-77
ZIF-8
ZIF-65
ZIF-67
frl
sod
Basolite Z1200
ZIF-72
ZIF-74
ZIF-75
ZIF-11
ZIF-12
ZIF-71
lcs
gis
rho
ZIF-3
ZIF-10
ZIF-60
ZIF-20
ZIF-21
ZIF-76
dft
mer
lta

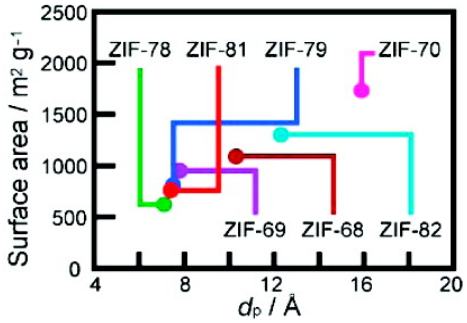
Zeolitic imidazolate Frameworks

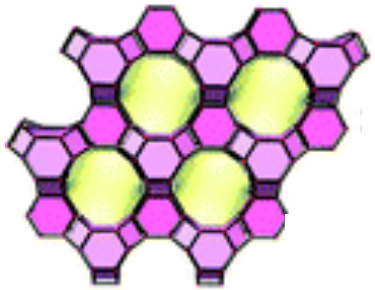
Large Pore GME ZIFs





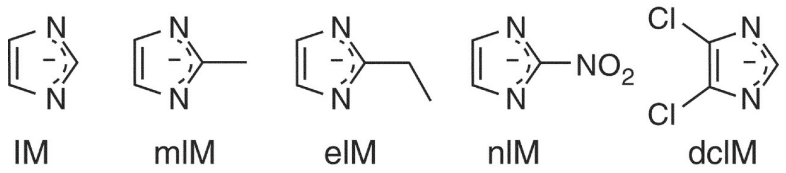


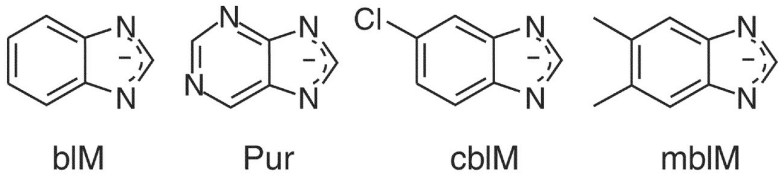


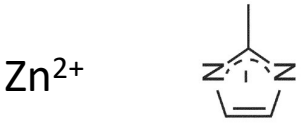


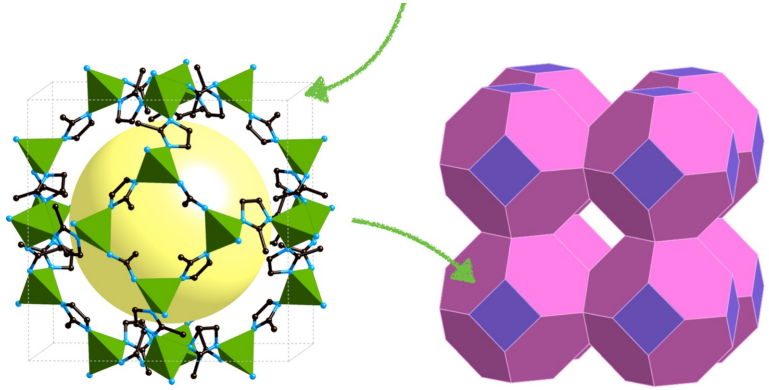
GME Pore apperture = 3.8 to 13.1 Å

SOD ZIFs









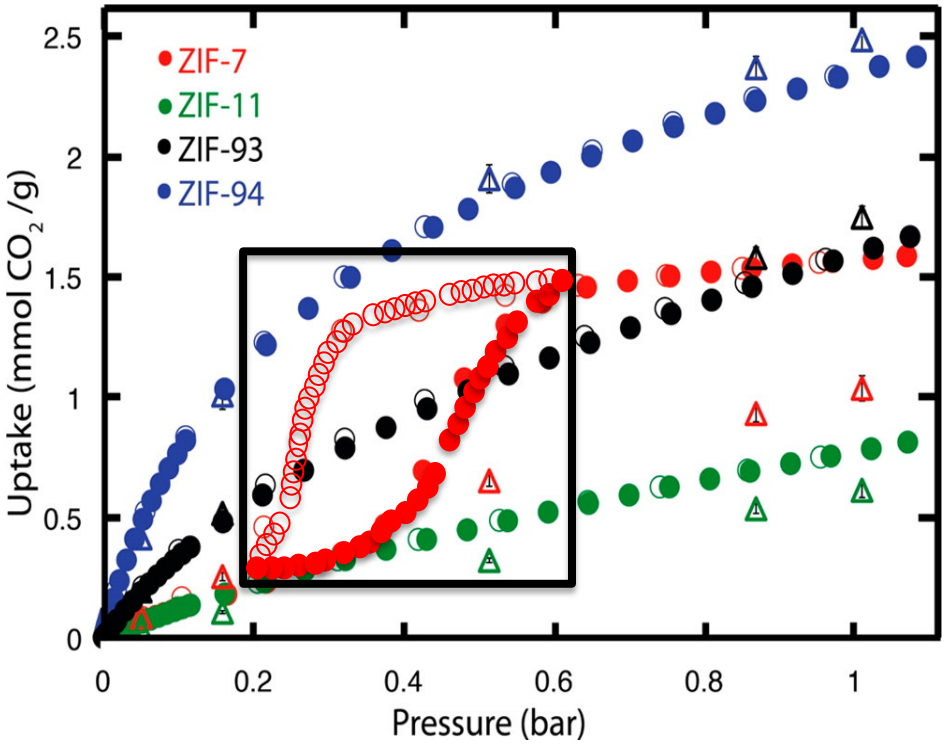
ZIF-8 cage diameter = 11.4

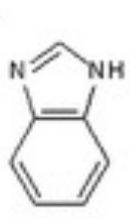
Kyo Sung Park et all, *PNAS*, **103**, 10186-10191
Xiao-Chun Huang, *Angew. Chem. Int. Ed.*, **45**, 1557-1559
Rahul Banerjee, *Science*, **319**, 939-943

Varying topology in ZIFs

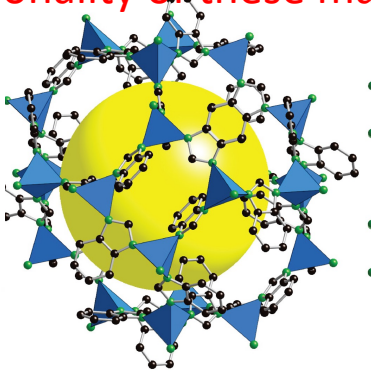
There are currently no studies to assess the functionality of these materials

ZIF	composition[a]	topology	density[a] (g cm^{-3})	pore volume[a,b] (cm^3 g^{-1})	pore diameter[a] (Å)
-7	$Zn(bIm)_2$	sod	1.24	0.207	7.5
-11	$Zn(bIm)_2$	rho	1.02	0.457	14.9
-93	$Zn(almeIm)_2$	rho	0.99	0.464	17.9
-94	$Zn(almeIm)_2$	sod	1.32	0.229	9.1

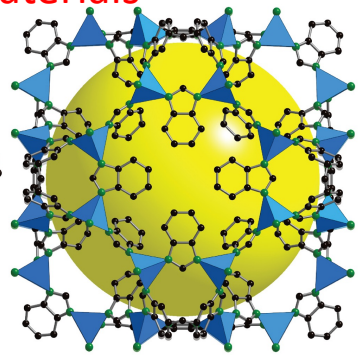




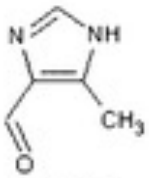
bIm



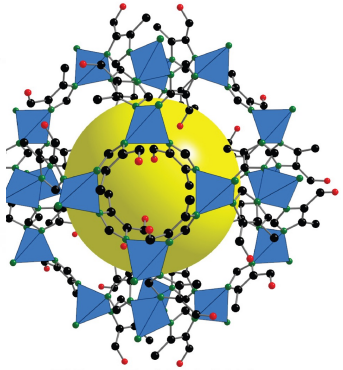
$ZIF\text{-}7\ Zn(C_7N_2H_5)_2$



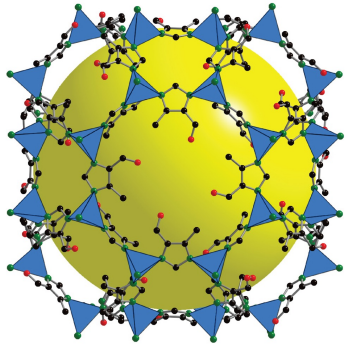
$ZIF\text{-}11\ Zn(C_7N_2H_5)_2$



almeIm

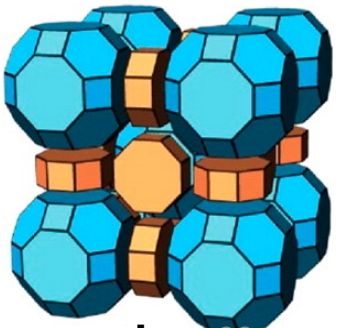


$ZIF\text{-}94\ Zn(C_5N_2OH_5)_2$



$ZIF\text{-}93\ Zn(C_5N_2OH_5)_2$

sod



rho

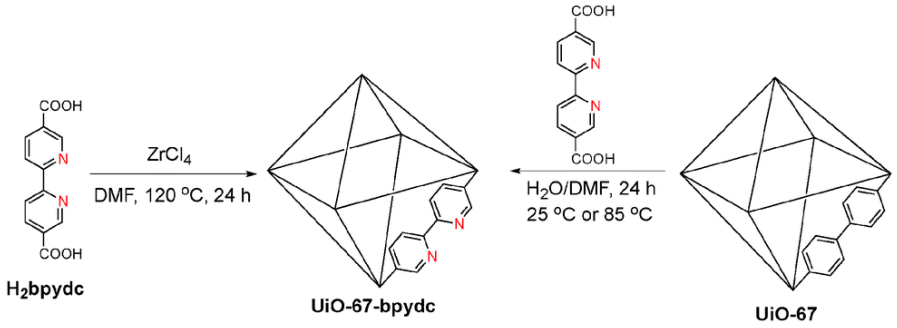
C. Gücüyener et al. *J. Am. Chem. Soc.* **2010**, 132, 17704.

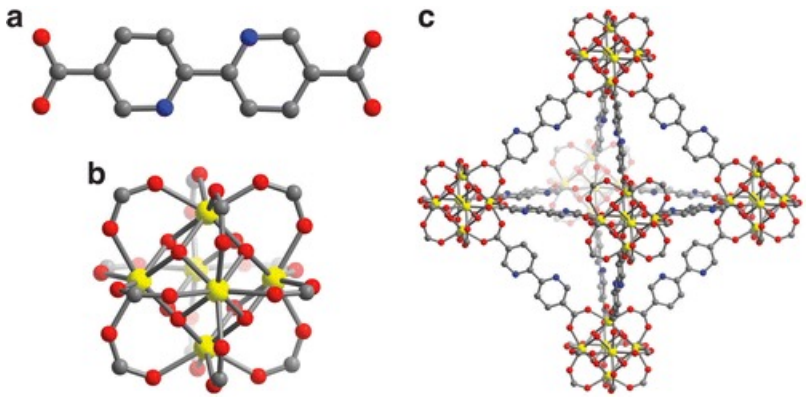
W. Morris et al. *J. Phys. Chem. C* **2012**; 116, 24084.

Post-Synthetic Modification

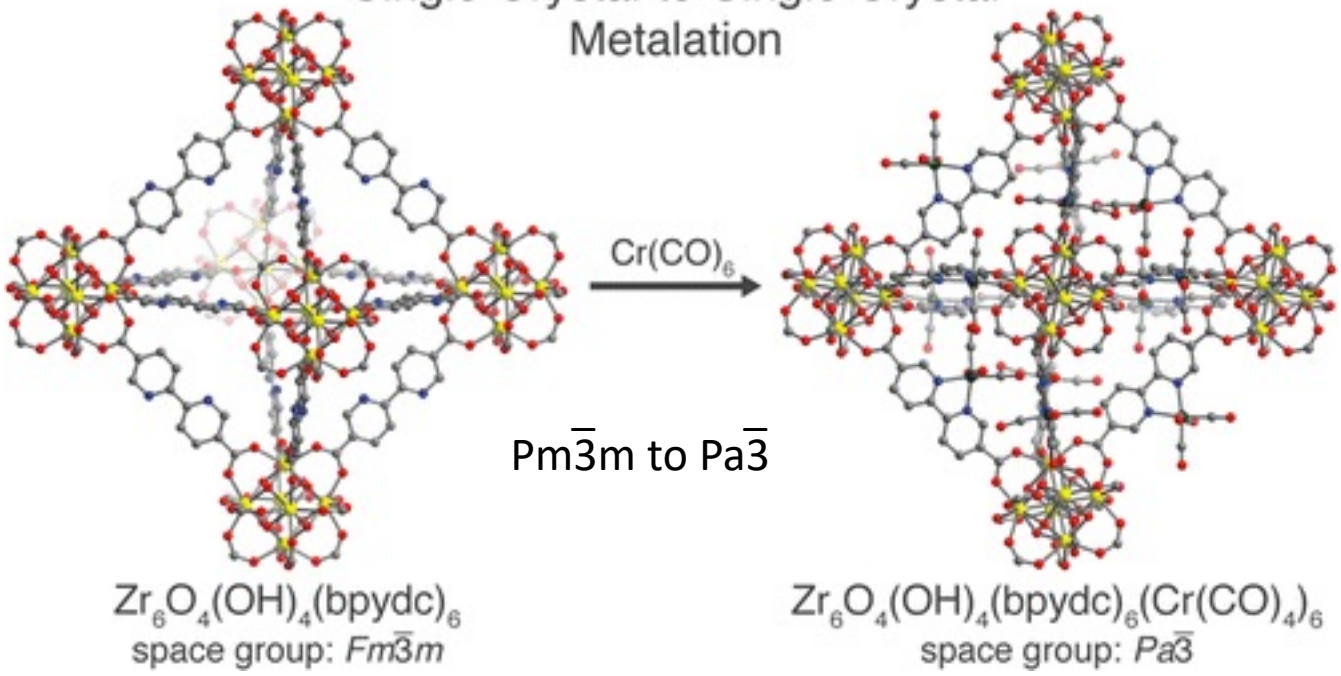
How many ways can we think of to change their properties?

Post-Synthetic Metalation and ligand exchange

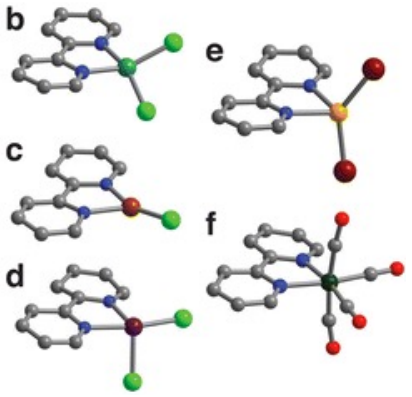




Single-Crystal-to-Single-Crystal Metalation

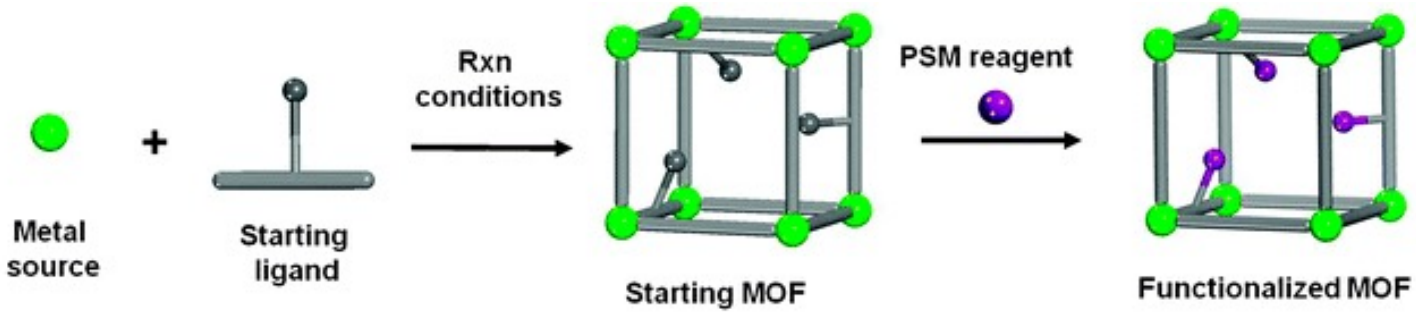


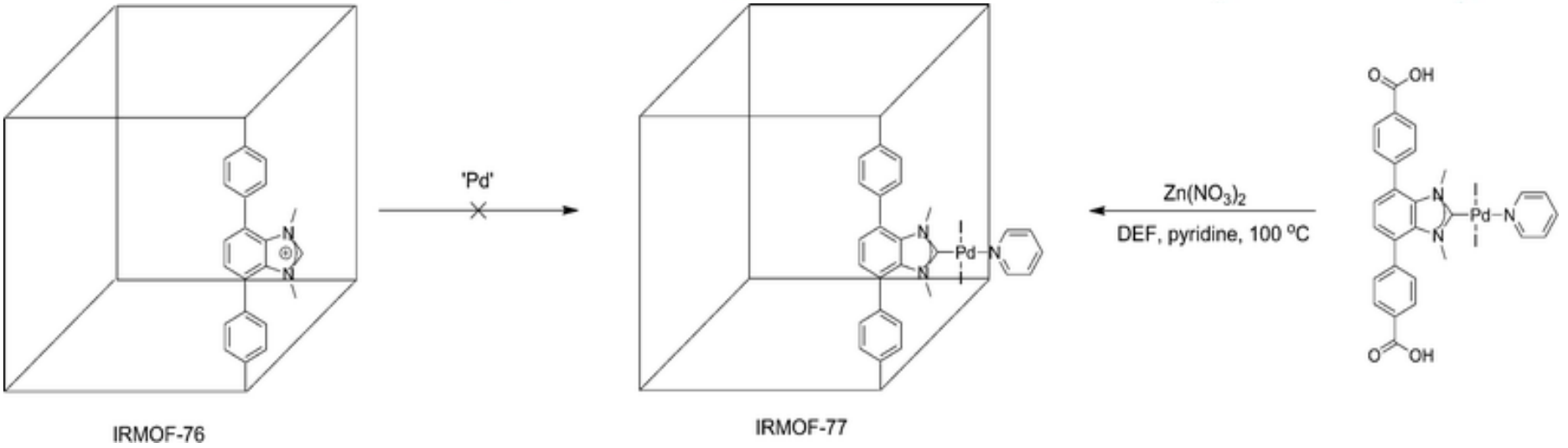
Pm3̄m to Pa3̄



Miguel I. Gonzalez et all, *Inorg. Chem.* ***54,*** *2995-3005*
Xinle Li et all, *ACS Catal.,* **6,** 6324-6328
Honghan Fei et all, *Chem. Commun,* **50,** 4810

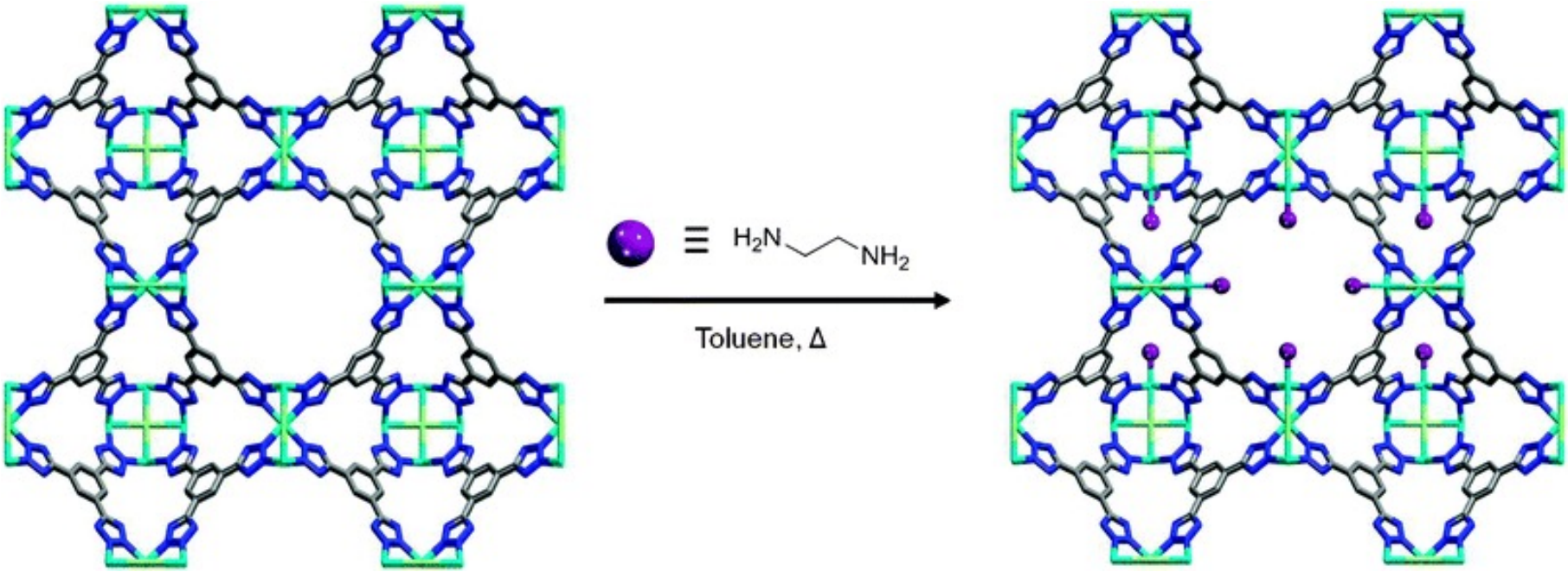
Modification methods





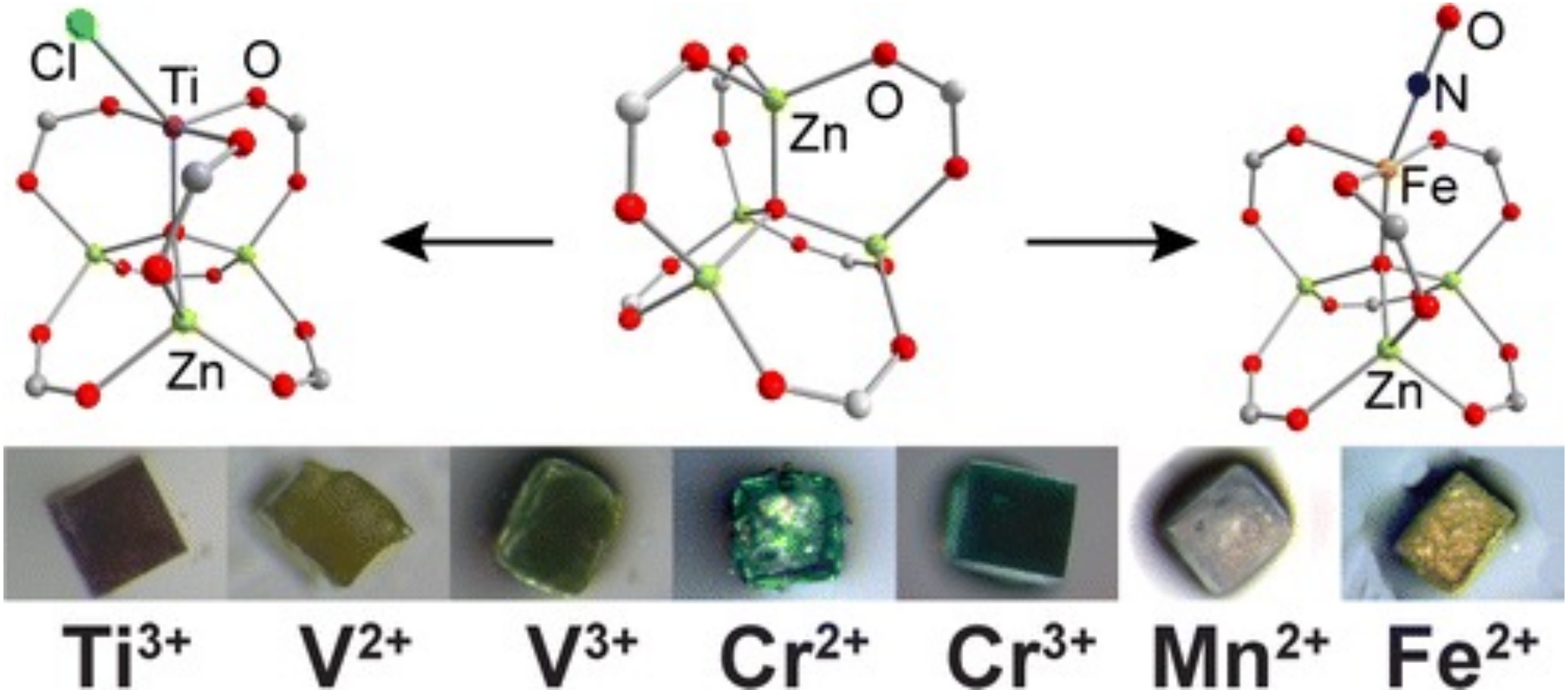
Tanabe et al, *Chem. Soc. Rev.*, **40**, 498-519

Post-synthetic appendage to open metals



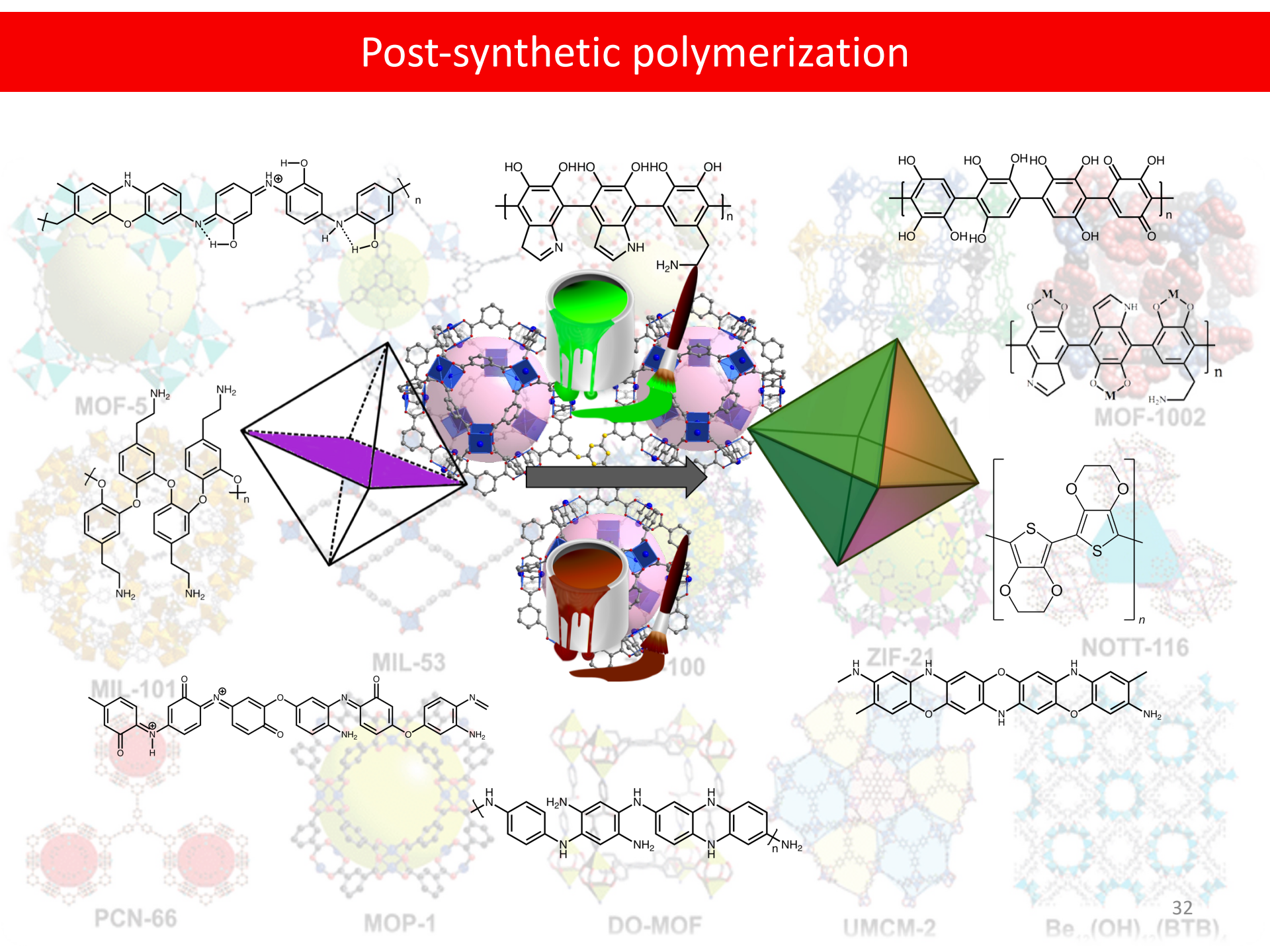
Thomas M. McDonald et all, *J. Am. Chem. Soc.,* **134**, 7056-7065
Thomas M. McDonald et all, *Nature*, **519**, 303-308

Post-synthetic metal exchange

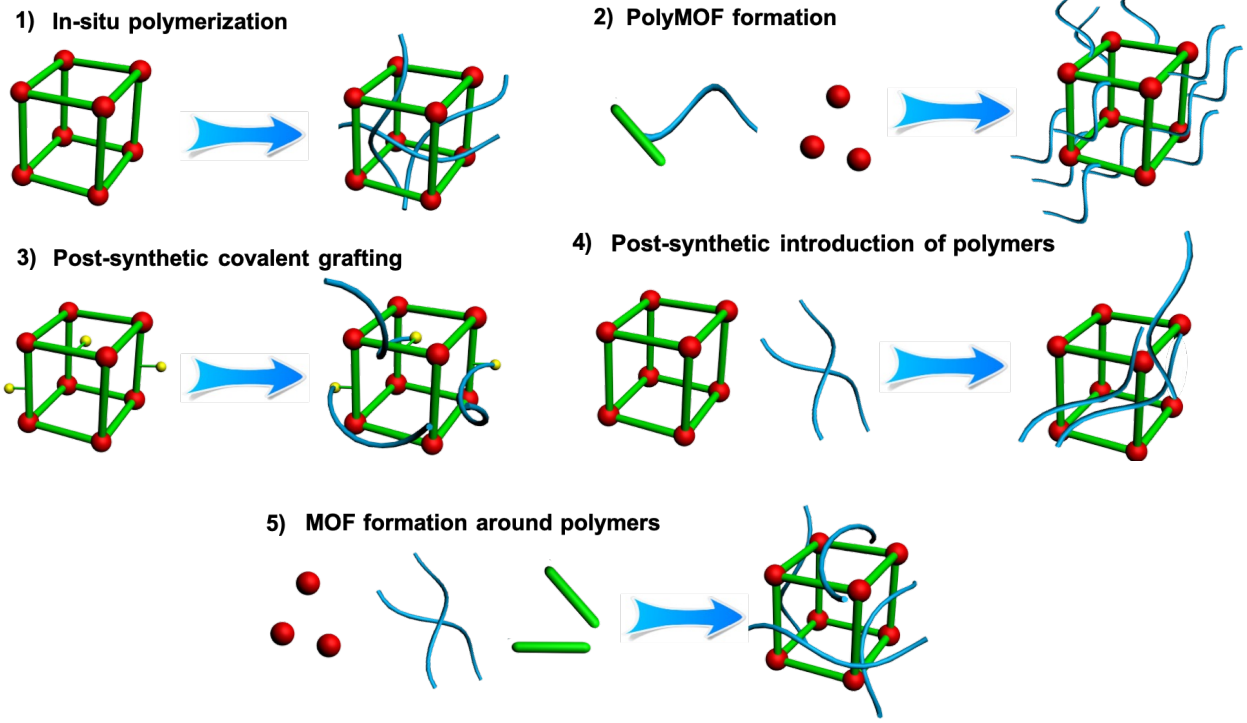


Broek, Dinca, *J. Am. Chem. Soc.*, 2013, 135 (34), 12886.
Brozek, Dinca, *Chem. Sci.*, 2012,3, 2110.

Post-synthetic polymerization



Post-synthetic polymerization



MOF Improvements

1. Mechanical stability
2. Chemical stability
3. Conductivity
4. Control dispersion
5. Control assembly
6. Enhance performance
7. Introduce non-native functionality
8. Shaping MOFs

Yang, Karve, Justin, Kochetygov, Espin, Asgari, Trukhina, Sun, Peng, Queen, *Coord. Chem. Rev.* **2021**, 427, 213525.
Uemura, Kitagawa, Horike, Kawamura, Kitagawa, Mizuno, Endo, Chem. Commun. **2005,** 5968.
Uemura, Yanai, Watanabe, Tanaka, Numaguchi, Miyahara, Ohta, Nagaoka, Kitagawa, *Nat. Commun.* **2010** 1, 83 .
Zhang, Nguyen, Miller, Cohen, *Angew. Chem. Int. Ed.,* **2015**, 54, 6152.