Towards a Taxonomy of MOF Structures

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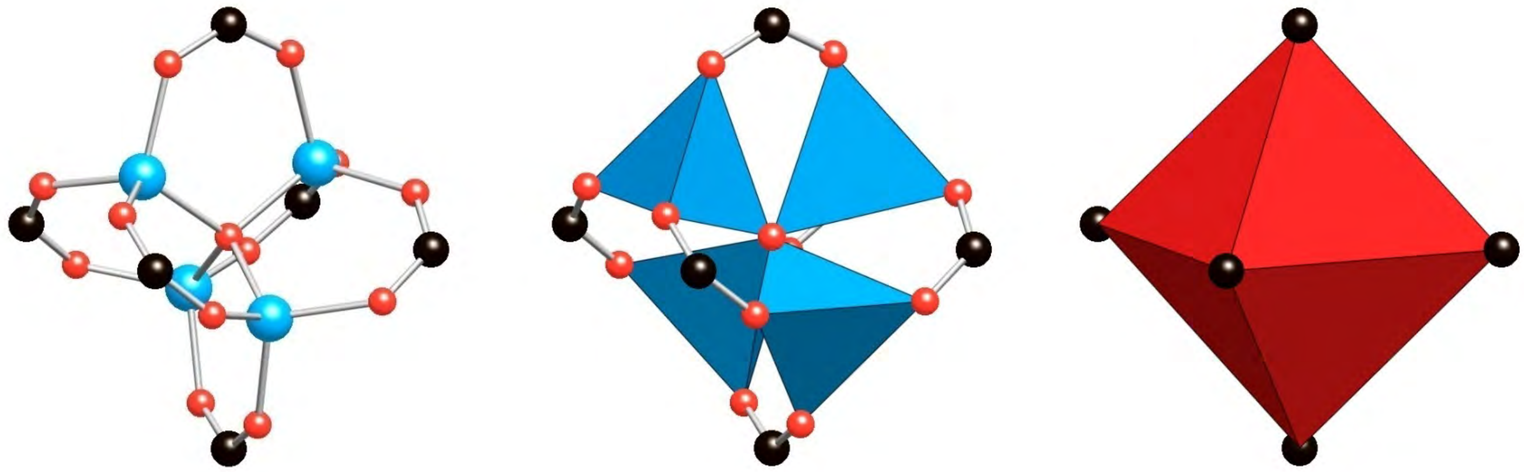
M. O'Keeffe & O. M. Yaghi, Chem. Rev. 112, 675 (2012)
M. Li, D. Li, M. O'K. & O. M. Y., Chem. Rev. 114, 1343 2014)

Nothing exists except atoms and empty space,

all else is opinion.

Democritus

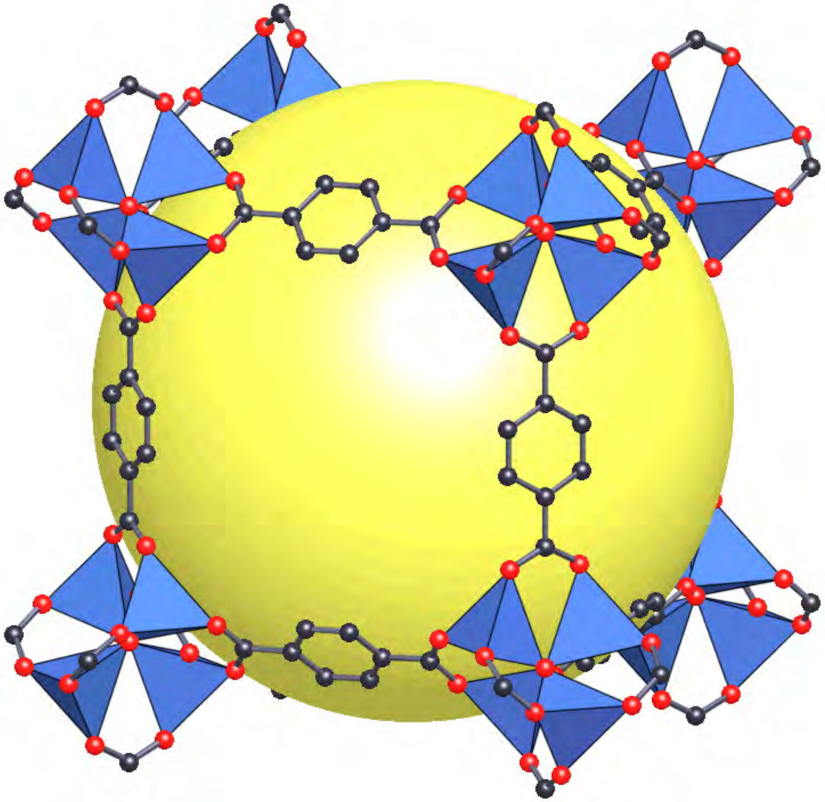
The cluster in basic zinc acetate (a salt!)



In the acetate each carboxylate C atom (black)
is joined to a methyl group -> discrete molecule
The C atoms are ***points of extension***

H. Koyama, Y. Saito, *Bull.Chem. Soc. Japan* **27**, 112 (1954)

In MOF-5 the basic zinc acetate clusters are joined by ditopic linkers (terephthalate) to make an infinite crystal.



H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature*, 1999, **402**, 276

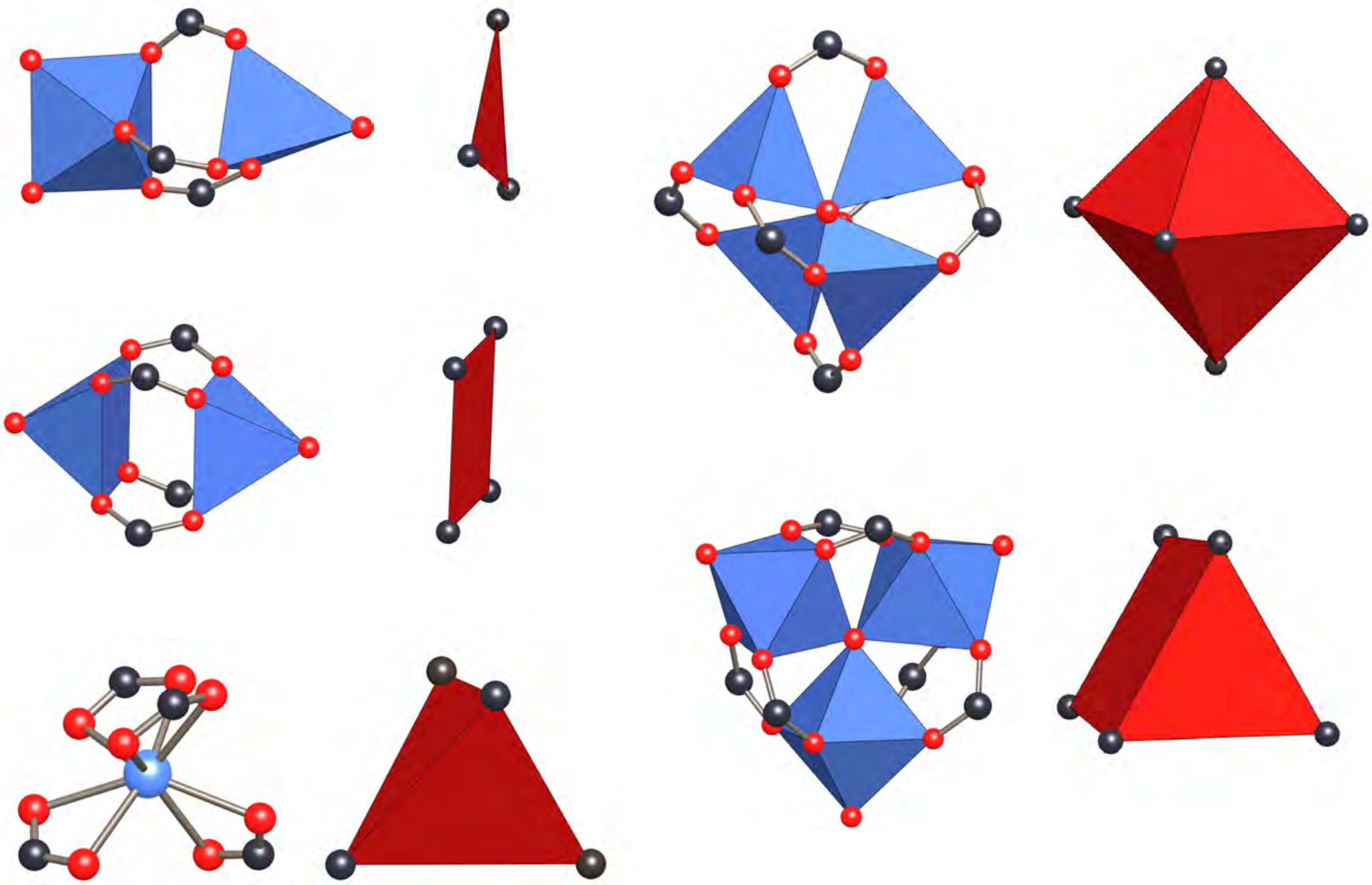
MOF has at least two components.
Secondary building units (SBUs)

1. metal-containing (“cation”)

0-periodic: single atom or cluster (may be a ring)
1-periodic: rod
2-periodic: layer
3-periodic: usually the whole crystal

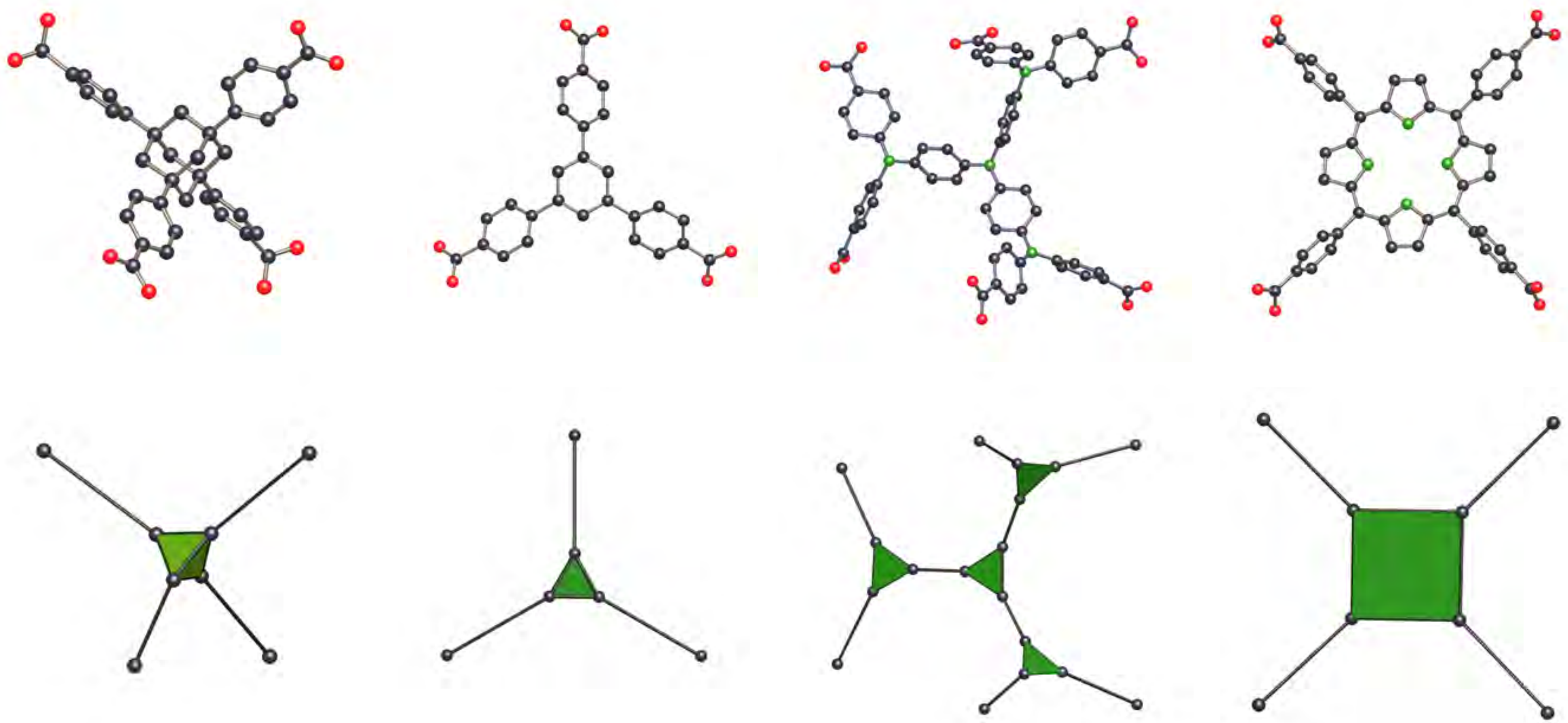
2. organic linker (anion”)

ditopic
polytopic
polytopic branched



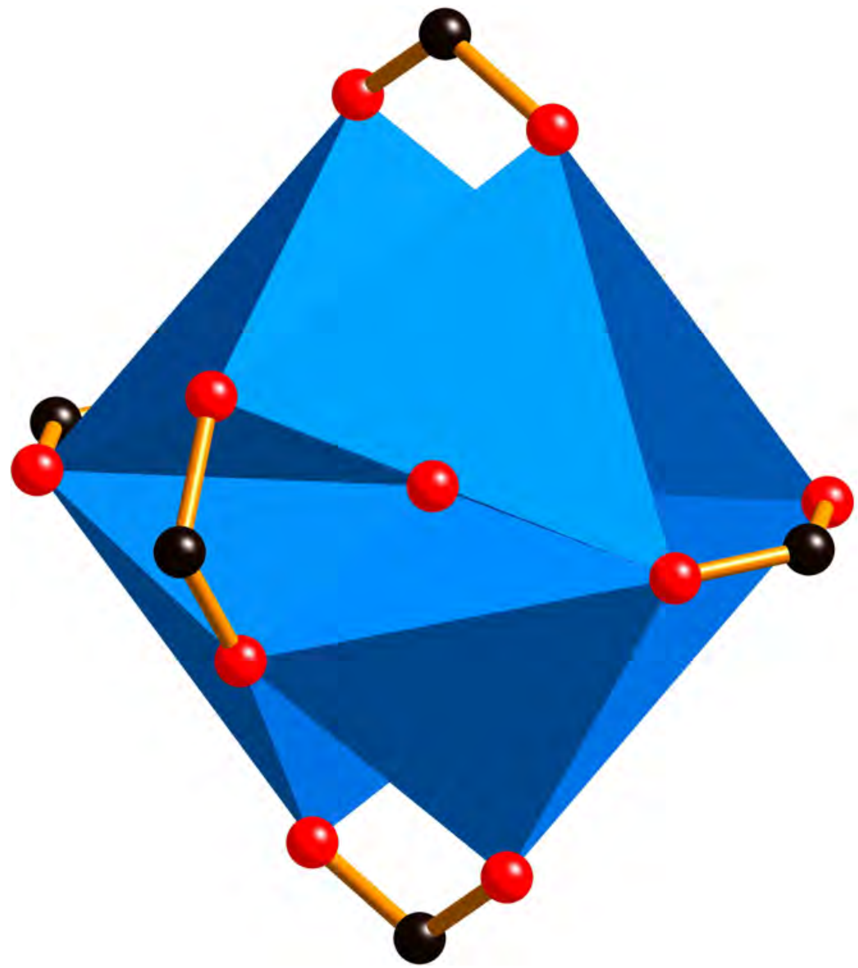
Cationic clusters and SBUs (red)

[SBU = Secondary Building Unit. Blue polyhedra are metal-O] metal atoms in an SBU have points of extension in common



Organic polytopic linkers (top) and SBUs (bottom)

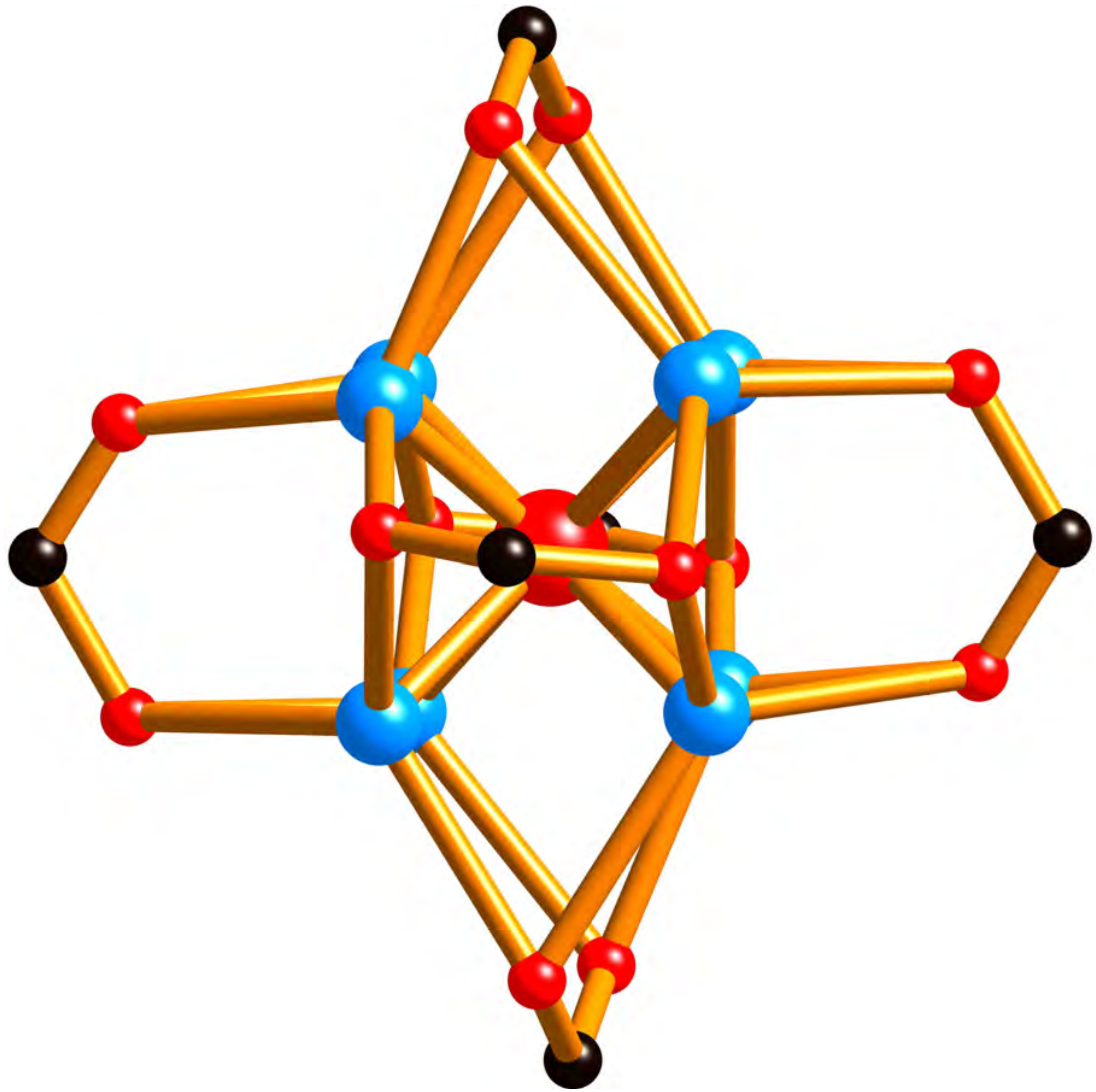
[SBU = Secondary Building Unit]



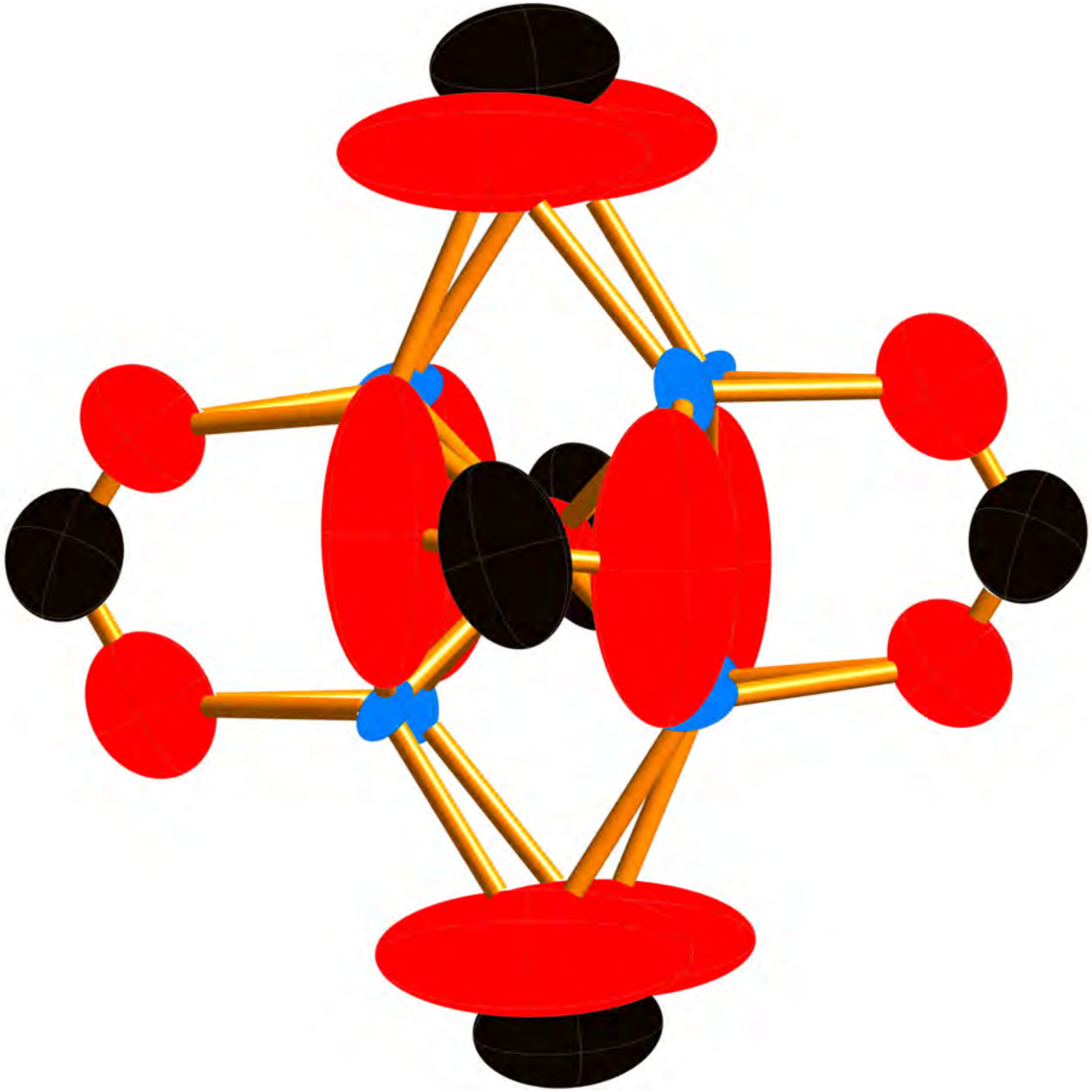
WARNING! An extraordinary Zn_8 SBU reported

Sen, S.; Nair, N. M.; Yamada, T.; Kitagawa, H.; Bharadwaj, K.

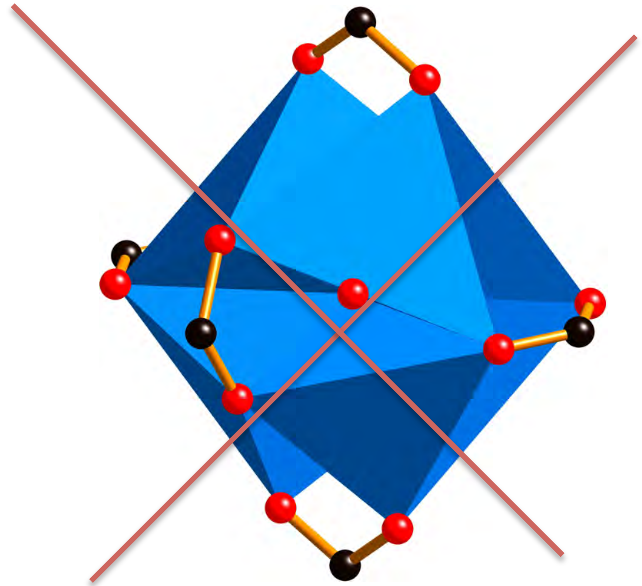
JACS **2012**, *124*, 19432-19437.

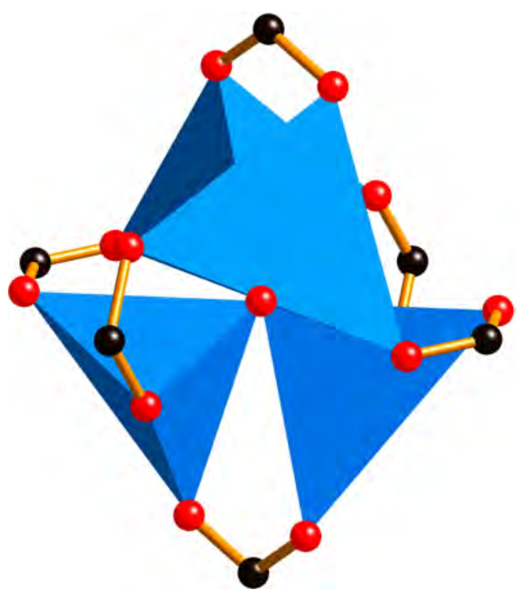


Ball and stick model $Zn_8O(\text{-}CO_2)_6$ Zn...Zn (blue) = 2.0 Å!

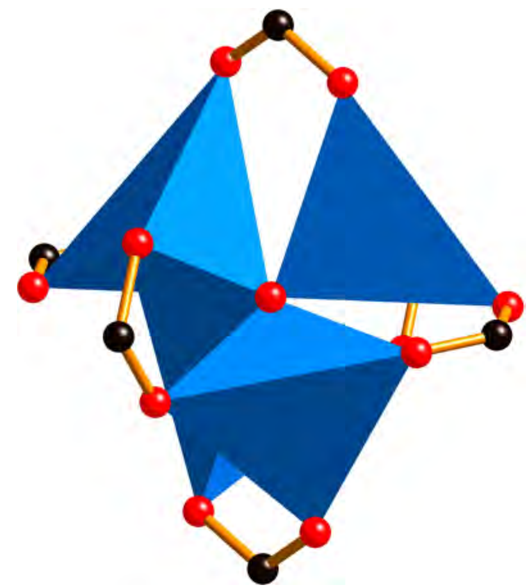


Look at thermal ellipsoids – give away for positional disorder!

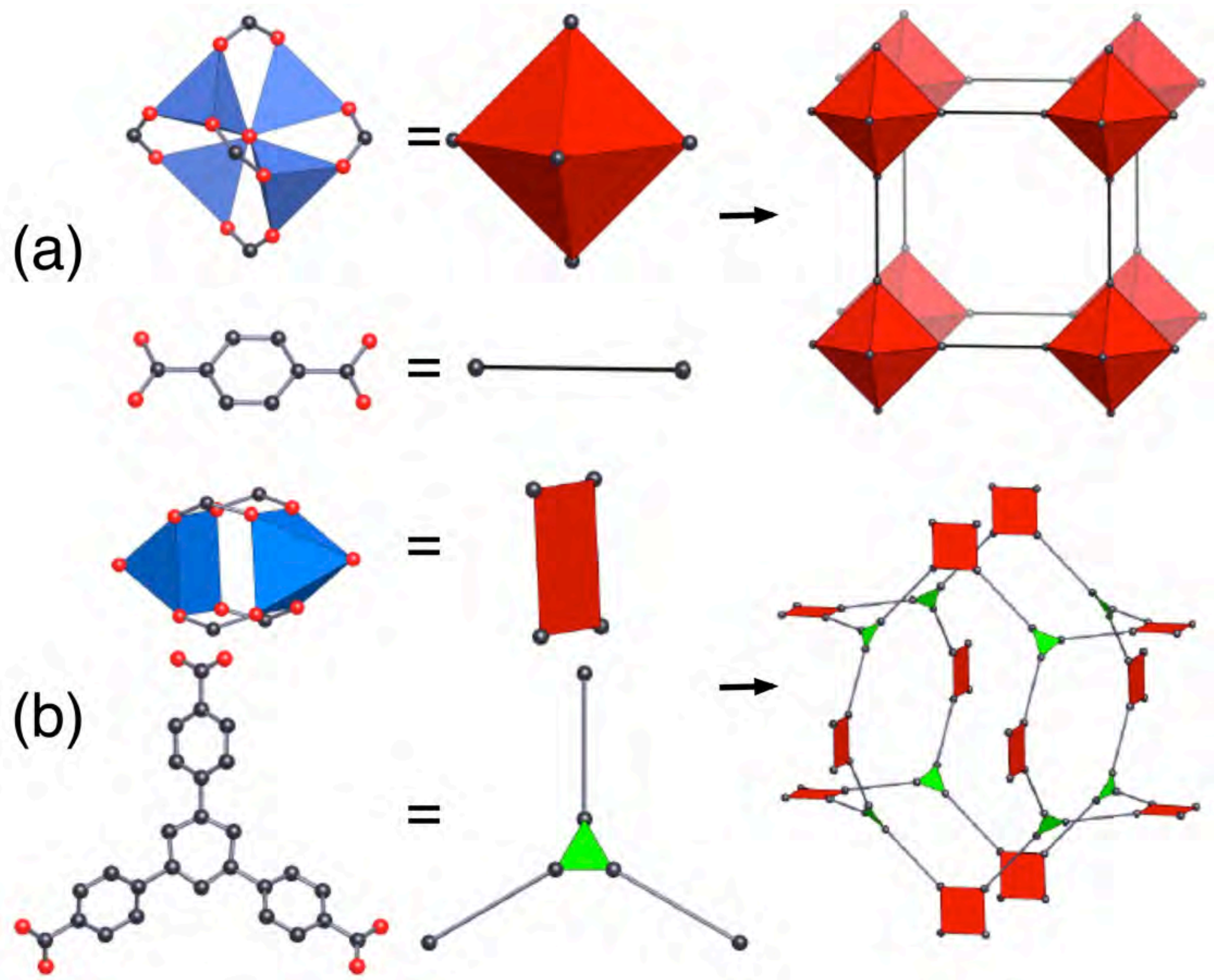




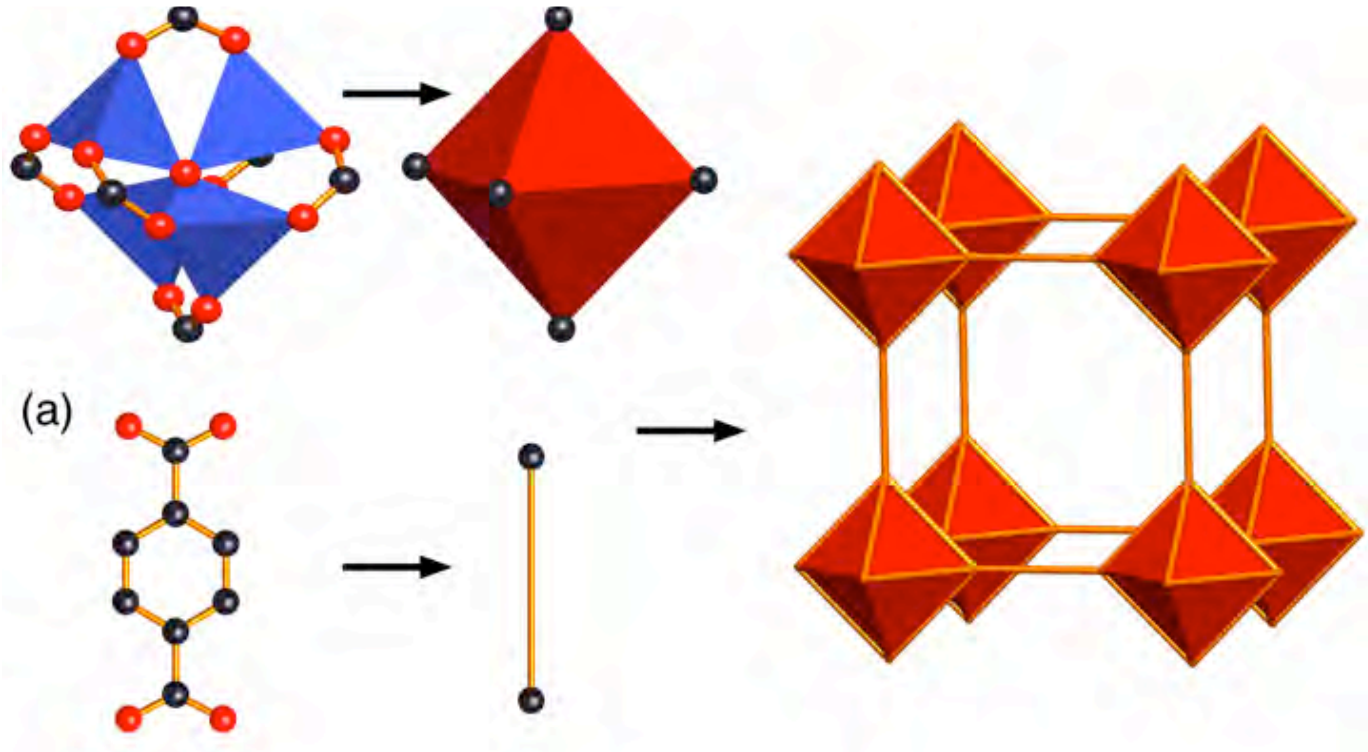
OR

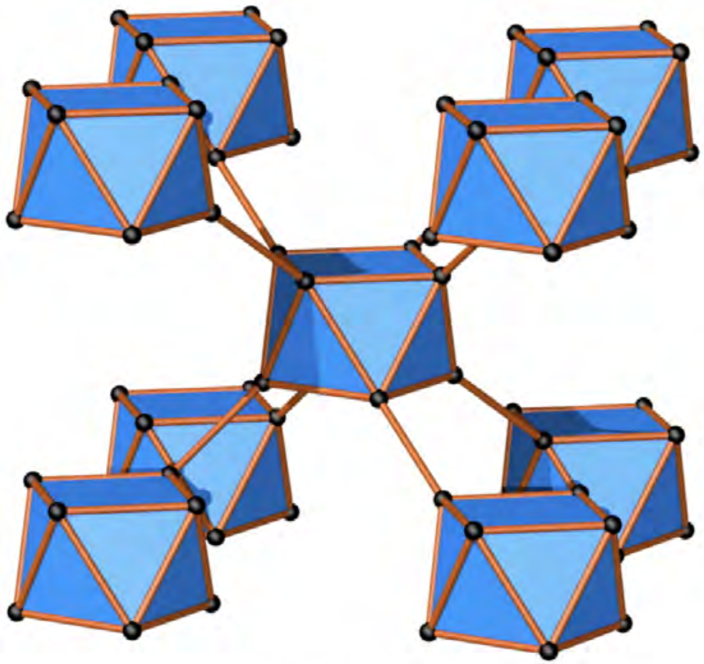


The two simplest types of MOF topology

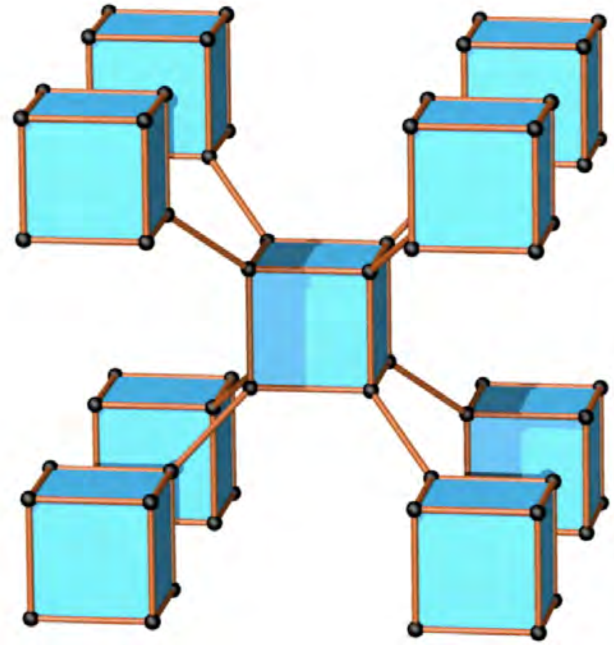


The simplest type of MOF topology



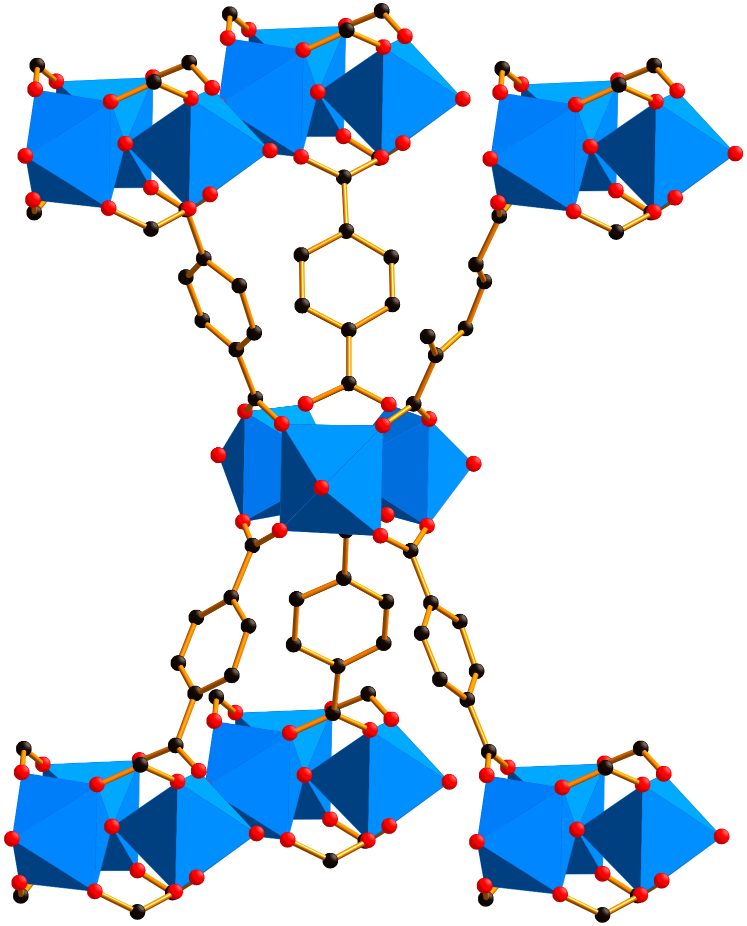


bcu-i

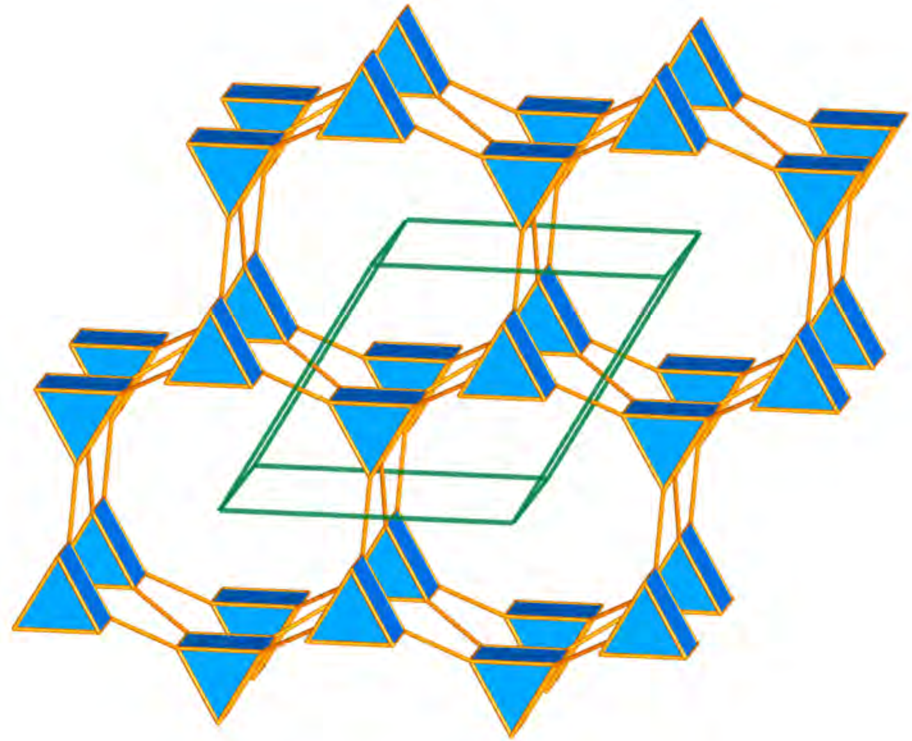


bcu-a = pcb

two structures with the same underlying topology (net)



An iron terephthalate
MOF-235 O. M. Yaghi group
Inorg. Chem. 44, 2998 (2005)



The underlying net **scs** shown as **acs-a**
The only way of linking trigonal prisms with one kind of link

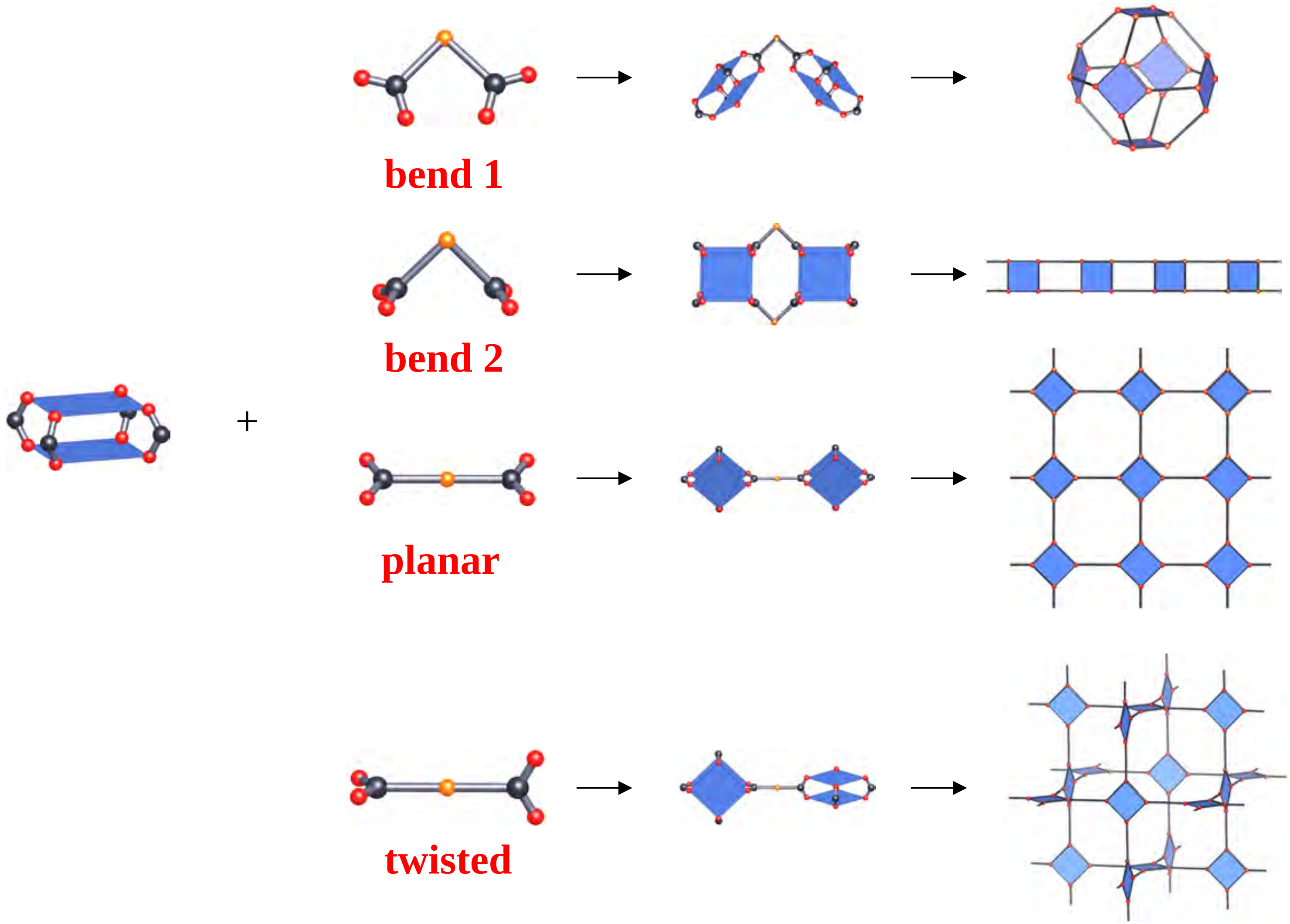
We know “all” the ways of linking shapes by one kind of linker. For example 9 ways of so linking squares.

Can we control which structure we get?

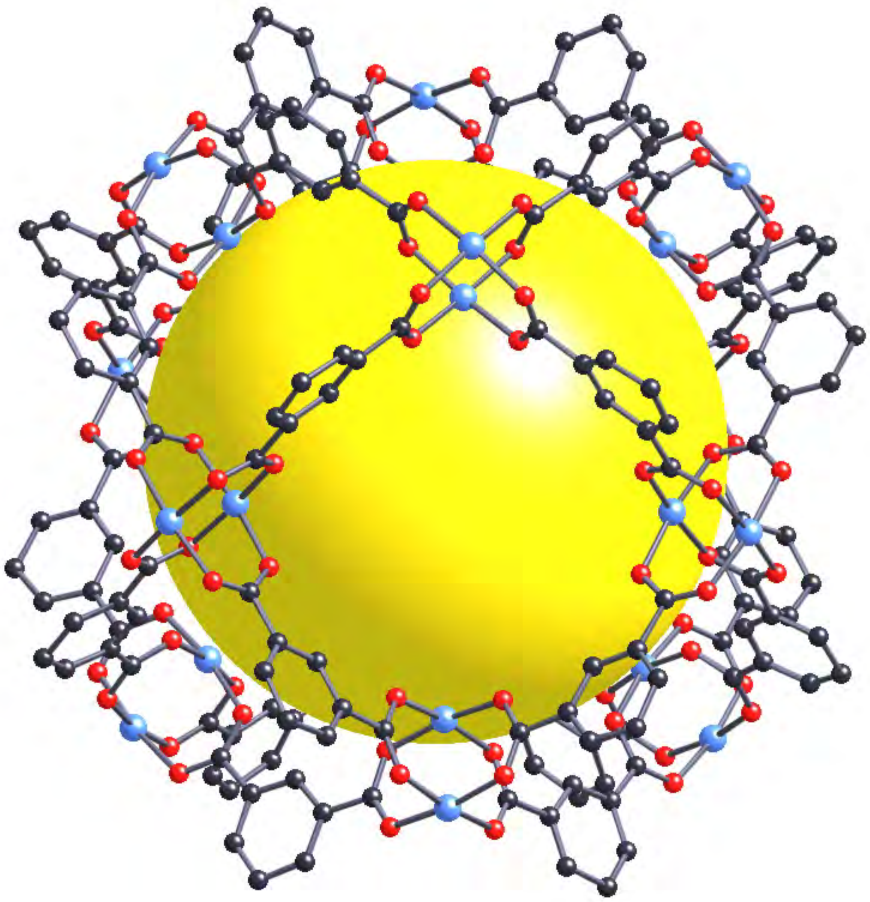
M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi et al. Proc. Natl. Acad. Sci. 99, 4000 (2002).

H. Furukawa, J. Kim, N, W. Ockwig, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* 130, 1650 (2008).

Control of periodicity
linking paddle wheels (squares) with dicarboxylic acids



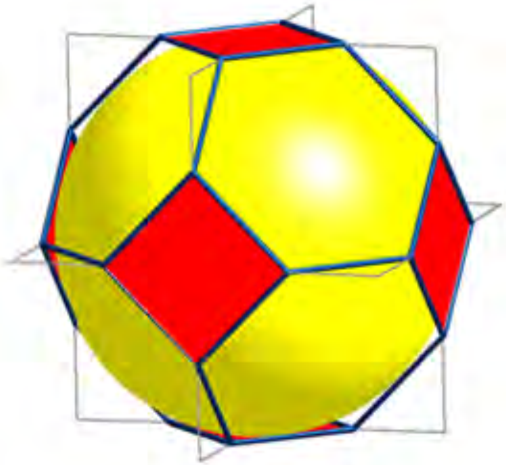
cuboctahedron

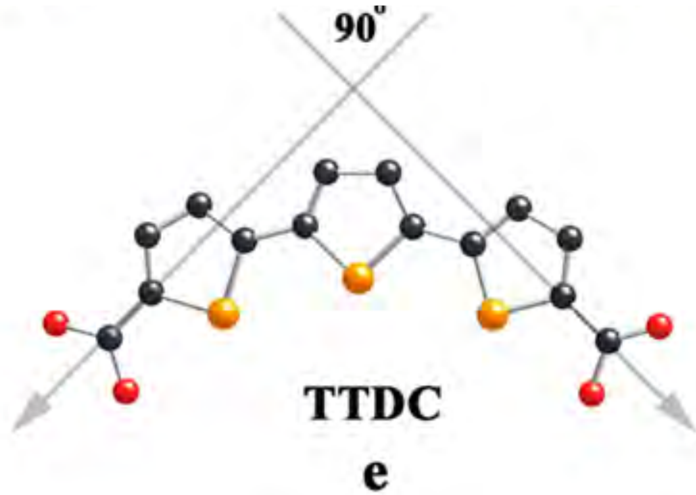


MOP-1 Framework = $[Cu_2(C_6H_4(COO)_2)_2]_{12}$

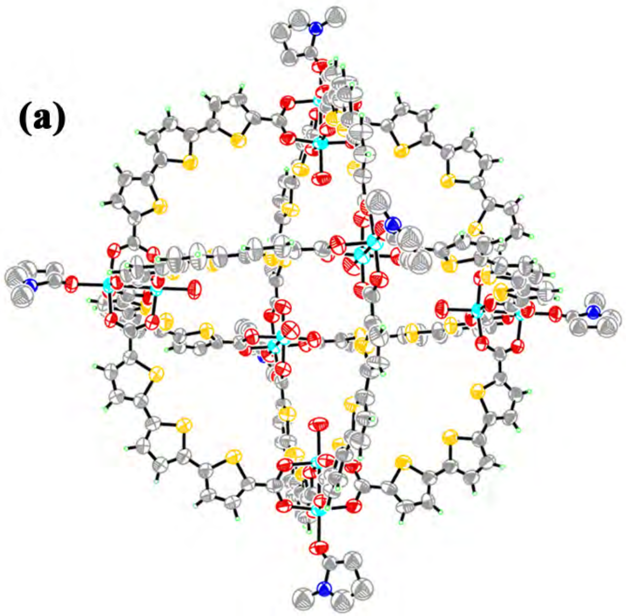
M. Eddaoudi, J. Kim, J. B. Wacher, H. K. Chae, M. O'Keeffe, O. M. Yaghi. *JACS*, 123, 4368-9 (2001).

truncated octahedron needs 90˚

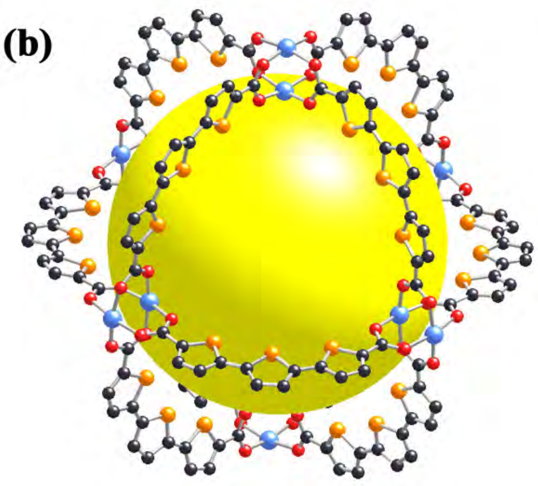




(a)

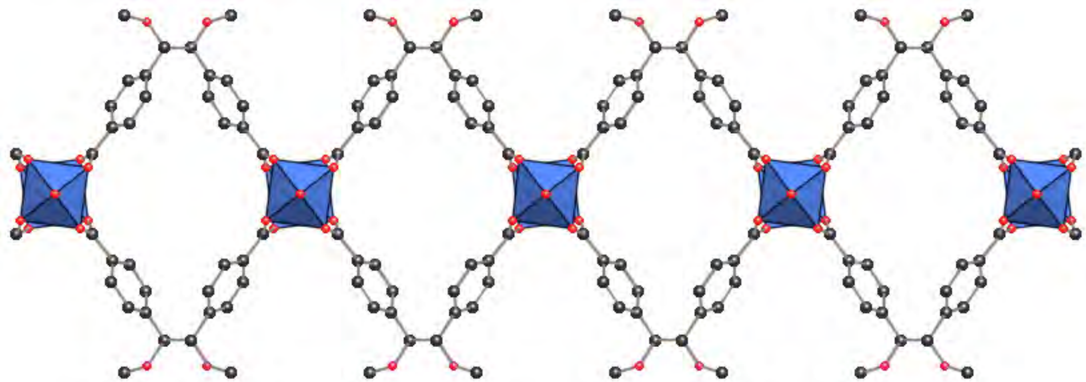


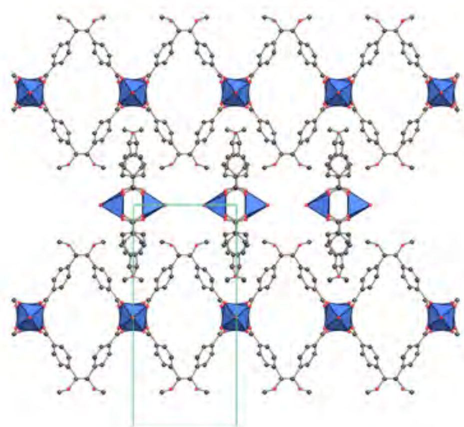
(b)



Z. Ni, O. M. Yaghi.et al. JACS 127, 12752 (2005)

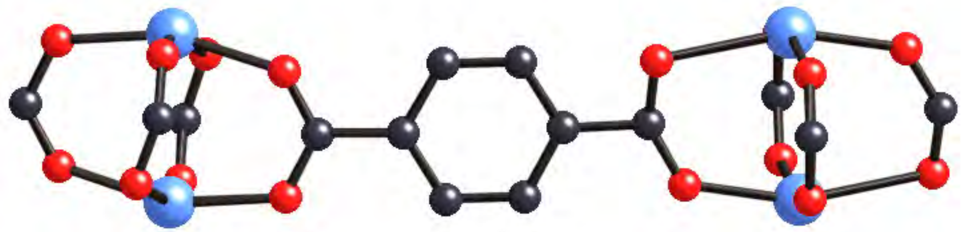
A 1-periodic (rod) structure

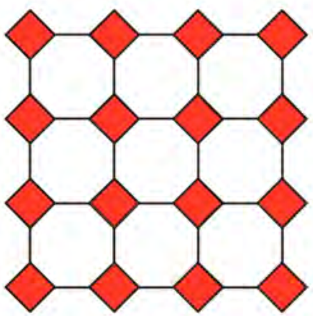


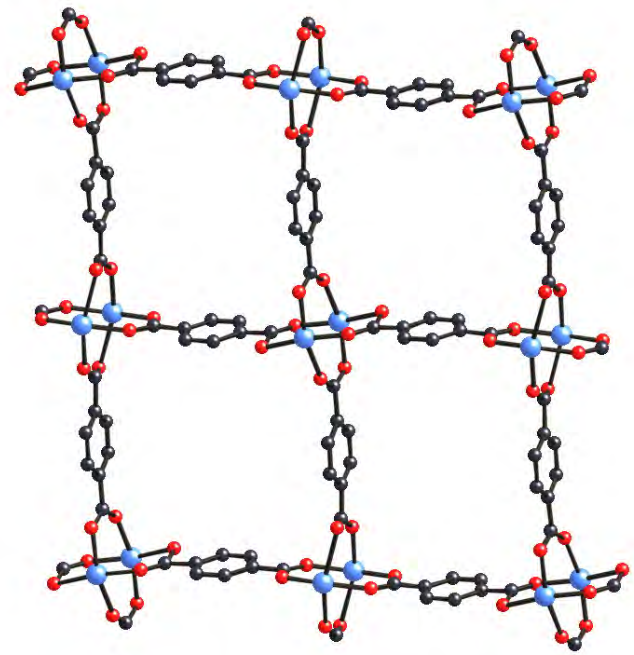


O. M. Yaghi group *J. Am. Chem. Soc.* 2008, **130**, 11650

A 2-periodic (planar) structure



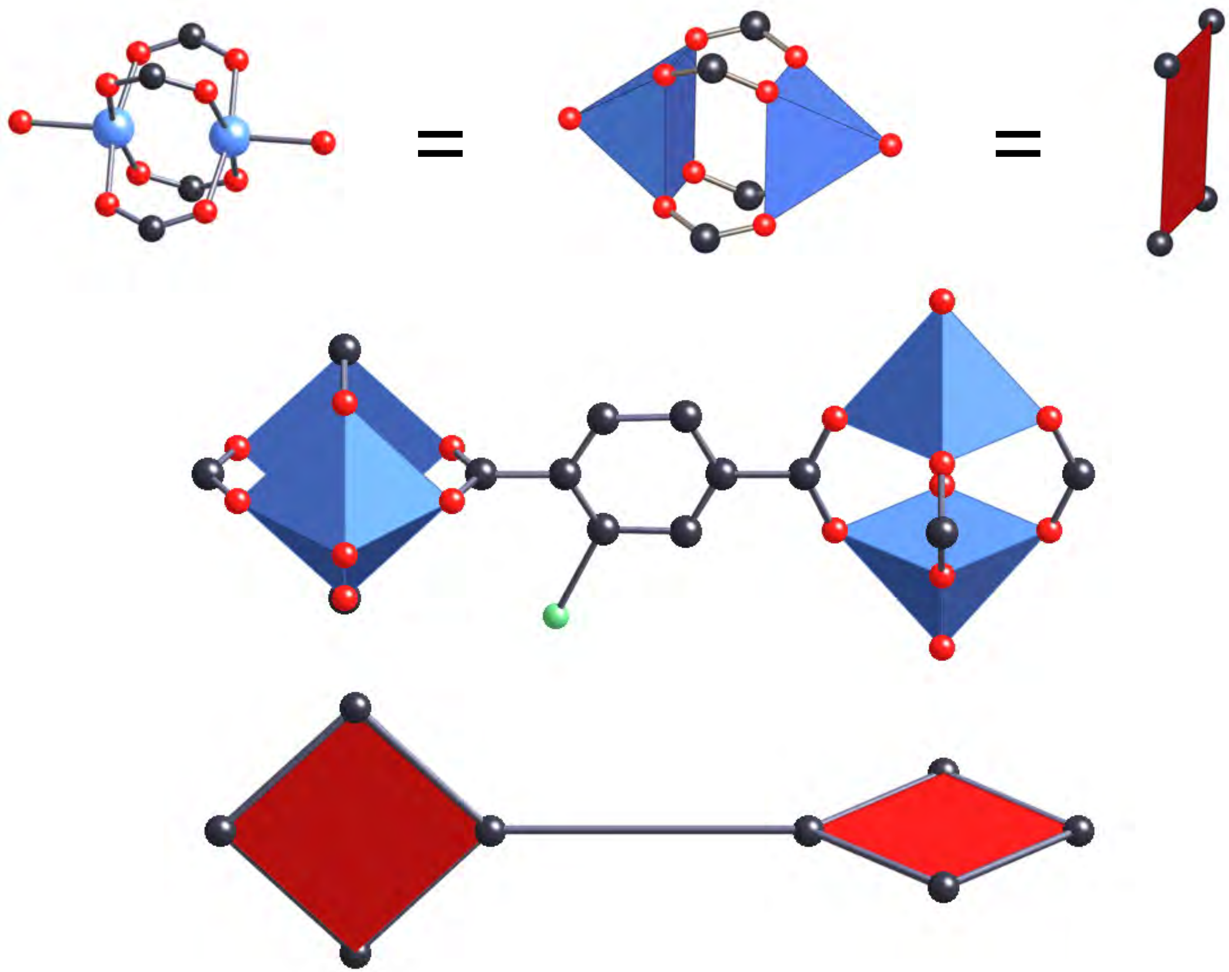




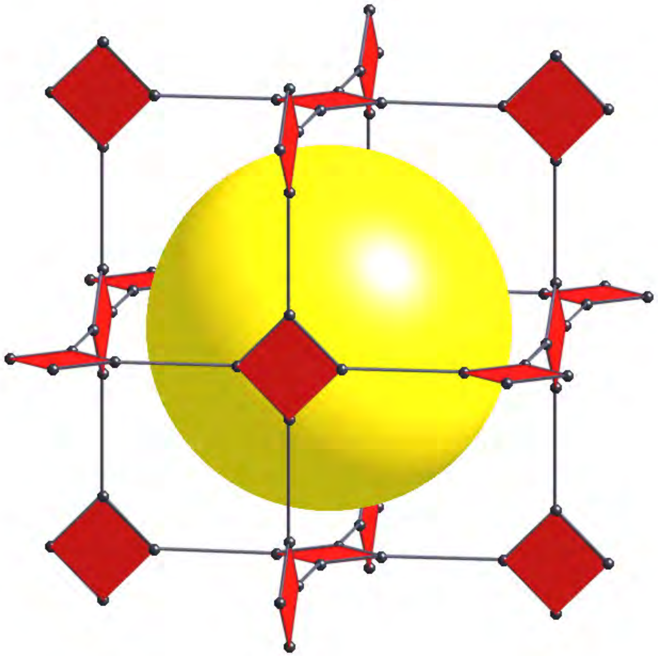
MOF-2 ZnBDC (BDC = benzenedicarboxylate

Li. H.; Eddaoudi, M.; Groy, T. L.; Yaghi, O. M. *JACS*, **1998**, *120*, 8571

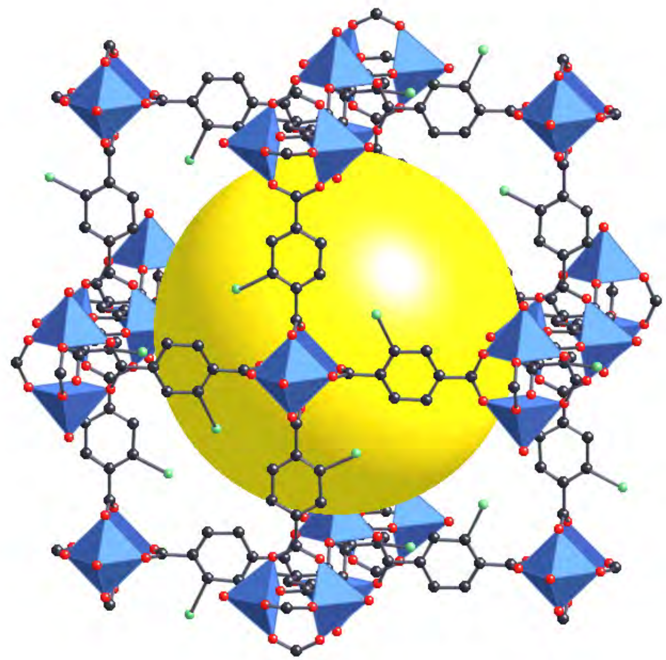
How to make a 3-periodic structure



Paddlewheels (square SBUs) linked with a twist to produce….



nbo-a



MOF-88 Cu(OOC-C_6H_3Br-COOO)·H_2O

Linked paddle-wheel clusters producing a decorated **nbo** net

M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* 124, 576 (2002)

Transitivity

vertex- (edge-) transitive means
one topological kind of vertex (edge)

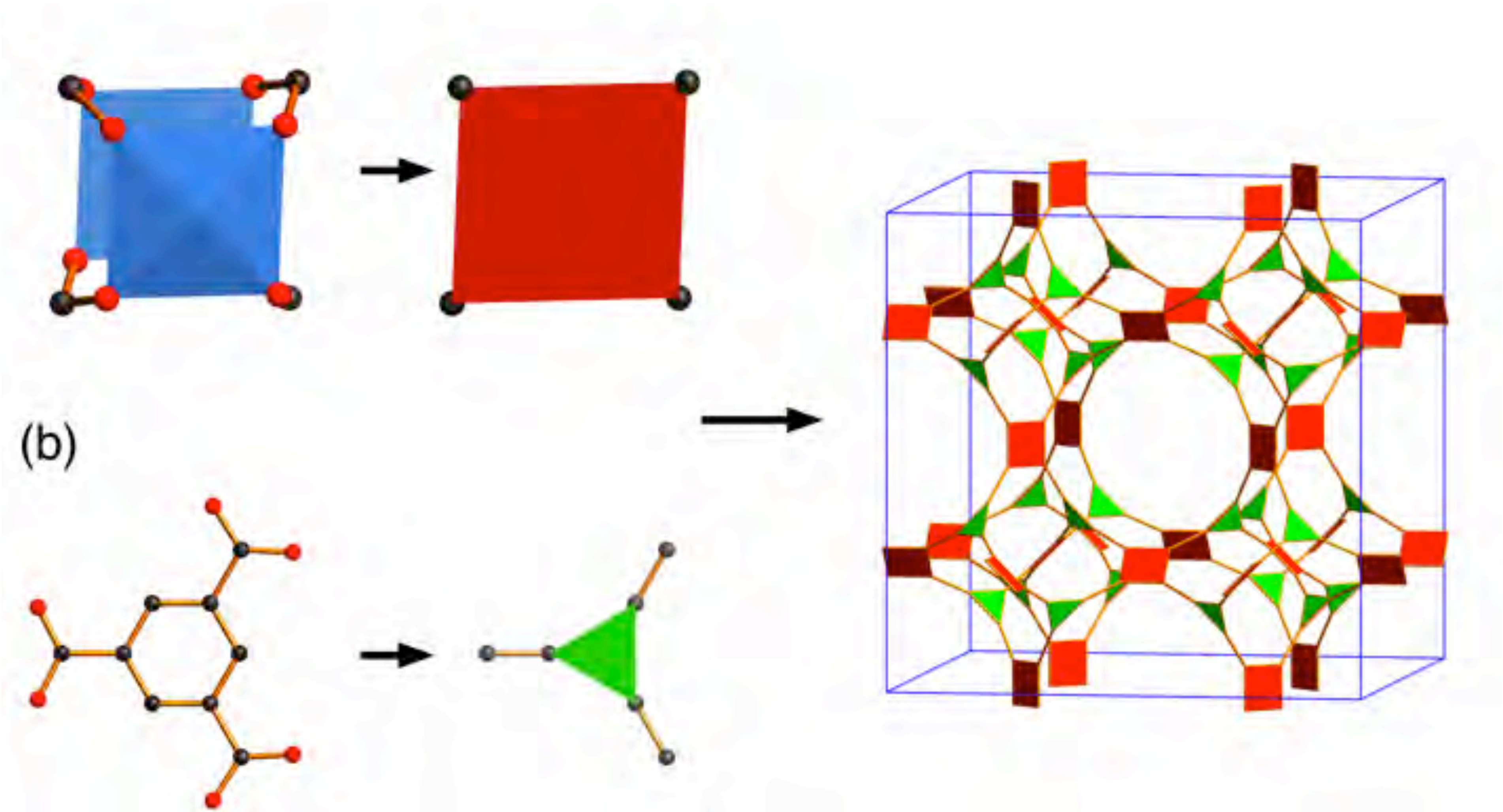
The most important nets with one or two kinds of vertex are edge-transitive

More complex nets are often

minimal transitivity

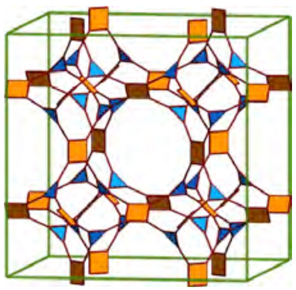
(see later)

A second simple type of MOF topology: two vertices one link

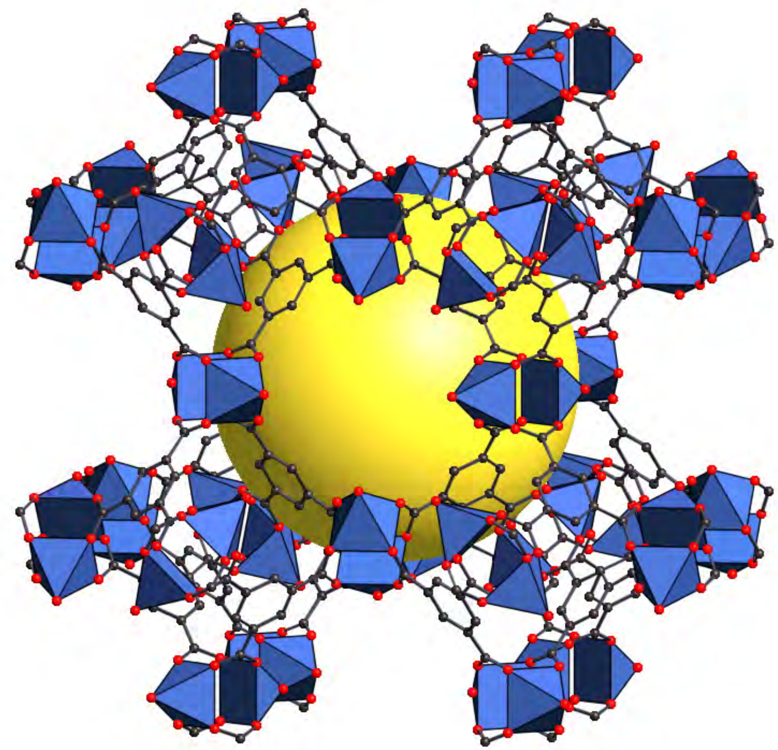


Net is **tbo-a**

linking square and triangle

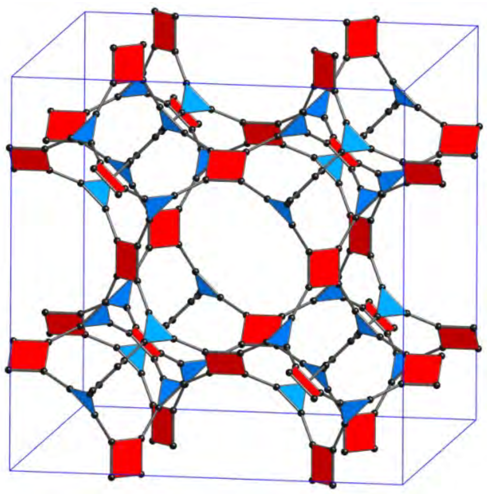


tbo-a

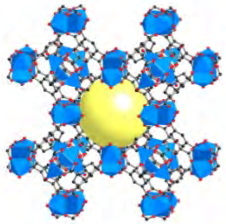


HKUST-1 linked paddlewheel and benzene tribenzoate $(Cu_2)_3(btb)_4$

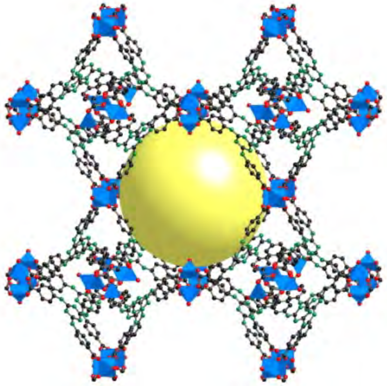
S. S.-Y. Chui, S. M. –F. Lo; J. P. H. Charmant, A. G. Orpen, I. D.Williams, *Science* **283**, 1148 (1999)



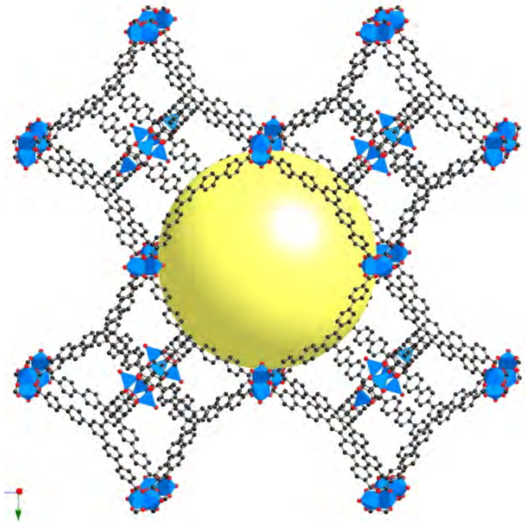
An isoreticular series based on tbo



HKUST-1
MOF-199

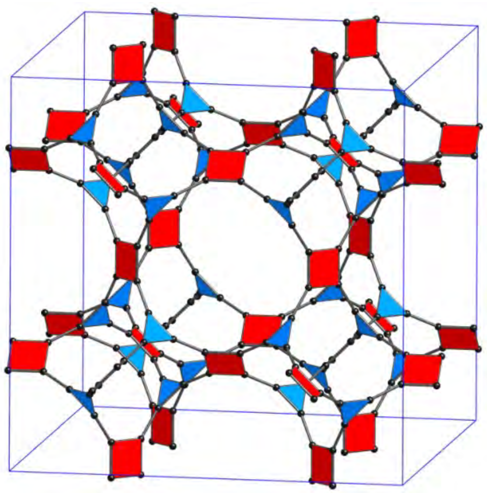


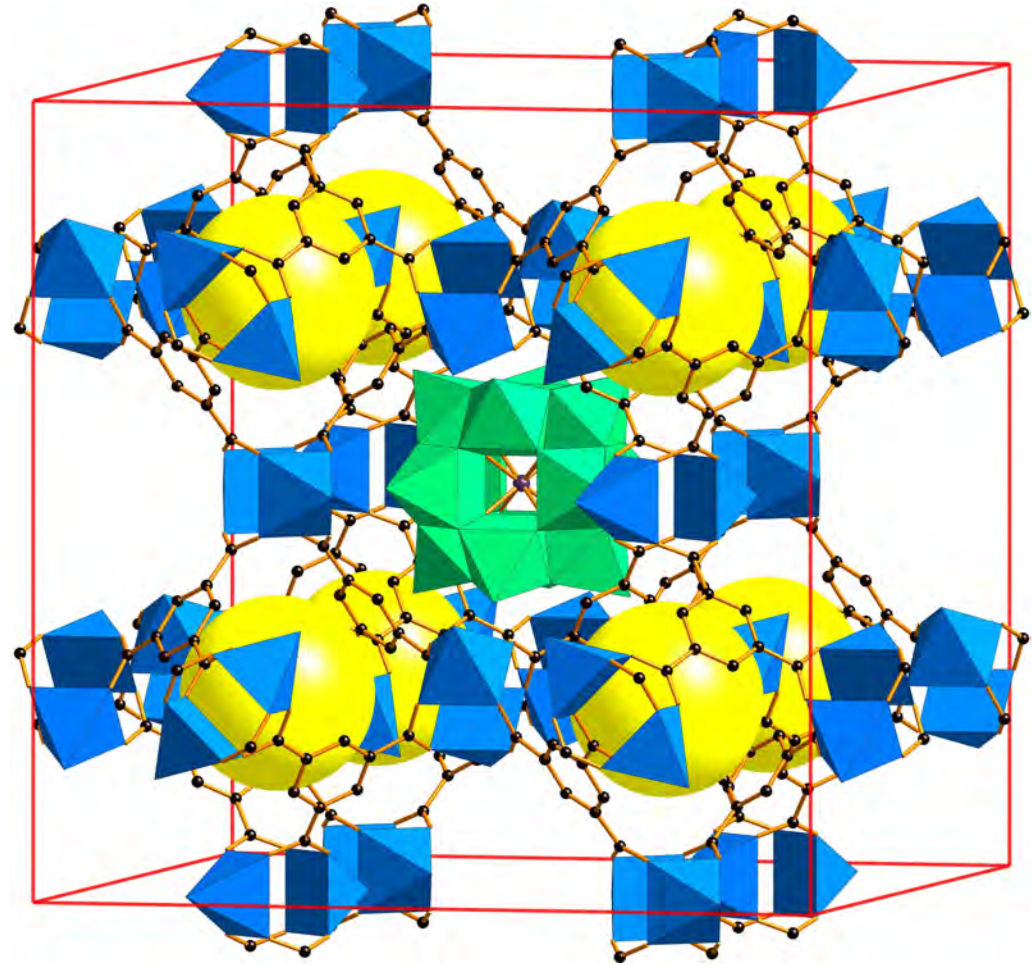
mesoMOF-1
H.C. Zhou



MOF-399

H. Furukawa etal. Inorg. Chem. 2011, *50*, 9147

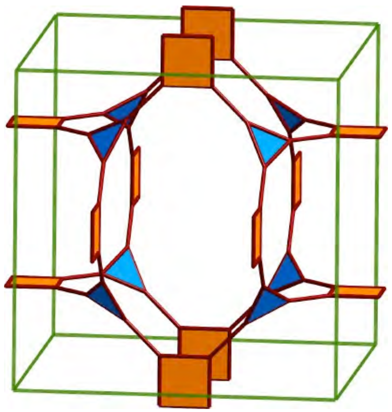




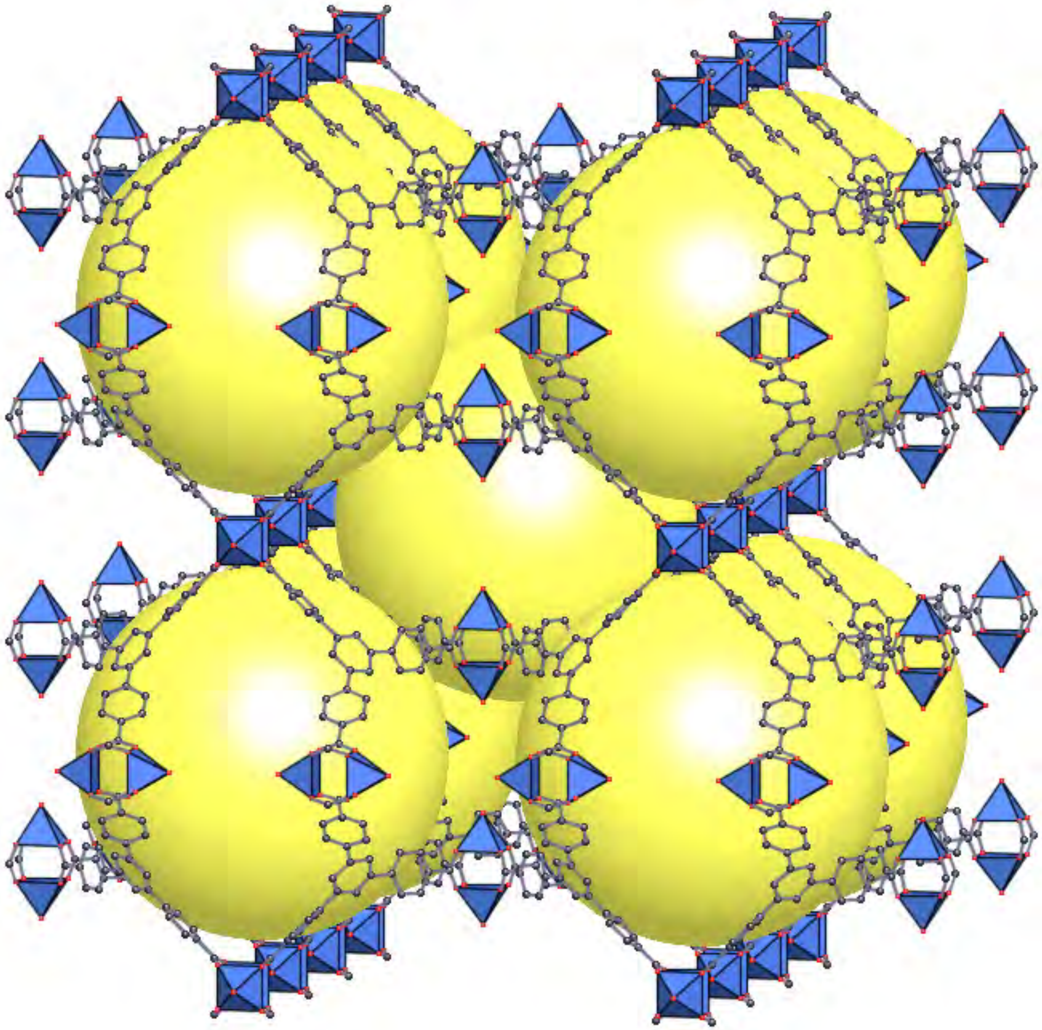
HKUST-1 very nicely has just the right space for Keggin ions

$AB_{12}O_{40}$ – A = P, As, Si, Ge (tetrahed.) B – Mo, W (octahed.)

Zhou-Min Su et al. JACS, 2009, 131. 1884 *linking square and triangle*

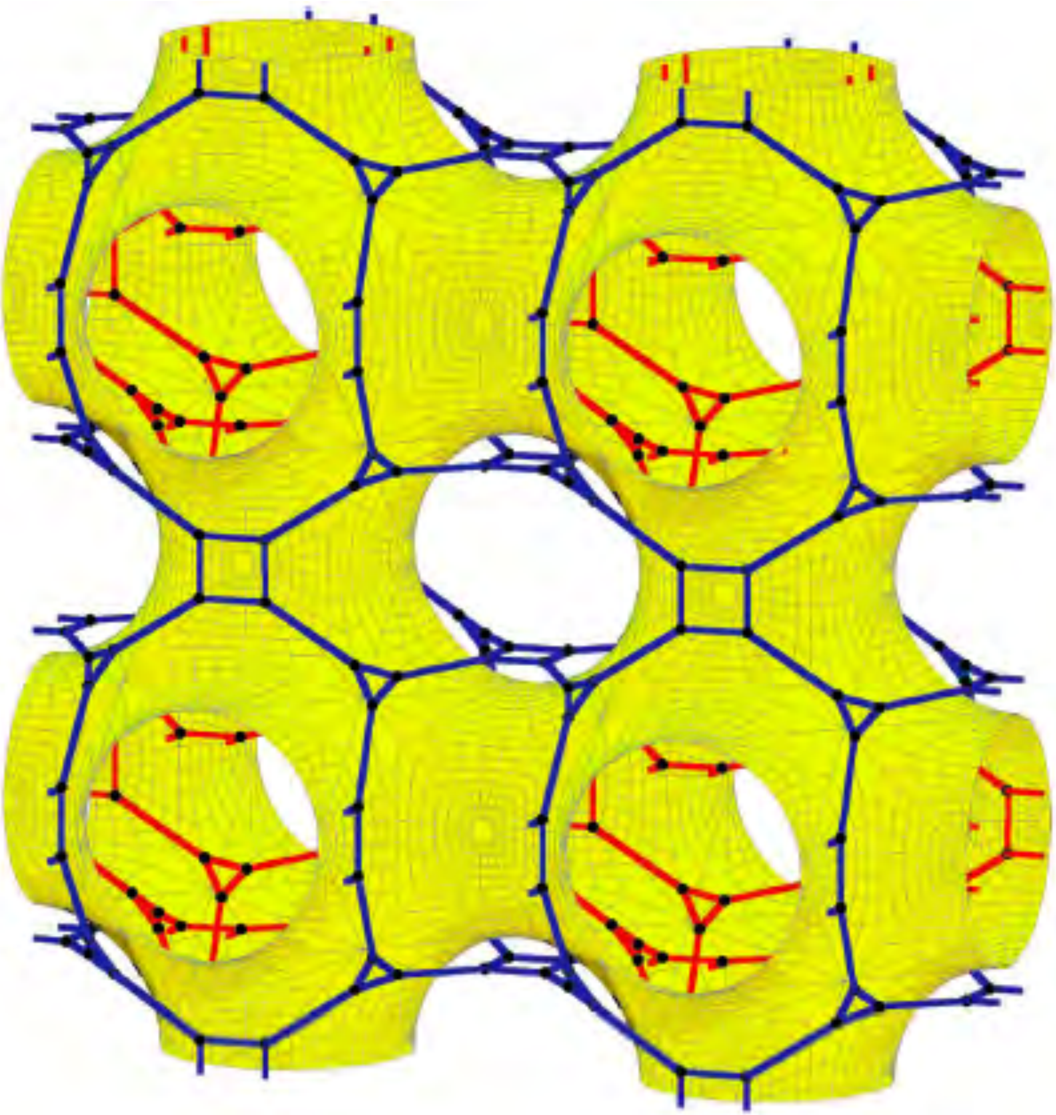


pto-a

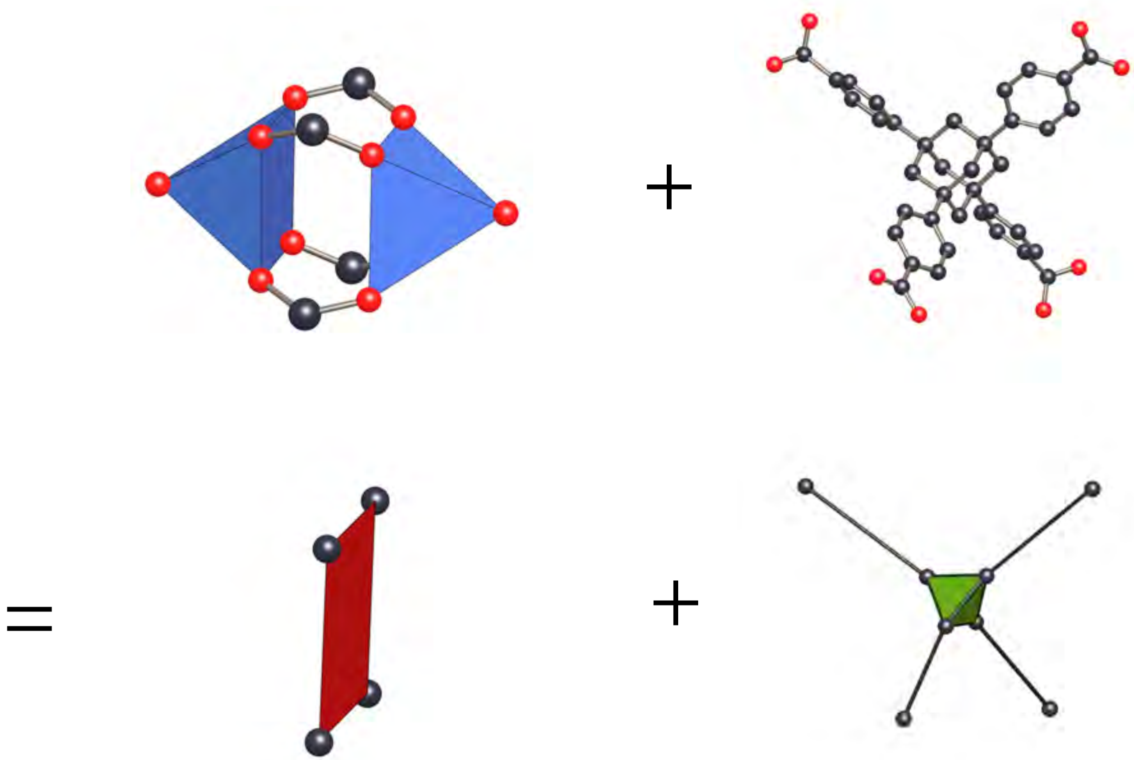


MOF-14A

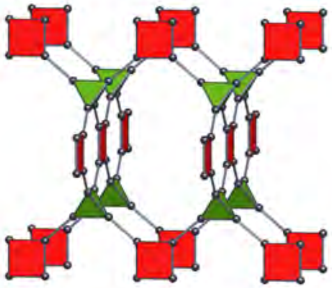
Fig. 2. Two MOF-14 frameworks (blue and red) interwoven about a *P*-minimal surface without intersecting the surface.

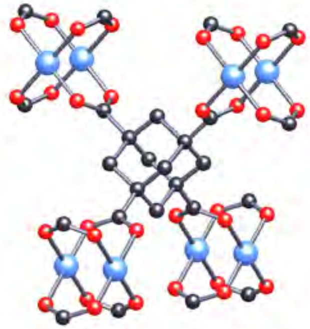


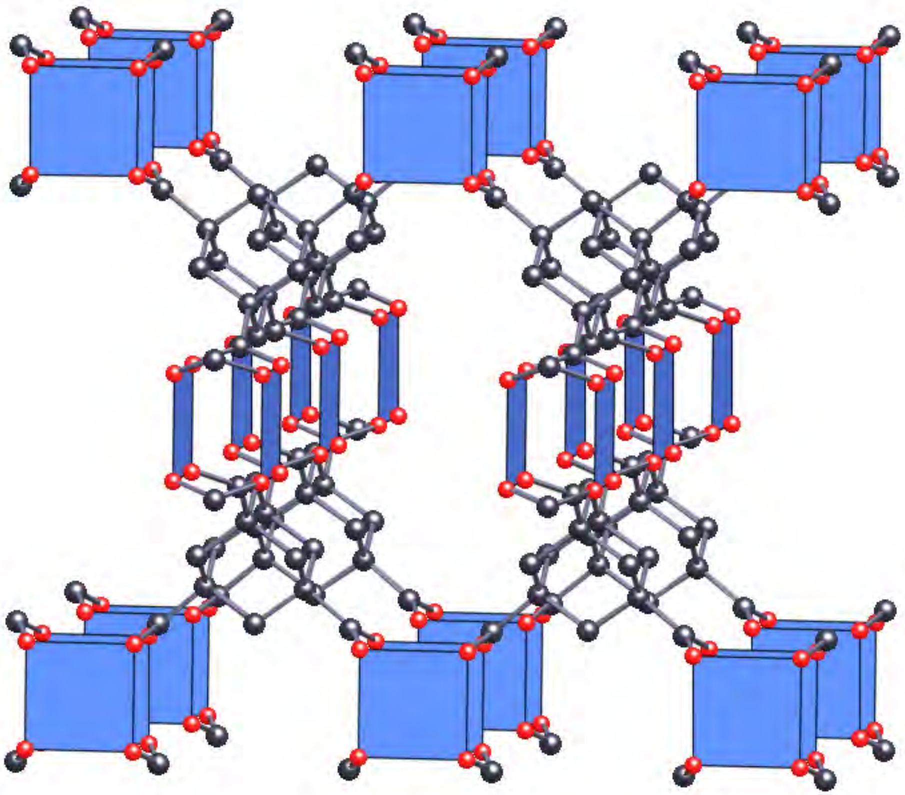
Banglin Chen,1 M. Eddaoudi, S. T. Hyde,2 M. O'Keeffe, O. M. Yaghi, Science, 291, 1021-1023 (2001), *Linking square and tetrahedron*



pts-a





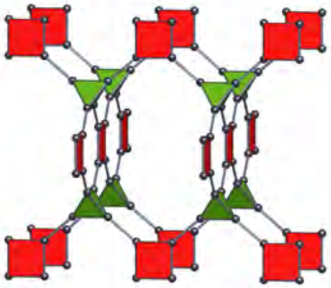


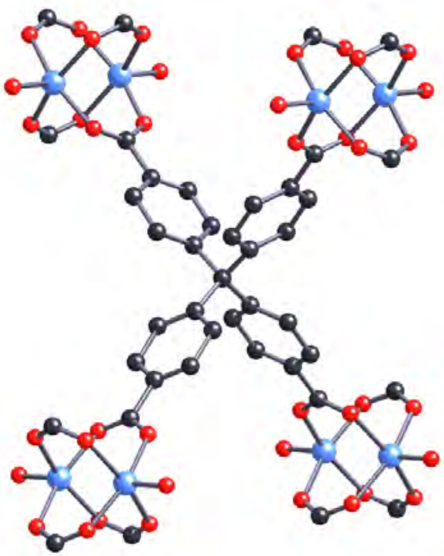
MOF-11 Cu_2(adamantane tetracarboxylate)

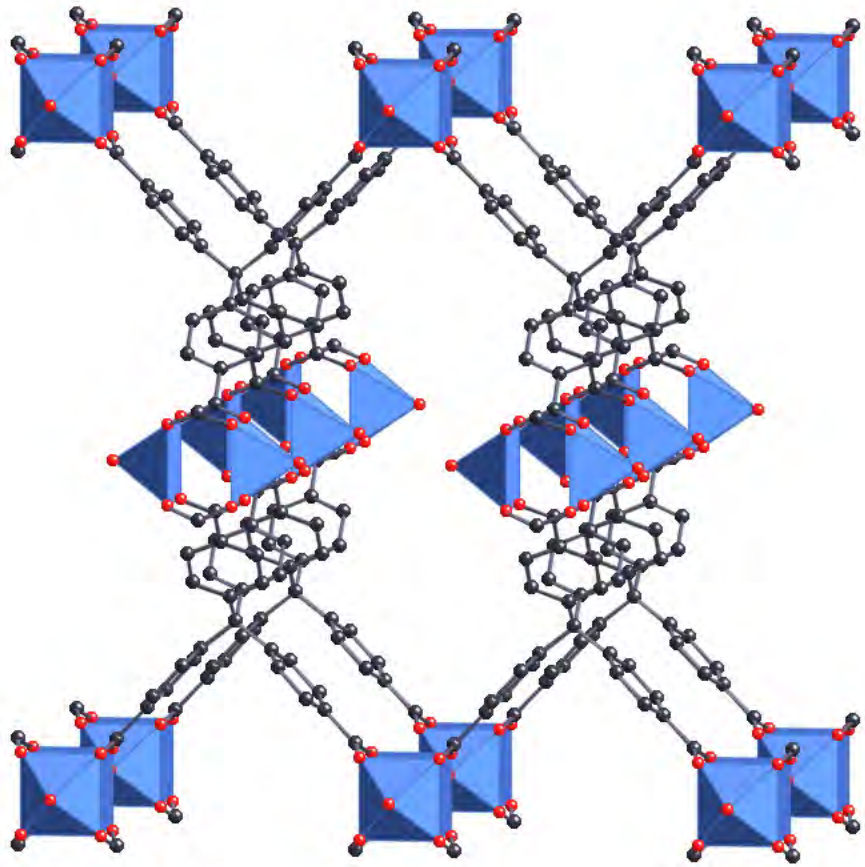
Notice that the Cu atoms in the paddle wheels are only 4-coordinated in the dehydrated form shown.

B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O'Keeffe, O. M. Yaghi
J. Am. Chem. Soc. 122, 11559 (2000)

pts-a



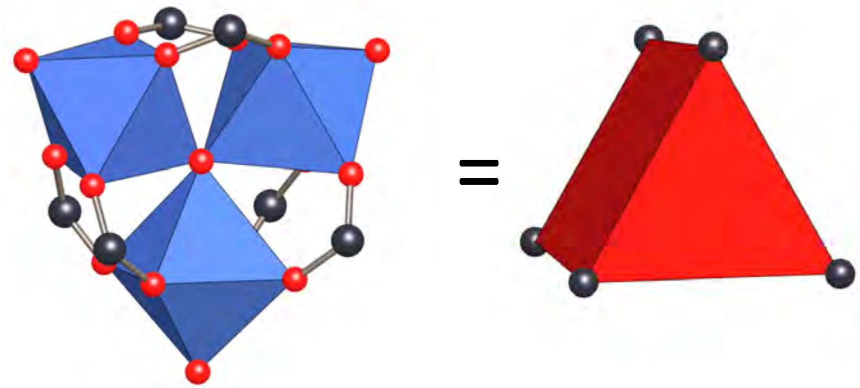


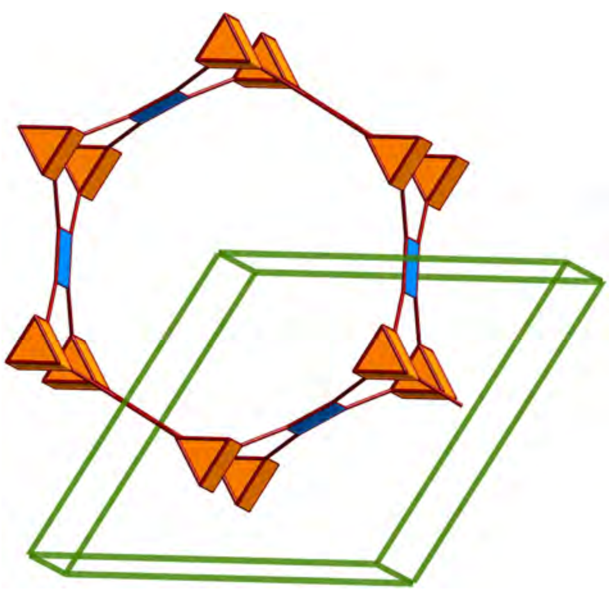


MOF-36 Cu_2(methane tetracarboxyllate) another decorated PtS

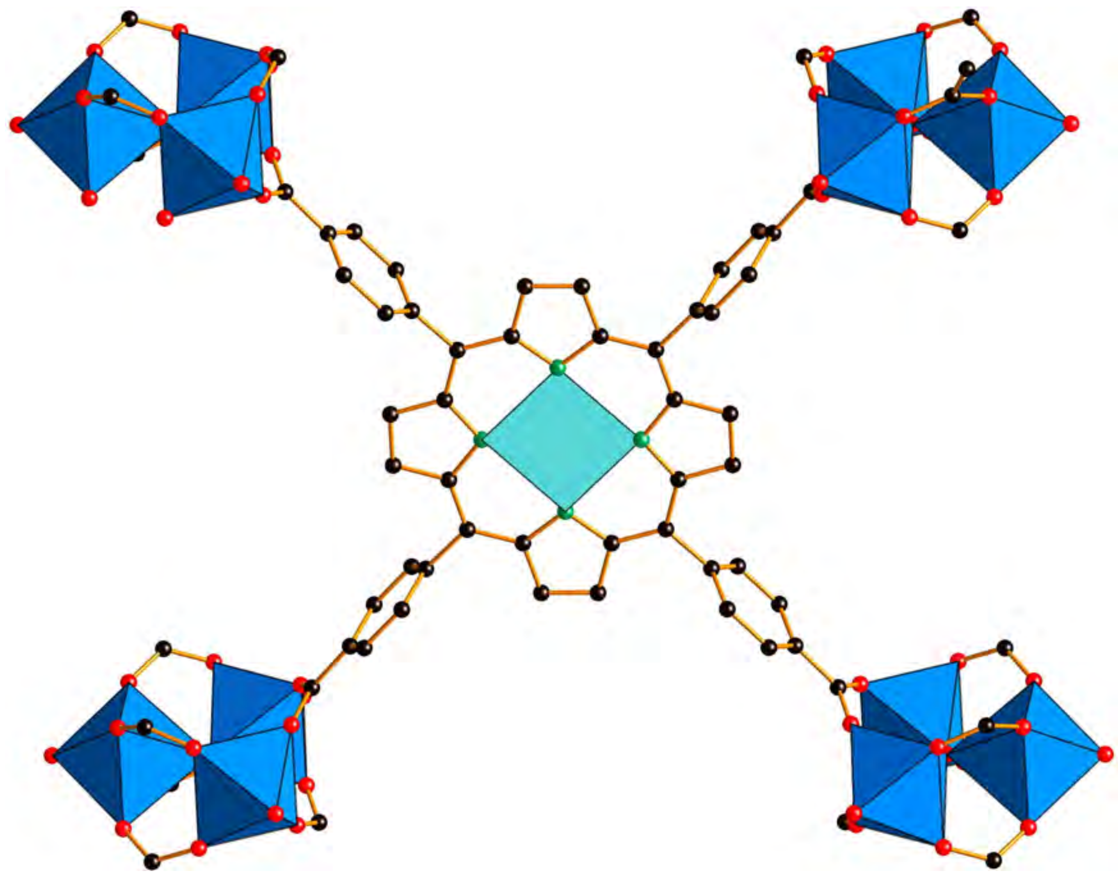
J. Kim, B. Chen, T. M. Reineke, H. Li, D. B. Moler, M. O'Keeffe, O. M. Yaghi
***J. Am. Chem. Soc.* 123, 8293 (2001)**

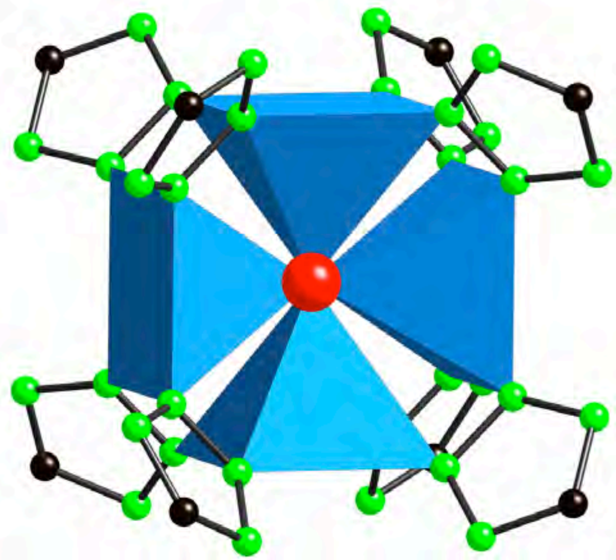
Linking square and trigonal prism
H.-C. Zhou et a;.
JACS 2014, 136, 3983





stp-a





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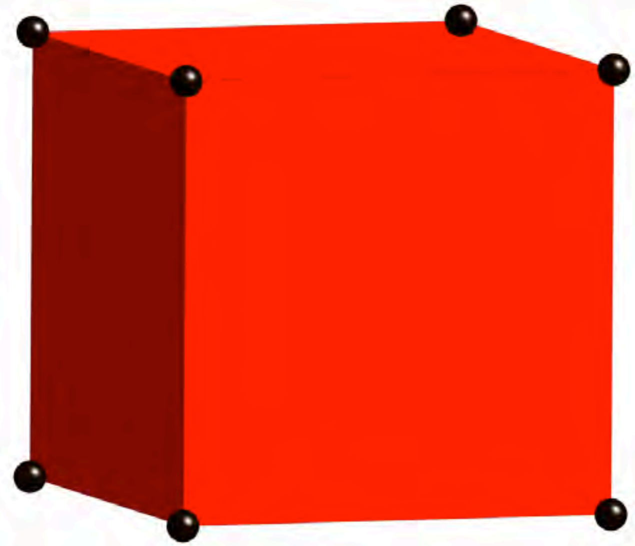
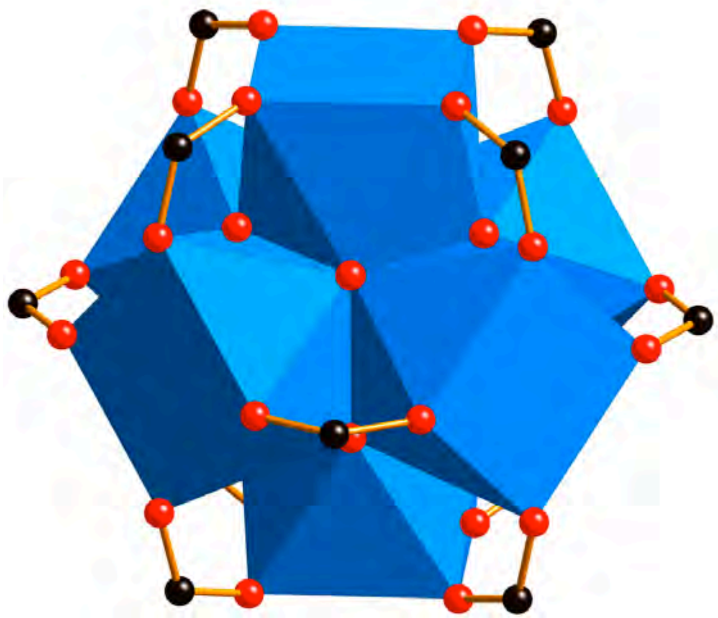


8-c SBU

Mn

Long group



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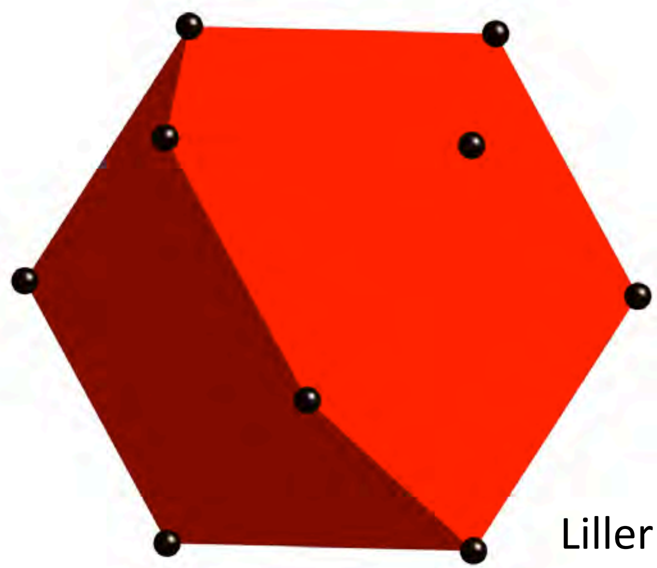
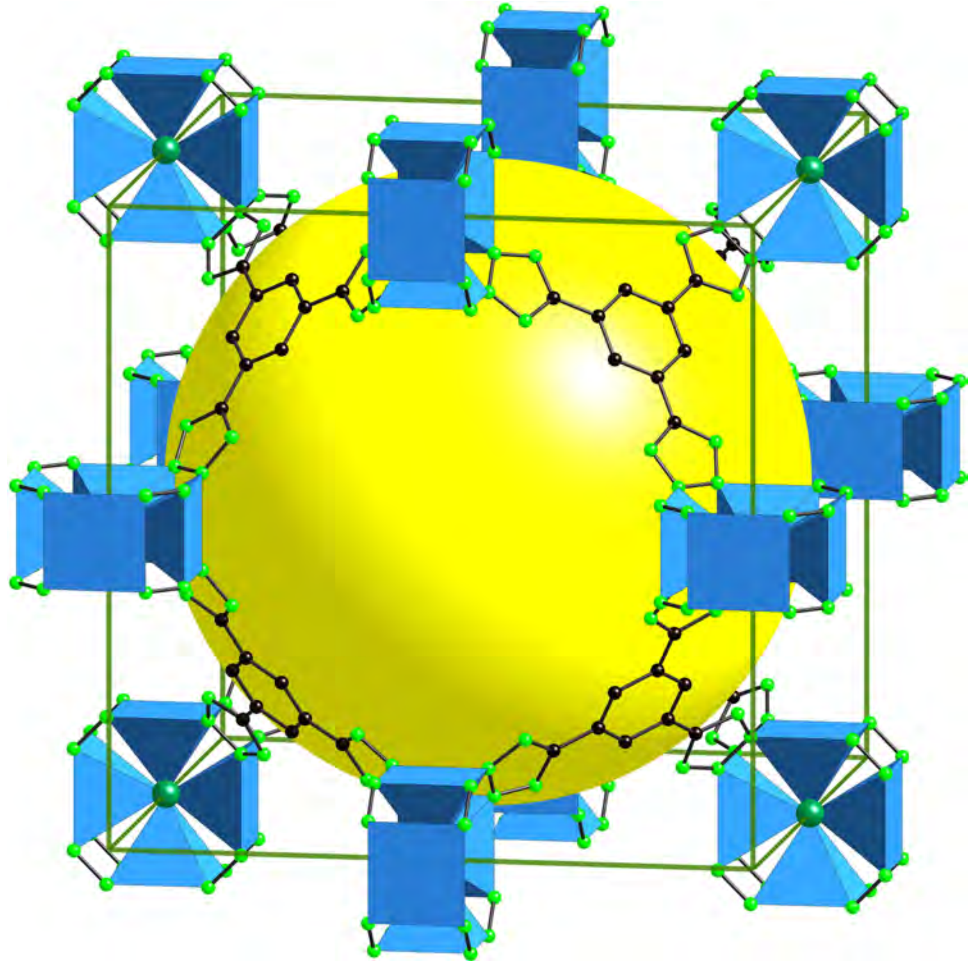


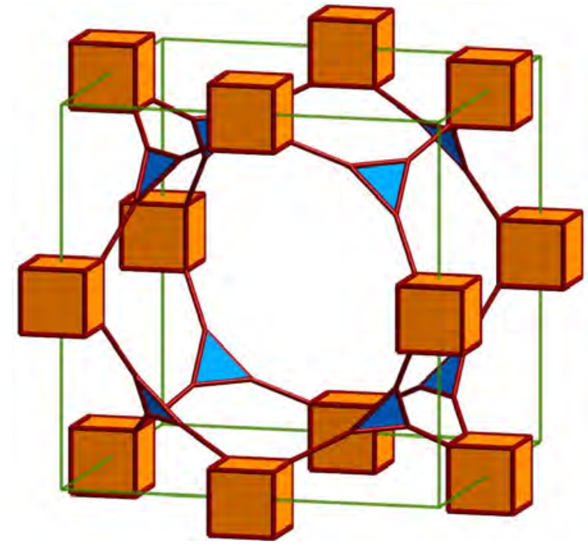
12-c SBU

Zr

UiO-6

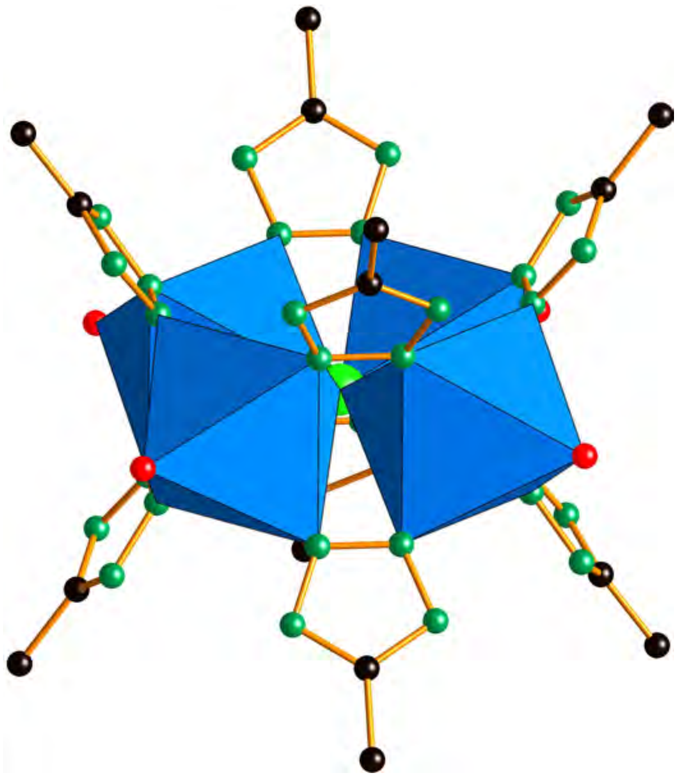
Lillerud group
JACS 2008, 130, 3850



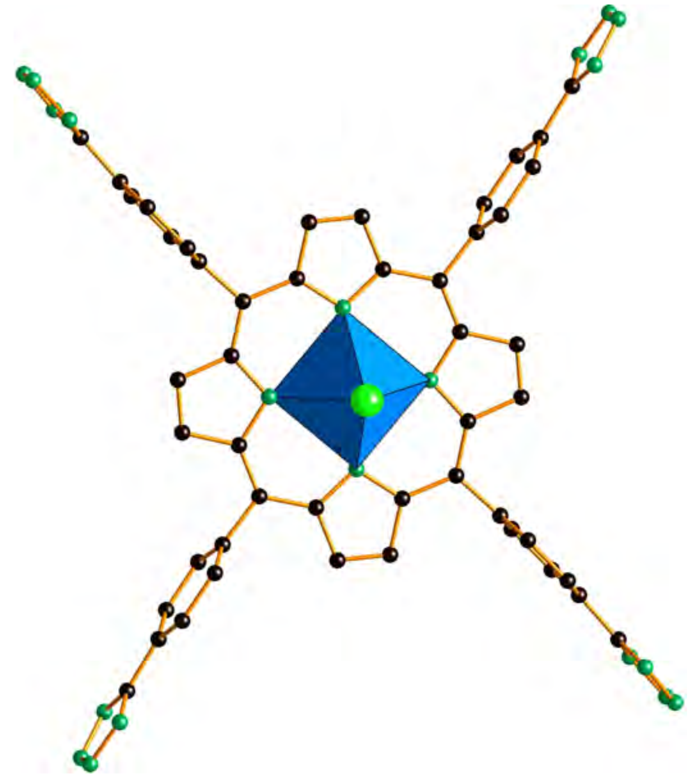


the-a

See J. R. Long group. JACS, 2006, 128, 16874
Angew. Chem int ed. 2007, 46, 419

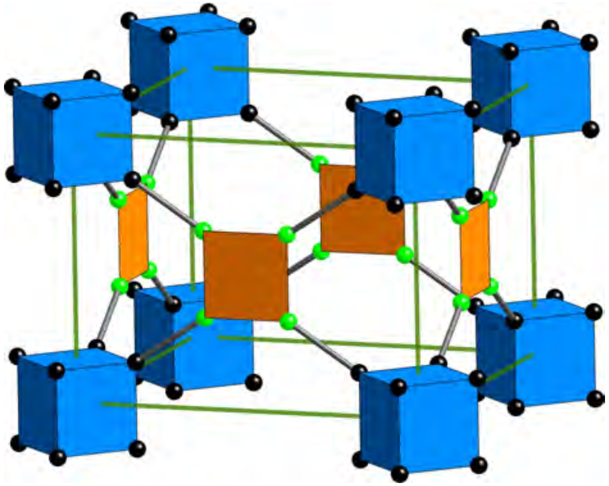


Essentially the same metal SBU but now octahedra

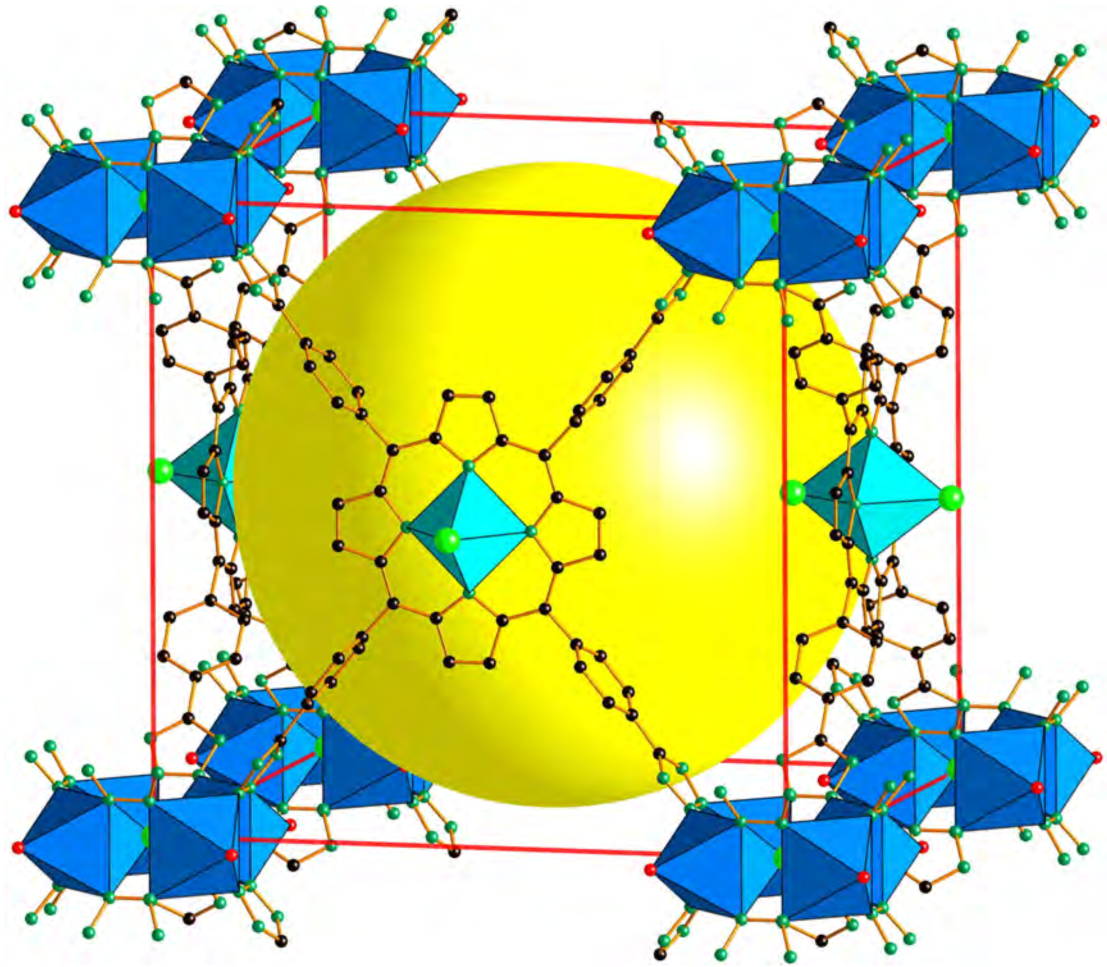


porphyin bases tetrazole square linker

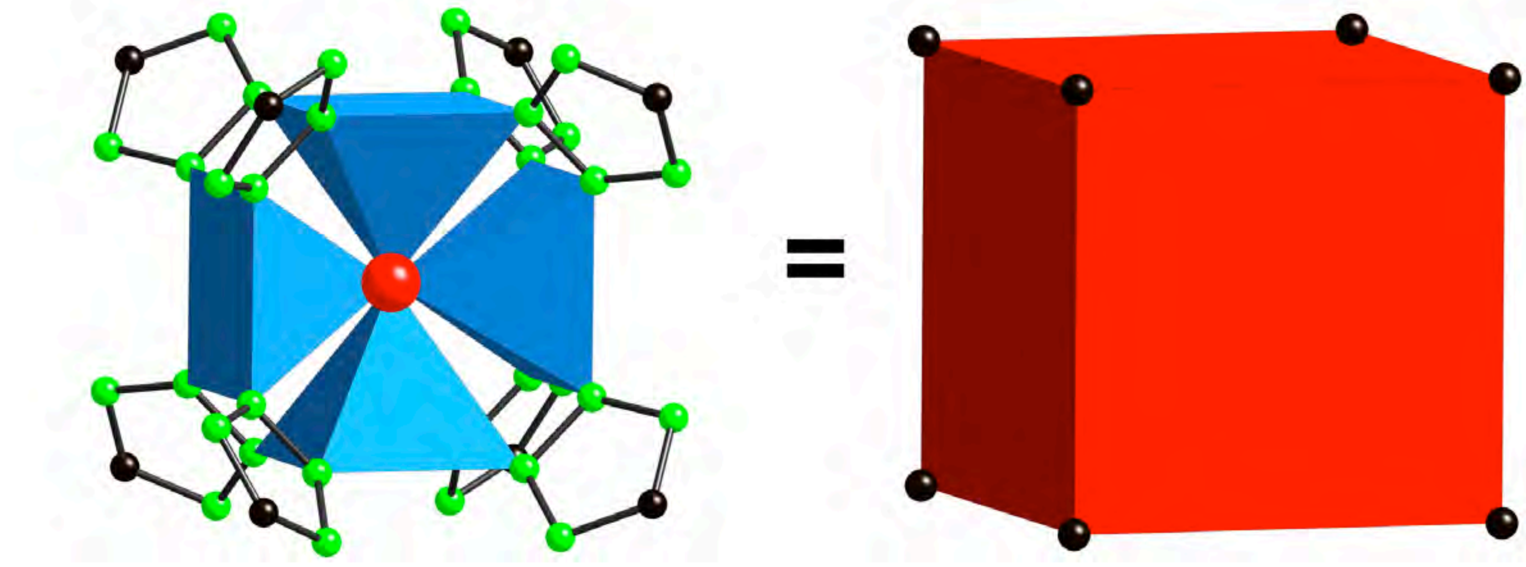
UTSA-57 Banglin Chen group *Inorg. Chem*. **2015**, *54*, 200



scu-a



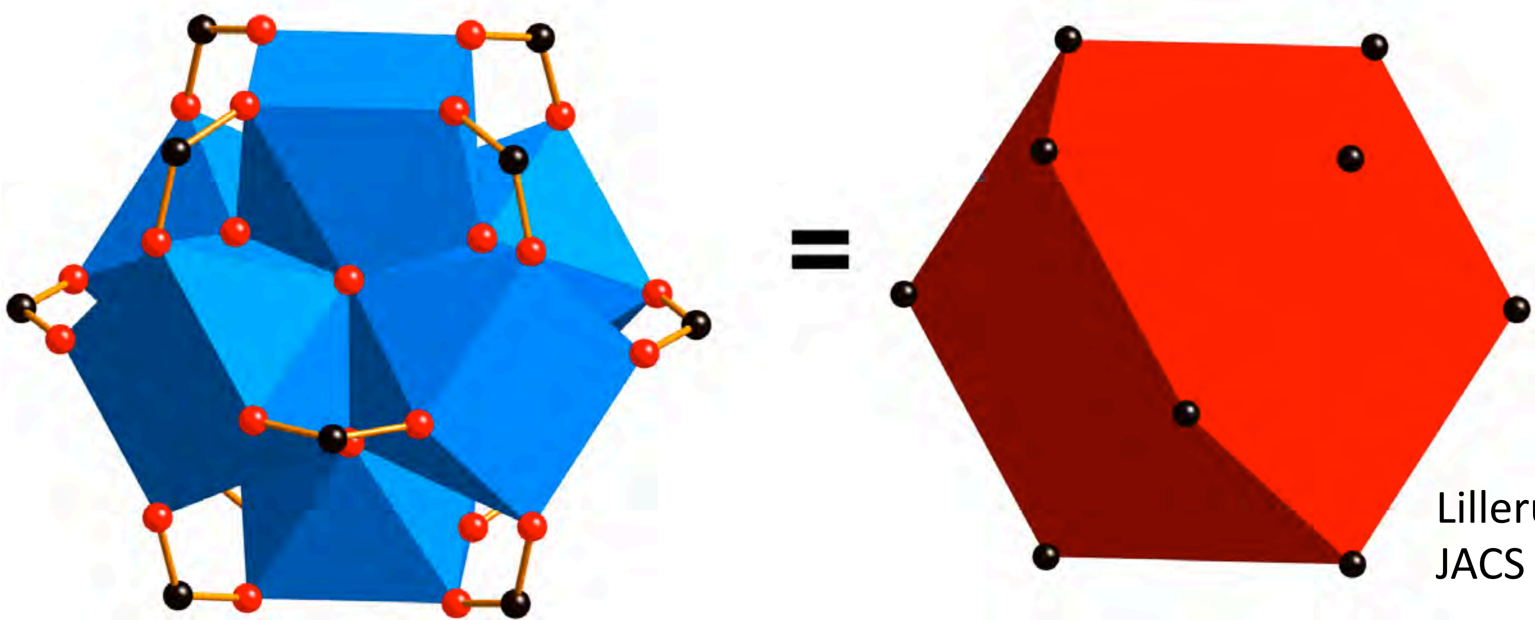
UTSA-57



8-c SBU

Mn

Long group

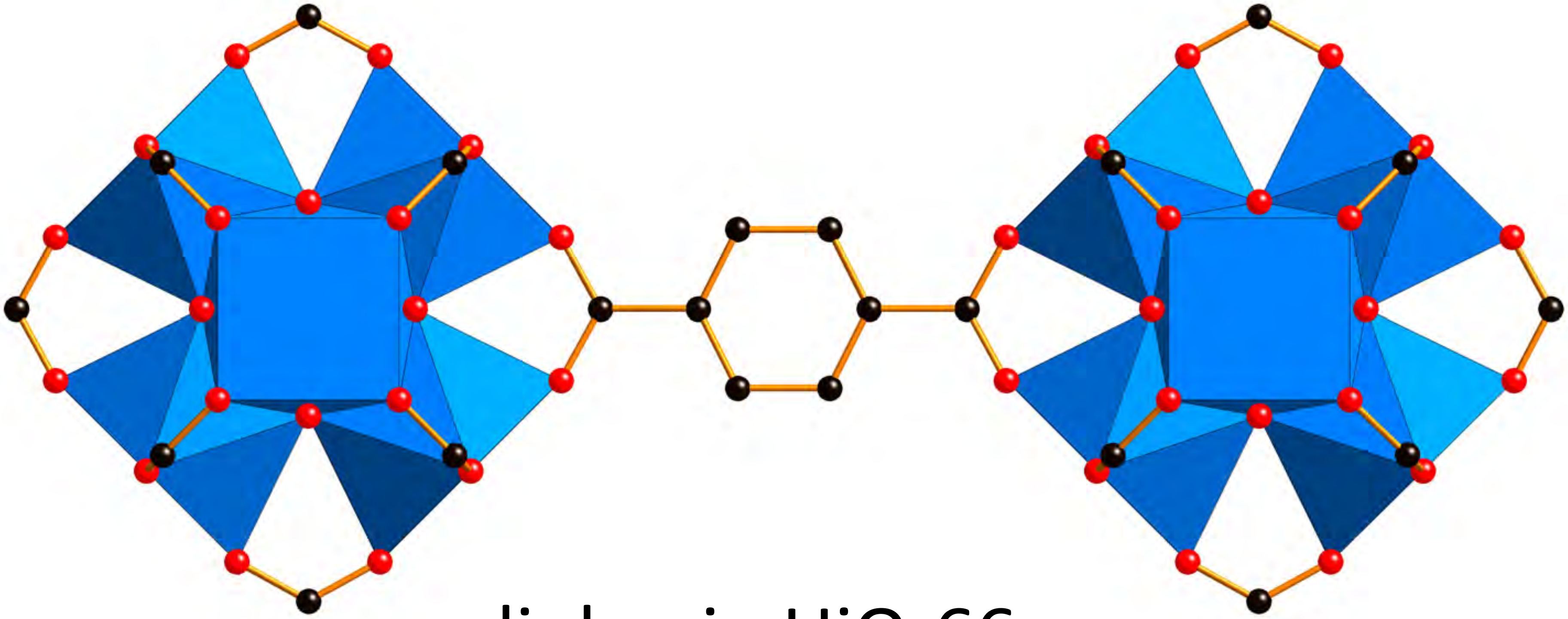


12-c SBU

Zr

UiO-6

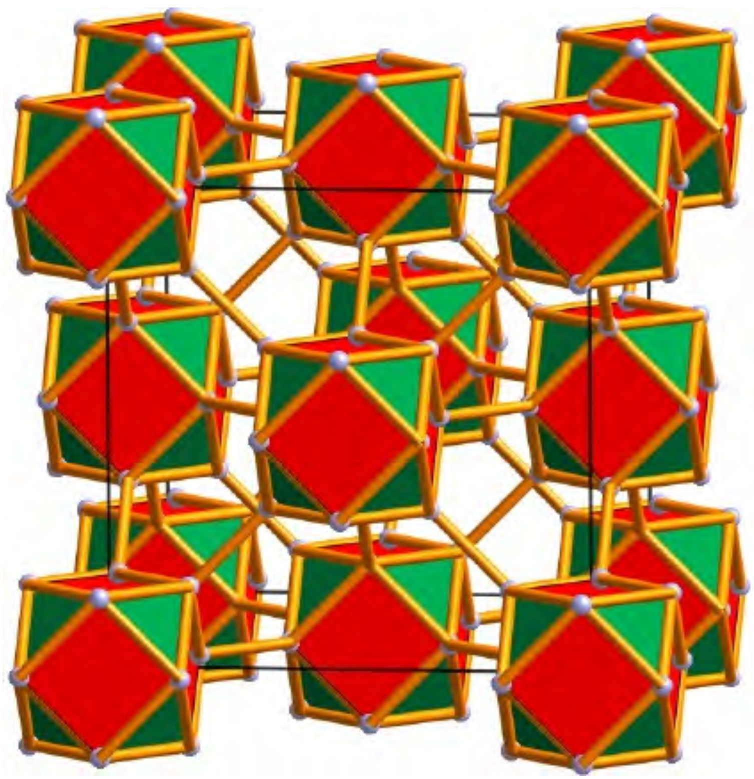
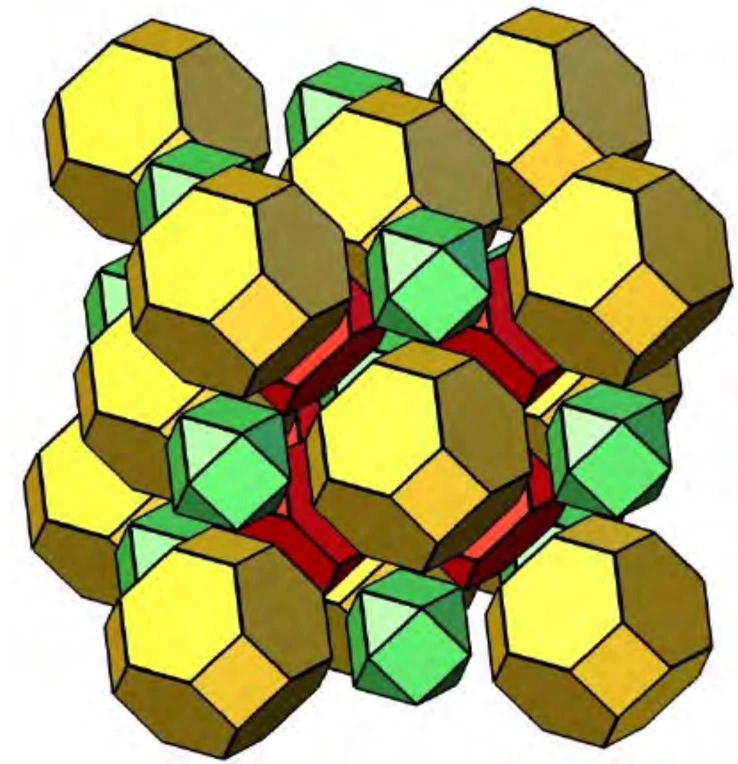
Lillerud group
JACS 2008, 130, 3850



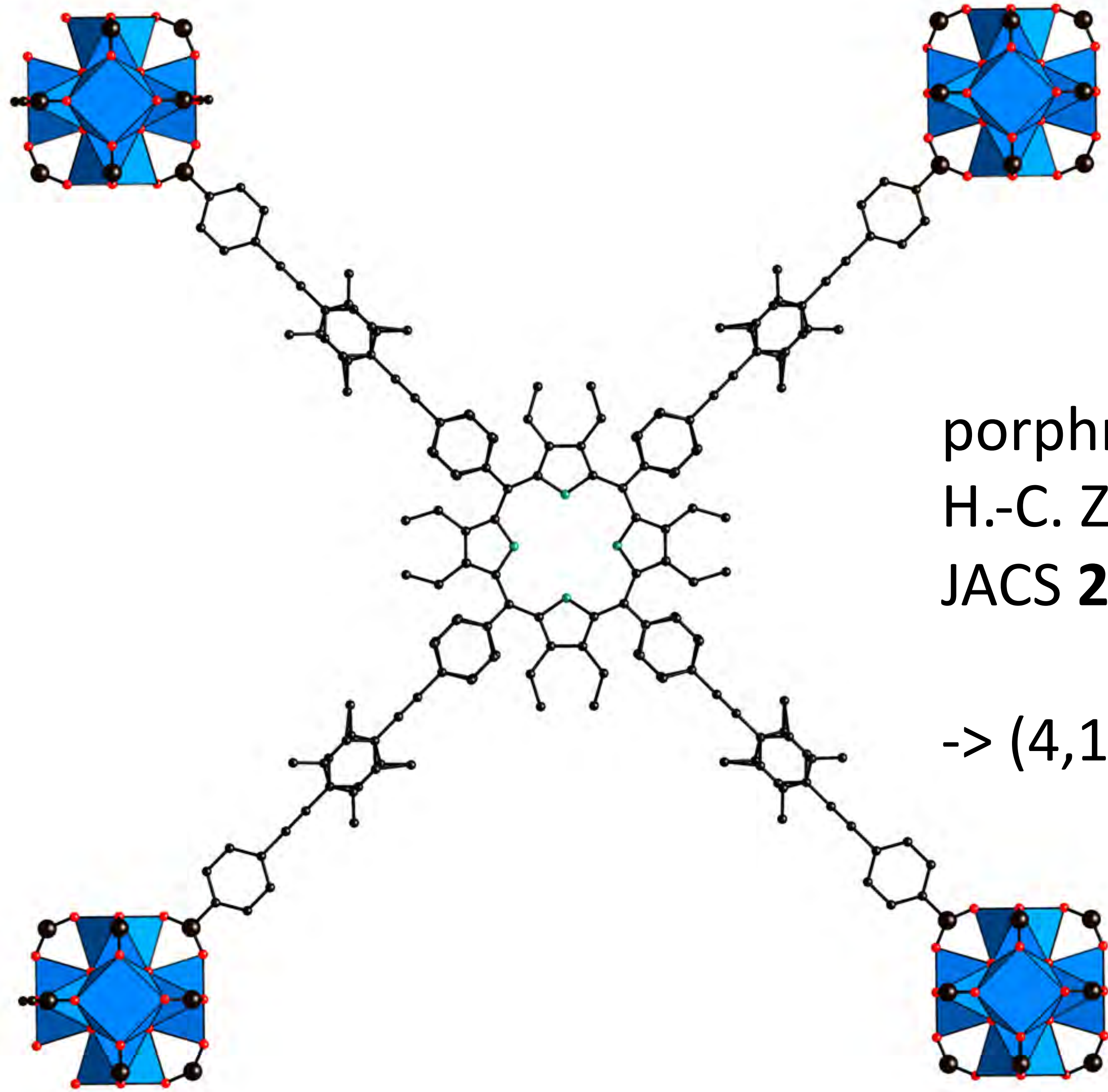
linker in UiO-66

basic Zr terephthalate

K. P. Lillerud group.JACS, 130, 13850 (3008)

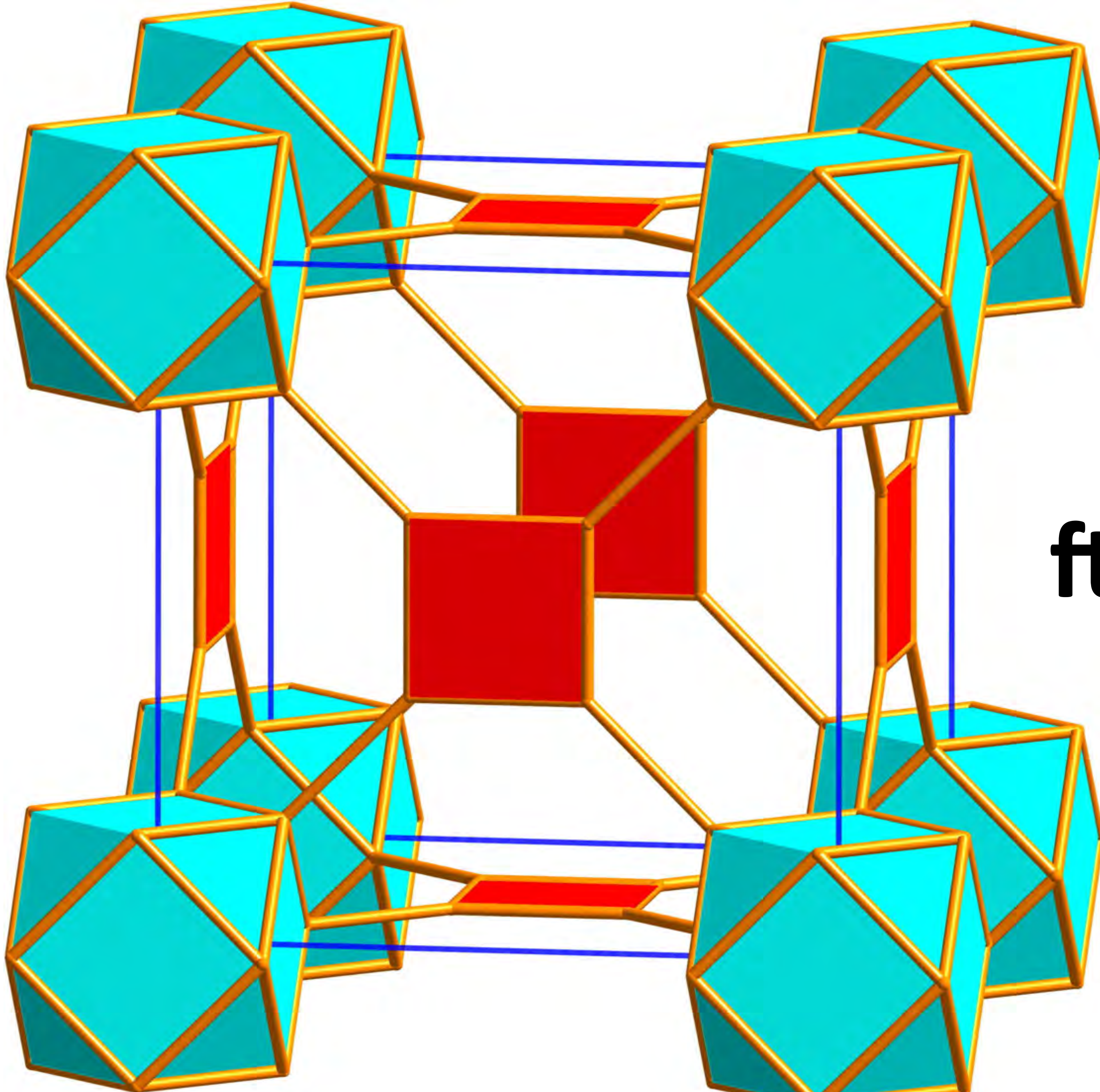
 

The underlying 12-c net of UiO-66 is **fcu** shown here in augmented form **fcu-a** = **ubt**. It is the B net un UB_{12} (hence the symbol. It is also a packing of archimedean polyhedra



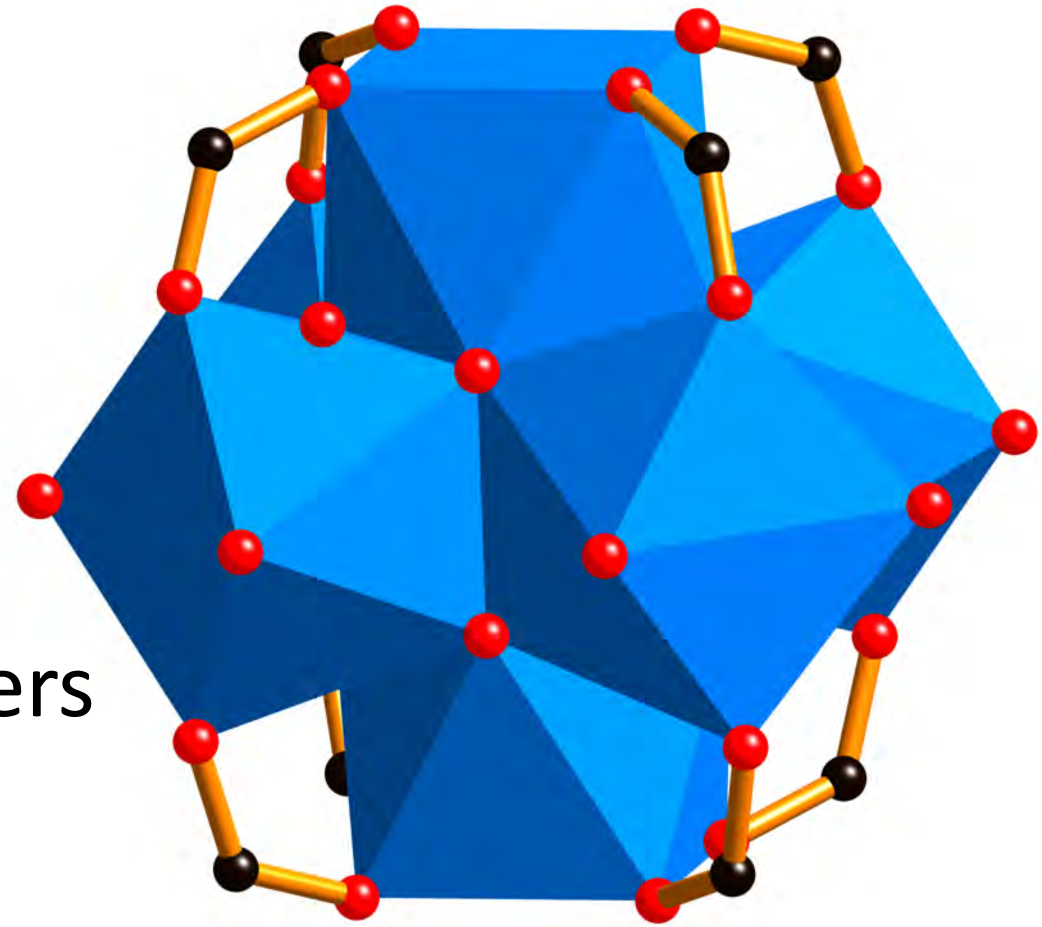
porphrin Zr MOF
H.-C. Zhou group
JACS **2015,** *137*, 413

-> (4,12)-c net **ftw**



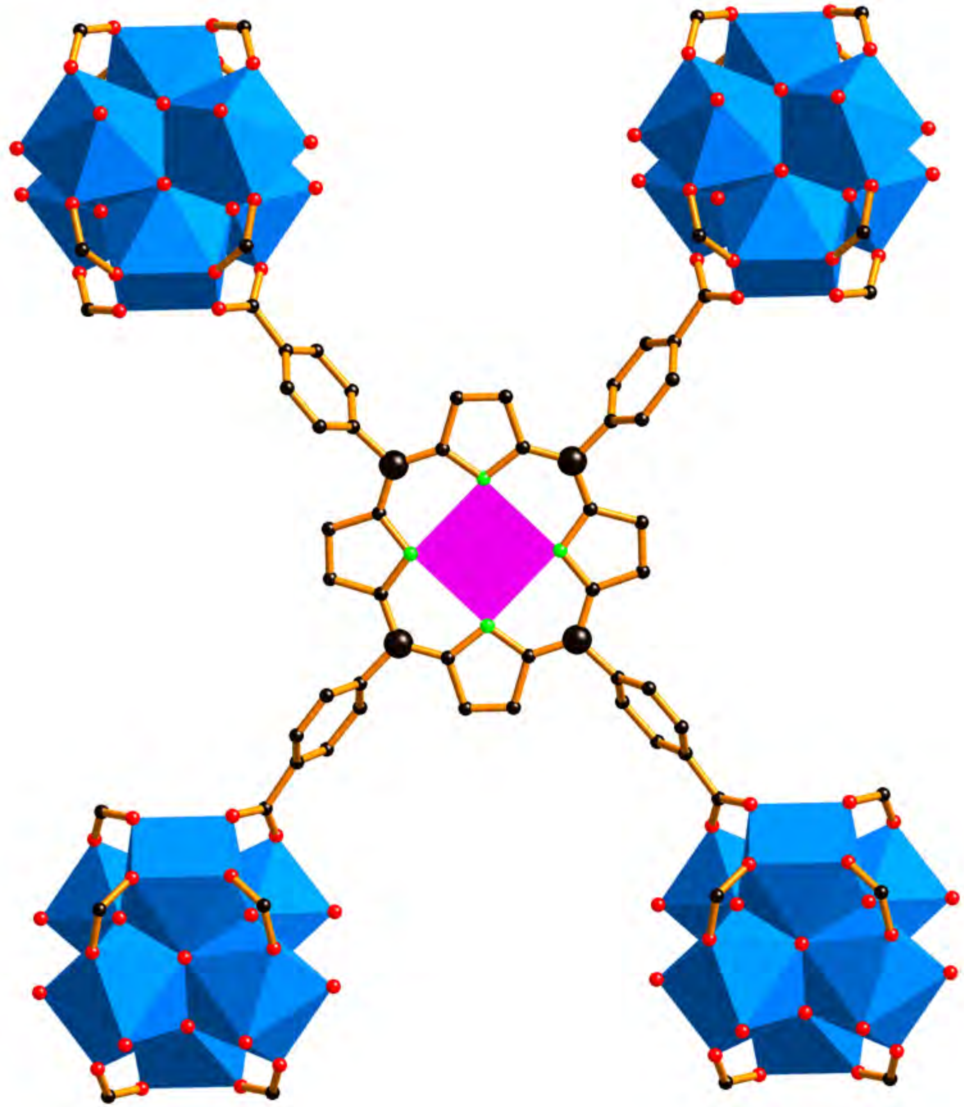
ftw-a

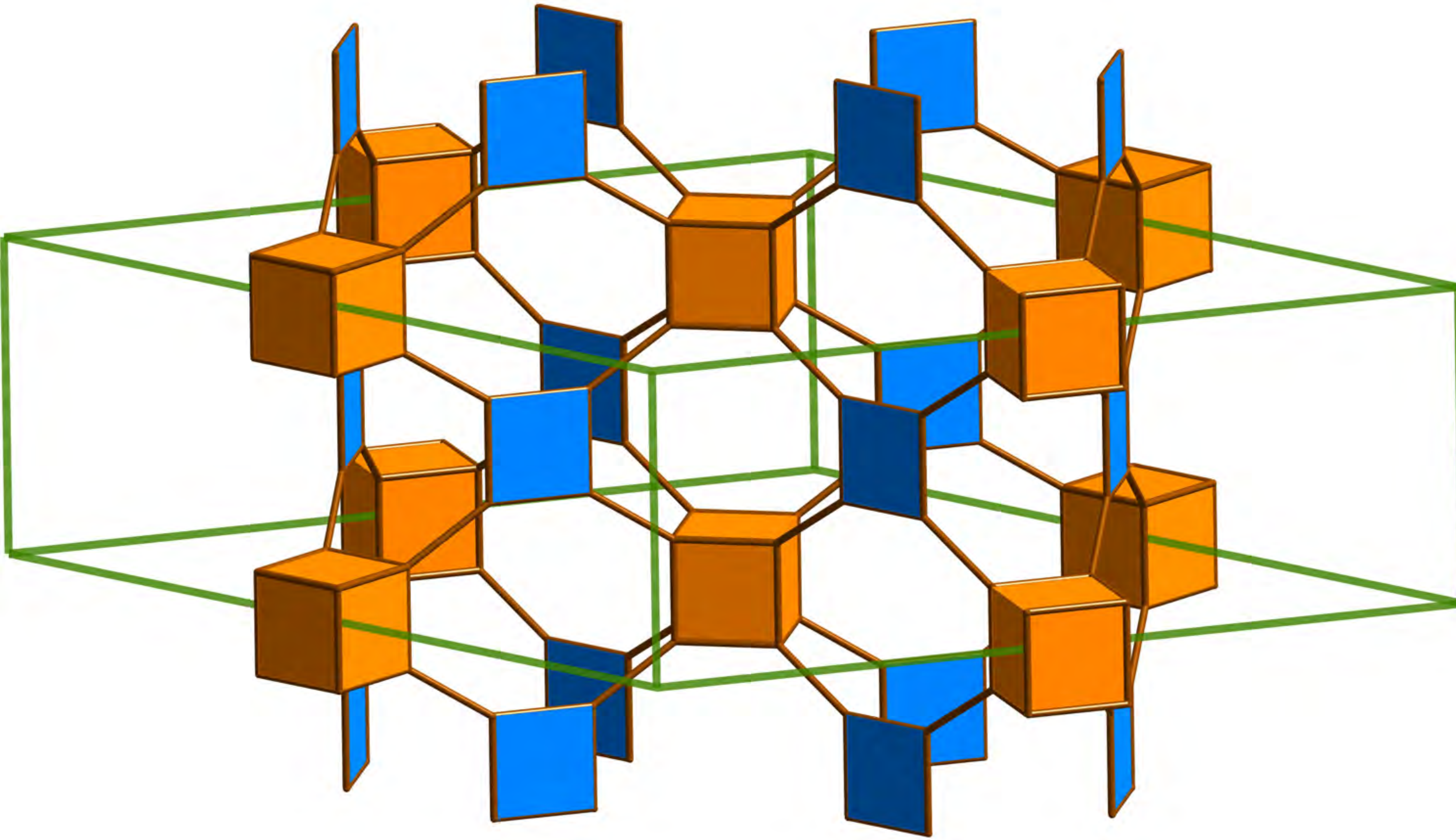
The Zr_6 cluster with eight points of extension in MOF-545 at corners of a cube.



O. M. Yaghi group
Inorg. Chem.51. 6443 (2012)

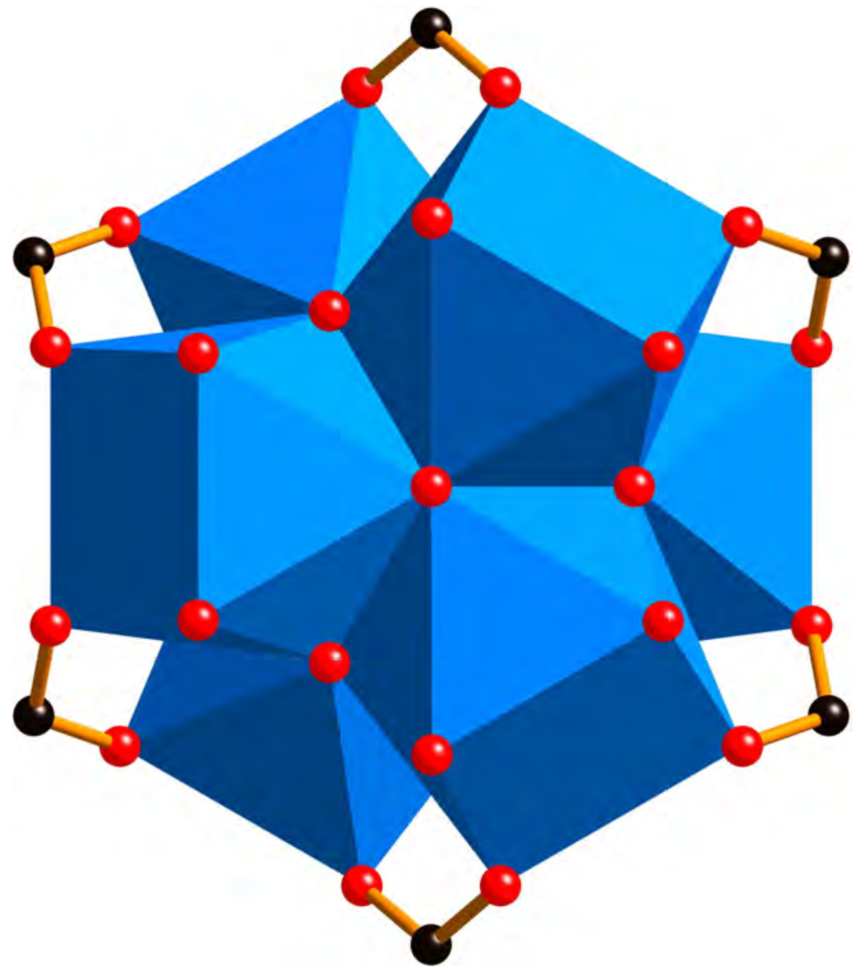
The linker in MOF-545 – an Fe porphyrin tetracarboxylate. A second way of linking square and cube





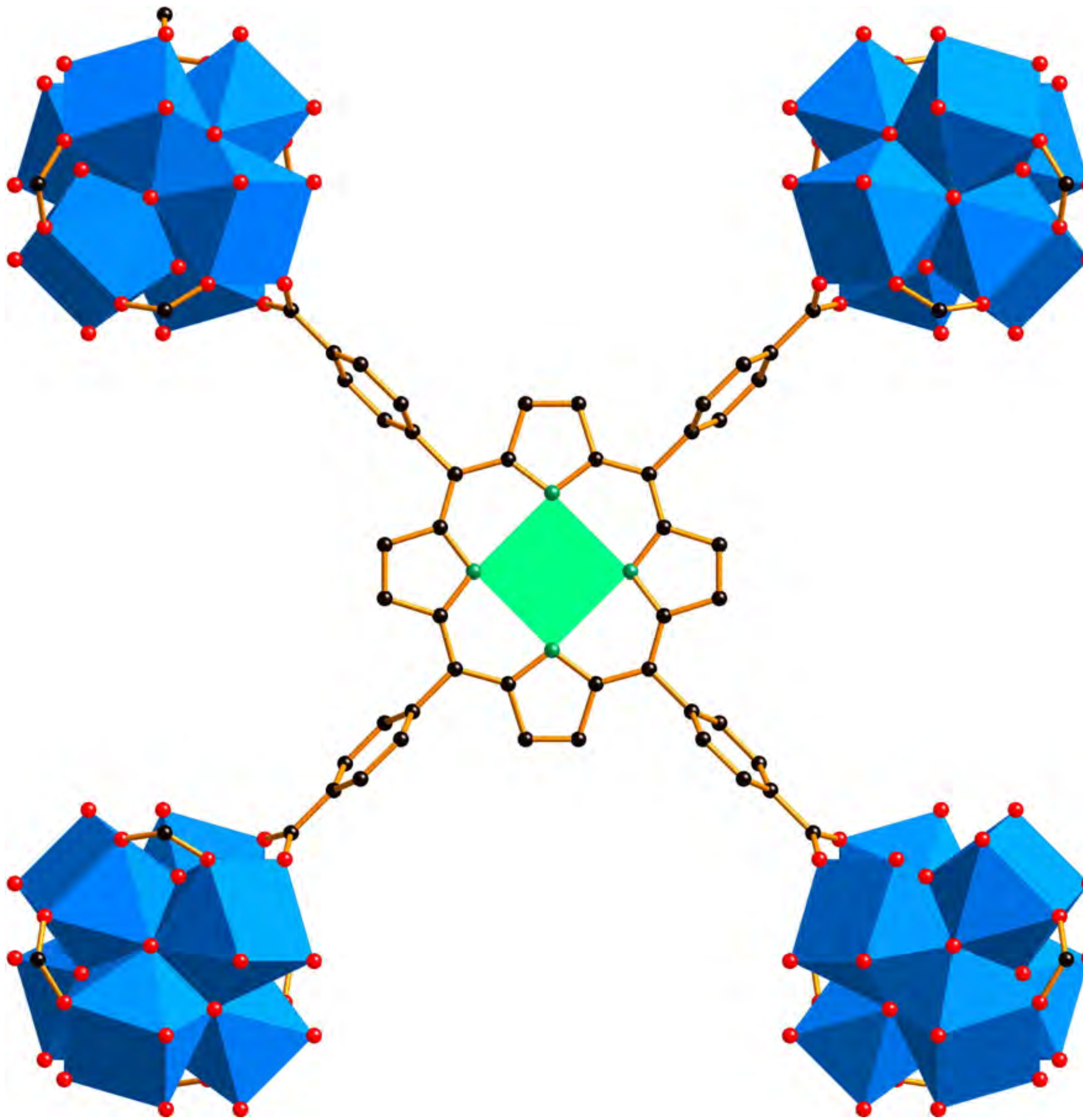
The underlying (4,8)-c net in MOF-545 shown as **csq-a**

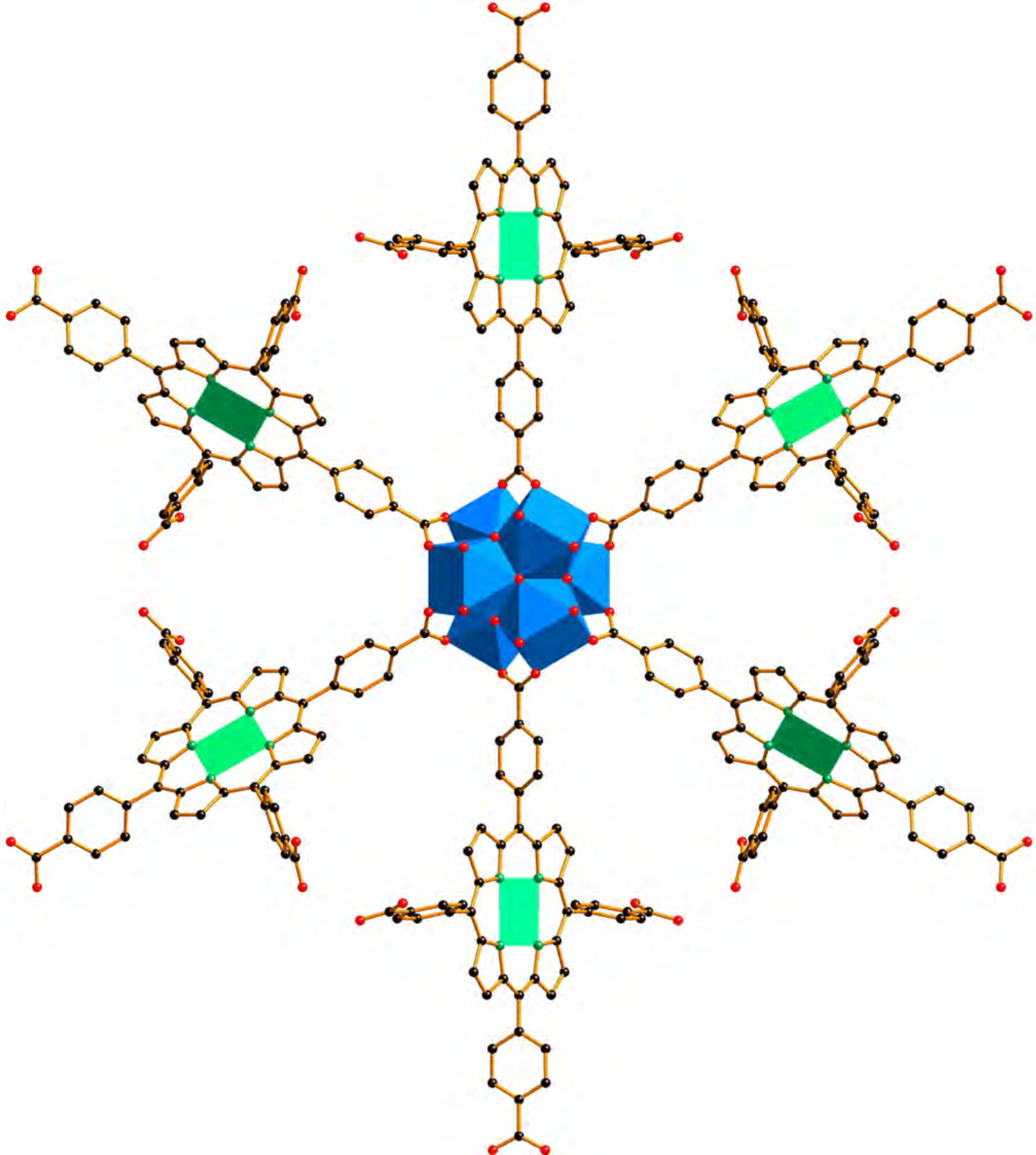
The same Zr_6 cluster but now only six points of extension forming a planar hexagon.



H.-C. Zhou group JACS, 135,17105 (2013)

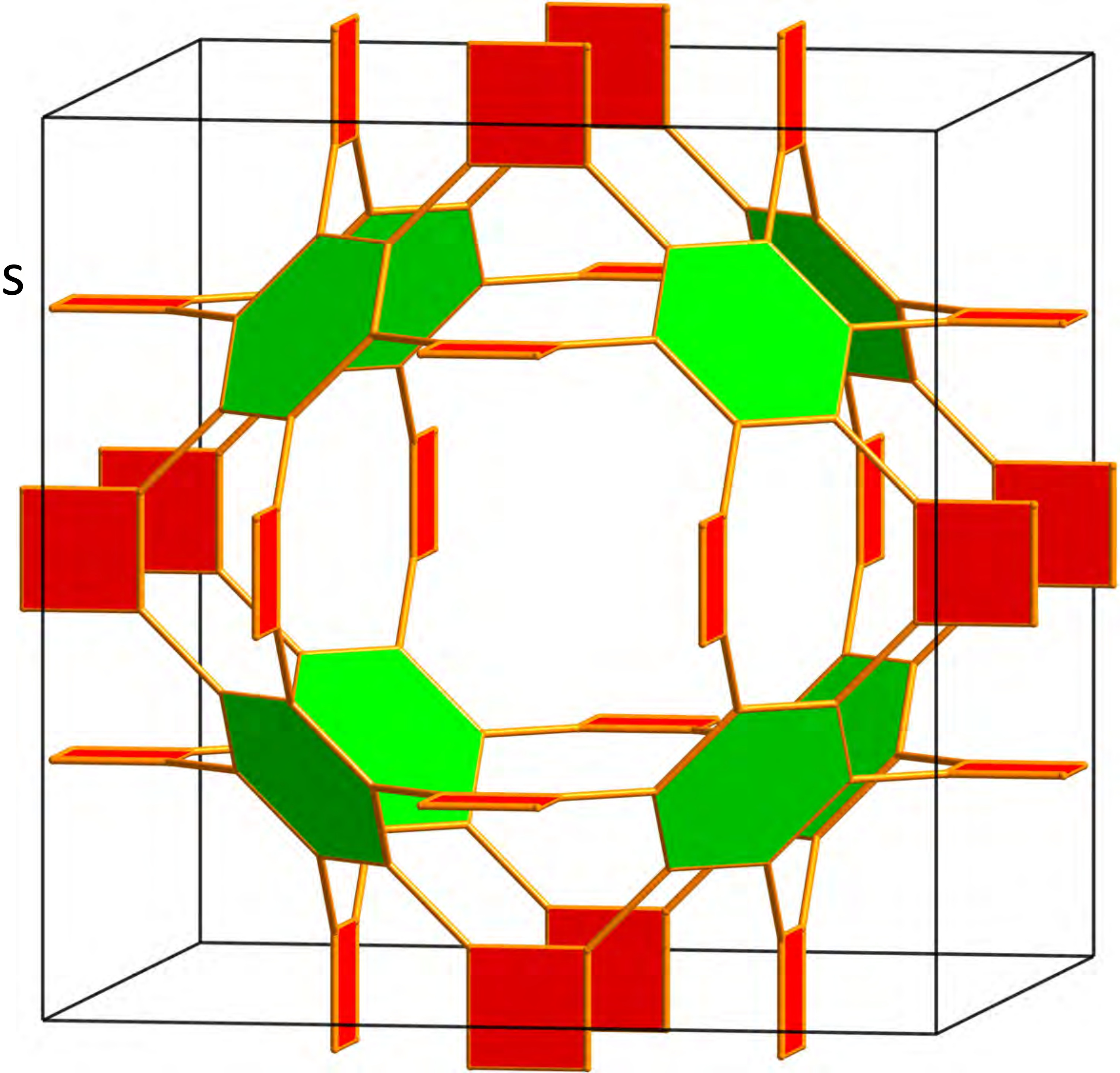
The linker is a nickel porphyrin tetracarboxylate

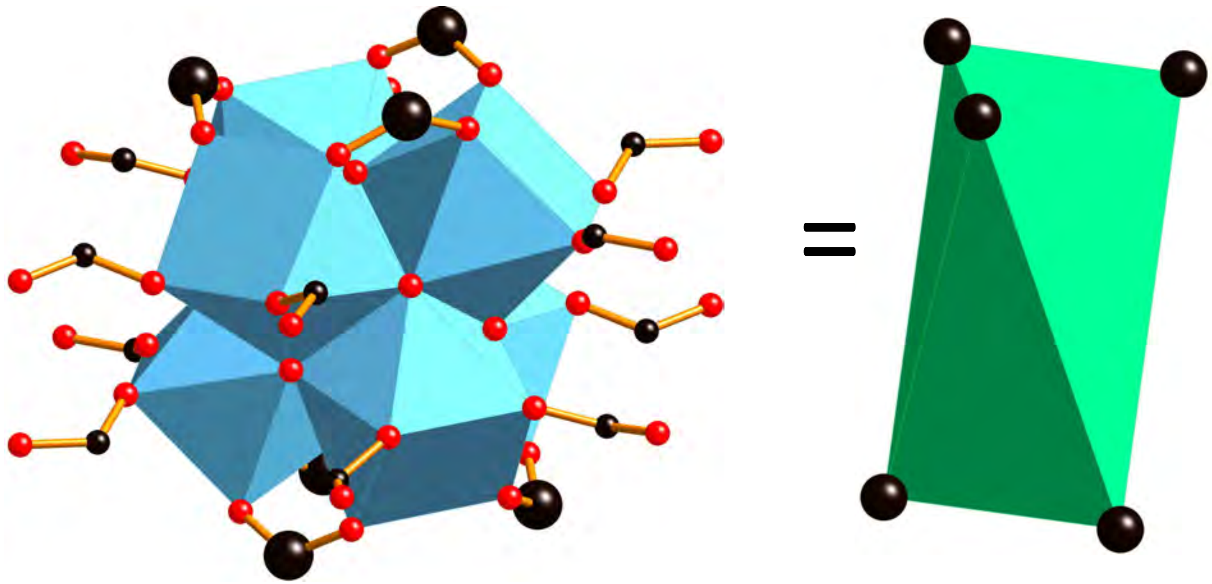




It’s really very beautiful

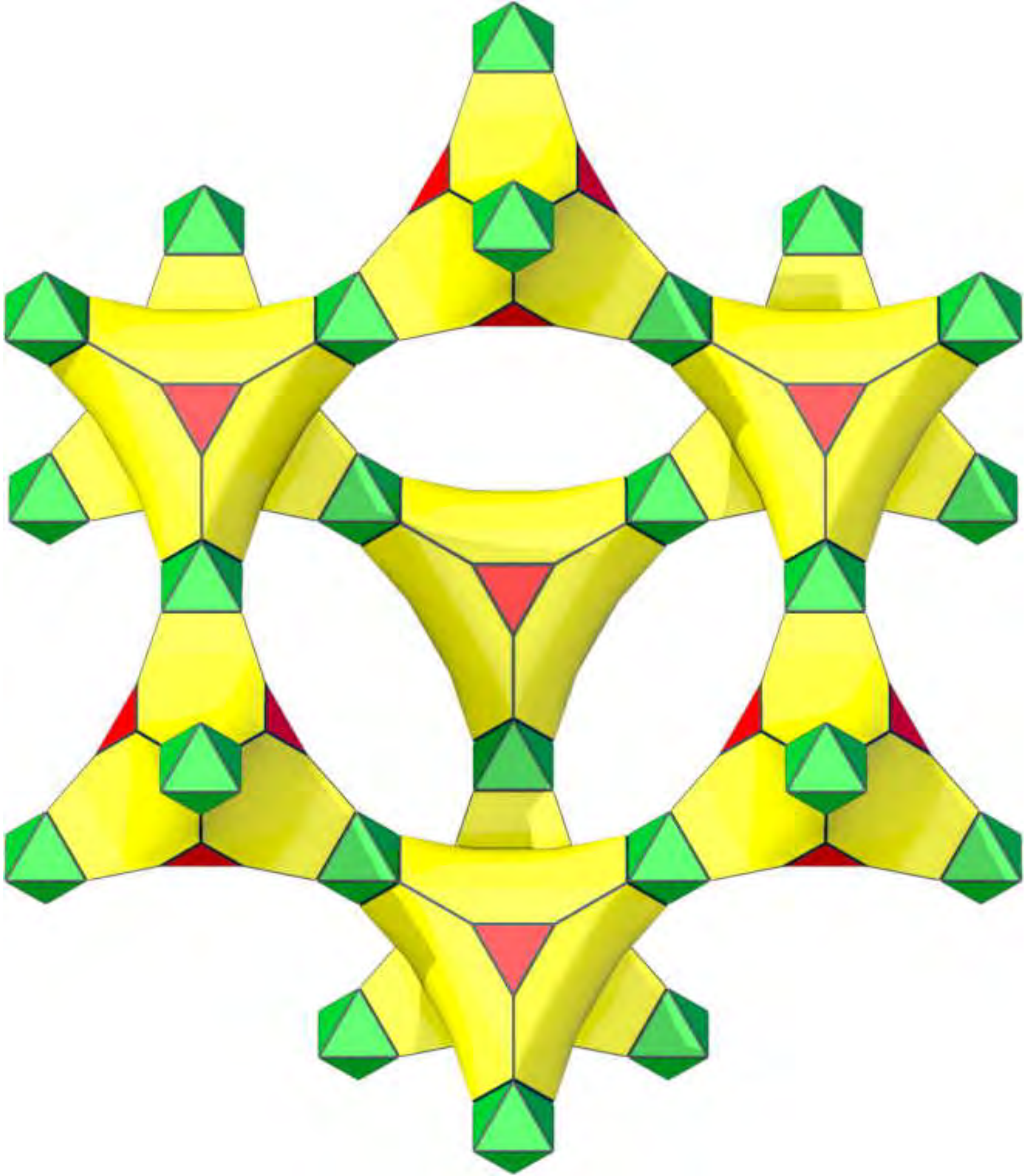
The net is **she**, shown here as **she-a**



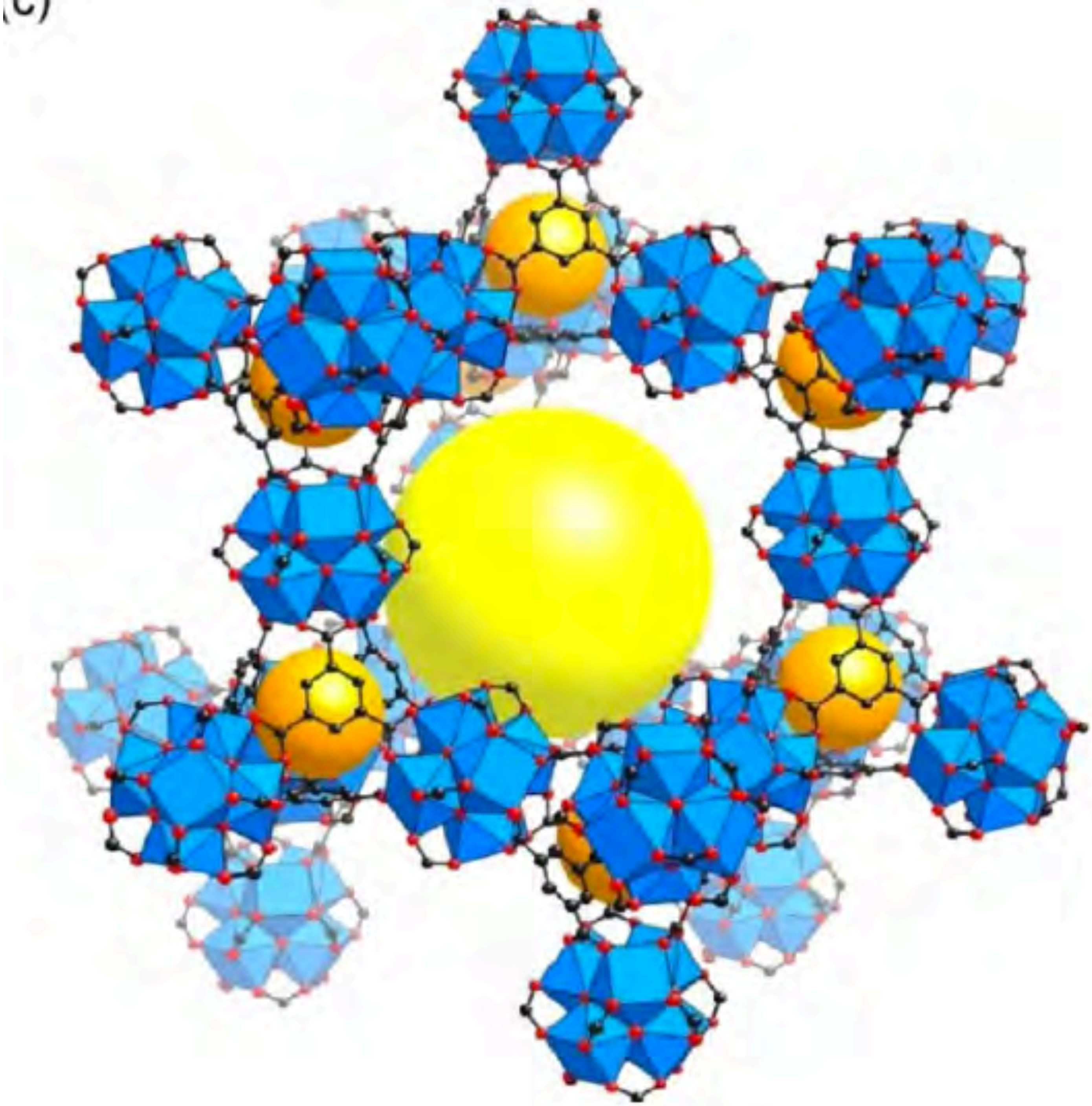


linker ->
(3,6)-c net

The same Zr_6 group but now with octahedral arrangement of points of extension (large balls)
The other ligands are formate. MOF-808
H. Furukawa et al. JACS, 136, 4369 (2014)

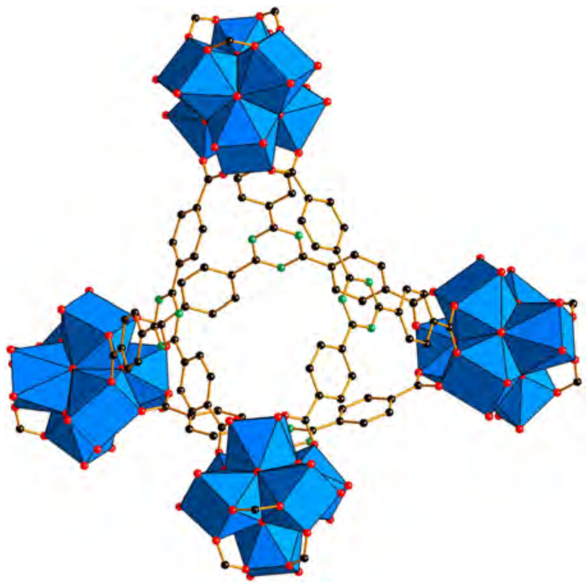


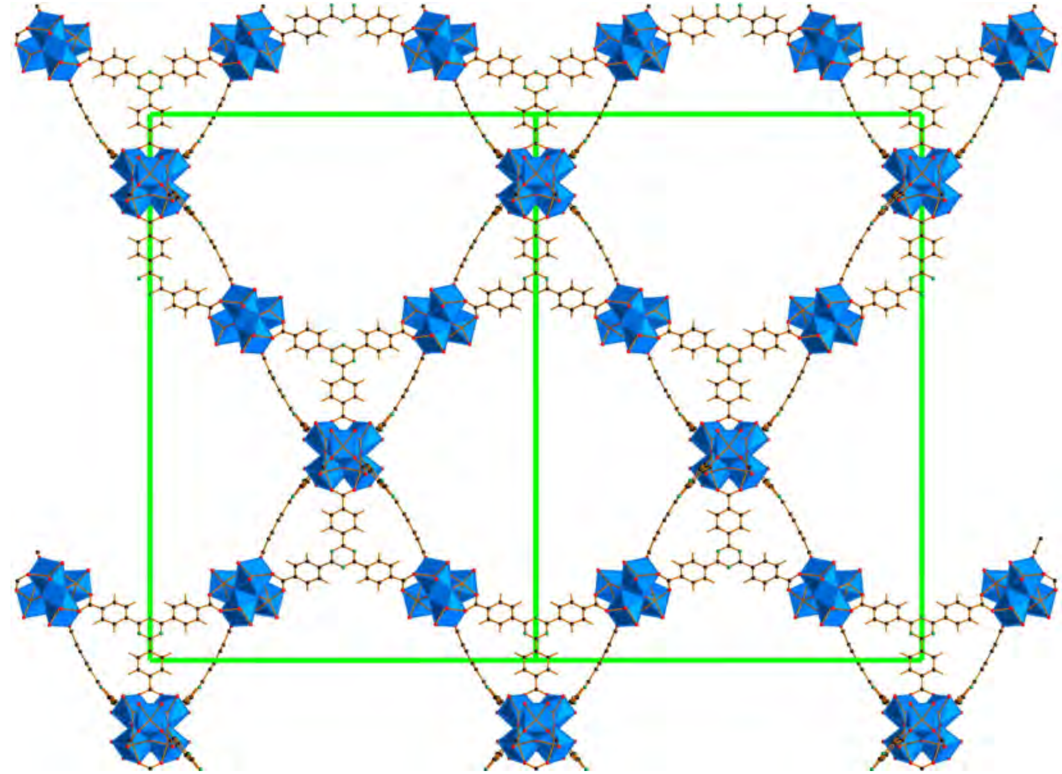
Net is edge-transitive **spn** shown here in augmented form



MOF-808

from paper

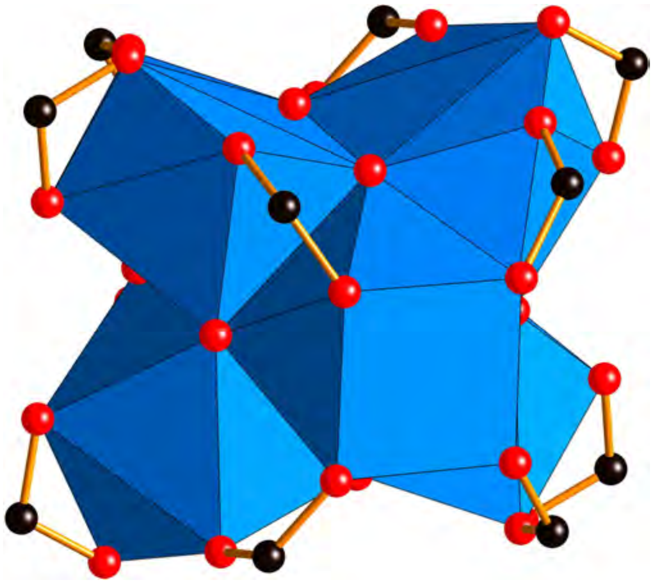




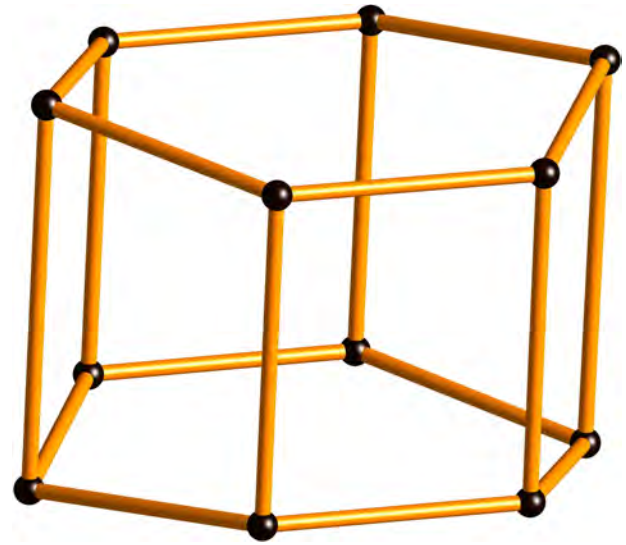
view down [110]

An isoreticular example – same Zr SBU
 but longer arms on the trtopic linker

X. Zou, H. C. Zhou et al. Angew. Chem **2015**, *54*, 149

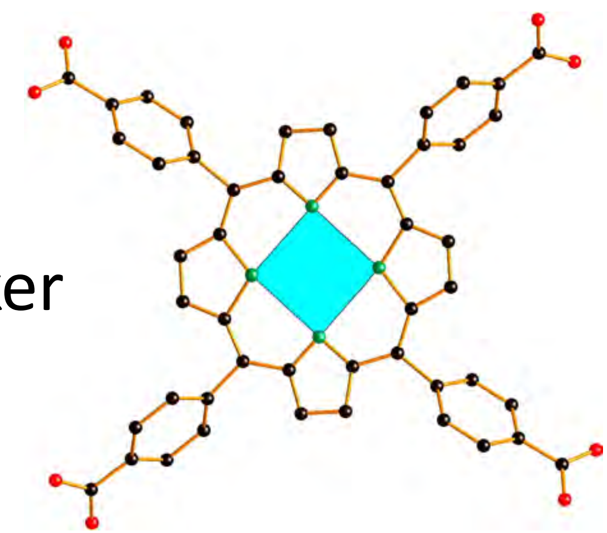


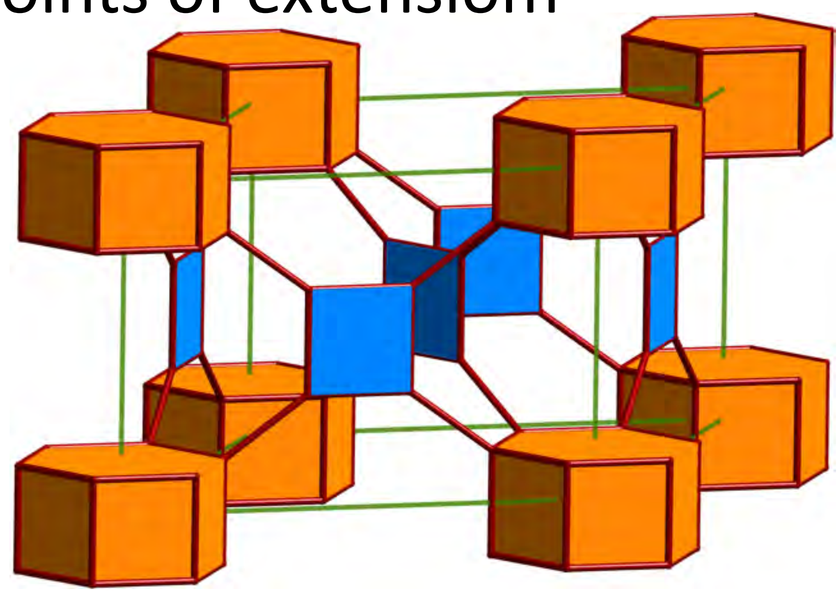
=



A fifferent Zr_6 SBU with 12 points of extensiom

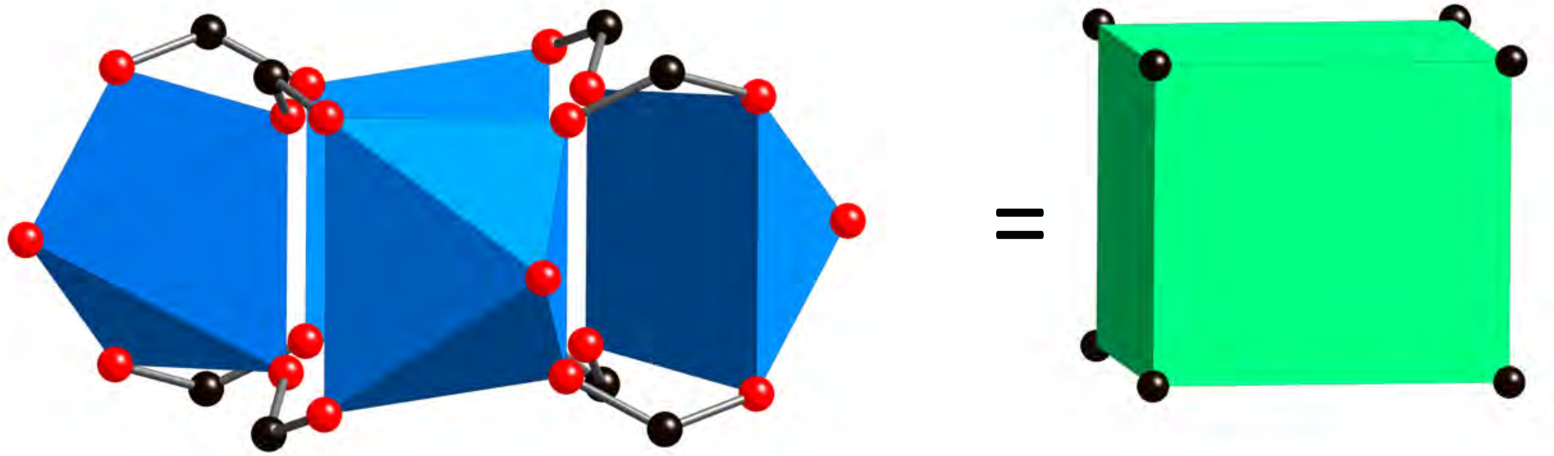
linker





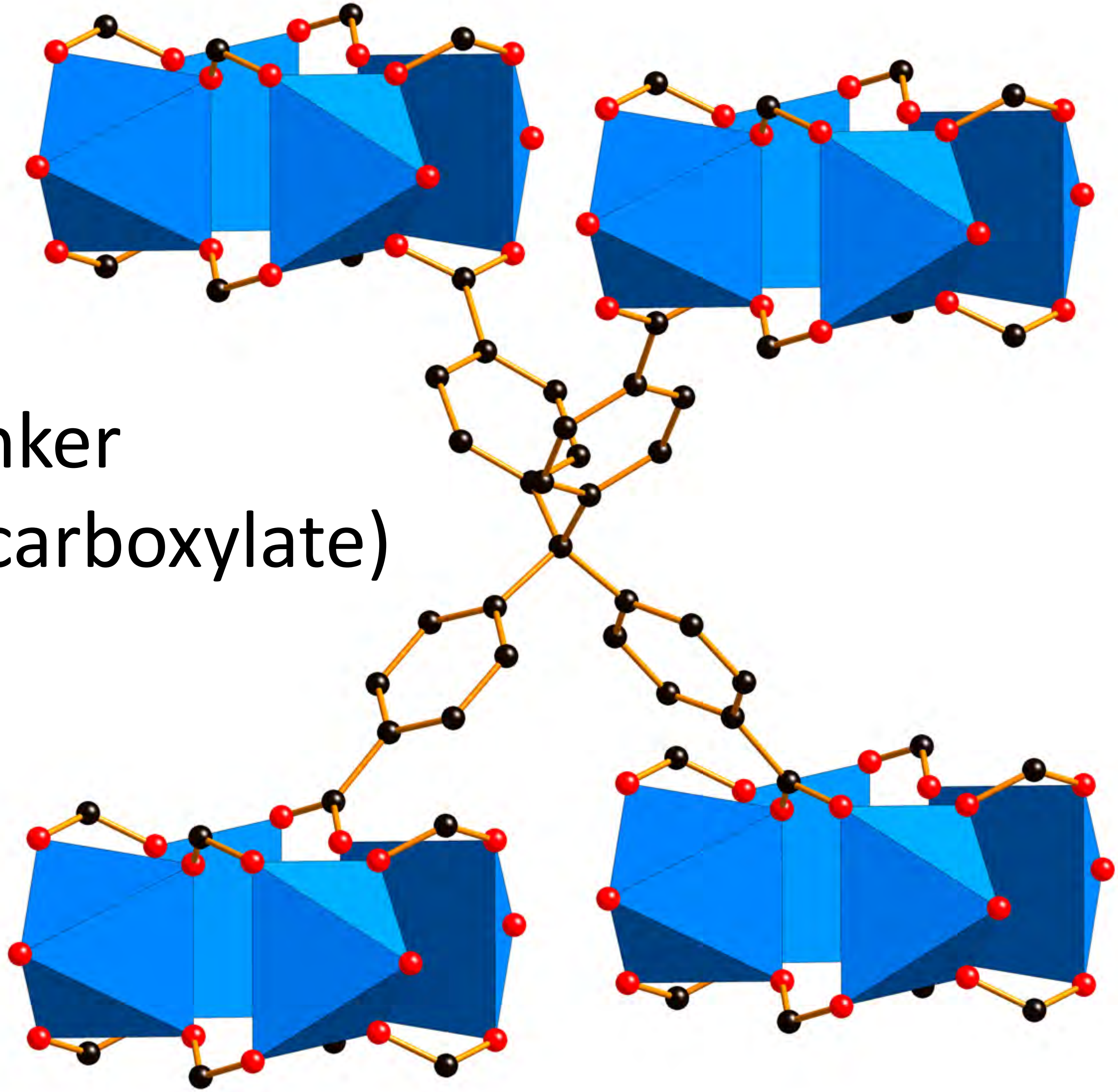
H.-C Zhou et al. JACS 2014, 136, 17714

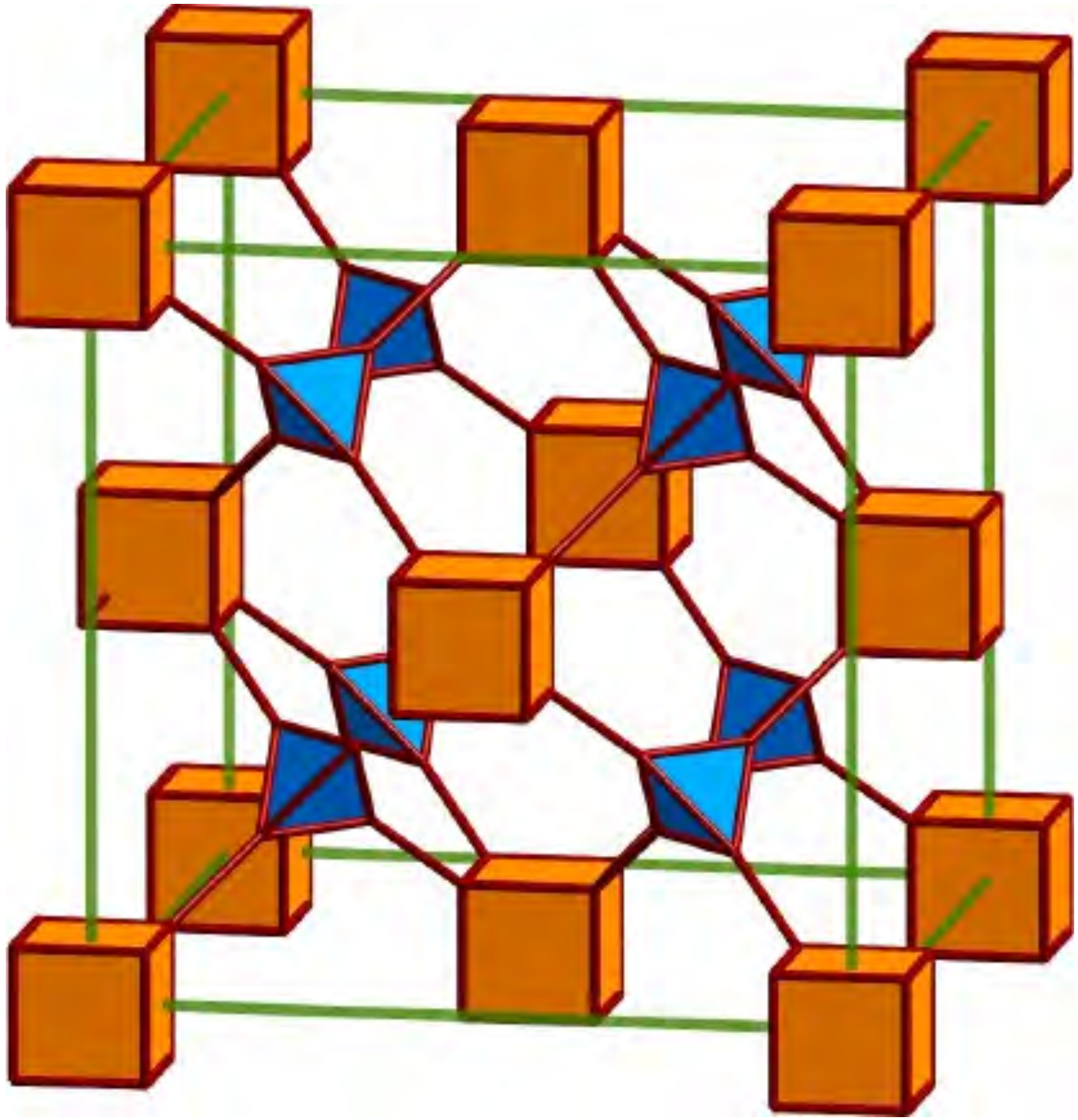
shp-a



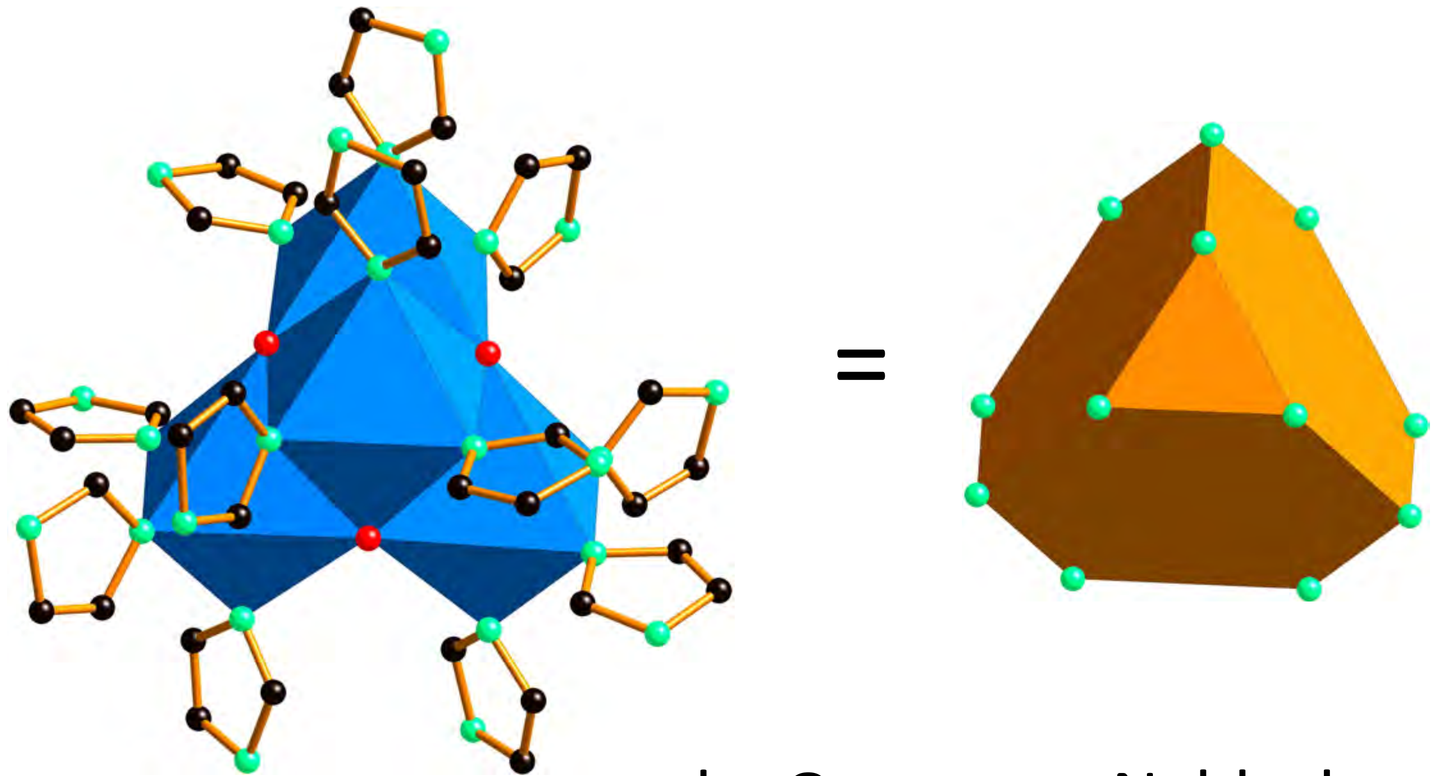
Cd_4 cluster with eight points of extension
Kimoon Kim group
Angew. Chem. Int. Ed. 43, 971 (2004)

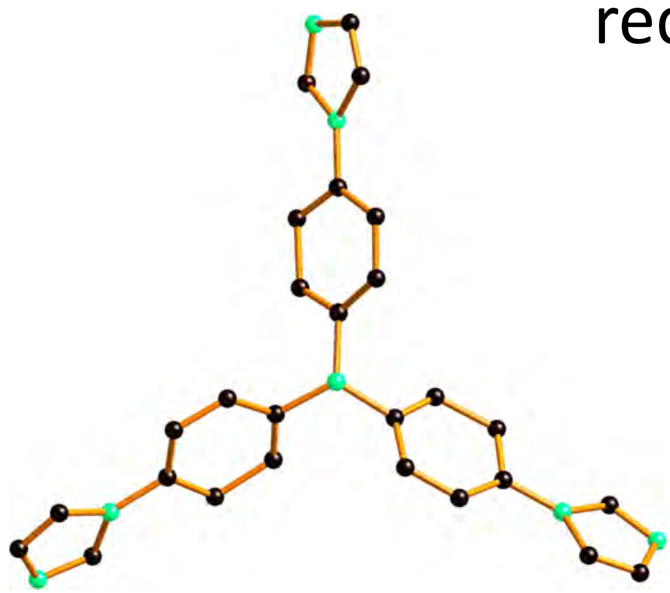
The linker
(tetracarboxylate)





The net, as expected is **flu** (fluorite) shown here as **flu-a**

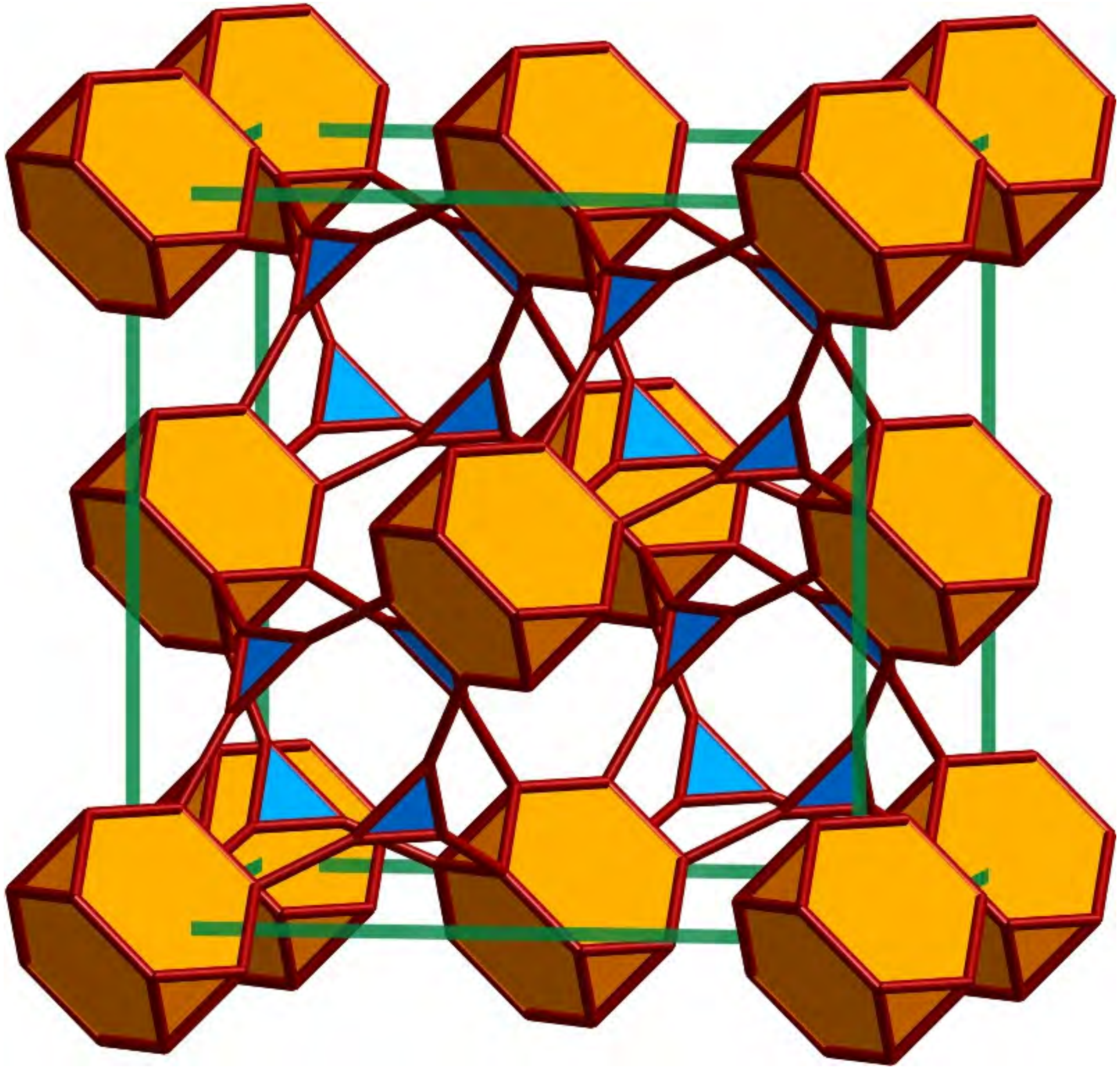




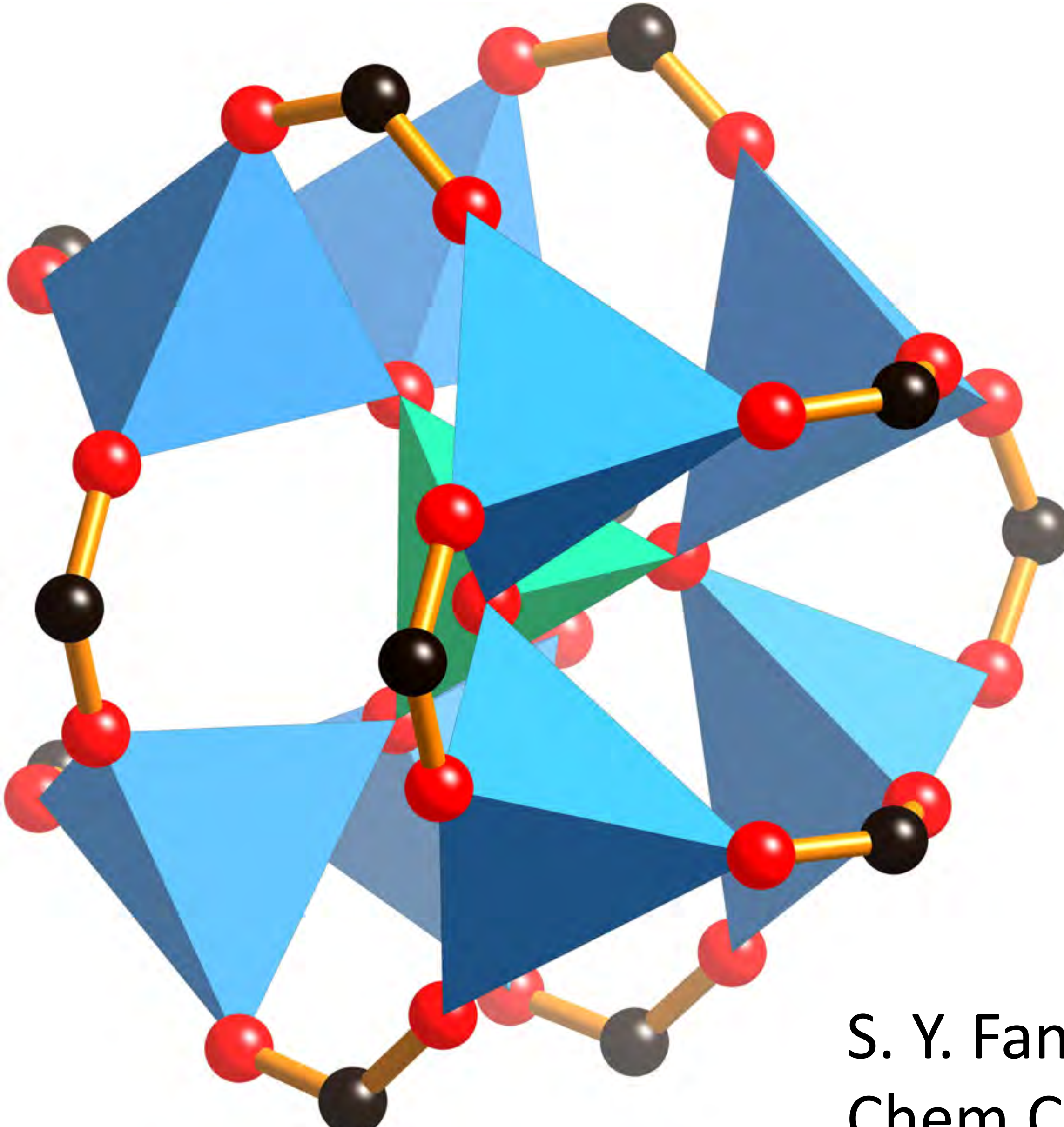
red = O, green = N, black = C

Cd MOF Di Sun et al.
CrystEngComm (2014), 16, 3829

truncated tetrahedra and
tritopic linker -> (3,12)-c net

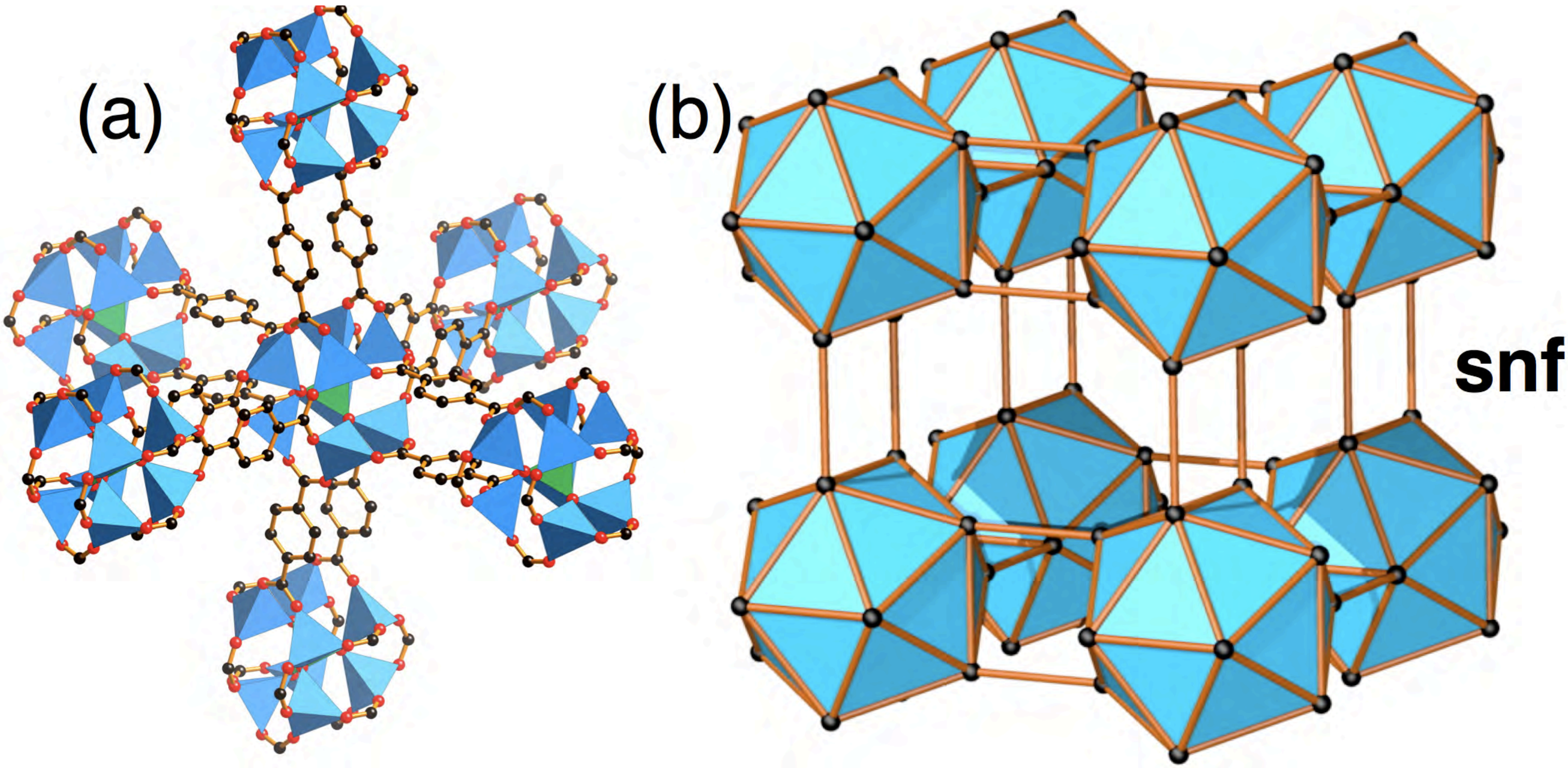


The edge-transitive net **ttt** shown as **ttt-a**



$SiZn_8(-CO2)_{12}$

S. Y. Fang *et al.*
Chem.Commun. 2002, 472.

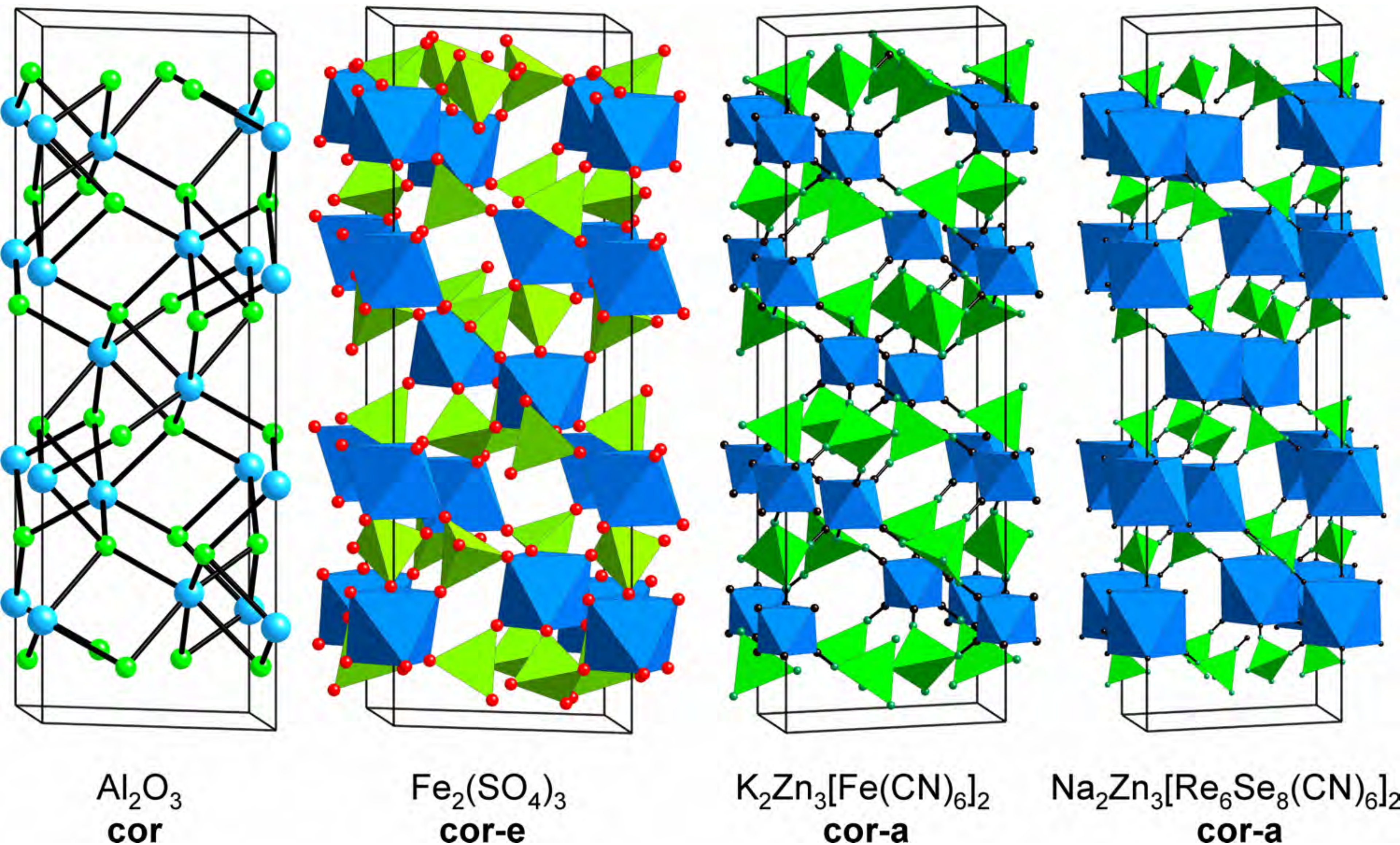


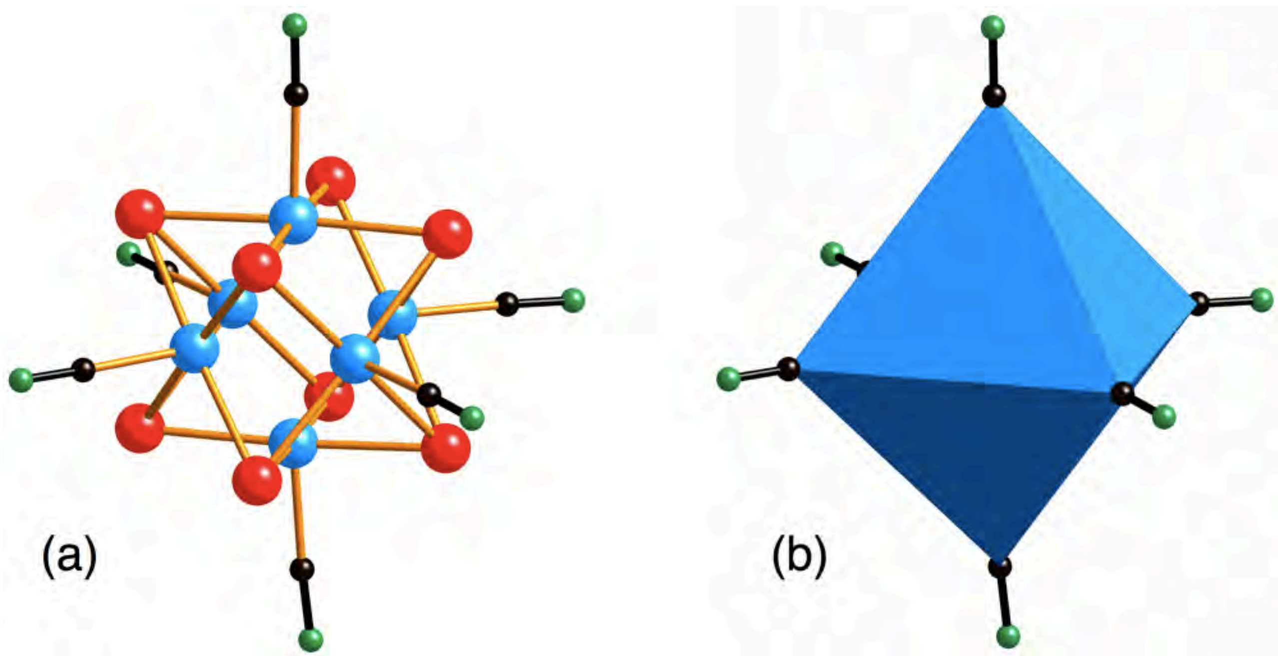
The net of points of extension is 6-**snu**

The net of linked SBUs is **pcu** – primitive cubic lattice net

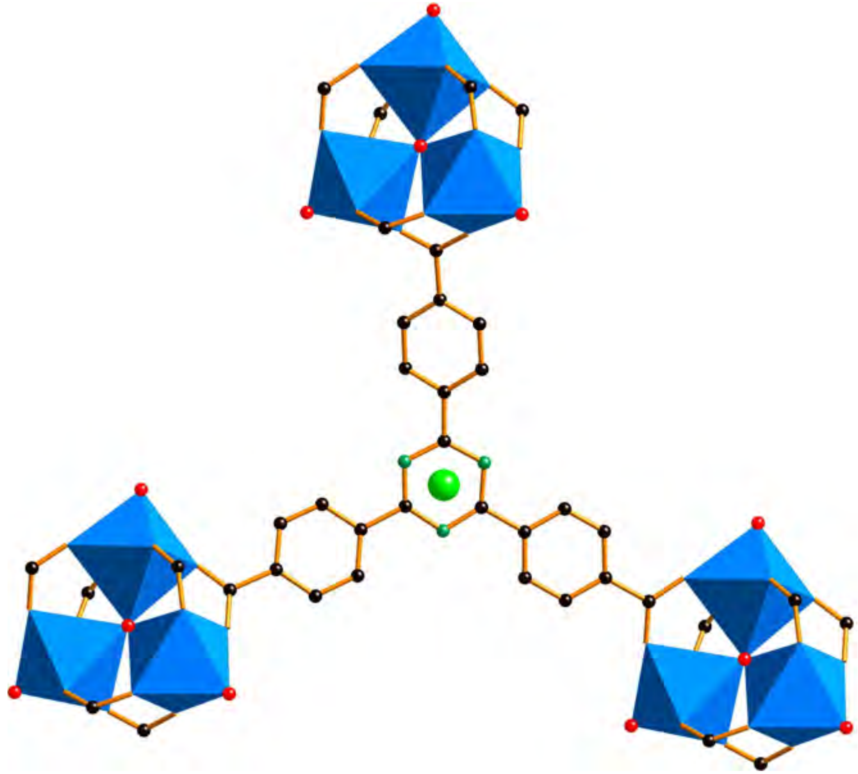
All the previous examples have been of edge-transitive nets

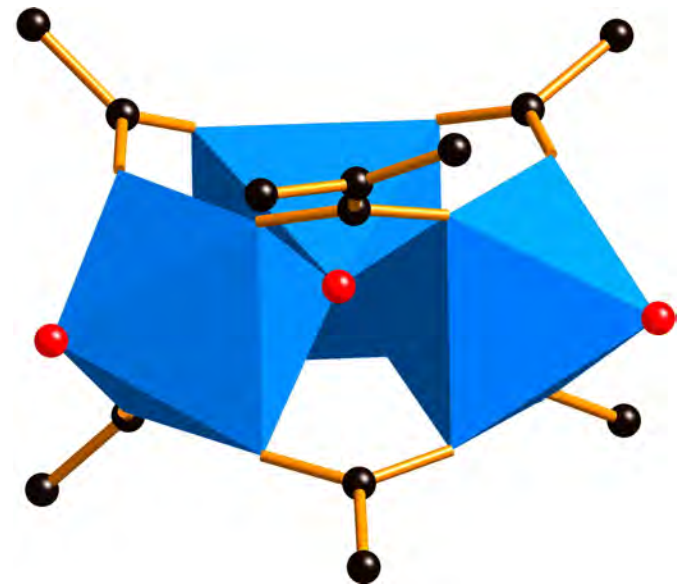
structures with the **cor** (corundum) topology





$Re_6Se_8(CN)_6$ SBU



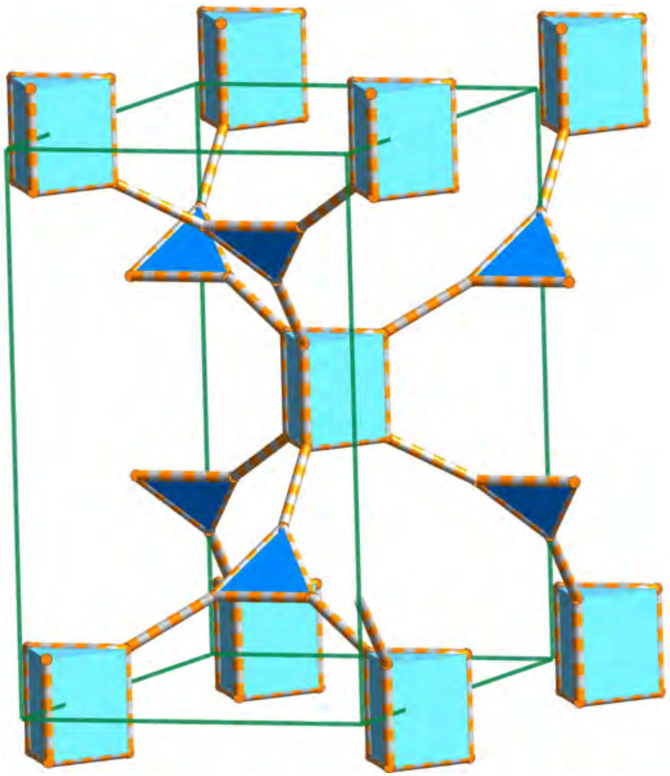


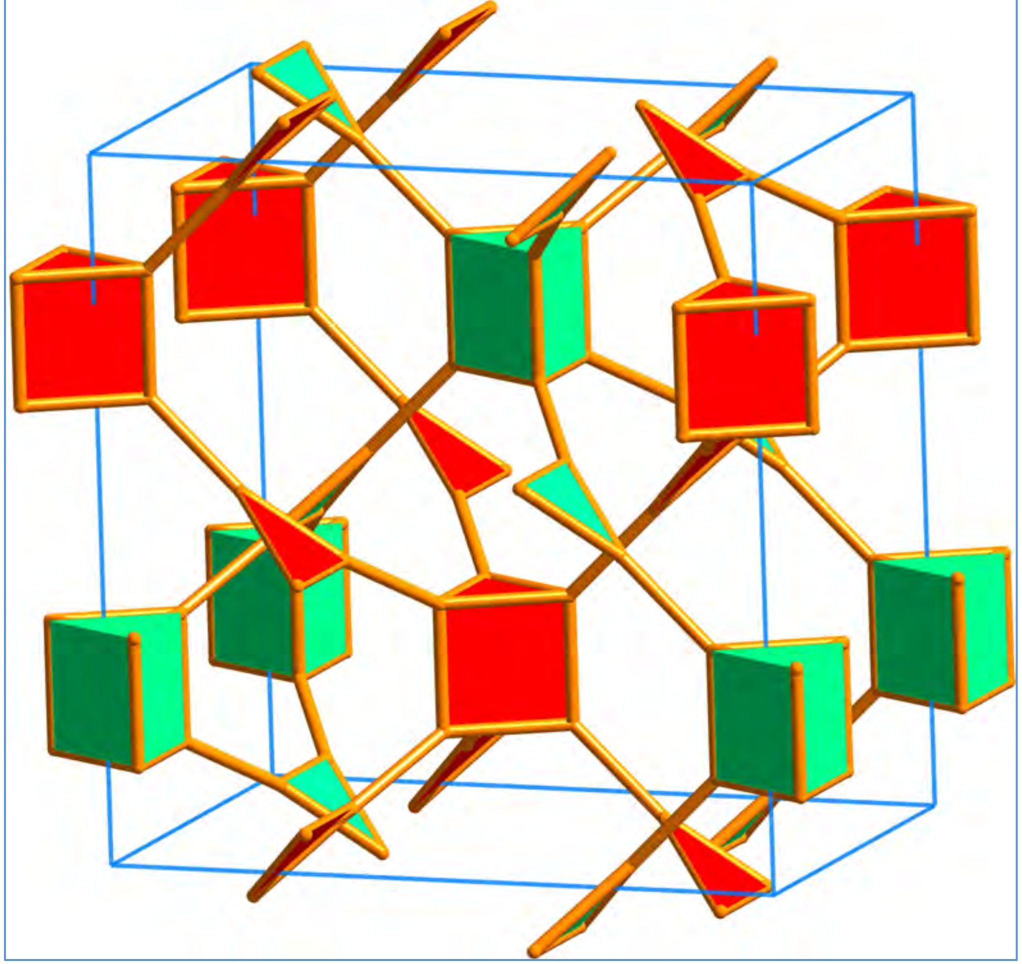
trigonal-prismatic SBU

Shenqian Ma et al (H.-C. Zhou group) Inorg. Chem. **2007**, 46, 3432

-> 93,6)-c net. There is no edge-transitive net for linking triangle with trigonal prism. Best is net **sit** that is edge 2-transitive.

First structure with this topology actually MOF-39 (Yaghi group JACS 2001, 123, 8239)



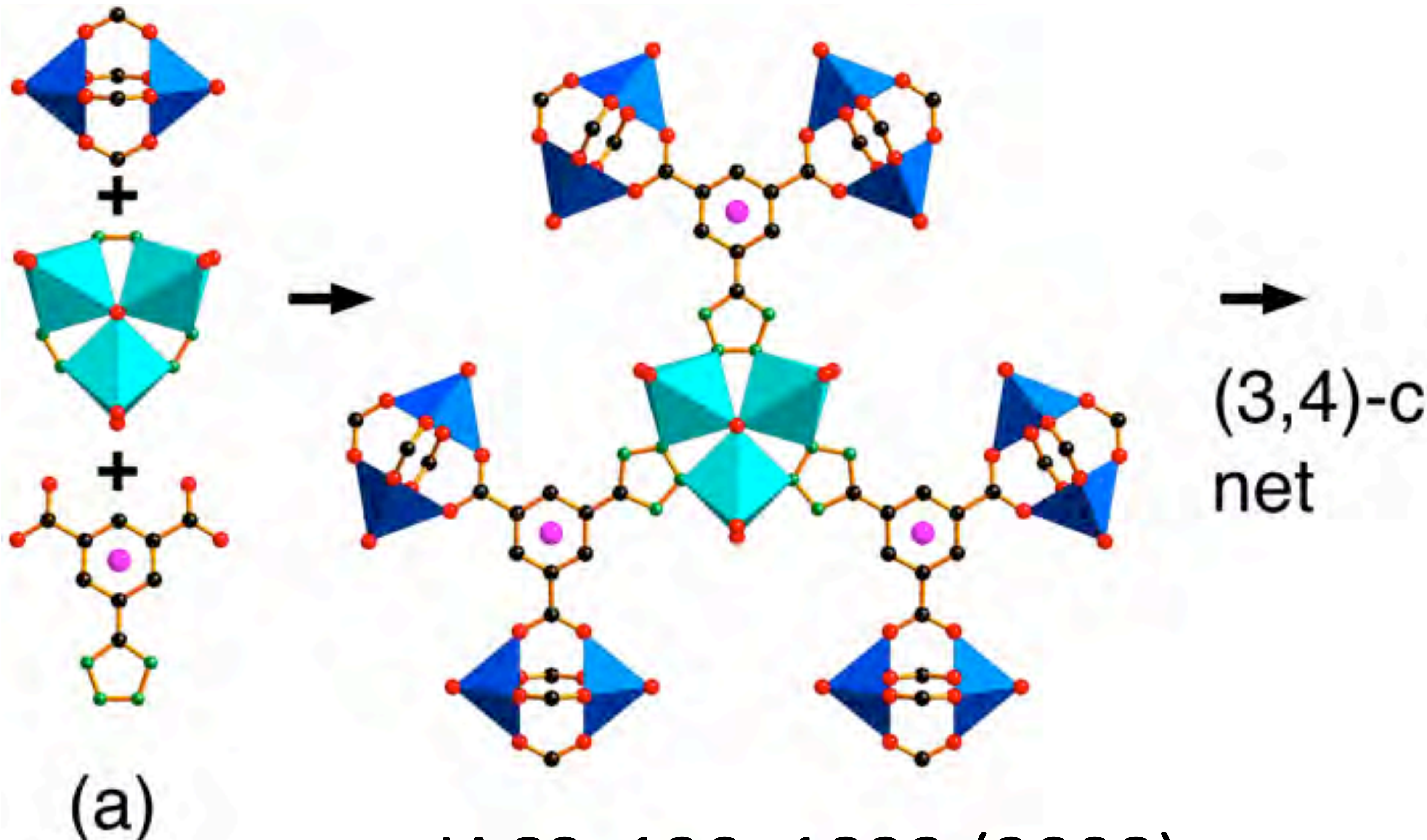


sit-a

sit-c-a

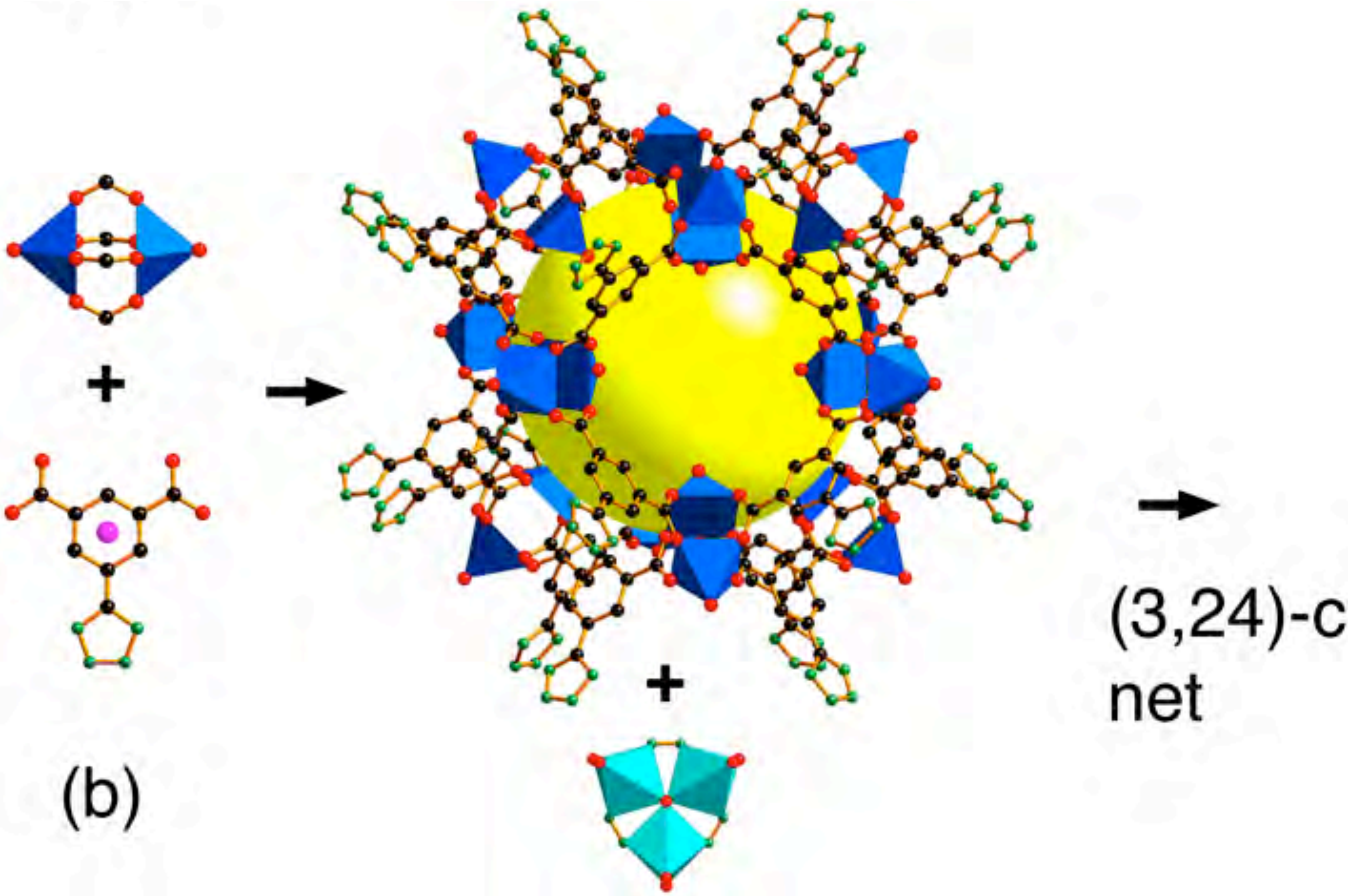
In every example to date **sit** nets are found to be interpenetrating pairs
sit is polar (symmetry *Imm*2) and pairs of opposite polarity intergrow (*Imma*)

A MOF with 3 SBUs – Eddaoudi group



JACS, 130, 1833 (2008)

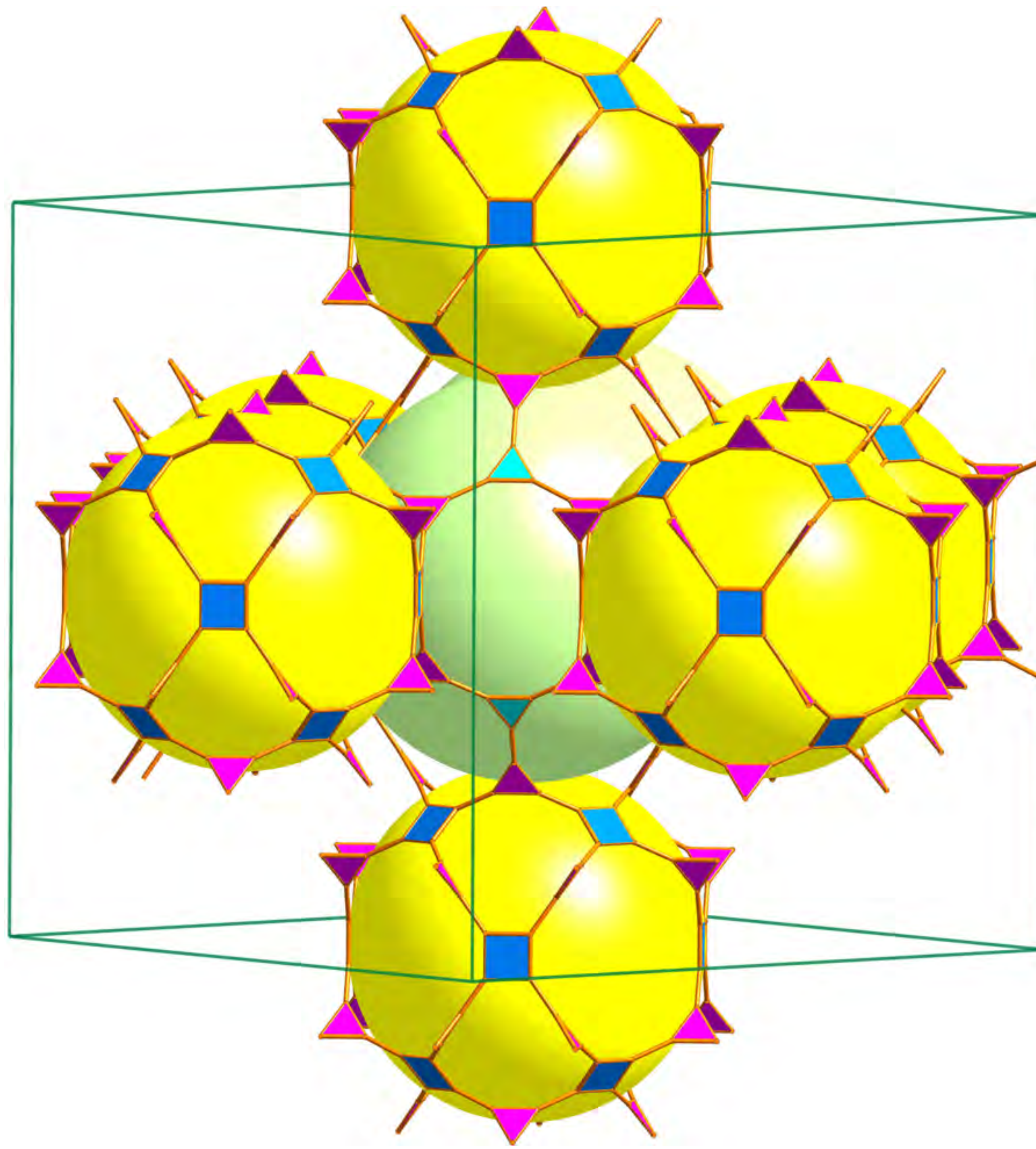
A second description with a 24-c tertiary building unit (TBU)



The (3,4)-c net

ntt-a

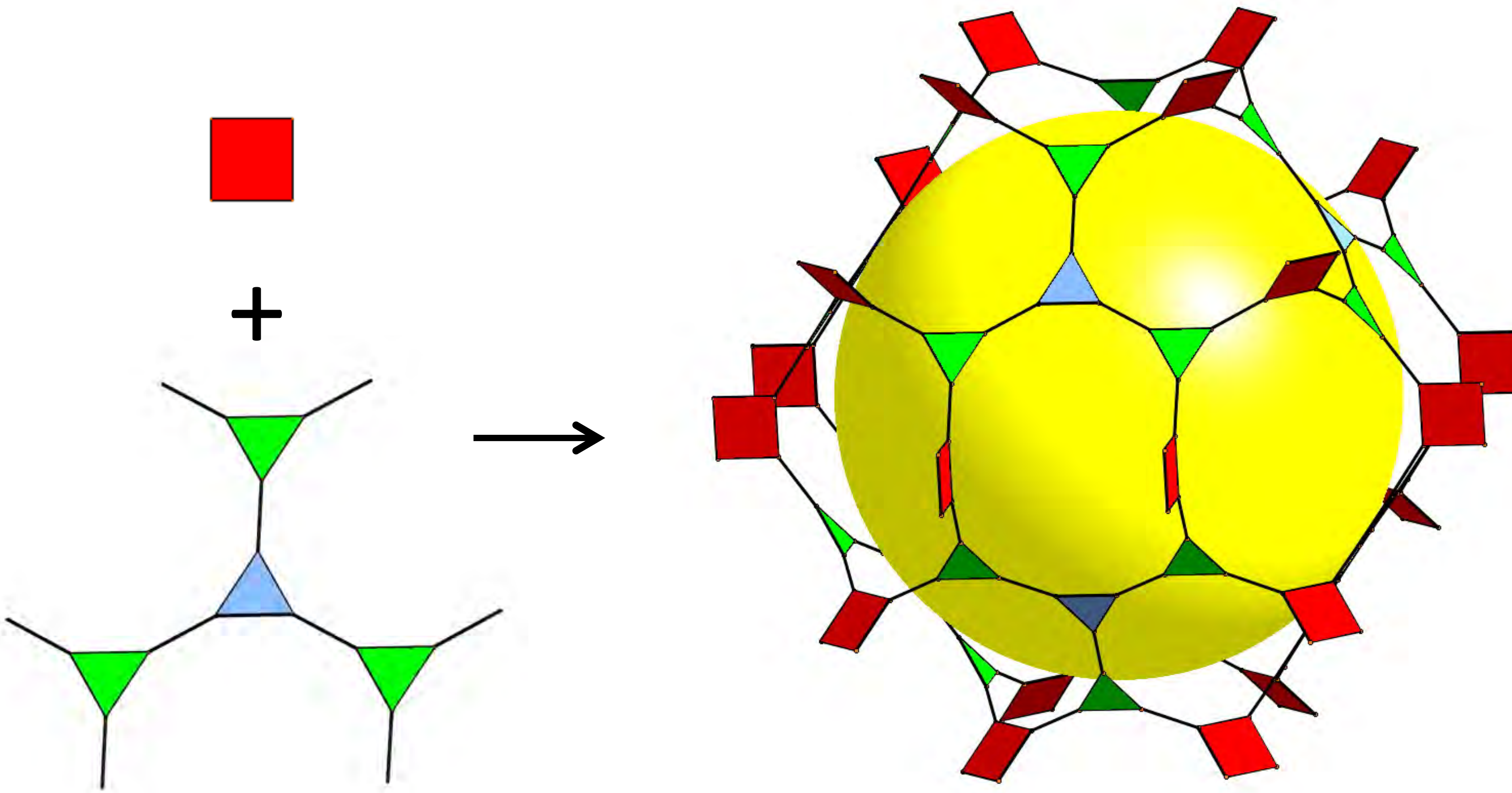
transitivity 3,2



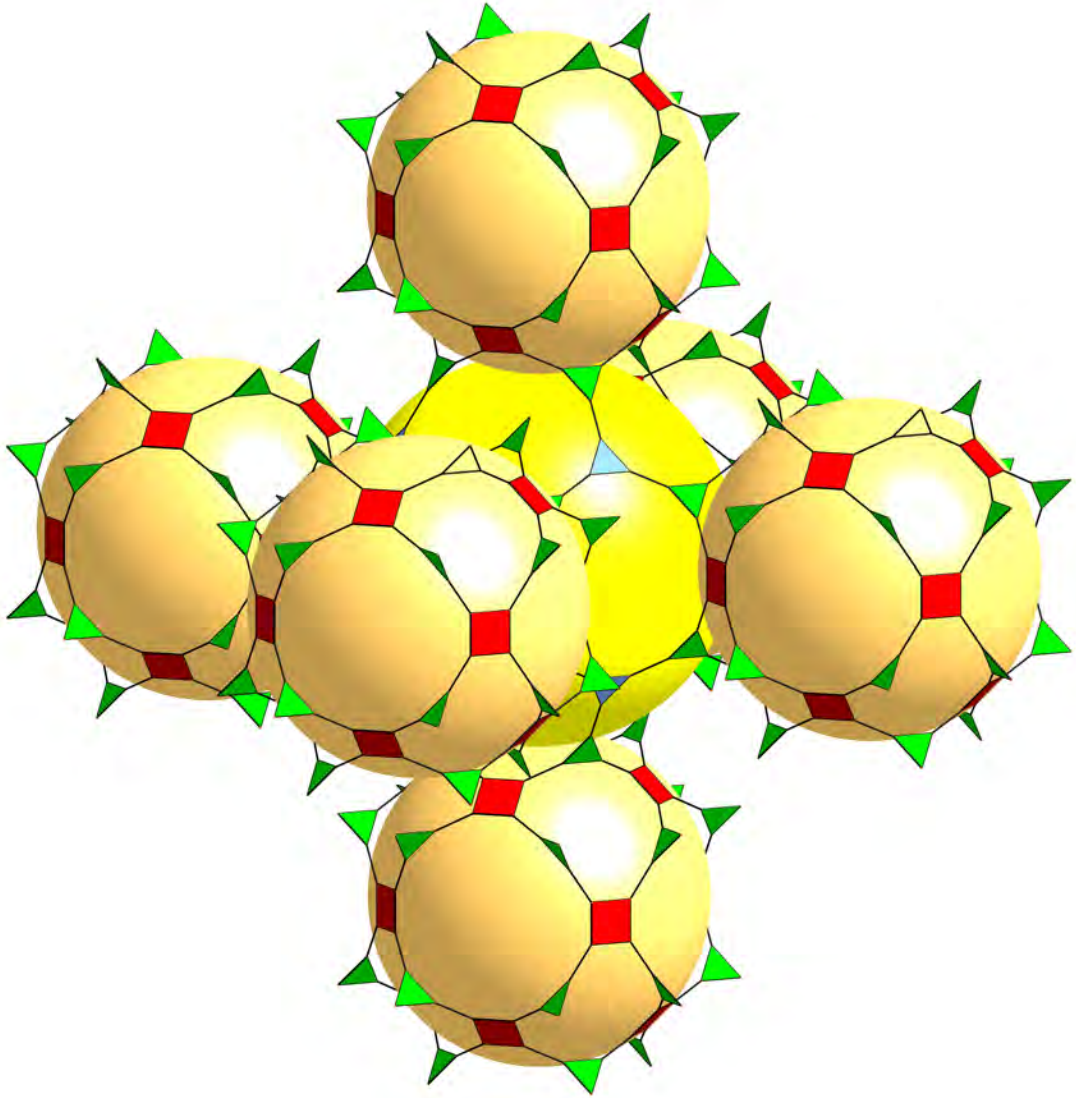
So we start a new chapter:

edge 2-transitive trinodal nets.

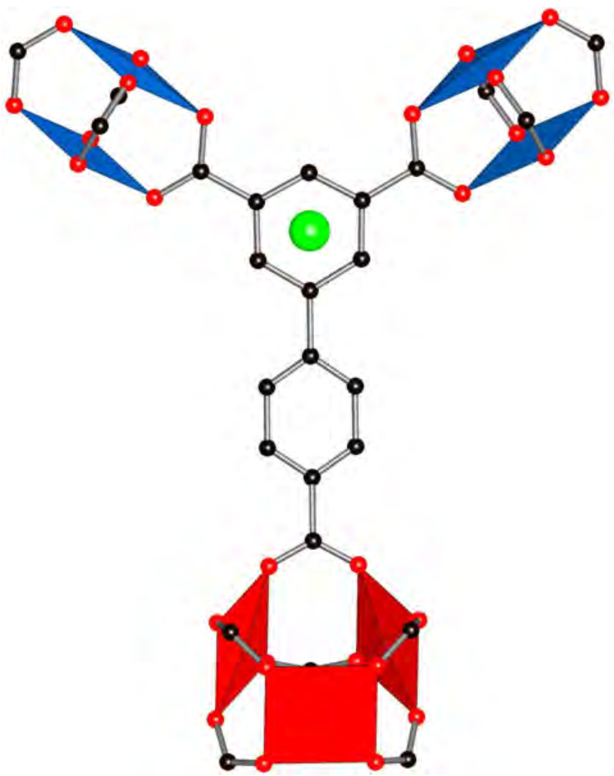
transitivity 3 2 *r s*

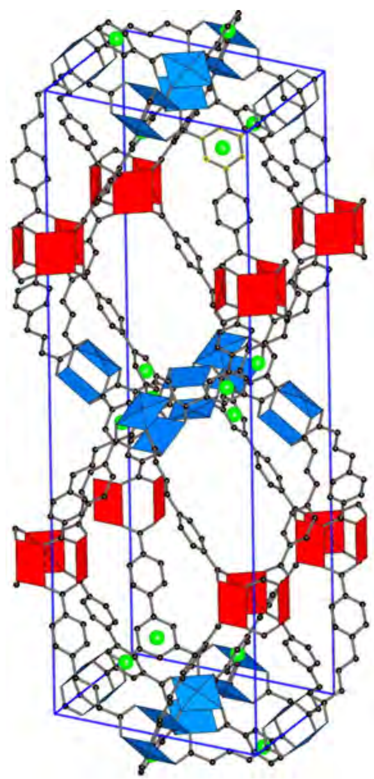


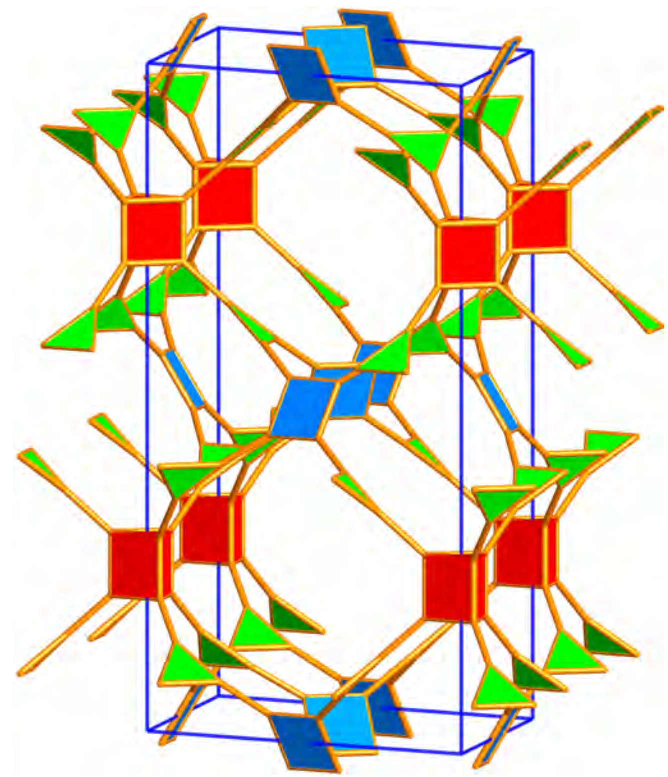
more of the same net. A cubic close packing of $(Cu_2)_{12}$ polyhedra



one more example of 3 vertices, two links, Matzger group



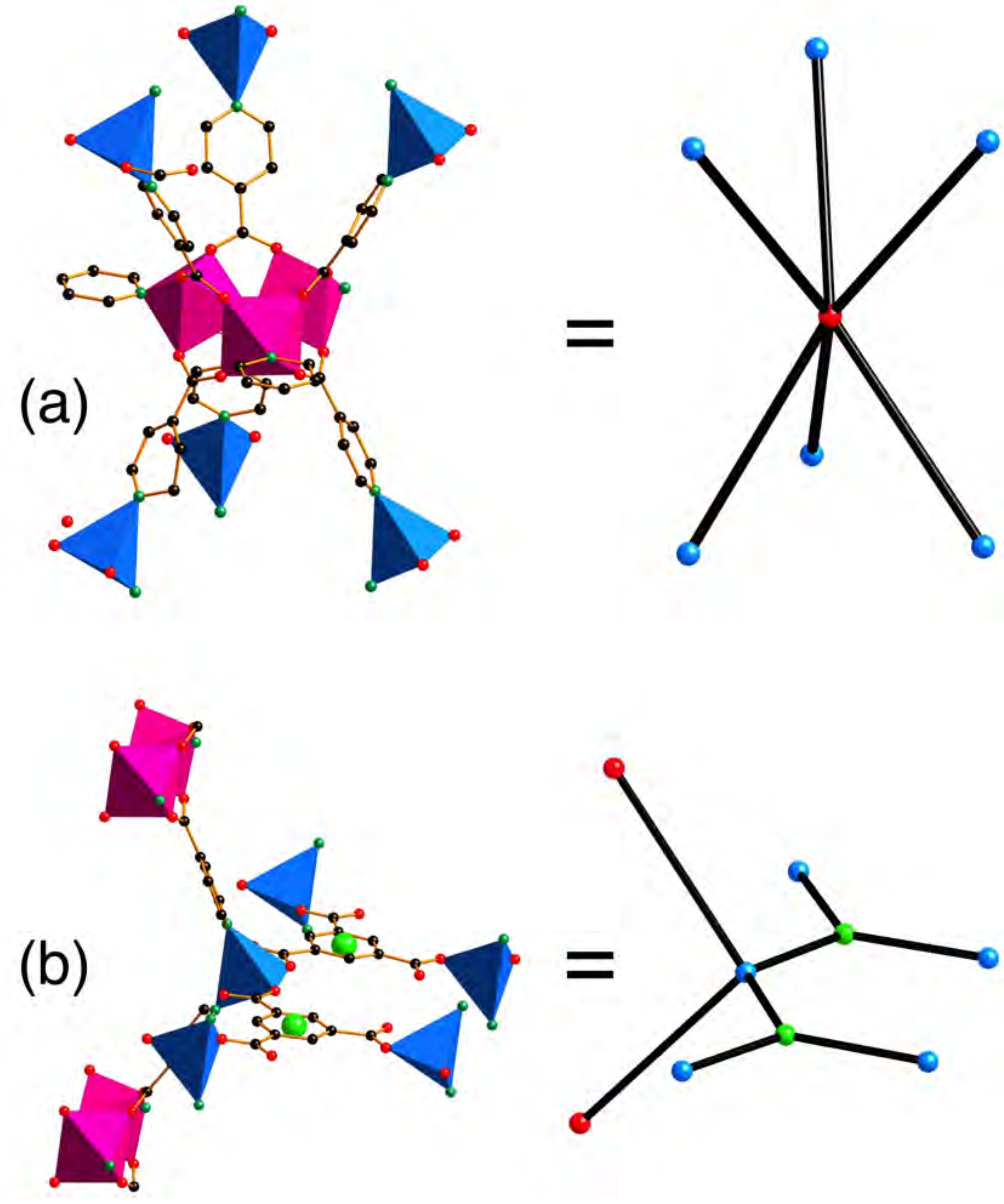


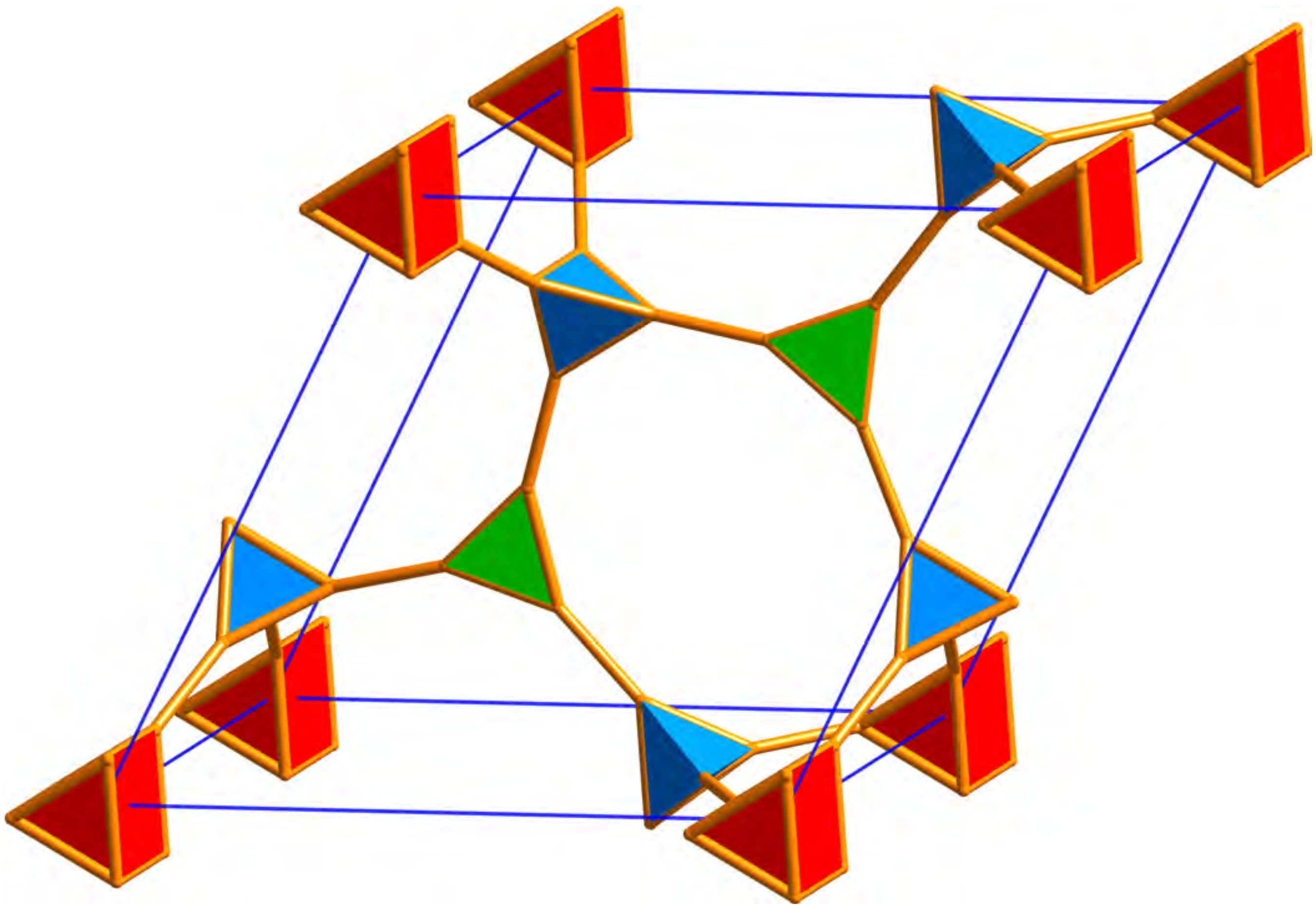


agw-a

transitivity 3,2

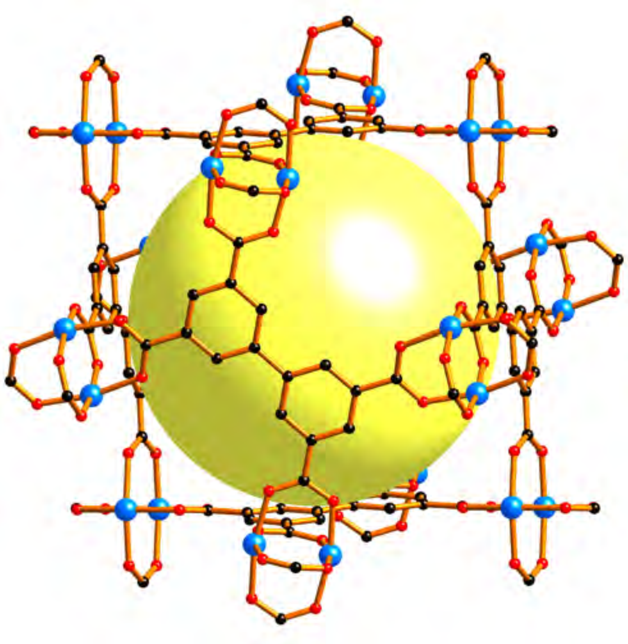
Another MOF with three SBUs from the USF group Eddaoudi-Zaworotko Angew, Chem. Int. Ed. 52, 2902 (2013).



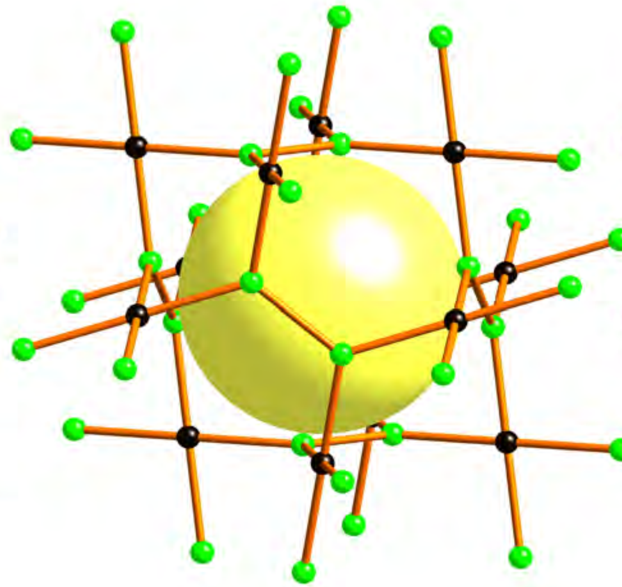


The net **asc-a** transitivity 3,2

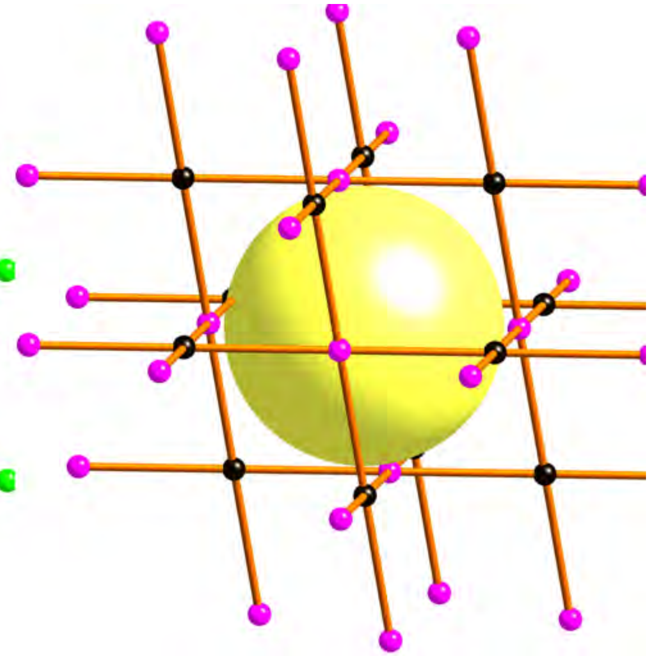
MOF-505. Two ways of deconstructing



structure



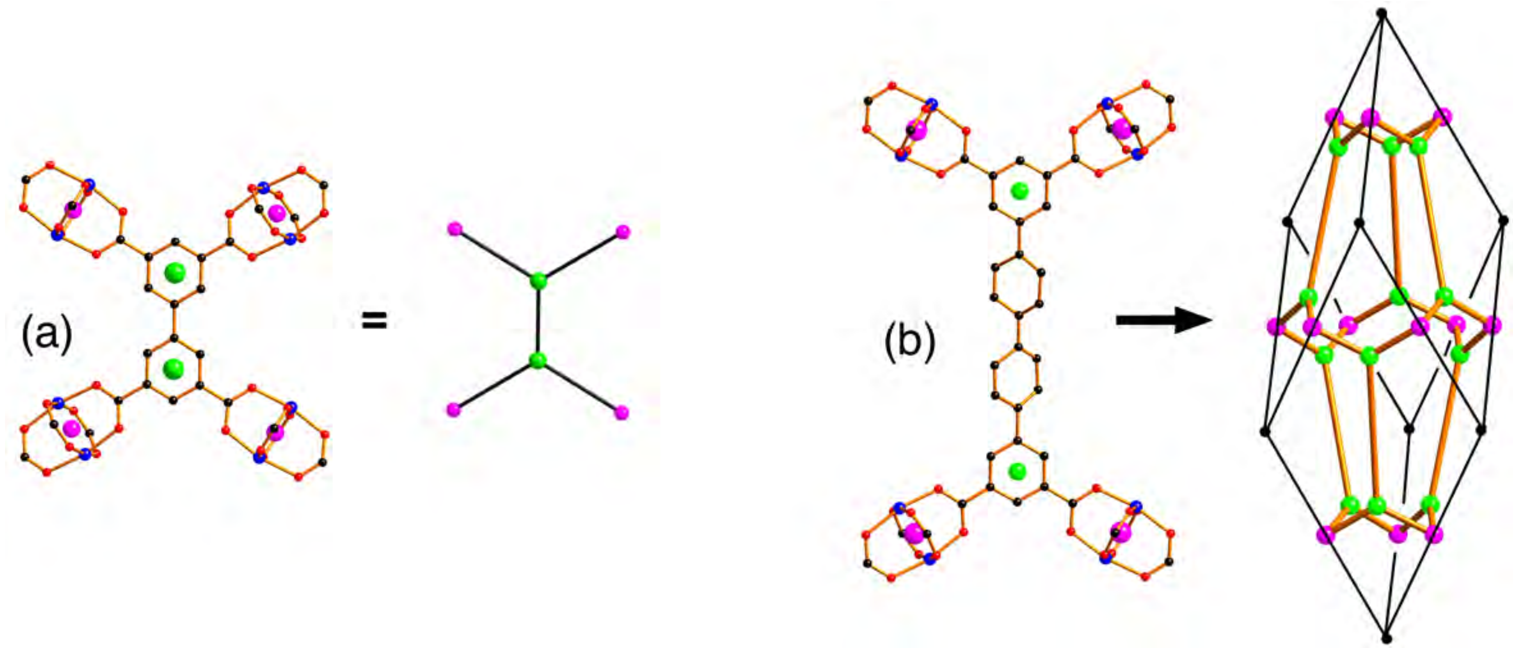
as (3,4)-c net (**fof**)



as 4-c net (**nbo**)

which way is best?

M. Li, D. Li, M. O'K. & O. M. Y., Chem. Rev. 114, 1343 2014)

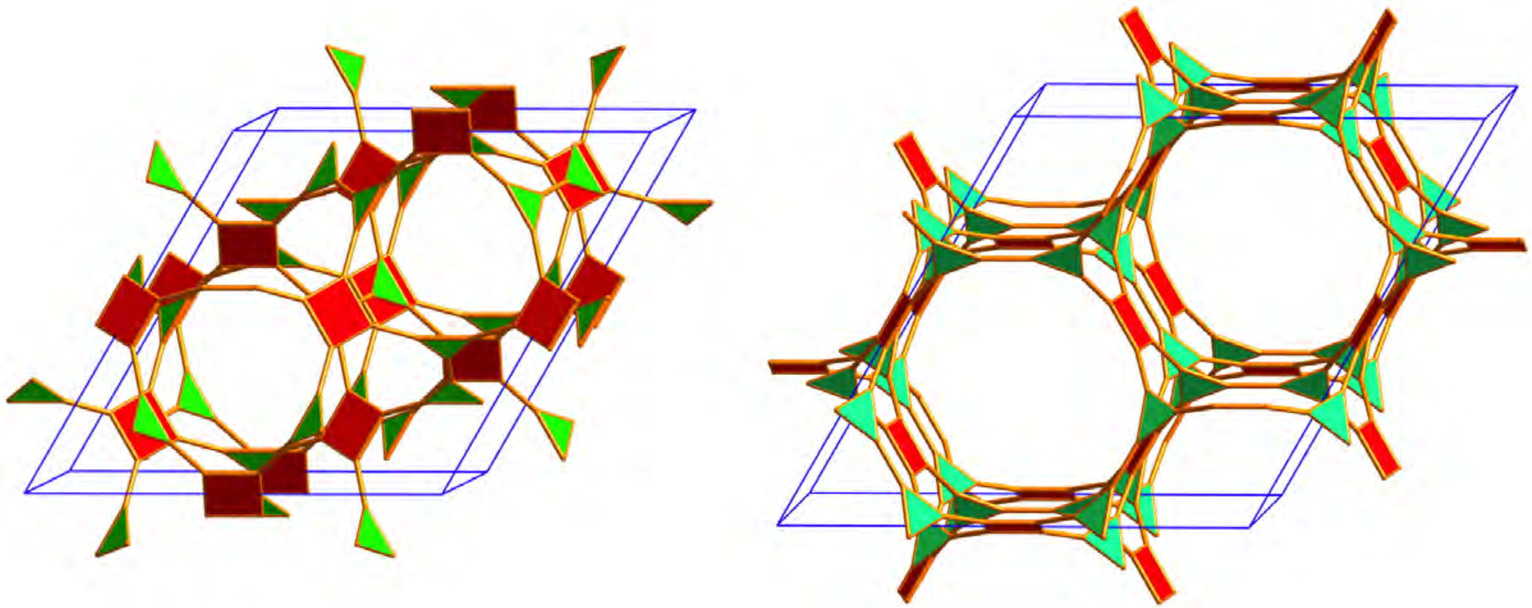


as central link is lengthened,
the structure gets far from cubic!

To retrieve fill topological information it is best to describe the (3,4)-c net derived from the 4-c net **nbo**

The reason for this is that there can be many derived nets....

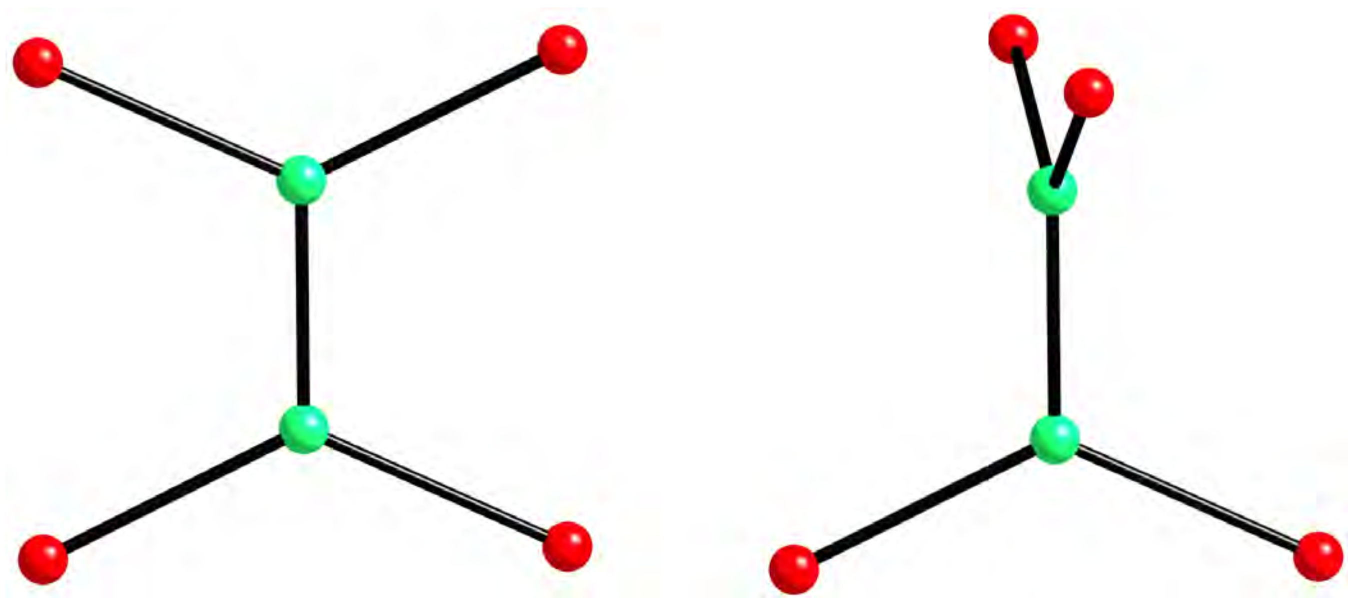
There are two (3,4)-c nets derived from **nbo** with the same symmetry *R*-3*m* and transitivity 2,2



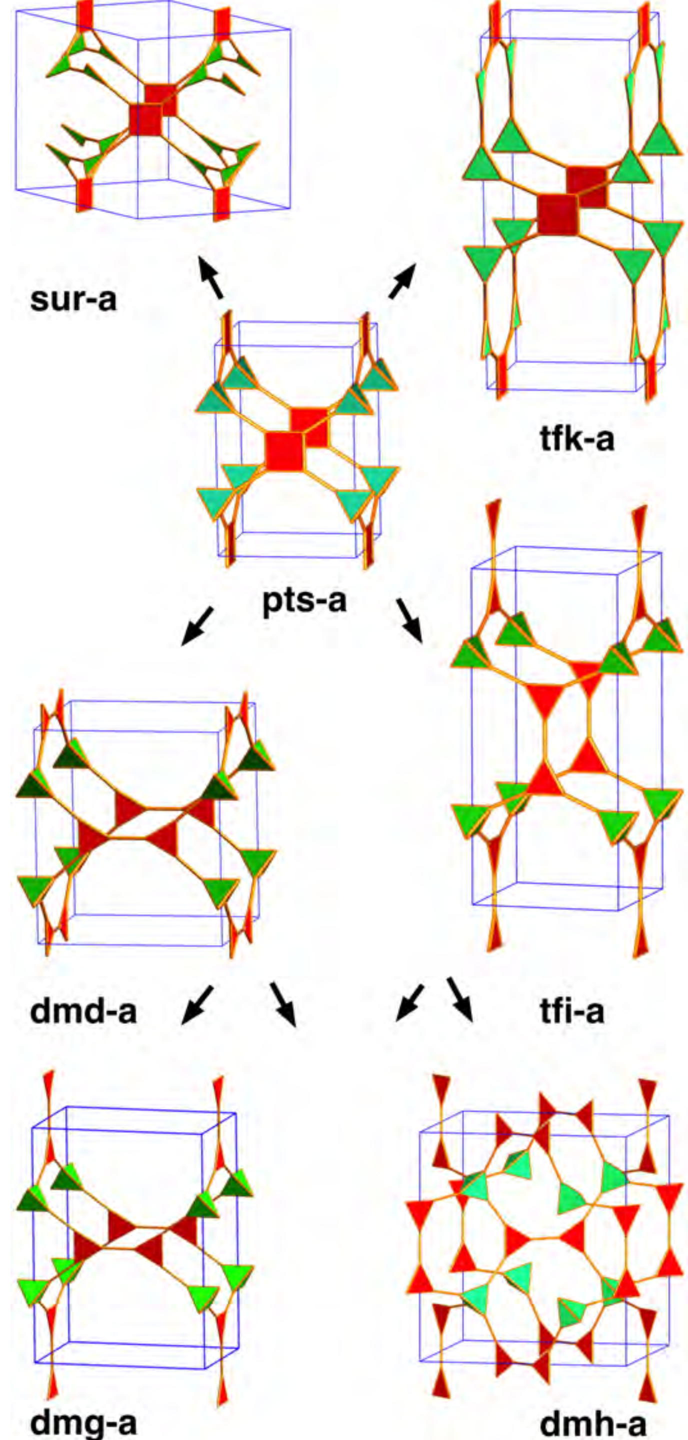
(a) **fof-a** (b) **fog-a**

Both are observed in real MOFs

basic net (4,*n*)-c, **derived net** (3,*n*)-c
replace square or tetrahedral node



(3,4)-c nets derived from **pts**

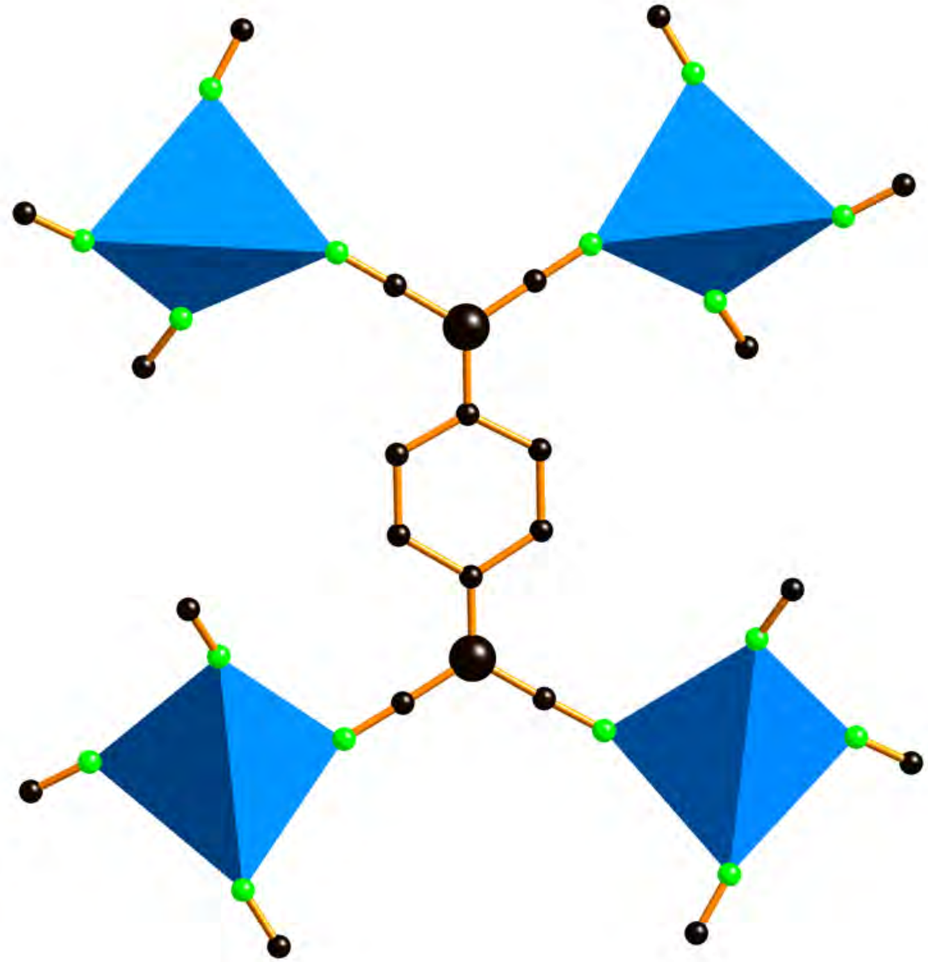


MTCNQ

M = Cu, Ag

->

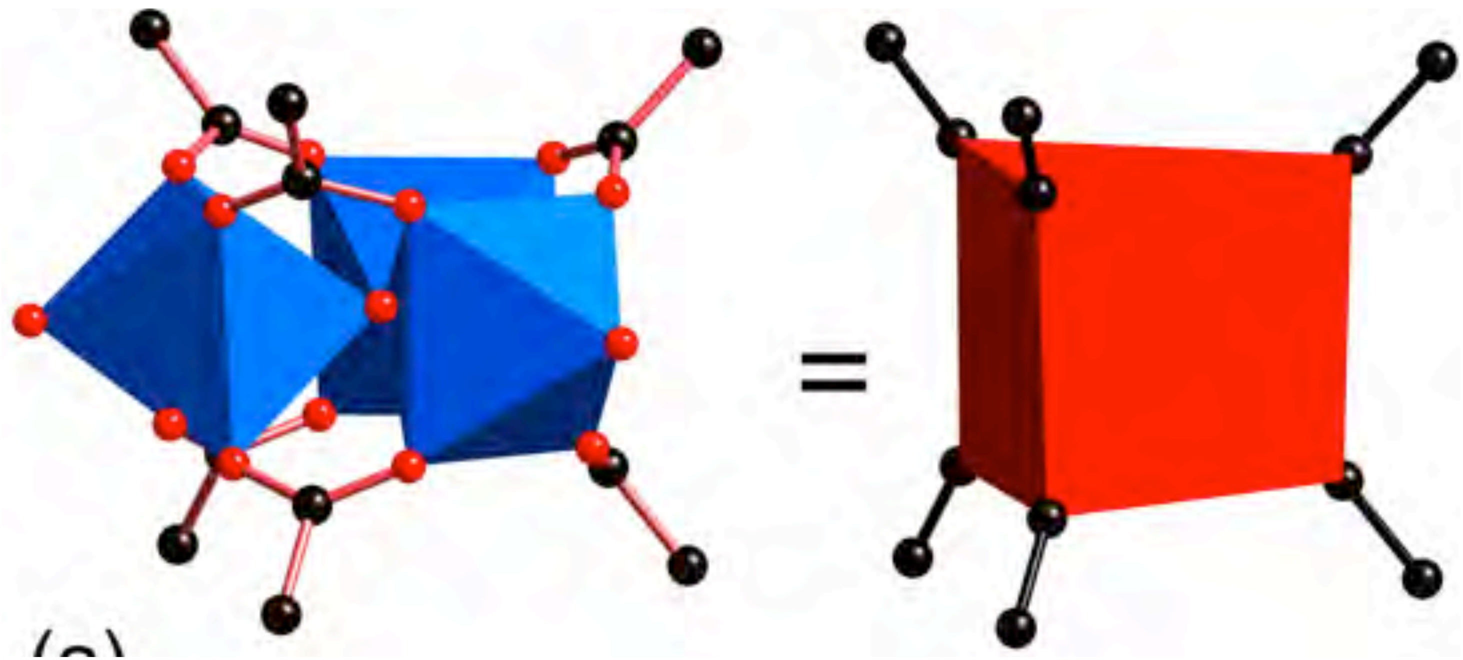
pts-derived nets



basic net	transitivity	coord	replace	derived nets	transitivity
nbo	1 1	4	square	†**fof**, †**fog**,†**tfb**	2 2
lvt	1 1	4	square	†**lil**, †**lim**	2 2
rhr	1 1	4	square	**ucp**	2 2
cds	1 2	4	square	†**gwg**	2 3
dia	1 1	4	tetrahedron	**tfa**	2 2
qtz	1 1	4	tetrahedron	**tfq**	2 2
sod	1 1	4	tetrahedron	**xbl**	2 2
lon	1 2	4	tetrahedron	†**zyl**	3 4
pts	2 1	4 4	square	†**dmd**, †**tfi**	2 2
			square	†**dmg**, †**dmh**	3 3, 3 4
			tetrahedron	†**sur**, **tfk**	2 2
pth	2 1	4 4	square	**hst**	2 2
			tetrahedron	†**phw**, **phx**	2 2
ssb	2 1	4 4	square 1	†**stu**, **stw**	2 2
			square 2	**stj**, †**stx**	2 2
ssa	2 1	4 4	square 1	†**sty**	2 2
stp	2 1	6 4	square	**ttp**, **ttx**	2 2
soc	2 1	6 4	square	†**edq**, **cdj**	2 2
scu	2 1	8 4	square	**tty**	2 2
csq	2 1	8 4	square	†**xly**, **xlz**	2 2
ftw	2 1	12 4	square	**ttv**	2 2
iac	2 1	6 4	tetrahedron	†**act**	2 2
toc	2 1	6 4	tetrahedron	**xab**	2 2
cor	2 2	6 4	tetrahedron	†**ttu**	2 3

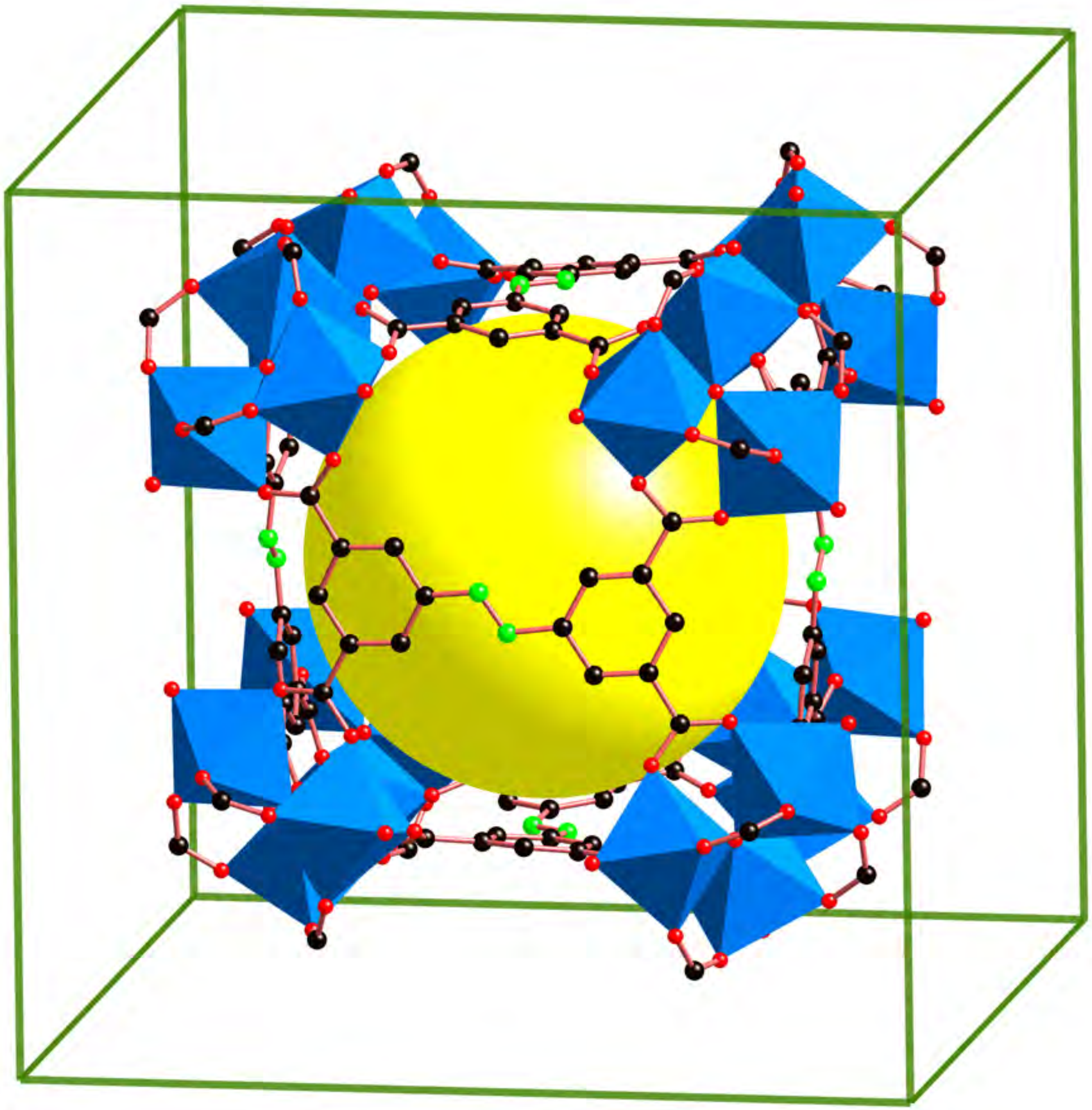
table from Li, M.; Li, D. O'Keeffe, M, Yaghi, O. m. *Chem. Rev.* b2014**, *114*,** 1343

The strange story of Eddaoudi's queer structure



First a reminder of a common SBU
with trigonal prismatic shape

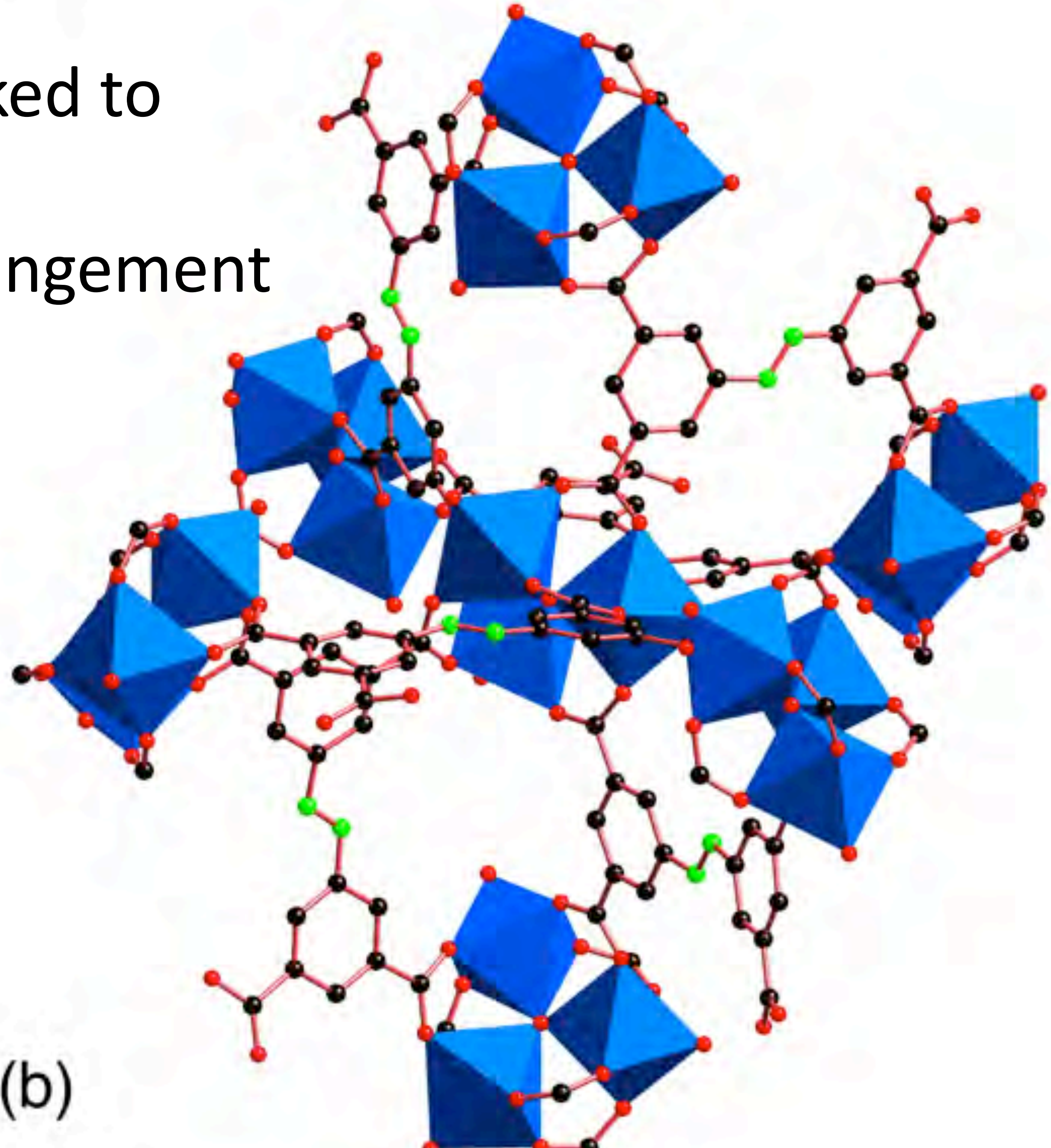
linked by a planar tetratopic linker -> a cubic structure!



(a)

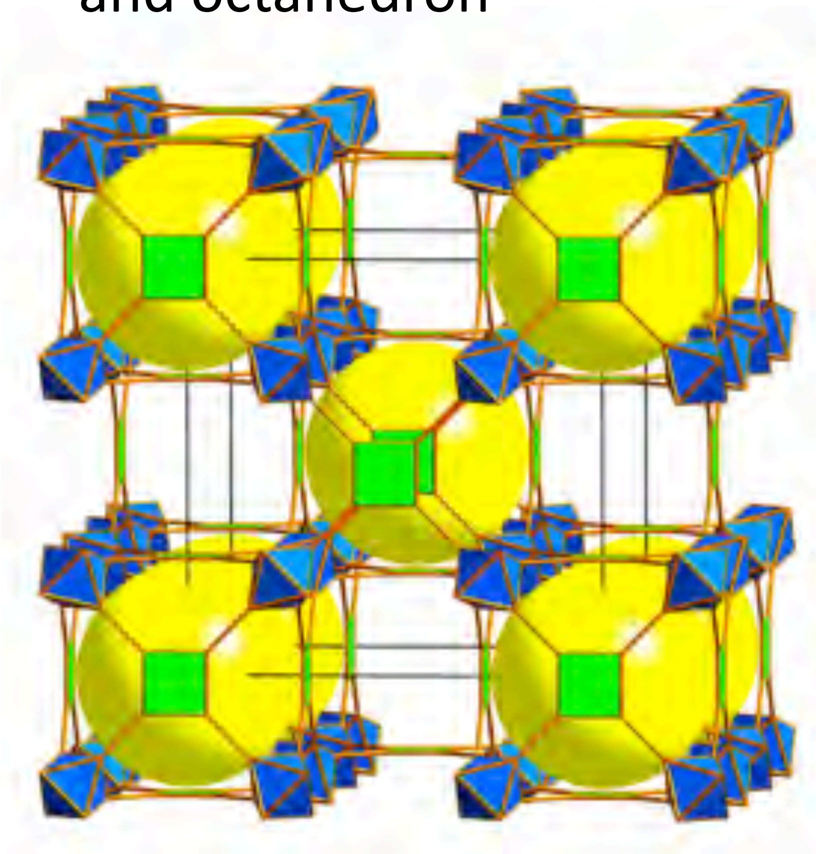
Each SBU is linked to six others in an octahedral arrangement

The basic net is (4,6)-c **soc** for linking square and octahedron

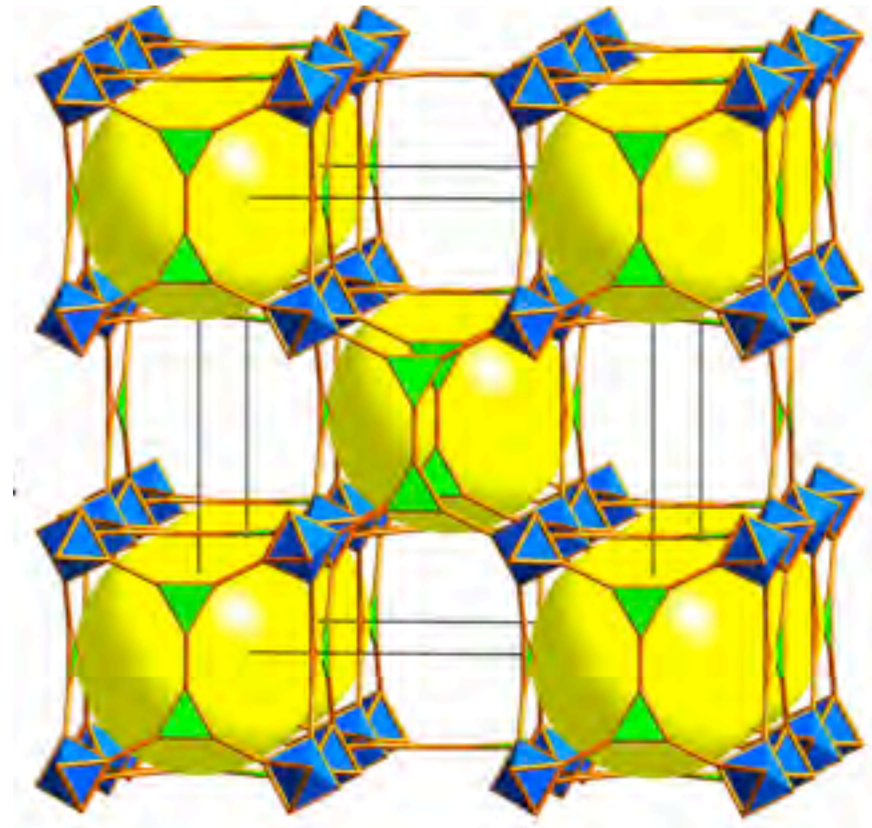


(b)

basic net linked square
and octahedron



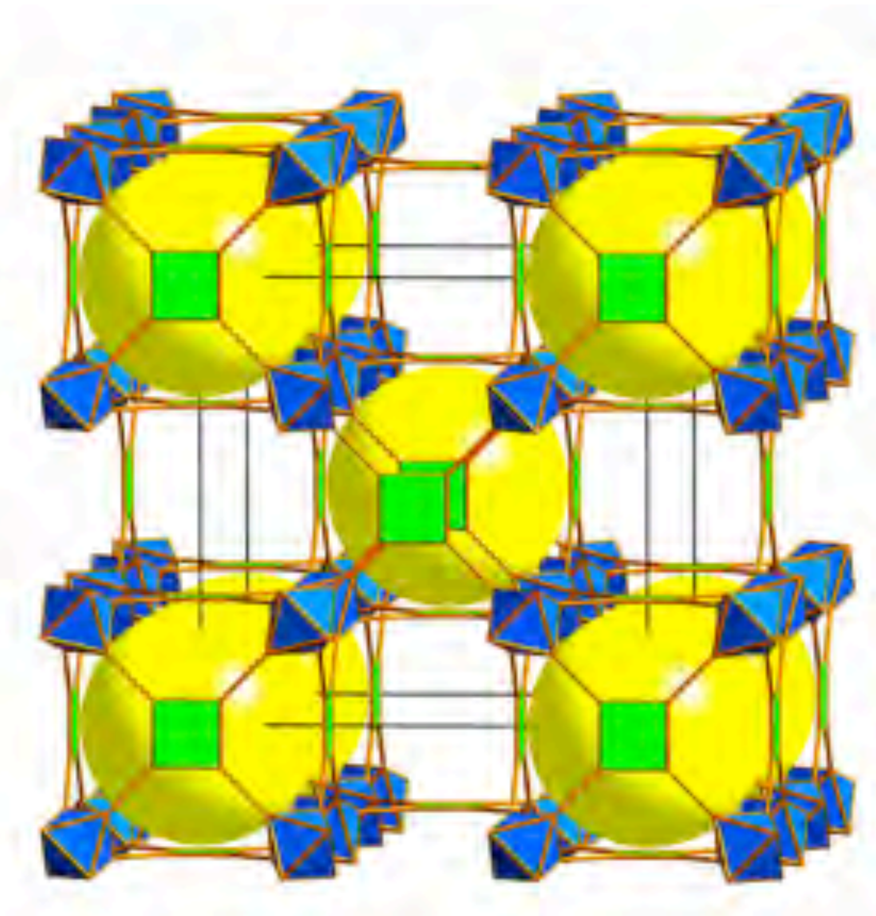
derived net



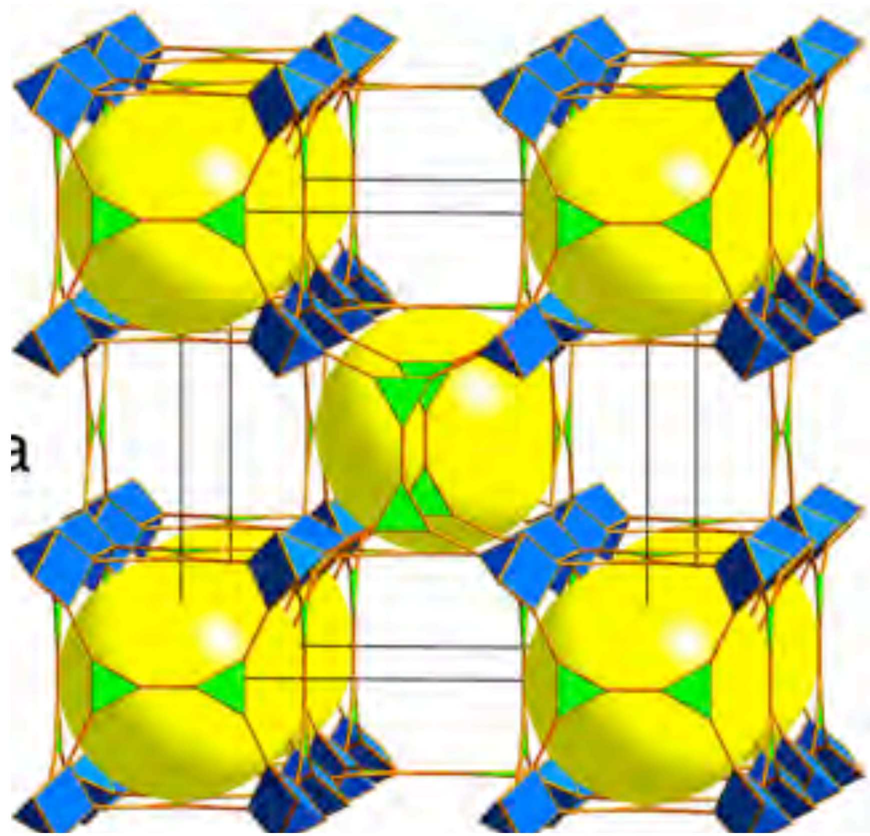
soc-a

cdj-a

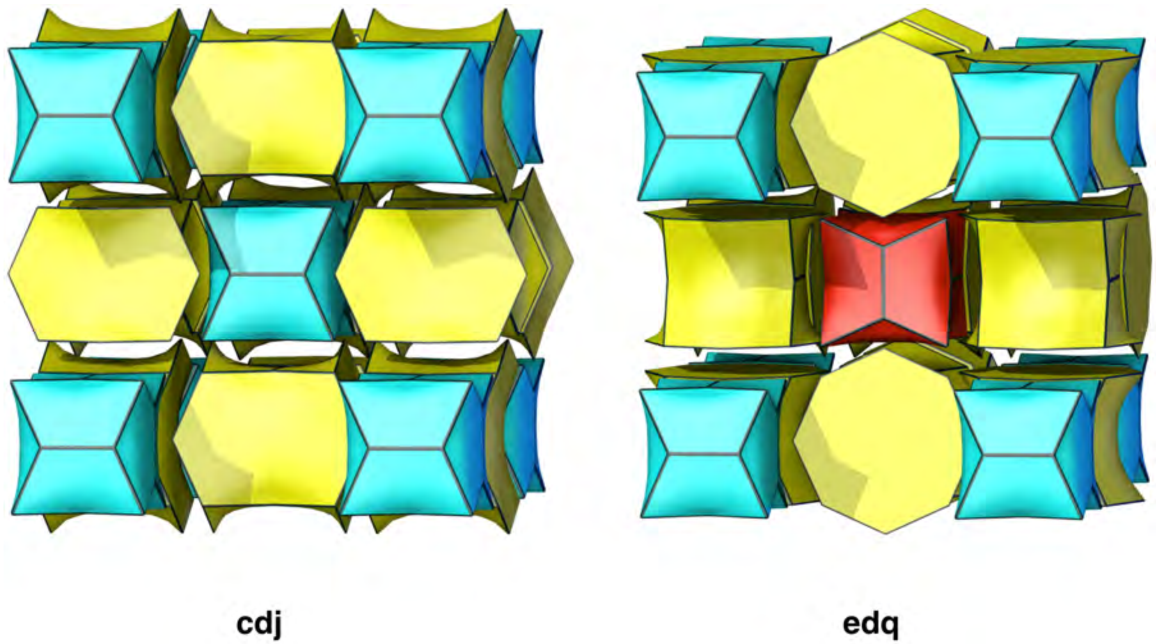
look the octahedra have
morphed into trigonal prisms!



soc-a

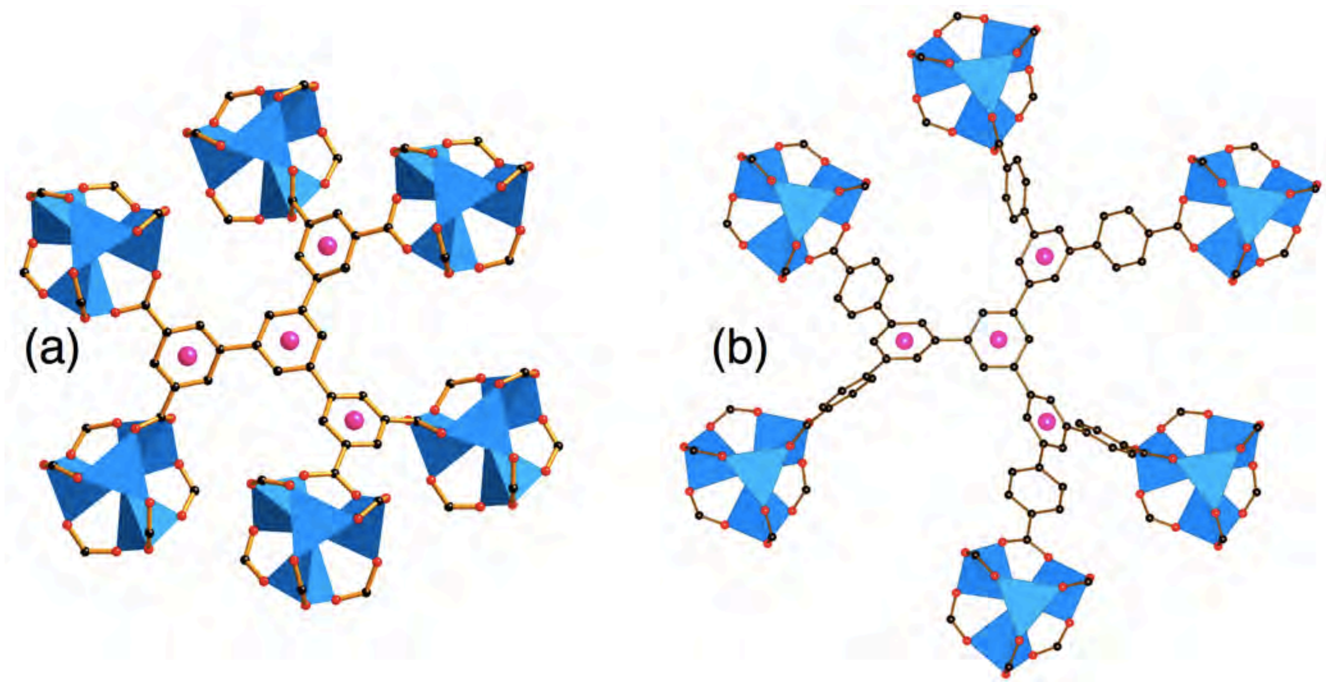


edq-a

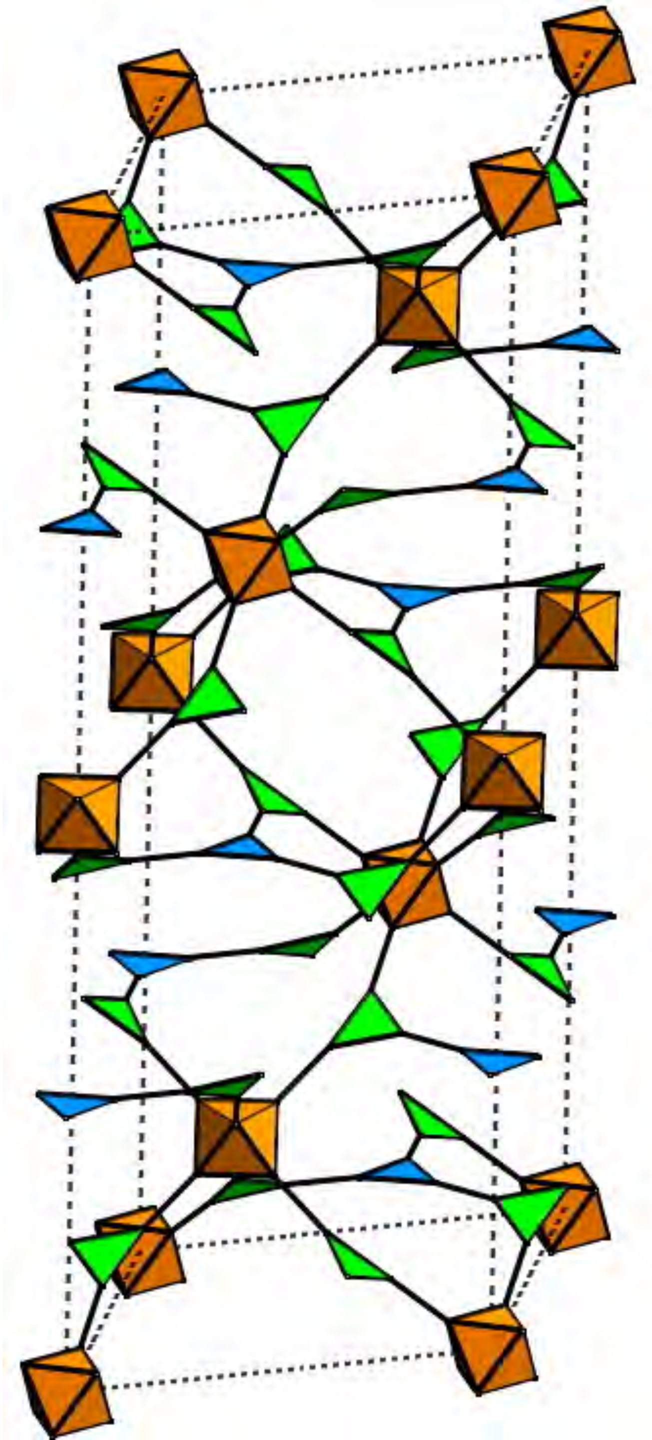


These two nets have the same vertex symbol and coordination sequence. But you can see they are different. (Different symmetry!)

hexatopic linker + octahedral SBU ->
another net with three vertices and two edges

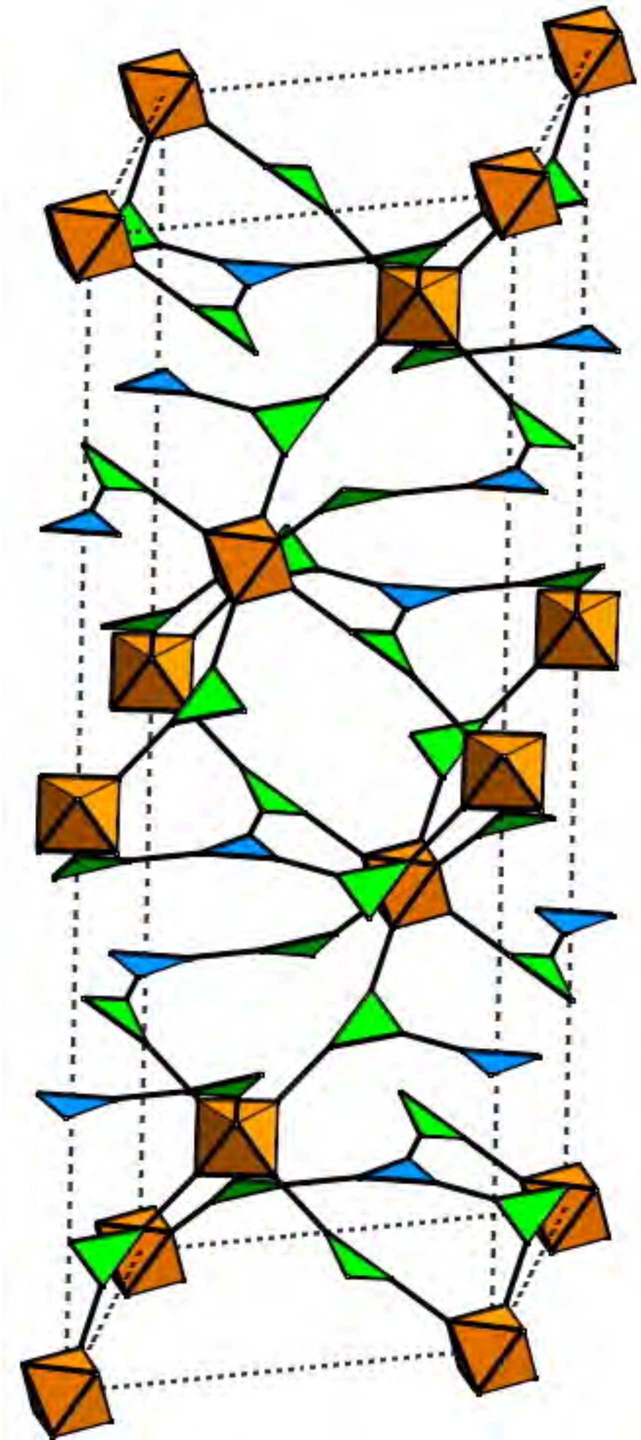


Banglin Chen group
Cryst. Growth Des. 10, 2775 (2010)



net is **zxc**

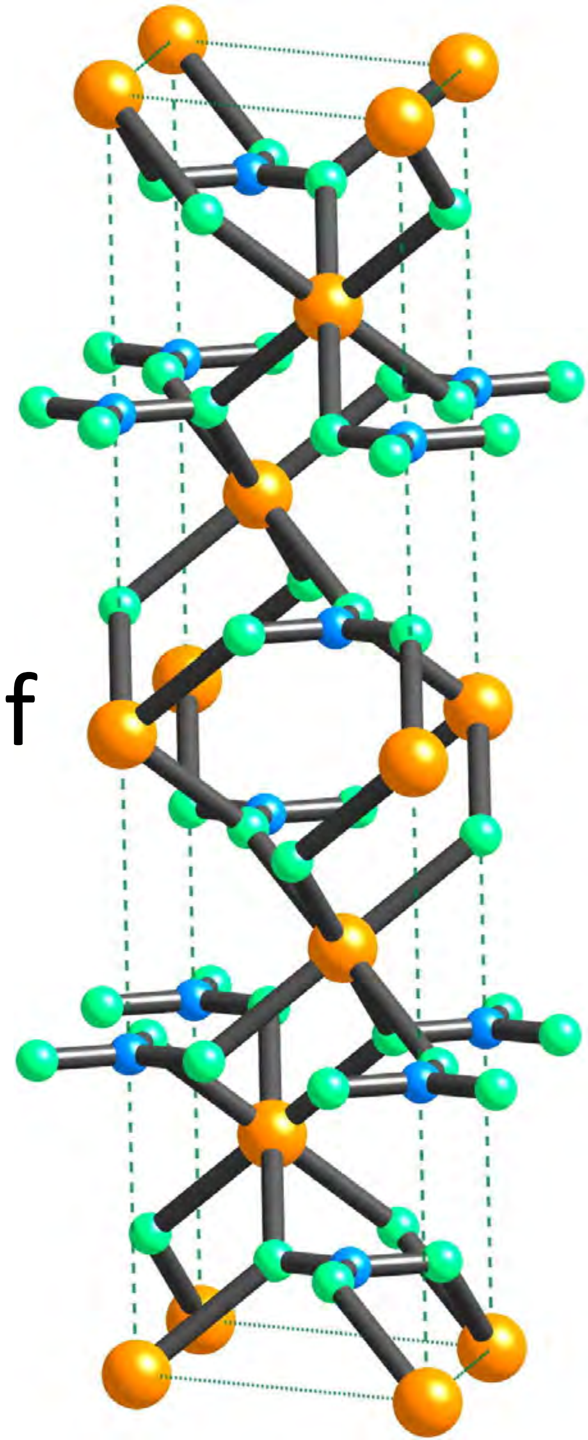
<-

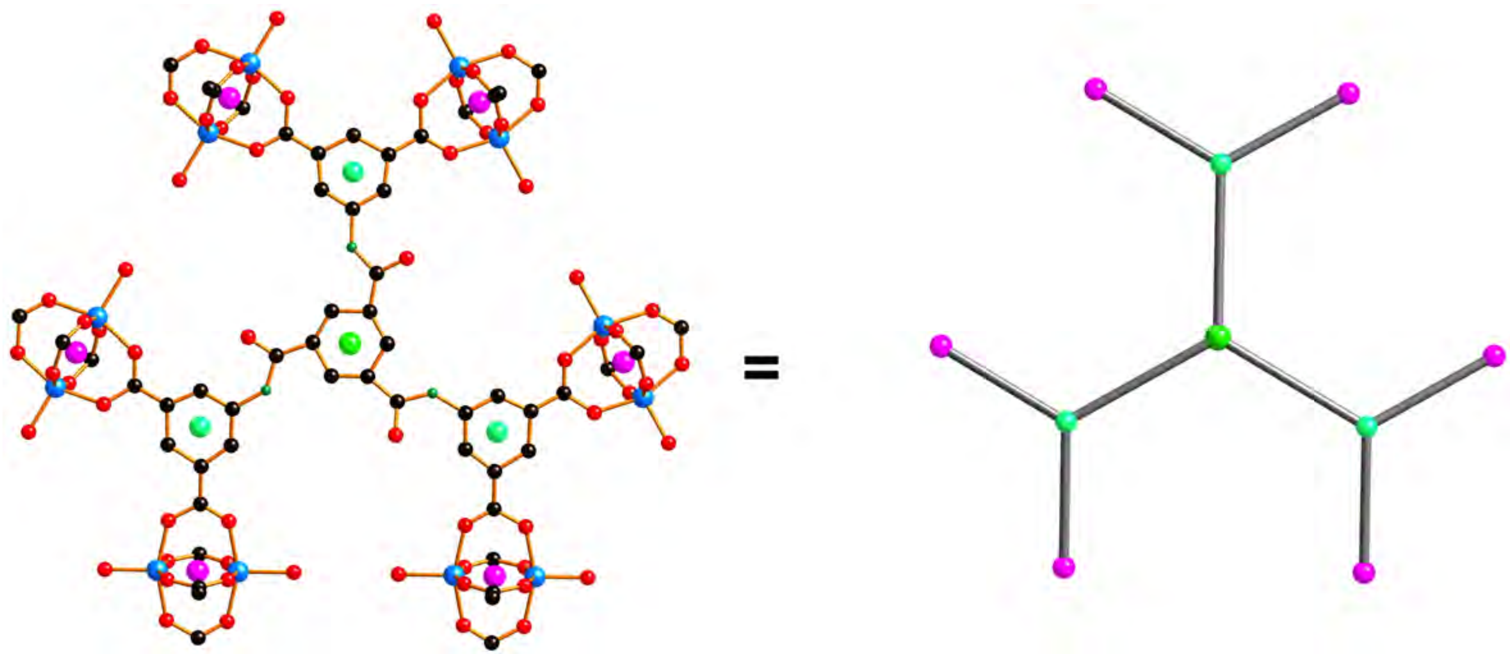


net is **zxc**

<-

structure of $CaCO_3$! ->

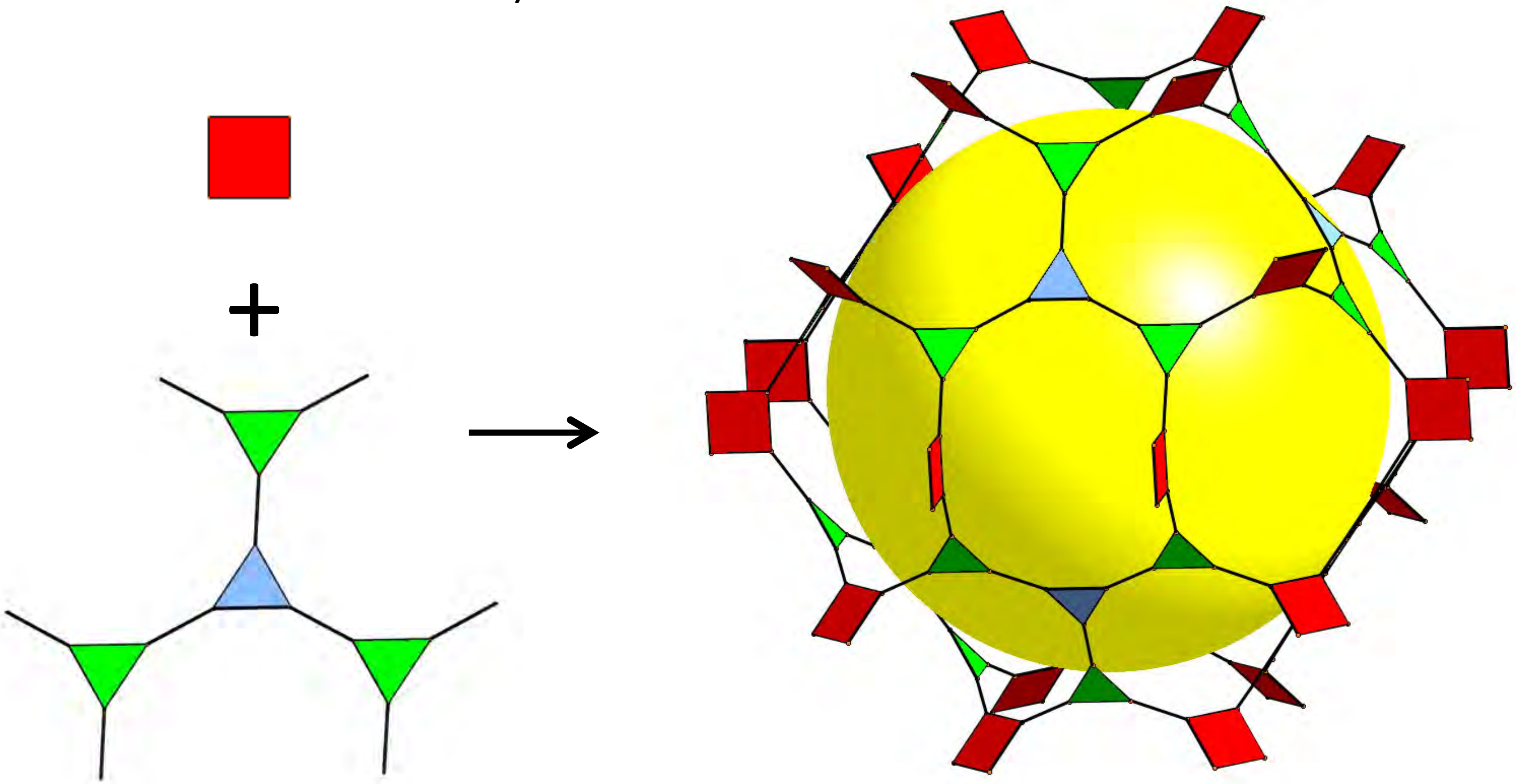




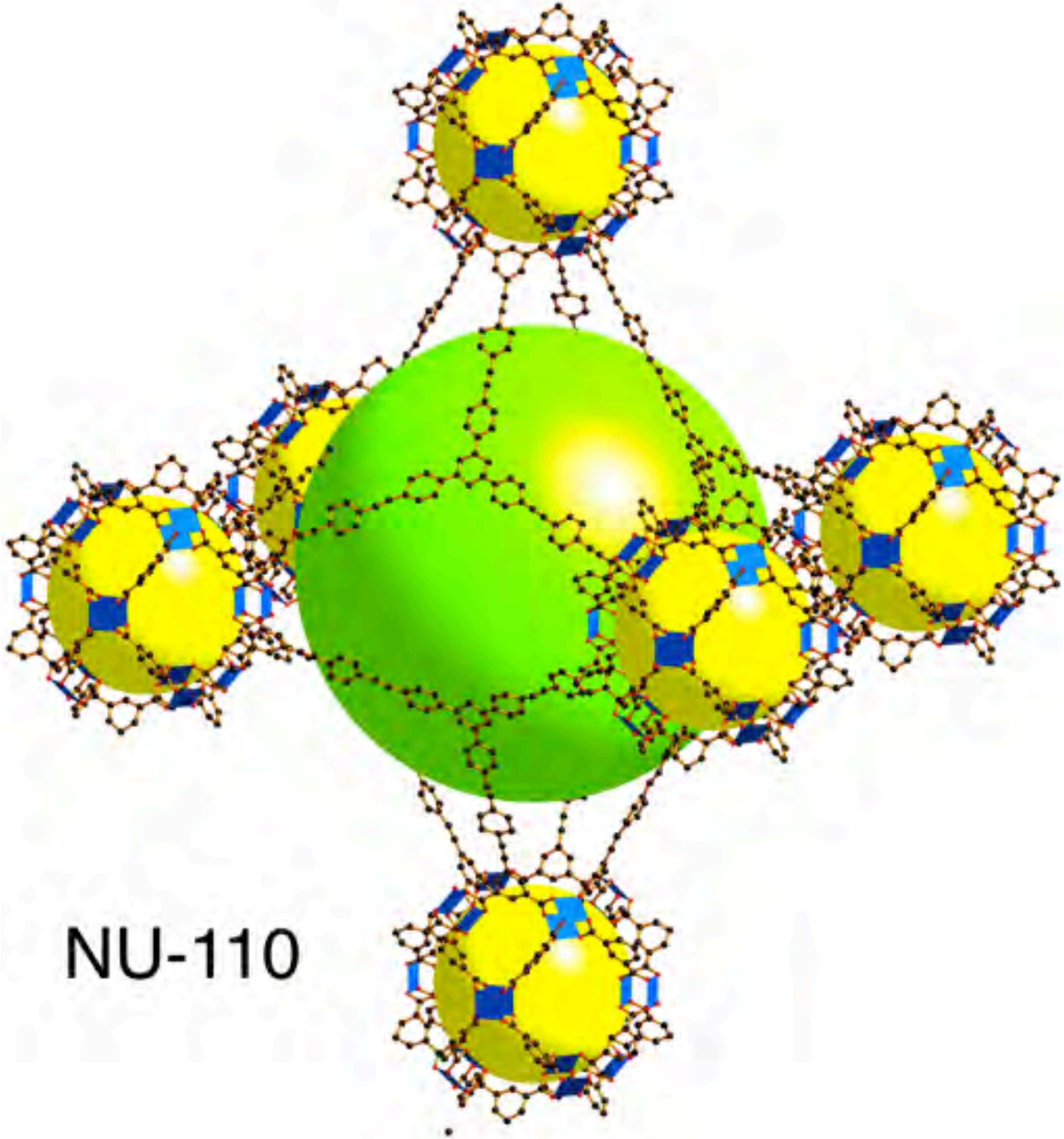
Planar hexatopic linker joined to paddlewheels
-> (3,4)-c net not derived from a known (4,6)-c net

Net is **ntt** again and may authors use (3,24)-c description edge 2-transitive trinodal nets.

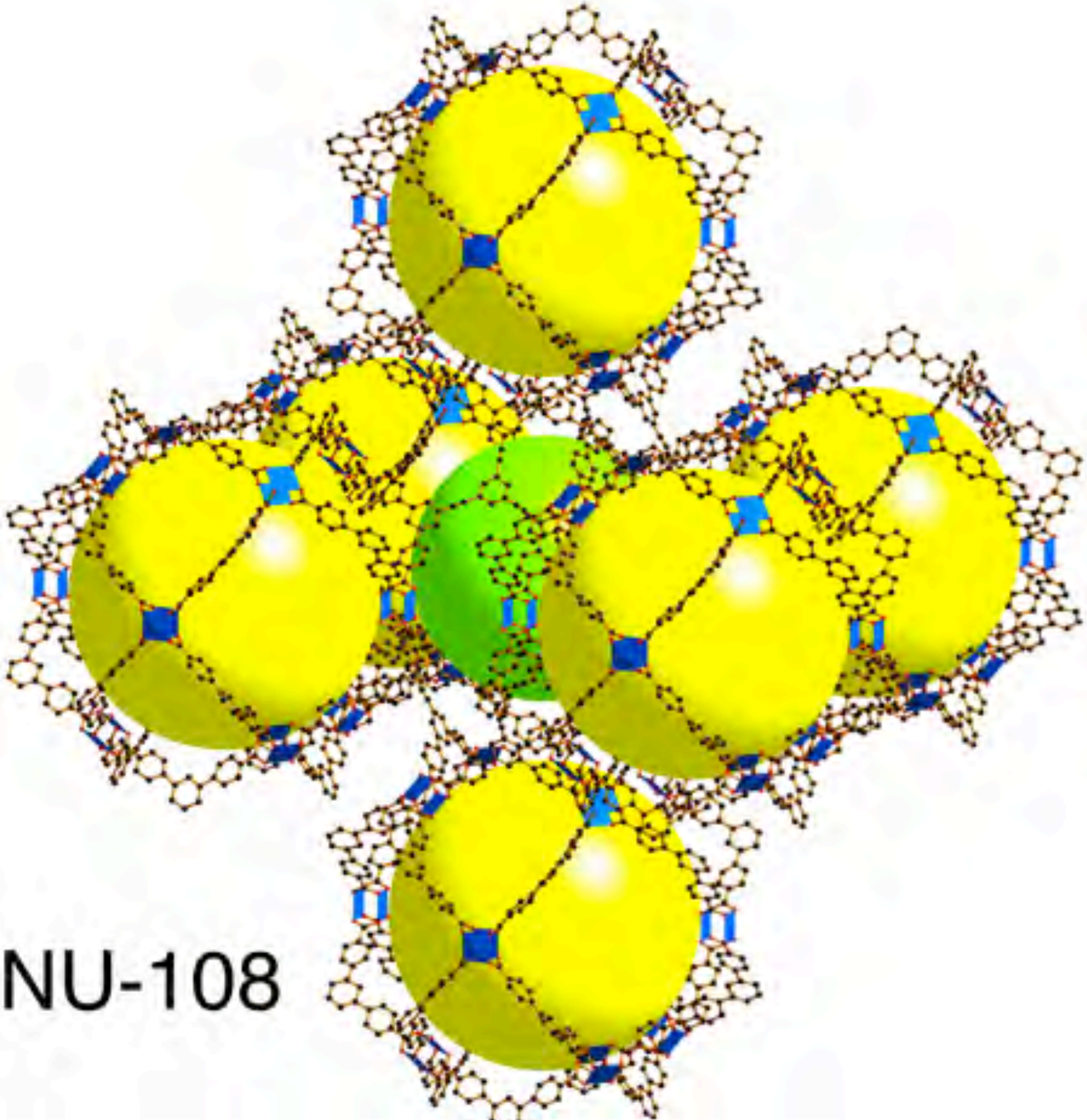
transitivity 3 2 *r s*



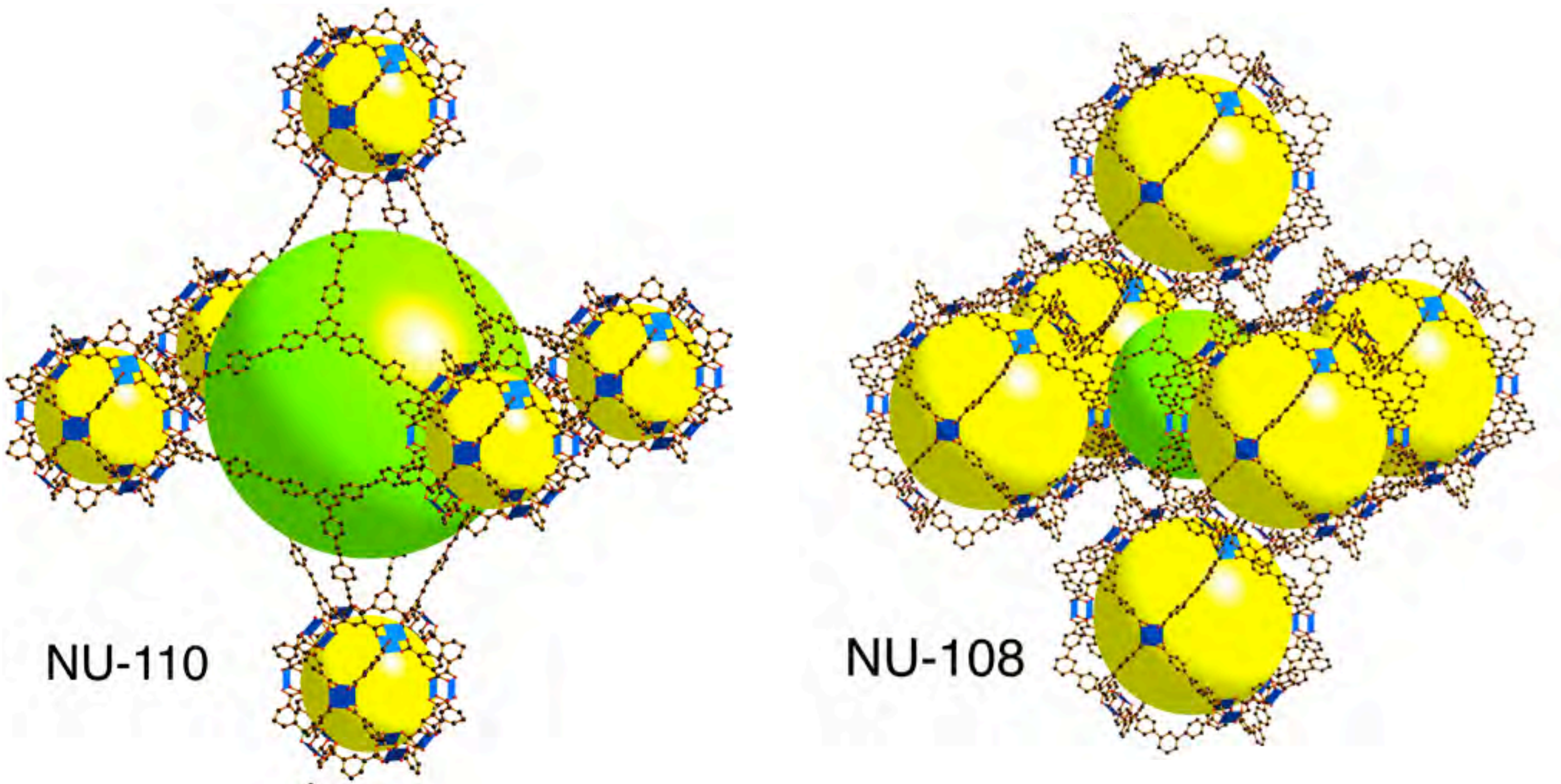
We want to use the description with two kinds of link



NU-110



NU-108

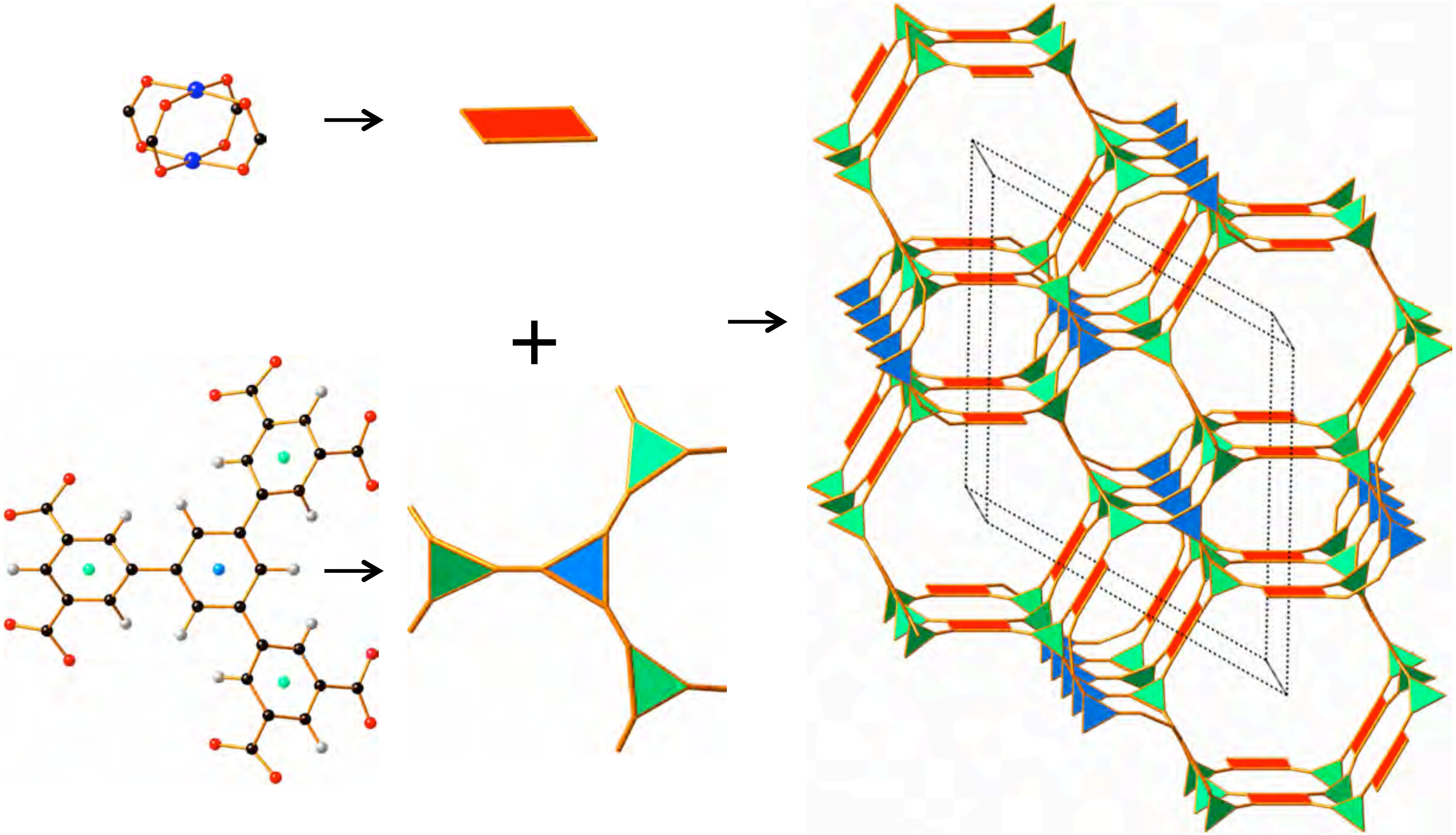


J. T. Hupp group.

Cryst. Growth Des. ***2012***, *12*, 1075

JACS **2012**, *134*, 15046

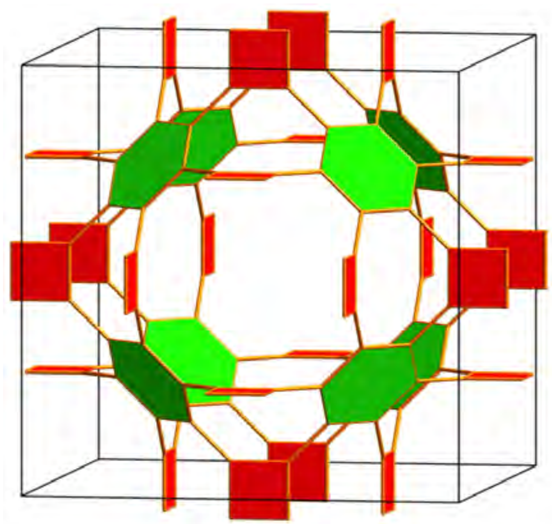
But a twist… Now the linker isn't planar.



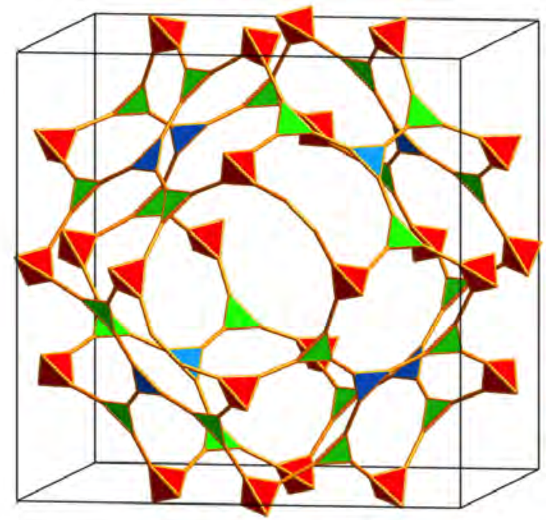
Banglin Chen group, Angew. Chem. 50, 3178 (2011)

But another net (**zyg**) with three vertices and two edges
i.e. minimal transitivity 3 2

Suppose you are designing a MOF with a square metal SBU and a planar hexatopic linker. The edge-transitive net for linking square and hexagon is **she**. But surprise! - the square morphs into a tetrahedron.

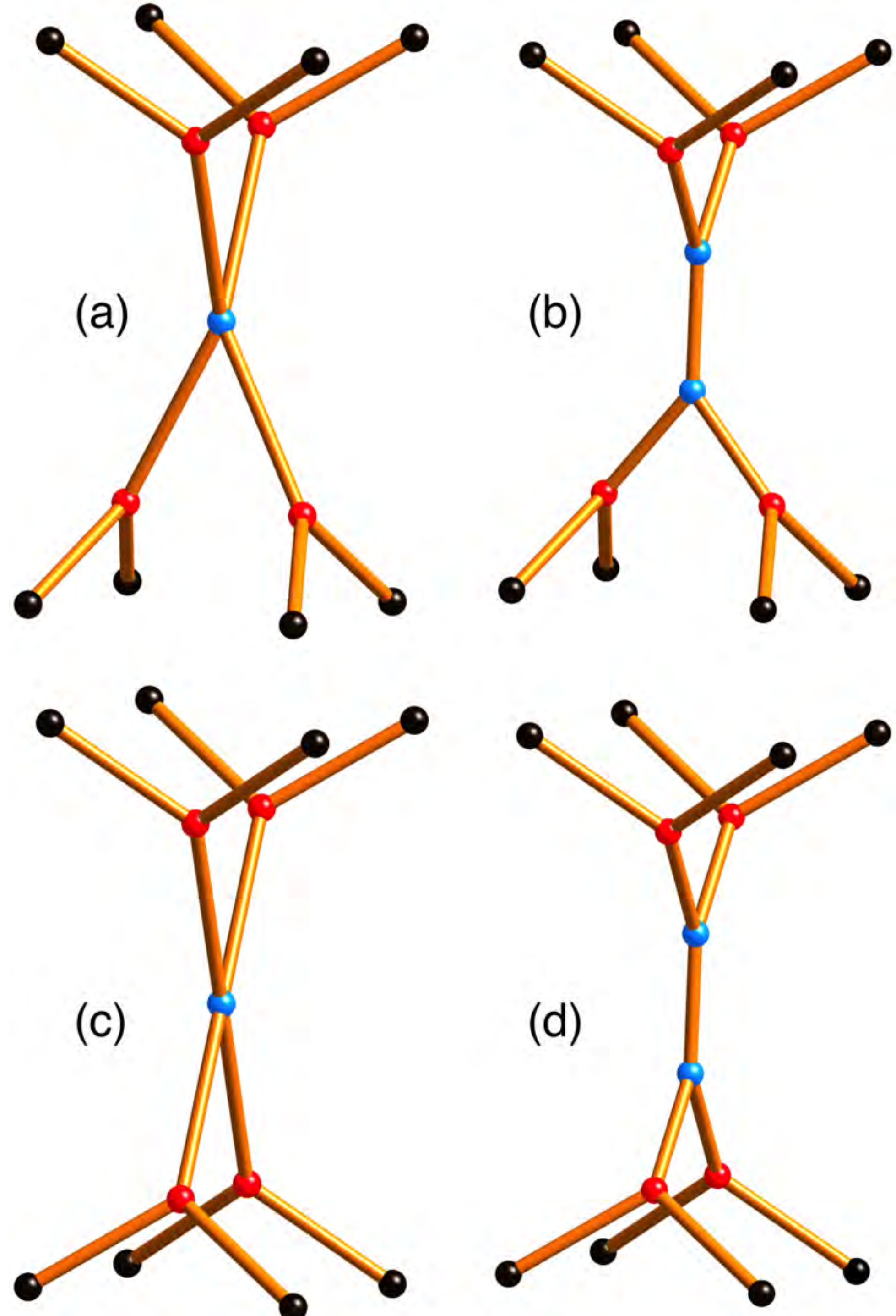


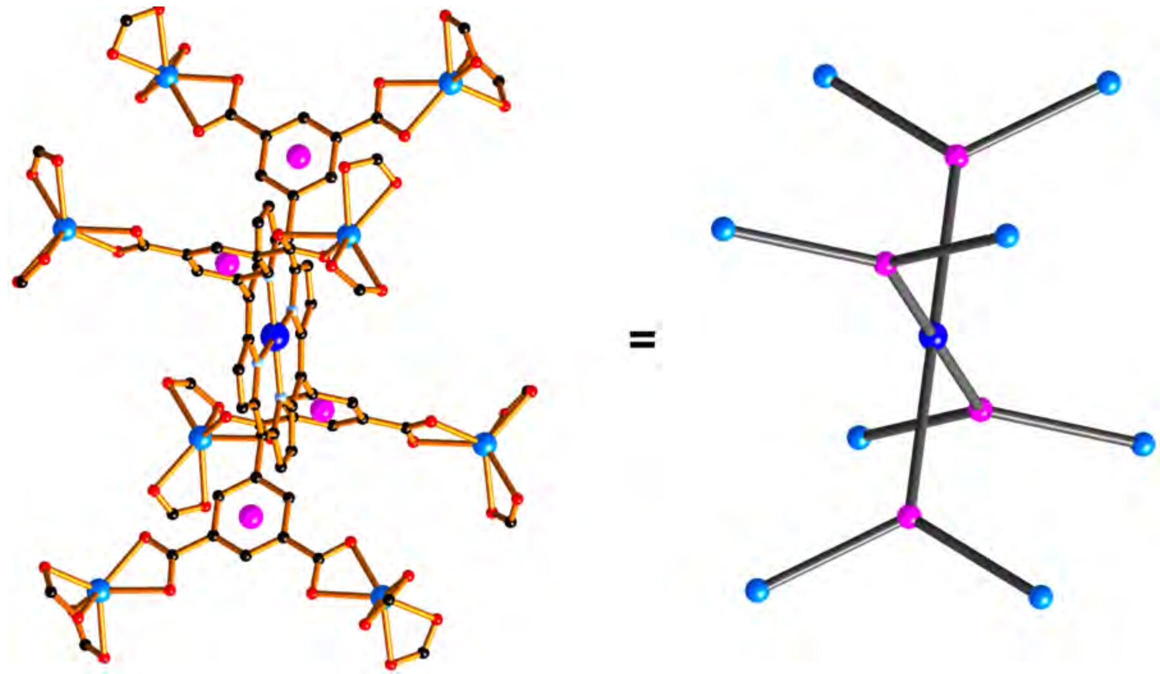
she-a



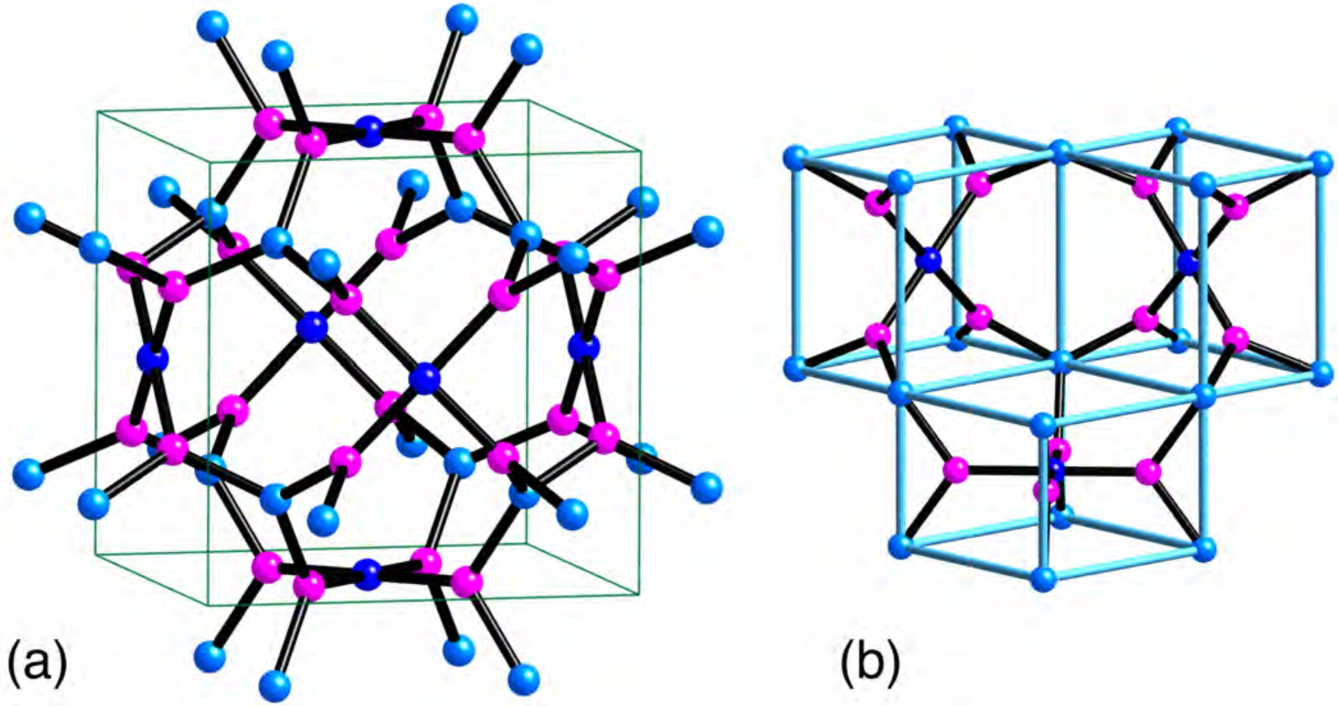
het-a

octatopic
linkers





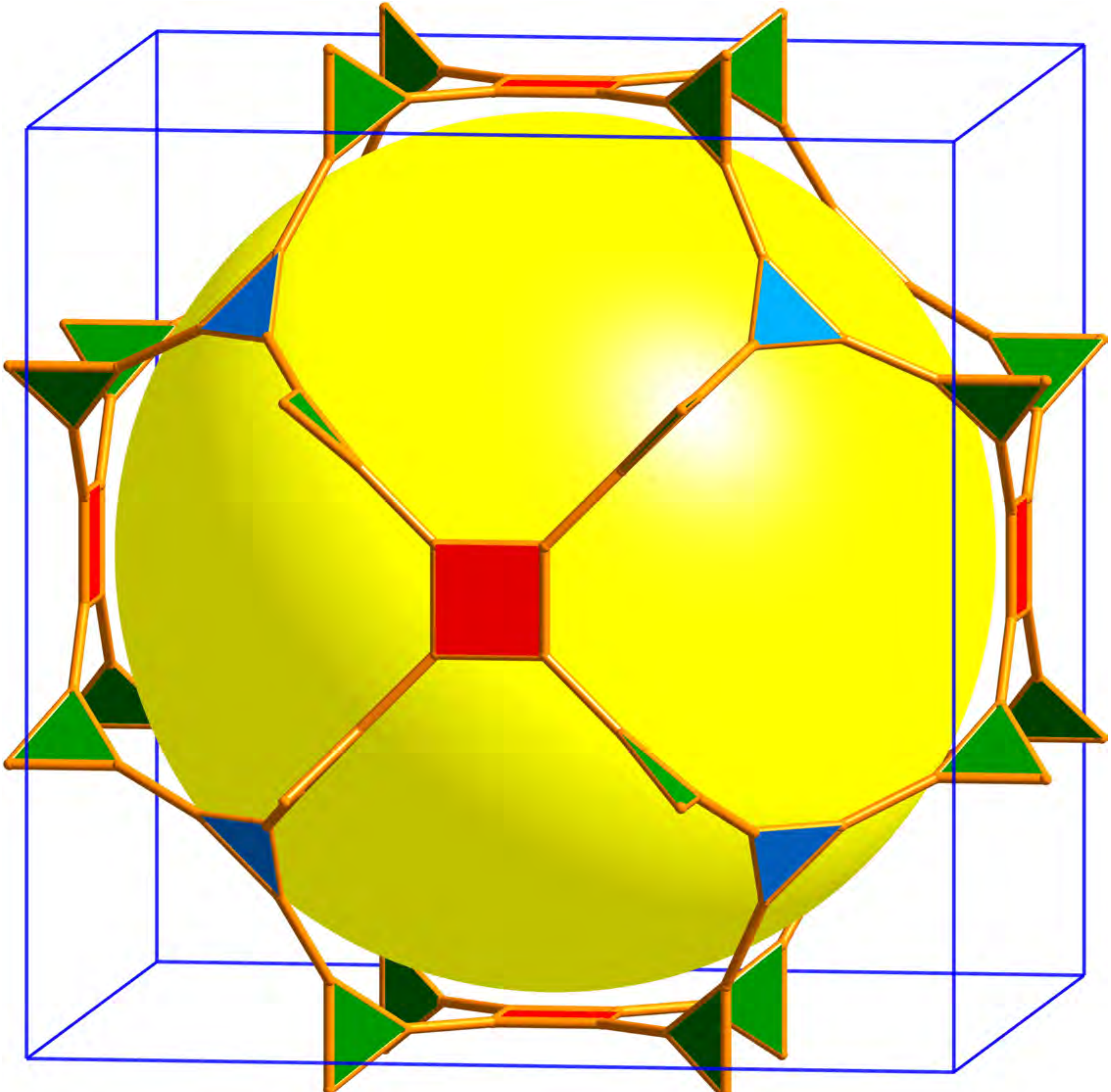
Example of an octatopic linker joining 3-c SBU’s
Wenbin Lin group

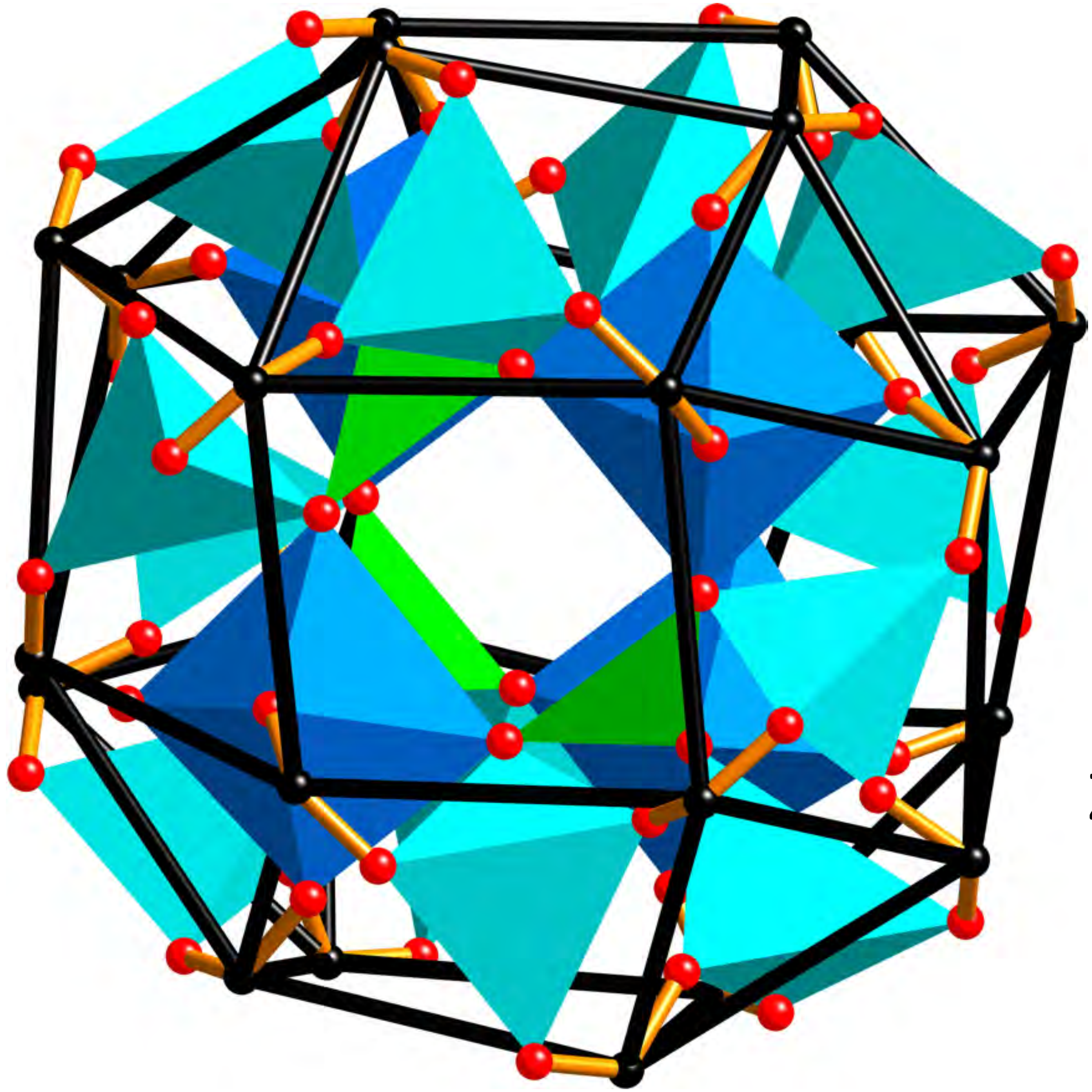


The (3,4)-c net **tfe** derived from the (3,8)-c net **the**

Transitivity 3 2

tfe-a

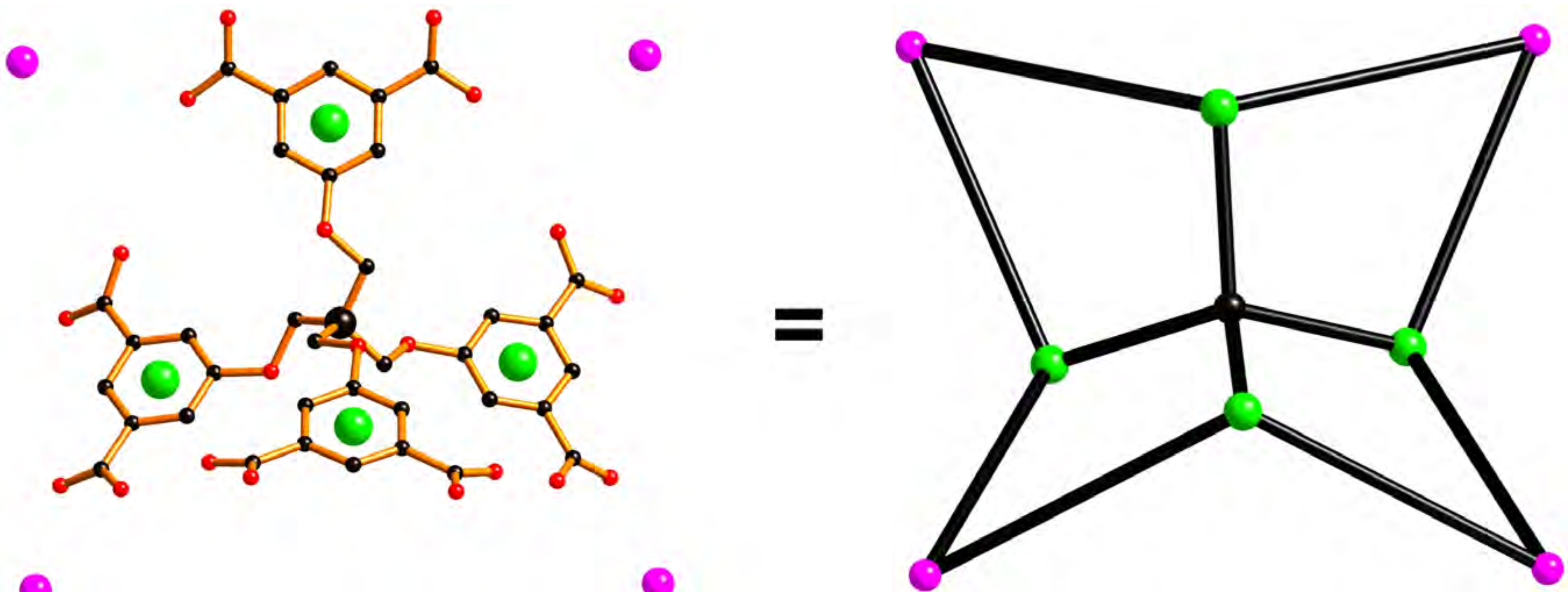




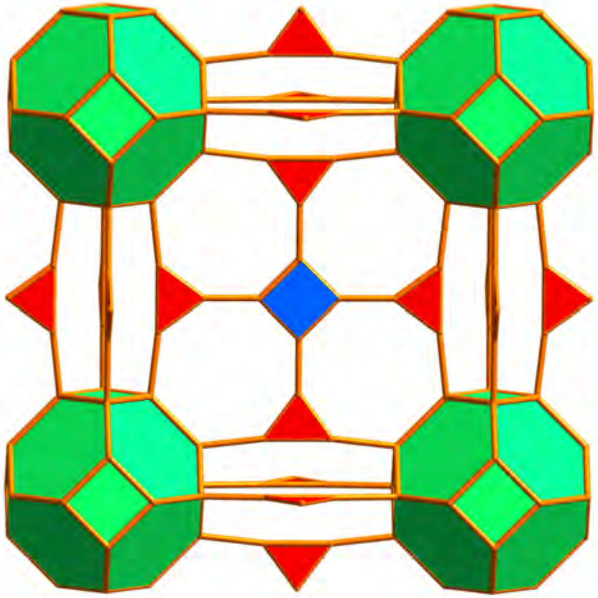
blue Zn
Green P
red O
black C

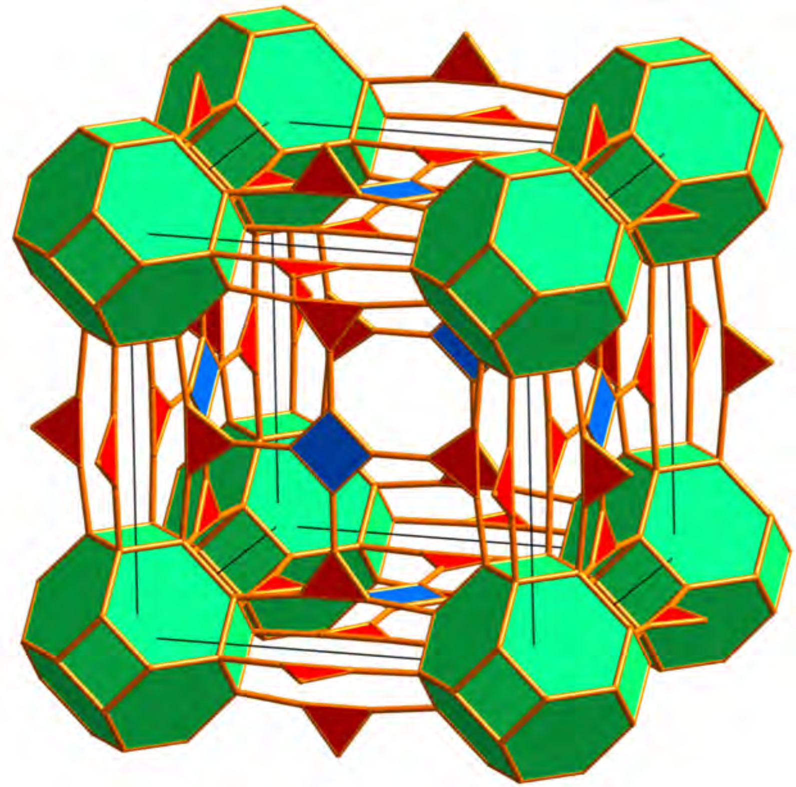
$Zn_{16}(HPO_3)_4(\text{-}CO_2)_{24}$

Unprecedented 24-c SBU in IFMC-200 .
D. –Y. Du et al. Sci. Rep. 2013, 3, 2616

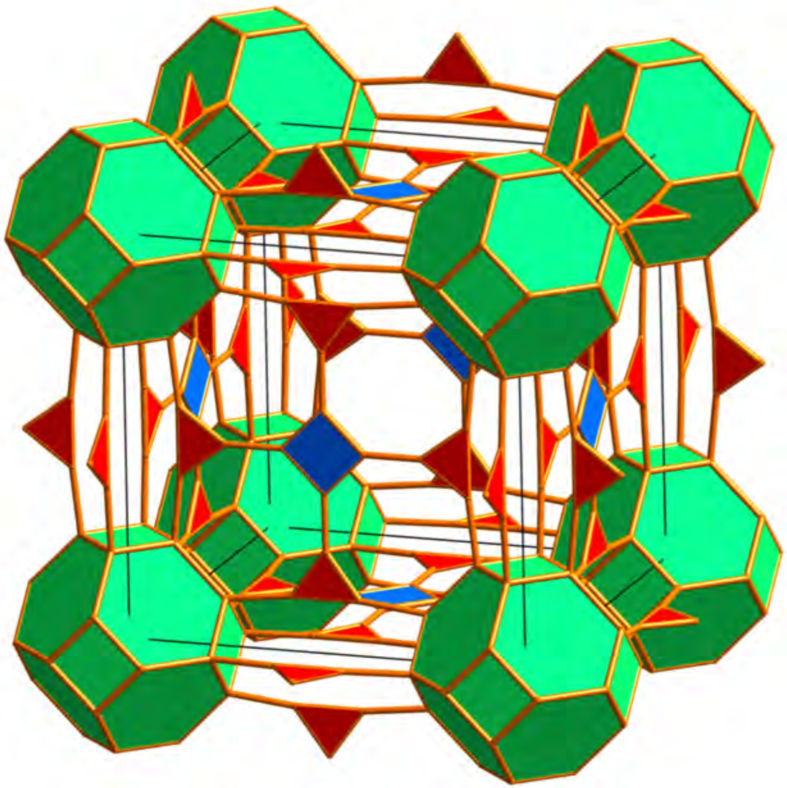


The linker in IFMC-200

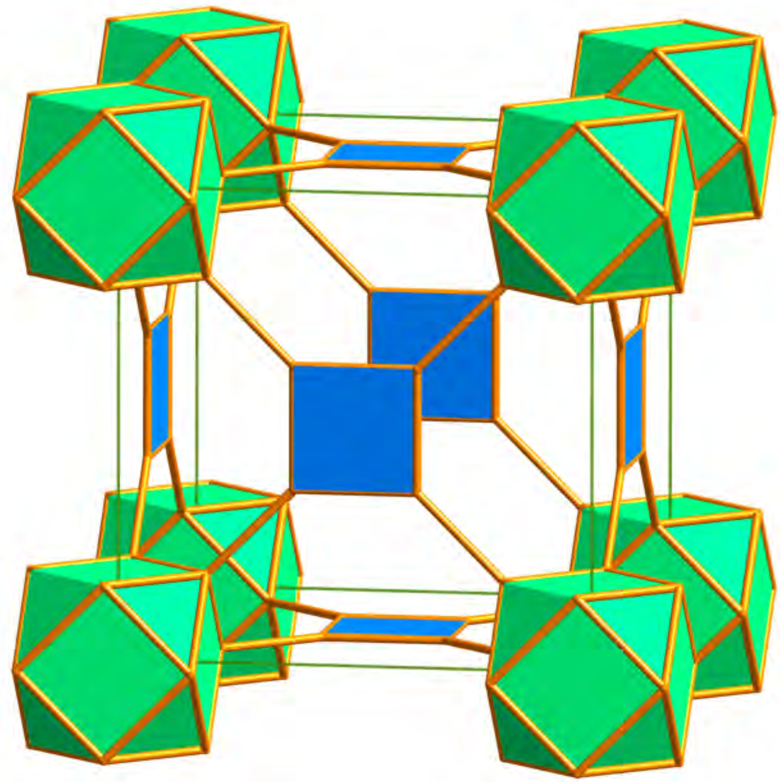




The net **ddy** in augmented form **ddy-a**



augmented 3,4,24-c net
ddy-a

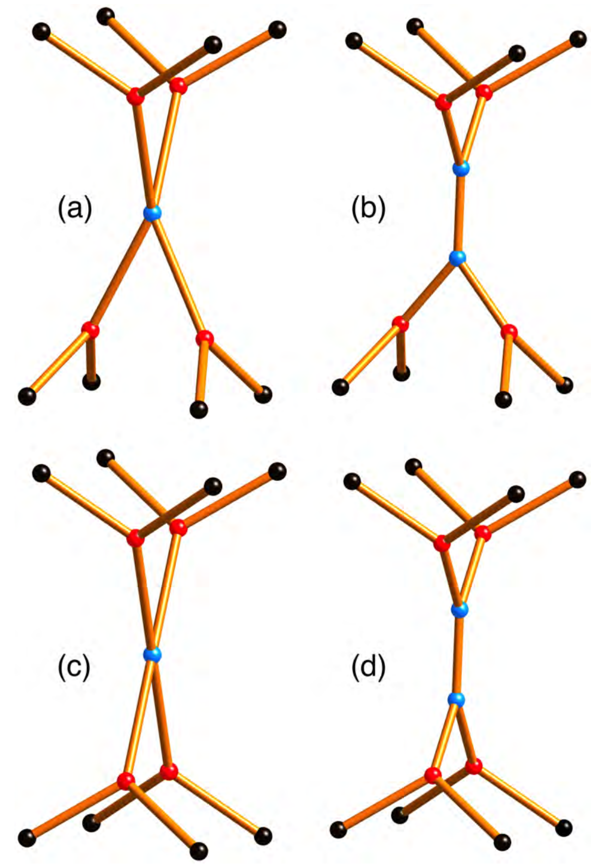


augmented 4,12-c net
ftw-a

Minimal transitivity. A minimal transitivity net has transitivity defined by the local arrangement of linkers and metal SBUs

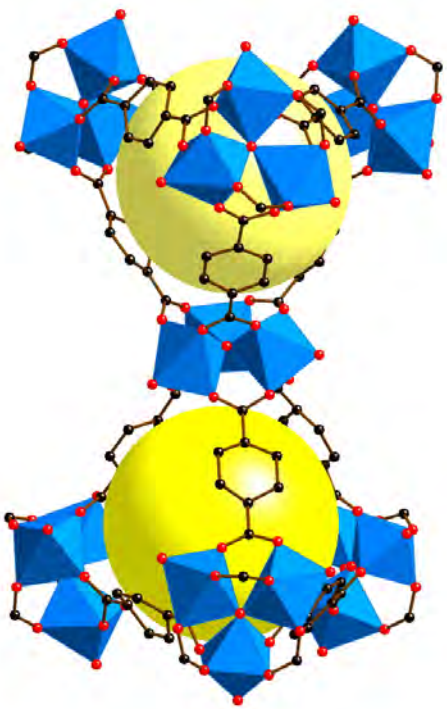
Example of an exception MOF-177 has 6-c metal SBUs joined by tritopic linkers. Minimal transitivity is 2,1

Real material has net **qom** with transitivity 5,5



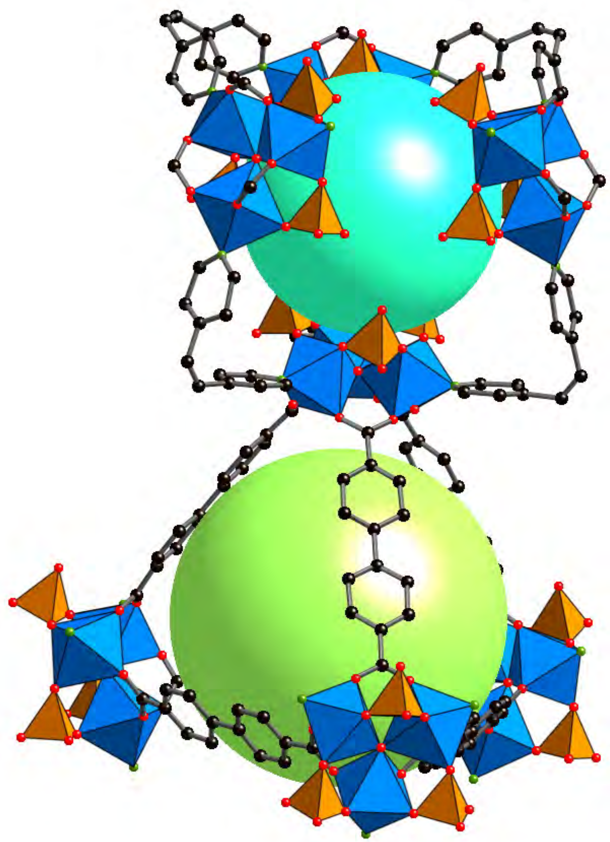
3, 2 3,3

The local geometry uniquely determines the structure
M. O'Keeffe. *Mat. Res. Bull.* **2006**, *41*, 911



MIL-101 Férey group

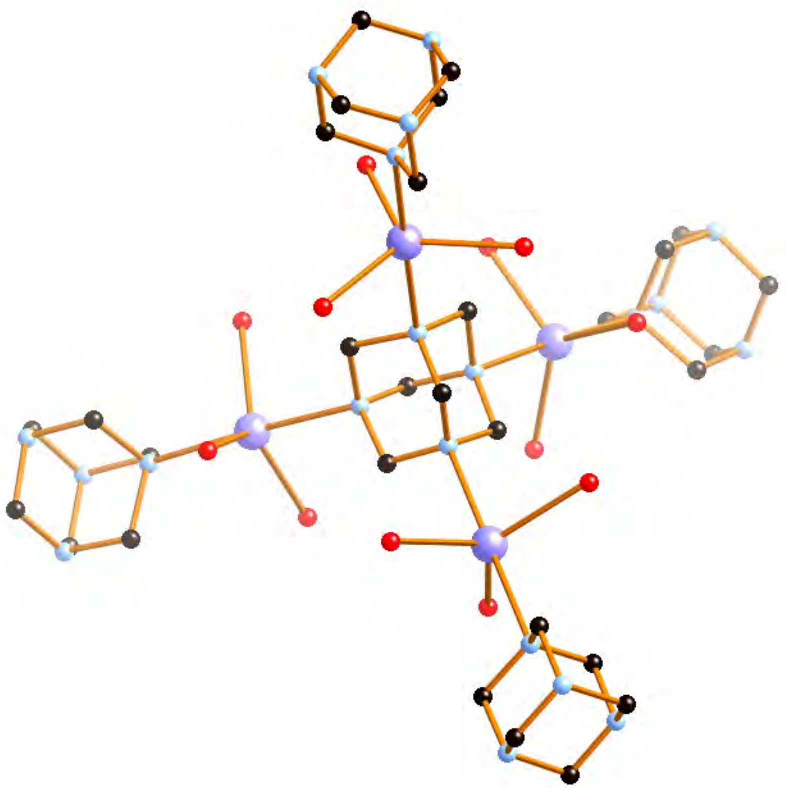
Angew. Chem 2004, 43, 6295
Science, 2005, 309, 2040

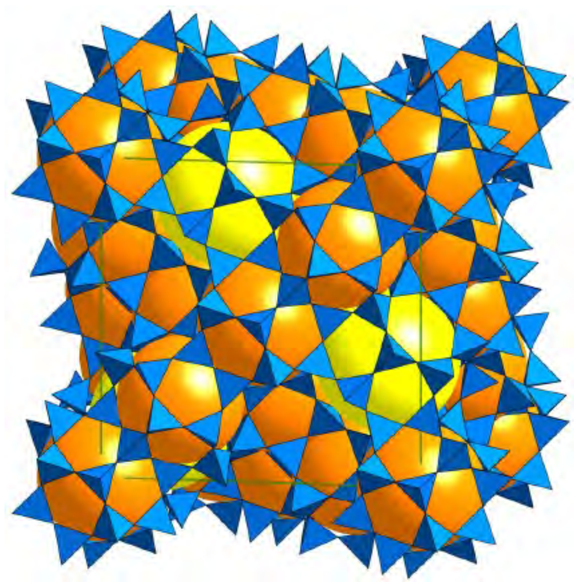


MOF-500 Yaghi group

Angew. Chem 2006, 46, 2528

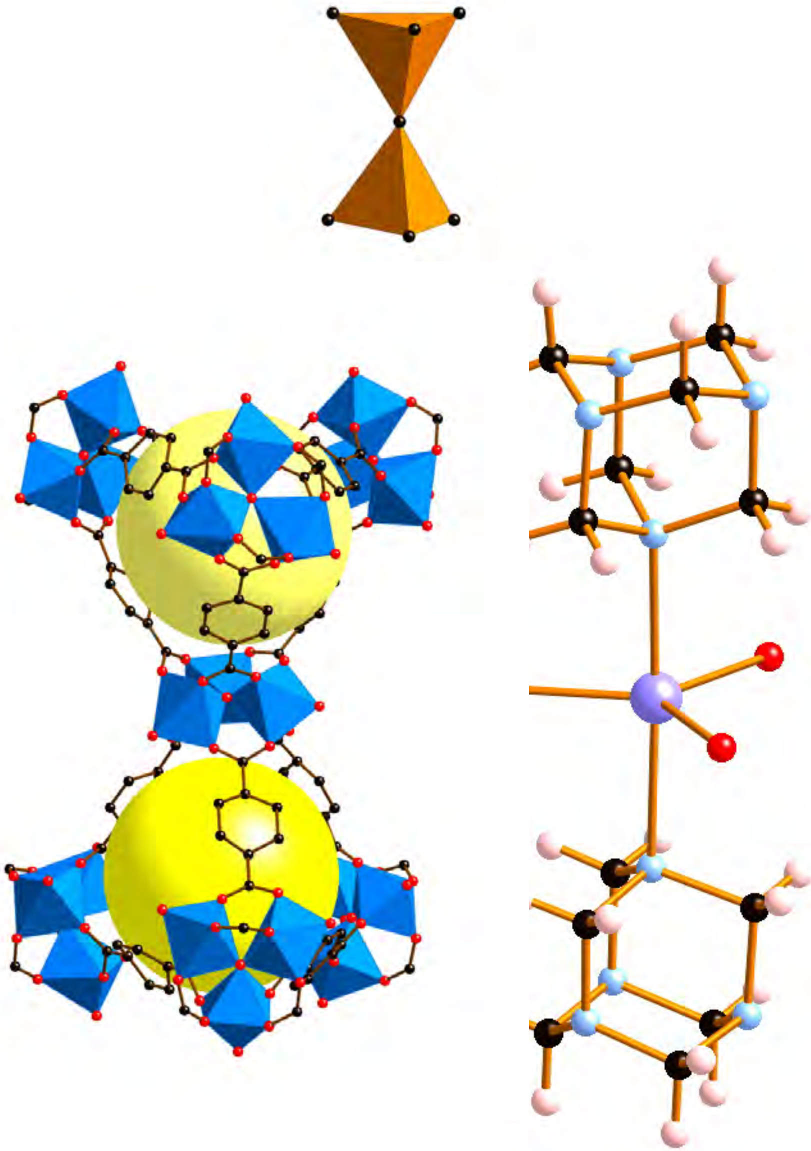
The Férey unit and this one (below) have the **mtn** topology
The Yaghi ubit had the **dia** topology. Why?



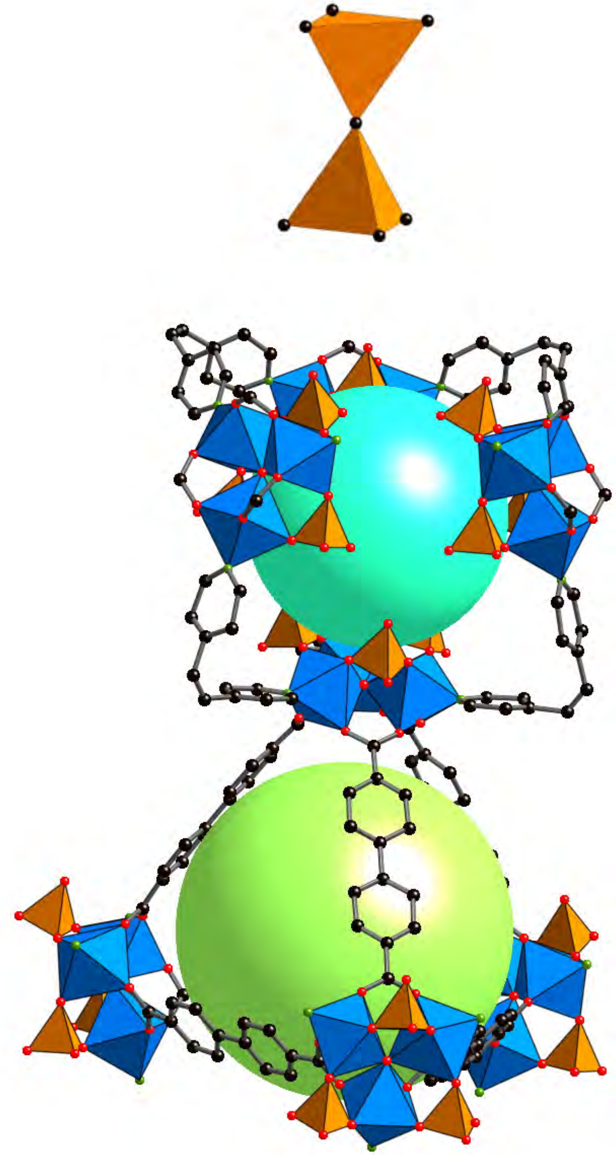


mtn-e

Hexamethylenetetramine linked by Cd atoms
Shilun Qiu et al. (Jilin)
Angew. Chem. Int. Ed. **2005**, 44, 3845.

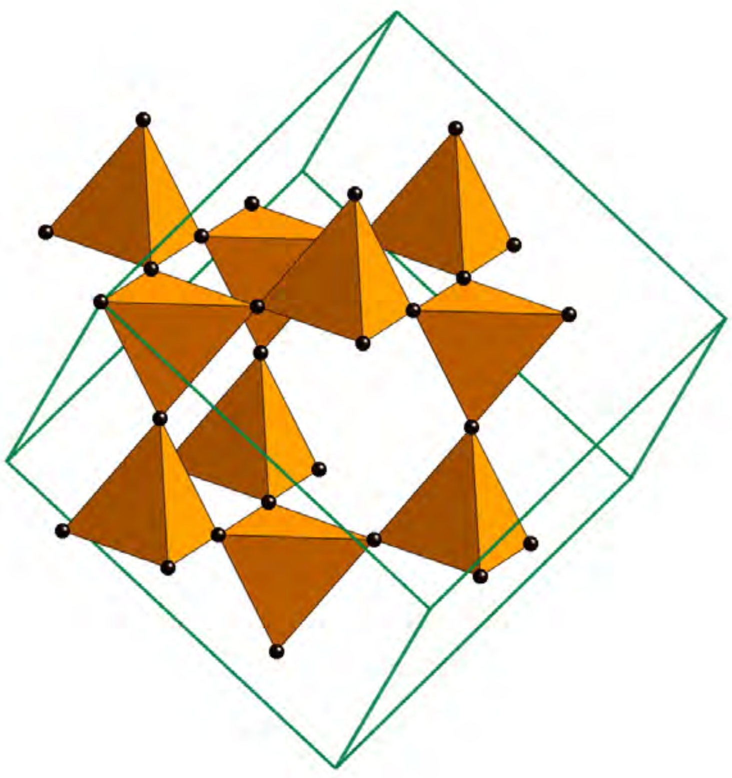


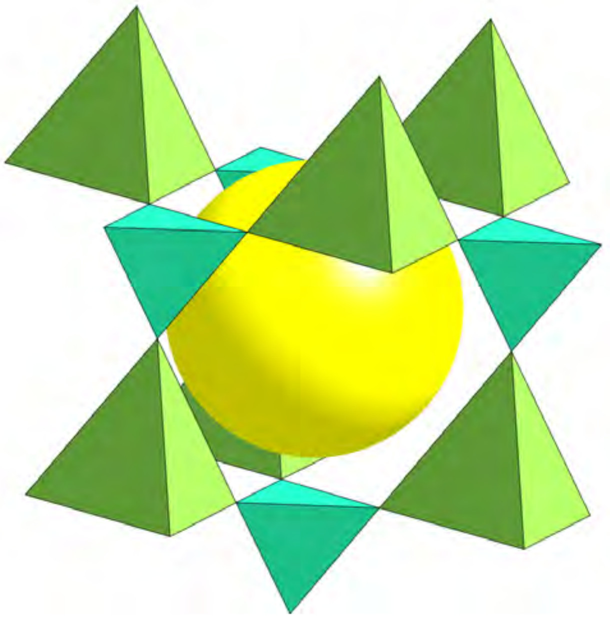
eclipsed



staggered

Linking staggered tetrahedra with T-X-T = 180°.
Only one solution:



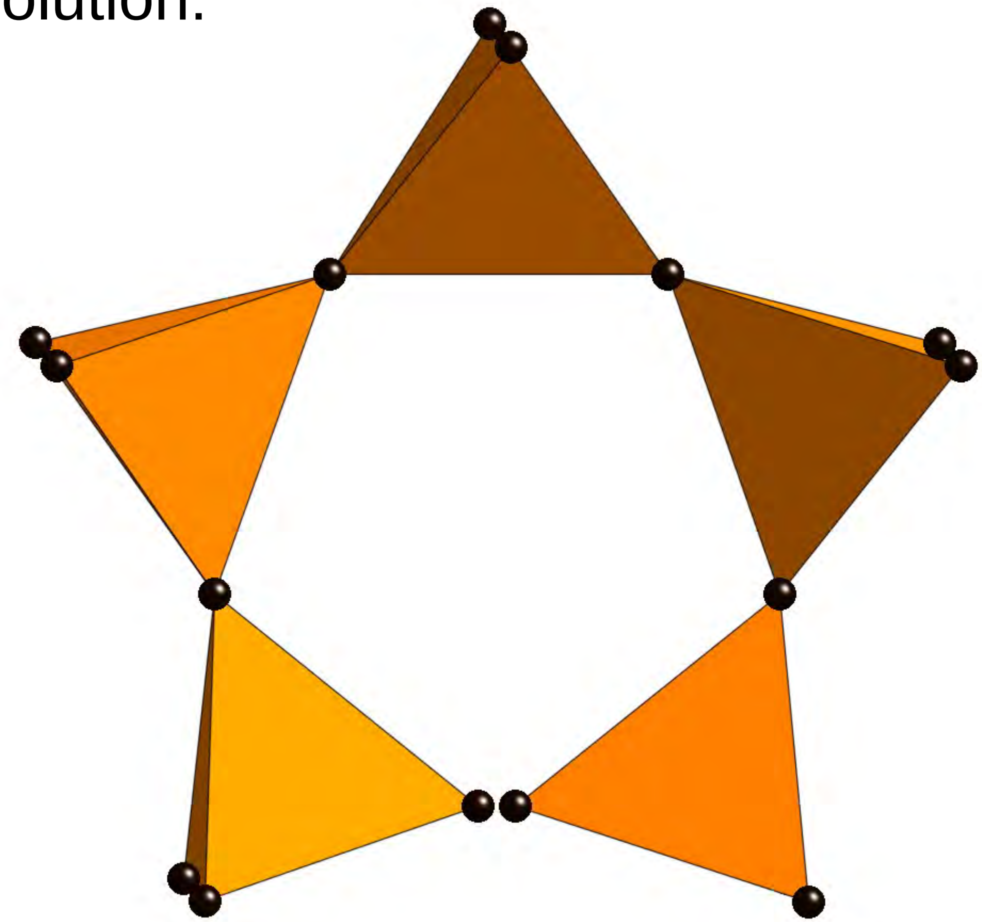


"cristobalite" *Fd*-3*m*   two kinds of tetrahedra *F*-43*m*

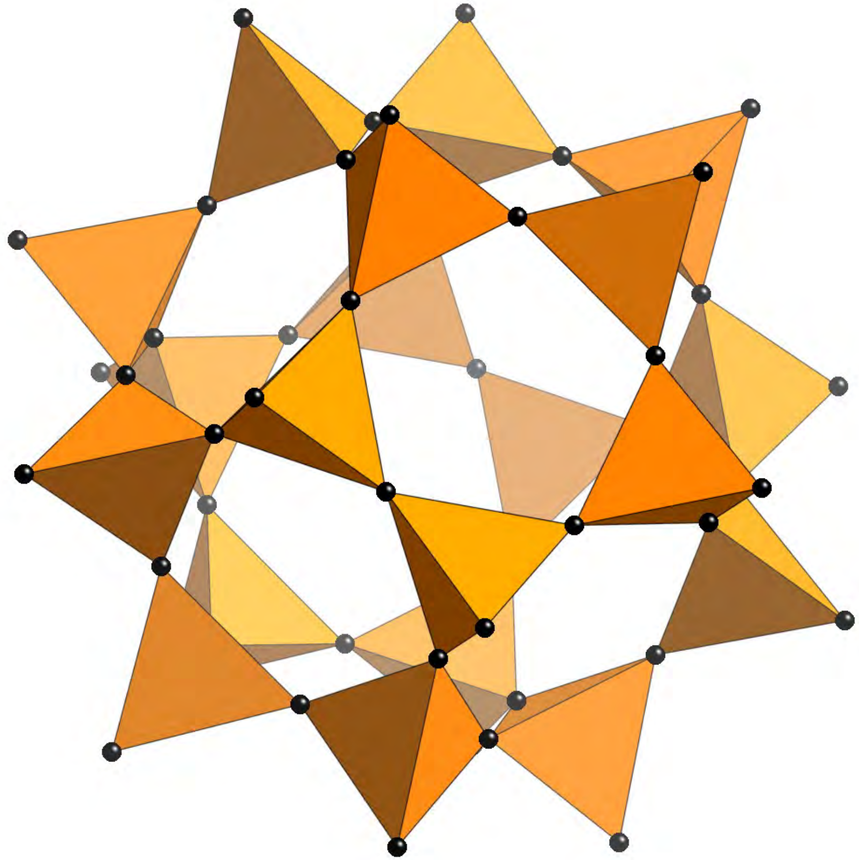
end of story for MOF-500

What about eclipsed tetrahedra and T-X-T = 180°?

No exact solution:



simple polyhedron with 5-sided fces



T-X-T = 177.1° with regular tetrahedra
OK we will take that, but...

The plot thickens.

If we pack dodecahedra so four meet at each vertex we get a finite structure in positively-curved space (a tiling of the 3-sphere = a 4-dimensional polytope).

To get a tiling of Euclidean 3-space we have to add in some polyhedra with six-sided faces.

So now we must ask what structures exist for simple tilings with 5- and six-sided faces?

Olaf Delgado to the rescue...

The dual problem is to find tilings by tetrahedra so that either five or six meet at an edge,

This has been done exhaustively for up to eleven kinds of tetrahedron.[Delgado-Friedrichs, O.; O'Keeffe, M. *Acta cryst.* **2010**, *A66,* 637*]*

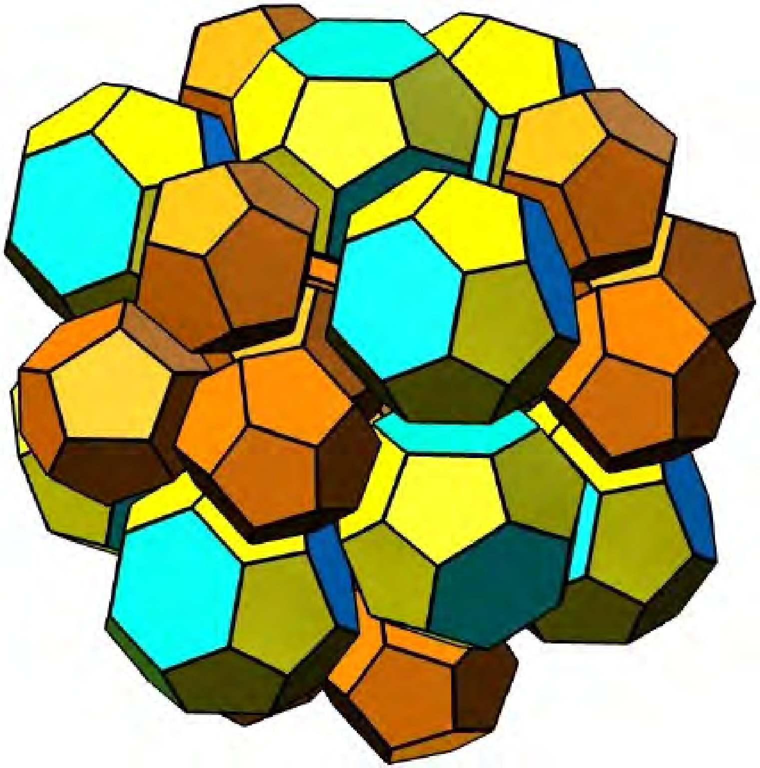
The two simplest have 3 kinds of tetrahedron and correspond to the well-known Frank-Kasper phases $MgCu_2$ and Cr_3Si. The duals are also well known as the Type I and Type II clathrate structures. Their nets have symbols **mtn** and **mep**.

At this point one can simply show that one of the two proposed structures exactly fits the powder pattern.

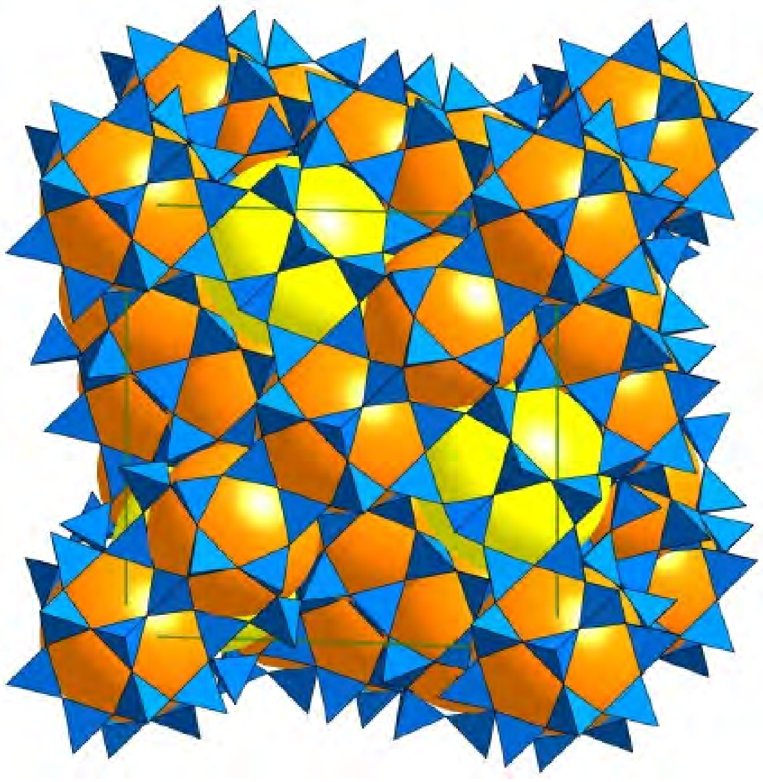
This is basically what was done by the Férey group. But note they found the candidate structures by an entirely different procedure.

The answer was a structure based on **mtn**

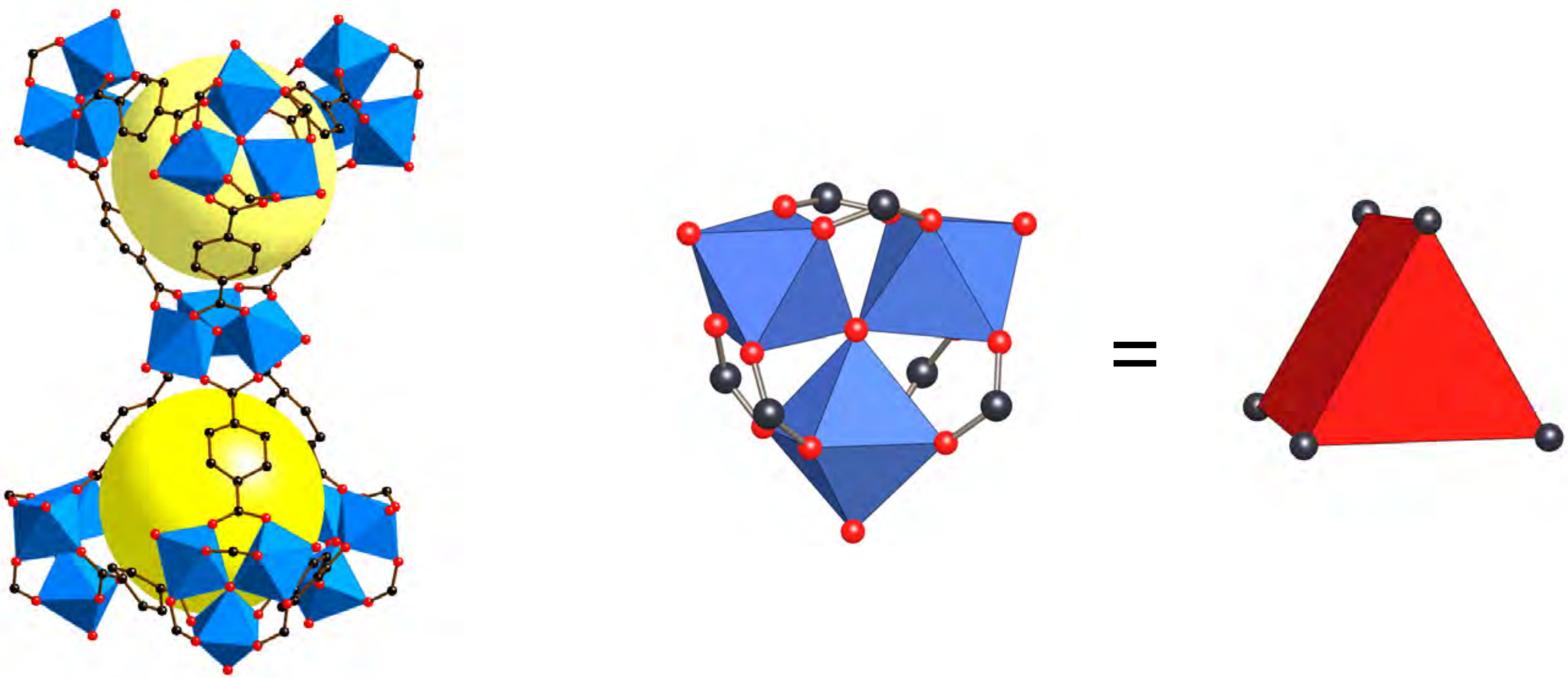
In fact we can show it is the preferred structure
- closest to regular tetrahedra and T-X-T = 180˚.



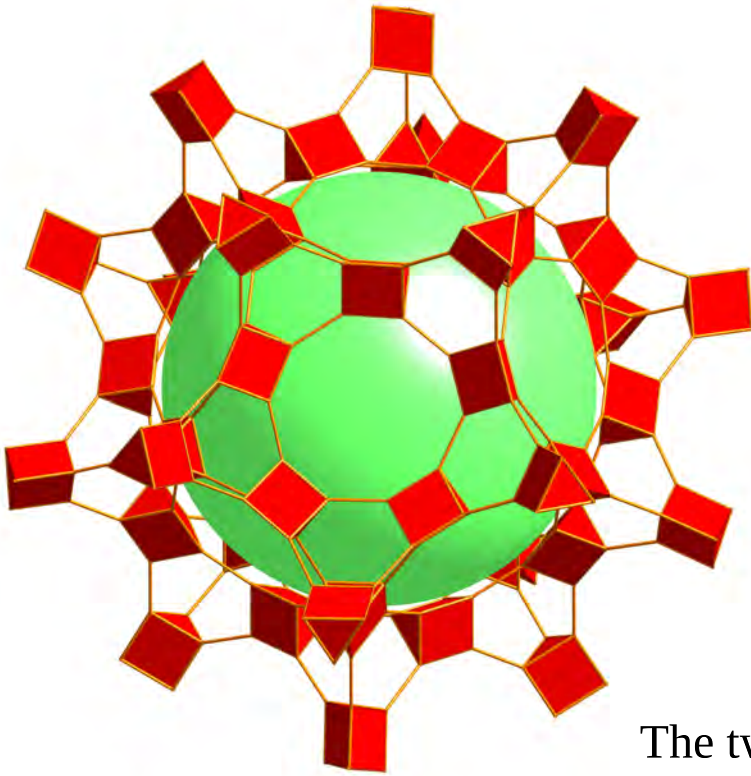
mtn

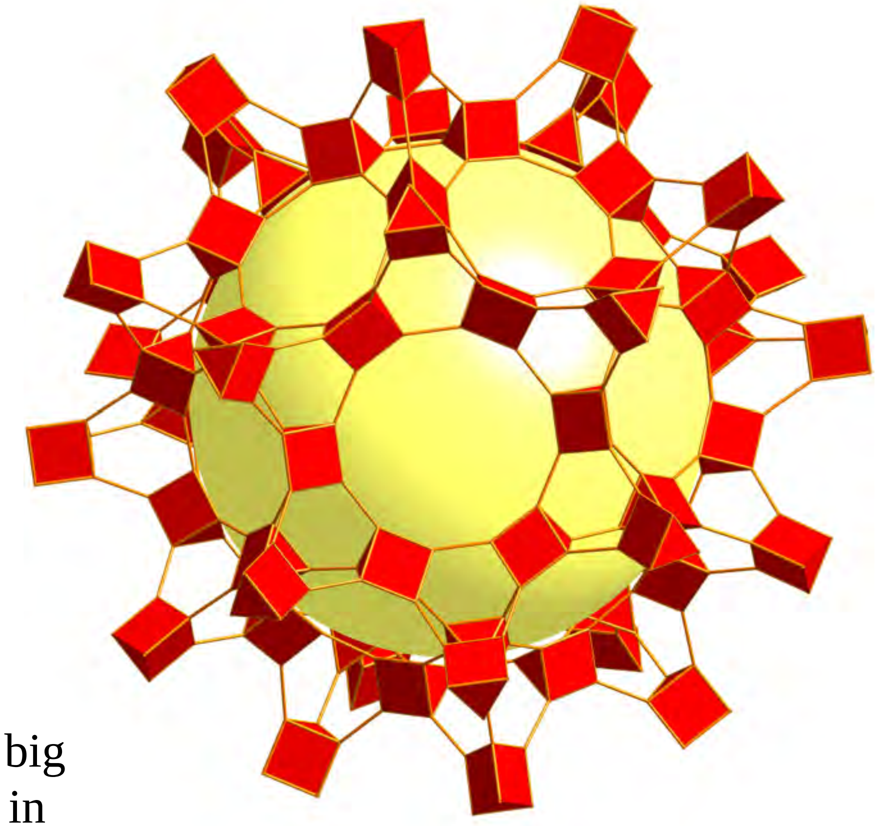


mtn-e

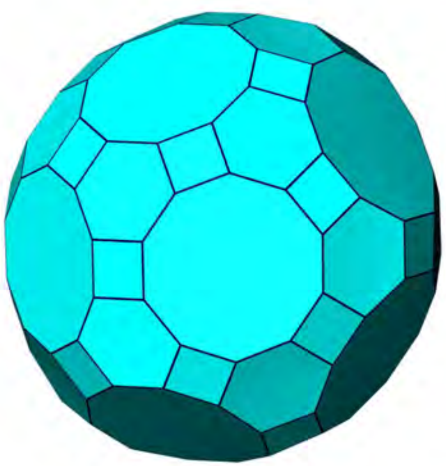


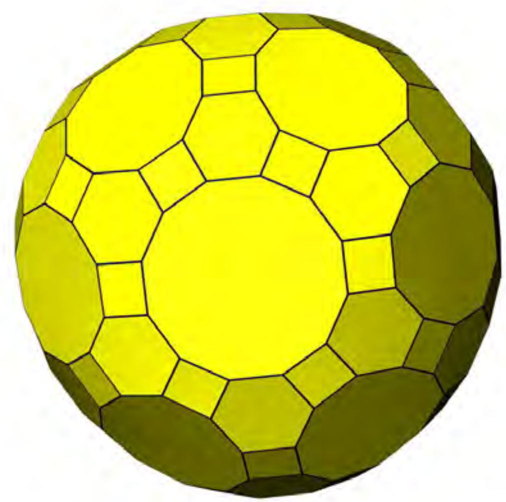
but the SBUs are really trigonal prisms.
net is mtn-e-a = mgc-x-d-e-a!



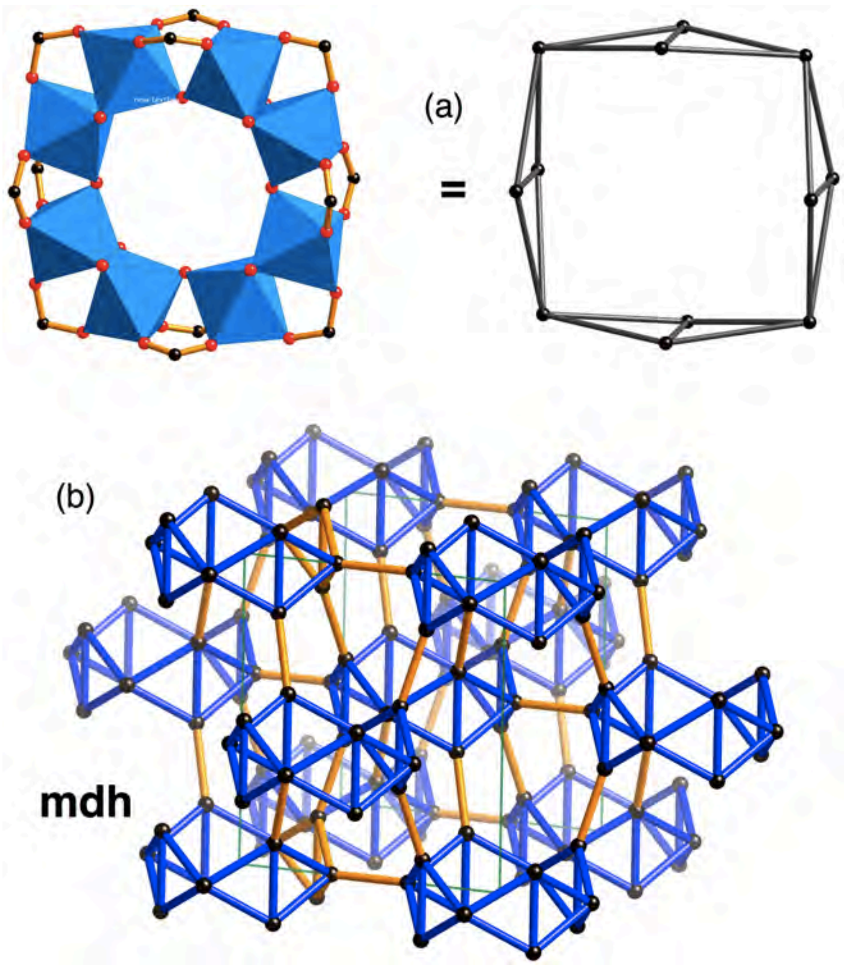


The two big cavities in **mtn-e-a**

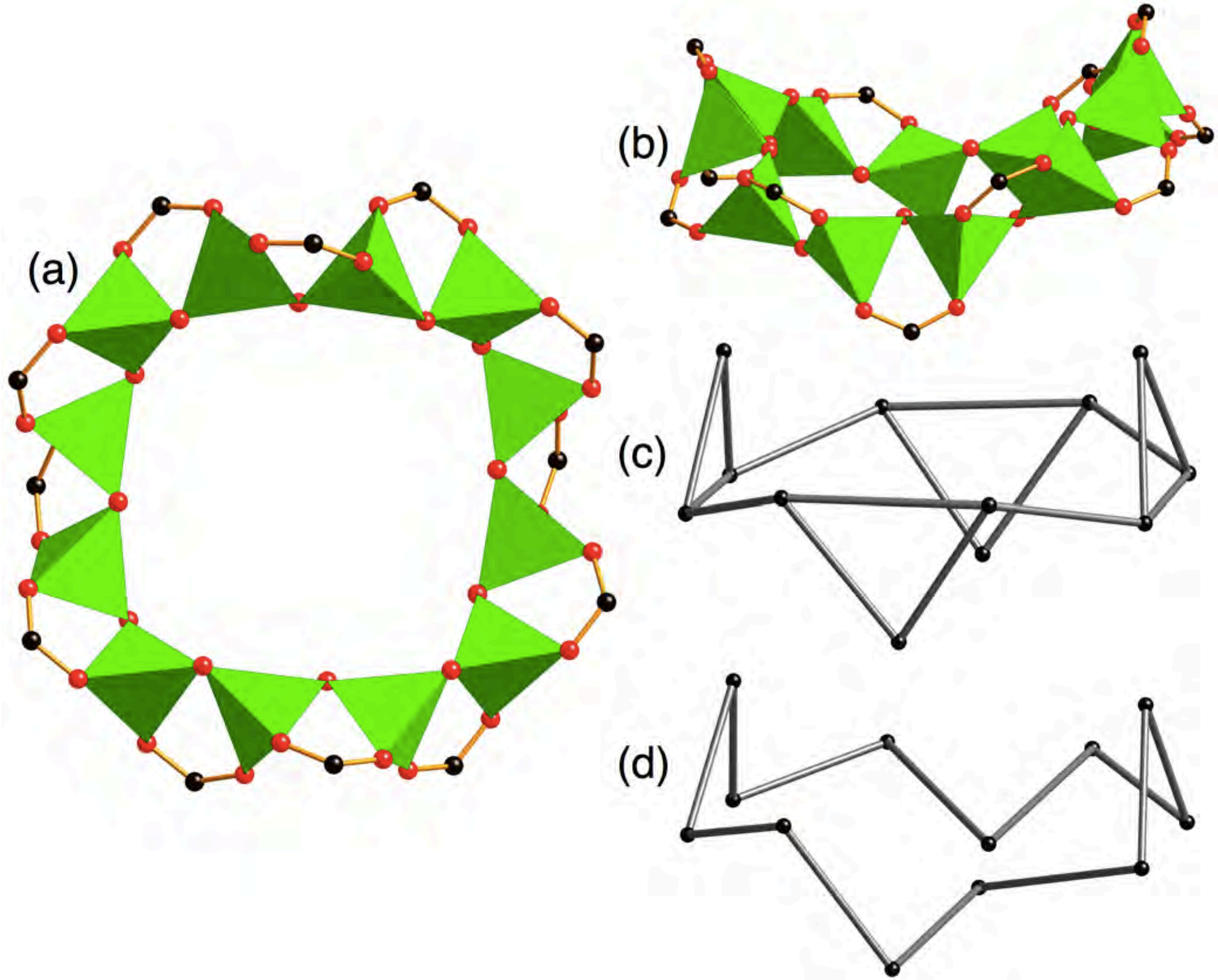




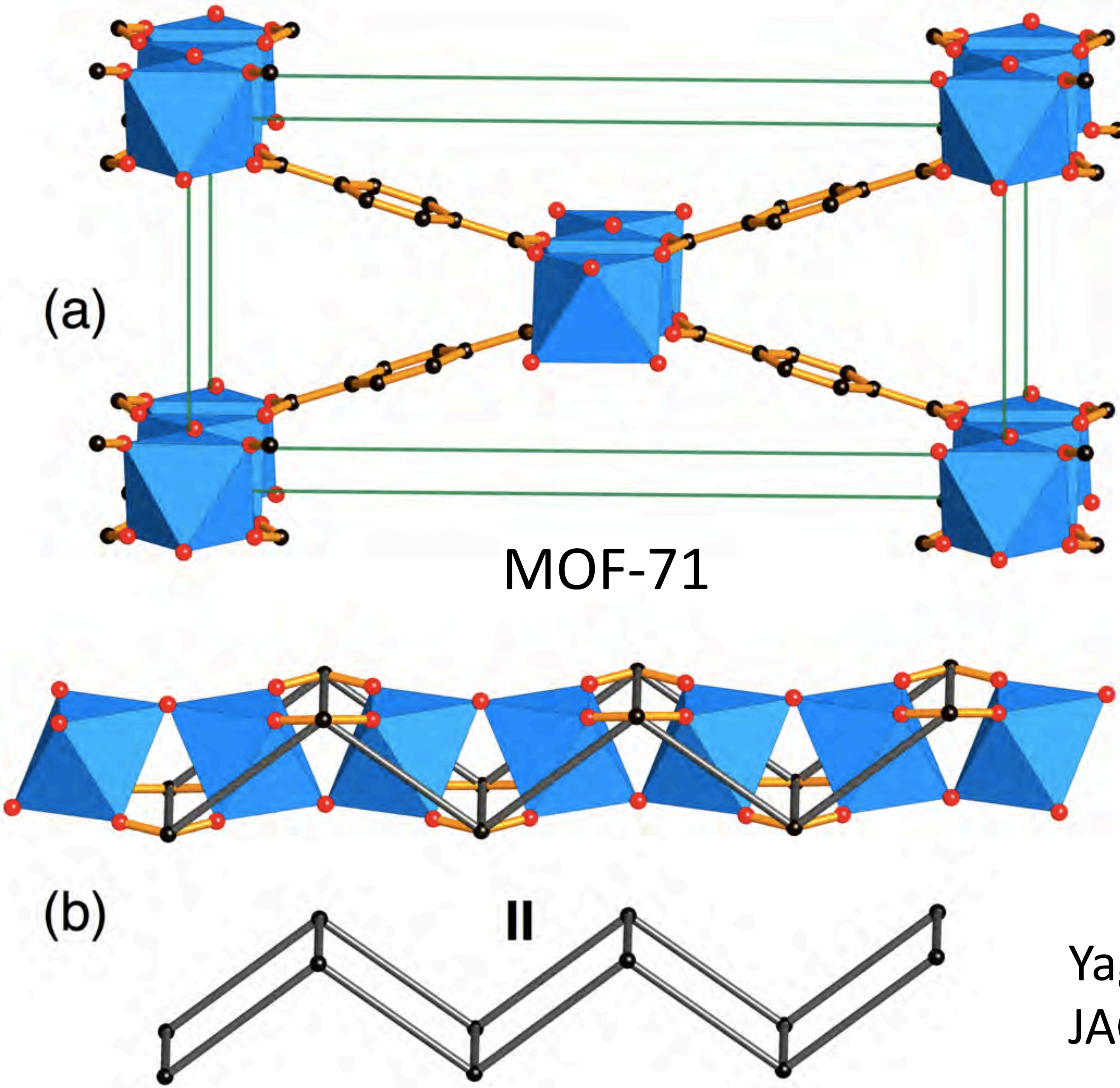
86 faces



SBU in Ti MOF from Férey group



Be MOF from Jeff Long group

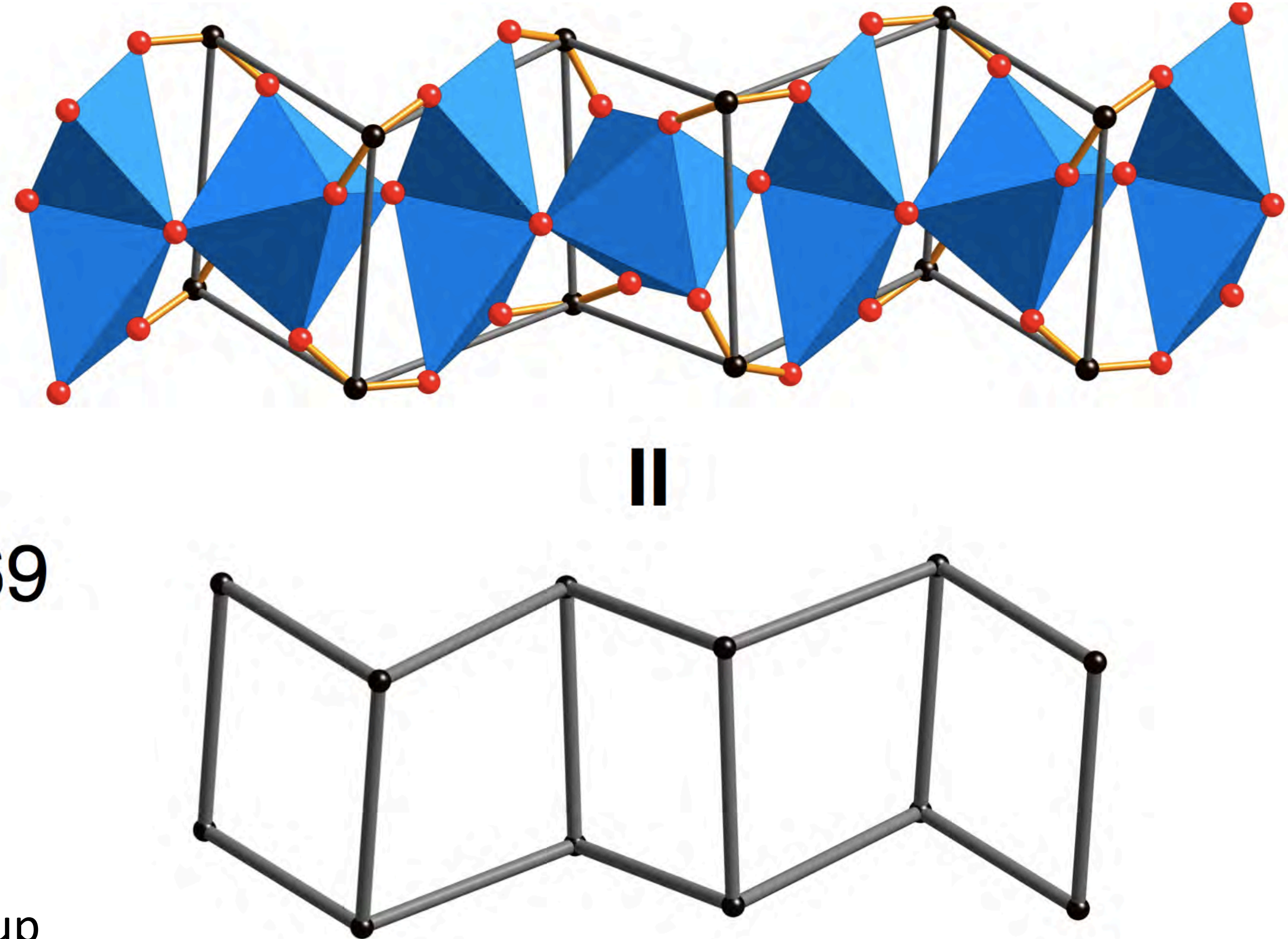


rod SBUs

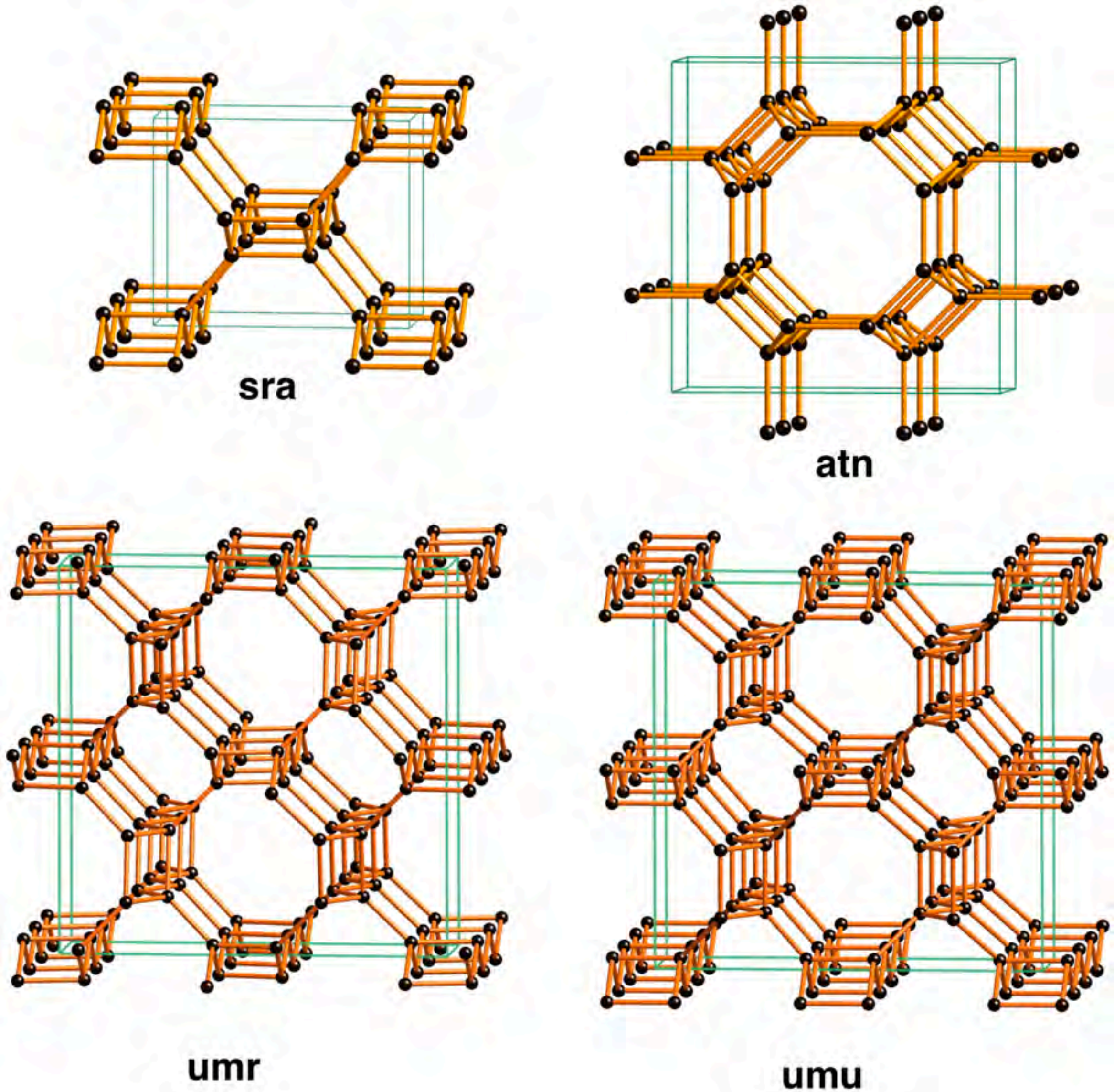
Yaghi Group
JACS **2005**, *127*, 1504

(a)

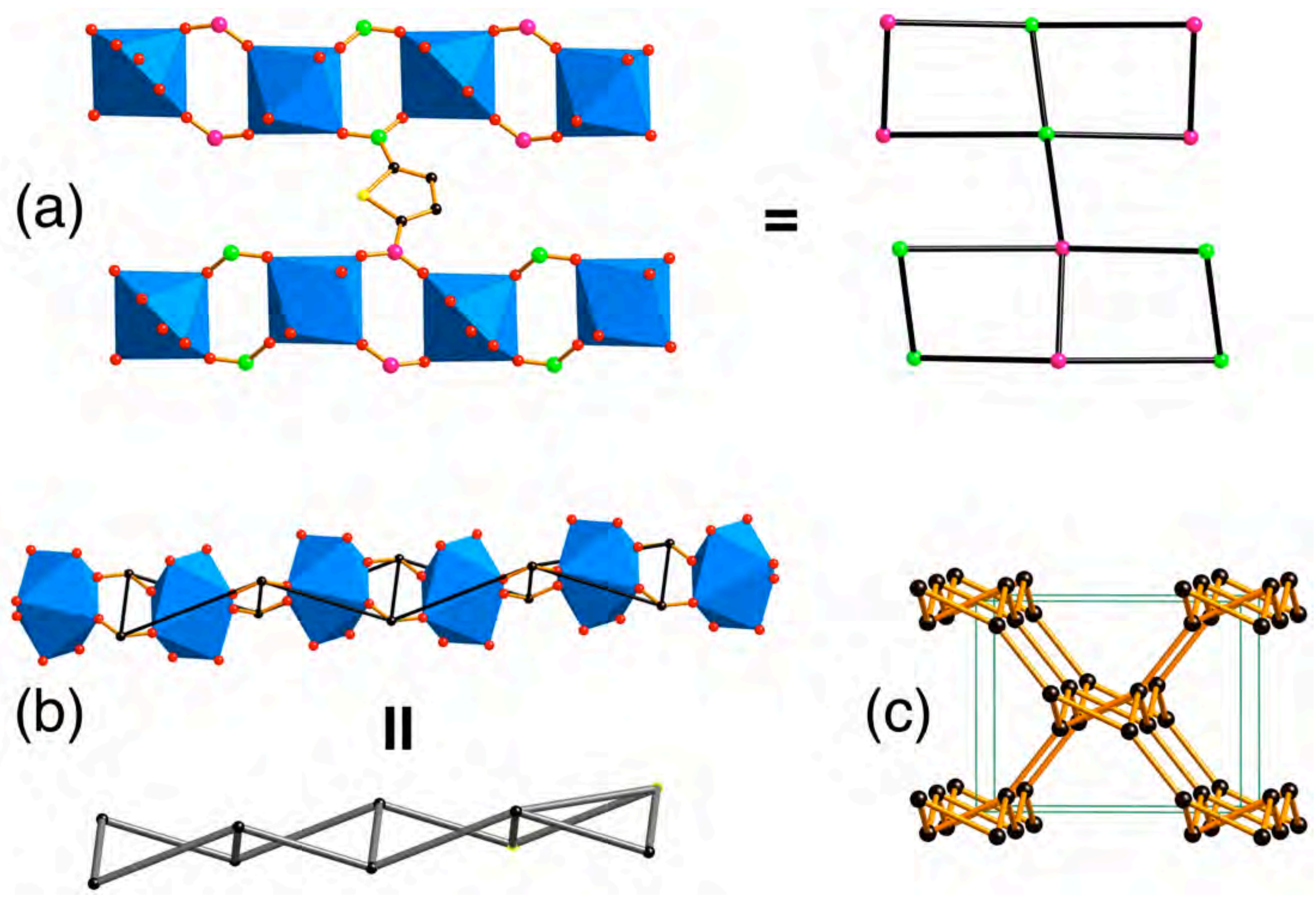
MOF-69



Yaghi Group
JACS **2005**, *127*, 1504

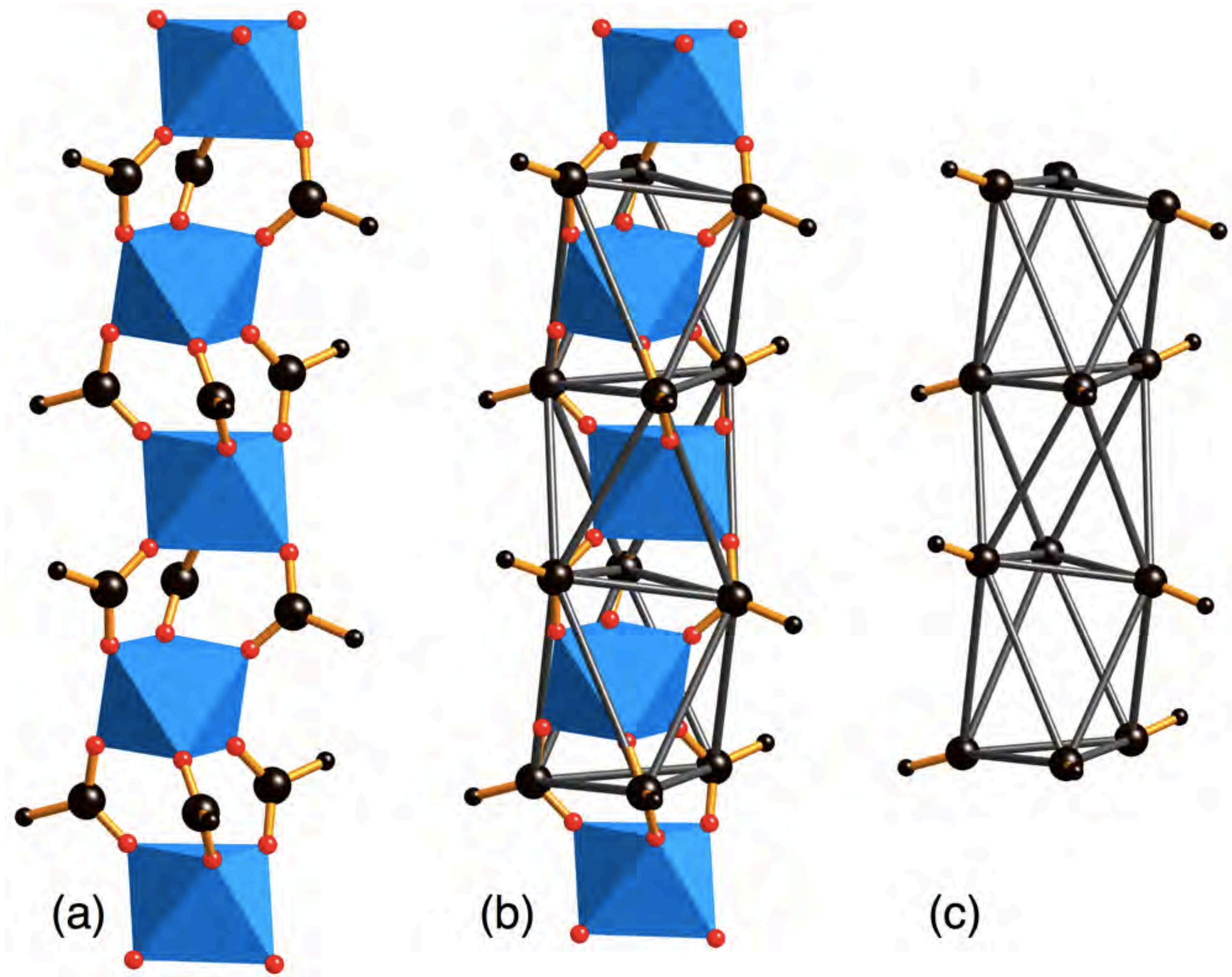


Some edge-transitive ways of linking ladders

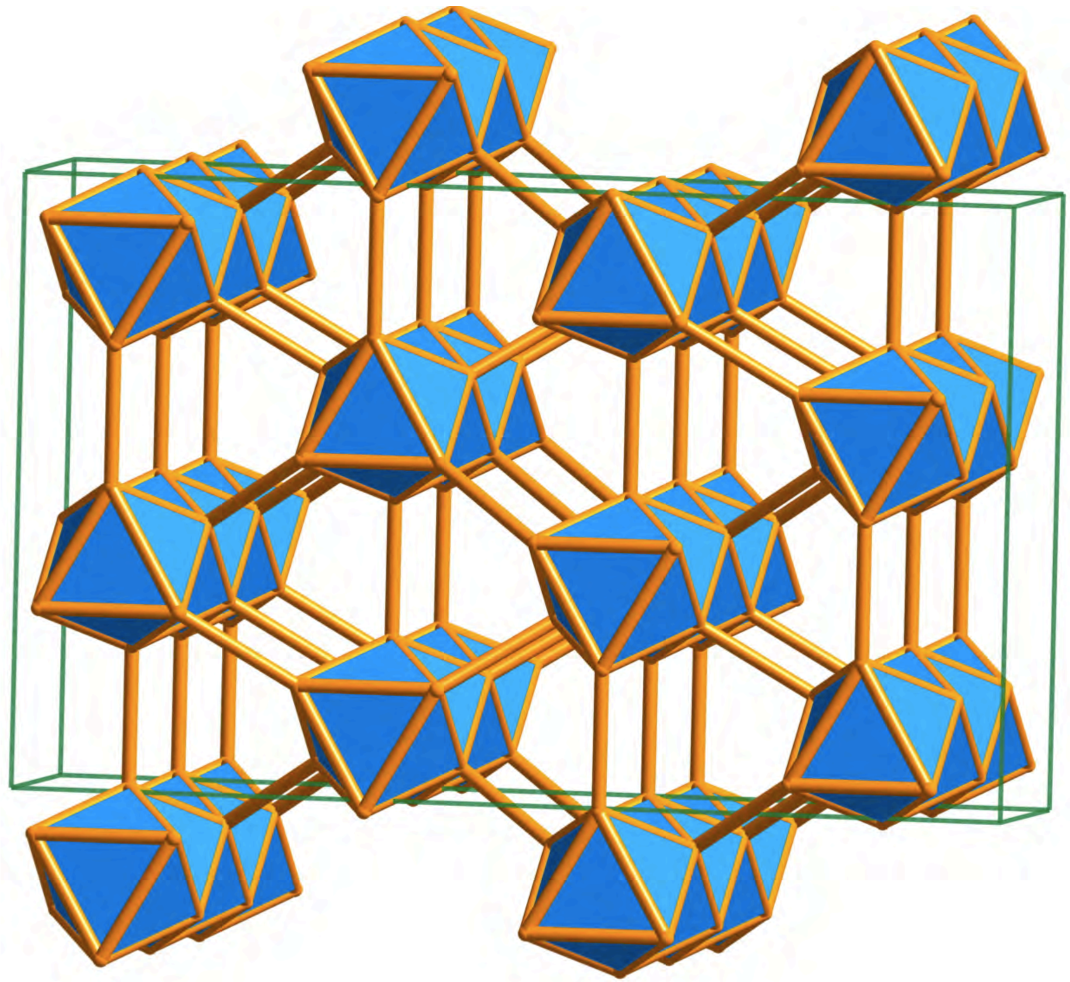


MOF-75 points of extension of rod form twisted ladder.
Net is **irl**.

Yaghi Group
JACS **2005**, *127*, 1504



Scandium terephthalate two groups, 2005



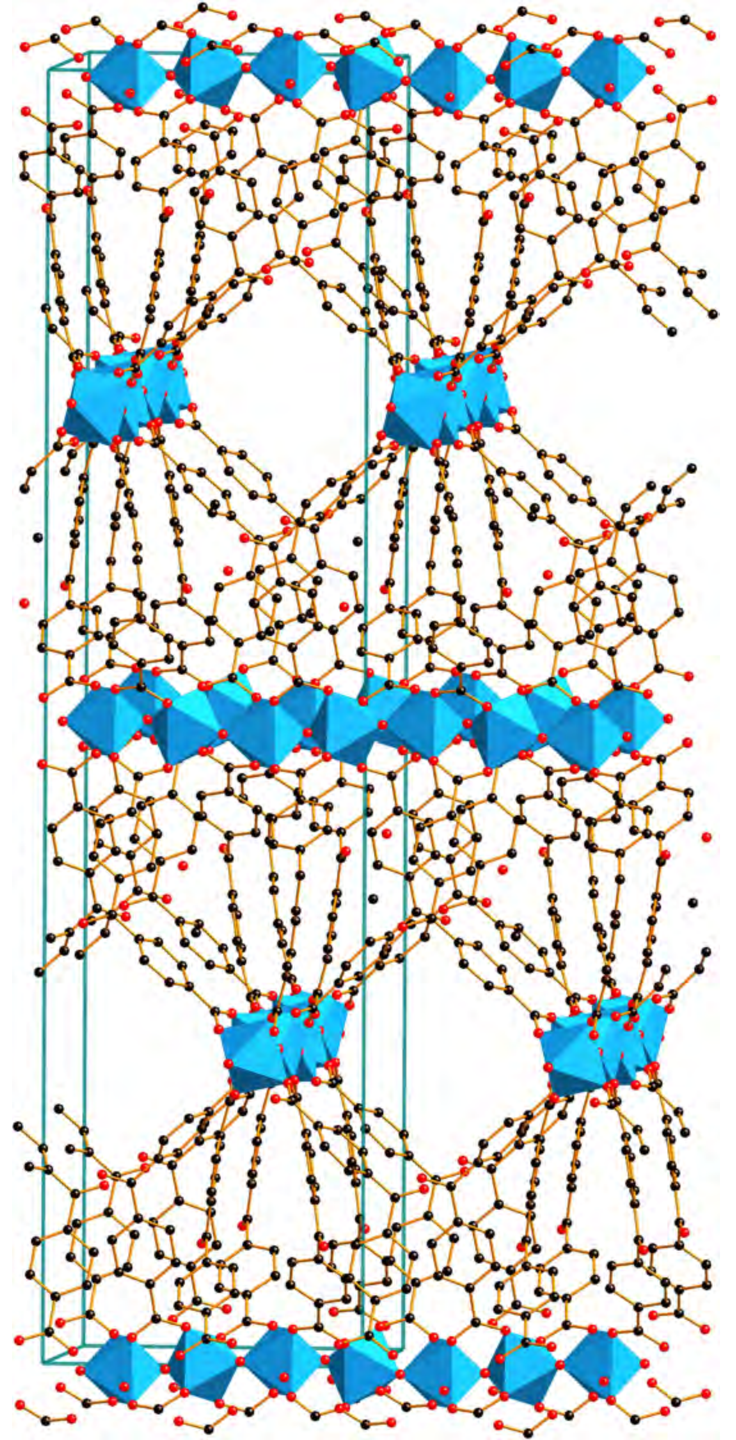
(a) **sct**

net of scandium terephthalate

First view of the structure

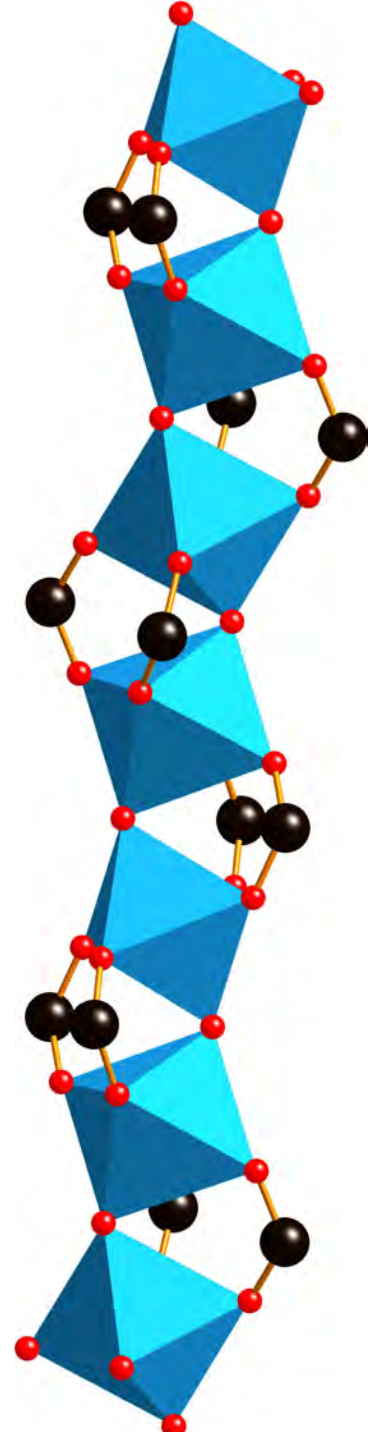
Rods of AlO_6 octahedra

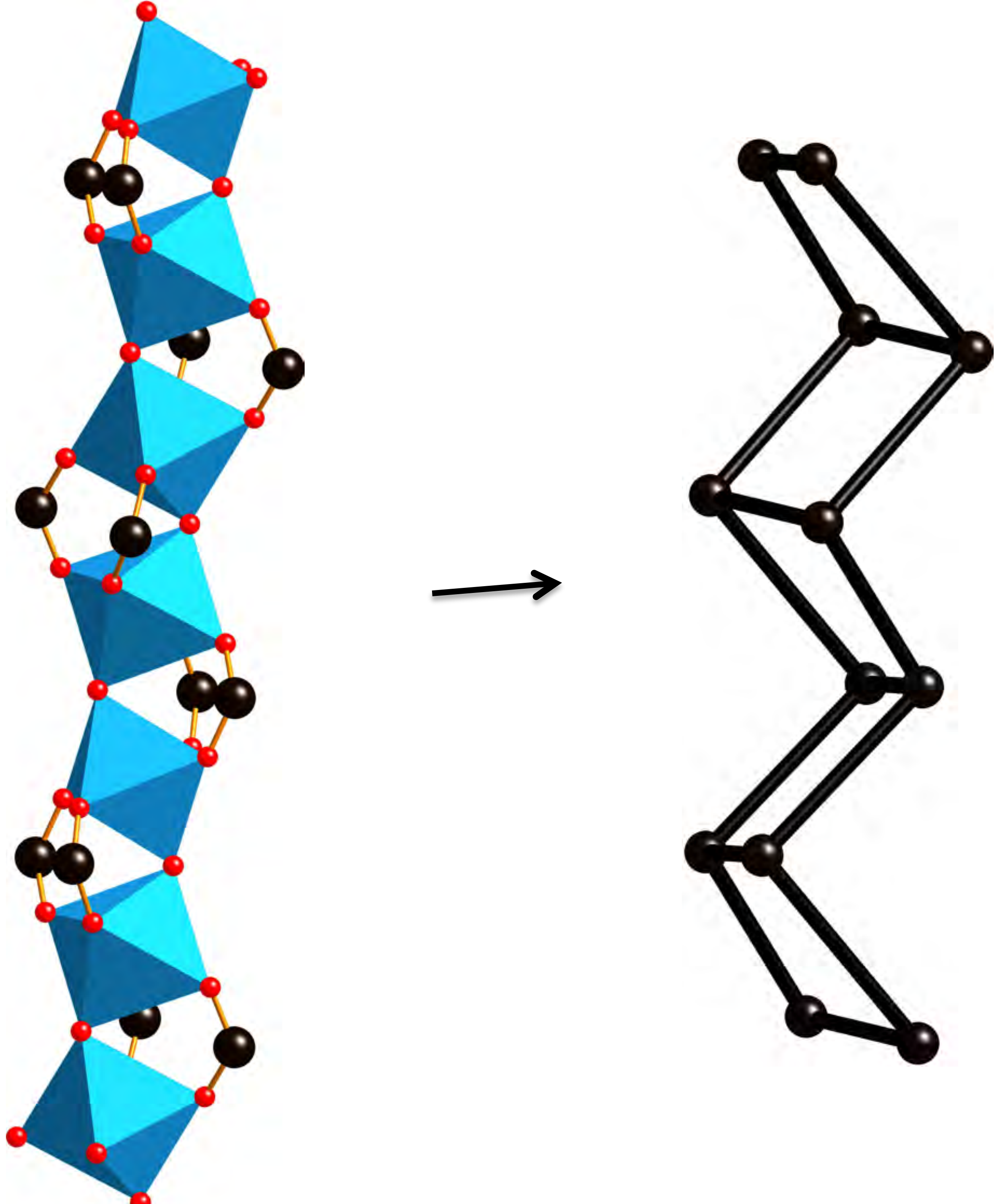
Norbert Stock group
Inorg. Chem. 52, 1854 (2013)

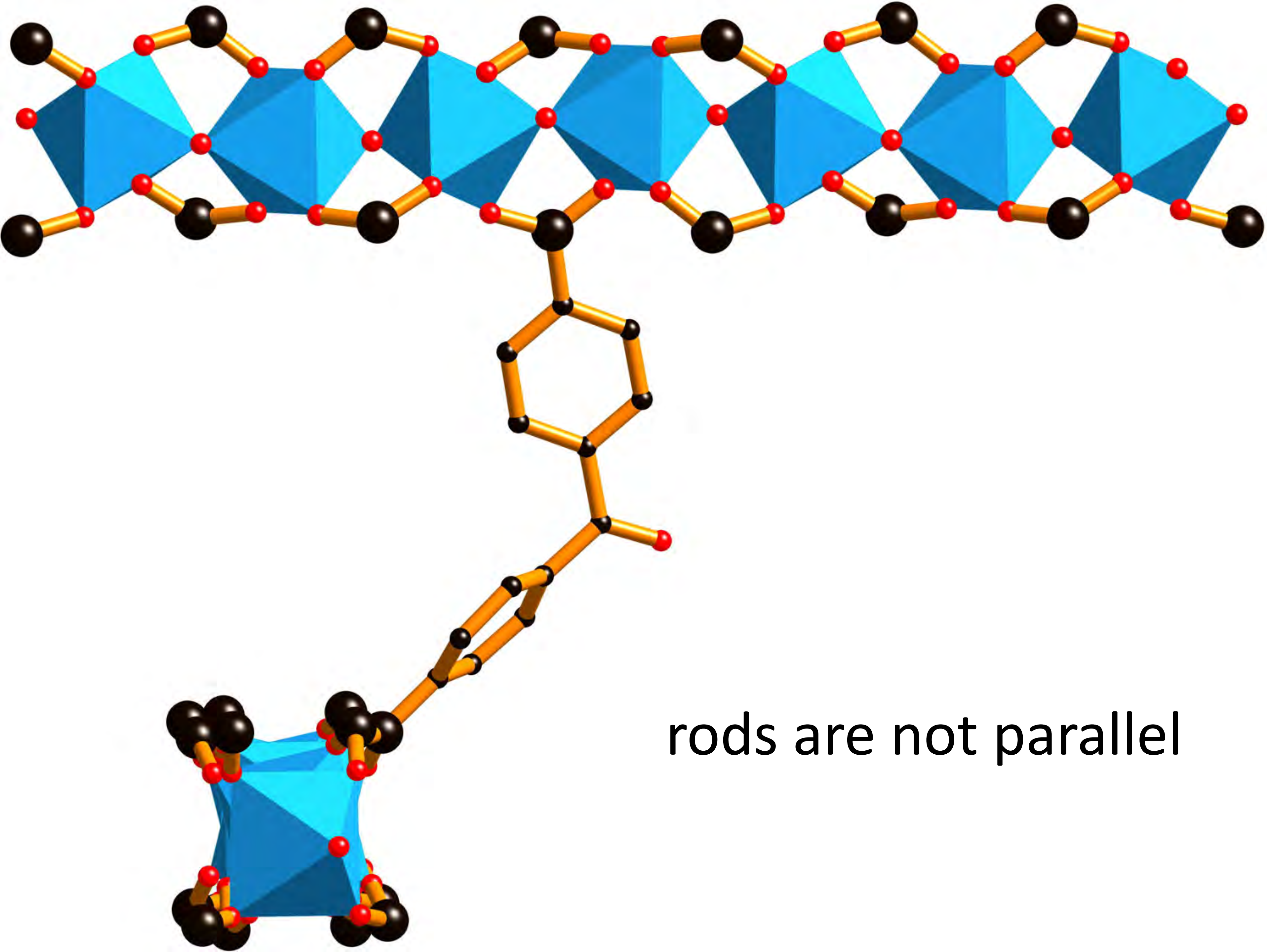


One rod

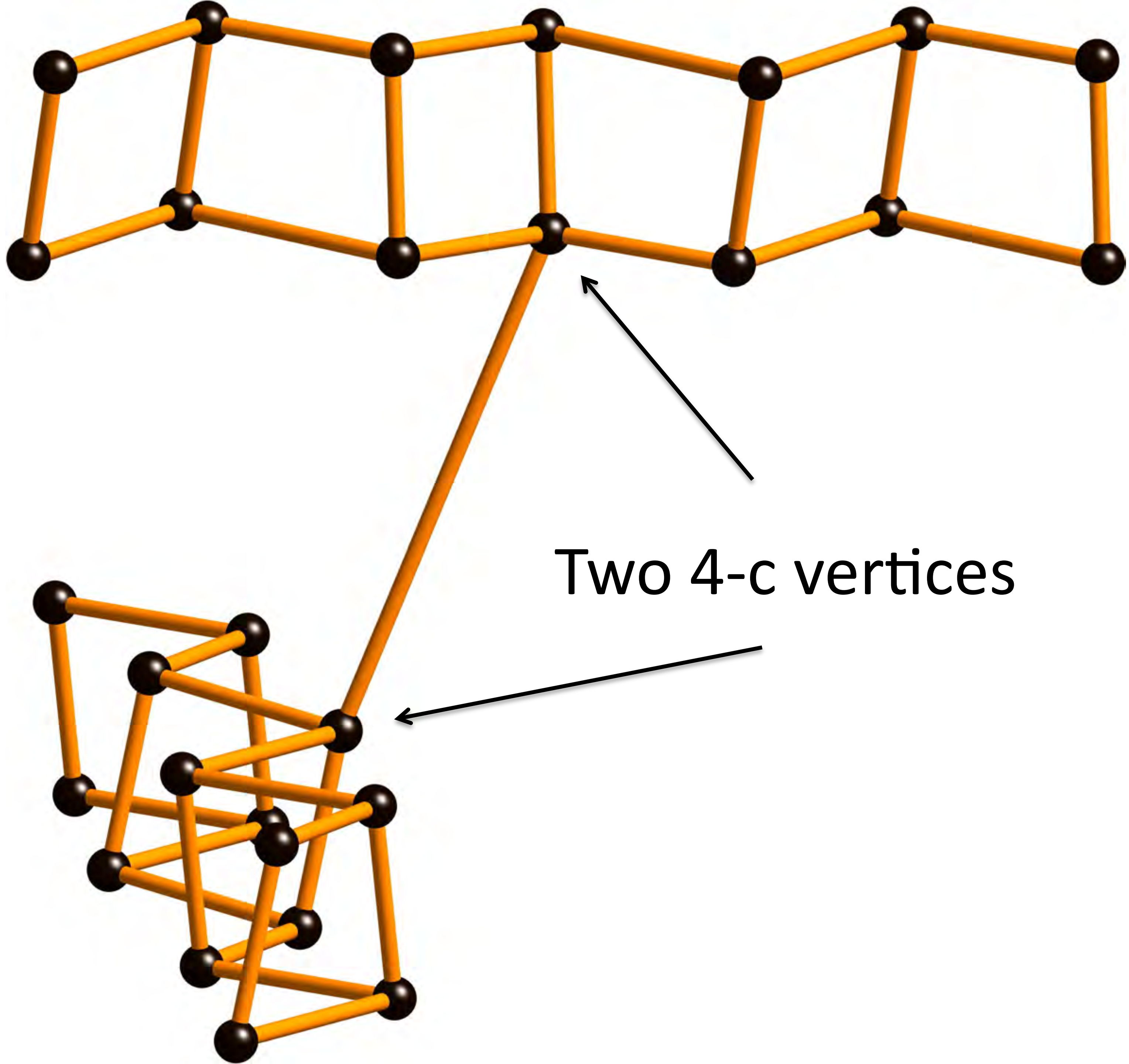
large black balls are points of extension



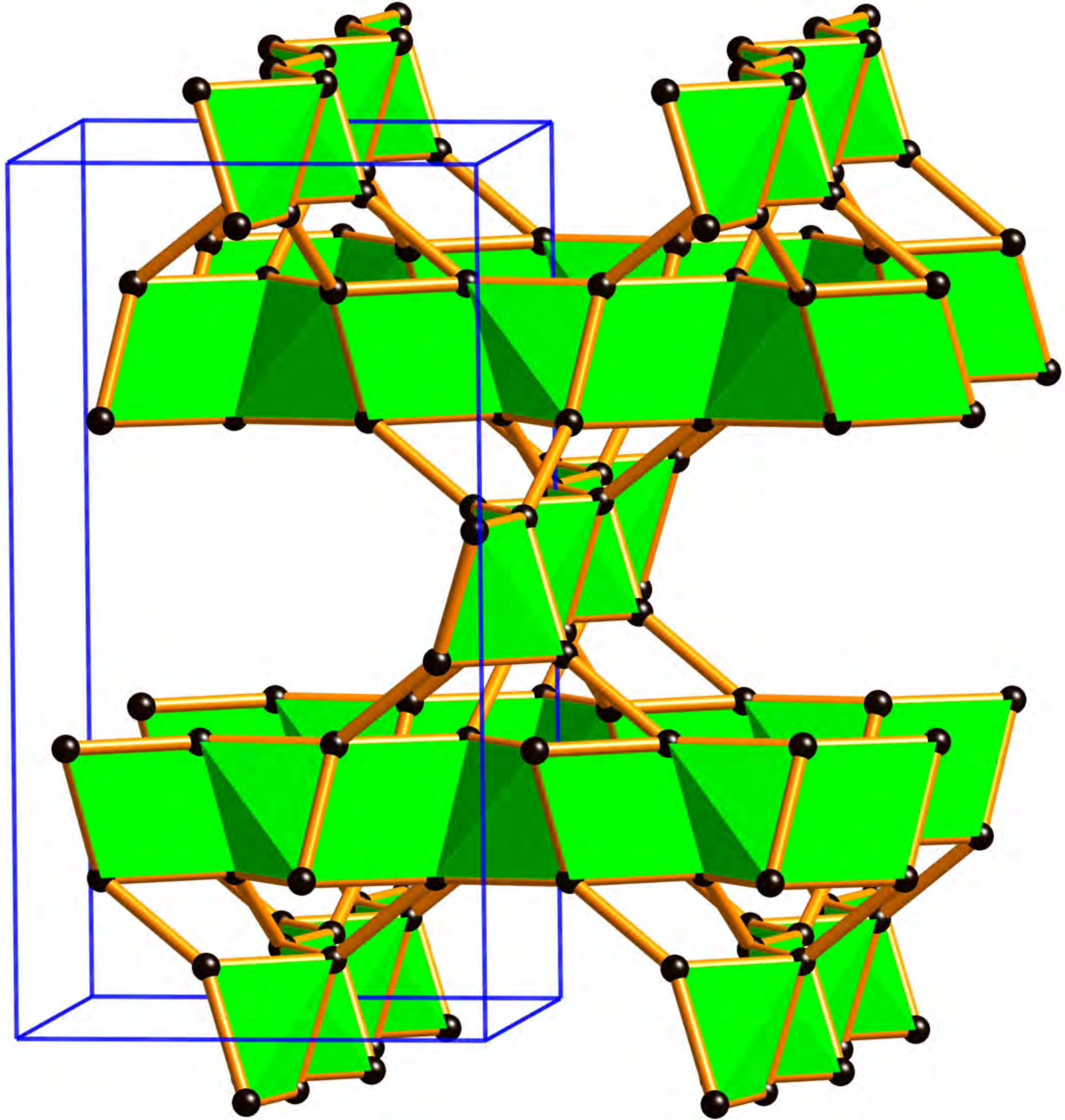


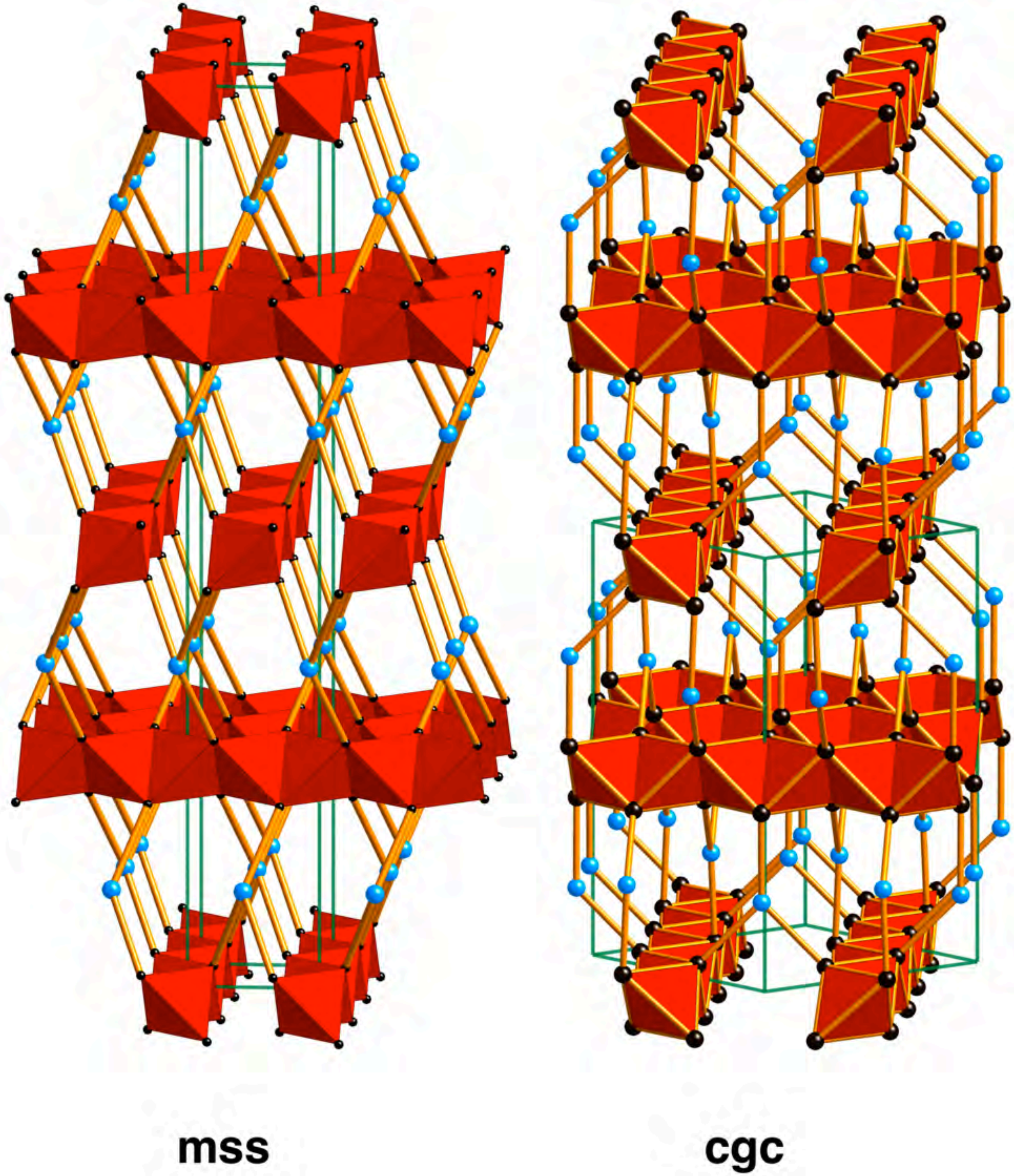


rods are not parallel


Two 4-c vertices

The binodal net **cua**

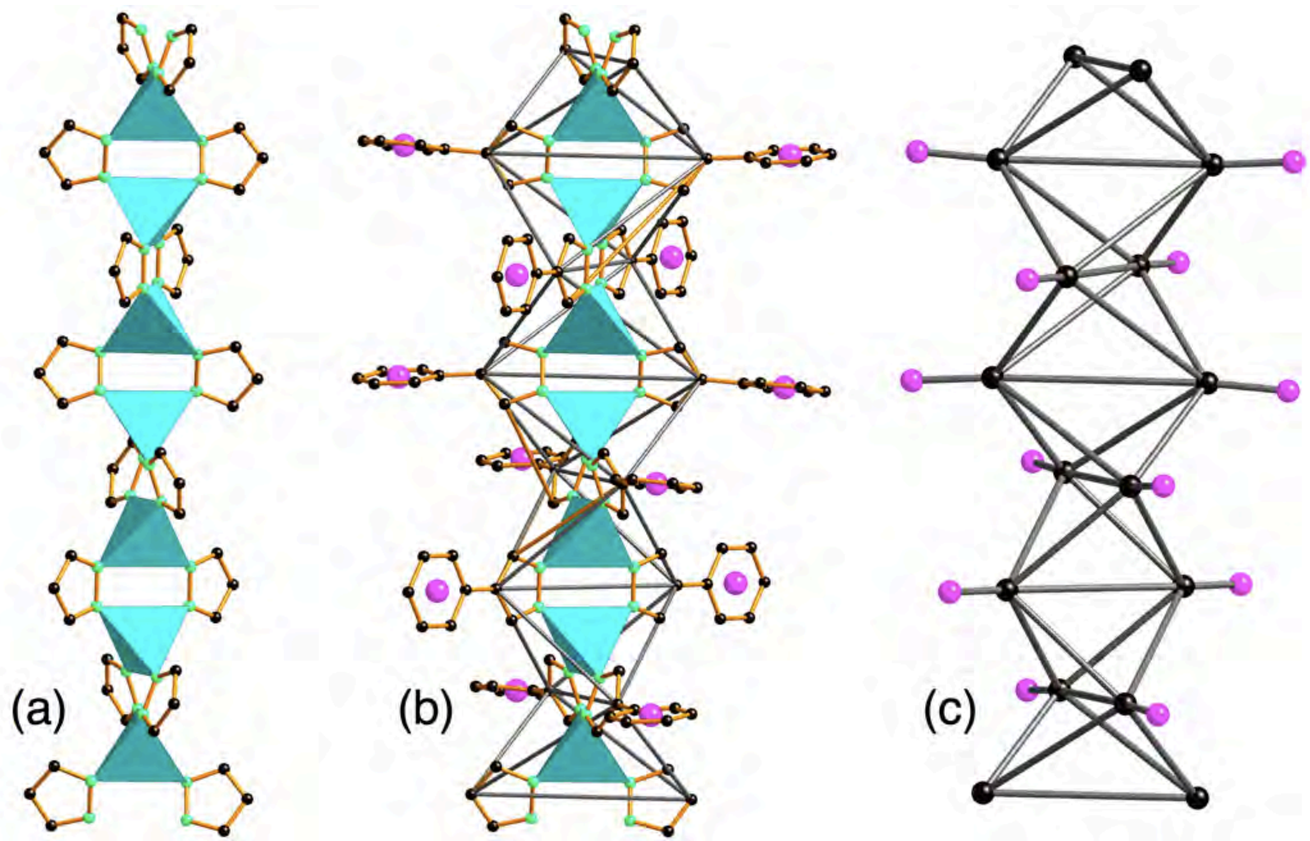




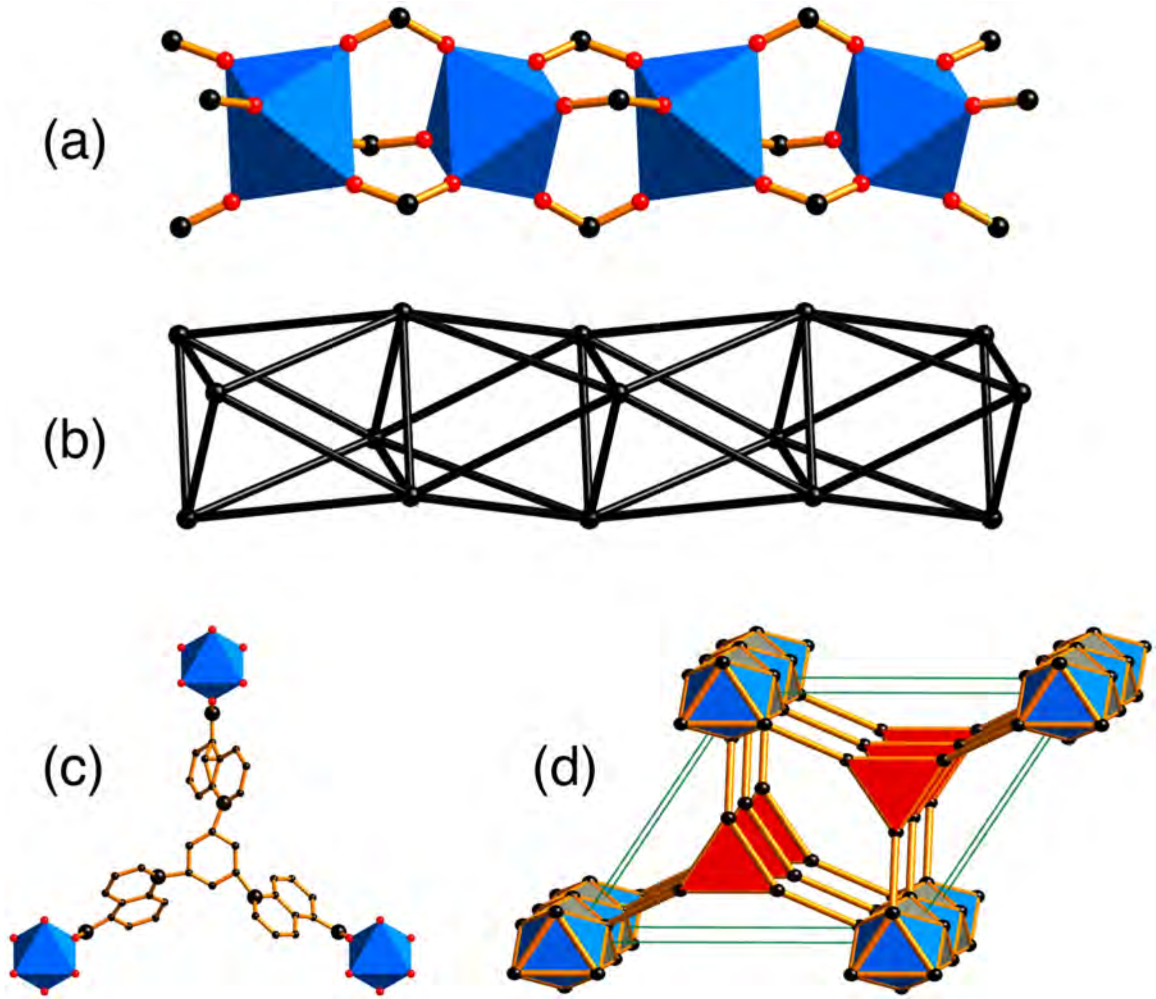
two distinct tetragonal rod packings

rods are edge-shared tetrahedra

pyrazole-based
linker



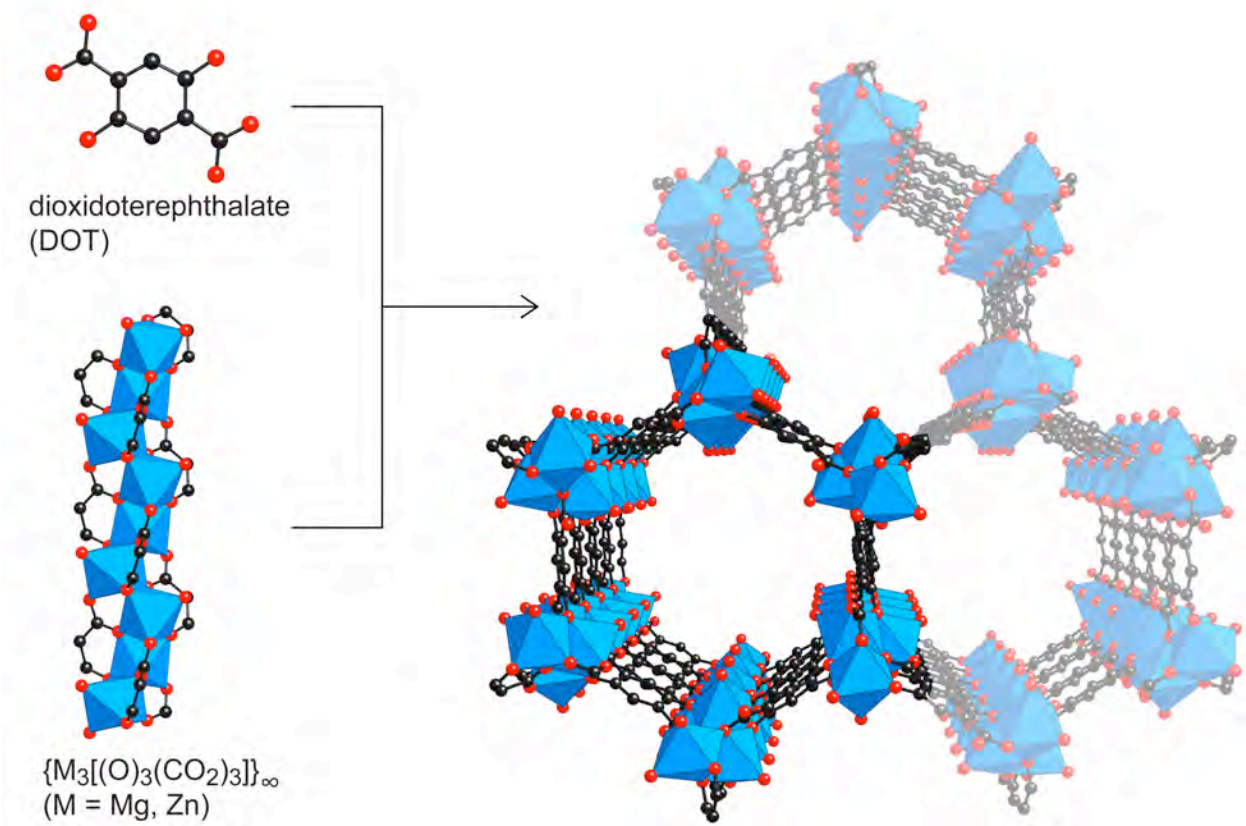
rod points of extension
are edge-sharing tetrahedra



Because we are taking points of extension as nodes of the net, it is in a sense alredy augmented. accordingly represent the 3-c ode a triangle

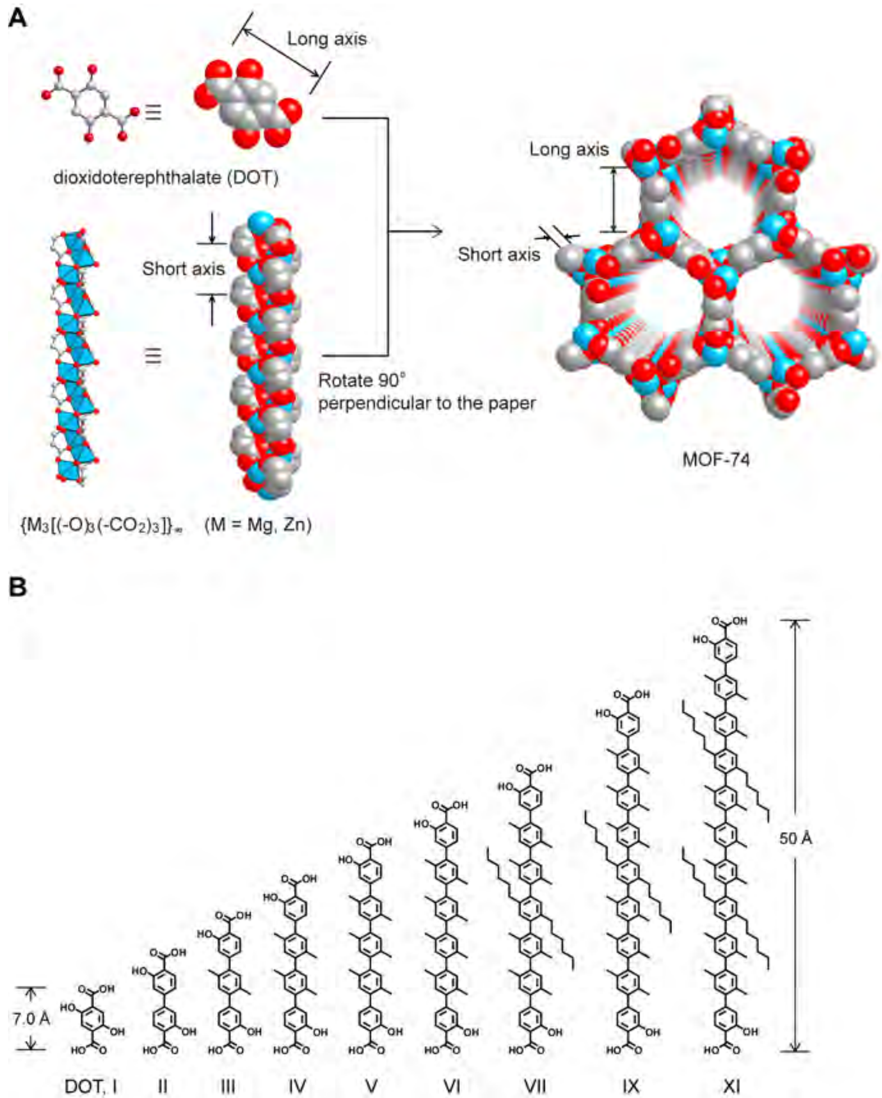
UTSA-30 Banglin Chen group. Net is **hyb**
Chem. Commun, 49, 10856 (2012)

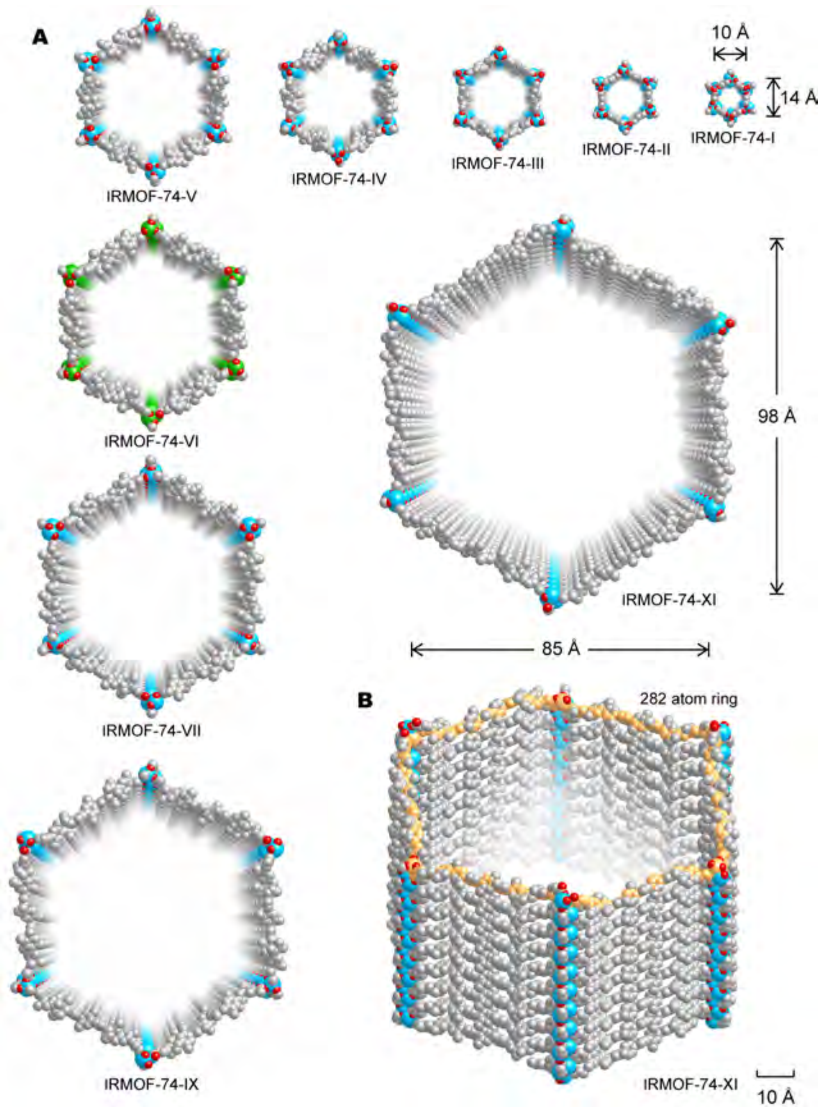
MOFs with rod SBUs



MOF-74. One of the most promising materials for gas storage/separations

N. Rosi, J. Kim, M. Eddaoudi, B. Chen, M.O'Keeffe, O. M. Yaghi, JACS 2005, 127, 1504

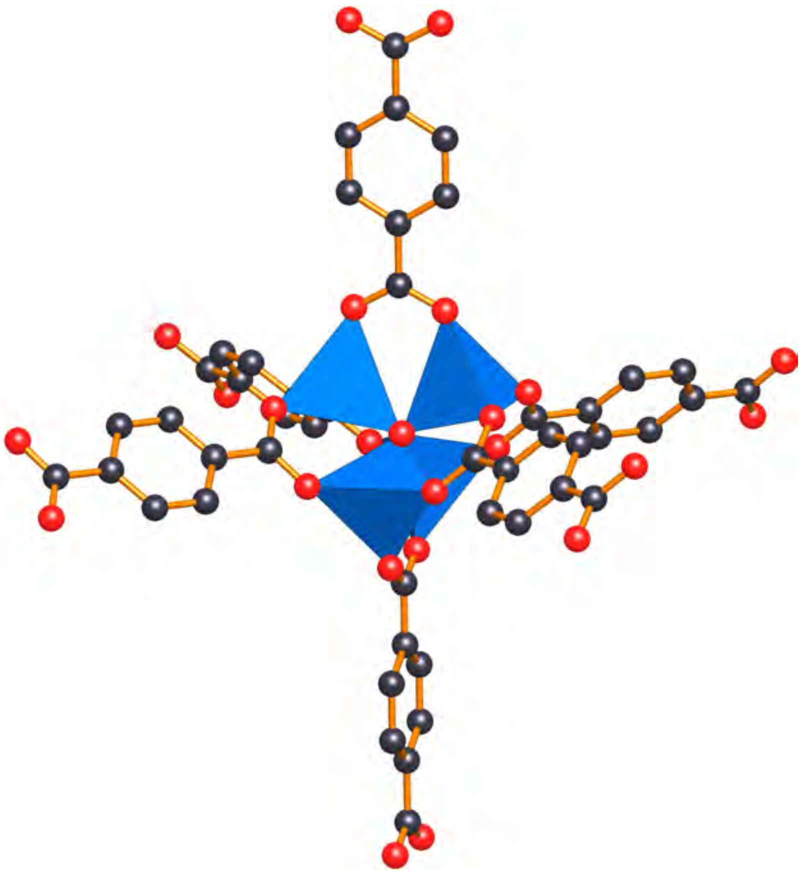

A
Long axis
dioxidoterephthalate (DOT)
Short axis
Rotate 90°
perpendicular to the paper
Long axis
Short axis
MOF-74
{M3[(-O)3(-CO2)3]}∞ (M = Mg, Zn)
B
7.0 Å
50 Å
DOT, I
II
III
IV
V
VI
VII
IX
XI

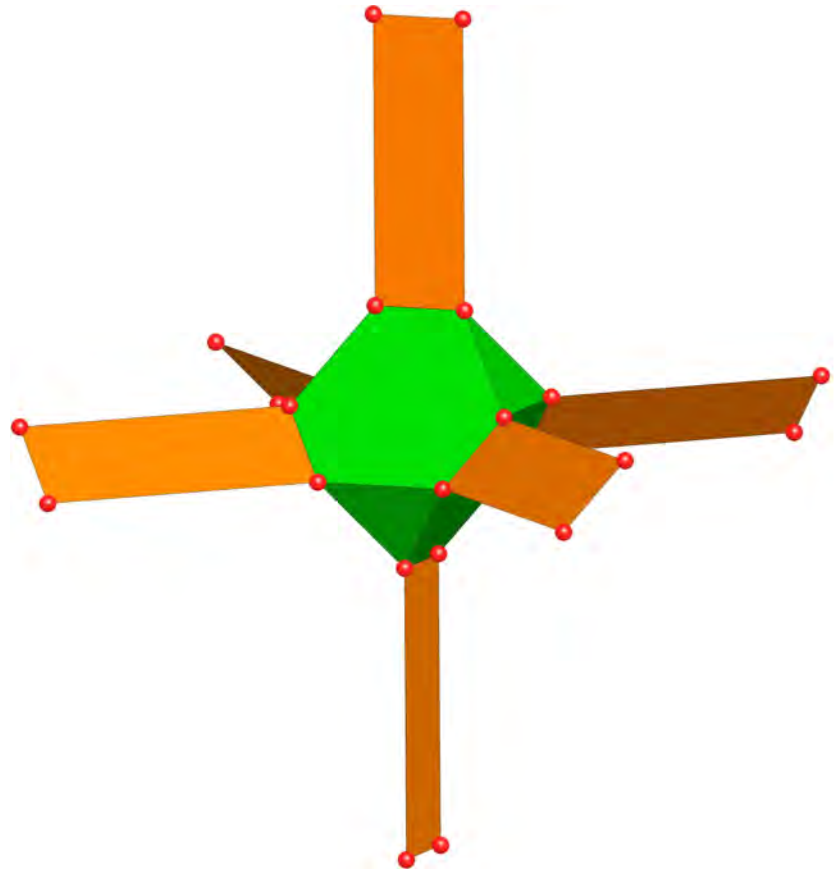


H. Deng, S. Grunder,
K. E. Cordova, C. Valente,
H. Furukawa, M. Hmadeh,
F. Gandara, A. C. Whalley,
Z. Liu, S. Asahina, H. Kazumori,
, M. O'Keeffe,O. Terasaki,
J. F. Stoddardt, O. M. Yaghi.
Science May 25, 2012.

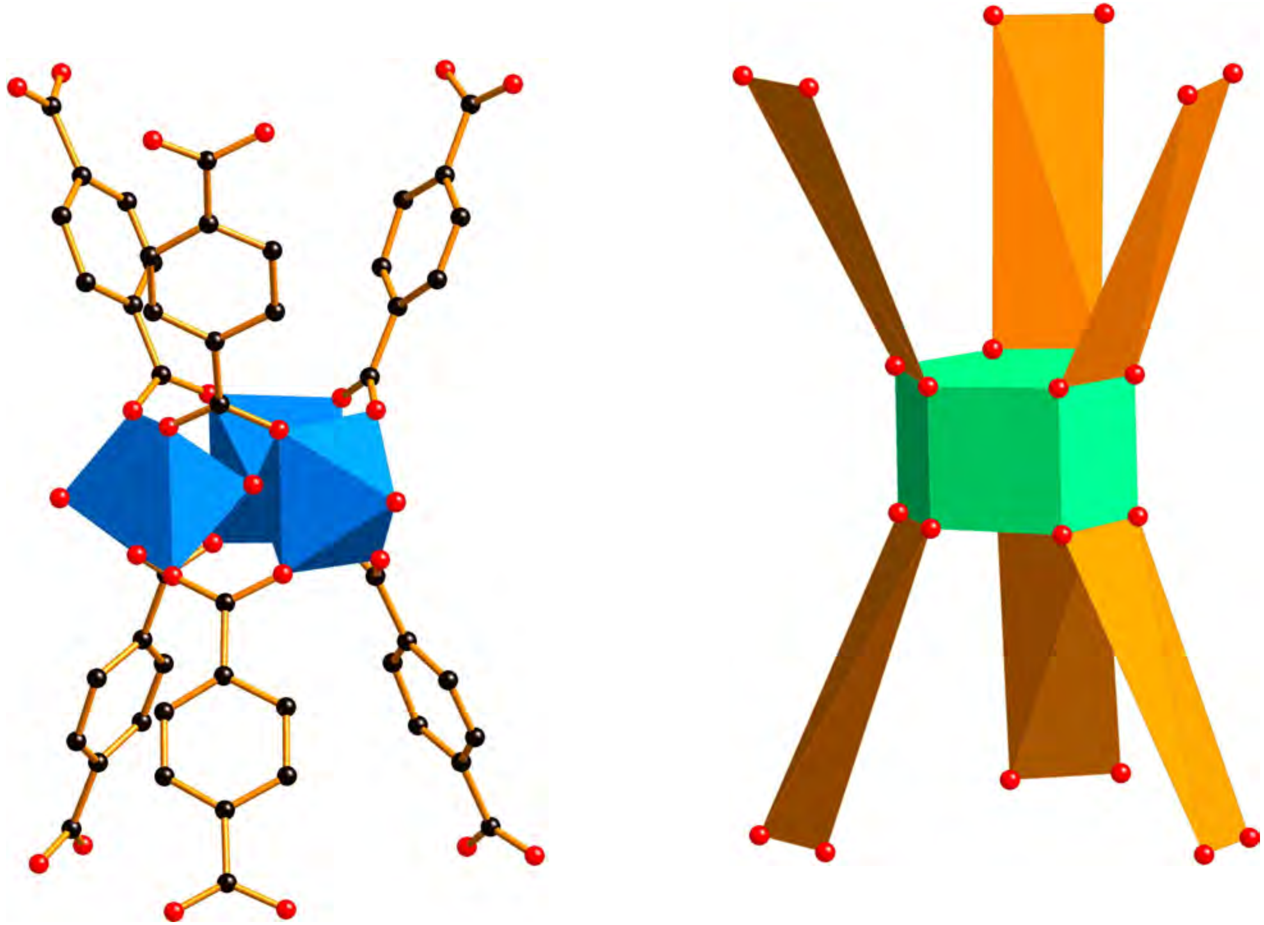
“breathing” MOFs, especially rod MOFs
G. Férey & C. Serre, *Chem. Soc. Rev*. 38, 380 (2009)

Special case of flexibility
We can consider carboxylate link as a hinge
Berend Smit *et al. JACS* 136. 2228 (2014)

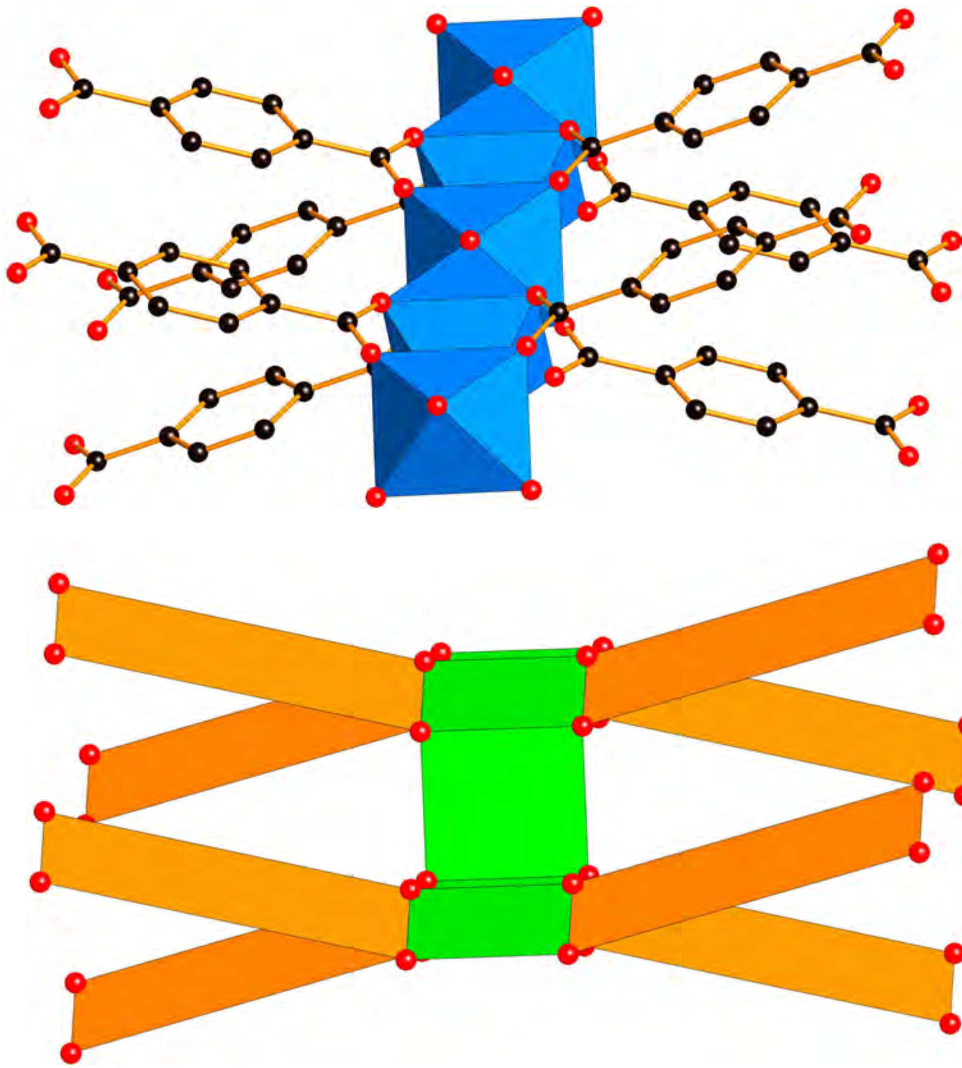




The case of MOF-5 planar terephthalate groups non coplanar (and opposed) hinges - RIGID



The case of MOF-2355 terephthalate again
6-c acs net - hinges in parallel planes - FLEXIBLE

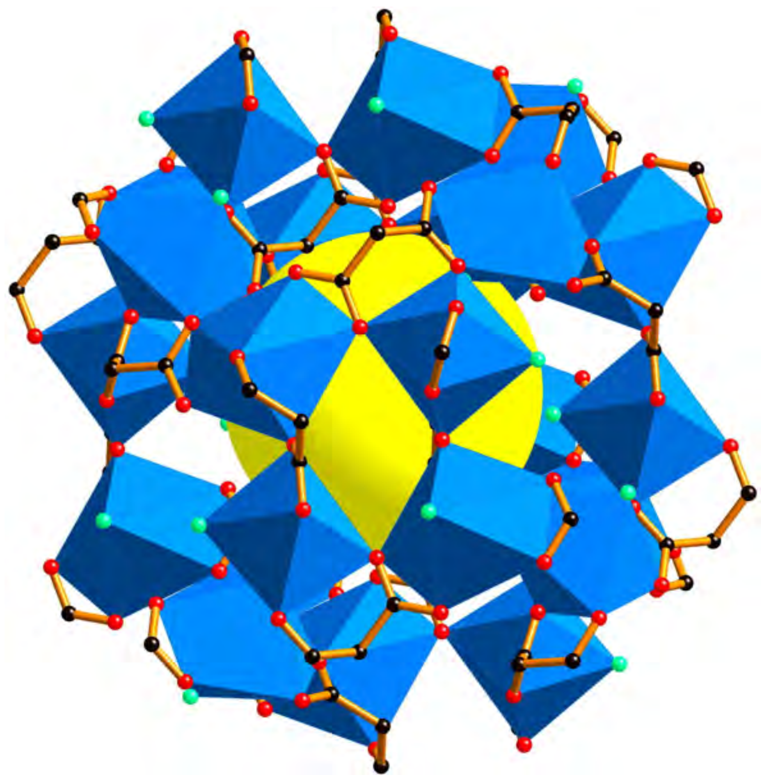


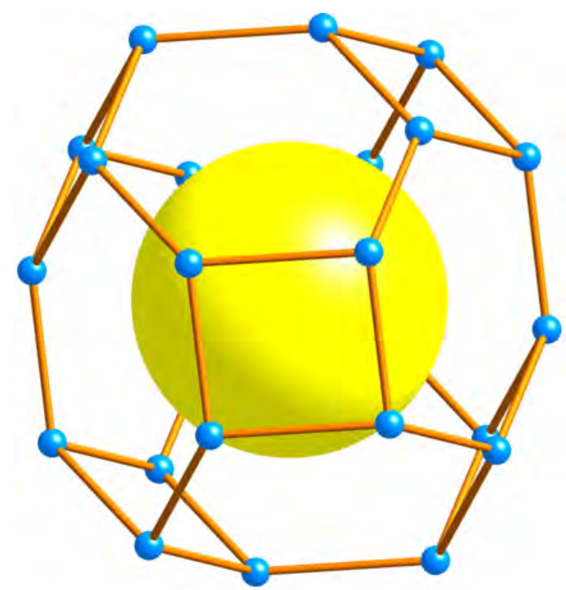
MOF-61, MOF-71, MIL-47, MIL-53 all have the **sra** net.

MIL-53 is the classical "breathing MOF"

rod MOFs. MOF-71 terephthalate again
4-c **sra** net - hinges in parallel planes - FLEXIBLE

3-periodic “SBU” Cd malonate



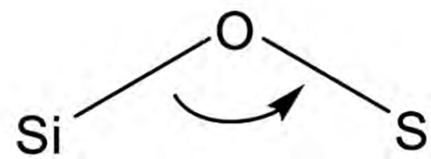


S. Yuan et al, *Acta cryst*. 2012 C68, m57 **sod** net

Zeolitic Imidazolate Frameworks (ZIFs)

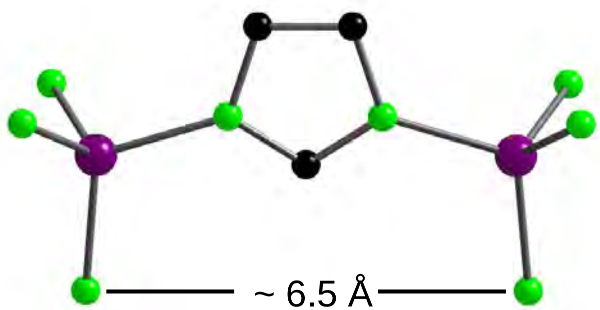
145 °
M - IM - M

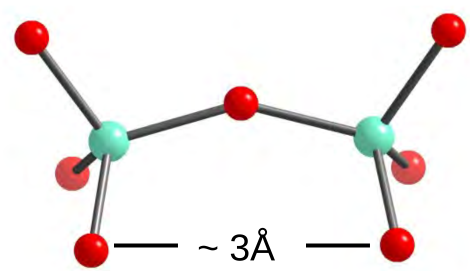
1



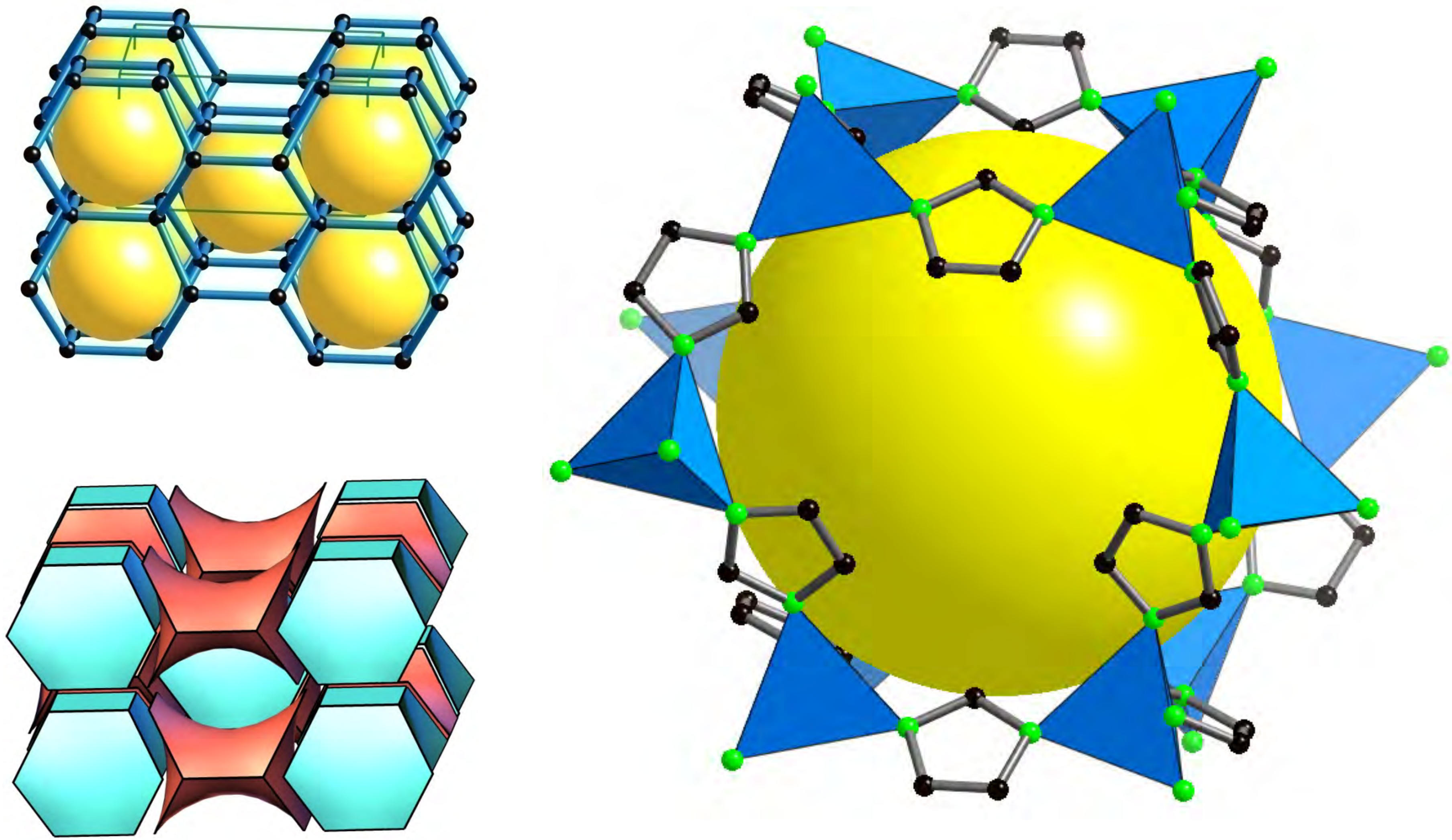
145 °
Si - O - Si

2

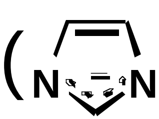


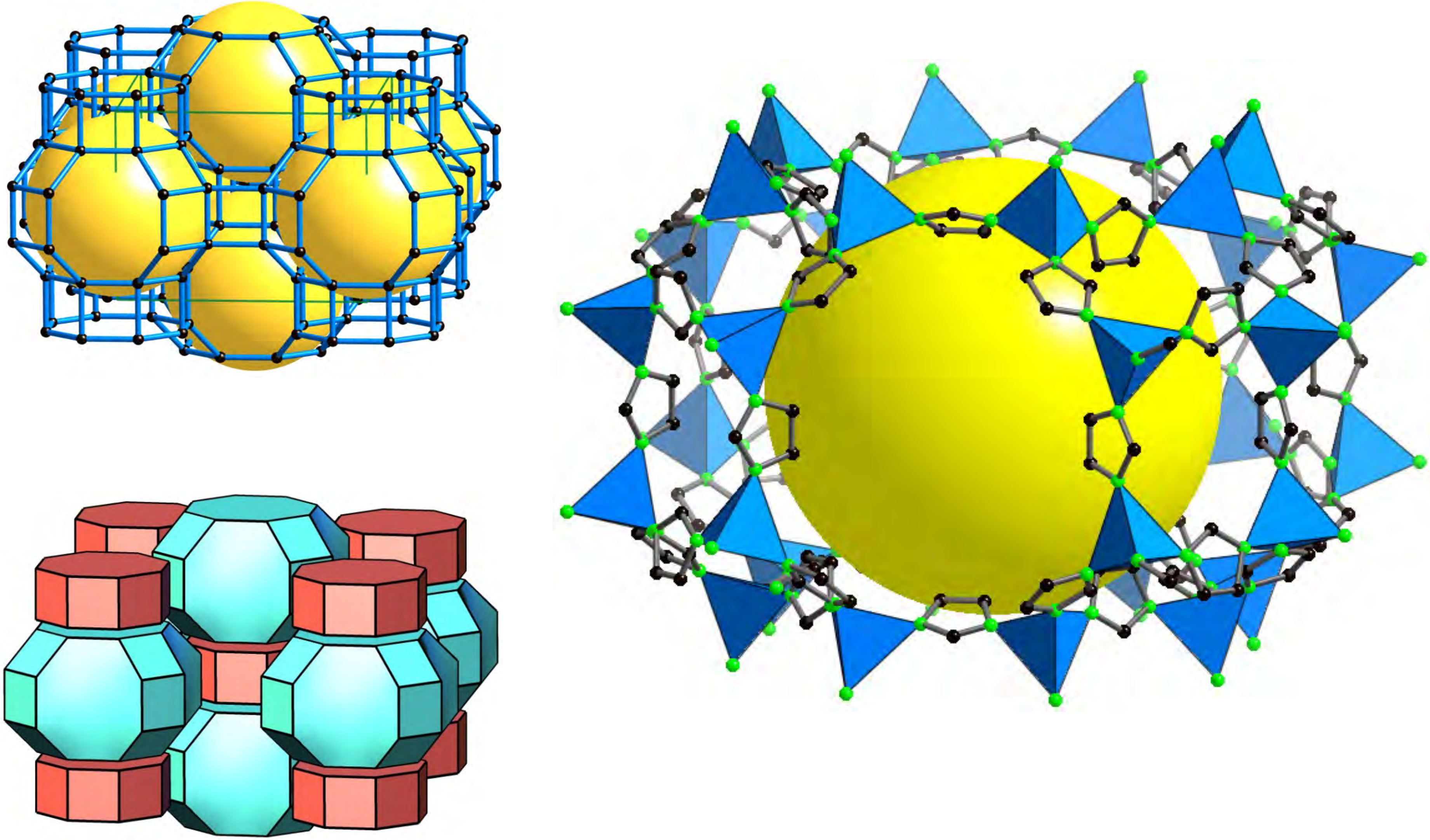


Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *PNAS,* 2006, 103, 10186.
A. Phan, C. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe, O. M.Yaghi, *Accts. Chem. Res*. 43, 59 (2010)

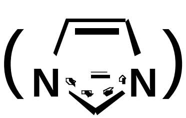


ZIF-2 (crb)

Zn()$_2$

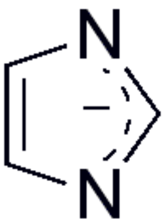


ZIF-10 (mer)

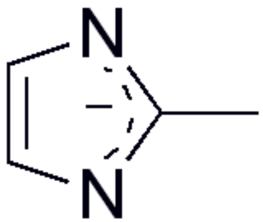
Zn(

$)_2$

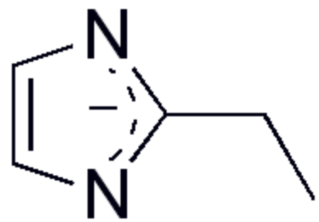
Extensive set of functionalized imidazolate links e.g.:



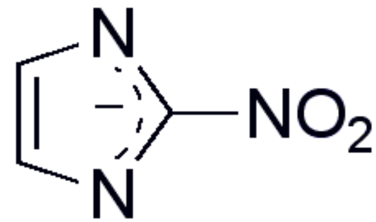
IM



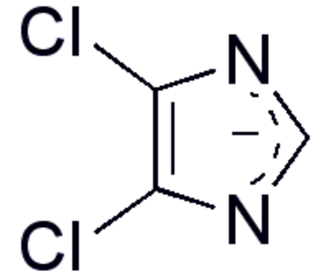
mIM



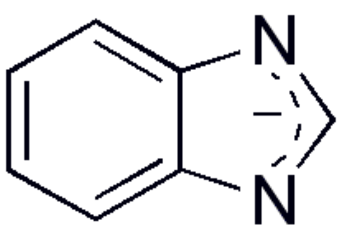
eIM



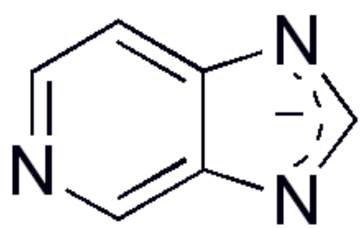
nIM



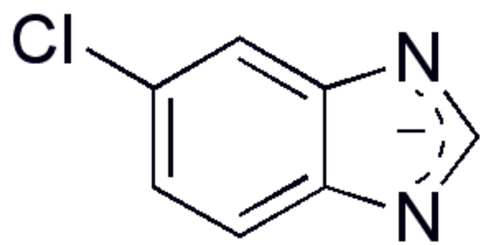
dcIM



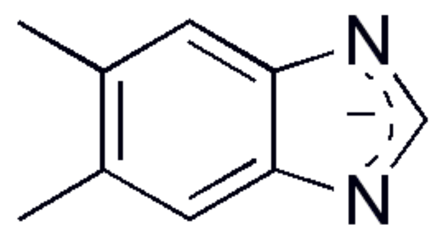
bIM



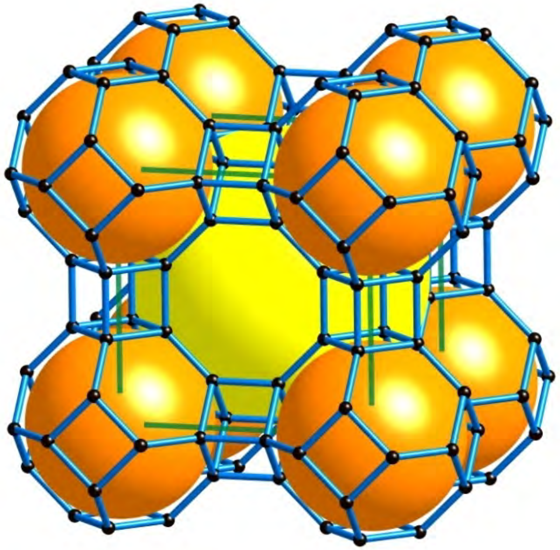
Pur

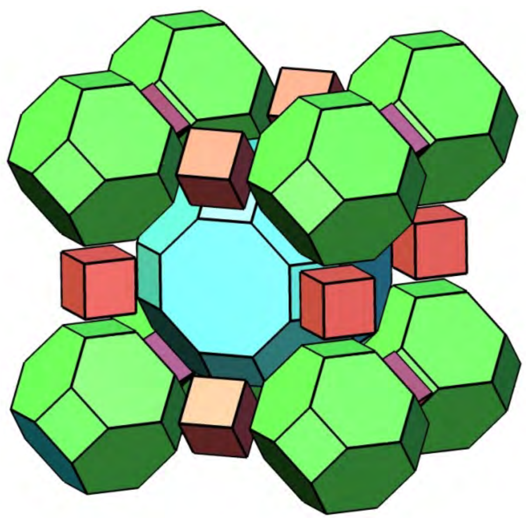


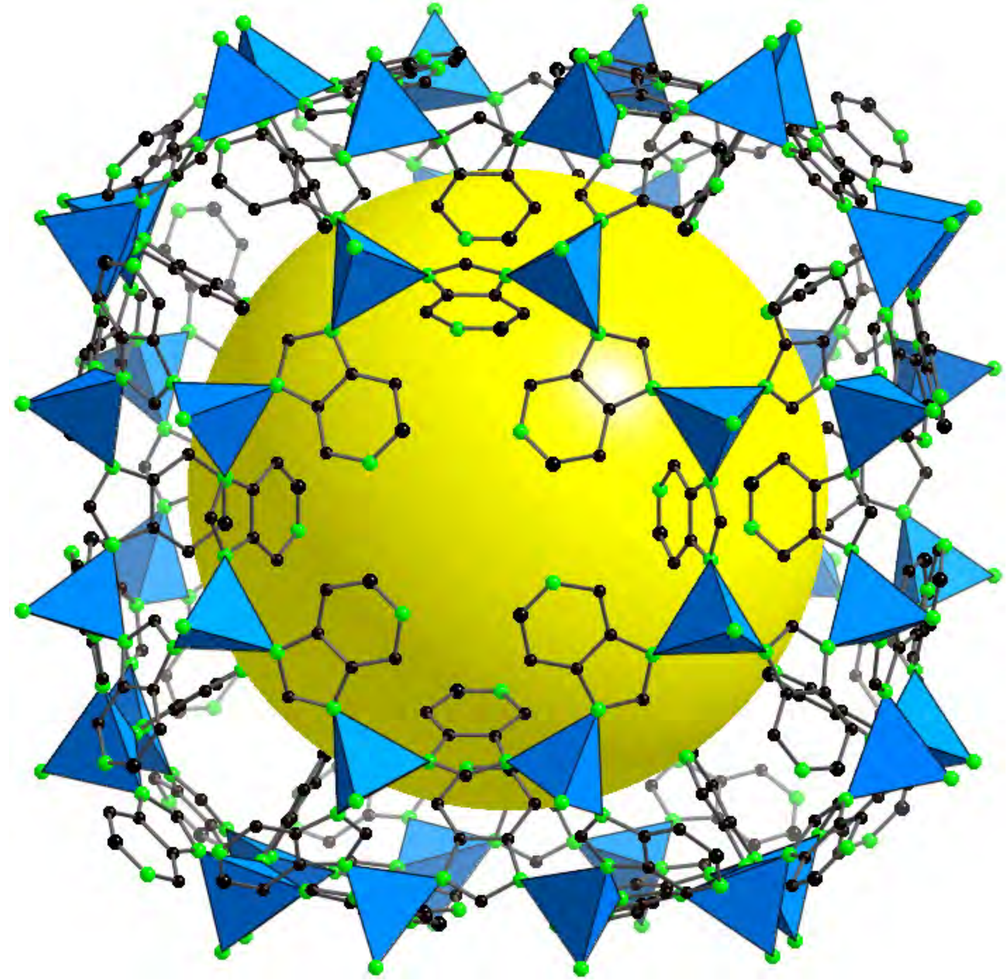
cbIM



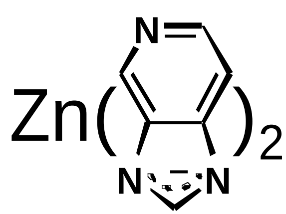
mbIM



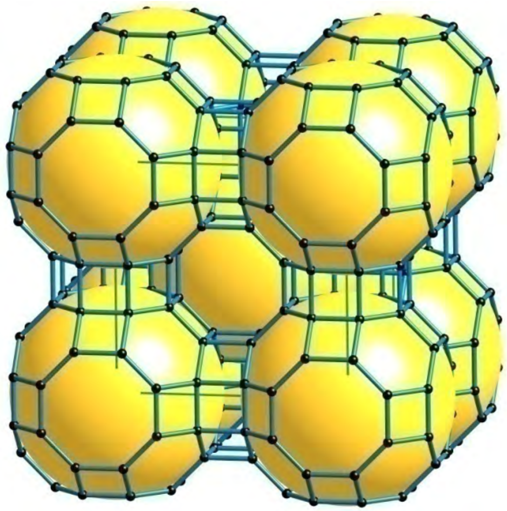


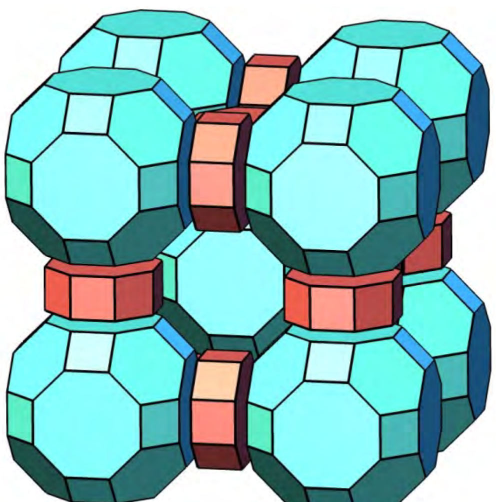


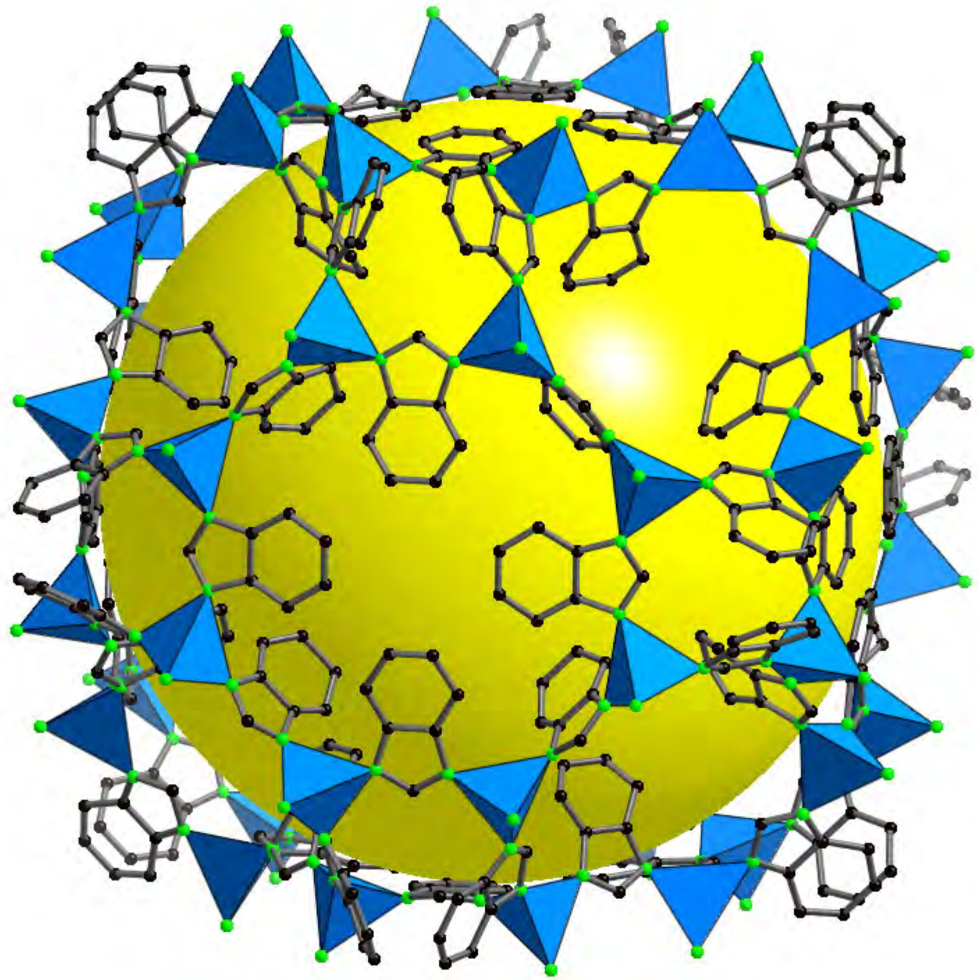
ZIF-20 (lta)



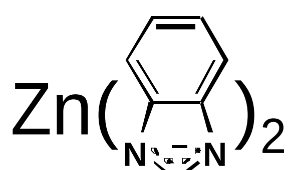
O. M. Yaghi, et al.
Nature Materials
2007, **6**, 501



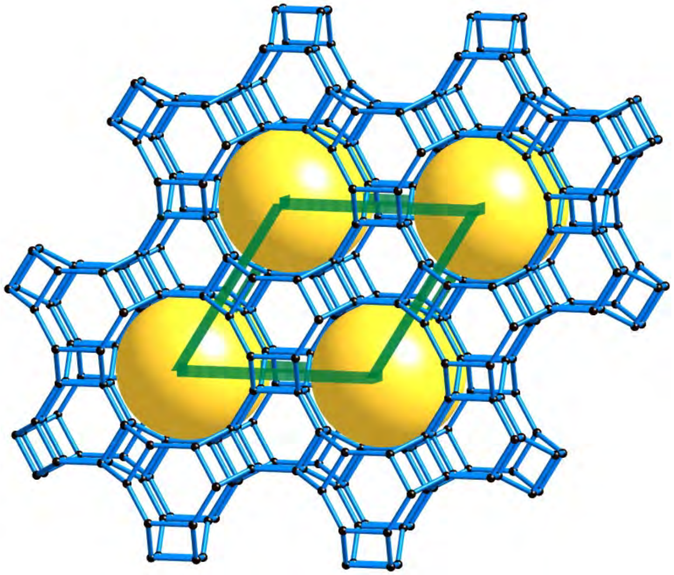


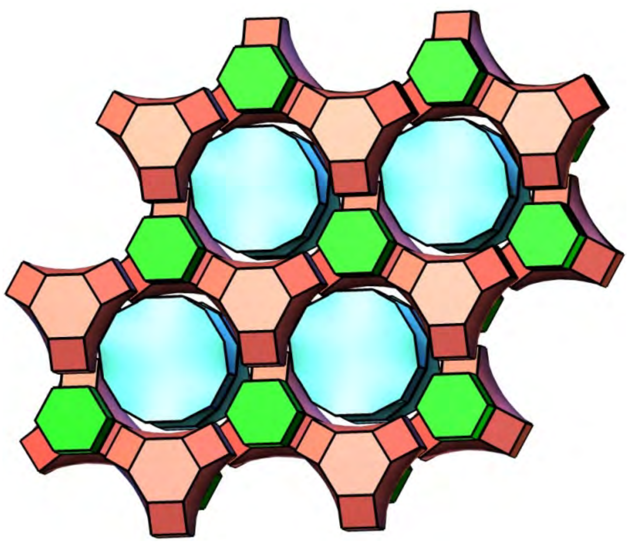


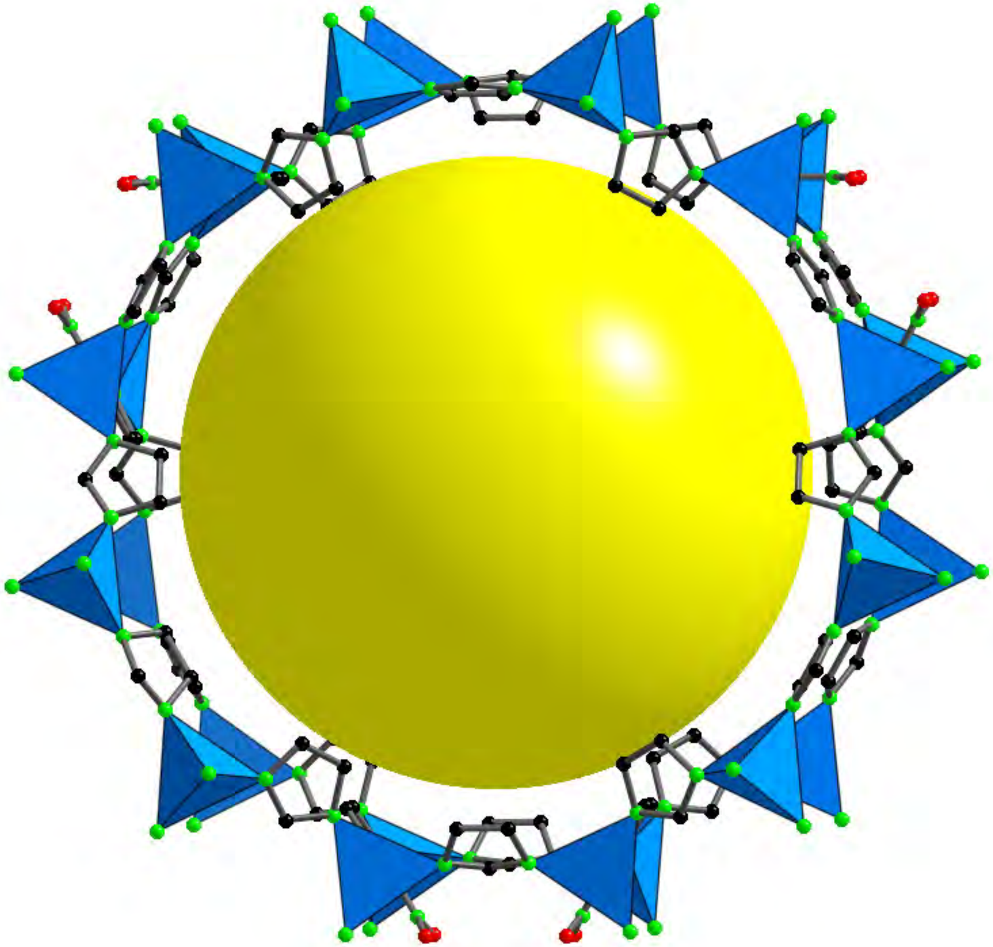
ZIF-11 (rho)



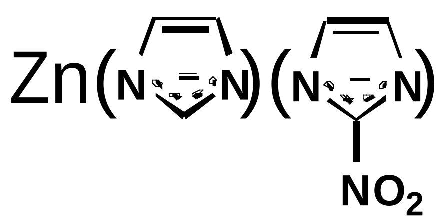
O. M. Yaghi, et al.
Science
2008, **319**, 939



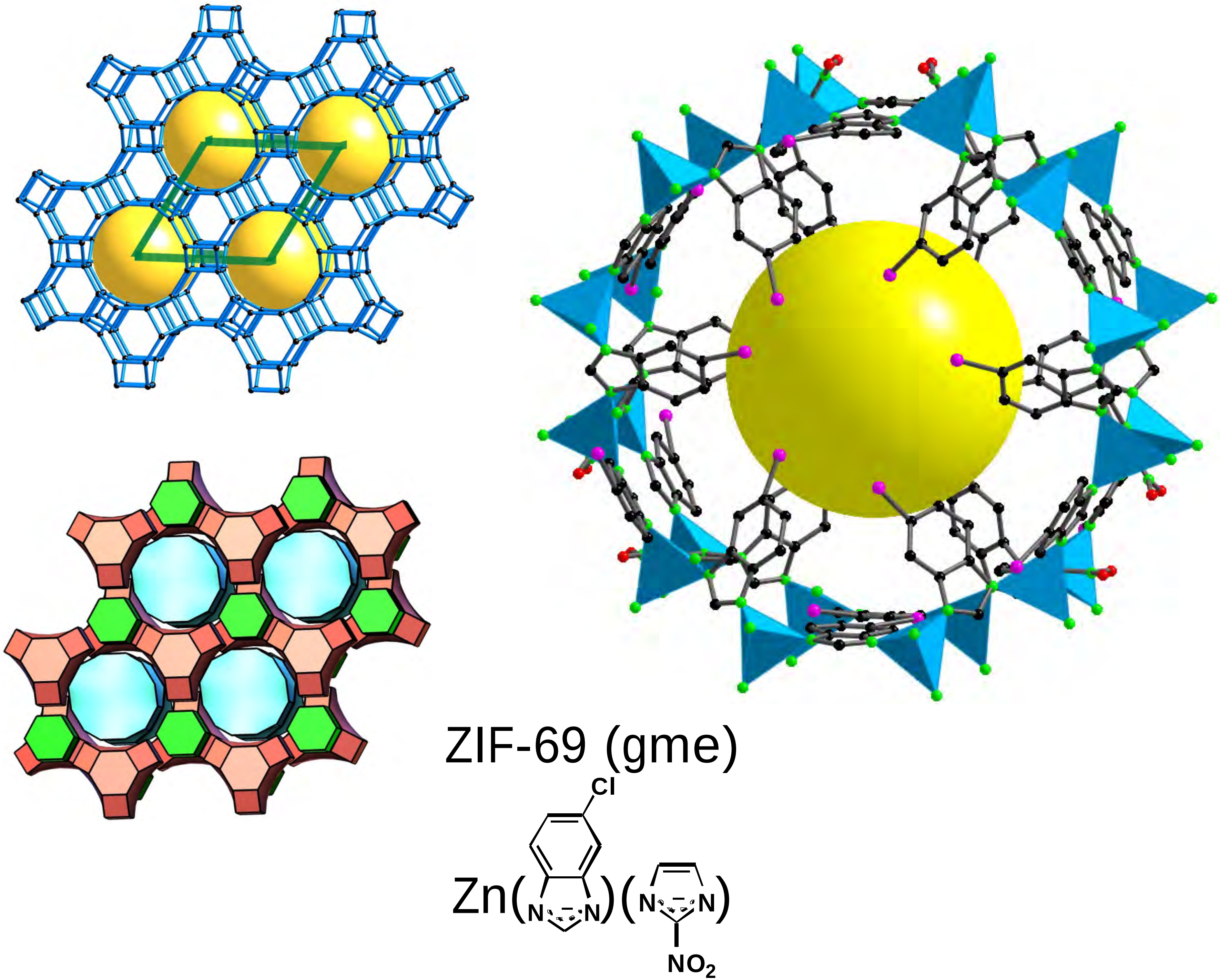




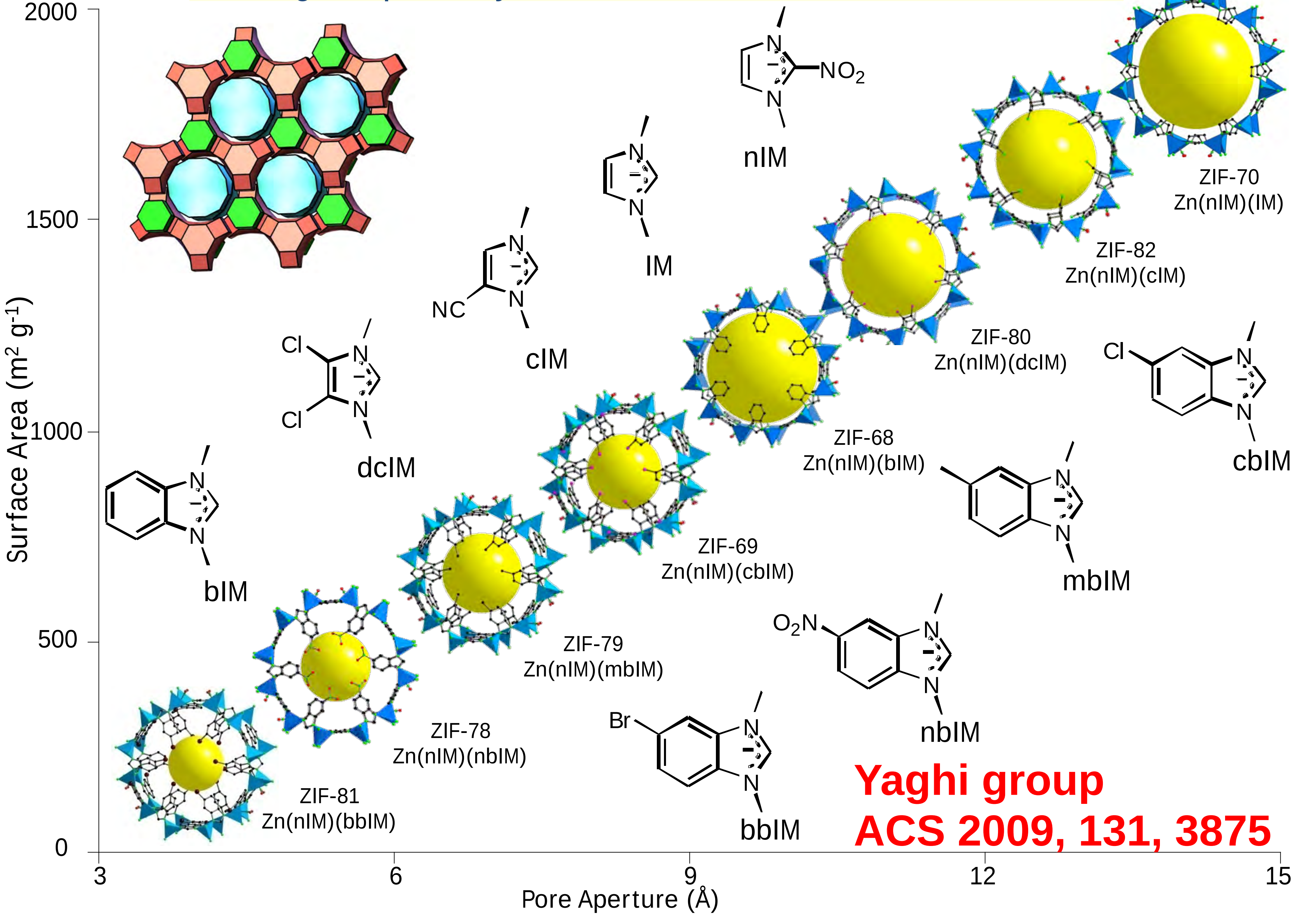
ZIF-70 (gme)



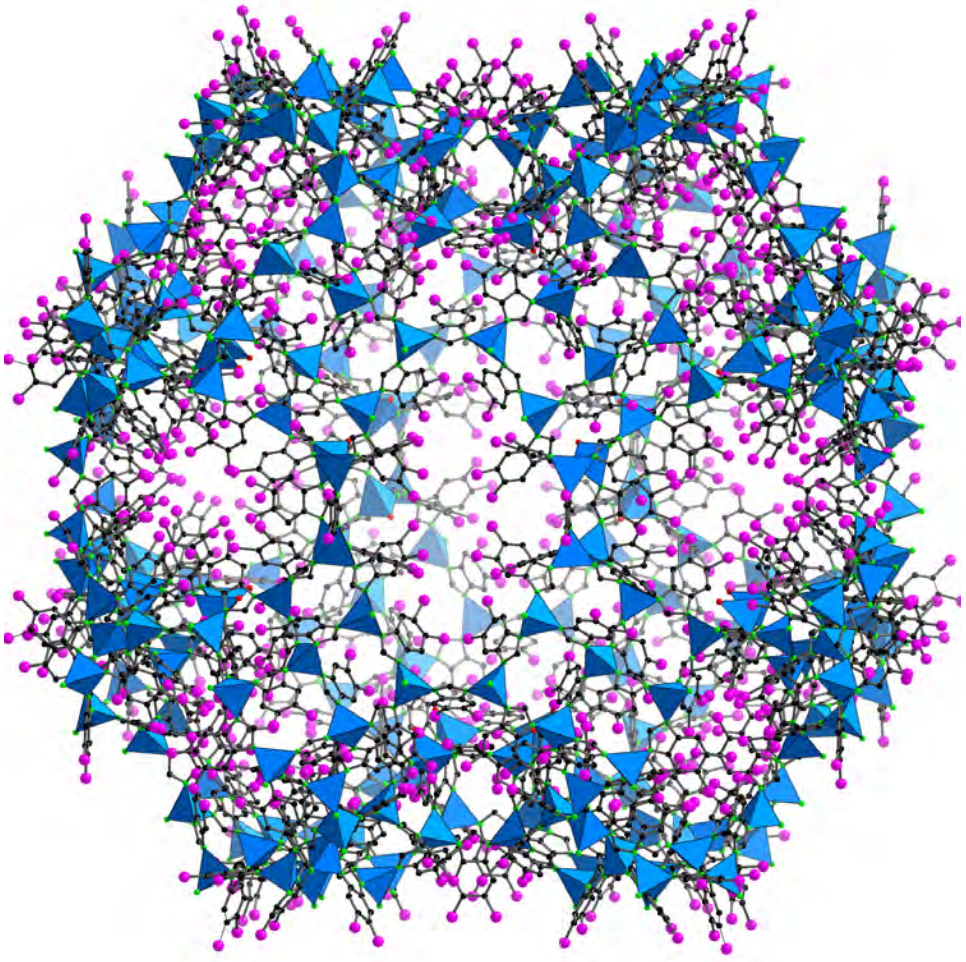
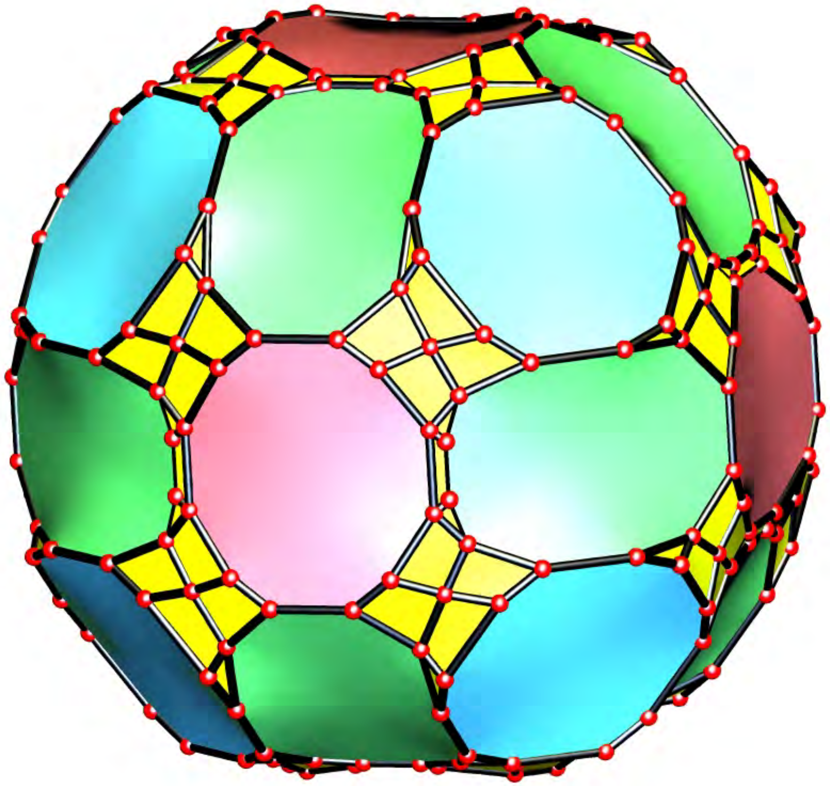
O. M. Yaghi, et al.
Science
2008, **319**, 939


ZIF-69 (gme)
Cl
Zn
N
N
N
N
NO2

Designed porosity in zeolitic imidazolate frameworks



Giant ZIFs - the cage in ZIF-100

M. O'Keeffe, O. M. Yaghi et al. *Nature*. 2008, **453**, 207 end