Lecture 1

Welcome to CH-405: Advanced Transition Metal Chemistry

Instructor:

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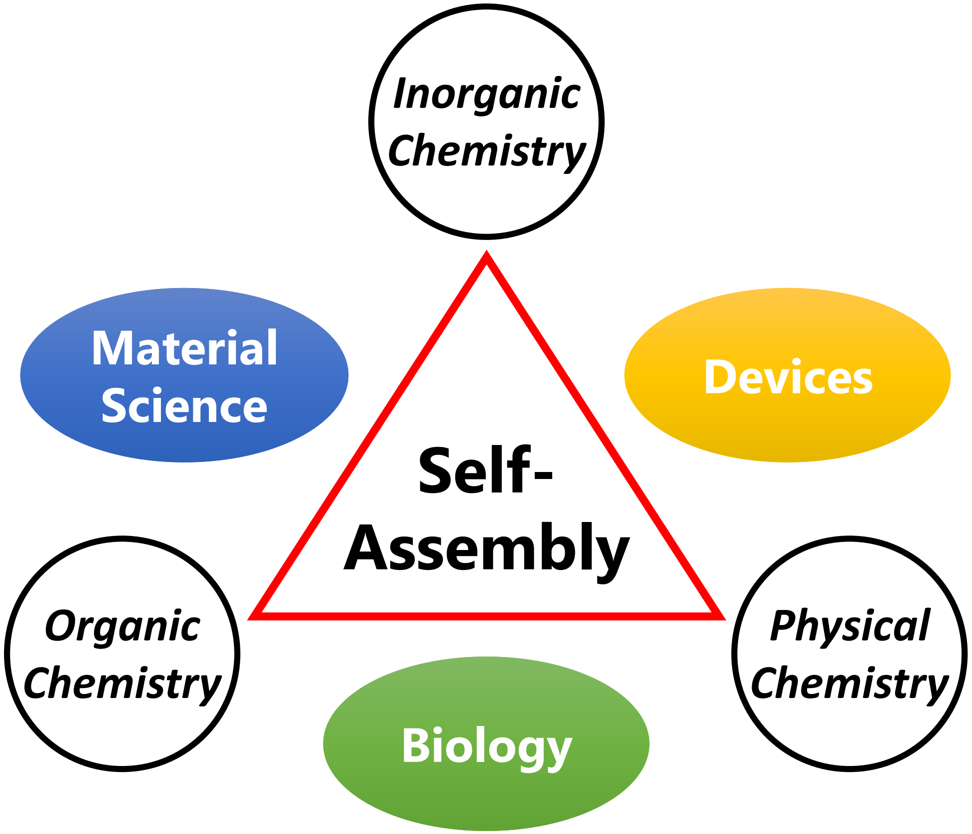
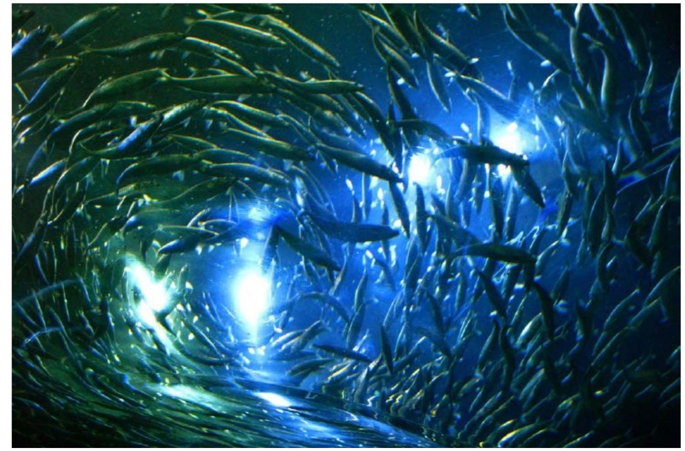
Self-assembly

- An inter-disciplinary research area that deals with chemical principals to <u>construct larger architectures from smaller entities – *Supramolecular Architectures*</u>.

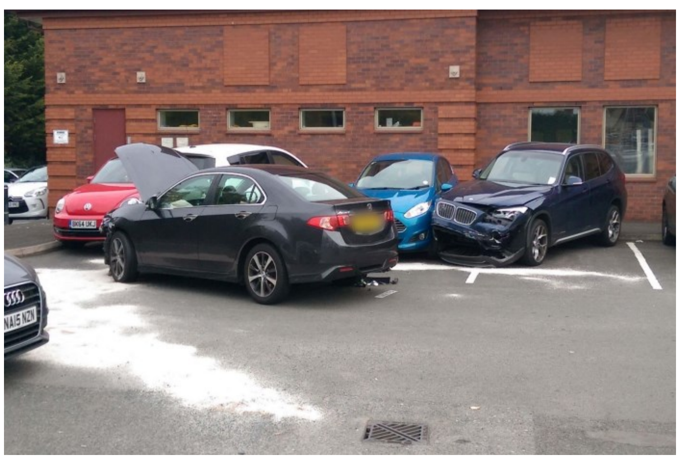


Self-assembly around us

Self-assembly of Bricks



Self-assembly of Fish



Random-assembly of Cars

Self-assembly of Cars

Self-assembly process depends on environment

Supramolecular Chemistry: Introduction

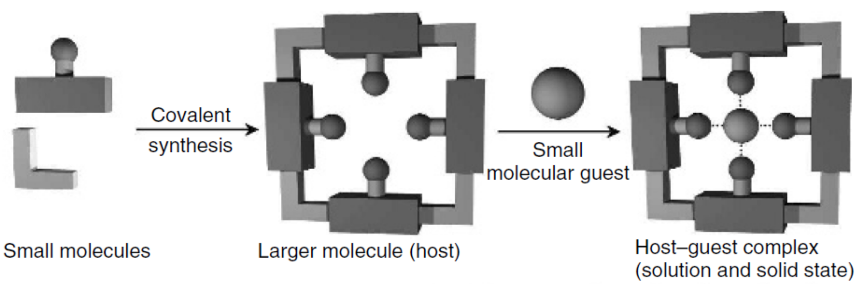
Supramolecular Chemistry

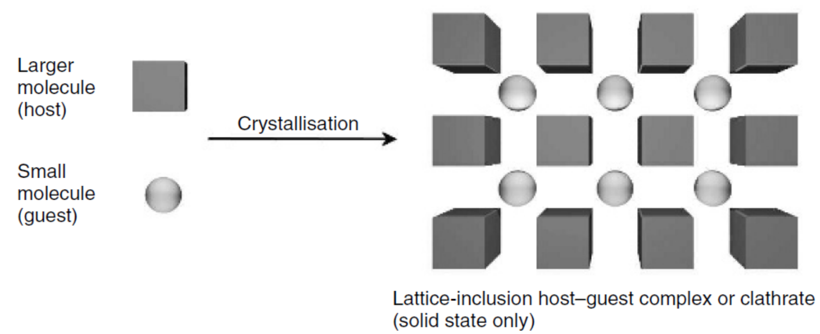
Host-guest Chemistry

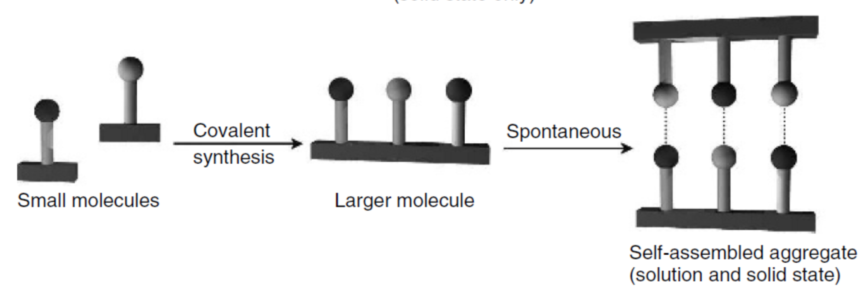
The study of large 'host' molecules that are capable of enclosing smaller 'guest' molecules *via* non-covalent interactions

Self-assembly

Spontaneous and reversible association of two or more components to form larger, non-covalently bound aggregates



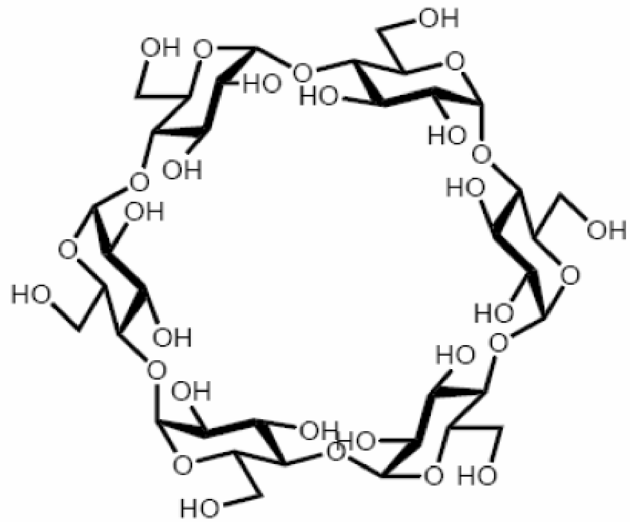




Core concepts in Supramolecular chemistry and Nano-Chemistry, J. W. Steed, D. R. Turner, Karl Wallace, (2007) 1st Ed. Wiley.

History of Supramolecular Chemistry

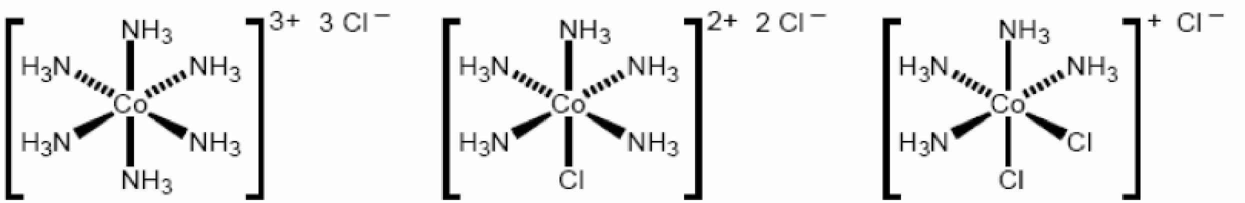
1891 A. Villiers; cyclodextrin synthesis & complexes — Host-Guest



1893 Alfred Werner (Uni ZH, Nobel Prize Chemistry 1913) — Affinity

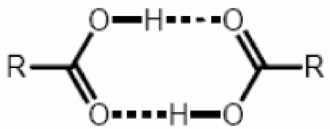
Coordination Chemistry: electronically saturated molecules can still bind if they have a 'mutual affinity' to form 'complexes' — Attraction

Complexation



History of Supramolecular Chemistry

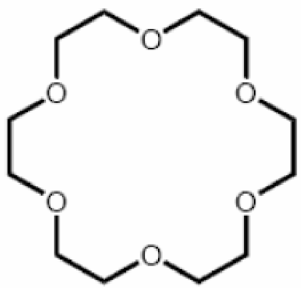
1894	Emil Fischer (Berlin, Nobel Prize Chemistry 1902)	Selectivity
	Enzyme-Substrate Interactions: 'lock-and-key' principle; 'binding must be selective', which requires size and shape complementarity	Recognition
1906	Paul Ehrlich (Berlin, Nobel Prize Medicine 1908)	Receptors
	Immunology: 'corpora non agunt nisi fixata', i.e., molecules do not react if they do not bind.	Fixation Reaction
1937	K. L. Wolf: "Übermoleküle" from carboxylic acid gas phase dimers	Supermolecules

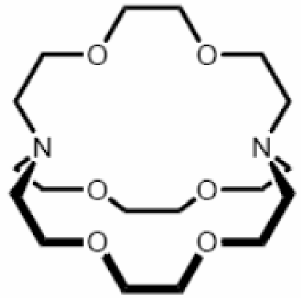


1939	Linus Pauling (Caltech, Nobel Prize Chemistry 1954)	Hydrogen Bond
	Bond Theory: 'hydrogen bonding' mentioned in The Nature of the Chemical Bond	

History of Supramolecular Chemistry

1967 Work by C. J. Pedersen J.-M. Lehn, and D. J. Cram 1973 on crown ethers and cryptands





Preorganization

Recognition

Templating

1987 Nobel Prize for J.-M. Lehn, D. J. Cram, C. J. Pedersen

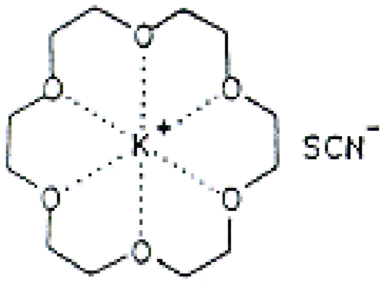
Supramolecular Chemistry

"Supramolecular chemistry is chemistry 'beyond the molecule', the science of non-covalent, intermolecular interactions."

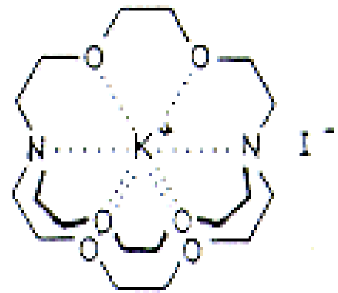
"Just as there is a field of molecular chemistry based on the covalent bond, there is a field of supramolecular chemistry, the chemistry of molecular assemblies and of the intermolecular bond."

and continuing…………..

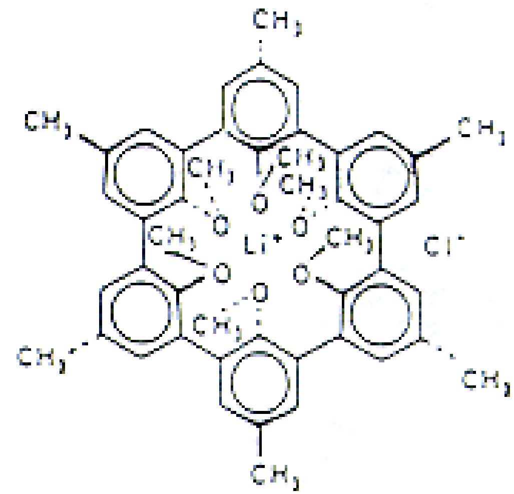
Nobel Prize for Chemistry in 1987



Crown ether complex
according to Pedersen



cryptand complex
= cryptate
according to Lehn



host-guest complex
according to Cram

https://www.nobelprize.org/prizes/chemistry/1987/summary/

In 1967, **Pedersen** observed that crown ether showed ***molecular recognition*** – the first artificial molecule found to do so.

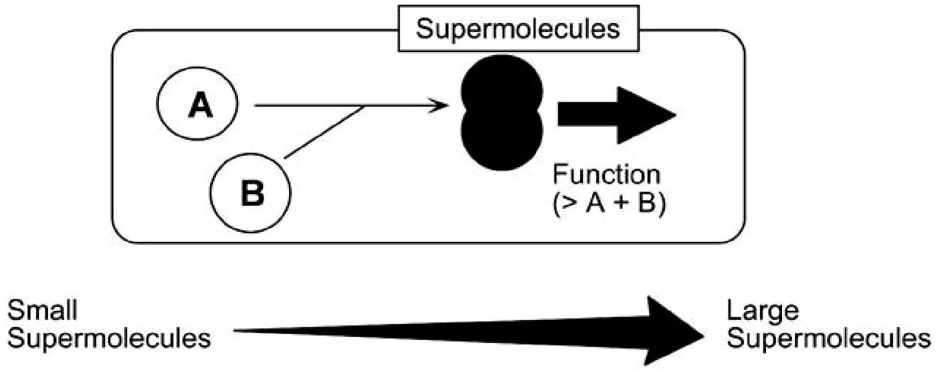
Cram established, ***host–guest chemistry***, where the host molecule can accommodate another guest molecule.

In 1978, **Lehn** proposed the term “***supramolecular chemistry***”.

Definitions

Supramolecular Chemistry: Supramolecular chemistry involves investigation of **molecular systems** in which the most important feature is that **components are held together by inter-molecular forces**, not by covalent bonds. (eg. hydrogen bonding, hydrophobic interactions, coordination bonds, etc.)

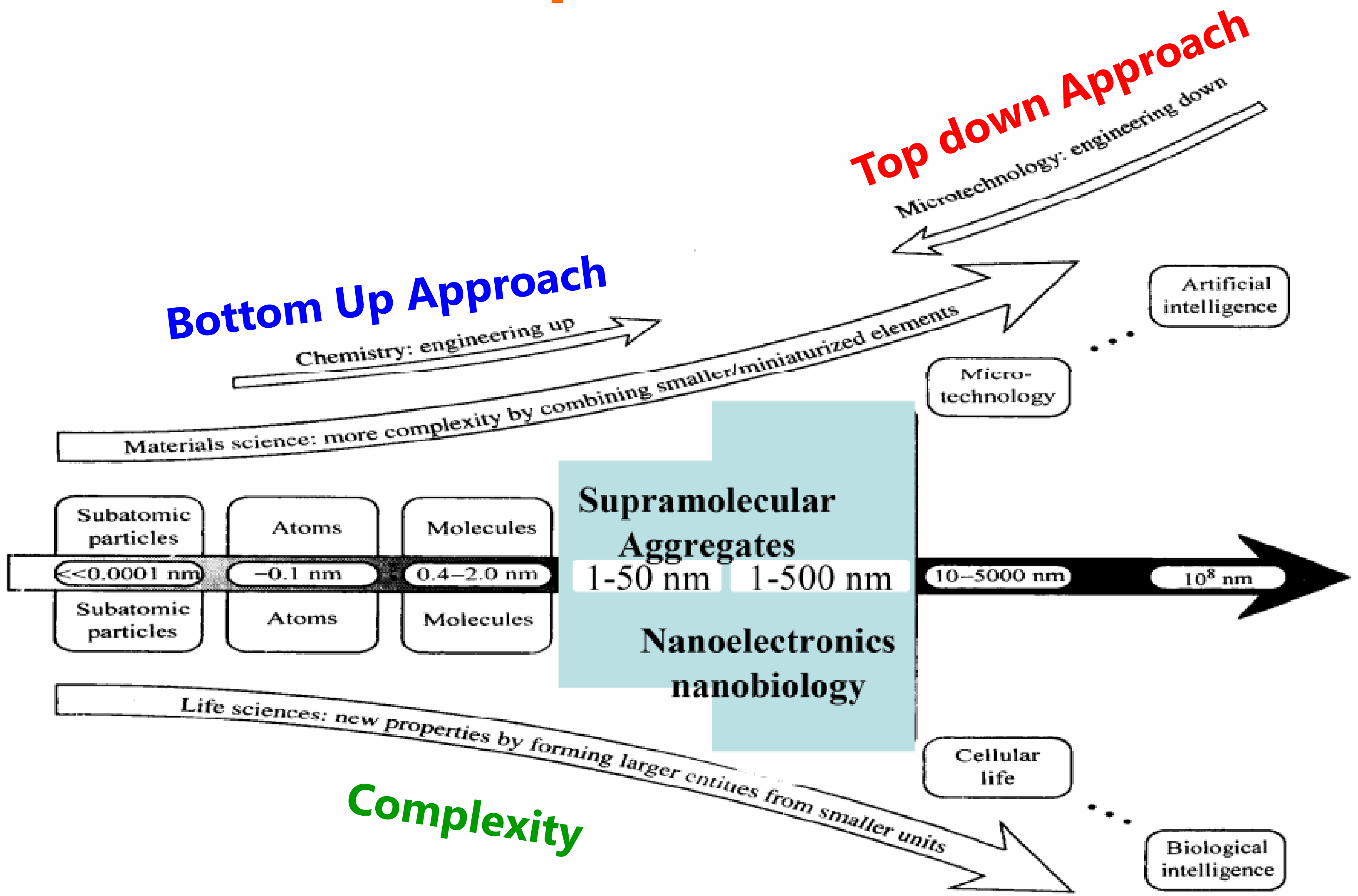
Supermolecule: A species that is held together by non-covalent interactions between two or more covalent molecules or ions.



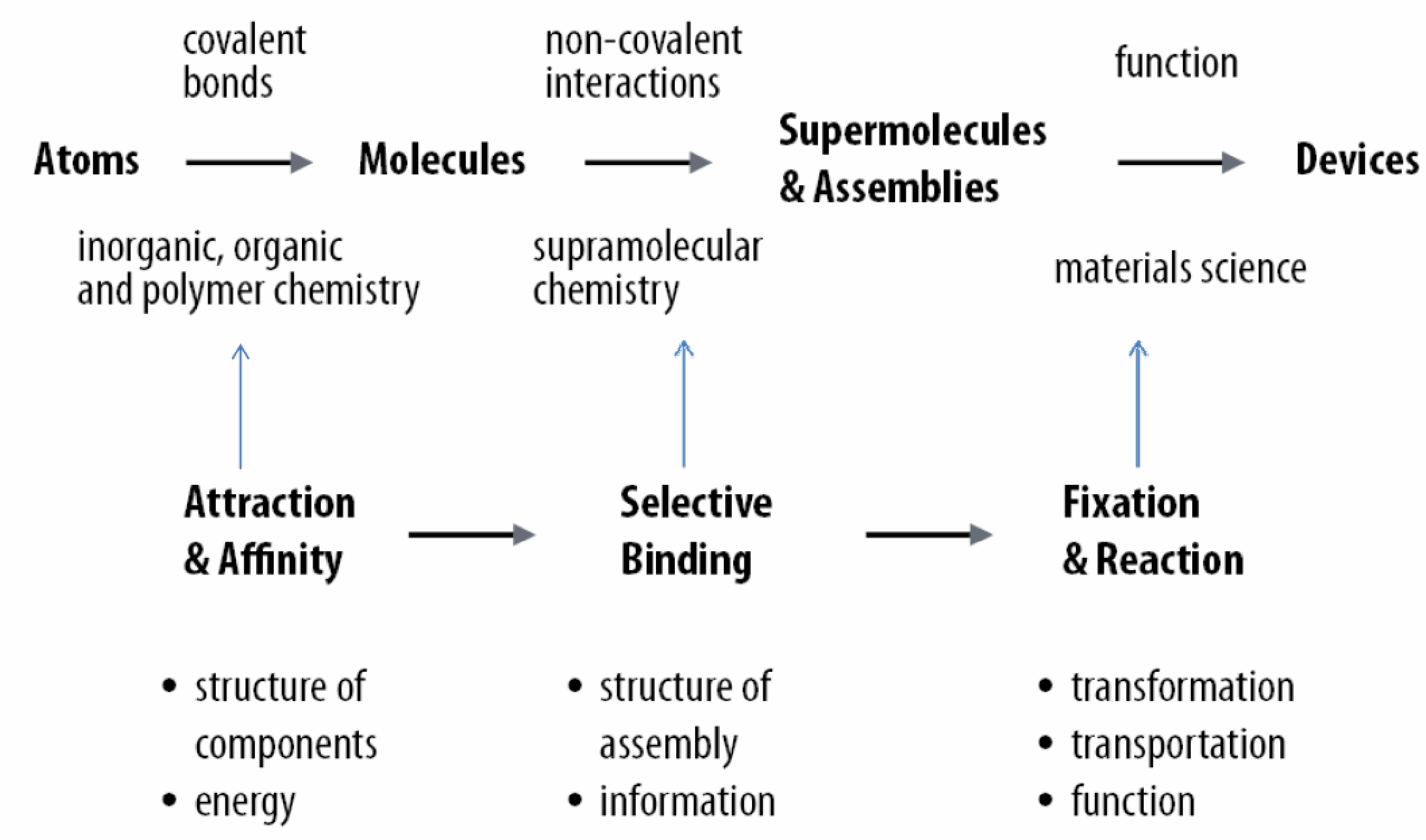
Self-assembly: Self-assembly **is a tool** to arrange covalent molecules/ions in space to get supramolecular material.

"Chemistry beyond the molecule"

Structural Perspective



Functional Perspective



"Molecular recognition is selective binding with a purpose"

J.-M. Lehn, *Pure Appl. Chem.* **1978**, *50*, 871.

Features of Self-assembly

- Self-assembly proceeds spontaneously

- Formation of the ordered structure may require energy (for example in the form of stirring), but once formed it is stable.

- The self-assembled structure is often at or close to thermodynamic equilibrium

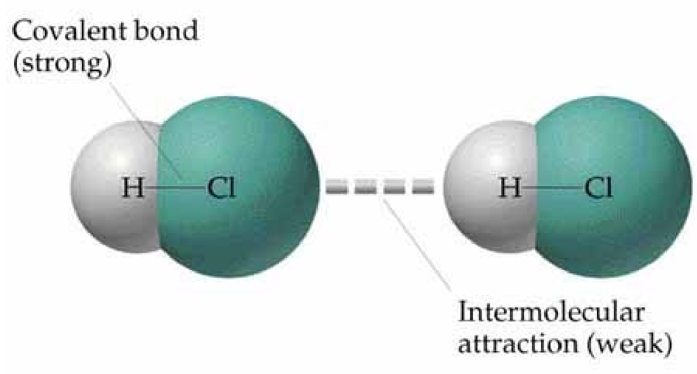
- Self-assembly tends to reject defects, and also has self-healing and self-sorting capability

- Self-assembly is one of the few practical strategies for making ensembles of nanostructures

Inter-molecular vs Intra-molecular

Intermolecular forces: forces of attraction and repulsion between molecules that hold molecules, ions, and atoms together.

Intramolecular forces: hold atoms together in a molecule.



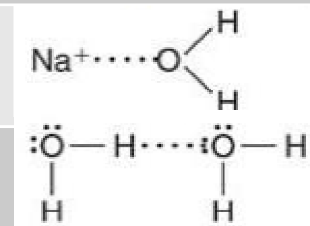
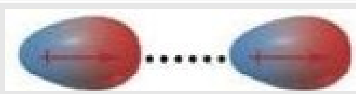
- **Intermolecular vs Intramolecular:**

Generally, **inter**molecular forces are much weaker than **intra**molecular forces.

- 41 kJ to vaporize 1 mole of water (**inter**)
- 930 kJ to break all O-H bonds in 1 mole of water (**intra**)

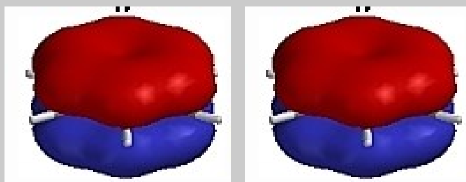
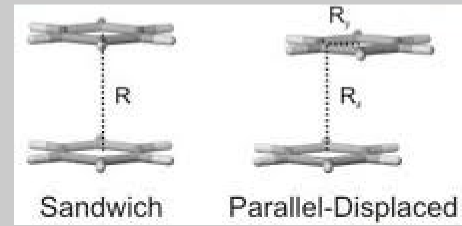
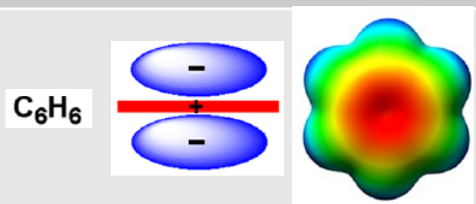
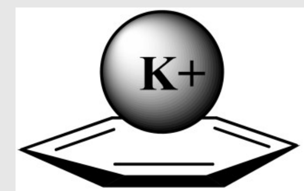
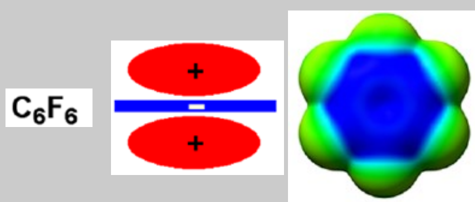
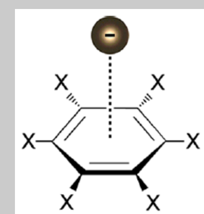
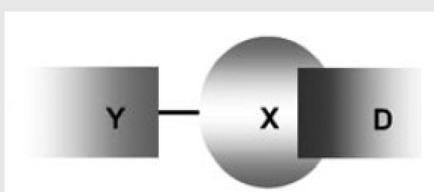
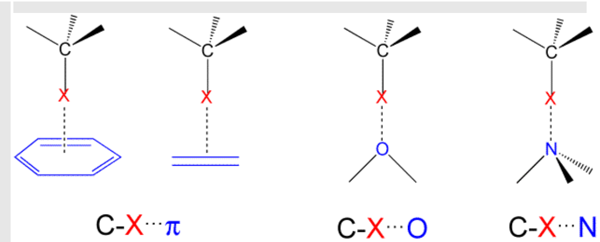
Non-covalent interactions

Types:

Force	Model	Energy	Example
Ion-Ion		200-300 kJ/mol	$—NH_3^+$ $^-OOC—$
Ion-Dipole		40-600 kJ/mol	
Hydrogen bond	δ− δ+ δ− —A—H·······:B—	10-40 kJ/mol	
Dipole-Dipole		5-25 kJ/mol	I—Cl·····I—Cl
Ion-Induced dipole		3-15 kJ/mol	Fe^{2+}·····O_2
Dipole-Induced dipole		2-10 kJ/mol	H—Cl·····Cl—Cl
Dispersion (London)		0.05-40 kJ/mol	F—F·····F—F

van der Waals forces

Noncovalent Interactions

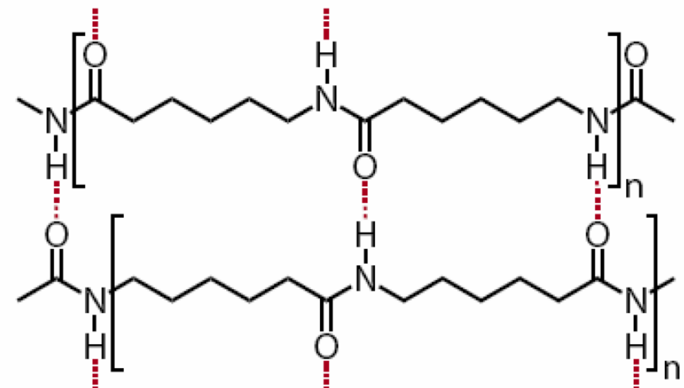
Force	Model	Energy	Example
Pi-Pi		0-50 kJ/mol	
Cation-Pi		5-80 kJ/mol	
Anion-Pi		20-70 kJ/mol	
Halogen bond	 Y = C, N, halogen, etc. D= N, O, S, Se, Cl, Br, I... I^-, Br^-, Cl^-, F^-...	10-200 kJ/mol	

Are they really weak?

Non-covalent interactions are weak !

Structure of Kevlar

https://en.wikipedia.org/wiki/Kevlar



Nylon-6

Structure of Nylon-6

Not really……. Individual non-covalent interaction may be weak, but when present in enough number and work together can stabilize the overall structure while allowing self-healing.

Lecture 2

Welcome to CH-405 Advanced Transition Metal Chemistry

Instructor:

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Supramolecular Chemistry: Introduction

Supramolecular Chemistry

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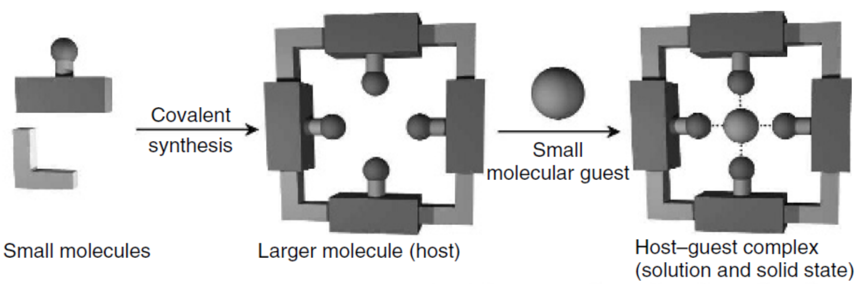
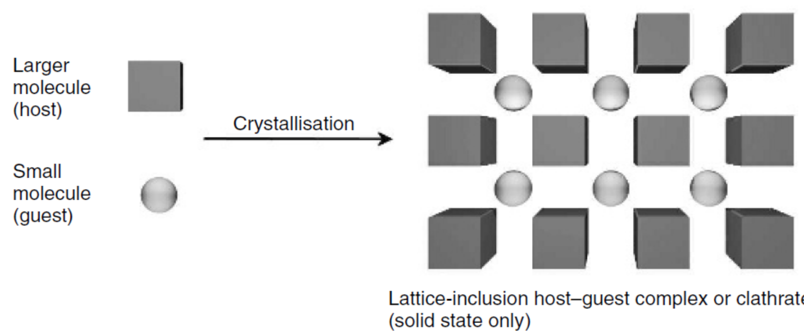
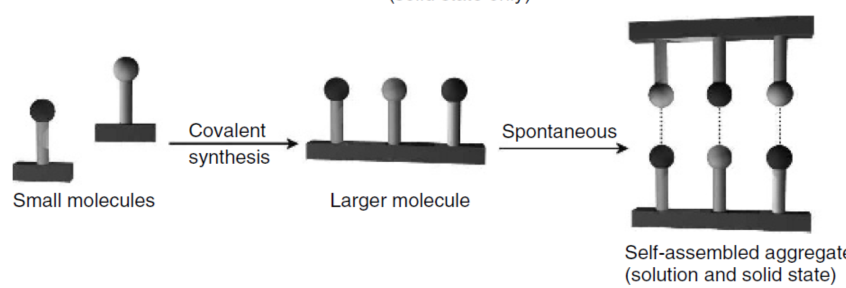


Self-assembly

Spontaneous and reversible association of two or more components to form larger, non-covalently bound aggregates





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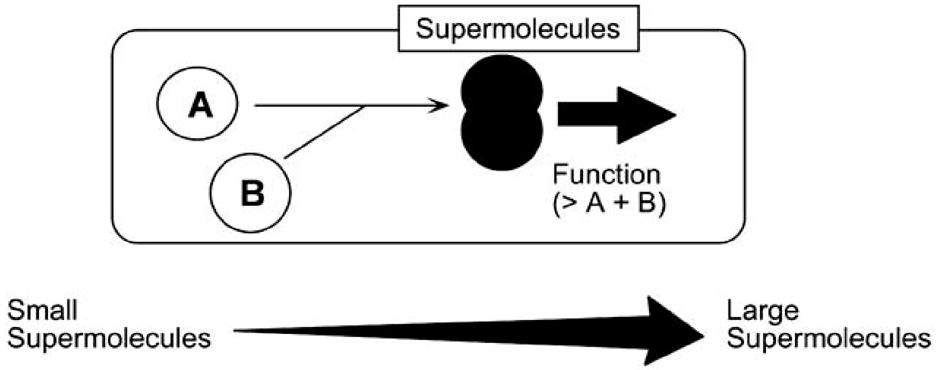

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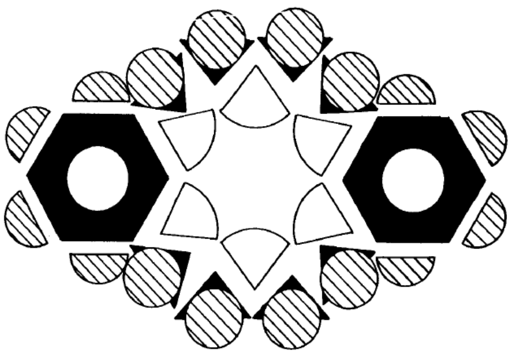
"Chemistry beyond the molecule"

Question: How to investigation of host-guest chemistry without X-ray crystallography?

Cyclic Polyethers and their complexes with metal salts C. J. Pedersen

J. Am. Chem. Soc. **1967**, *89*, 7017–7036

1) Molecular model to predict the size of Cavity ion size from literature



2) Change in IR (wag, twist, rock modes)

Identification of Cyclic Polyethers. The proof of the structure of the cyclic polyethers is based on elementary composition, molecular weight, and nmr spectrum. Some of these data are listed in Table III. All nmr spectra obtained in deuteriochloroform are consistent with the proposed structures as shown for some of the aromatic compounds in Table IV. These spectra establish the absence of terminal groups, such as hydroxyl and alkoxy.

Molecular weight distinguishes compounds having the same composition, such as benzo-9-crown-3 (I) and dibenzo-18-crown-6 (XXVIII) and cyclohexyl-15-crown-5 (VII) and dicyclohexyl-30-crown-10 (XXXIX).

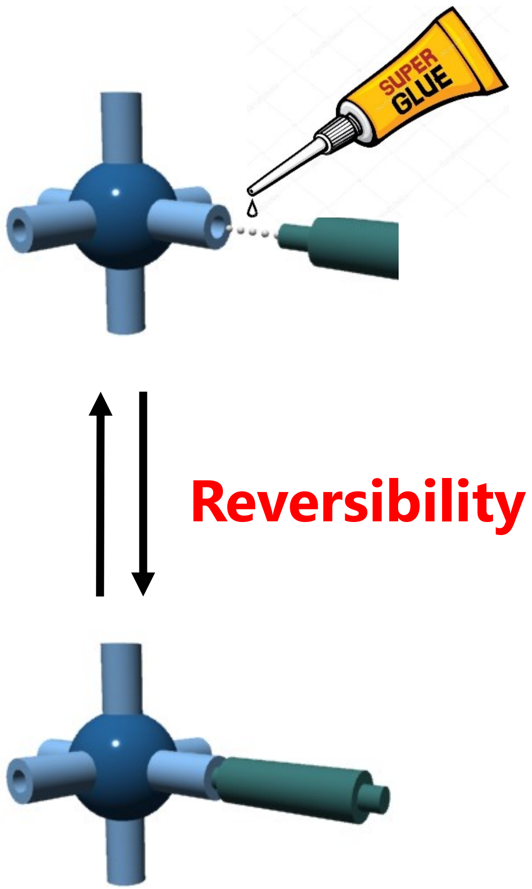
Infrared and ultraviolet spectra were also obtained.

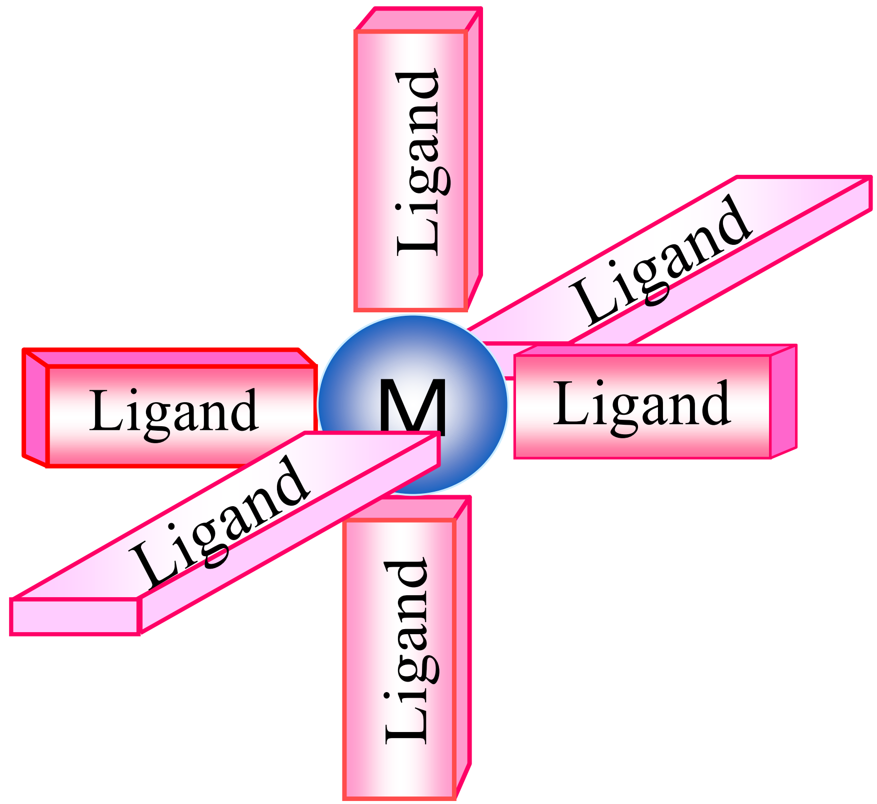
Formation of Salt Complexes. Three criteria are used for the formation of complexes between the cyclic polyethers and salts: (a) changes in the solubilities of the polyethers and salts in different solvents, (b) characteristic changes in the ultraviolet spectra of the aromatic polyethers, and (c) isolation of the complexes as pure compounds. The most positive test is c but some

Today’s Topic

Coordination Compounds

Key : <u>Coordination bond</u> 'glue' to link building blocks

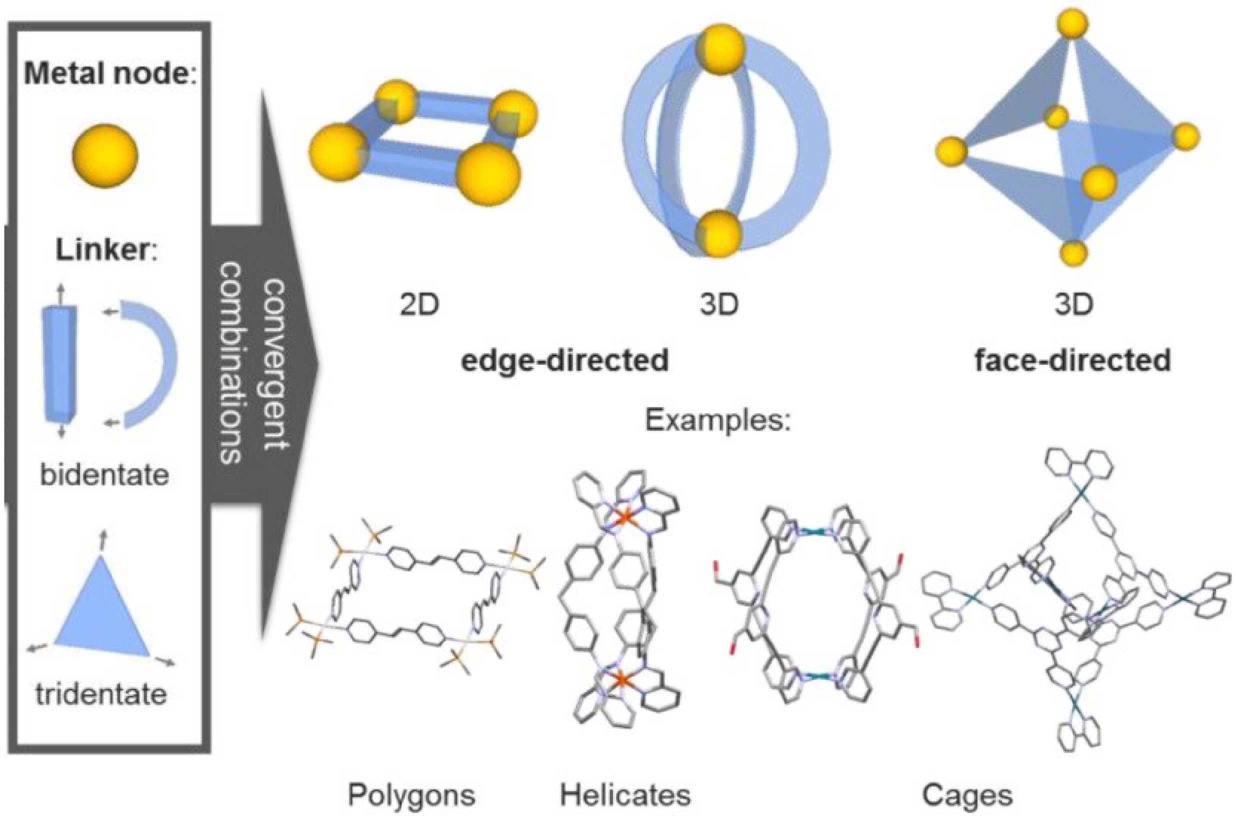




Coordination Compound

Metallo-supramolecular Chemistry

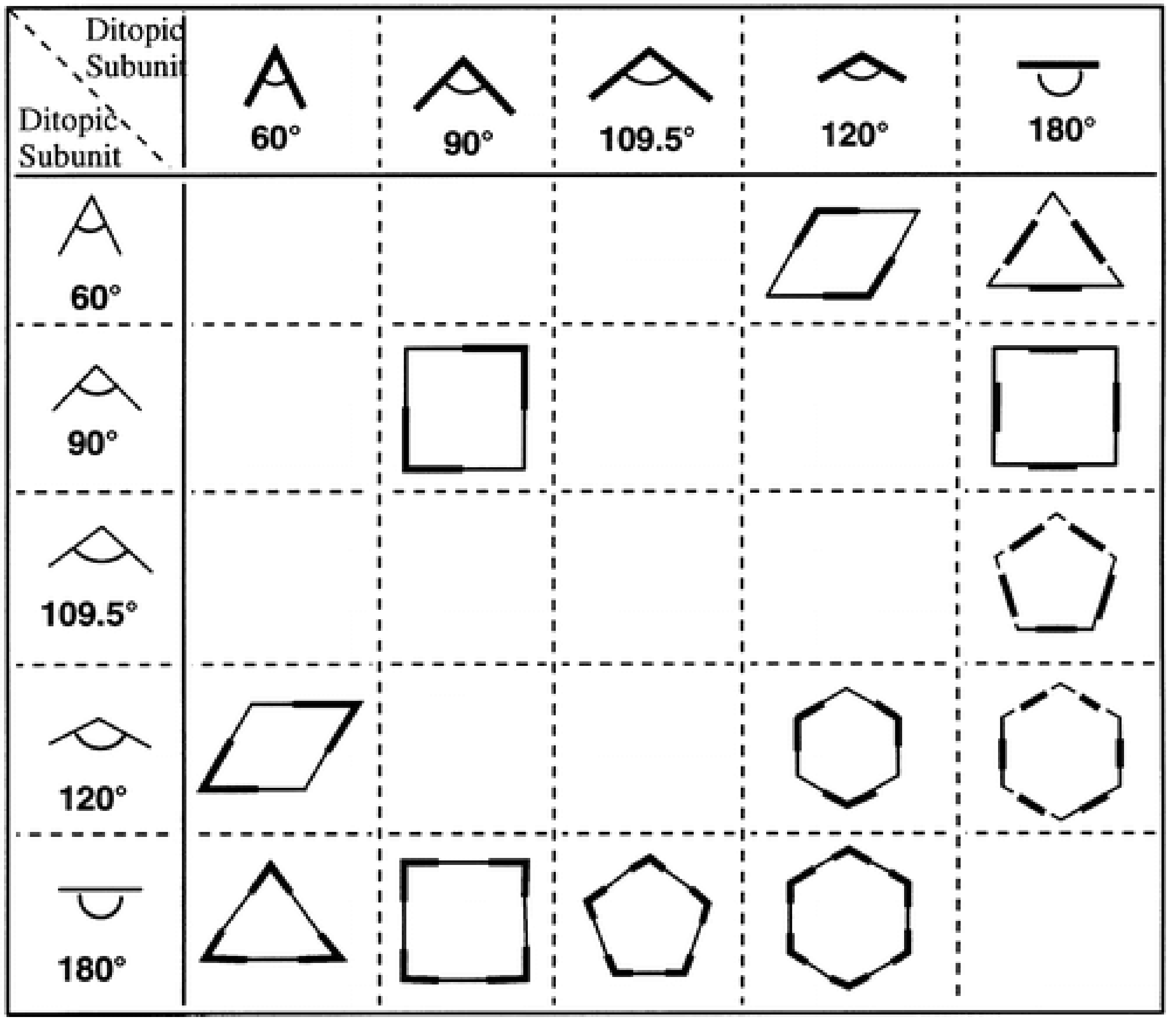
By employing donor groups in **organic molecules** (ligands) that bridge **more than one metal centre** it is possible to construct one-, two-or three dimensional architectures, based on M-L interactions.



Angela Casini* *et al. Theranostics* **2019**, *9*, 3150

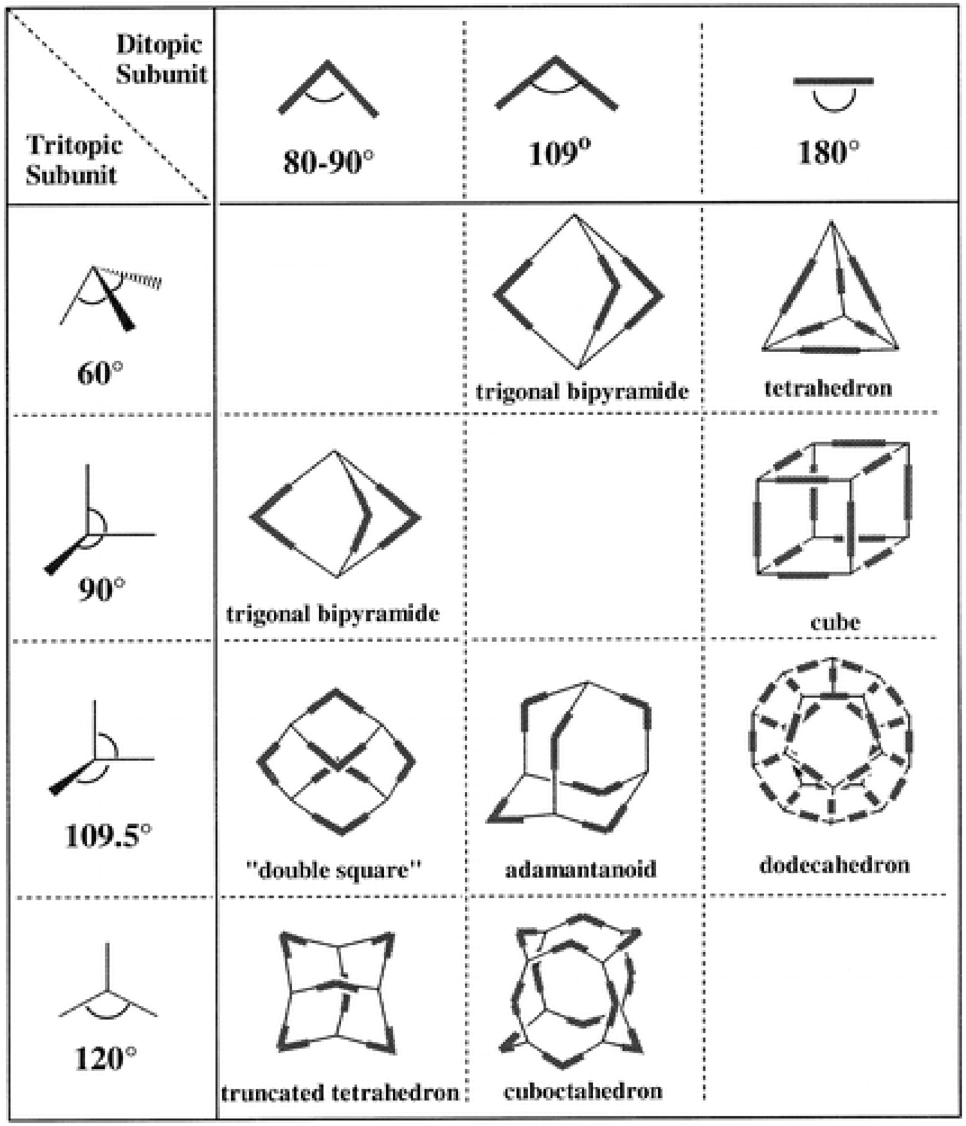
✓ **Discrete Complex with defined molecular Composition**

Molecular Library Model



P. Stang* *et al.* Chem. Rev. **2000**, *100*, 853.

Molecular Library Model



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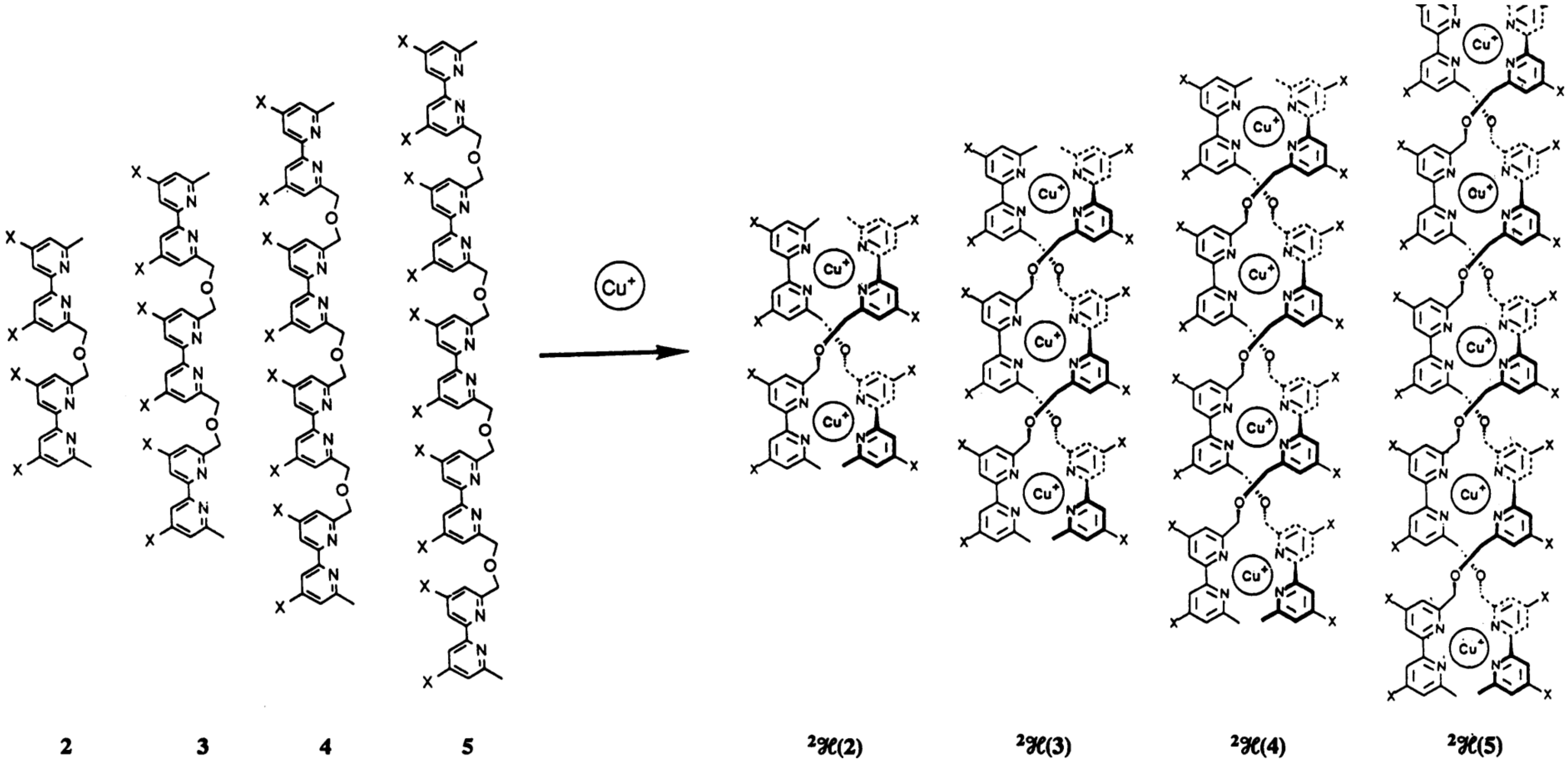
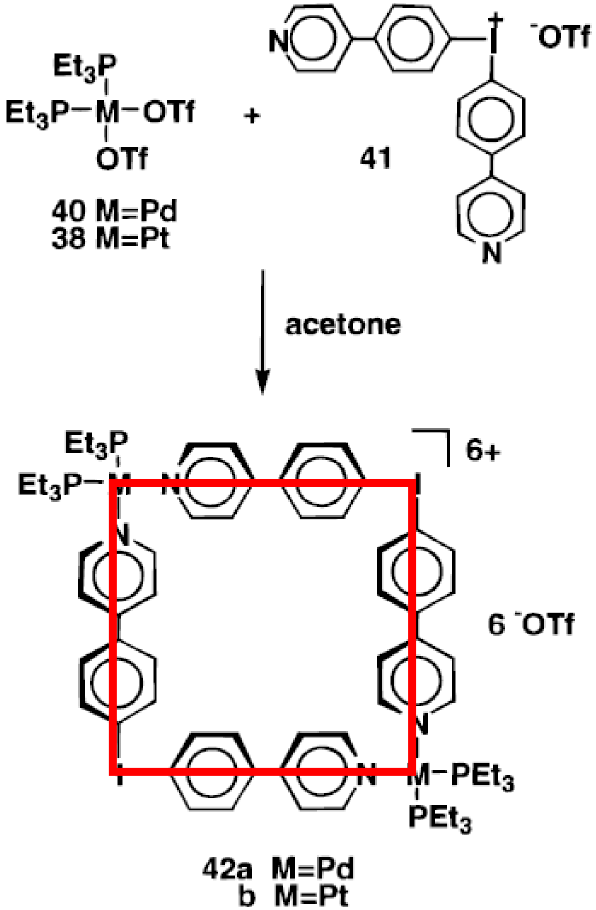
1D Helical chains

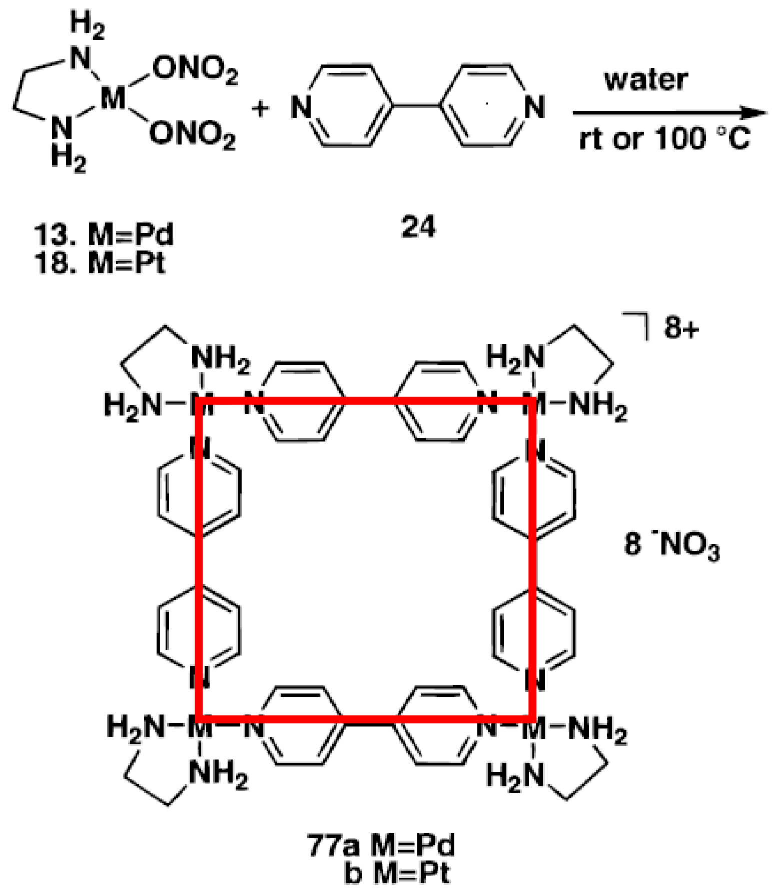


J. M. Lehn* *et al. Proc. Natl. Acad. Sci. USA* **1993**, *90*, 5394

Polygons

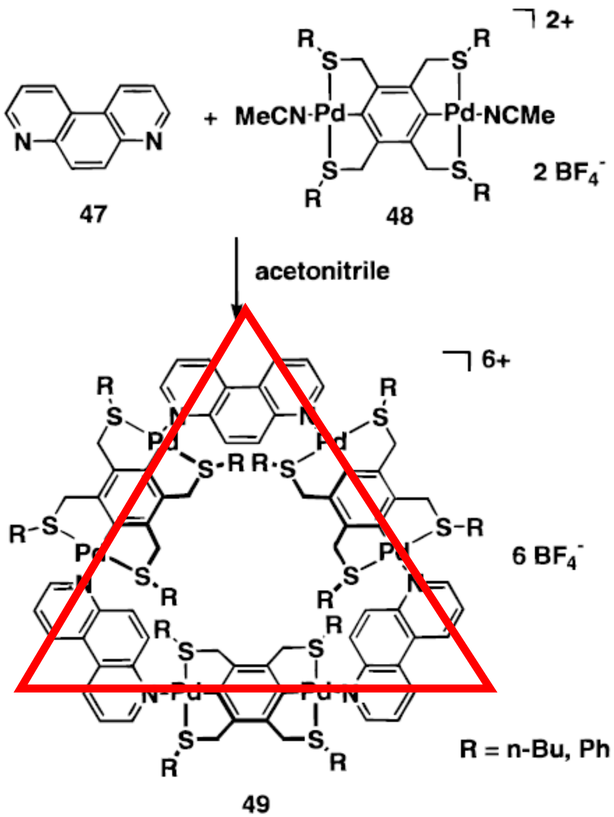


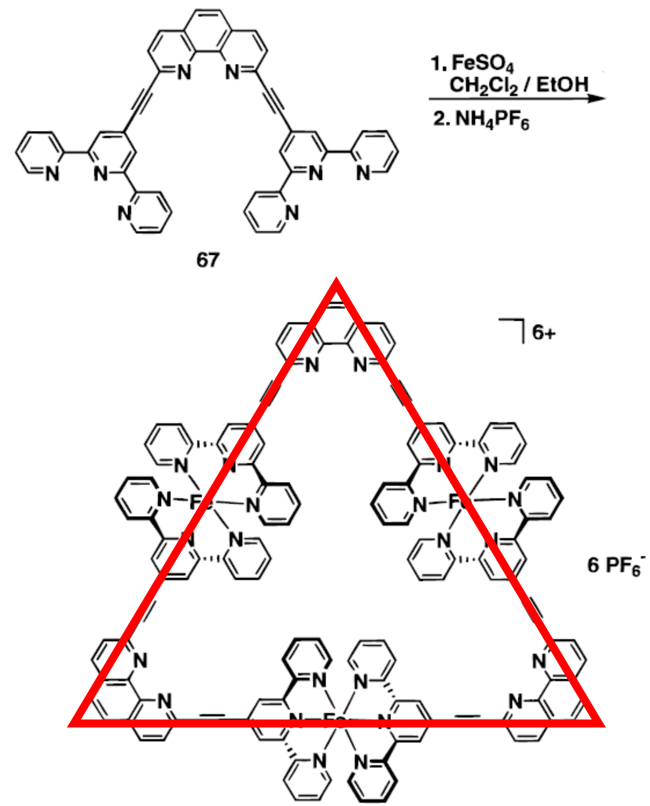
Rhomboid



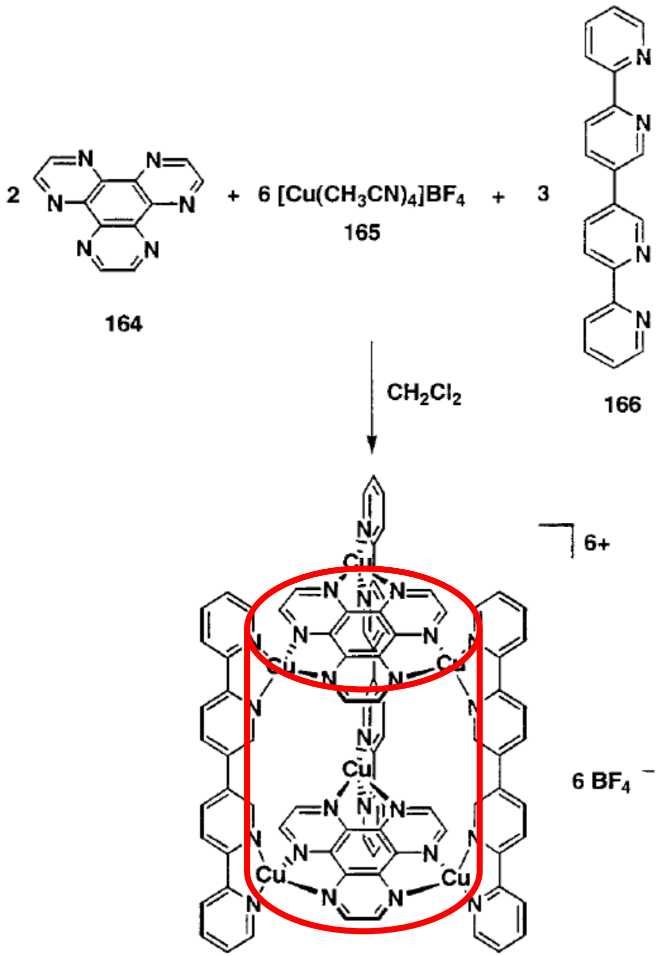
Molecular Square

Molecular Triangle

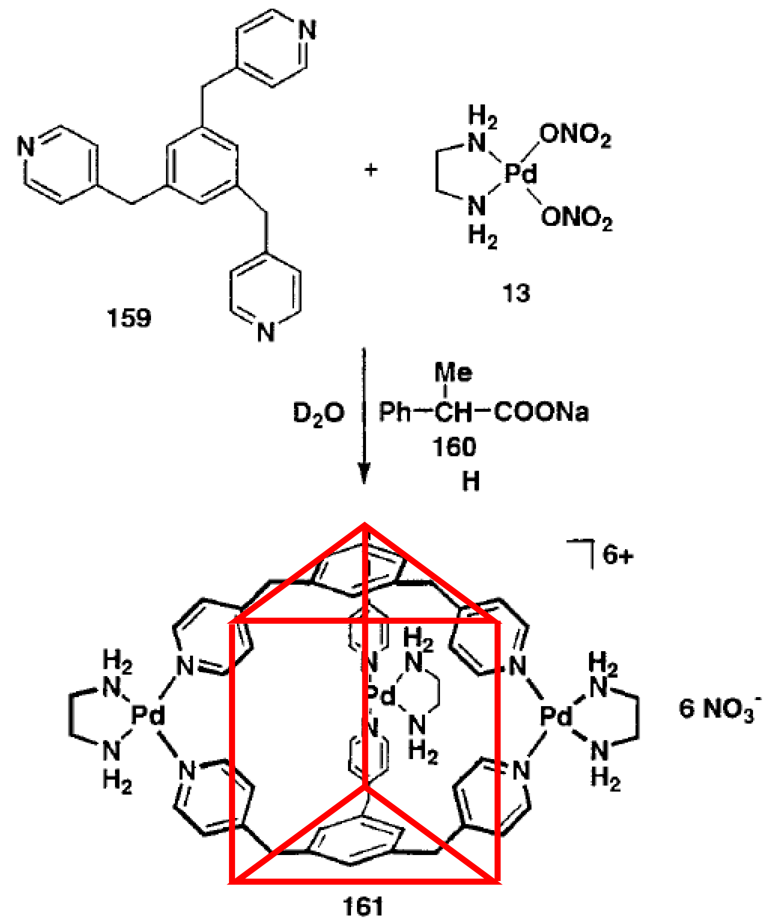




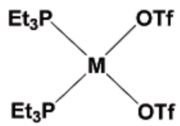
Prism and Cylinder



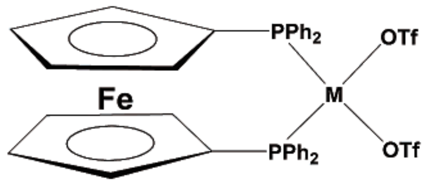
Cylinder



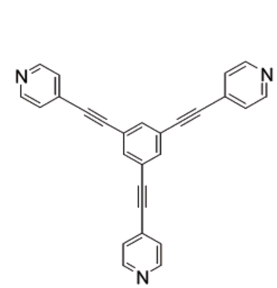
Trigonal Prism



1: M = Pt
2: M = Pd



4: M = Pd
5: M = Pt



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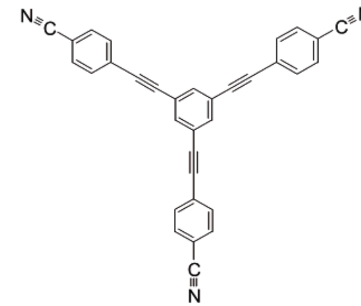

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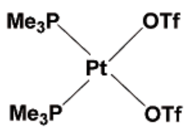

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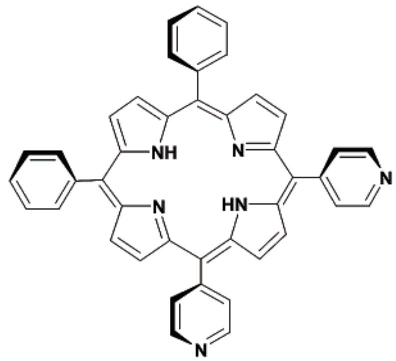

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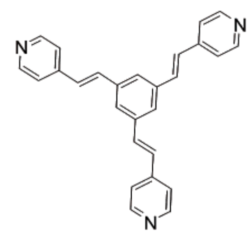

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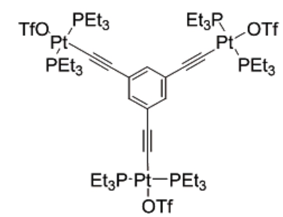
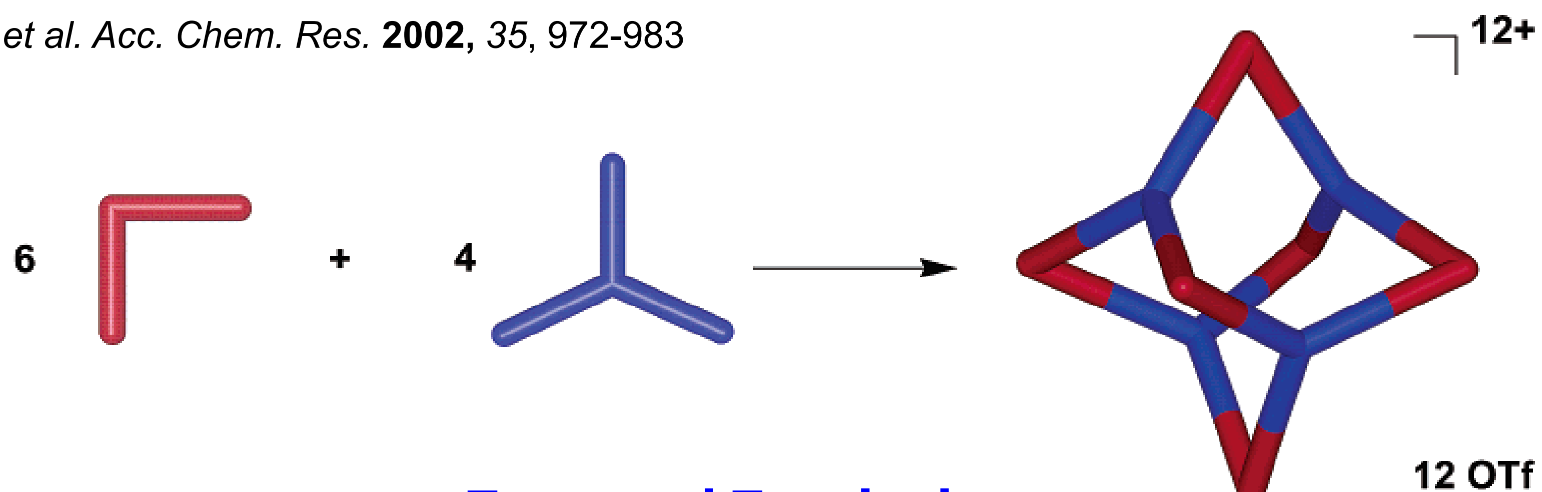
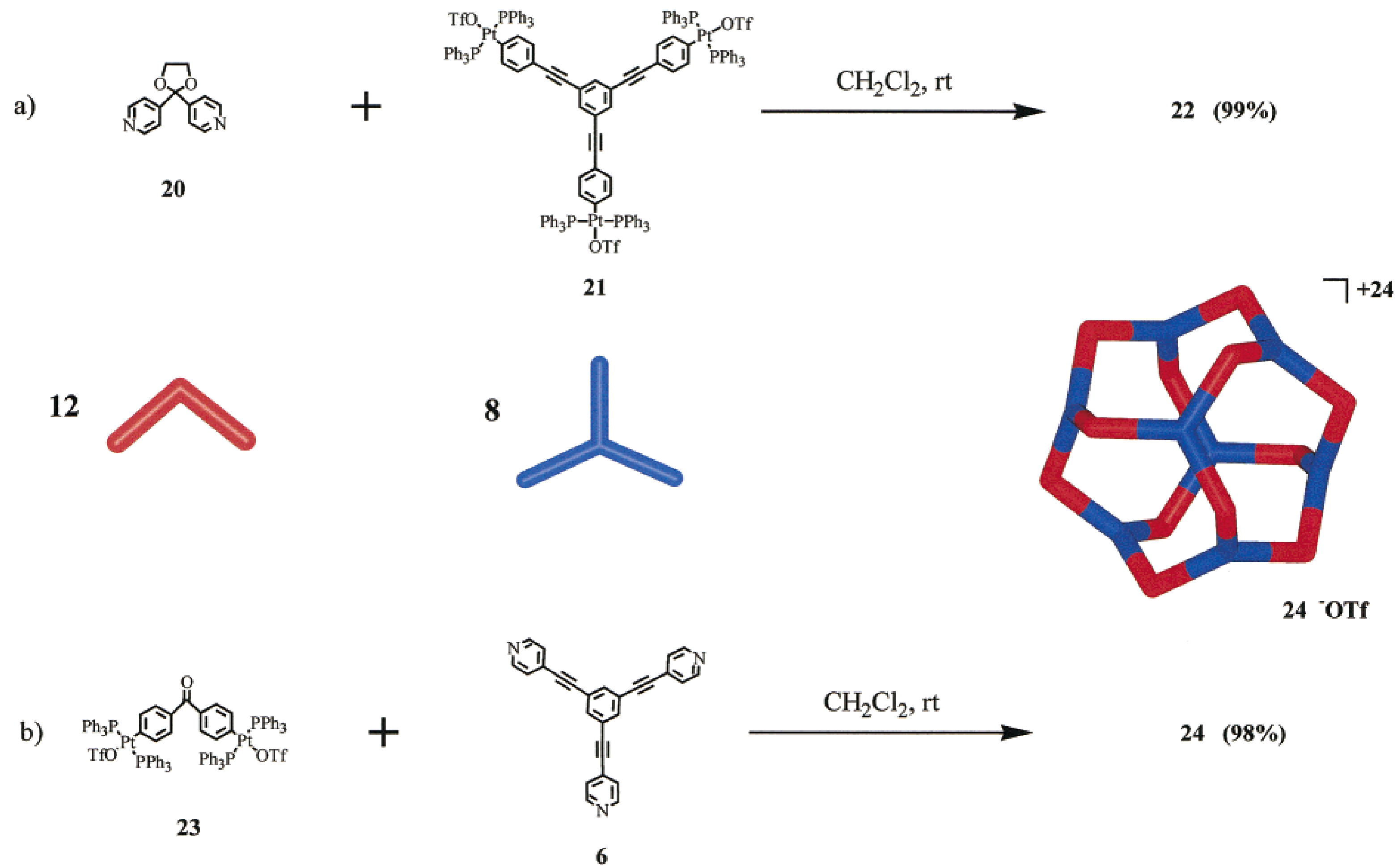


18

P. Stang* *et al. Acc. Chem. Res.* **2002,** *35*, 972-983

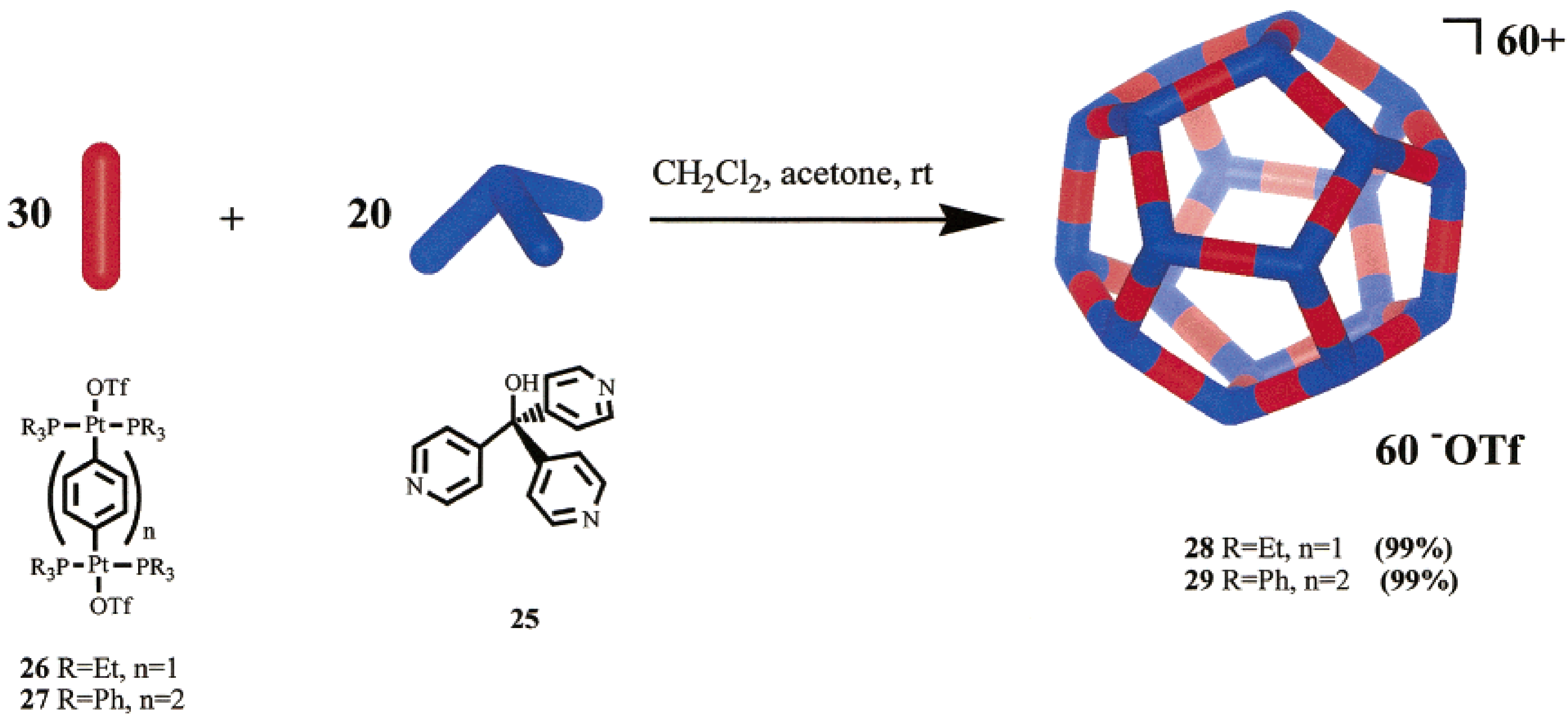


Truncated Tetrahedra



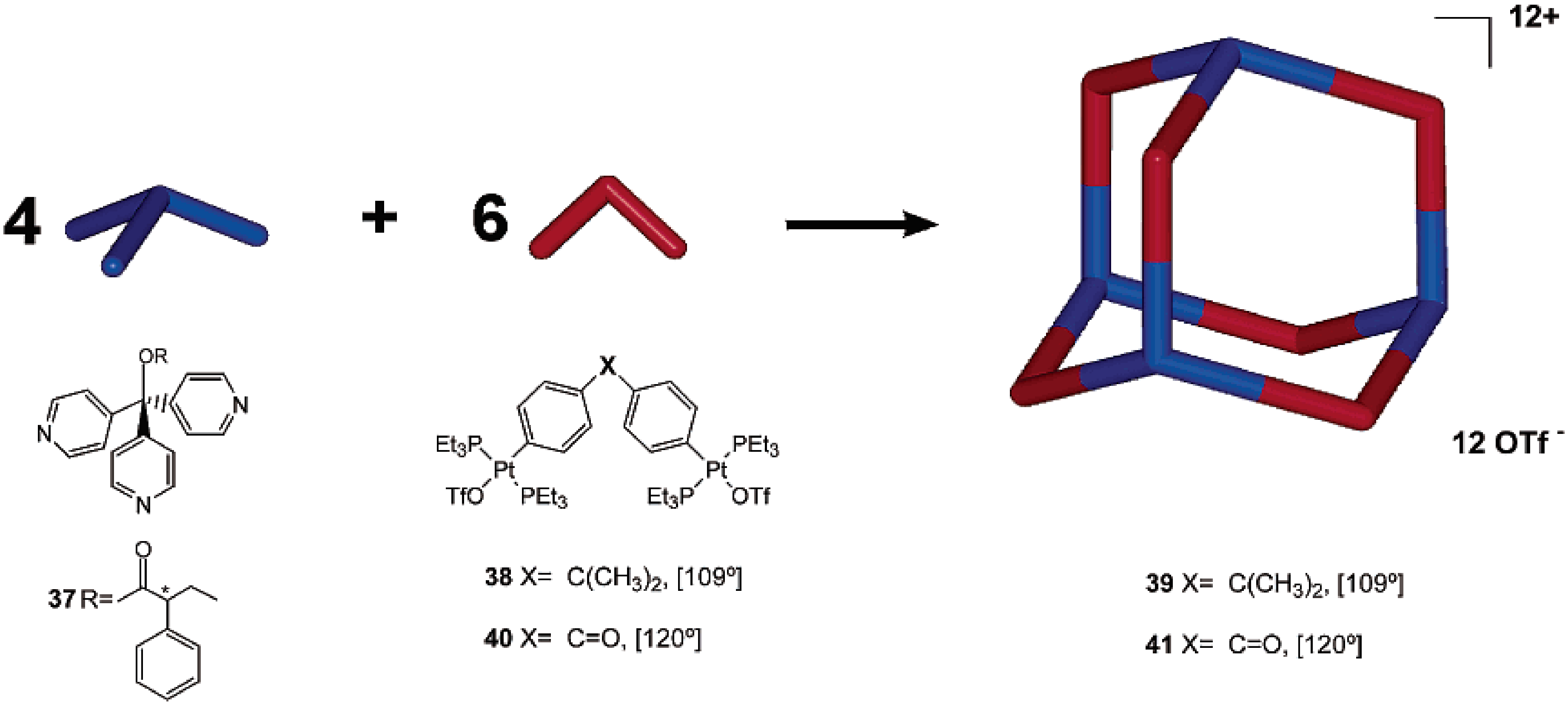
Cuboctahedra

P. Stang* *et al. Acc. Chem. Res.* **2002,** *35*, 972-983



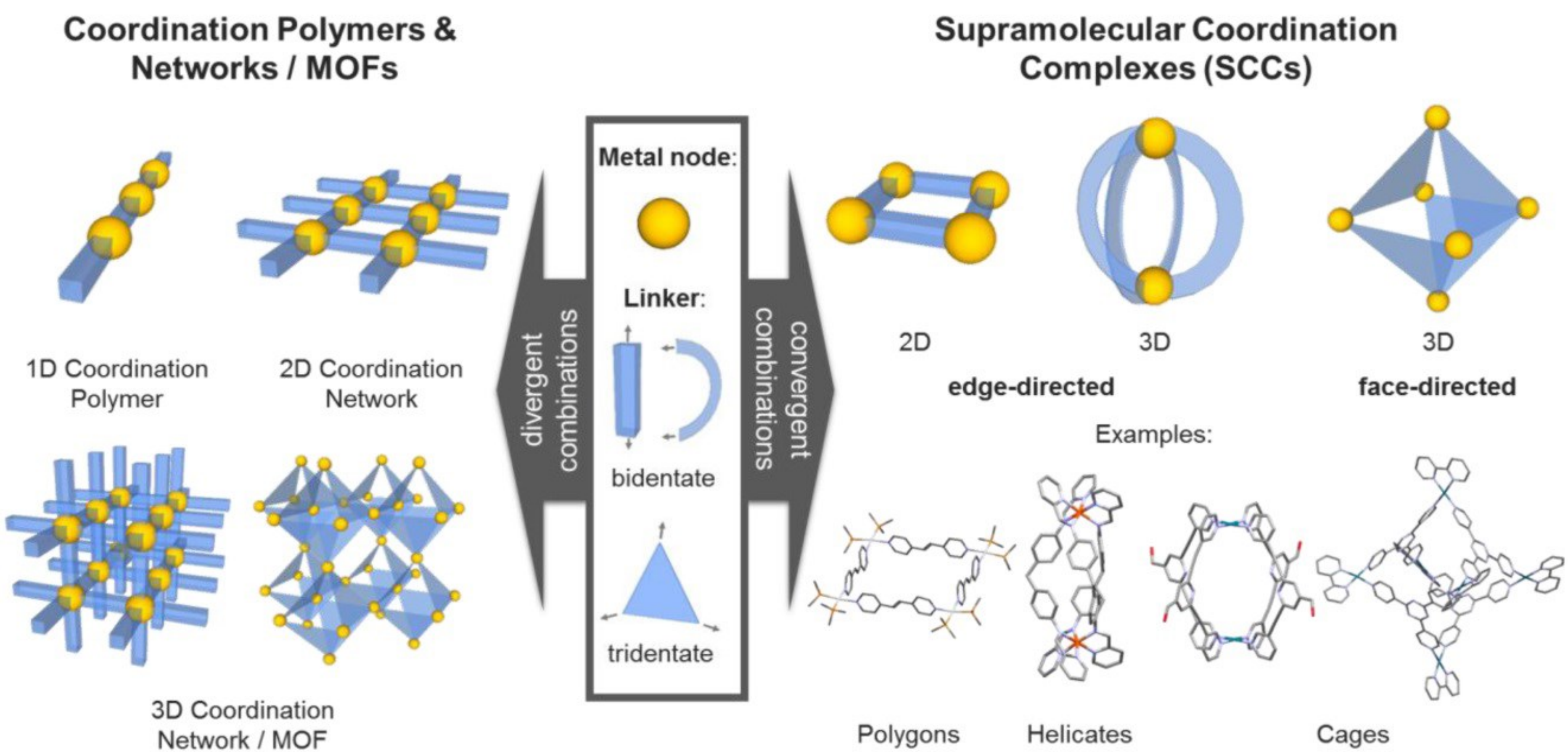
Dodecahedra

P. Stang* *et al. Acc. Chem. Res.* **2002,** *35*, 972-983



Adamantanoids

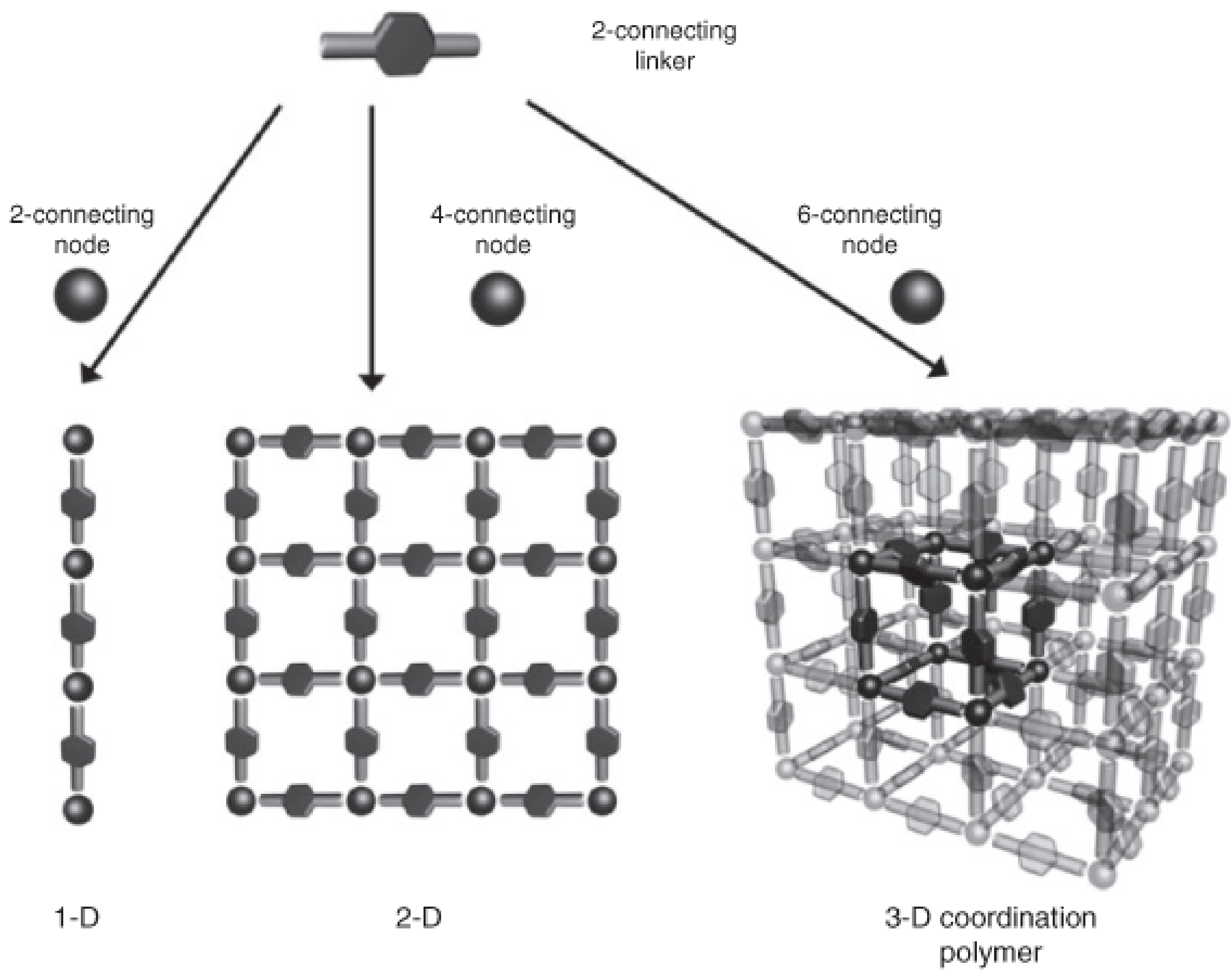
Coordination Complex to Coordination Polymers (CP)



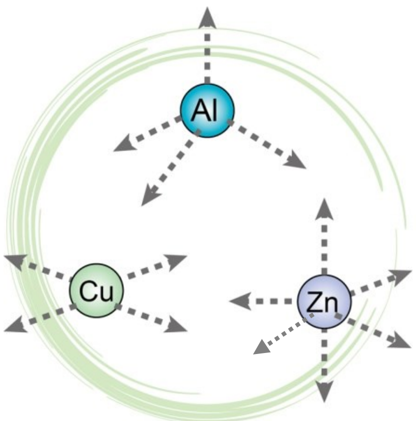
Coordination Compound as Repeating Unit

(a) B. F. Hoskins, R. Robson*; *J. Am. Chem. Soc.* **1990**, *112*, 1546; (b) S. R. Batten, R. Robson*, *Angew. Cheme. Int. Ed.* **1998**, *37*, 1460; (c) Angela Casini* *et al. Theranostics* **2019**, *9*, 3150.

Coordination Polymers (CPs)

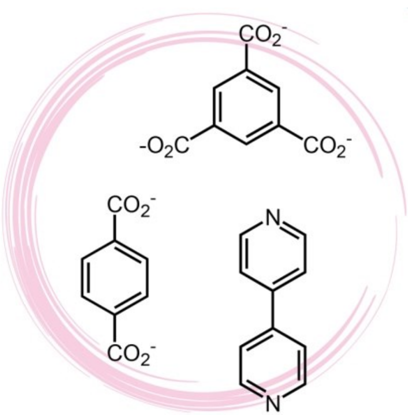


Coordination Polymer (CP): Designable Structure

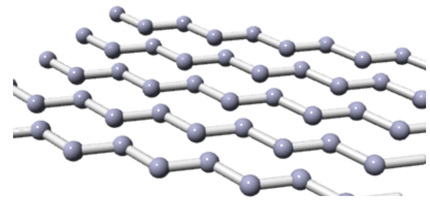


Metal ions

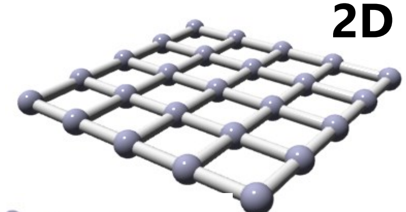
+



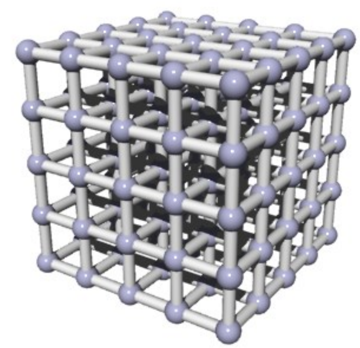
Ligands



1D

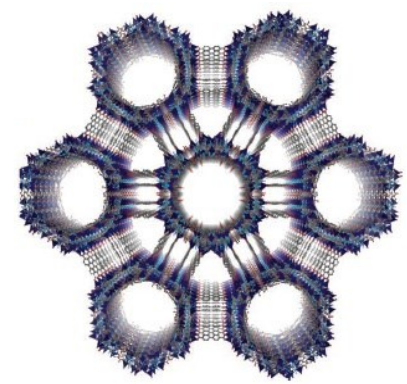


2D



3D

Bio-MOF-1



"Highly ordered framework structures"

B. F. Hoskins, R. Robson*; *J. Am. Chem. Soc.* **1990**, *112*, 1546; S. R. Batten, R. Robson*, *Angew. Cheme. Int. Ed.* **1998**, *37*, 1460;
S. Horike, S. Kitagawa* *et al.*, *Acc. Chem. Res.* **2013**, *46*, 2376; O. M. Yaghi* *et al.*, *Science* **2013**, *341*, 1230444;
G. K. H. Shimizu* *et al.*, *Science*, **2013**, *341*, 354.

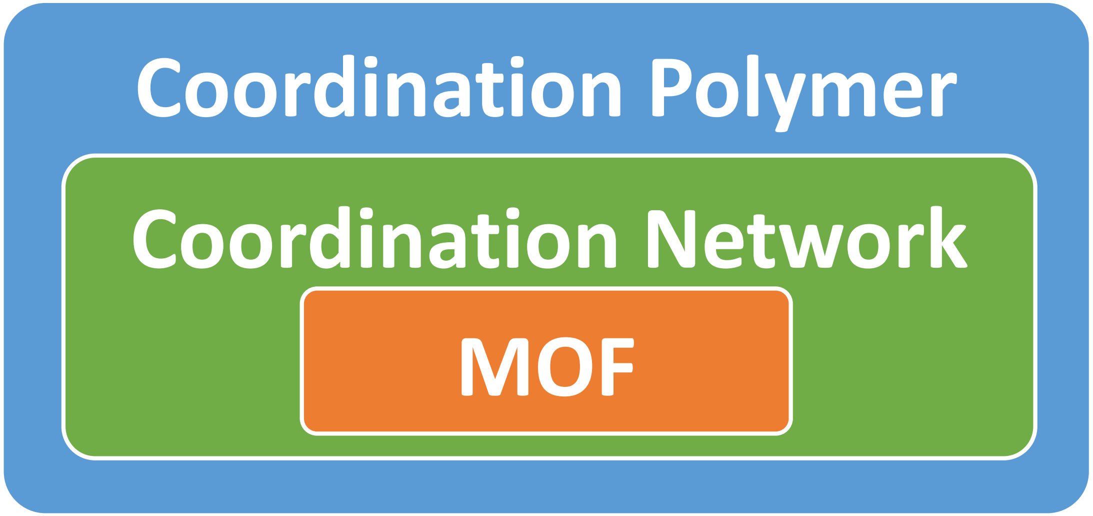
Definitions (IUPAC)

❖ **Coordination Polymers (CPs)** is a "*coordination compound with repeating coordination entities extending in **1**, **2**, or **3** dimensions*"

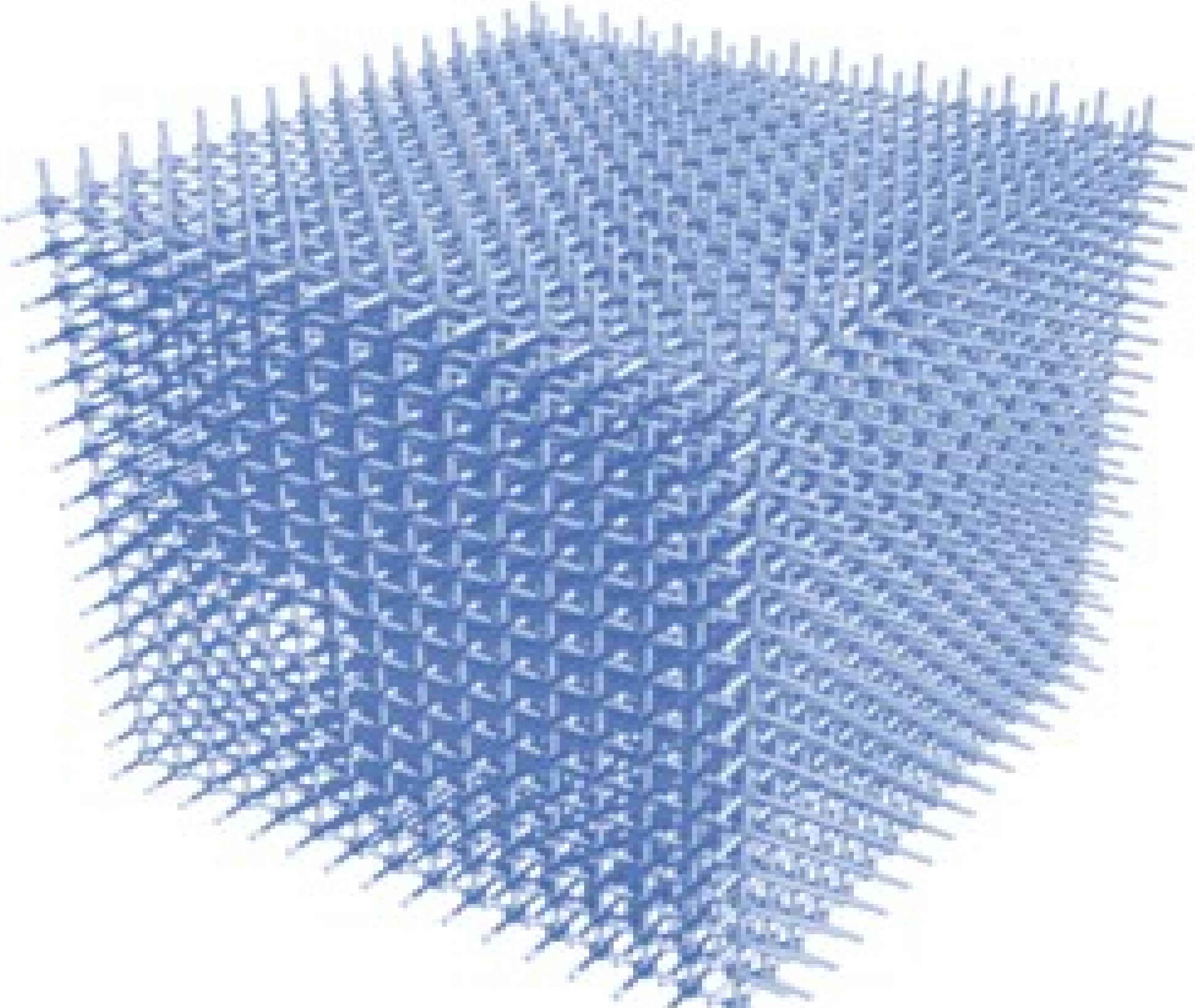
❖ **Coordination Network** is "*a coordination compound extending through repeating coordination entities in **2** or **3** dimensions*"

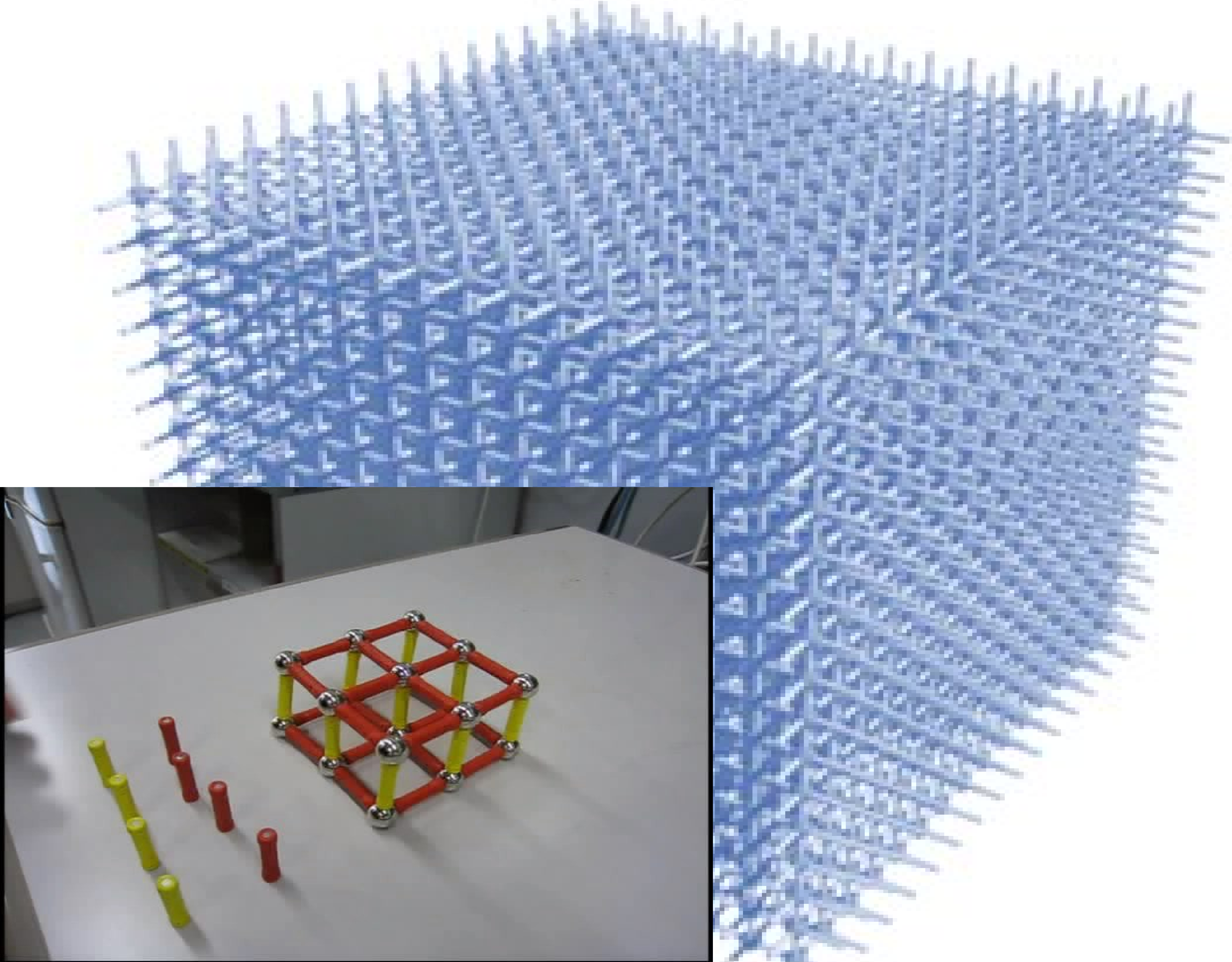
❖**Metal–Organic Framework (MOF)** is a subset of coordination networks, defined as "*coordination network with **organic ligands** containing **potential voids***"

❖ **Neither CP nor MOFs need to be crystalline.**

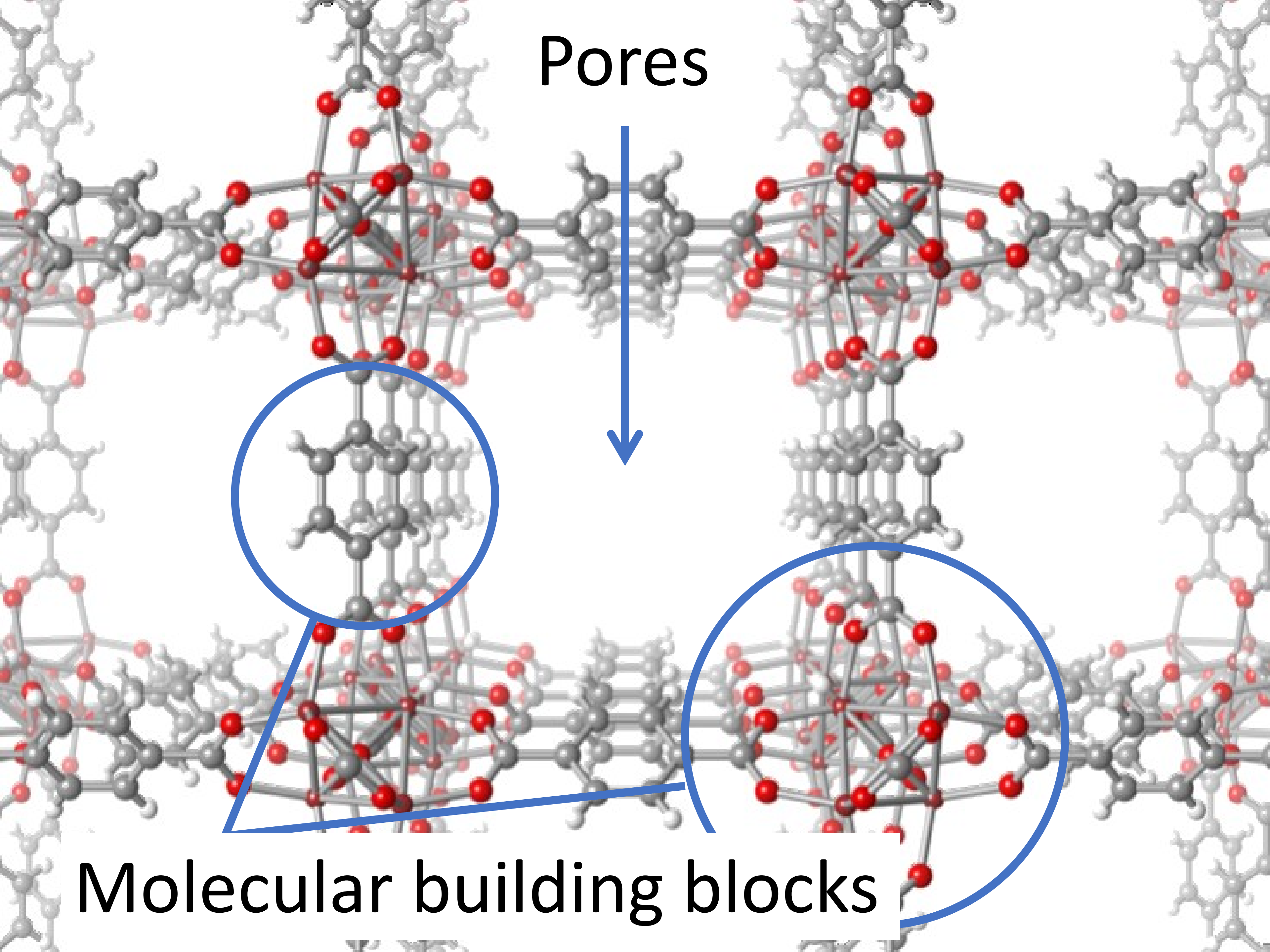


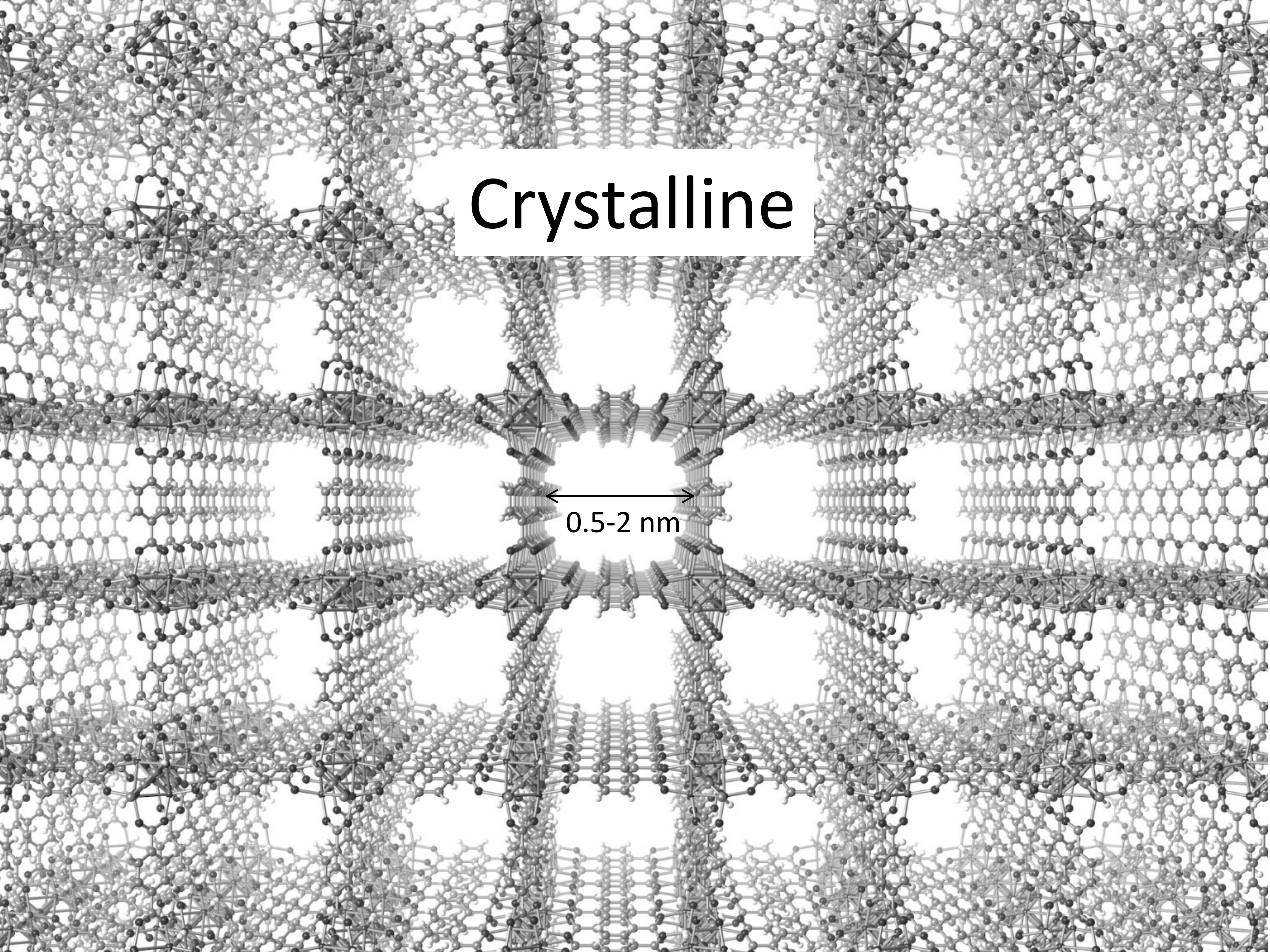
S. R. Batten, N. R. Champness, X.-M. Chen, J. G.-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M. P. Suh and J. Reedijk, *Pure Appl. Chem.* **2013**, *85*, 1715.

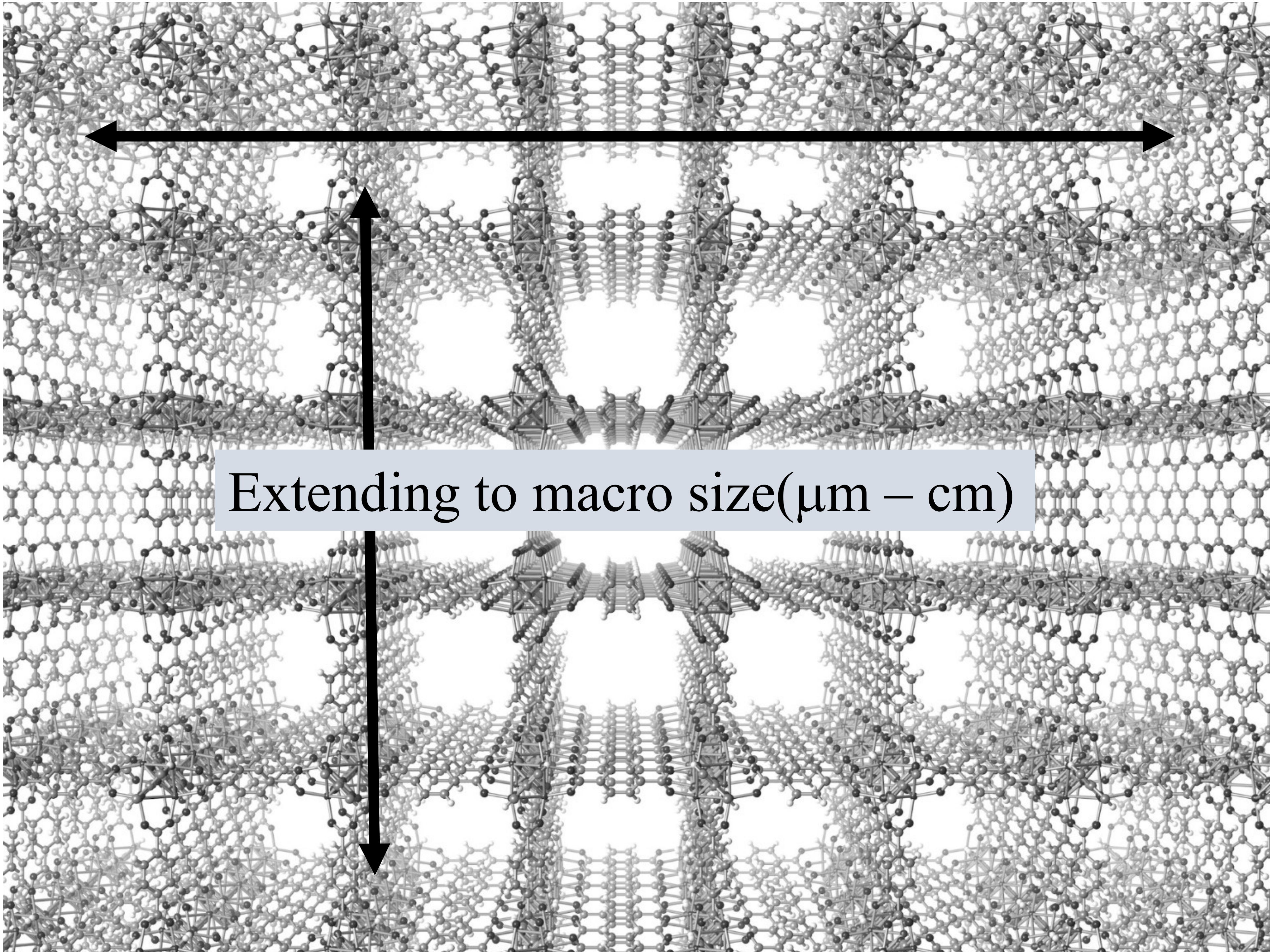


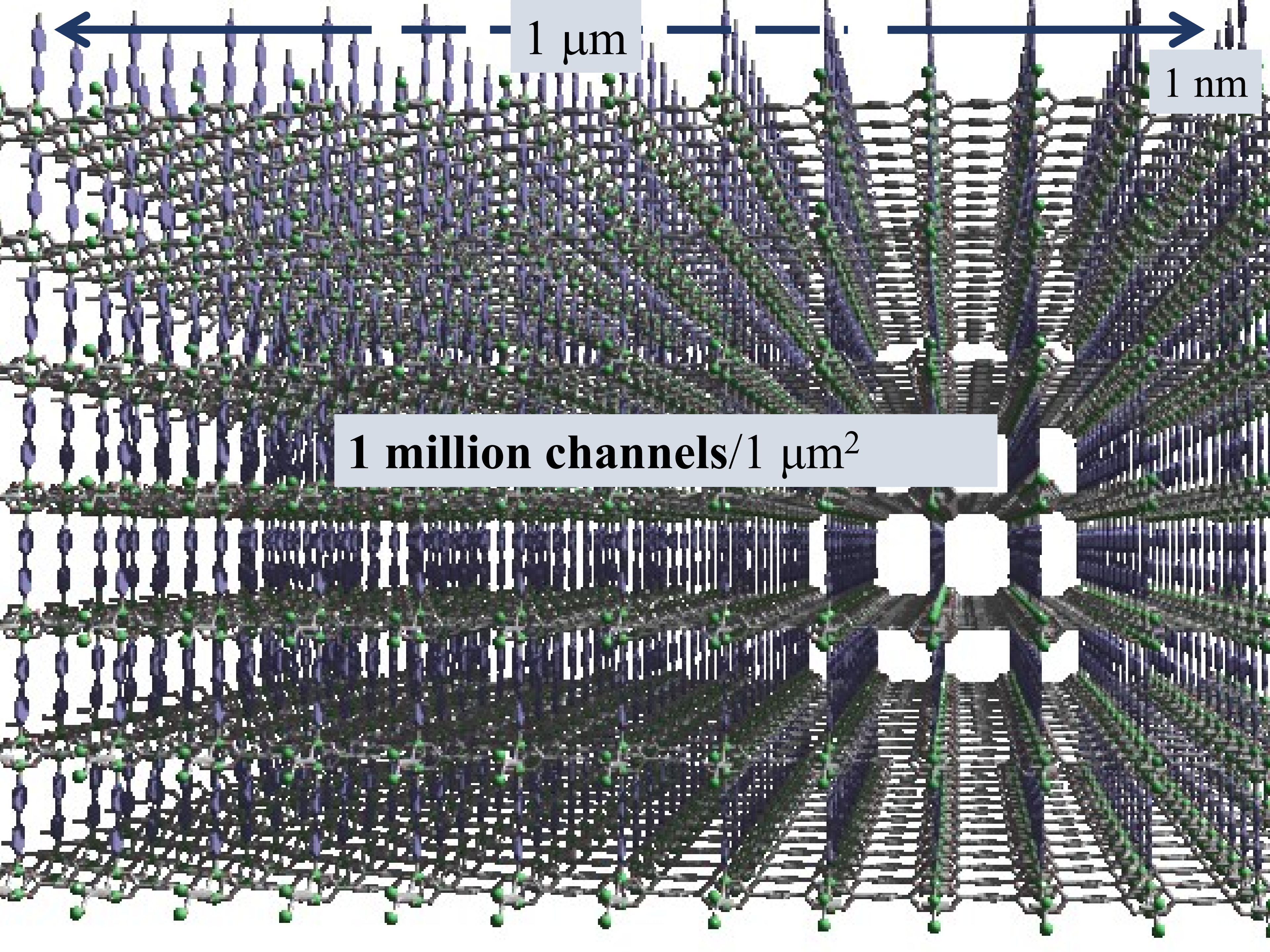



50


Pores
Molecular building blocks


Crystalline
0.5-2 nm


Extending to macro size(μm – cm)

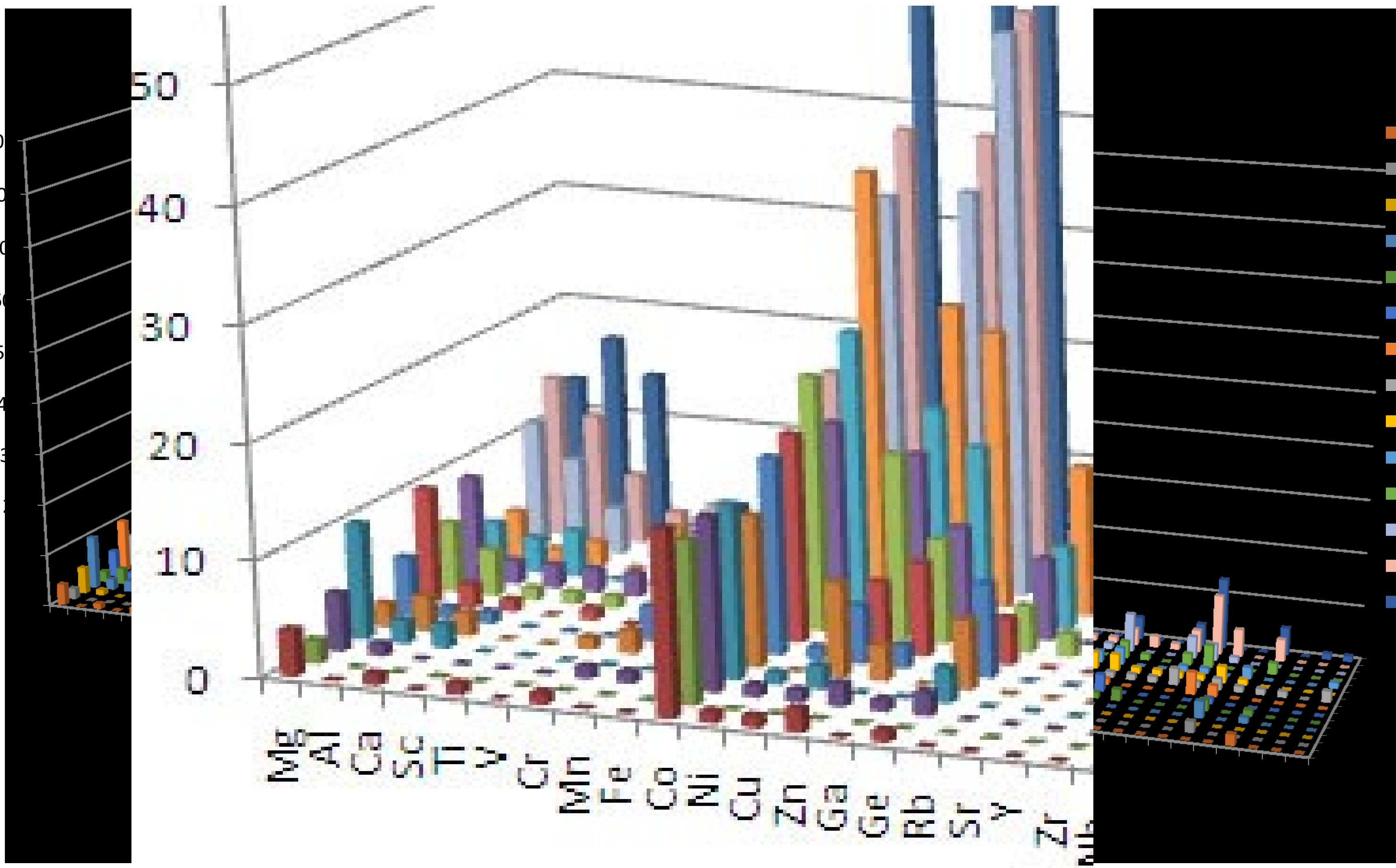


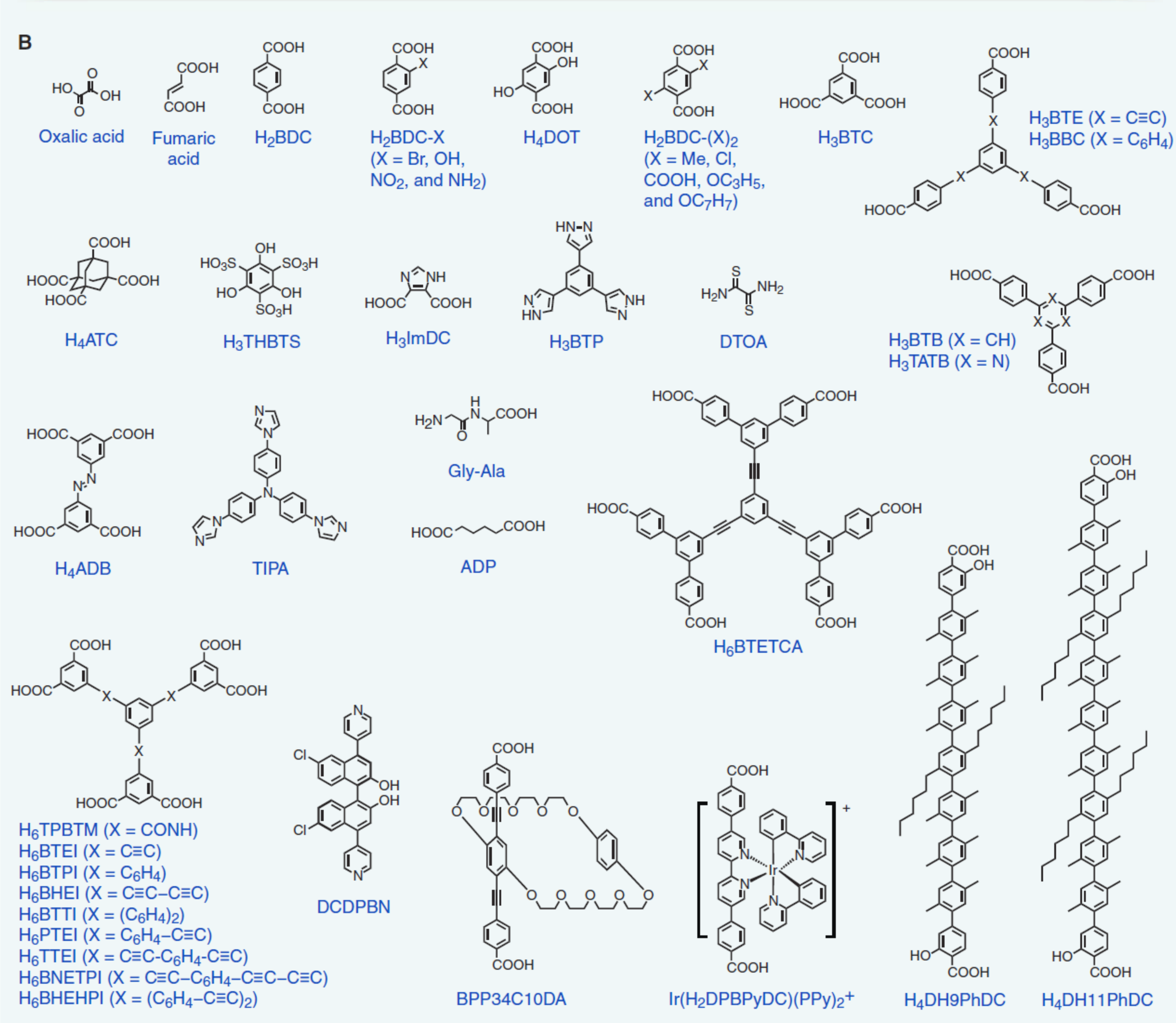
1 μm
1 nm
1 million channels/1 μm^2

PCPs / MOFs

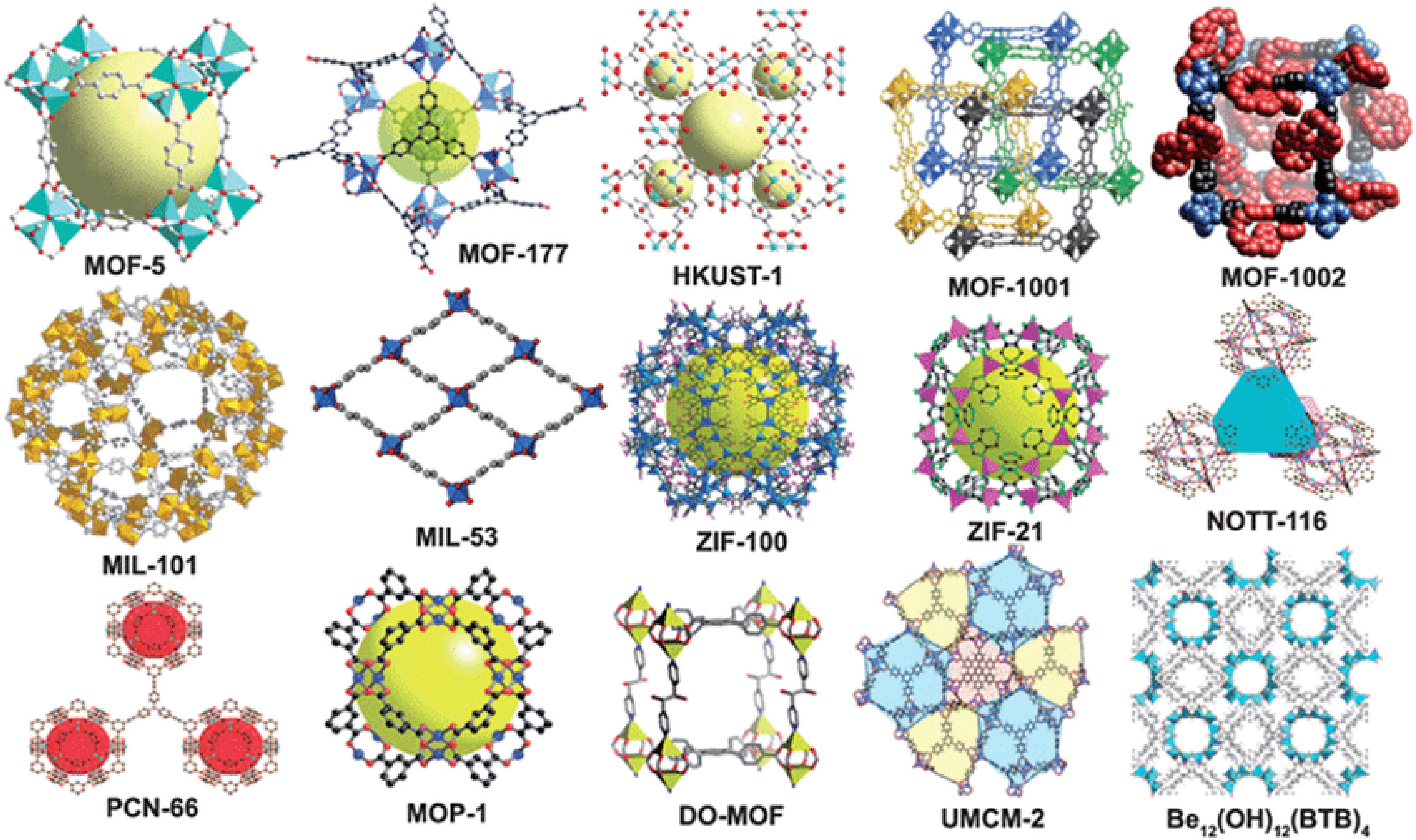
organic molecules and metal ions

Metal ion as a connector




B
Oxalic acid
Fumaric acid
H_2BDC
H_2BDC-X (X = Br, OH, NO_2, and NH_2)
H_4DOT
H_2BDC-(X)$_2$ (X = Me, Cl, COOH, OC_3H_5, and OC_7H_7)
H_3BTC
H_3BTE (X = C≡C)
H_3BBC (X = C_6H_4)
H_4ATC
H_3THBTS
H_3ImDC
H_3BTP
DTOA
H_3BTB (X = CH)
H_3TATB (X = N)
H_4ADB
TIPA
Gly-Ala
ADP
$H_6BTETCA$
H_6TPBTM (X = CONH)
H_6BTEI (X = C≡C)
H_6BTPI (X = C_6H_4)
H_6BHEI (X = C≡C–C≡C)
H_6BTTI (X = $(C_6H_4)_2$)
H_6PTEI (X = C_6H_4–C≡C)
H_6TTEI (X = C≡C-C_6H_4-C≡C)
$H_6BNETPI$ (X = C≡C–C_6H_4–C≡C–C≡C)
$H_6BHEHPI$ (X = $(C_6H_4–C≡C)_2$)
DCDPBN
BPP34C10DA
$Ir(H_2DPBPyDC)(PPy)_2^+$
$H_4DH9PhDC$
$H_4DH11PhDC$

Various MOF structures



Molecules **2019**, *24*, 4525

Research Activity in MOFs/CP area