COORDINATION POLYMERS(CPs)

Professor: José Antonio Real

Colaborator: Carlos Bartual Murgui

ADVANCED INORGANIC CHEMISTRY
COORDINATION POLYMERS(CPs)

Resultados del Aprendizaje

- Know the contextual facts, ideas and concepts that have paved the way for the chemistry of CPs metal-organic frameworks (MOFs).

- Identify the most relevant types of CPs/MOFs and their intrinsic properties (rigidity, flexibility, interpenetration, porosity, etc).

- Analyse relevant types of bridging ligands, nature of involved metal ions and introduce the concept of secondary building units (SBUs).

- Describe and analyse the most representative 0-3Dimensional objects in terms of geometry and topology.

- Account of the most relevant MOFs and their physico-chemical properties (inclusion, adsorption, selectivity, reactivity, chirality, luminiscence, magnetism, etc).

- Methods of synthesis.

INDEX PART ONE

INDEX PART TWO

Description, classification, topology of nets and significant examples

- Concept of network as a set of nodes and links. Schläfli's topological symbols
    - a) Regular uninodal systems:
        - i) Platonic solids.
        - ii) Two-dimensional networks.
    - b) Semi-regular systems
        - i) Archimedian and catalan solids.
        - ii) Two-dimensional networks.

- Topological analysis: Euler and Schläfli's formulas.

- Description and symbols for 2D, 3D networks and polihedra
    - i) Schläfli's symbol.
    - ii) Vertex symbol (M. O'Keeffe).
    - iii) Point symbol (A. F. Wells).

- Examples of most common networks found in CPs/MOFs

NbO, Sodalite, Diamond, Quartz (SiO_2), Moganite (SiO_2), $SrAl_2$, tri- and tetra-connected nets, etc

- Means available for the topologycal analysis of networks derived from CPs/MOFs

- Bibliography of interest on coordinación networks and polymers

INDEX PART THREE

Review of significant MOFs

- Introduction: i) Motivations that have led to the explosive expansion of the research area of MOFs; ii) Importance of the nature of the node (fragility vs robustness). Examples of simple SBUs ($[Fe(tvp)_2(NCS)_2$ y $Fe(piracina)[M^{II}(CN)_4]$).

- Selection of networks based on polynuclear SBUs :

i) MOF-2.
ii) HKUST-1.
iii) MOF-14 (extension of the trivalent node of HKUST-1 and interpenetration).
iv) Importance of bridge geometry : OD→2D→3D.
v) MOF-5. Properties.
vi) Iso-reticular series IRMOFs.
vii) MOF-177.
viii) Series MIL: MIL-101 y MIL-5 (flexibility).
ix) Series UiO y PCN based on Zr^{IV} SBUs
x) Serie NU-nº
xi) MOFs with unsaturated coordination centers : $H_2[Co_4O(TAT)_{8/3}]_n$.
xii) ZMOFs: $[Cu^I(pyrimidine)_2]_n(BF_4)$; $[Co_5(imidazole)]_n$; $[Zn(bim)_2]_n$.
xiii) ZIFs
xiv) Covalent organic frameworks (COFs).

INDEX PART FOUR
SYNTHESIS OF PCS/MOFS

INDEX PART FIVE   MOF AND PHOTONICS

1- Inclusion of soluble fluorophore. System $[Cd_3(bpdc)_3(DMF)_3]$/Rhodamine-6-G.

2- Inclusion of sublimable molecules in MOF-5, MOF-177, UMCM-1 y MIL-53 (Al).

3- Doping an anionic MOF with lanthanides in MOF $\{[NH_4]_2[Zn(btc)]\cdot 6H_2O\}_n$.

4- Exciplex emission induced by guest molecules. Charge transfer:

4-a) System $\{ [Zn(bipy)]_{1.5}(NO_3)_2\}\cdot CH_3OH\cdot 0.5$pyrene.
4-b) System $[Zn_2(adc)_2(dabco)]_n$ /aniline.
4-c) Molecular decodification in MOF $[Zn_2(bdc)_2(dpNDI)]_n$.

5- Photocatalysis in MOF UiO-67. Incorporation of catalytic centres in the pores of the network:

5-a) Oxidation of H_2O.
5-b) Reduction of CO_2.
5-c) Reduction of H^+.

6- Photo-oxidation of alcohols. Other photoinduced reactions.

Advanced Inorganic Chemistry

Chapter 4th: Coordination Polymers

Part 1

Instituto de Ciencia Molecular
Departamento de Química Inorgánica
Universidad de Valencia

INDEX CHAPTER ONE

- Introduction. Definition of coordination polymer.

- Coordination compounds versus inorganic solids (essential differences).

- Terminology: Coordination polymers (PC) versus metal-organic frameworks (MOFs).

- Historical Background:
  - i) Prussian Blues.
  - ii) Hofmann Clathrates.

- Motivations that stimulated the development of CPs.
  - i) Crystal engineering: “mineralomimetic” view of CPs.
  - ii) Molecular magnetism.
  - iii) Relationships between crystal engineering, supramolecular chemistru and metalo-supramolecular chemistry. Examples.

- Concept of Net as a tool to describe and design CPs/MOFs:
  - i) First examples arisen from the structure of diamond.
  - ii) Definition of net.
  - iii) Geometry versus topology. Bridging ligands more investigated.
  - iv) Conectivity and molecular geometry : building blocks and secondary building units (SBUs). Examples.

BIBLIOGRAFÍA

Libro- S. R. Batten, S. M. Neville, D. R. Turner; *Coordination Polymers*. Design, Analysis and Application, RSC Publishing, 2009………………

Libro- *The Chemistry of Metal-Organic Frameworks: Synthesis, Characterization, and Applications Wiley Online Library, 16 JUN 2016, Edited by S. Kaskel* (libre todos los pdf en internet: http://onlinelibrary.wiley.com/book/10.1002/9783527693078).

Revista- *Chemical Reviews* 2012, Vol. 112 (2), pag. 673-1268. Contiene unos 18 artículos escritos por los grupos más activos en el campo y discute aspectos: Estructurales; de simulación de adsorción (H_2, CH_4, CO_2, C_2H_2); adsorción de CO_2, de H_2 de hidrocarburos, de alcoholes; diseño de MOFs para procesos de separación química, métodos de síntesis de MOFs; modificación post-sintética de MOFs; MOFs basados en ligandos azolato; crecimiento epitaxial de MOFs en films nanométricos; propiedades ópticas y optoelectrónicas en MOFs; MOFs y sensores químicos, MOFs y luminiscencia, propiedades ferroeléctricas en MOFs, MOFs homoquirales, MOFs y biomedicina.

Revista- *Chem. Soc. Rev*. 2014, Vol. 43,…..; ZMOFs; nuevas rutas de diseño; POMs; transformaciones estructurales y RX; membranas y separación; MOFs basados en elementos del grupo 3p; MOFs y flexibilidad; adsorción de H_2O; catálisis heterogénea; propiedades electrónicas y optoelectrónicas, fotosíntetsis y fotocatálisis; etc.

Revista- Trabajos originales o de revisión que se irán citando.

Introducción Polímeros de Coordinación (PC)
Redes Metal-orgánicas (MOFs)

Definition of CP/MOF

- A CP/MOF can be defined as an array of metallic ions held together through bridging ligands which afford one-, two- or thre-dimensional infinite networks .

- Metal ions are mostly transition metals (1st, 2nd and 3rd series), lanthanides, Zn, Cd and Hg, Al and alkaline earth metals and to a lesser extent alkaline.

- Ligands are generally constituted by functional groups derived from pyridine, pyrimidine, pyrazine, pyridazine, imidazole, triazole, tetrazole, pyrazole, nitriles, cyanides, carboxylates, etc.

- This definition excludes compounds that have a much more inorganic character such as halides, oxides, hydroxides, alkoxides, sulphides, phosphates, sulphates, poly-oxometalates, etc.

Coordination compounds vs inorganic solids

In general, no correlation between the structure of the starting reagents and products is required in the synthesis of inorganic solids the structure of the precursor reagents is not conserved during the reaction and therefore there is.

In contrast…

In contrast…

- The synthetic methods derived from coordination chemistry are essentially based on the intrinsic "rigid" nature of selected molecular building units that keep their structural integrity during the synthesis process.

- This rigidity confers directionality to the coordination bonds, an essential feature of CPs since it conveys predictability to the geometry around the metal centres and allows a certain degree of guarantee in the design.

In addition…

- Coordination bonds, in general, are sufficiently robust to impart reasonable thermal and mechanical stability providing, in addition, electronic and elastic communication between the metal centres to CPs.

However…

- Comparatively CPs are thermally less robust than metallic oxides and other similar inorganic solids characterized by predominant ionic interactions. Besides, oxides, among other binary compounds, have much higher thermal stability as well as physicochemical properties of industrial relevance [magnetic, electrical (semiconductor, conductive), optical (thermo-, photo- and piezo-chromism), photonic (luminescence, laser), catalytic, etc.] as well as very different methods of synthesis and characterization from those used in CPs.

- Porous CPs (i.e. MOFs) have been compared with zeolytic compounds (aluminosilicates) that are characterized by much more covalent bonds (see later…).

Introduction CPs versus MOFs

Terminology

- Terminological ambiguity: CP vs MOF

- Currently, the IUPAC considers that the general term Coordination Polymer contains a subclass of porous compounds popularized with the name of MOFs of the English "metal-organic frameworks”.

- Number of citations obtained for CPs and MOFs in a search using the Sci-Finder database.

Periodo	PC	MOF
Hasta 1950	1	0
1951-1960	12	0
1961-1970	175	0
1971-1980	130	0
1981-1990	154	0
1991-2000	531	8
2001-2008	3348	687
2009-2016	12474	13356

Historical Precedents :

Prussian Blue
and
Hofmann Clathrates

Prussian Blue

First records of PCs and current MOFs goes back to 1704-1705 when Prussian Blue was discovered. Apparently it was J. L. Frish who reported for the first time on the discovery of Prussian Blue (*"Notitia Caerulei Berolinensis Nuper Inventi," Miscellanea Berolinensia ad incrementum Scientiarum, 1710, 1, 377-378*).

First page of the J. L. Frish's report about discovery of Prussian Blue

377

SERIUS EXHIBITA.

Notitia Cœrulei Berolinenſis nuper inventi.

Pictores, qui coloribus ſuis oleum admiſcent, paucos illorum habent, quibus cœrulea exprimant: eosque tales, ut jure commodiores deſiderent. Ex vulgaribus enim alius mixturam cum oleo non reſpuit quidem, ſed non diu in opere durat; ſubviridis, ſubpallidus, ferrugineus, aut planè ſordidus fit: Alius conſtans quidem & ſatis pulcher, ſed arenoſus eſt, & hoc vitium, quò ad ſubtiliorem artificis laborem eſt incommodus, ſi vel anni ſpatium in eo terendo conſumeretur, non tolli poteſt. Optimus omnium, quem vulgo Ultramarinum ſive Azurinum vocant, qui ex lapide Lazuli conficitur, non modo pretio ſuo multos deterret; ſed & aliorum colorum mixturam non libenter admittit; & hinc tantum in eminentiis pulchritudinem ſuam monſtrare poteſt: ad umbras in utilis eſt. Hoc juſtum artificum deſiderium cœruleus color, qui ante aliquot annos hic Berolini inventus eſt, & nunc, poſt varia variorum accuratiſſima examina, audacter in ſcenam prodit; ſi non explere, certè lenire poteſt. Nihil enim harum incommoditatum habet: In oleo ſplendorem ſuum potiſſimum oſtendit. Ubique vero, in aqua, in oleo, & aliis liquoribus, quibus pingi poteſt, tam durabilis reperitur, quam qui maxime. Aqua illa fortis, ut à Chymicis appellatur, quæ omnia arrodit aut diſſolvit, eum adeò non mutat, multo minus exſtinguit, ut potius lucidiorem reddat. Et ut quædam cærulei coloris genera in encauſtica pictura (Schmeltz-Werck / *email*,) adhiberi poſſunt, & igne, ut ita dicam, ſicco non delentur: ſic novus hic color igni humido (quod nomen aquæ illi forti & omnia deſtruenti, meritò dari poteſt) fortius reſiſtit, quem vix alius ex omnibus colorum generibus perferre poteſt. Hinc multo minus leviores & communiores pictorum explorationes timet, ut: ſuccum ex malis citreis expreſſum &c. Non mutatur in loci, aut aeris ſive tempeſtatis mutatione. Vivit in calce viva, ejusque album,

Bbb ut

(*Caerulei* = azul; *Berolinensis* = Berlin; *Nuper* = reciente)

Additional historical information:
(A. Kraft "*On the discovery and history of Prussian Blue*" *Bull. Hist. Chem., VOLUME 33, Number 2008, 2, 61-67*).

Prussian Blue

As described by G. E. Stahl in "*Experimenta, Observationes, Animadversiones, CCC Numero Chymicae et Physicae, Ambrosius Haude, Berlin*, **1731**, 280-283.

Inventors: Dippel and Diesbach (Berlin) discovered PB when using a K_2CO_3 accidentally contaminated with potassium ferrocyanide.

- Pigment of great importance due to stability of its colour. It was used in paints and inks. More recently, it has been also employed in cellular dyes, detoxification by radioactive isotopes Tl^+, Cs^+. Prussian blues (PBs) have been investigated for their gas storage (especially H_2) properties but also for their magnetic and photomagnetic properties among others.

- Its chemical composition has been a source of discussion for a long time. There are at least two generic forms: i) a soluble form that contains alkaline ions and ii) an insoluble form that contains only H_2O molecules.

- Its structure was resolved about 273 years after its discovery:

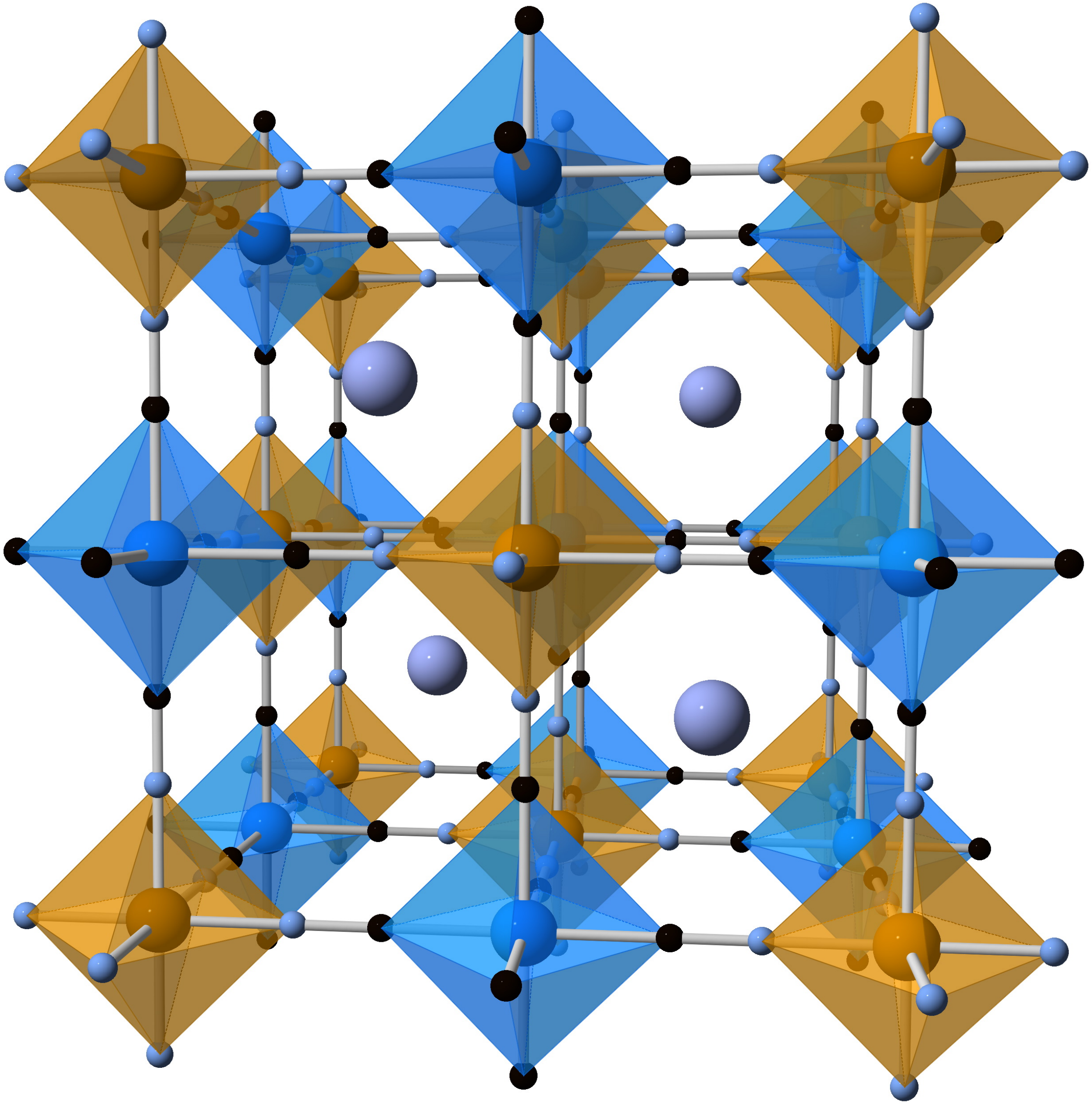
i) J. F. Keggin and F. D. Miles proposed for the first time a cubic structure from an RX analysis of samples containing alkali metals, $K\{Fe^{III}Fe^{II}(CN)_6\}\cdot xH_2O$; Nature 1936, 137, 577-578.

ii) A. Ludi et al. solved and described, for the first time, the structure of the insoluble form formulated $\{Fe^{III}_4[Fe^{II}(CN)_6]_3\}\cdot xH_2O$ (x = 14-16) from single crystal X-ray diffraction methods, H. J. Buser, D. Schwarzenbach, W. Petter, A. Ludi, Inorg. Chem. 1977, 16, 2704-2710.

- Oxidation state. It is a mixed valence complex in which the electronic density is widely delocalised through the CN bridge. In fact, the characteristic blue colour is the result of the absorption of the visible (orange) spectrum due to the process: $Fe^{II}\text{-CN-}Fe^{III} + h\nu \longrightarrow Fe^{III}\text{-CN-}Fe^{II}$.

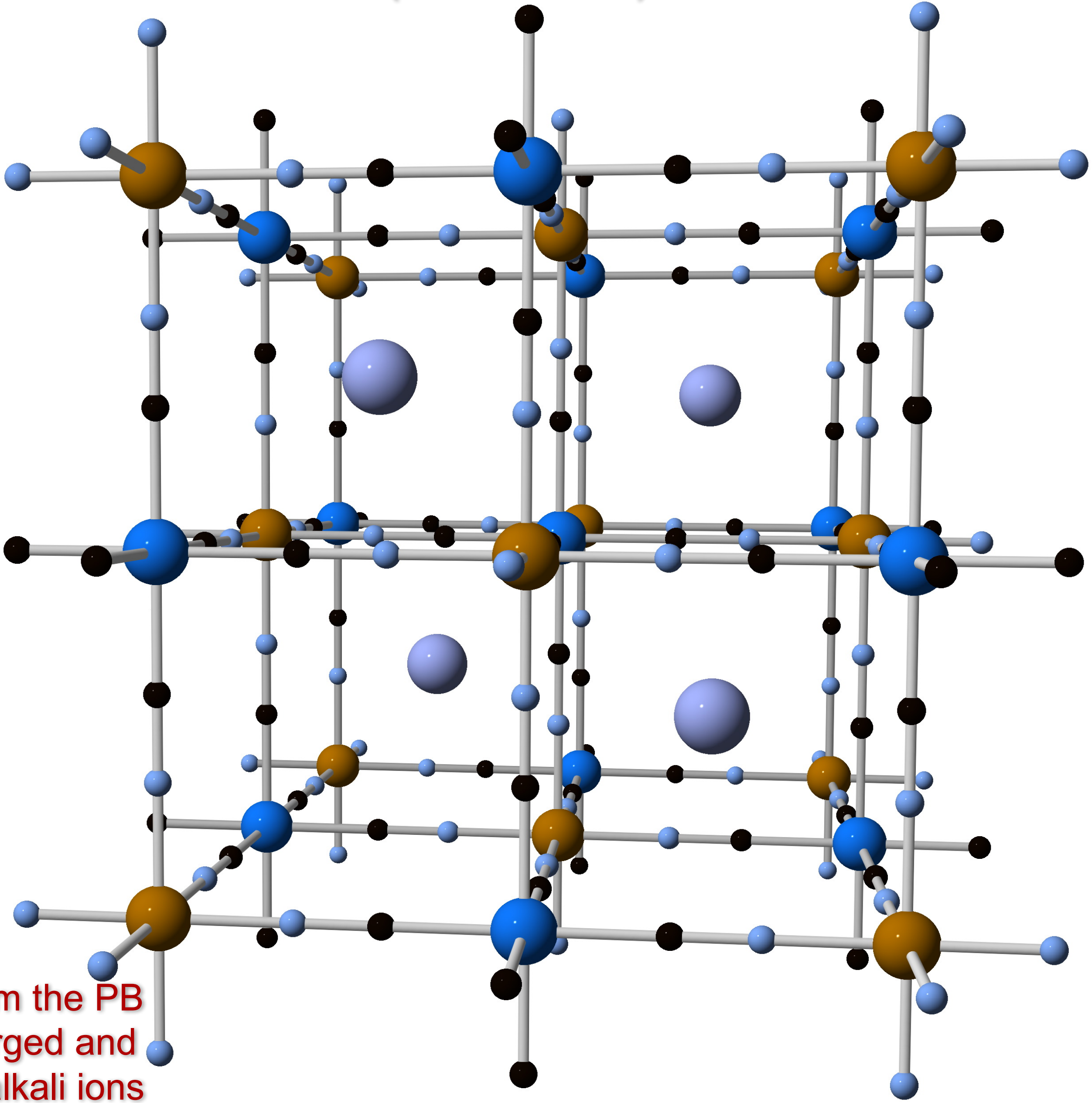
Prussian Blue: $K\{Fe^{III}Fe^{II}(CN)_6\} \cdot xH_2O$

(Soluble form)



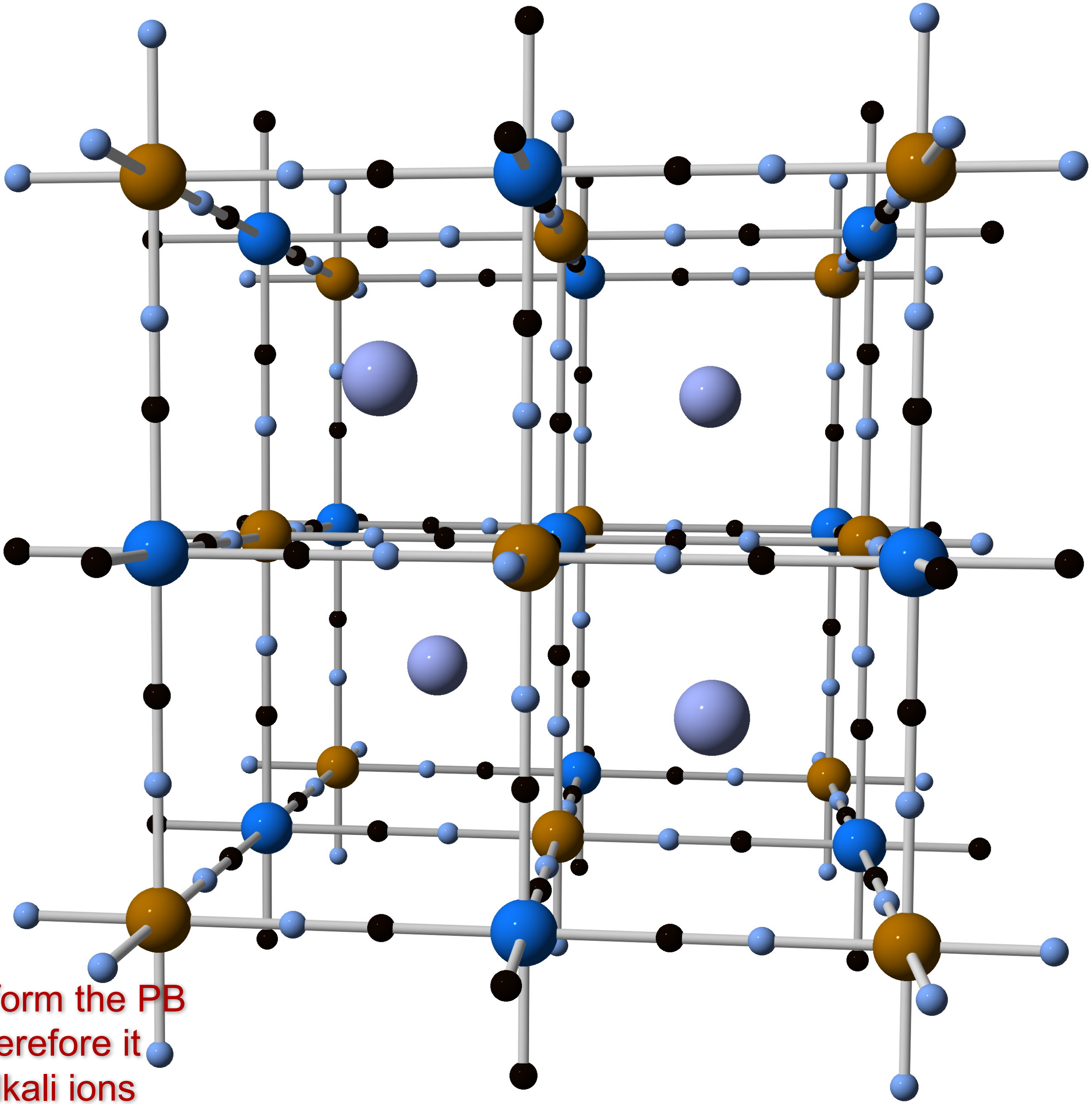
Prussian Blue: K{$Fe^{III}Fe^{II}(CN)_6$}·xH_2O

(Soluble form)



In the soluble form the PB is negatively charged and neutralizes with alkali ions

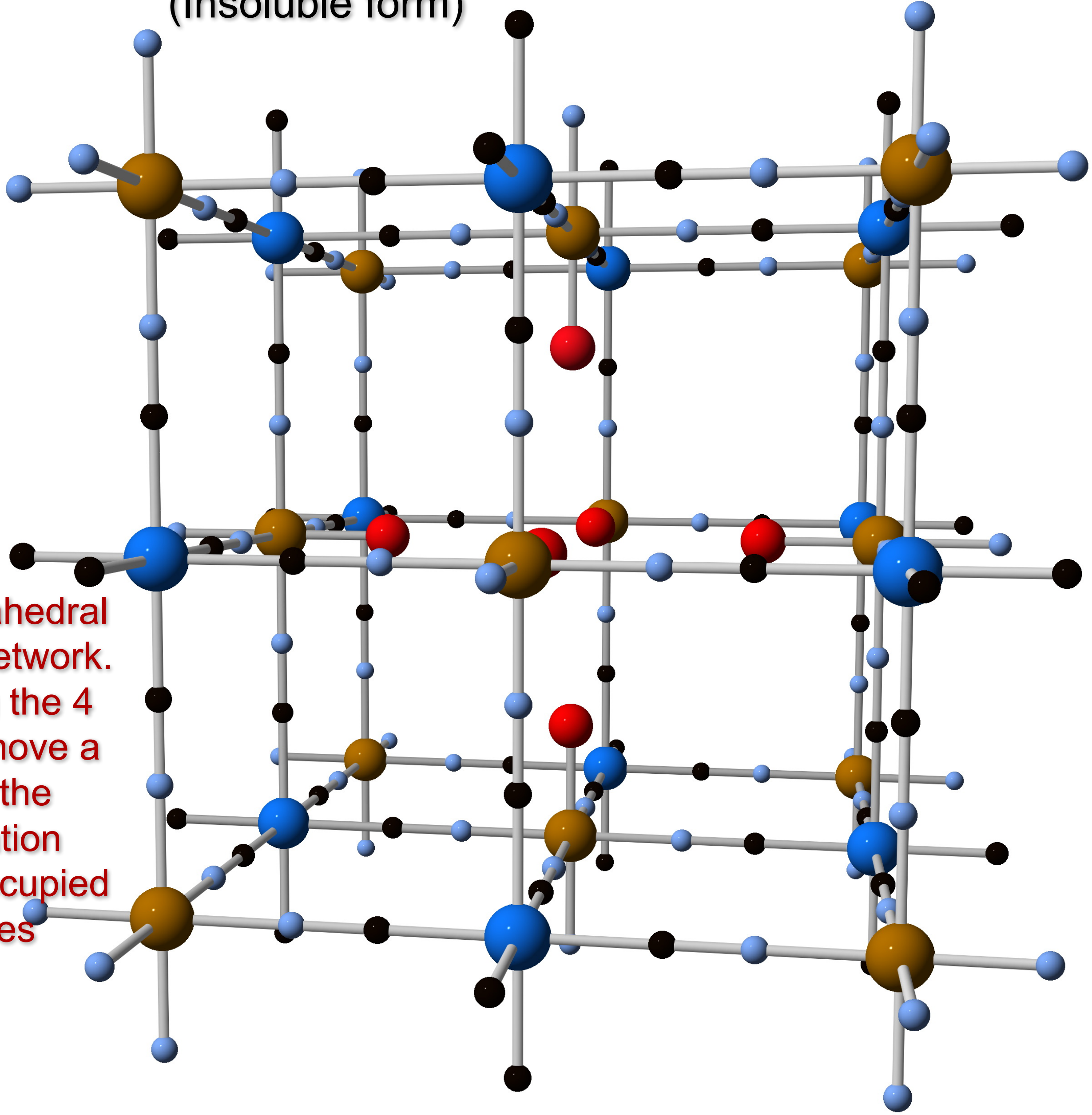
Prussian blue: Relation between soluble and insoluble forms



In the insoluble form the PB is neutral and therefore it does not have alkali ions

Prussian Blue: $\{Fe^{III}_4[Fe^{II}(CN)_6]_3\} \cdot xH_2O$ (x = 14-16)

(Insoluble form)



Generating octahedral defects in the network. When removing the 4 M^+ we must remove a $[Fe(CN)_6]^{4-}$ and the vacant coordination positions are occupied by H_2O molecules

Hofmann Clathrates

They also belong generically to the family of metallocyano complexes.

Synthesis:

The first compound was published by K. A. Hofmann and F. A. Küspert, Z. Anorg. Allg. Chem. 1897, 15, 204. It was formulated $[Ni(NH_3)_2Ni(CN)_4]\cdot 2G$ and the authors observed that this compound had the singular feature of adsorbing aromatic molecules such as G = benzene, pyrrole, thiophene, furan, etc..

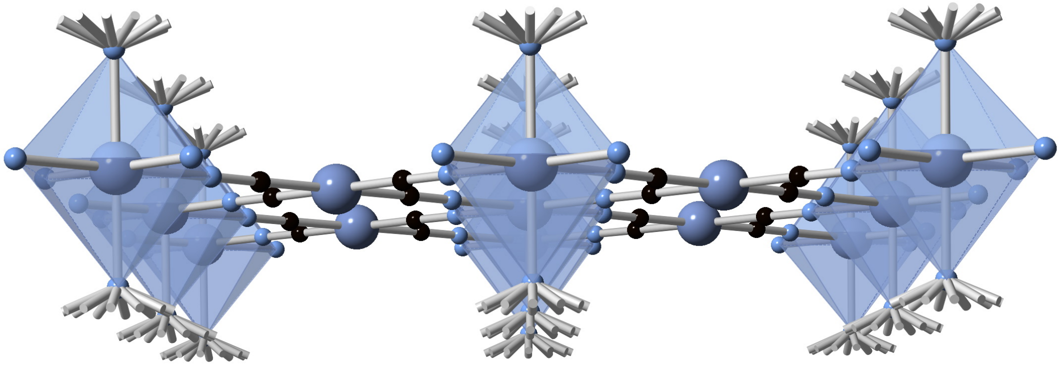
Structure:

Its structure was published by H. M. Power and J. H. Rainer more than 50 years later (Nature 1949, 163, 566, J. Chem. Soc. 1952, 319).

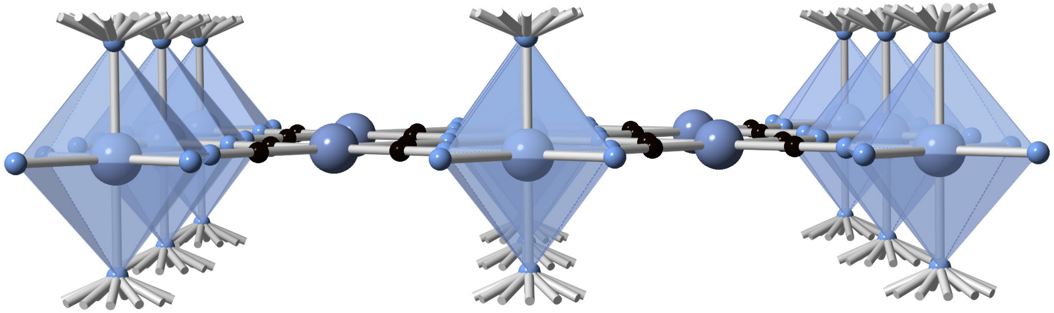
Systematic investigation of new Hofmann Clathrates:

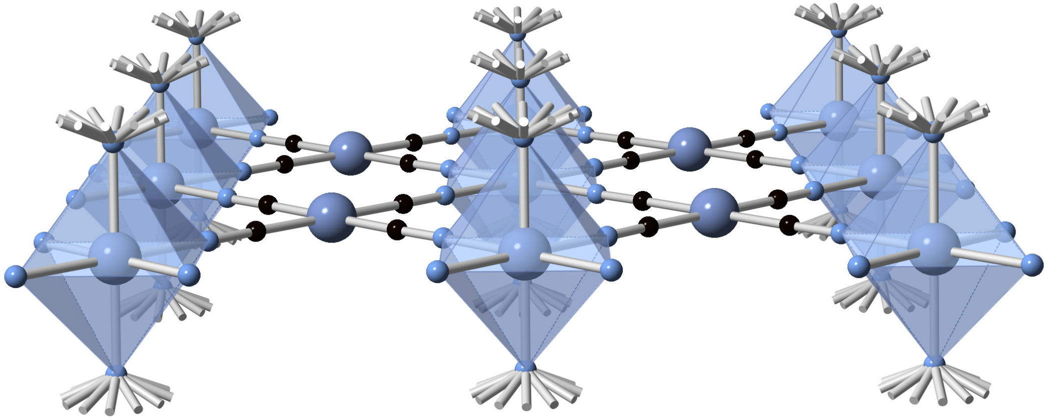
T. Iwamoto y colaboradores….1970-1995

Hofmann Clathrate $Ni(NH_3)_2[Ni(CN)_4] \cdot$ Benzene

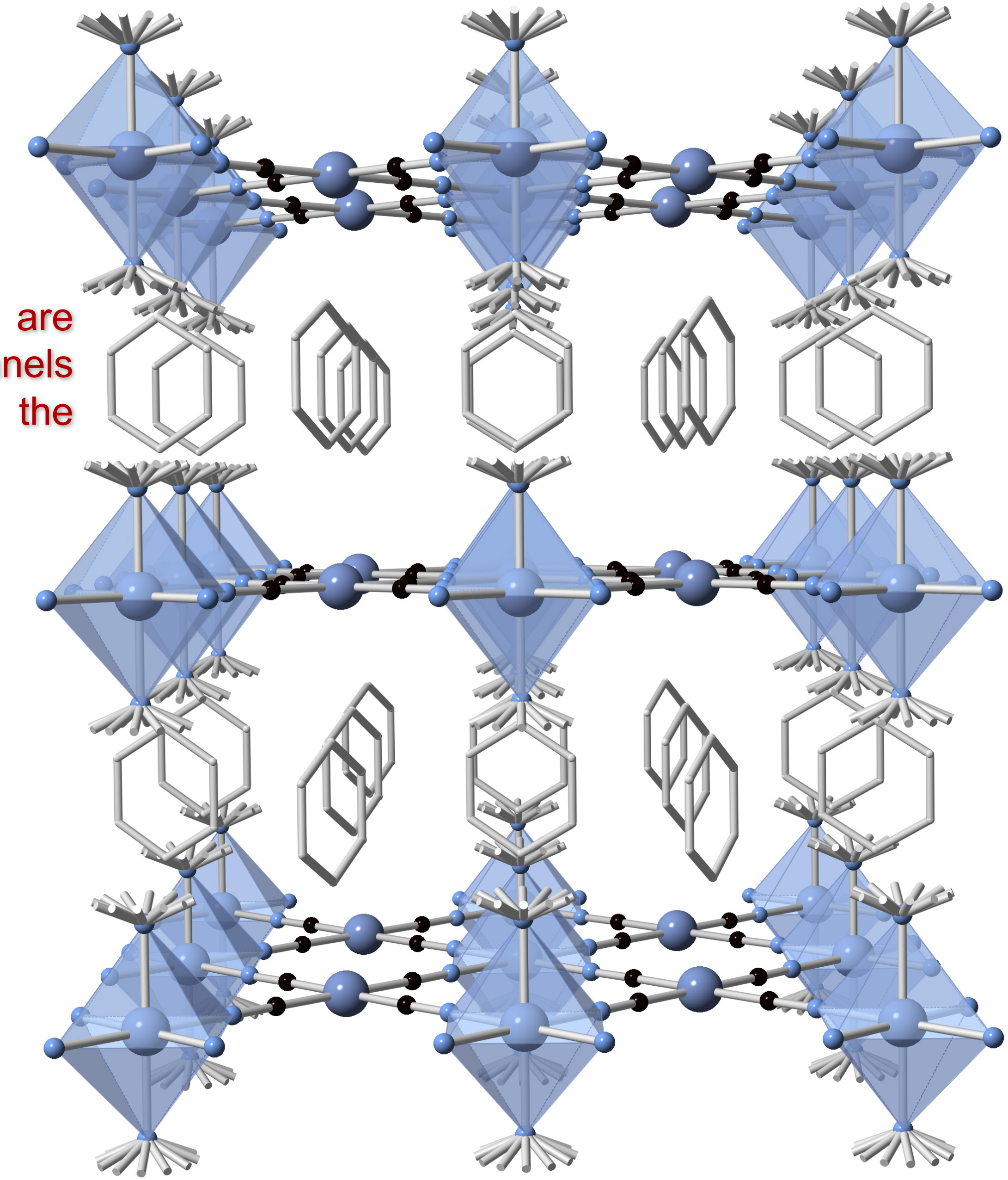


2D networks extending on the xy plane and stacked along z



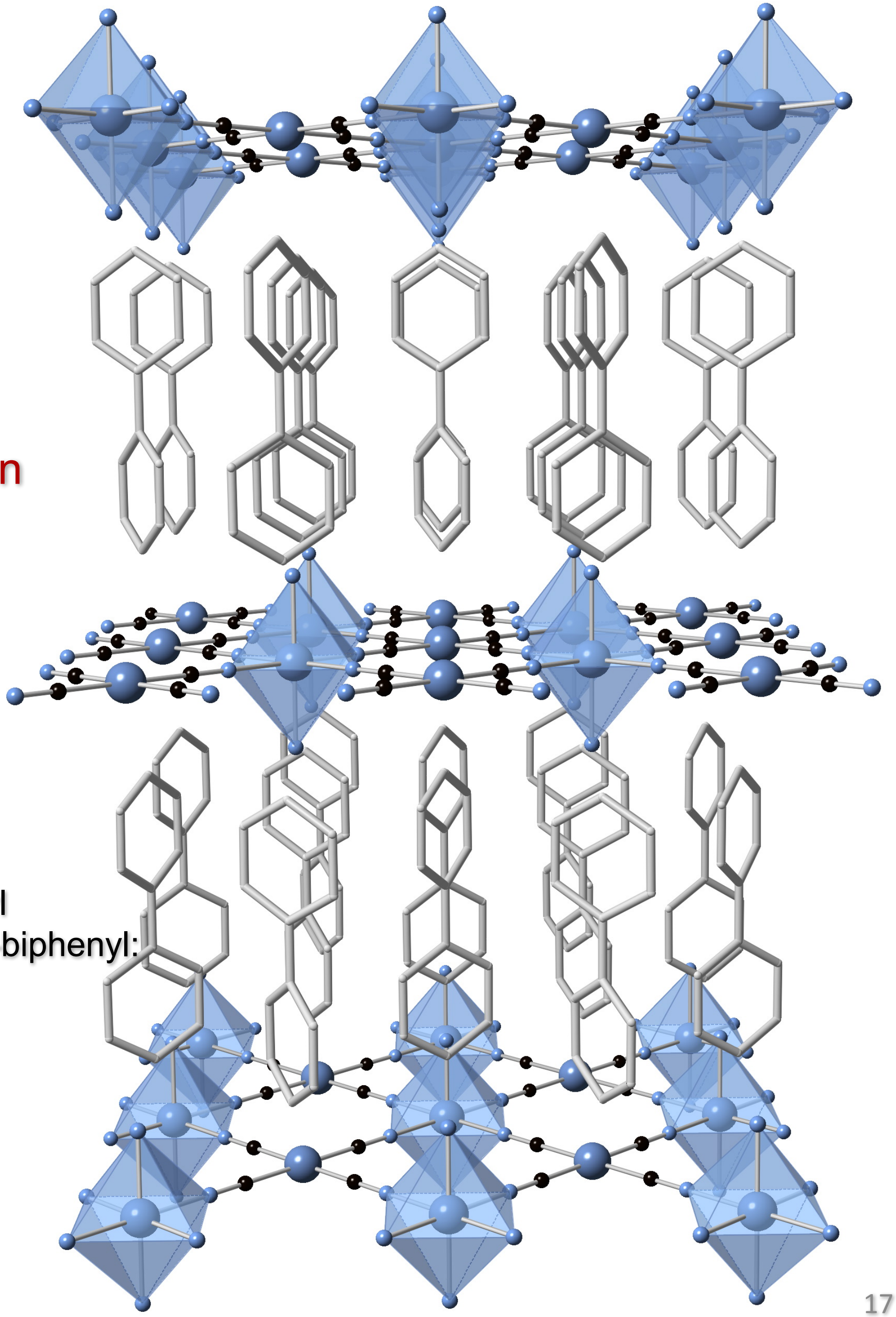


Hofmann Clathrate $Ni(NH_3)_2[Ni(CN)_4]\cdot$Benzene



Invited molecules are located in the channels that run along the directions x and y

Hofmann Clathrate $Ni(NH_3)_2[Ni(CN)_4]\cdot$Biphenyl

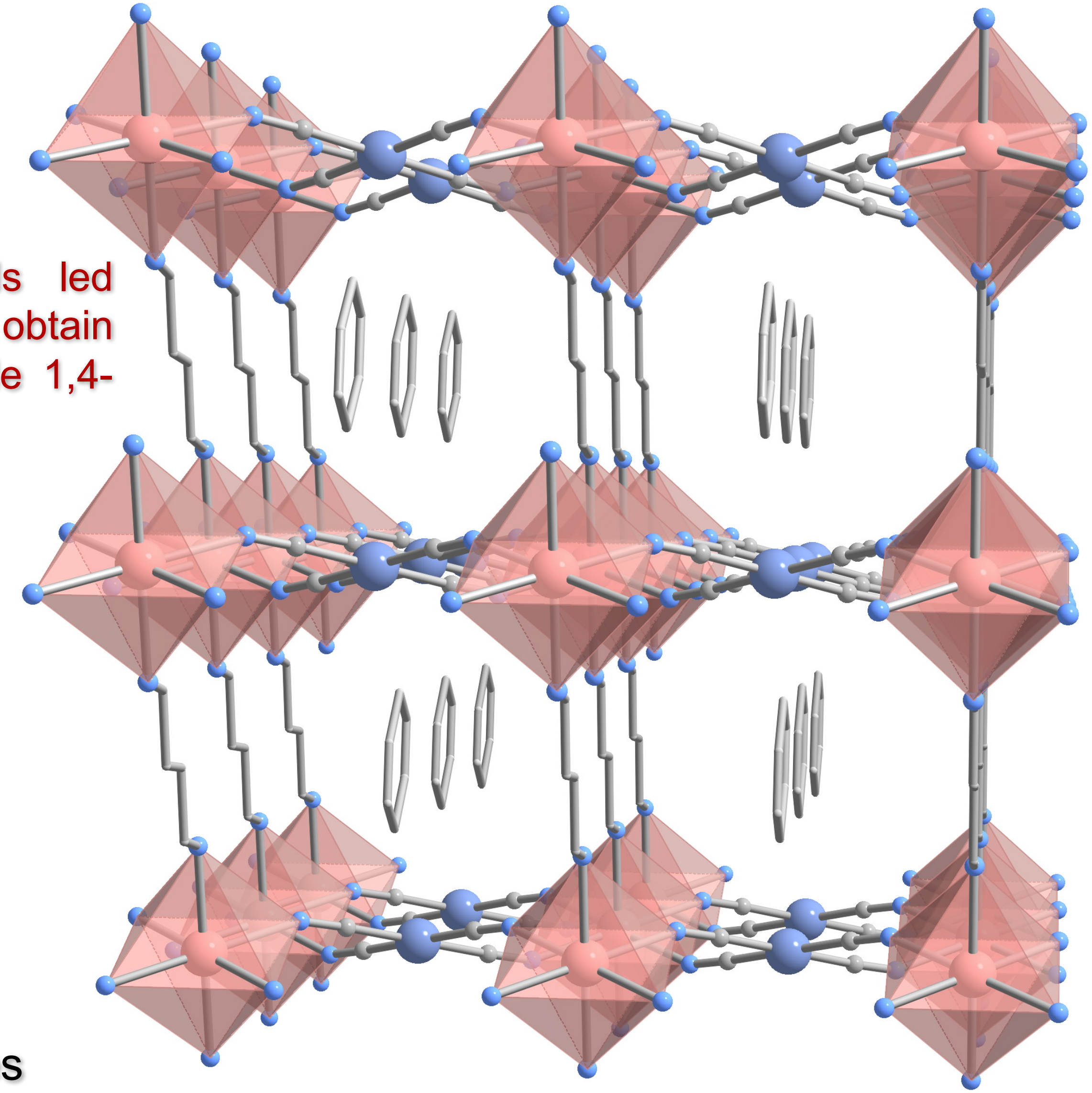


Even larger molecules such as biphenyl can be inserted.

T. Iwamoto, T. Miyoshi, Y. Sasaki
"The Metal Ammine Cyanide Aromatic Clathrates.
XIII. The Crystal Structure of the Hofmann-type Biphenyl Clathrate, Diamminenickel(II) Tetraeyanonickelate(II) Di-biphenyl: $Ni(NH_3)_2Ni(CN)_4\cdot 2C_{12}H_{10}$",
Acta Cryst. (1974). B30, 292-295

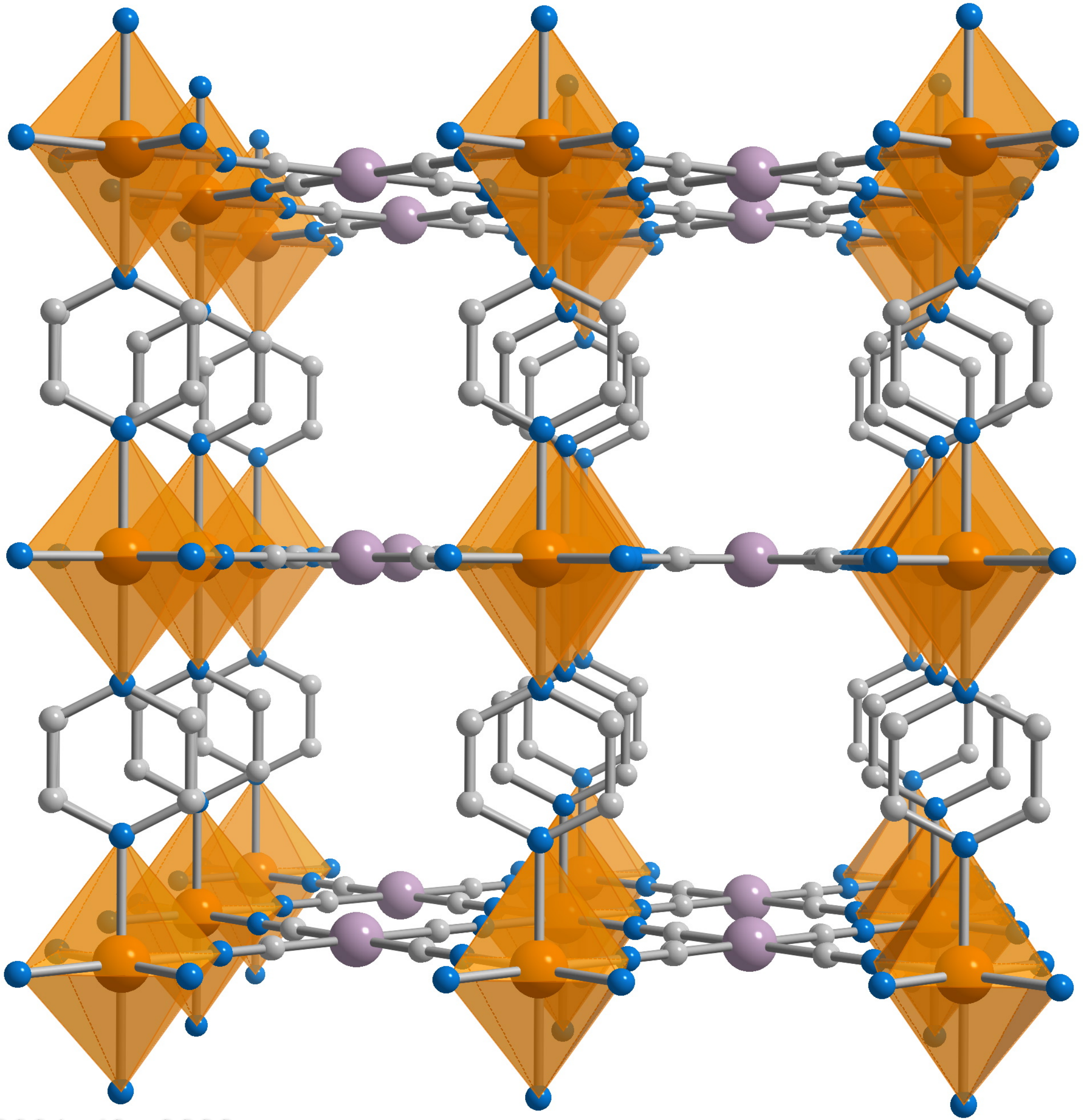
Hofmann Clathrate $Cd(NH_2(CH_2)_4NH_2)[Ni(CN)_4]\cdot$Benzene

The use of bridge ligands led Iwamoto and collaborators to obtain 3D networks. In this example 1,4-diaminobutane was used



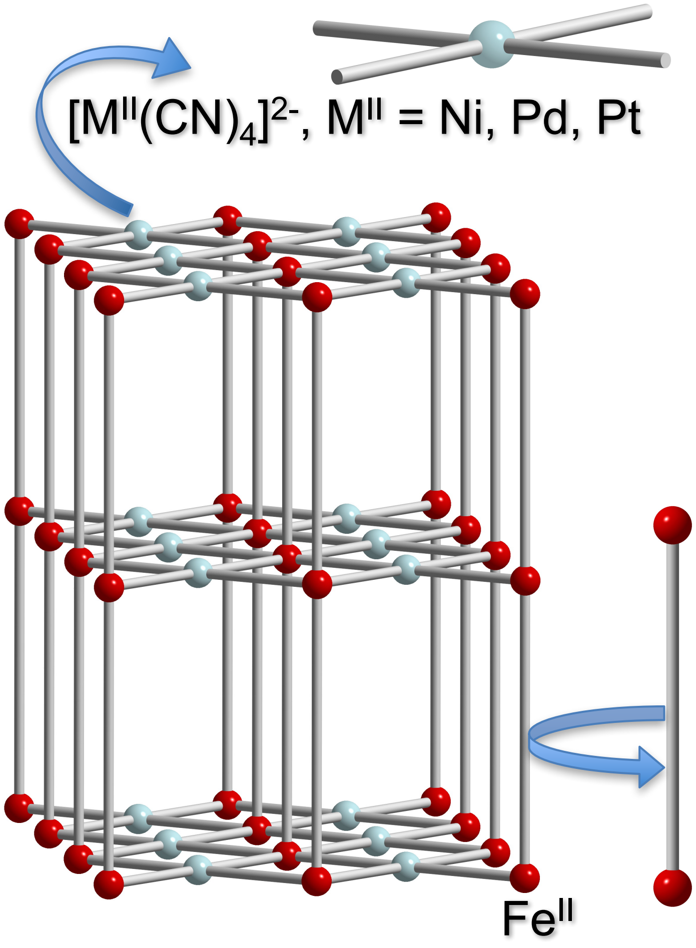
T. Iwamoto y colaboradores

Hofmann Clathrate
$\{Fe(pyrazine)[M^{II}(CN)_4]\cdot G$; M^{II} = Ni, Pd, Pt



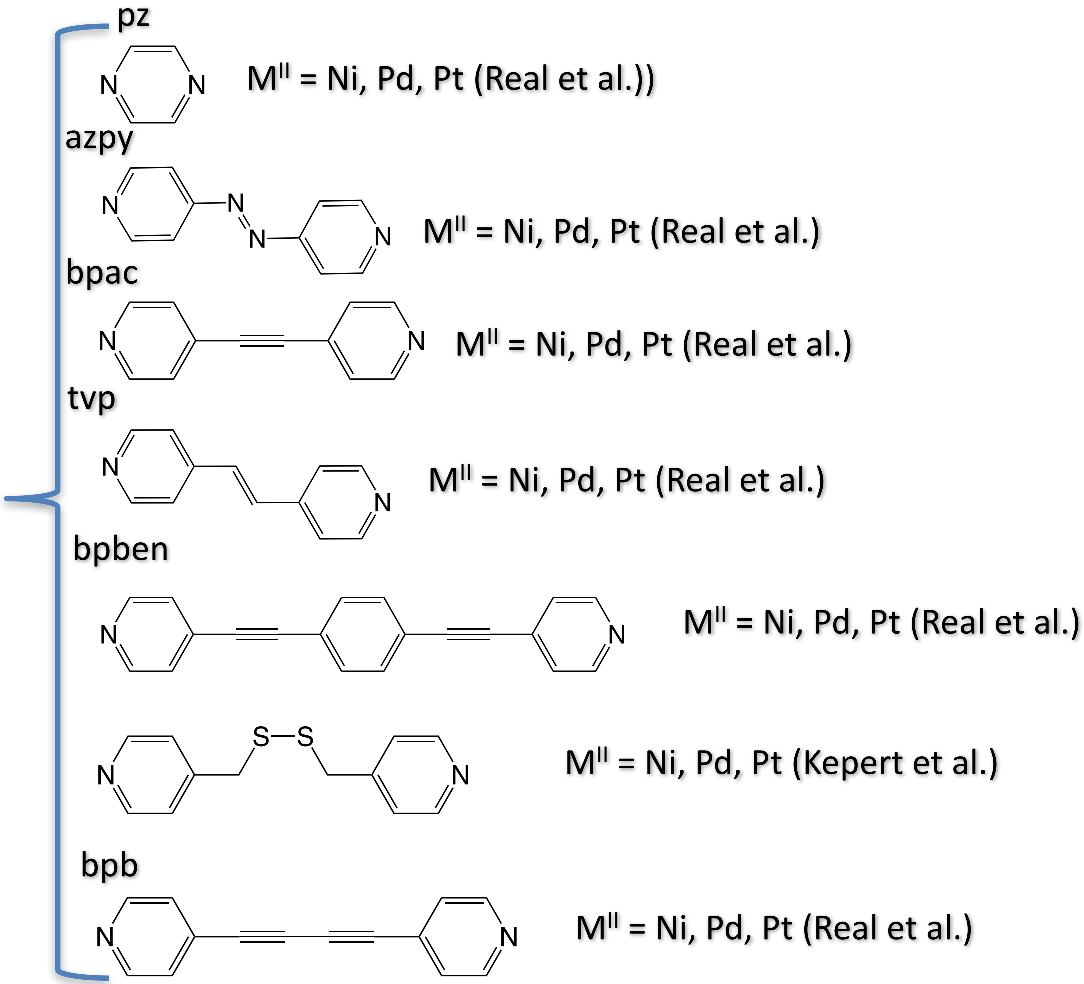
J. A. Real, y col. *Inorg. Chem. 2001, 40 , 3838*

3D Hofmann Porous Coordination Polymers with SCO



$[M^{II}(CN)_4]^{2-}$, M^{II} = Ni, Pd, Pt

Fe^{II}



pz

M^{II} = Ni, Pd, Pt (Real et al.))

azpy

M^{II} = Ni, Pd, Pt (Real et al.)

bpac

M^{II} = Ni, Pd, Pt (Real et al.)

tvp

M^{II} = Ni, Pd, Pt (Real et al.)

bpben

M^{II} = Ni, Pd, Pt (Real et al.)

M^{II} = Ni, Pd, Pt (Kepert et al.)

bpb

M^{II} = Ni, Pd, Pt (Real et al.)

Motivations that stimulated the development of CPs

Decade 1990 -1999

i) Crystal Engineering, Supramolecular Chemistry

Mineralo-mimética vision of CPs: Synthesis of the new CPs with recognizable structures in elements and binary archetypal compounds (**C(d)**, **C(g)**, **PtS**, **NbO**, **ReO_3**, **$CdSO_4$**, **SiSr**,……). Conceptual correlations with Crystal Engineering and Supramolecular Chemistry.

ii) Molecular Magnetism

i.a) Search for connectivity between paramagnetic metal ions (spin coupling, magnetic exchange) and magnetic ordering in (0-3D) systems.

i.b) Search for connectivity between metal ions capable of presenting spin transitions (elastic coupling), cooperativity and ordering of spin states in (0-3D) systems.

iii) Chemistry of Metallosupramolecules

Synthesis of coordination polyhedra as examples of growth control of discrete fragments of 3D networks.

Decade 1990-2000

Mineralomimetic perspective, synthesis and systematic study of CPs

- ✔ The mineralomimetic view of the CPs is essentially (although not fully) due to B. F. Hoskins and R. Robson (J. Am. Chem. Soc. 1989, 111, 5962; J Am. Chem. Soc.1990, 112, 1546).

- ✔ These authors opened new perspectives to the Coordination Chemistry based on:

i) Mimesis of known type networks in classical binary compounds as strategy to stimulate the synthesis of unknown (not experimentally described) CPs .

ii) Provide a systematic classification / study / structural rationalization of the PCs.

iii) Design and deliberate synthesis of new types of functional CPs with interesting properties such as porosity, catalysis, etc.

- ✔ Hoskins y Robson were inspired by the theoretical analyses carried out by the structural inorganic chemist A. F. Wells, whose activity was developed in the 1950-1970s (author of some classic books on Inorganic Structural Chemistry).

- ✔ The work by Hoskins and Robson stimulated many other authors among the most active are: Zaworotko, O. Yaghi, M. Fujita, S. Kitagawa, Proserpio, Blatov, etc ... ..)

Conceptual relationship between Crystal Engineering / Supramolecular Chemistry / Metalsupramolecules

It has been already mentioned that the development of the CPs chemistry was reinforced by the parallel growth of the concepts stemming from: Supramolecular Chemistry and Crystal Engineering.

Crystal Engineering seeks to understand why molecules are packaged in the crystal the way they do and use that knowledge to control such supramolecular organizations, which indeed requires to control the intermolecular interactions in the solid state.

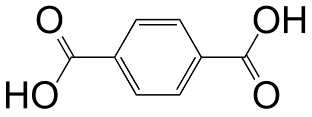
It is well known that the properties of a solid can dramatically depend on the mode in which the molecules organise in the crystal. Therefore, the control of intermolecular interactions can lead to new compounds with applied interest.

In Crystal Engineering, intermolecular interactions are weak [H bridges, π interactions or even inter-metallic interactions d^{10}-d^{10}] but they are capable of generating structures that have inspired or have been found in CPs. In many examples, the resulting CPs are magnified versions of known simple networks such as C(g) and C(d) for example ....

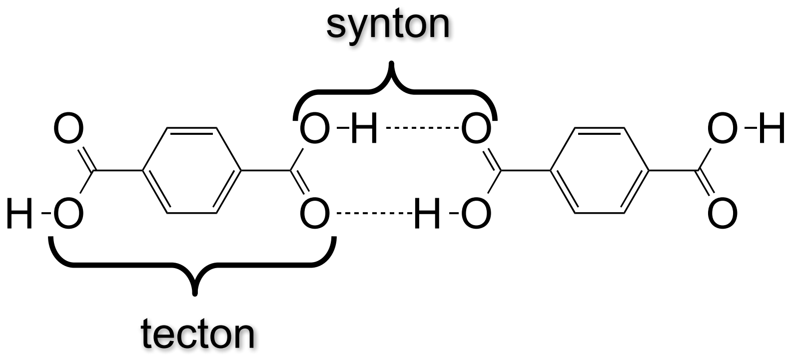
Examples….

Some examples of Crystal Engineering based on hydrogen bonds:

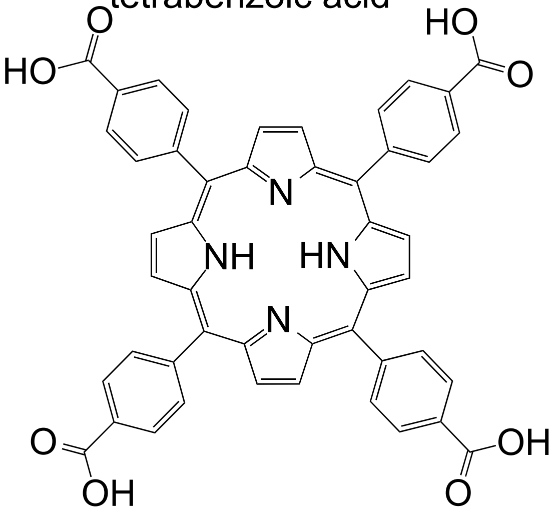
Tectons and syntons

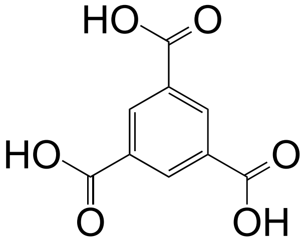


Benzene 1,4-dicarboxylic acid
(Ácido terephthalic)

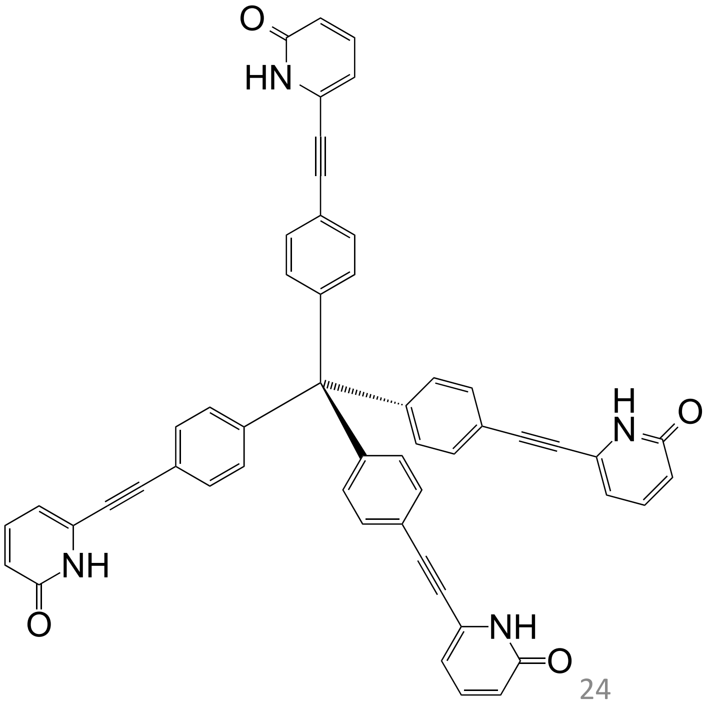


4,4',4'',4'''-(porphyrin-5,10,15,20 tetrayl)
tetrabenzoic acid



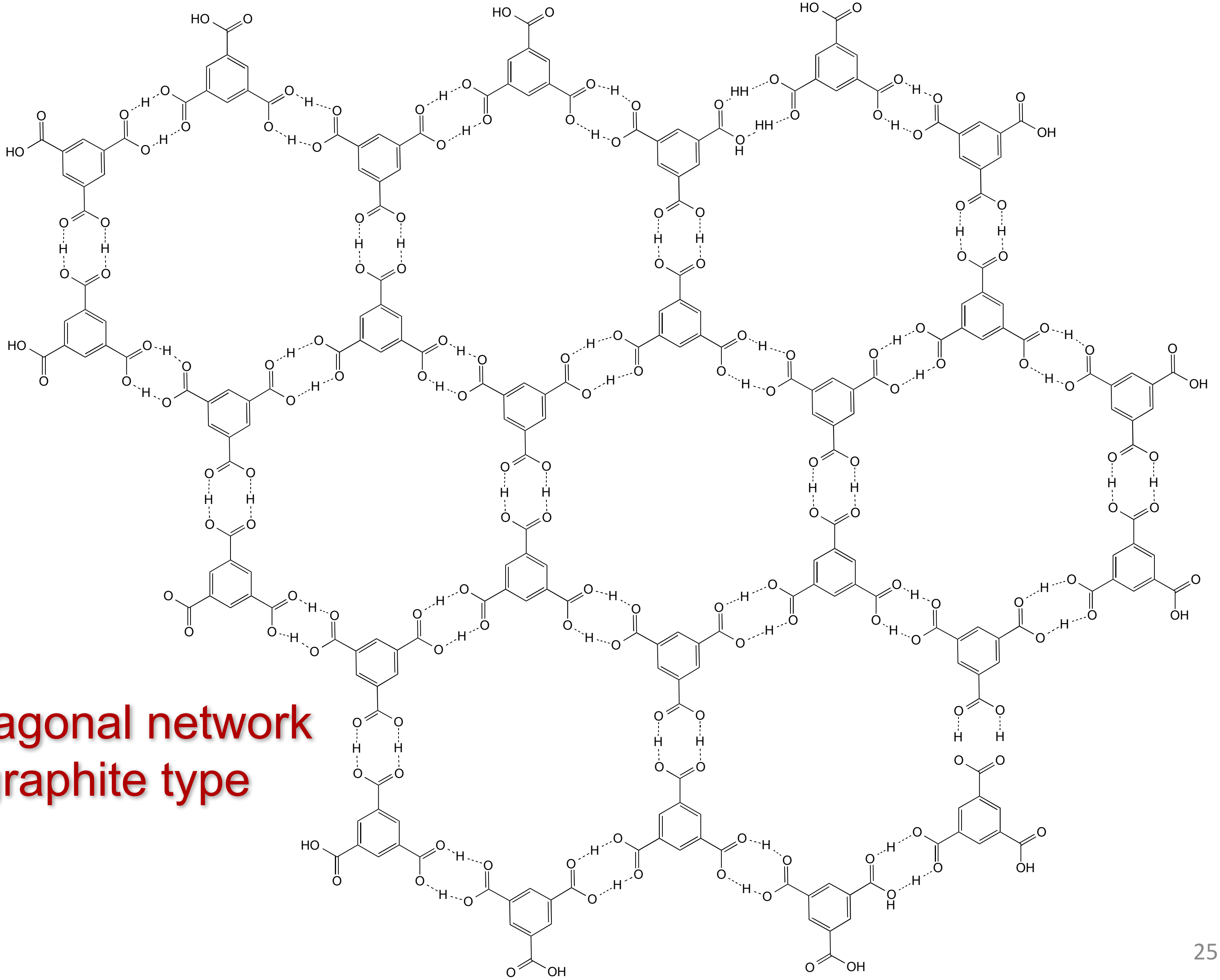


Ácido benceno 1,3,5-tricarboxílico
(o ácido trisimético)



Supramolecular / self-assembly organization of trisimetic acid

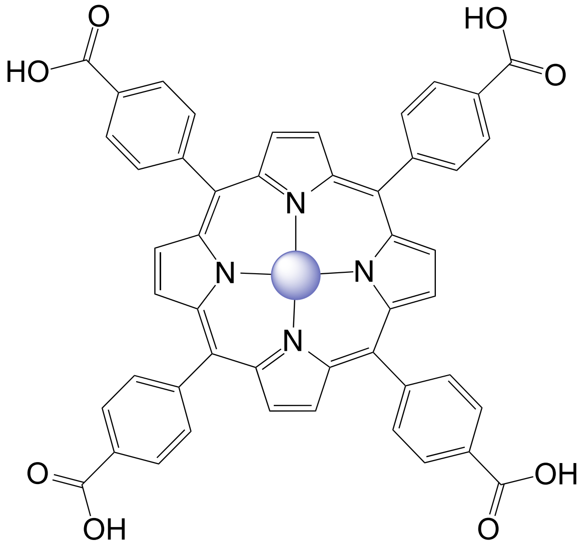
D. J. Duchamp; R. E. Marsh *Acta Cryst*. **1969**, B25, 5

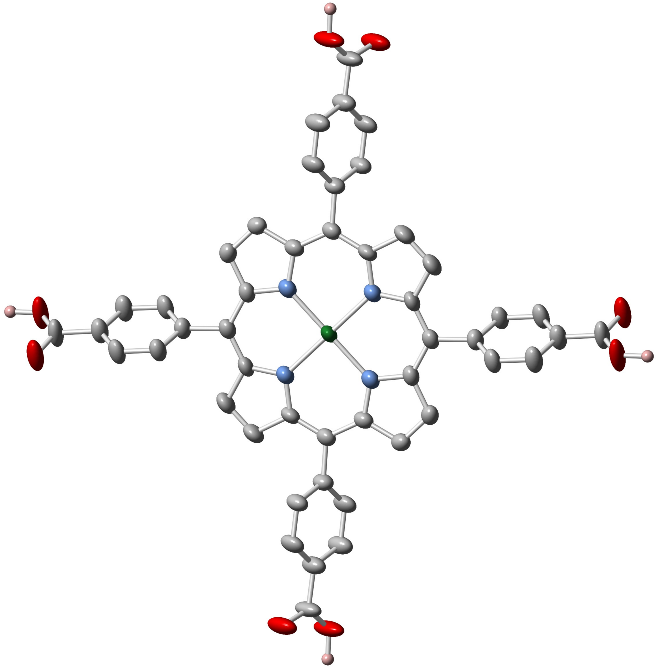


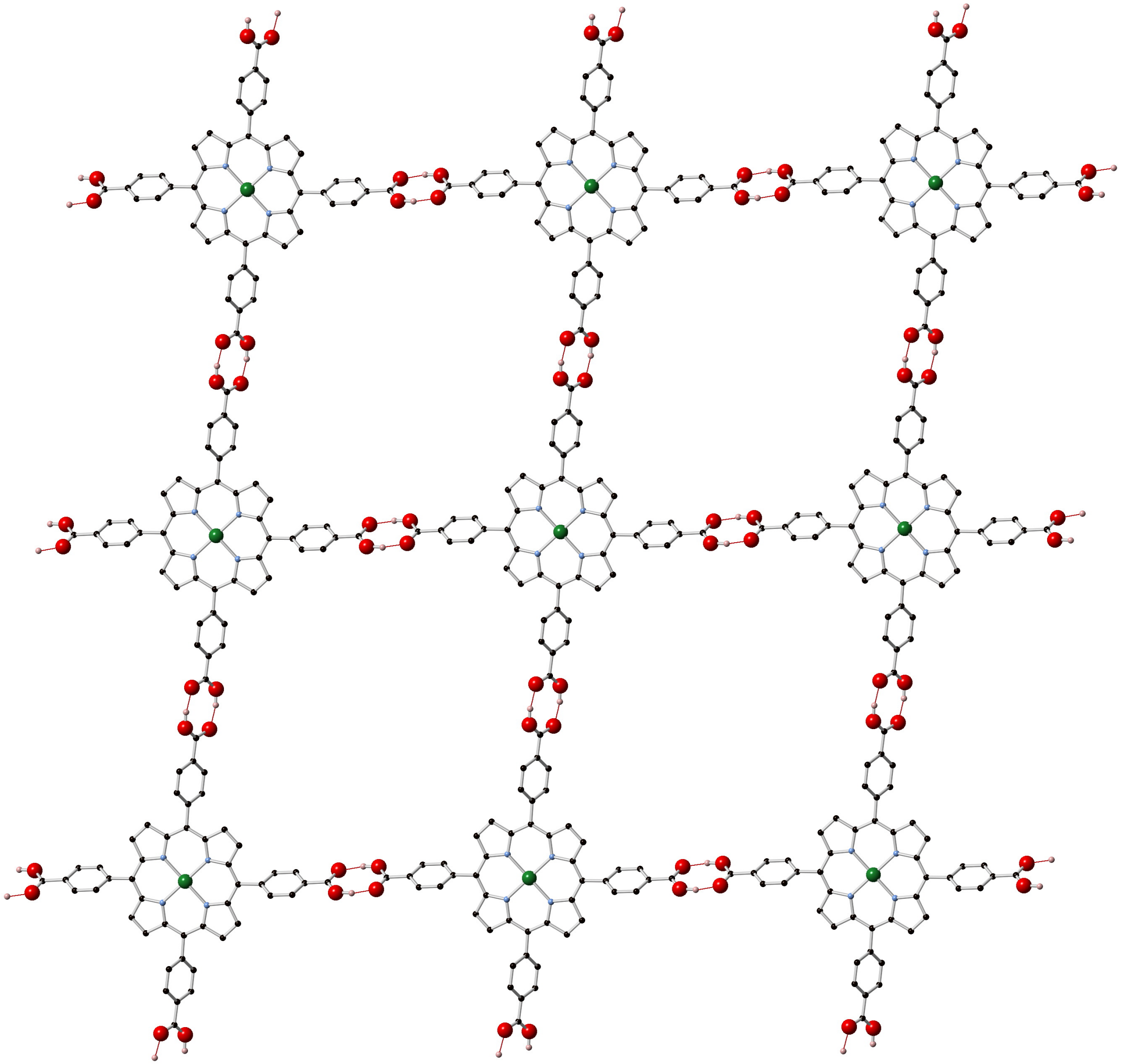
hexagonal network
graphite type

Supramolecular / self-assembled organization Porphyrinato de Zn (II)

Y. Diskin-Posner; I. Goldberg *Chem. Commun*. **1999**, 1961



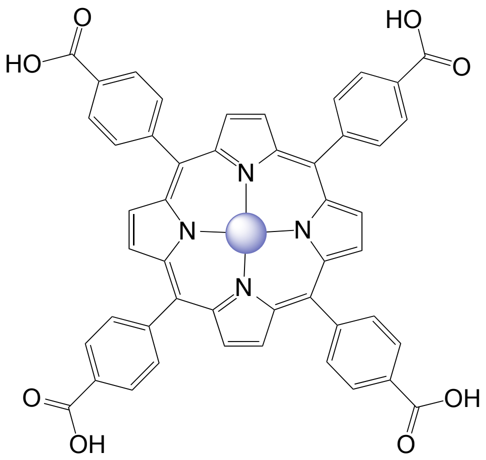


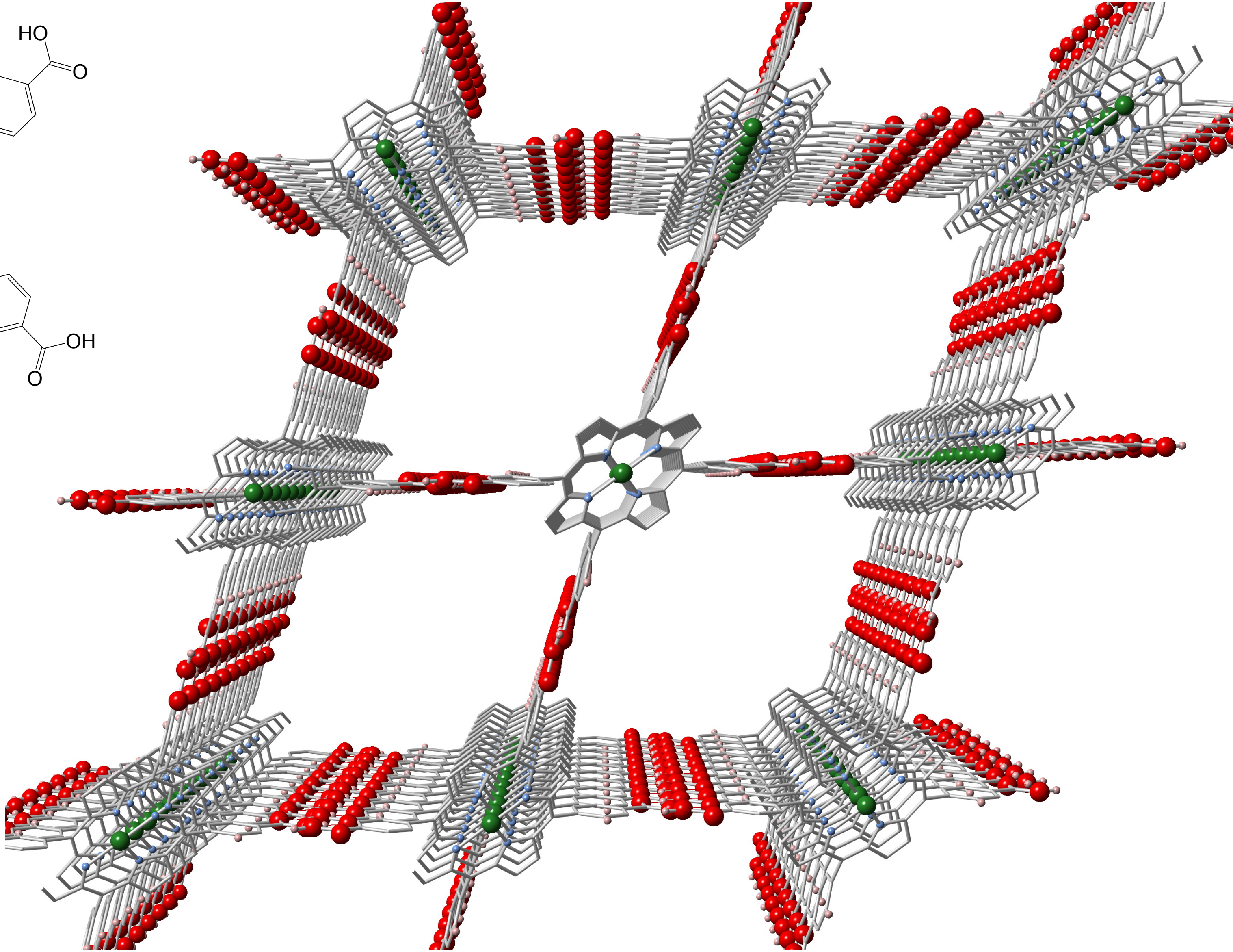


Square network

Supramolecular/self-assembly of Porphyrinato de Zn(II)

Y. Diskin-Posner; I. Goldberg *Chem. Commun*. **1999**, 1961





Crystal packing of ZnTPC square networks complexes linked by hydrogen bonds originates a CP with wide pores

Supramolecular Chemistry

- In contrast to Crystal Engineering for which the crystalline state is a fundamental feature, that is not an essential factor for Supramolecular Chemistry.

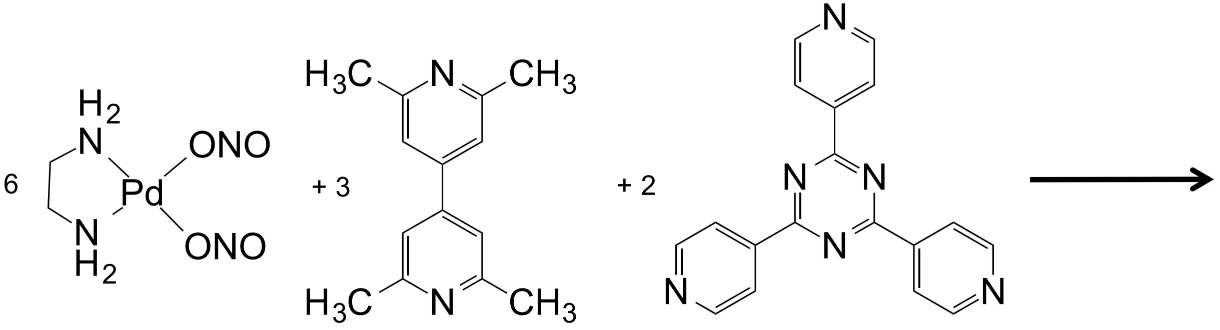
- Despite this, the differences between the two areas can be very subtle in many cases since in Supramolecular Chemistry chemists not only use non-covalent interactions but also coordination bonds.

- The use of metal complexes in supramolecular chemistry has given rise to the chemical term "metallosupramolecular" to distinguish it from purely "supramolecular chemistry" devoted to molecular recognition between organic species and / or inorganic anions etc. However, the term metallosupramolecular is used in a wide range of situations including CPs.

- Conceptually metallosupramolecular chemistry fits the requirements of coordination polymer chemistry, however metallosupramolecular systems are discrete species that exist both in solution and in a crystalline state. Most active researchers in this field: J. M. Lehn, P. Stang, M. Fujita, J. R. Nitschke ... ...

- Let's see some examples that illustrate this last situation….

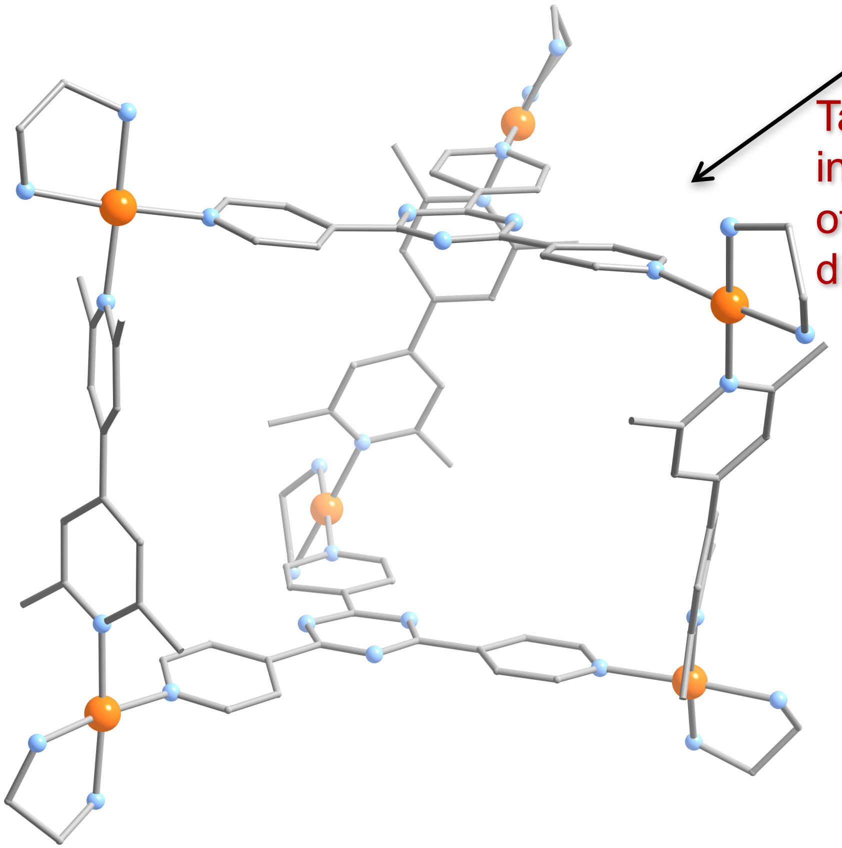
Polyhedra versus Coordination Polymers



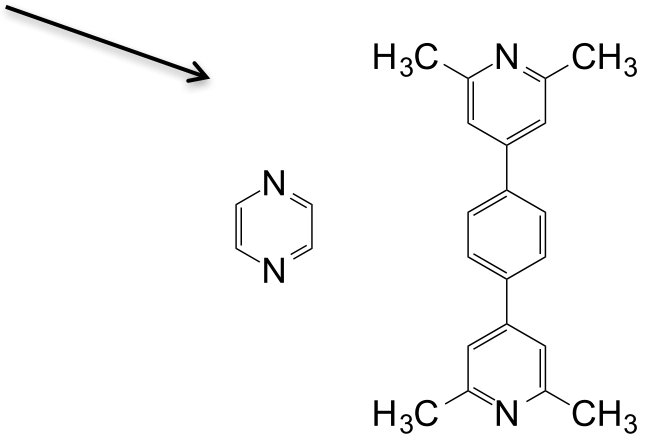
2,2',6,6'-tetramethyl-4,4'-bipyridine

2,4,6-tri(pyridin-4-yl)-1,3,5-triazine

$\{[Pd(en)]_6(44'bipy)_3(tpt)_2\}^{12+}$

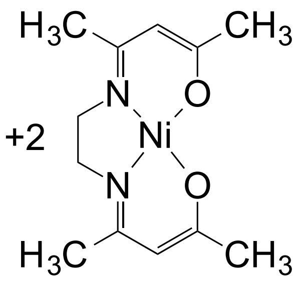


Taking advantage of the chemical inertia and the flat-square geometry of the Pd^{II} $[Kr]4d^8$ (strong field, diamagnetic)



Solutions and colourless crystals (the cage is stable in solution)

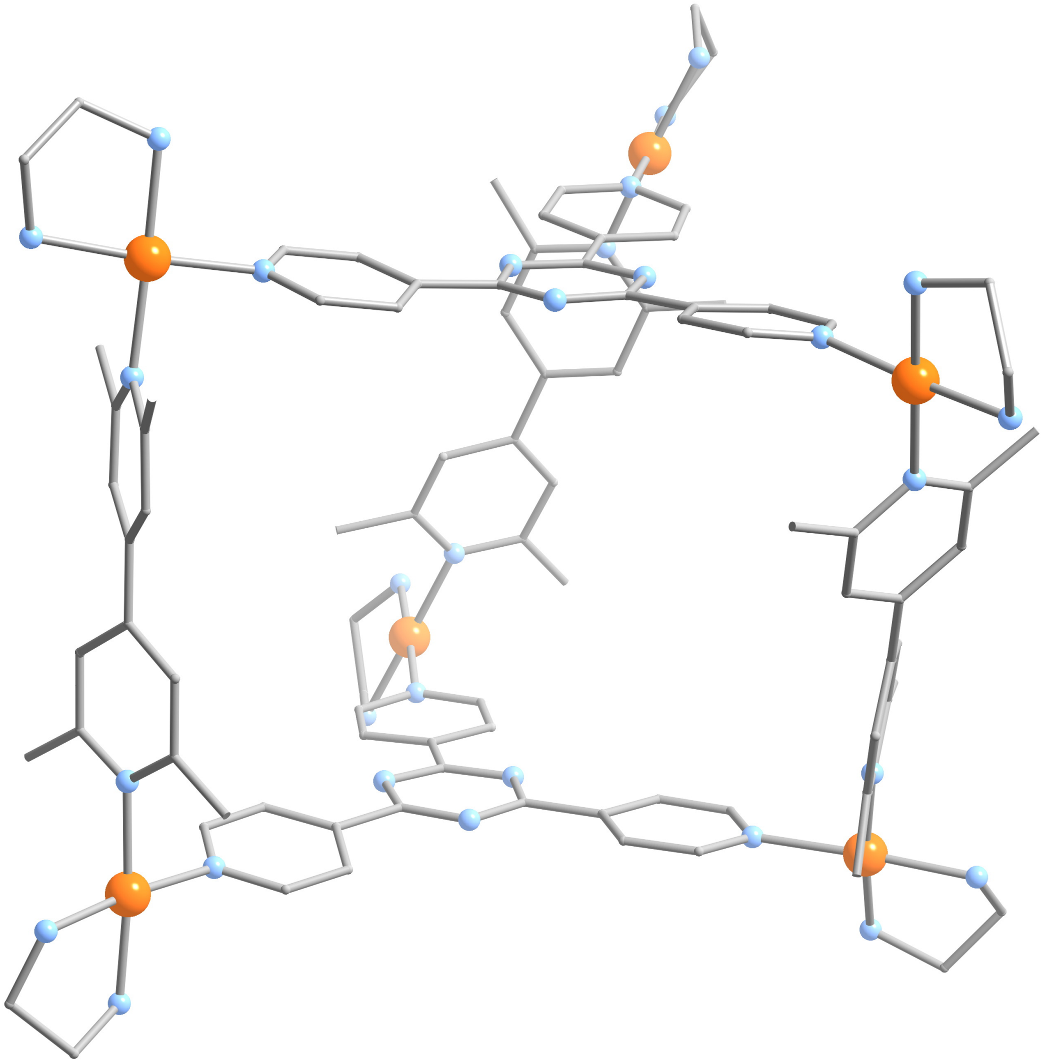
Encapsulation of different molecules by molecular recognition



Ni(II)(acen) (deep red / diamagnetic)
(acen = N,N′-ethylenebis(acetylacetoneiminate))

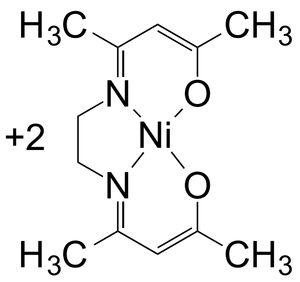
suspended in a solution of

$\{[Pd(en)]_6(44'bipy)_3(tpt)_2\}^{12+}$



K. Ono, M. Yoshizawa, M. Akita, T. Kato, Y. Tsunobuchi, S. Ohkoshi, Makoto Fujita, *J. Am. Chem. Soc*. **2009**, *131*, 2782.

Encapsulation of different molecules by molecular recognition

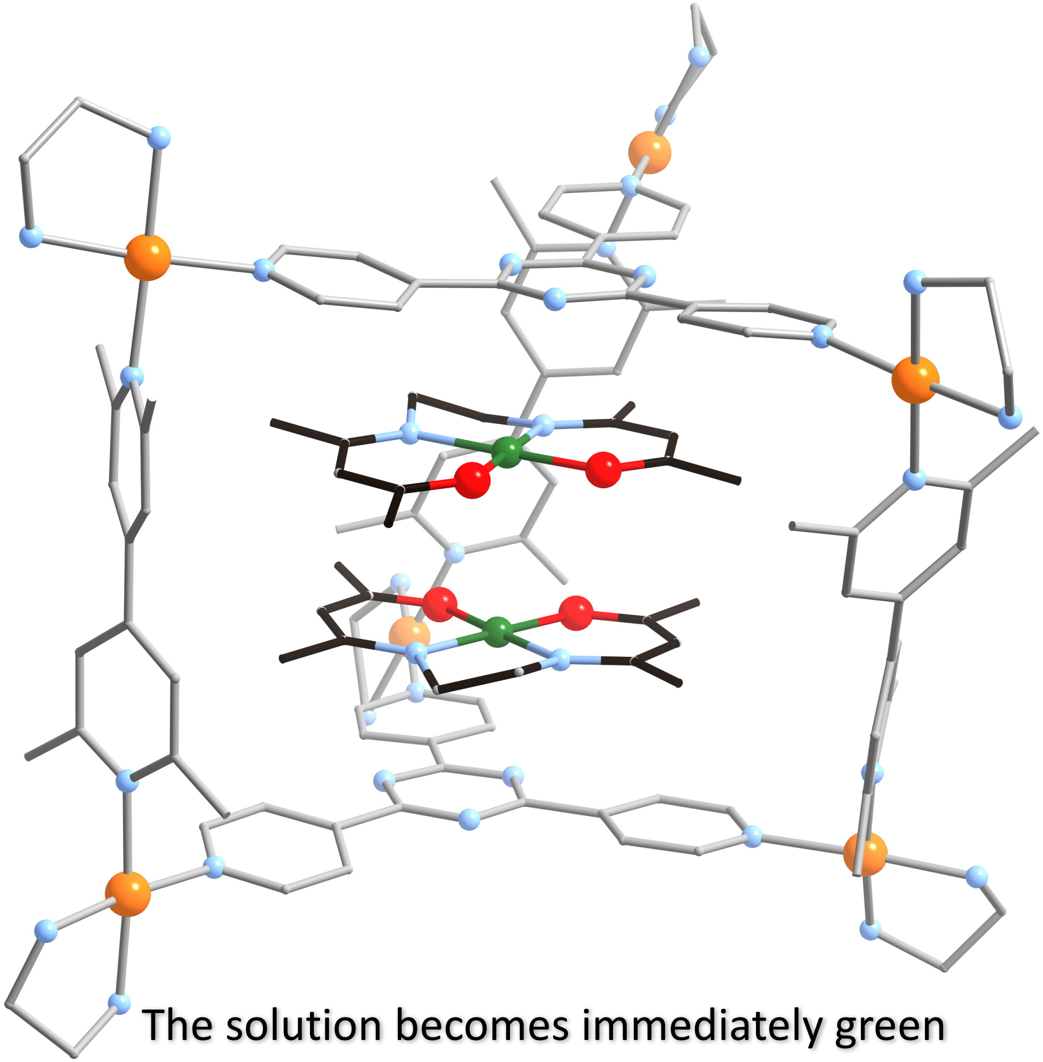


Ni(II)(acen) (deep red / diamagnetic)

(acen = N,N′-ethylenebis(acetylacetoneiminate))

suspended in a solution of

$\{[Pd(en)]_6(44'bipy)_3(tpt)_2\}^{12+}$

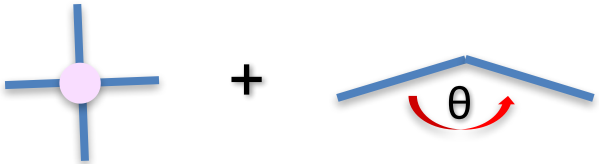


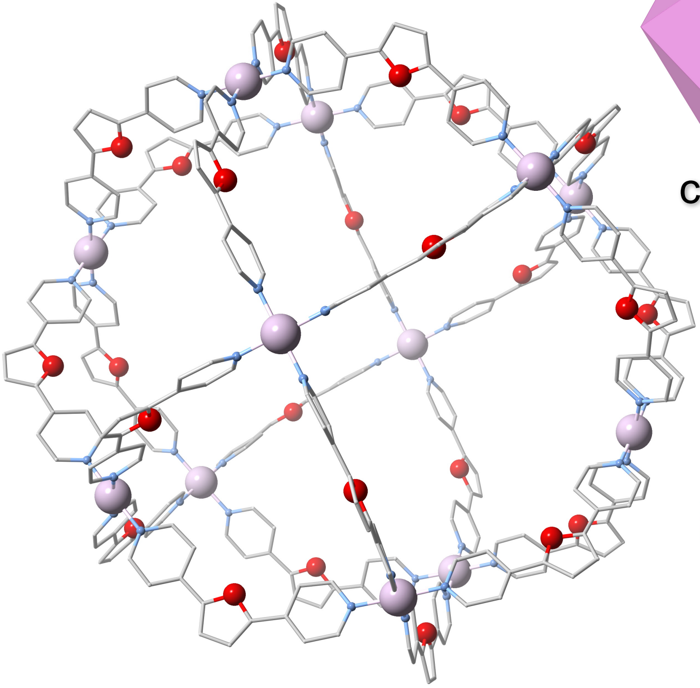
The solution becomes immediately green

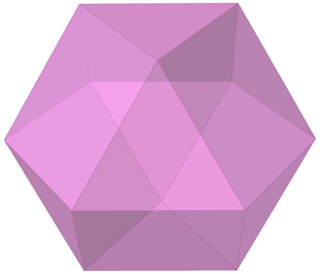
K. Ono, M. Yoshizawa, M. Akita, T. Kato, Y. Tsunobuchi, S. Ohkoshi, Makoto Fujita, *J. Am. Chem. Soc*. **2009**, *131*, 2782.

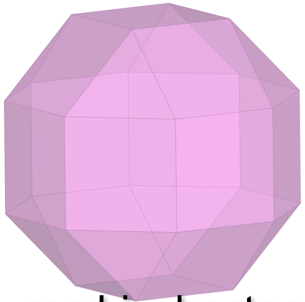
Polyhedra versus Coordination Polymers

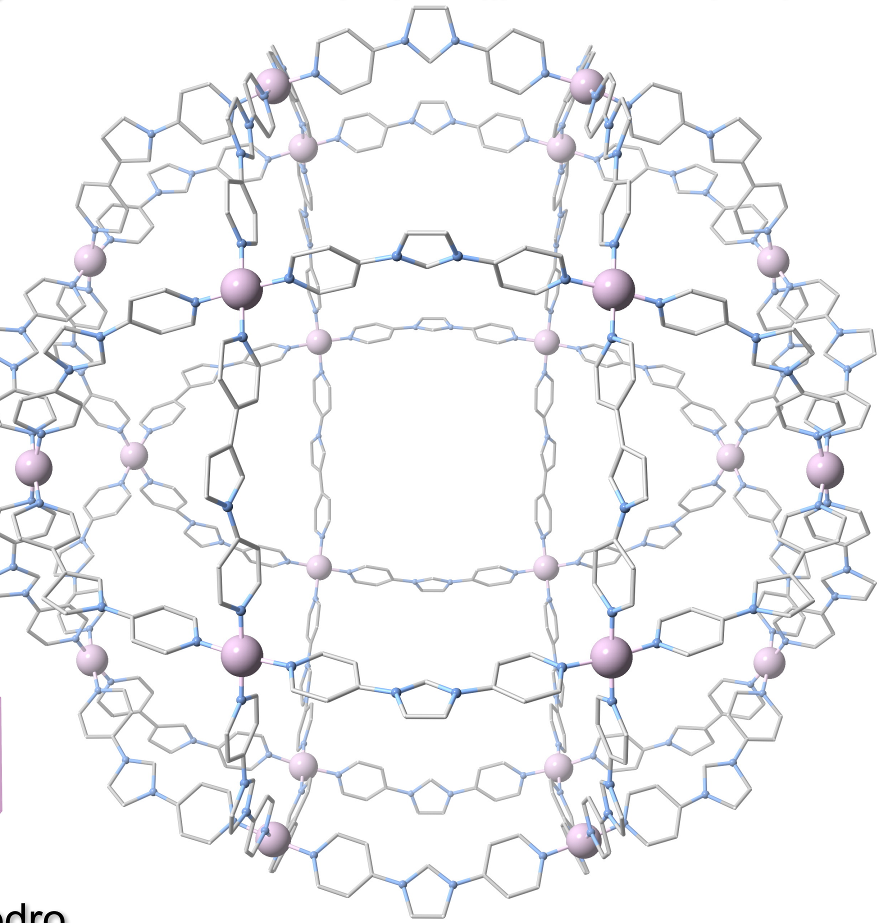
M. Fujita y col., *Angew. Chem. Int Ed.* **2012**, *51*, 3161;;; *Science* **2006**, *313*, 1273.

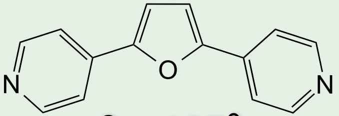


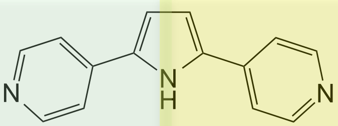


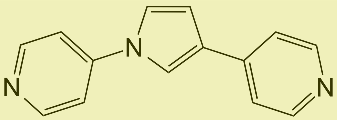

cuboctaedro

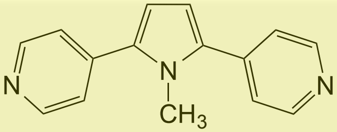

rombicuboctaedro

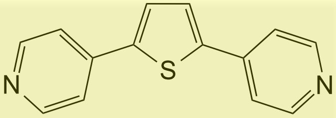



θ = 127°


θ = 135°


θ = 143°

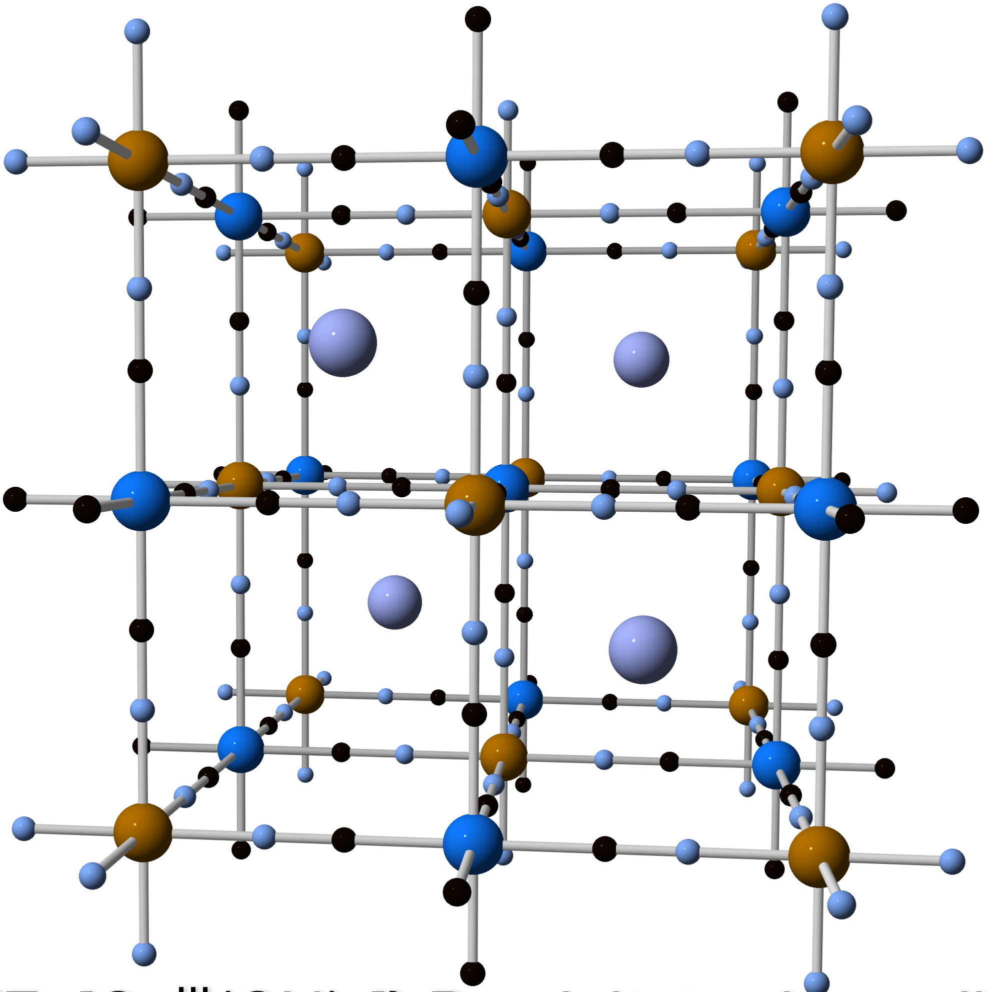

θ = 147°


θ = 149°

127° ← Pd$_{12}$L$_{24}$ → 131° 134° ← Pd$_{24}$L$_{48}$ → 149°

CPs / MOFs and Metalsupramolecular Chemistry
Polyhedra versus Coordination Polymers

$[Co^{III}(CN)_6]^{3-}$ (ac) + Fe^{II} (ac) + M^{I} (ac) }



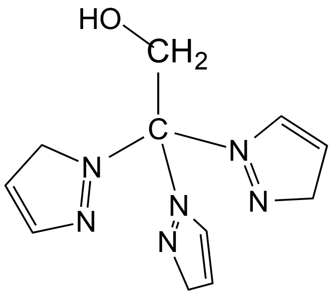
3D

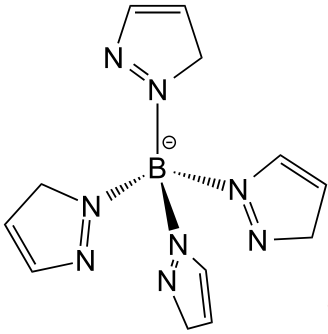
$M\{Fe[Co^{III}(CN)_6]\}$ Precipitates immediately

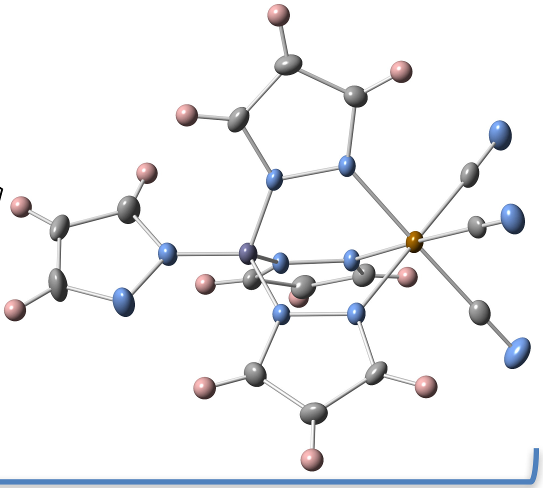
CPs / MOFs and Metalsupramolecular Chemistry Polyhedra versus Coordination Polymers

Protection of the coordination centres enable us to access ever smaller fragments of the counterpart structure of Prussian Blue

2,2,2-tris(pyrazolylethanol) + $Co^{II}(ClO_4)_2 \cdot 6H_2O$ +[(tetrapyrazolylborate)$Fe^{III}(CN)_3]^-$



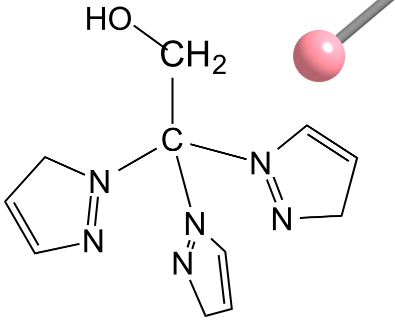


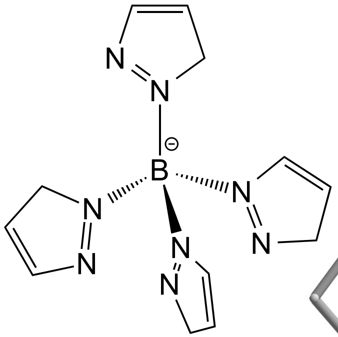


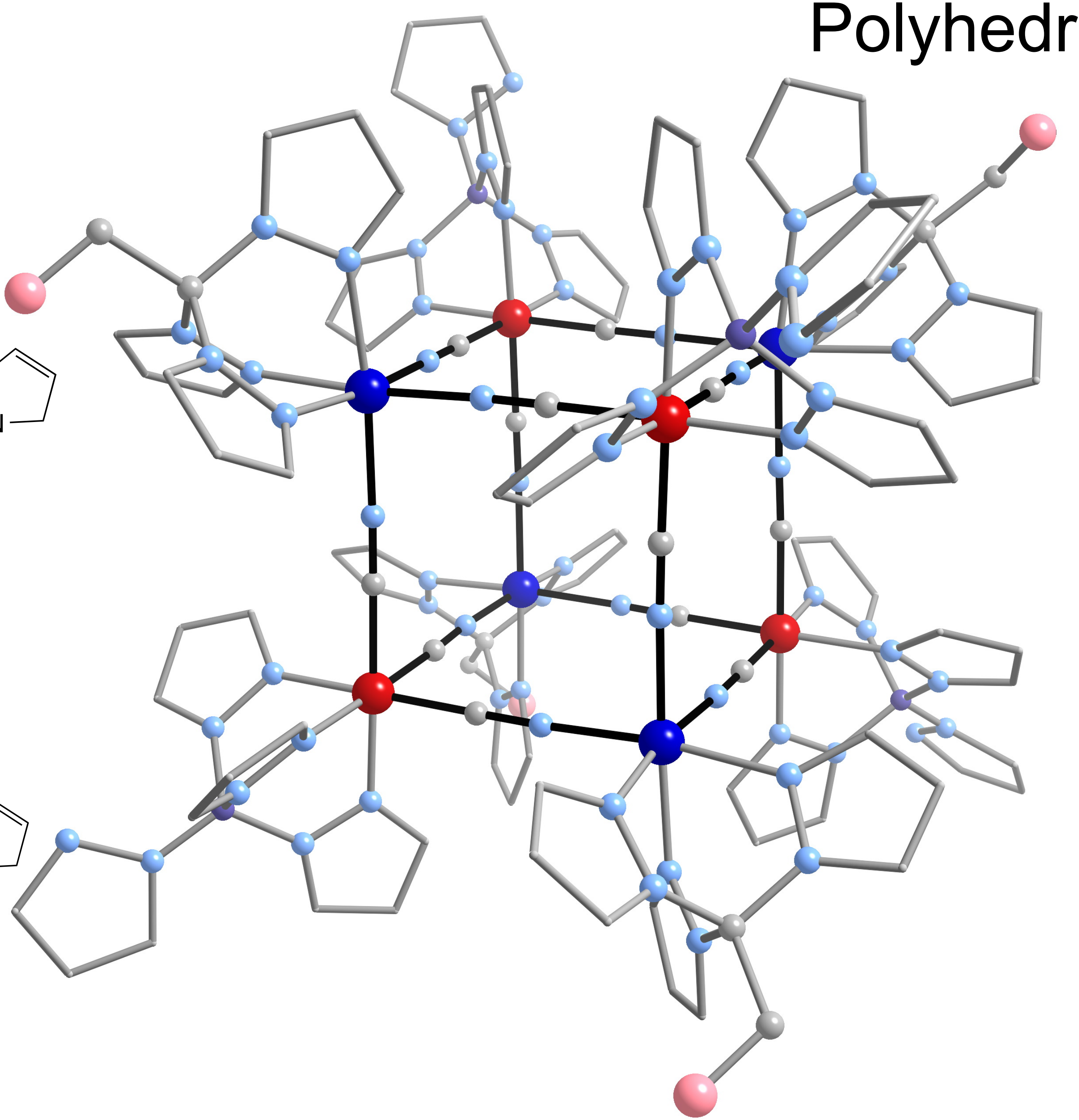
$\{[(pzTp)Fe^{III}(CN)_3]_4[Co^{II}(pz)_3\text{-}CCH_2OH]_4[ClO_4]_4 \cdot 13DMF \cdot 4H_2O$

D. Li, R. Clérac, O. Roubeau, E. Harté, C. Mathonière, R. Le Bris, S. M. Holmes, *J. Am. Chem. Soc.* **2008**, *130*, 252-258.

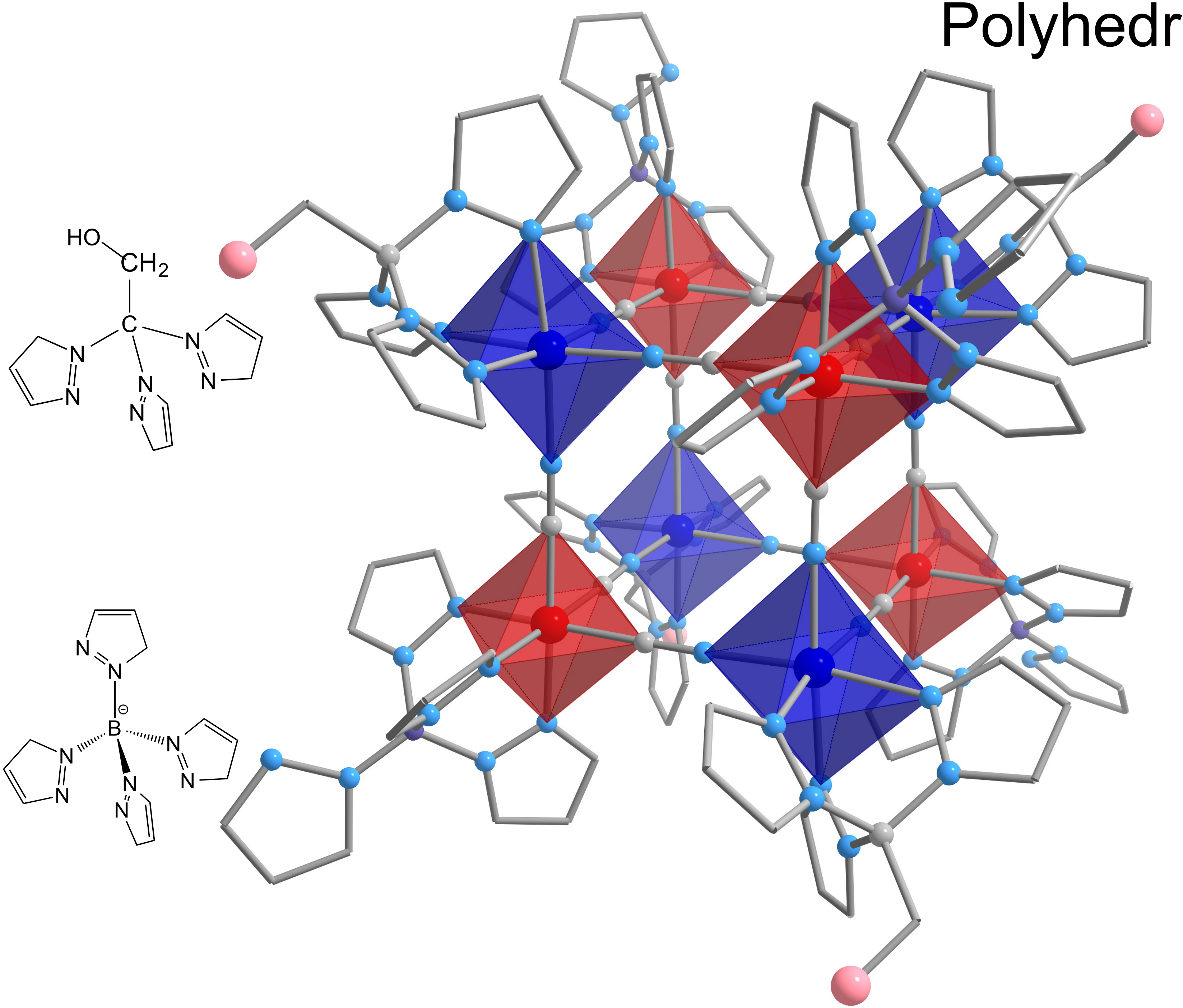
Polyhedron 0D



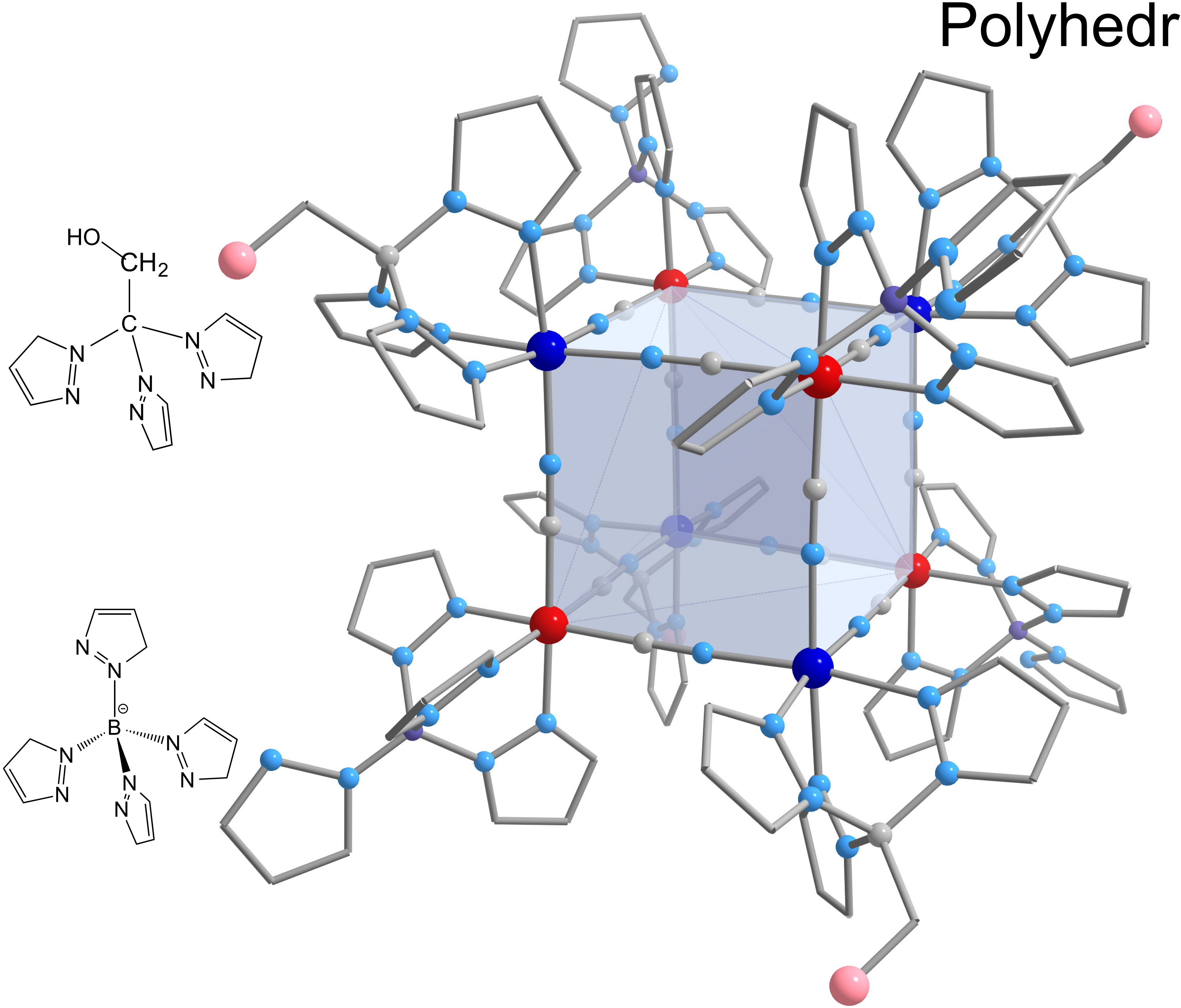




Polyhedron 0D



Polyhedron 0D



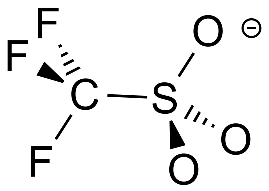
CPs / MOFs and Metalsupramolecular Chemistry

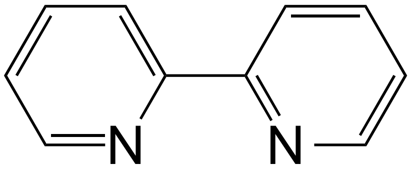
Polyhedra versus Coordination Polymers

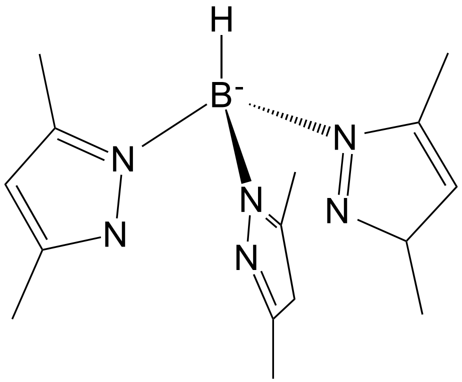
Protection of coordination centres give access to smaller molecular fragments of the CP (in this case Prussian Blue)

1 Co^{II}(OTf)$_2$ + 2 (2,2'bipy) +1 [(Hidro-tris(3,5-dimetil)pirazolil borato)Fe^{III}(CN)$_3$]$^-$

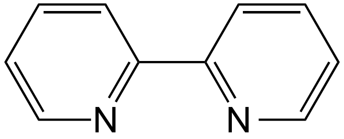
Otf = trifluoromethanesulphonate

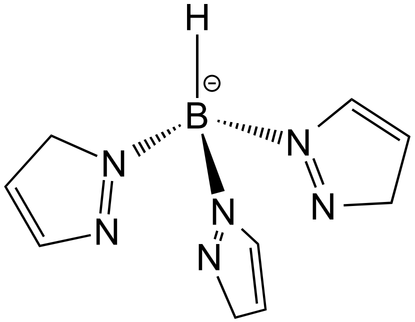


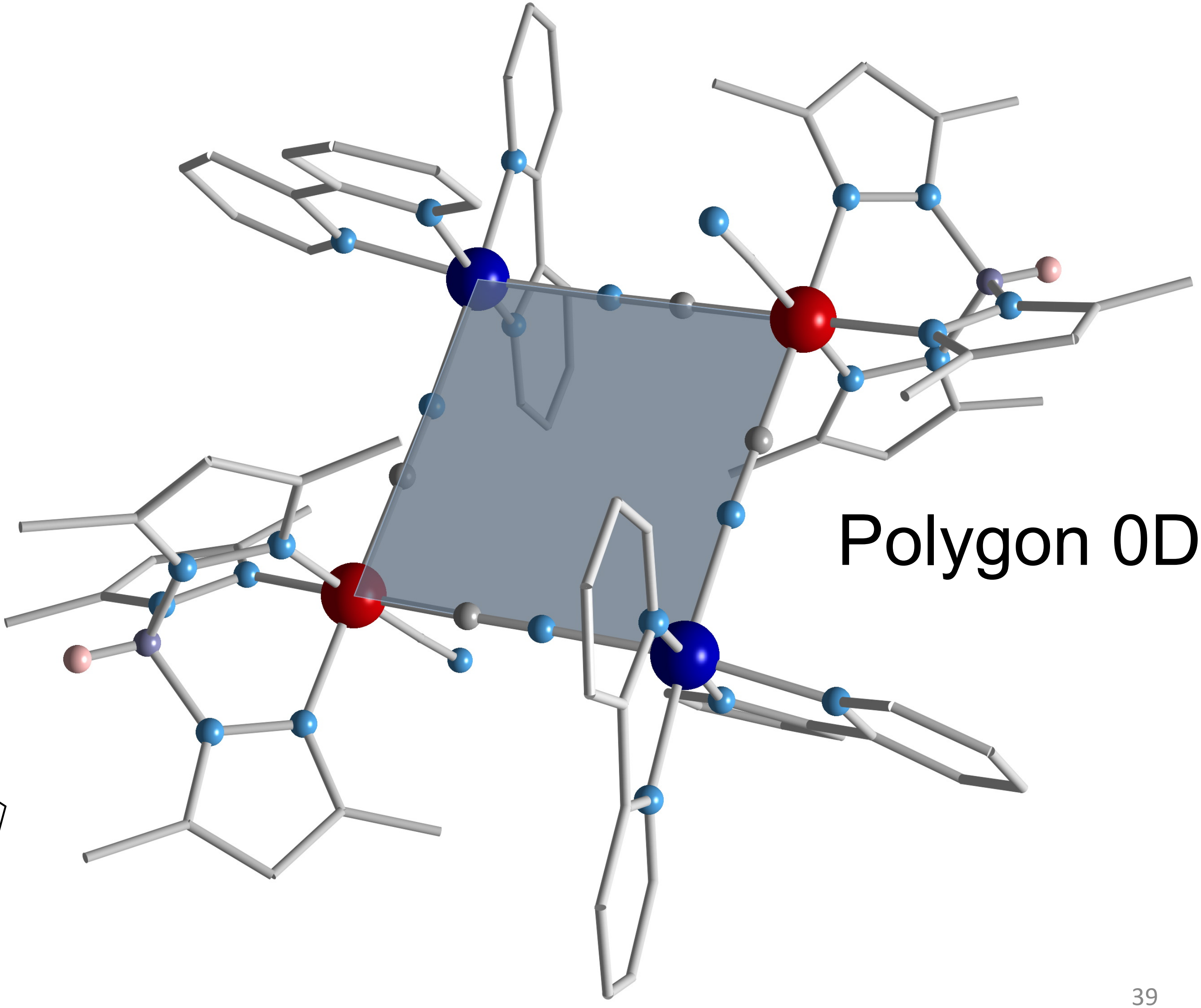




[{(Tp*)Fe^{III}(CN)$_3$}$_2${Co^{II}(bpy)$_2$}$_2$][OTf]$_2$·4DMF·2H$_2$O

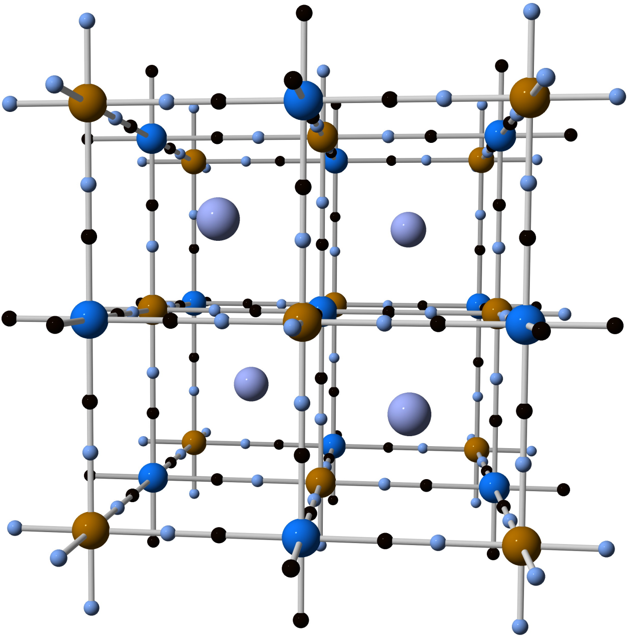




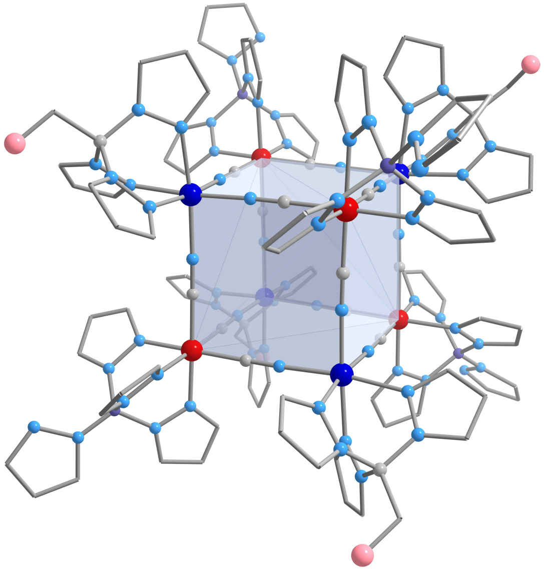

Polygon 0D

Y. Zhang, D. Li, R. Clérac, M. Kalisz, C. Mathonière, S. M. Holmes, *Angew. Chem. Int. Ed*. **2010**, *49*, 3752-3756

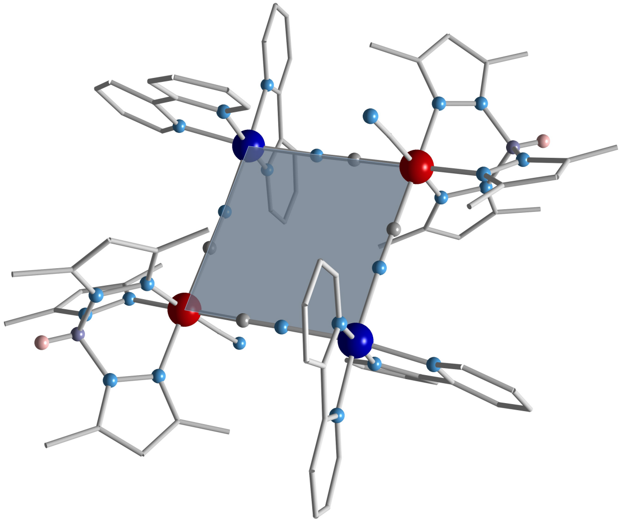
Three-dimensional network



0-D Polyhedron



0-D Polygon



Relevant references about Coordination Polyhedrons

M. Fujita, M. Tominaga, A. Hori, B. Therrien *Acc. Chem. Res.* **2005**, *38*, 369.
*(http://fujitalab.t.u-tokyo.ac.jp/research_e/)

A. J. McConnell, C. S. Wood, P. P. Neelakandan, **J. R. Nitschke** *Chem. Rev.*, **2015**, *115*, 7729.
S. Zarra, D. M. Wood, D. A. Roberts, **J. R. Nitschke** *Chem. Soc. Rev.*, **2015**, *44*, 419–432.
*(https://www.nitschkegroup-cambridge.com)

R. Chaktabarty, P. S. Mukherjee, **P. Stang** *Chem. Rev*. **2011**, *111*, 6810.
T. R. Cook, Y.-R. Zheng, **P. Stang** *Chem. Rev*. **2013**, *113*, 734.

Concept of Network:

Tool to describe and design coordination polymers

One of the most powerful techniques in Crystal Engineering with analytical and design potential of crystalline solids is the reduction of its crystalline structures to "simple" networks.

This strategy helps to i) describe and understand complicated structures; ii) certify the discovering of new networks and iii) establish property structure correlations.

Background: This approach stems from the seminal work carried out by A. F. Wells during the period 1950-1970 ... However, it was in the years 1989-1990 when Robson and Hoskins and collaborators (and subsequent works) published two articles:

B. F. Hoskins, R. Robson, *“Infinite Polymeric Frameworks Consisting of Three Dimensionally Linked Rod-like Segments”, J . Am. Chem. Soc.* **1989**, *111* , 5962-5964.

B. F. Hoskins, R. Robson “Design and Construction of a New Class of Scaffolding-like Materials Comprising Infinite Polymeric Frameworks of 3D-Linked Molecular Rods. A Reappraisal of the $Zn(CN)_2$ and $Cd(CN)_2$ Structures and the Synthesis and Structure of the Diamond-Related Frameworks $[N(CH_3)_4][Cu^{I}Zn^{II}(CN)_4]$ and Cu^{I}[4,4”4”,4”’-tetracyanotetraphenylmethane] $(BF_4)\cdot C_6H_5NO_2$, *J. Am. Chem. Soc.* **1990**, *112*, 1546-1554

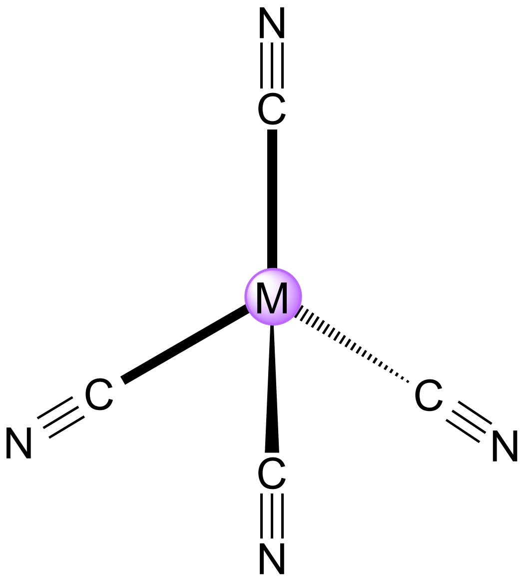
Where they apply the ideas of Wells to the Crystal Engineering of Polymers of coordination.

These authors emphasize that:
Structures with precise topologies can be designed and realized through the use of metal ions and ligands with appropriate coordination geometries.

Examples…

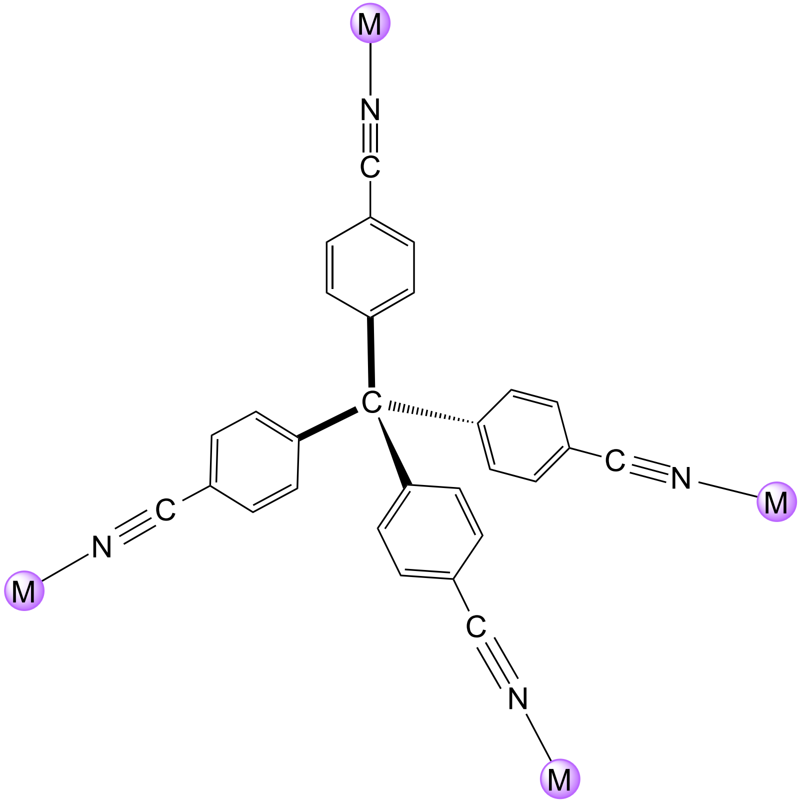
Network:
Tool to describe and design coordination polymers. Example: Diamond Network

Example: Diamond type networks can be generated by choosing metal ions that have a preference for coordination number 4 and tetrahedral geometries such as Cu(I), Zn(II) and Cd(II) together with linear ligands such as CN^- or designing more sophisticated ligands with tetrahedral geometry such as 4,4',4",4"'-tetracyanotetraphenylmethane:



M can be assimilated to **C** (diamond)
The **CN** group adopts the role of **C-C** bond

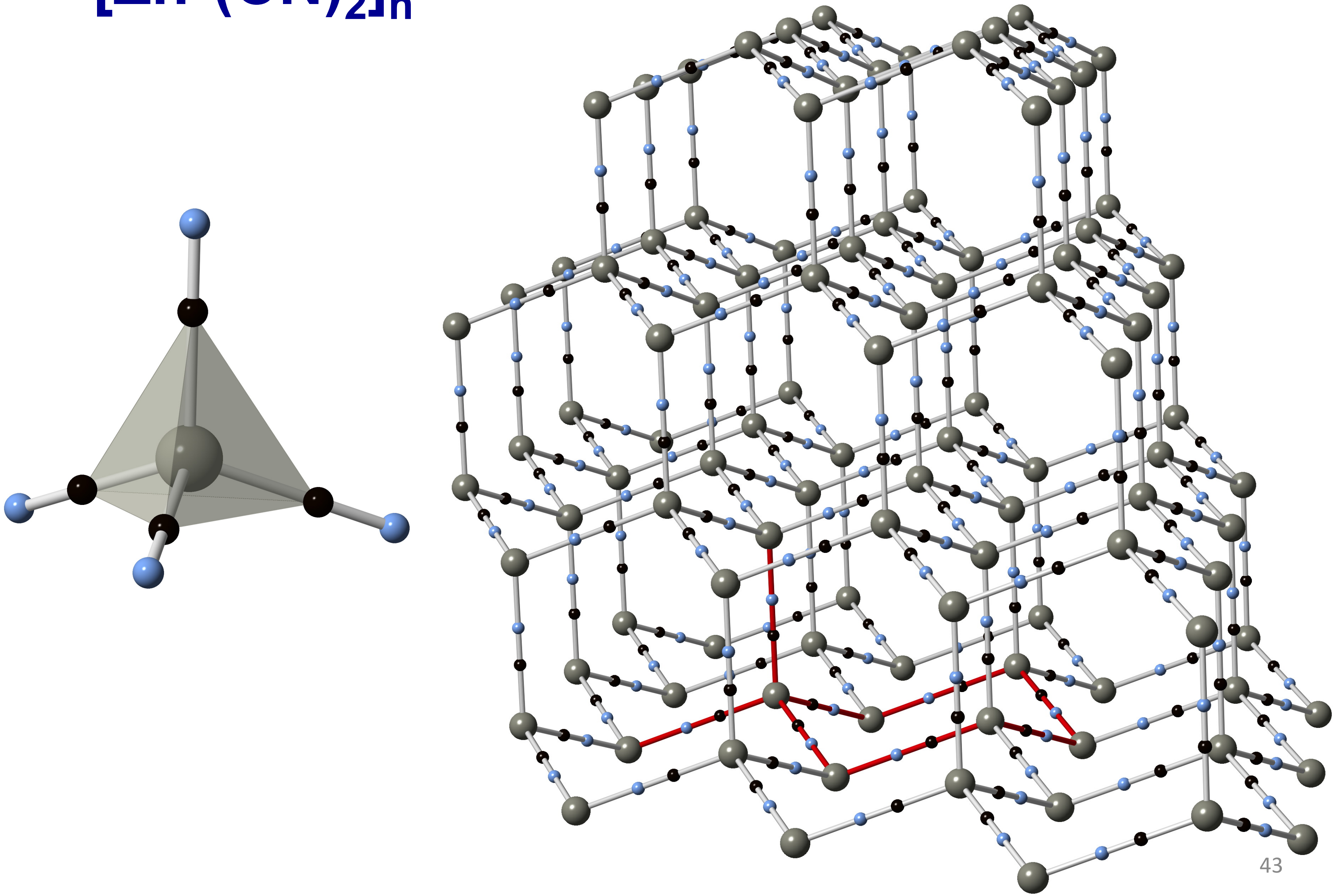
$Zn^{II}(CN)_2$, $Cd^{II}(CN)_2$, $\{[Zn^{II}(CN)_4]Cu^{I}\}[N(CH_3)_4]$



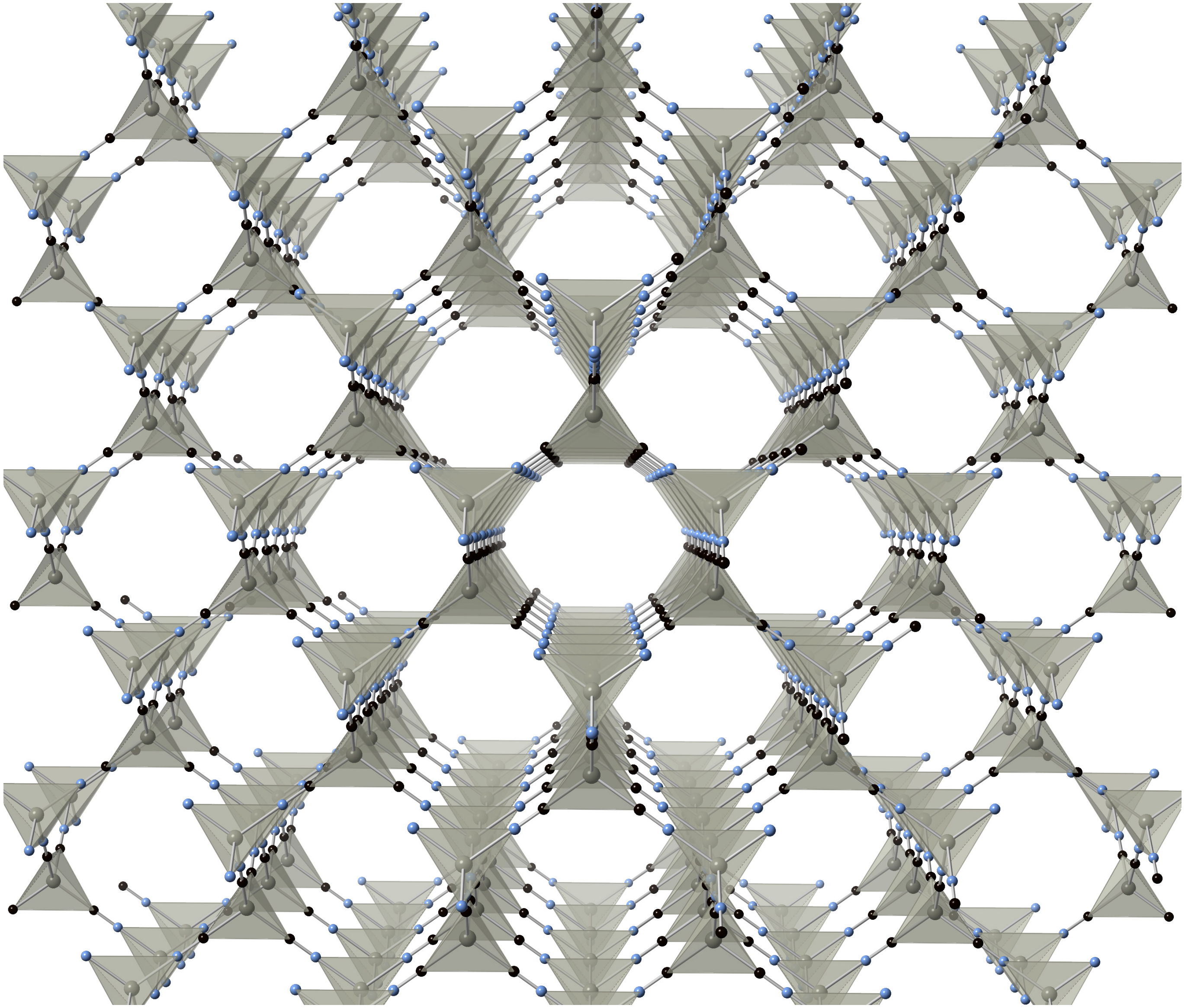
The **C** centres of diamond are replaced with **M** and the ligand **$[C(PhCN)_4]$**

$Cu^{I}[C(PhCN)_4](BF_4)\cdot nPhNO_2$ (n>7)

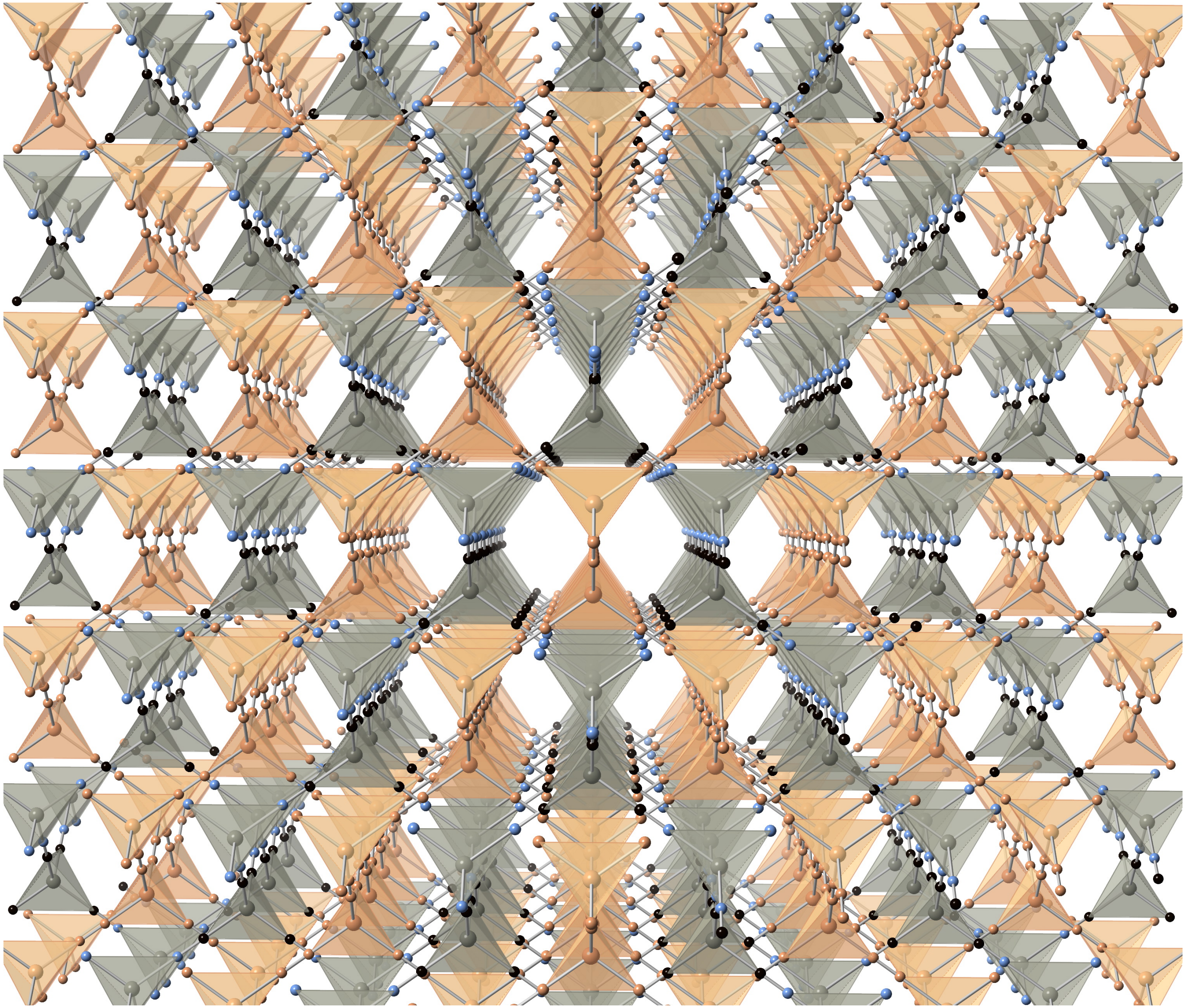
$[\mathrm{Zn^{II}(CN)_2}]_n$



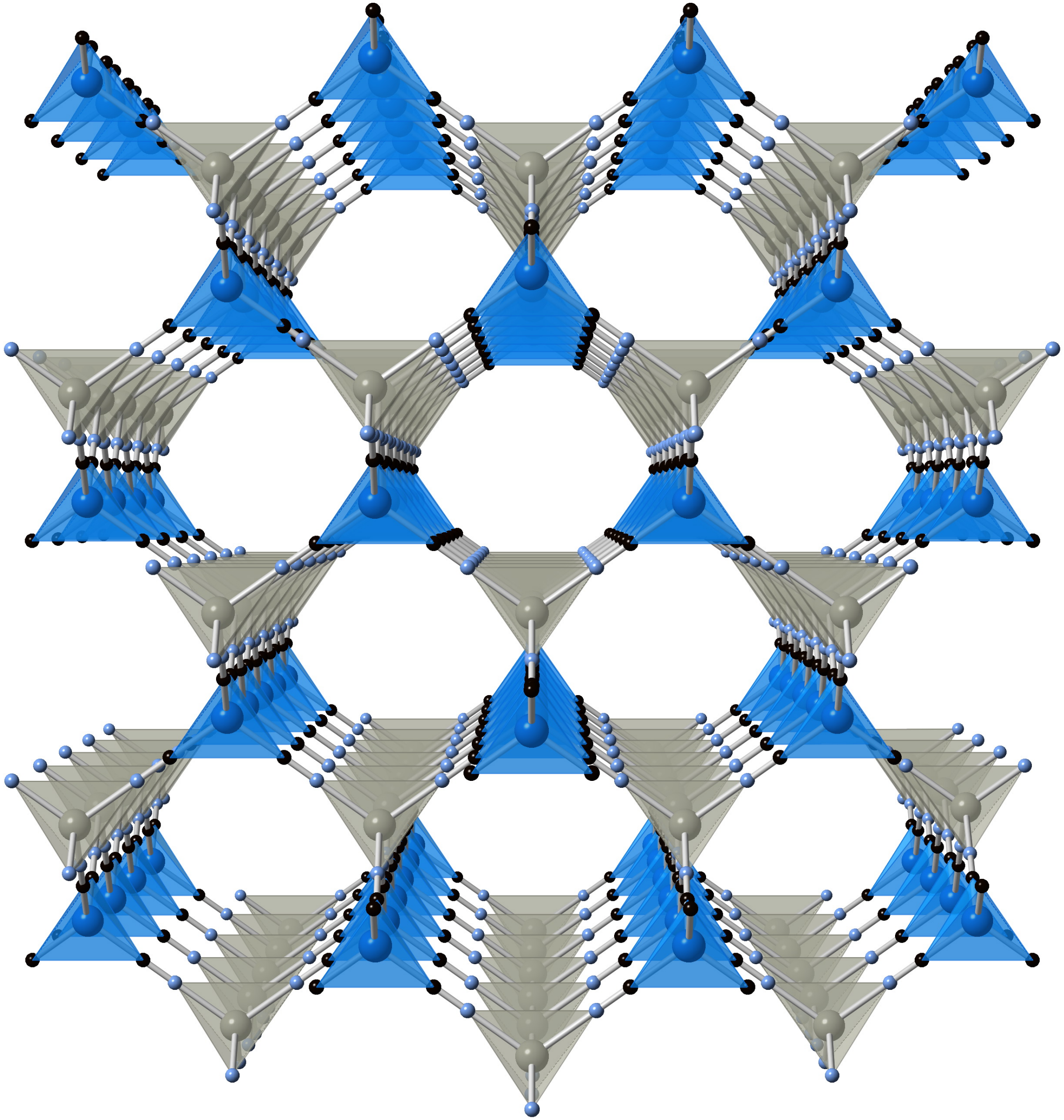
Network Interpenetration Phenomenon



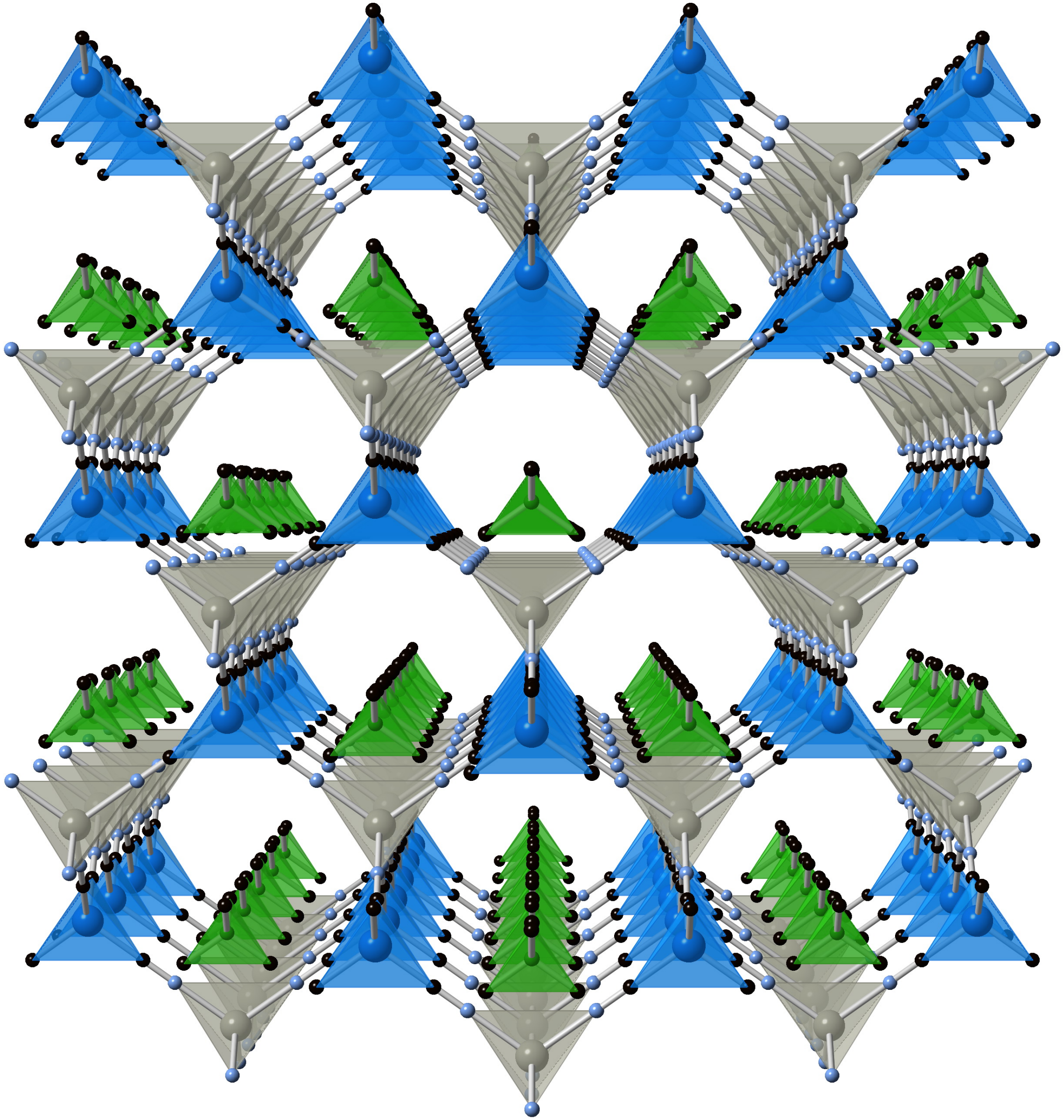
Network Interpenetration Phenomenon



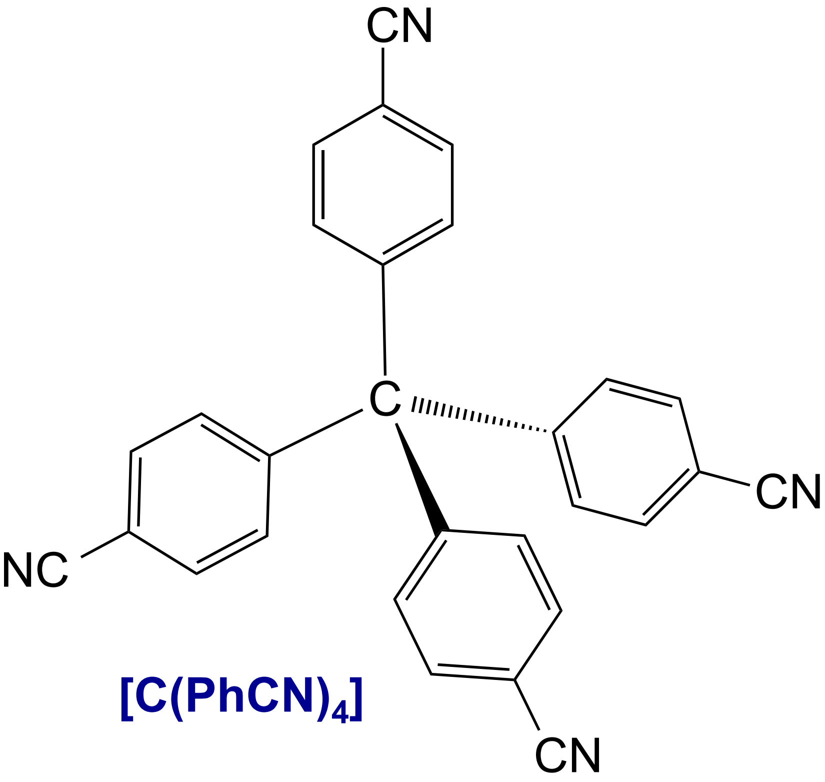
$\{[\mathrm{Zn^{II}(CN)_4}]\mathrm{Cu^{I}}\}[\mathrm{N(CH_3)_4}]$ Avoids Interpenetration



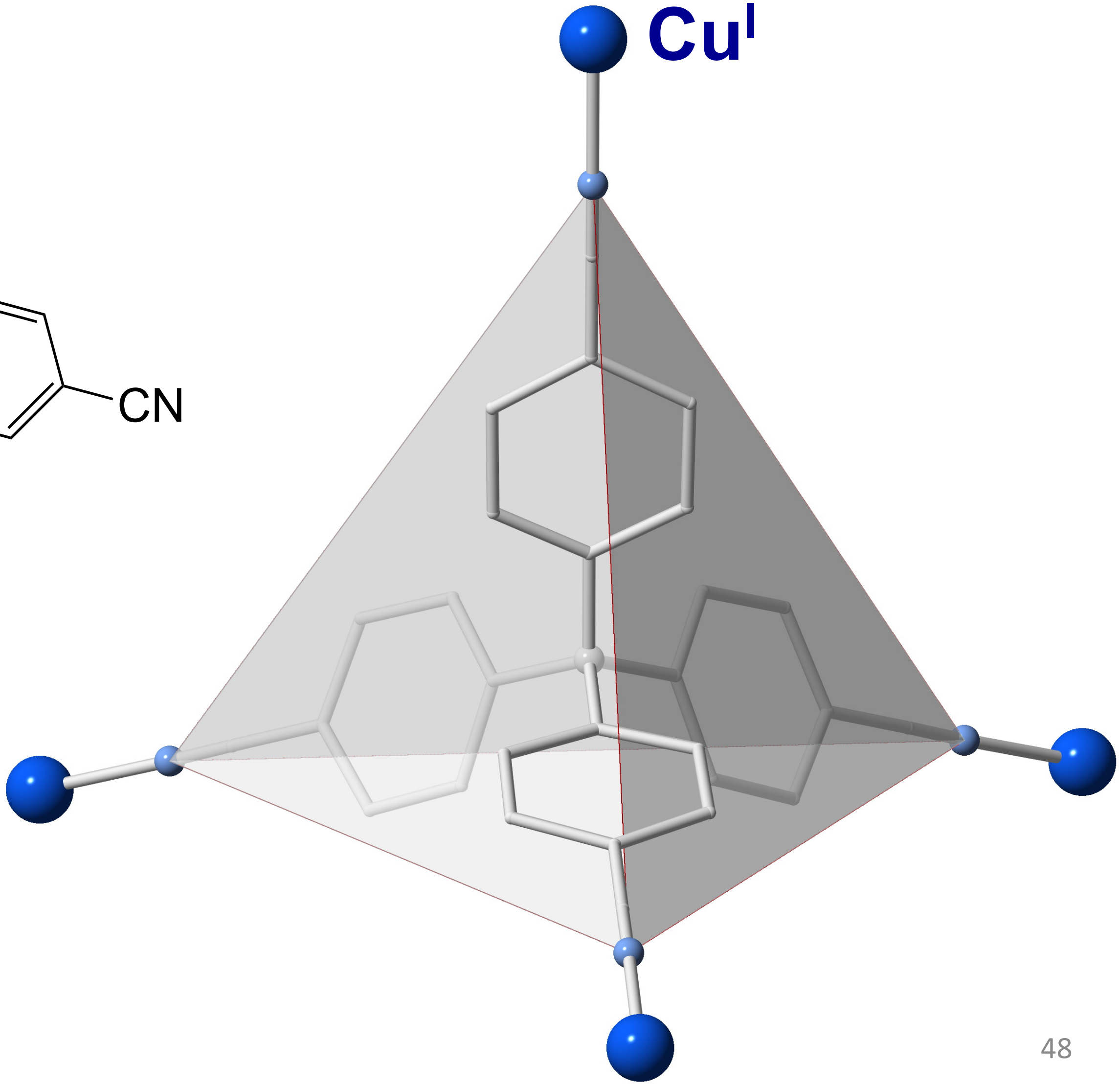
$\{[Zn^{II}(CN)_4]Cu^{I}\}[N(CH_3)_4]$ Avoids Interpenetration



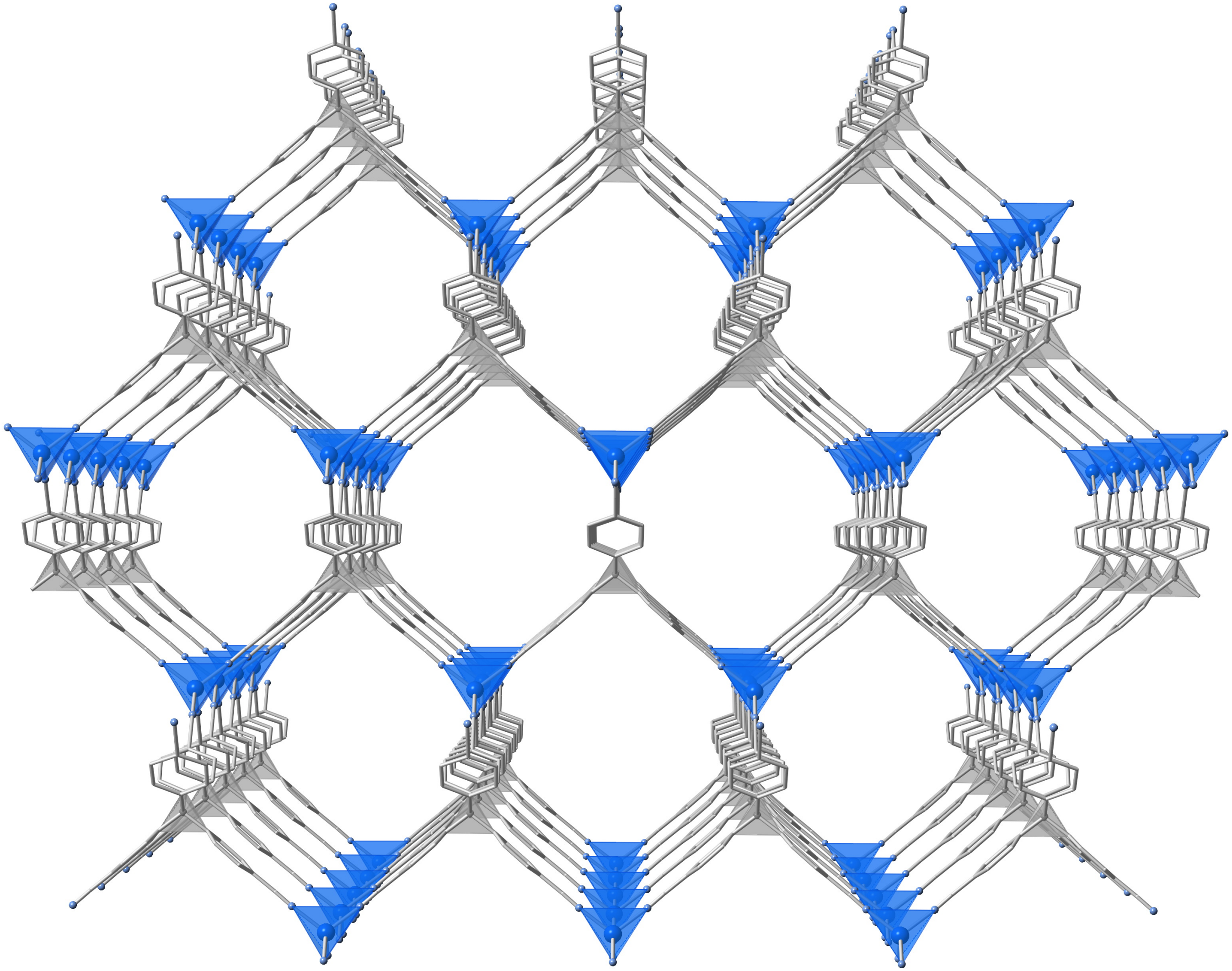
Expansion of the Diamond type network
$Cu^{I}[C(PhCN)_4](BF_4)\cdot nPhNO_2$ (n>7)



$[C(PhCN)_4]$



Expansion of the Diamond type network $Cu^I[C(PhCN)_4](BF_4)\cdot nPhNO_2$ (n>7)



Definition of Network

i) A network is a polymeric collection of interlaced nodes.

ii) Each link connects 2 nodes and each node is linked to 3 or more nodes.

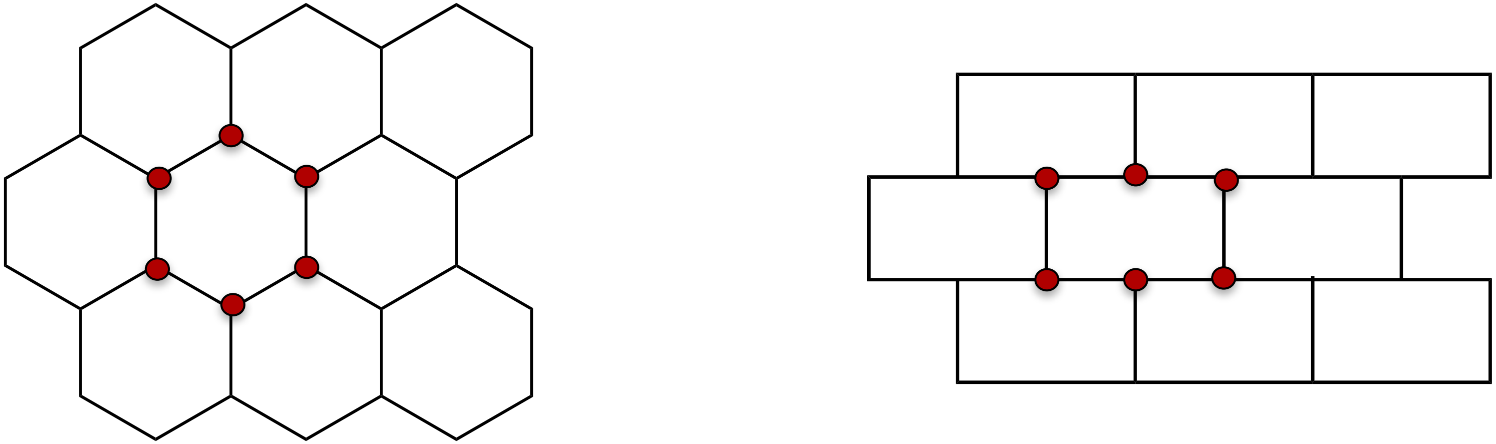
iii) A node can not be connected to only 2 nodes because it becomes a link.

iv) A link can only connect to 2 nodes; if it were connected to more nodes (eg 3) it would become a node.

v) The network must have an order that is repeated by an infinite number of links and nodes.

Every network has two essential concepts associated
a) Geometry
b) Topology

Example: both networks are topologically identical but geometrically different. They consist of three-connected nodes, in one case the connection is regular trigonal and in the other is T shaped. Both networks can be interconverted if they break links. Note that the shortest circuit joining the nodes contains 6 nodes in both networks.



From a topological point of view there is no difference between a tetrahedron and a square. The regular connection of tetrahedral centres gives rise to a 3D network of the diamond type. But square connections give rise to a square 2D network. This is a difficulty in the description of the networks but in spite of that the topological analysis is very useful as demonstrated by A. F. Wells.

Connectivity versus Geometry

- ✓ In the topological approach is the connectivity and not the geometry the element of description of a network.

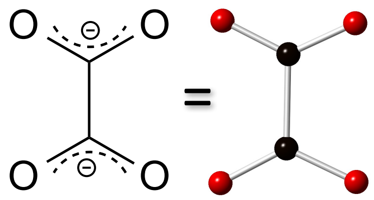
- ✓ In a network there are two essential elements: ligands and metal centres and both determine the geometry and topology of the network.

- ✓ For the reduction of a coordination polymer / MOF in a network, it is necessary to identify the nodes and the links that define it on the basis of metal centres and ligands.

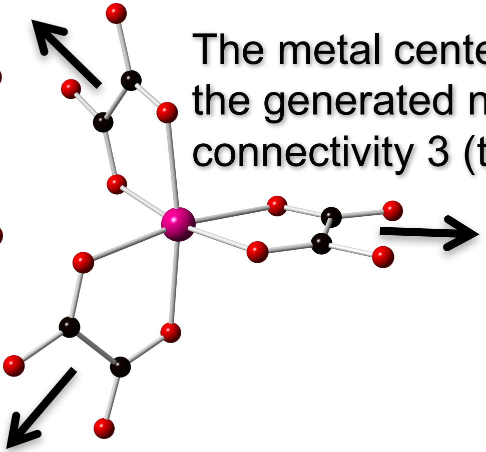
- ✓ This reduction can be very simple in certain cases but it is not simple in general. Consequently, it is important to keep in mind that the connectivity of a node can be very different from the local geometry of the centre that originates it (coordination index).

Connectivity versus Geometry

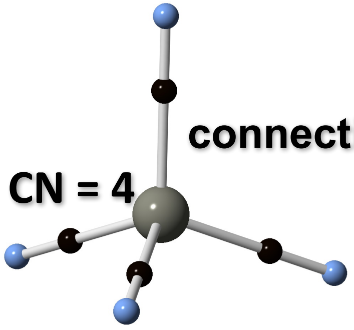
Examples of coordination and connectivity centres:

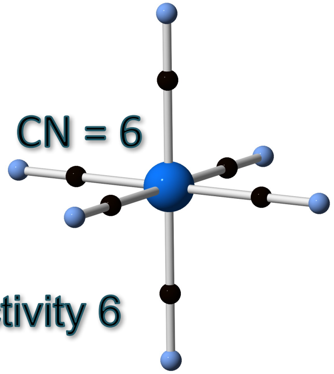


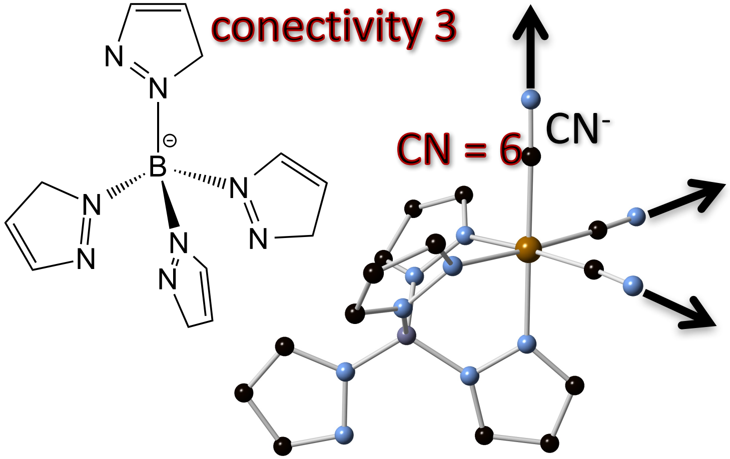
Ion Oxalate
$C_2O_4^{2-}$

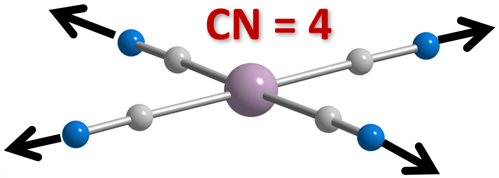


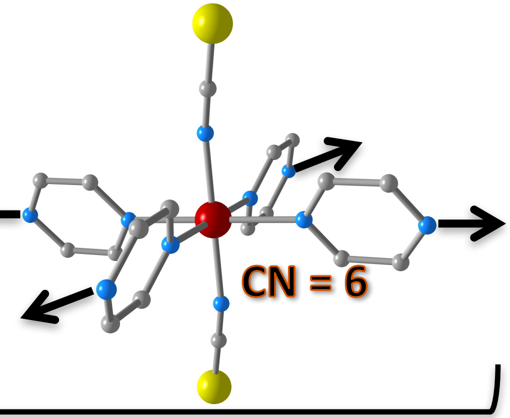
The metal center has a CN = 6, but the generated node has connectivity 3 (trigonal)











The generated node has connectivity 4 (square)

Selection of Most Studied Ligands (Connectors, Nodes)

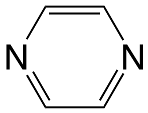
✓ N-donor ligands derived from pyridine.

✓ N-donor ligands derived from azoles (imidazole, triazole and tetrazole) and their deprotonated forms (azolate groups).

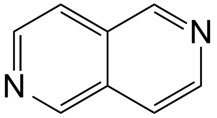
✓ O-donor ligands derived from the carboxylate function.

Examples of Ditopic Connectors of the Pyridine Type

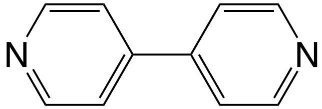
The sp^2 electronic pair of the N-donor atom facilitates a predictable coordination towards the metal atom. Being non-deprotonable ligands, the complexes require coordinating (or non-coordinating) anions to compensate the charge. The saturation of the metal coordination sphere with these ligands is unusual. In absence of another type of bridging ligands generally negatively charged, these ligands derived from pyridine generate 1D or 2D coordination polymers.



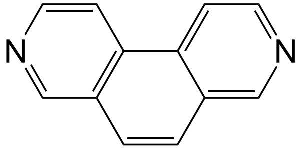
pyrazine



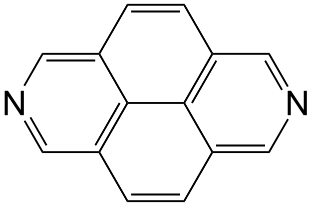
2,6-naphthyridine

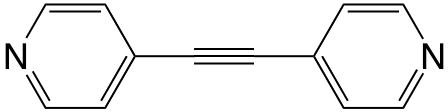


4,4'-bipyridine

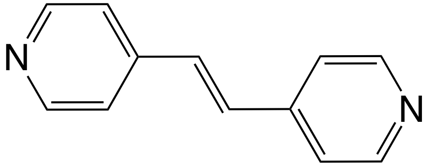


8-phenanthroline

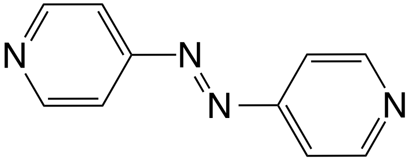




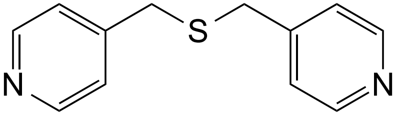
1,2-di(pyridin-4-yl)ethine



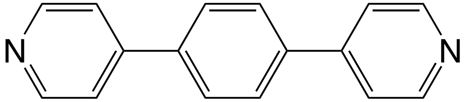
trans-(4,4'-vinylendipyridina))



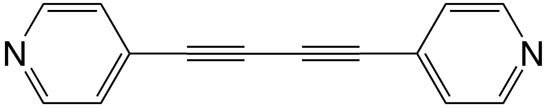
trans-(4,4'-azopyridine))



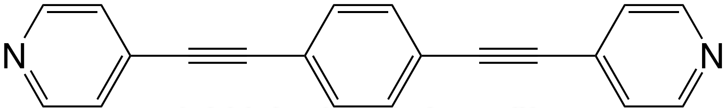
Bis(pyridin-4-ylmethyl)sulphane



1,4-di(pyridin-4-yl)benzene



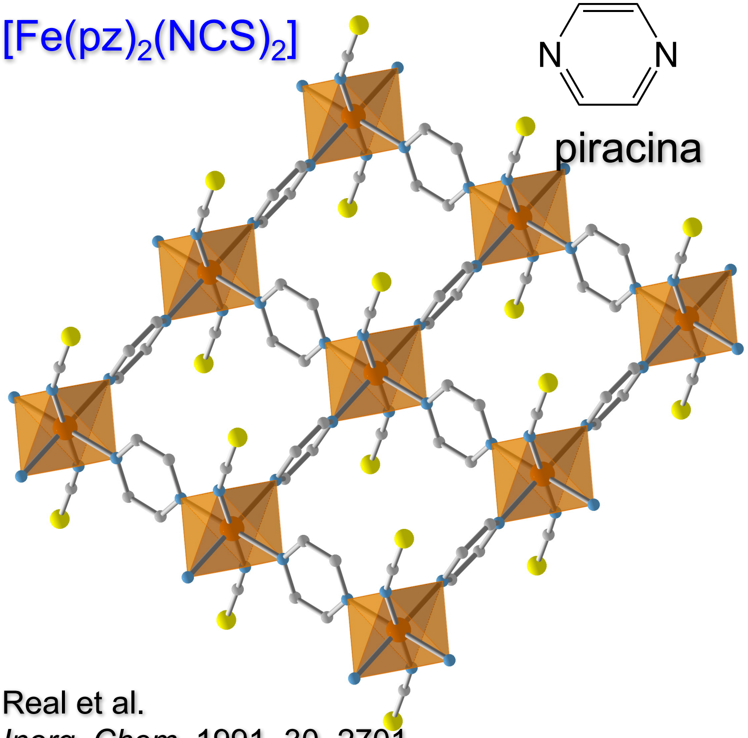
1,4-di(pyridin-4-yl)buta-1,3-diine



1,4-bis(pyridin-4-yletenyl)benzene

Examples of 2D complexes

$[Fe(pz)_2(NCS)_2]$

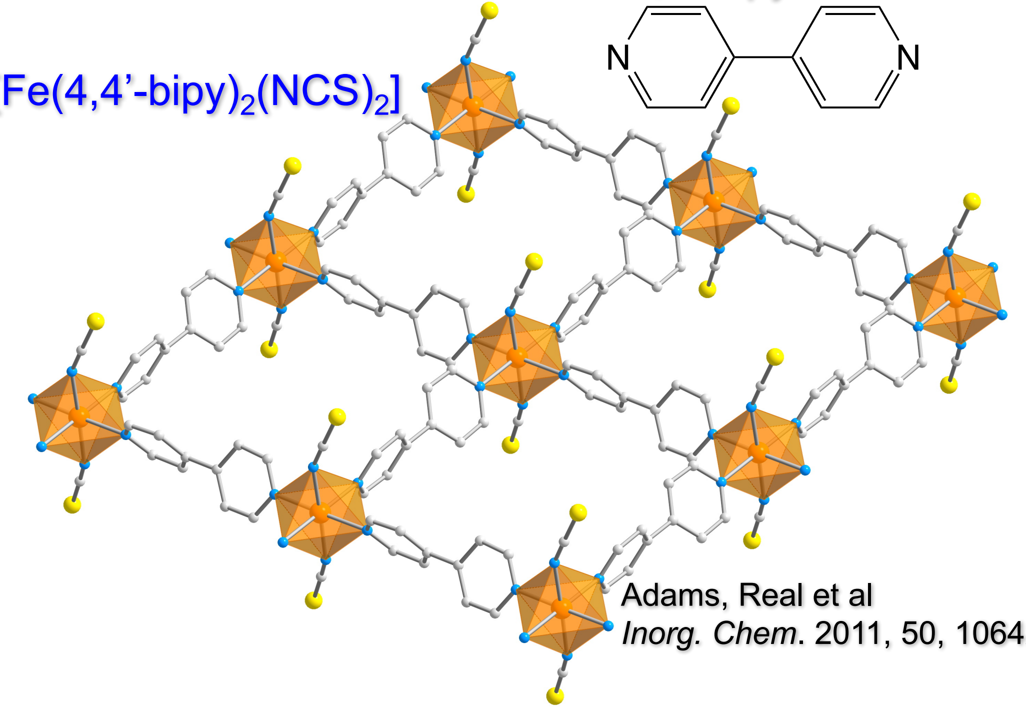


piracina

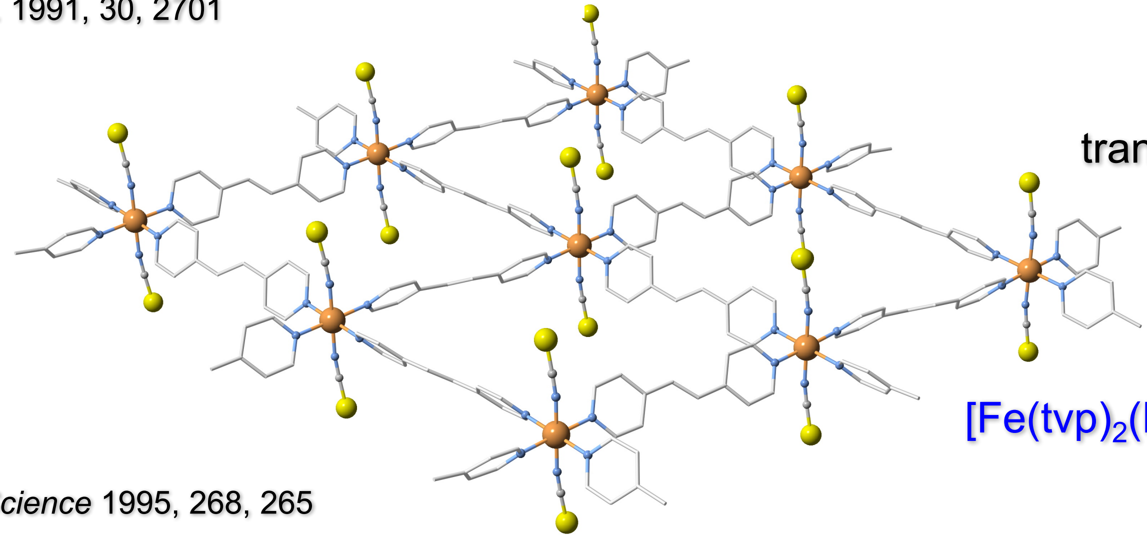
Real et al.
Inorg. Chem. 1991, 30, 2701

4,4'-bipyridine

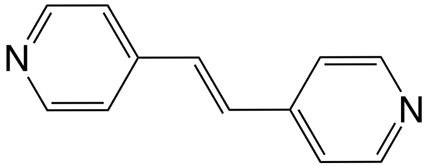
$[Fe(4,4'\text{-bipy})_2(NCS)_2]$



Adams, Real et al
Inorg. Chem. 2011, 50, 10642



trans-(4,4'-vinylendipyridine))

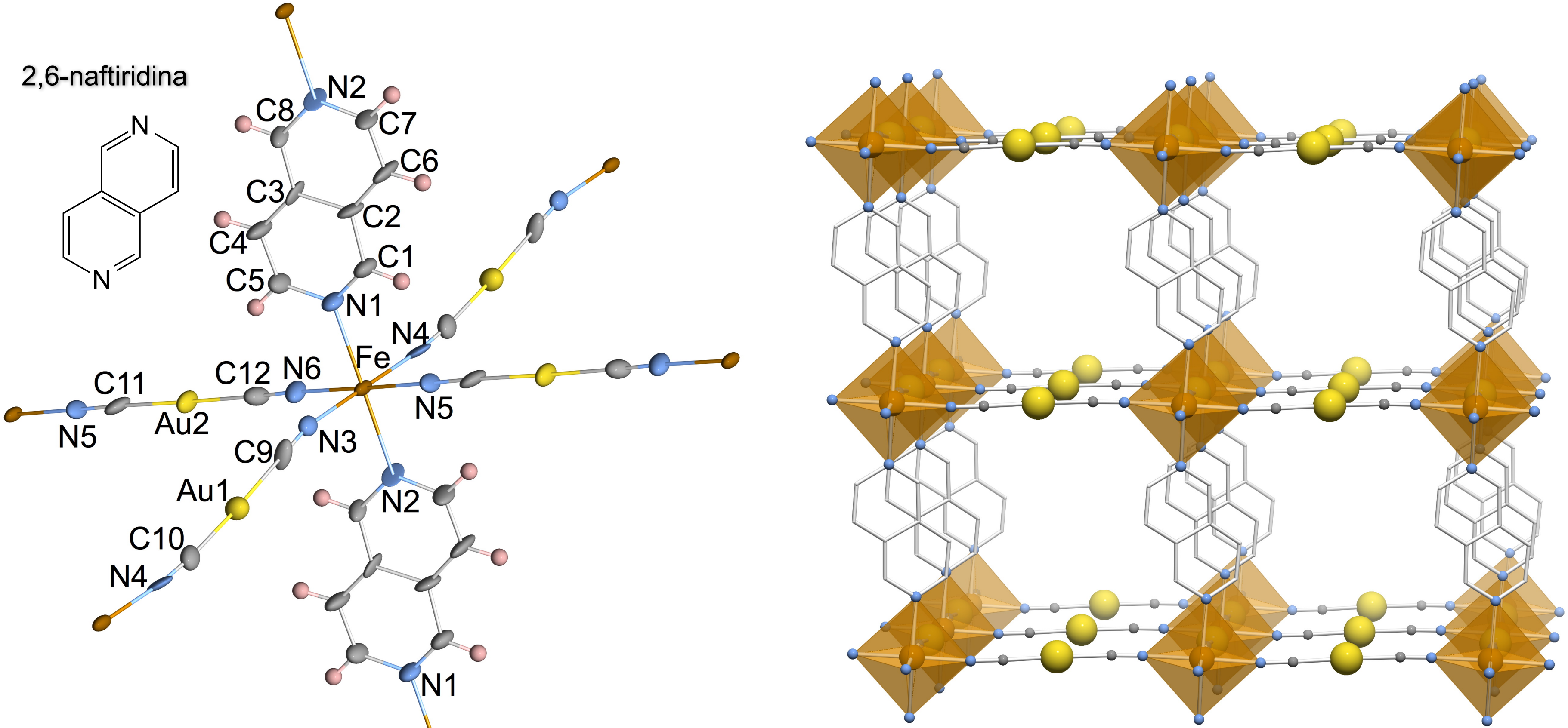


$[Fe(tvp)_2(NCS)_2]$

Real et al *Science* 1995, 268, 265

Examples of 3D complexes

The use of negatively charged ligands or metallo-ligands causes 3D networks. Among these we find ligands of the type [SCN^-, CN^-, $[M(CN)_2]^-$ (M = Cu^I, Ag^I, Au^I), $[M(CN)_4]_2^-$ (M = Ni^{II}, Pd^{II}, Pt^{II}), $[M(CN)_6]^{x-}$ (M = Cr^{III}, Fe^{III}, etc) , $[M(CN)_8]^{(4,3-)}$ (M = $Mo^{IV,V}$, $W^{IV,V,}$, Nb^{IV}), $[N(CN)_2]^-$, etc,]. 3D networks are usually formed by stacking 2D subnets generated by the pseudo-halide and the metal linked by the organic ligand:

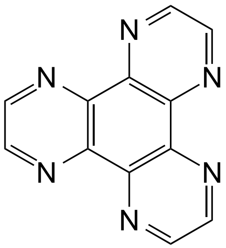


$Fe(naphthyridine)[Au(CN)_2]_2$

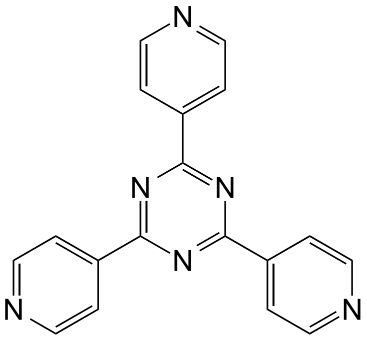
Real et al Eur. J. Inorg. Chem. 2018

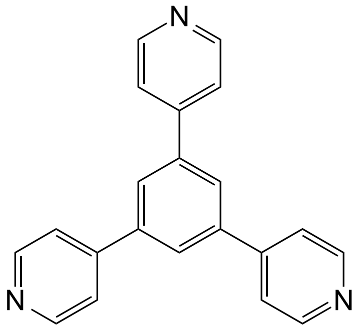
Tri- and Tetra-Topic Nodes of the Pyridine Type

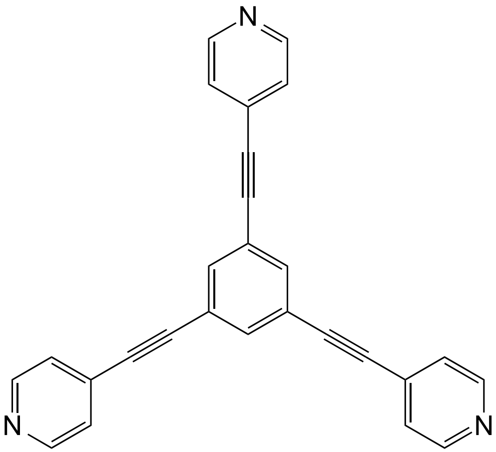
These ligands can no longer be considered as connectors since when connecting more than two nodes they become nodes.

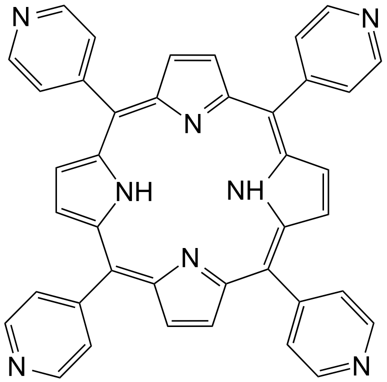


Ver R. Robson et al.,
J. Chem Soc., Chem. Commun.
1990, 762-763; [AgHAT](ClO_4).Solv
structure type SiSr (10,3)-a

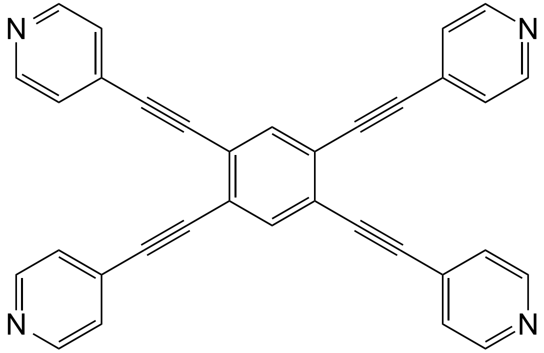


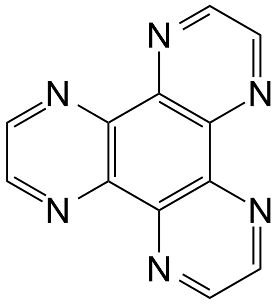




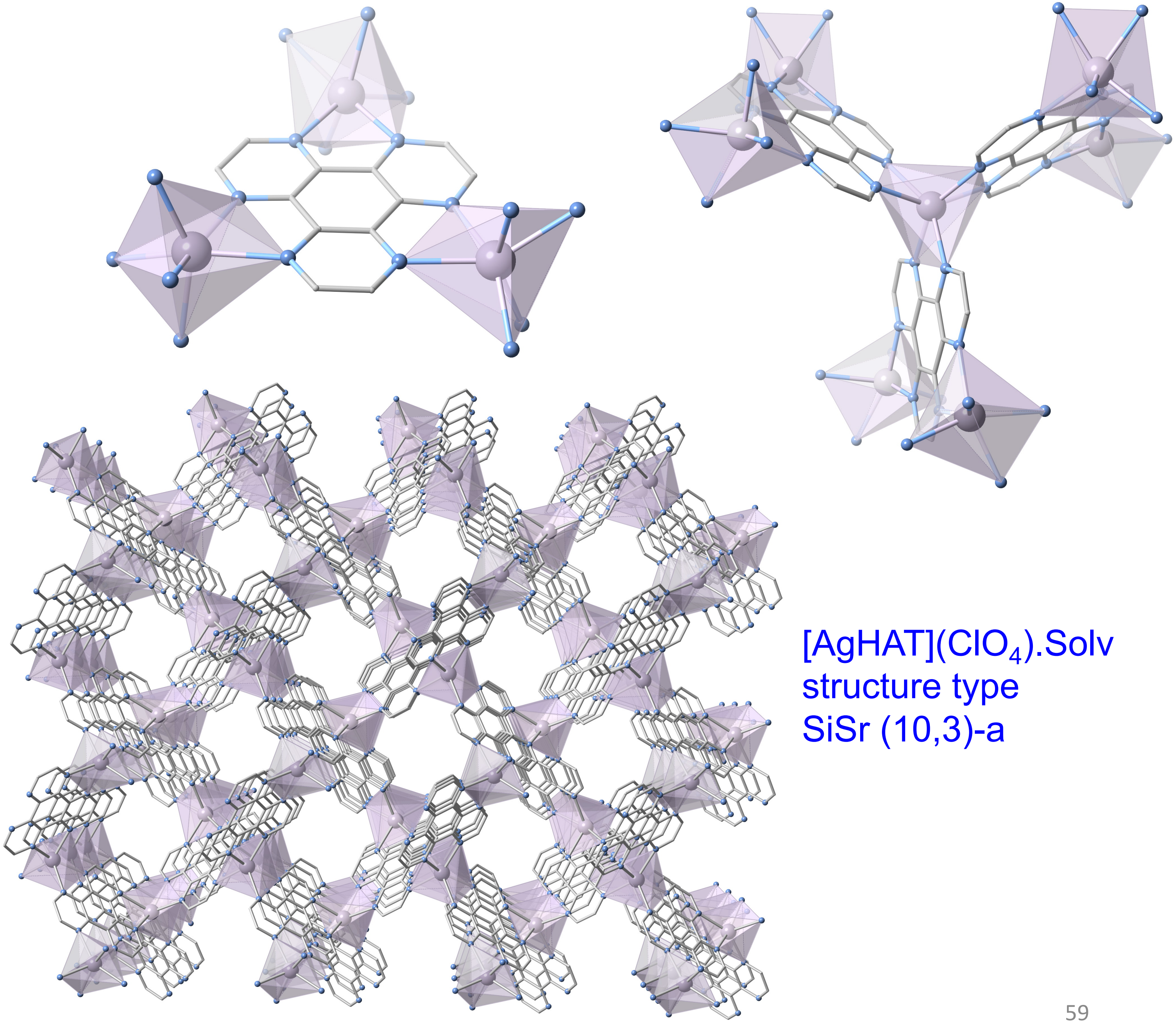


Ver R. Robson et al., Nature 1994, 369, 727
$\{[Cu^{II}(tpp)]Cu^{I}\}_n$ structure type PtS (D_{4h}-Td)





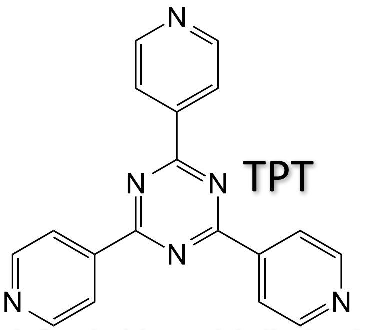
HAT



[AgHAT](ClO_4).Solv
structure type
SiSr (10,3)-a

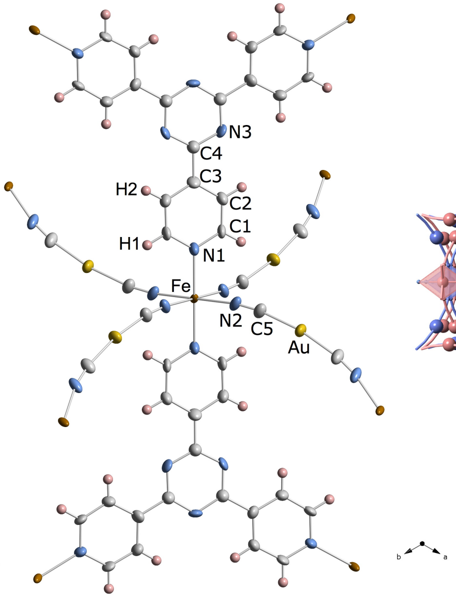
R. Robson et al., J. Chem Soc., Chem. Commun.1990, 762-763

Example Node TPT:

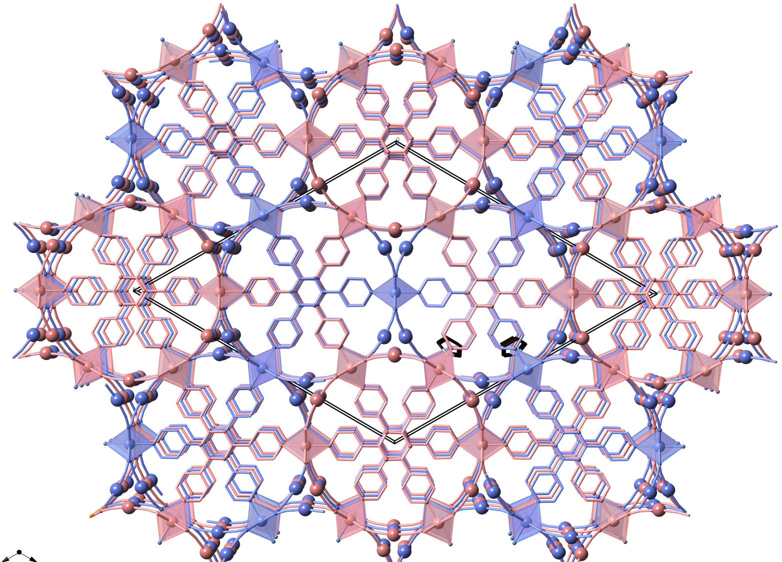


2,4,6-tris(4-pyridyl)triazine

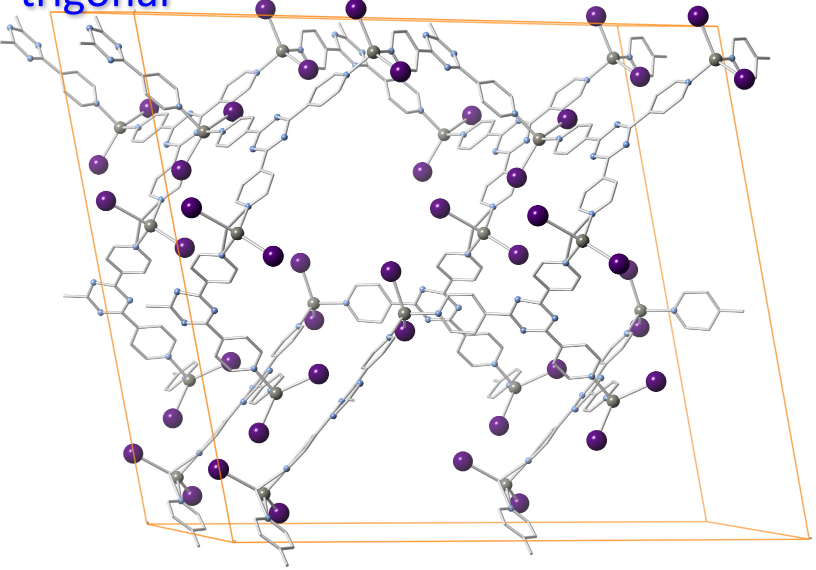
Note that there is a coordination node Zn(II) CN = 4, but there is only one node in the network which is trigonal



Connectivity 6 y 3

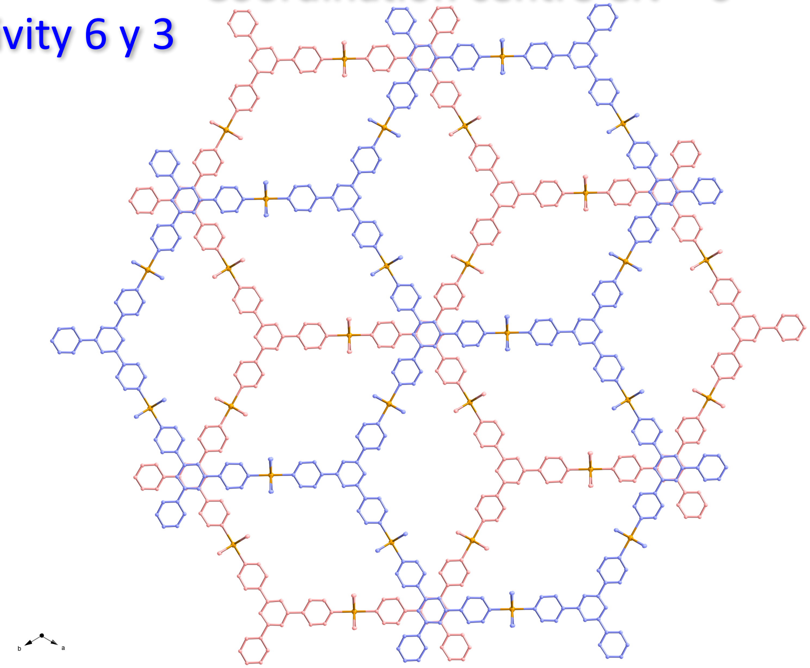


Coordination centre CN = 6



$[(ZnI_2)_3(TPT)]\cdot 6PhNO_2$

Fujita et al Angew. Chem. Int. Ed. 2002, 41, 3392

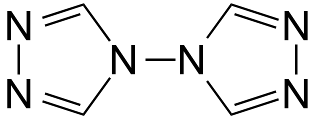


$[Fe(TPT)_{2/3}\{M^I(CN)_2\}_2]\cdot nSolv$

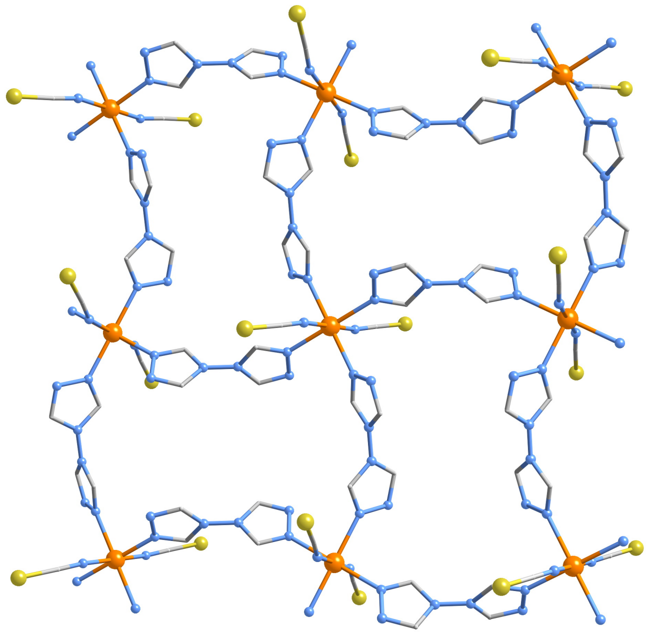
Real et al Chem. Eur. J. 2013, 19, 6851

Connectors derived from Triazole

These N-substituted ligands act in a similar way to the pyridine derivatives. But, the fact of having a smaller ring seems to facilitate the coordinative saturation of the metal ion (structure on the right)

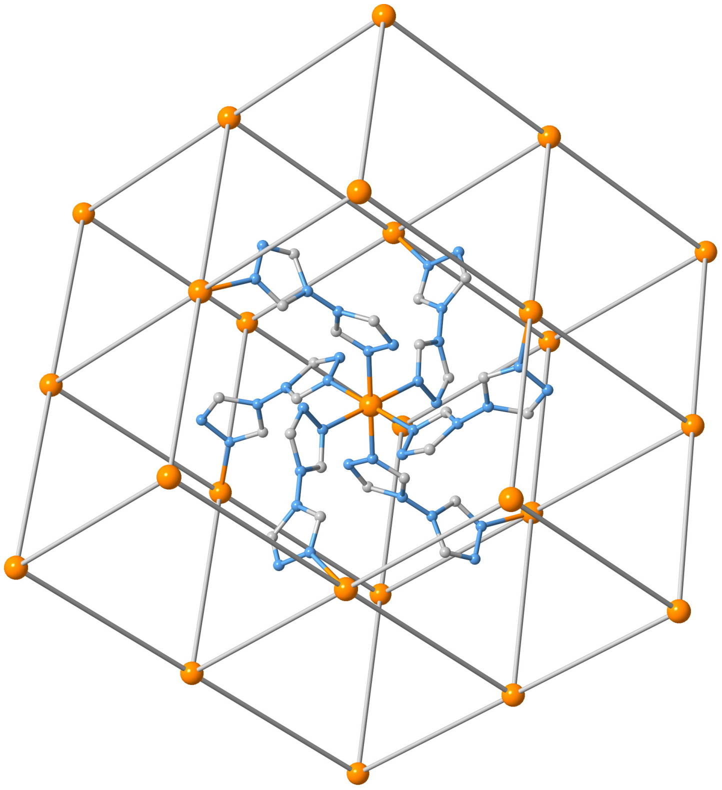


4,4'-bi(1,2,4-triazole)



$[Fe(btr)_2(NCS)_2]$
2D Coordination Polymer

Haasnoot et al *Polyhedron* 1999

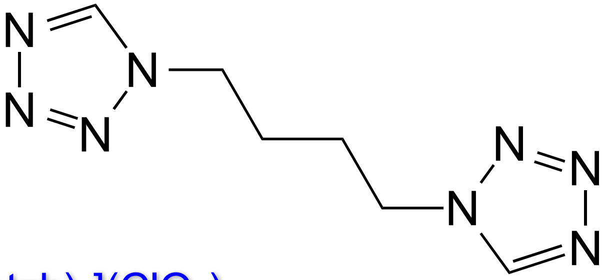


$[Fe(btr)_3](ClO_4)_2$
3D Coordination Polymer

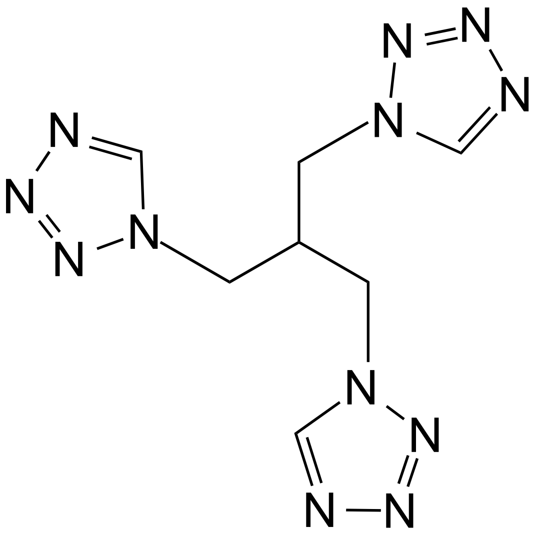
Kahn et al *Inorg. Chem*. 1999

Examples of bridging ligands derived from Tetrazol

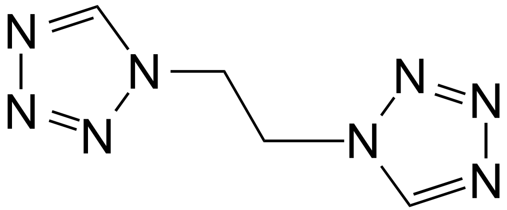
These N-substituted ligands act in a similar manner to the triazole derivatives. Some examples:



$[Fe(btzb)_3](ClO_4)_2$
3D Coordination Polymer
Konigsbruggen et al *J. Chem. Dalton Trans*. 2001, 466



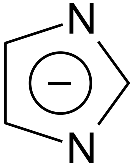
$[Fe(ttz)_3](ClO_4)_2$
2D Coordination Polymer
Bronisz et al *Inorg. Chem*. 2011, 51, 237

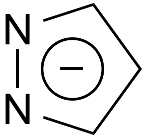


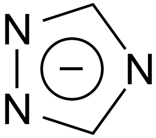
$[Fe(btre)_2(propionitrilo)_2](ClO_4)_2$
1D Coordination Polymer
Bronisz et al *Inorg. Chem*. 2012, 51, 12630

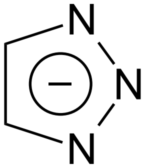
Azolate function

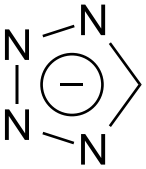
In general, azolate functions are N-donor ligands formed by 5-membered heterocyclic rings that have 2, 3 or 4 N atoms. In its neutral form one of the N is protonated and behave like very weak acids that can be deprotonated by the action of coordination with metals under appropriate conditions:


imidazolate

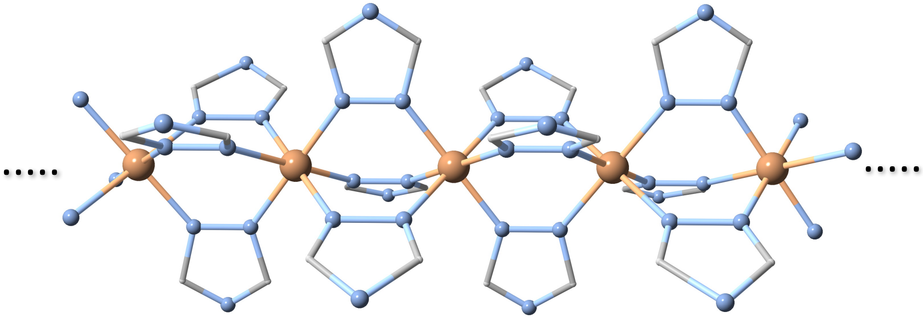

pyrazolate


1,2,4-triazolate


1,2,3-triazolate


tetrazolate

These ligands can act as bridges between metals giving rise to coordination polymers. The following example corresponds to the 1D complex [Fe(Htrz)$_2$(trz)](BF$_4$):



Azolate function

Azolate groups are relevant in the construction of porous coordination polymers (MOFs):

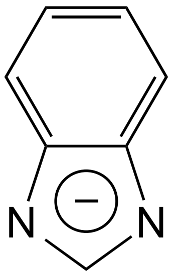
i) As in pyridine derivatives, the N(sp^2) atoms of the azole groups coordinate a single metal with the direction defined by the lone pair. This is significantly different from the O atom of the carboxylates that has three available electron pairs. From that point of view, the direction of the coordination bond of the azolato groups is more predictable. This fact is of great importance in the rational design of new MOFs with specific structures. In this sense, the most predictable are the pyrazolate and imidazolate groups because they only have two N atoms. The triazolates can act with three, two or sometimes an N atom (it depends on the metal ion, and the triazole substituents). Tetrazolate groups often resemble pyrazoles in how to coordinate.

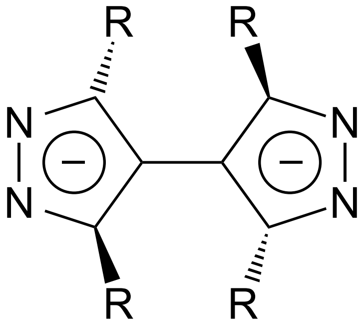
ii) Deprotonation of the azoles activates the coordination of an additional N and increases the basic character of the ligand and evidently neutralizes the M charge, giving rise to quite insoluble species. **MOFs** generated by azolates are often referred to as **MAFs** but also have other names such as **ZIFs** ... .. They tend to have high chemical and thermal stability.

iii) Imidazolate groups invariably exhibit a coordination that is equivalent to the *syn-syn* of the carboxylates.

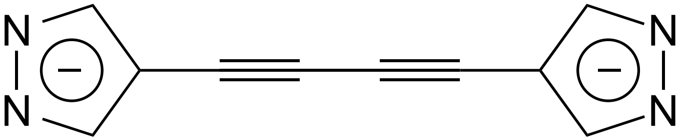
iv) Generally, triazolates and tetrazolates do not use all of their N atoms and, consequently, the uncoordinated N atoms can contribute with their lone pairs to enhance the host-guest affinity in the cavities of the MOF.

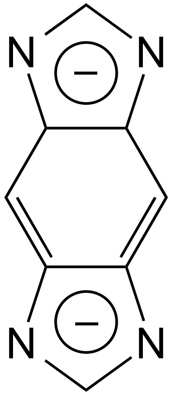
Ejemplos de funciones imidazolato y pirazolato

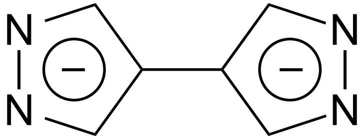


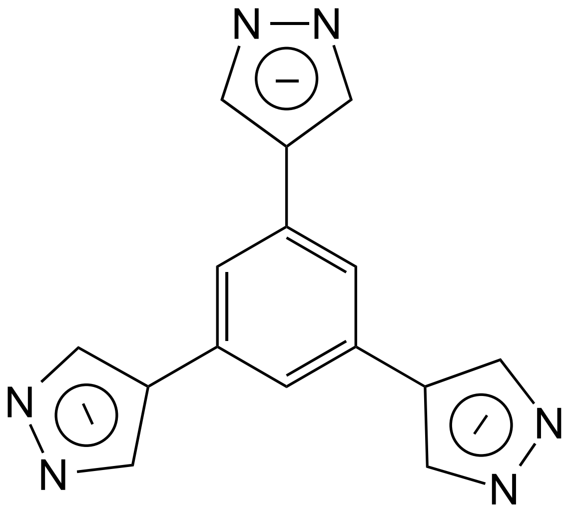


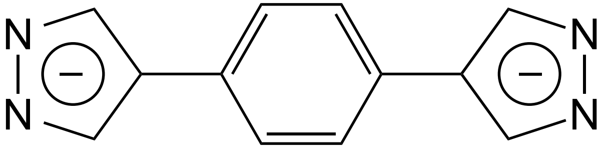
R = Me, Et, Ph







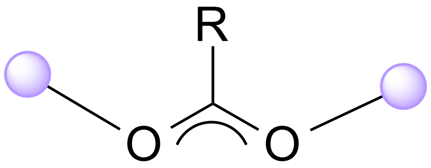




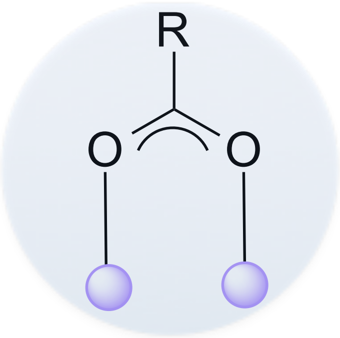
(more information see chapter 11 of the book edited by S. Kaskel)

Carboxylate function

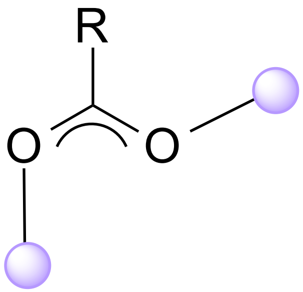
The coordination of the carboxylate group is less predictable than that of the azolates due to the greater number of lone pairs. The most common coordination modes of the bridge carboxylate group are:



anti-anti

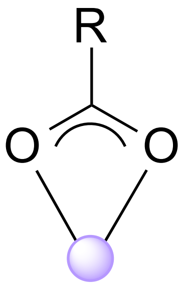


syn-syn

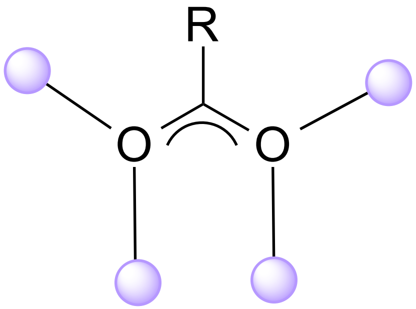


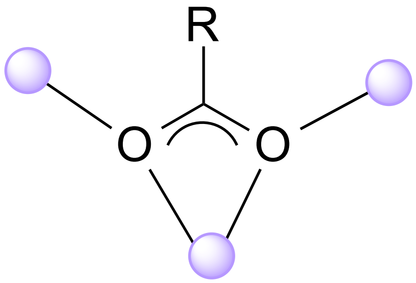
anti-syn

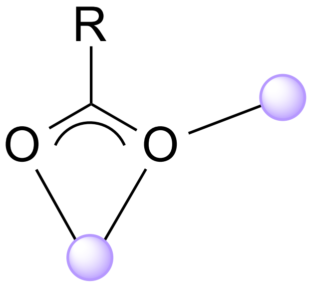
But it can also be found other modes such as:

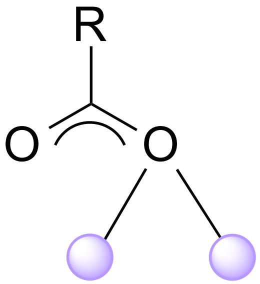


chelate







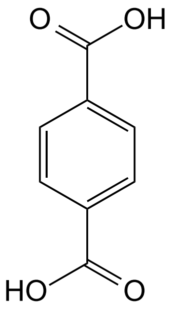


monodentate

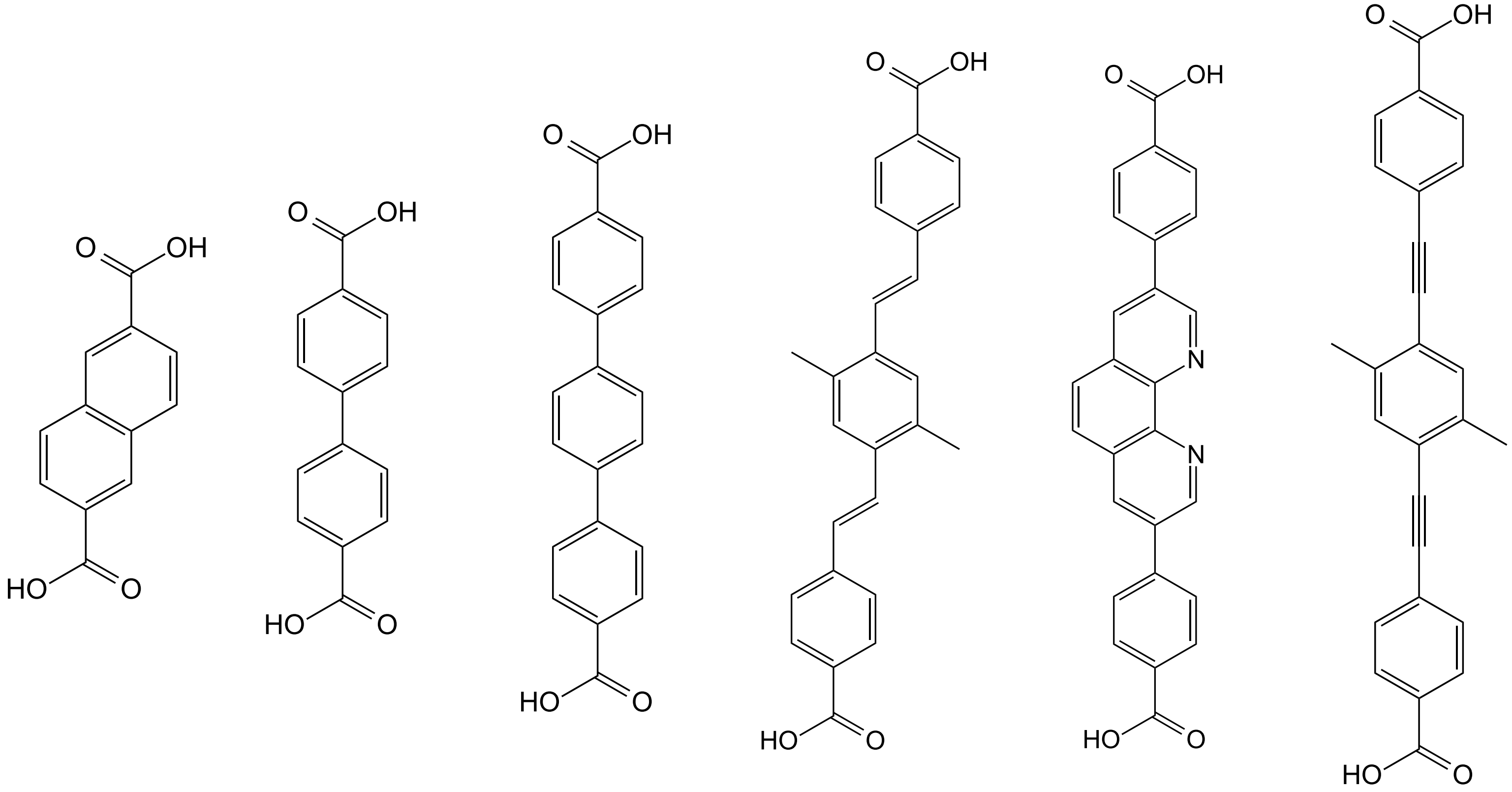
Carboxylate function

Systematic design of ligands with carboxylate functions: control of the size, shape and functionalization of the pores of the MOF

Ditopic connectors

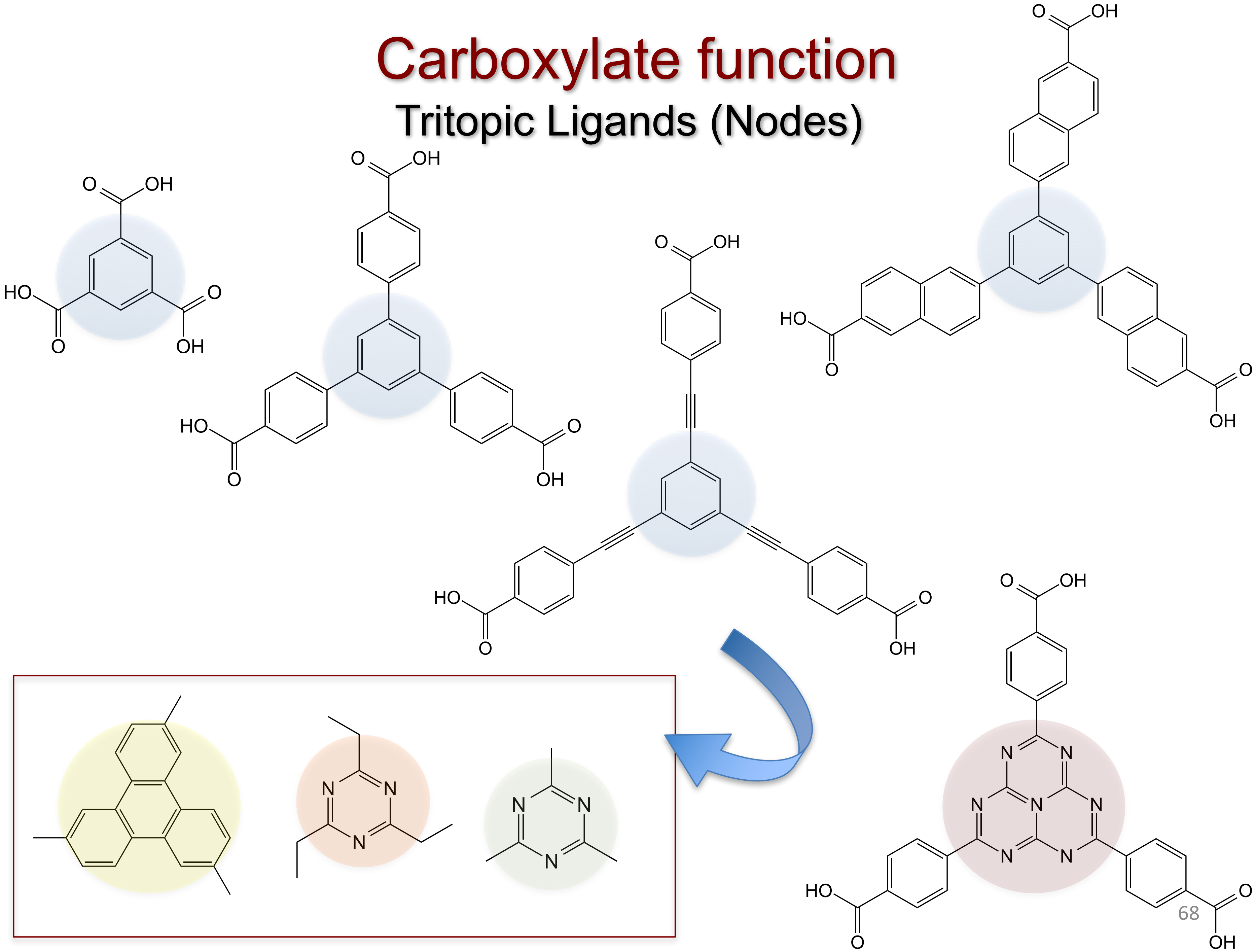


BDC



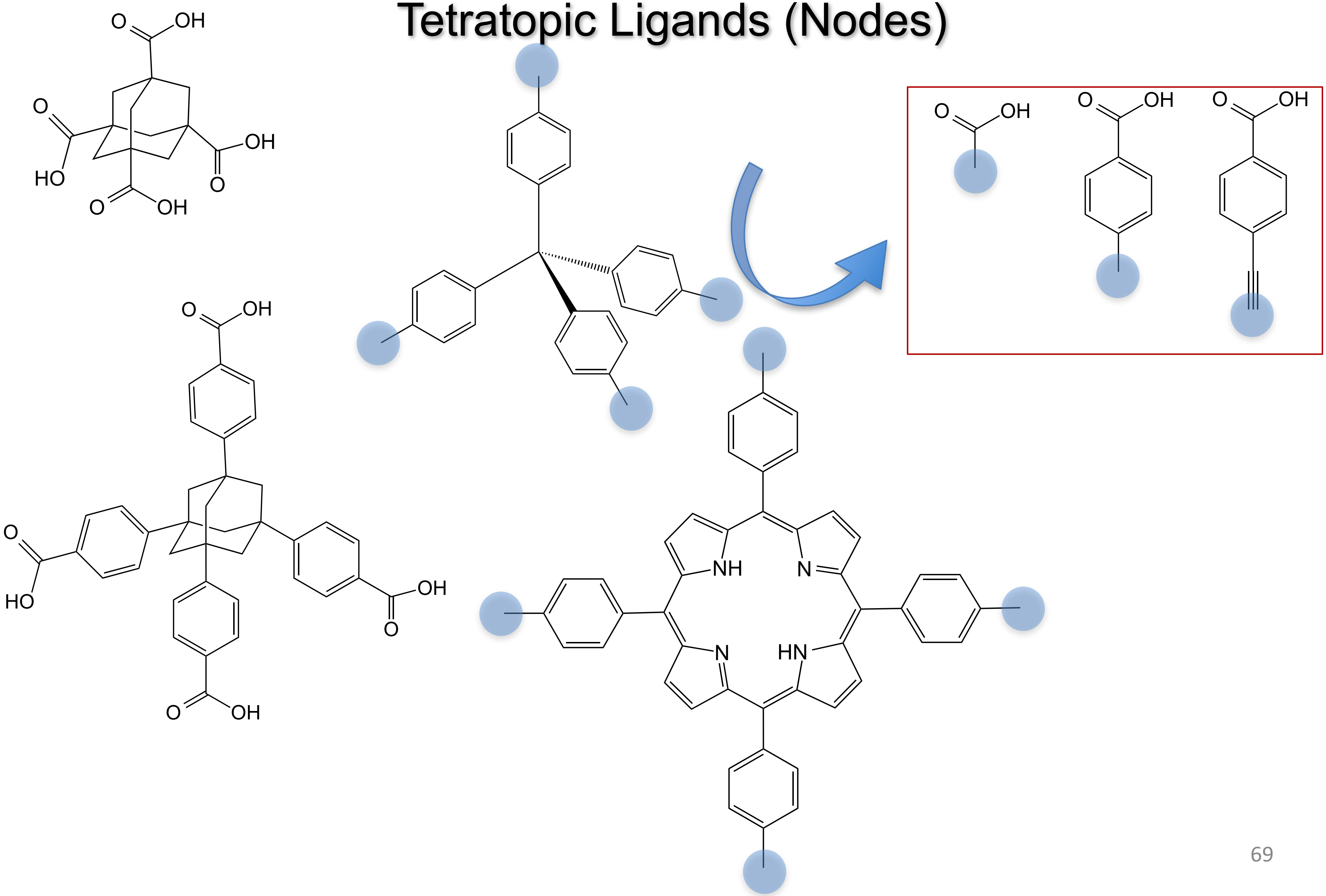
Carboxylate function

Tritopic Ligands (Nodes)



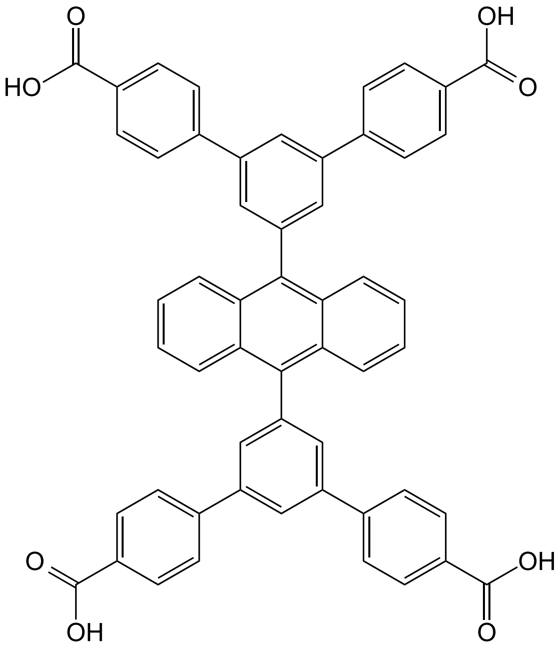
Carboxylate function

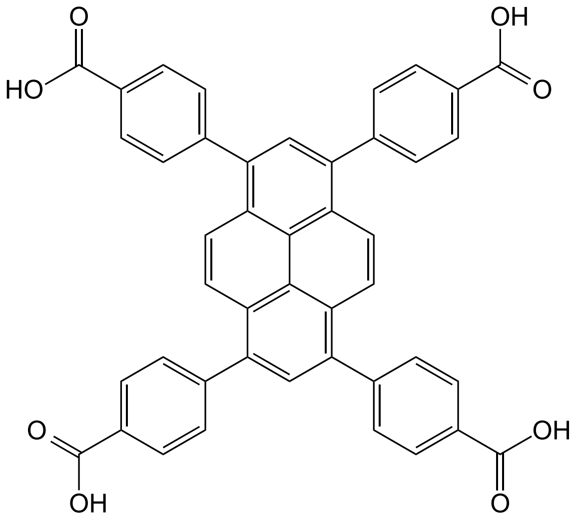
Tetratopic Ligands (Nodes)

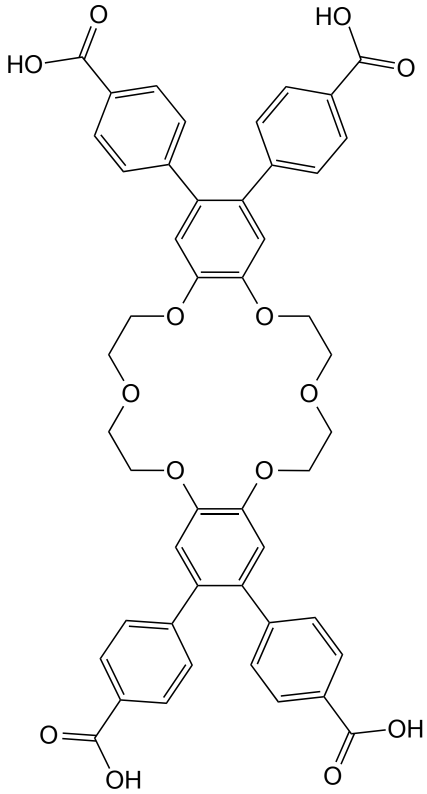


Carboxylate function

Tetratopic Ligands (Nodes)







…. Connectors Penta-, Hexa, Hepta, Octa-, Dodeca-topic

(see chapter 10 of the book edited by S. Kaskel)

Secondary Construction Units

(Secondary Building Units; SBUs)

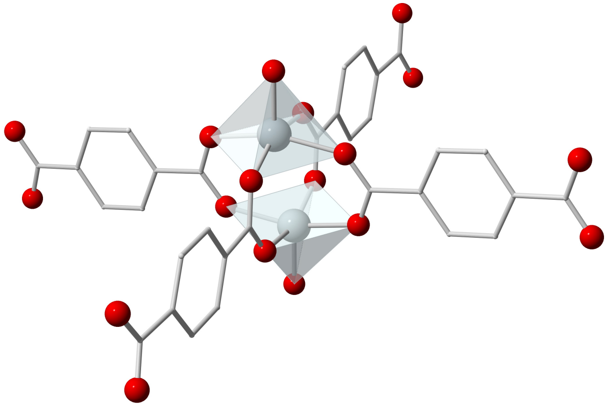
for the construction of MOFs

One of the results that has contributed most to the development of MOFs in the last 2 decades has been the observation of permanent porosity in [Zn (BDC)] called MOF-2 (Yaghi et al J. Am. Chem. Soc. 1998, 120, 8571). Although this compound has a discrete Langmuir surface (270 m^2 g^{-1}), it paved the way to the synthesis of stable MOFs with surfaces greater than 4500 m^2 g^{-1}.

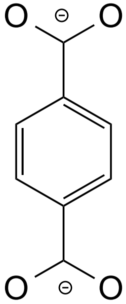
The idea underlying in this work by Yaghi and collaborators is the concept of SBU.

(more information see chapter 3 of S. Kaskel's book)

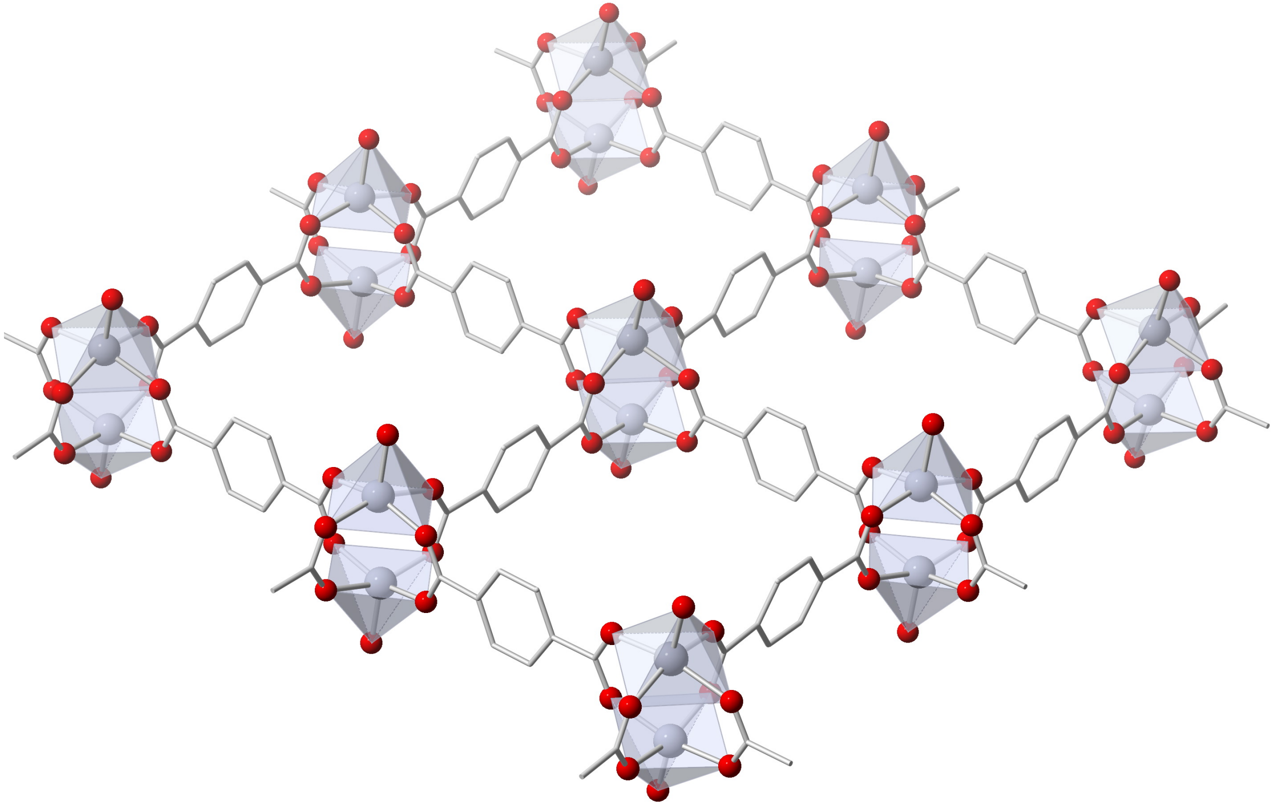
MOF-2: [Zn(BDC)]



“Node connectivity 4”



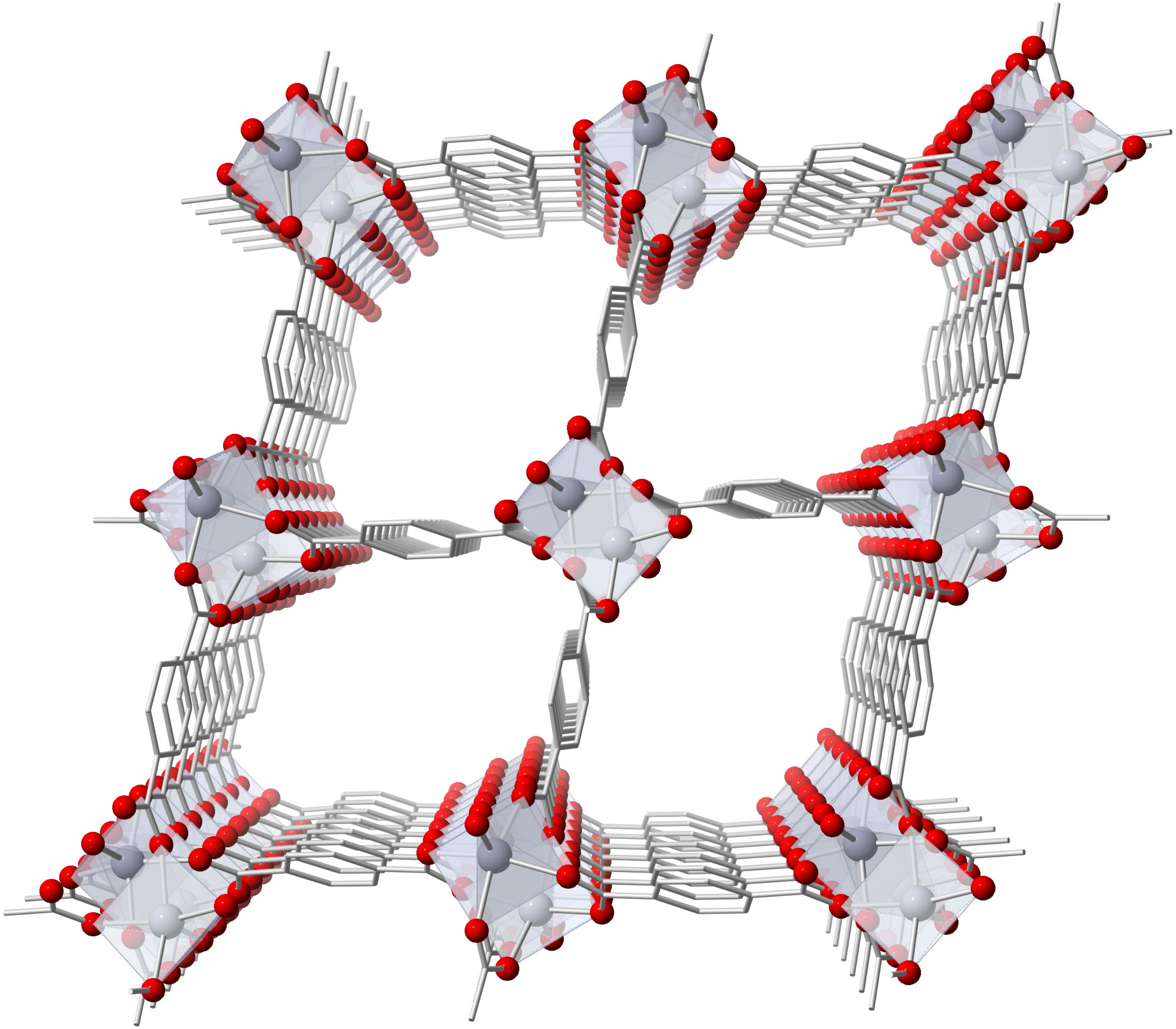
“linear bond”



Metal centers with IC = 5 form dimers that generate a connectivity node 4 (SBU) and define a 2D coordination polymer with square windows.

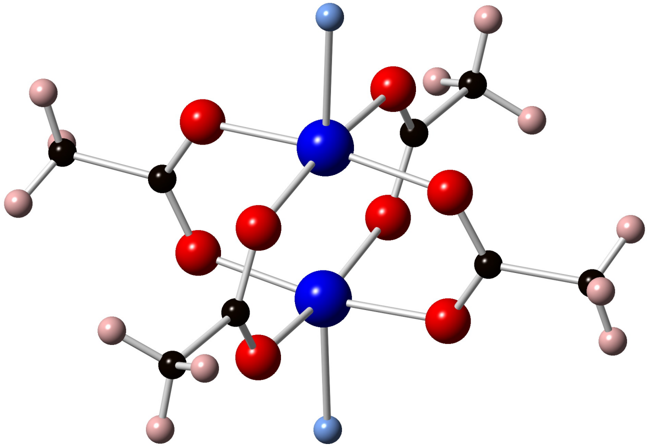
H. Li, M. Eddaoudi, T. L. Groy, O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 8571-8572

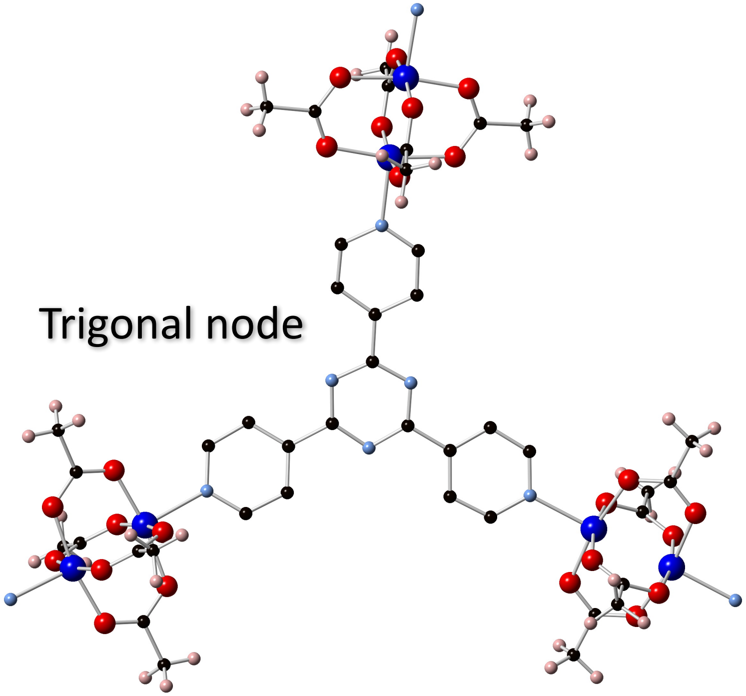
The stacking of the 2D layers in the perpendicular direction occurs in such a way that the layers eclipse each other defining channels.



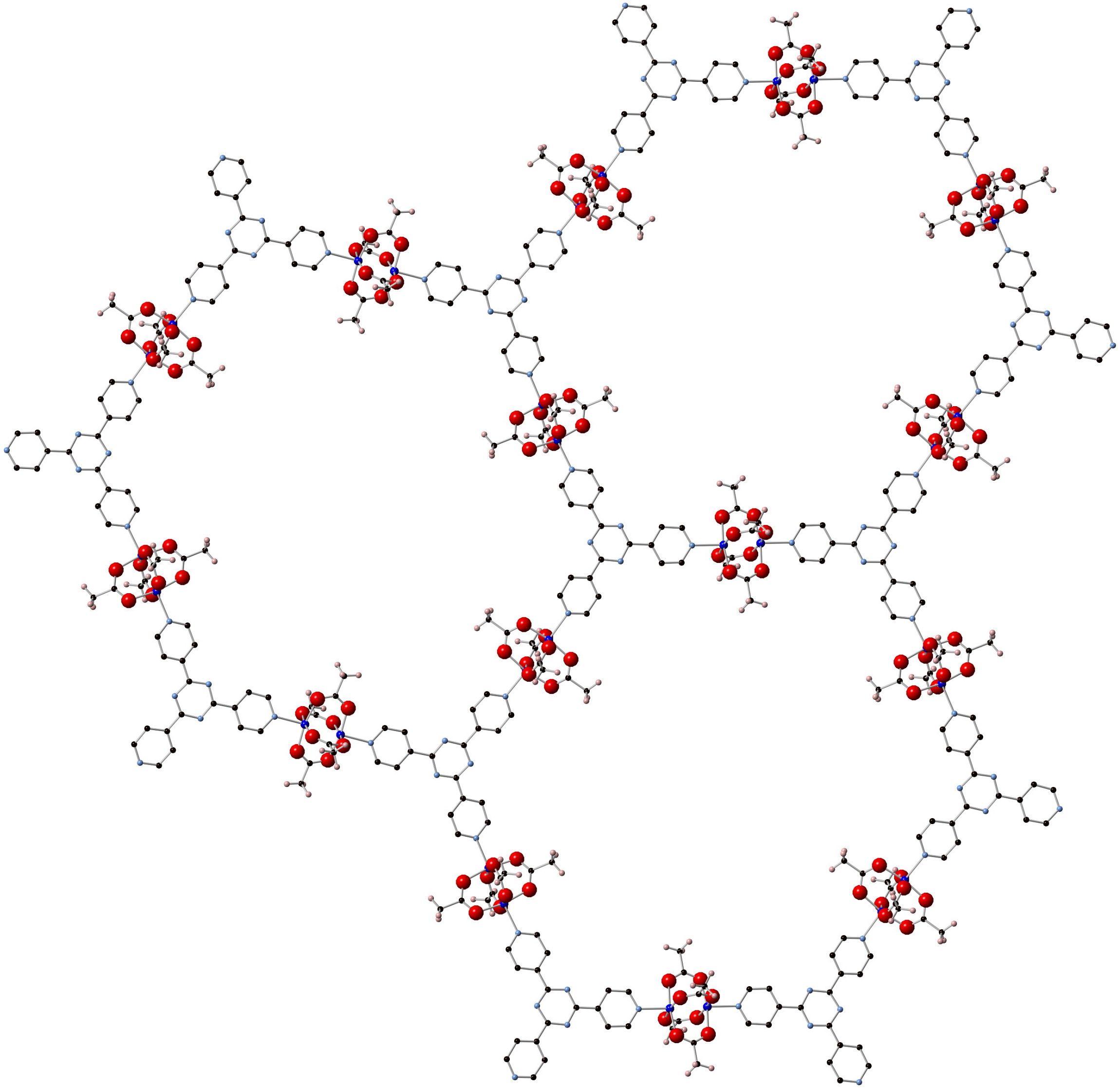
H. Li, M. Eddaoudi, T. L. Groy, O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 8571-8572

in this case the SBU is blocked by CH_3 groups but can polymerise using a suitable axial ligand such as the TPT that acts as a node with connectivity 3



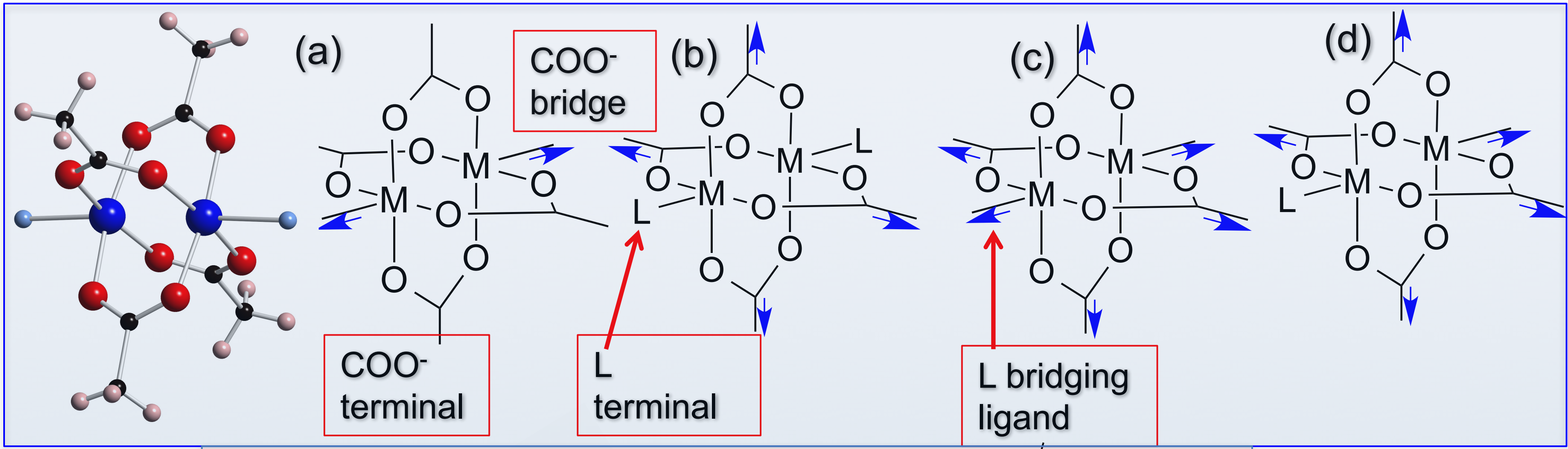


Trigonal node



S. R. Batten, B. F. Hoskins, Boujemaa Moubaraki, K. S. Murray, R. Robson, *Chem. Commun*. **2000**, 1095-1096

SBUs Based on Carboxylates

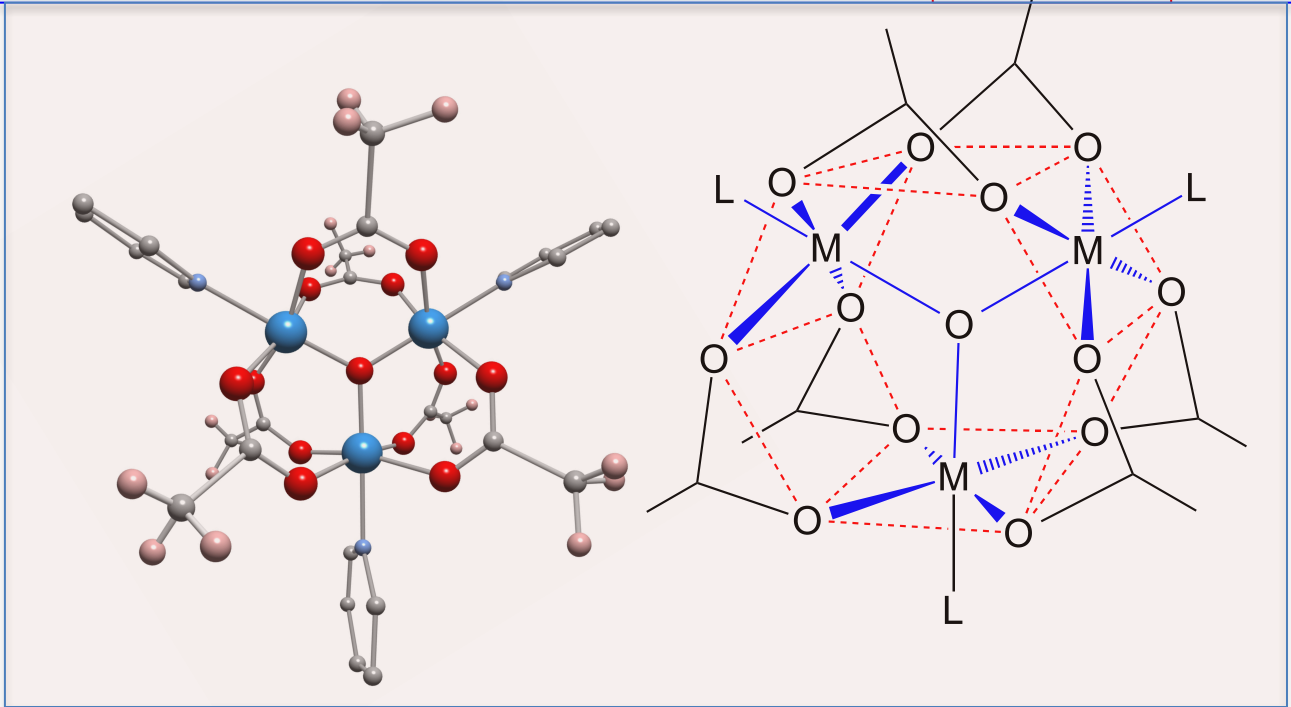


COO- bridge

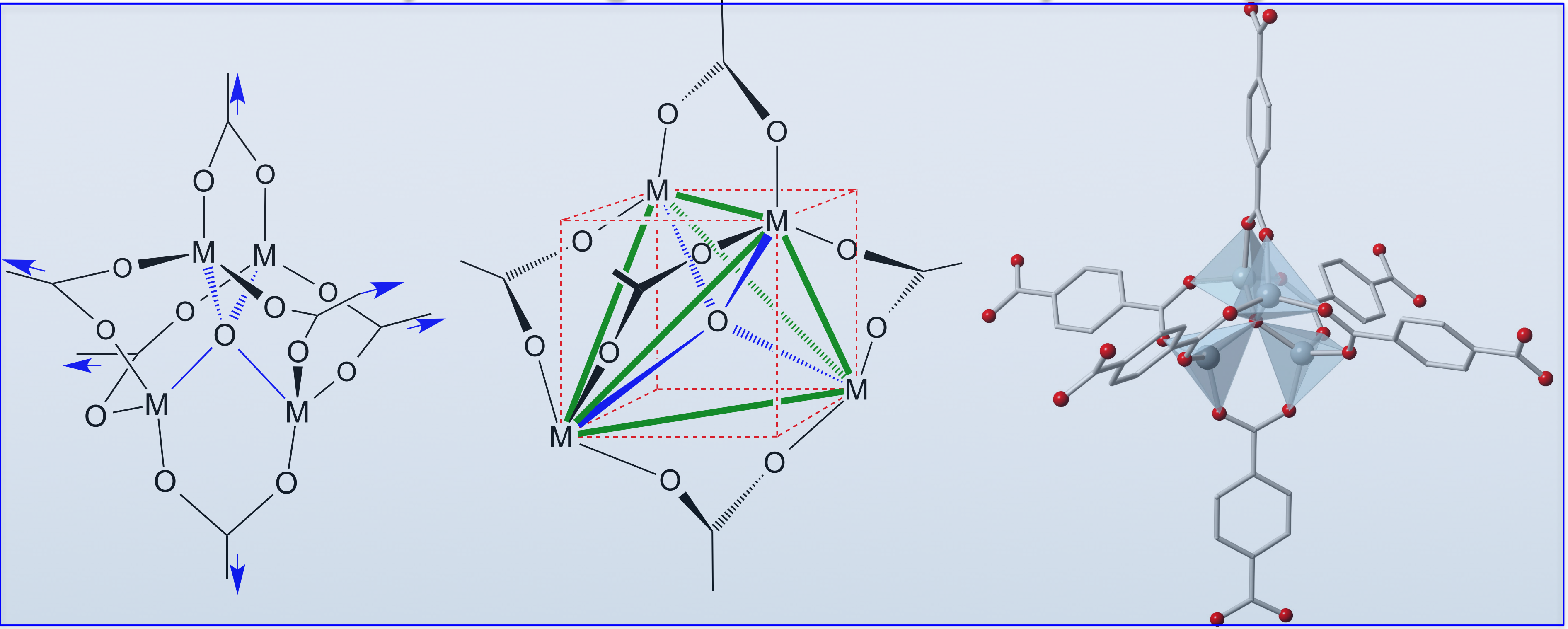
COO- terminal

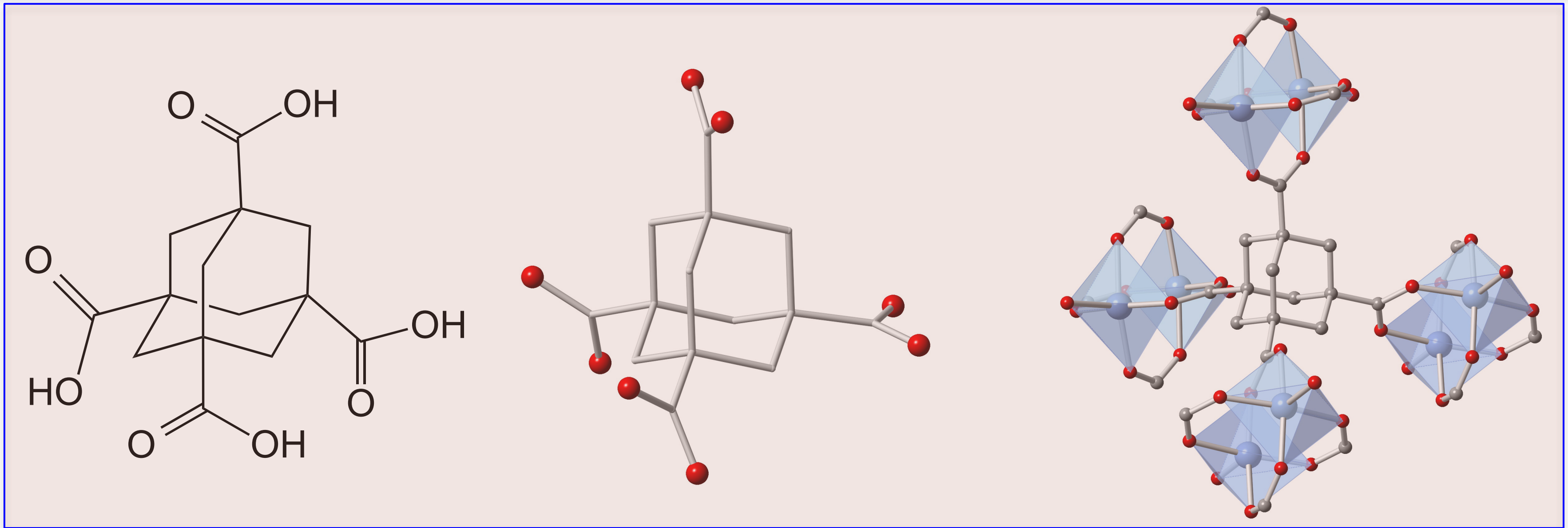
L terminal

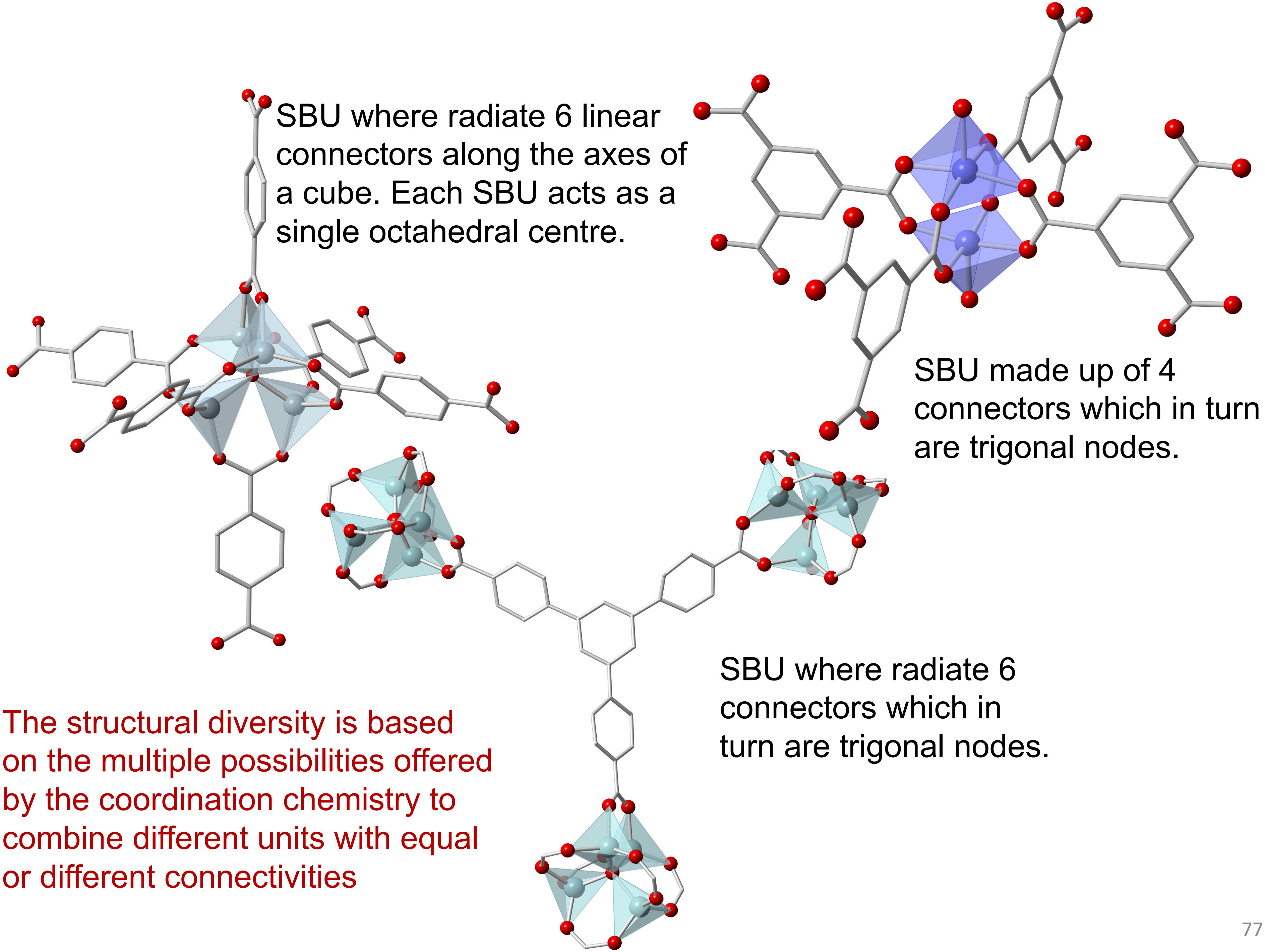
L bridging ligand



Secondary Building Units / Secondary Building Units







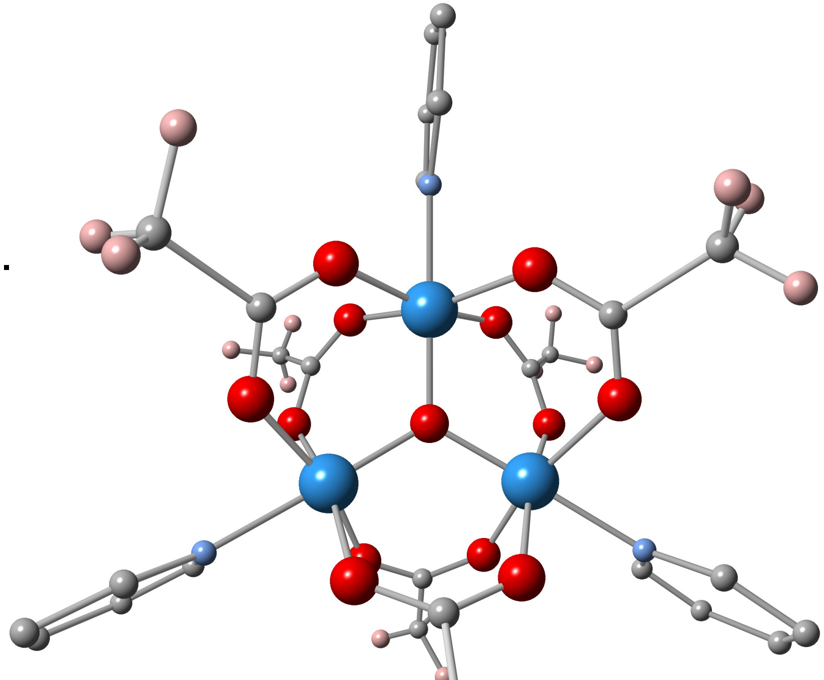
SBU where radiate 6 linear connectors along the axes of a cube. Each SBU acts as a single octahedral centre.

SBU made up of 4 connectors which in turn are trigonal nodes.

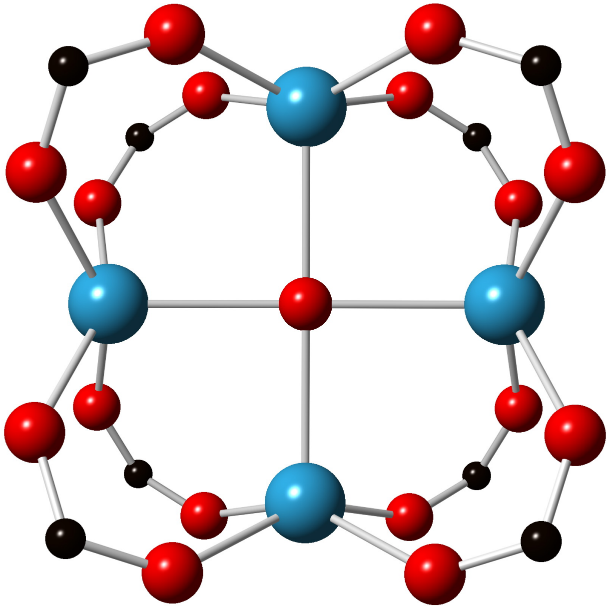
SBU where radiate 6 connectors which in turn are trigonal nodes.

The structural diversity is based on the multiple possibilities offered by the coordination chemistry to combine different units with equal or different connectivities

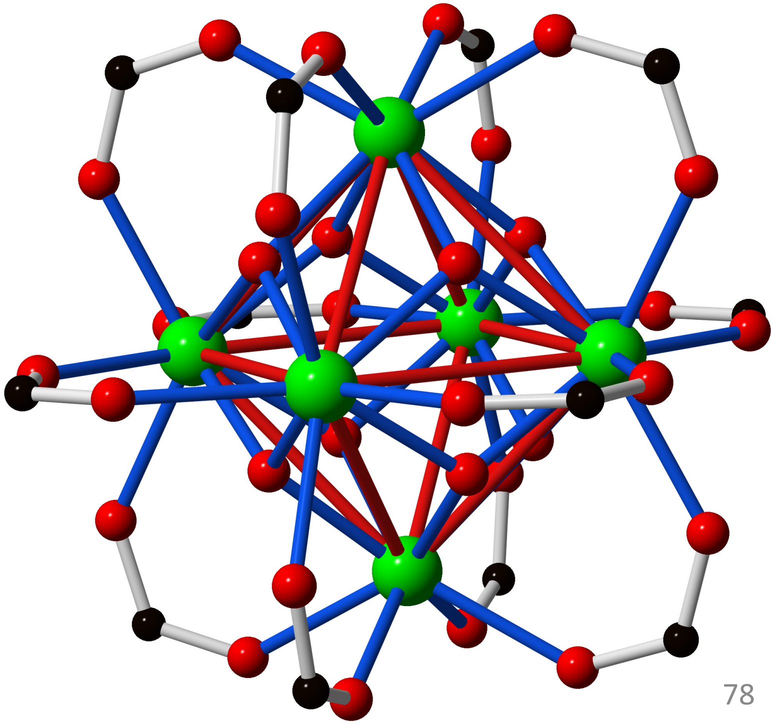
Potential trigonal
SBU with
6+3 connectors….



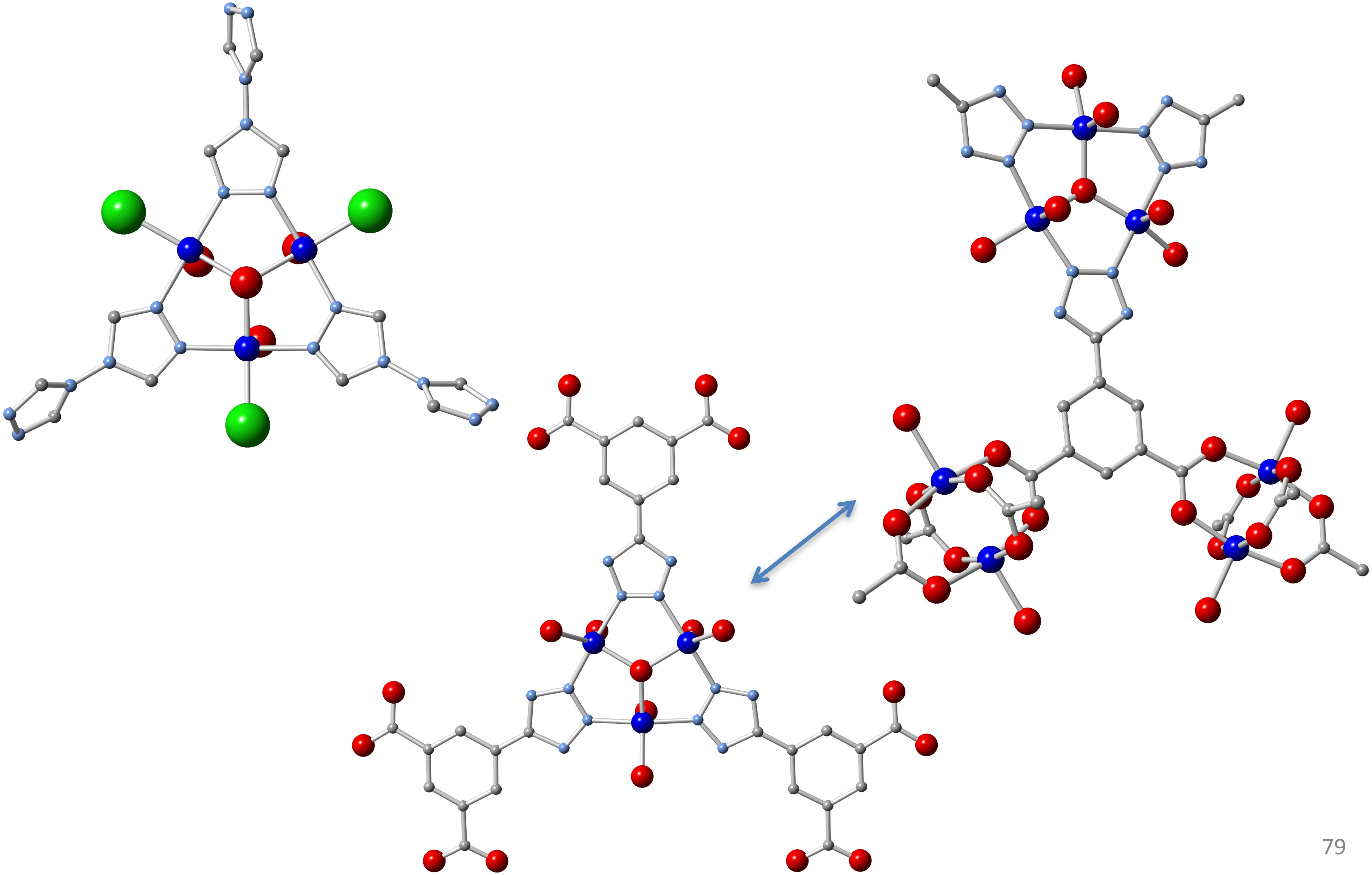
Square SBU with 8 connectors



Octahedral SBU with
12 connectors



SBUs Based on Azolates and Carboxylates



Advanced Inorganic Chemistry

Chapter 4th: Coordination Polymers

Part 2

Instituto de Ciencia Molecular
Departamento de Química Inorgánica
Universidad de Valencia

INDEX PART TWO

Description, classification, topology of nets and significant examples

- Concept of network as a set of nodes and links. Schläfli's topological symbols
    - a) Regular uninodal systems:
        - i) Platonic solids.
        - ii) Two-dimensional networks.
    - b) Semi-regular systems
        - i) Archimedian and catalan solids.
        - ii) Two-dimensional networks.

- Topological analysis: Euler and Schläfli's formulas.

- Description and symbols for 2D, 3D networks and polihedra
    - i) Schläfli's symbol.
    - ii) Vertex symbol (M. O'Keeffe).
    - iii) Point symbol (A. F. Wells).

- Examples of most common networks found in CPs/MOFs

NbO, Sodalite, Diamond, Quartz (SiO_2), Moganite (SiO_2), $SrAl_2$, tri- and tetra-connected nets, etc

- Means available for the topologycal analysis of networks derived from CPs/MOFs

- Bibliography of interest on coordinación networks and polymers

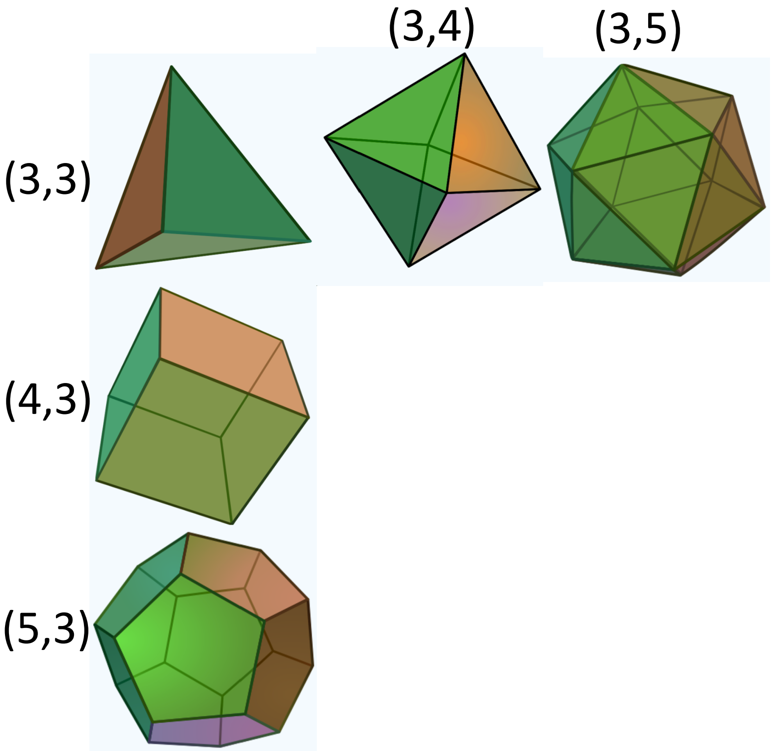
DESCRIPTION, CLASSIFICATION, NETWORK TOPOLOGY

Since the first articles of AF Wells in the 1950s polyhedral complexes and coordination polymers have been described in terms of node connectivity and number of nodes in the shortest circuit containing a given "spacer-node-spacer” unit.

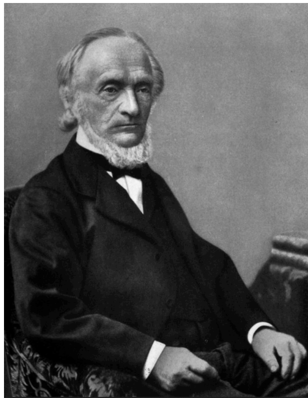
Wells based its description on the nomenclature (**n,p**) previously introduced by Schläfli in the field of topology to describe these objects, being **n** the poligonality (the number of connections/sides in the smallest circuit) and **p** the connectivity of the nodes.

Only 5 simple convex polyhedrons (**n,p**) have all their faces of the same type (same type of polygons, **n**-gonos) and the same number (**p**) of them coming together in the same vertex (node). They are known as Platonic solids:

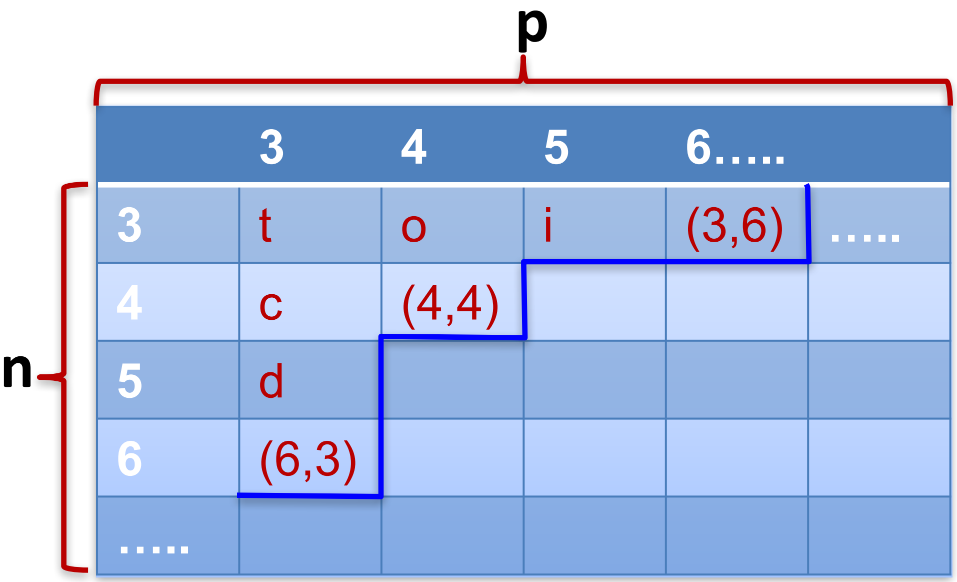
p →			
n ↓	(3,3)	(3,4)	(3,5)
	(4,3)	?	?
	(5,3)	?	?



Ludwig Schläfli
1814-1895

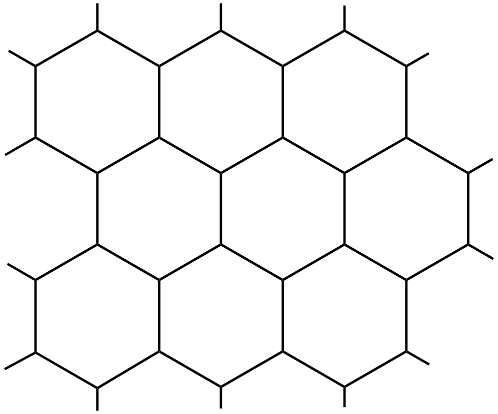


As we progress through the table that defines the Schläfli’s space (**n,p**), we move from the Platonic polyhedrons to three regular flat networks (3,6), (4,4) and (6,3). These represent the only examples of flat networks that have all polygons converging on the same vertex identical. These surfaces, like Platonic solids, are called regular for obvious reasons.

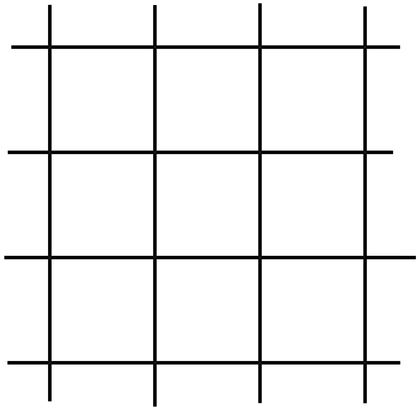


	3	4	5	6…..	
3	t	o	i	(3,6)	…..
4	c	(4,4)			
5	d				
6	(6,3)				
…..					

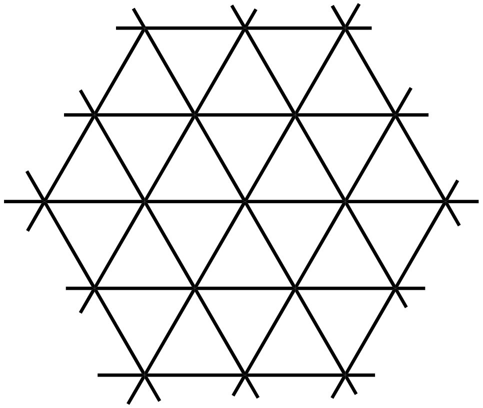
(6,3)



(4,4)

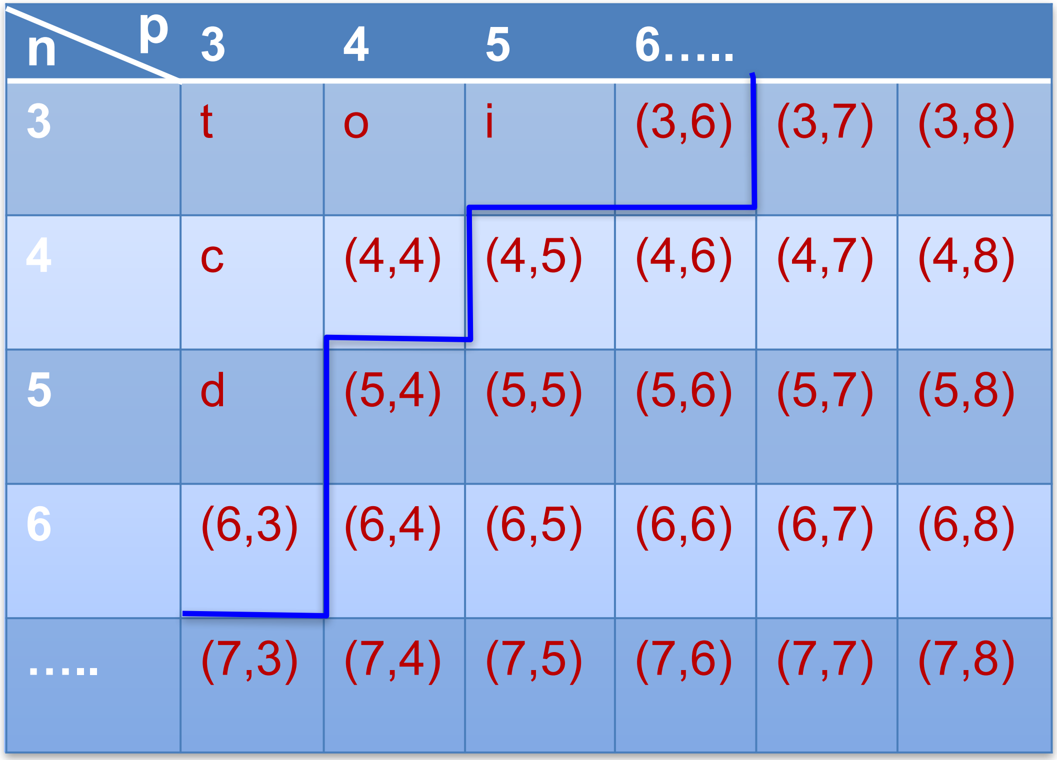


(3,6)



-Wells investigated the nature of 3-connected networks (**p** = **3**) in which the value of **n** > **6**. That is, the pairs (**n,3**). These regular networks are called **Uniform Three-connected Networks**.

-Wells also investigated the opposite situation paying special attention on the polygons (shorter circuits) that form the surface of the object. Namely, when one gathers in a node (**p** = **3**, **4** or **5**) equilateral triangles (**n** = **3**), one defines a tetrahedron, octahedron or an icosahedron, respectively. But what happens if we join **6** (**p** = **6**)?. In this case is easy to see that it is not possible to form a convex polyhedron but an infinite plane (since the triangles are equilateral, the plane is regular/uniform (**3,6**)). When we increase **p** at values **p** > **6** in the space (**3,p**) the surface cannot be anymore flat and can be closed giving complex geometries.

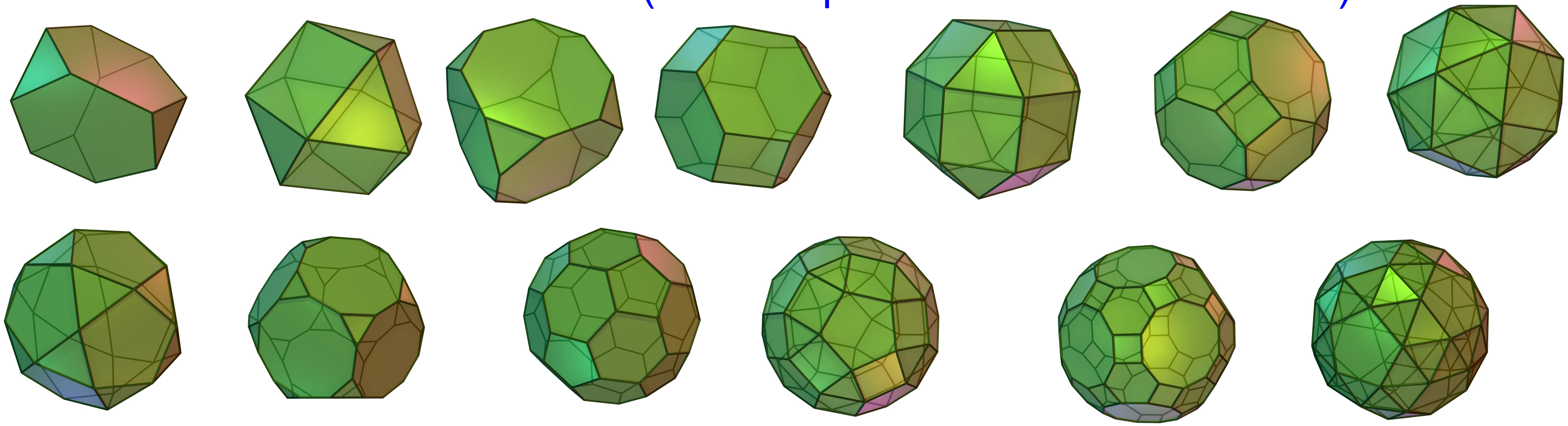


p n	3	4	5	6…..		
3	t	o	i	(3,6)	(3,7)	(3,8)
4	c	(4,4)	(4,5)	(4,6)	(4,7)	(4,8)
5	d	(5,4)	(5,5)	(5,6)	(5,7)	(5,8)
6	(6,3)	(6,4)	(6,5)	(6,6)	(6,7)	(6,8)
…..	(7,3)	(7,4)	(7,5)	(7,6)	(7,7)	(7,8)

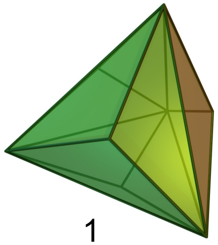
POLYHEDRONS

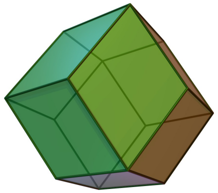
In addition to the **platonic solids/polyhedrons** there is a series of solids known as **semiregular**. **Archimedean** solids are characterized by non-integer values of **n**, these combine in a congruent way polygons of different number of edges/links but with a fixed value of **p**. **Catalan** solids (Eugène Catalan) are characterized by fractional values of **p** but integer values of **n** (different types of nodes and a single type of polygon). (This also applies to two-dimensional and three-dimensional networks).

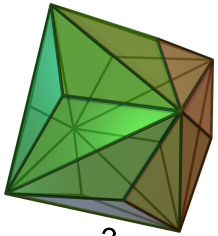
Archimedean Solids (see Wikipedia for more information)

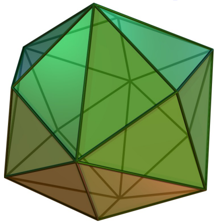


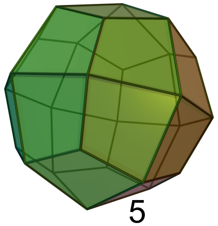
Catalan Solids (see Wikipedia for more information)

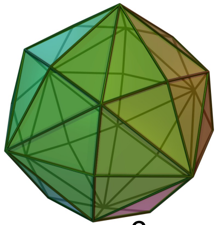

1

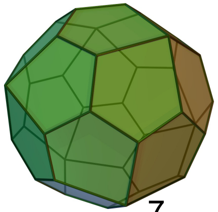

2

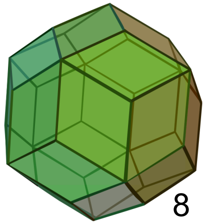

3

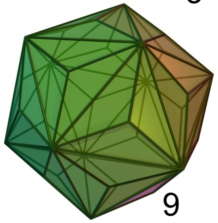

4

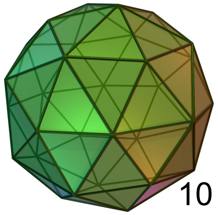

5

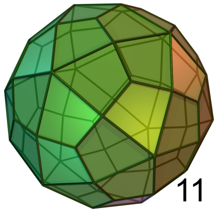

6

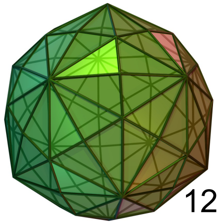

7

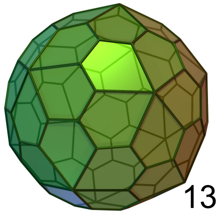

8


9


10

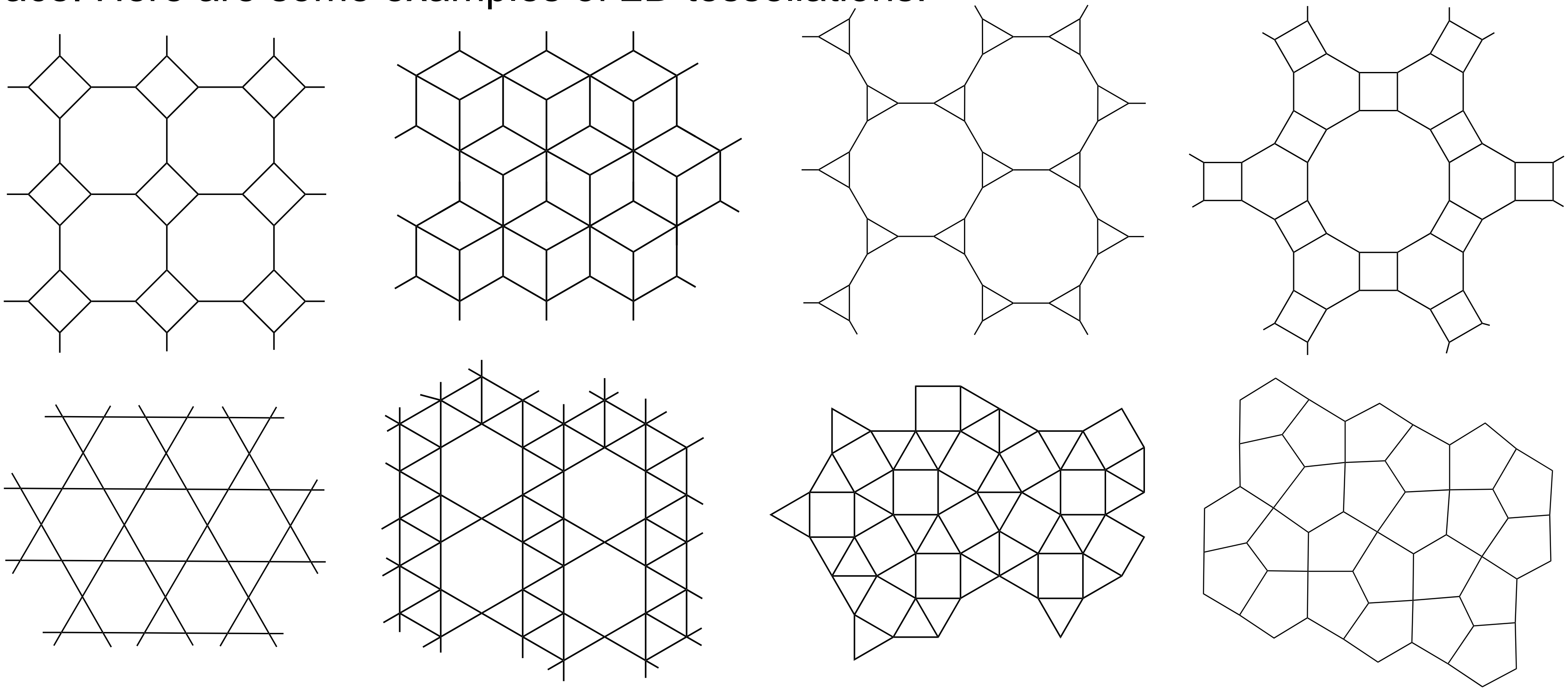

11

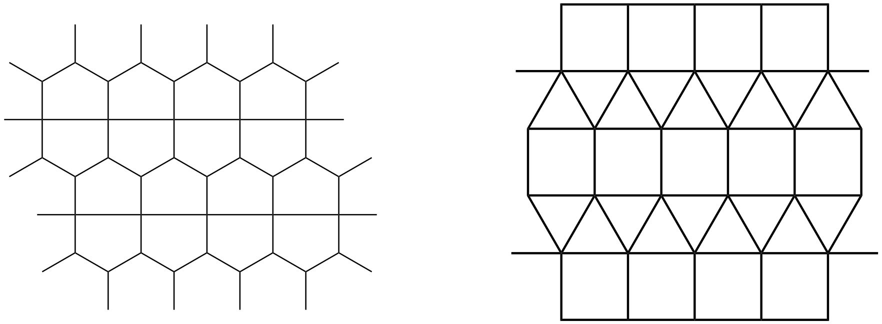

12


13

TESSELLATION OF THE 2D SPACE: 2D PERIODIC NETWORKS

Geometric motifs related to those found in Platonic, Archimedean and Catalan solids can be generated in the 2D space by creating non-regular polygonal tessellations of the space. Here are some examples of 2D tessellations:





PCs are known to adopt many of these forms in versions more or less distorted

TOPOLOGICAL ANALYSIS OF POLYHEDRA AND NETWORKS

The analysis of all these geometric objects (polyhedrons, 2D and 3D networks) can be rationalized by the principles of topology, mathematical branch that rests on Euler's formula (1707-1783): $V - E + F = 2$ (1)

(V = vertices, E = edges/links, F = faces/polygons)

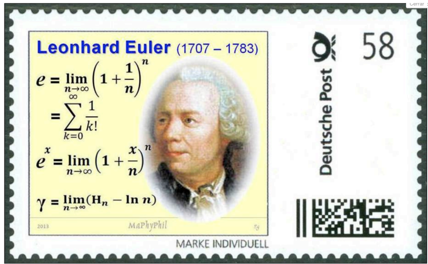
In addition it is complemented with the conclusions of Schläfli (1814-1895):

$$n \cdot F = 2E \qquad (2)$$

$$p \cdot V = 2E \qquad (3)$$

$$V = \frac{4n}{4 - (n-2)(p-2)}\ ;\ E = \frac{2np}{4 - (n-2)(p-2)}\ ;\ F = \frac{4p}{4 - (n-2)(p-2)} \qquad (4)$$

(Exercise: check these formulas with platonic solids)



Schläfli substituted his two expressions (Eqs 2 and 3) in the Euler relation (Eq 1) to obtain the expression:

$$(1/n) + (1/p) = (1/2) + (1/E)$$

and since E is necessarily positive, this expression is simplified as follows:

$$(1/n) + (1/p) > (1/2)$$

From this expression one quickly realise that there can only be 5 regular polyhedrons. To do so, one should take into account that the simplest object has poligonality 3 and connectivity 3. Thus one can realise that only the pairs (**3.3**), (**4.3**), (**3.4**), (**5.3**), (**3.5**) (Schläfli symbols), which are tetrahedron, cube, octahedron, dodecahedron and icosahedron, respectively, meet this condition.

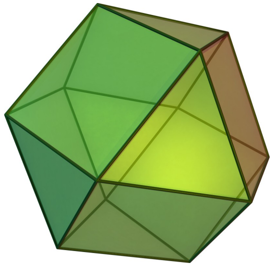
It is also interesting to observe with expressions (4), where V, E and F are defined according to the topological parameters **n** and **p**, that for $(n-2)(p-2) < 4$, finite values of V are obtained (it is possible to check for any of the presented polyhedrons). When $(n-2)(p-2) = 4$, the values V = E = F equal to infinite and corresponds to the 2D networks: (**6**,**3**), (**4**,**4**) and (**3**,**6**). Expressions (4) are also applicable to semi-regular Archimedean and Catalan systems if the mean values of **n** and **p** are taken into account. Example:

(see Wikipedia for more information)

The 13 archimedean solids have values of **p** = **3**, **4**, or **5** (like the Platonic ones) but with values of **n** in the interval **3-10** and therefore non-integer values of $\mathbf{n}_{\mathbf{med}}$. Conversely, the catalan solids are the duals of the archimedeans, that is, **n = 3**, **4**, or **5**, but with values of **p** in the interval **3-10** and therefore with values of $\mathbf{p}_{\mathbf{med}}$. For example:

V	n	p		
12	24/7	4	cuboctahedron	(n-2)(p-2) = 20/7
14	4	24/7	Rhombic Dodecahedron	

cuboctahedron

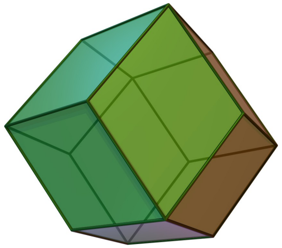


n = 3, 4; p = 4

There are 6 squares and 8 triangles with 6•**4** or 8•**3** = 24 edges that are divided into triangles (3) and squares (4). Therefore $\mathbf{n}_{\mathbf{med}}$ = 24/7

(24/7, 4)

Rhombic
dodecahedron



n = 4; p = 3, 4

There are 6 vertices **p** = **4** and 8 **p** = **3**; 6•**4** or 8•**3** = 24 vertices that are distributed in connectivity centres **3** and **4**. Therefore $\mathbf{p}_{\mathbf{med}}$ = 24/7

(4, 24/7)

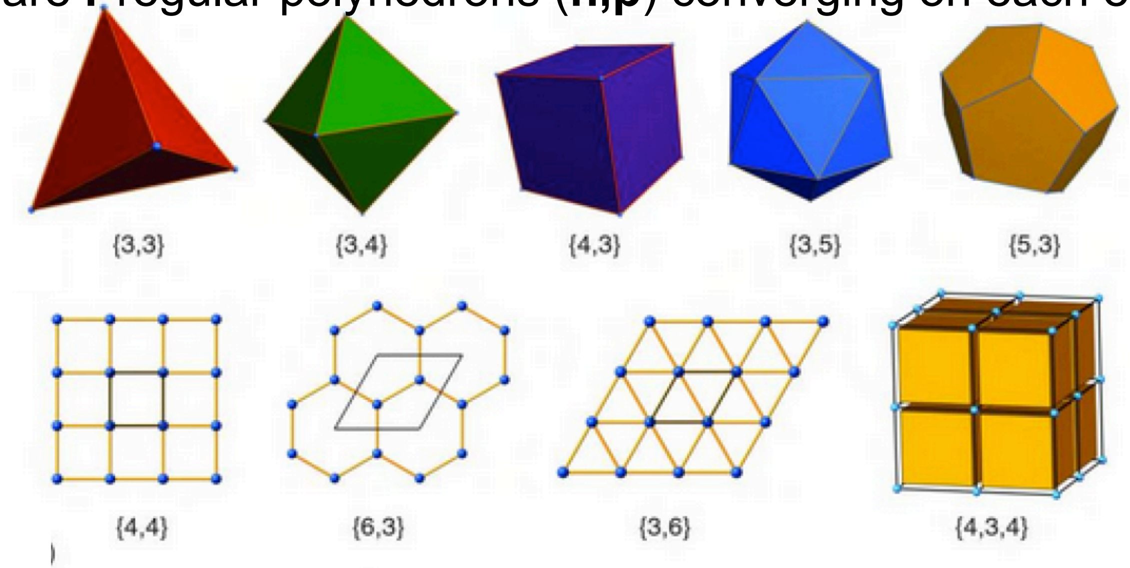
DESCRIPTION AND SYMBOLS FOR NETWORKS AND POLYHEDRONS

Schläfli's symbols: they have in general three or two entries (**n,p,r**) or (**n,p**) that refer to the tessellation of the 3D/2D space or discrete polyhedrons with regular geometry. The idea of the Schläfli's space (**n,p,r**)/(**n,p**) is to find the **circuits** that define the sides of the polygons and the faces of the polyhedrons that determine the tessellation of the 3D/2D space in regular objects (polygons/polyhedra).

In this way a tessellation 1D of the space corresponds to a regular polygon of **n**-sides: (**3**), (**4**), (**5**), (**6**), etc (triangle, square, pentagon, hexagon, etc).

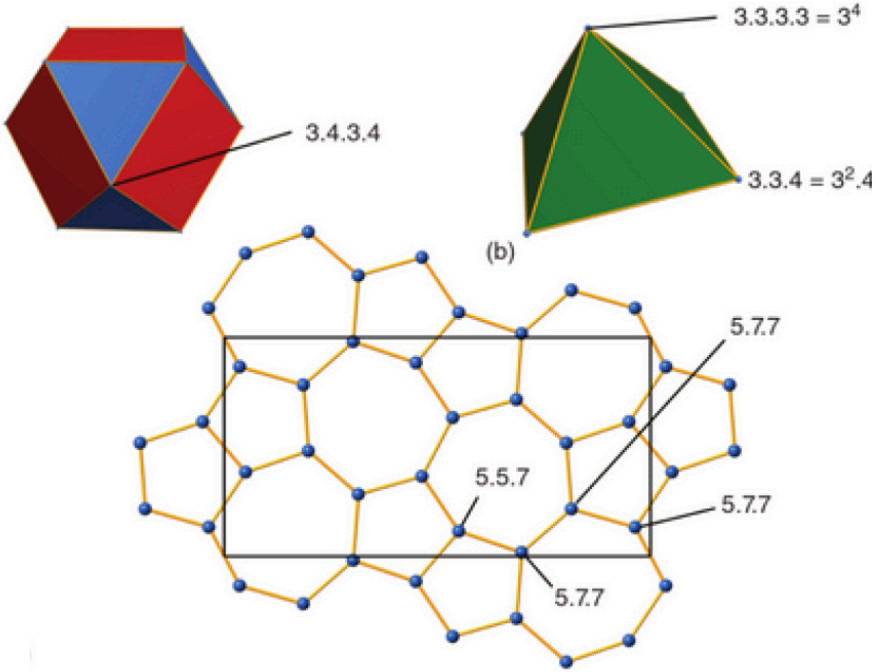
The symbol (**n,p**) describes regular polygons or a regular tessellations of the 2D space. Recall that the value of **n** refers to the poligonality and symbol **p** indicates how many **n**-gons converge in each vertex.

In 3D networks (**n,p,r**) represents the tessellation of the 3D space in polyhedrons and indicates that there are **r** regular polyhedrons (**n,p**) converging on each edge.



Vertex Symbol (VS): it can be applied to the vertices of polyhedrons and 2D-3D periodic networks **whether or not they are regular**. The notation for polyhedrons and periodic 2D networks on the one hand and 3D notation on the other have slightly different indexes and in the case of 3D the notation is also dependent on the coordination number of the centres that generate the vertices. This ambiguities have led to confusion in the literature. The methodology to obtain the symbol of a determined **node/vertex** is to consider all the possible **angles of pairs of edges** or **sides that converge** in a given **node/vertex**. The number of such angles for a **p-coordinated node** is **p (p-1) / 2** and the shorter rings (polygons) are examined. The **VS** symbols have the form $\mathbf{a^n.b^m.c^o.d^p}$ .... Where **a**, **b**, **c**, **d** ... represent the type of polygons that converge in each singular vertex and the superscript reflects the number of those polygons that coincide in the considered vertex. The symbol is organized from lower to higher polygonality:

Examples:



Tetrahedron: $3.3.3 = 3^3$

Cube: $4.4.4 = 4^3$

Octahedron: $3.3.3.3 = 3^4$

Cuboctahedron: 3.4.3.4

Square-based Pyramid: $(3.3.3.3)(3.3.4)_4 = (3^4)(3^2.4)_4$

2D Network **n** = 5, 7: (5.5.7)(5.7.7)

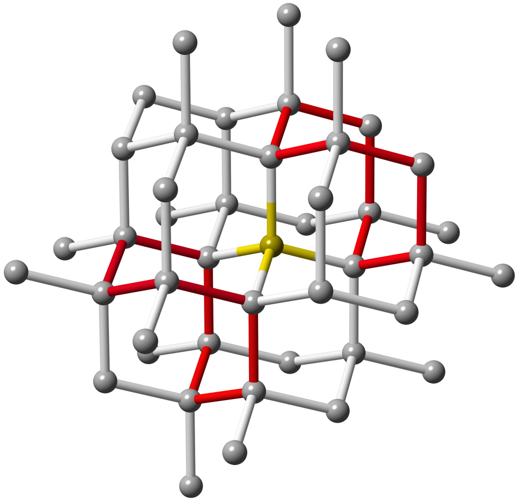
etc.

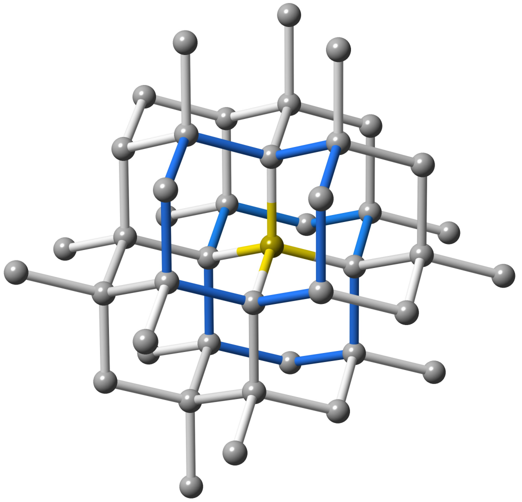
More about the Vertex Symbol (VS)

The VS is easy for polyhedrons and flat networks, however it is more complex for 3D networks because the selected angle can be involved in more than one ring. For 3D networks it is also necessary to consider that:

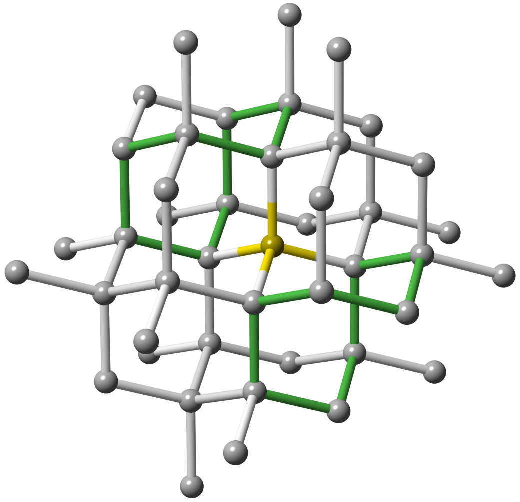
i) The symbols are never grouped (in 3D networks).

ii) When a node connectivity is greater than 3 the cyclic order is not possible and for 4-coordinate centres O'Keeffe has proposed to group the 6 angles into pairs of opposite angles (those that do not have any common axis).





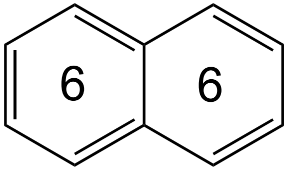
$6_2.6_2.6_2.6_2.6_2.6_2$



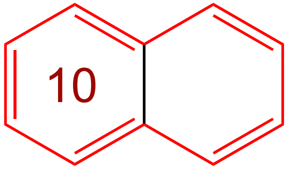
iii) When an angle does not give rise to a ring, an asterisk is placed indicating that a cycle with "shortcuts" originates ....

......The **vertex symbol** (O'Keeffe) differentiates between **rings** and **circuits**. A **ring** has the meaning that we all understand but a **circuit** can have shortcuts.... **Example**: naphthalene defines a circuit of 10 centers but is made up of two rings of 6:

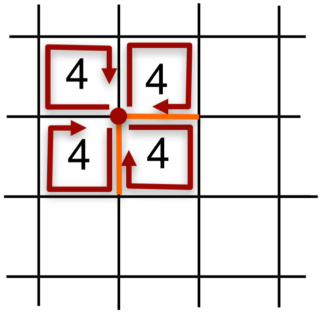
Two six-membered rings



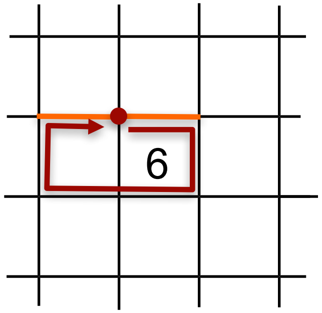
1 circuit of 10 links



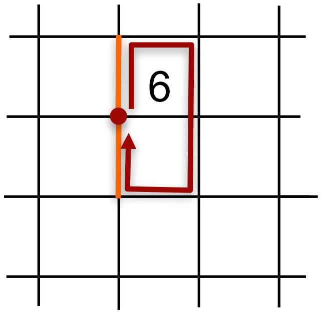
Therefore, the **Vertex method** inspects only the **smallest rings for each angle** in which the chosen node is located (there are **p(p-1)/2** angles for a node **p**), and specifies the size of the ring/or the number of vertices. **Example**:



Angle of 90º
4 rings of 4:
4.4.4.4
But we have two left angles [p(p-1)/2] = 6



These are:
Angles of 180º
2 circuits of 6:
6.6



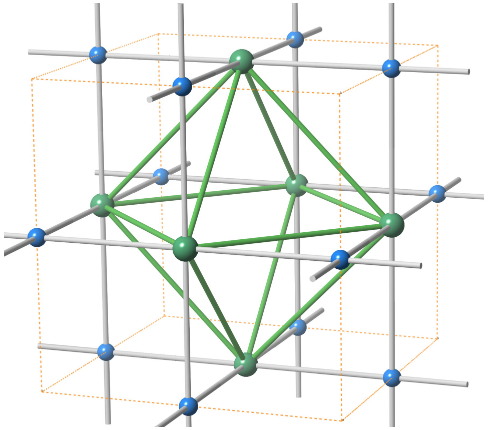
The Vertex Symbol for this 2D layer is: 4.4.4.4. *. * since VS does not consider circuits. The two asterisks are added to be consistent with p(p-1)/2. It is important to note that the VS does not explicitly contain the connectivity of the nodes, it only specifies the poligonality. However, the value p(p-1)/2 is the sum of the "exponents" of the corresponding symbols (including asterisks).

EXERCISES

Application of the VS to unimodal (p = 4) 3D Networks

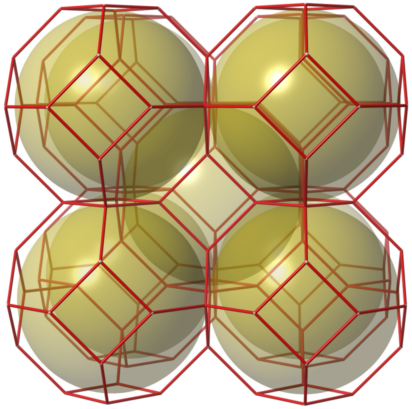
NbO

$6_2\cdot6_2\cdot6_2\cdot6_2.8_2\cdot8_2$



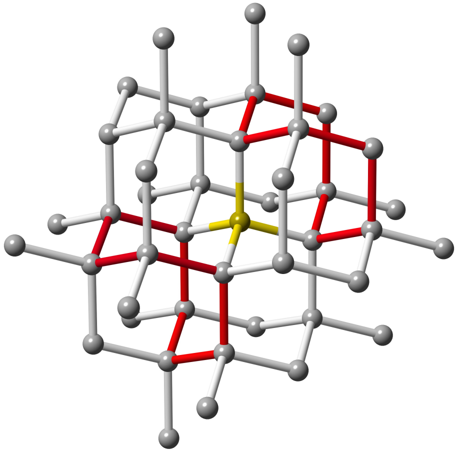
Sodalite ($Na_8Al_6Si_6O$)

$4\cdot4\cdot6\cdot6\cdot6\cdot6$



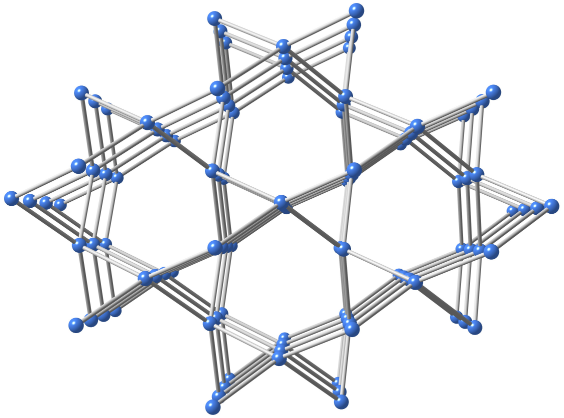
Diamond (C)

$6_2\cdot6_2\cdot6_2\cdot6_2\cdot6_2\cdot6_2$



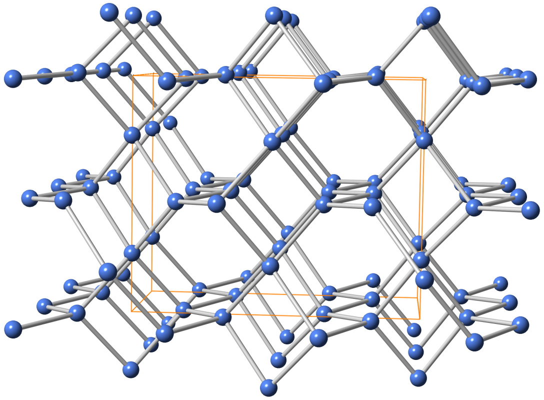
Quartz (SiO_2)

$6\cdot6\cdot6_2\cdot6_2\cdot8_7\cdot8_7$



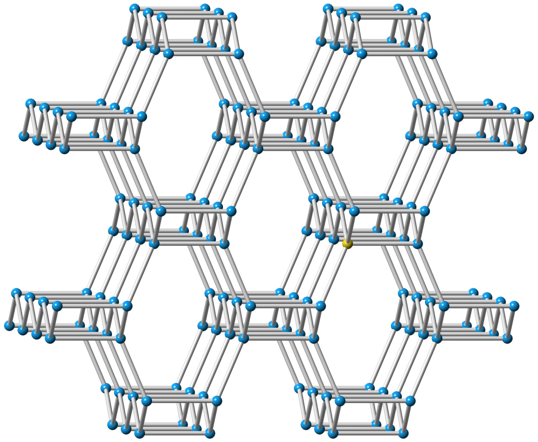
Moganite (SiO_2)

$4\cdot4\cdot6_2\cdot6_2\cdot8_4\cdot8_4$



$SrAl_2$

$4\cdot6\cdot4\cdot6\cdot6\cdot8_2$



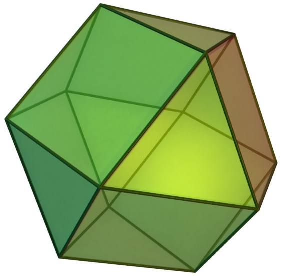
Point Symbol (PS): It was introduced by A. F. Wells especially to describe **non-uniform networks** where rings of different polygonality converge at their vertices/nodes. The basic procedure of **PS** is very similar to that of **VS**: analysing all possible pairs of edges meeting around each singular vertex and accounting for the generated polyhedrons. However, the essential difference between **VS** and **PS** is that the shortest rings defined by the angles of a given vertex have to be polygons (fundamental circuits). In contrast, **PS** refers to shortest circuits whether or not they are natural polygons. This means that we search for each single node the link angles the shortest possible circuit to return to the starting point. The **PS** applies equally to polyhedrons and 2D and 3D networks. It does not take into account the considerations discussed above for the **VS** and usually simplifies the simbology, for example, in the square network analysed previously we would have 4.4.4.4.6.6 (we consider rings and circuits) and write ($4^4.6^2$). **PS** notation seems to be more reasonable than **VS** and that is why **PS** is mostly used.

As already mentioned, the number of ways to select two links/edges that are in a node of **p**-connectivity is expressed: **p(p-1)/2**. For example, in the case of the tetrahedron with Schläfli symbol (**3,3**), **p** = **3**, therefore the number of ways to select the two links is **3(3-1)/2 = 3**. The **PS** for the tetrahedron will be $\mathbf{3^3}$. In general a node **p** = **3** generates three elementary circuits that can coincide with regular polygons or not.

It is important to observe how the number of circuits of a node grows rapidly with its connectivity :

p = 3, 4, 5, 6,….
p(p-1)/2 = 3, 6, 10, 15,….

Comparison of the three systems of topological description: Schläfli, Vertex and Point in some regular and semiregular polyhedrons



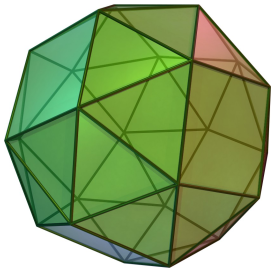
cuboctahedron

Schläfli: (24/7, 4)

Vertex Symbol: 3.4.3.4

Point Symbol: $3^2.4^2$

Tetrahedron, (3,3)	Octahedron, (3,4)	Icosahedron (3,5)
3.3.3	3.3.3.3	3.3.3.3.3
3^3	3^4	3^5



Snub Cube

Schläfli: (60/38, 5)

Vertex Symbol : 3.3.3.3.4

Point Symbol : $3^4.4$

Some analysed networks: comparison between VS and PS

NbO: (VS) $6_2.6_2.6_2.6_2.8_2.8$ (PS) $(6^4.8^2)$

Sodalite: (VS) 4.4.6.6.6.6 /// (PS) $(4^2.6^4)$

Diamond: (VS) $6_2.6_2.6_2.6_2.\ 6_2.6_2$ /// (PS) (6^6)

SiO_2-Quartz: (VS) $6 \cdot 6 \cdot 6_2 \cdot 6_2 \cdot 8_7 \cdot 8_7$ /// (PS) $(6^4.8^2)$

SiO_2-Moganite: (VS) $4 \cdot 4 \cdot 6_2 \cdot 6_2 \cdot 8_4 \cdot 8_4$ (the same pair of links are involved in two distinct circuits)
(PS) $(4^2.6^2.8^2)$

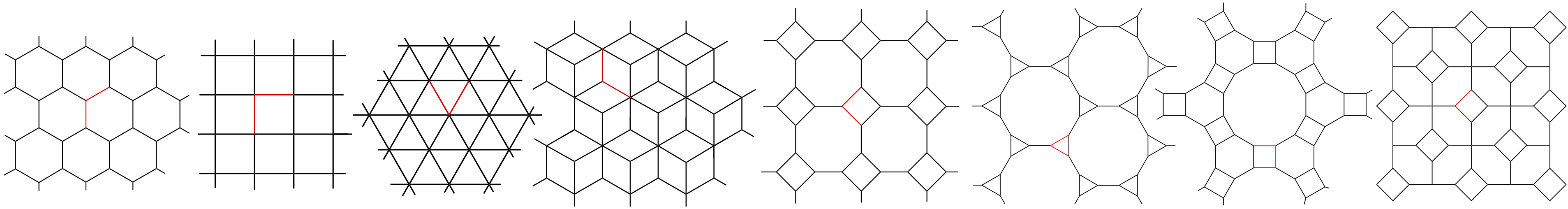
$SrAl_2$: (VS) $4 \cdot 6 \cdot 4 \cdot 6 \cdot 6 \cdot 8_2$ /// (PS) $(4^2.6^3.8)$

$CdSO_4$: (VS) 6.6.6.6.6.* /// (PS) $(6^5.8)$

PtS: (VS) $4.4.8_2.8_2.8_2.8_2$ /// (PS) $(4^2.8^4)(4^2.8^4)$ nodes T_d y D_{4h}

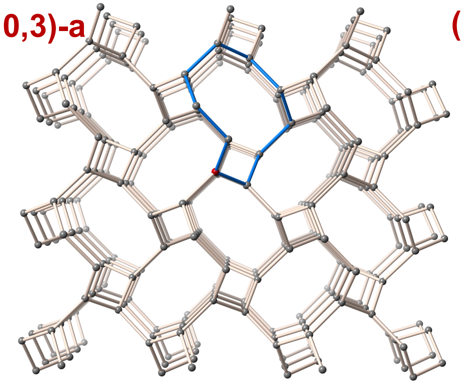
EXERCICES

TESSELLATION OF THE 2D SPACE

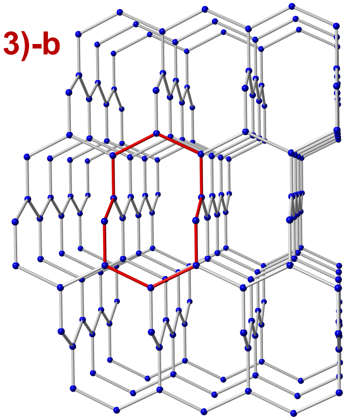


TESSELLATION OF THE 3D SPACE (COMMON 3D NETWORKS)

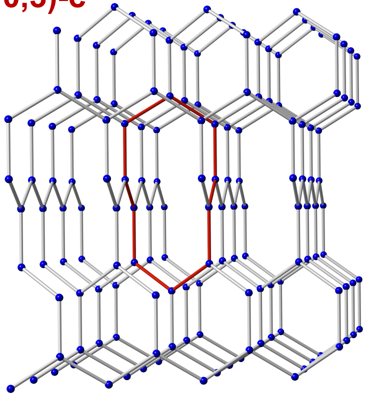
(10,3)-a



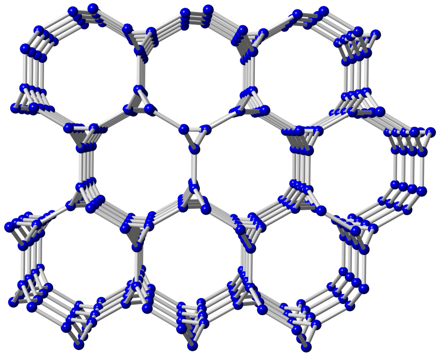
(10,3)-b



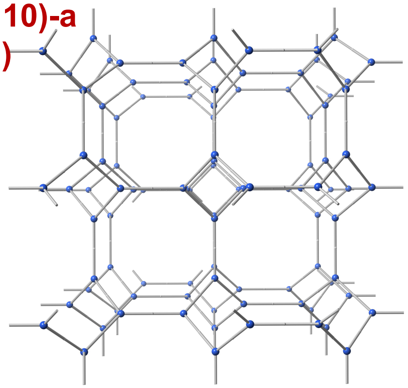
(10,3)-c

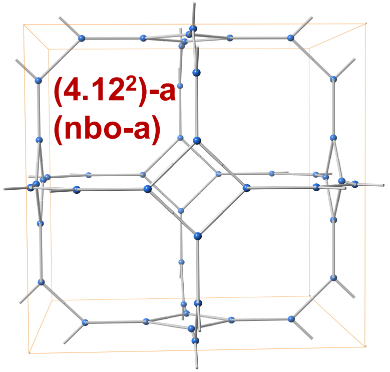


(8,3)-c

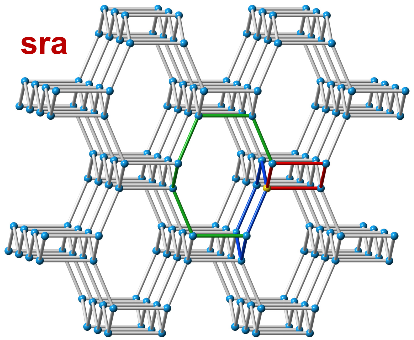


$(8^{2}.10)$-a
(lig)

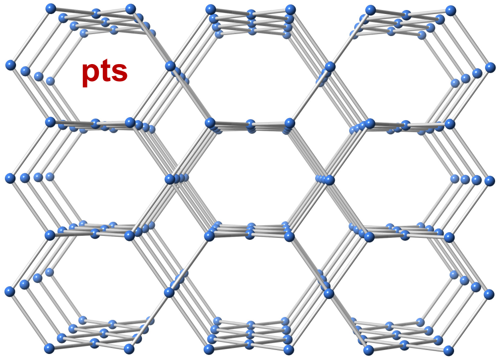




(4.12^{2})-a
(nbo-a)



sra



pts

Available means for the topological analysis of networks in coordination polymers

The graphical and the topological analysis are necessary tools for the classification and discovering of new networks.

The first steps in this direction were given by A. F. Wells in a series of articles and books published in the period 1950-1980 (eg. *Three-dimensional Nets and Polyhedra*, Wiley-Interscience, New York, 1977).

More recently have been published important monographies by M. O'Keeffe y B. G. Hyde (*Crystal Structures.I. Patterns and Symmetry* , Mineralogical Society of America Monograph, Washington, DC, 1996) and L. Öhrström y K. Larsson (*Molecule-based Materials, the Structural Network Approach*, Elsevier, Amsterdam, 2005).

Of great importance are the data base "*Reticular Chemistry Structure Resource* (RCSR)" http://rcsr.anu.edu.au (O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. *Accts. Chem. Res.* **2008**, *41*, 1782-1789) and the TOPOS software http://topospro.com (V. A. Blatov et al. *J. Appl. Crystallogr*. 2000, 33, 1193).

Relevant References

F. Hoffmann, M. Fröba
Network Topology in The Chemistry of Metal-Organic Frameworks:Synthesis, Characterization, and Applications Wiley Online Library, 16 JUN 2016, Edited by S. Kaskel (libre todos los pdf en internet: http://onlinelibrary.wiley.com/book/10.1002/9783527693078)

M. O’Keeffe, M. Eddaoudi, H. Li, T. Reineke, O. M. Yaghi,
Frameworks for Extended Solids: Geometrical Design Principles
Journal of Solid State Chemistry 152, 3-20 (2000).

Omar M. Yaghi, Michael O’Keeffe, Nathan W. Ockwig, Hee K. Chae, Mohamed Eddaoudi, Jaheon Kim.
Reticular synthesis and the design of new materials
Nature 2003, 423, 705-714.

Michael O’Keeffe, Omar M. Yaghi
Deconstructing the Crystal Structures of MetalOrganic Frameworks and Related Materials into Their Underlying Nets
Chem. Rev. 2012, 112, 675-702

Timothy R. Cook, Yao-Rong Zheng, and Peter J. Stang
Metal−Organic Frameworks and Self-Assembled Supramolecular Coordination Complexes: Comparing and Contrasting the Design, Synthesis, and Functionality of Metal−Organic Materials
Chemical Reviews 2013, 113, 734-777.

INDEX PART THREE

Review of significant MOFs

- Introduction: i) Motivations that have led to the explosive expansion of the research area of MOFs; ii) Importance of the nature of the node (fragility vs robustness). Examples of simple SBUs ([Fe(tvp)$_2$(NCS)$_2$ y Fe(piracina)[M^{II}(CN)$_4$]).

- Selection of networks based on polynuclear SBUs :

  i) MOF-2.
  ii) HKUST-1.
  iii) MOF-14 (extension of the trivalent node of HKUST-1 and interpenetration).
  iv) Importance of bridge geometry : OD→2D→3D.
  v) MOF-5. Properties.
  vi) Iso-reticular series IRMOFs.
  vii) MOF-177.
  viii) Series MIL: MIL-101 y MIL-5 (flexibility).
  ix) Series UiO y PCN based on Zr^{IV} SBUs
  x) Serie NU-nº
  xi) MOFs with unsaturated coordination centers : $H_2[Co_4O(TAT)_{8/3}]_n$.
  xii) ZMOFs: $[Cu^I(pyrimidine)_2]_n(BF_4)$; $[Co_5(imidazole)]_n$; $[Zn(bim)_2]_n$.
  xiii) ZIFs
  xiv) Covalent organic frameworks (COFs).

INTRODUCTION

Storage of molecular hydrogen is one most relevant driving forces that have propelled the field of MOFs during the last 10 years. Besides the difficulties of finding efficient methods of H_2 generation it is the problem of storing H_2 under conditions competitive with current storage methods (energy storage). In the case of H_2:

** 1 kg of H2 generates 120 MJ (gravimetric density of excellent energy)

but the problem is that

** 1 kg of H_2 occupies 11 m^3 (STP) (very low volumetric energy density compared to other fuels).

Then, there is the need for finding methods to group H_2 molecules more efficiently than with the methods used today: 1) compression, 2) liquefaction, 3) solid state. An efficient solution could be Fisisorción in solid state.

In the solid state, C (active), metal hydrides, clathrates, microporous polymers, zeolites, etc. have been tested. The problem of C (active) is the lack of a long-range porous structure and zeolites, metal hydrides and clathrates are based on chemisorption processes that make the recovery of stored H_2 difficult.

Given the limitations of these traditional materials, MOFs seem to have certain advantages:

1) Crystallinity and structural diversity.
2) Permanent long-range porosity.
3) Almost infinite compositional diversity derived from the combination of different metal centers and ligands.
4) Ability to design and decorate the pores by unsaturation strategies of the coordination centers, functional groups, post-synthetic modifications.
5) These characteristics are also advantageous for:

These characteristics are also advantageous for:

i) Storage of CH_4 (energy).
ii) CO_2 sequestration; of volatile organic compounds (VOC) (safety, health ...).
iii) Selective separation of substances of industrial interest.
iv) Catalysts in heterogeneous catalysis processes through the specific design of pores (eg metallic nano-crystals).
v) Drug dispensers (biocompatible MOFs).
vi) Implementation of interesting physical properties (luminescent, magnetic, ionic transport, electronic, etc.) that depend on the nature of the molecules included in the pores (sensors, devices).

MOFs BASED ON POLYNUCLEAR SECONDARY BUILDING UNITS (SBUs)

All these attributes have contributed to intense activity carried out in the design of coordination polymers leading to spectacular advances in the synthesis of new porous MOF materials, as well as to the development of new rational synthetic strategies in which stability, control of pore size, organic functionality etc are fundamental aspects.

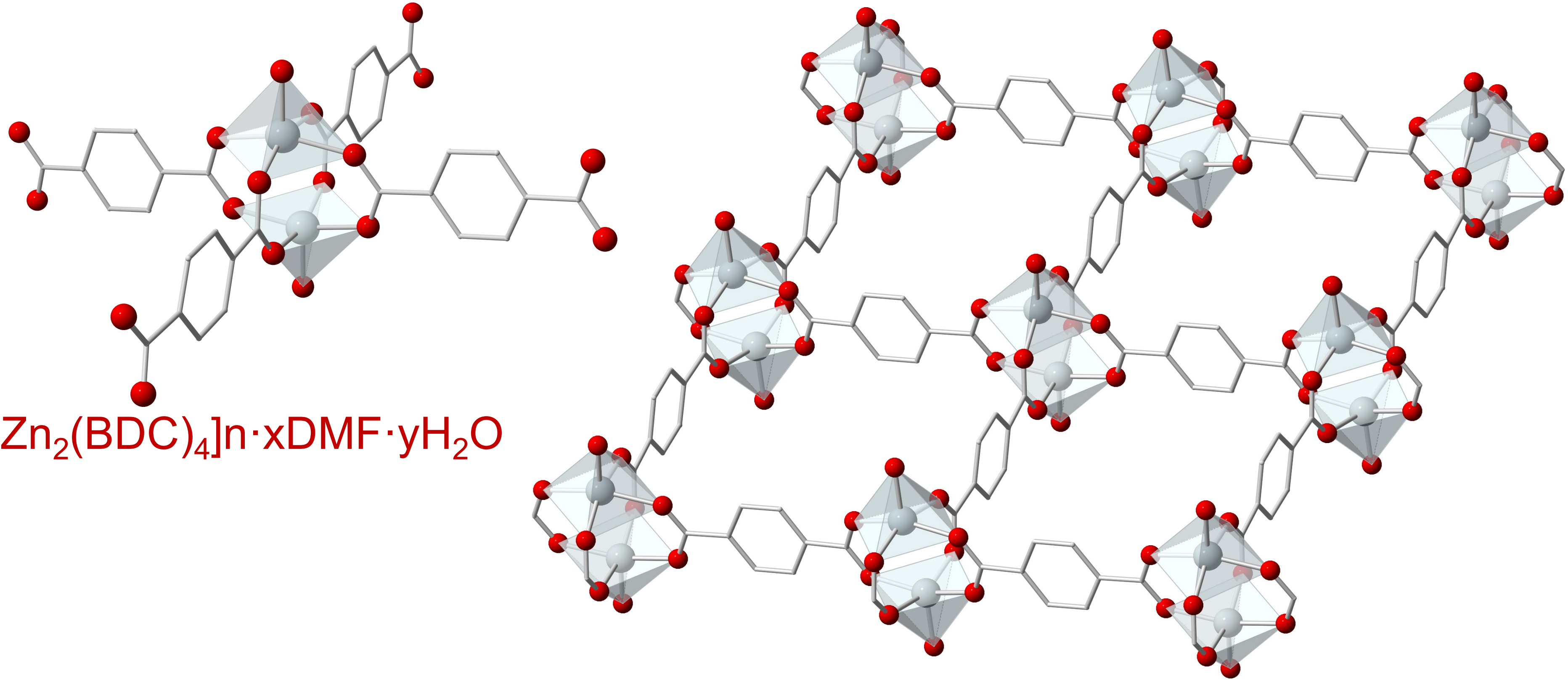
These strategies include methods to avoid interpenetration of networks or collapse of the framework when the solvent molecules located in the channels are evacuated (many of them have to be "emptied" by soft methods such as liophilization or using critical CO_2).

It has been concluded that simple Metal-Ligand coordination links as generators of the network nodes are in many cases not robust enough due in part to the lability of the metal coordination sphere, which possibly confers fragility to empty MOFs structures.

The discovery of metallic polynuclear units as robust nodes in porous networks (SBUs), is possibly one of the ideas that have most influenced the evolution of research in the last 10-15 years and, together with the aspects mentioned above, continues being one of the main axes of research into MOFs.

SELECTION OF SOME SIGNIFICANT MOFs

The concept of SBU was presented for the first time by O. Yaghi and collaborators (Li, H., Eddaoudi, M., Groy, TL & Yaghi, OM "Establishing microporosity in open metal-organic frameworks: gas sorption isotherms for Zn(BDC) (BDC = 1,4-benzenedicarboxylate)" *J. Am. Chem. Soc*. 1998, 120, 8571-8572 ... It gives origin to the so-called MOF-2, which is a typical square network (4.4). The most significant feature are the nodes of the network made up of SBUs formulated $[Zn_2(CO_2)_4]$ instead of a single metal ion.

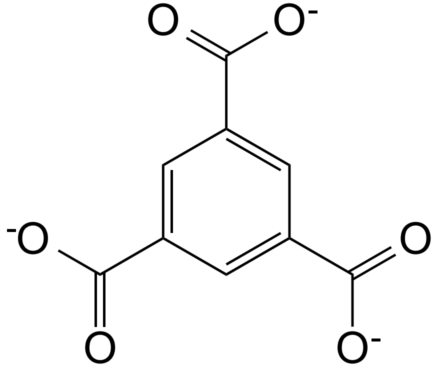


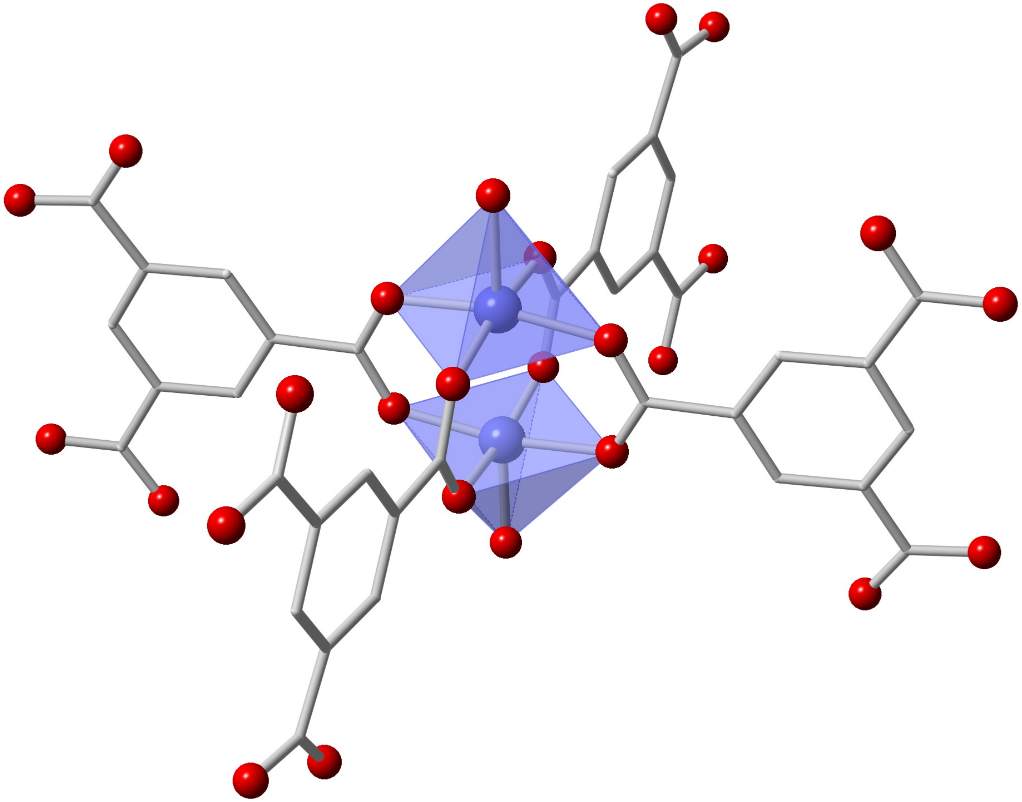
$[Zn_2(BDC)_4]n \cdot xDMF \cdot yH_2O$

After removing the DMF and H_2O molecules included between the 2D layers the resulting formulated compound $[Zn(BDC)_2]_n$ is thermally stable in the temperature range 190-315 °C

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

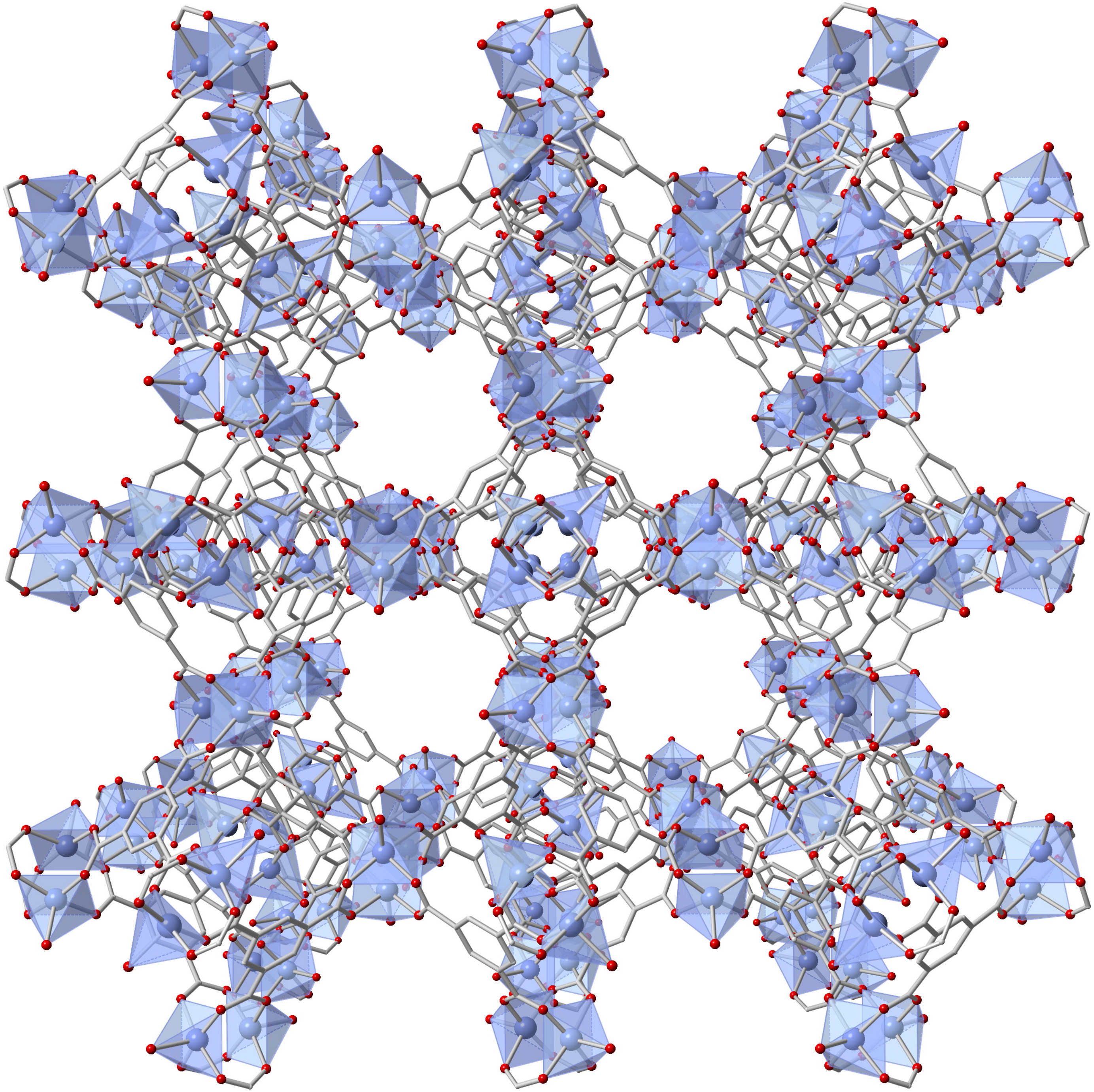
Almost at the same time a group composed of the universities of Hong Kong and Bristol reported one of the most studied MOFs called HKUST-1 of the Hong Kong University of Science and Technology. The formula of this compound is $[Cu_3(TMA)_2(H_2O)_3]_n$ where TMA is benzene-1,3,5-tricarboxylate. In this case the organic molecule acts as an IC3 node that alternates with IC4 nodes provided by the SBU $[Cu_2(CO_2)_4]$ giving rise to a porous 3D network.



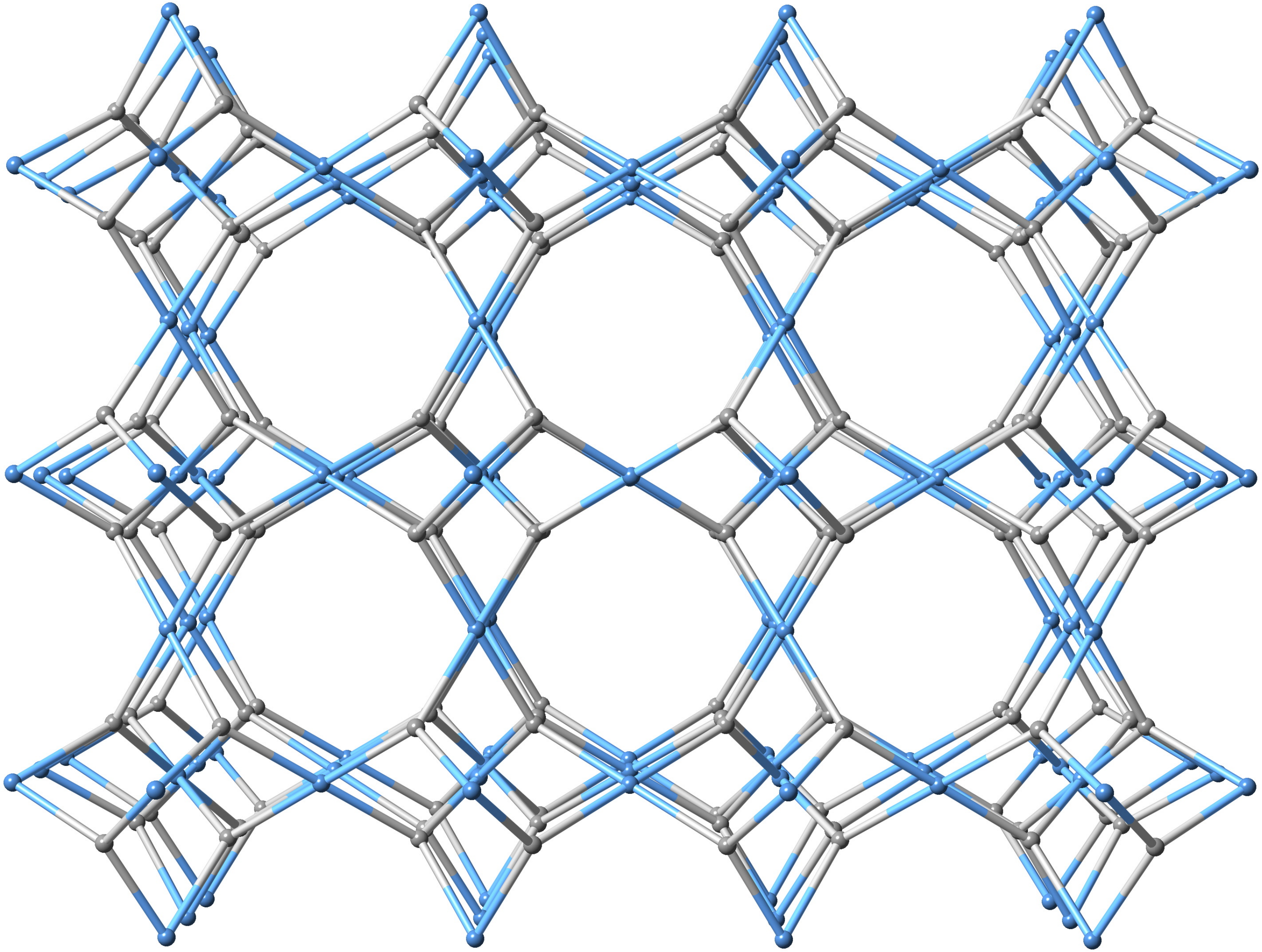


S.S.Y. Chui, S.M.F. Lo, J. P. H. Charmant, A.G. Orpen, I. D. Williams "A Chemically Functionalizable Nanoporous Material $[Cu_3(TMA)_2(H2O)_3]_n$" *Science* 1999, 283, 1148-1150.

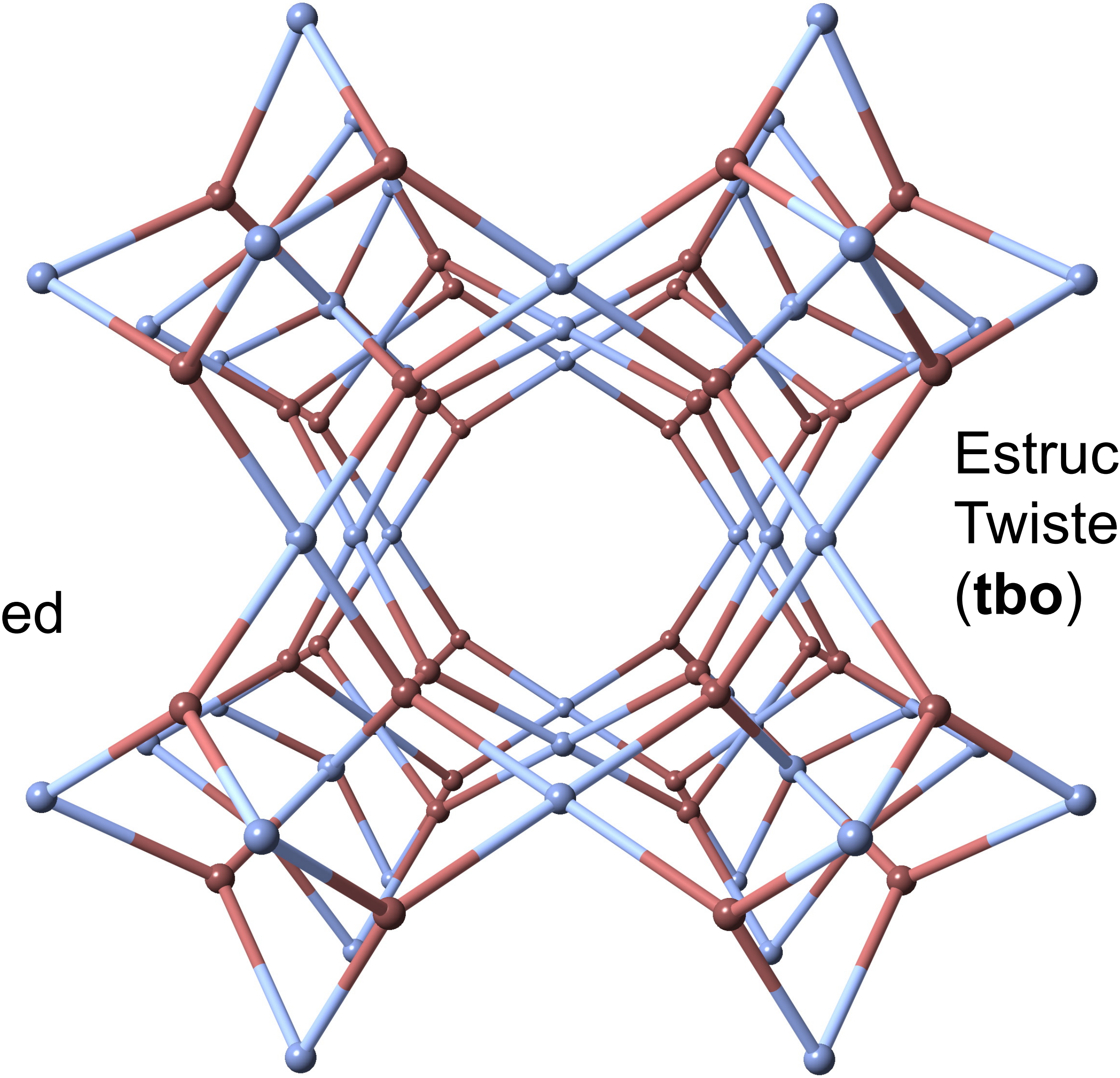
HKUST-1



HKUST-1



HKUST-1

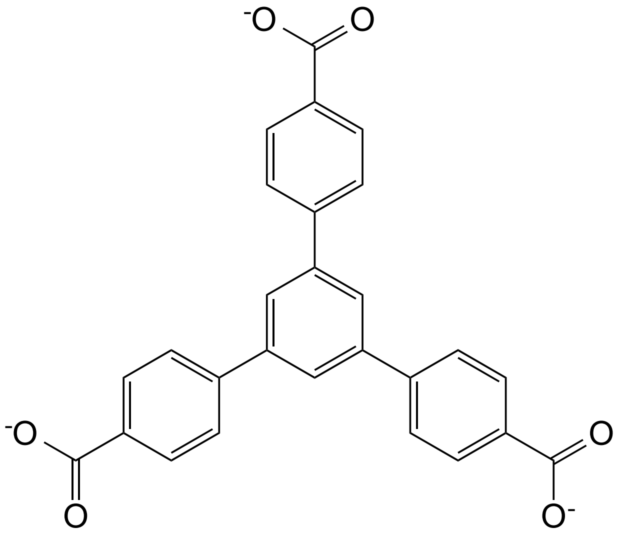


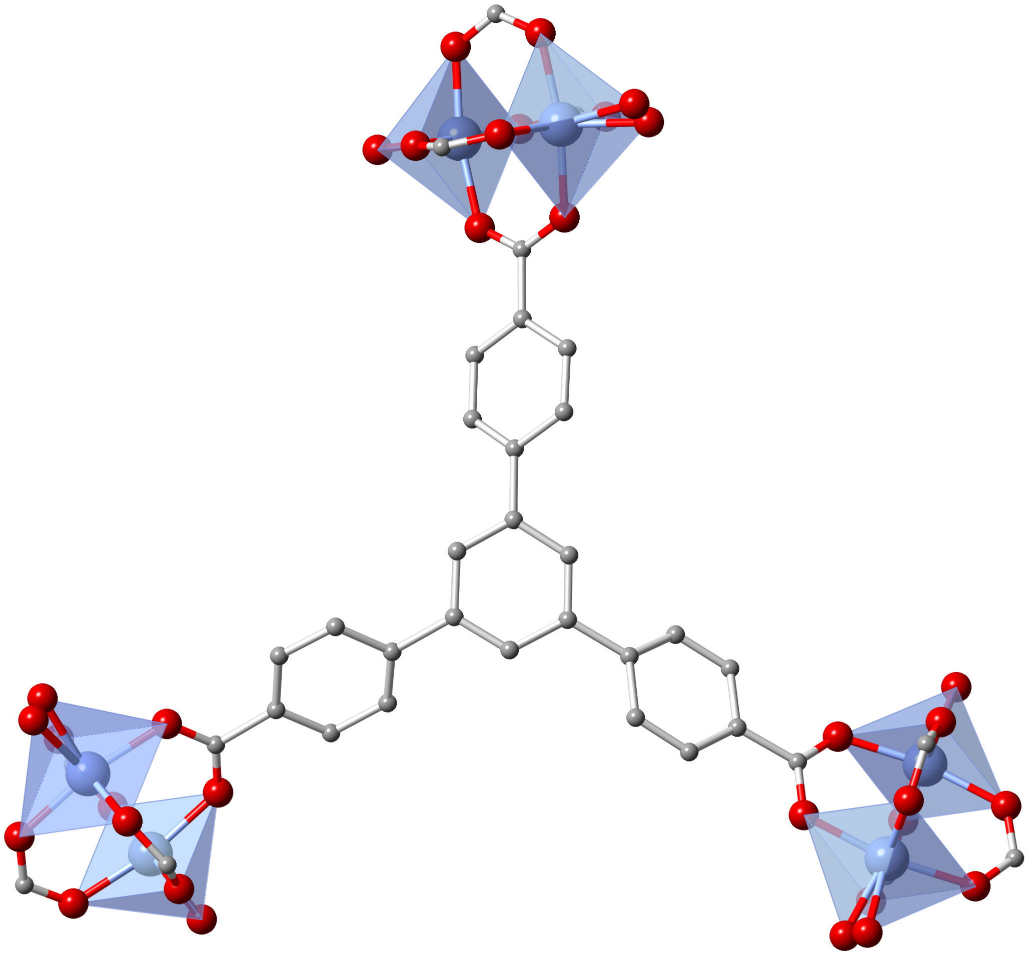
Network
3,4 connected

Estructure type :
Twisted boracite
(**tbo**)

MOF-14

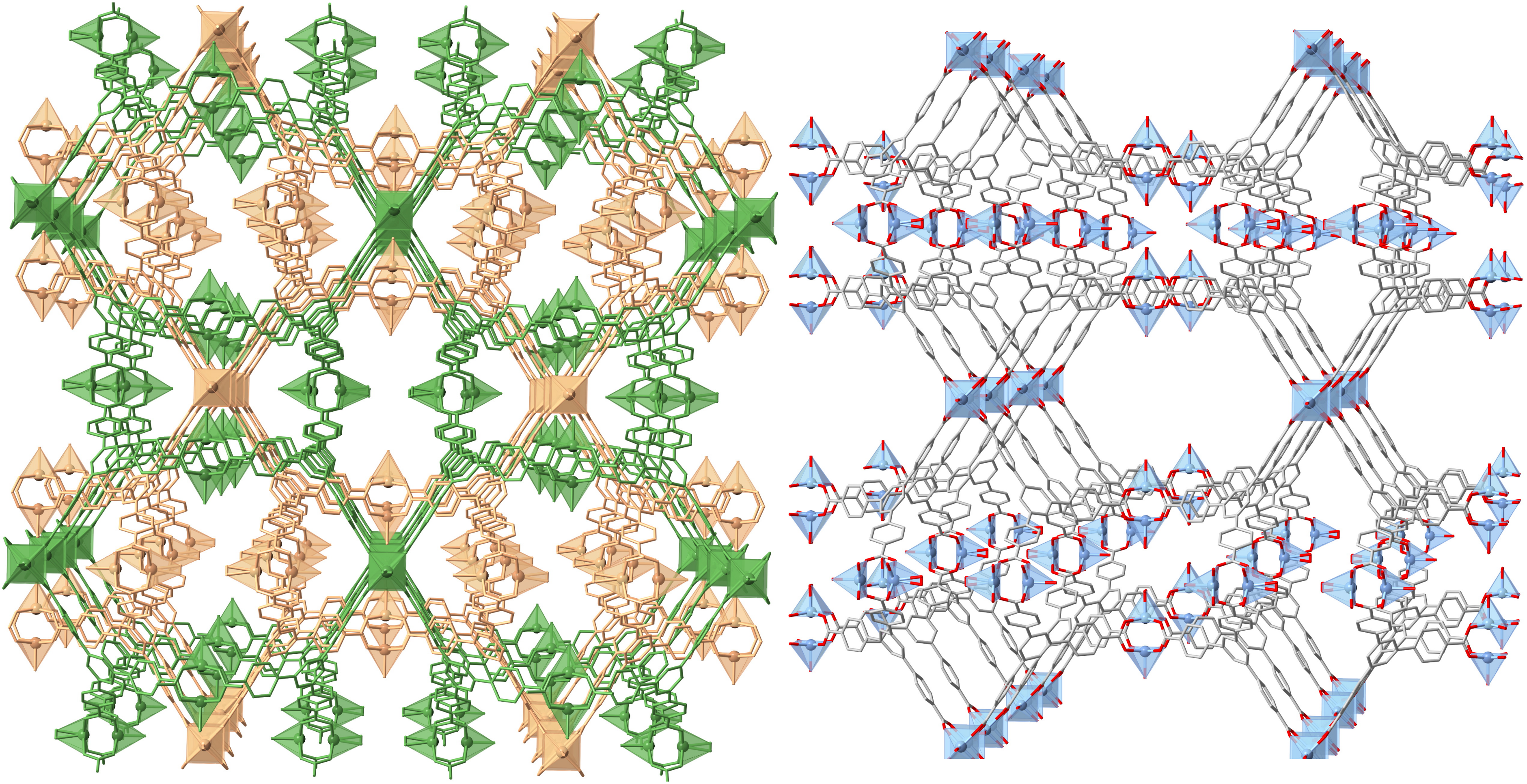
A variant of the HKUST-1 system was published B. Chen, M. Eddaoudi, ST Hyde, M. O'Keeffe, OM Yaghi, "Interwoven Metal-Organic Framework on a Periodic Minimal Surface with Extra-Large Pores" *Science* 2001,291,1021-1023. These authors combine 1,3,5-benzene-4,4',4"-tribenzoic acid (BTB) with $Cu^{II}(NO_3)\cdot 4H_2O$ and DMF to get the compound $Cu_3(BTB)_2(H_2O)_3\cdot(DMF)_9(H_2O)_2$ (MOF-14).



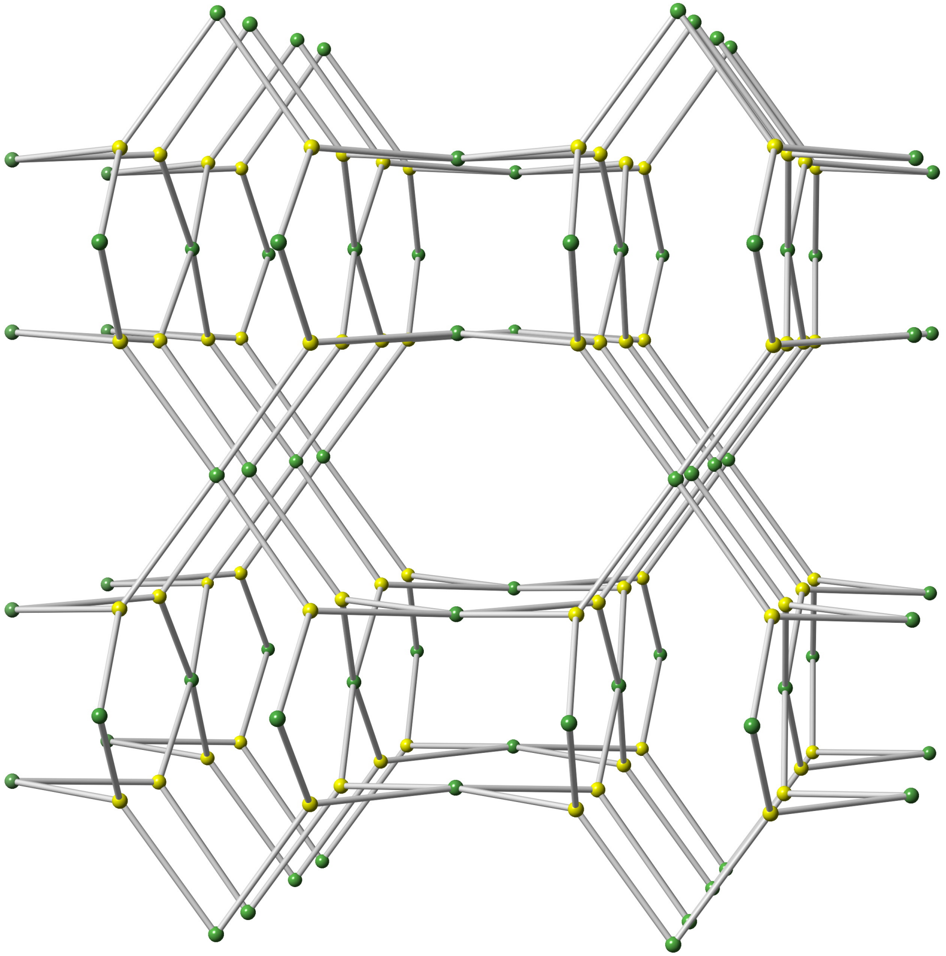


MOF-14

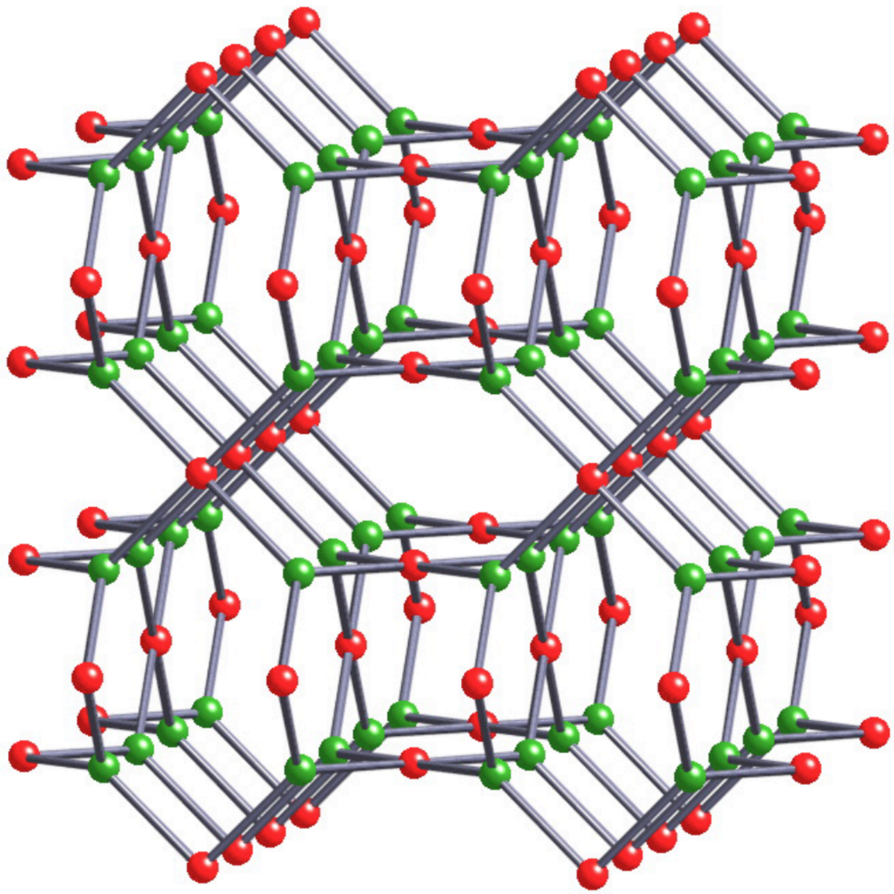
This is a case of two identical interpenetrated networks



Network 3.4 connected with the type structure of Pt_3O_4



Pt_3O_4 structure from MOF-14

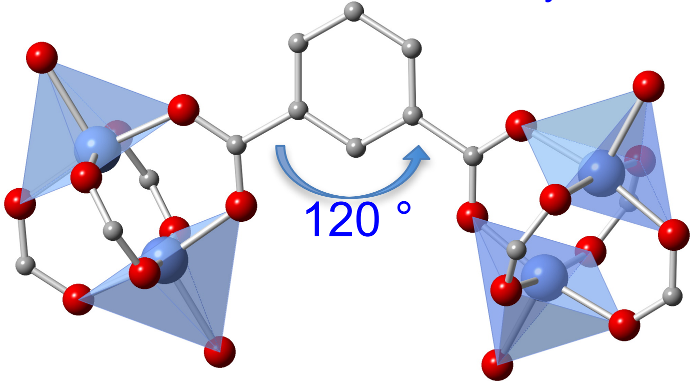


Structure of Pt_3O_4

IMPORTANCE OF BRIDGE LIGAND GEOMETRY

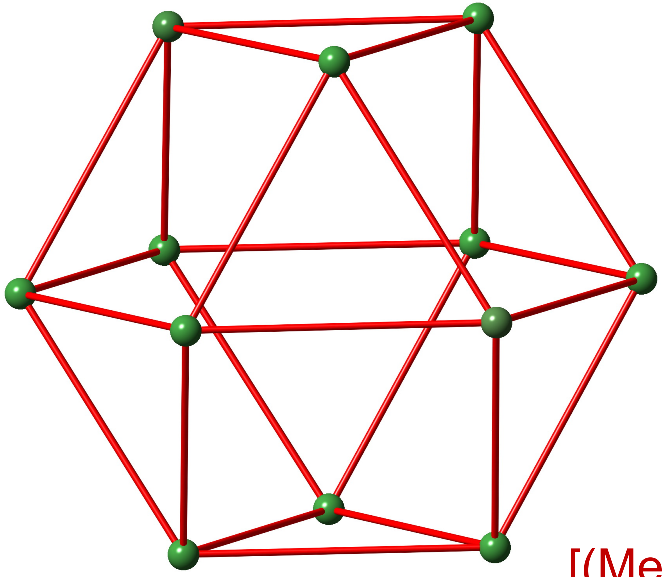
For a given SBU cationic unit, the geometry of the organic unit is essential in the final result

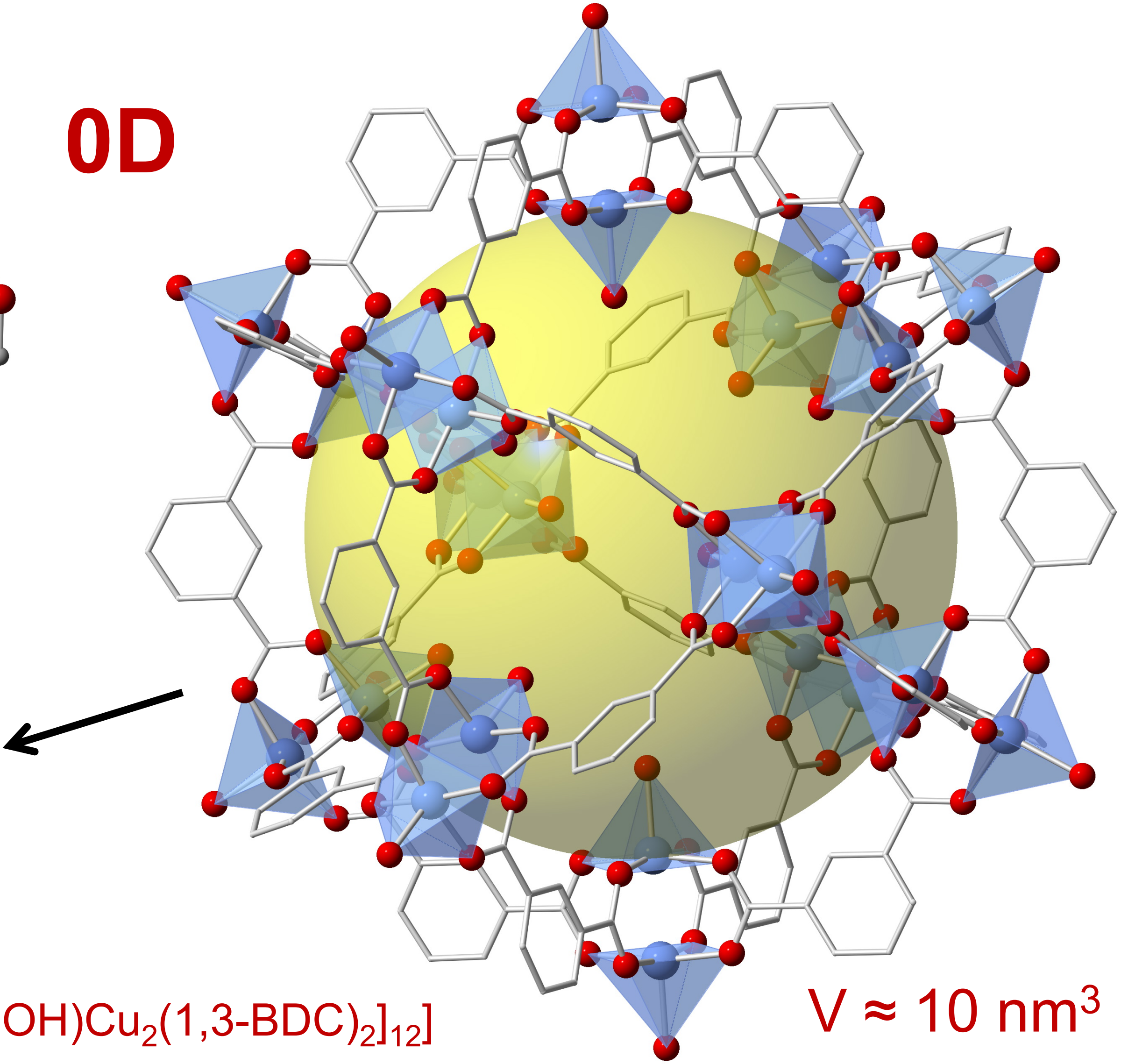
Benzene 1,3-dicarboxylate



0D

Cuboctahedron



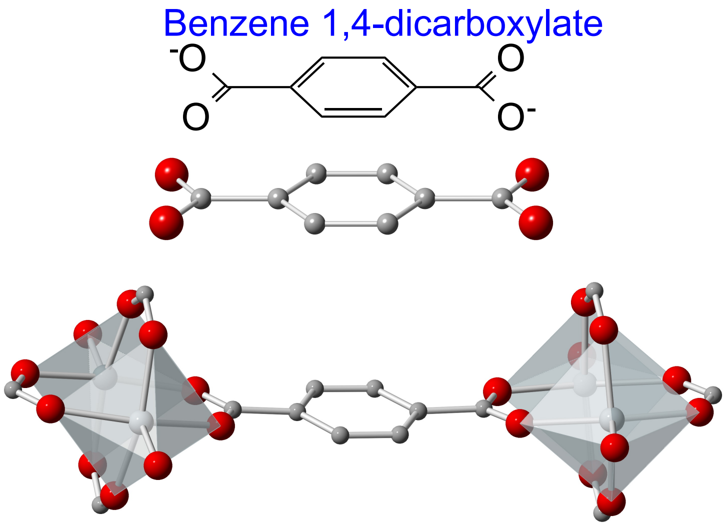


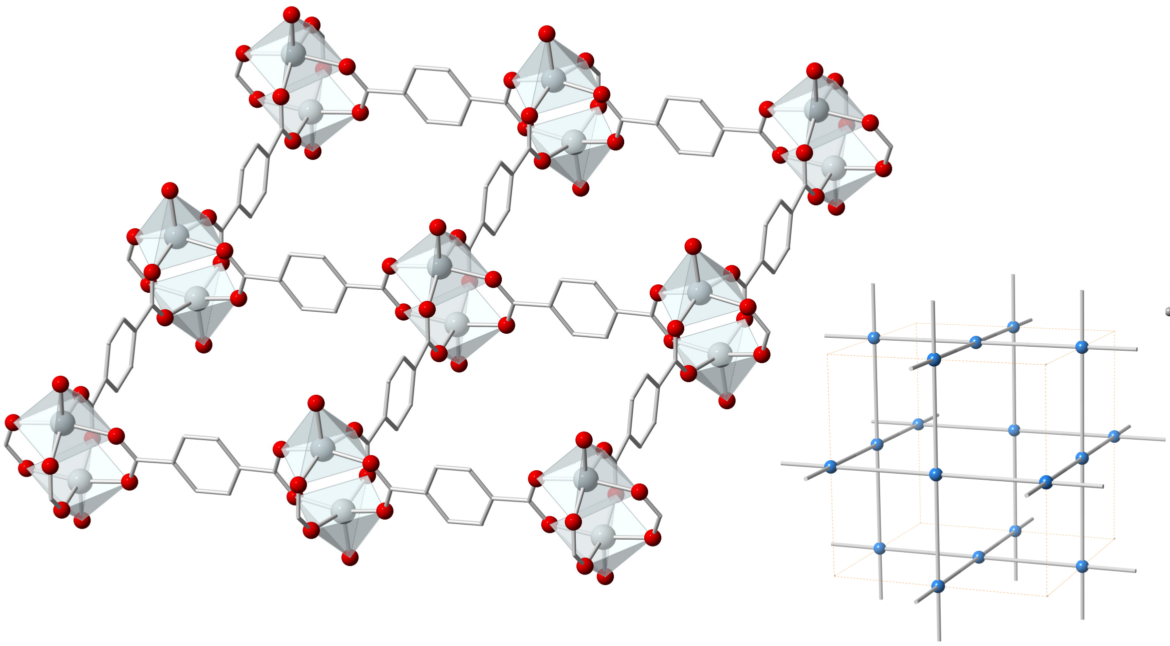
$[(MeOH)Cu_2(1,3\text{-}BDC)_2]_{12}]$

$V \approx 10\ nm^3$

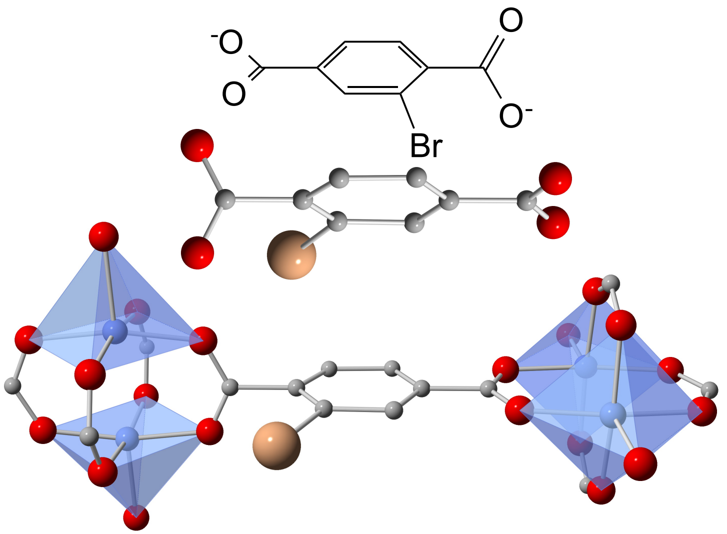
B. Moulton, J. Lu, A. Mondal, M. J. Zaworotko “Nanoballs: nanoscale faceted polyhedra with large windows and Cavities” Chem. Commun., 2001, 863-864

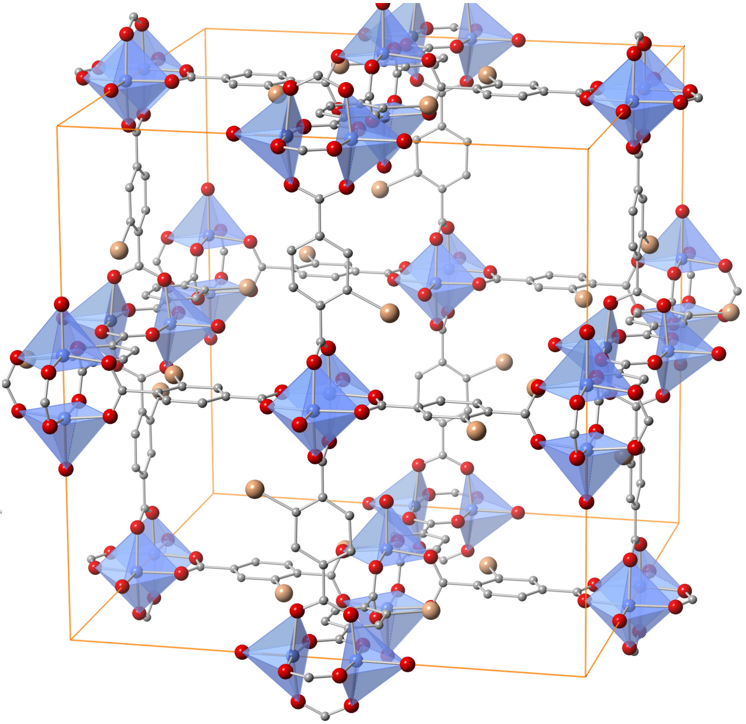
Red 2D (4,4)





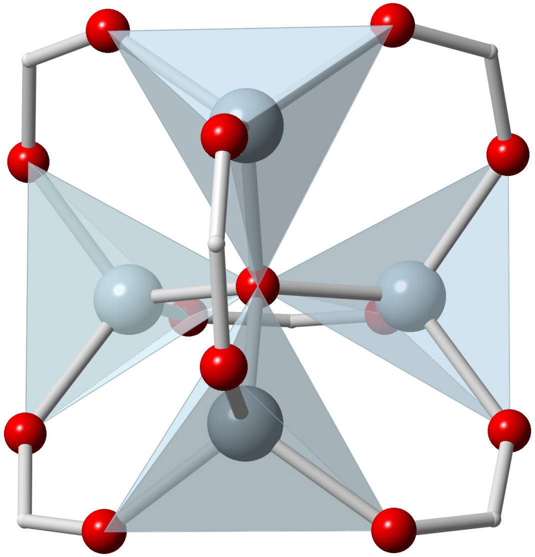
Red 3D NbO

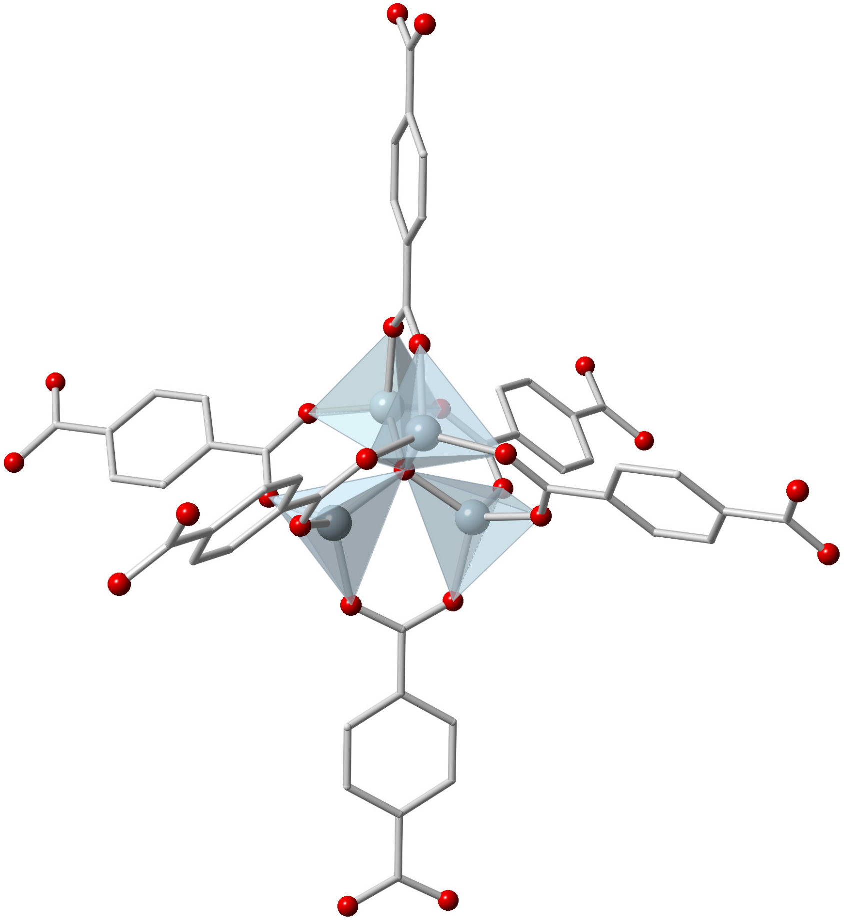




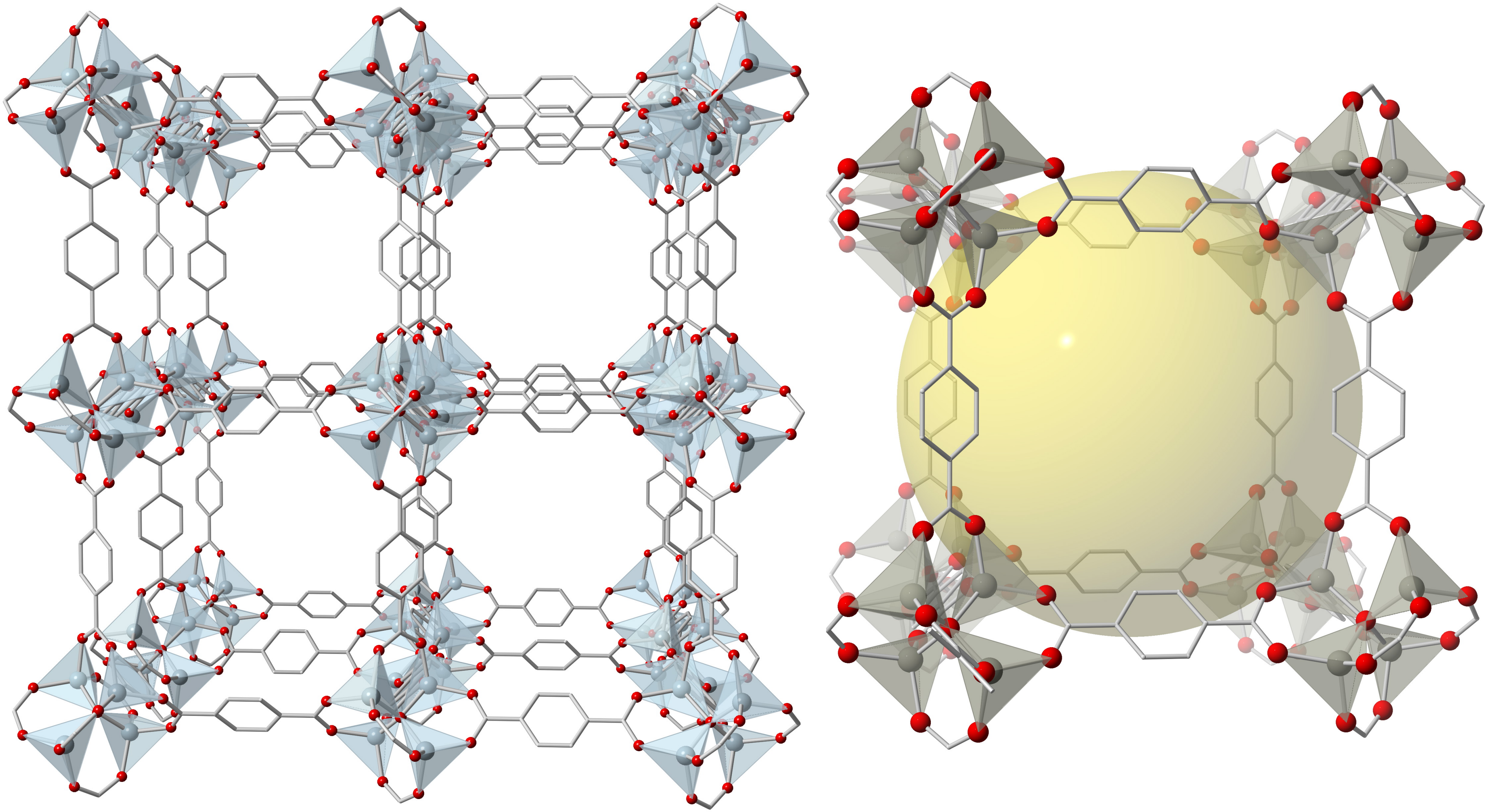
MOF-5

The Yaghi's team studied the synthesis conditions to generate in situ tetranuclear SBU nodes formulated $[Zn_4O(CO_2)_6]$ which consist in ZnO_4 tetrahedrons linked by a common vertex and six carboxylate groups that define the axes of an octahedron. Therefore, the SBU extends the structure, resulting in a much more regular cubic 3D network than MOF-14. The compound is formulated $Zn_4O(BDC)_3{\cdot}(DMF)_8(C_6H_5Cl)$ (H. Li, M. Eddaoudi, M. O'Keeffe & O. M. Yaghi "Design and synthesis of an exceptionally stable and highly porous metal-organic framework" Nature **1999**, 402, 276-279).





MOF-5



This network has high porosity and stability

PROPERTIES OF MOF-5

Once removed the solvent molecules from MOF-5 at around 350°C, the activated compound is able to adsorb enormous amounts of Ar, N_2 or solvents such as CH_2Cl_2, $CHCl_3$, C_6H_6, CCl_4, C_6H_{12} (see table). Assuming that the ideal conditions of the Langmuir isotherm are met (it is not very correct for very large pores) a specific pore area of 2900 m^2/g is estimated.

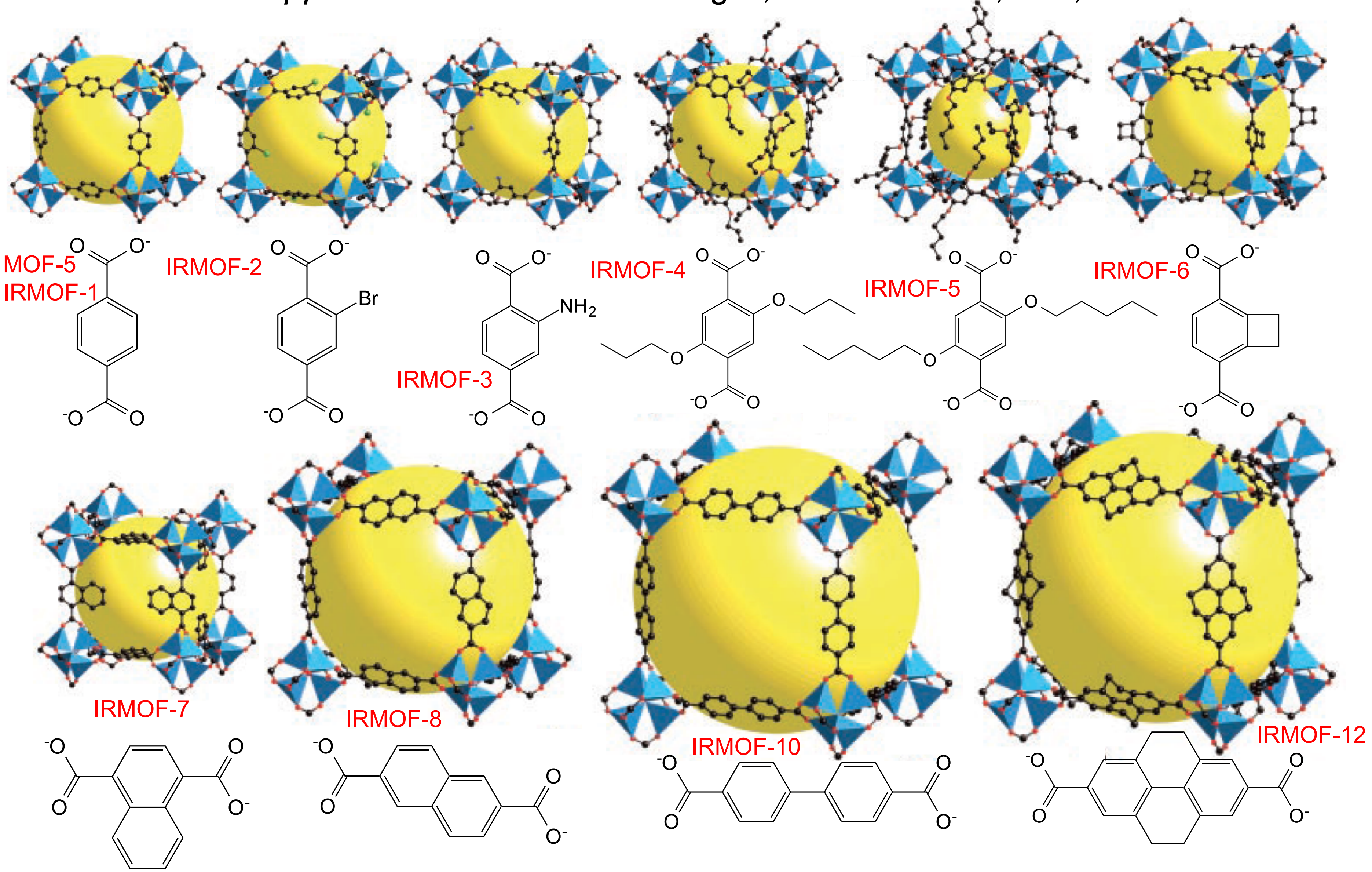
Adsorbate	T/°C	Amount Ad. (mg/g)	Molec. unit cell
Ar	-194	1492	230
N_2	-194	831	183
CH_2Cl_2	22	1211	88
$CHCl_3$	22	1367	71
C_6H_6	22	802	63
CCl_4	22	1472	59
C_6H_{12}	22	703	51

(In 2003 adsorption of H_2 record 7.1% weight at 77 K y 40 bar)

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

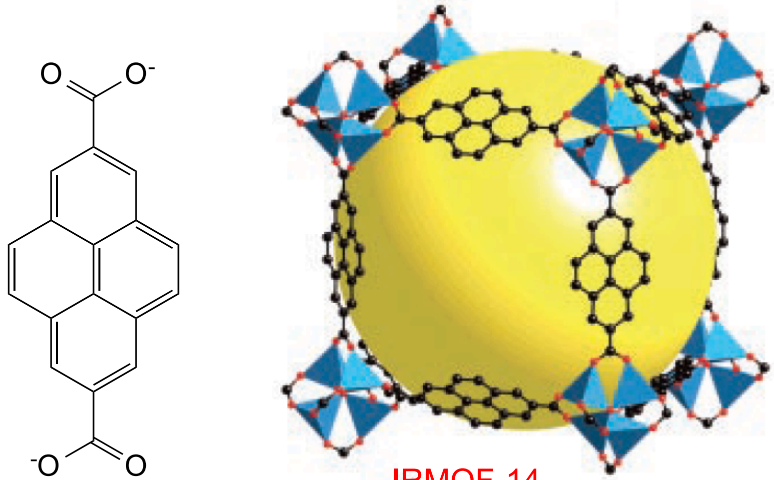
SERIE ISORETICULAR

O. M. Yaghi et al. “*Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage*”, Science 2002, 295, 469-472

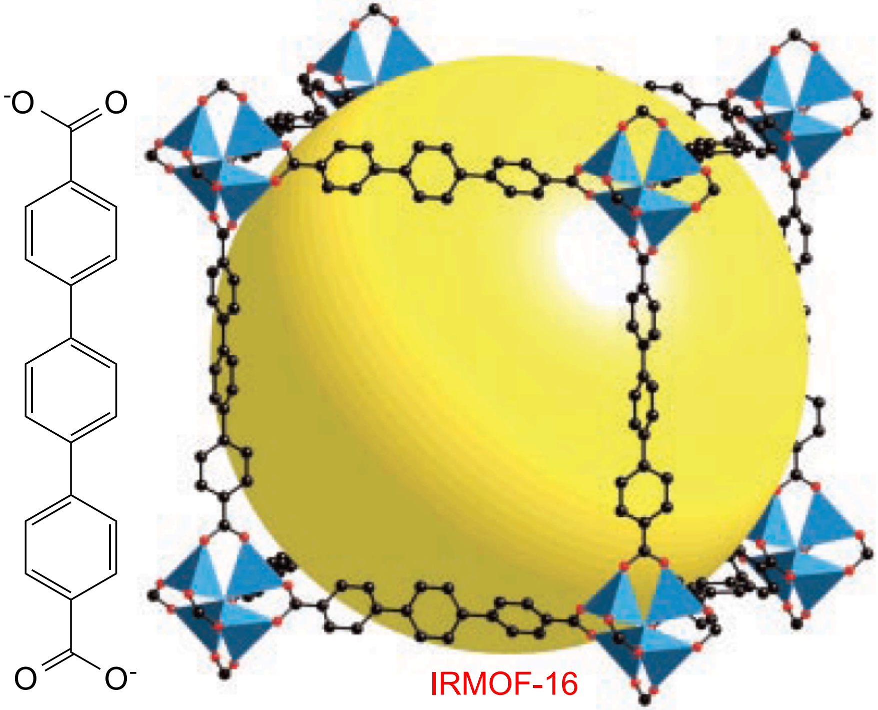


SERIE ISORETICULAR

O. M. Yaghi et al. "*Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage*", Science 2002, 295, 469-472



IRMOF-14

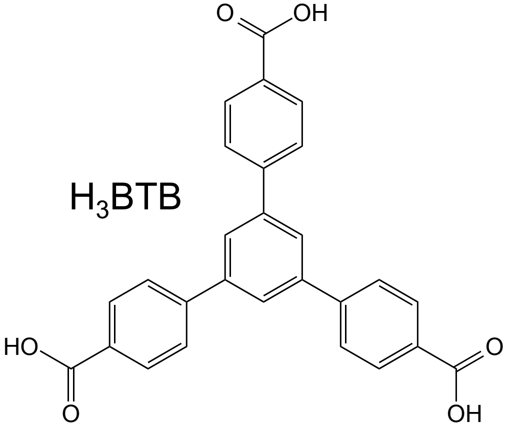


IRMOF-16

The members of this series with longer bridge ligands have pore sizes in the range of mesoporous materials (> 20 Å) and the lowest density observed for a crystalline material (so far, 2002). In particular IRMOF-6 presents the ability to adsorb CH_4 to the greatest extent. During the preparation of this series the synthesis of MOF-5 was improved: $Zn(NO_3)_2 \cdot 4H_2O$ + 1,4-benzenedicarboxylic acid (BDC) in DEF, heated (85°-105° C) in autoclave.

MOF-177

Once demonstrated that the SBU [$Zn_4O(CO_2)_6$] units are stable and afford robust MOFs with linear ligands of benzene-1,4-dicarboxylate type, a furhter step was to prove that this SBU could give stable networks with expanded ligands of different symmetry. To do this, 1,3,5-benzenetribenzoic acid (H_3BTB) was chosen, which reacts in DEF at 100°C with $Zn(NO_3)_2{\cdot}6H_2O$ to get $Zn_4O(BTB)_2{\cdot}(DEF)_{15}(H_2O)_3$ (H. K. Chae, D. Y. Siberio-Pérez, J. Kim, Y. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe, O. M. Yaghi, "A route to high surface area, porosity and inclusion of large molecules in crystals", Nature, 2004, 427, 523-527).

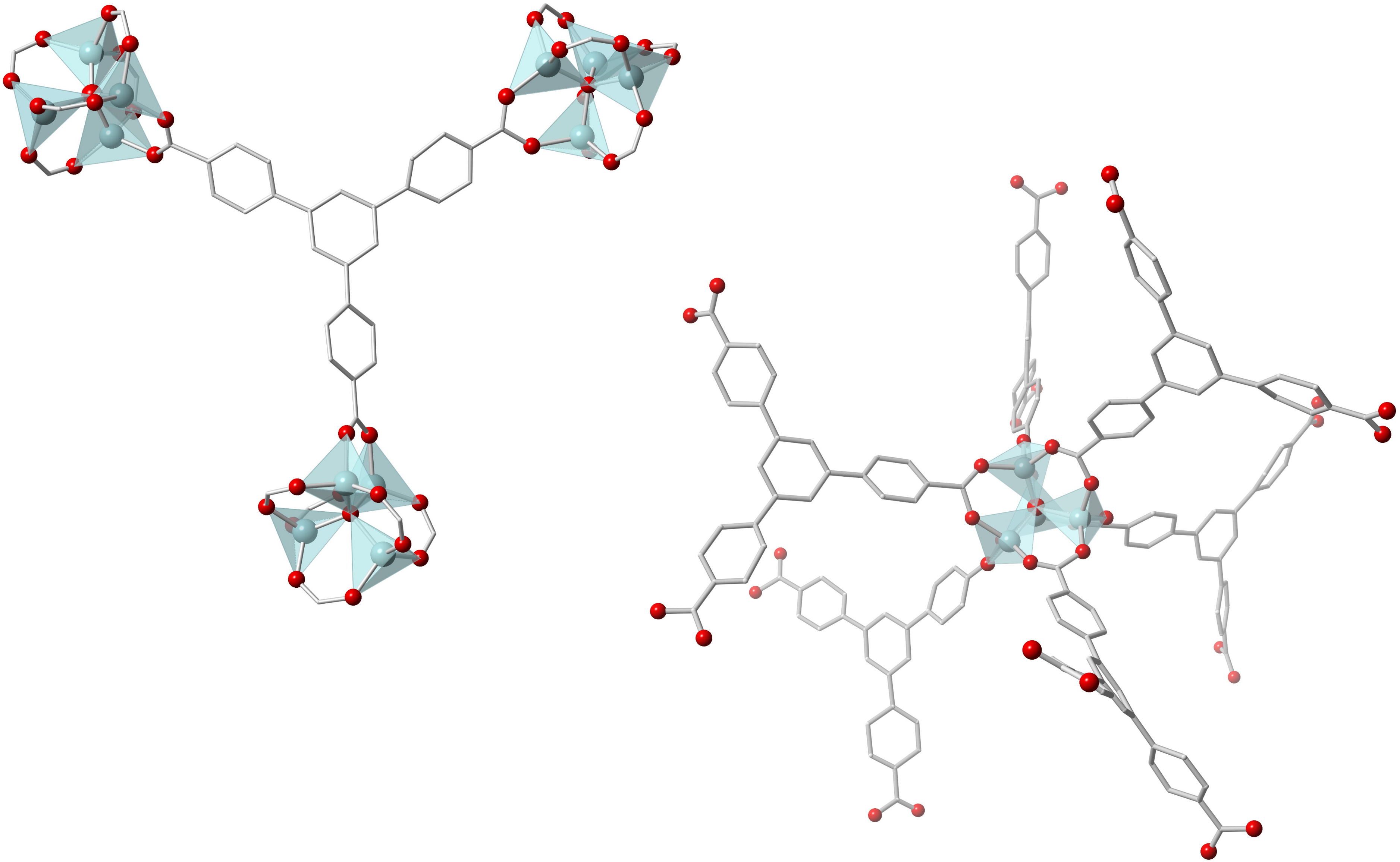


The thermal analysis shows that 48% of the mass is lost between 50° and 100°C, which corresponds to the solvent molecules located in the pores. The compound is thermally stable up to 350°C and once evacuated has a specific area (Langmuir) record of 4500 m^2/g deduced from the adsorption of N_2 (l) at 78 K.

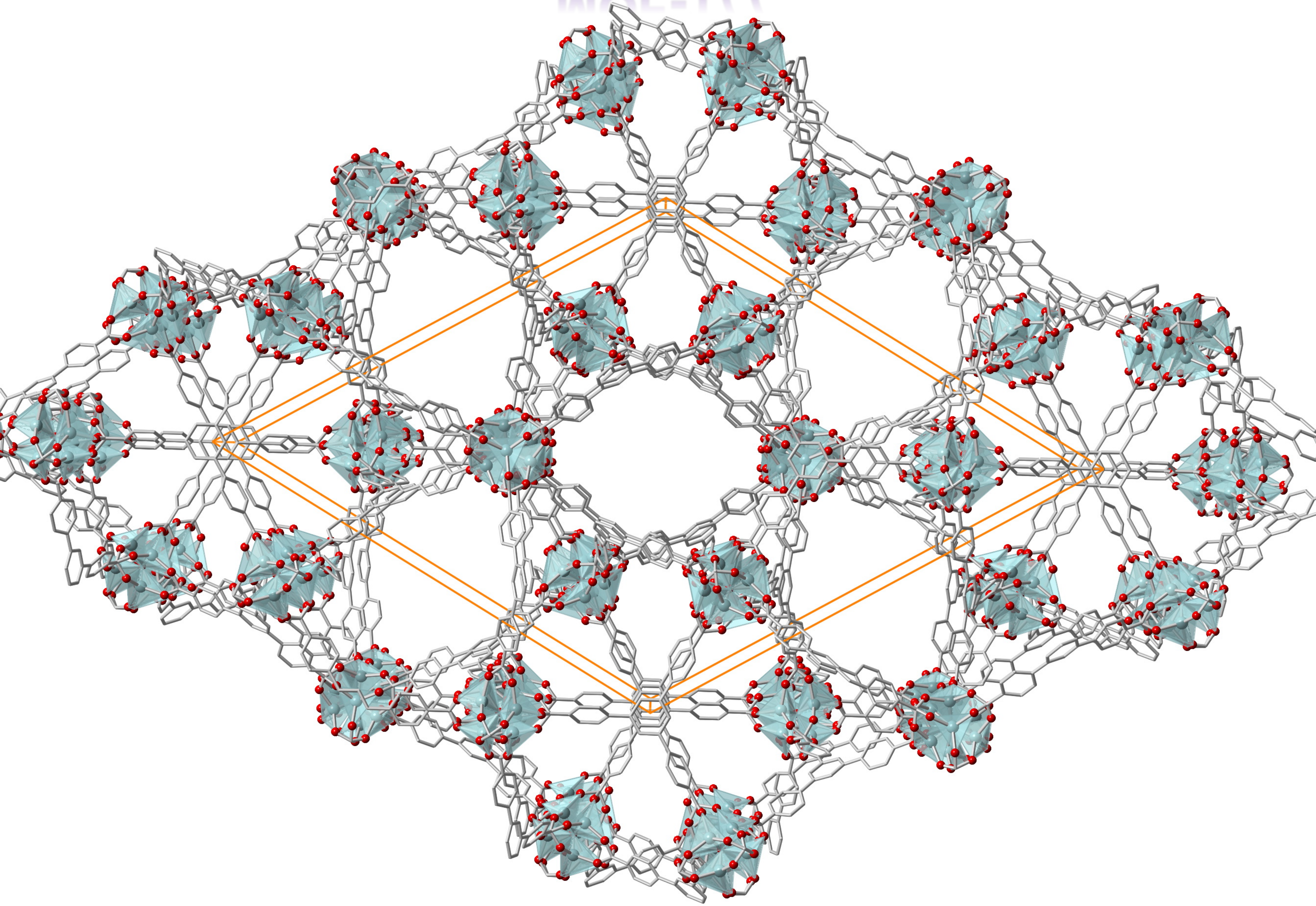
This compound also has the ability to adsorb large organic molecules. The experiments were carried out with single crystals directly observing the colour change of the crystals. Submerging the crystals in a solution of C_{60} in toluene, the C_{60} is installed in the pores in a few days, the same happens with other large polycyclic dyes.

MOF-177

It is a 3,6-connected network (left), each BTB act as an IC = 3 node, while each SBU $[Zn_4O(CO_2)_6]$ acts with IC = 6 (right).



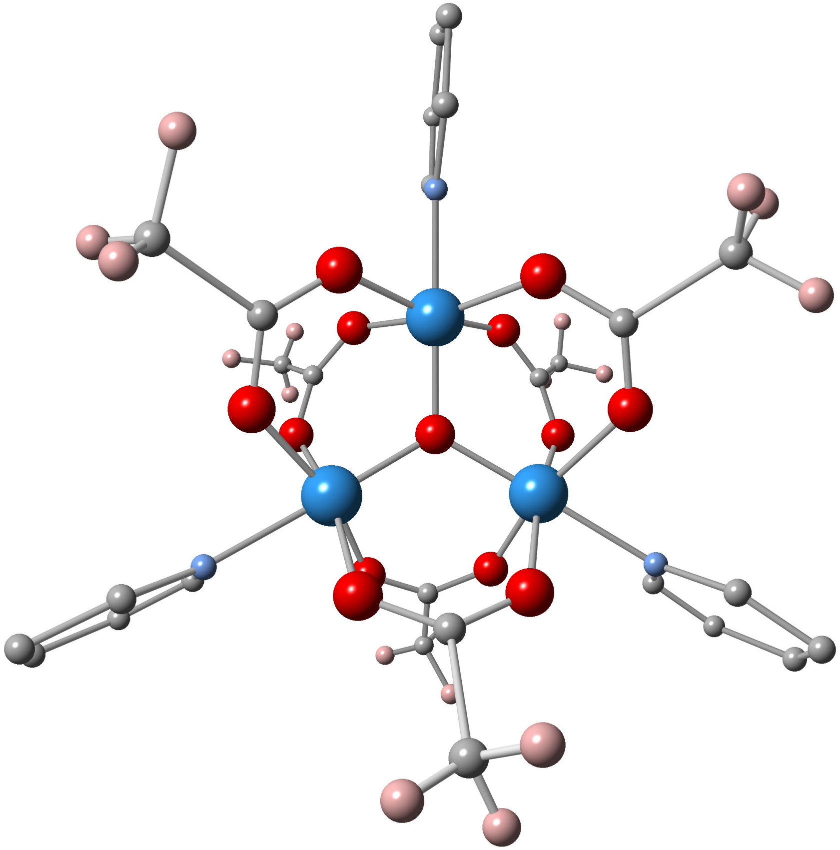
MOF-177



SERIES MIL-N

(Matériaux de l’Institut Lavoisier- U. Versailles Saint Quentin)

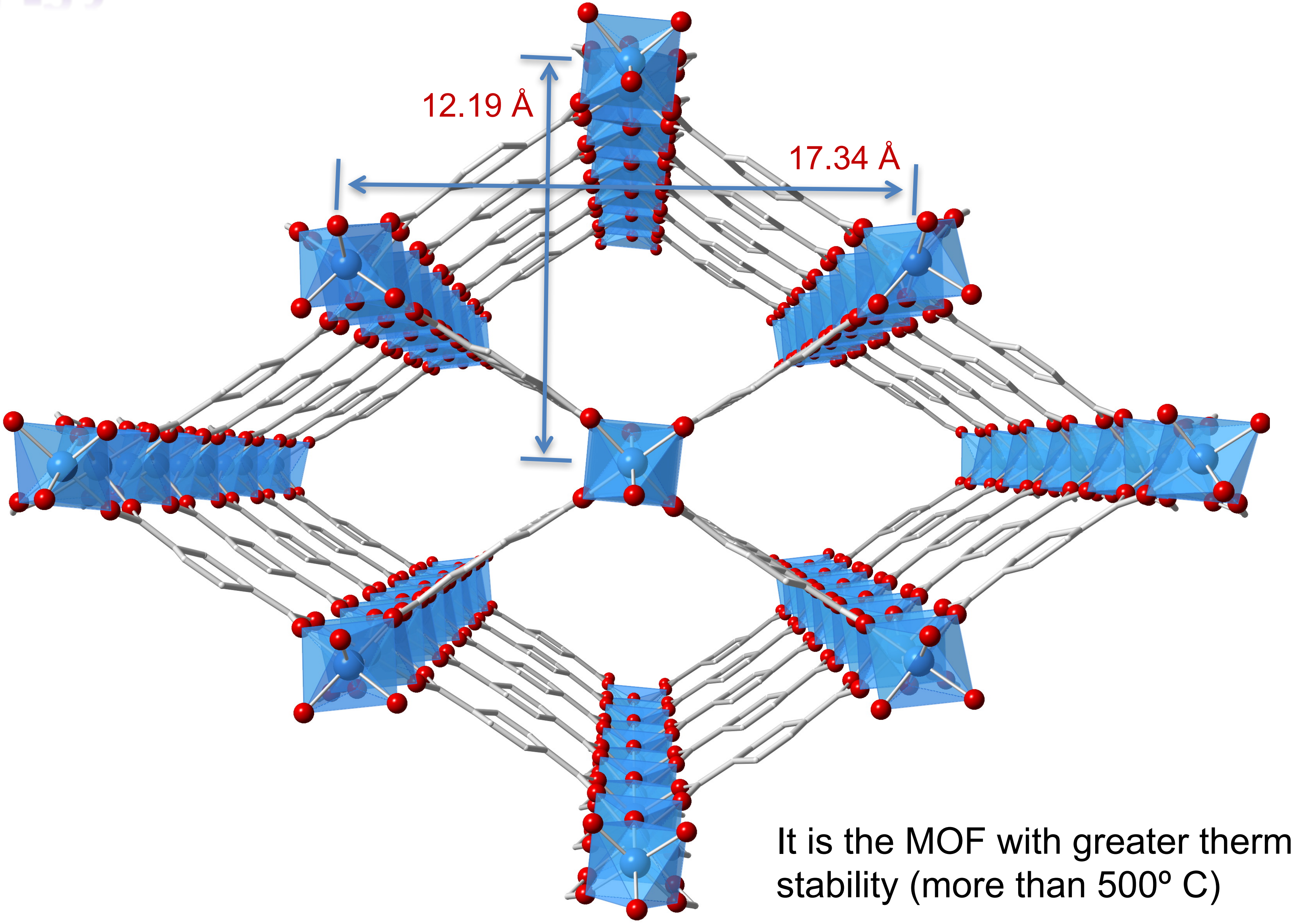
It is well known that trivalent ions V(III), Cr(III), Mn(III), Fe(III), Al(III), Ga(III) or In(III) easily form polioxo-especies. Particularly interesting are those formed in presence of acetate groups because they generate trinuclear complexes $M_3(\mu\text{-}O)(RCO_2)_6L_3$ typically L is pyridine.



Substitution of the acetate groups by polycarboxylic ligands such as benzene-1,4-dicarboxylate (BDC) gives rise to porous networks.

MIL-53

Paradigm of flexibility in a crystalline compound

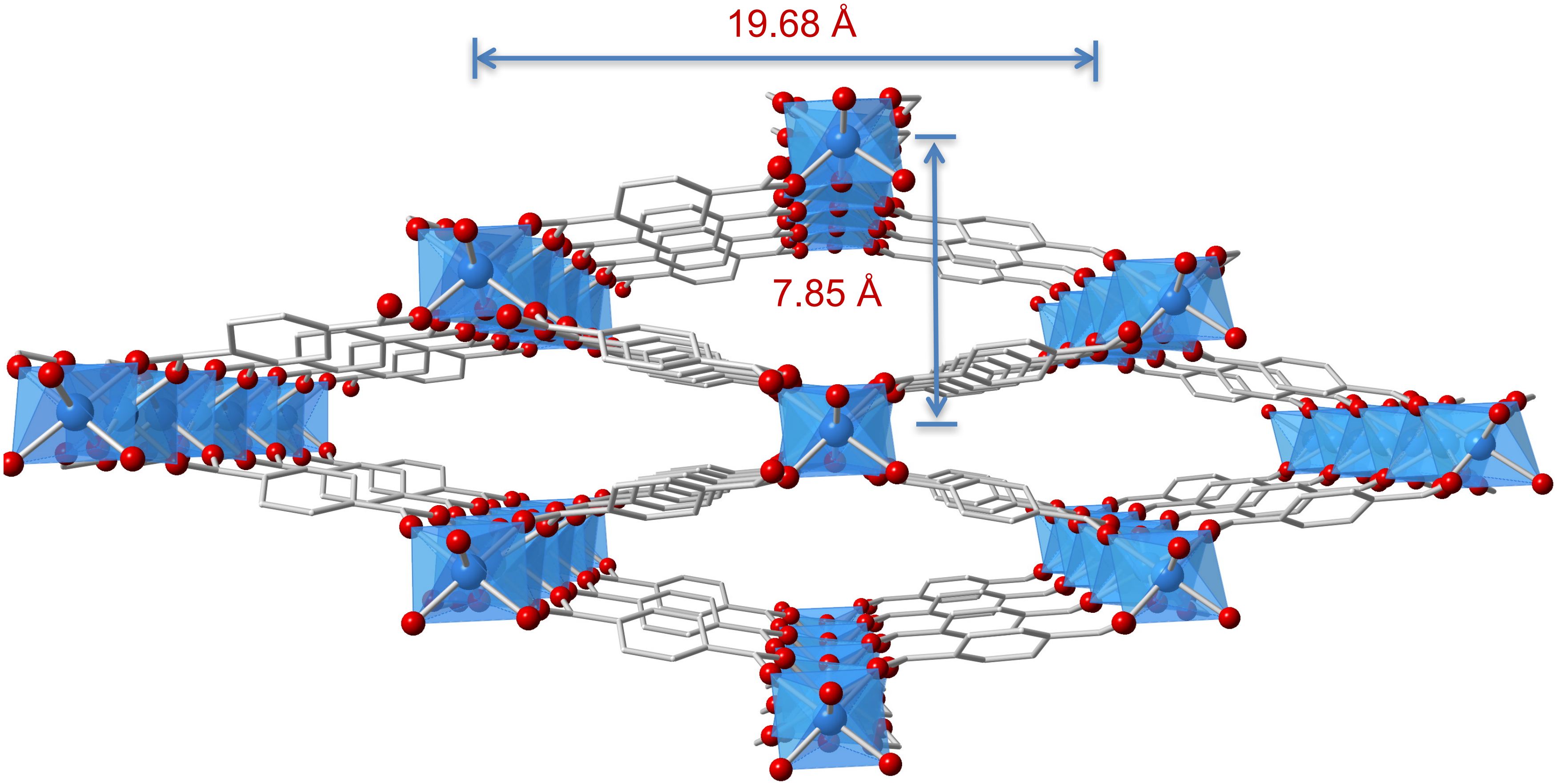


It is the MOF with greater thermal stability (more than 500º C)

$\{Cr^{III}(OH)(BDC)\} \longleftrightarrow \{Cr^{III}(OH)(BDC)\}\cdot H_2O$

MIL-53

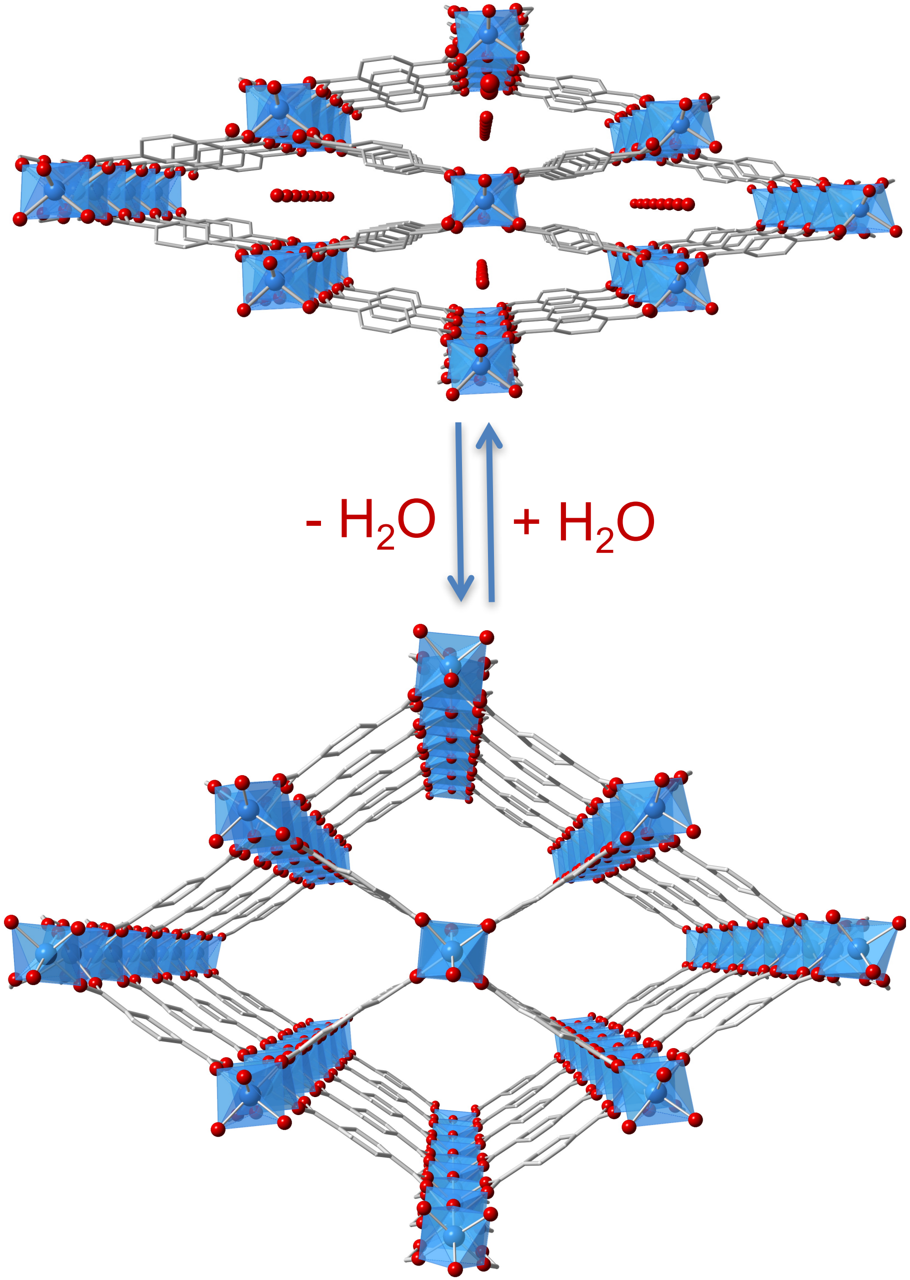
Paradigm of flexibility in a crystalline compound



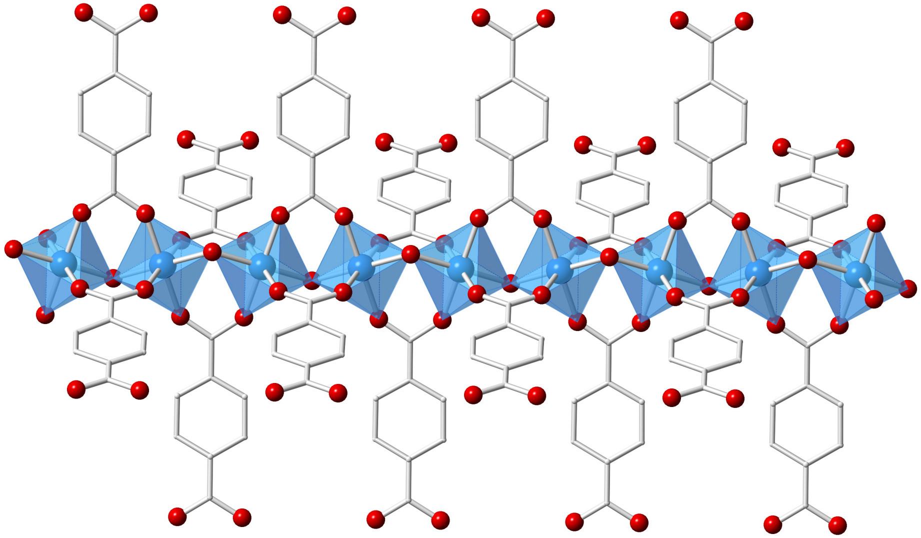
It is the MOF with greater thermal stability (more than 500º C)

$\{Cr^{III}(OH)(BDC)\} \longleftrightarrow \{Cr^{III}(OH)(BDC)\}\cdot H_2O$

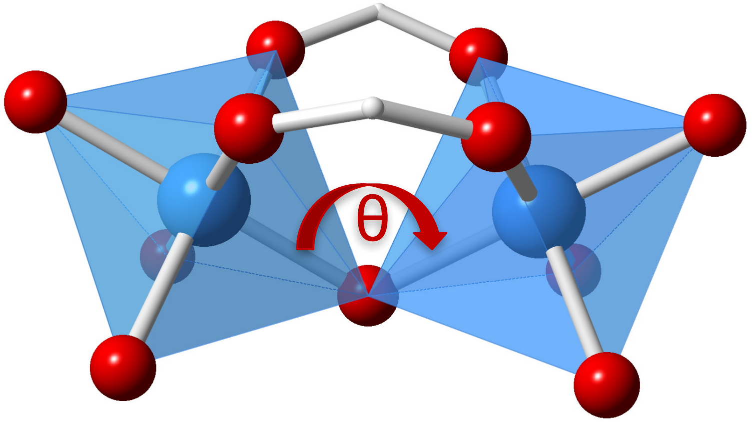
MIL-53



The trinuclear SBU are not formed,
Indeed form infinite chains



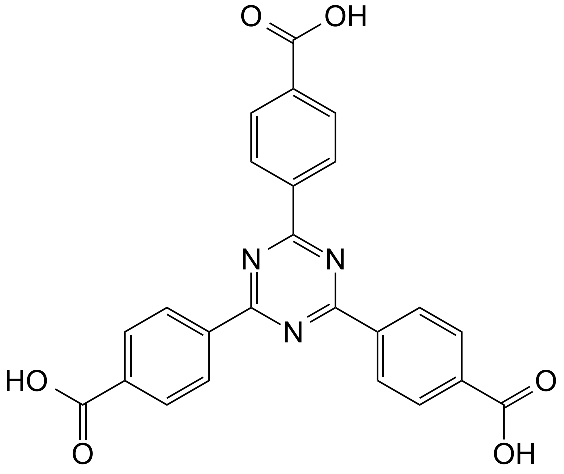
Mechanism associated with flexibility



θ = 121.7° dehydrated
θ = 126.4° hydrated

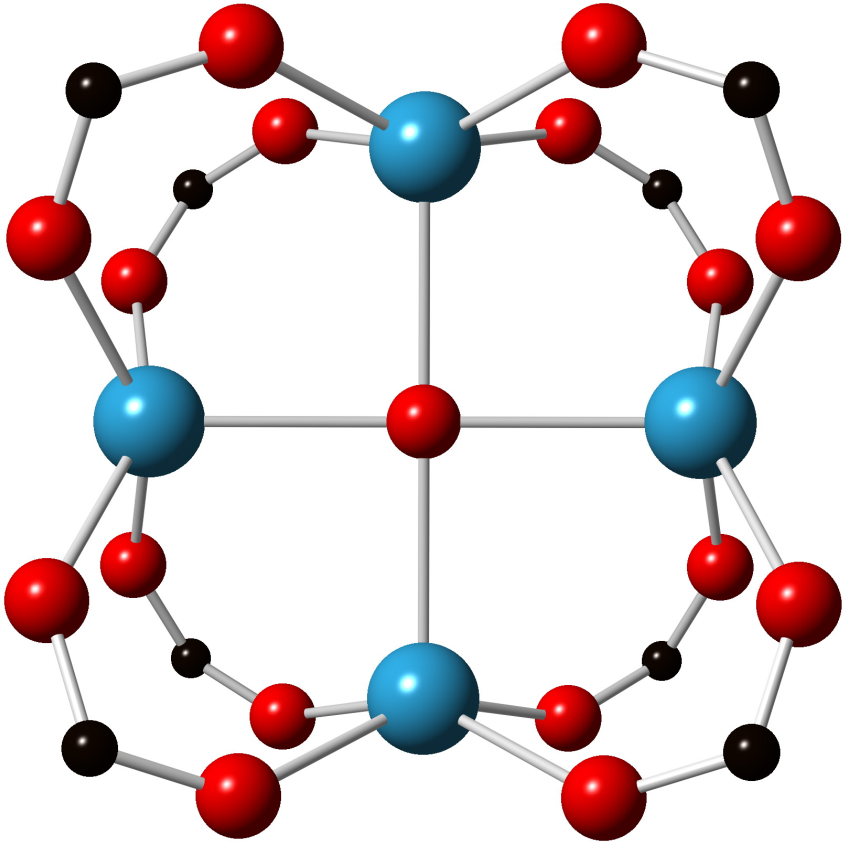
$H_2[Co_4O(TATB)_{8/3}]$:
MOF with unsaturated metallic centers (UMCs)
SBU $Co_4(\mu_4\text{-}O)(CO_2)_8$

Triconnected node



TATB = 4,4',4''-s-triazine-2,4,6-triyltribenzoate

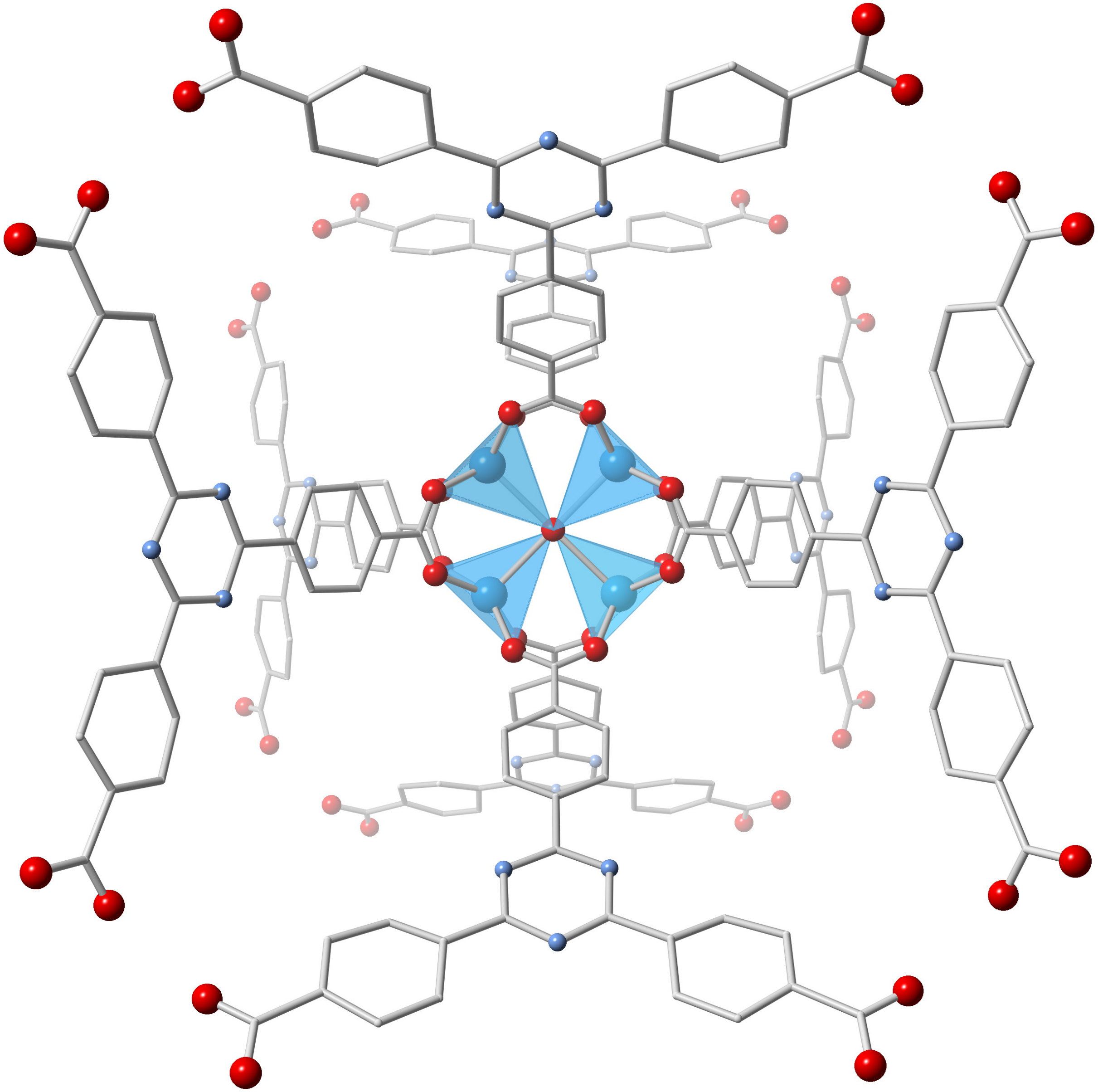
Octaconnected node



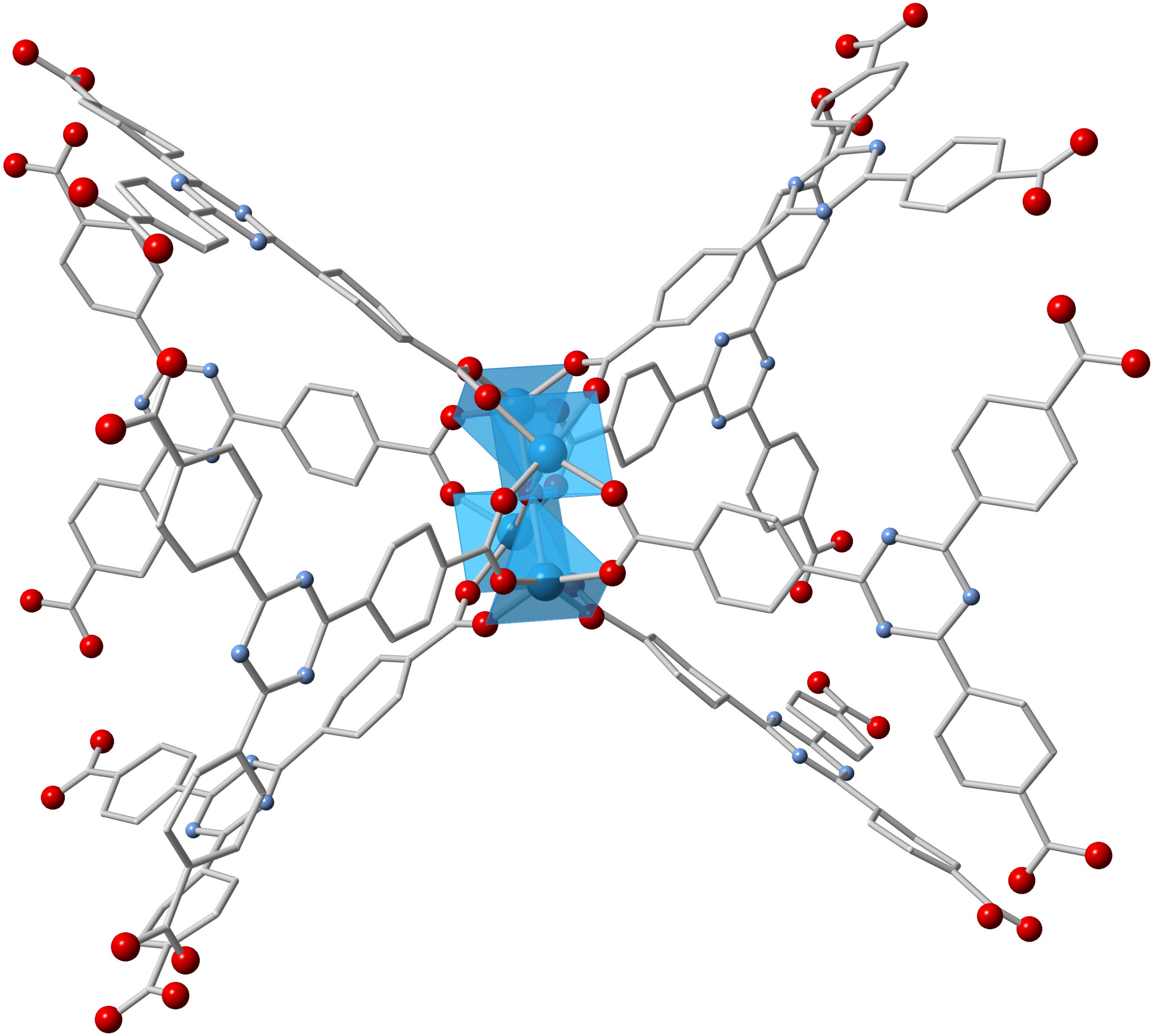
S. Ma and H-C. Zhou
"A Metal-Organic Framework with Entatic Metal Centers Exhibiting High Gas Adsorption Affinity"
J. Am. Chem. Soc. 2006, 128, 11734-11735

The atoms of Co(II) are pentacoordinated and define square-base pyramids, thereby leaving a sixth position free for the coordination of invited molecules.

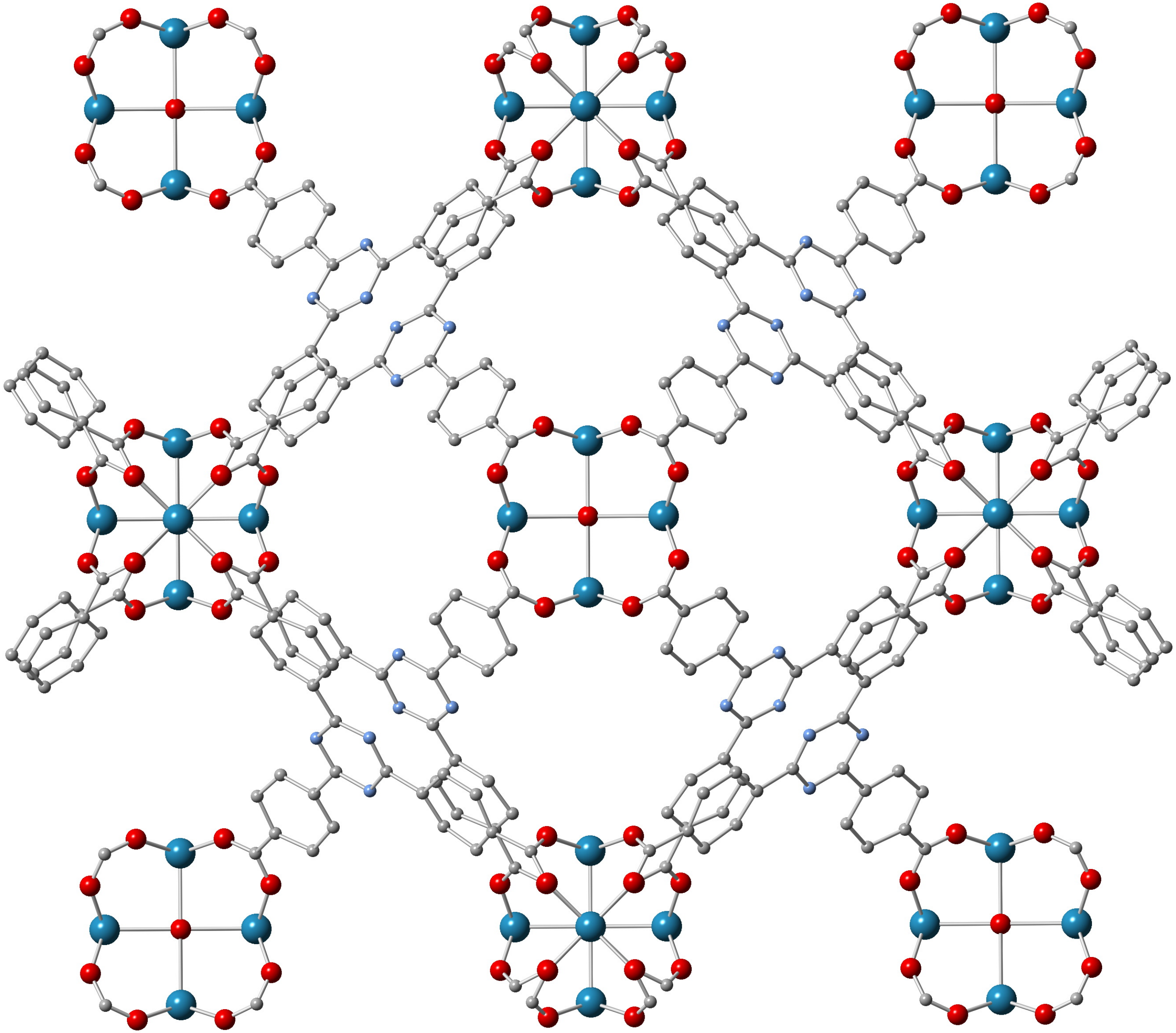
$H_2[Co_4O(TATB)_{8/3}]$



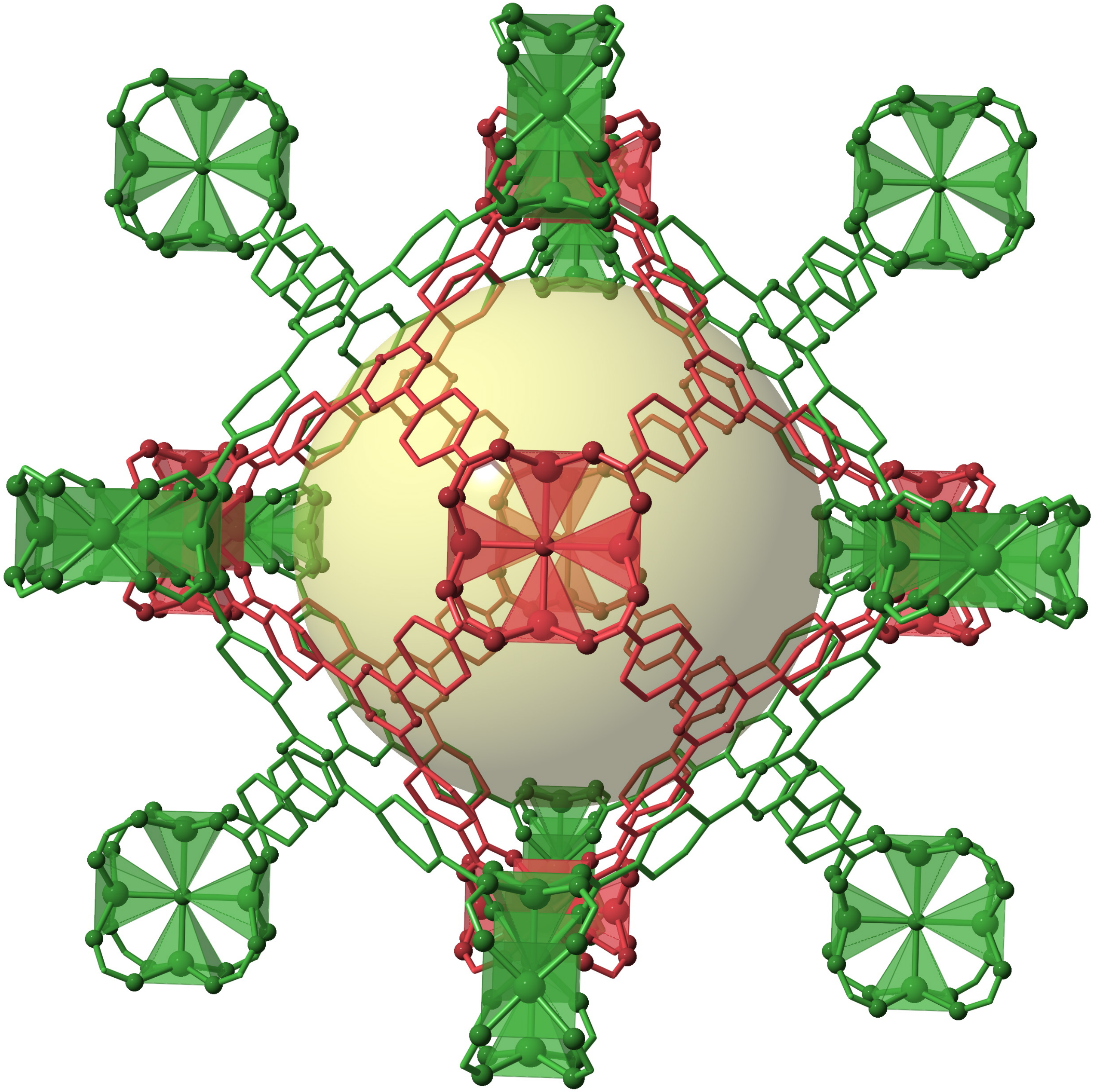
$H_2[Co_4O(TATB)_{8/3}]$



$H_2[Co_4O(TATB)_{8/3}]$ is a network with (8,3) topology

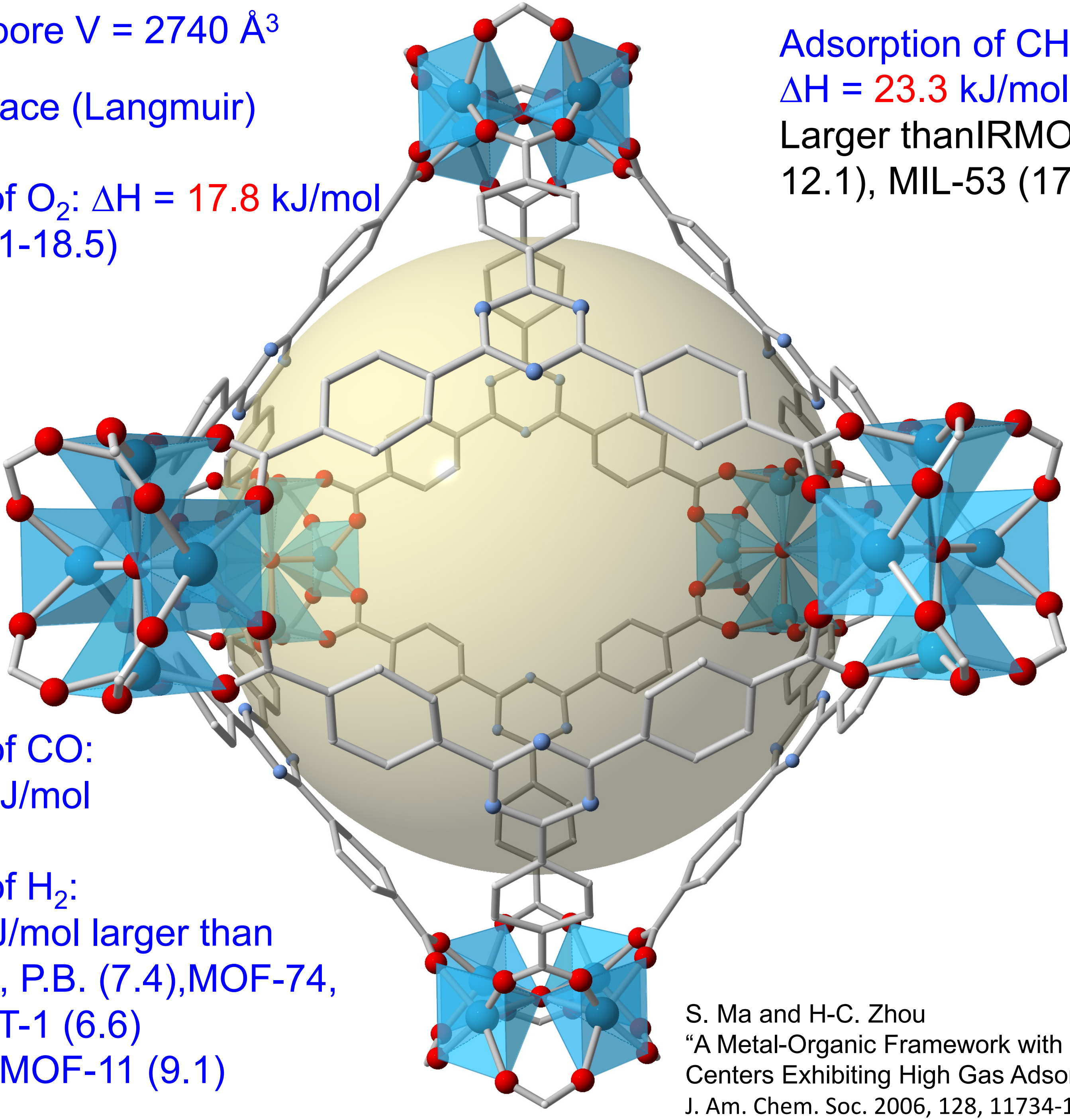


There are to identical networks interpenetrated



Octahedral pore V = 2740 Å^3

Specific surface (Langmuir)
1355 m^2/g.
Adsorption of O_2: ΔH = 17.8 kJ/mol
(zeolites 15.1-18.5)



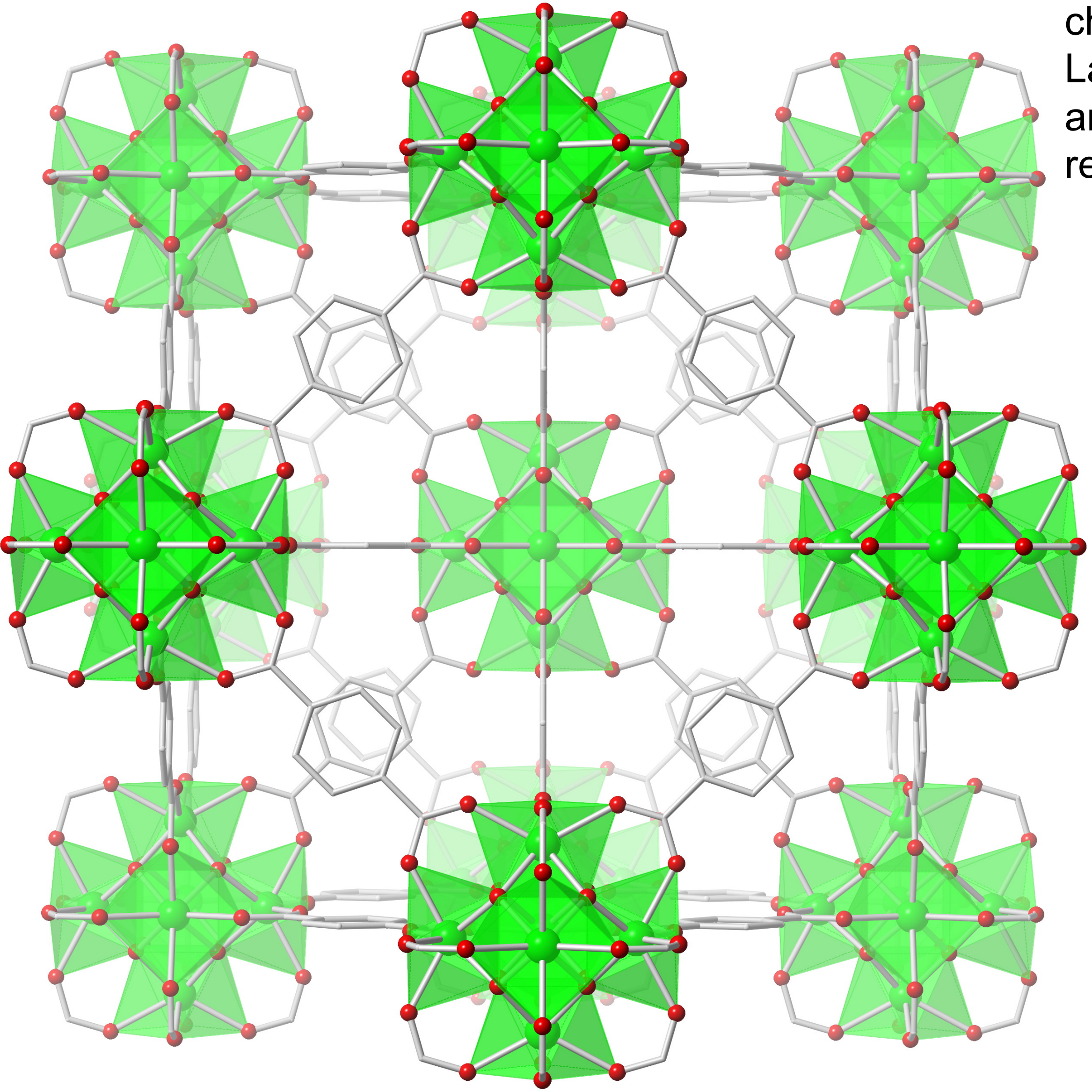
Adsorption of CH_4:
ΔH = 23.3 kJ/mol
Larger thanIRMOF-6
12.1), MIL-53 (17)

Adsorption of CO:
ΔH = 21.0 kJ/mol

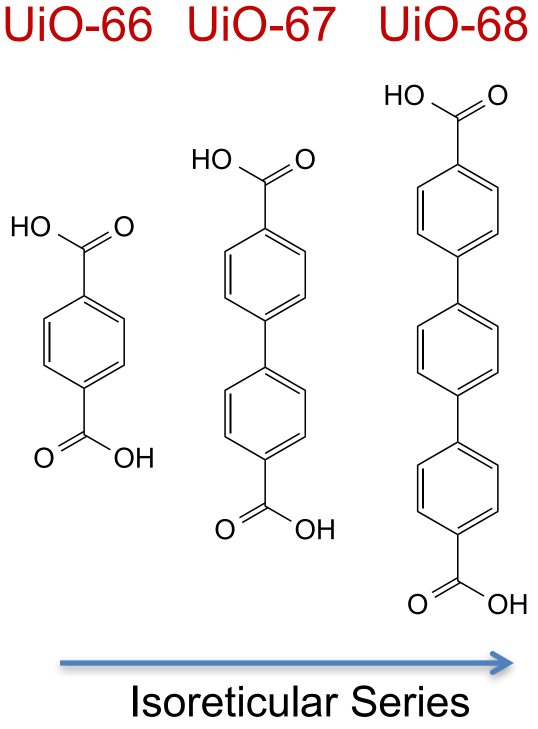
Adsorption of H_2:
ΔH = 10.1 kJ/mol larger than
MOF-5 (5.2), P.B. (7.4),MOF-74,
(8.3), HKUST-1 (6.6)
Similar to IRMOF-11 (9.1)

S. Ma and H-C. Zhou
“A Metal-Organic Framework with Entatic Metal
Centers Exhibiting High Gas Adsorption Affinity”
J. Am. Chem. Soc. 2006, 128, 11734-11735

SBUs based on Zr^{IV} with nodes $Zr_6O_4(OH)_4(CO_2)_{12}$ (IC=12) (Series UiO-n)



characterized by a T_{descp} = 540°C and Langmuir surface 1187m^2/g, 3000 m^2/g and 4170 m^2/g for UiO-66, -67 and -68, respectively

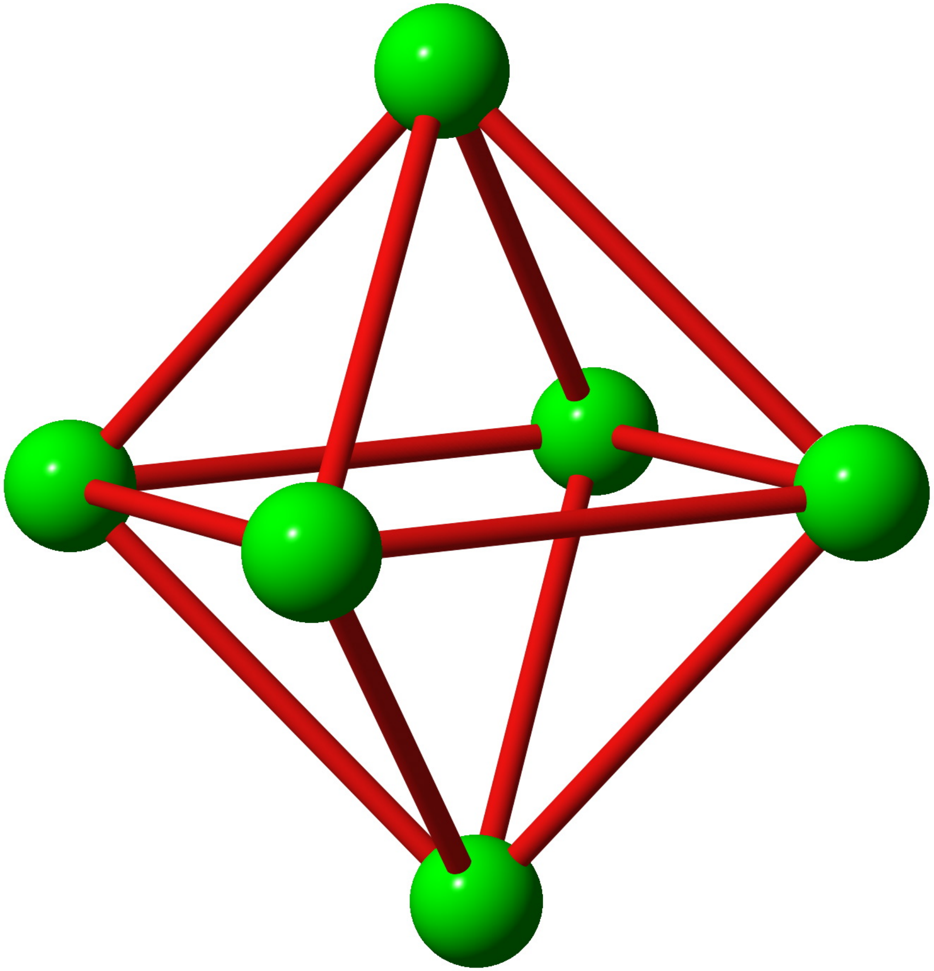


Isoreticular Series

J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, Karl P. Lillerud, “A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability” J. Am. Chem. Soc. 2008, 130, 13850-13851

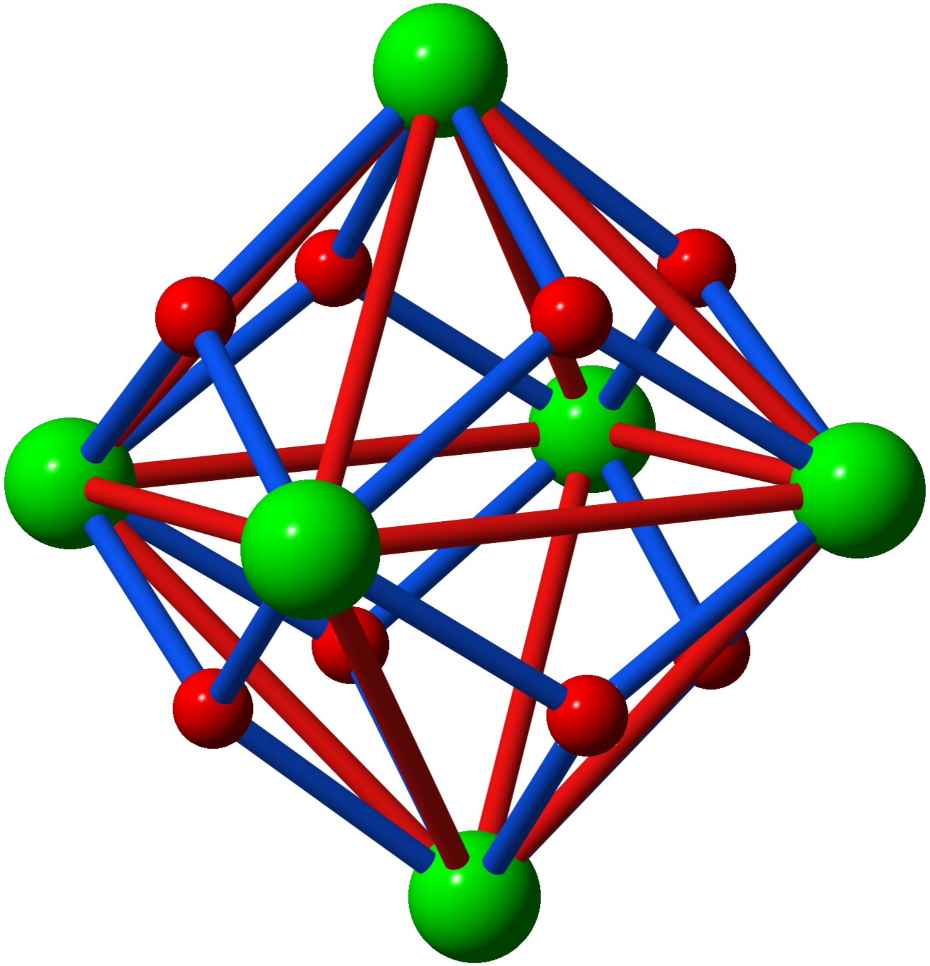
Series UiO-n

SBU: $Zr_6O_4(OH)_4(CO_2)_{12}$



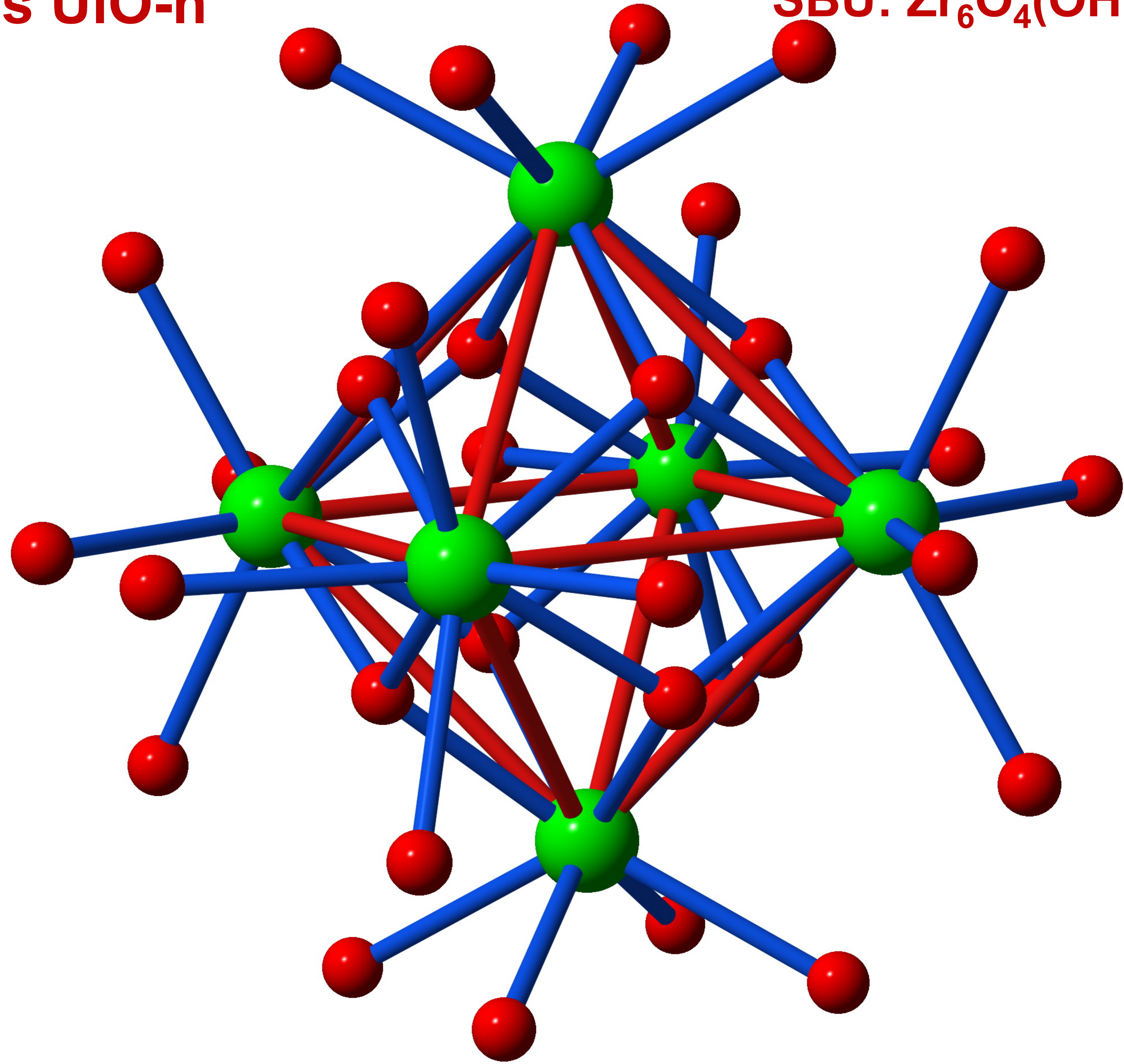
Series UiO-n

SBU: $Zr_6O_4(OH)_4(CO_2)_{12}$



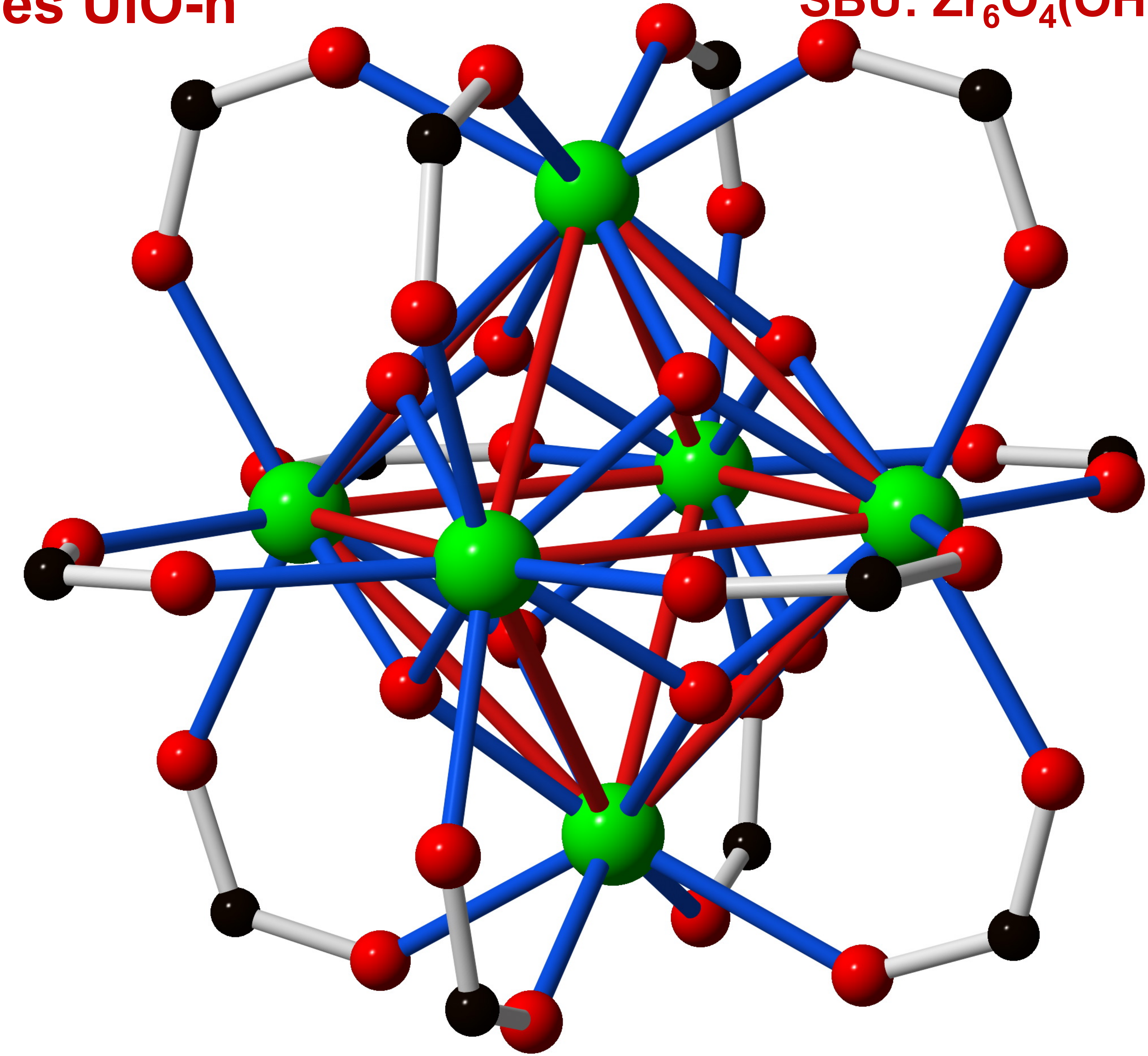
Series UiO-n

SBU: $Zr_6O_4(OH)_4(CO_2)_{12}$

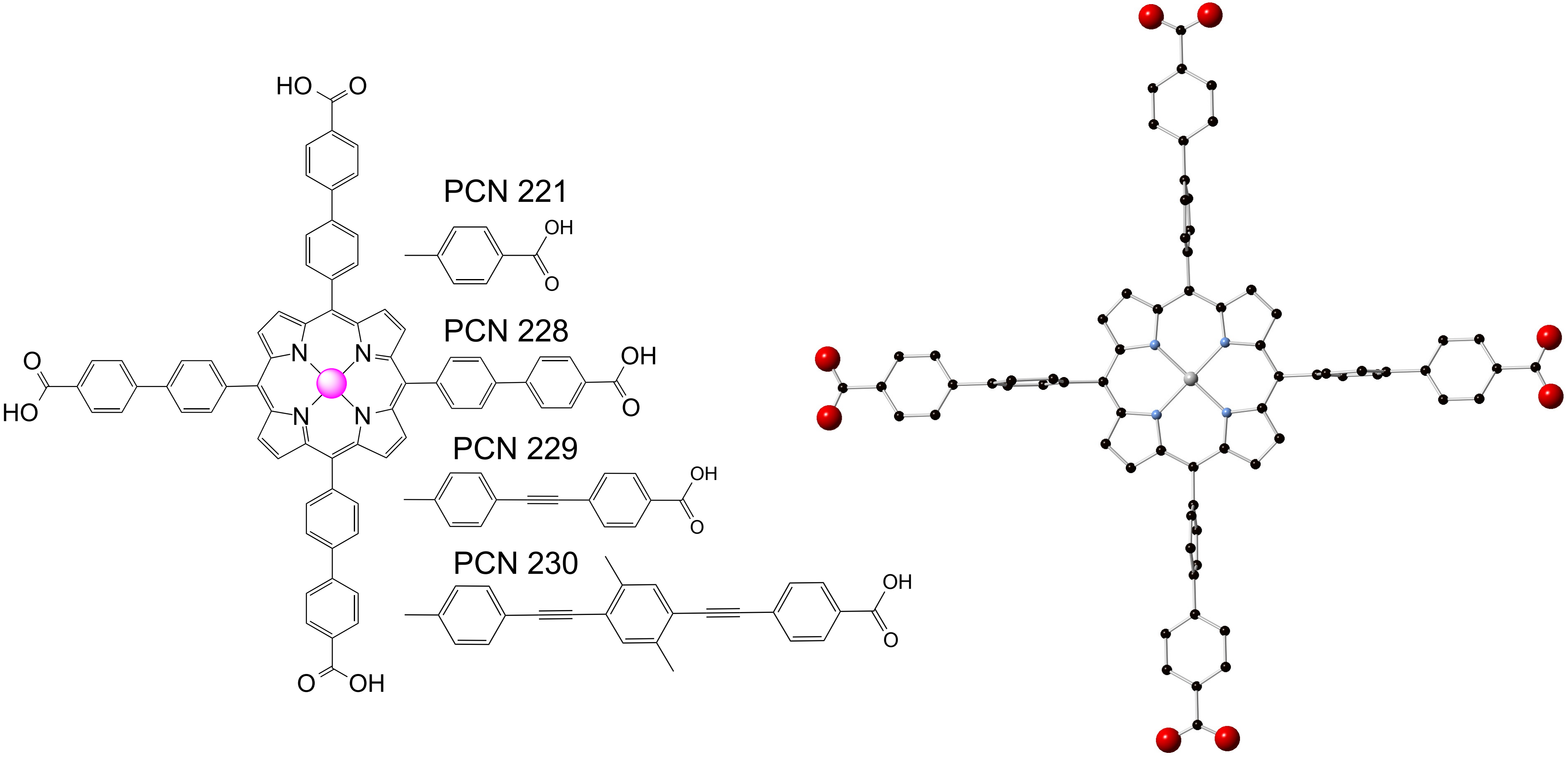


Series UiO-n

SBU: $Zr_6O_4(OH)_4(CO_2)_{12}$

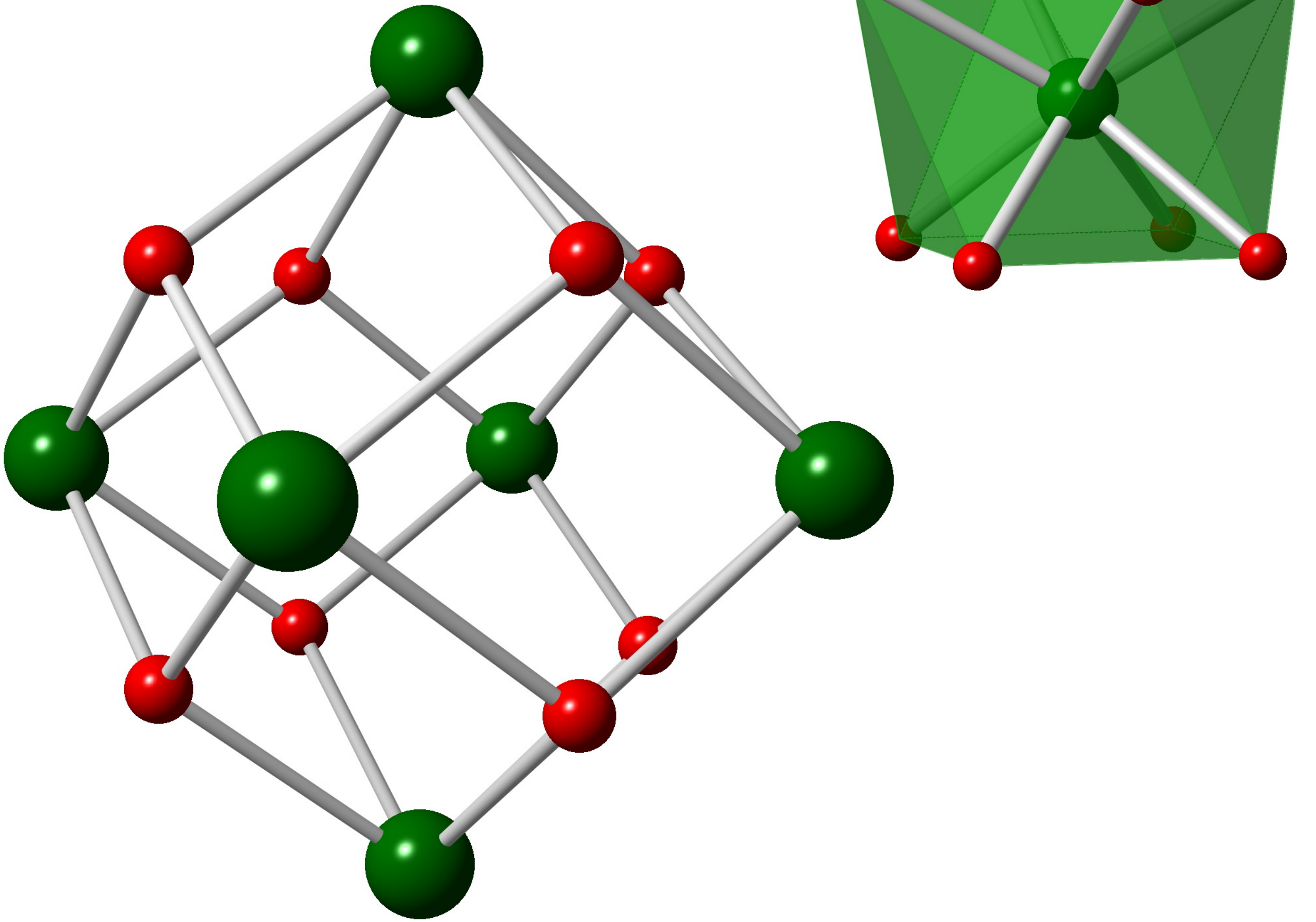


Networks PCN 221, 222, 228, 229, 230

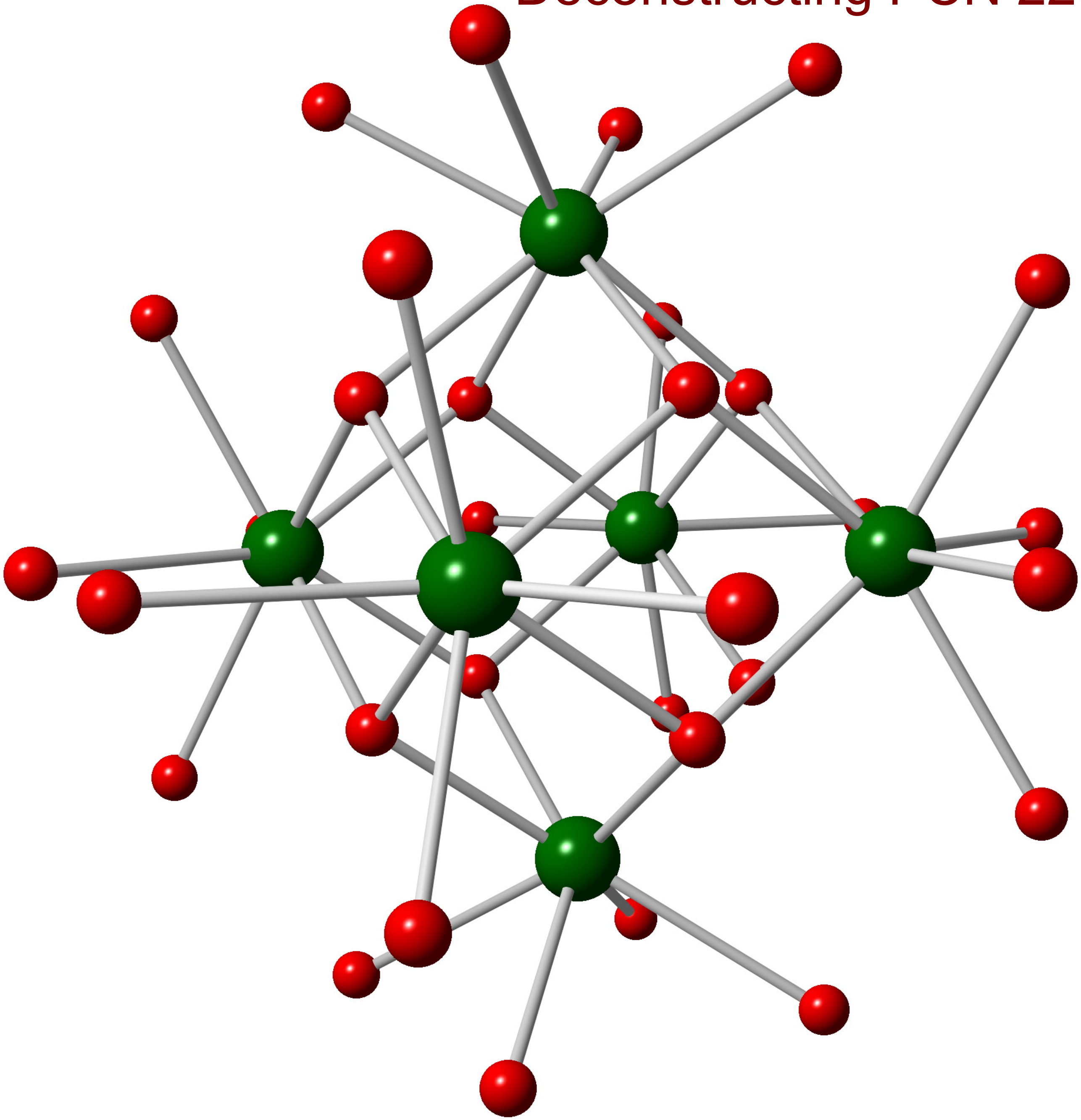


Topology-Guided Design and Syntheses of Highly Stable Mesoporous Porphyrinic Zirconium Metal−Organic Frameworks with High Surface Area H.-C. Zhou et al *J. Am. Chem. Soc.* **2015**, *137*, 413-419; Metal−Organic Frameworks Based on Previously Unknown Zr8/Hf8 Cubic Clusters, H.-C. Zhou et al *Inorg. Chem.* **2013**, *52*, 12661-12667.

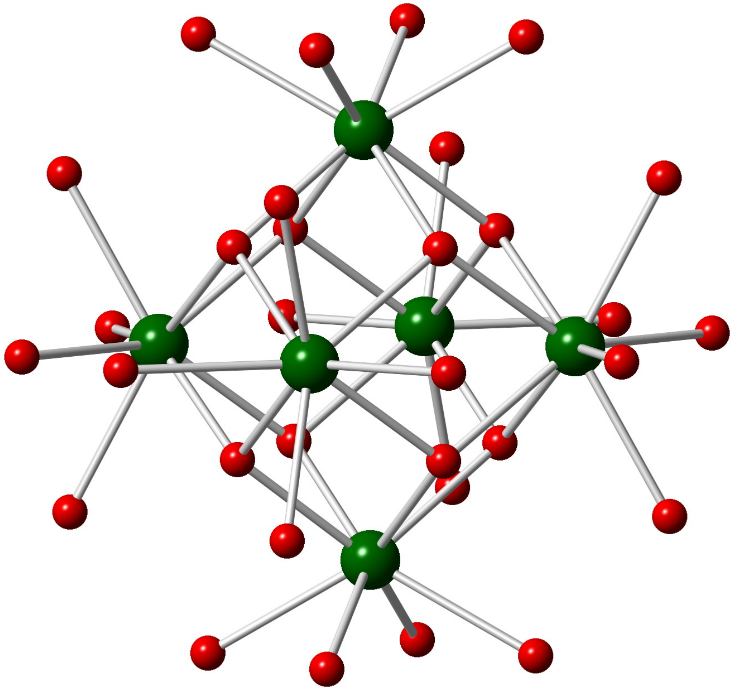
Deconstruting PCN 228, 229, 230

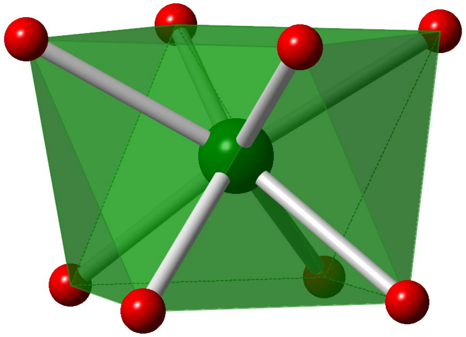


Deconstructing PCN 228, 229, 230

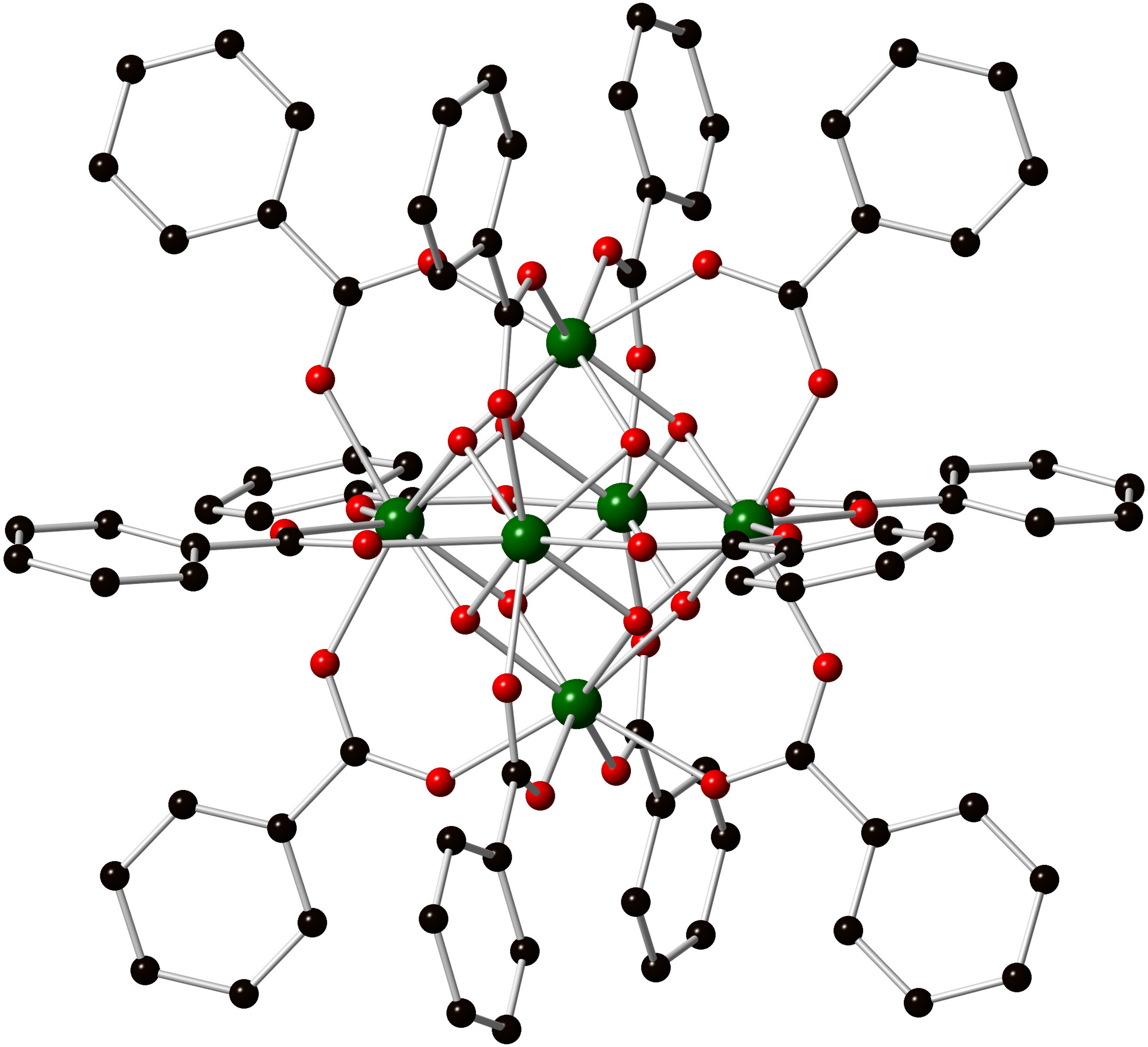


Deconstructing PCN 228, 229, 230

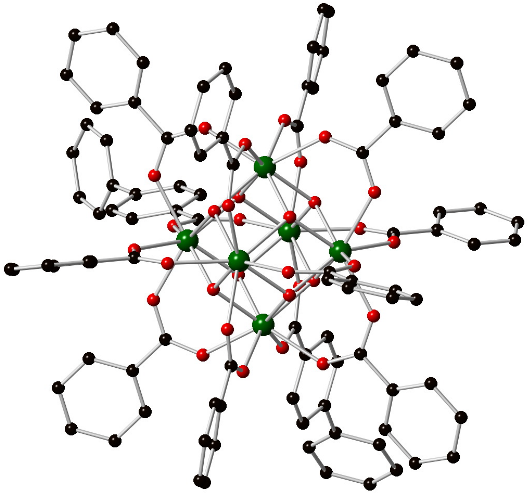




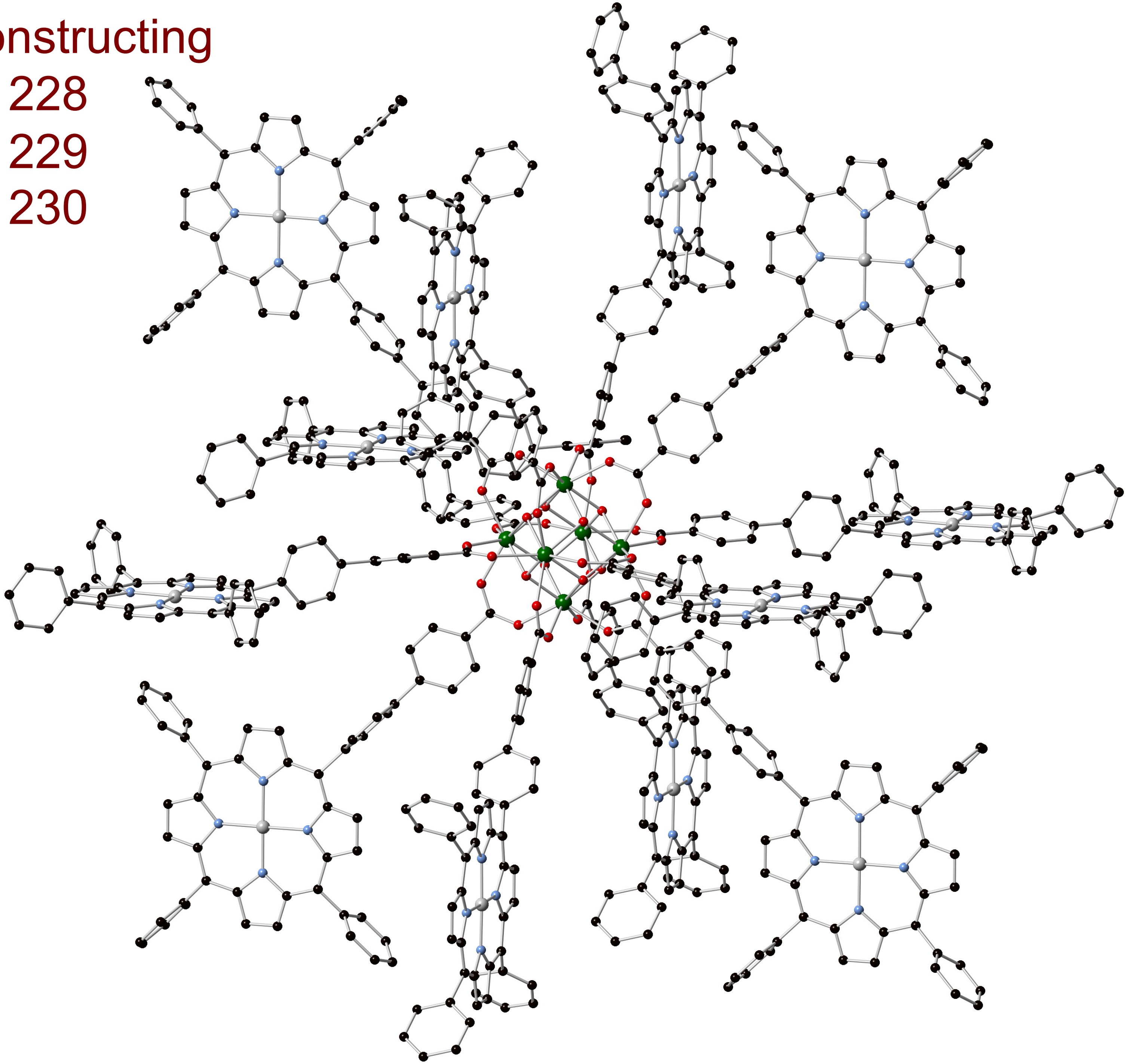
Deconstructing PCN 228, 229, 230



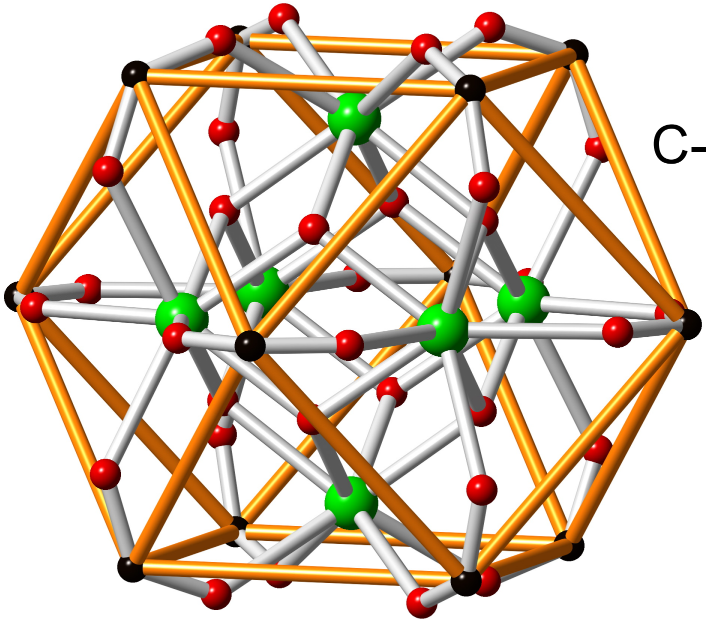
Deconstructing PCN 228, 229, 230



Deconstructing
PCN 228
PCN 229
PCN 230



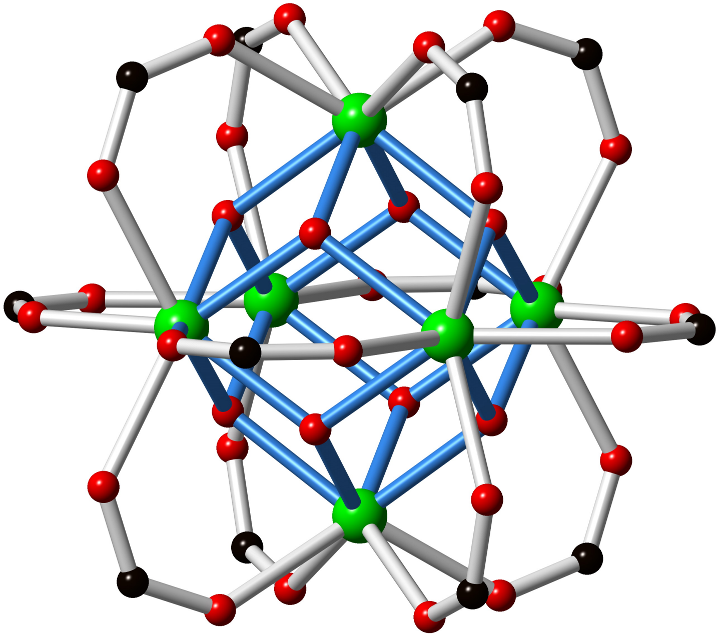
Defined Polyhedrons



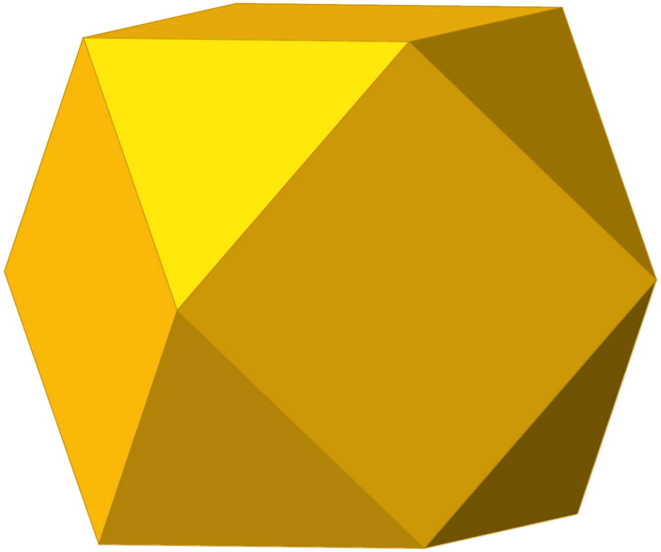
C-C: Cuboctahedron

Zr-Zr: Octahedron

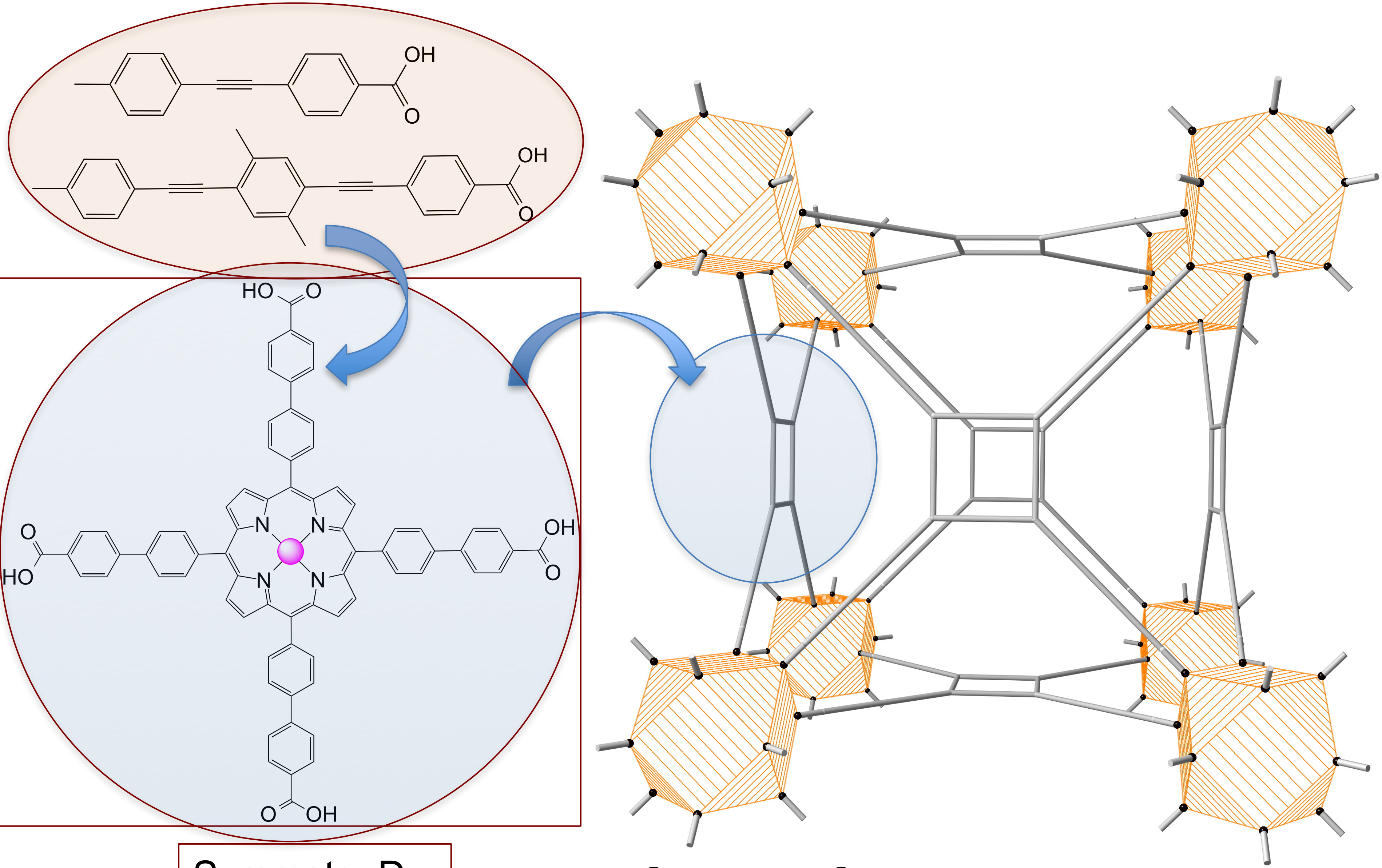
Zr-O: Rhombic dodecahedron



Symmetry O_h



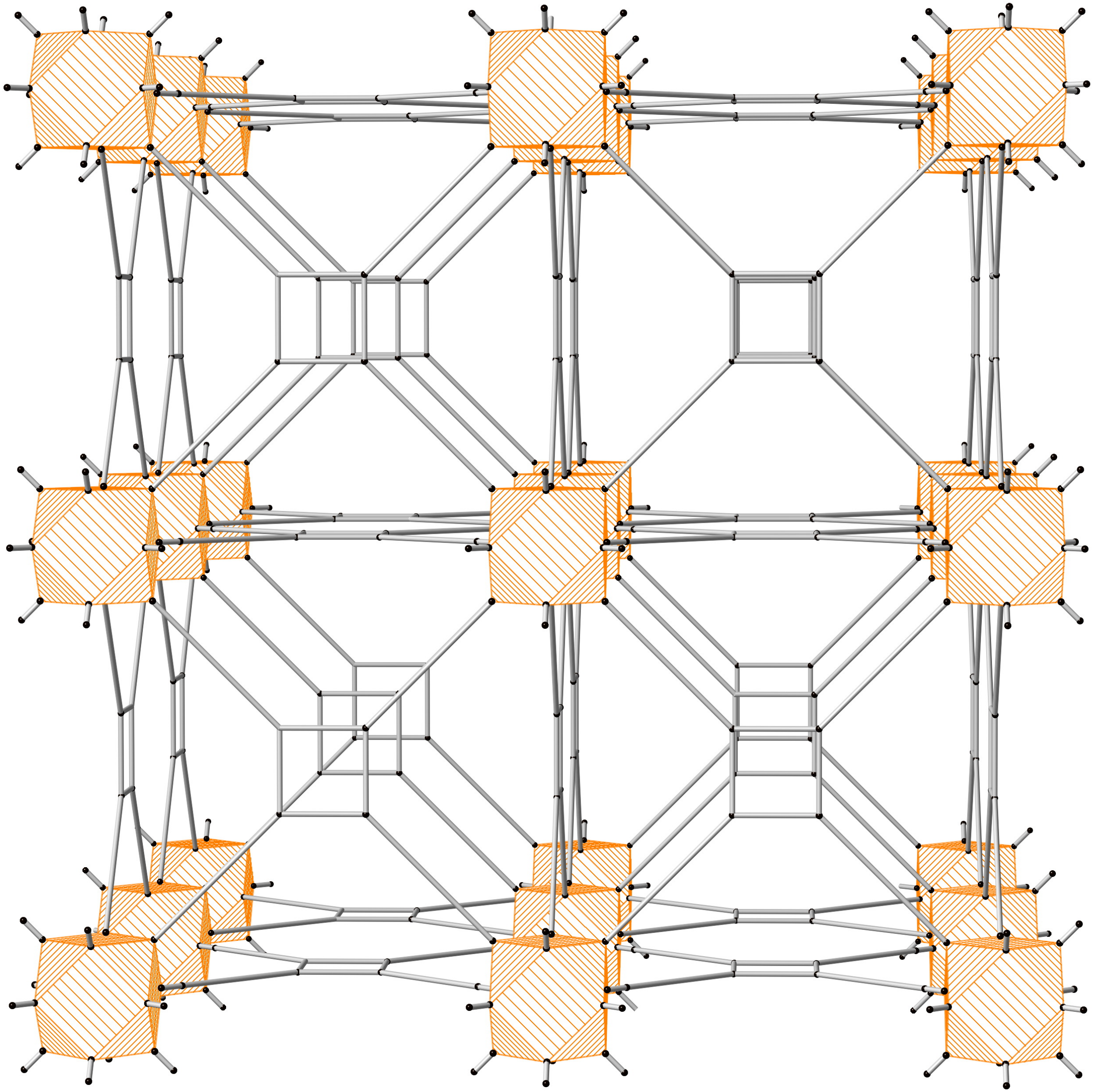
Reduction of MOF in a Network: Nodes + Links



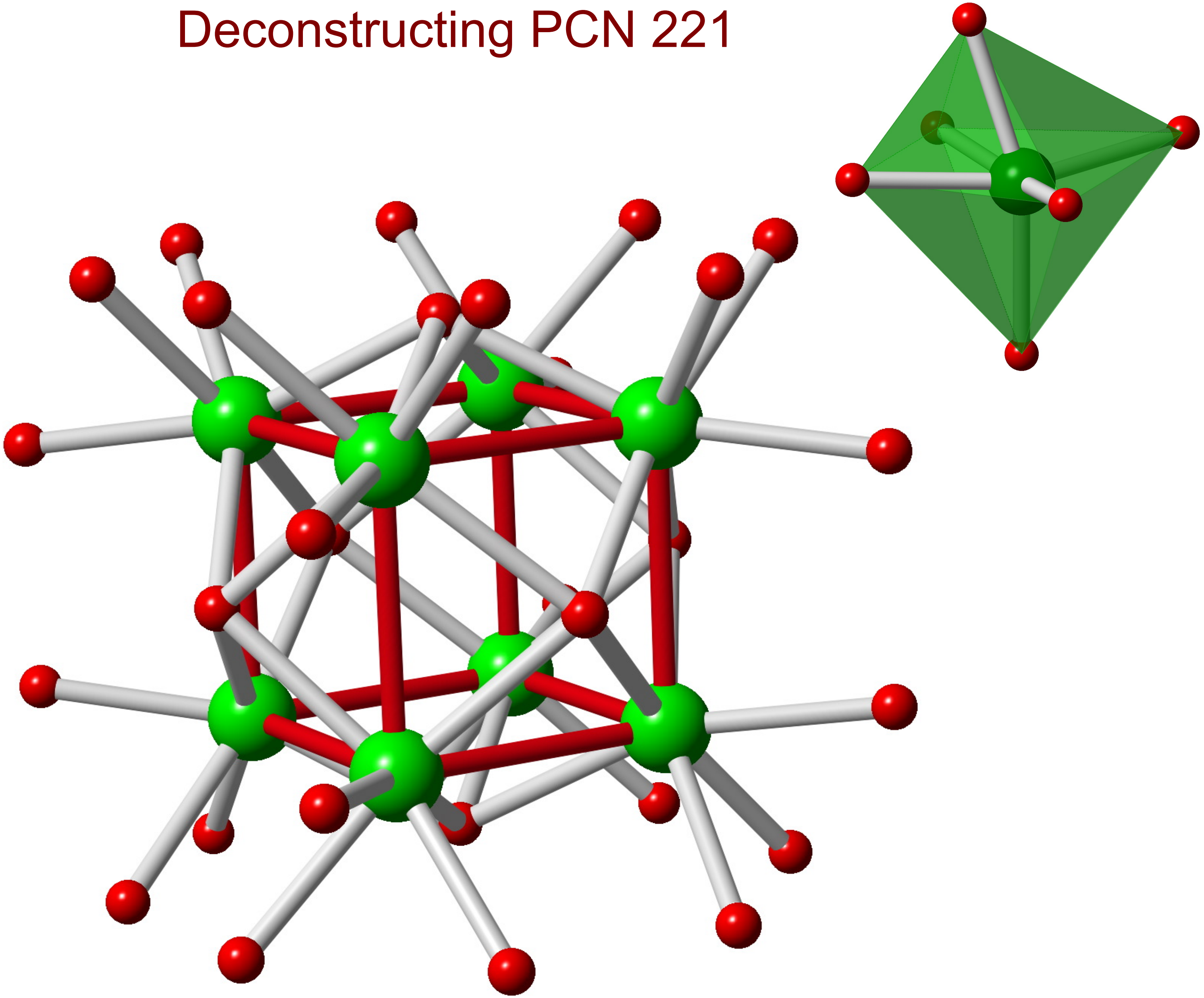
Symmetry D_{4h}

Symmetry O_h

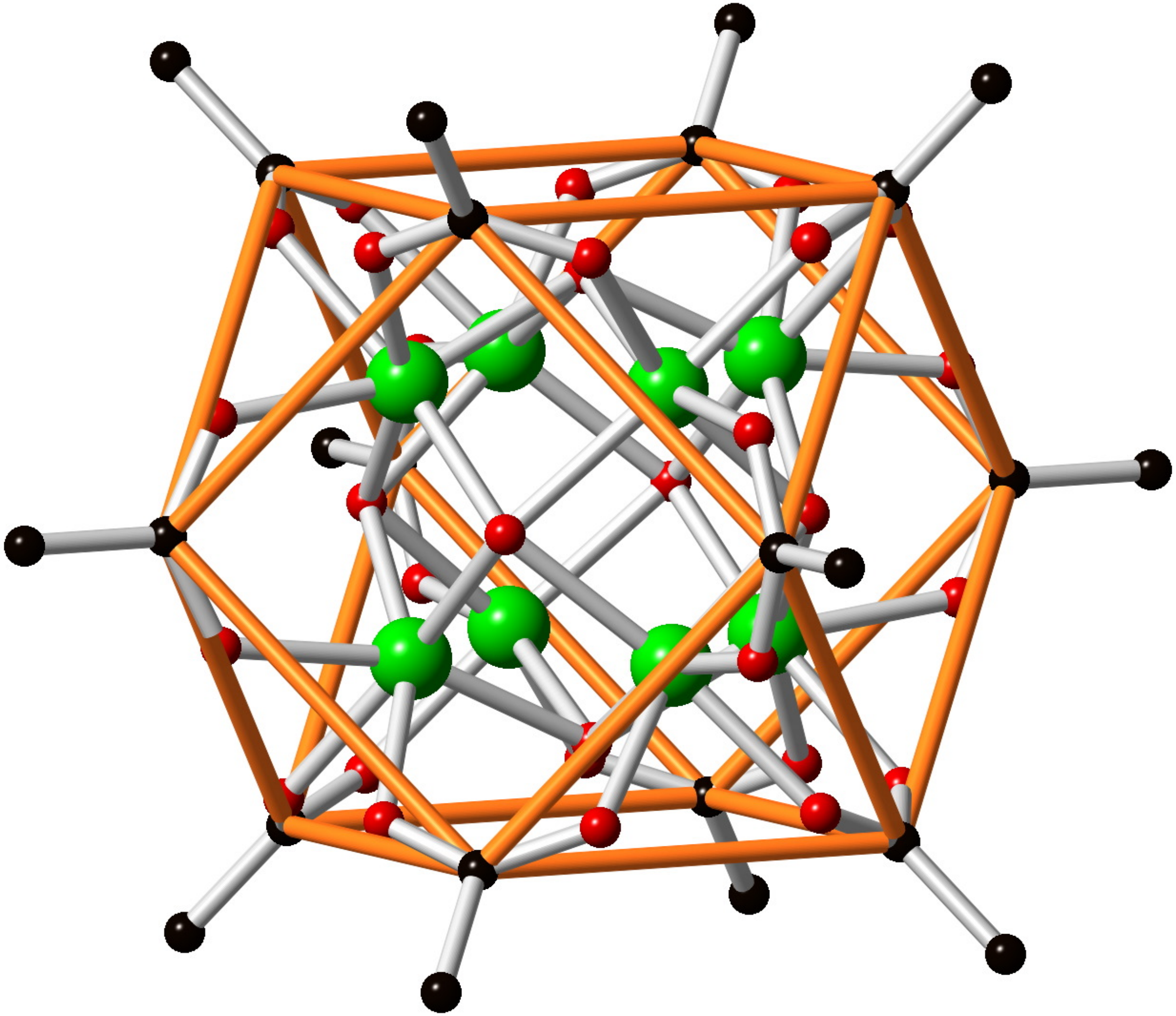
Reduction of MOF in a Network: Nodes + Links



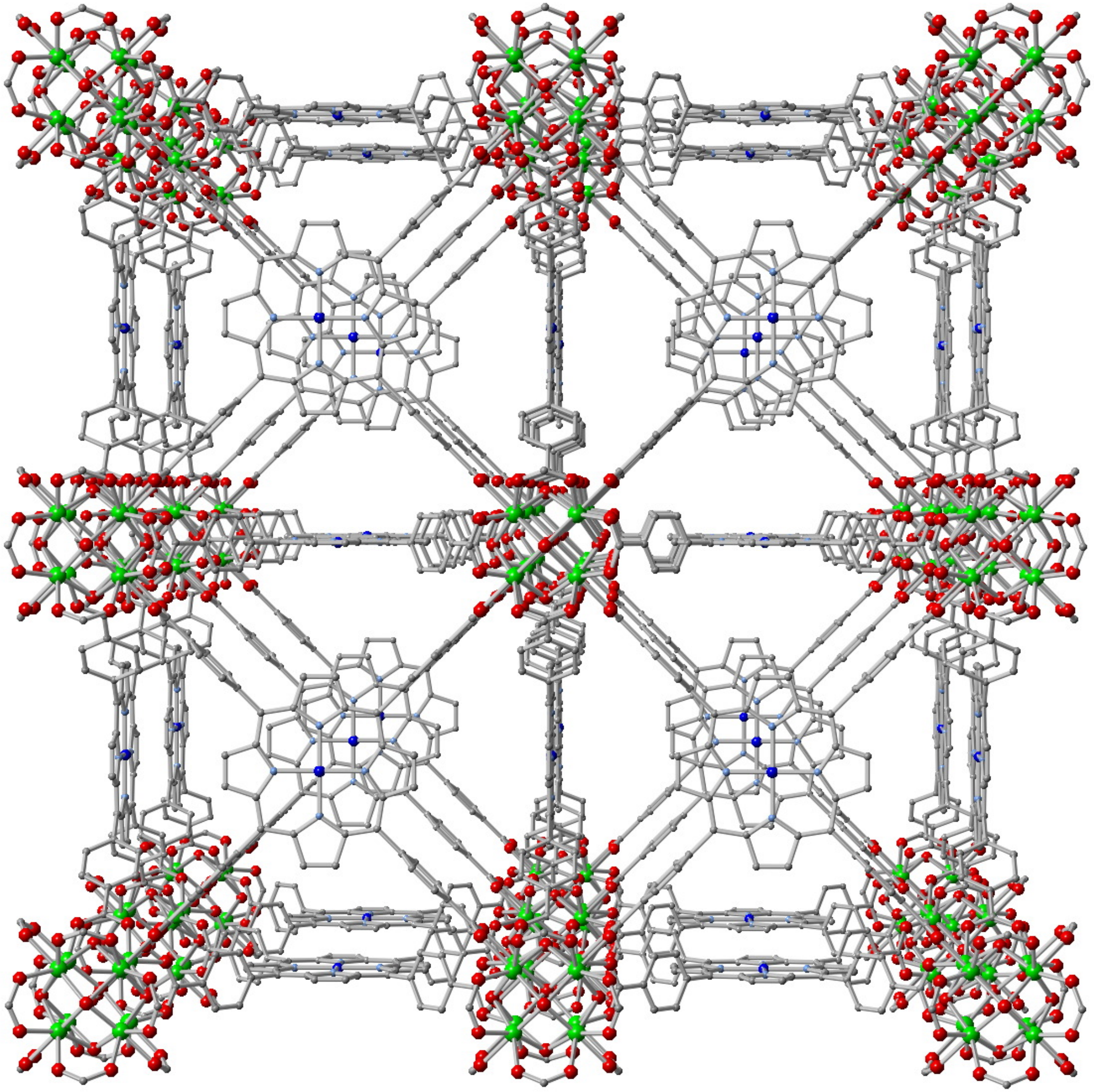
Deconstructing PCN 221



Deconstructing PCN 221



Deconstructing PCN 221

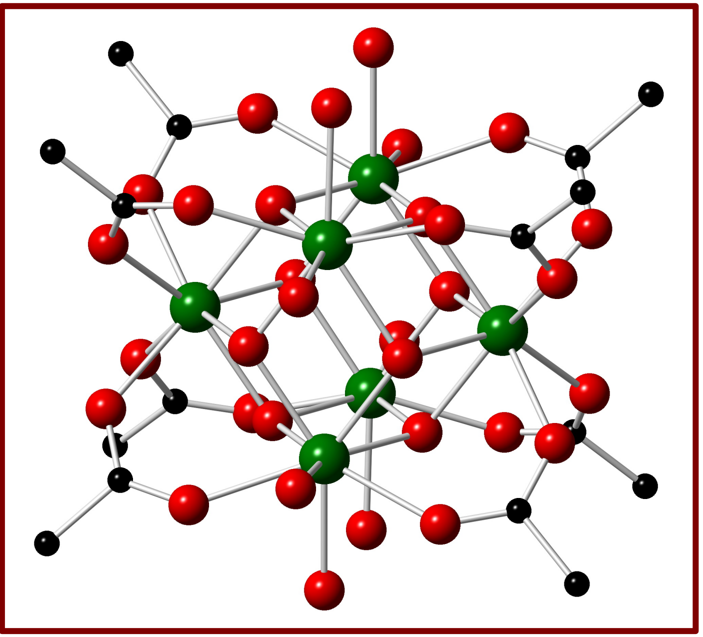


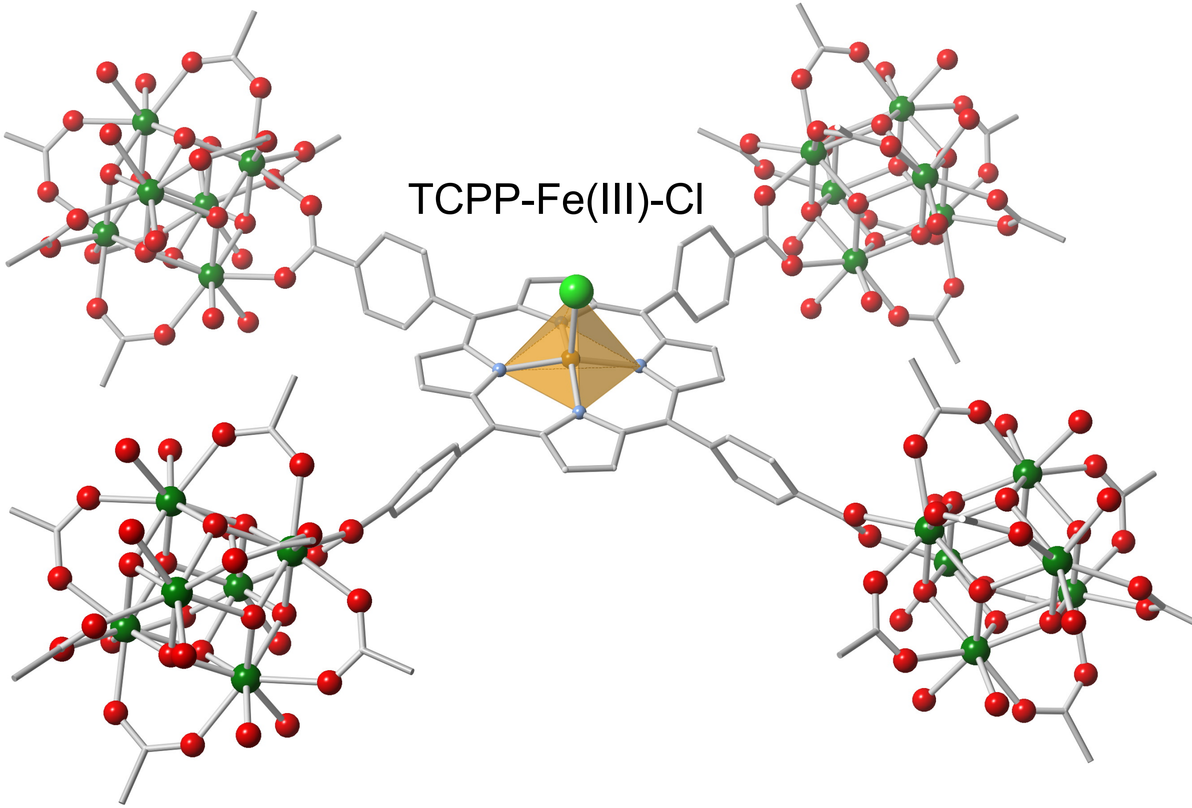
PCN-222: MOF with catalytic properties

PCN-222 is constituted of SBUs type $Zr_6(\mu_3\text{-}O)_8(\mu_2\text{-}CO_2)_8$ and of [5,10,15,20-Tetrakis(4-methoxicarbonylphenyl)porphyrinate]-Fe(III) Chloride].

Synthesis: solvothermal of M-TCPP (M=Fe, Mn, Co, Ni,Cu, Zn, H2) (50 mg), $ZrCl_4$ (70 mg) and benzoic acid (2.7 g) in N,N-dimethylformamide (48 h a 120º C).

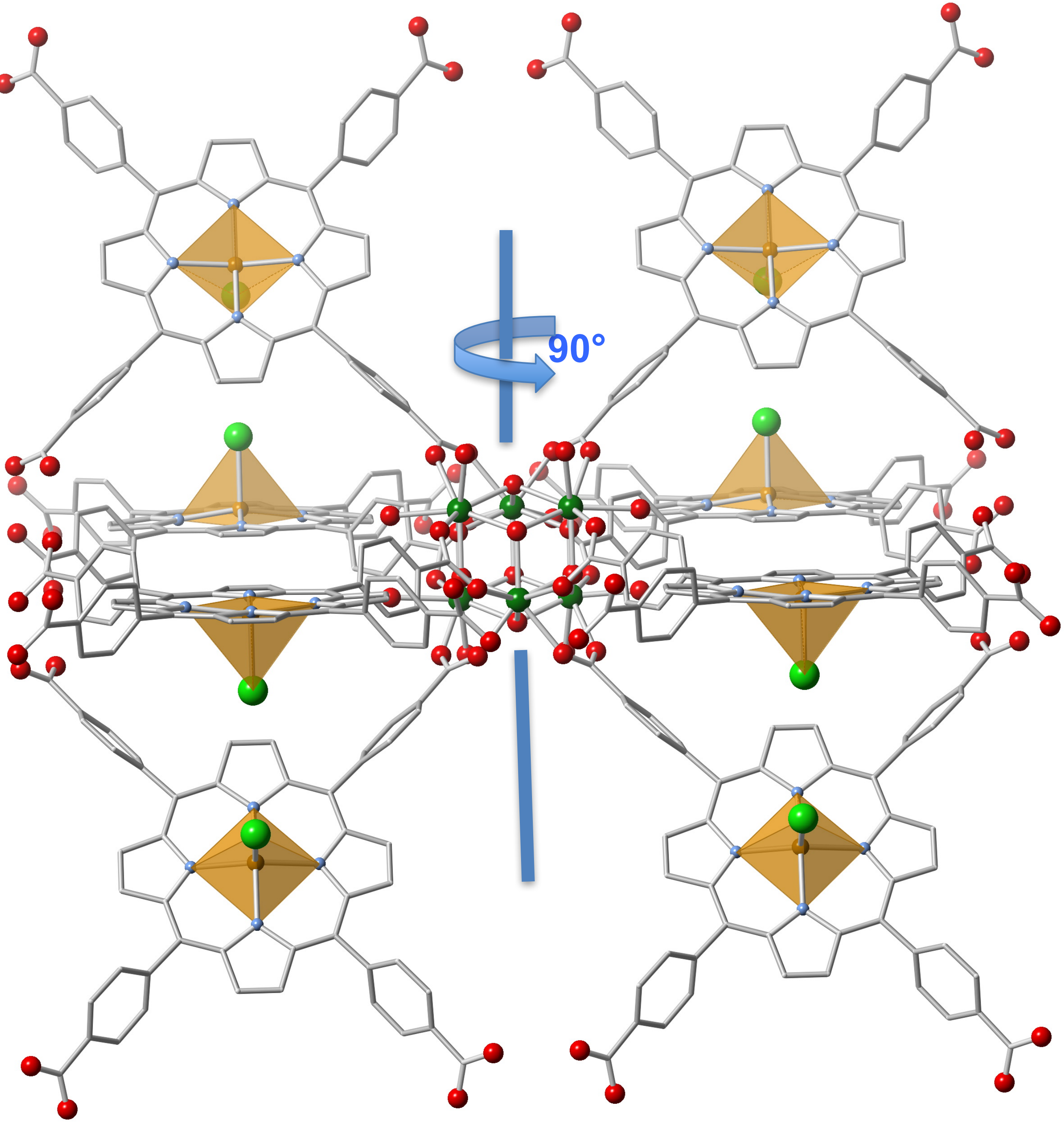
SBU $Zr_6(\mu_3\text{-}O)_8(\mu_2\text{-}CO_2)_8$



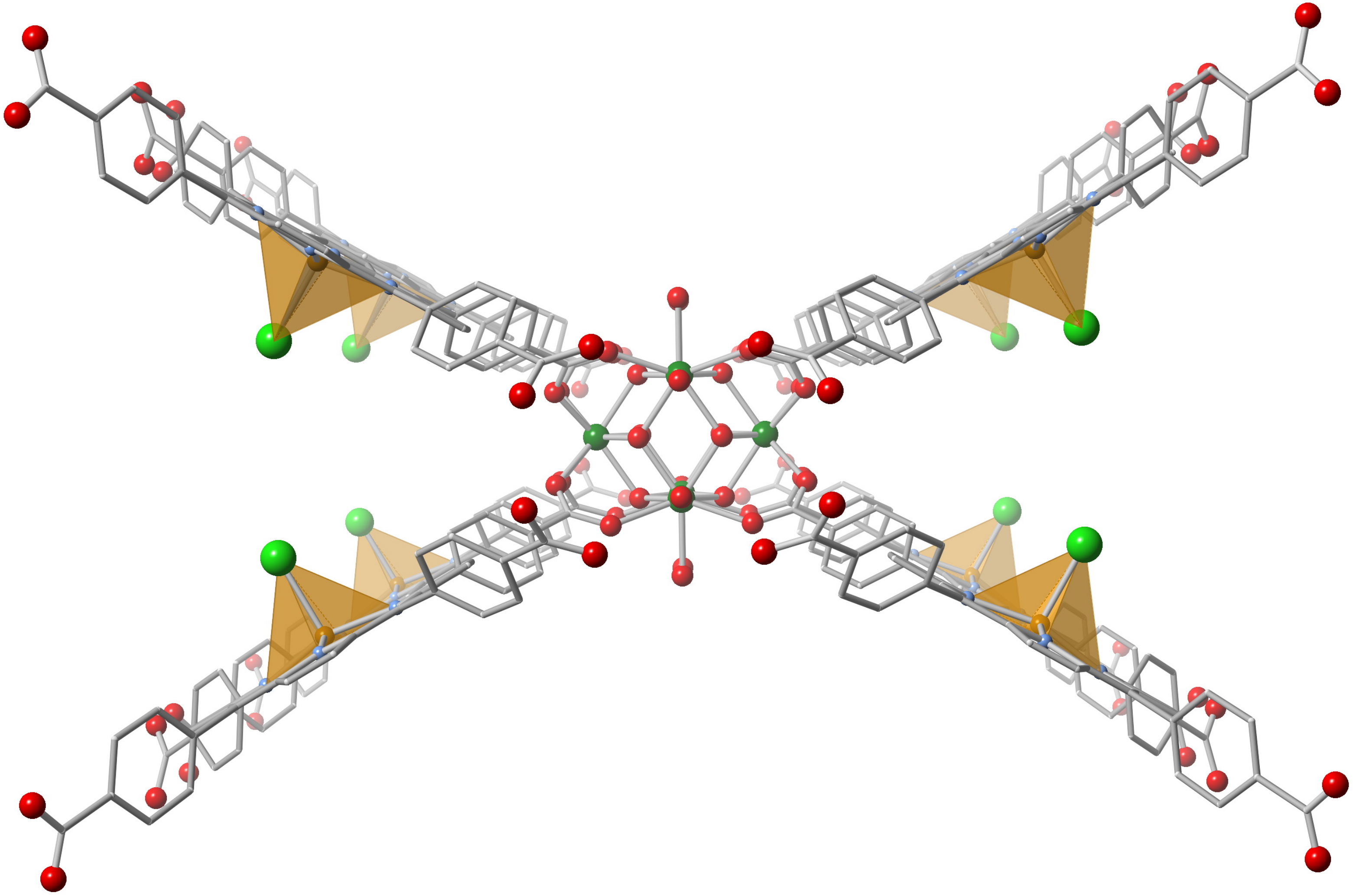


Zirconium-Metalloporphyrin PCN-222: Mesoporous Metal–Organic Frameworks with Ultrahigh Stability as Biomimetic Catalysts; H.-C. Zhou et al. *Angew. Chem. Int. Ed*. **2012**, *51*, 10307-10310

PCN-222

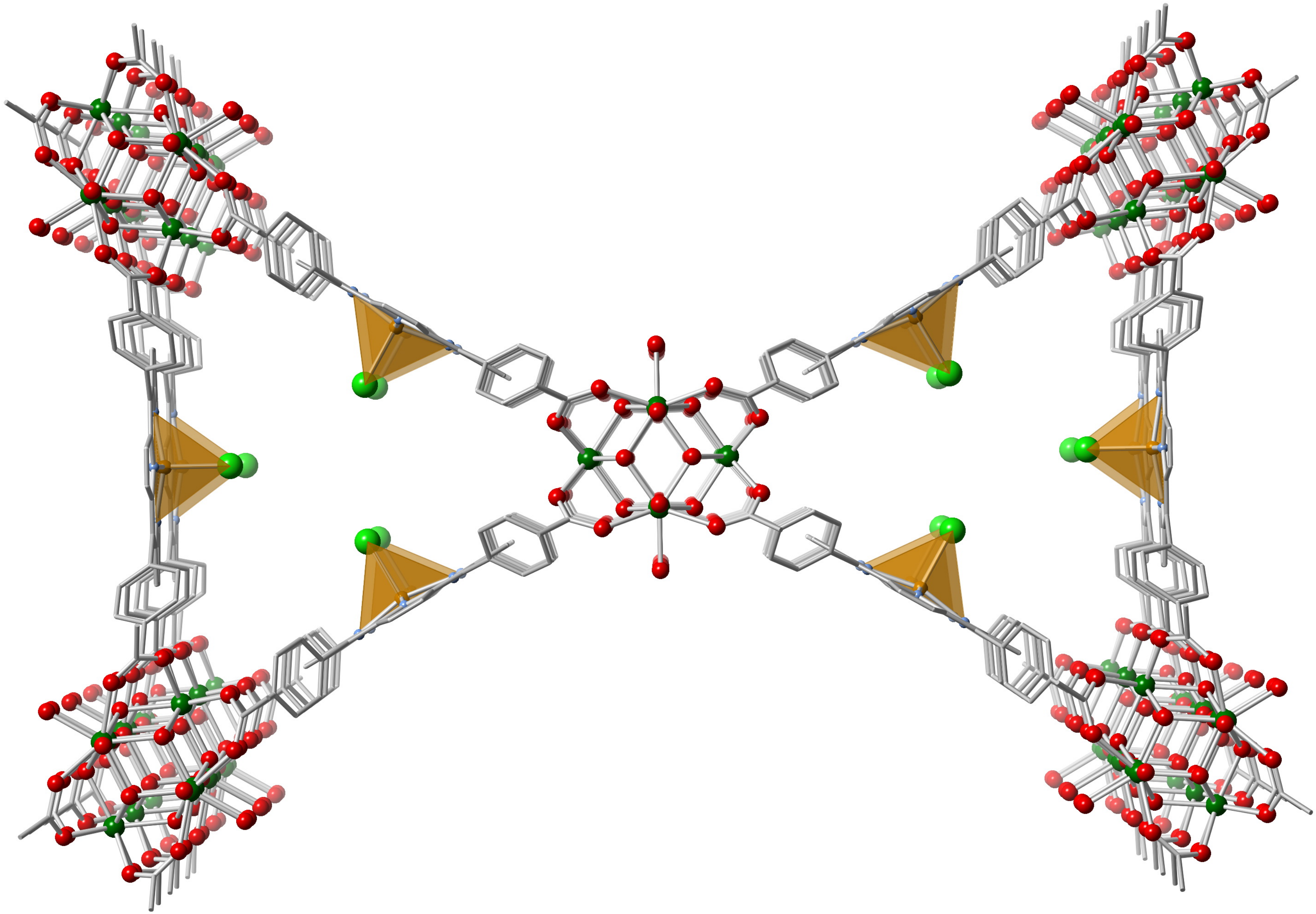


PCN-222 SBU $Zr_6O_8(CO_2)_8$ MOF

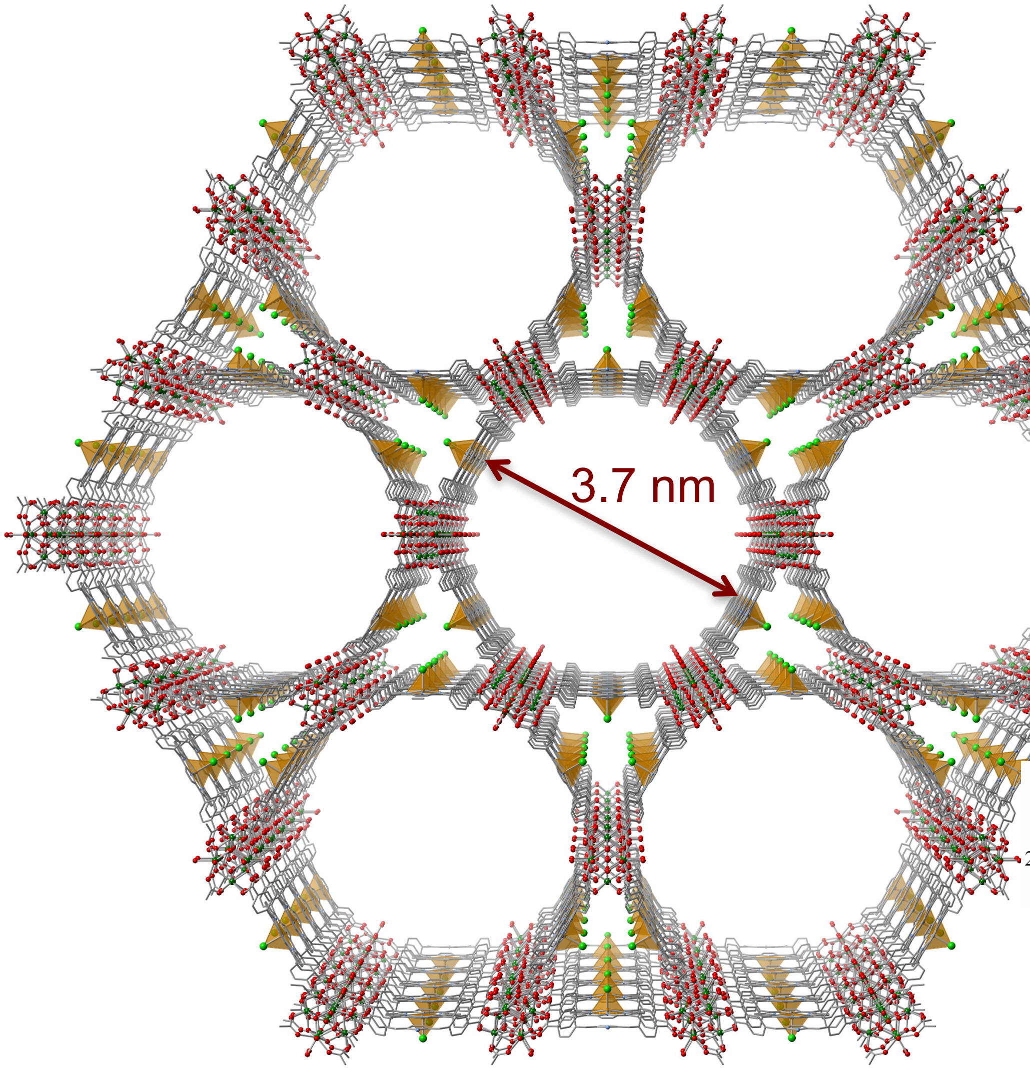


Zirconium-Metalloporphyrin PCN-222: Mesoporous Metal–Organic Frameworks with Ultrahigh Stability as Biomimetic Catalysts; H.-C. Zhou et al. *Angew. Chem. Int. Ed*. **2012**, *51*, 10307-10310

PCN-222 SBU $Zr_6O_8(CO_2)_8$ MOF



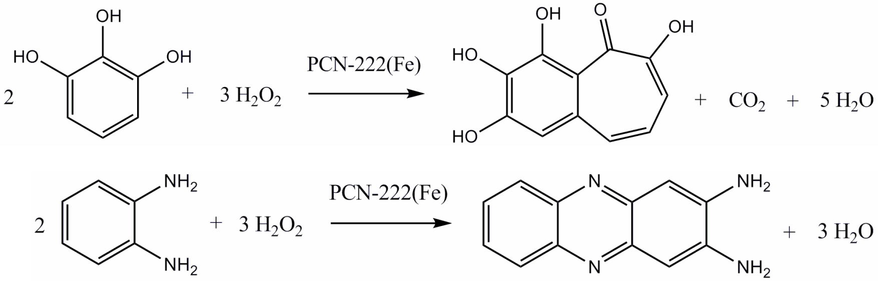
PCN-222:



Structure type Kagome (**kgm**)

Specific surface
Brunauer-Emmett-Teller (BET)
2200-2300 m^2/g

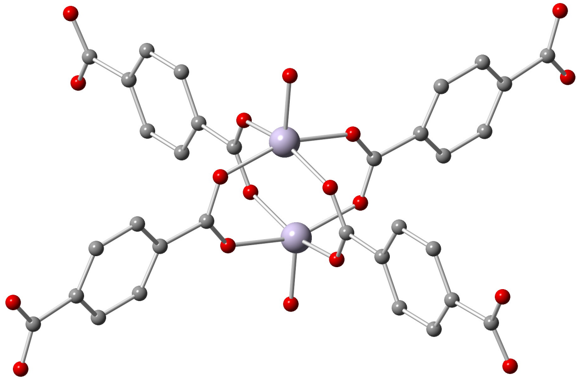
PCN-222(Fe) catalyzes the oxidation of a variety of substrates acting in a similar way as peroxidase



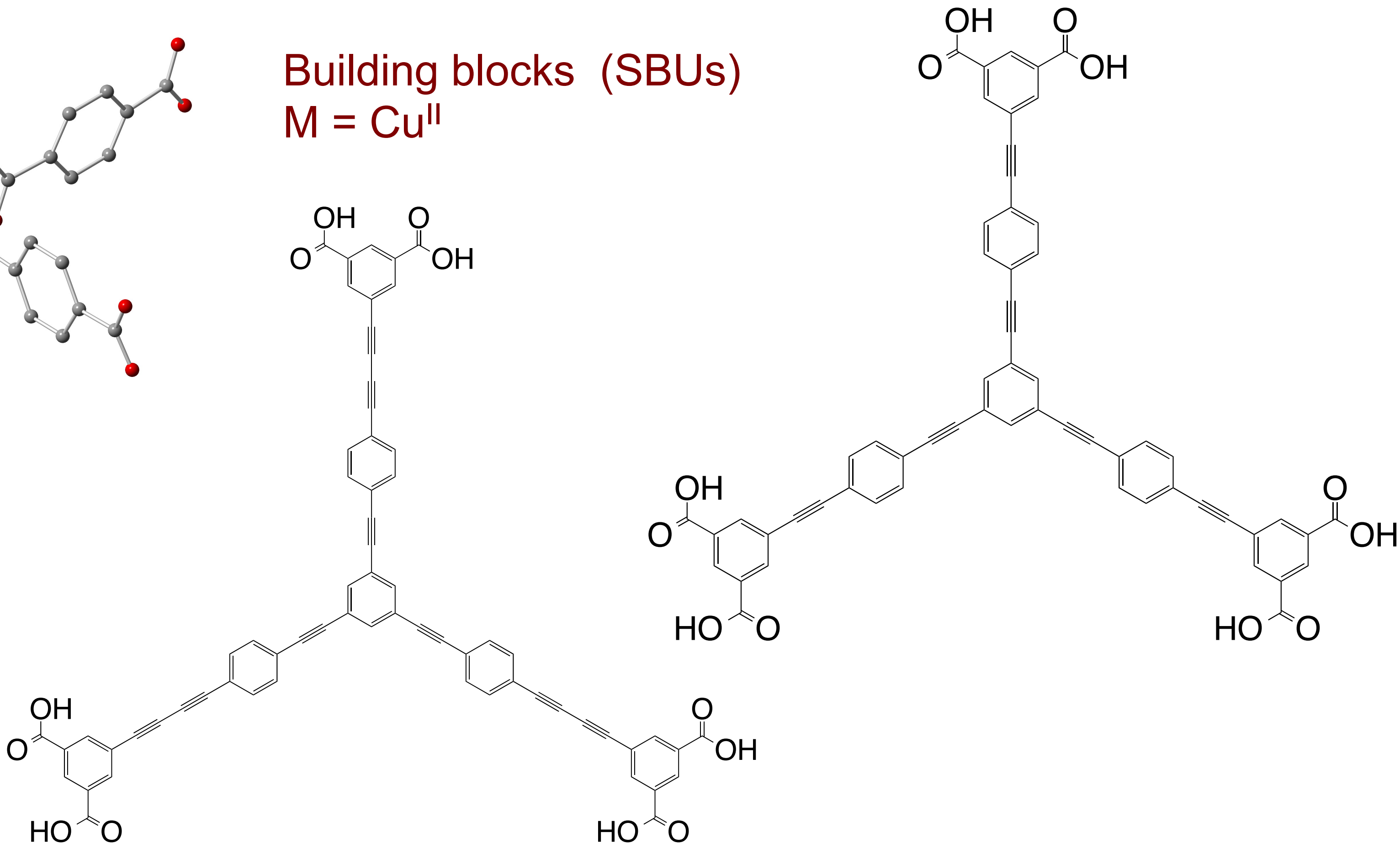
H.-C. Zhou et al. *Angew. Chem. Int. Ed*. **2012**, *51*, 10307-10310

Series NU: NU-109 y 110

3,24-connected networks with **rht** topology



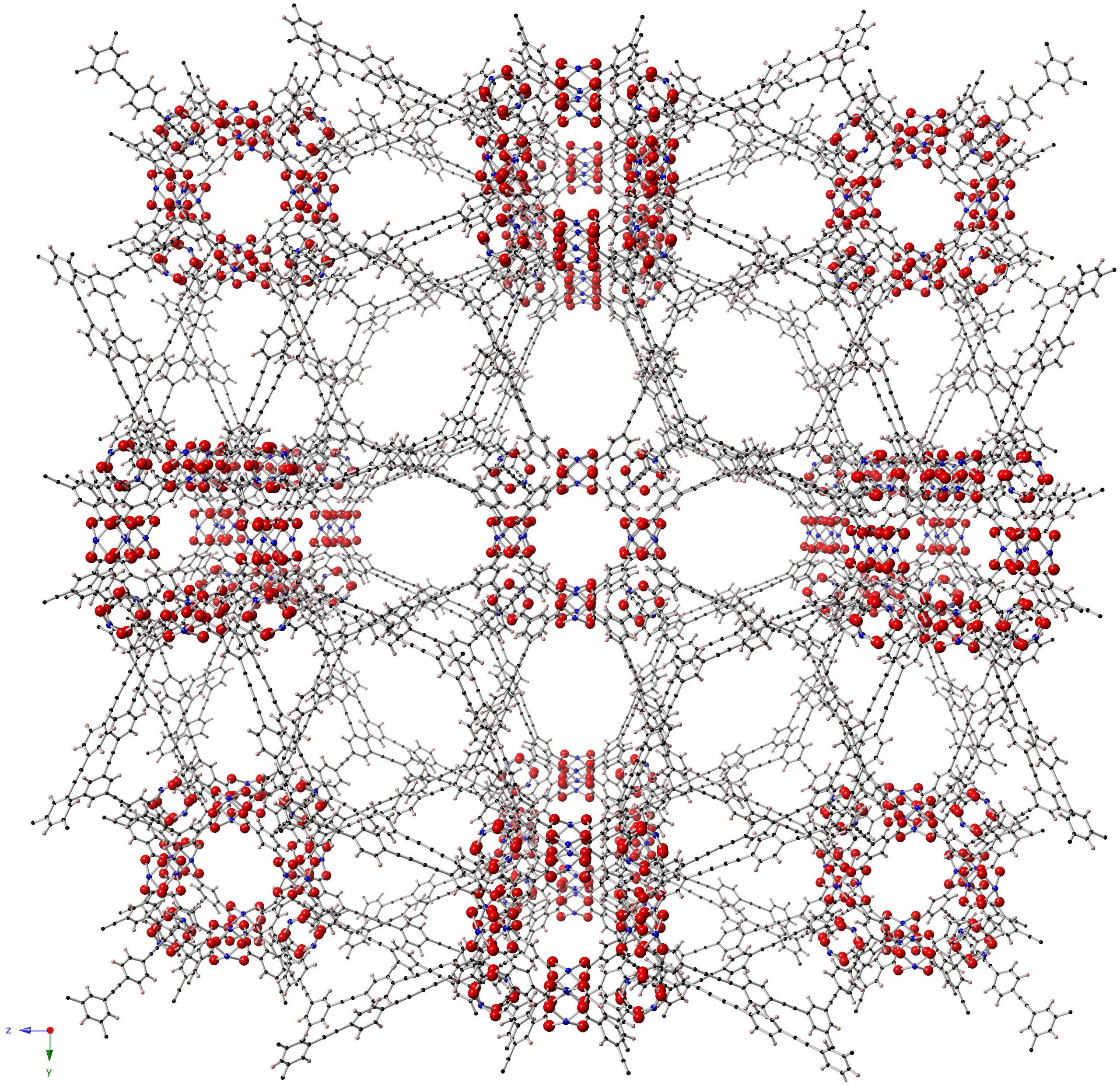
Building blocks (SBUs)
M = Cu^{II}



A. Ö. Yazaydin, J. T. Hupp et al. Metal−Organic Framework Materials with Ultrahigh Surface Areas: Is the Sky the Limit? *J. Am. Chem. Soc*. **2012**, *134*, 15016−15021

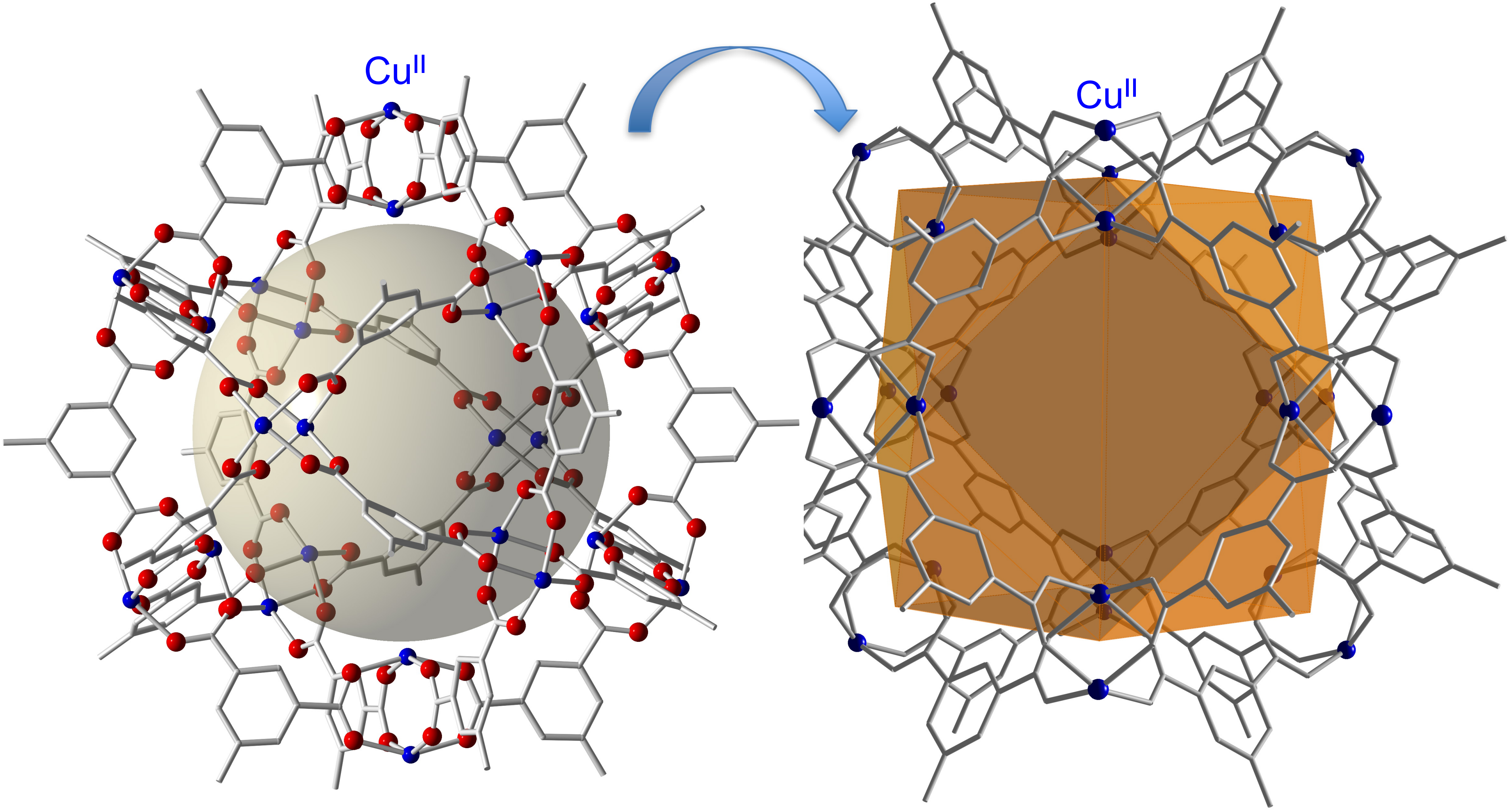
Deconstruction of NU-109 y 110

Networks (**3,24**)
with **rht** topology

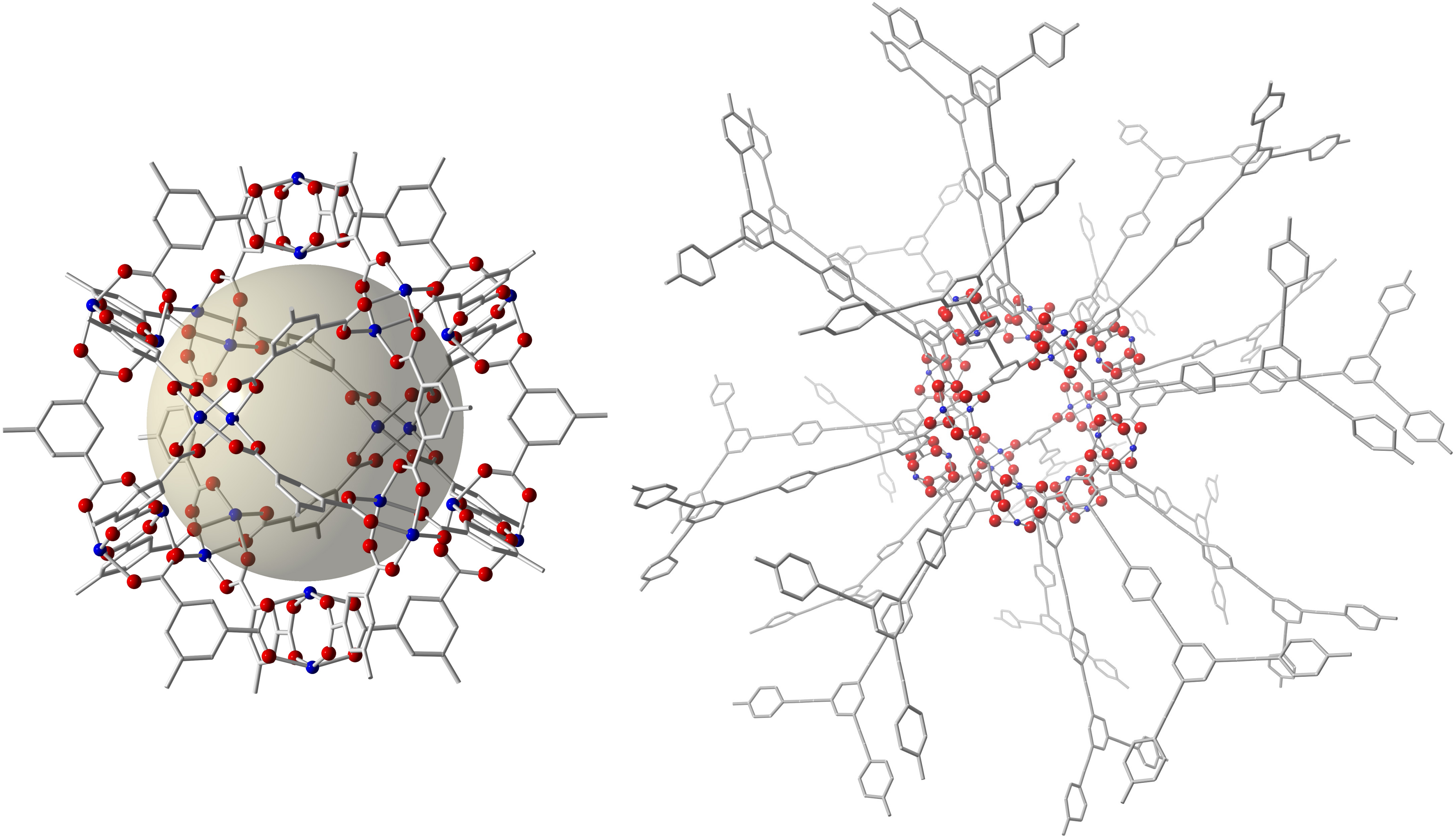


A. Ö. Yazaydin, J. T. Hupp et al. Metal−Organic Framework Materials with Ultrahigh Surface Areas: Is the Sky the Limit? *J. Am. Chem. Soc*. **2012**, *134*, 15016−15021

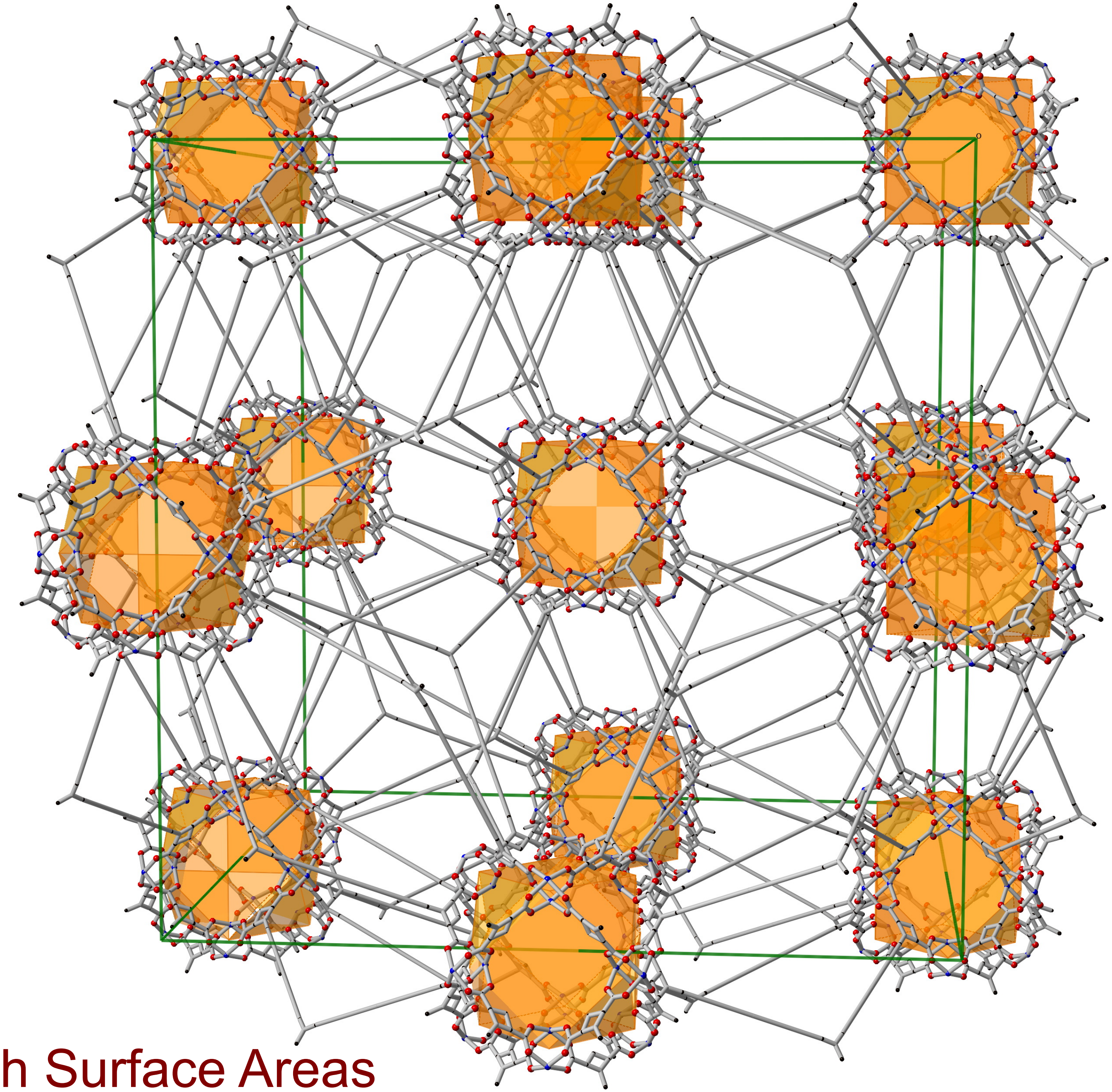
Generates expanded cuboctahedrons acting as nodes of connectivity 24



From the cuboctahedrons radiate 24 ligands acting each as nodes of connectivity 3



Simplification of the network in cuboctahedrons and trigonal connectors



Ultrahigh Surface Areas

Specific surface (BET) and pore volume for highly porous MOFs

MOF	Superficie específica (m^2g^{-1})	Volumen de poro (cm^3g^{-1})	
MFU-4 L	2750	1.26	Chem. Eur. J. 2011, 17, 1837
NOTT-102	2940	1.14	J. Am. Chem. Soc. 2009, 131, 2159
PCN-61	3000	1.36	J. Am. Chem. Soc. 2009, 131, 9186
$Cu_{24}(TPBTM)_8(H_2O)_{24}$	3160	1.27	J. Am. Chem. Soc. 2011, 133, 748
SNU-77	3670	1.52	Chem. Eur. J. 2011, 17, 7251
NOTT-112	3800	1.62	Chem. Commun. 2009, 1025
MOF-5	3800	1.55	J. Am. Chem. Soc. 2007, 129, 14176
UMCM-1-NH_2	3920		Chem. Eur. J. 2010, 16, 212
PCN-66	4000	1.36	J. Am. Chem. Soc. 2009, 131, 9186
$Be_{12}(OH)_{12}(BTB)_{24}$	4030		J. Am.Chem. Soc. 2009, 131, 15120
UMCM-1	4160		Angew. Chem., Int. Ed. 2008, 47, 677
MIL-101c	4230	2.15	Science 2005, 309, 2040
Bio-MOF-100	4300	4.3	Nat. Commun. 2012, 3, 604
MOF-205	4460	2.16	Science 2010, 329, 424
MOF-177	4750	1.59	J. Mater. Chem. 2007, 17, 3197
DUT-23-Co	4850	2.03	Chem. Eur. J. 2011, 17, 13007
NOTT-116	4660	2.17	Angew. Chem., Int. Ed. 2010, 49, 5357
PCN-68	5110	2.17	J. Am. Chem. Soc. 2010, 132, 4092
UMCM-2	5200	2.32	J. Am. Chem. Soc. 2009, 131, 4184
NU-100	6140	2.82	Nat. Chem. 2010, 2, 944
MOF-210	6240	3.6	Science 2010, 329, 424
NU-109E	7010	3.75	*J. Am. Chem. Soc.* **2012**, *134*, 15016
NU-110E	7140	4.4	*J. Am. Chem. Soc.* **2012**, *134*, 15016

Materiales porosos convencionales		
Zeolitas	≈ 900	0.30
Sílicas	≈ 1000	1.15
Carbonos	≈ 1500	0.60

Table partially adaptaded from:
J. Am. Chem. Soc. **2012**, *134*, 15016

Este material docente ha sido elaborado en el marco de una convocatoria de ayudas para el desarrollo de proyectos de innovación educativa y mejora de la calidad docente (convocado por el Vicerectorat de Polítiques de Formació i Qualitat Educativa de la Universitat de València, en el curso 2017-2018). Código: UV-SFPIE_RMD17-725369

Estas diapositivas forman una parte del contenido docente de la asignatura "Química Inorgánica Avanzada" del Máster Universitario en Química.