# Porosity in Metal-organic compounds

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# Introduction to Reticular Chemistry of Metal-organic frameworks (MOFs)

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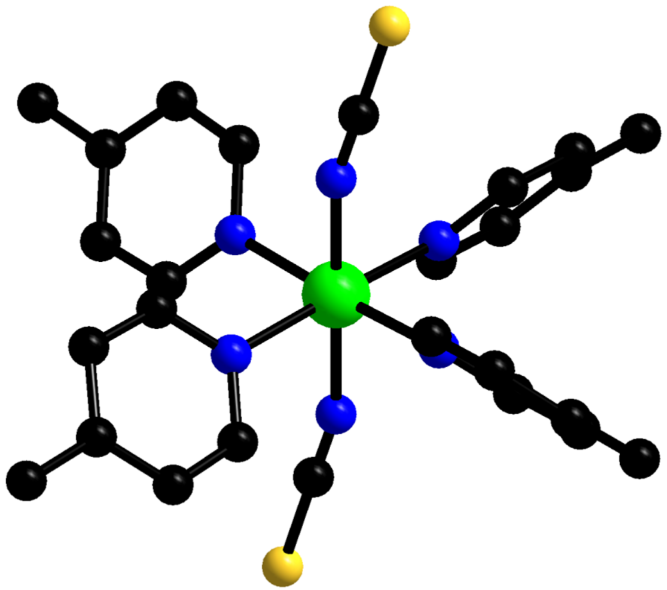
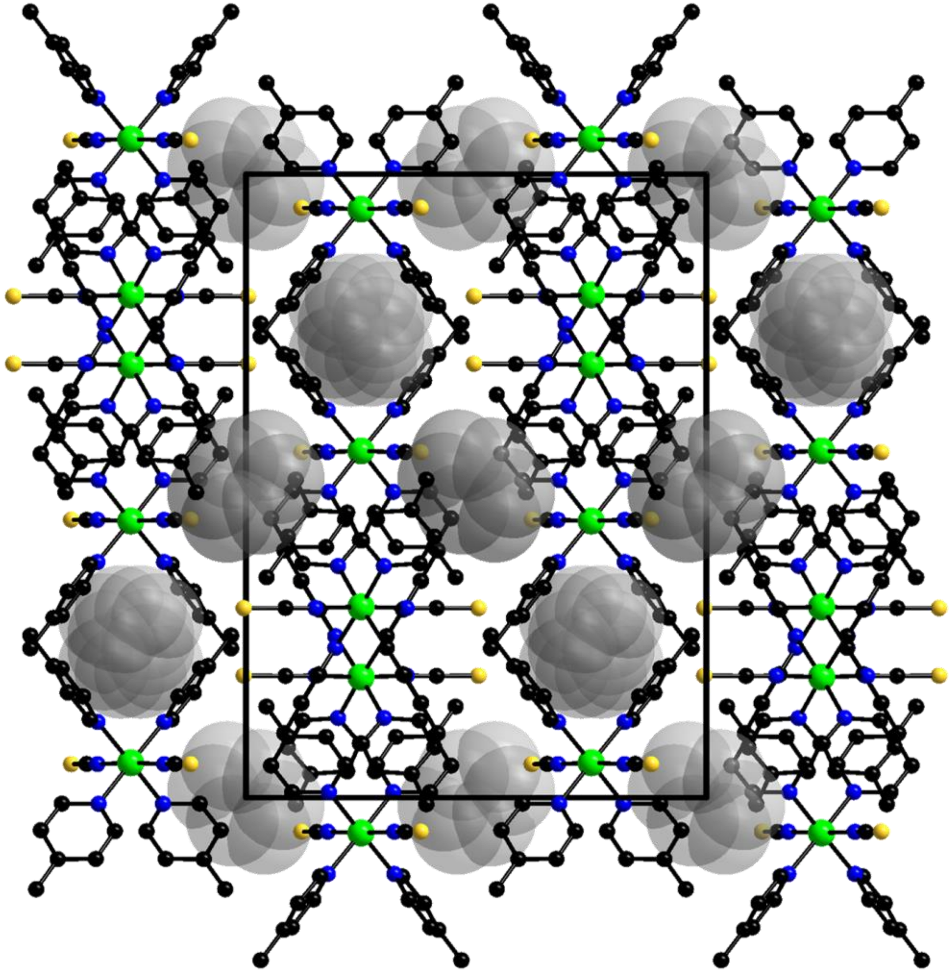
March 12th 2015

# Porosity in Metal-organic compounds

# Werner complexes



*ß*-M(4-MePY)$_4$(NCS)$_2$
(M = $Ni^{2+}$, $Co^{2+}$)

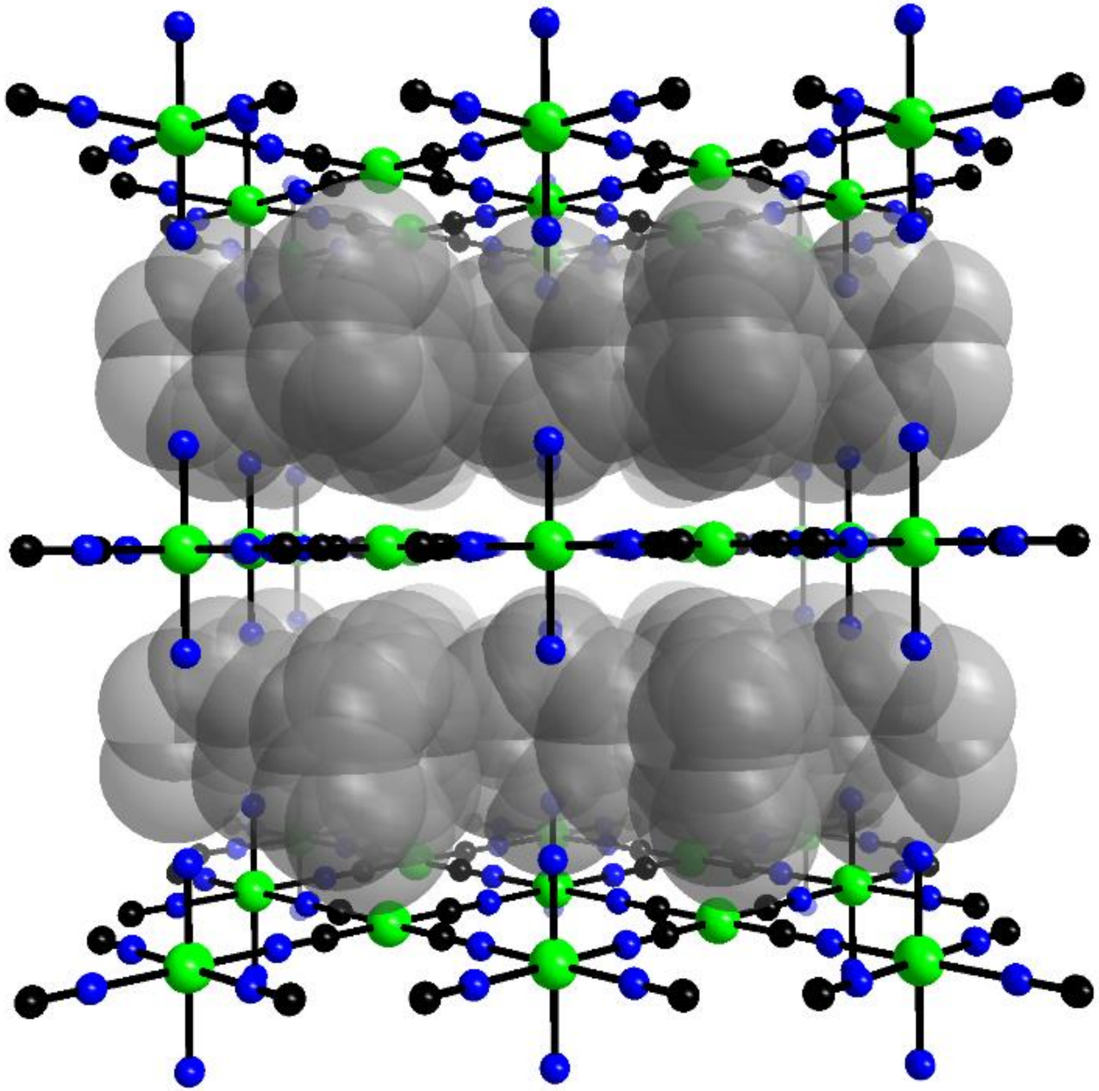


- zigzag channels occupied with benzene
- Barrer (1969): Porosity towards $N_2$, $O_2$, noble gases and hydrocarbons.

Christian *et al., J. Am. Chem. Soc.* **1957**, *79*, 5870; Barrer *et al., J. Chem. Soc. A* **1969**, 1717.

# Hofmann clathrates

$[Ni(CN)_2(NH_3)]\cdot C_6H_6$

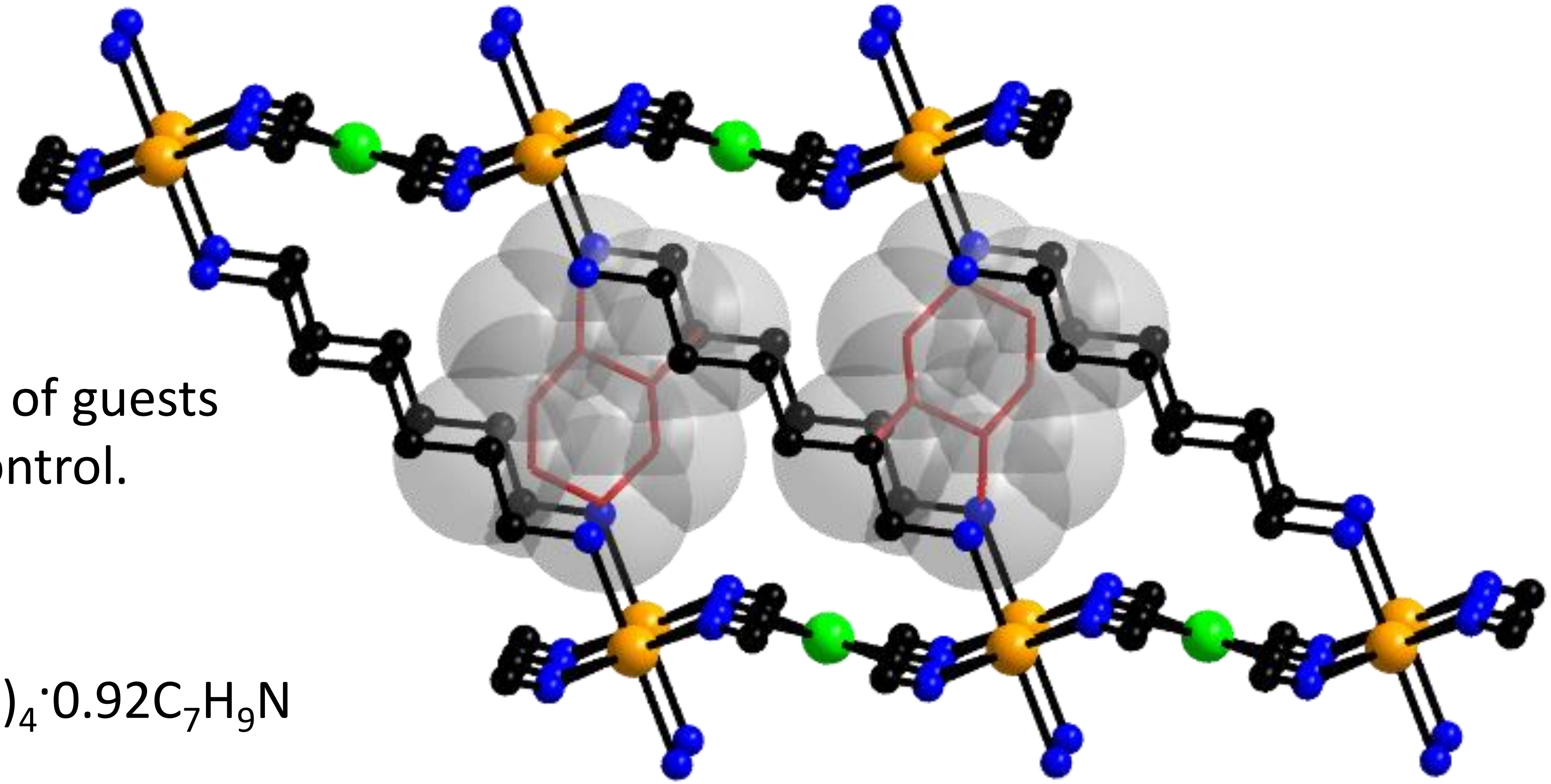


- General formula: $[M^1(NH_3)_2M^2(CN)_4]^{\cdot}G$
- Firstly prepared in 1897
- Structure determination by Powell in 1952
- Encapsulation of aromatic guests such as aniline, benzene, thiophene or pyrrole.

Hofmann *et al., Z. Anorg. Chem.* **1897**, *15*, 204; Powell *et al., J. Chem. Soc.* **1952**, 319; Iwamoto *et al., Inorg. Chim. Acta* **1968**, *2*, 313

# Hofmann clathrates

α,ω-diaminoalkanes



- Selective encapsulation of guests through linker length control.
- Here *o*-toluidine

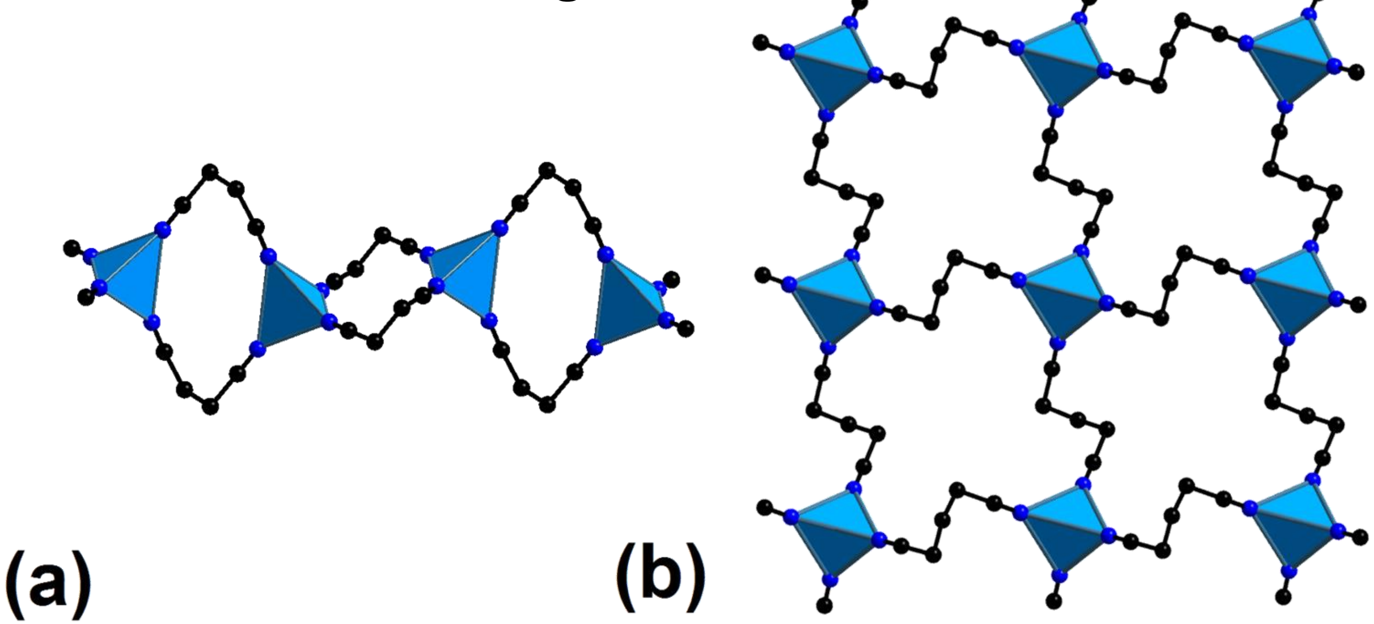
$Cd[NH_2(CH_2)_6NH_2]Ni(CN)_4 \cdot 0.92C_7H_9N$

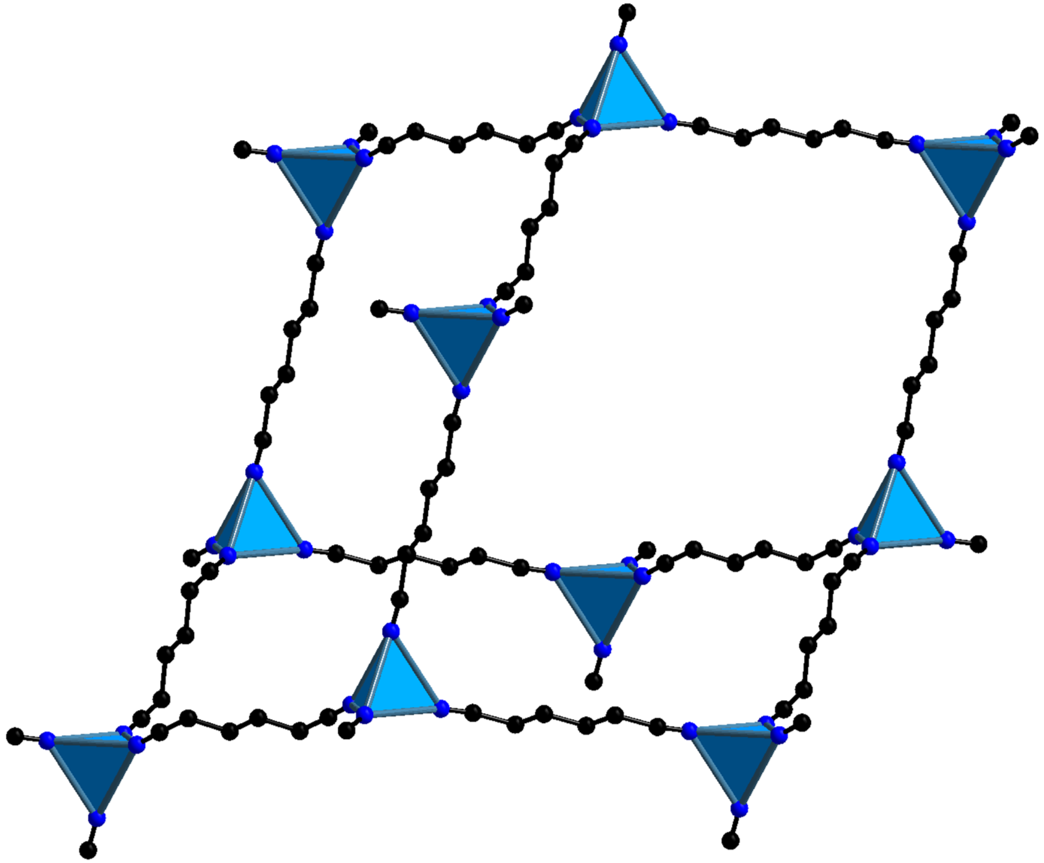
Mathey *et al., Inorg. Nucl. Chem. Lett.* **1977**, *13*, 1; Mathey *et al., Can. J. Chem.* **1977**, *55*, 17; Iwamoto *et al., J. Incl. Phenomena* **1984**, *2*, 351; Iwamoto *et al., Chem. Lett.* **1985**, *14*, 1659.

# Coordination polymers

$[Cu(-CN)_4]^+$

tetrahedral building blocks



1-D chains: succinonitrile

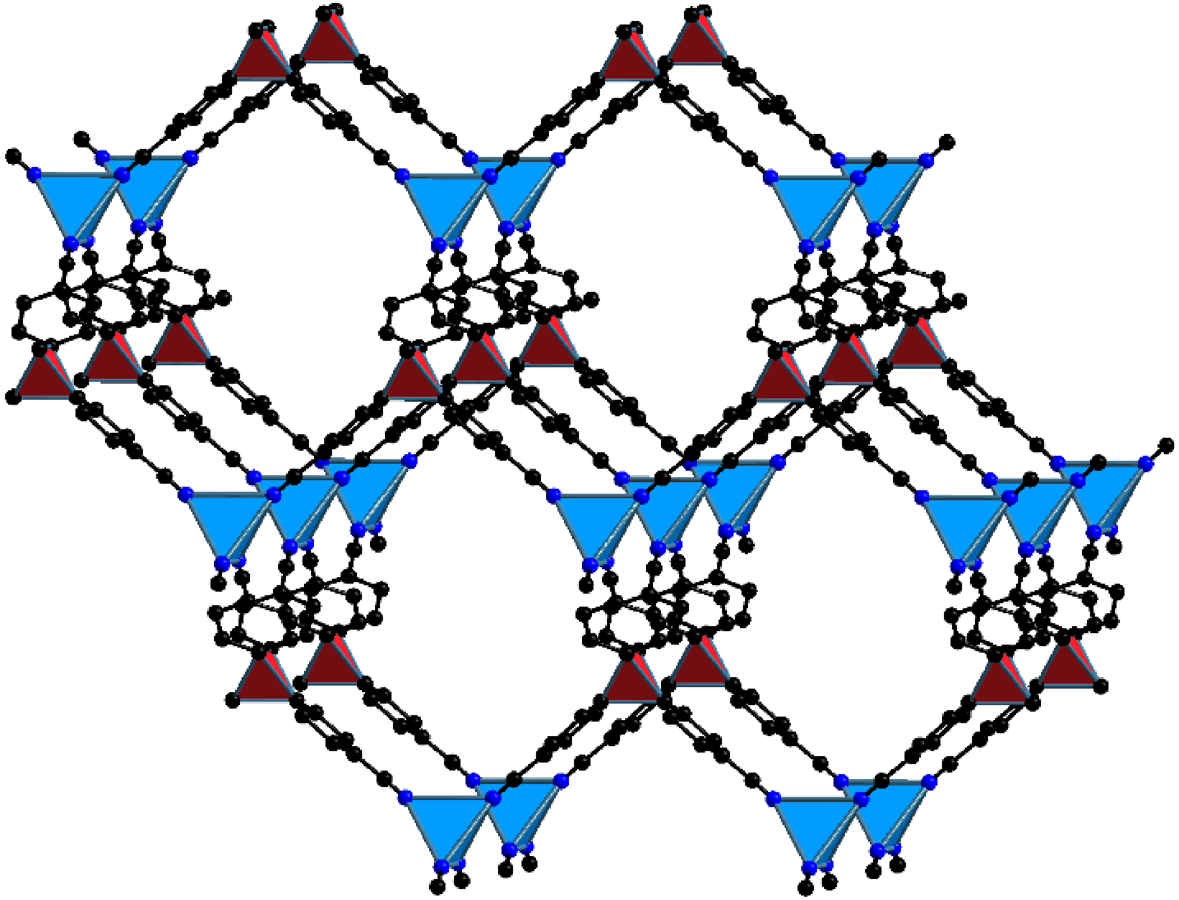
2-D square grid: glutaronitrile

3-D networks: adiponitrile

Saito *et al.*, *Bull. Chem. Soc. Jap.* **1959**, *32*, 741; *Bull. Chem. Soc. Jap.* **1959**, *32*, 1216; *Bull. Chem. Soc. Jap.* **1959**, *32*, 1221.

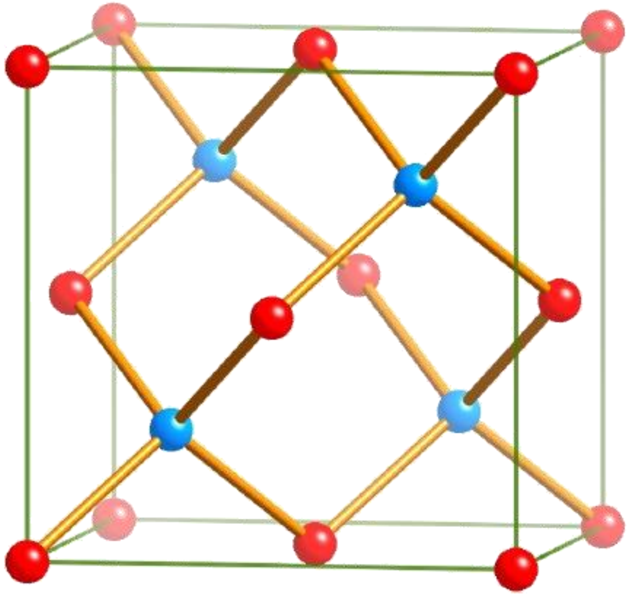
# Coordination polymers – Deliberate Design

$[Cu(-CN)_4]^+$ and $[C(C_6H_4CN)_4]$ tetrahedral building blocks



**Robson (1989)**

$\{Cu[C(C_6H_4CN)_4]\}^+$
**dia-b**



- adamantine cavity ~ 700Å³
- charge balancing $BF_4^-$ counteranions
- exchangeable through $PF_6^-$

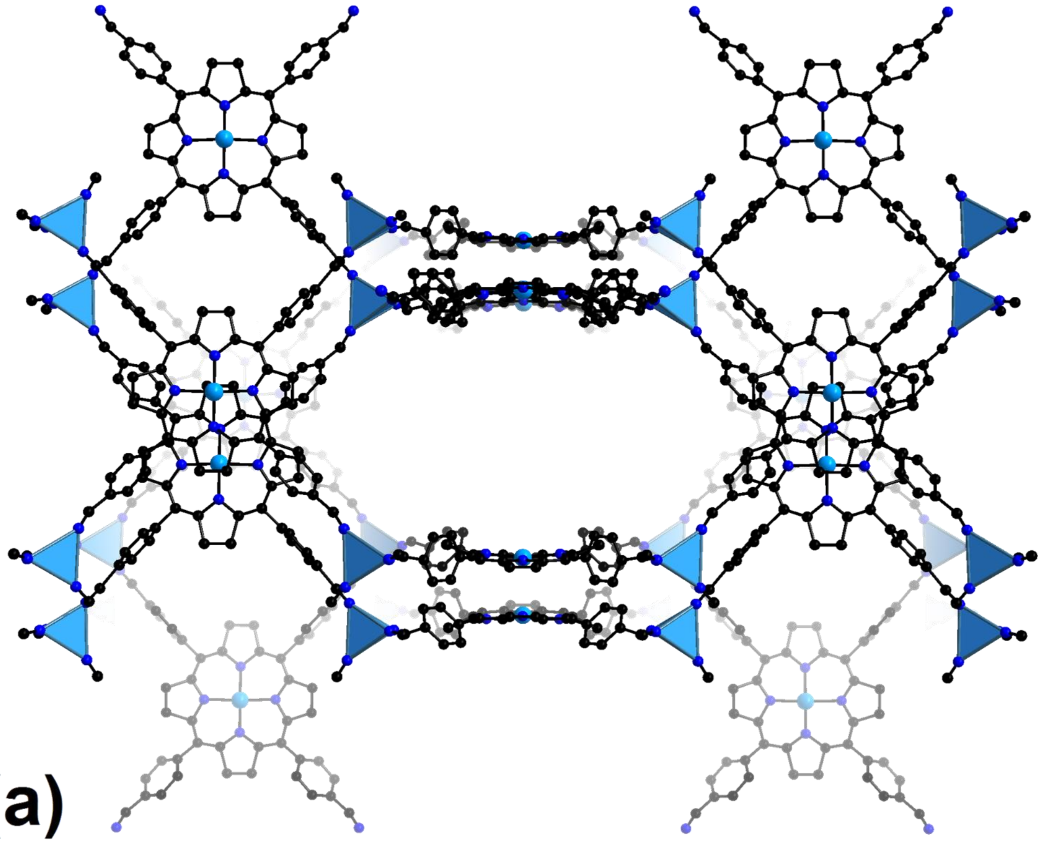
Robson *et al., J. Am. Chem. Soc.* **1989**, *111*, 5962; *J. Am. Chem. Soc.* **1990**, *112*, 1546; Iwamoto *et al., Chem. Lett.* **1988**, *17*, 1729.

# Coordination polymers – Deliberate Design

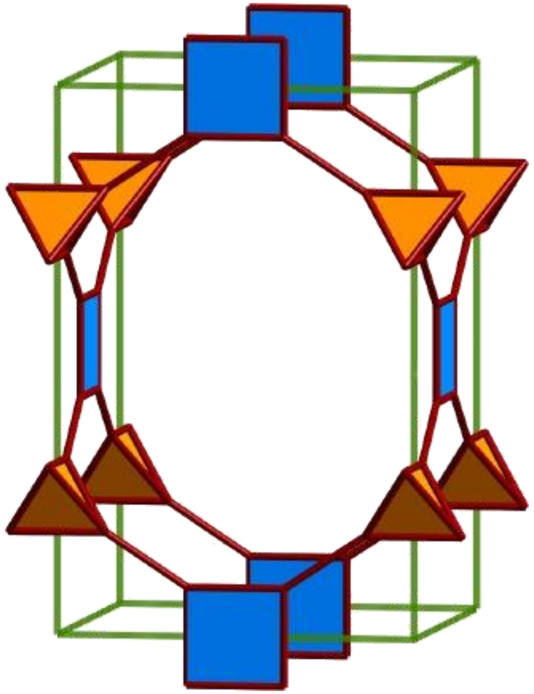
$[Cu(-CN)_4]^+$ - tetrahedral building blocks
tcp (porphyrin) – square planar building blocks

$[Cu^{II}(tcp)Cu^{I}BF_4]$
**pts**

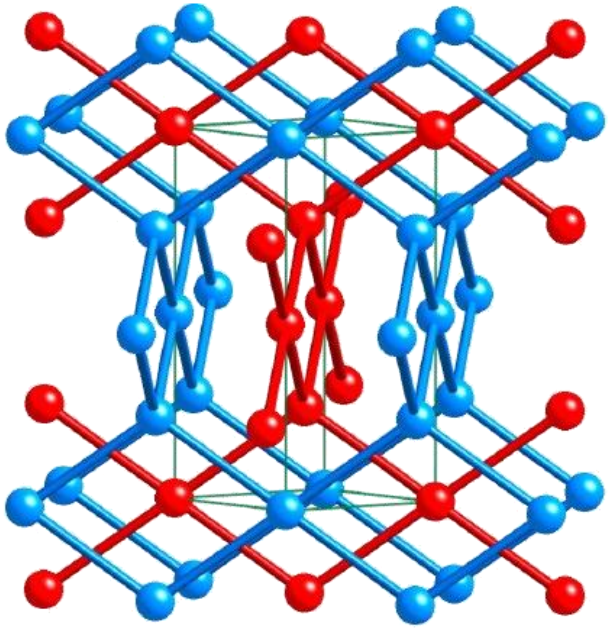
**Robson (1994)**



(a)



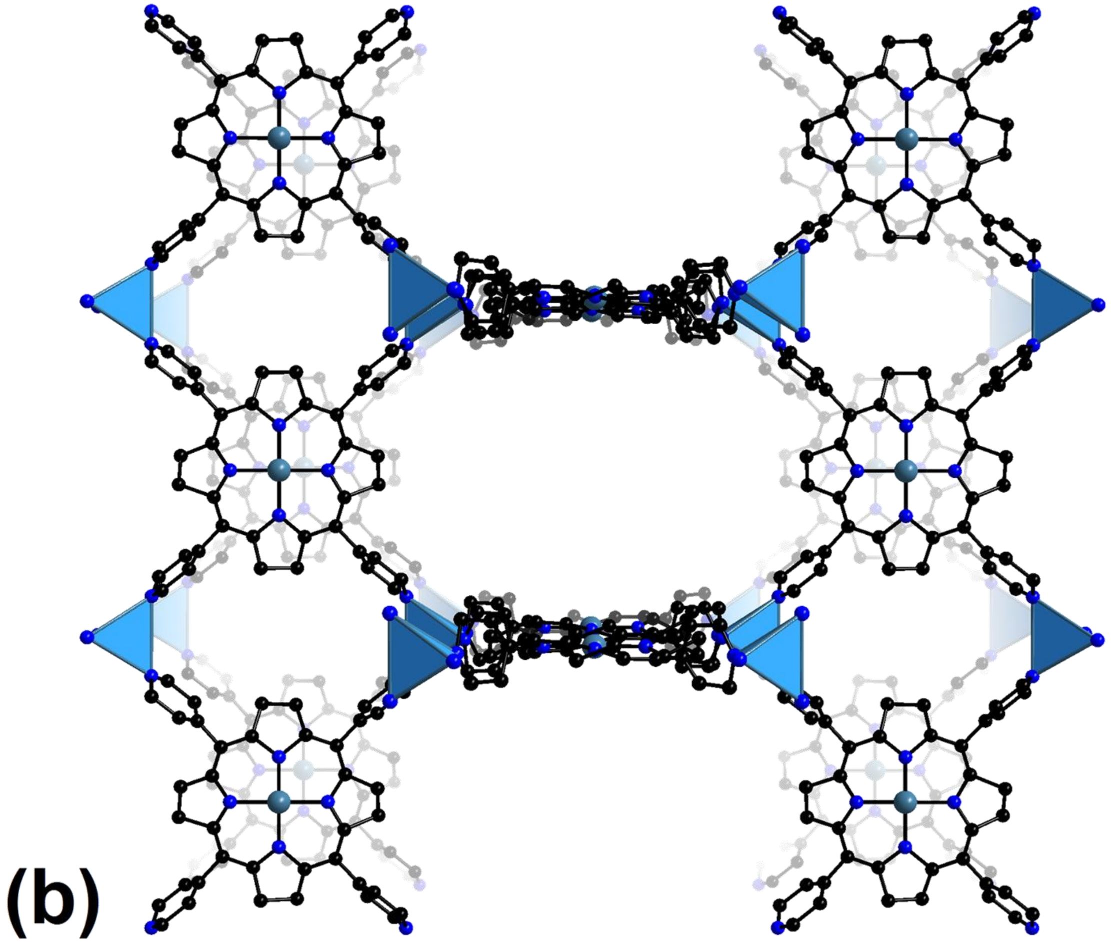
**pts-a**



**pts-c**
2-fold interpenetrated

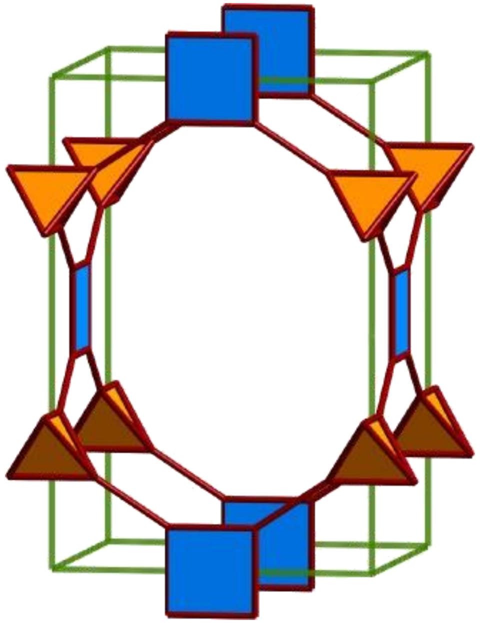
Robson *et al., Nature* **1994**, *369*, 727.

# Interpenetration in PtS nets




$[Cu(\text{-PY})_4]^+$ - tetrahedral building blocks

tpp (porphyrin) – square planar building blocks



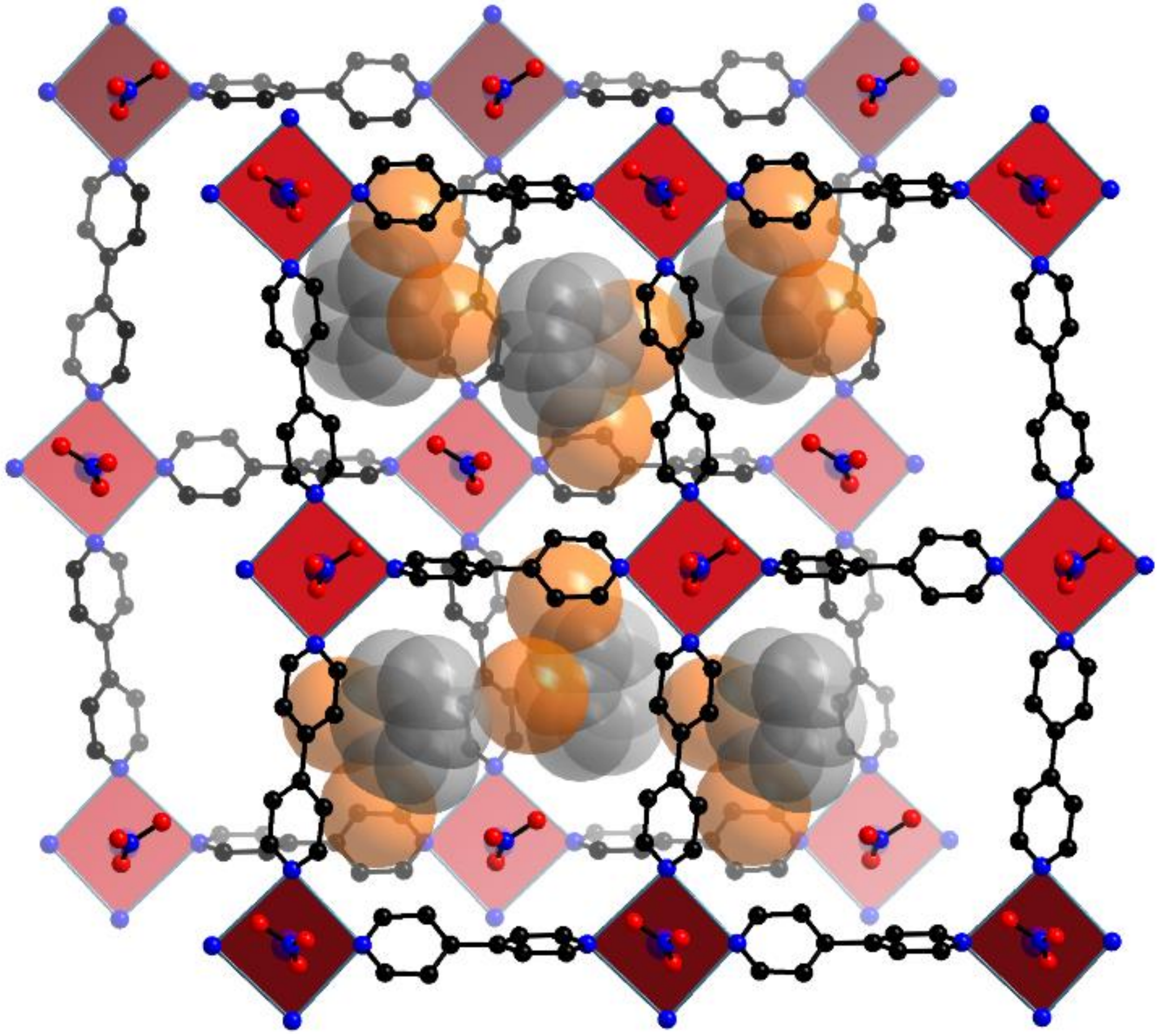
$[Cu^{II}(tpp)Cu^{I}BF_4]$

**pts**

- Single **pts** net
- Bulky PY groups prevent interpenetration

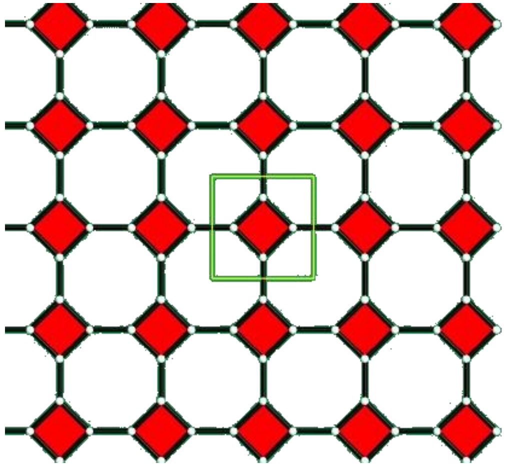
Robson *et al., Nature* **1994**, *369*, 727.

# Functional coordination polymers



**Fujita (1994)**

$[Cd(bipy)_2(NO_3)_2]$
**sql**



**sql-a**

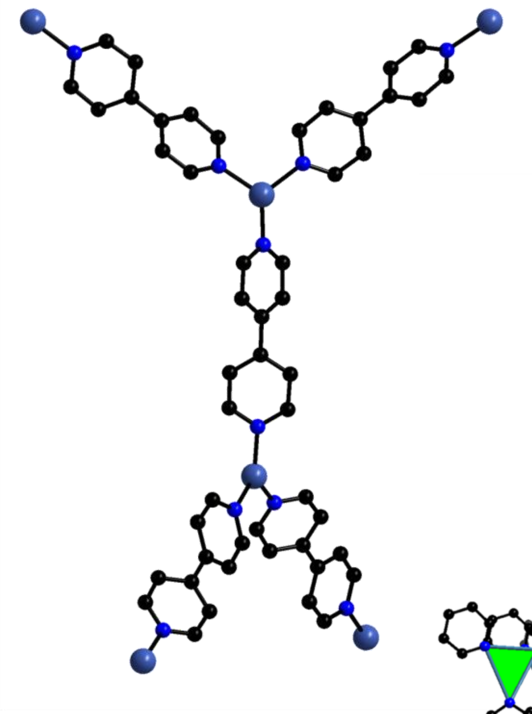
**First ever catalytic reaction in a CP!**

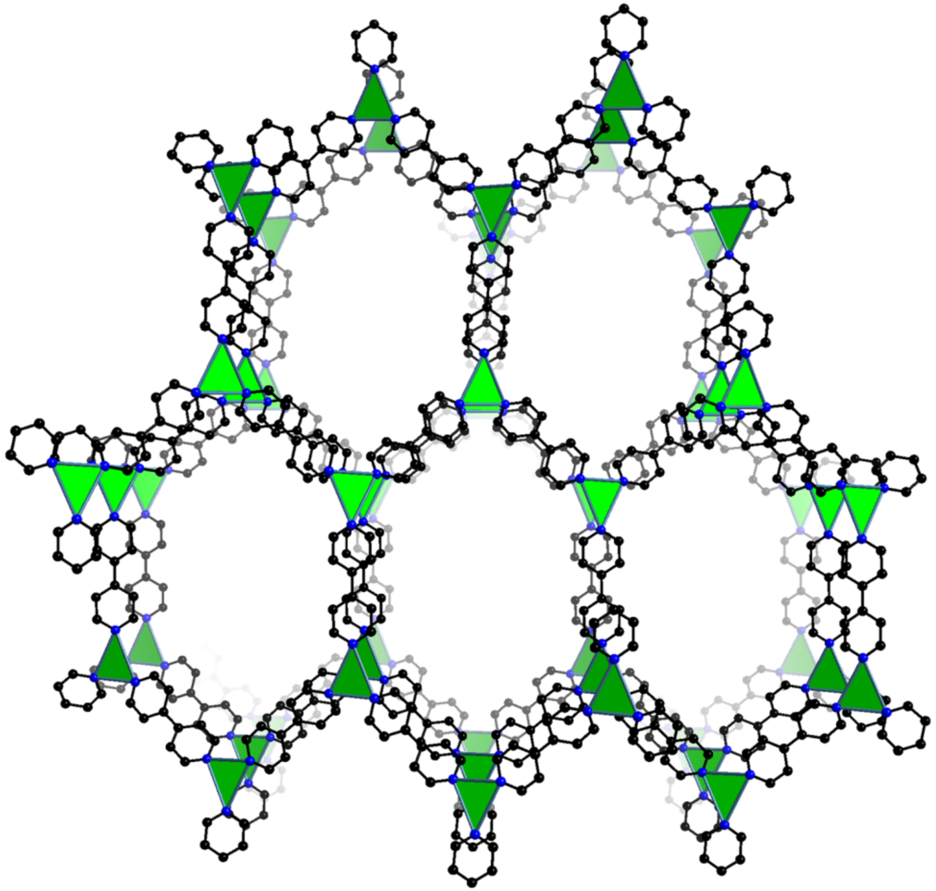
- Non-interpenetrated net
- Clathrate with *o*-dibromobenzene
- Cyanosilylation of benzaldehyde and imines

Fujita *et al., J. Am. Chem. Soc.* **1994**, *116*, 1151.

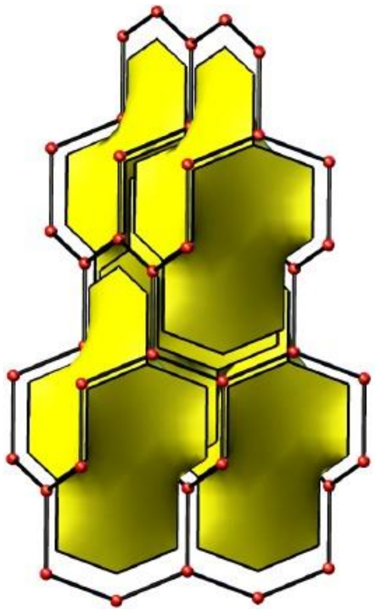
# The first MOF

**The term ‘Metal-organic framework’ (MOF) was coined in 1995.**





$[Cu(bipy)_2(PF_6)]$
**ths**



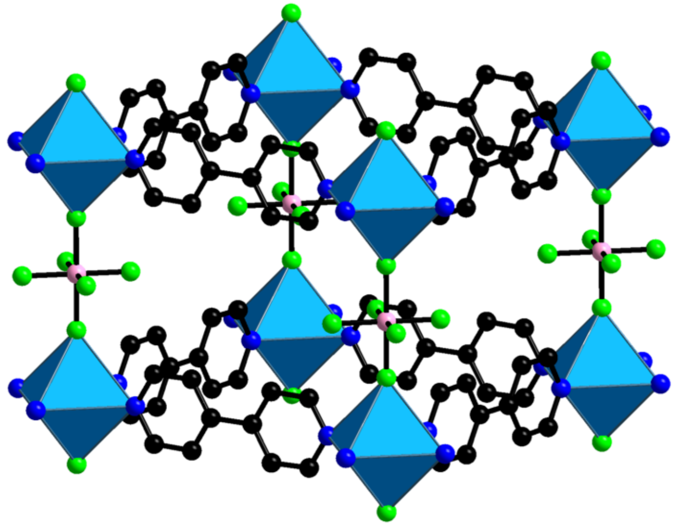
**Yaghi (1995)**

$ThSi_2$
**ths**

- Six-fold interpenetrated
- Rectangular channels: 3×6 and 6×6 Å
- Charge balancing nitrates
- Anion exchange with $BF_4^-$ or $SO_4^{2-}$.

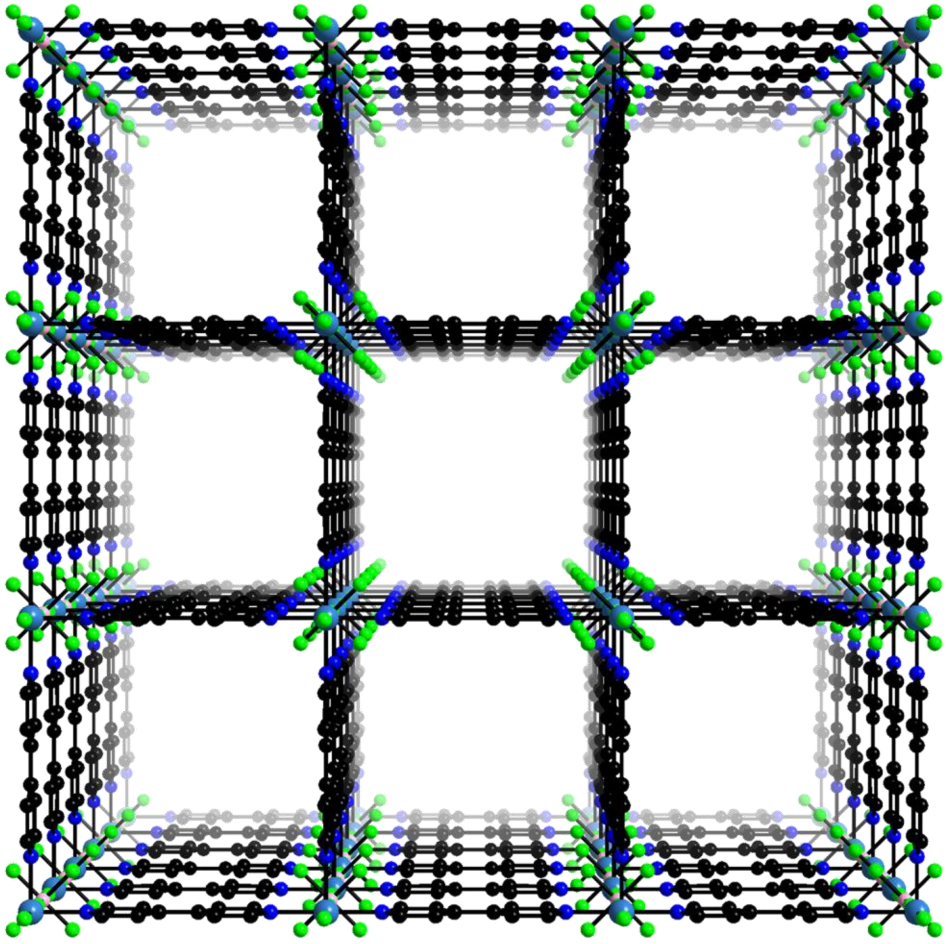
Yaghi *et al., J. Solid State Chem.* **1995**, *117*, 256.

# $[M(bipy)_2(SiF_6)]$ – primitive cubic net



**Zaworotko (1995)**
**Kitagawa (2000)**
**Zaworotko (2013)**
**Eddaoudi (2014)**

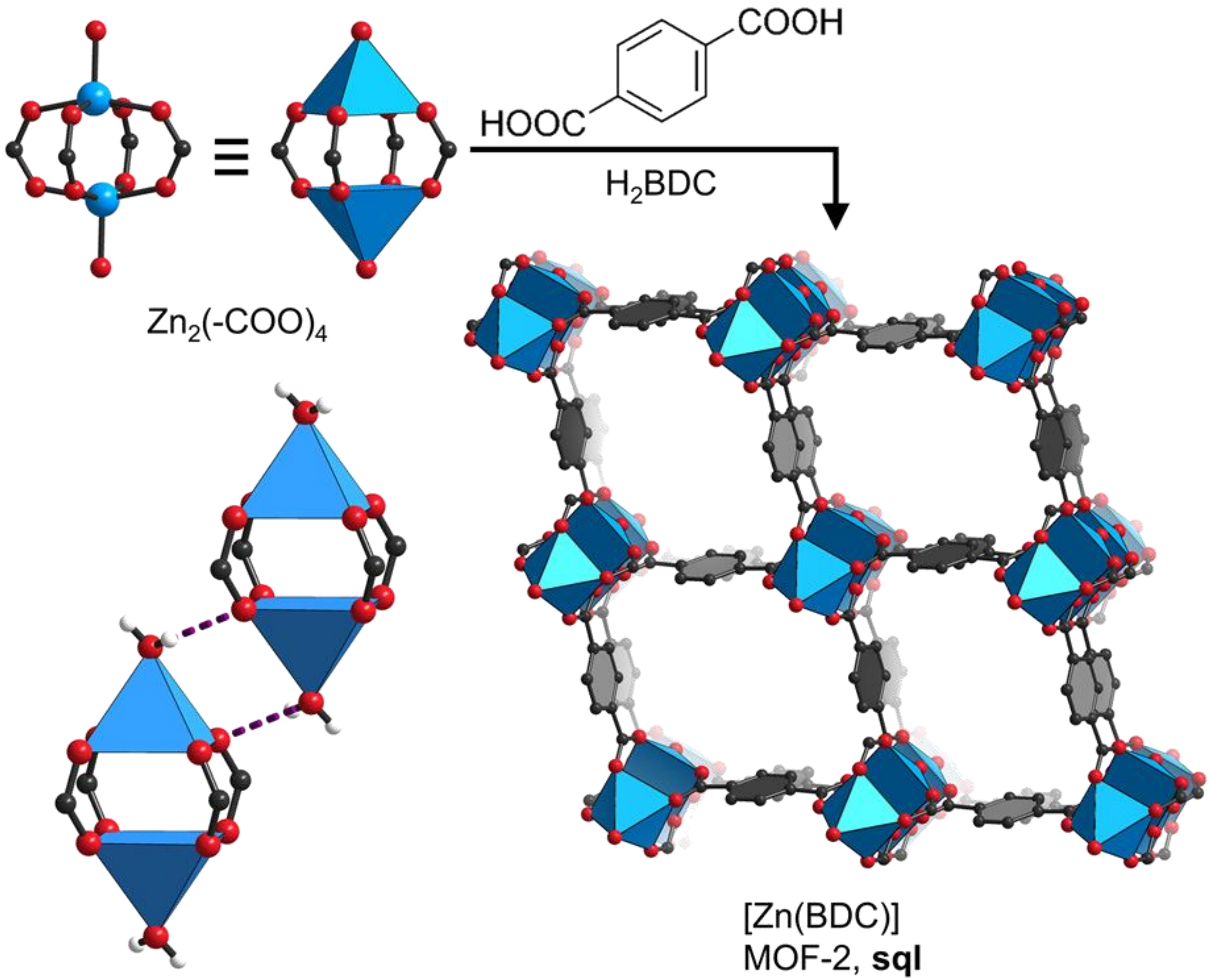
- 8×8 Å channels
- ~50% of empty space
- unstable upon evacuation
- Cu-analogue: surface area of 1337 $m^2/g$
- exceptional CO2 uptake/separation



**pcu**

Zaworotko *et al., Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2127; Kitagawa *et al., J. Am. Chem. Soc.* **2002**, *124*, 2568; Zaworotko *et al., Nature* **2013**, *495*, 80; Eddaoudi *et al., Nat. Commun.* **2014**, *5*.

# Discovery of microporosity in MOFs – MOF-2




**Yaghi (1998)**

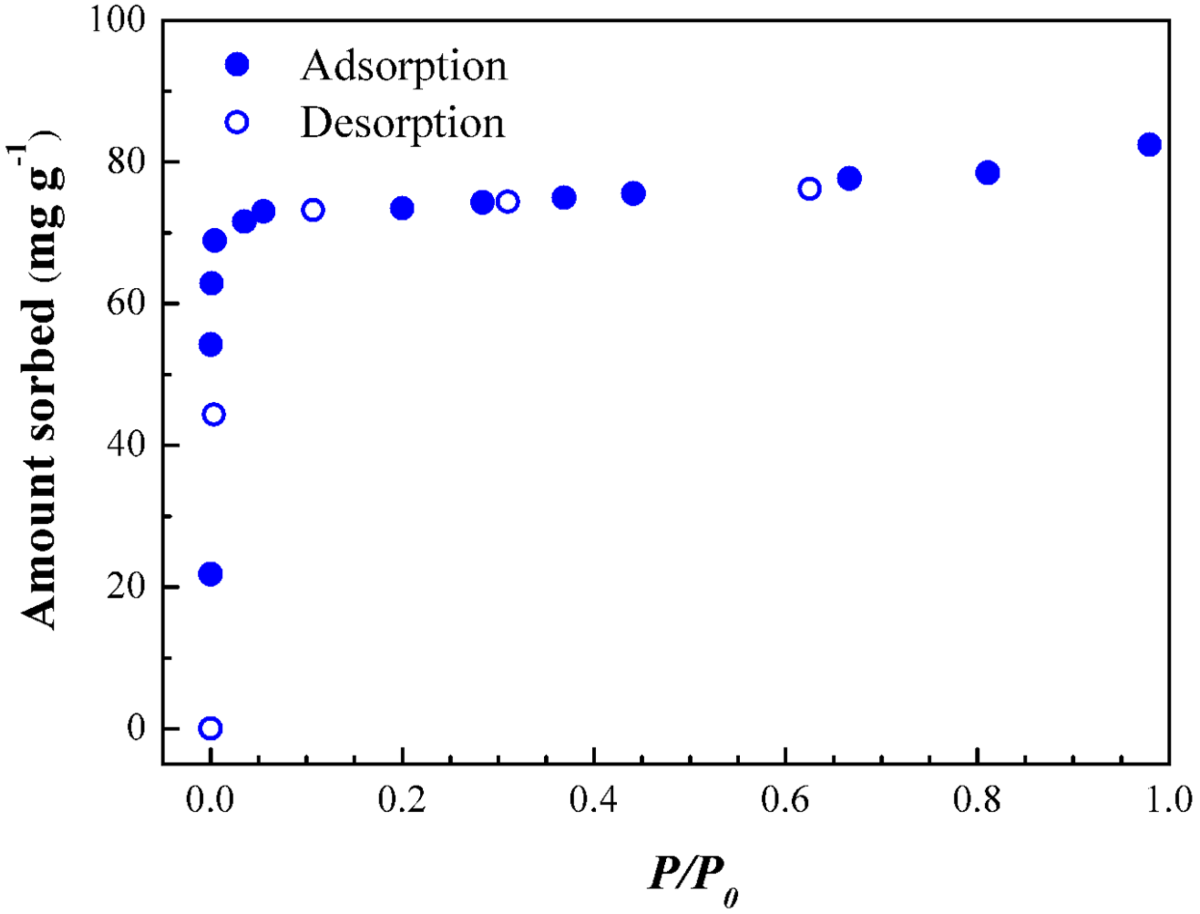
$[Zn(BDC)]\cdot(DMF)\cdot(H_2O)]$
**sql**

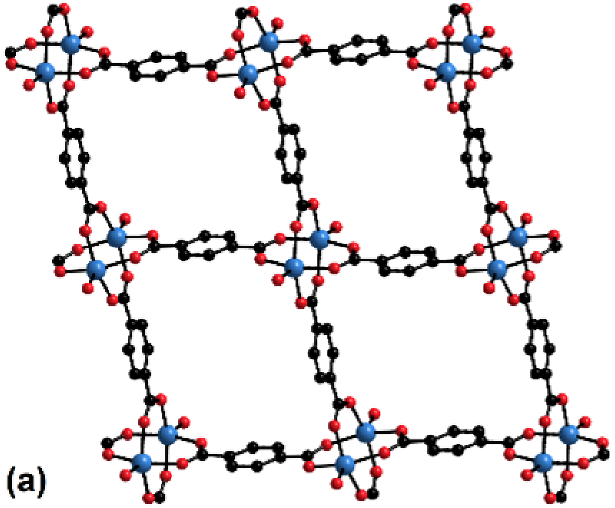
- additional stability through strong hydrogen bonding interactions
- voids filled with guest molecules, (DMF) and $H_2O$.

Yaghi *et al., J. Am. Chem. Soc.* **1998**, *120*, 8571.

# Discovery of microporosity in MOFs – MOF-2

**Yaghi (1998)**



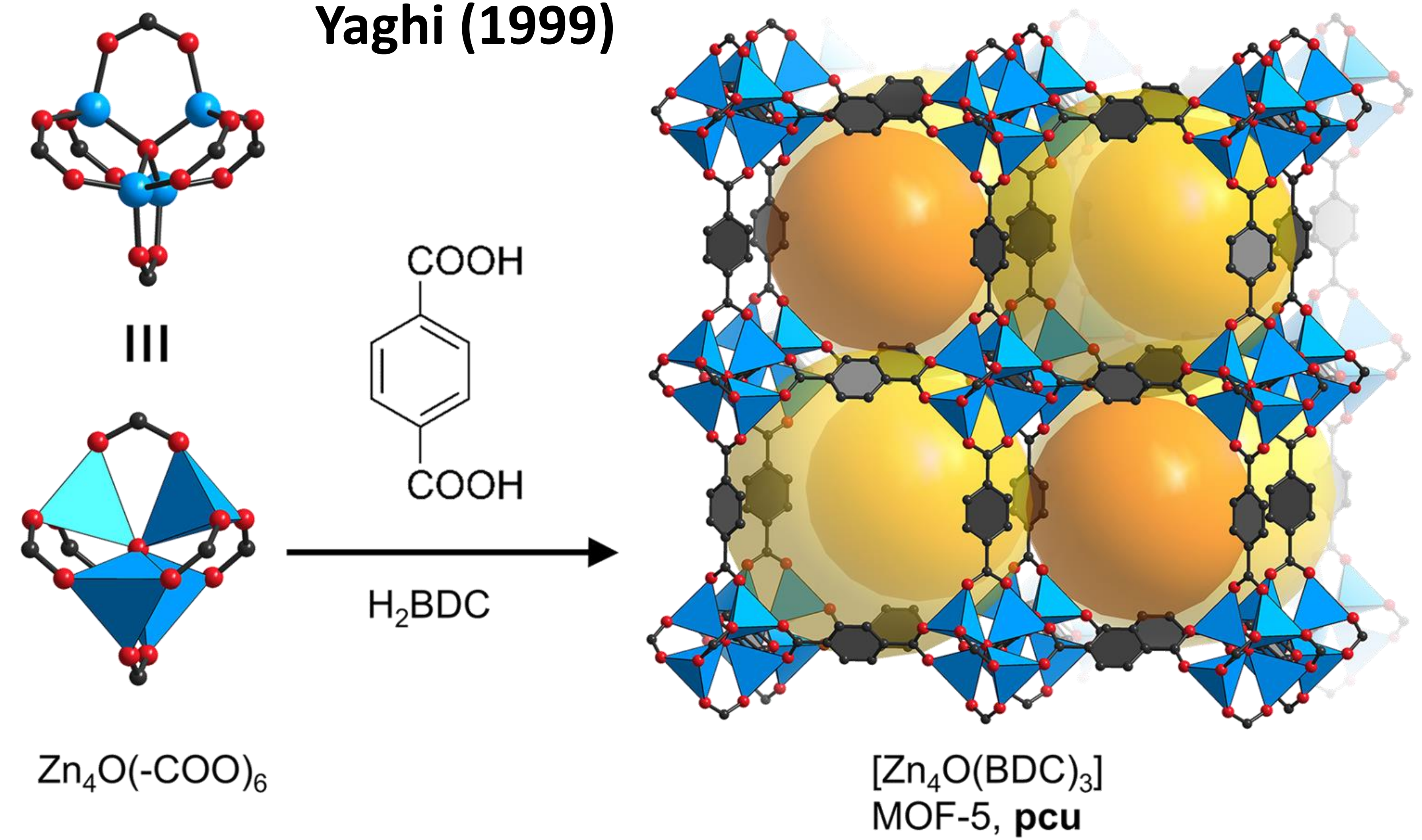

Empty framework
[Zn(BDC)]

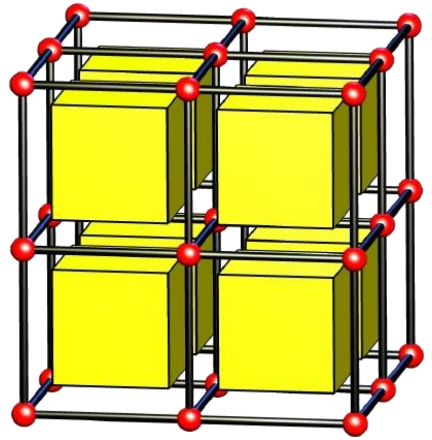
- Guest removal: evacuation, heat
- Isotherm with $N_2$ at 77K
- Type I behavior
- Langmuir area: 270 and 310 $m^2/g$.

Yaghi *et al., J. Am. Chem. Soc.* **1998**, *120*, 8571.

# High surface area MOFs – MOF-5

## Yaghi (1999)



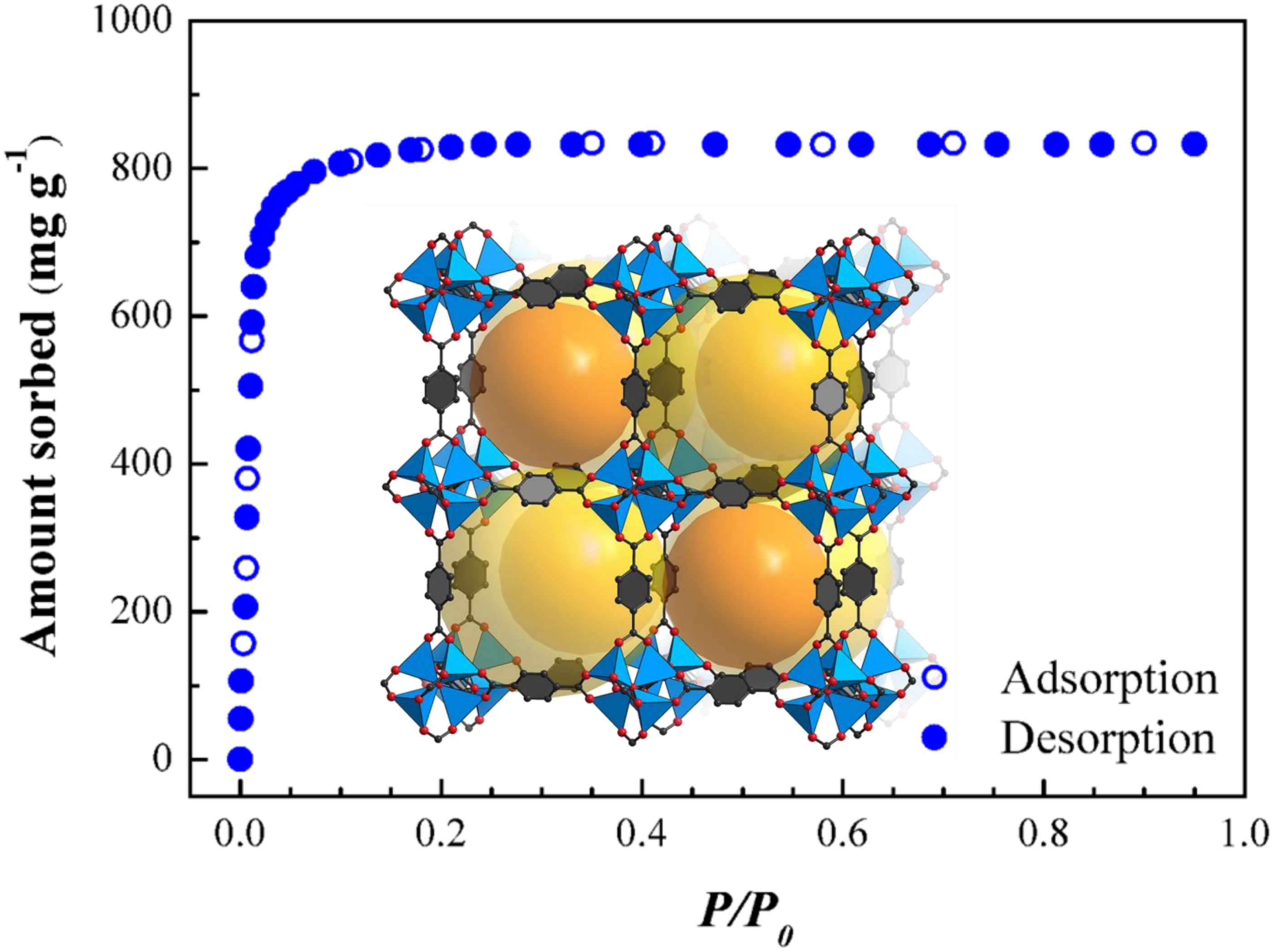



**pcu**

- $Zn(NO_3)_2$ + 1,4-$H_2BDC$
- Voids filled with DMF/chlorobenzene
- 2 types of cavities

Yaghi *et al.*, *Nature* **1999**, *402*, 276.

# High surface area MOFs – MOF-5

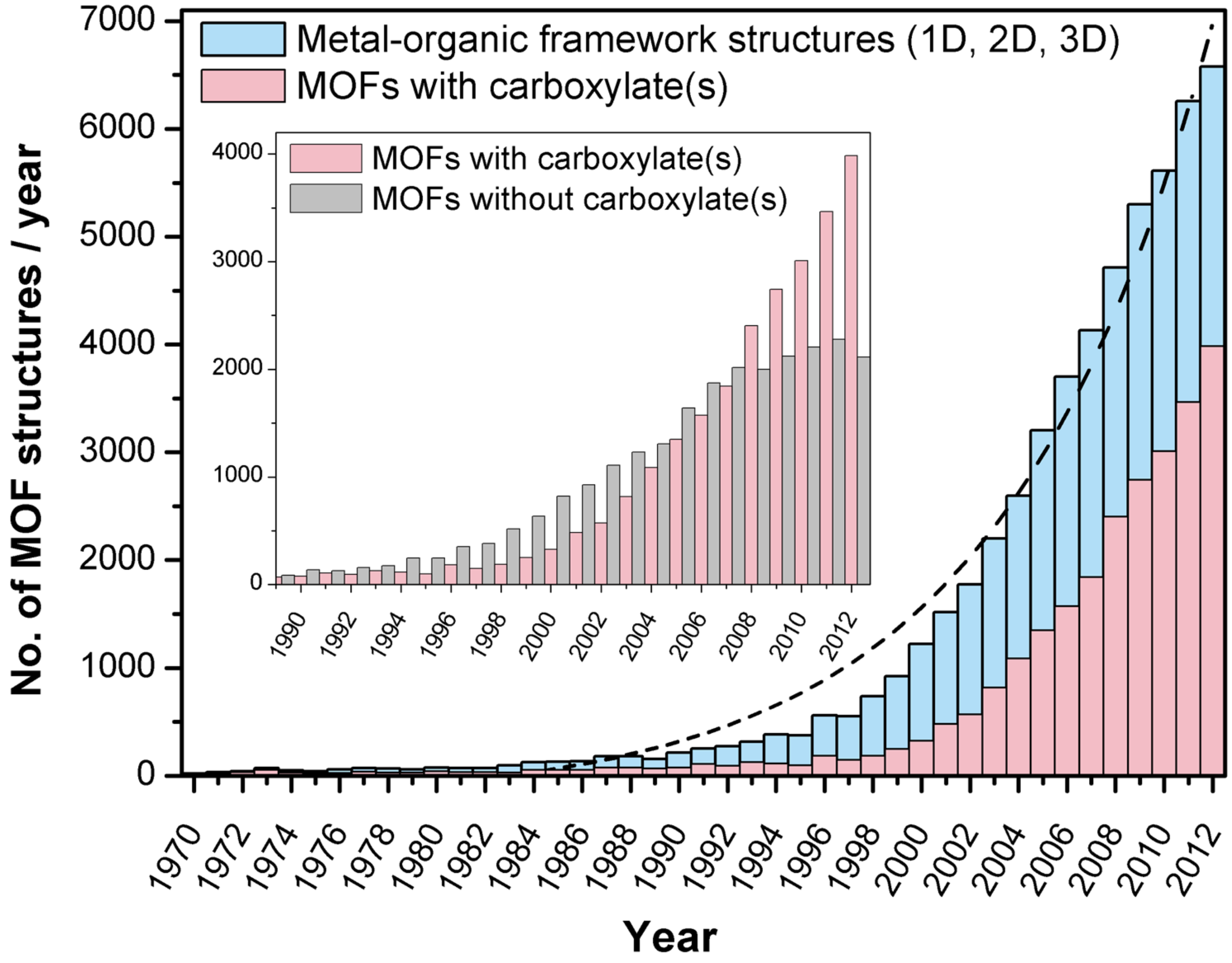



- Robust framework
- Type I isotherm ($N_2$, 77K)
- Langmuir surface area of 2,900 $m^2/g$, pore volume of 1.04 $cm^3/g$.
- modular structure
- Control of linker length and functionality

Yaghi *et al.*, *Nature* **1999**, *402*, 276.

# Introduction to Reticular Chemistry of Metal-organic frameworks (MOFs)

# Reticular Chemistry

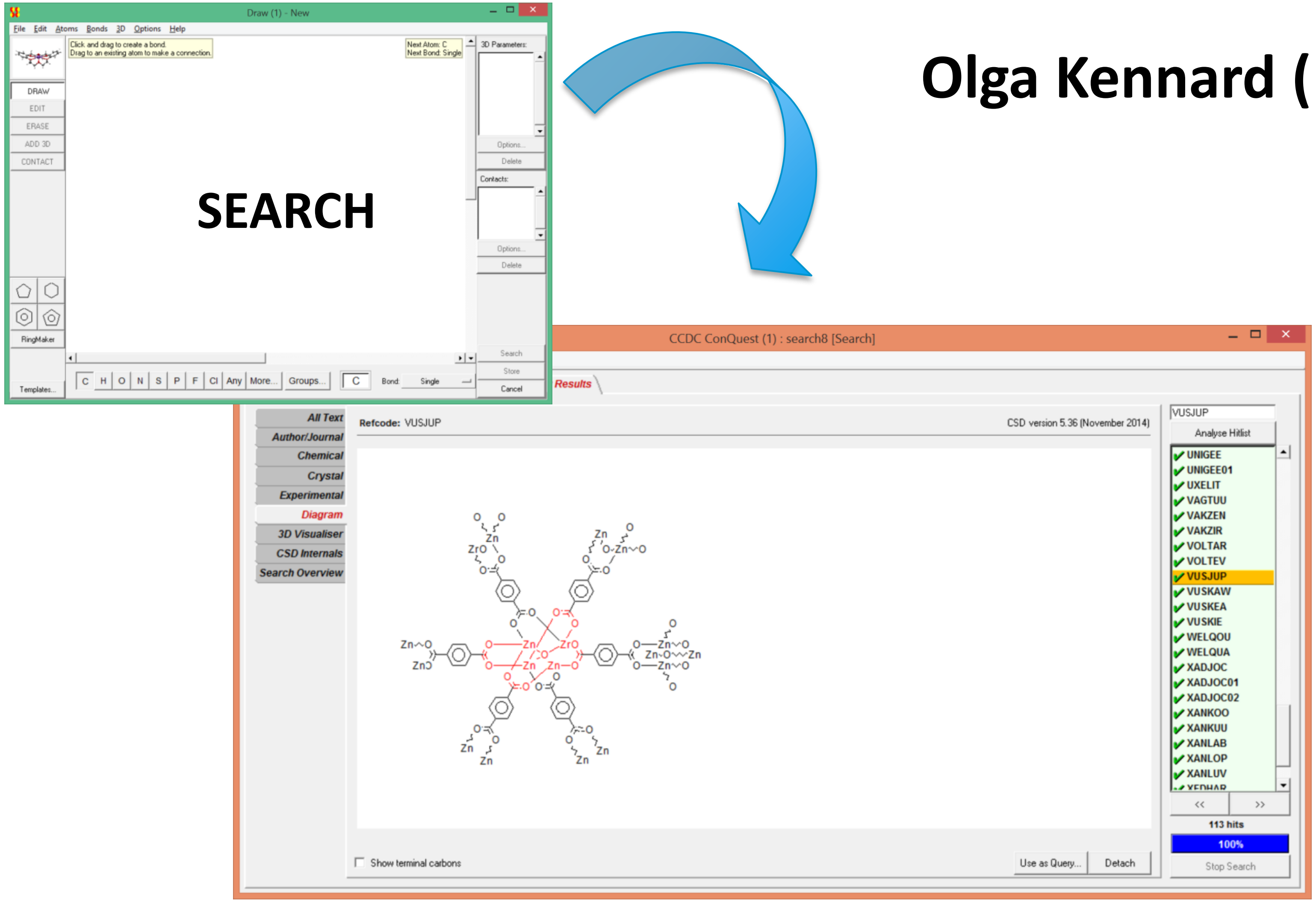



**Definition:** Reticular chemistry is concerned with **linking** of **molecular building blocks** (organic molecules, inorganic clusters, dendrimers, peptides, proteins, ...) into **predetermined structures** in which such units are **repeated** and are held together by **strong bonds**.

**Strong bonds and inorganic clusters are important**

Yaghi *et al., Acc. Chem. Res.* **2005**, *38*, 176; *Science* **2013**, *341*, 1230444.

# The Cambridge Structural Database (CSD)

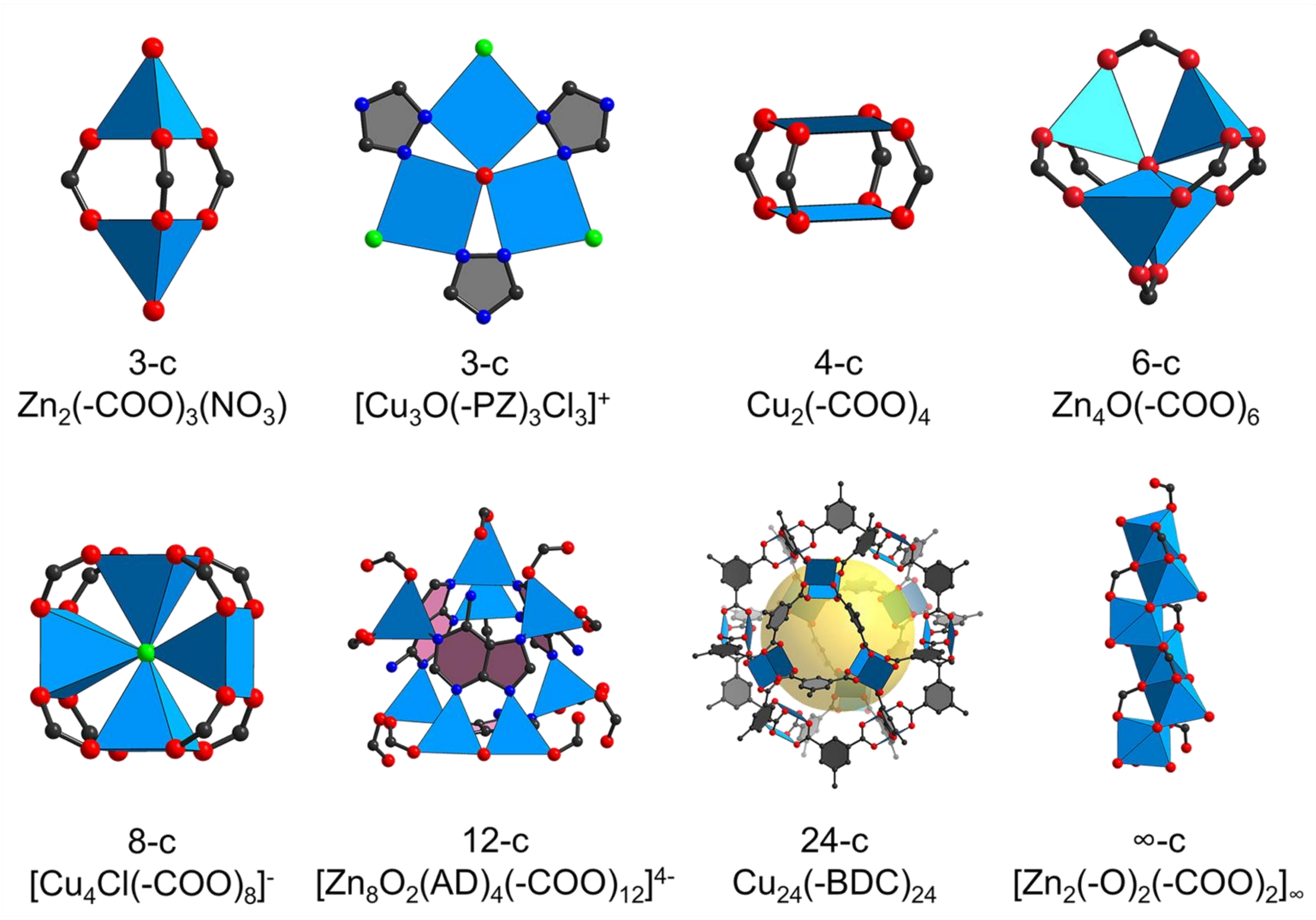



**Olga Kennard (1965)**

- crystallographic information files (.cif) for each structure
- Six letter codes
- 2-D diagram and 3-D visualizer
- Literature reference
- Many search capabilities

Allen, *Acta Crystallogr. B* **2002**, *58*, 380; Allen *et al.*, *Angew. Chem. Int. Ed.* **2014**, *53*, 662; http://www.ccdc.cam.ac.uk/pages/Home.aspx

# Secondary Building Units (SBUs)

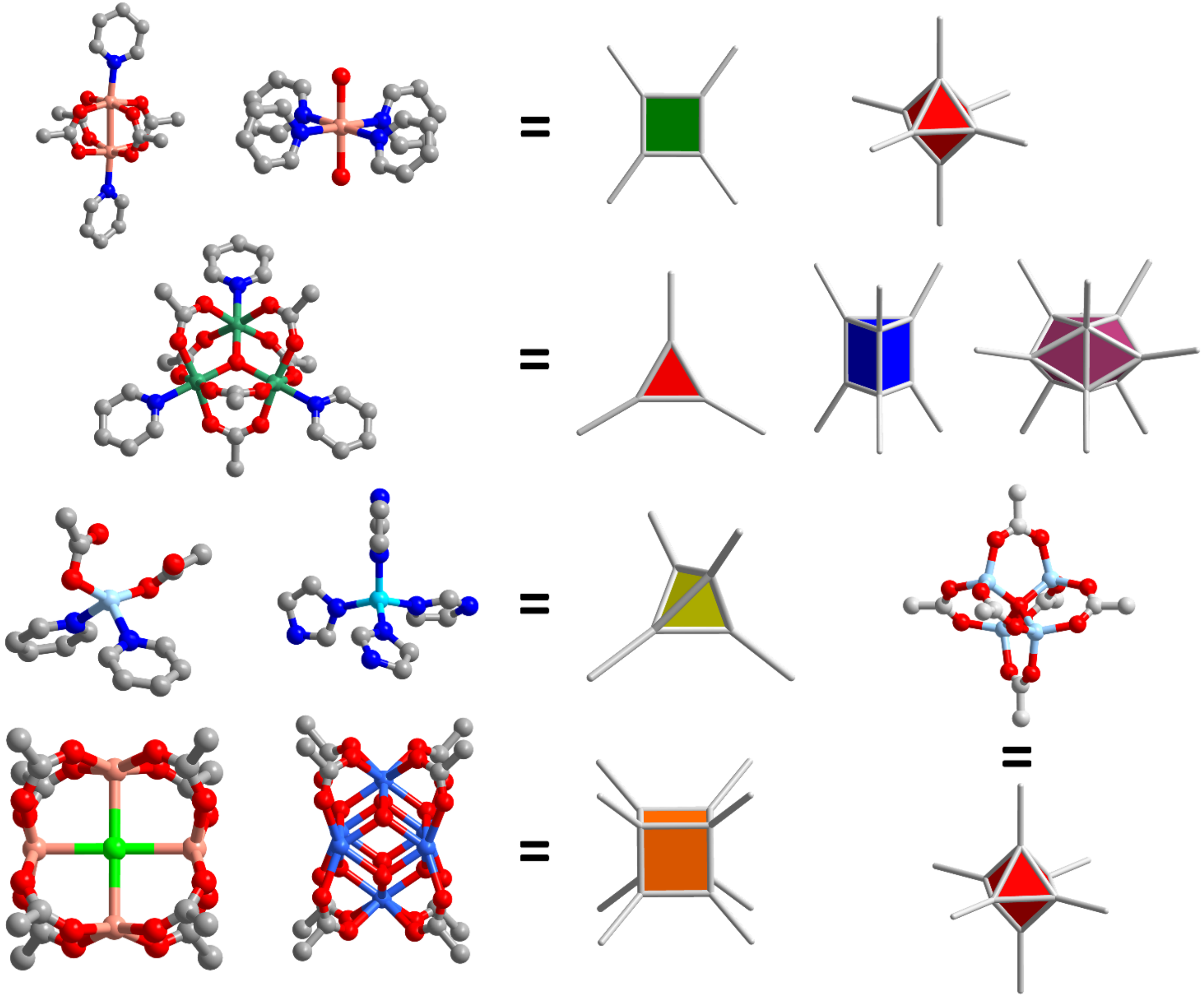



**Definition:** SBUs are defined as an aggregate of metal ions together with multi-dentate functional groups, such as carboxylates, into clusters.

SBUs can then serve as rigid vertices propagated into a framework by rigid organic struts and due to strong bonding account for a high structural stability.

Yaghi *et al., Acc. Chem. Res.* **2001**, *34*, 319-330.

# Points of extension



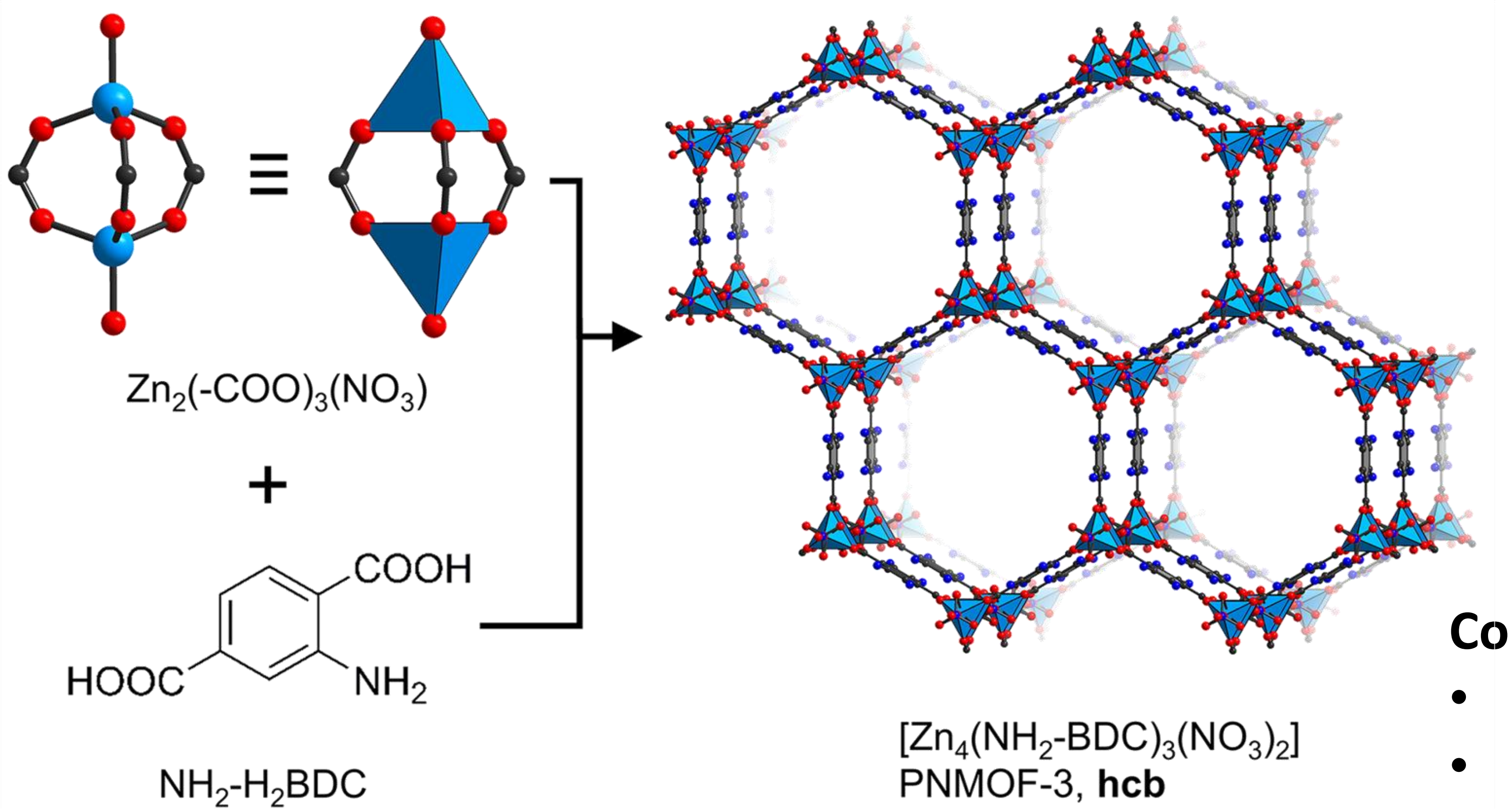

**Definition:** Points of extension in MOF chemistry means the number of possible connections between one metal cluster to other metal clusters through organic linkers.

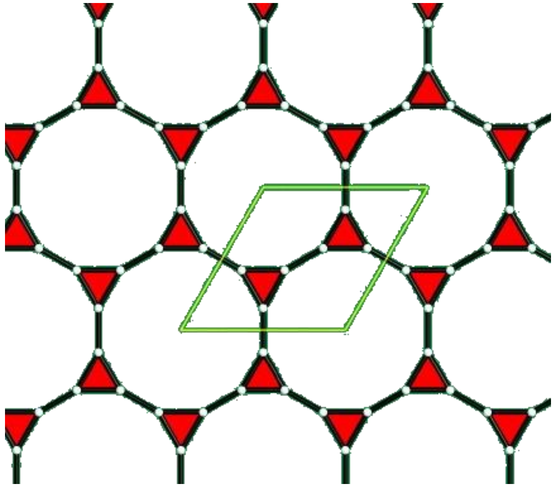
Coordination chemistry defines the geometry of the SBU.

Three up to 24 points of extension.

Yaghi *et al., Chem. Soc. Rev.* **2009**, *38*, 1257; Zaworotko *et al., Chem. Sci.* **2014**, *5*, 1269.

# Three points of extension – PNMOF-3



**hca**

**Copolymer:**

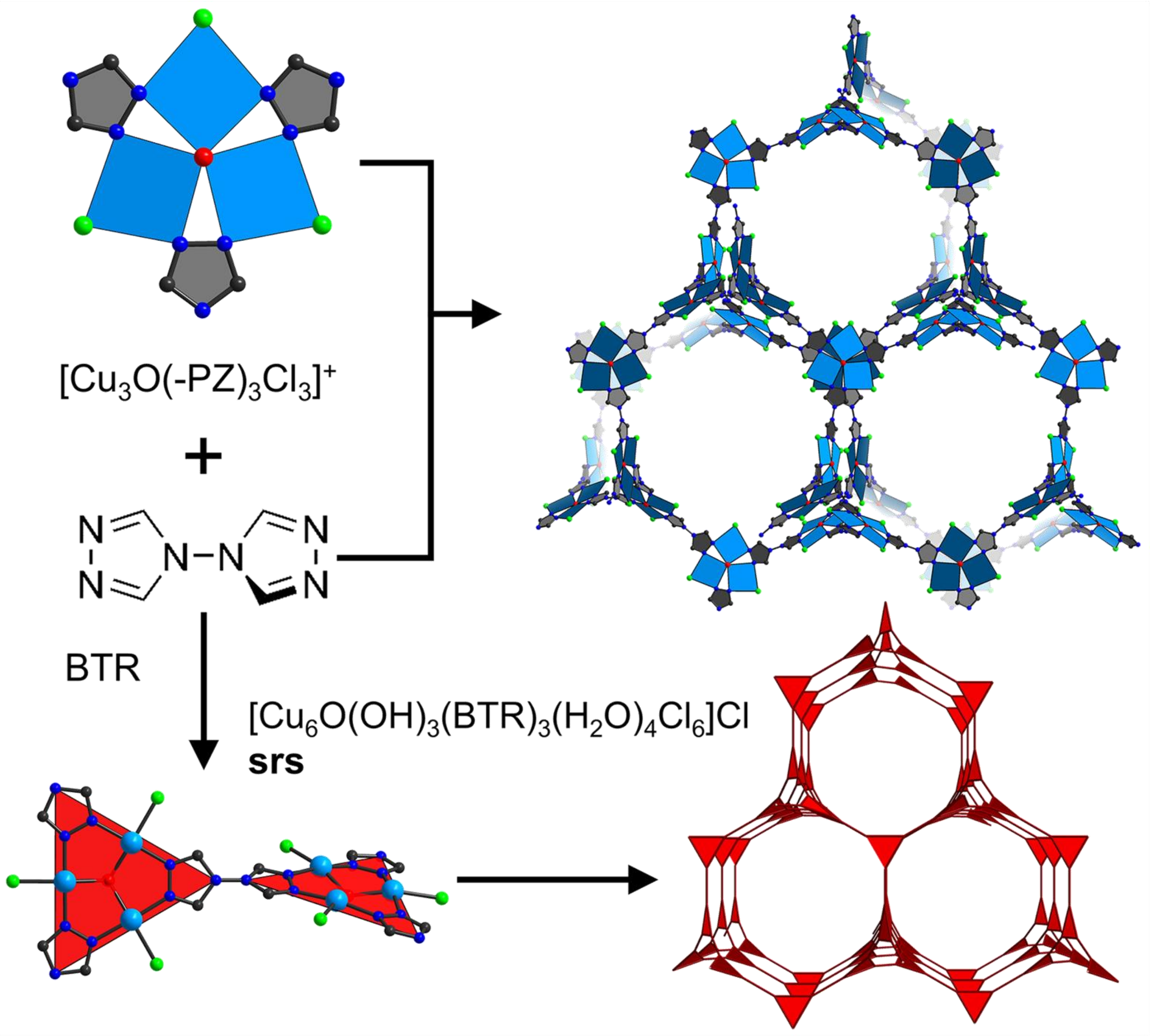
- methacrylic acid (MAA)
- divinylbenzene (DVB)

**Yaghi and Matzger (2006)**

conventional: IRMOF-3

Yaghi, Matzger *et al., Angew. Chem. Int. Ed.* **2006**, *45*, 2553-2556; **IRMOF-3:** Yaghi *et al., Science* **2002**, *295*, 469-472.

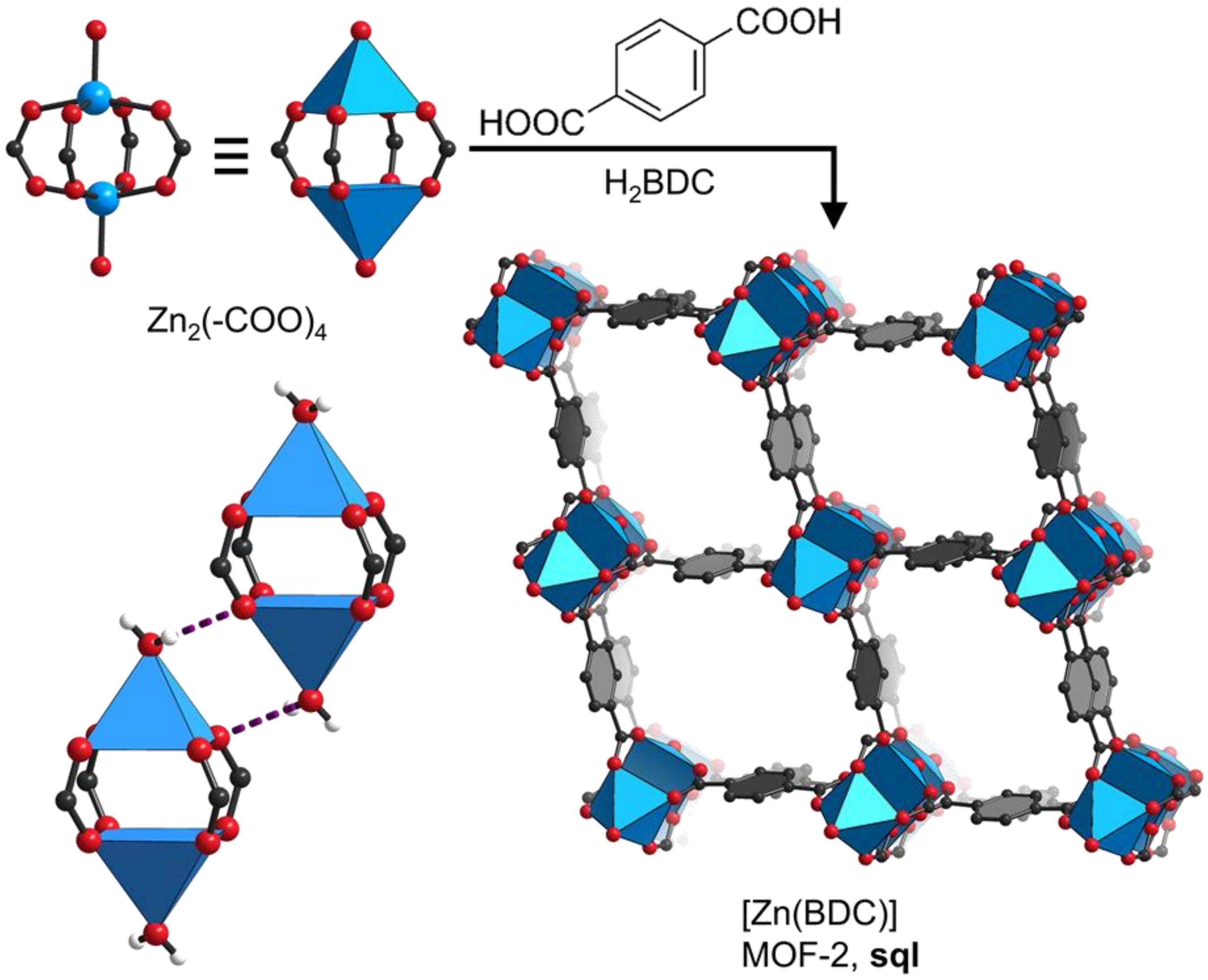
# Three points of extension



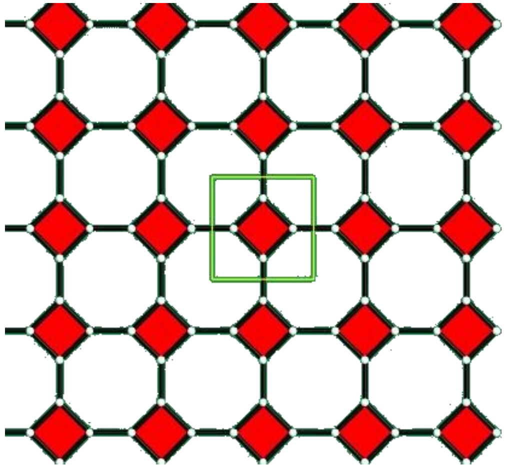

- SrSi$_2$ (**srs**) net
- Eight fold interpenetrated
 **srs** is self-dual
- Non-planar geometry generates **srs** rather than **hcb**.

Domasevitch *et al., Dalton Trans.* **2006**, 3772-3776.

# Four points of extension – MOF-2




**Yaghi (1998)**

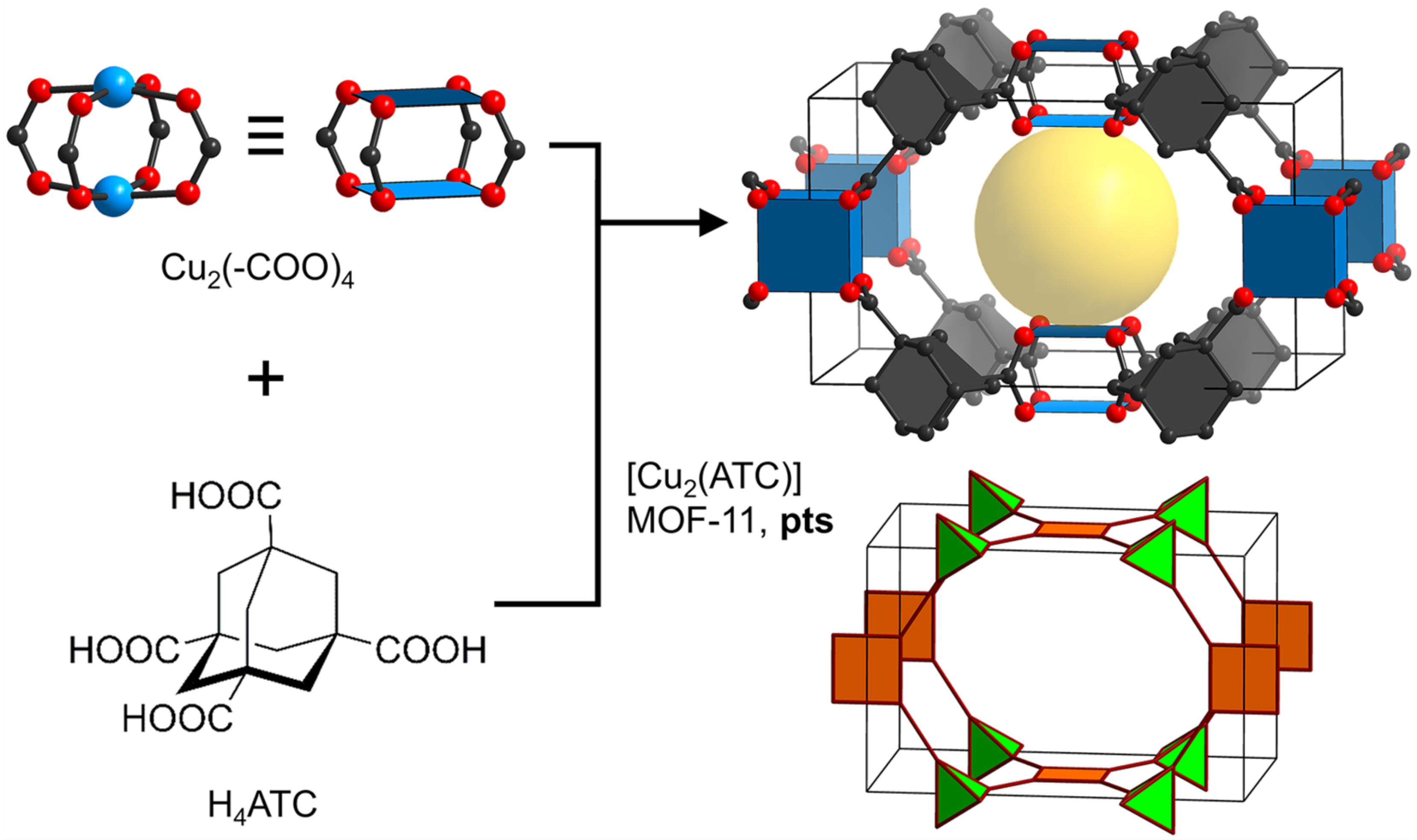


**sql-a**

- paddlewheel is long and well known: $Cu_2(OAc)_4$, $Cr_2(OAc)_4$, $Rh_2(OAc)_4$.
- Langmuir area: 270 and 310 m²/g.

Yaghi *et al., J. Am. Chem. Soc.* **1998**, *120*, 8571; **Discrete clusters:** A. F. Wells, *Structural Inorganic Chemistry* **5th ed.**, *Oxford University Press: Oxford*, 1984; Schoening *et al., Nature* **1953**, *171*, 36-37.

# The discovery of open metal sites (OMS)

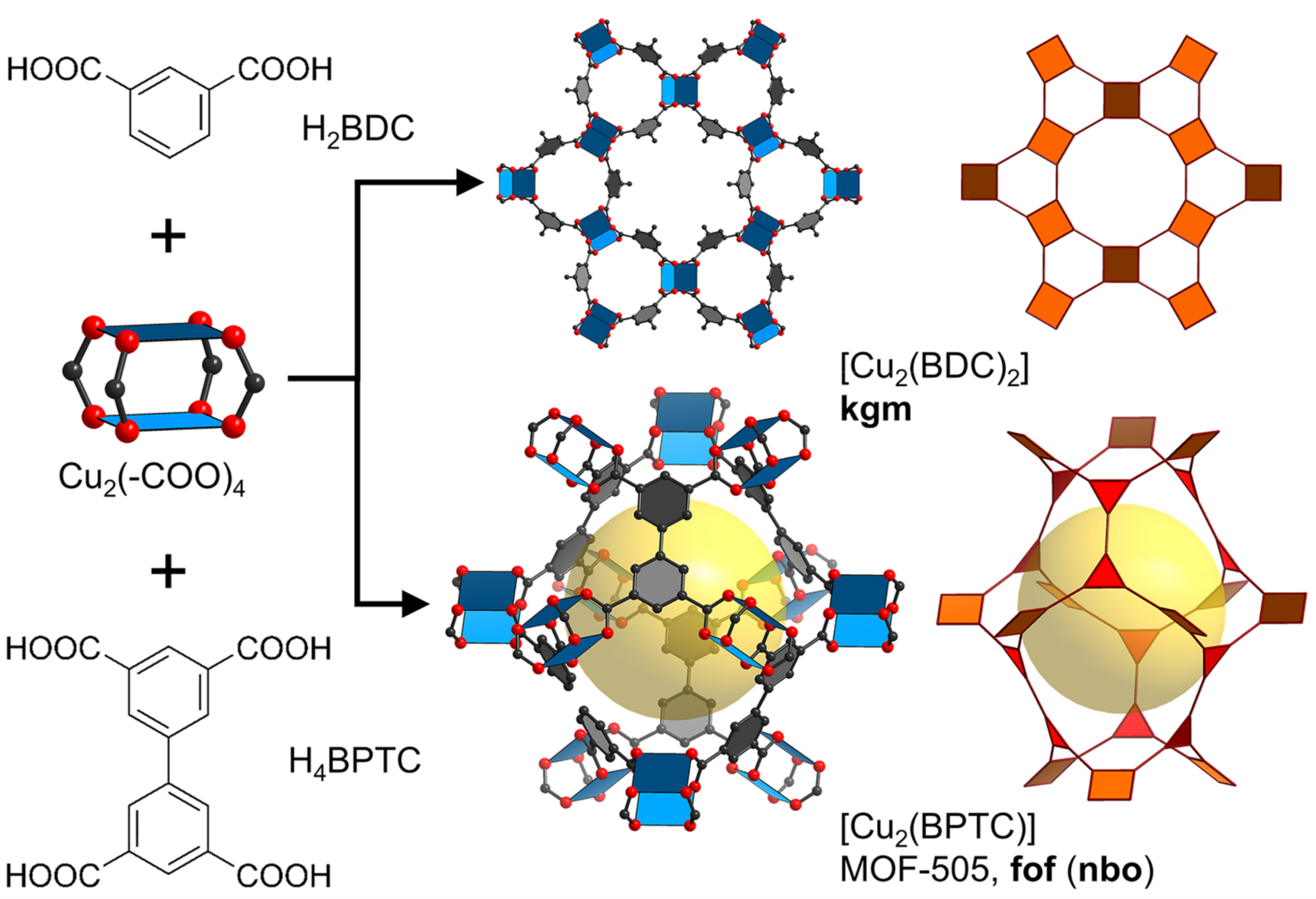



**Yaghi (2000)**

- First permanently porous material with OMS
- Langmuir area: 560 $m^2/g$

Yaghi *et al., J. Am. Chem. Soc.* **2000**, *122*, 11559-11560.

# Why are OMS important?



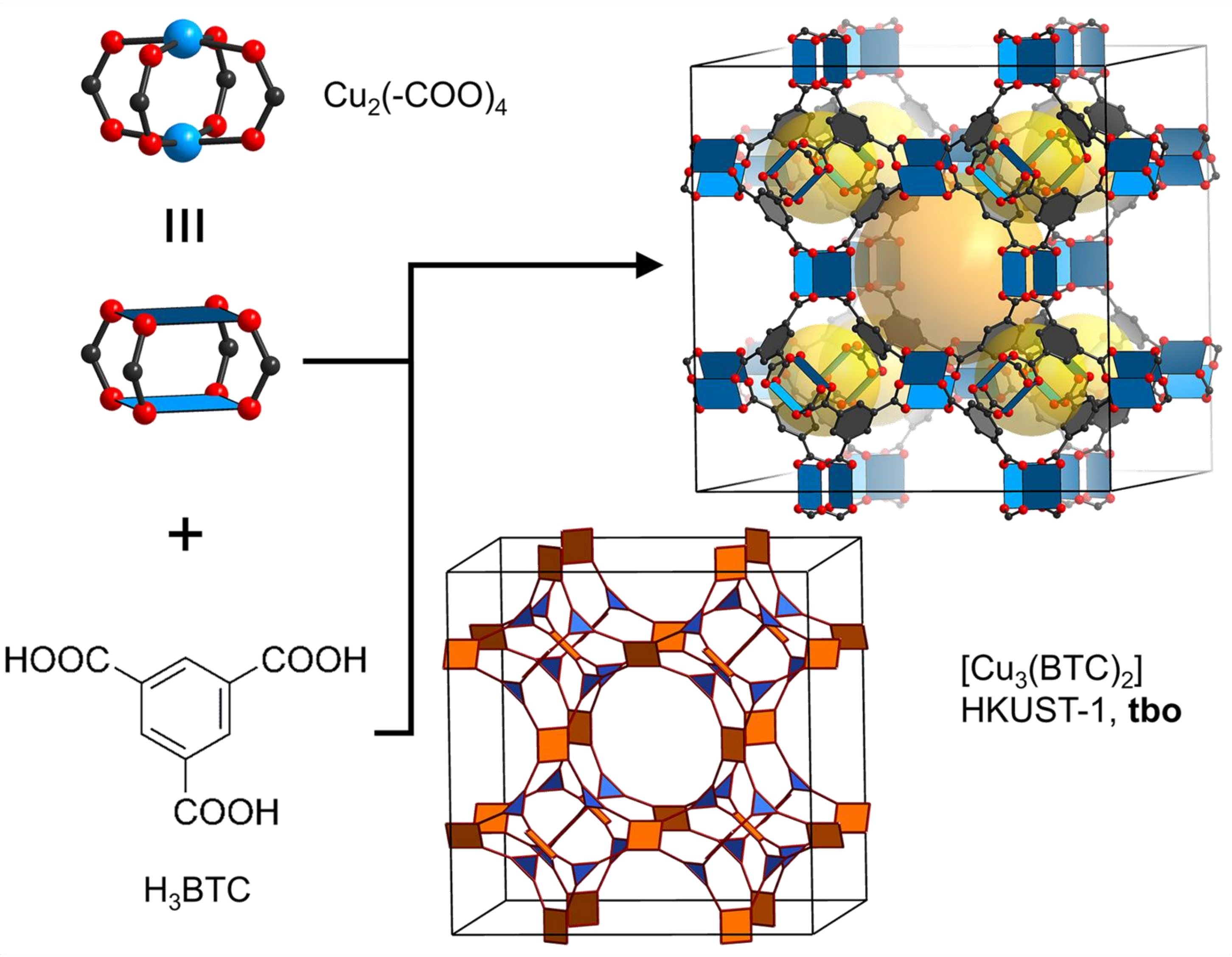

**Chen and Yaghi (2005)**

- Topology: 4,4-c net (**nbo**)
- Deconstruction to 3,3,4-c net (**fof**)
- Linker to linker cross-linked **kgm** nets.

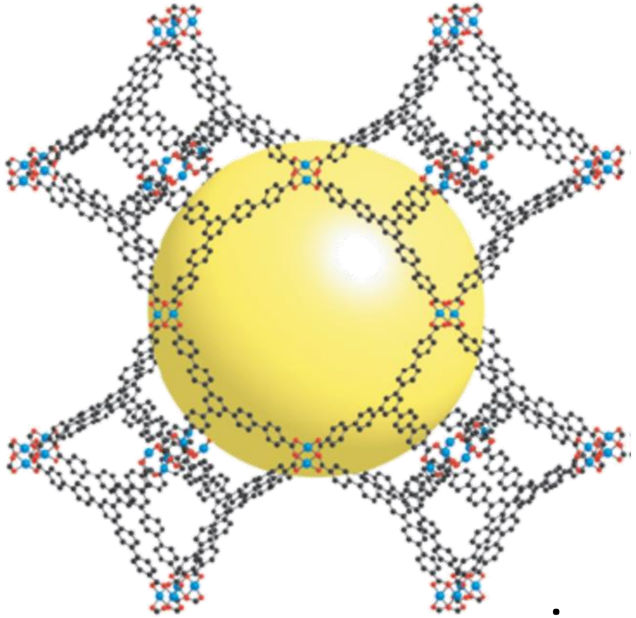
- Langmuir area: 1830 $m^3/g$
- **Enhanced $H_2$-sorption at 77K: 2.47wt%**

Chen, Yaghi *et al., Angew. Chem. Int. Ed.* **2005**, *44*, 4745-4749; **Kagomé:** Zaworotko *et al., Angew. Chem. Int. Ed.* **2002**, *41*, 2821-2824; **Deconstruction:** O'Keeffe, Yaghi, *Chem. Rev.* **2012**, *112*, 675-702.

# HKUST-1 – A prototypal MOF



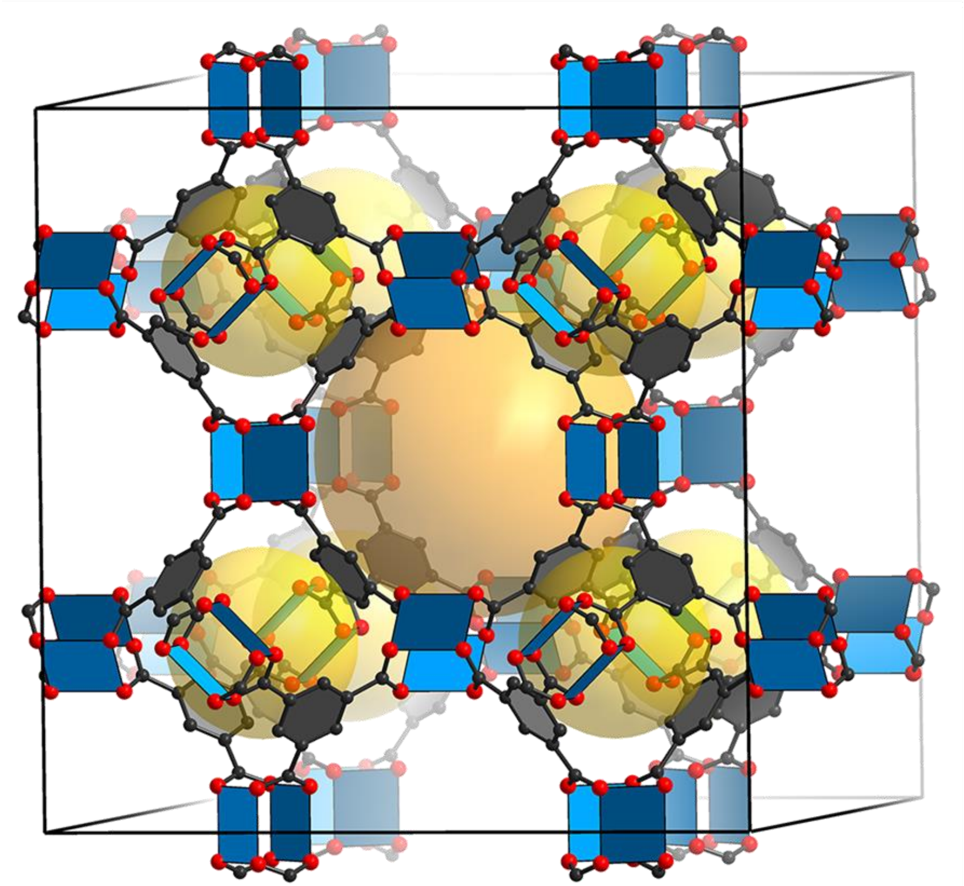

**Williams (1999)**
**Yaghi (2011)**



isoreticular
MOF-399
**tbo**
d = 0.126 g/cm³

Williams *et al., Science* **1999**, *283*, 1148-1150; Yaghi *et al., Inorg. Chem.* **2011**, *50*, 9147-9152.

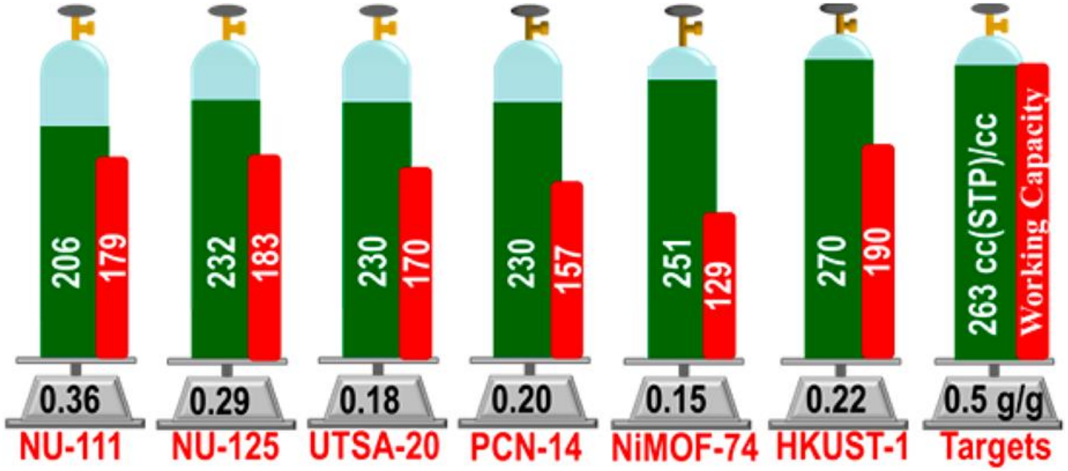
# HKUST-1 – Features



BET (Brunauer-Emmett-Teller) area:

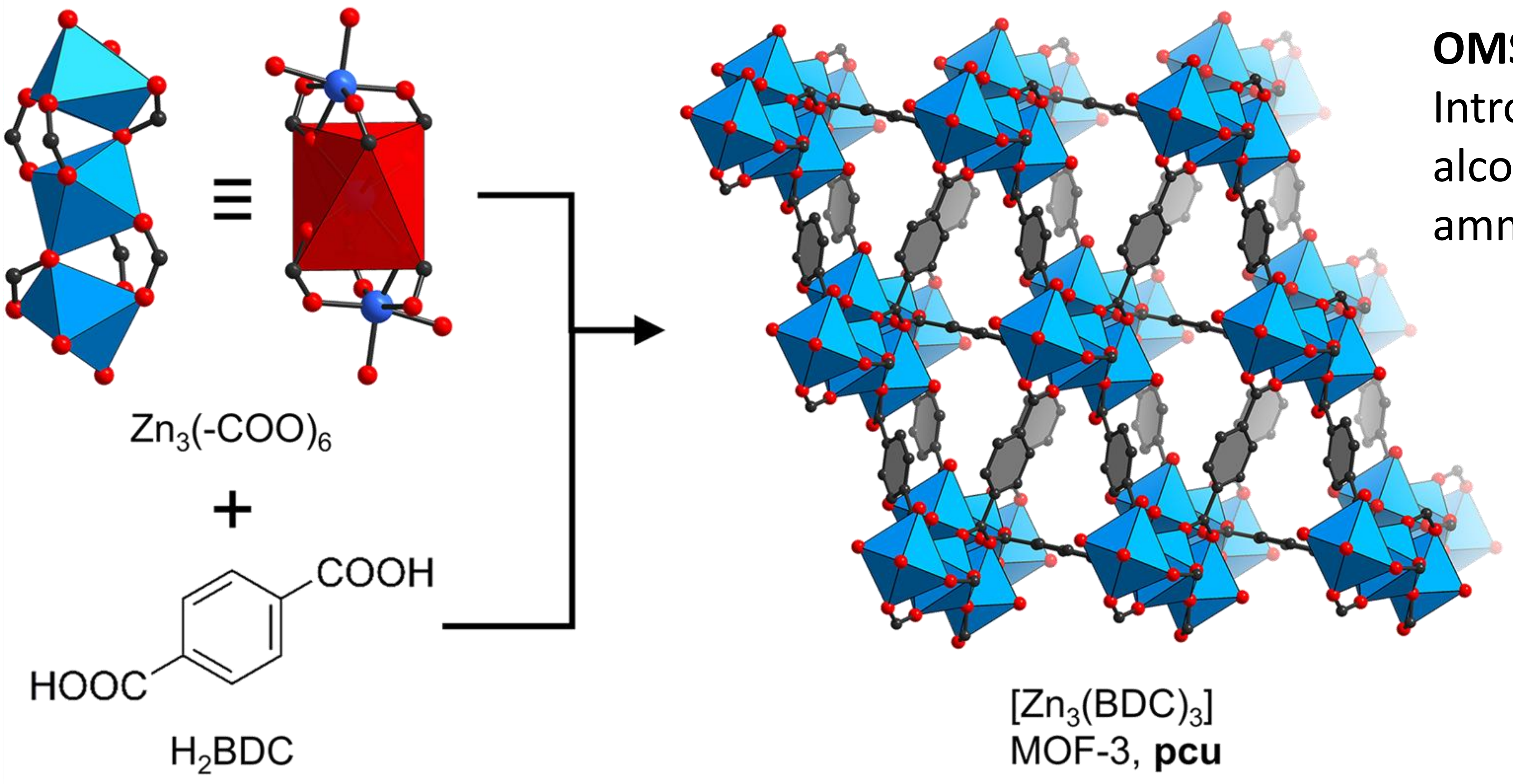
- Original: 700 m²/g
- Full activation: 1800 m²/g

High methane storage capacity (65 bar):




Yaghi *et al., J. Am. Chem. Soc.* **2005**, *127*, 17998-17999; Hupp, Farha, Yildirim *et al., J. Am. Chem. Soc.* **2013**, *135*, 11887-11894.

# Six points of extension – MOF-3



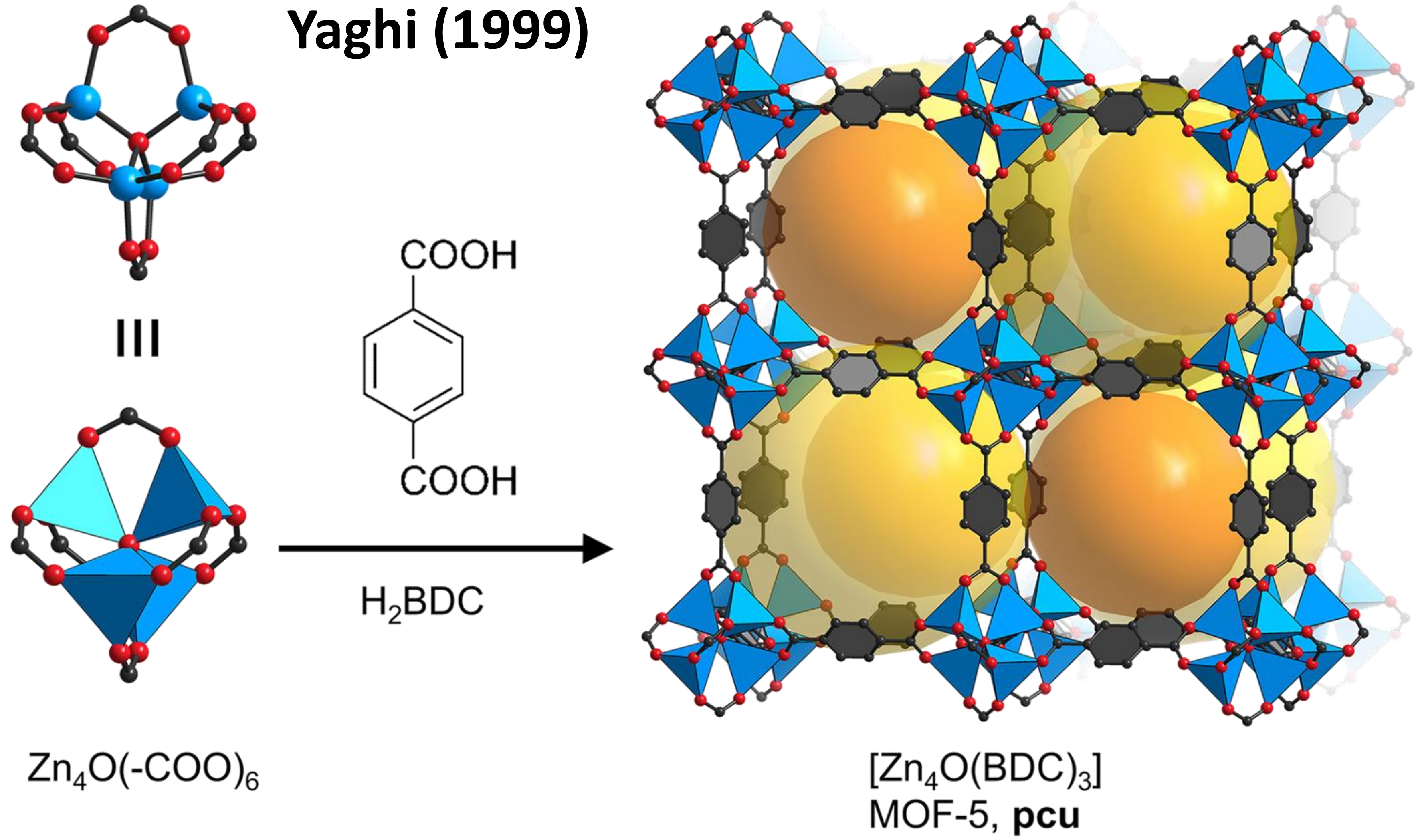

**OMS:**
Introduction of alcohols, amines and ammonia in solution

**1998 Yaghi**

Yaghi *et al., J. Am. Chem. Soc.* **1998**, *120*, 2186-2187.

# Six points of extension – MOF-5

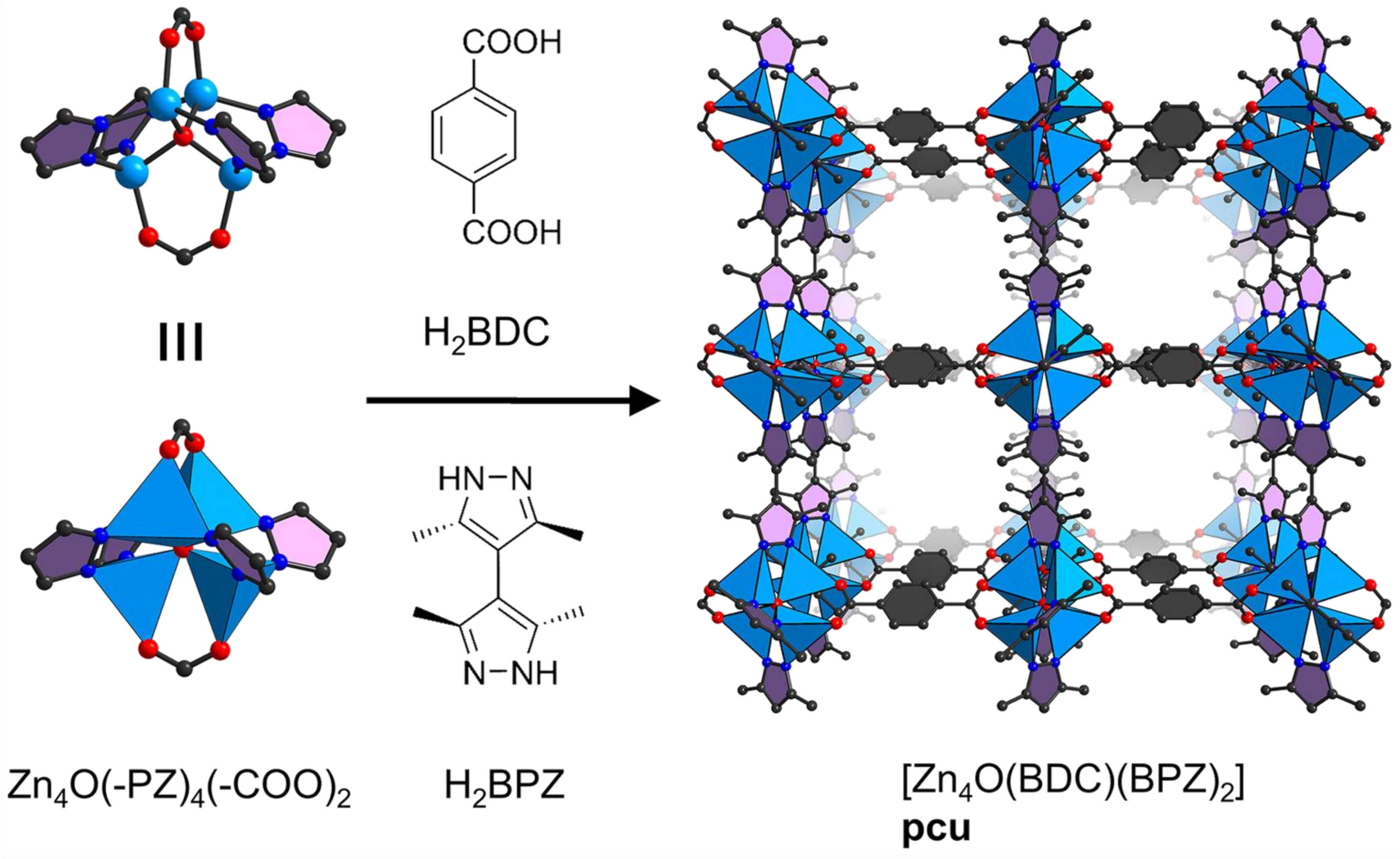
**Yaghi (1999)**




Yaghi *et al., Nature* **1999**, *402*, 276.

- Robust framework
- Type I isotherm ($N_2$, 77K)
- Langmuir surface area: 2,900 $m^2/g$.
- Pore volume: 1.04 $cm^3/g$.
- modular structure
- Control of linker length and functionality

# Replacement of carboxylates

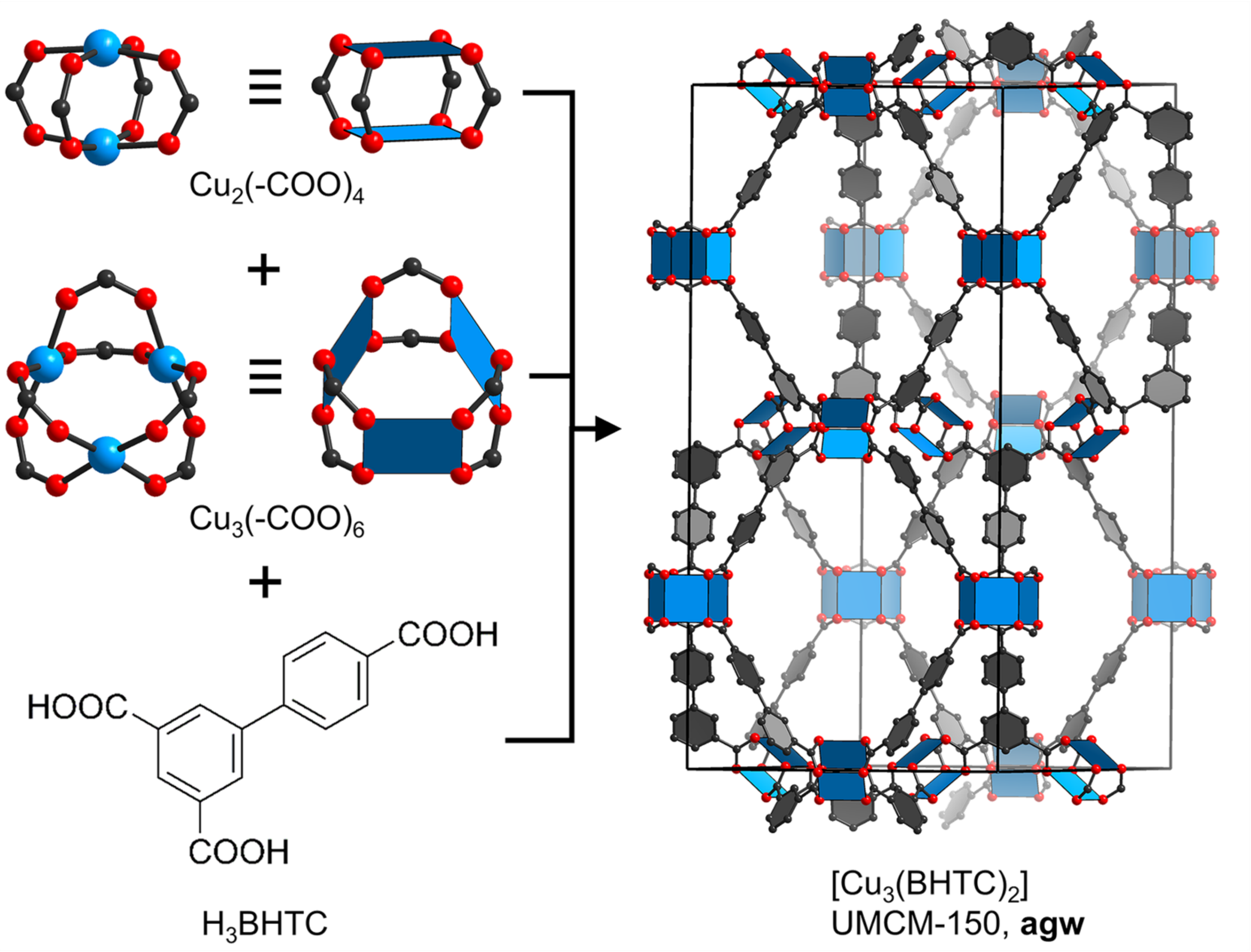



**X.-M. Chen (2008)**

- Symmetry reduction to tetragonal.
- Langmuir surface area: 1,900 $m^3/g$ .
- Pore volume: 0.58 $cm^3/g$.

Chen *et al.*, *Inorg. Chem.* **2008**, *47*, 1346-1351.

# Linker-directed vertex desymmetrization

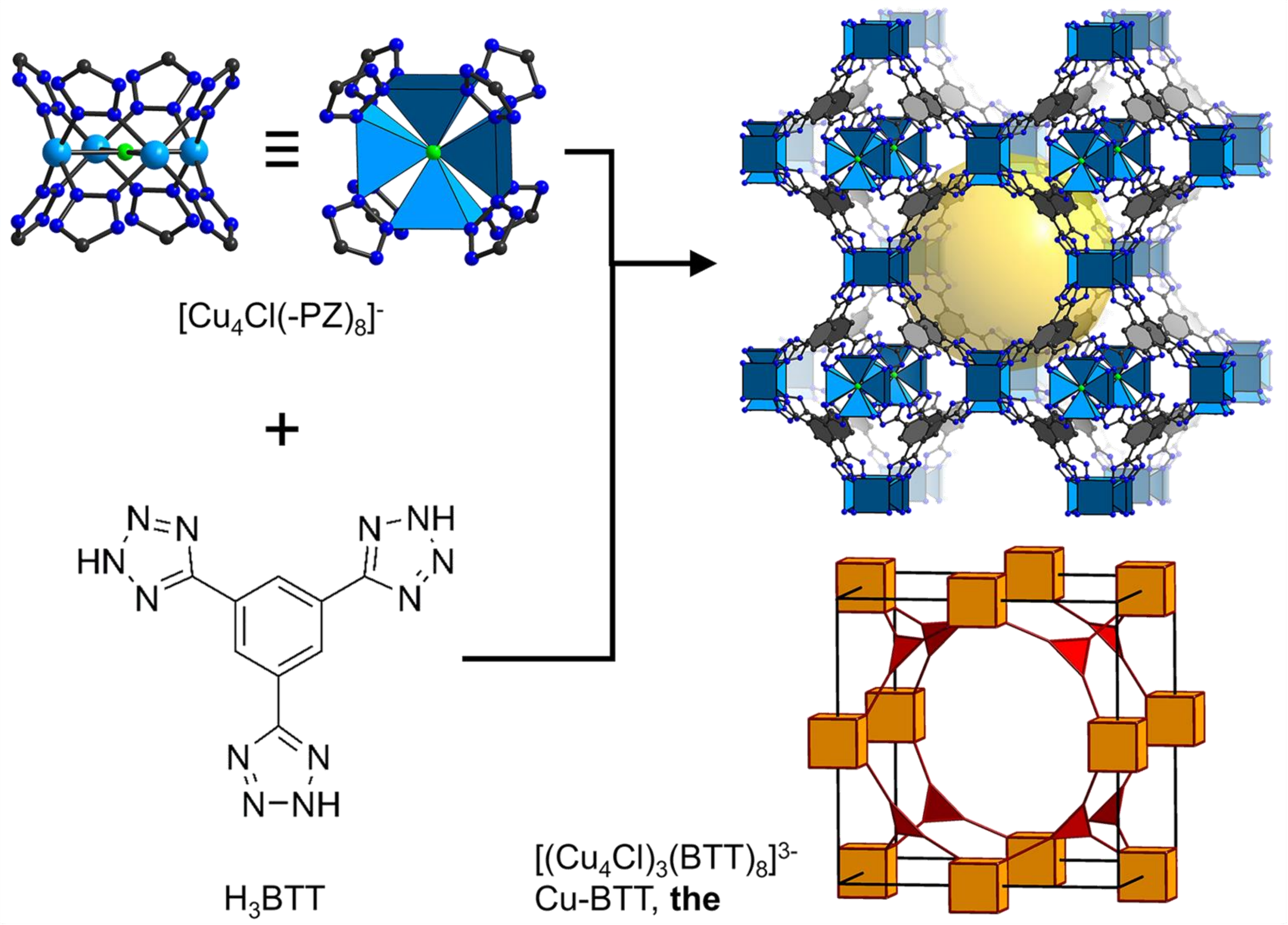



**Matzger (2010)**

- Symmetry reduction of the linker ($D_{3h}$ → $C_{2v}$).
- Trinodal, edge-two transitive net.
- Trigonal prisms are geometric perquisites of cross-linked **kgm**.
- BET area: 3,000 $m^3$/g.

Matzger *et al., J. Am. Chem. Soc.* **2010**, *132*, 13941-13948.

# Eight points of extension



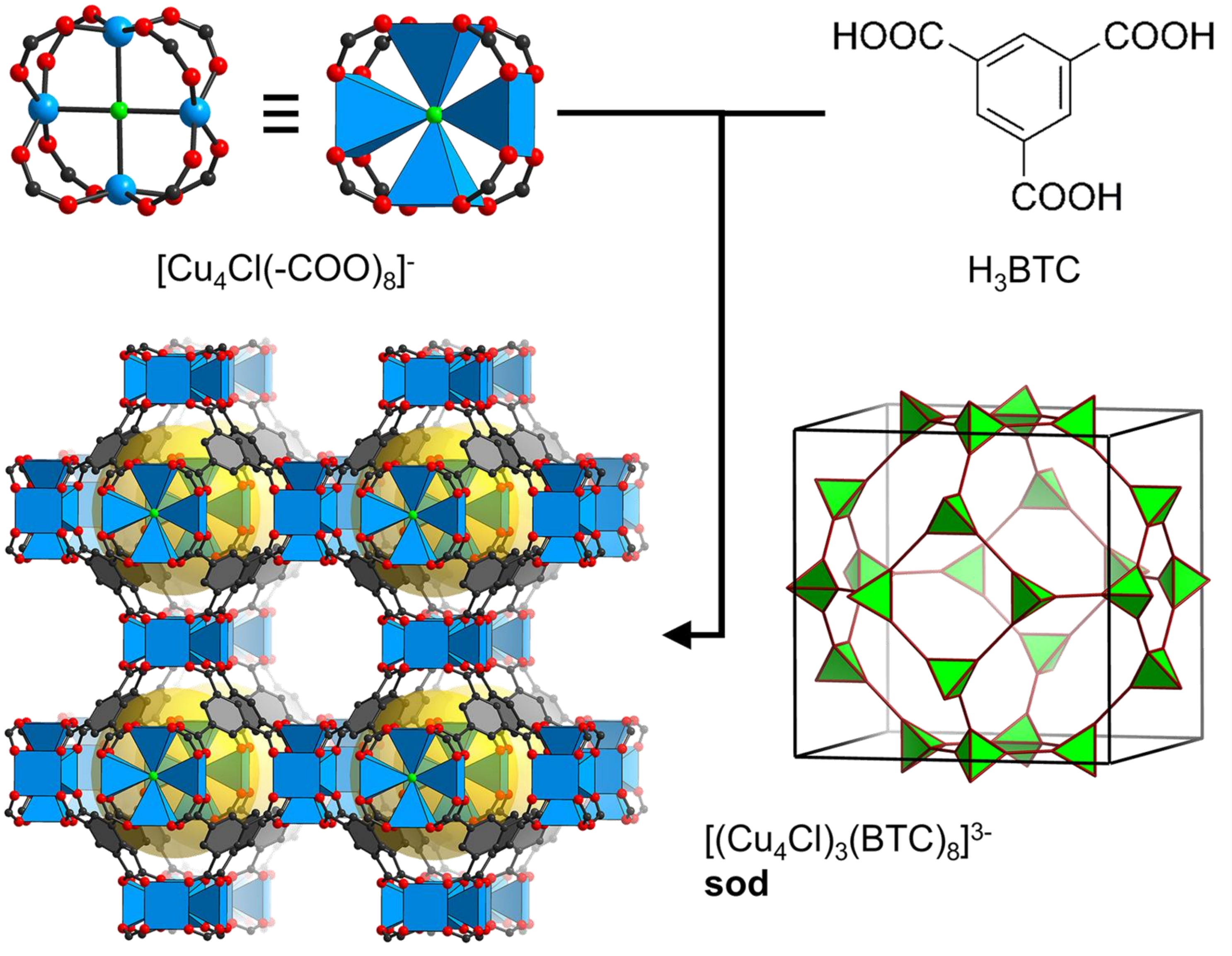

**Long (2006)**

- Anionic framework
- Isostructural to Mn-BTT.
- BET area: 2,100 m³/g.
- High $H_2$-uptake: 2.42 wt%
- $Q_{st}$ = 6 kJ/mol

Long *et al., Angew. Chem. Int. Ed.* **2007**, *46*, 1419-1422; *J. Am. Chem. Soc.* **2006**, *128*, 16876-16883.

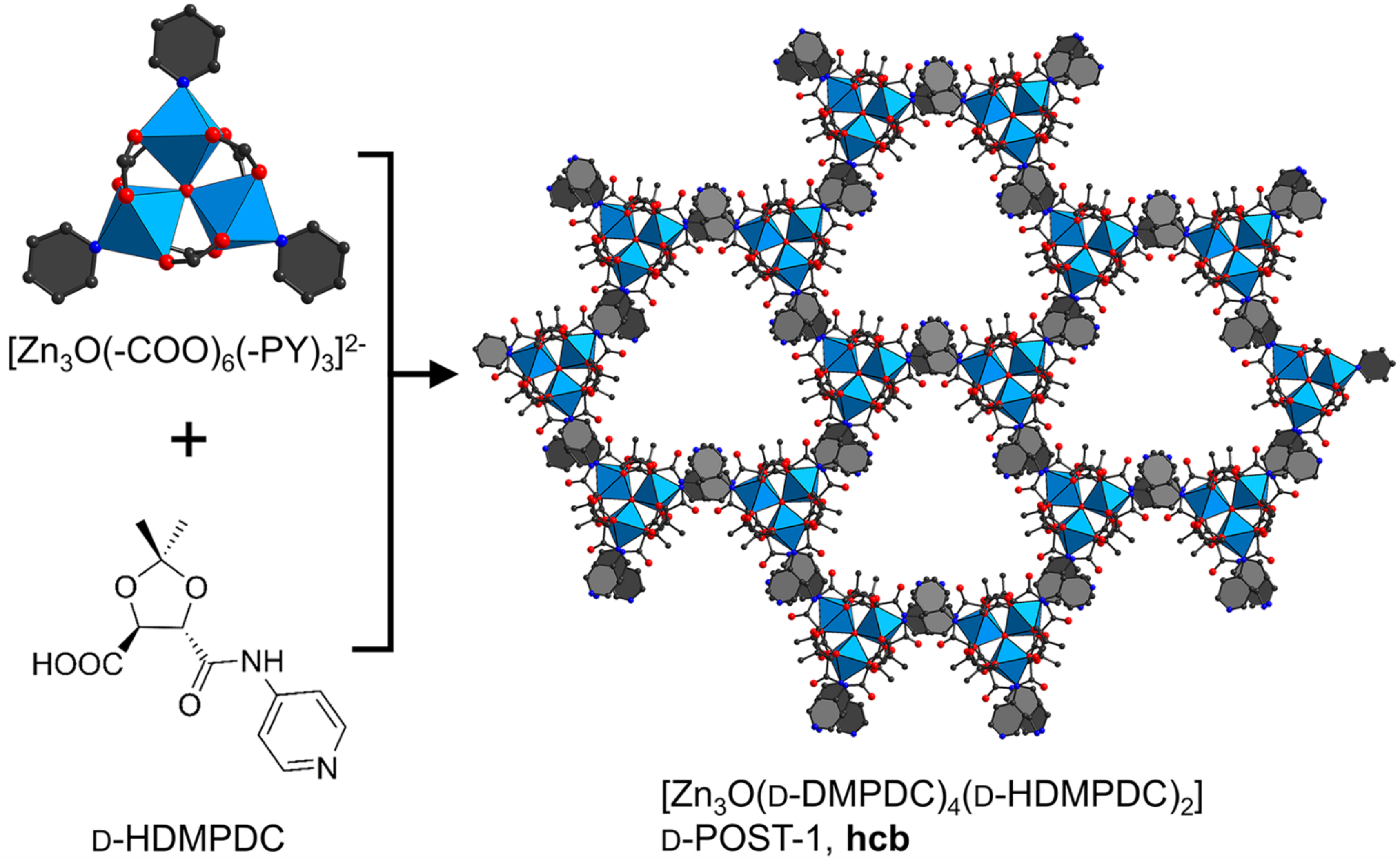
# Eight points of extension

- Anionic framework
- $BTT^{3-}$ replaced by $BTC^{3-}$
- BET area: 800 m³/g.
- Pore partitioning effect
- Described as **sod**, but **the** more accurate.




Zhang *et al., Chem. Commun.* **2011**, *47*, 10647-10649.

# Nine points of extension – POST-1

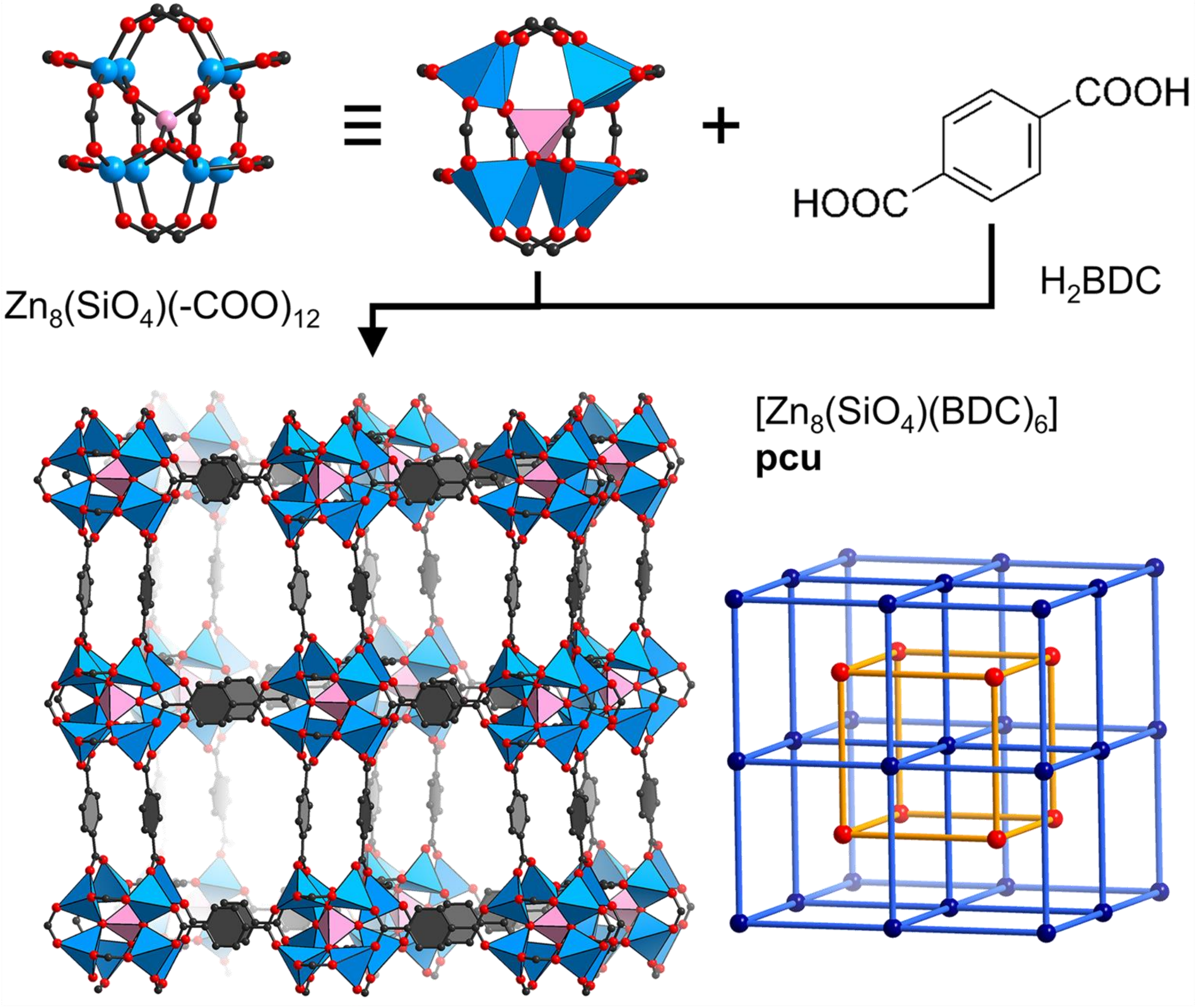



**K. Kim (2000)**

- Only net reported with Zn-trigonal prism
- Chiral linker affords chiral framework (**always**)
- First asymmetric induction in MOF catalysis.

K. Kim *et al., Nature* **2000**, *404*, 982.

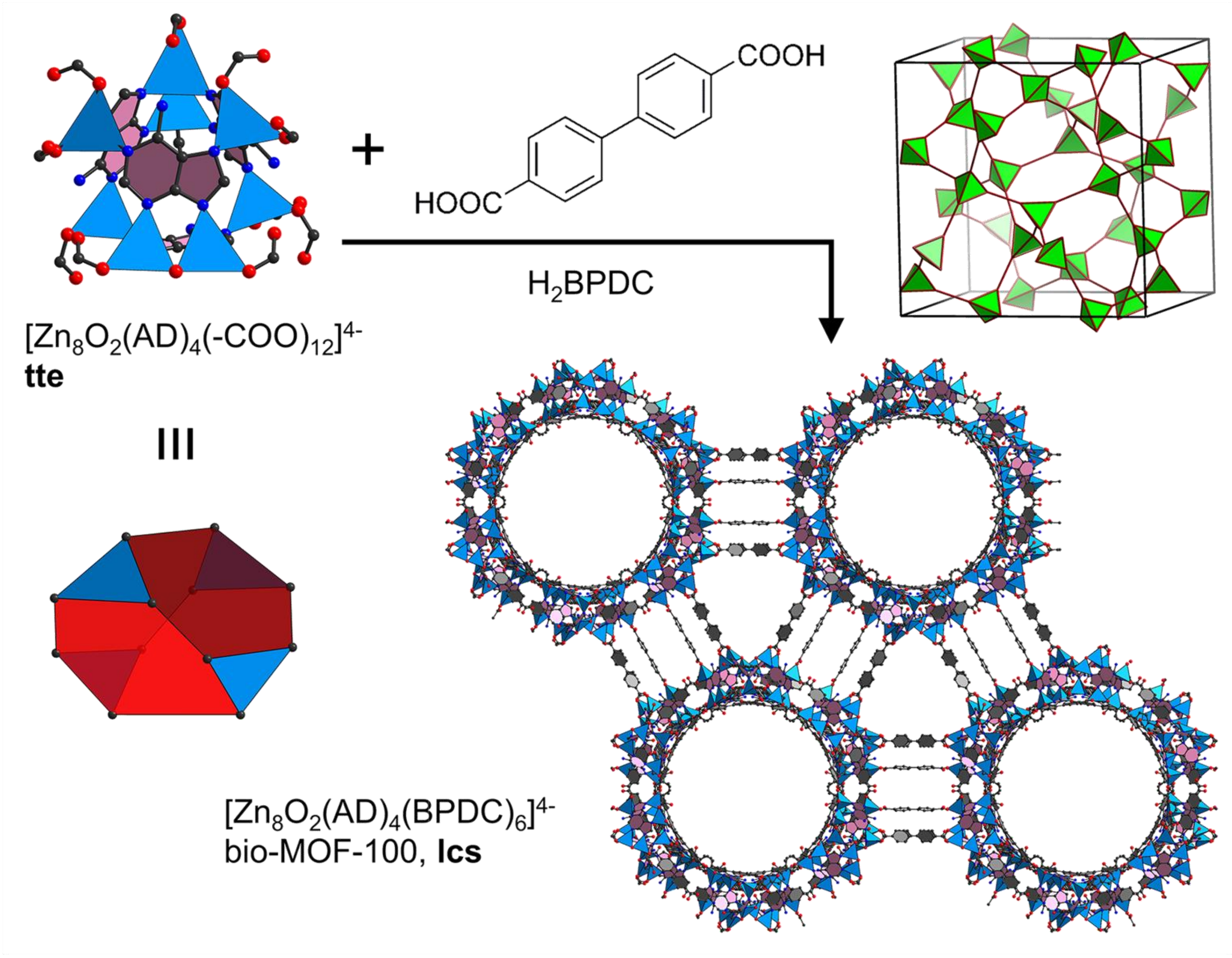
# Twelve points of extension – composite SBUs




- tetrahedral $SiO_4^{4-}$ core.
- double cross-linking, overall 6-c **pcu** net
- 2-fold interpenetration
- High stability up to 520°C

Zheng *et al., Chem. Mater.* **2002**, *14*, 3229-3231.

# Twelve points of extension – bio-MOF-100

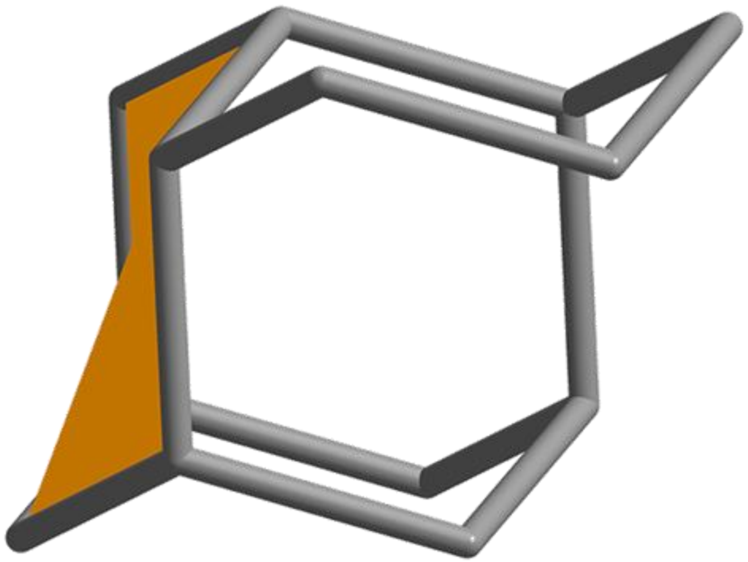



**Rosi (2012)**

- Triple cross-linking, overall 4-c **lcs** net.
- only mesopores.
- BET area: 4,300 $m^2/g$.
- Pore volume: 4.3 $cm^3/g$.
- Post-synthetic linker exchange possible

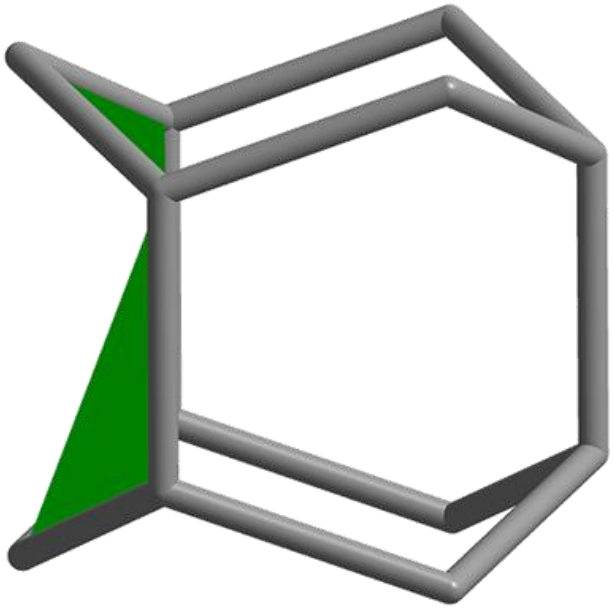
Rosi *et al., Nat. Commun.* **2012**, *3*, 604; **Linker exchange:** Rosi *et al., J. Am. Chem. Soc.* **2013**, *135*, 11688-11691.

# Topology of dia, lon and lcs



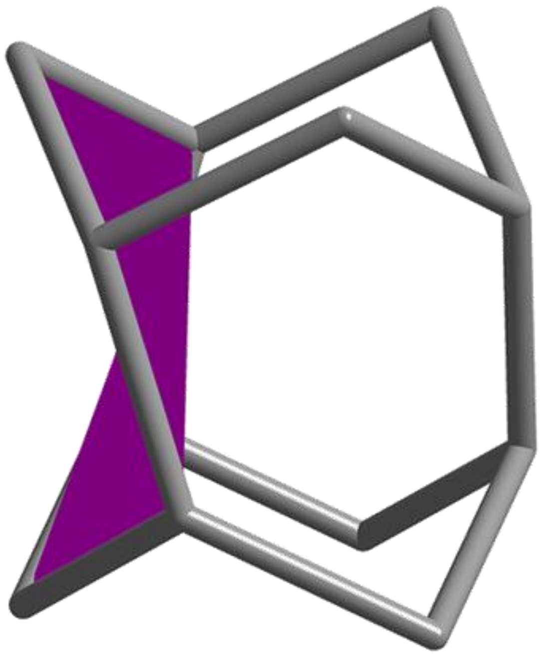
**dia**

Chair



**lon**

Boat

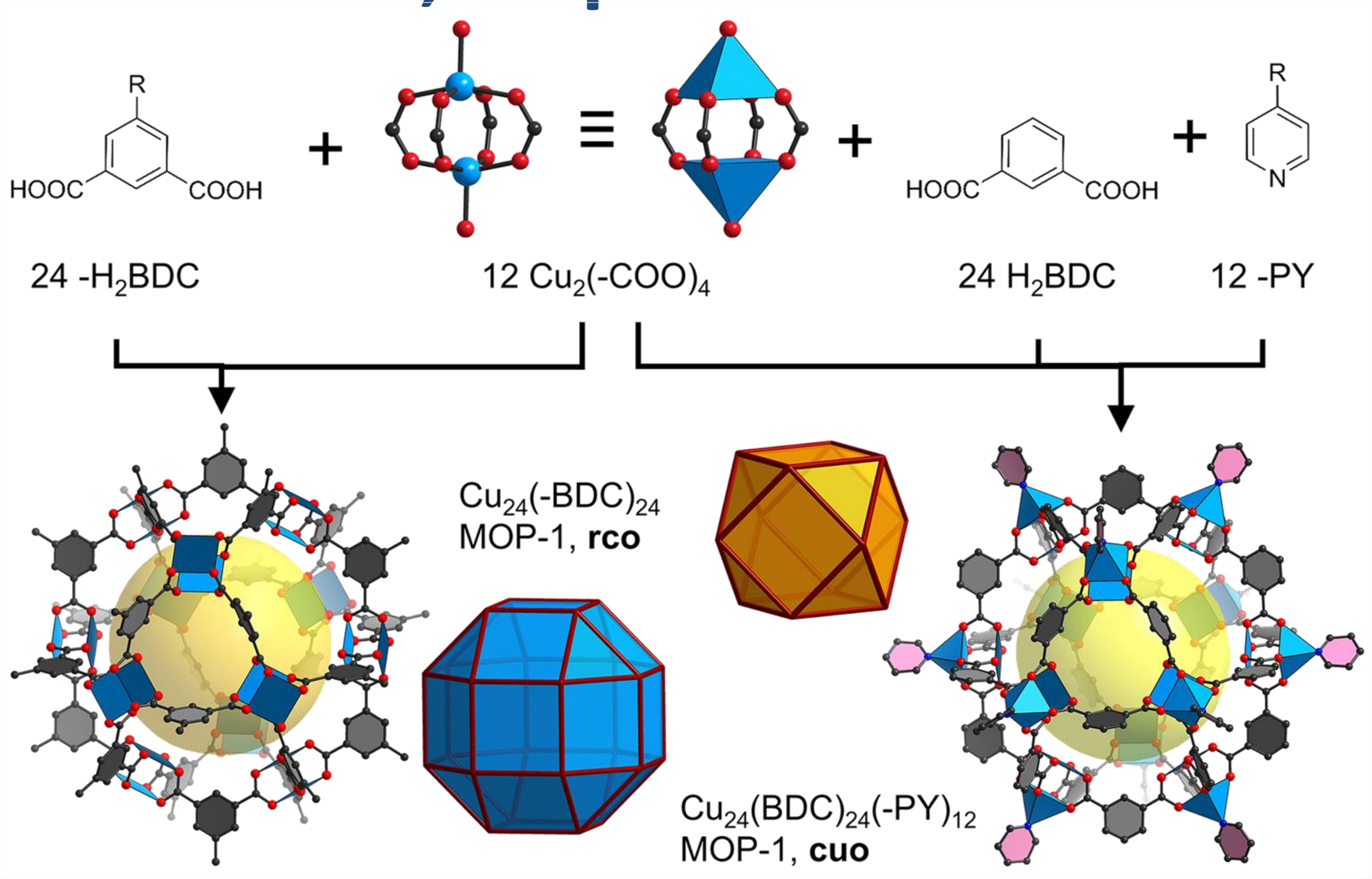


**lcs**

Twist-boat

**dia**: http://rcsr.net/nets/dia; **lon**: http://rcsr.net/nets/lon; **lcs**: http://rcsr.net/nets/lcs.

# 12, 24 points of extension – MOPs

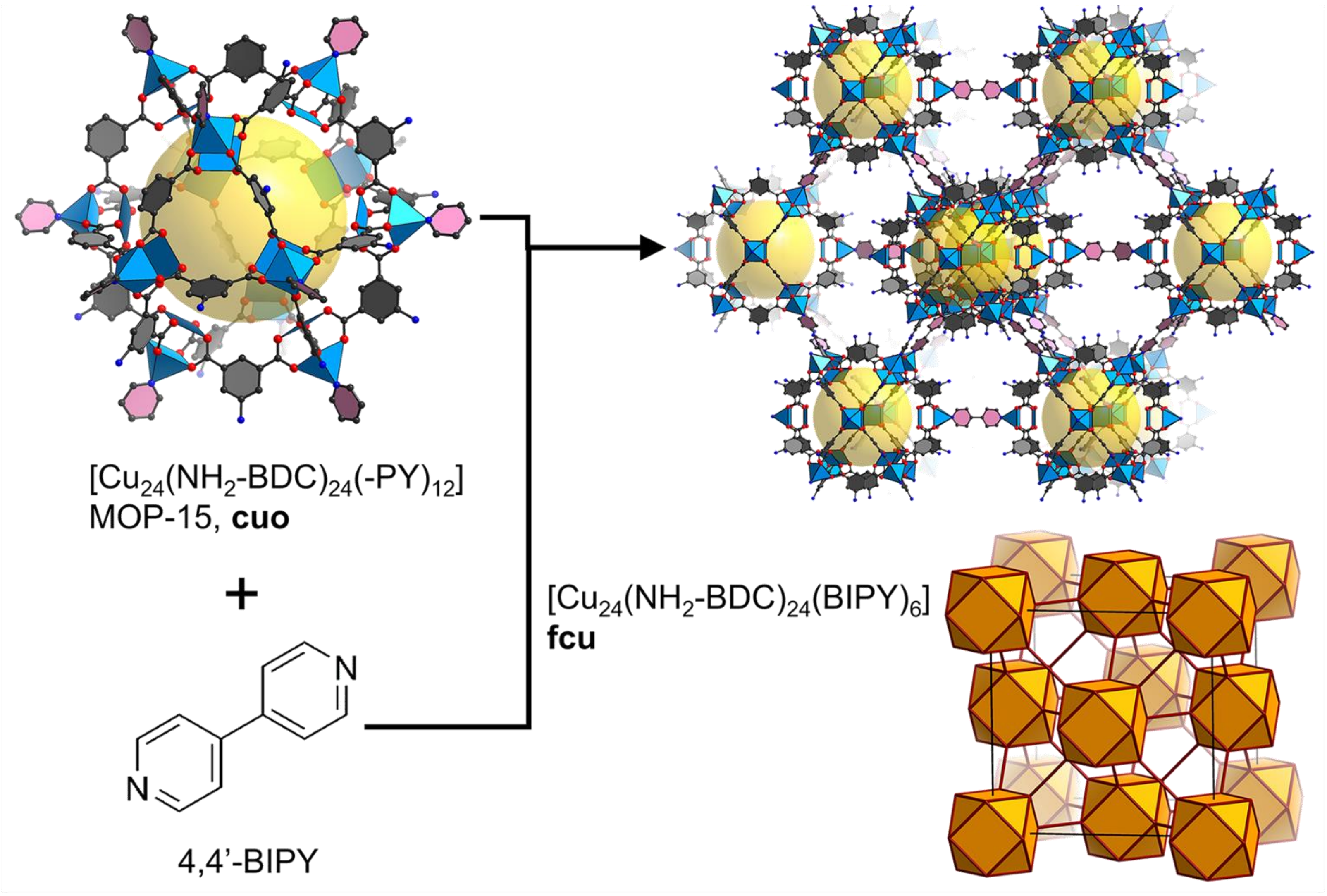



**Yaghi (2001)**

- Metal-organic polyhedra
- 15Å inner diameter
- 12-c cuboctahedron (**cuo**)
- 24-c rhombicuboctahedron (**rco**)

Yaghi *et al., J. Am. Chem. Soc.* **2001**, *123*, 4368-4369; Zaworotko *et al., Chem. Commun.* **2001**, 863-864; Yaghi *et al., J. Am. Chem. Soc.* **2008**, *130*, 11650-11661; Zhou *et al., Nat Chem* **2010**, *2*, 893-898.

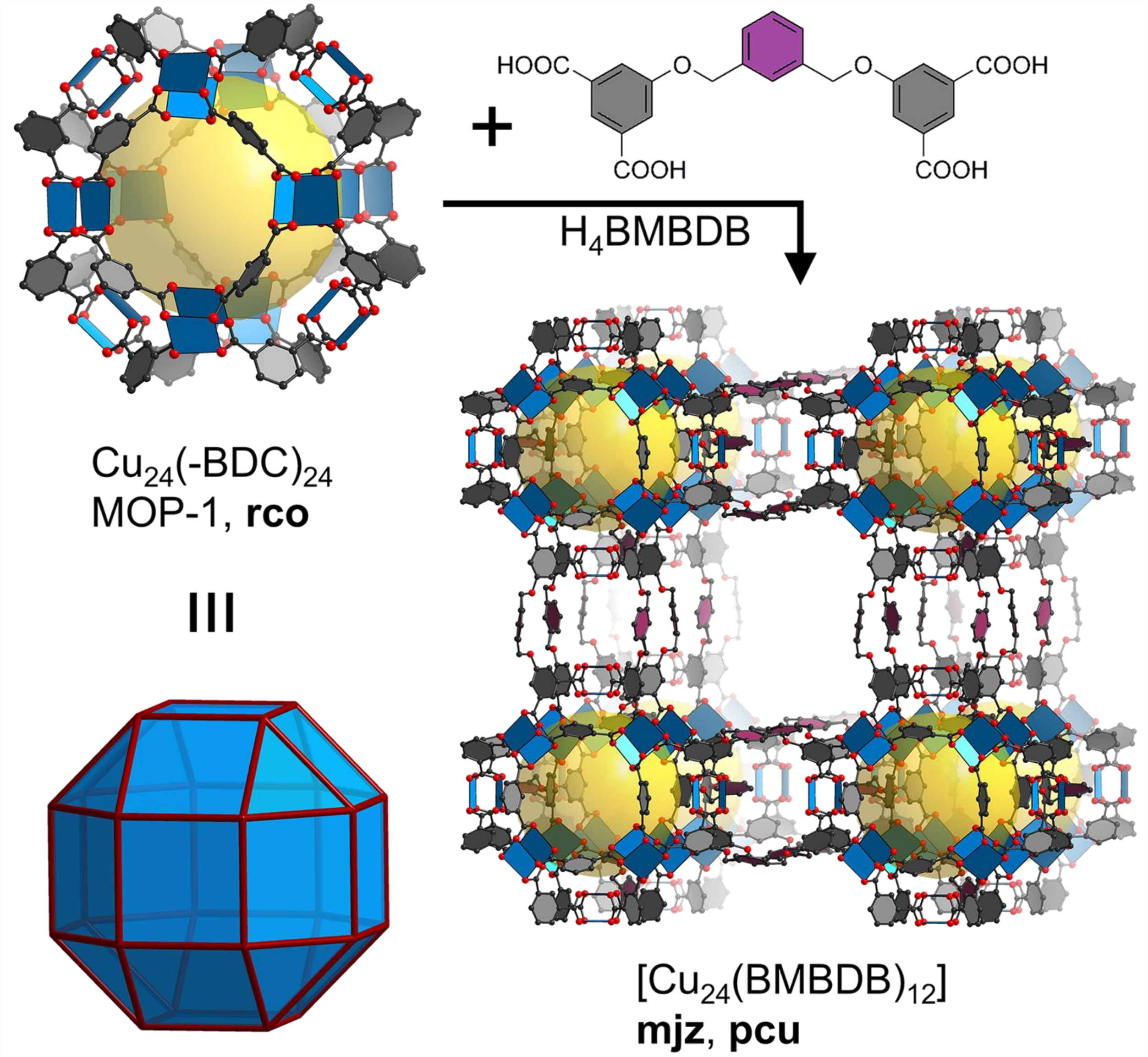
# Decoration of MOPs – cuboctahedron




- Linking through exo-position of paddlewheels
- Mesoporous, octahedral cage

Wang *et al., Chem. Commun.* **2011**, *47*, 7128-7130; Yaghi *et al., J. Am. Chem. Soc.* **2008**, *130*, 11650-11661.

# Rhombicuboctahedron – quadruple cross-linking

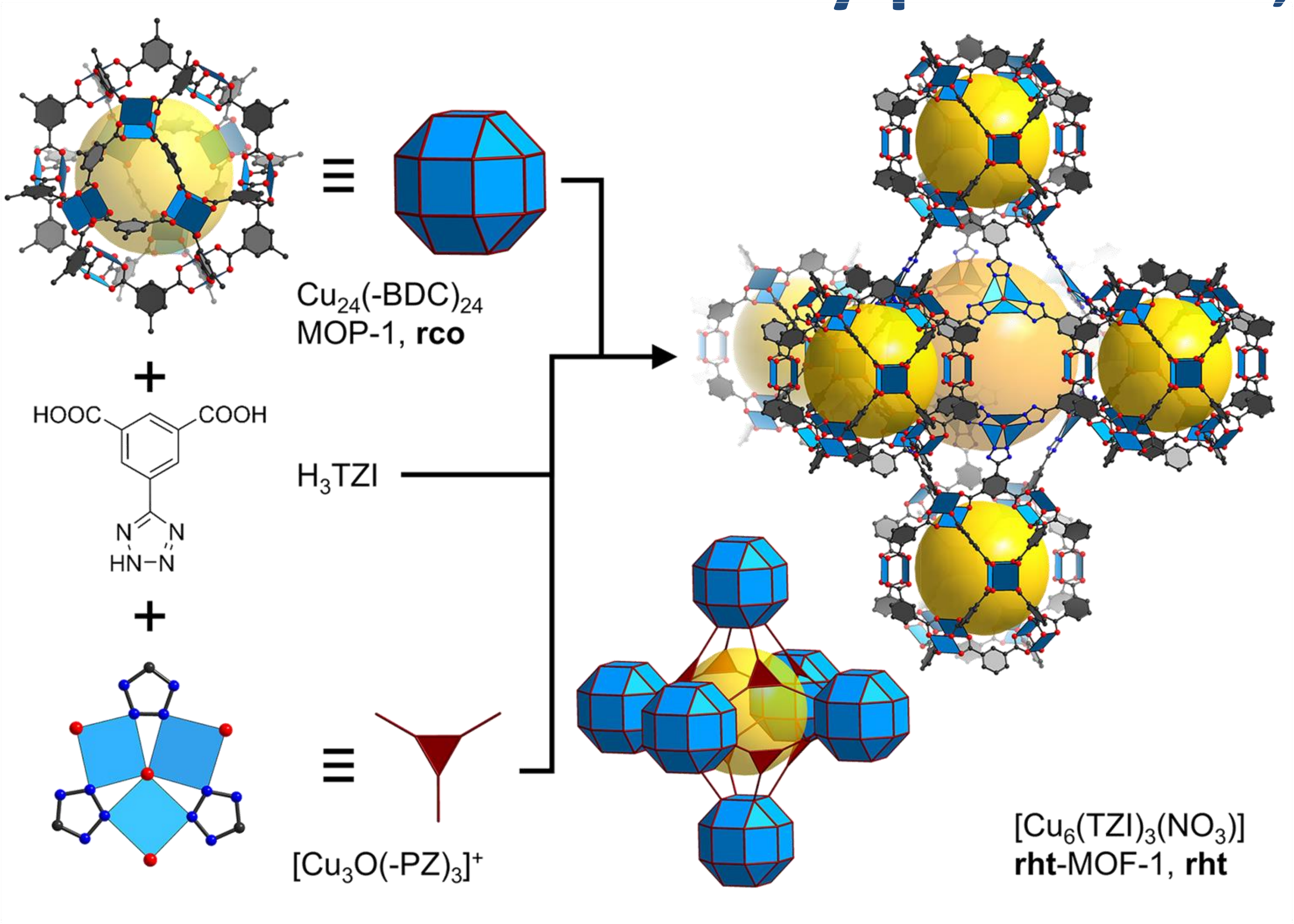



**Zaworotko (2007)**

- Flexible, tetratopic linker.
- Quadruple cross-linking
- Each MOP connected to six neighbors.
- Overall **pcu**-net (each **rco** is 6-c).
- 2-fold interpenetration.

Zaworotko *et al.*, *J. Am. Chem. Soc.* **2007**, *129*, 10076-10077.

# rht – The only possible 3,24-c net




**Eddaoudi (2008)**

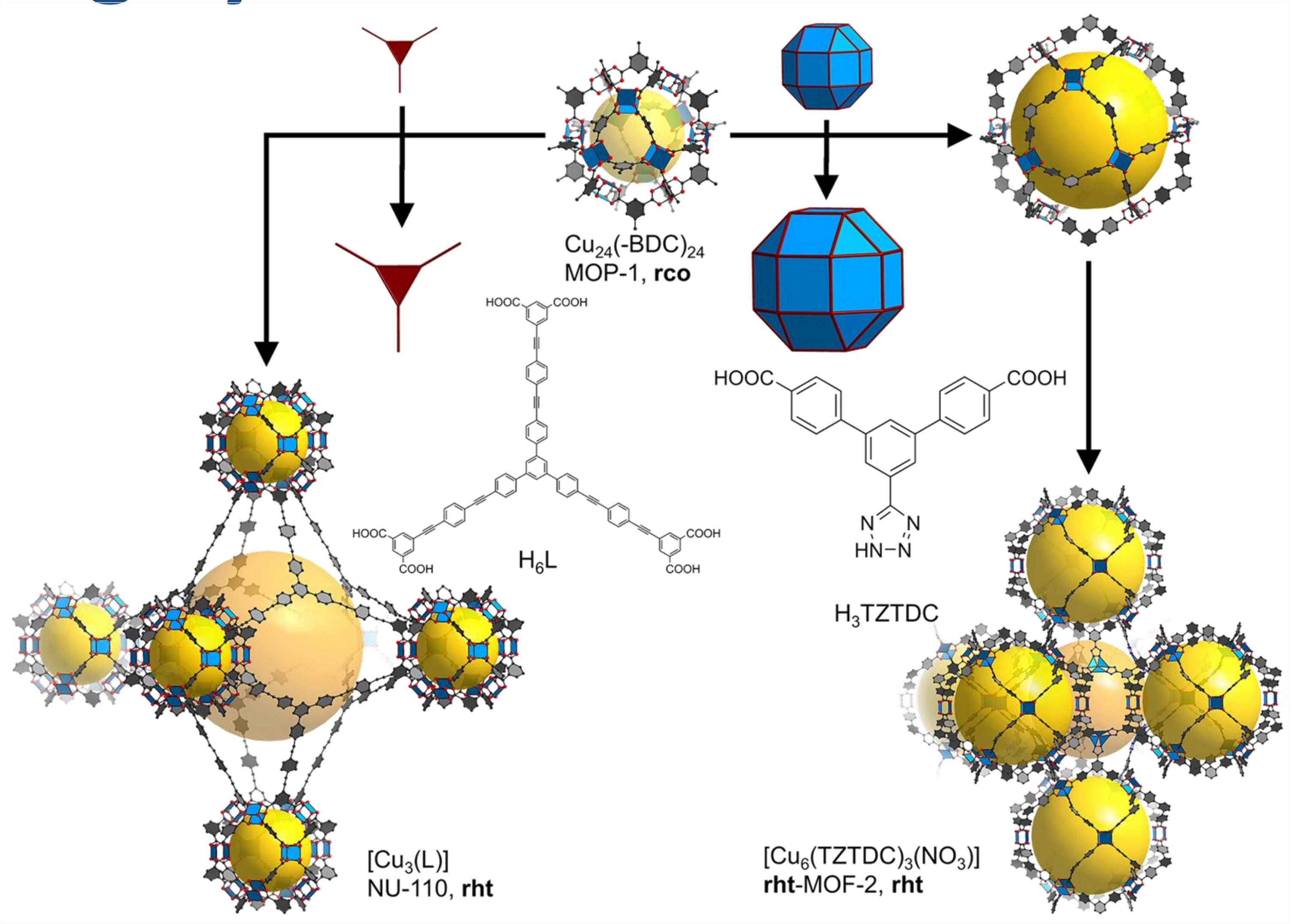
- Minimal transitive net (**rco** and triangle with one kind of edge)
- BET area: 2,847 m²/g
- highly modular
- Fine tunable: sorption of $H_2$, $CO_2$, $CH_4$, …

Eddaoudi *et al., J. Am. Chem. Soc.* **2008**, *130*, 1833-1835.

# rht – A highly modular MOF

**Eddaoudi (2011)**
**Farha (2012)**

- Isoreticular expansion
- Interpenetration precluded (**rht** not self dual)
- NU-110
  - BET area: 7,140 m²/g
  - Pore volume: 4.40 cm³/g

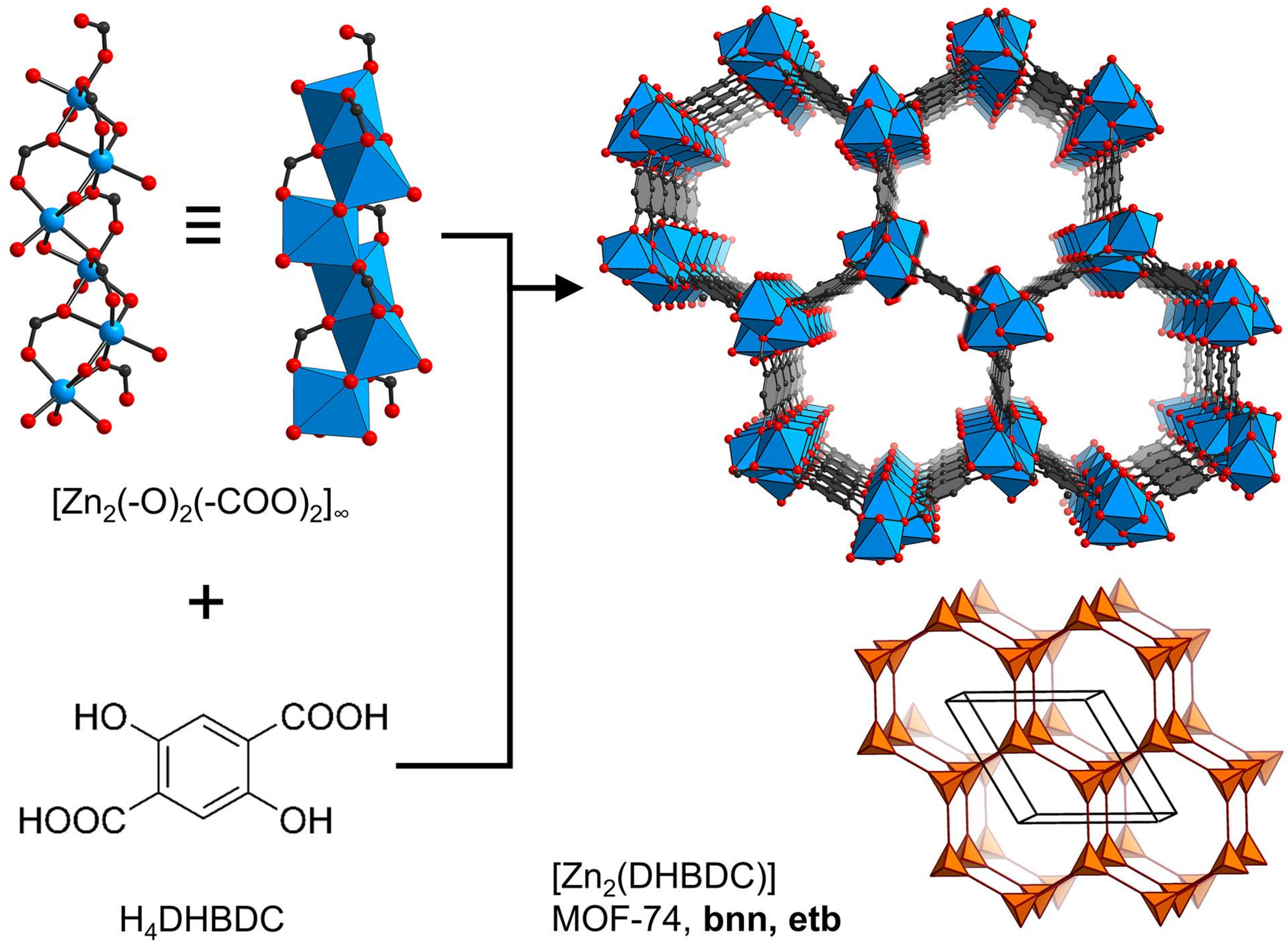



Eddaoudi *et al., J. Am. Chem. Soc.* **2011**, *133*, 17532-17535; Farha *et al., J. Am. Chem. Soc.* **2012**, *134*, 15016-15021.

# Infinite SBUs – MOF-74

**Yaghi (2005)**

- Rod-like SBUs.
- Interpenetration precluded.
- 10.3 x 5.5 Å channels.
- Described as 5-c (**bnn**) or 3-c (**etb**) net.
- Highly modular.

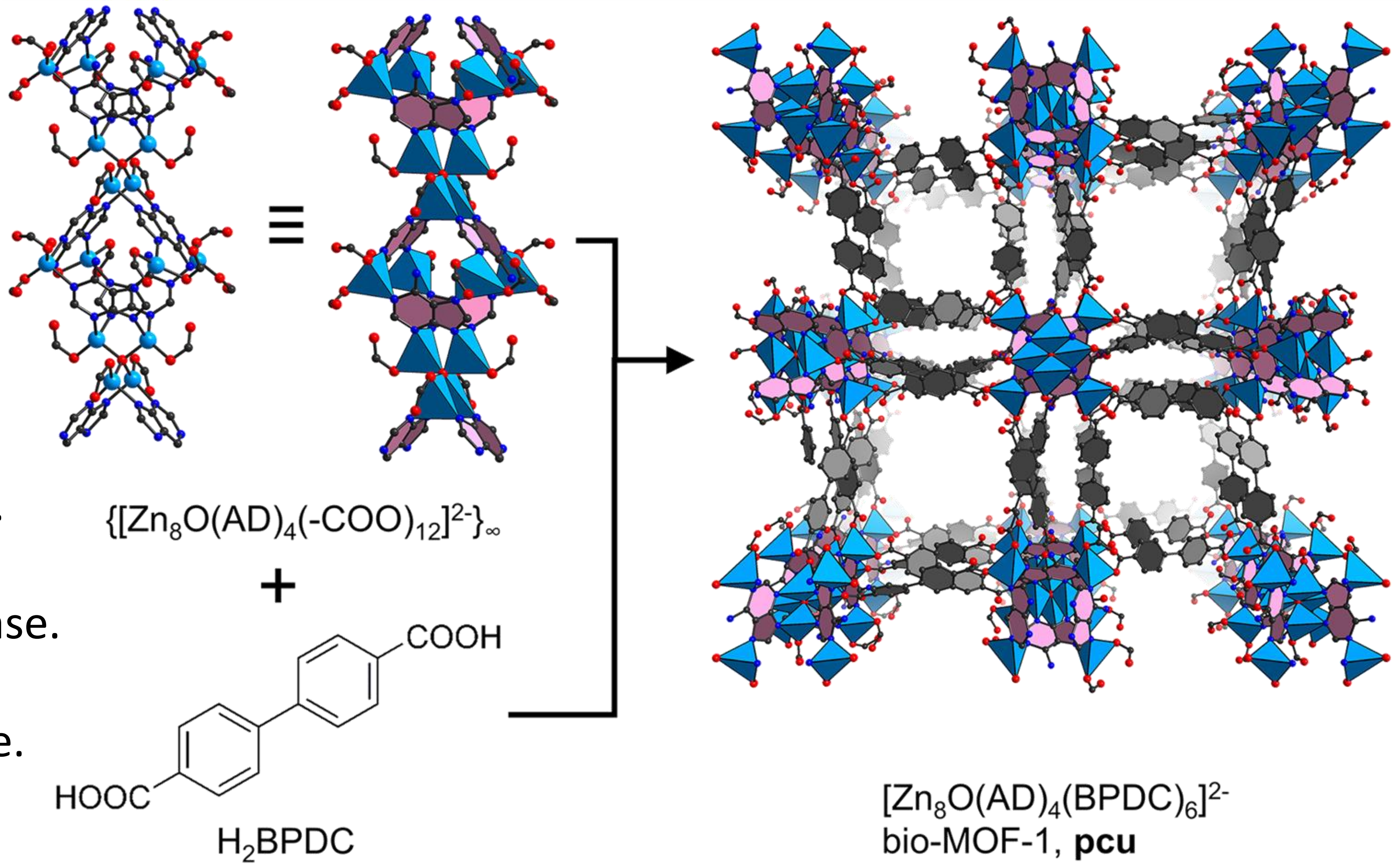



Yaghi *et al., J. Am. Chem. Soc.* **2005**, *127*, 1504-1518; **Isoreticular expansion:** Yaghi *et al., Science* **2012**, *336*, 1018-1023.

# Infinite SBUs – bio-MOF-1

**Rosi (2009)**

- Rod-like SBUs.
- Double cross-linking.
- BET area: 1,700 m²/g.
- Controlled drug release.
- Cations exchangeable.




Rosi *et al.*, *J. Am. Chem. Soc.* **2009**, *131*, 8376-8377; *J. Am. Chem. Soc.* **2010**, *132*, 5578-5579.

# Overview – important SBUs and related MOFs

| Points of extension | SBU | Compound name | Topology (RCSR) | REFCODE (CSD) |
|---|---|---|---|---|
| | | | | |
| 3 | $Cu(-PY)_3$ | | **ths** | ZIBRAD |
| | $Zn_2(-COO)_3(NO_3)$ | PNMOF-3 | **hcb** | ICITOE |
| | $[Cu_3O(-PZ)_3Cl_3]^+$ | | **srs** | WELTIR |
| | $Zn_2(-COO)_3(-COO)_2$ | MOAAF | 3,3,4,5-c | PEJNUP |
| | | | | |
| 4 | $Zn_2(-COO)_4$ | MOF-2 | **sql** | GECXUH |
| | $Cu_2(-COO)_4$ | HKUST-1 | **tbo** | FIQCEN |
| | $Cu_2(-COO)_4$ | PCN-6' | **tbo** | NIBHOW |
| | $Cu_2(-COO)_4$ | MOF-399 | **tbo** | BAZGAM |
| | $Cu_2(-COO)_4$ | MOF-11 | **pts** | BIMDIL |
| | $Cu_2(-COO)_4$ | MOF-101 | **nbo** | YIXBIQ |
| | $Cu_2(-COO)_4$ | MOF-505 | **nbo, fof** | LASYOU |
| | $Cu_2(-COO)_4$ | kagomé | **kgm** | PACFOP |
| | $Cu_2(-COO)_4$ | MOP-1 | **cuo, rco** | MIQCEU |
| | $Cu_2(-COO)_4$ | MOP-15 | **cuo, rco** | KOJXAJ |
| | | | | |
| 6 | $Zn_4O(-COO)_6$ | MOF-5 | **pcu** | SAHYIK |
| | $Zn_4O(-COO)_6$ | MOF-177 | **qom** | ERIRIG |
| | $Zn_4O(-COO)_6$ | MOF-180 | **qom** | CUSXIY |
| | $Zn_4O(-COO)_6$ | MOF-200 | **qom** | CUSXOE |
| | $Zn_4O(-COO)_6$ | MOF-210 | **toz** | CUSYAR |
| | $Zn_3(-COO)_6$ | MOF-3 | **pcu** | PURSOK |
| | $Zn_4O(-PZ)_4(-COO)_2$ | | **pcu** | WIYFAM |
| | $Cu_3(-COO)_6$ | UMCM-150 | **agw** | UKIQOV |

| Points of extension | SBU | Compound name | Topology (RCSR) | REFCODE (CSD) |
|---|---|---|---|---|
| | | | | |
| 8 | $Cu_4Cl(-PZ)_8$ | Cu-BTT | **the, sod** | VEXYON |
| | $Cu_4Cl(-COO)_8$ | | **the, sod** | ABEMIF |
| | | | | |
| 9 | $[Zn_3O(-COO)_6(-PY)_3]^{2-}$ | POST-1 | **hcb** | UHOPUC |
| | | | | |
| 12 | $Zn_8(SiO_4)(-COO)_{12}$ | | **pcu** | OGIYEI |
| | $Cu_{24}(BDC)_{24}(-PY)_{12}$ | | **fcu** | IVEKEA |
| | $[Zn_8O_2(AD)_4(-COO)_{12}]^{4-}$ | bio-MOF-100 | **lcs** | SAPBIW |
| | | | | |
| 24 | $Cu_{24}(-BDC)_{24}$ | | **mjz, pcu** | CILLAL |
| | $Cu_{24}(-BDC)_{24}$ | **rht**-MOF-1 | **rht, ntt** | LIZWEX |
| | $Cu_{24}(-BDC)_{24}$ | **rht**-MOF-2 | **rht, ntt** | ADASAB |
| | $Cu_{24}(-BDC)_{24}$ | NU-110 | **rht, ntt** | SEMNIJ |
| | | | | |
| ∞ | $[Zn_2(-O)_2(-COO)_2]_\infty$ | MOF-74 | **bnn, etb** | FIJDOS |
| | $\{[Zn_8O(AD)_4(-COO)_{12}]^{2-}\}_\infty$ | bio-MOF-1 | **pcu** | NUDLAA |