The Importance of Shape – A Primer for Chemical Consultants

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Chemical Consultants Network Meeting

Philadelphia 12/12/12

What I learned from Wolfgang Pauli

When Pauli's wife left him for a chemist he remarked in wonder to a friend:

"Had she taken a bullfighter I would have understood. But a *chemist…*"

Bill Bryson, A Short History of Nearly Everything, 2003, p.180

What I learned from Jeremy Knowles

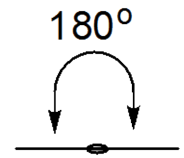
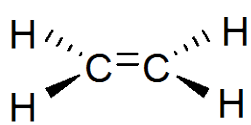
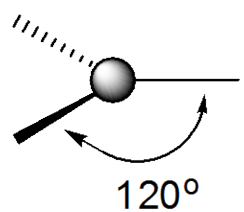
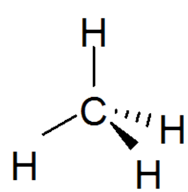
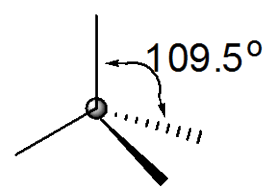
“What really interests me is whether God could have created the world any differently; in other words, whether the demand for logical simplicity leaves any freedom at all.”

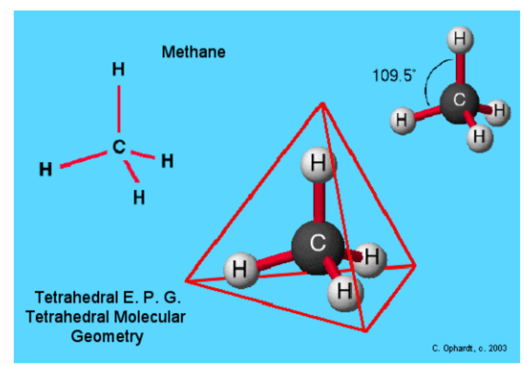
Albert Einstein

Outline

- Geometry surrounding atoms (electron geometry)
- Equivalents of regular solids that have been synthesized
- Rotaxanes, catenanes, knots, etc.
- Stereochemistry (cis/trans, E/Z, R/S)
- Polymers
  - Natural and synthetic polymers,
  - Macromolecules that are not polymers
  - Dendrimers and related (highly branched) polymers
- Self-assemblies (metal-organic frameworks, supramolecular coordination complexes)
- (Macro)molecules to be synthesized

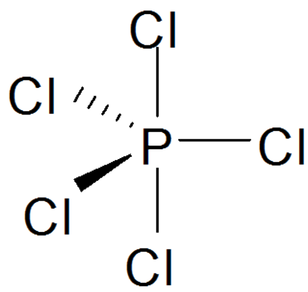
Atoms' geometry (I)

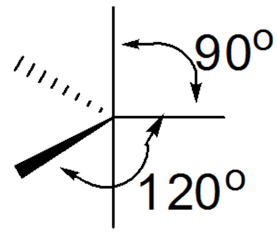
Central Atom Geometry	Example	Angle between bonds
linear	O=C=O	
trigonal (triangular) planar		
tetrahedral		

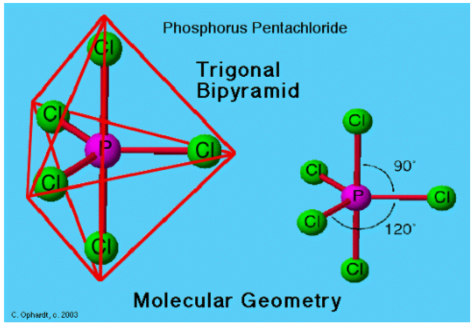


Atoms' geometry (II)

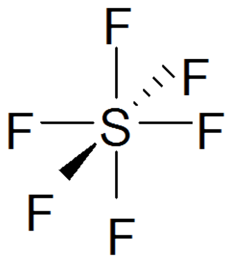
trigonal
pyramidal

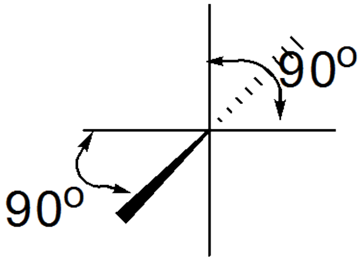




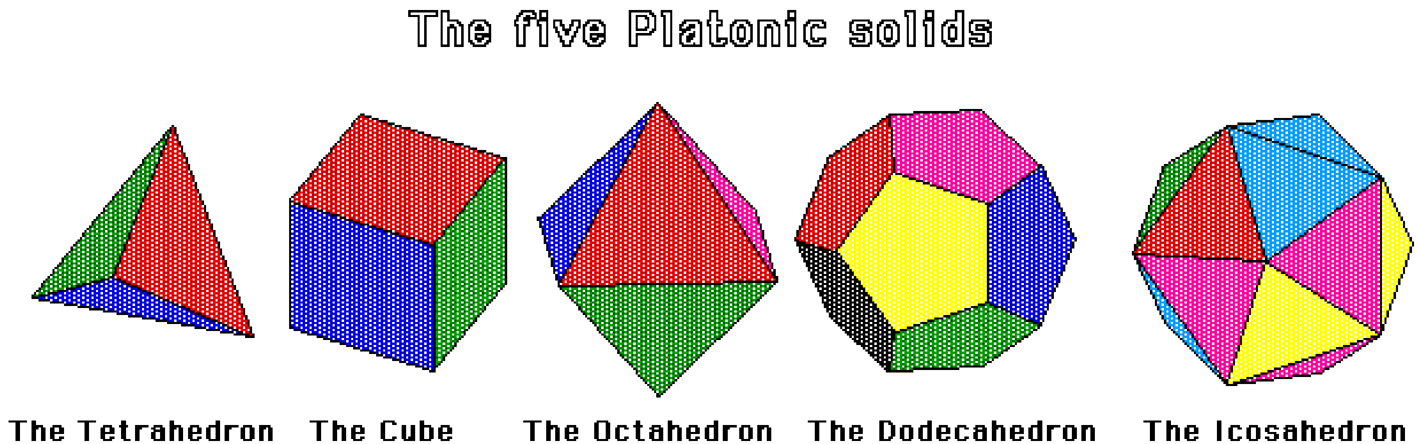


octahedral





Regular polyhedra – Platonic solids



The five regular solids discovered by the Ancient Greek mathematicians are:

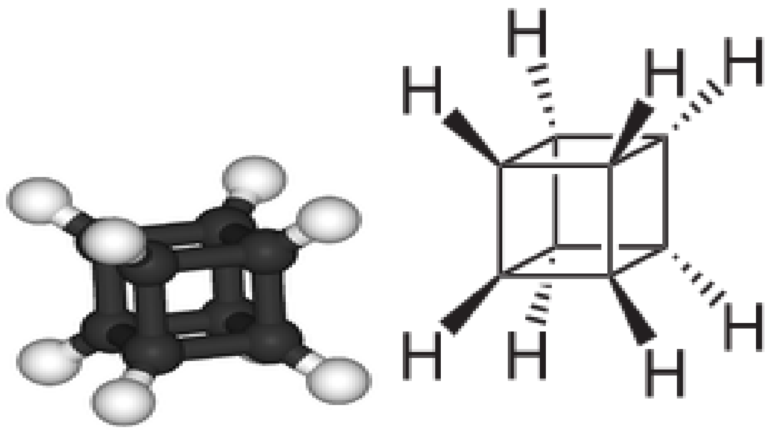
The **Tetrahedron**:	4 vertices	6 edges	4 faces	each with 3 sides
The **Cube**:	8 vertices	12 edges	6 faces	each with 4 sides
The **Octahedron**:	6 vertices	12 edges	8 faces	each with 3 sides
The **Dodecahedron**:	20 vertices	30 edges	12 faces	each with 5 sides
The **Icosahedron**:	12 vertices	30 edges	20 faces	each with 3 sides

The solids are regular because the same number of sides meet at the same angles at each vertex and identical polygons meet at the same angles at each edge.
These five are the only possible regular polyhedra.

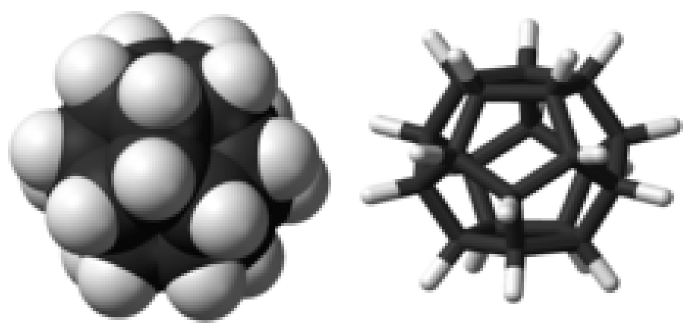
http://maths-wiki.wikispaces.com/Regular+Polyhedra

F –E +V = 2

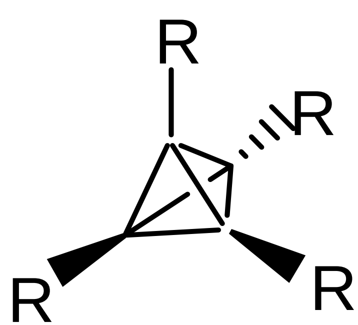
Synthesized regular solids



CUBANE (C_8H_8)



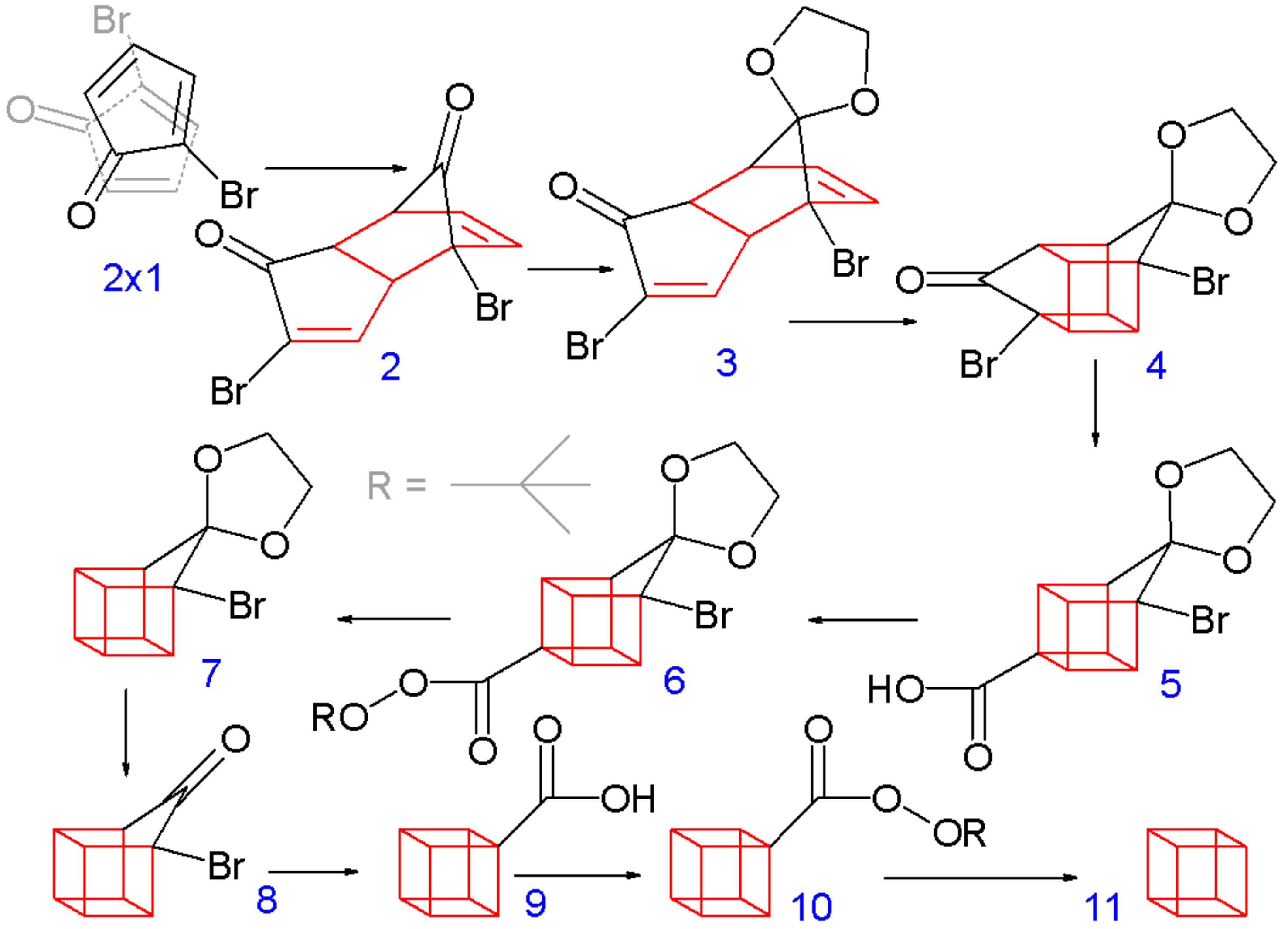
DODECAHEDRANE ($C_{20}H_{20}$)



TETRAHEDRANE

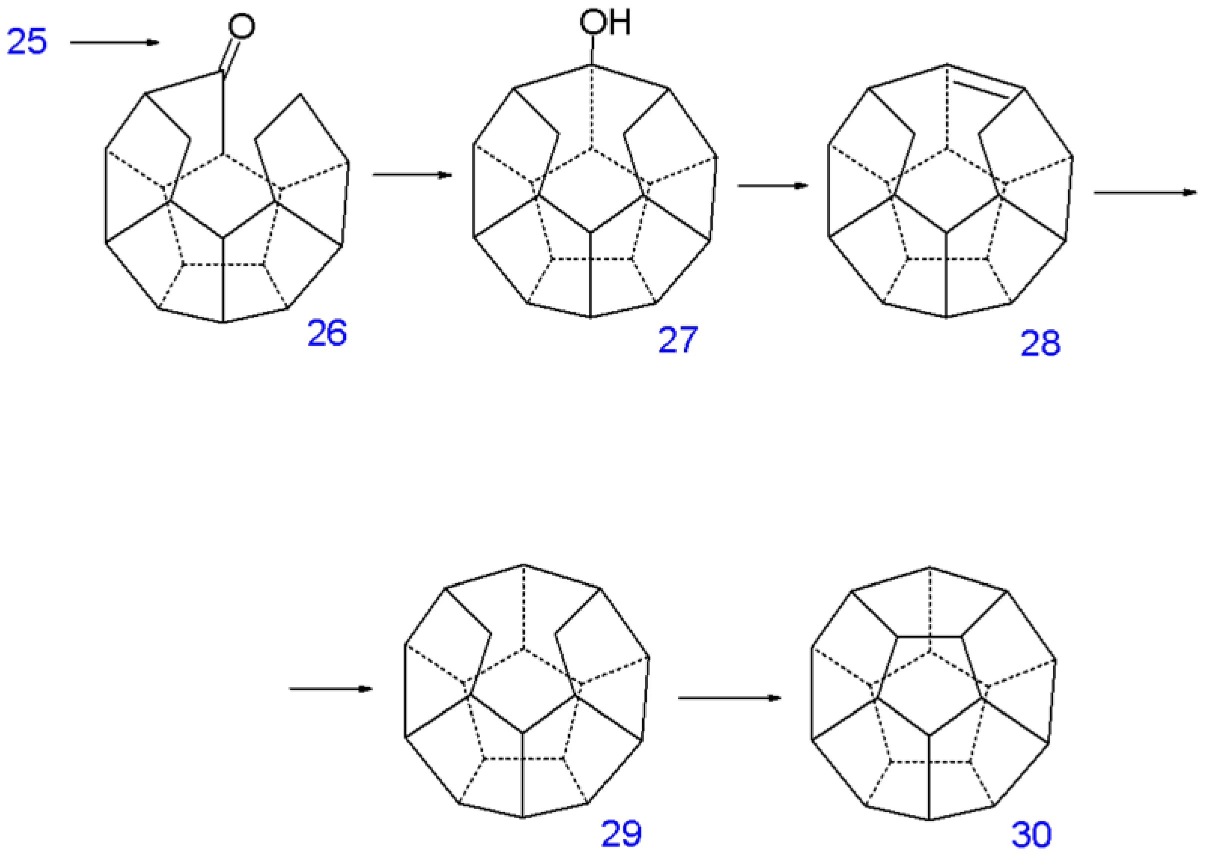
Eaton's synthesis of cubane (1964)

(about 12 steps)

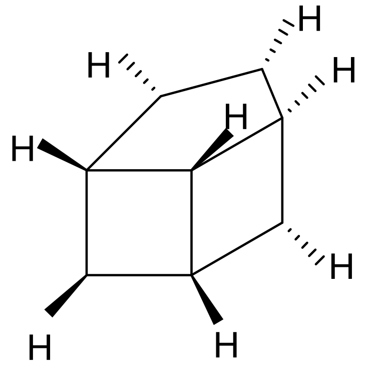


Paquette's synthesis of dodecahedrane (1982)

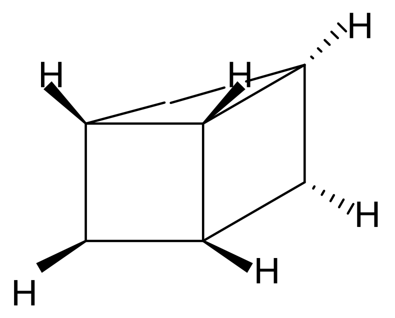
(29 steps)



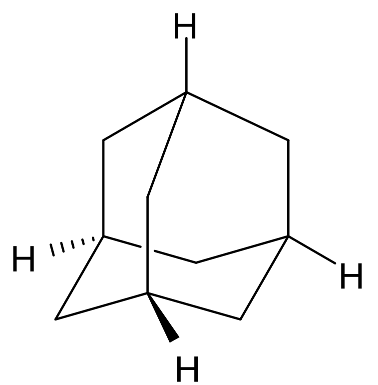
A few more



PENTAPRISMANE ($C_{10}H_{10}$)



PRISMANE (C_6H_6)

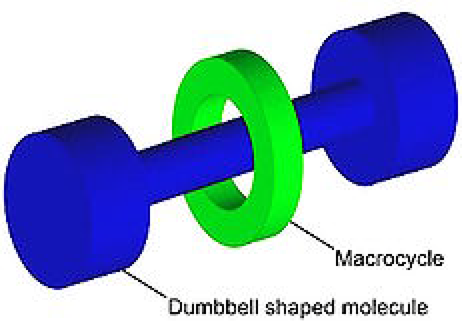


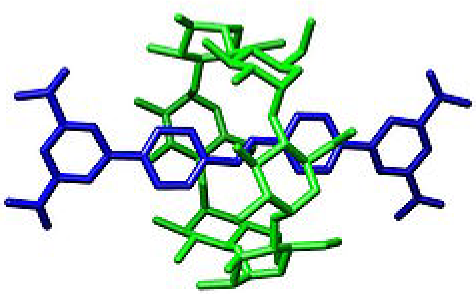
ADAMANTANE ($C_{10}H_{14}$)

Catenanes, Rotaxanes ……

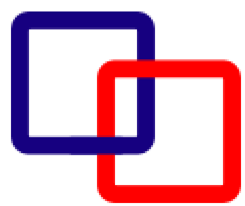
Video - http://en.wikipedia.org/wiki/Catenane

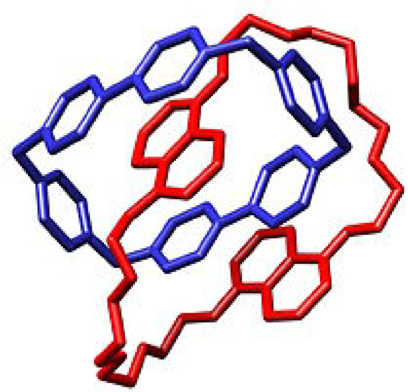
- Rotaxane Catenane Pretzelane



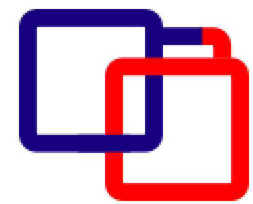


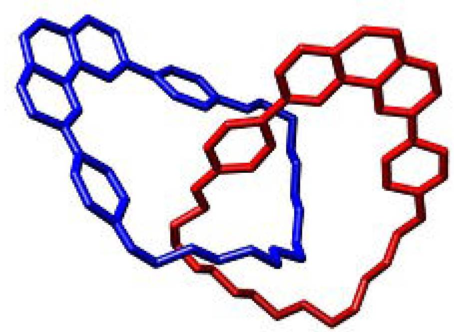
W. Clegg et al., *Chem. Commun*., **2001**, 493.





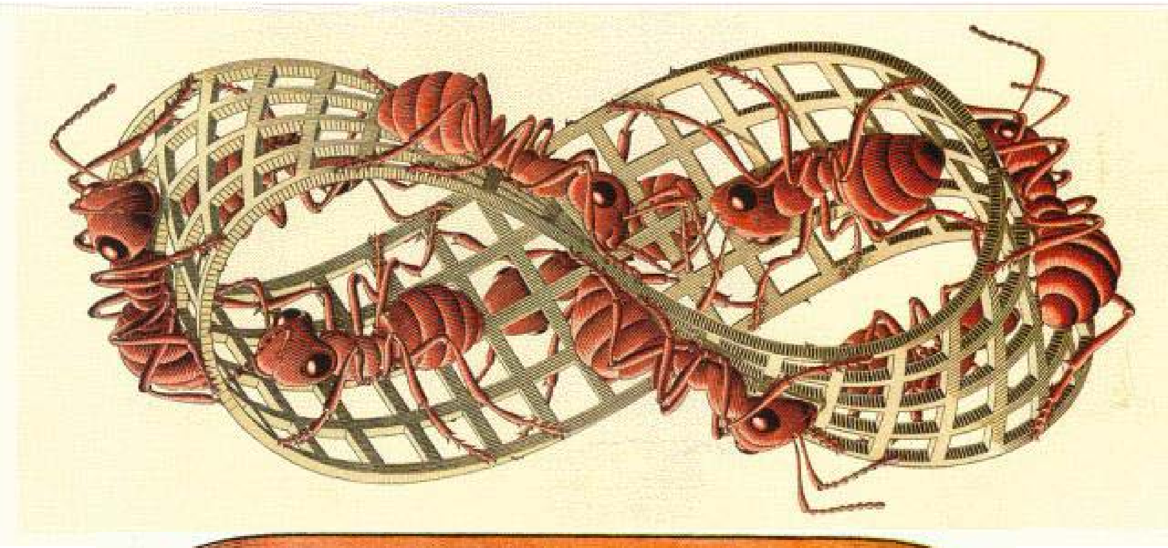
J.F. Stoddart et al., *Chem. Commun*., **1991**, 634.

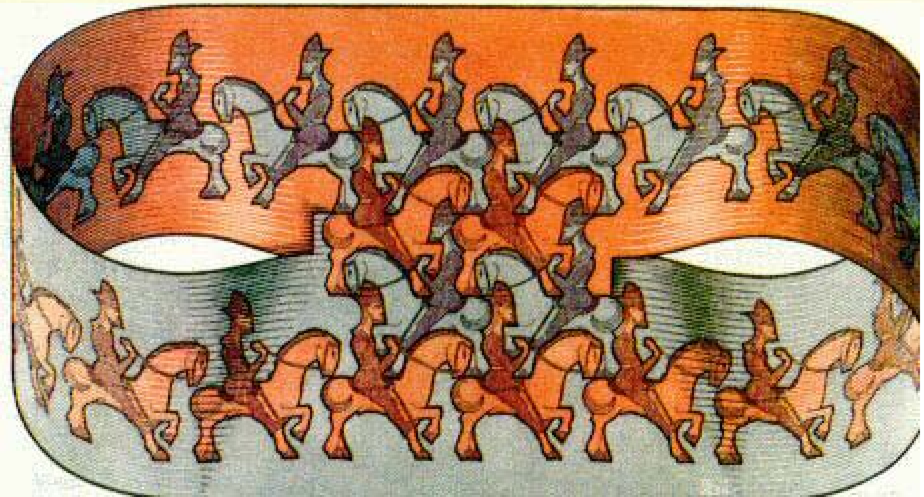


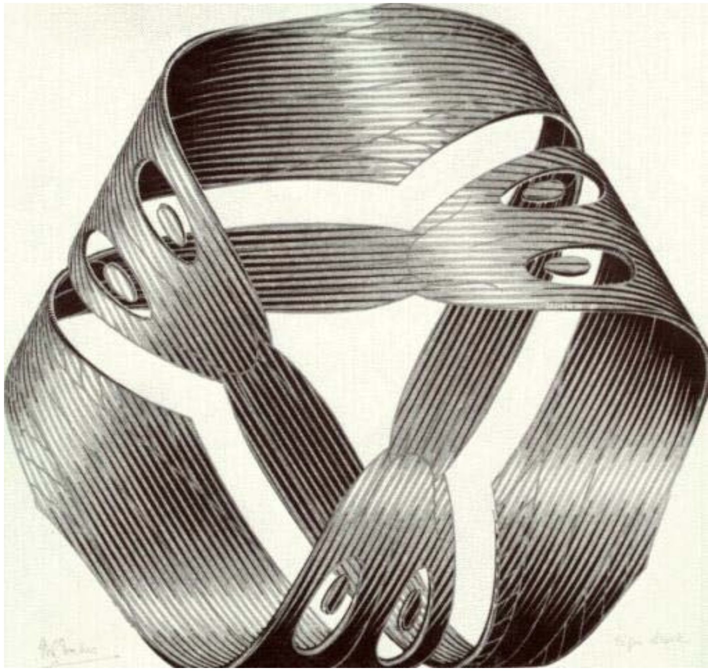


J-P.Sauvage et al.,
Chem. Commun, **1985**, 244.

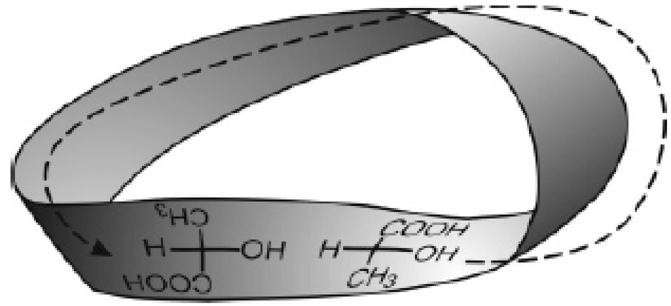
Escher’s Möbius strips







Möbius molecules



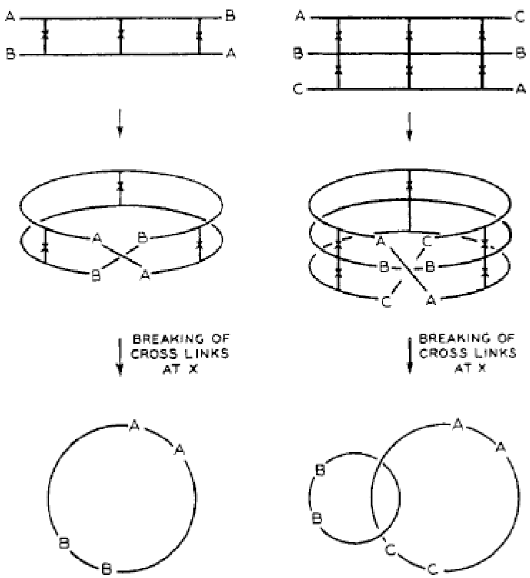
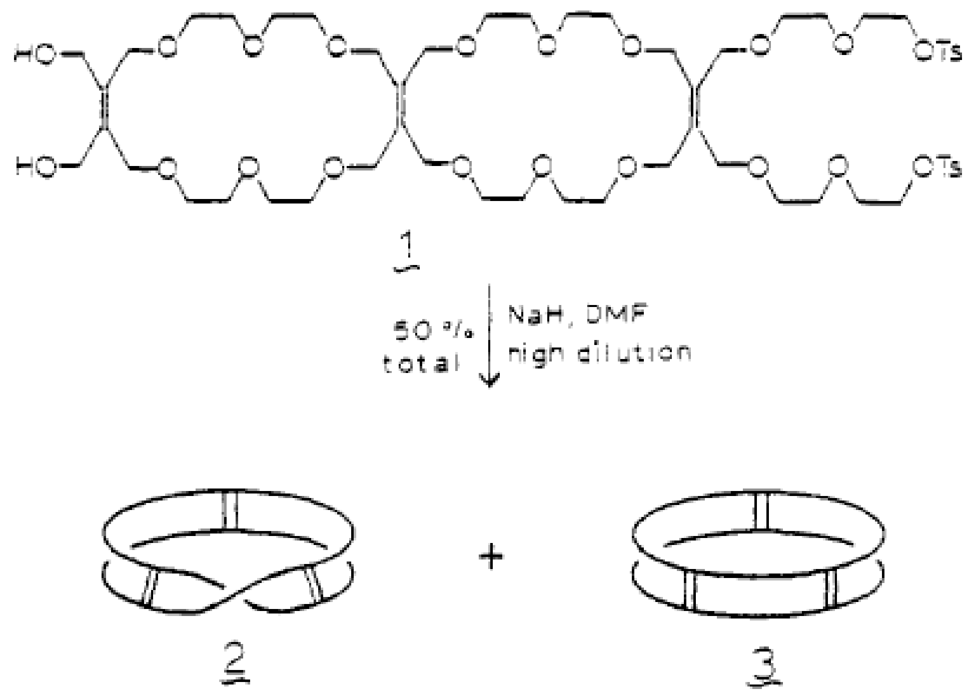


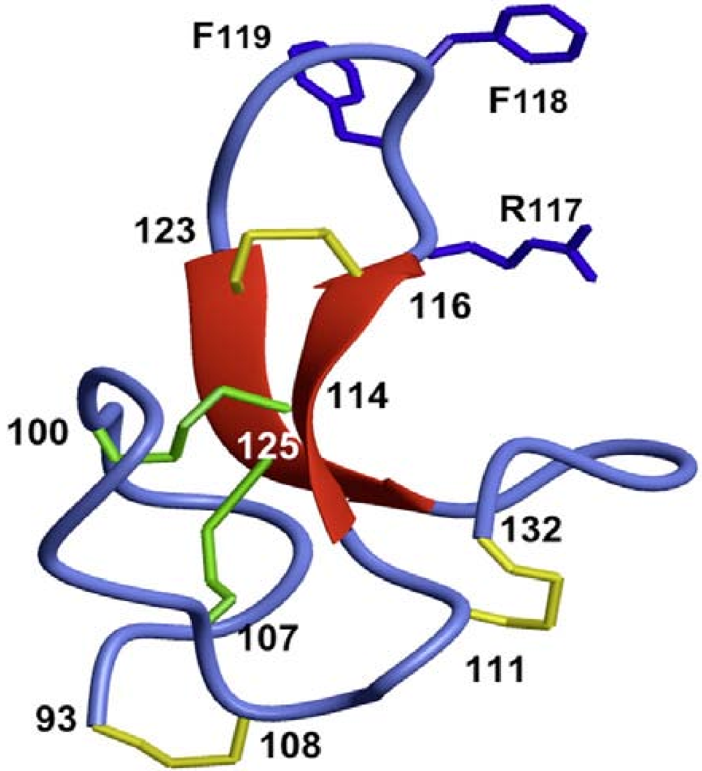
Fig. 2.—Möbius strips.

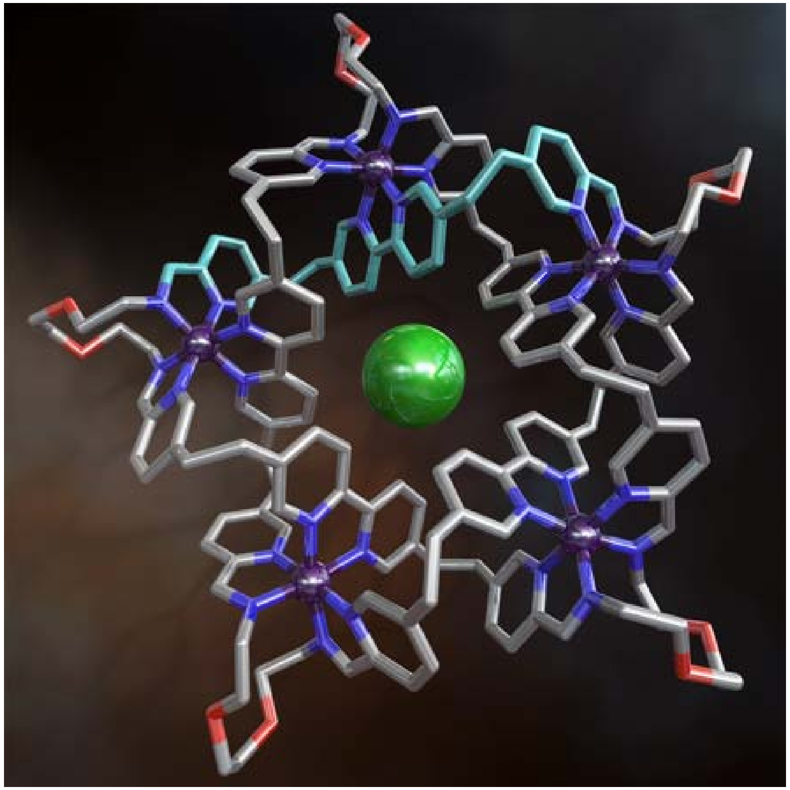
Scheme I



Wasserman, E. et al. *JACS,* **1961**, *83*, 3789.
Walba, D. et. Al. *JACS* **1982**, *104*, 3219
http://www.scs.illinois.edu/denmark/presentations/2008/Collins-1.pdf

Knots

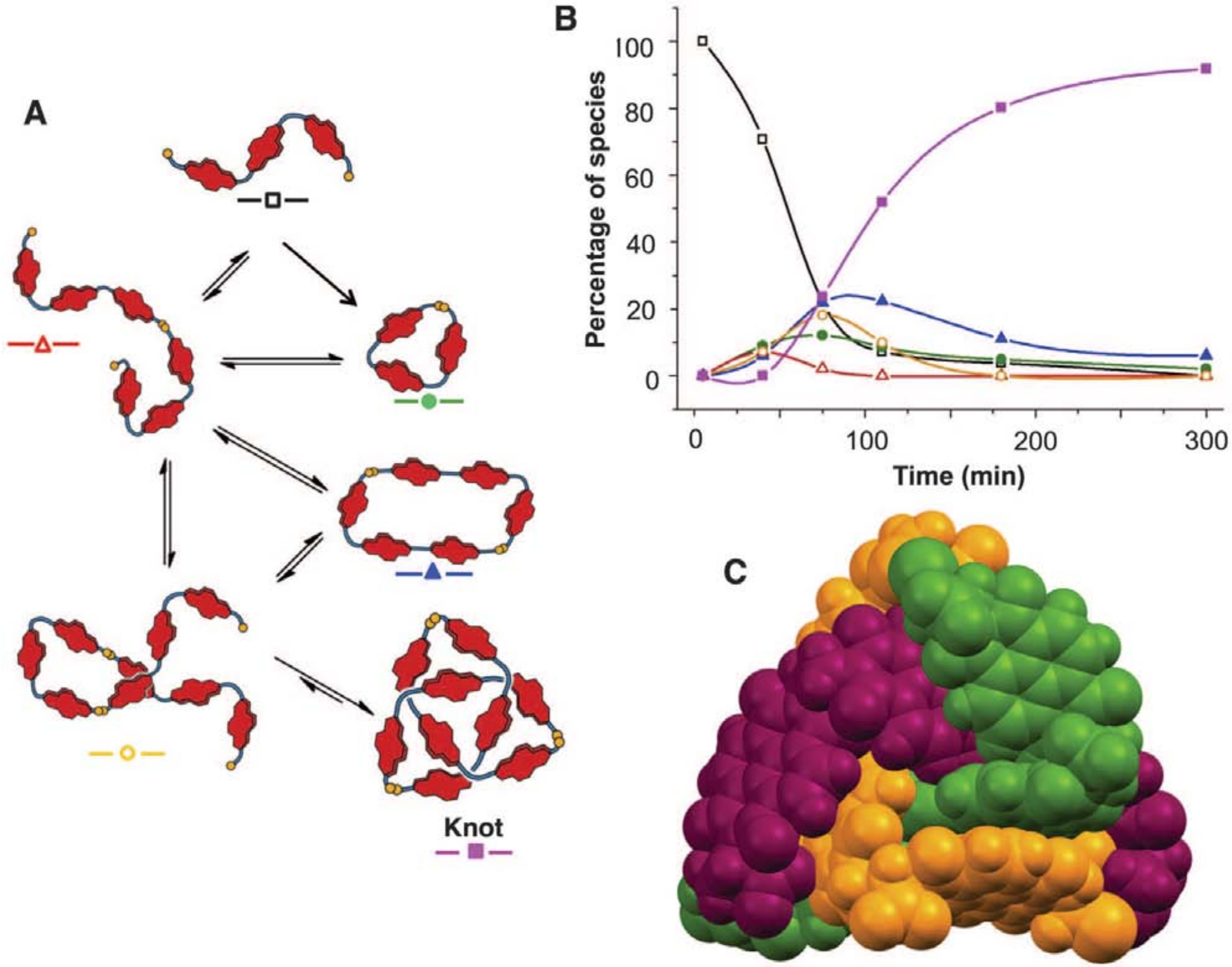




B. Yu, G. L. Millhauser, *FEBS Letters*, **2007**, 581, 5561

Leigh et al., *Nature Chemistry*, **2012**,4, 15.

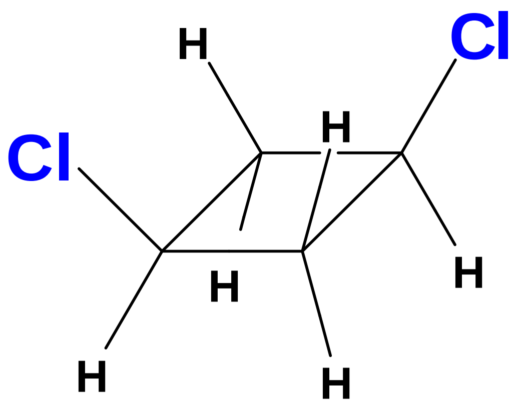
Building blocks may assemble into knots spontaneously



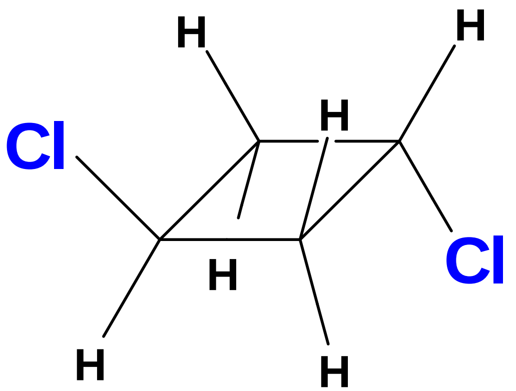
naphthalenediimide-based aqueous disulfide and amino acids

J.K.M. Sanders et al., *Science* **2012,** 338, 783.

Stereochemistry (I) – cis/trans

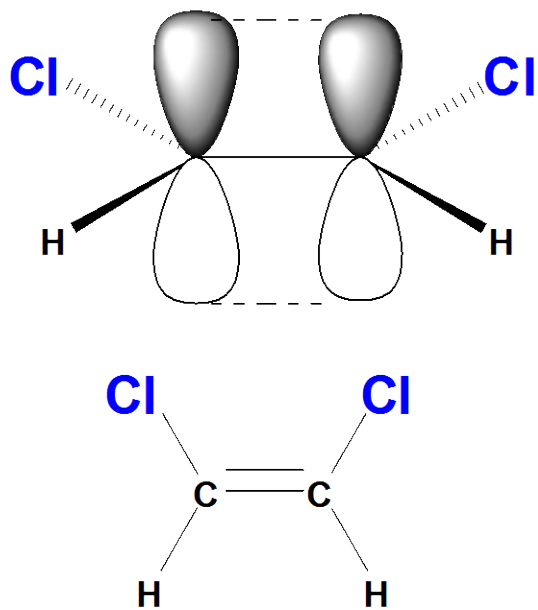


cis-1,3-dichlorocyclobutane



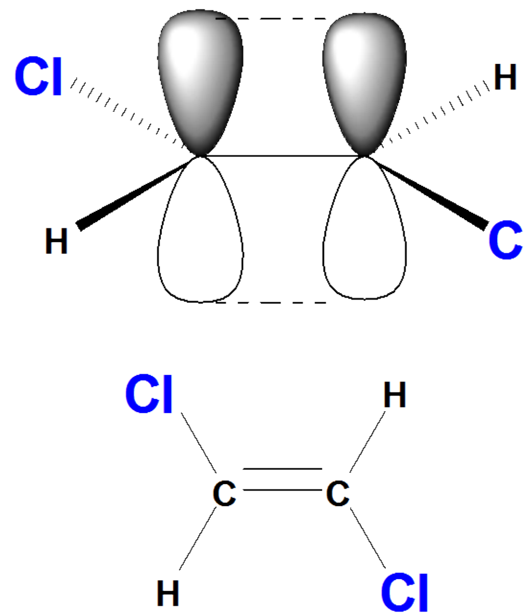
trans-1,3-dichlorocyclobutane

Stereochemistry (II) – E/Z



Z-1,2-dichloroethene

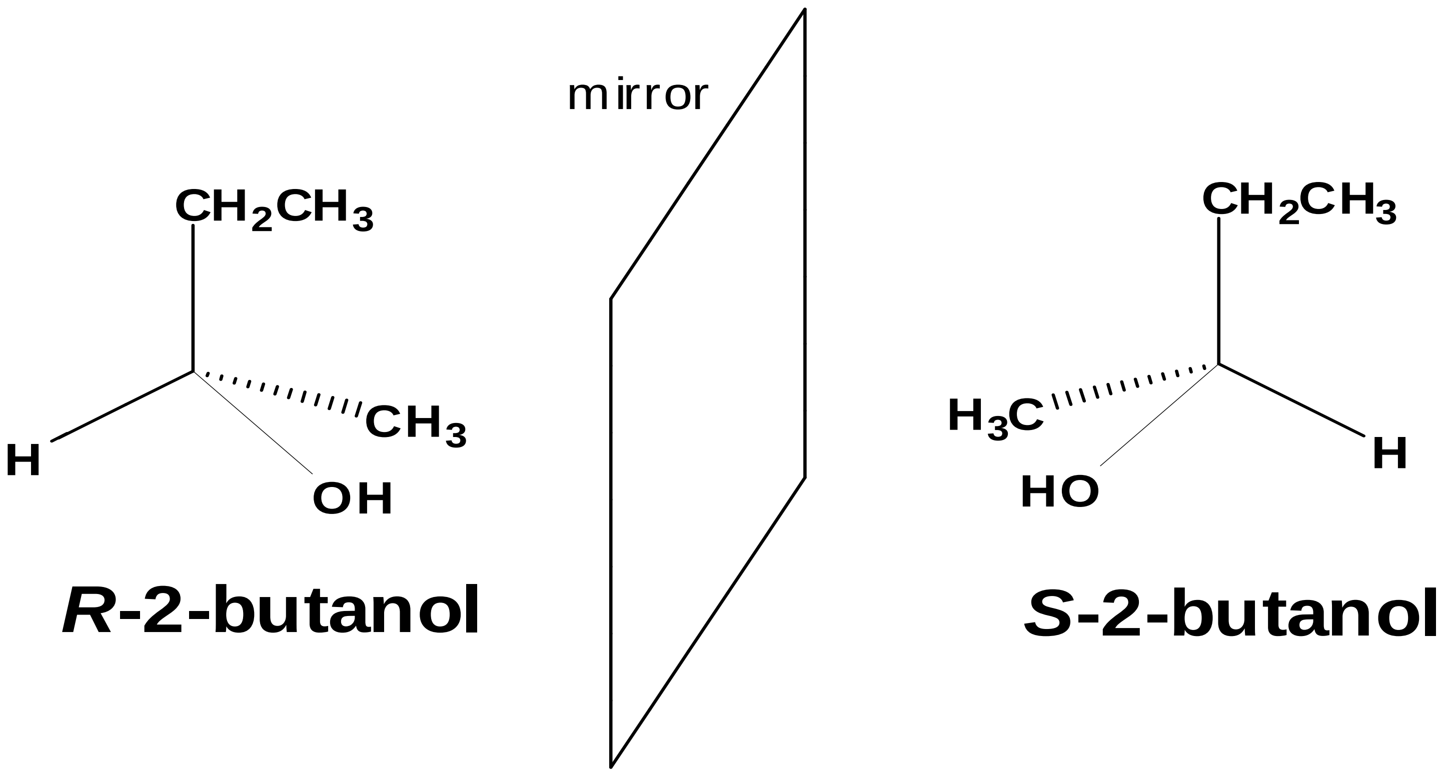
This is not (!!!) *cis*
-1,2-dichloroethene



E-1,2-dichloroethene

This is not (!!!) *trans*
-1,2-dichloroethene

Stereochemistry (III) – R/S

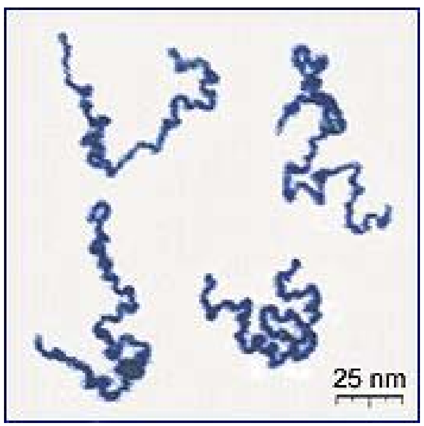


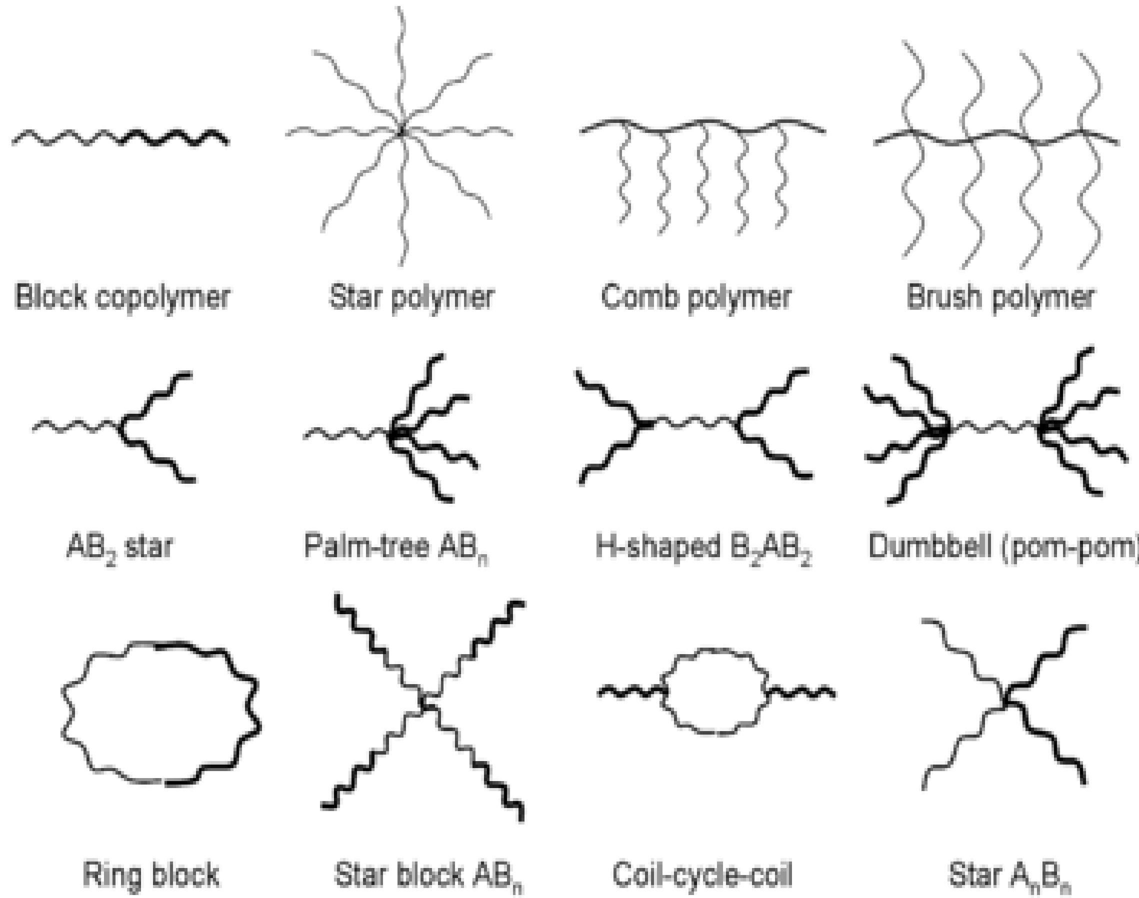
***R*-2-butanol**

***S*-2-butanol**

Polymers

Polymer chains



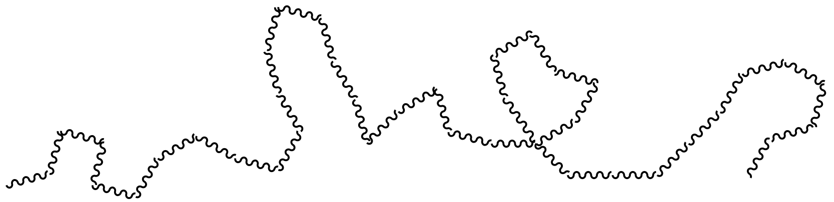


Polymer architectures

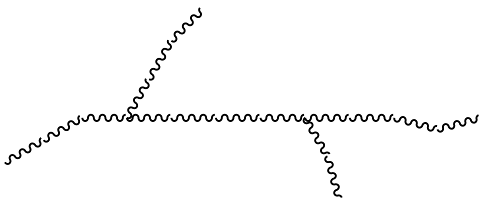
Wikipedia

Real polymers

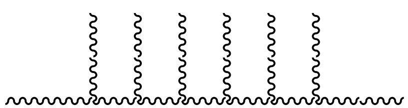
polymer



the real thing

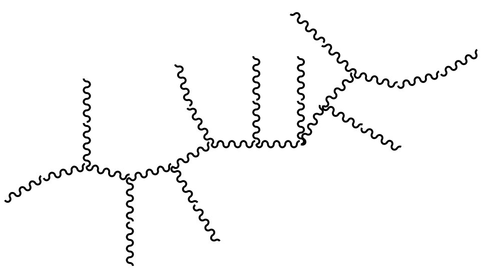


branched polymer



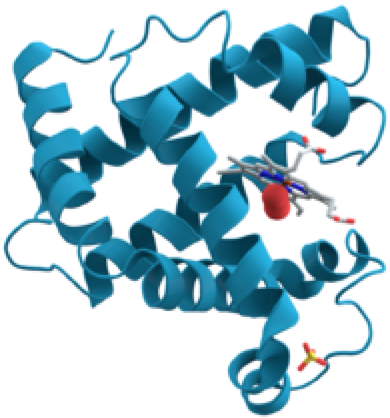
comb

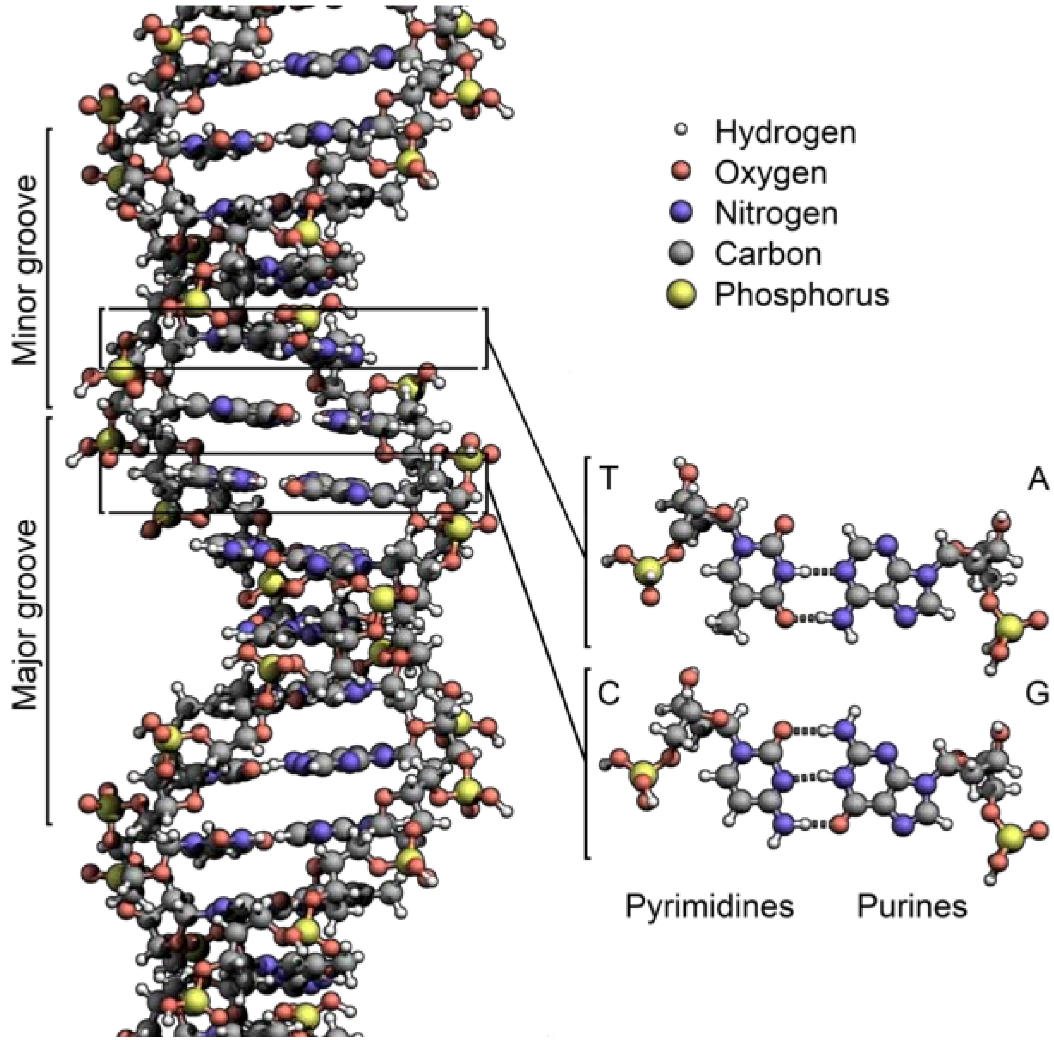
=



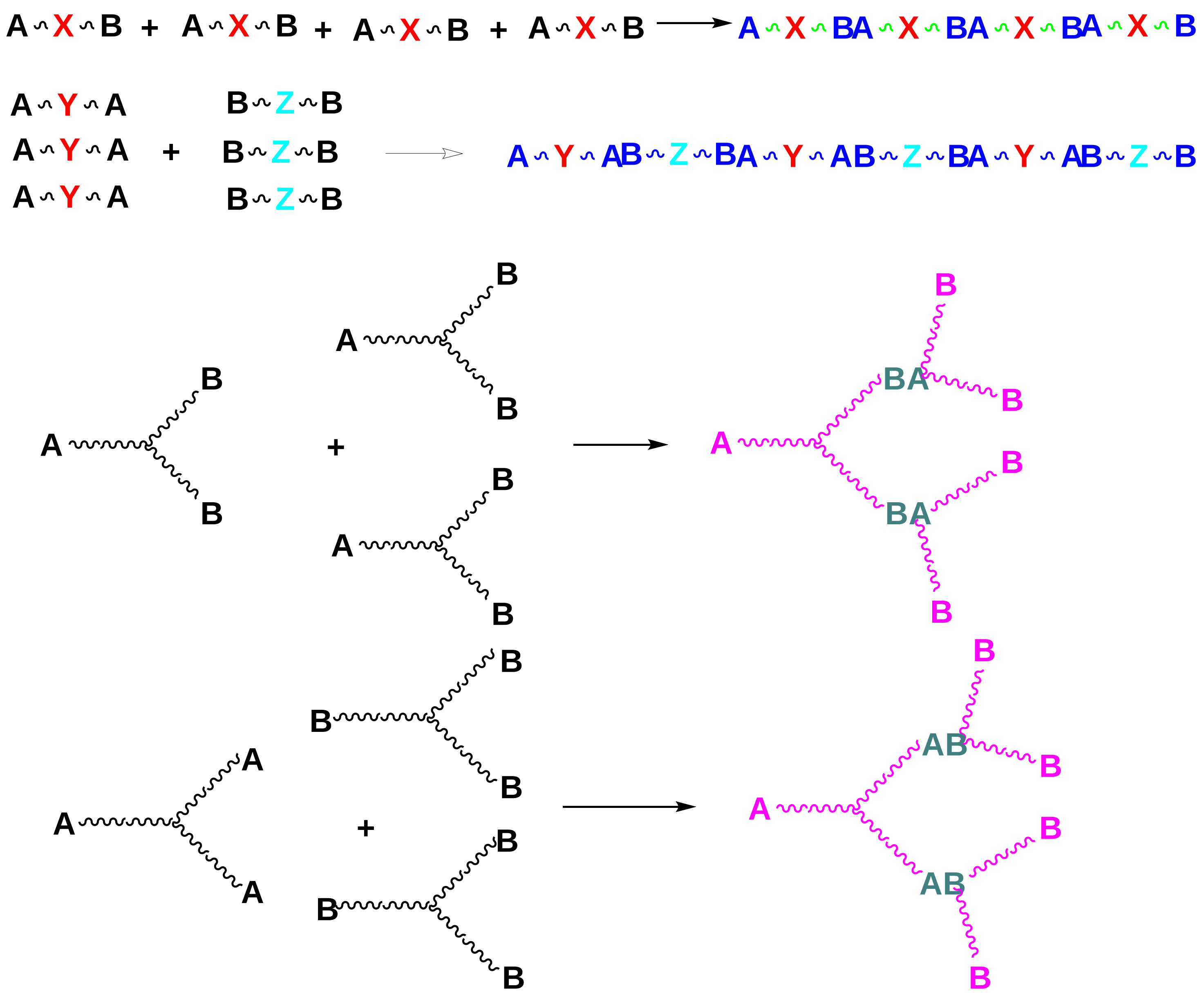
Natural macromolecules

- Myoglobin

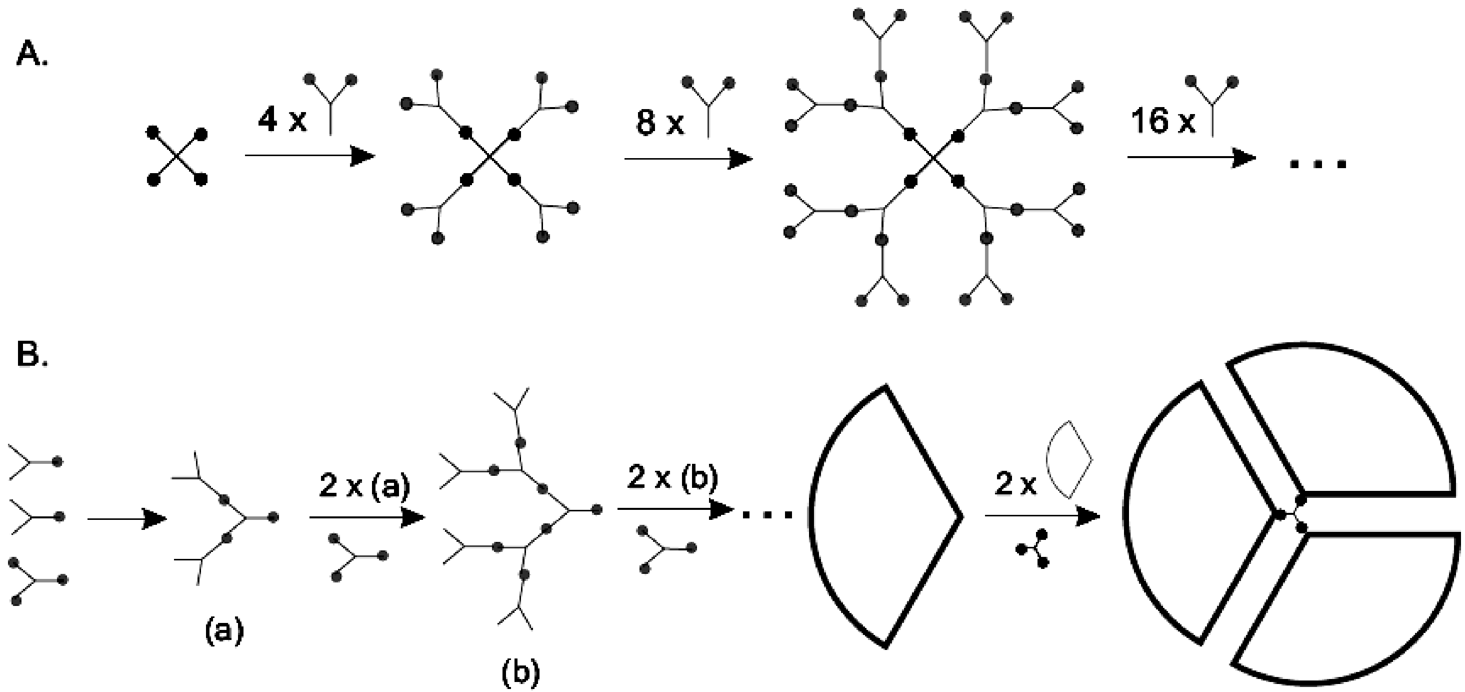




Polymerizations



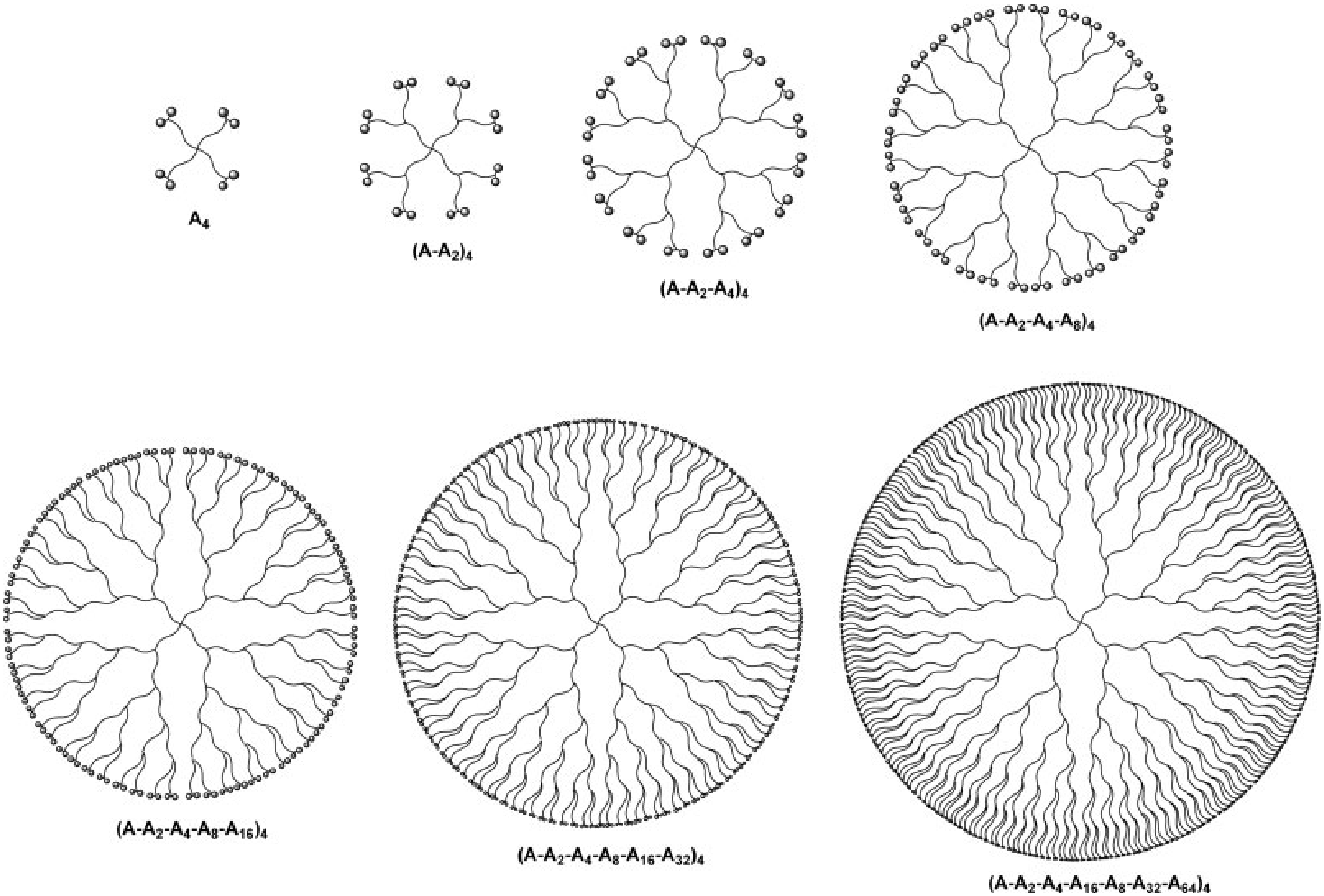
Dendrimer synthesis



A. The divergent growth method **B. The convergent growth method**

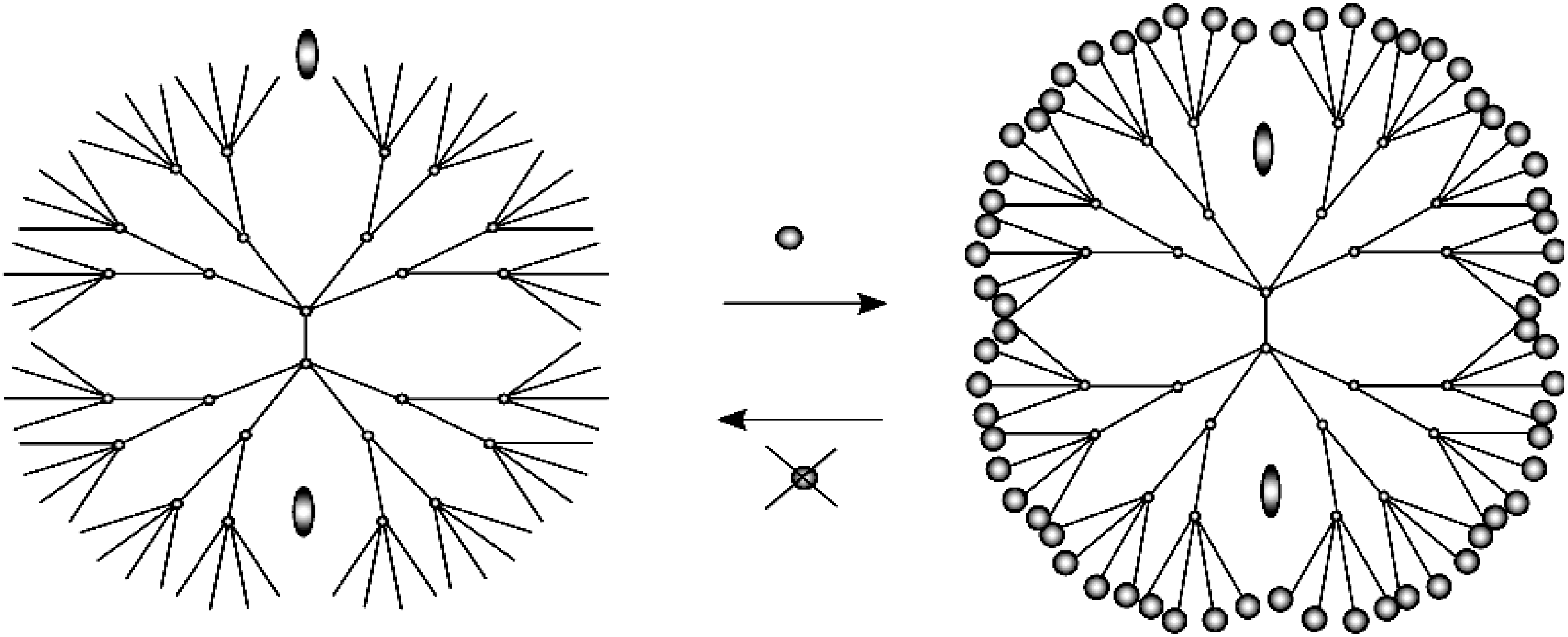
S. Ashvini, S. Asheesh, C. Dharmendra, N. Ritu, *IJRPS*, 2012, 2, 44.

Dendrimer-like star-branched architectures of G-1 to G-7



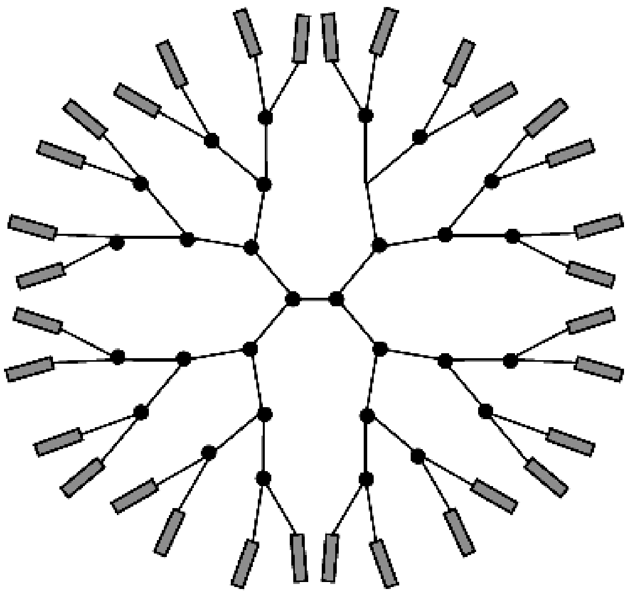
A. Hirao et al.,*J. Polym. Sci. Part A: Polym. Chem*., **2006**, 44 , 6659

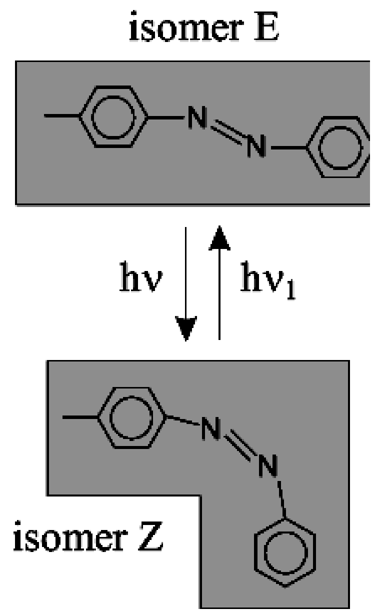
Dendritic box, encapsulating guest drug molecules



S. Asheesh et al., *Int. J. Res. Pharm. Sci.*, **2012**, 2, 44

How the release is controlled?

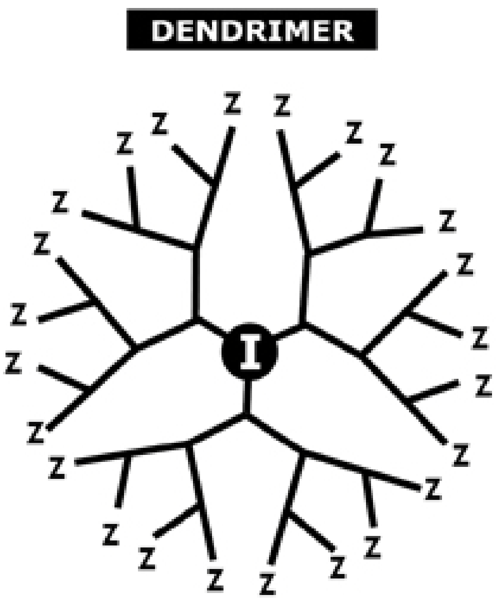




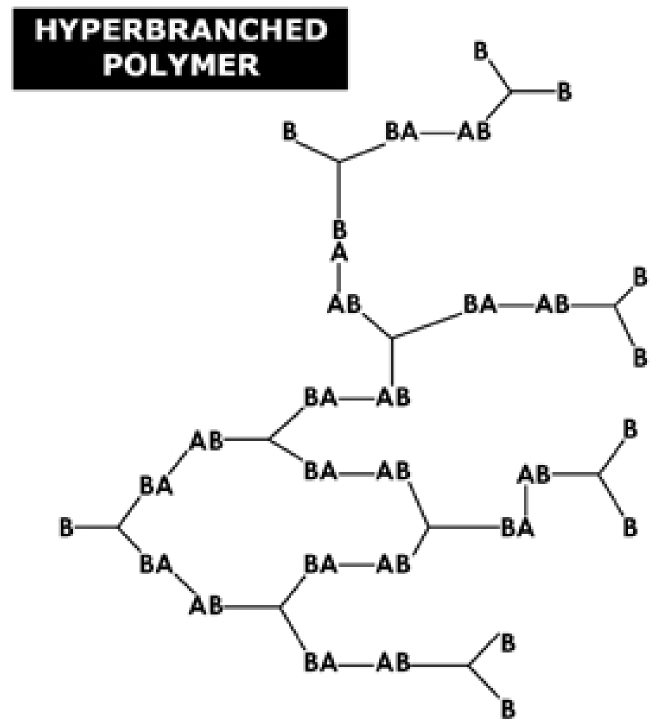
E **to** ***Z*** **at 313 nm**
Z **to** ***E*** **at 254 nm or heating**

S. Asheesh et al., *Int. J. Res. Pharm. Sci.*, **2012**, 2, 44

Dendrimers and hyperbranched polymers



- Well-defined core (I)
- Maximum branching
- Isomolecularity
- Large-number of end-groups (Z)
- Almost spherical shape
- Intramolecular cargo space



- No core
- High degree of branching
- Polymolecularity
- Large number of end-groups (B)
- Distribution of globular shapes
- Less well-defined intramolecular cargo space

Dendrimers' properties

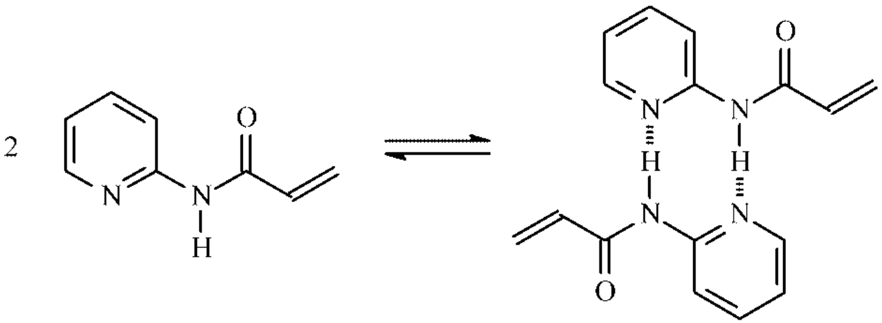
- Monodisperse macromolecules (as opposite to "normal" polymers)
- Tightly packed balls in solution (as opposite to coils)
- Significantly lower viscosity than comparable linear polymers
- Significantly higher solubility (50 – 10^5 times higher as compared with a linear equivalent)
- Due to globular shape and presence of internal cavities ability to control encapsulated guest molecules

Hyper branched polymers in *Extractive distillation*

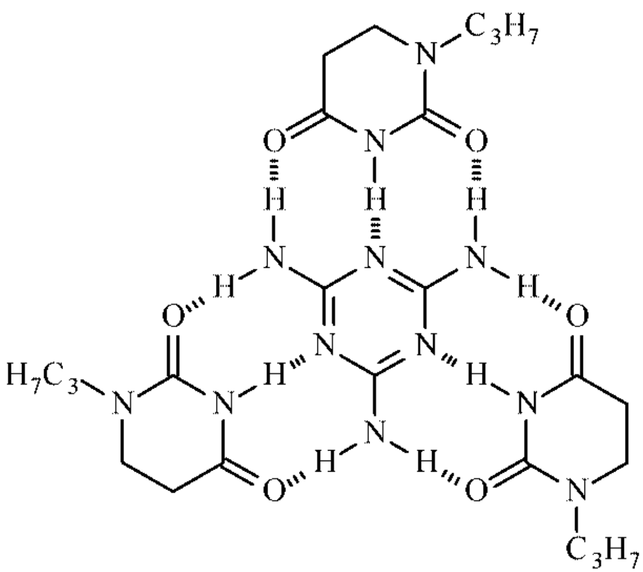
- a remarkable solubility (because of their large number of functional groups);
- a comparatively low solution viscosity (due to the highly branched topology);
- a remarkable thermal stability (up to 823K = 545ºC=1013ºF for hyper branched polyphenylenes);
- an increasing variety and large-scale availability at low cost (currently≥4 EUR/kg);
- noncorrosive behavior;
- no or tunable reactivity and toxicity;
- adjustable physical and chemical properties.

M.Seiler, *Fluid Phase Equilibria* 241 (2006) 155–174

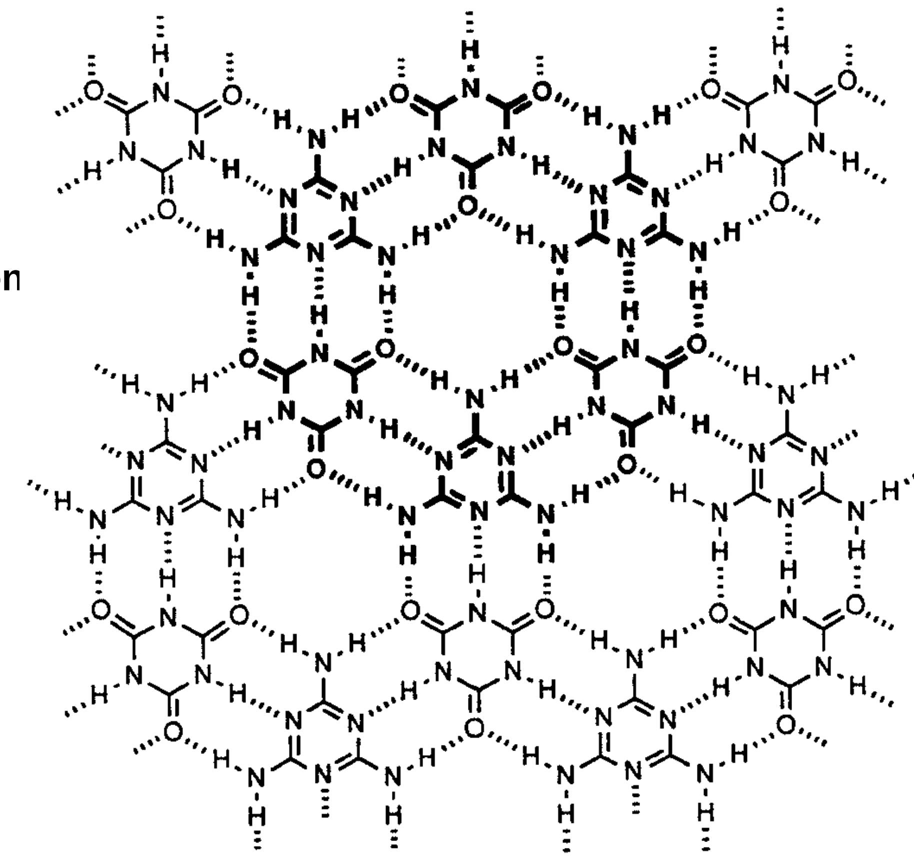
Self-assembly *via* multiple hydrogen bonding interactions



Self-association of 2-acrylaminopyridine in solution



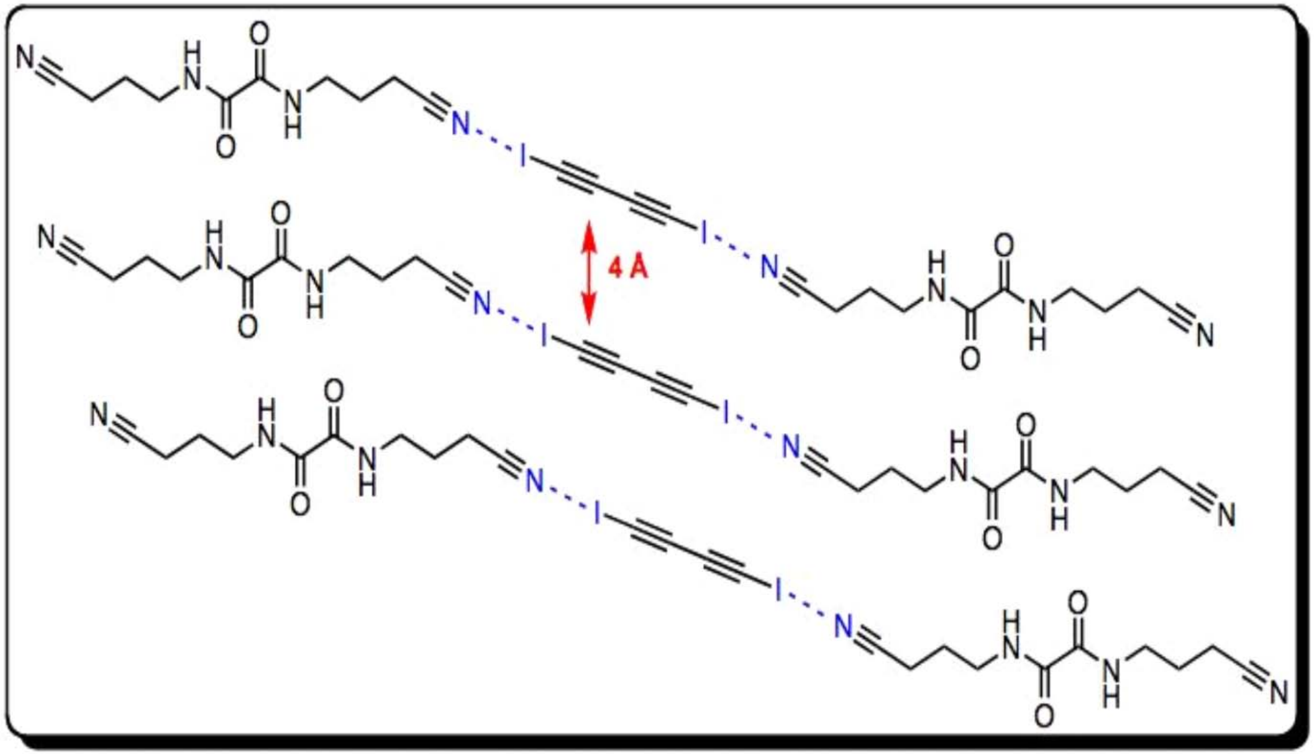
The 1+3 complex between melamine and 1-*N*-propylthymine



Cyanuric acid–melamine lattice12 (cyclic hexamer shown in bold)

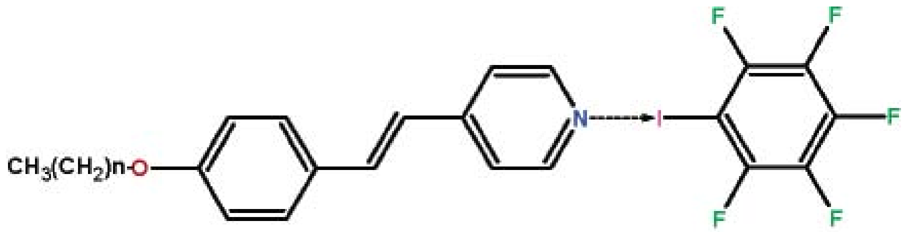
D. C. Sherrington, K. A. Taskinen, *Chem. Soc. Rev.*, **2001**, 30, 83.

Hydrogen and Halogen Bonding

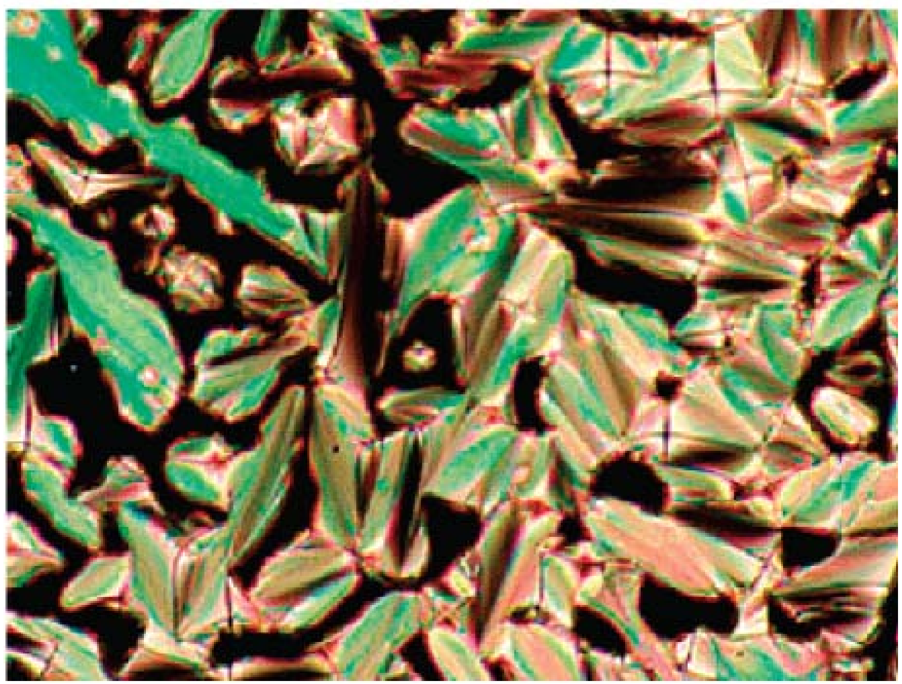


http://en.wikipedia.org/wiki/File:Monomerand6.jpg

Halogen bonding assisted liquid crystals



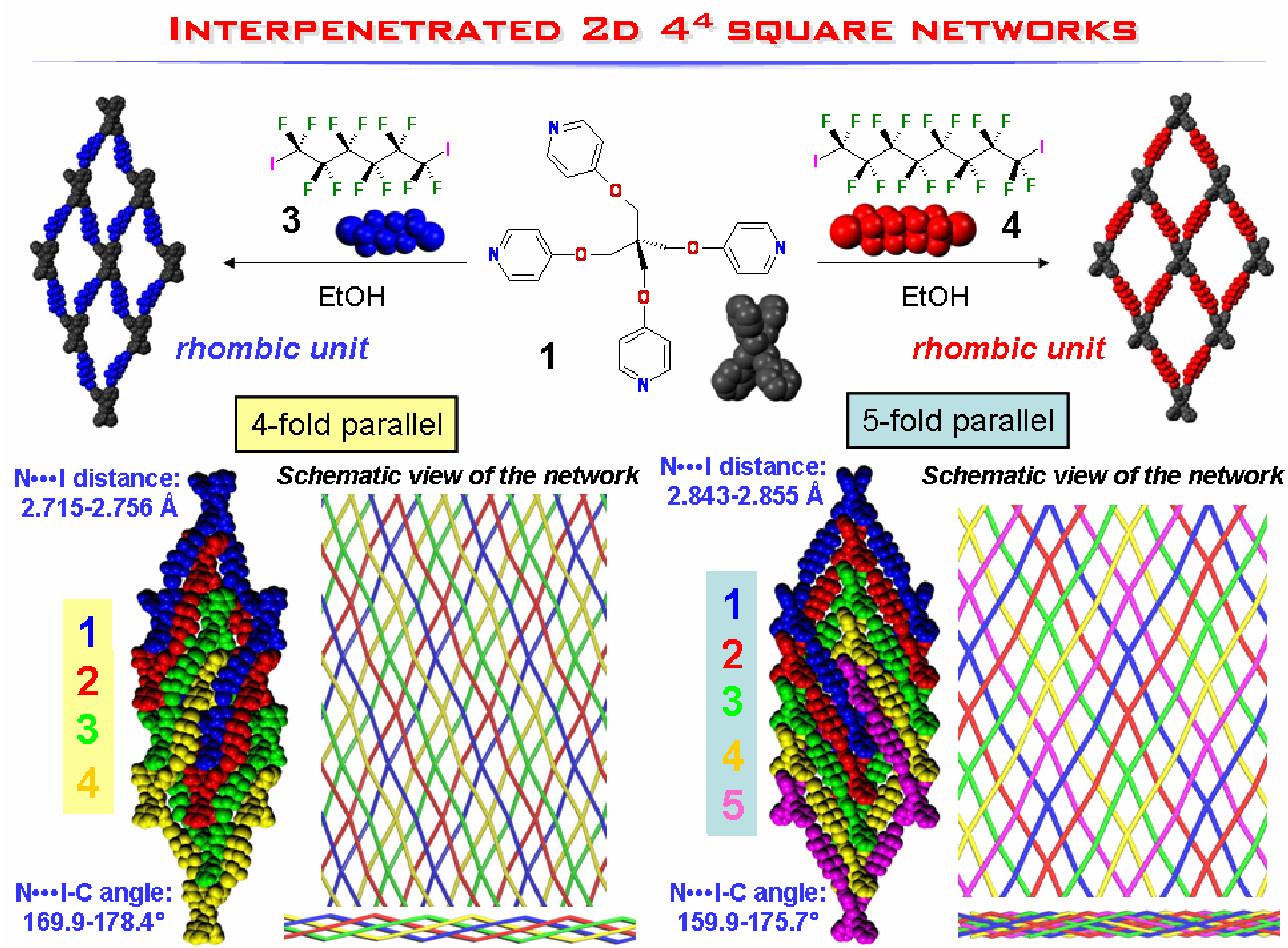
	16a	16b	16c	16d	16e	
n =	3	5	7	9	11	9d



16b-9d   Cr-SmA (77 °C)   SmA-I (80 °C)

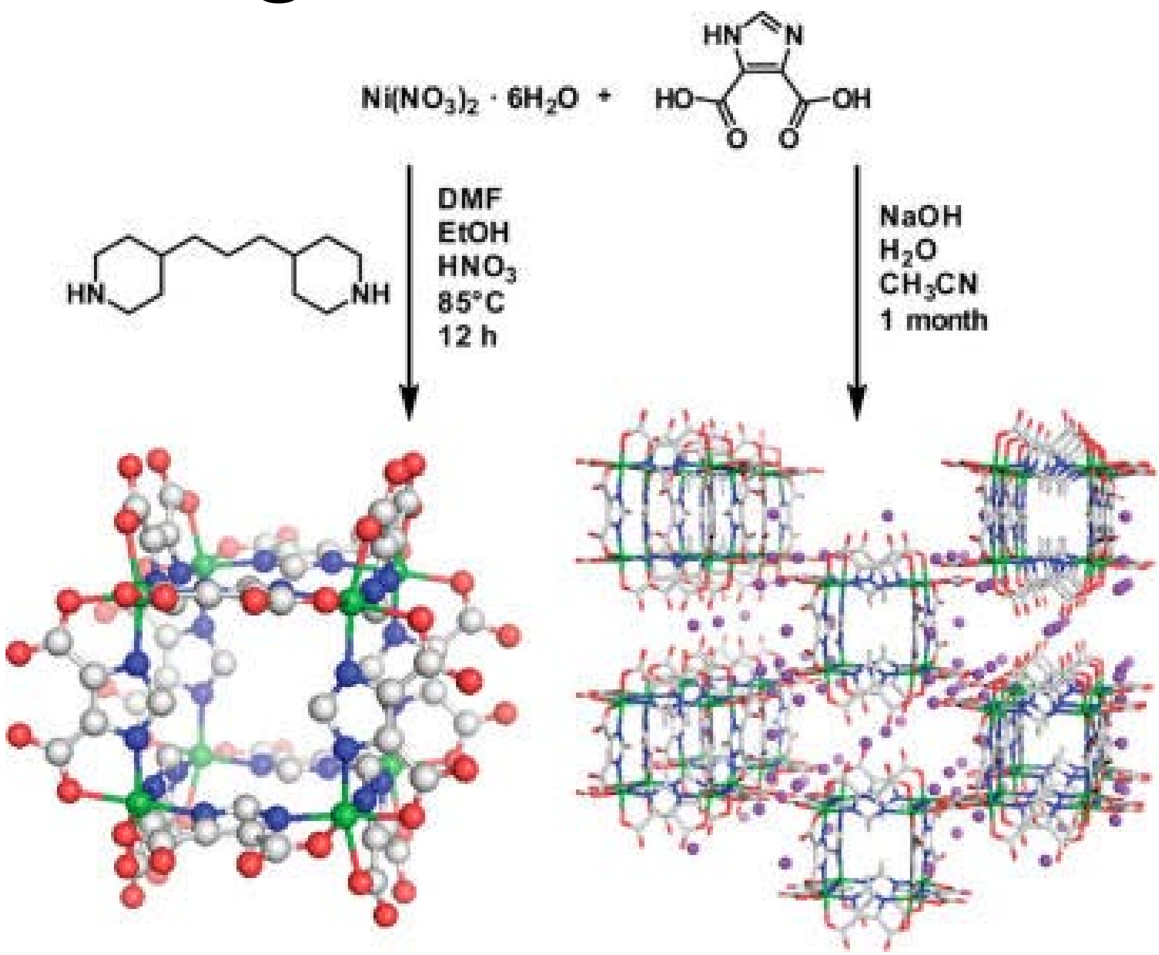
P. Metrangolo, G. Resnati et al., *Acc. Chem. Res*. **2005,** 38, 386.

Halogen bonding based network



http://www.dtic.mil/cgi-bin/GetTRDoc?AD=ADA503707

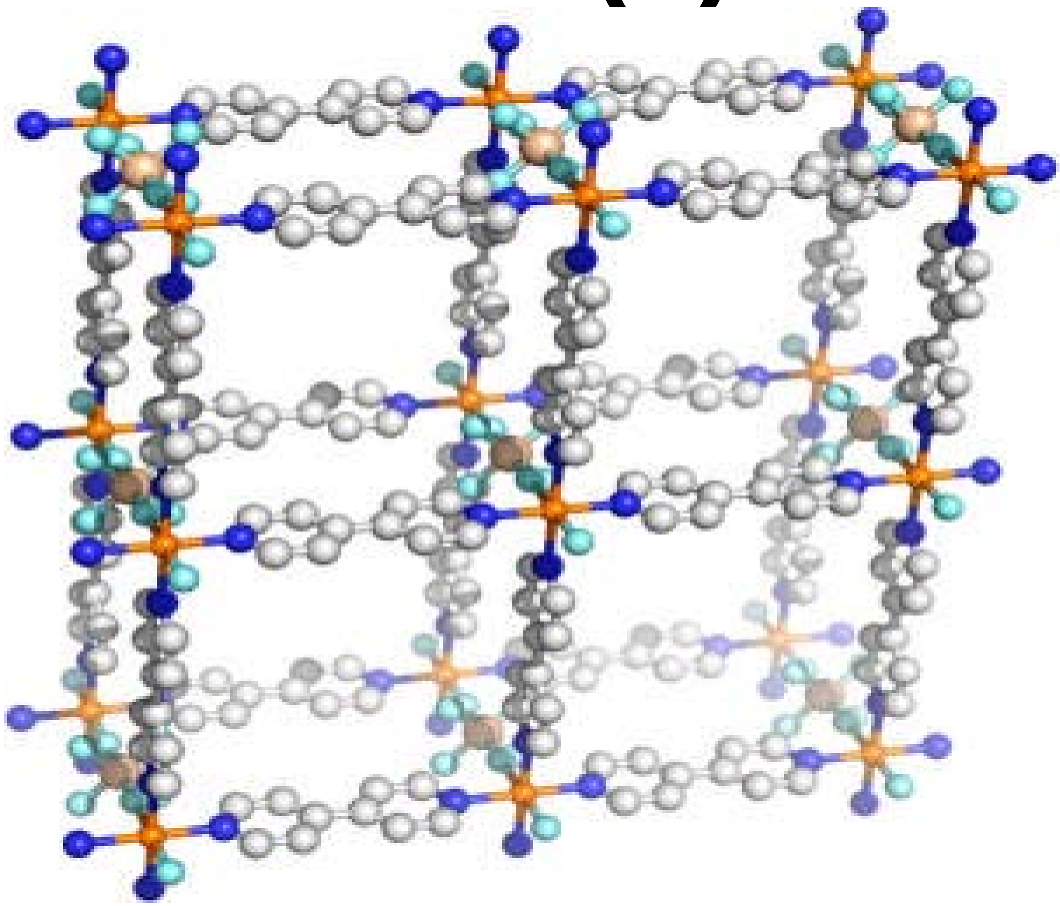
Metal-Organic Frameworks (I)



Treatment of nickel nitrate with 4,5-imidazoledicarboxylic acid generates cubic clusters. Depending on the reaction conditions, a discrete cube (left) or an extended cubic network bridged by sodium atoms (right) can be isolated.

P.Stang et al., *Chem. Rev.*, **2012**. doi.org/10.1021/cr3002824

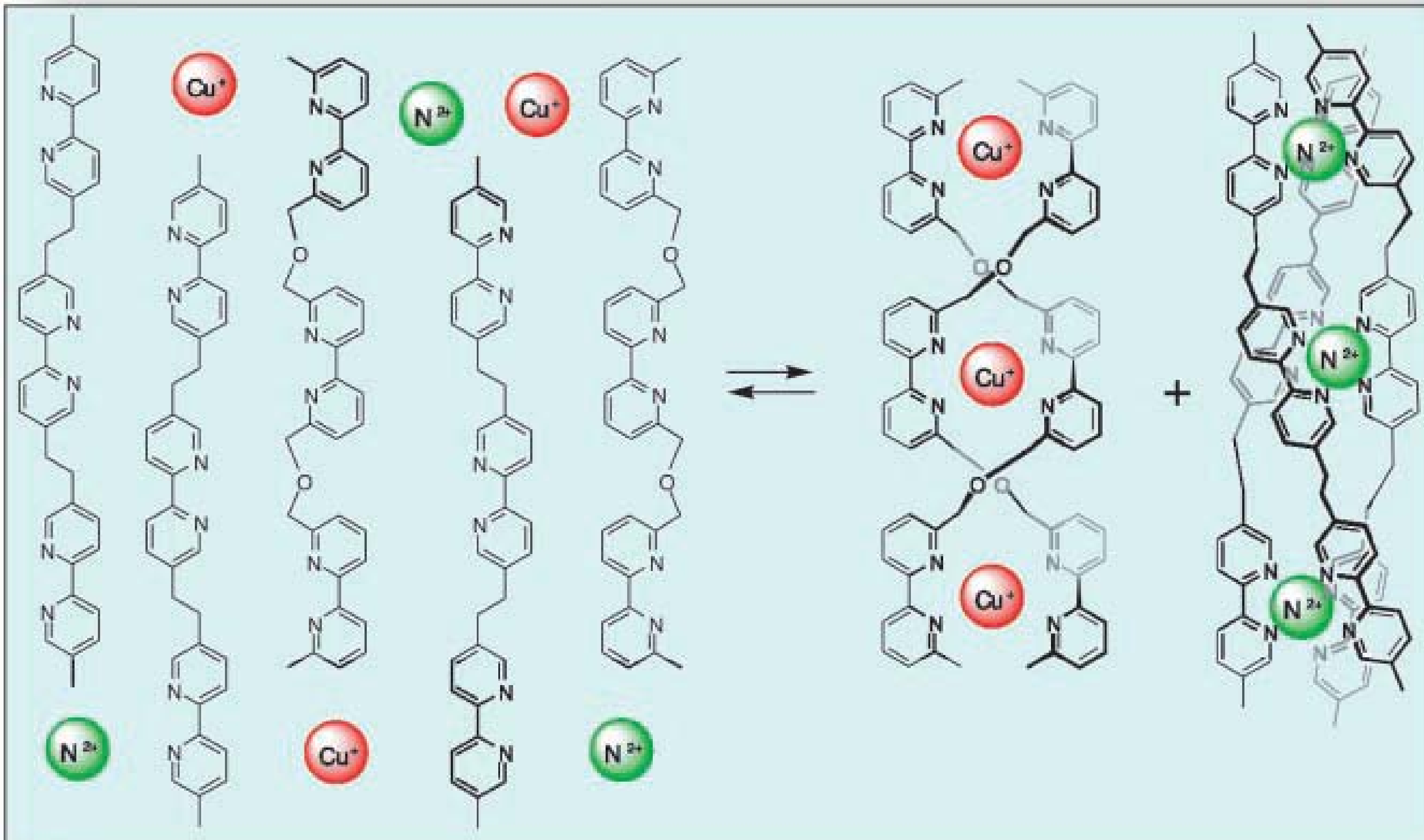
MOFs (II)



[Zn(4,4′-bpy)$_2$(SiF$_6$)]$_n$ network
Element (color): Zn (orange), N (blue), C (gray), Si (tan), F (teal)

P.Stang et al. Chem. Rev., **2012**. doi.org/10.1021/cr3002824

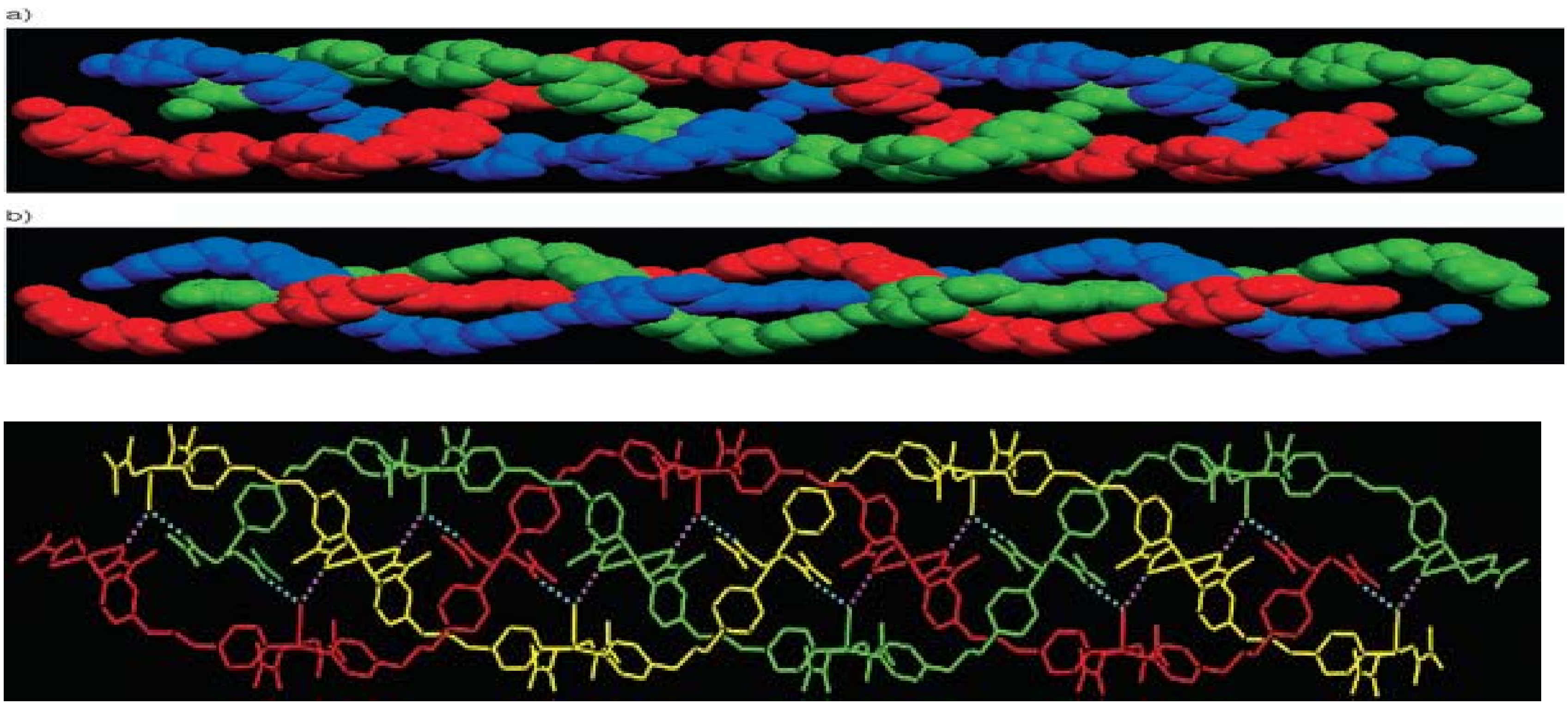
Toward Self-Organization and Complex Matter



Parallel formation of a double helicate and a triple helicate from a mixture of two different ligands and two different types of metal ions that present specific processing/coordination algorithms. Cu(I) and Ni(II) have tetrahedral and octahedral coordination, respectively.

J-M. Lehn, *Science*, **2002**, 295, 2400; J-M. Lehn et al., *PNAS USA*,. **1993***,* 90, 5394.

Triple-stranded molecular bride through hydrogen-bonding interactions



14.760A; 44.28A

X-J. Luan, Y-Y Wang, D-S. Li, P. Liu, H-M. Hu, Q-Z. Shi, S-M. Peng, *Angew. Chem. Int. Ed*. **2005**, 44, 3864.

“Architectures” to be created

- Double Möbius strip
- Catenanes made of Möbius strips
- Polymers made of catenanes
- Truly 2-dimensional polymers
- Truly 1-dimensional ladders
- Spirals (which is a 2-dimensional object)
- Combs

Thank you for your attention

Merry Christmas!!!