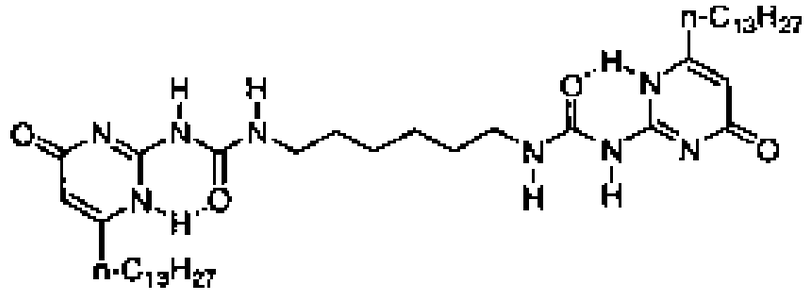
examples of supramolecular chemistry

A



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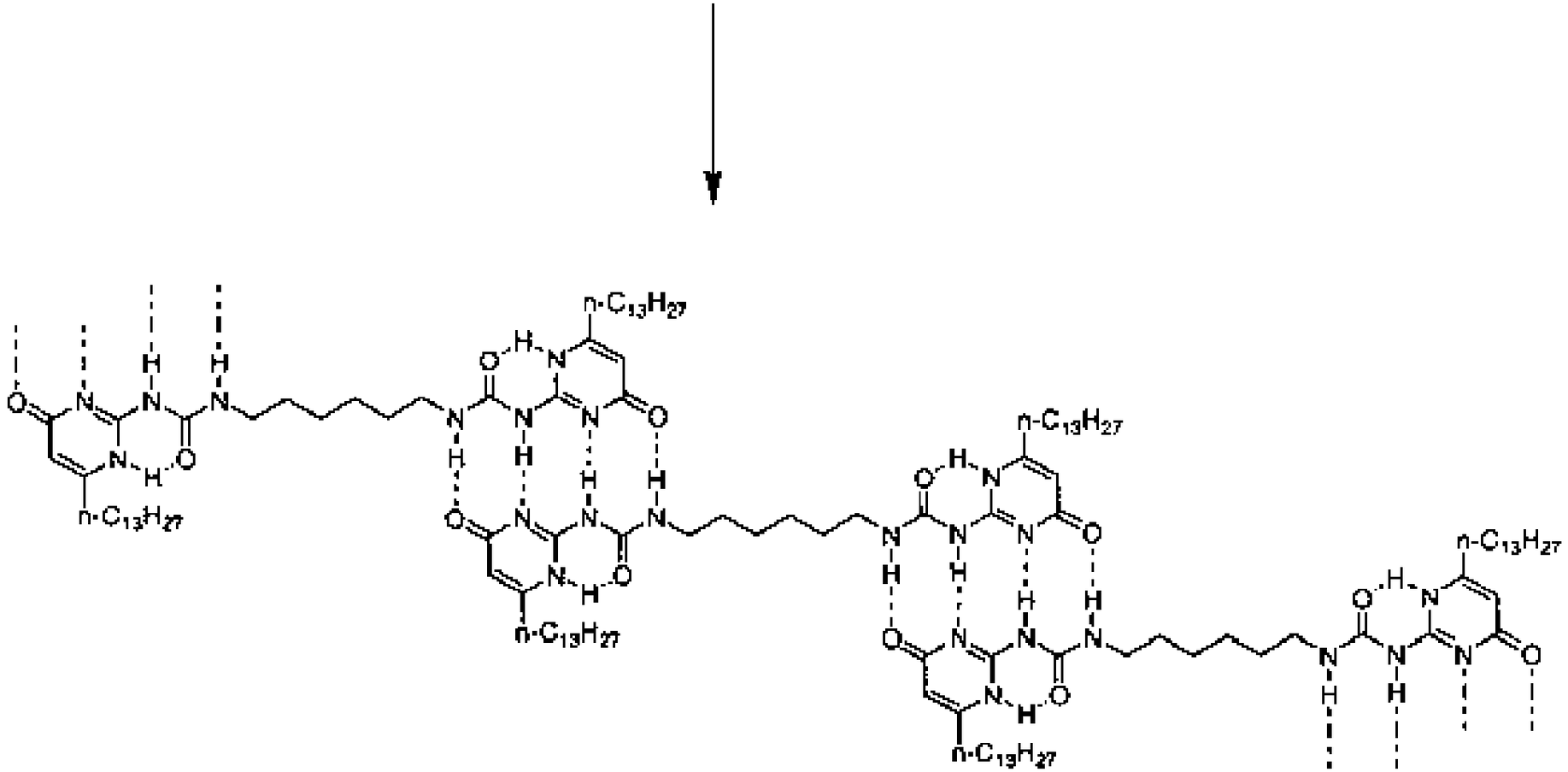
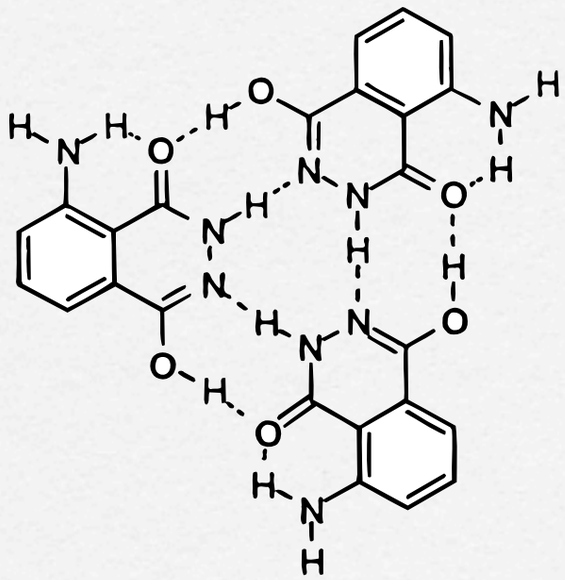
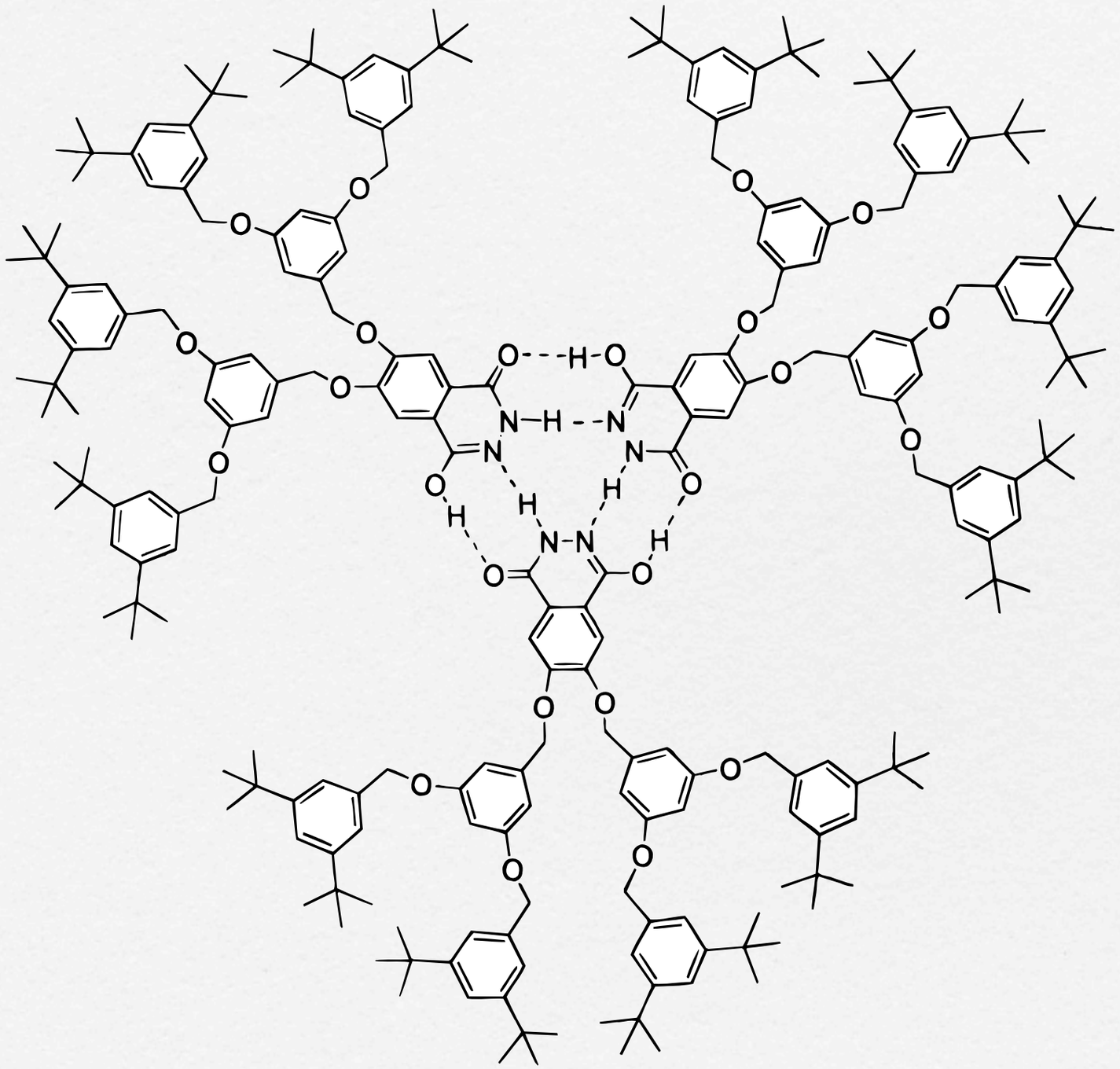
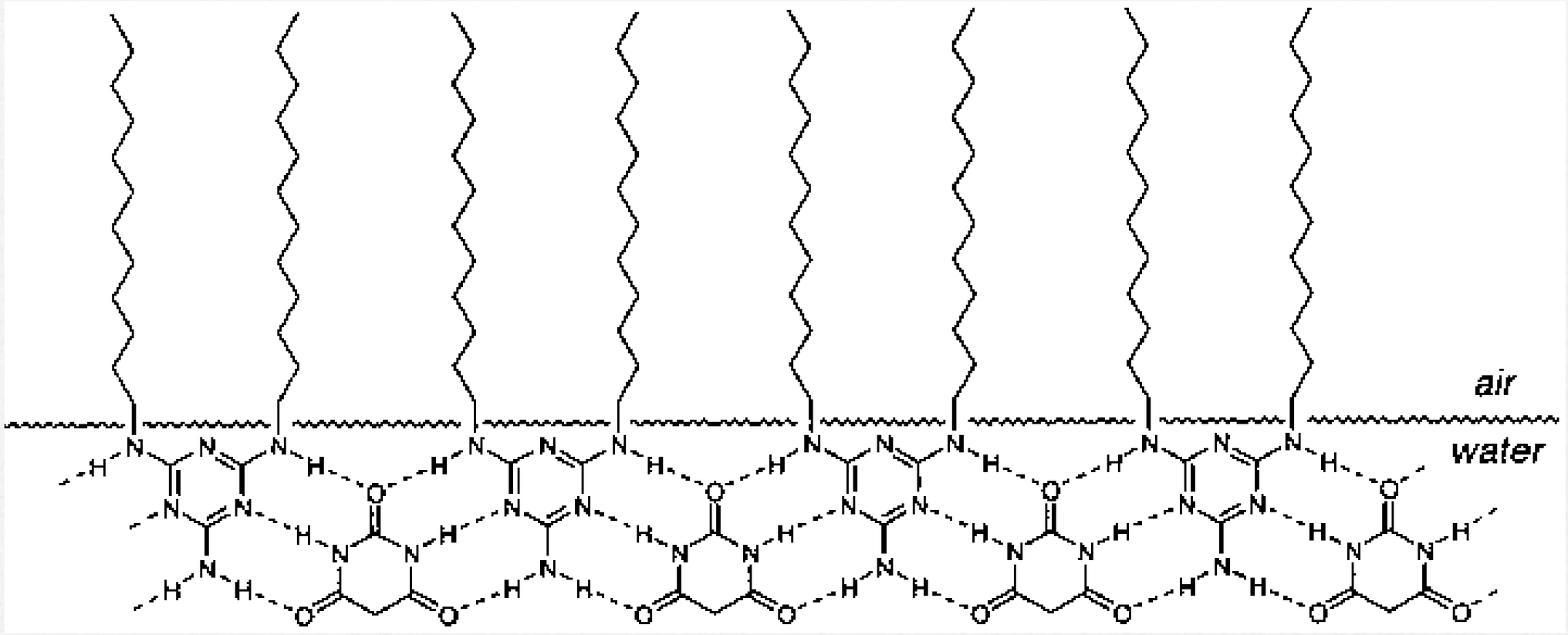
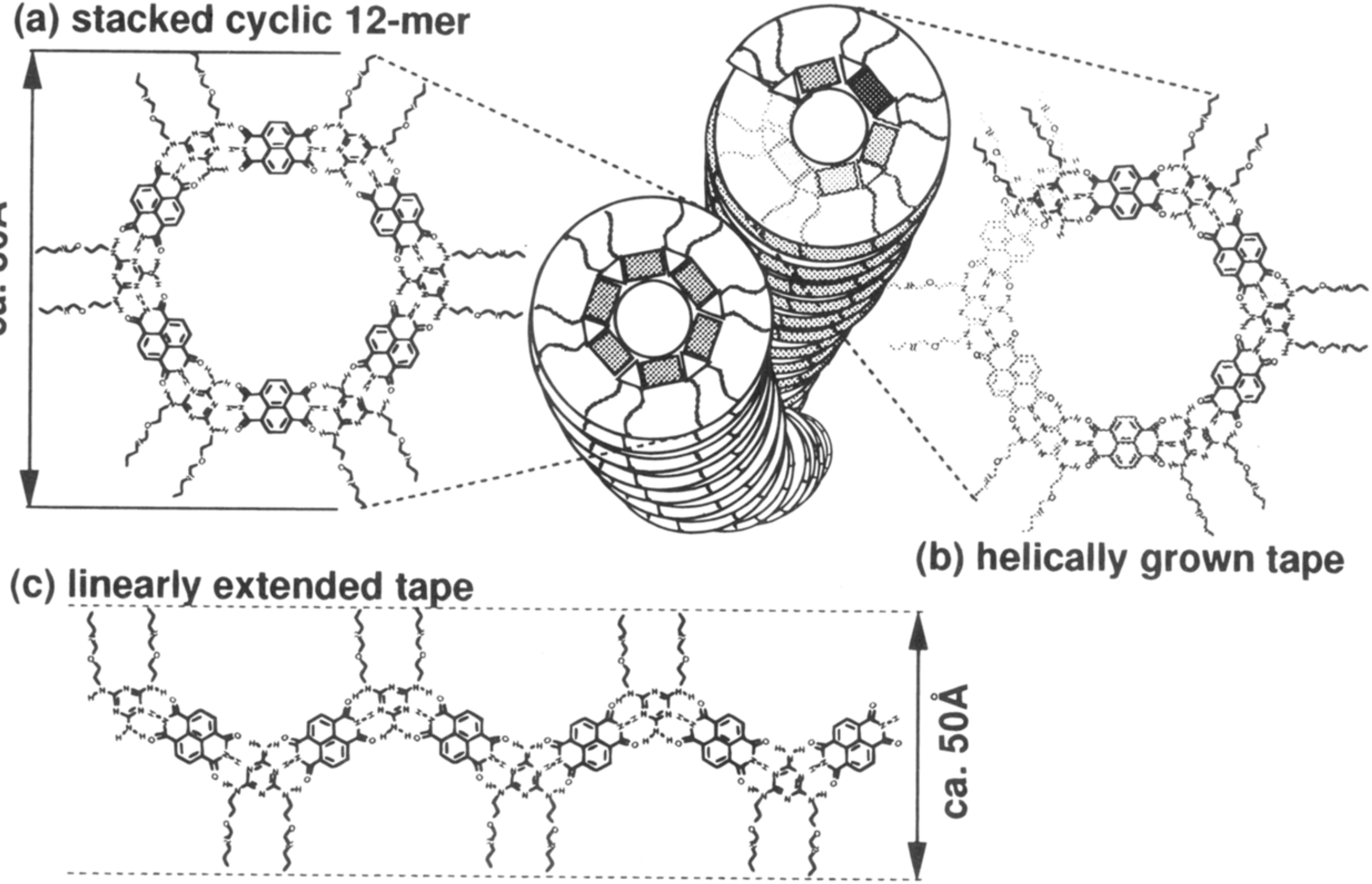







air
water


(a) stacked cyclic 12-mer
ca. 80Å
(b) helically grown tape
(c) linearly extended tape
ca. 50Å

MOFs

Metal-Organic Frameworks

MOFs – what is it ?

- „Metallorganic networks“

  → frames of a metal center (Atom or Cluster), which are connected coordinative by an organic linker

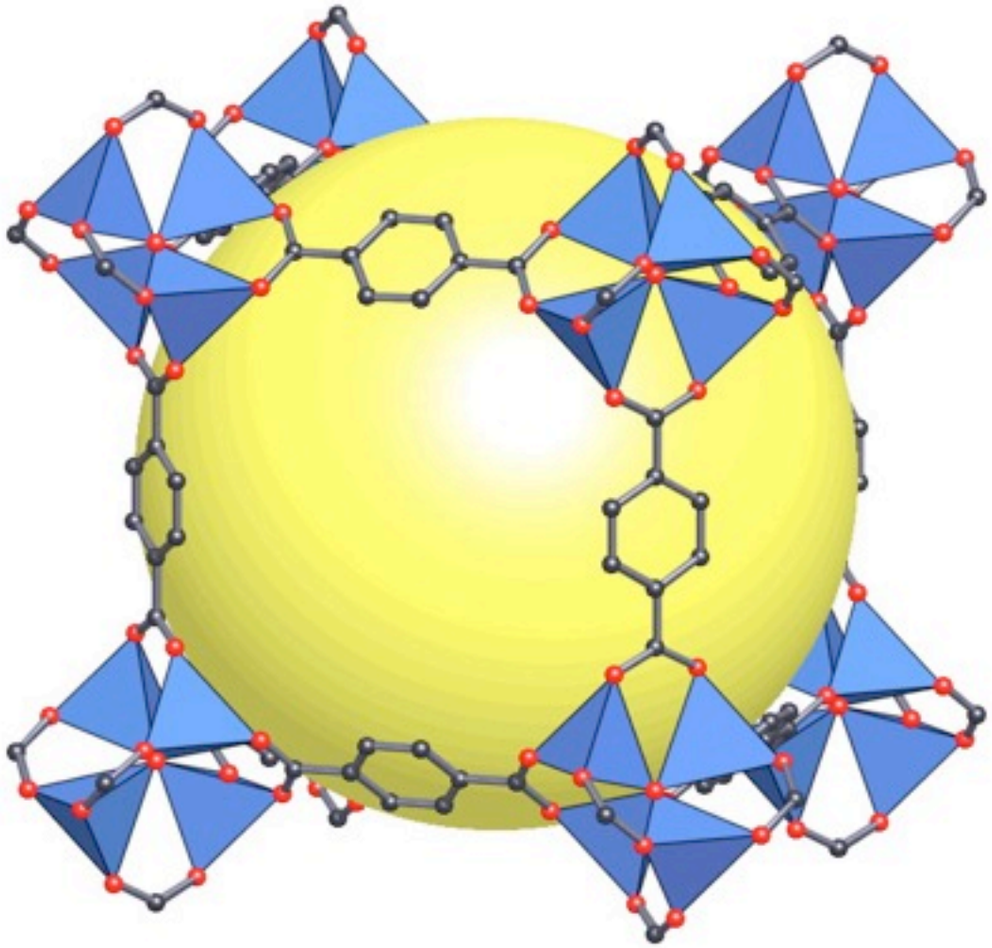
  → one-, two- or three-dimensional networks

  → often porous materials, sometimes exchange of guest molecules possible (adsorption of gases)

  → alternative name: „hybrid frameworks“ or „coordination polymers“

MOF-5: THE example

$Zn_4O(BDC)_3 \bullet (DMF)_8\text{-}(C_6H_5Cl)$



metall center: Zn^{2+}

linker: 1,4-benzenedicarboxylate

guest molecules can be removed without the loss of stability

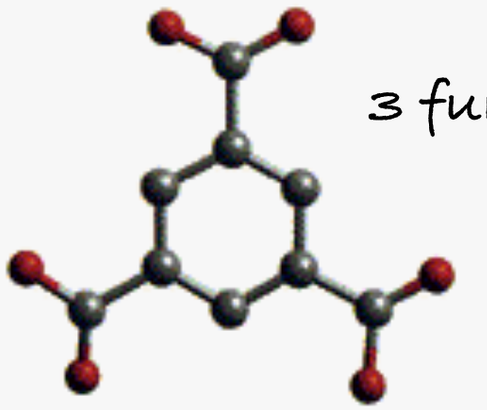
→ Adsorption of gases

ligands = linker

2 functions

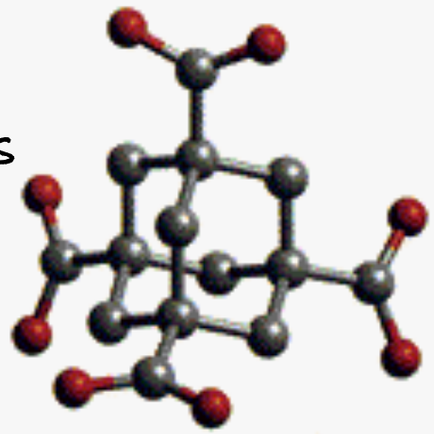
1,4-benzenedicarboxylate
(BDC)

1,4-azodibenzoate
(ADB)



3 functions

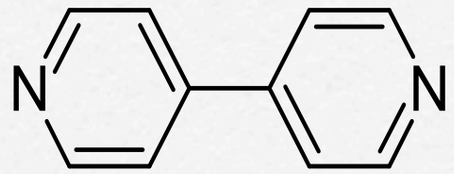
4 functions



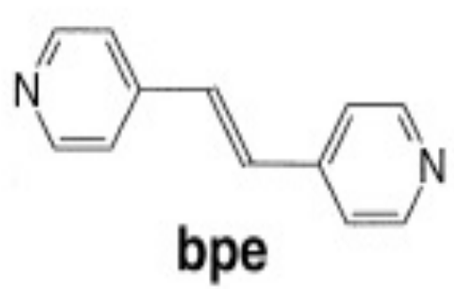
1,3,5-benzenetricarboxylate
(BTC)

1,3,5,7-adamantanetetracarboxylate
(ATC)

ligands = linker



4, 4'-Bipyridine (4,4'-bipy)



bpe

diaz

SBU

organic bridges

dimer

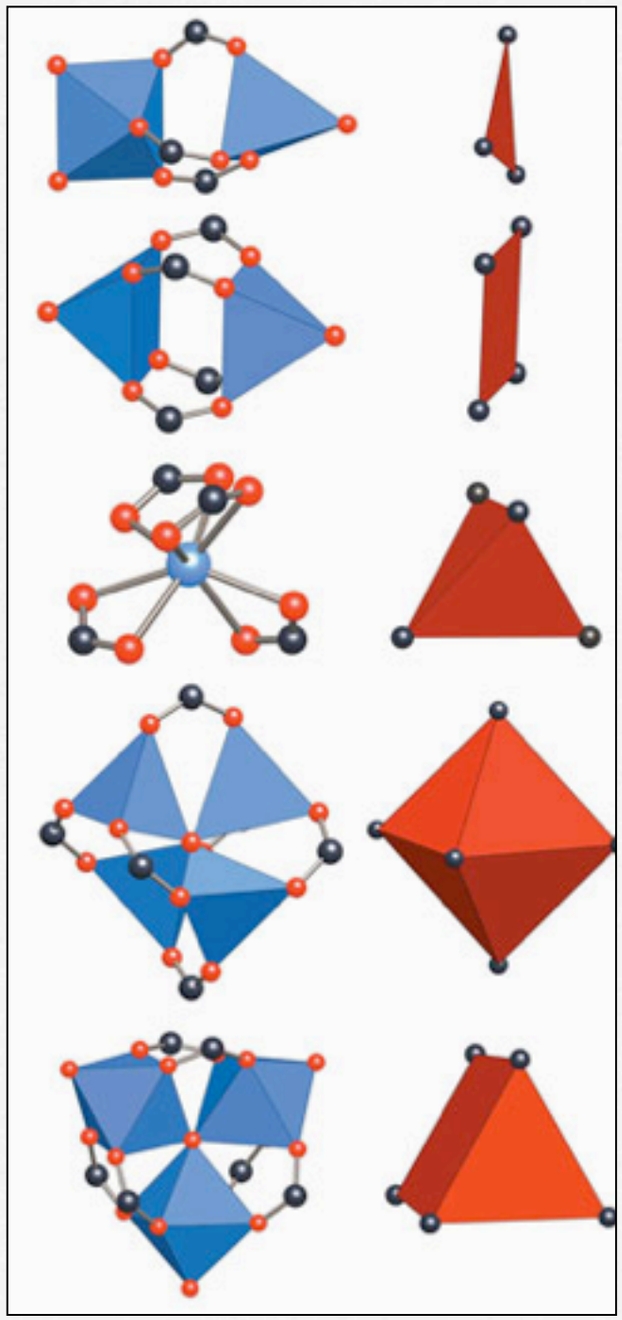
$Zn_2(COO)_4$

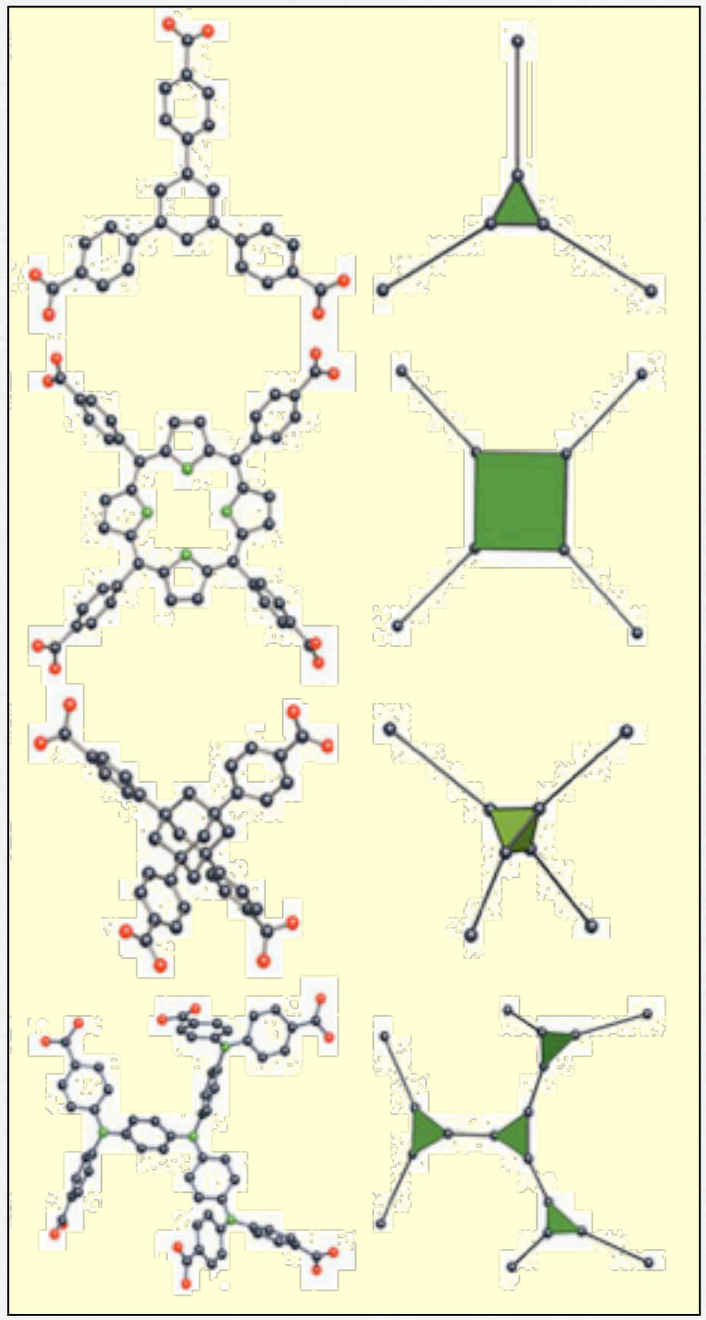
trimer

$Zn_3(COO)_6$

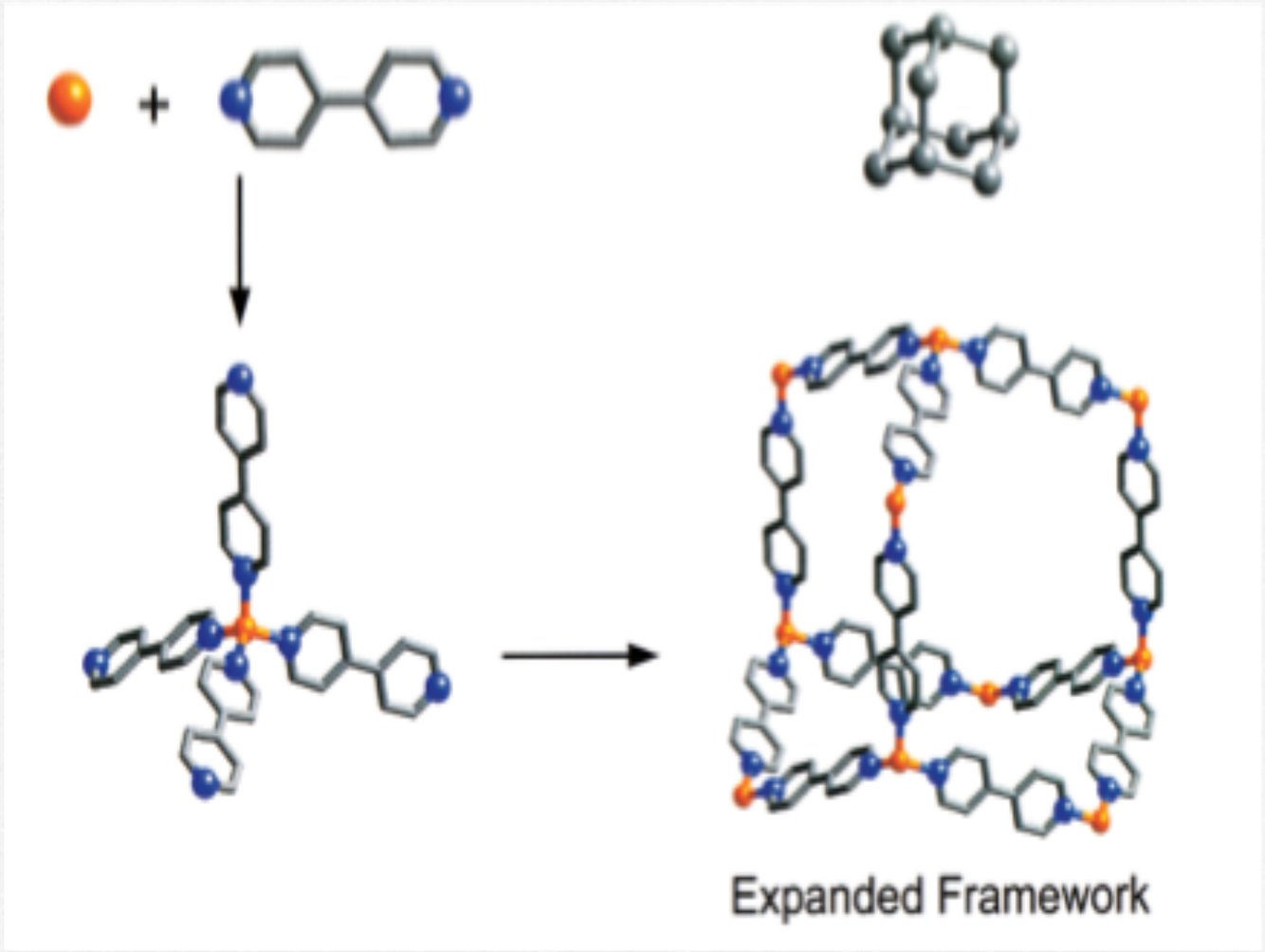
tetramer

$Zn_4(COO)_6$





module chemistry



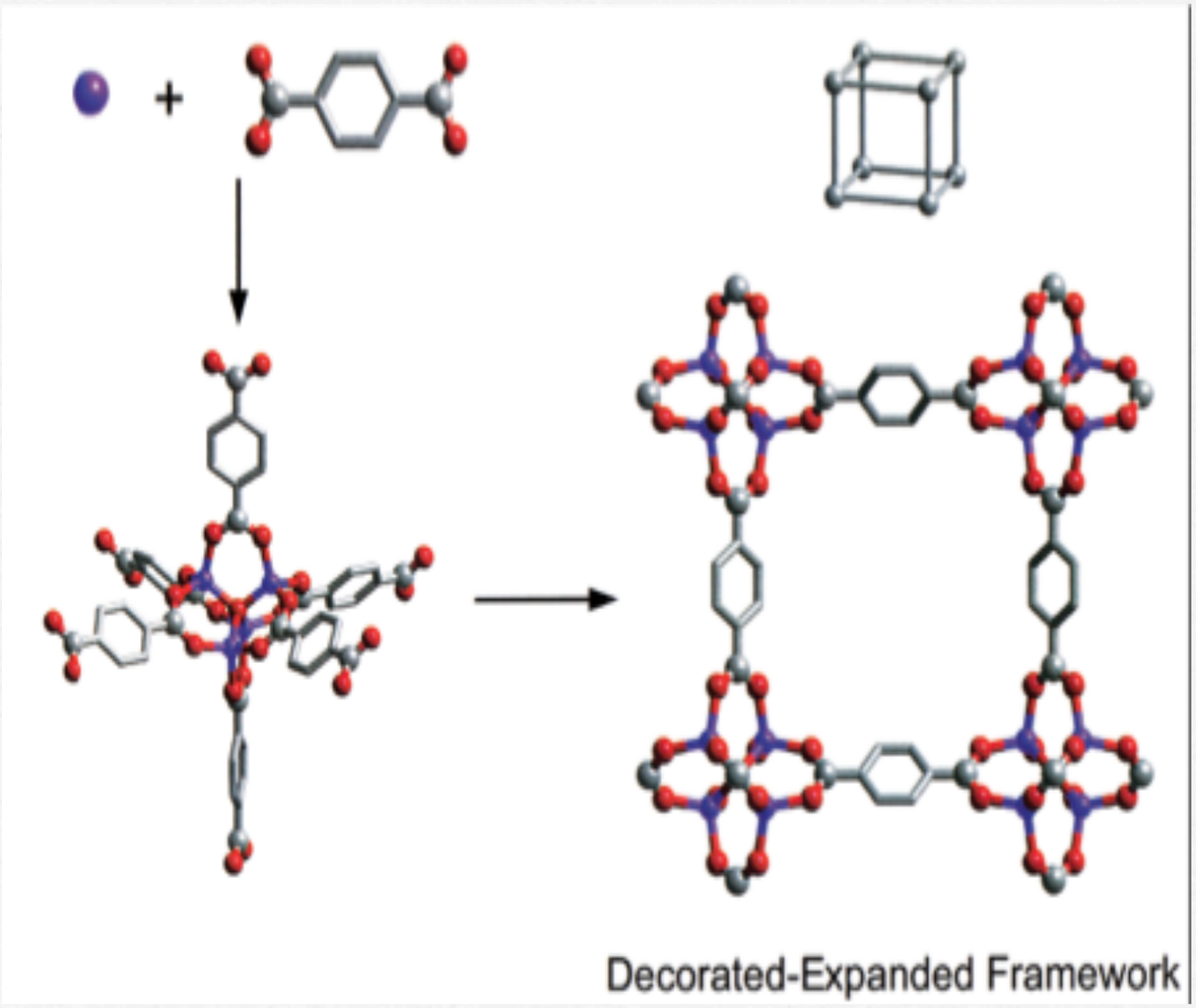
expanded networks:

→ a structure will be recreated by SBU (example diamand structure)

→very large pores possible

→disadvantage: interpenetration of networks

module chemistry



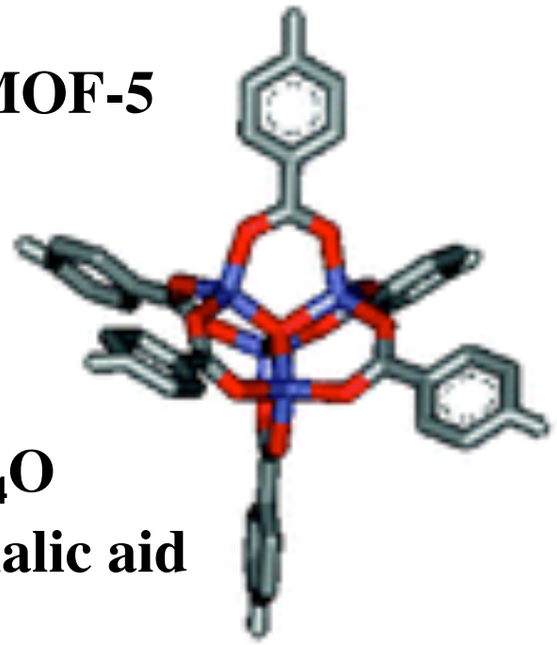
→decorated networks:

→ a given basic structure will be decorated by SBU

→ stable networks without „interpenetration“

→combination with expansion possible

MOF-5



Zn_4O

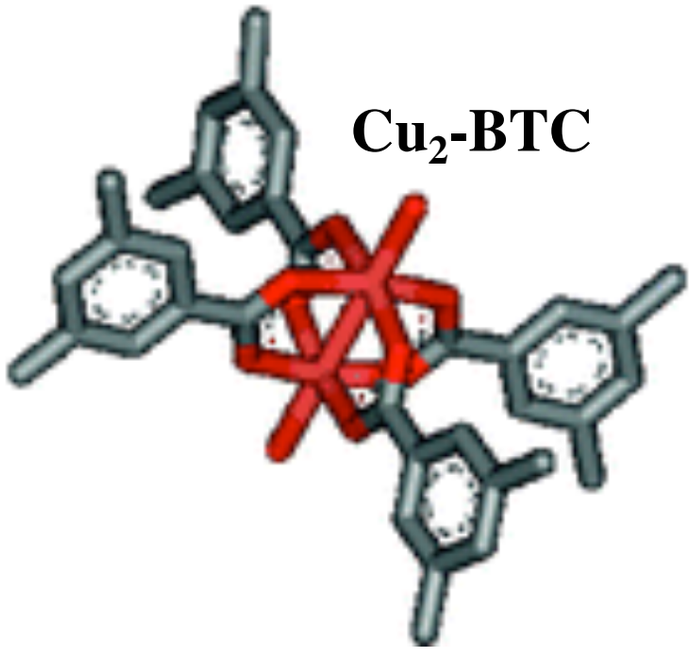
terephthalic aid

IRMOF-8

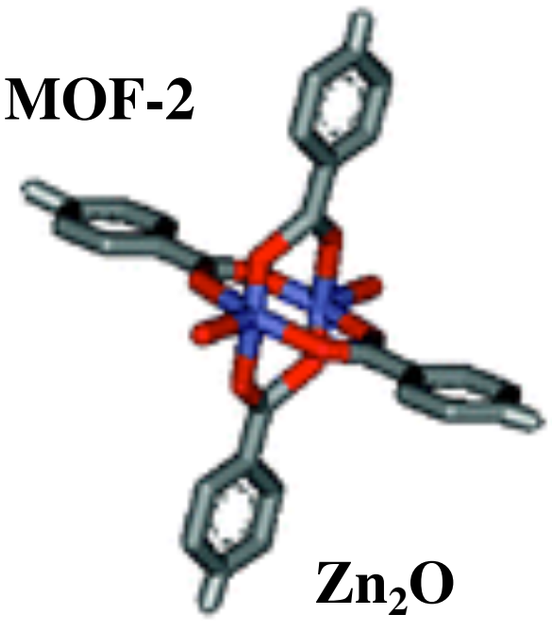
Zn_4O

2,6-naphtalene dicarboxylic acid

Cu_2-BTC

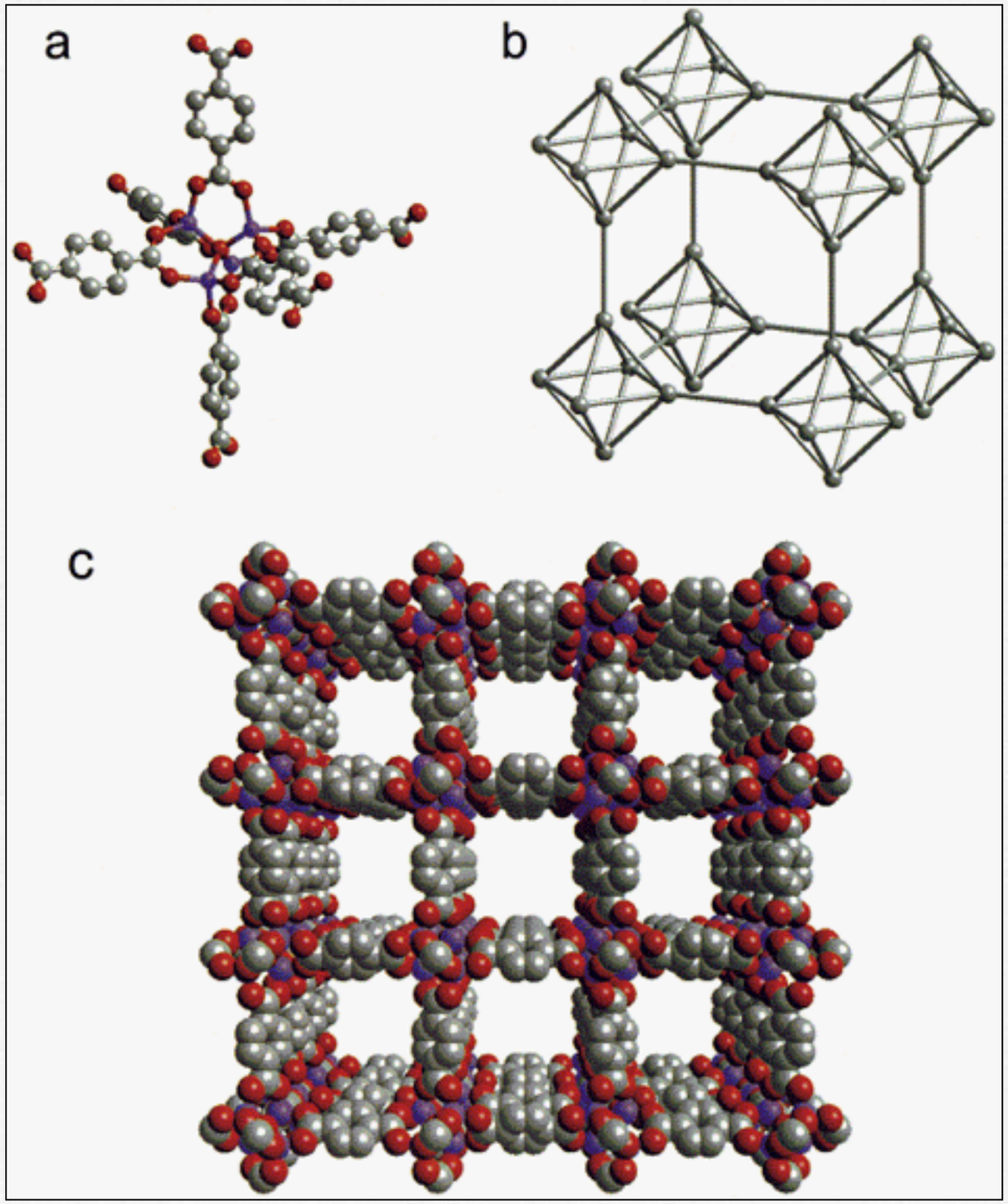


MOF-2



Zn_2O

terephthalic acid



MOF-5

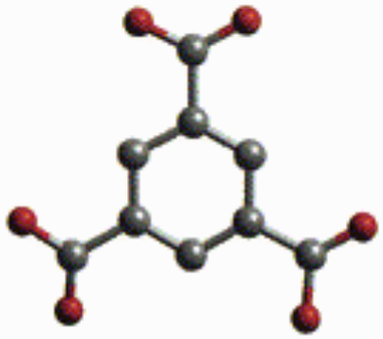
expansion and decoration shown at the example MOF-5

a) octahederic SBU with octahedral coordination of the carboxylate-carbons

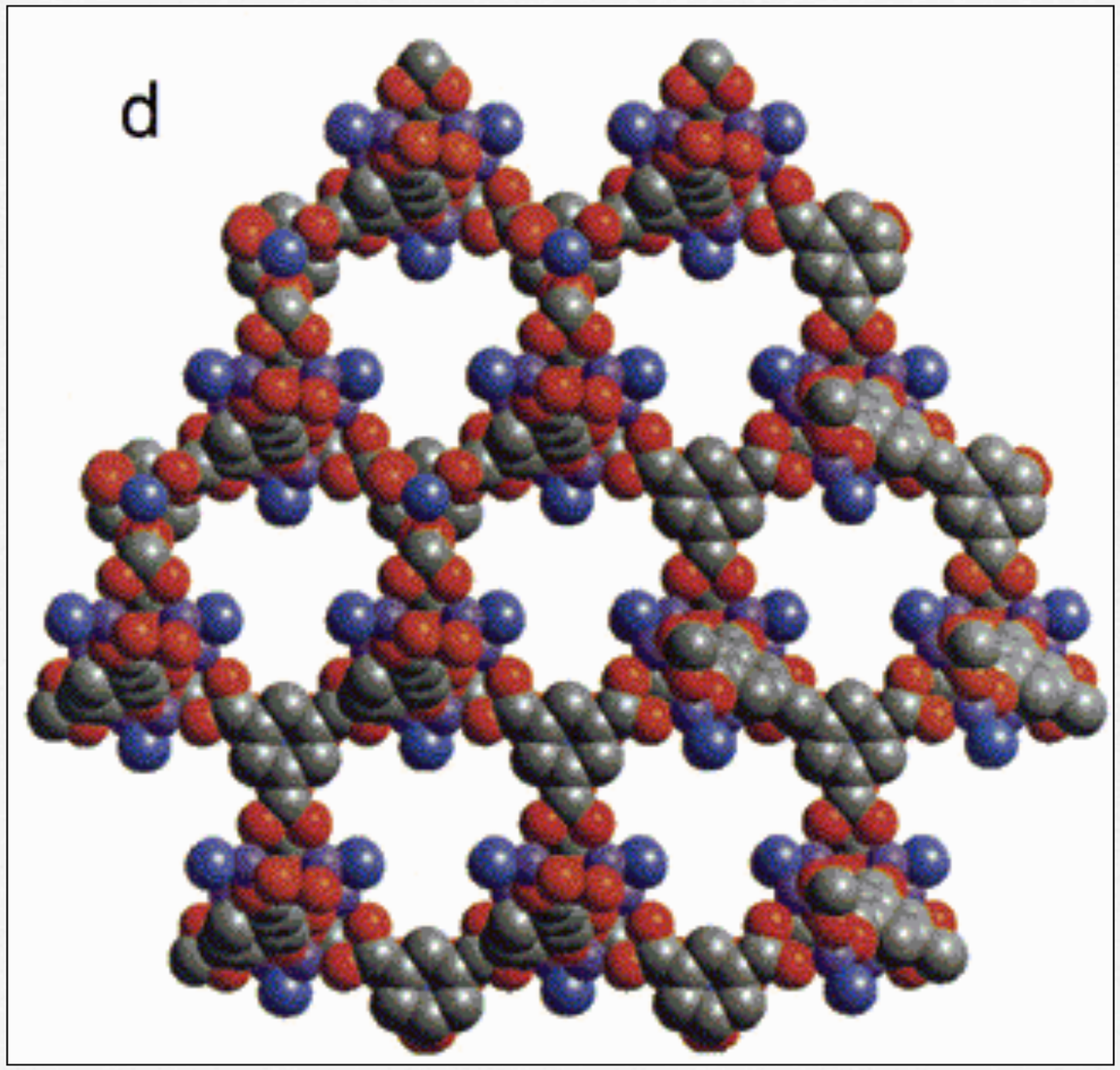
b) cubic-primitive lattice with decorating SBUs

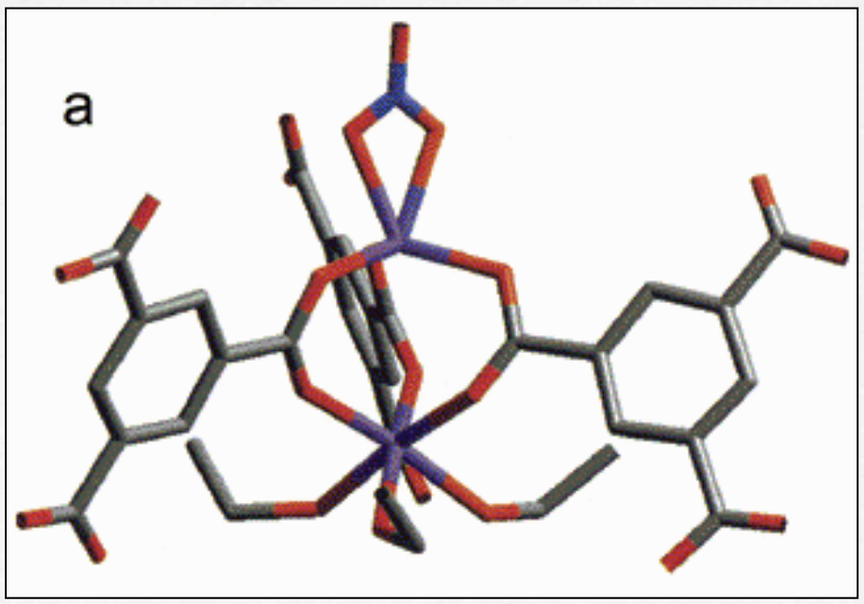
c) porous crystal

MOF-4



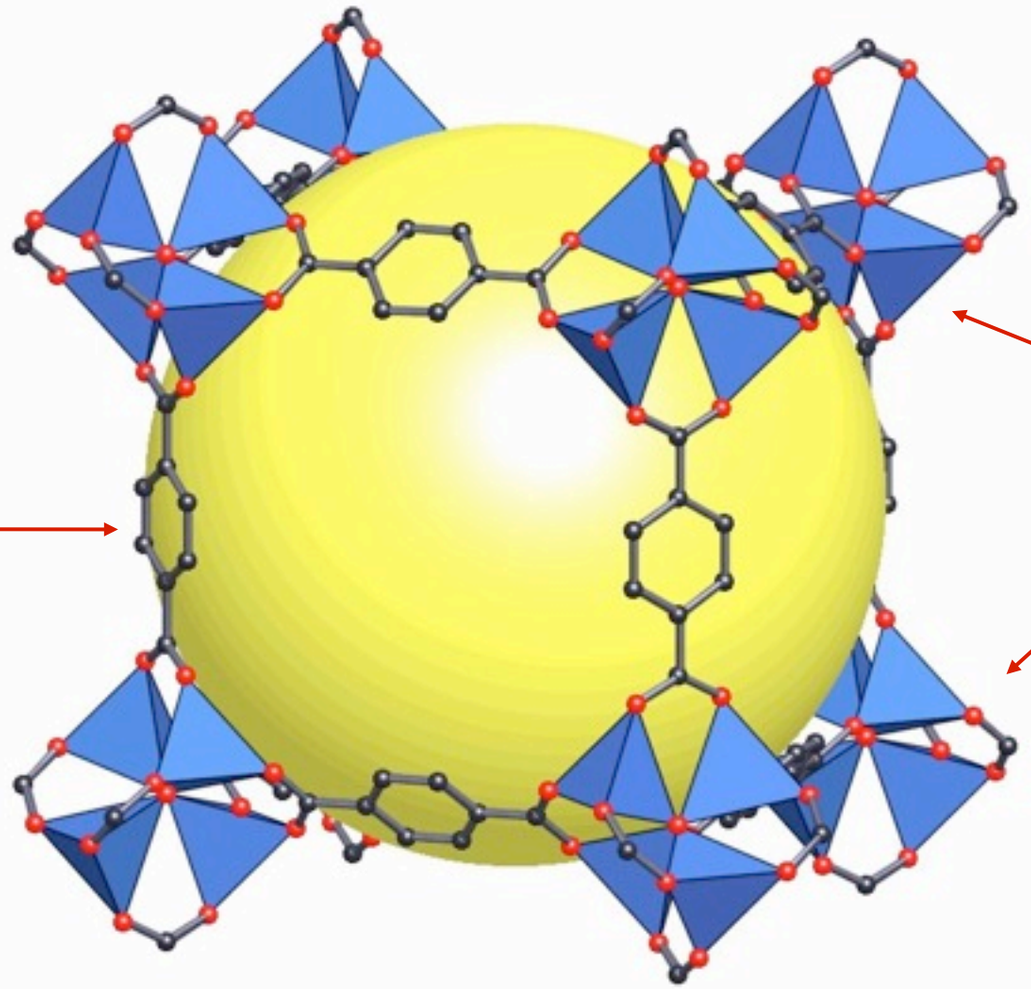
1,3,5-benzenetricarboxylate
(BTC)





$Zn_2(BTC)(NO_3)(EtOH)_5(H_2O)$

MOF-5

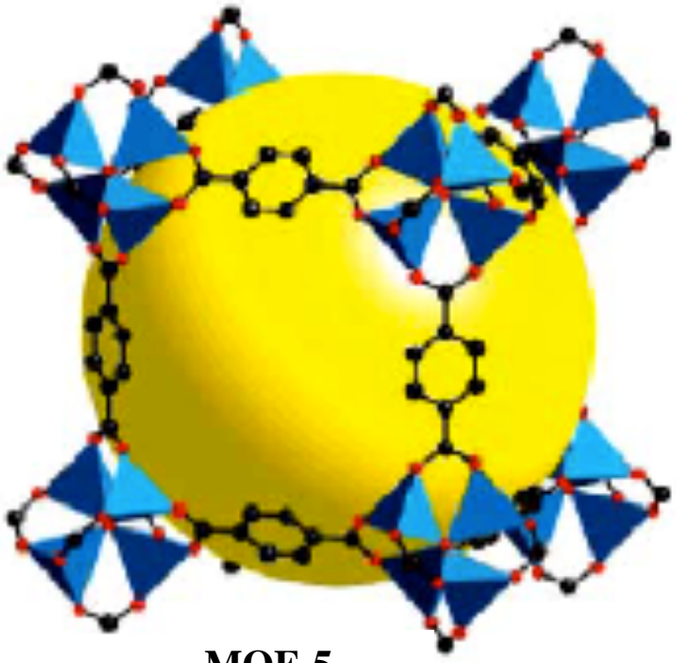


organic bridge

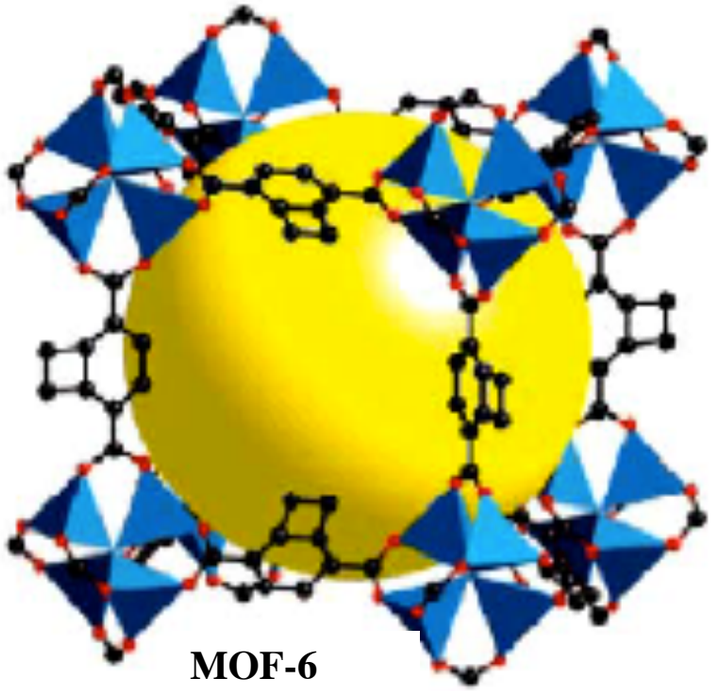
mineral Zn_4

d = 18,5 Å S = 2900 m²/g

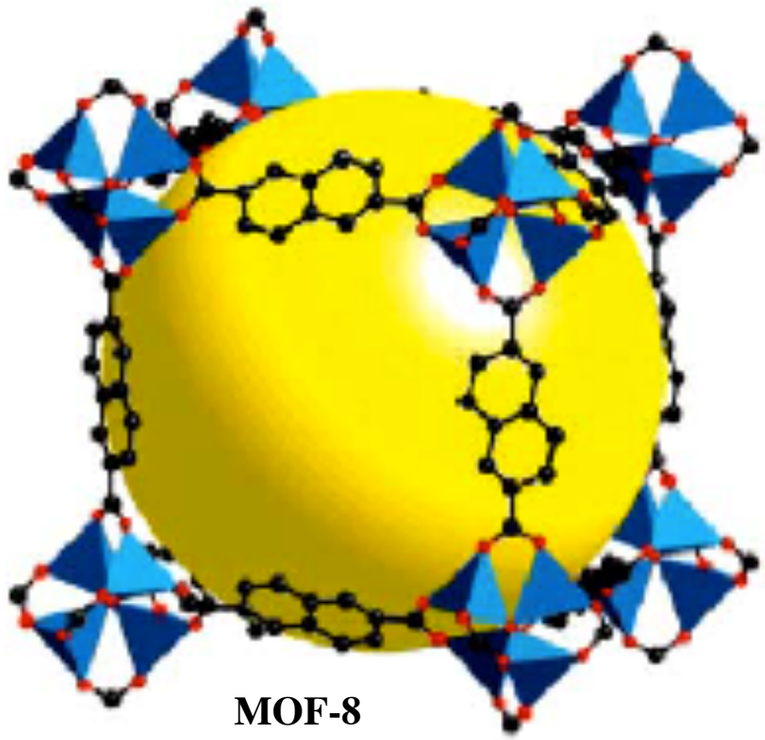
$[Zn_4O]$ - bridged carboxylates



MOF-5

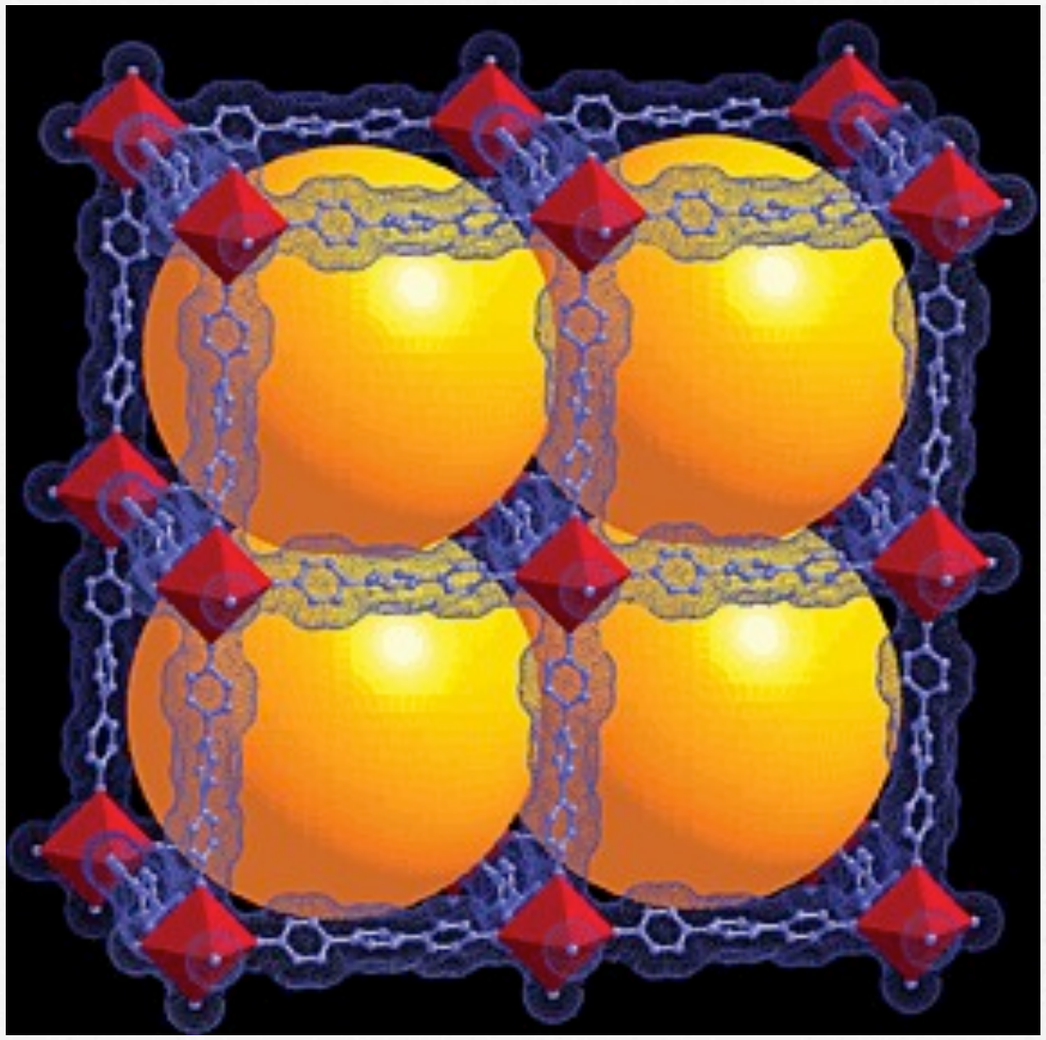


MOF-6



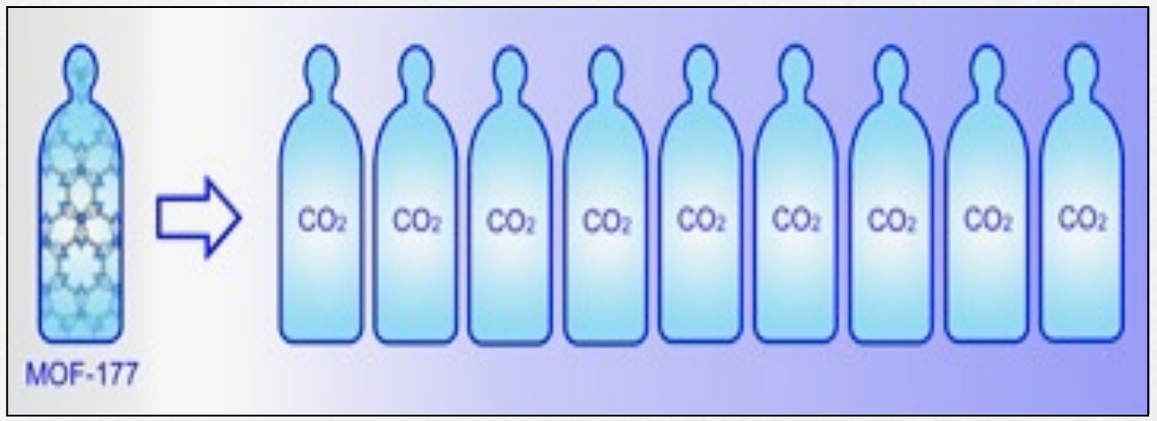
MOF-8

CH_4 - CO_2 - H_2



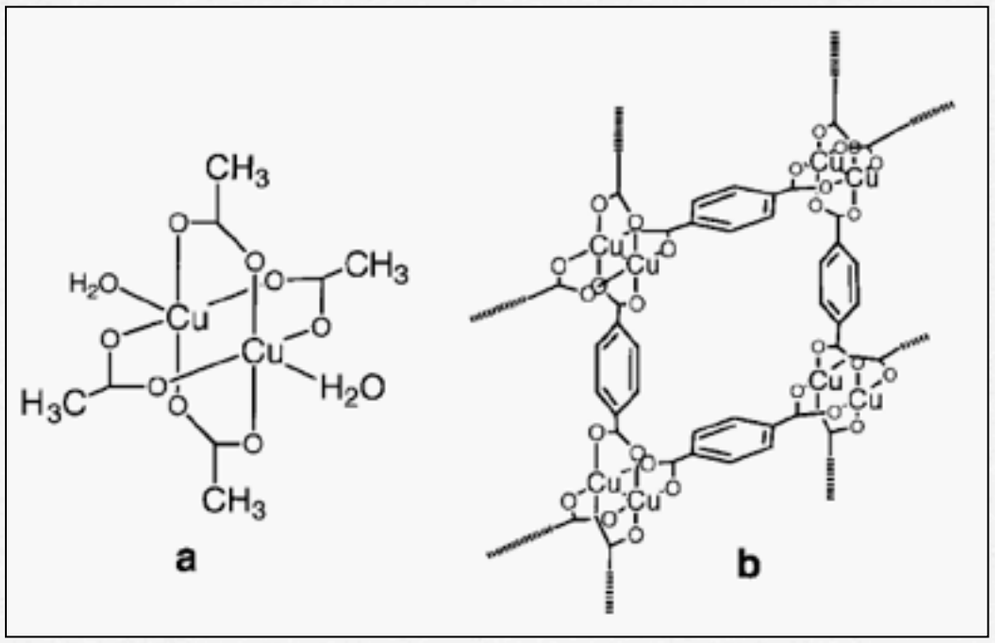
crystal sponges

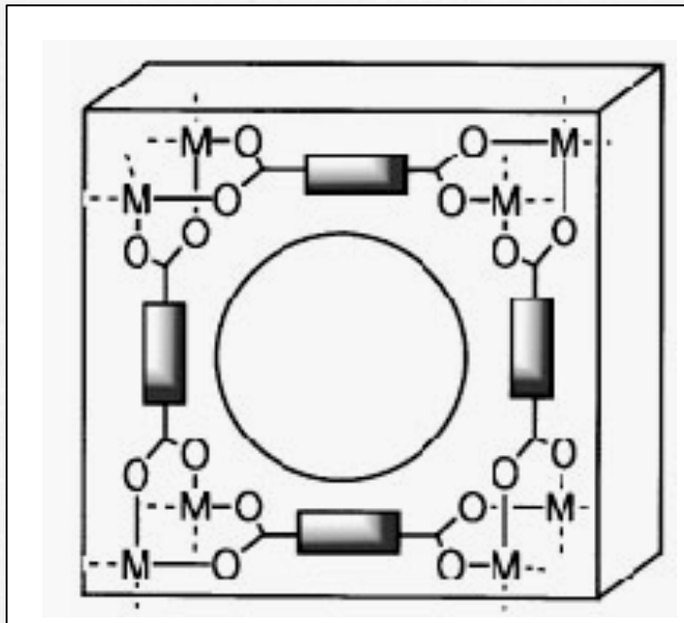
MOF-177

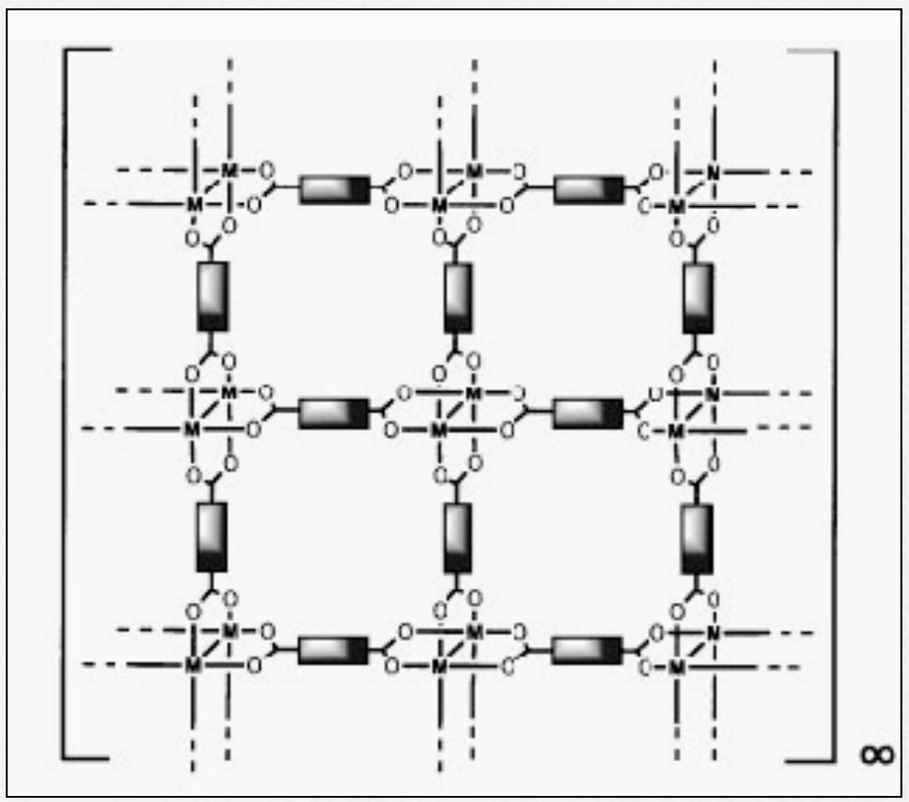


one container of MOF-177
can uptake up to 9 containers of gas

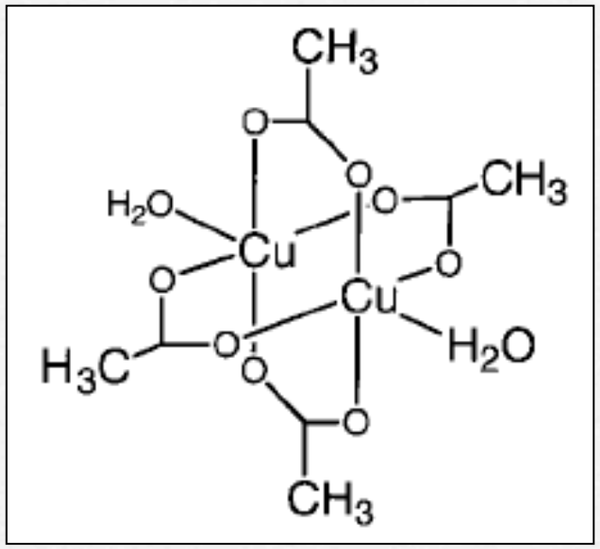
terephthalic acid

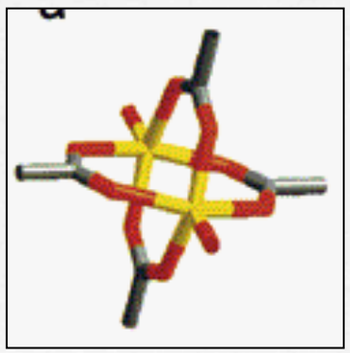




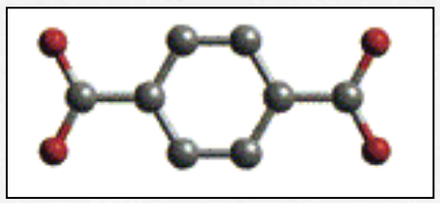


terephthalic acid

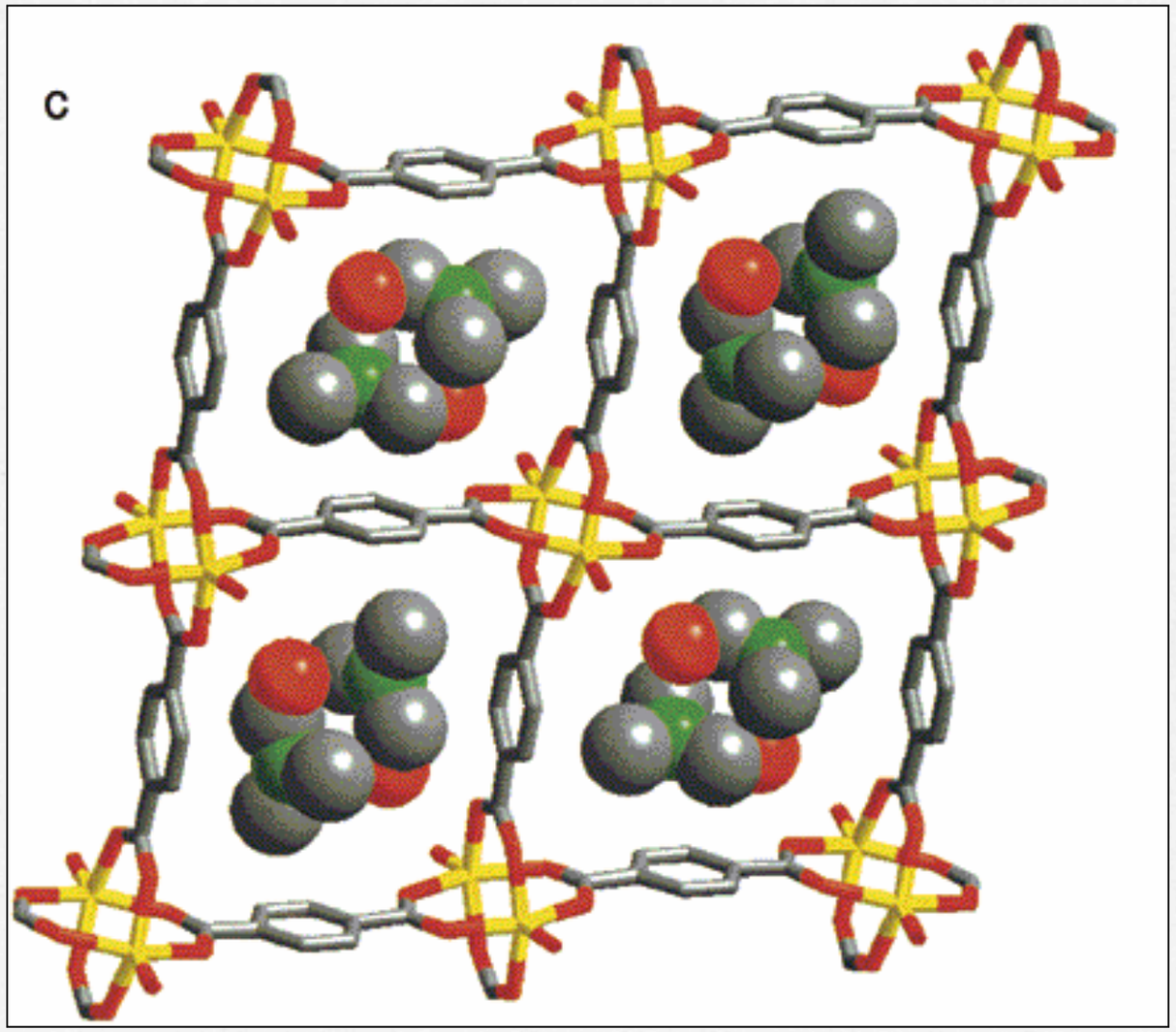




+

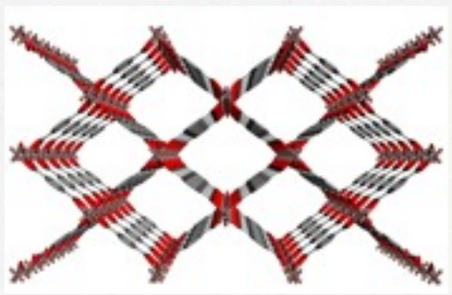


BDC



terephthalic acid

$AlCl_3$ +

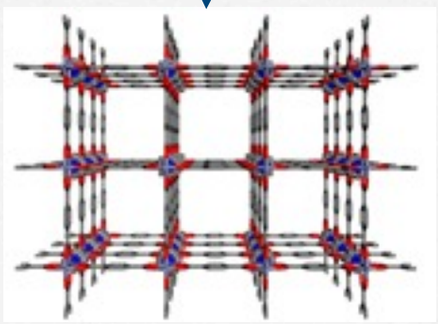


USO-1-Al (MIL-53)

1300 m^2/g

$Ni(NO_3)_2$ +

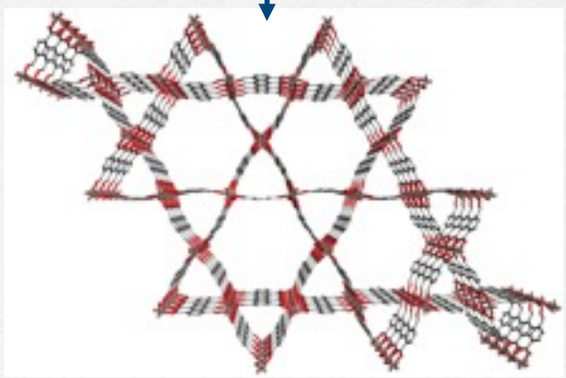
+



USO-2-Ni

1925 m^2/g

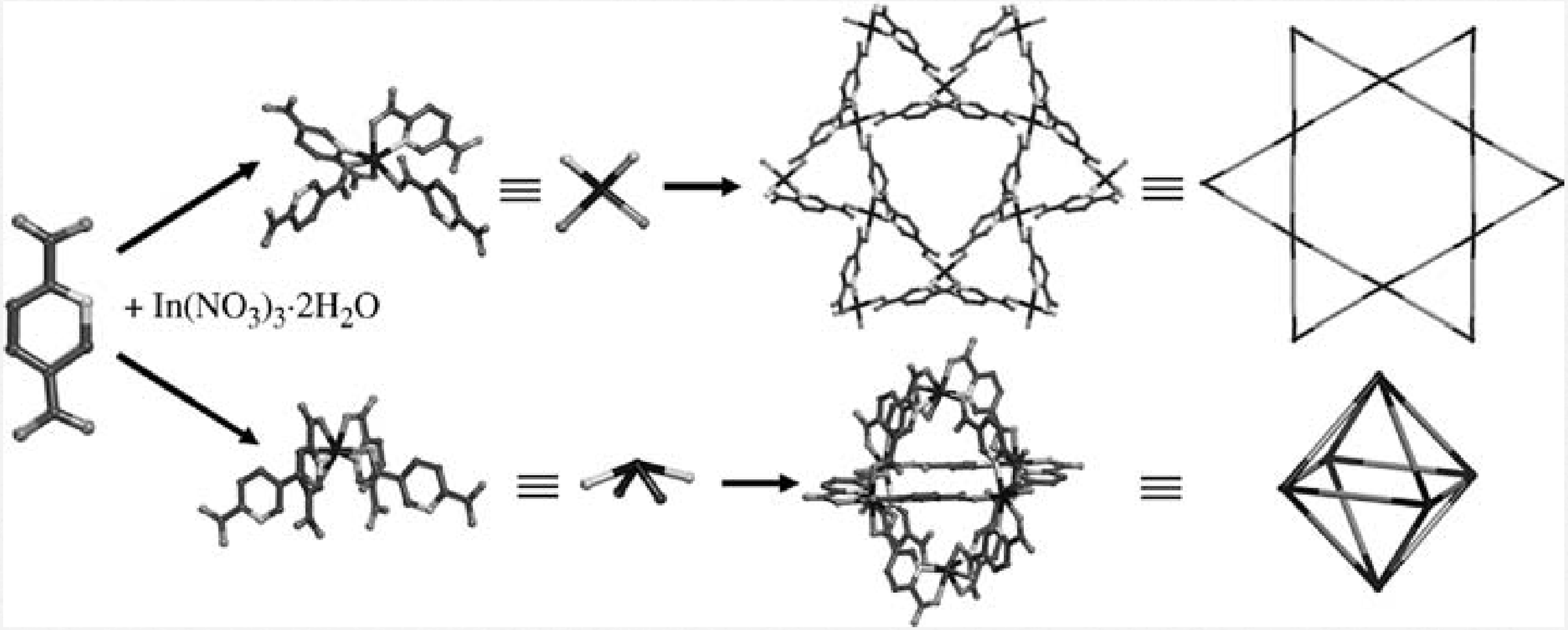
$InCl_3$ +



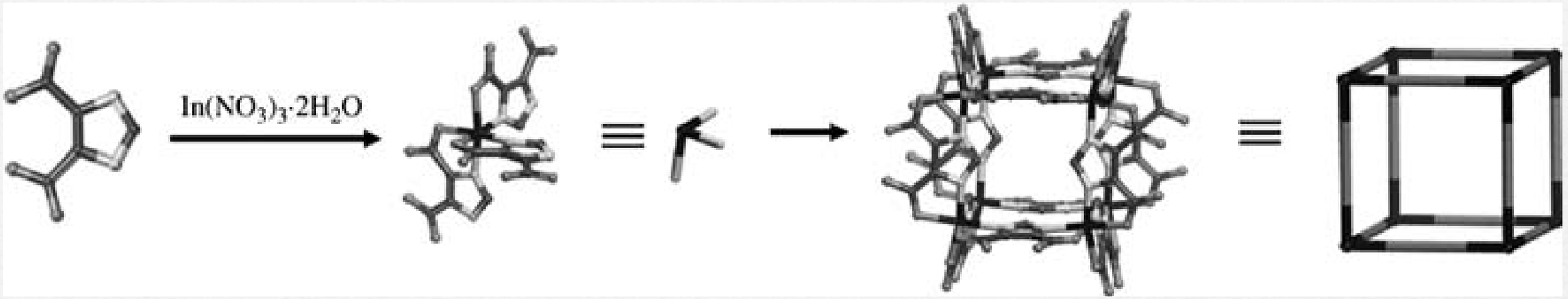
USO-3-In (MIL-68)

930 m^2/g

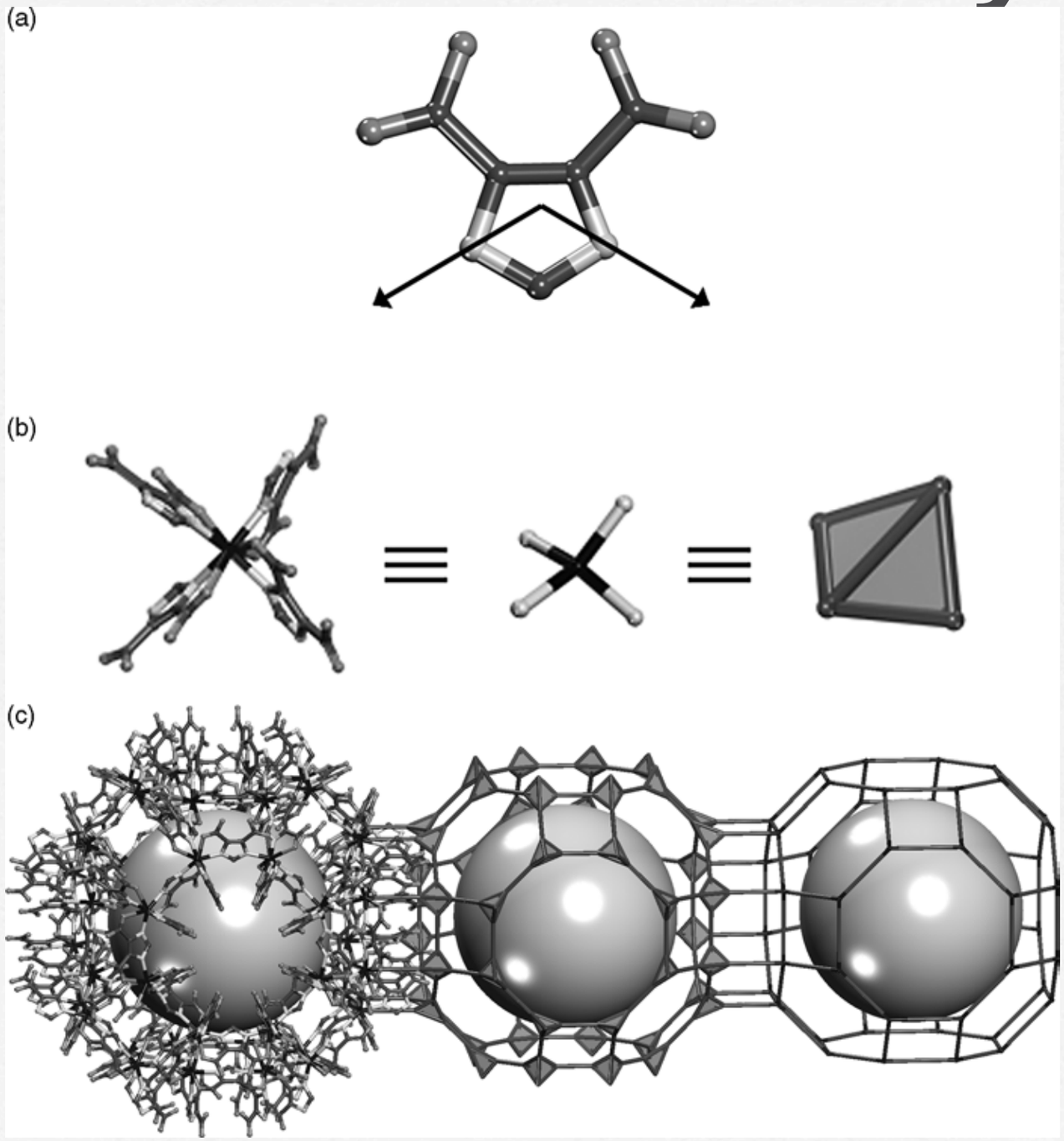
terephthalic acid



Imidazole dicarboxylic acid



Imidazole dicarboxylic acid

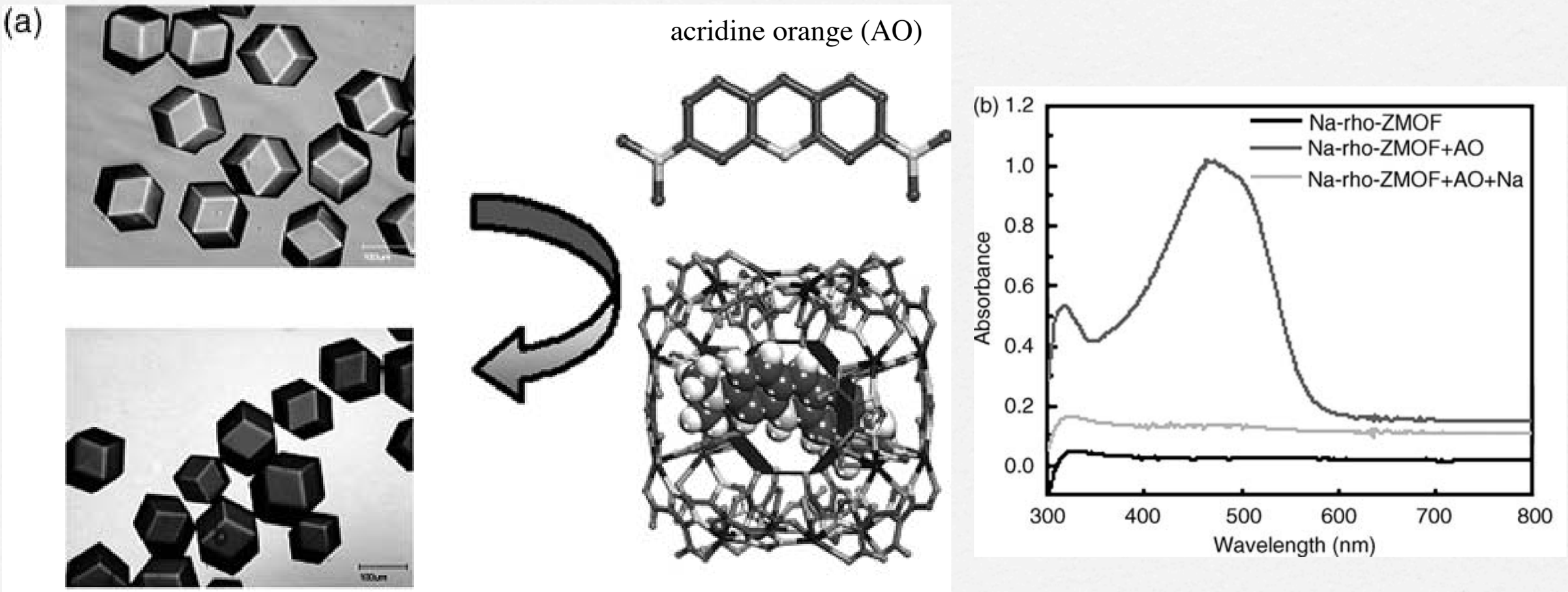


four $HImDC^{2-}$ ligands

rho-ZMOF

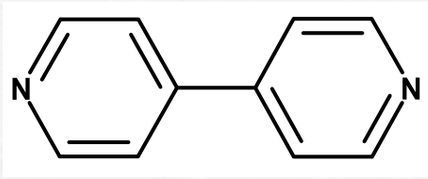
rho-ZMOF

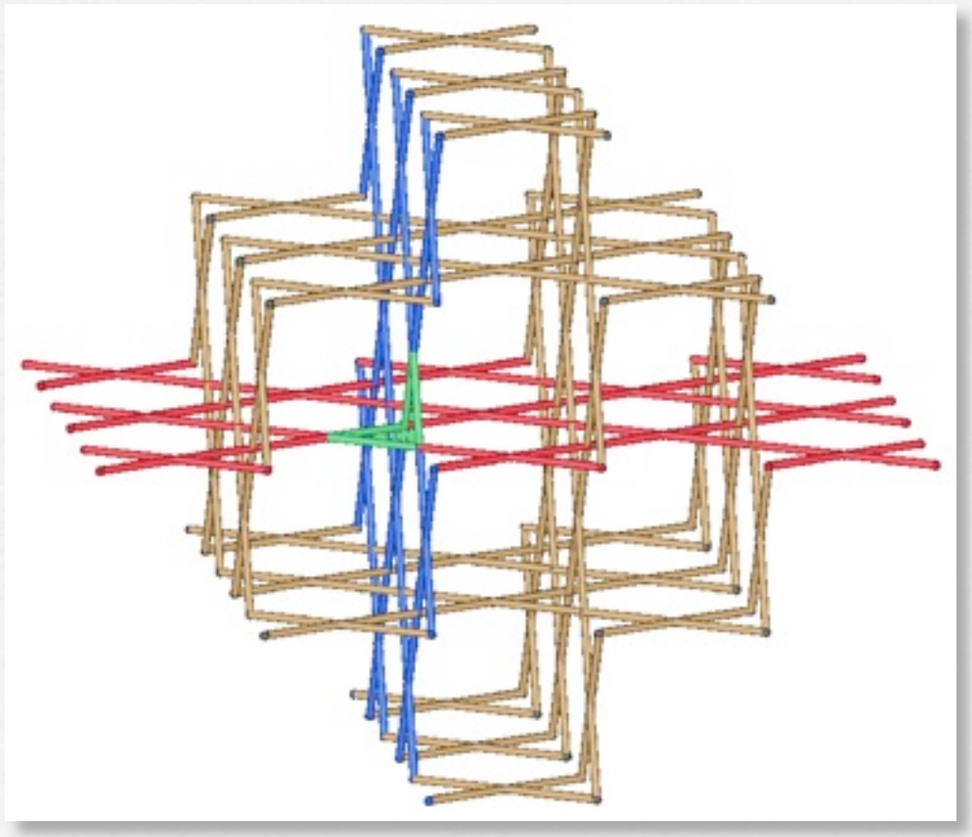
Guest Sensing



interpenetration

$[Cu(4,4'\text{-bipy})_2(CF_3SO_3)_2]\cdot 2CH_2Cl_2\cdot H_2O$
lvt- 2f





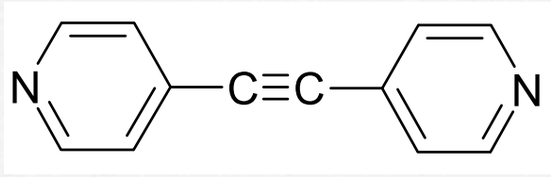
lvt - $4^2\cdot 8^4$
$4\cdot 4\cdot 8_4\cdot 8_4\cdot 8_8\cdot 8_8$

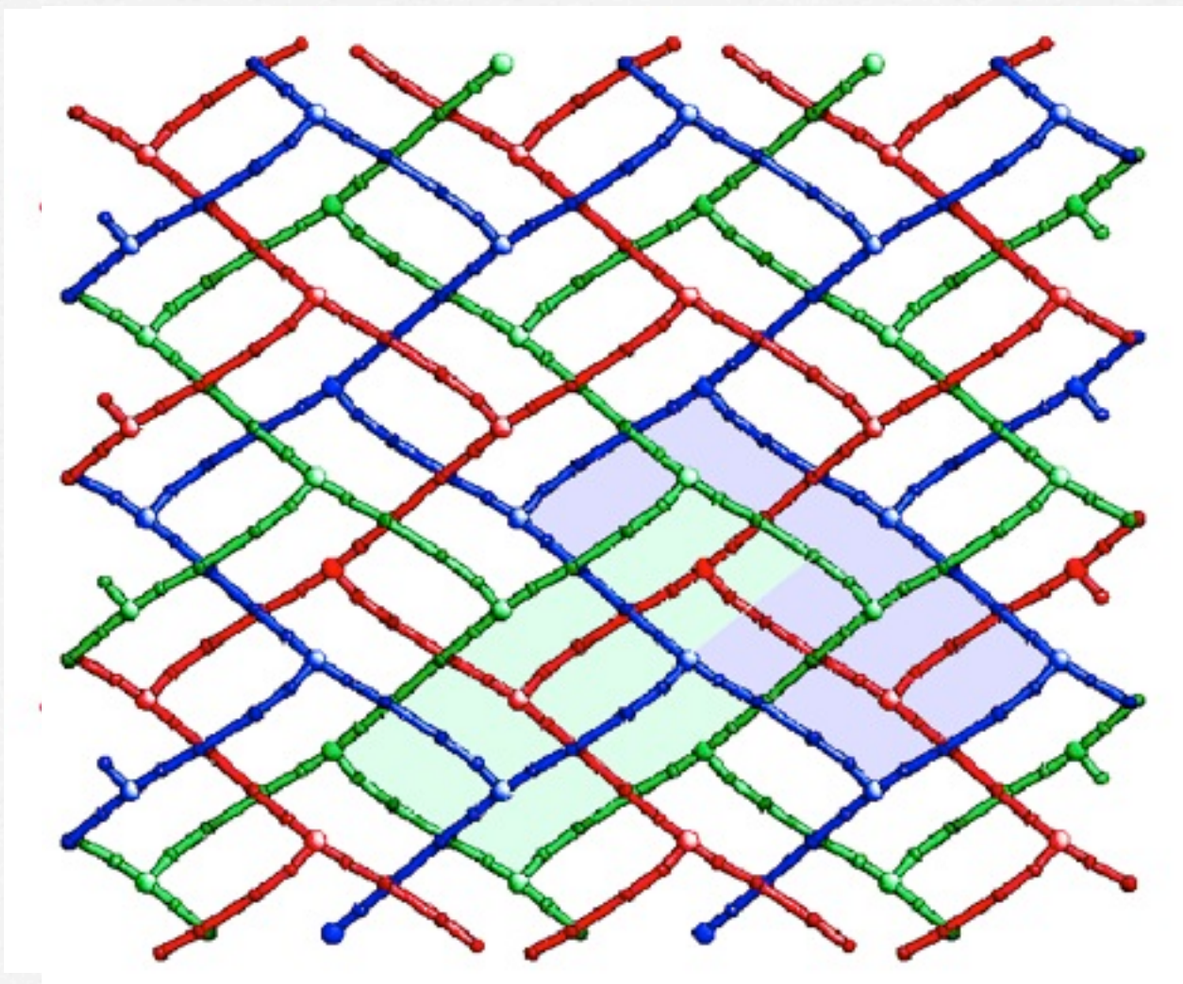
L. Carlucci, N. Cozzi, G. Ciani, M. Moret, D.M. Proserpio, S. Rizzato, *Chem*. Commun, 1354 (2002)

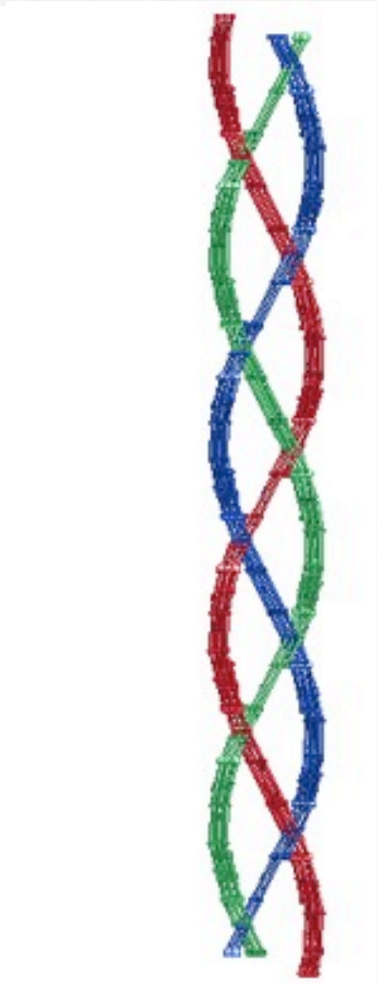
interpenetration

$[Cd_2(bpethy)_3](NO_3)_4$

2D // 2D ⇒ 2D-3f



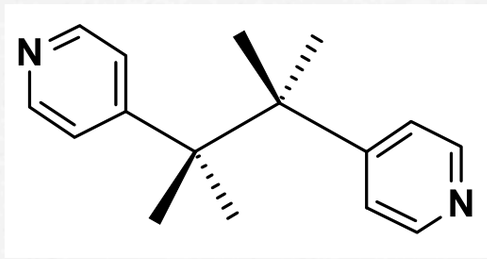


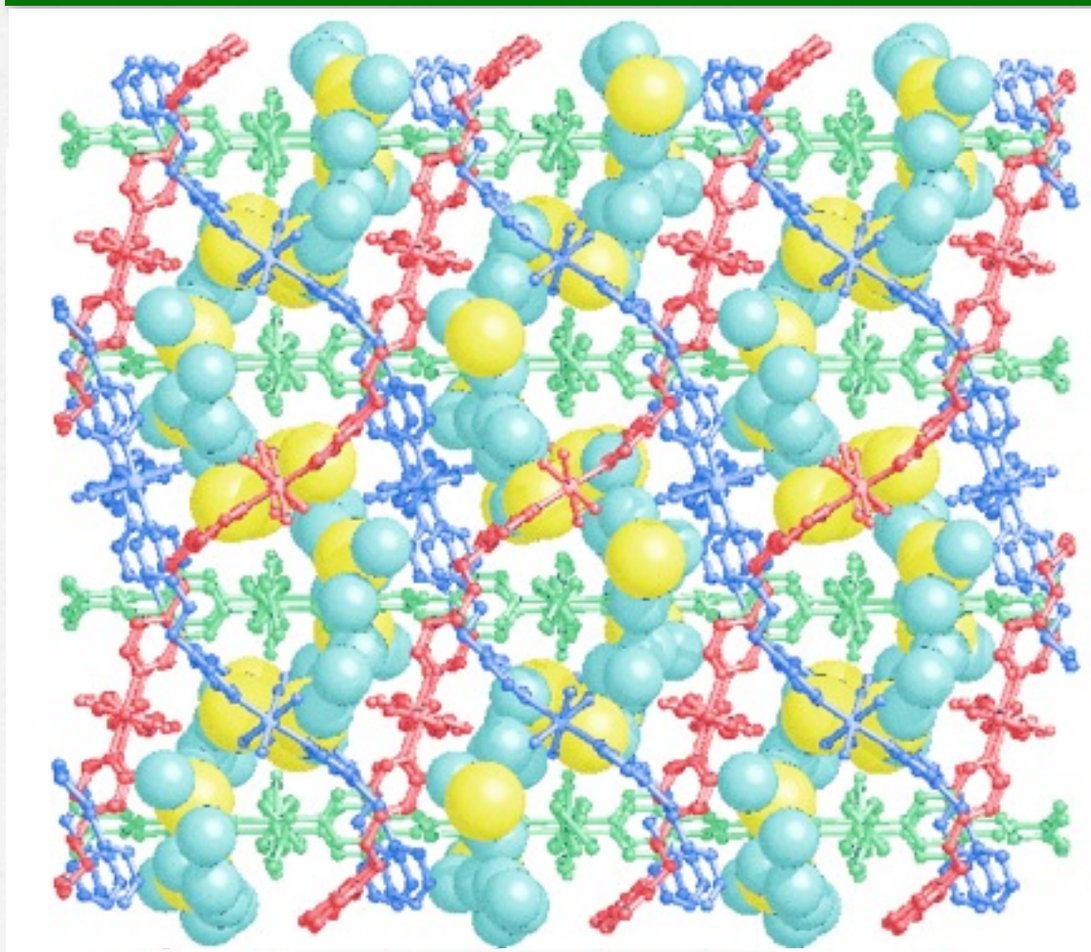


interpenetration

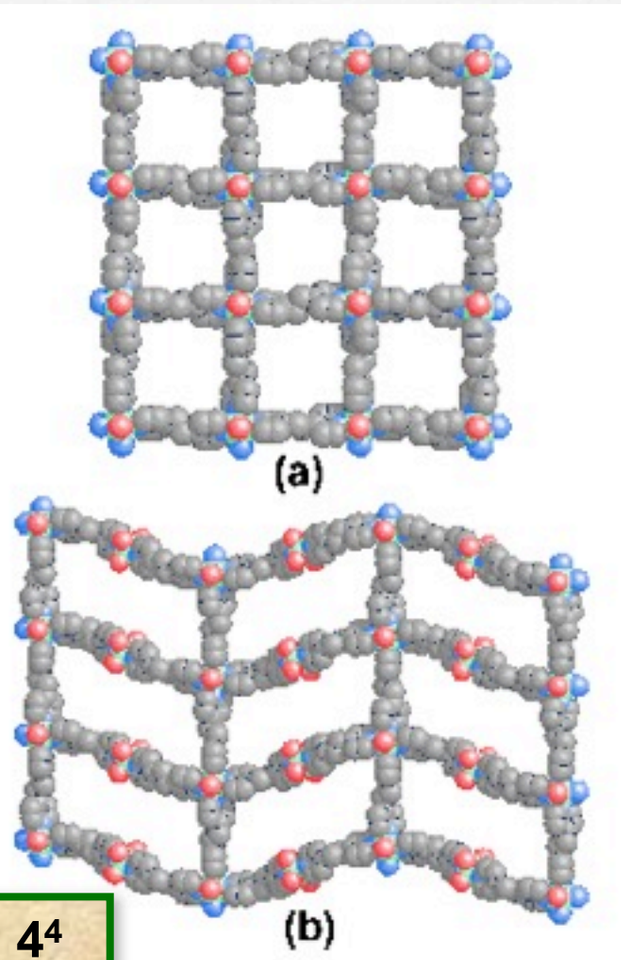
$[Ni_6(bpe)_{10}(H_2O)_{16}](SO_4)_6 \cdot nH_2O$

(2D ⊥ 2D ⊥ 2D) ⇒ ***3D polycatenation***





Voids 20%



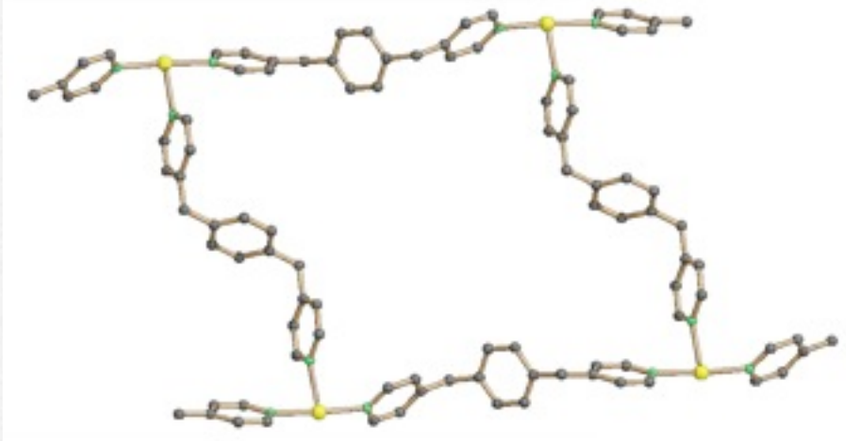
4^4

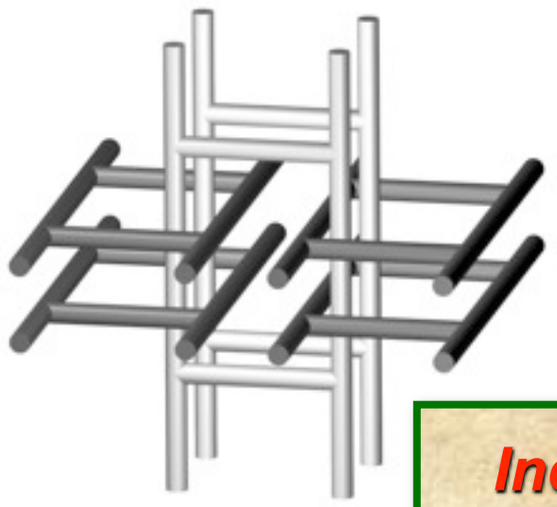
interpenetration

3D ⟵ ***polycatenation of 1D ladders*** ⟶ 2D

$[Cd(L)_{1.5}](NO_3)_2$

Fujita group, 1995

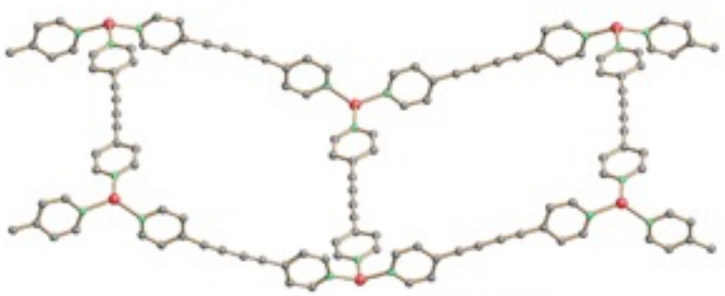


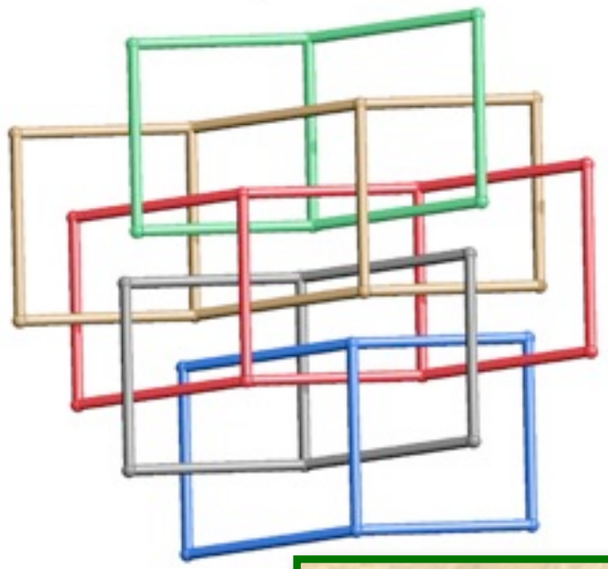


Inclined ⇒ 3D

$[Cu_2(MeCN)_2L_3](PF_6)_2$

Schröder group, 1997

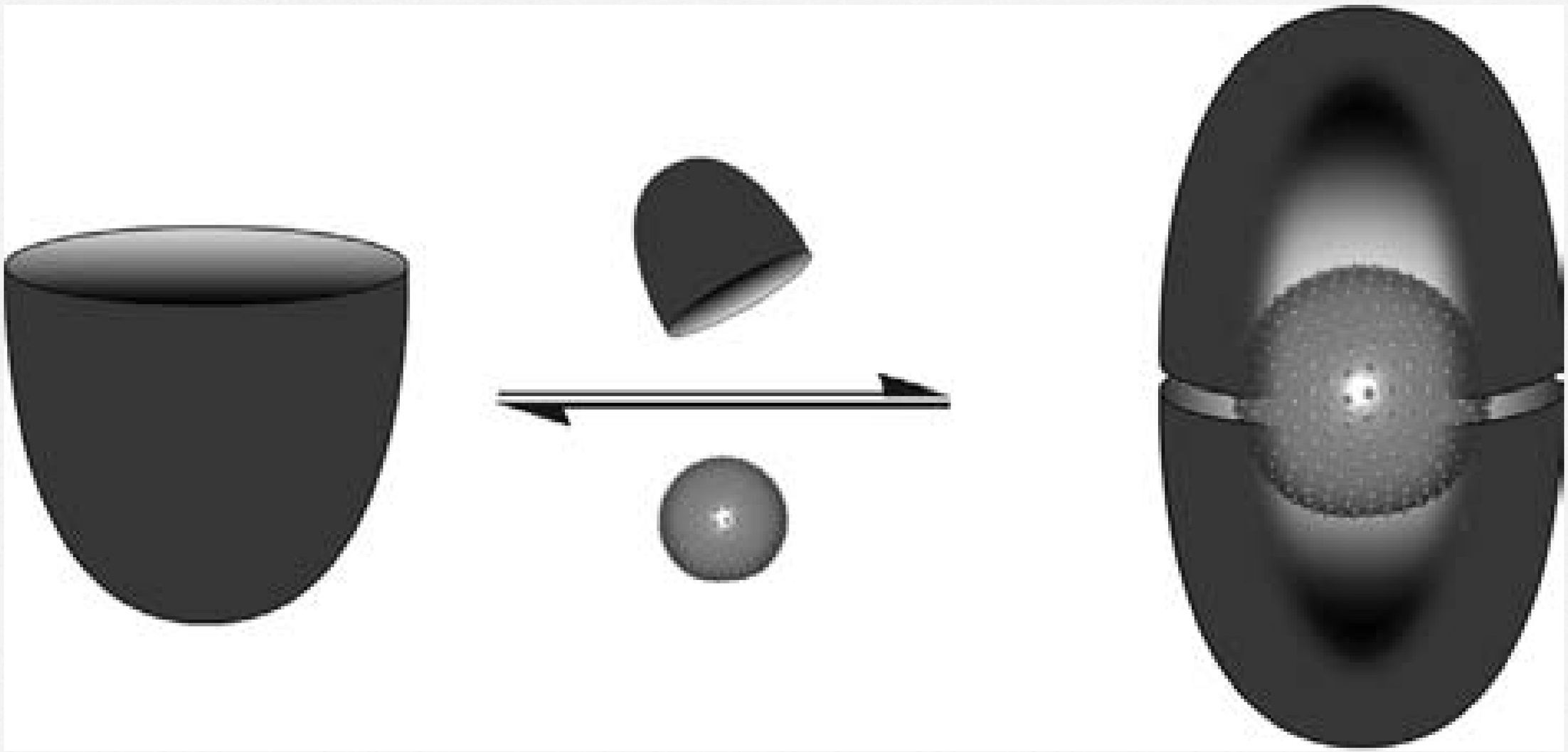




Parallel ⇒ 2D

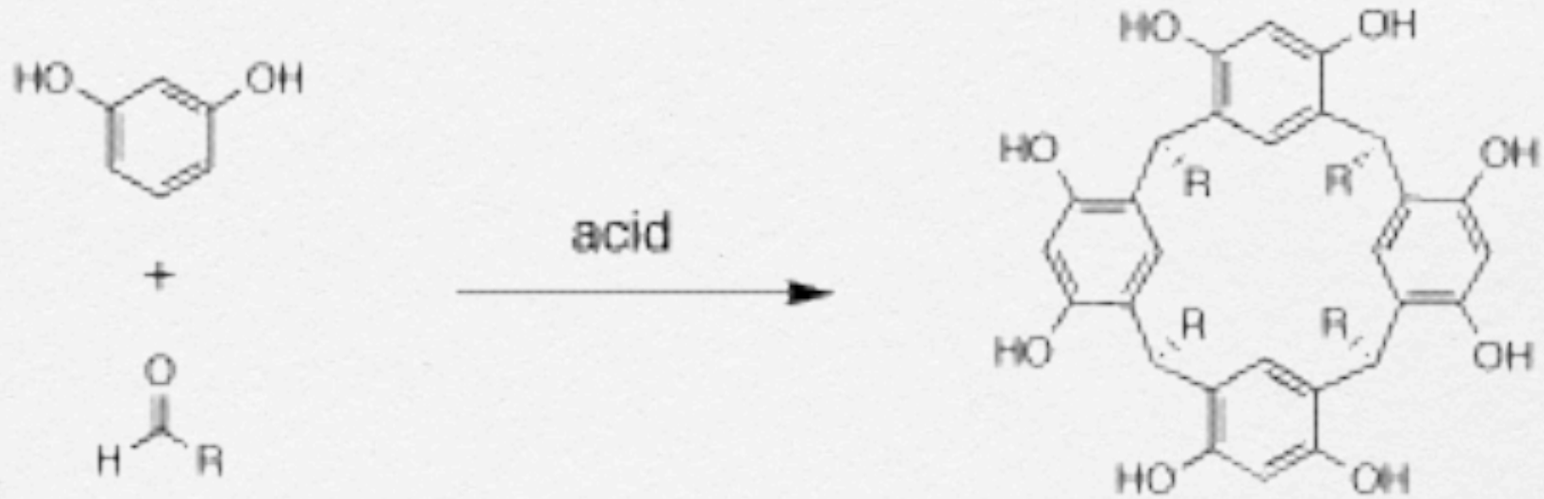
Nano-capsules

the concept

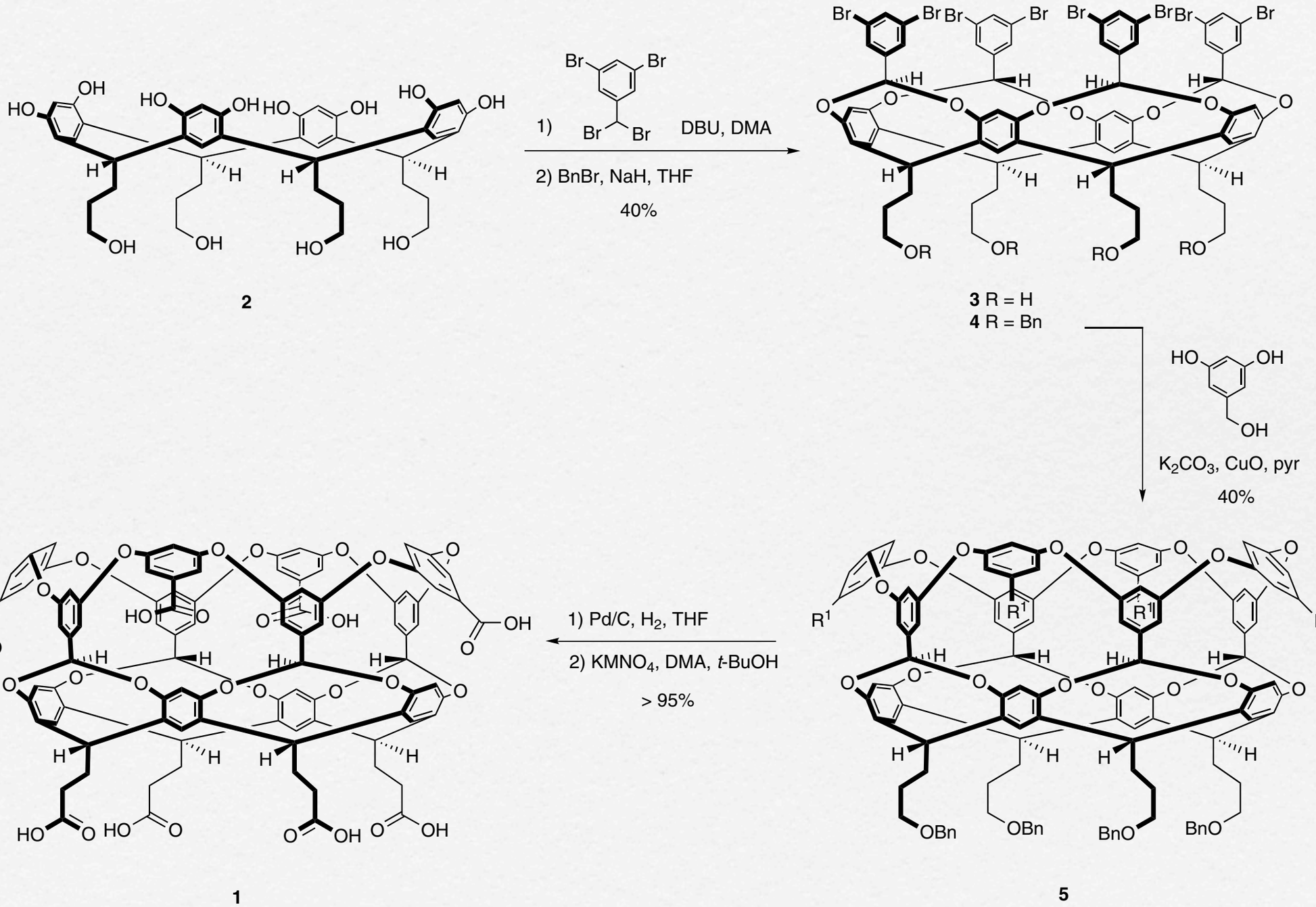


synthesis

resorcinarene macrocycle: condensation of resorcinol and an aldehyde in concentrated acid solution

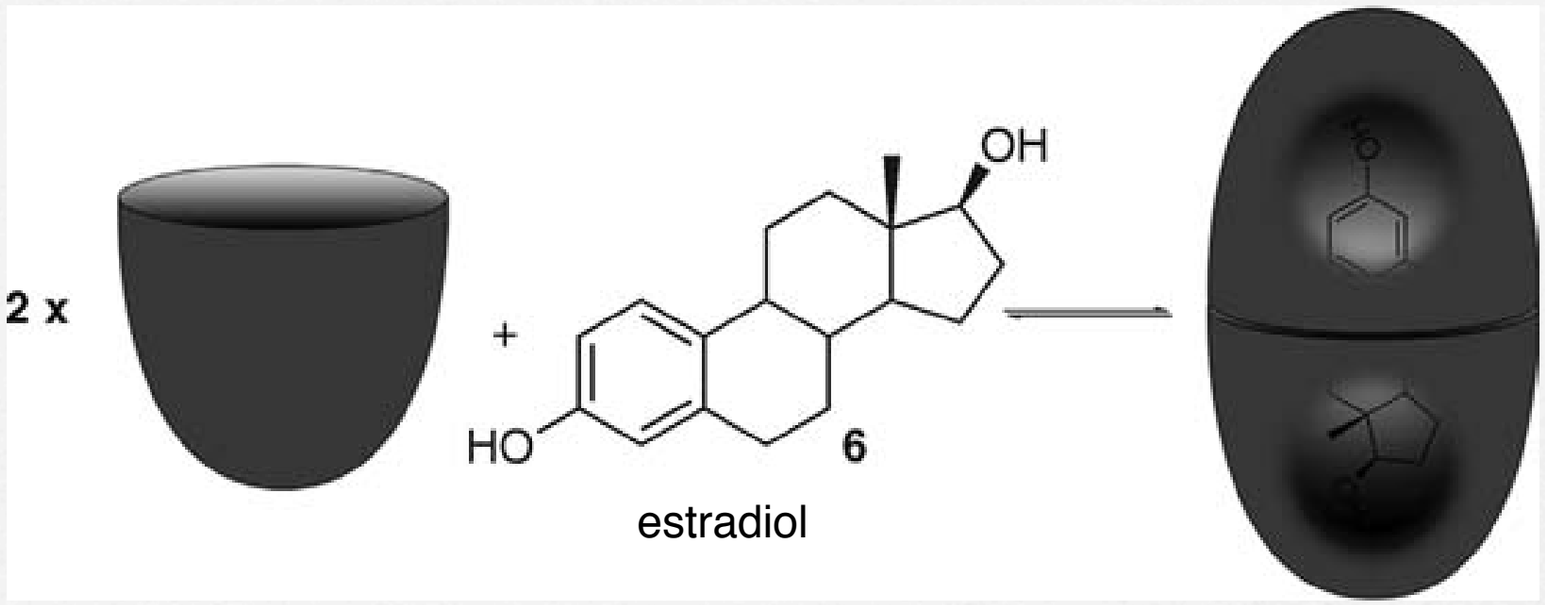


synthesis



Scheme 12.1 Synthesis of octa-acid cavitand **1**.

encapsulation



encapsulation

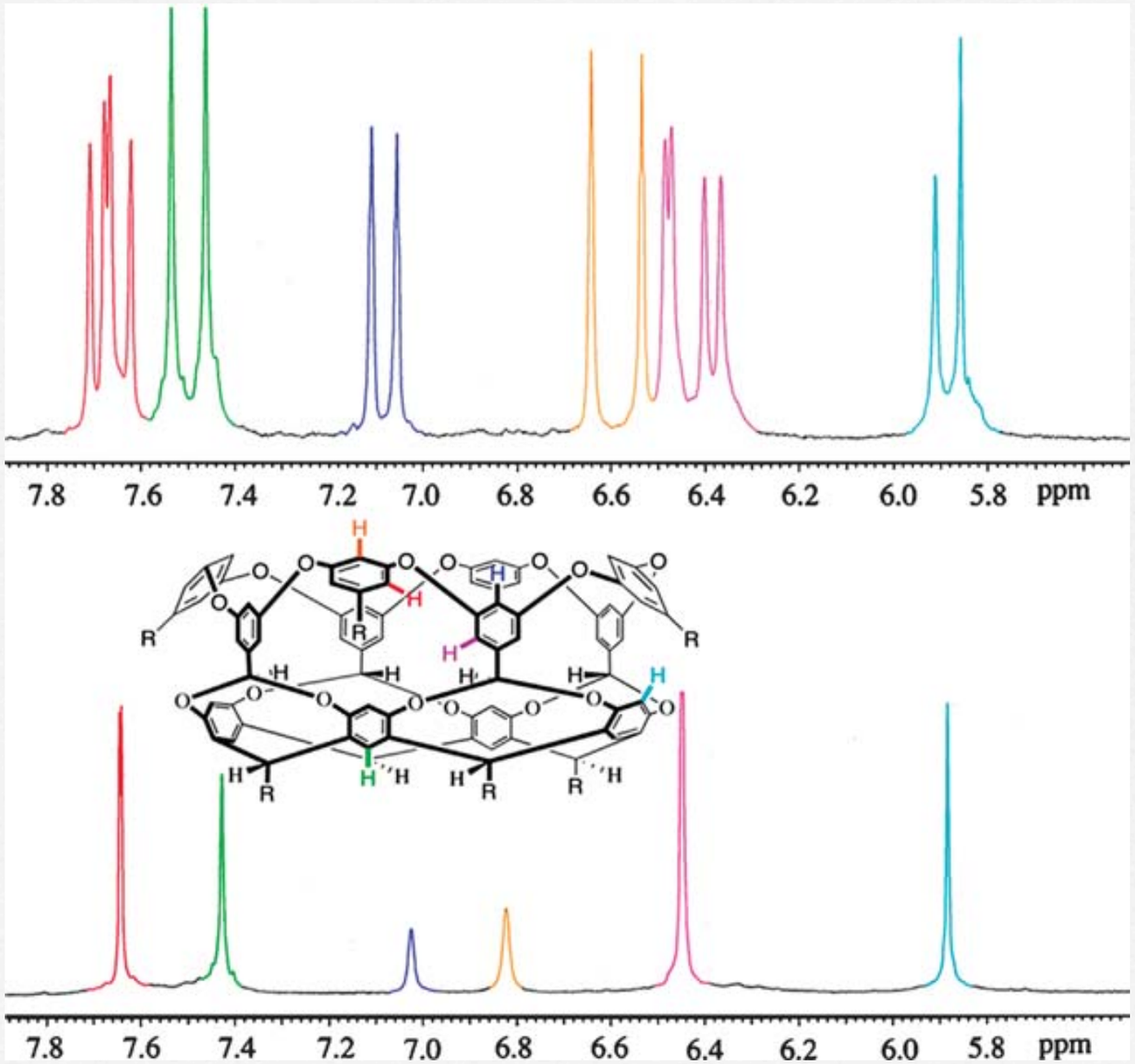
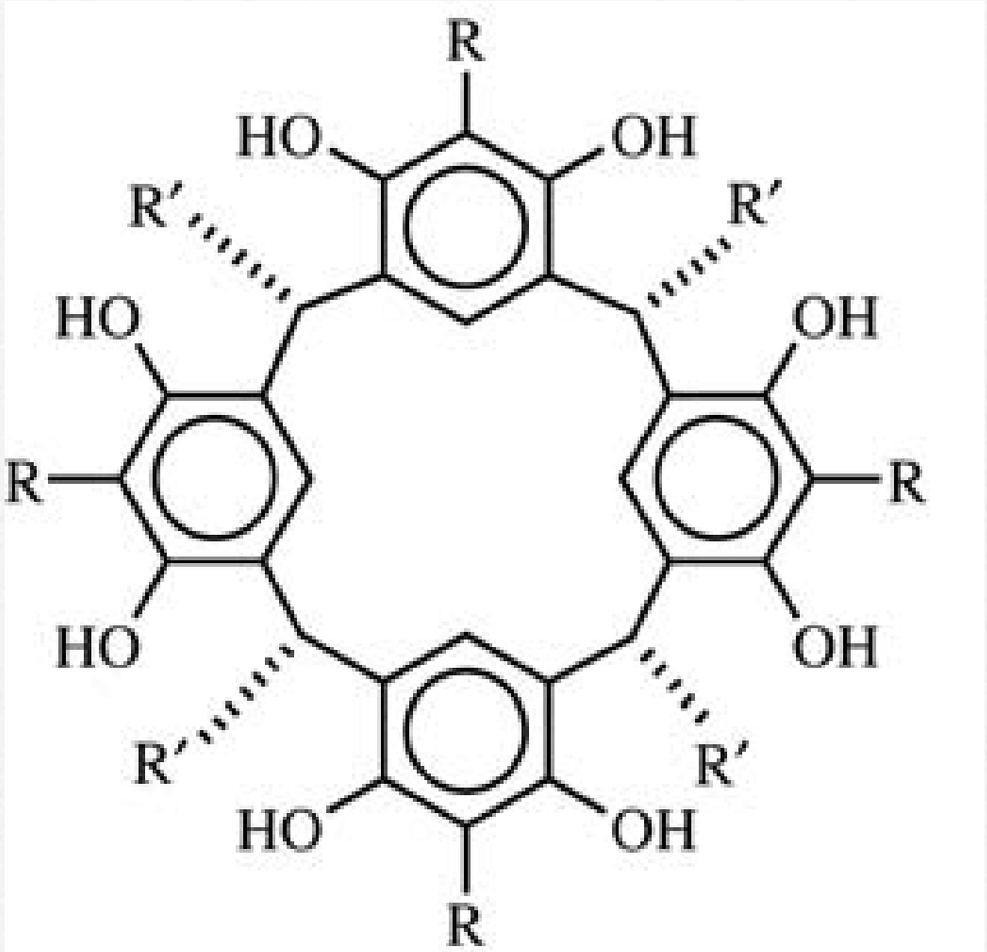


Figure 12.5 Selected region of the ^{1}H NMR spectrum of cavitand **1** (lower trace) and its 2:1 complex with estradiol **6** (upper trace).

C-hexylpyrogallol[4]arene



R = OH, R' = C_6H_{13}

C-hexylpyrogallol[4]arene

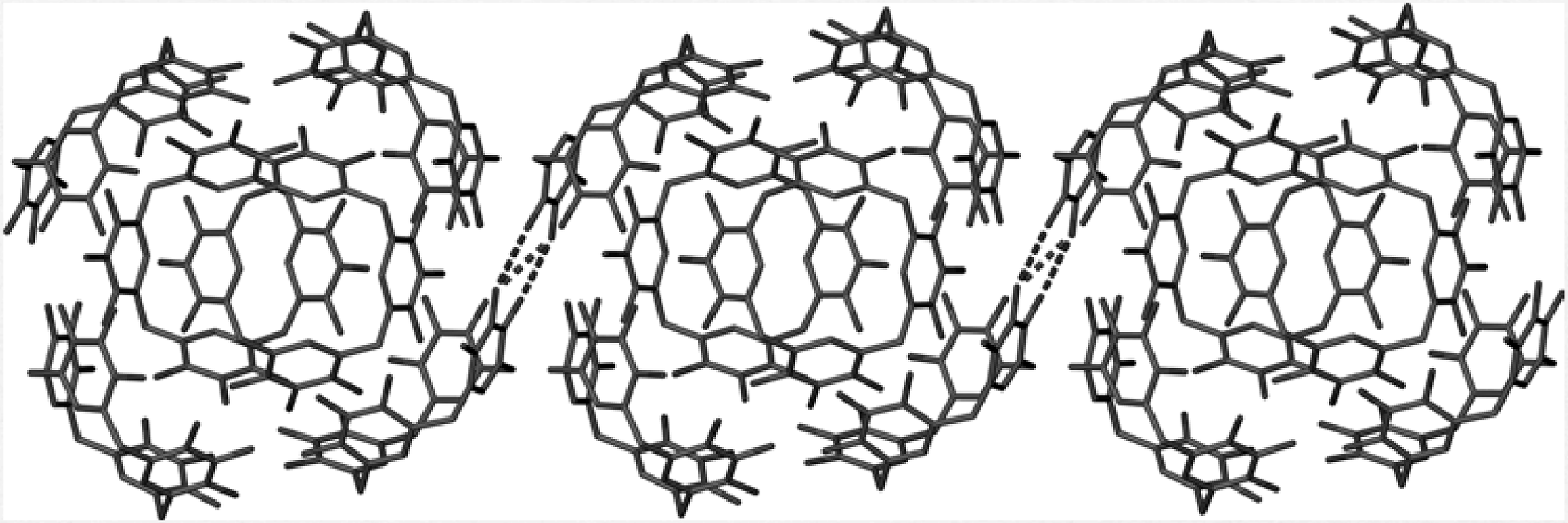
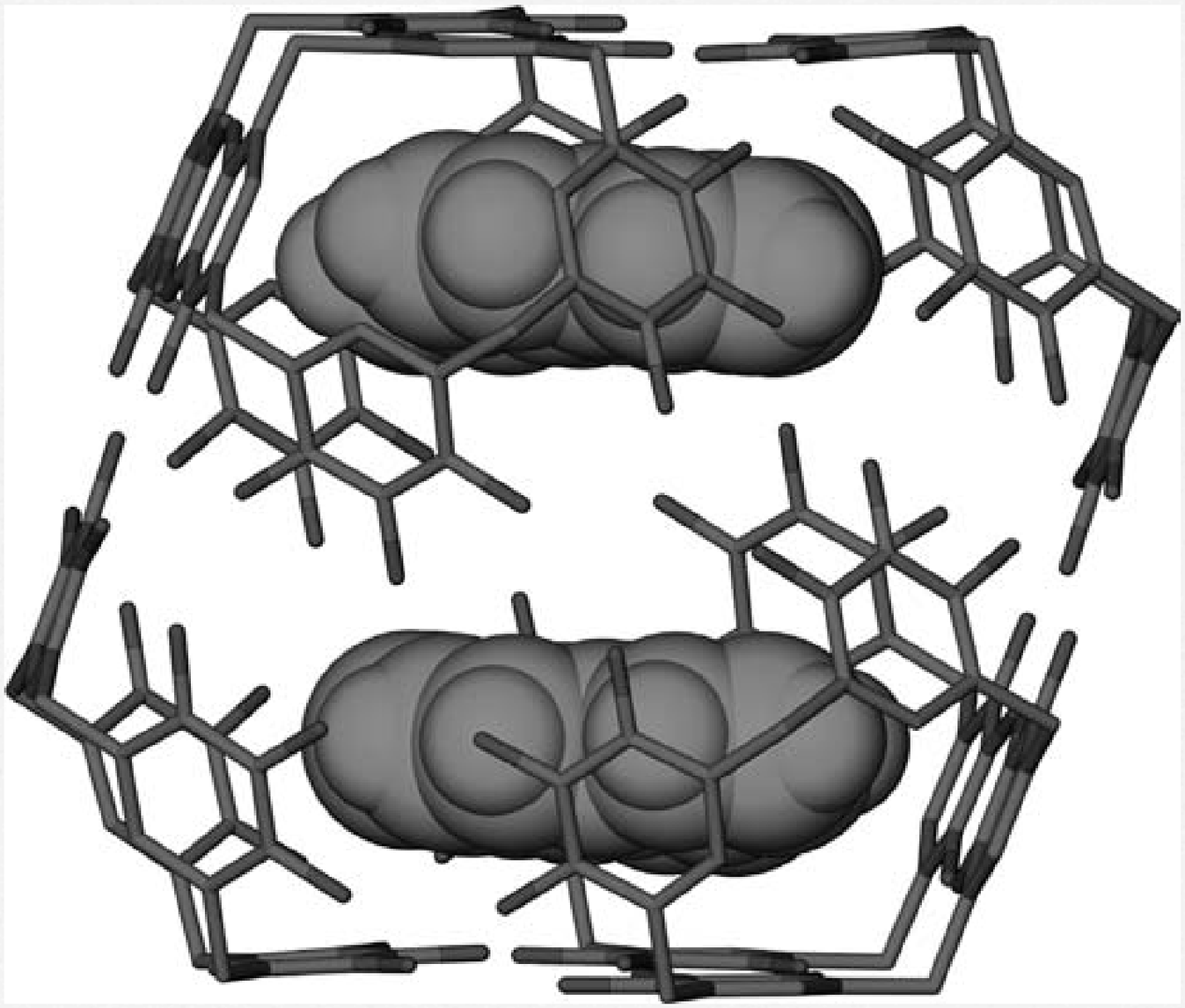


Figure 14.7 Some of the hydrogen bonding interactions found between nanocapsule walls when *C*-hexylpyrogallol[4]arene is crystallized from ethyl acetate [21].

C-hexylpyrogallol[4]arene



C-hexylpyrogallol[4]arene hexameric nanocapsule shrouding two pyrene butyric acid molecules

C-hexylpyrogallol[4]arene

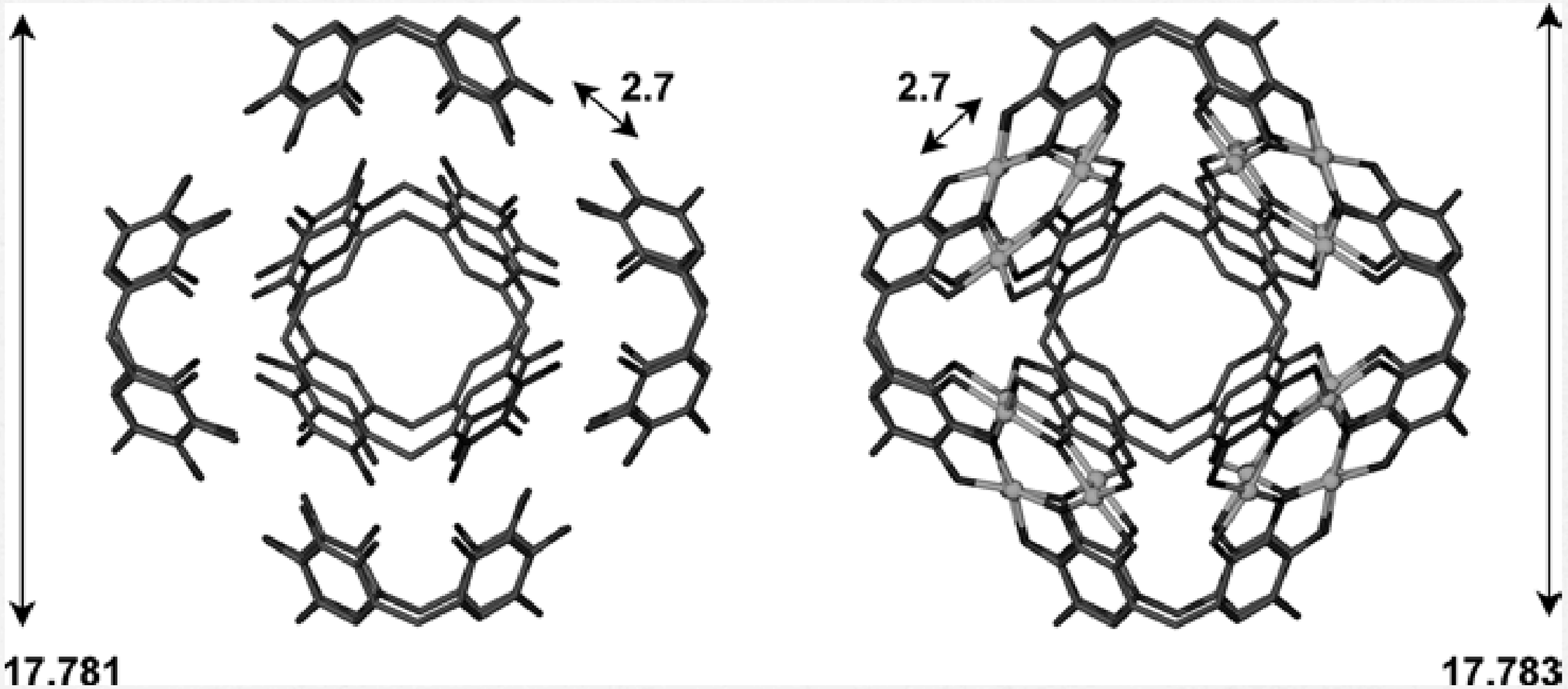
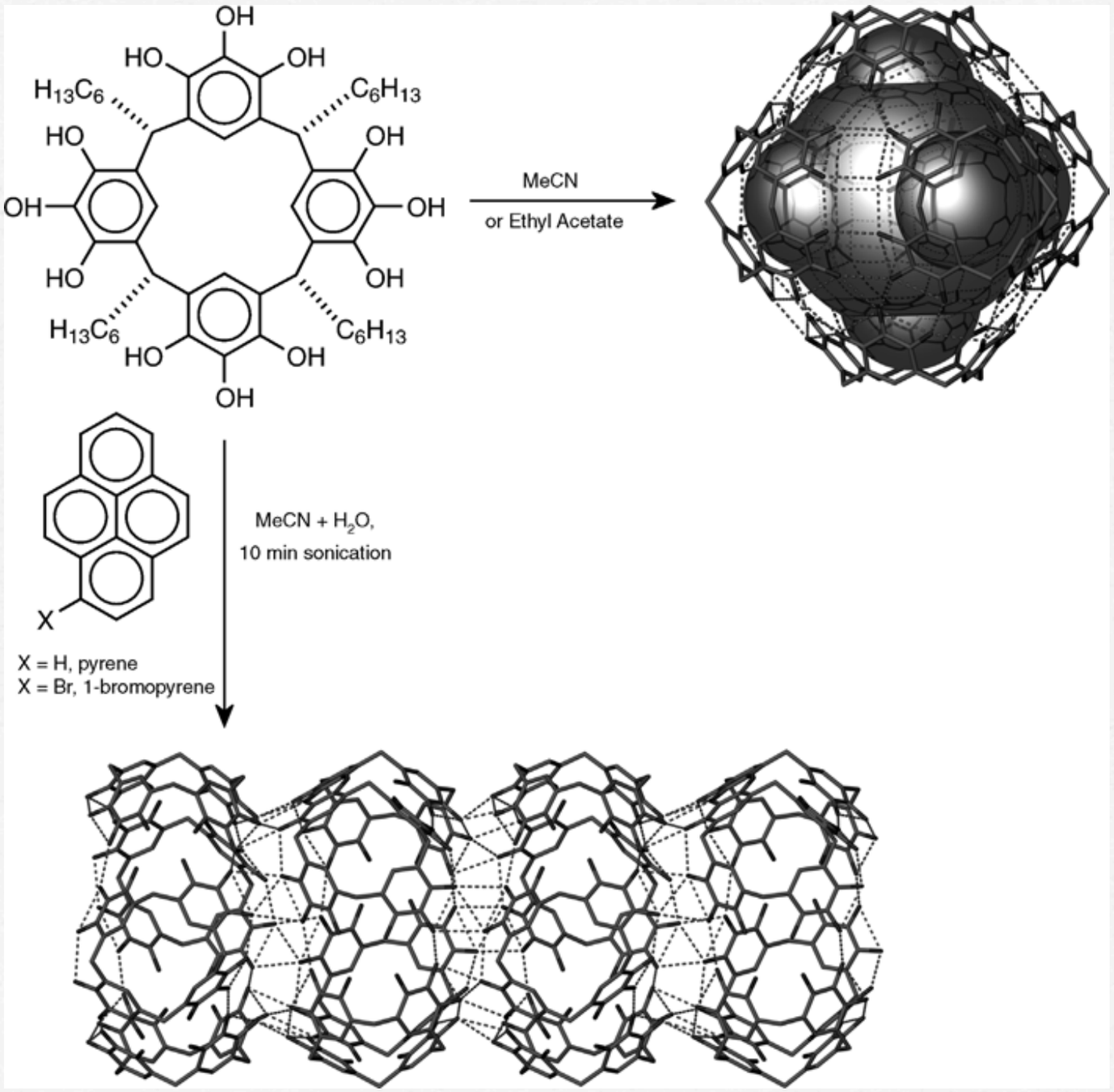


Figure 14.13 Comparison between the hydrogen-bonded (left) and copper bound (right) nanocapsules showing similarities in structure, shape and size of each assembly. Distances shown are in ångstroms [37].

C-hexylpyrogallol[4]arene



The conditions required to form either nanocapsules or nanotubular arrays of C-hexylpyrogallol[4]arene. In the latter, pyrene or 1-bromopyrene acts as a type of molecular glue on the exterior of the nanotubular assembly, interacting through many van der Waals interactions