CHM 696-11: Week 5

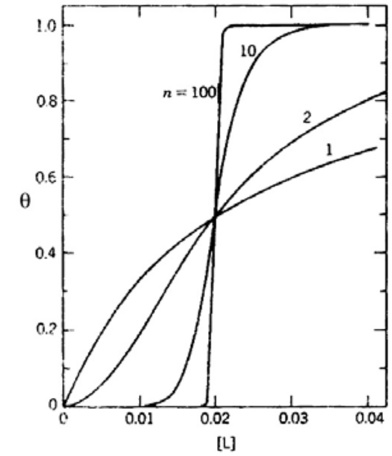
Instructor: Alexander Wei

Supramolecular Materials: Self-assembly in 2 and 3 dimensions

Crystal Engineering and Metal-Organic Frameworks

Supramolecular assemblies

The "*n* effect": model of positive cooperativity in an *n*-bodied system at a critical concentration



Types of supramolecular materials:

Liquid crystals: low-dimensional (1D or 2D) systems of oriented molecules in an ordered state

Crystals (solid-state engineering): well-defined 3D lattice structure, based on directional intermolecular forces (hydrogen bonding, etc.)

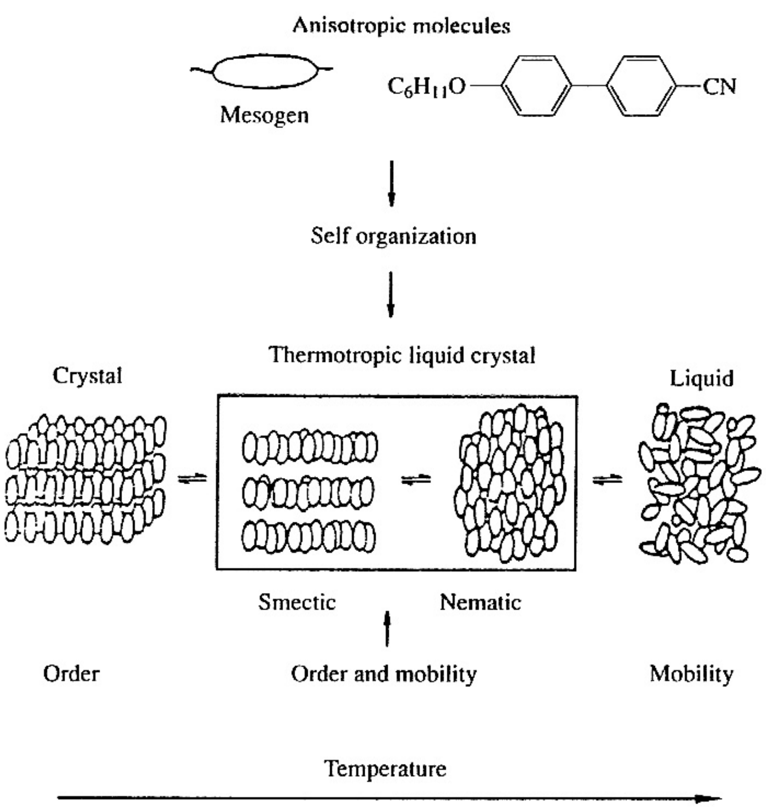
Self-assembled monolayers (SAMs): 2D systems assembled at interfaces (esp. metal surfaces and air-water interfaces)

Micelles, bilayer membranes: comprised of amphiphilic molecules which form self-organized assemblies in 2D and 3D at a critical aggregation concentration (CAC)

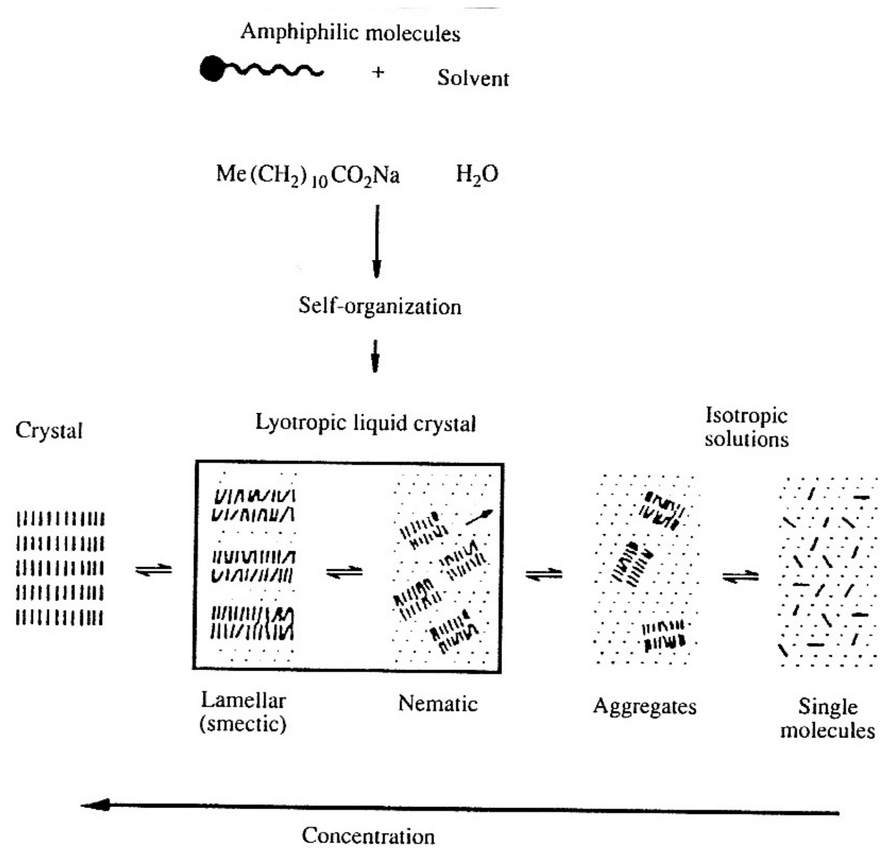
(nano)Fibers: 1D ensembles of molecules which undergo "non-covalent polymerization" at a critical concentration

Liquid Crystals

Self-organization of “mesogens” into (thermotropic) liquid crystals:



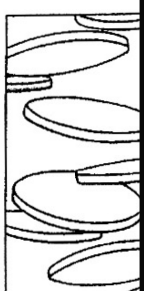
Self-organization of amphiphiles into (lyotropic) liquid crystals:



Calamitic Liquid Crystals

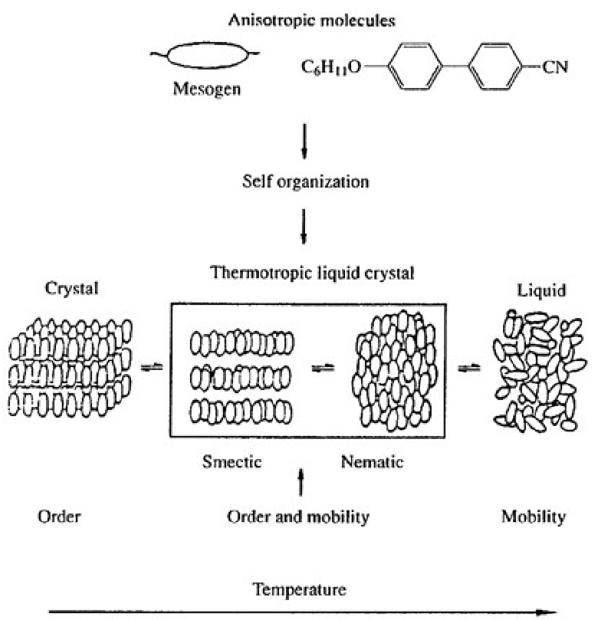
Example

1D: Ne

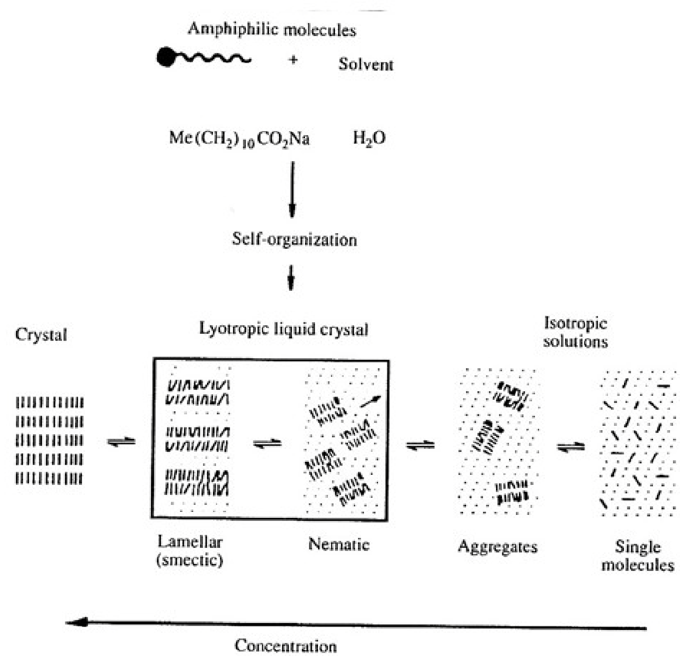


Liquid Crystals

Self-organization of "mesogens" into (thermotropic) liquid crystals:



Self-organization of amphiphiles into (lyotropic) liquid crystals:



Disordered layer structure of the smectic C phase, where the molecules are tilted

S_c

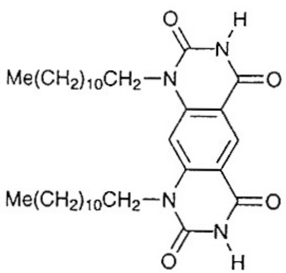
Discotic Liquid Crystals

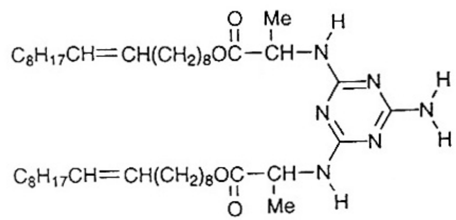
Examples of discotic LC phases

Discotics: Columnar phases (fiber-forming)

Nematic columnar phase

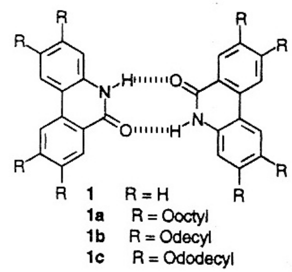
Hexagonally-packed discotics





Kimizuka et al, *Chem. Commun.* **1997**, 2103.
(structural characterization by SEM)

"Supramolecular" discotics:



Kleppinger et al, *JACS* **1997**, *119*, 4097

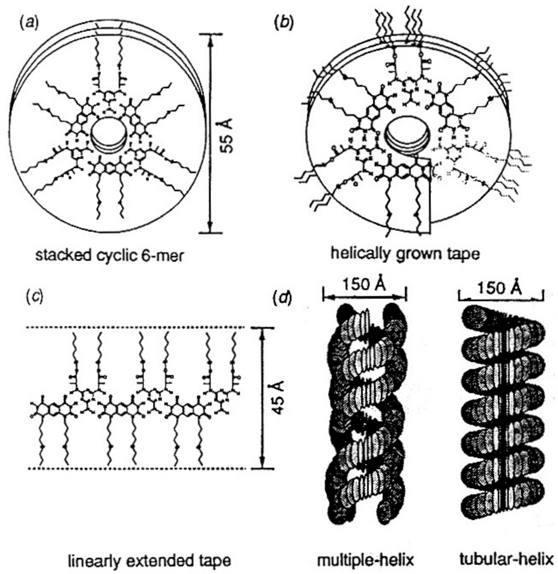


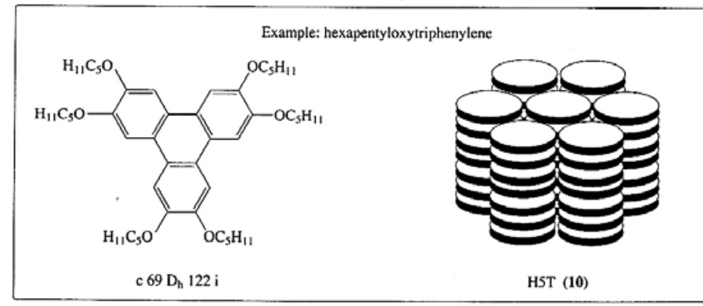
Fig. 3 Schematic illustration of possible mesoscopic superstructures

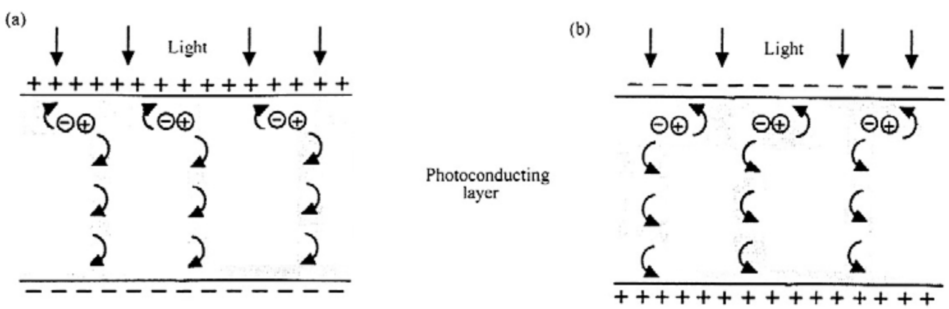
Some applications of liquid crystals

For more details, see *Liquid crystals: applications and uses* (Ed. Bahadur, B.), World Scientific Press, c. 1990.

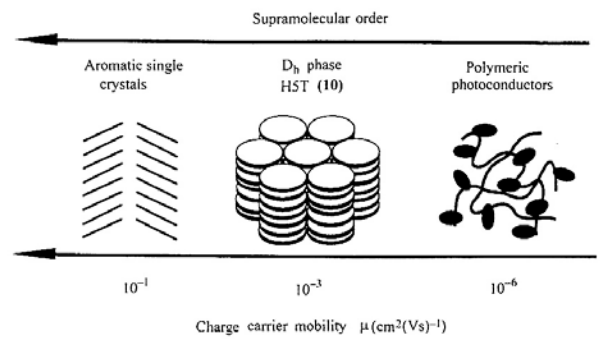
1. Electrochromic and thermochromic displays (typically involves cholesteric phases)

2. Photoconductivity in discotic phases





Hole or electron migration occurs when thin film in an electric field is photo-irradiated



Discotic H5T as hole-carrier material: Moderate electron transport possible

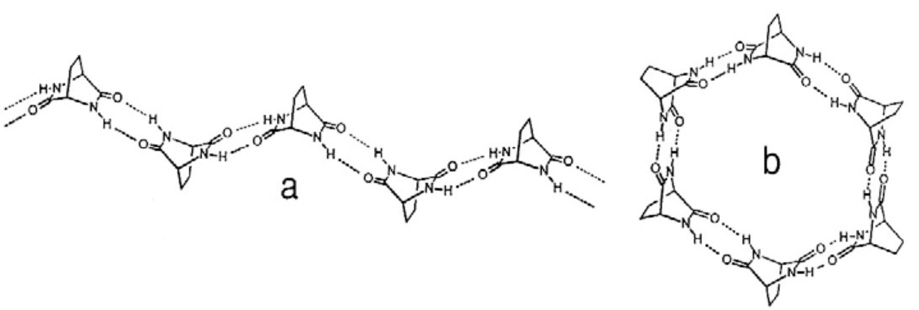
Solid-state Crystal Engineering

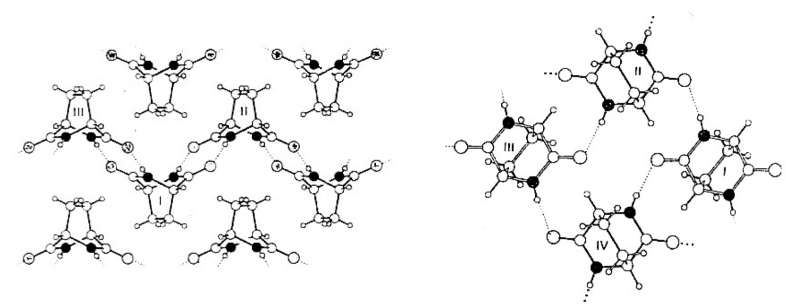
Overview: Steed and Atwood, *Supramolecular Chemistry*, 2nd Ed., Chapters 7 & 8.

<u>α, β, and γ-networks</u>: Crystalline solids with well-defined intermolecular periodicity in 1, 2, and 3 dimensions

Challenges in designing supramolecular crystals:
1) Predicting the effect of solvent inclusion
2) Interpenetration
3) Predicting the influence of secondary interactions
4) Understanding and controlling polymorphism

<u>Example</u>: “designed” supramolecular motifs (a,b) vs. actual crystal polymorph

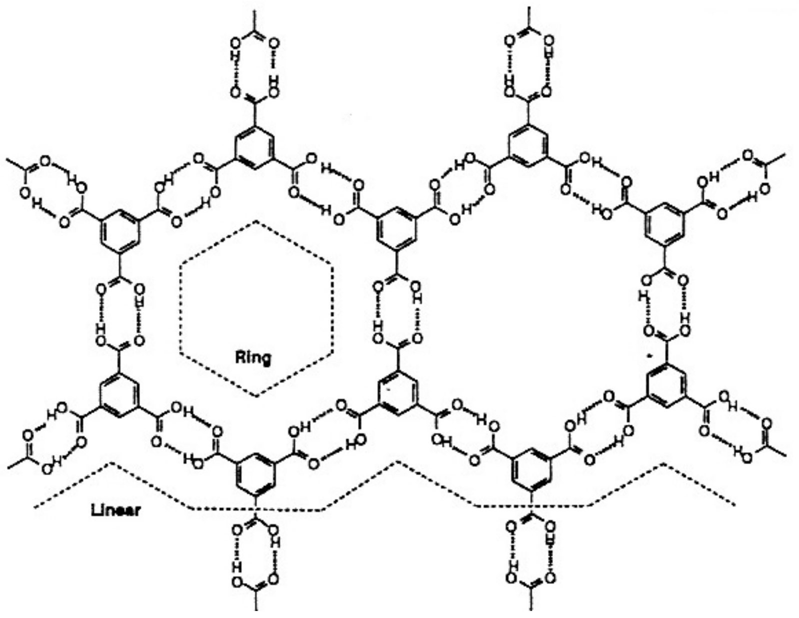


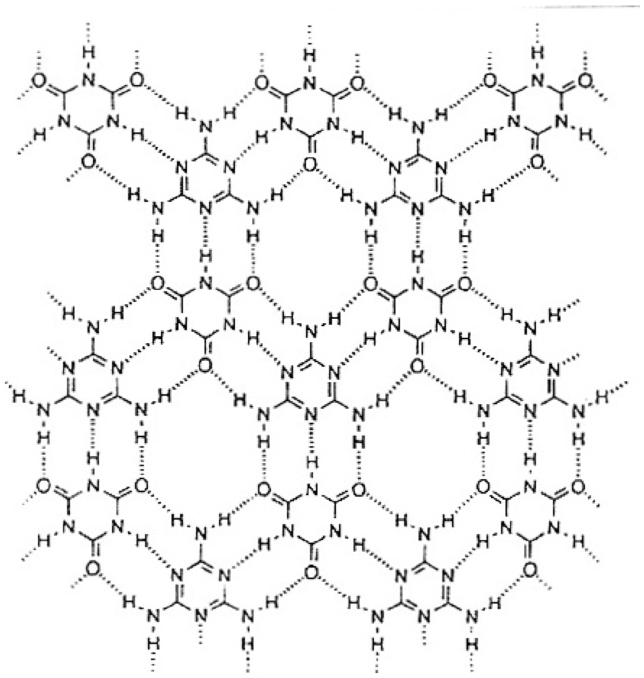


Brienne et al, *Tetrahedron Lett.*, **1996**, *35*, 8157

Design aspects in β-networks

I: Incorporation of highly symmetrical components



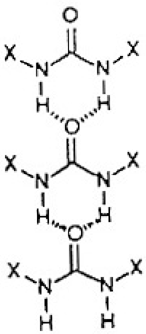


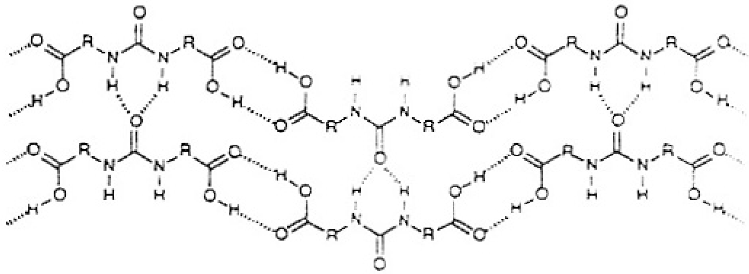
Trimesic acid (β-network sheet)

Melamine + cyanuric acid

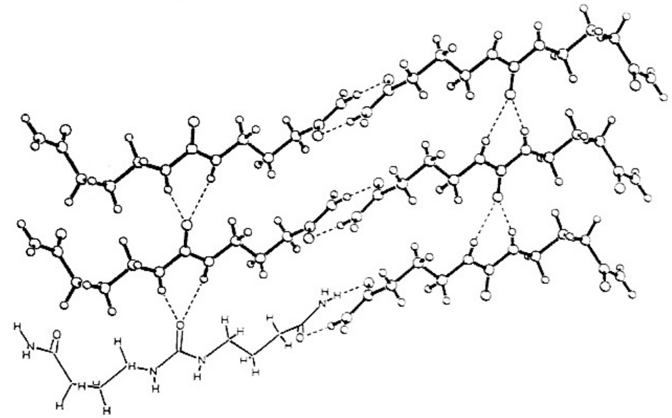
Design aspects in β-networks

II: symmetrical vs. unsymmetrical β-networks:



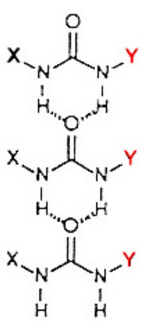


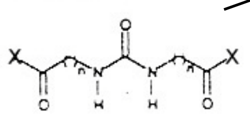
R = $-CH_2-$ (1), $-CH_2CH_2-$ (2), $-CH_2CH_2CH_2-$ (3)



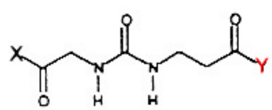
α: urea bifurcated hydrogen bonds

β: amide-amide hydrogen bonds

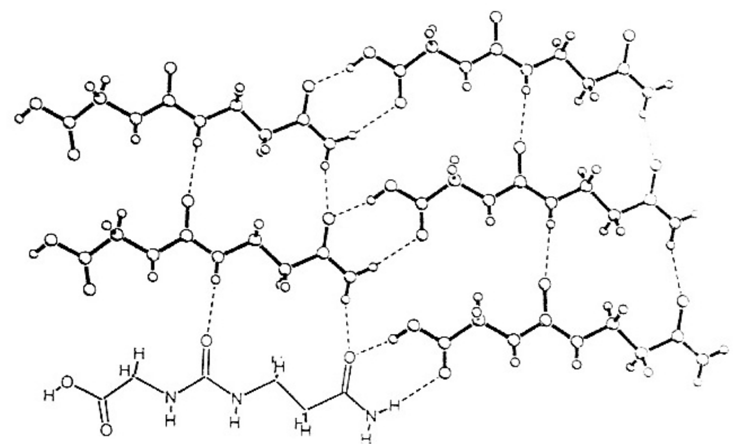




X = NH_2, n =3



X = OH, Y = NH_2



Chang et al, *JACS* **1993**, *115*, 5991

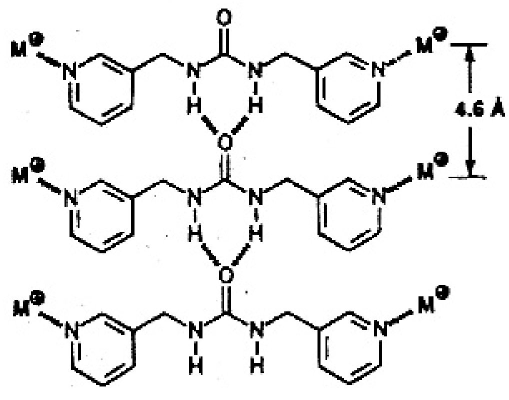
Coe et al, *JACS* **1997**, *119*, 86

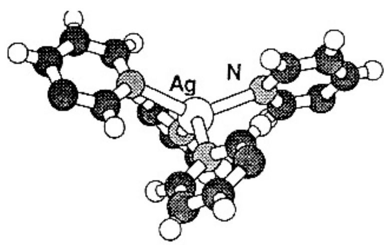
α: urea NH…O hydrogen bonds

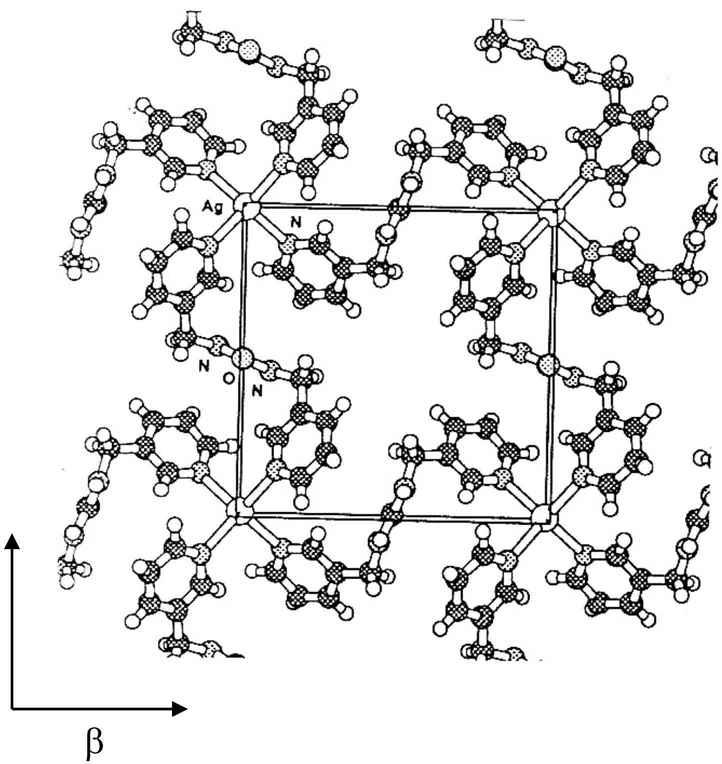
β: acid-amide hydrogen bonds

Design aspects in γ-networks

Successful example of γ-network using urea H-bonding + coordination chemistry





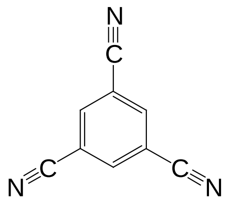


Looking down P_2 axis of urea α–network

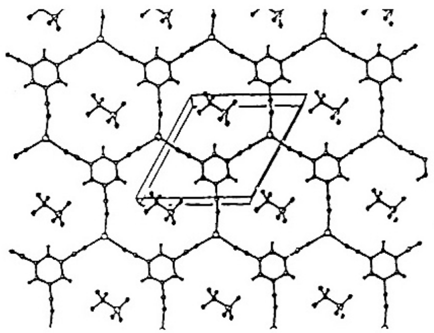
Schauer et al, *JACS*, **1997**, *119*, 10245

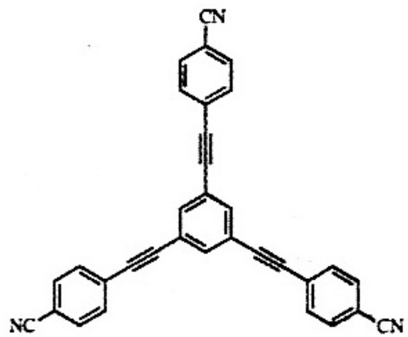
Engineering porous solids

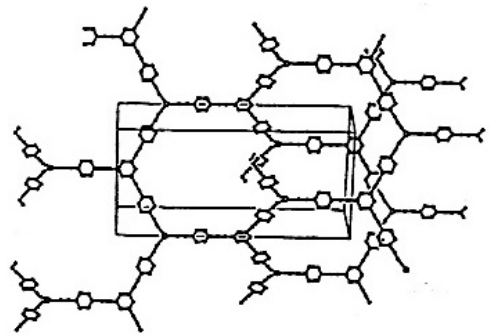
Creating unoccupied cavities by limiting structural complementarity



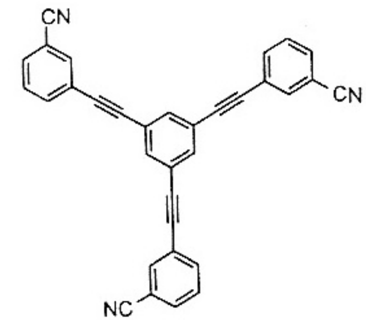
• AgOTf

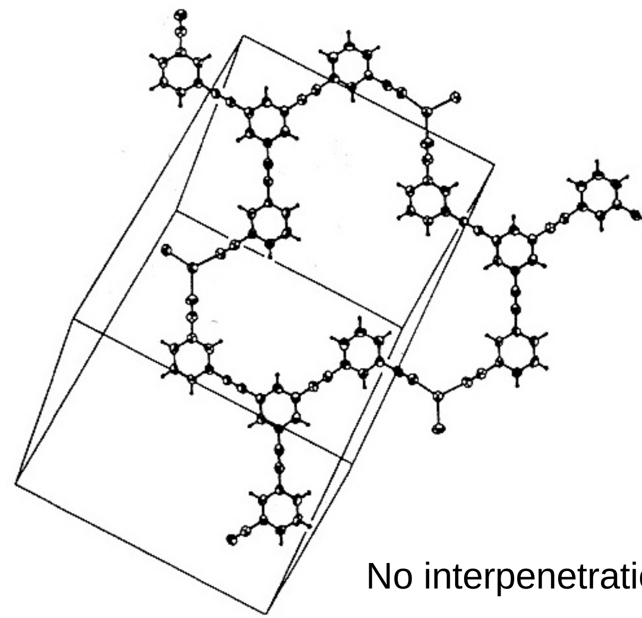






(interpenetrating lattices)





No interpenetration!

Venkataraman et al, *JACS* **1995**, *117*, 11600

Gardner et al, *Nature* **1995**, *374*, 792