Fundamentals of Nanoscience SMBS813

Supramolecular nanochemistry: from self-assembly to molecular devices

Prof. Maija Nissinen
YN233
E-mail: maija.nissinen@jyu.fi

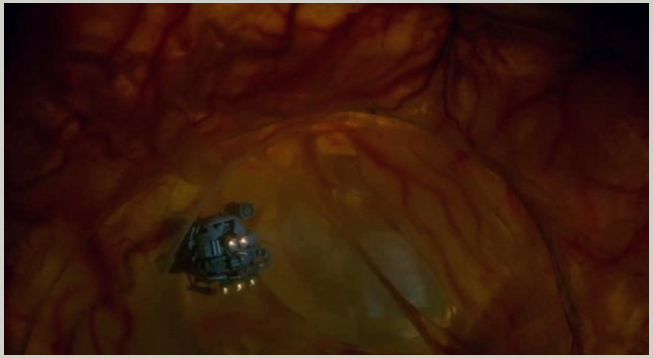
Contents

- Introduction
- Weak interactions
- Self-assembly
- Molecular devices
- Monolayers
- Liquid crystals
- Dendrimers
- Fibres and gels

Introduction to supramolecular nanochemistry

- Nanochemistry: chemistry of nanometer scale synthesis, nanoscale materials and devices (e.g. switches, sensors) → nanotechnology.
- Nanophysics: top-down approach, for example by cutting, etching, slicing and other microfabrication techniques → limits the size at dimensions of below 100 nm.
- Nanochemistry: bottom-up approach by synthesis utilizing the supramolecular and biomimetic materials → from atomic scale (10^{-10} m) to nanometer scale.
- Advantage: Not limited to existing properties of materials.

Bottom-up approach

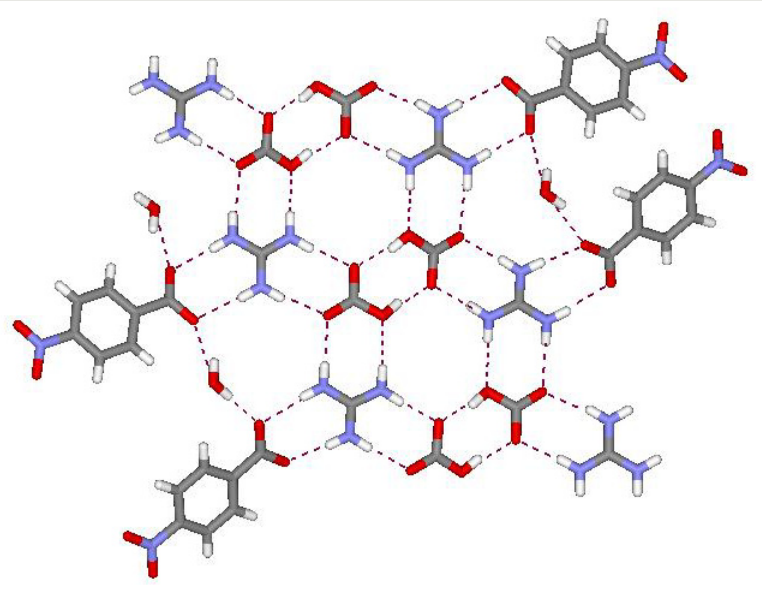


- Drexler 1980’s: nanorobots, which build up copies of themselves by picking up atoms.
- Nanomaterials are built up from smaller building blocks with the help of self-assembly or traditional chemical synthesis.
- Molecules are more suitable building blocks than single atoms: atoms are too reactive and difficult to handle while molecules have exact shapes and properties.

→ Link to supramolecular chemistry.

Concept: Supramolecular chemistry

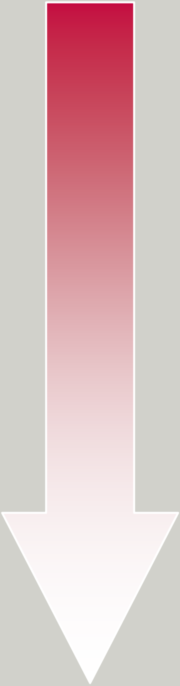
- Supramolecular chemistry: chemistry beyond molecule, chemistry of weak, non-covalent intermolecular interactions.



T. Mak and F. Xue, J. Am. Chem. Soc., 2000.

Concepts: weak interactions

- Classification of the weak interactions:
  - (Ion-ion interactions 200-300 kJ/mol)
  - Ion-dipole interactions 50-200 kJ/mol
  - Dipole-dipole interactions 5-50 kJ/mol
  - Hydrogen bonding 4-120 kJ/mol
  - Interactions involving π-systems 0-80 kJ/mol
  - Van der Waals forces < 5 kJ/mol
  - (Close packing)
  - Hydrophobic effects

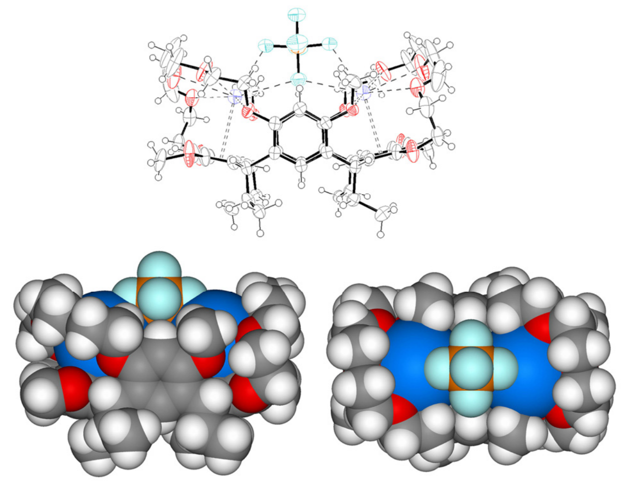


Classification is not unambiguous!

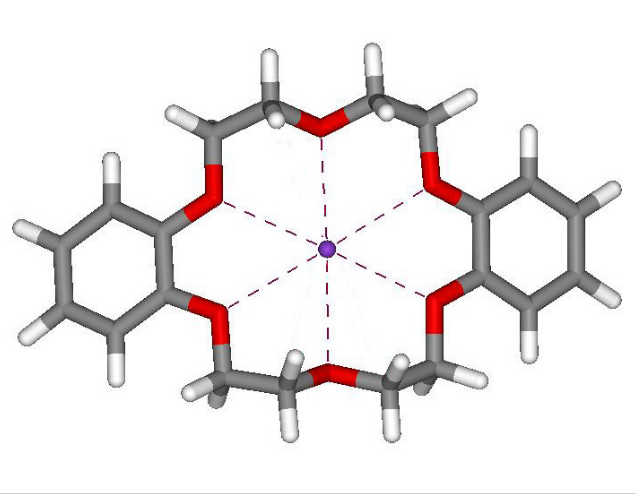
Note: weak interactions are cooperative.

Ion-dipole interactions

- Based on Coulombic attraction between opposite charges.
- An ion interacts with a polar part of a molecule.
- Orientation dependent.
- Typical examples are crown ether – alkali metal complexes.



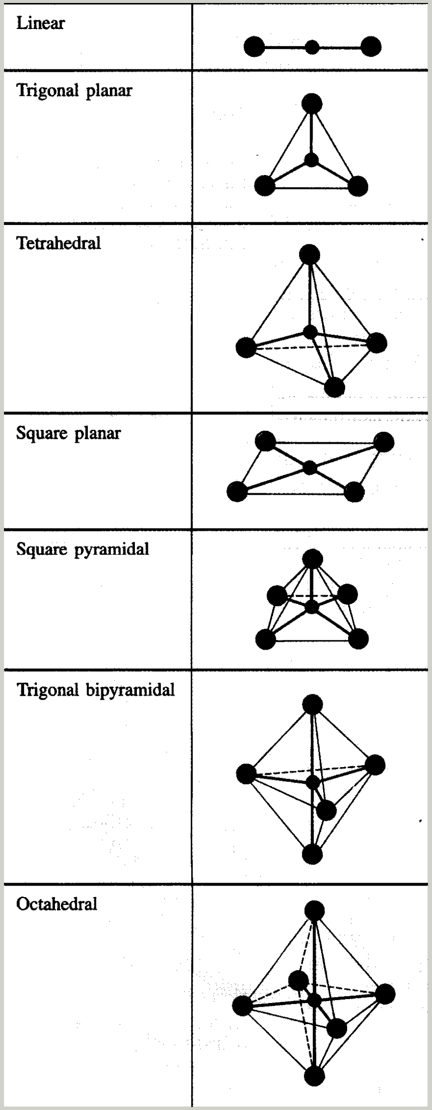
K. Salorinne & M. Nissinen, Tetrahedron, 2008.



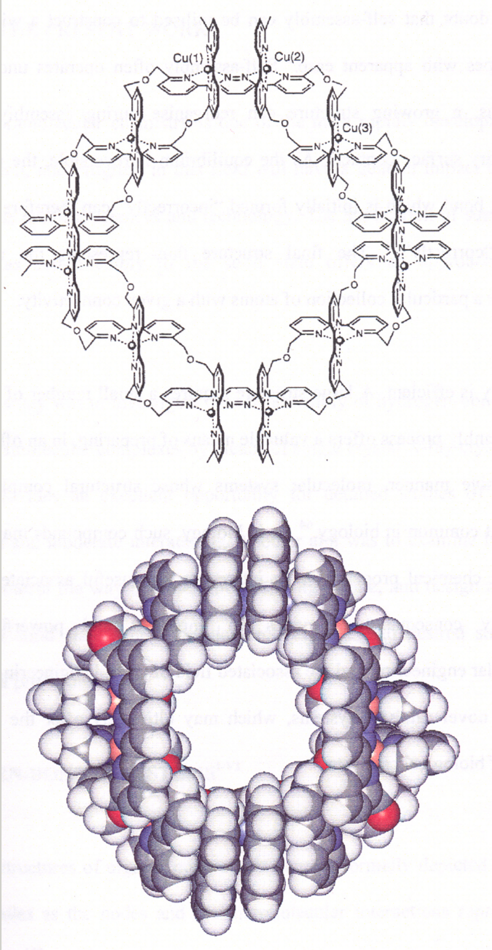
R. Hilgenfeld & W. Saenger, Angew. Chem. Int. Ed., 1981.

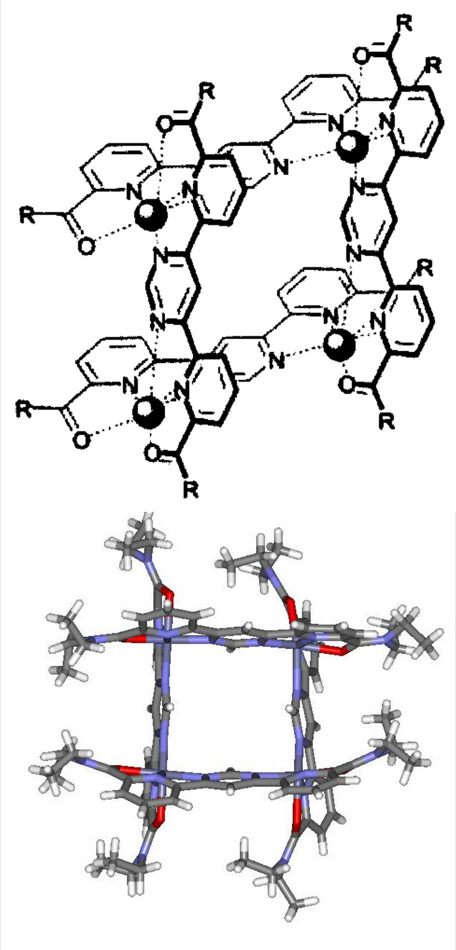
Ion-dipole interactions

- Another important example is metal coordination between nonpolarizable metal cations and lone-pair electrons of hetero-atoms.
- Coordinative bonds have significant covalent component, which causes the bonds to be strong and well-defined geometries (coordination number of metals) → useful in crystal engineering and synthesis.



Ion-dipole interactions





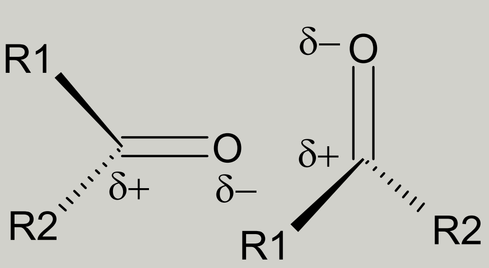
Examples of metal coordination

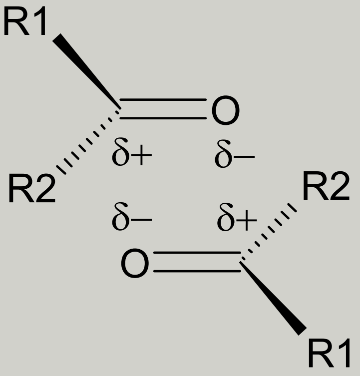
J.-M. Lehn et al., Chem. Eur. J., 1997.

J.-M. Lehn, M. Nissinen,
K. Rissanen et al., Eur. J. Inorg. Chem. 2004.

Dipole-dipole interactions

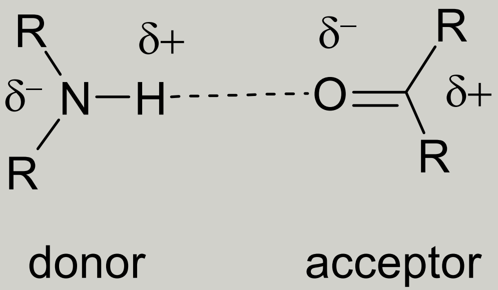
- Typical with organic carbonyl compounds
- Useful in bringing species into alignment
- Strength 5-50 kJ/mol, directional

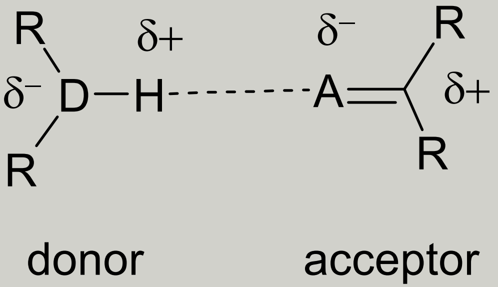




Hydrogen bonding

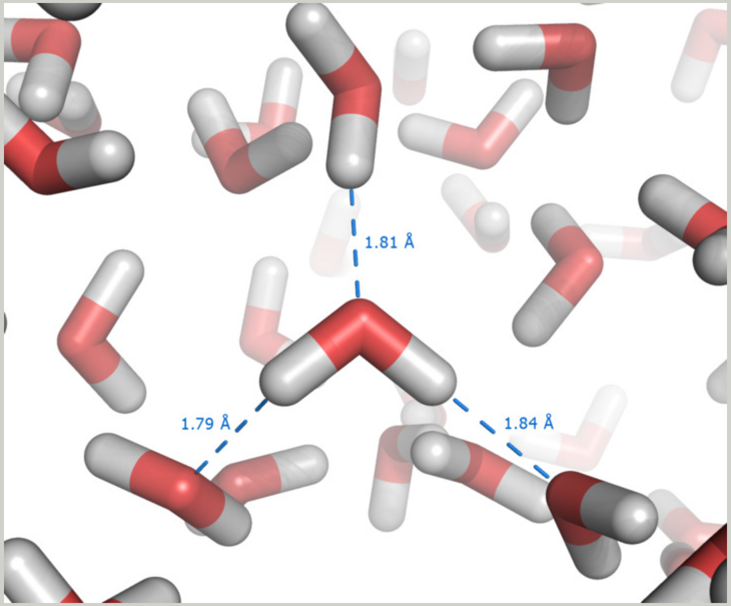
- Hydrogen bonding is a particular kind of dipole-dipole interaction with high degree of directionality, electrostatic nature and a certain geometry.
- Donor: partially positively charged hydrogen due to large difference in electronegativity of hydrogen and the atom to which it is attached to (typically O, N, S, F, (C)) → highly polarized covalent bond.
- Acceptor: (partially) negative atom with unshared valence electrons or polarizable π-electrons.

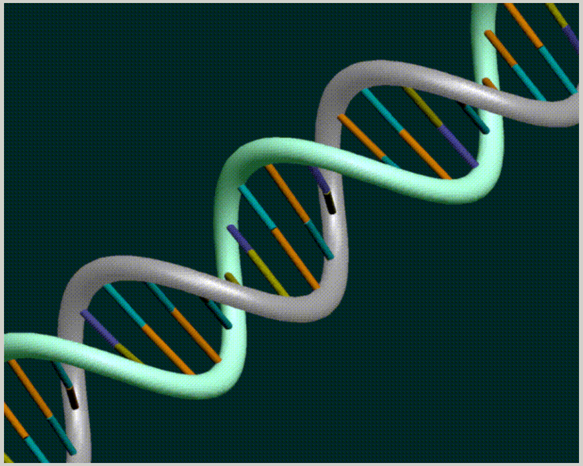


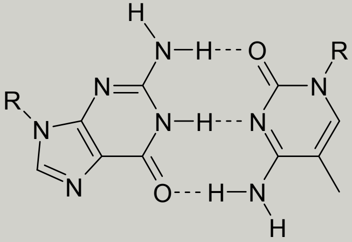


Hydrogen bonding

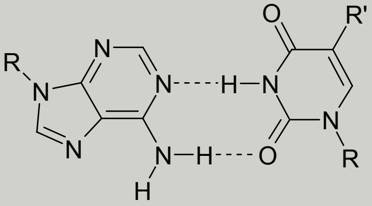
REMEMBER: HYDROGEN BONDING IS VERY IMPORTANT INTERACTION FOR LIFE (E.G. DNA, PROTEIN FOLDING, PROPERTIES OF WATER)!







guanine cytosine



adenine

R' = H: uracil
R' = CH_3 : thymine

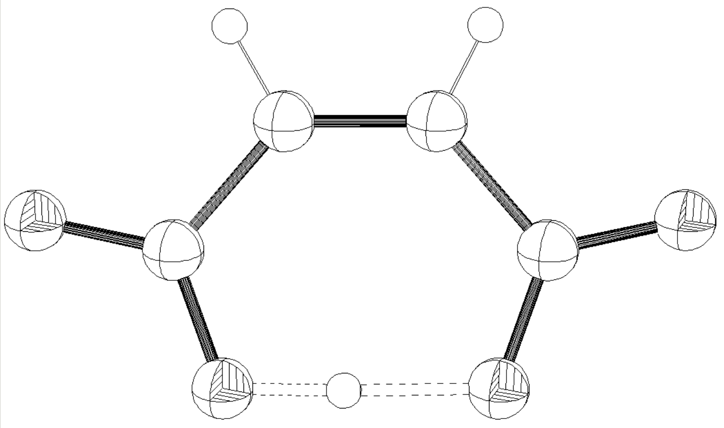
Hydrogen bonding

- Classification: strong, moderate and weak
- Strong H-bonds are formed when

  a) donor is electron density deficient.

  b) acceptor has an excess of electron density.

  c) configuration or conformation of the molecule forces the donor and acceptor closer than normal H-bonding distance.



M. James & M. Matsushima, Acta Crystallogr. B32 (1976) 1708.

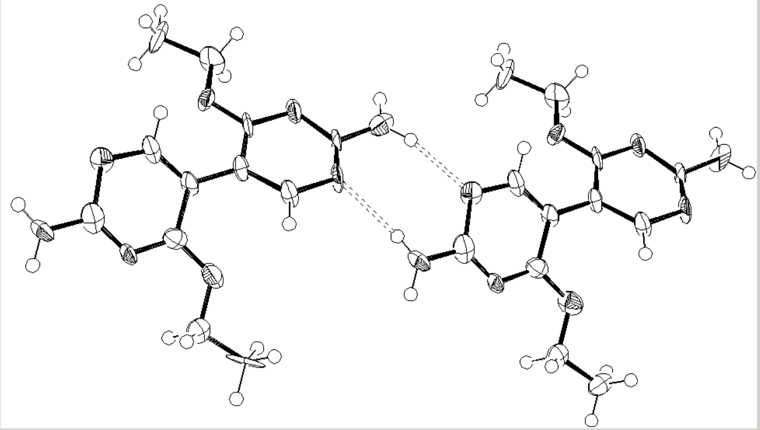
Hydrogen bonding

- Moderate bonds (most common type) form typically between neutral groups.
- Weak H-bonds are formed when

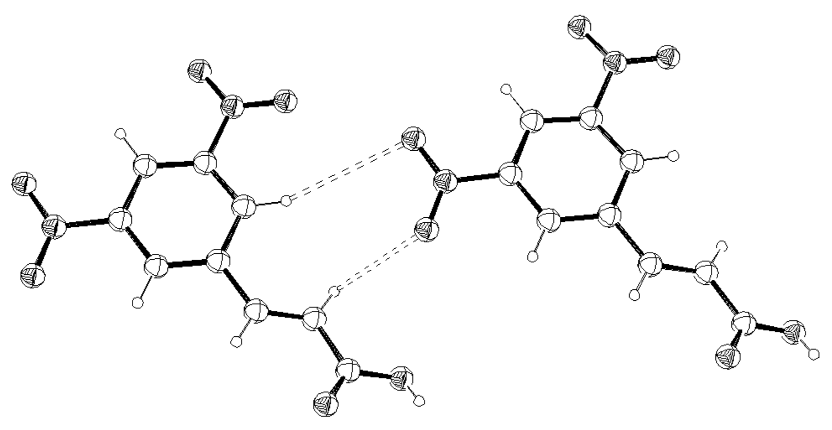
  a) hydrogen is bonded to only slightly more electronegative atom (C, Si).

  b) acceptor has π-electrons instead of lone-pairs.

  c) acceptor is otherwise poor acceptor (Br, Se).



J.-M Lehn, M. Nissinen, K. Rissanen et al., Helv. Chim. Acta, 1998.

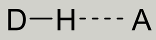


G. Desiraju & C. Sharma, J. Chem. Soc. Chem. Commun., 1991.

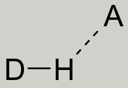
	Strong	**Moderate**	**Weak**
D-H···A interaction	Mostly covalent	Mostly electrostatic	Electrostatic
Bond length	D-H ≈ H···A	D-H < H···A	D-H << H···A
H···A / Å	~ 1.2 - 1.5	~1.5 – 2.2	2.2 – 3.2
D···A / Å	2.2 - 2.5	2.5 – 3.2	3.2 – 4.0
Bond angle / °	175 – 180	130 – 180	90 – 150
Bond energy / $kJmol^{-1}$	60 – 170	17 – 63	< 17
Examples	Gas phase dimers of strong acids and bases, acid salts, HF complexes	Acids, alcohols, phenols, hydrates, all biological molecules	Gas phase dimers of weak acids and bases, C-H···O/N/Cl and N/O-H···π interactions

Hydrogen bonding

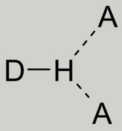
Primary hydrogen bonding geometries:



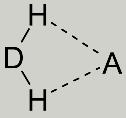
linear



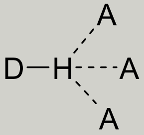
bent



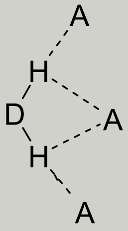
donating bifurcated



accepting bifurcated

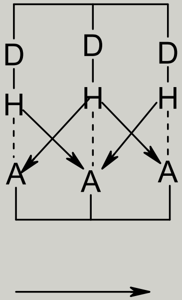


trifurcated

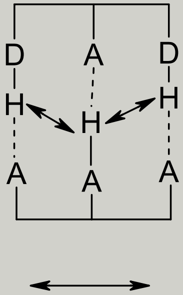


three-center bifurcated

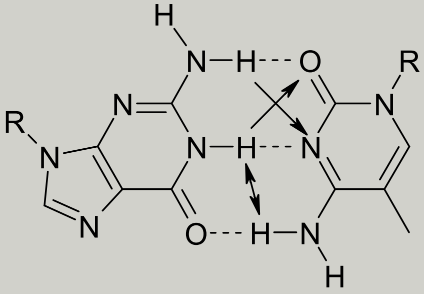
Secondary hydrogen bonding geometries:



attractive interaction



repulsive interaction

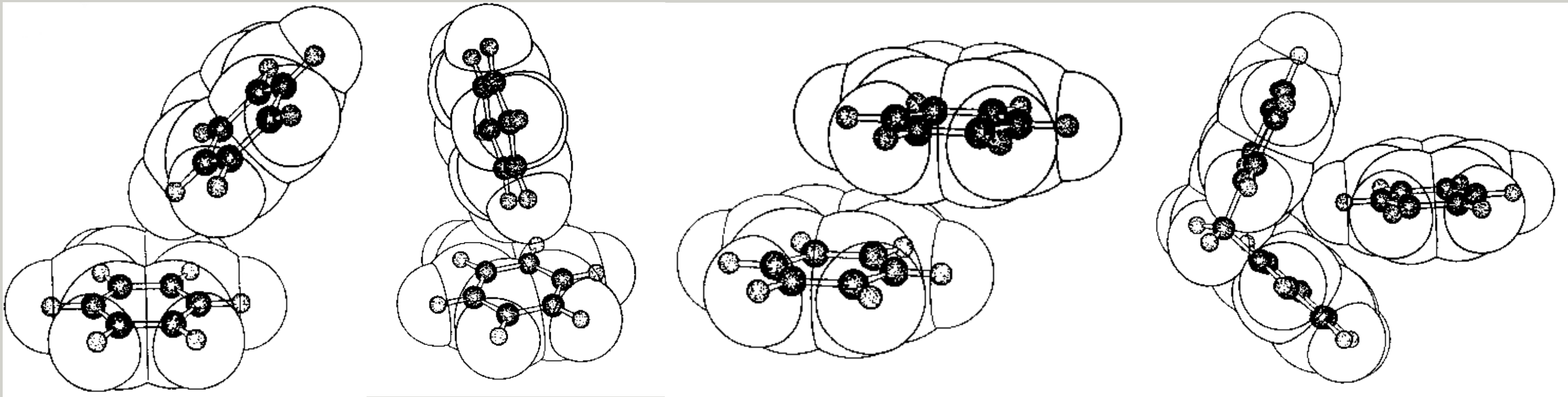


guanine

cytosine

Interactions involving π systems

- Categories: D-H···π, π···π and cation···π interactions
- Note: D-H···π could also be classified as weak H-bonding.
- π···π interaction (π-stacking; 0-50 kJ/mol) is non-directional, electrostatic, attractive force, which occurs when attraction between π-electrons and σ-framework overcome the unfavorable π-π repulsions.



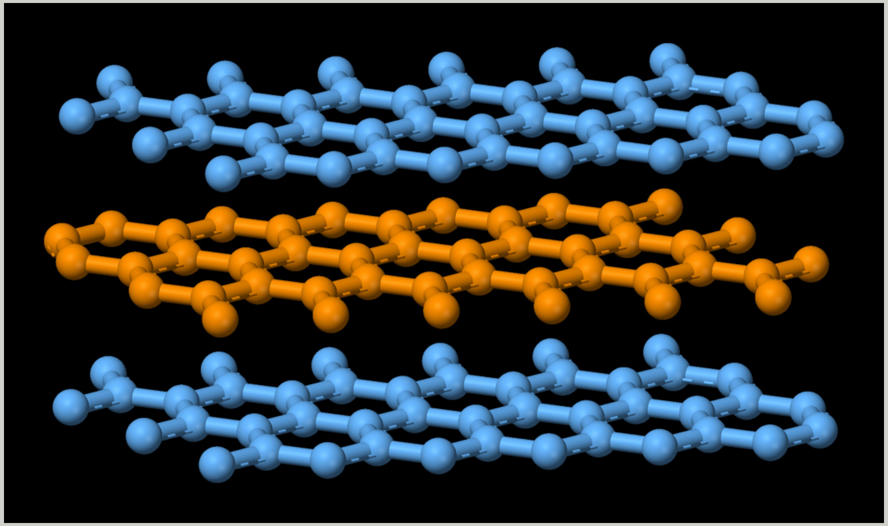
edge-to-face

edge-to-face
(T-stacking)

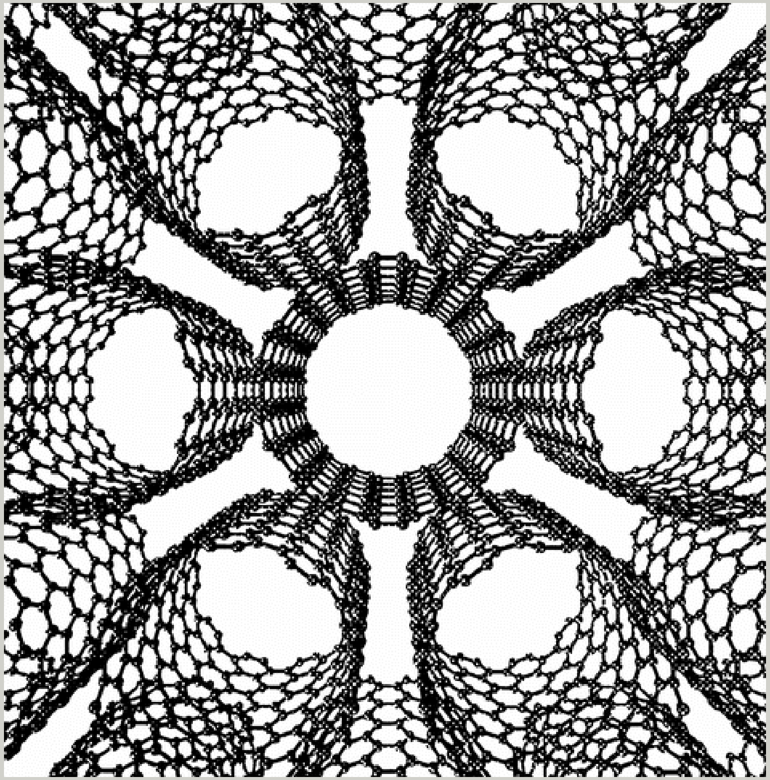
offset face-to-face

edge-in-angle

Interactions involving π systems



Structure of graphite

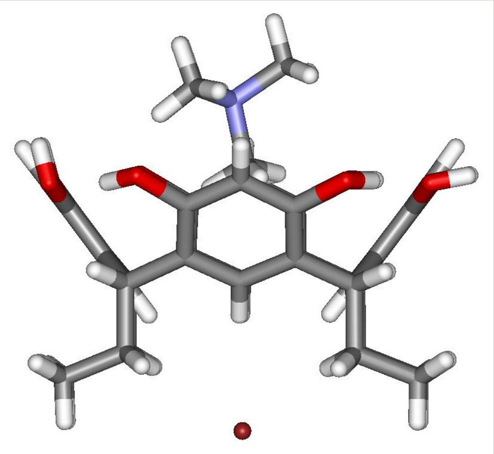


A rope of carbon nanotubes

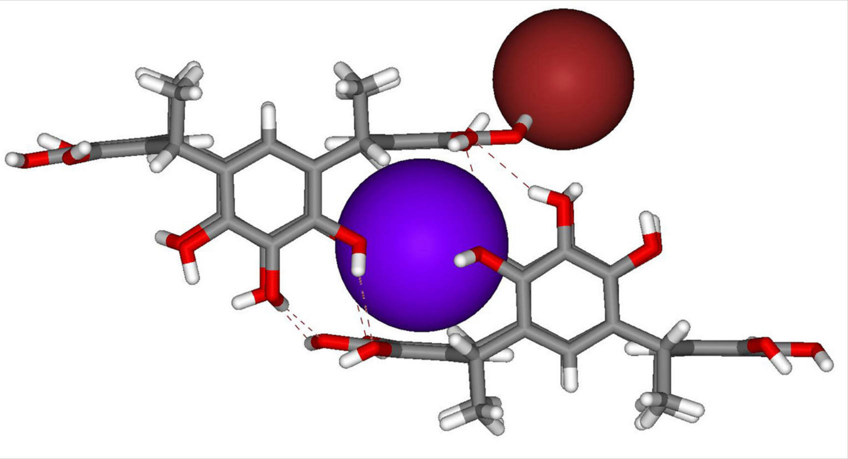
M.L. Cohen et al. Nature 1998.

Interactions involving π systems

- Cation···π interactions (5-80 kJ/mol) occur between metallic or organic cations and aromatic or double/triple bonded regions of the molecule.
- Electrostatic force, but relates also to the polarizability of the aromatics (ion-induced dipole, donor-acceptor, charge transfer or dispersion force).



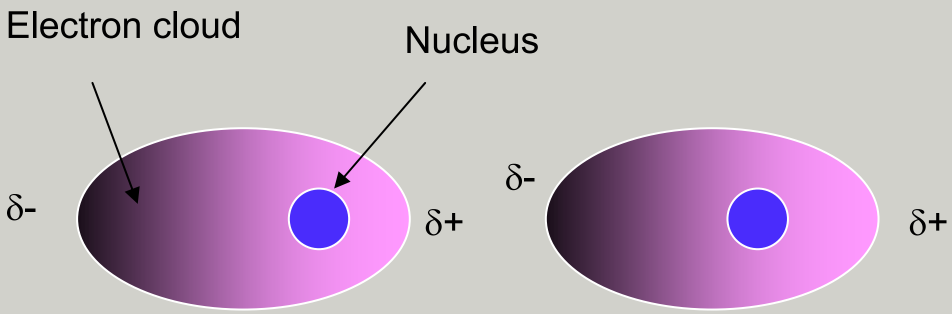
M. Mäkinen, M. Nissinen, K. Rissanen & P. Vainiotalo, J. Am. Soc. Mass Spec., 2003.



A. Åhman, M. Nissinen, Chem. Commun. 2006.

Van der Waals forces

- A collective name for non-directional dispersion forces which are weakly bonding at long distance and strongly non-bonding at short distances.
  1) London interactions
  2) Exchange and repulsion interactions
- Arise from the fluctuations of the electron distribution between species that are in close proximity.

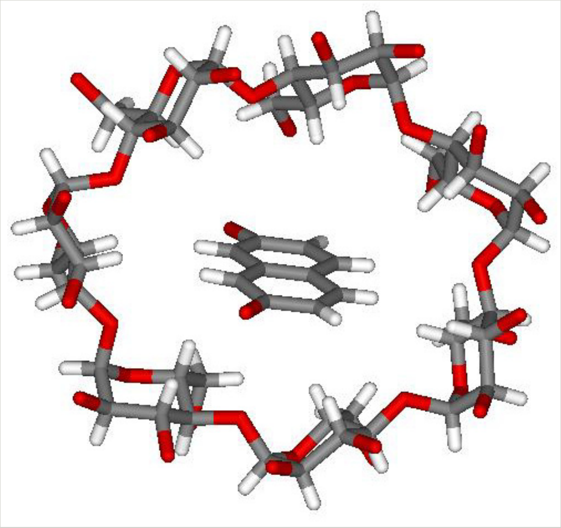


Van der Waals forces

- The strength depends on the polarizability of the molecule and is proportional to the size of the molecule and inversely proportional to the sixth power of distance.
- Repulsive forces balance the dispersion forces and define molecular shape and geometry → important in crystal packing and in inclusion complexes.
- Usually term ”VDW-forces” refers to C···C, C···H and H···H interactions.

Hydrophobic effects

- Relate to the exclusion of large or weakly solvated (hydrophobic) species from polar media.
- Enthalpic effect: stabilization of polar solvent excluded from the cavity upon guest binding.
- Entropic effect: combination of host and guest results in less disruption to the solvent structure → entropic gain.
- Typical examples: Binding of organic guests by cyclodextrins or cyclophanes in water, micelle formation.



M. Anibarro et al. Carbohydr. Res. 2001.

Literature about weak interactions

- G.A. Jeffrey: *An Introduction to Hydrogen Bonding*, Oxford University Press, 1997.
- J.C. Ma & D.A. Dougherty: *The cation-π interactions*, Chem. Rev. 1997 (97) 1303.
- C.A. Hunter et al.: *Aromatic Interactions*, J. Chem. Soc. Perkin Trans. 2, 2001, 651.
- J.-M. Lehn, J.L. Atwood, J.E.D. Davies, D.D. MacNicol & F. Vögtle: *Comprehensive Supramolecular Chemistry*, Wiley, 2000.
- J.W. Steed & J.L. Atwood: *Supramolecular Chemistry*, Chapter 1, Wiley, 2000.

Self-assembly

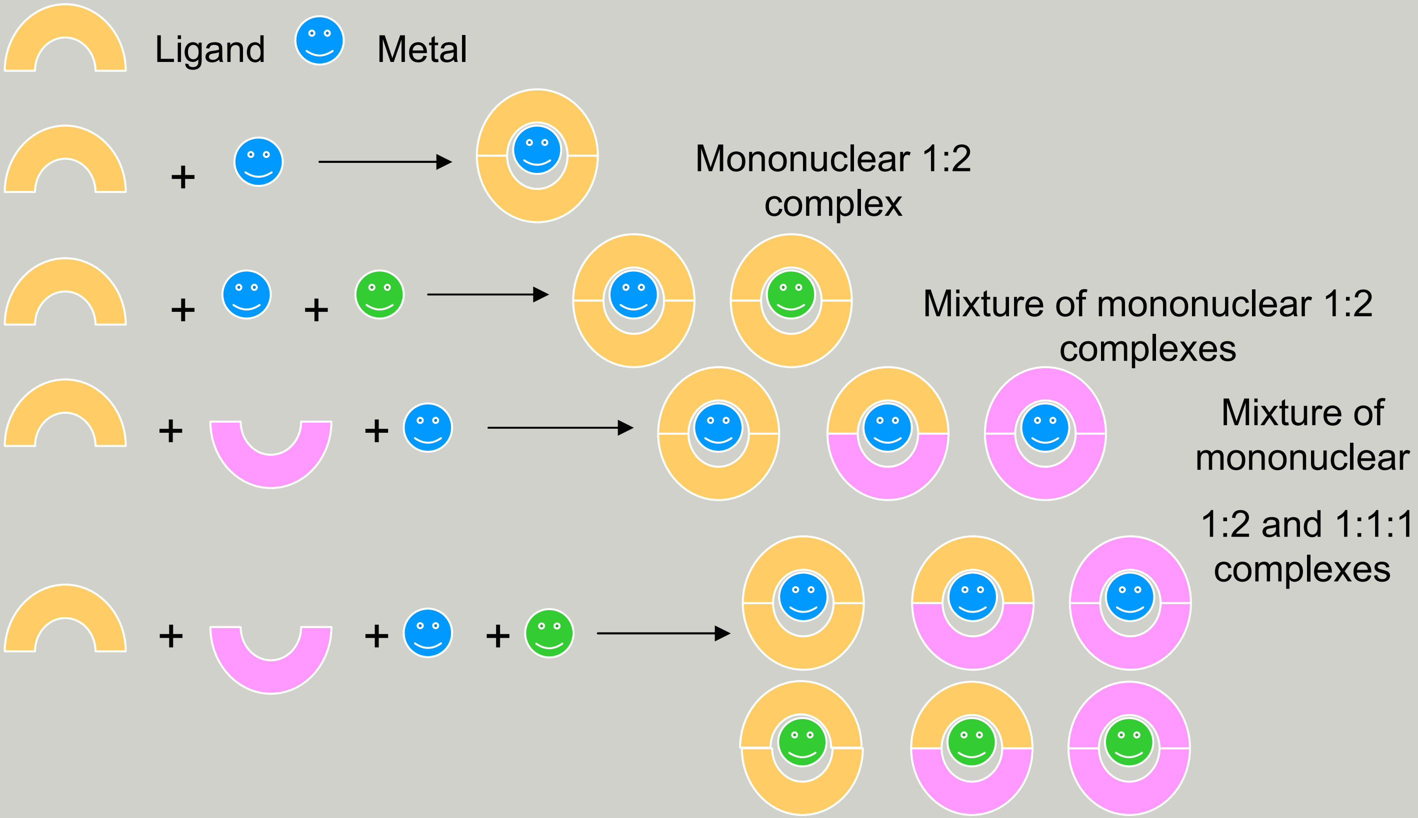
- Supramolecular self-assembly: Reversible, recognition-directed spontaneous association of two or more components to a larger aggregate controlled by weak, non-covalent, intermolecular interactions → self-repairable.
- The idea: To get pre-programmed systems in which small easily prepared components (tectons) automatically converge to produce larger and more complicated assemblies (which could perform a certain function) → ”synthesise up”.
- Pre-programmed (convergent and predictable): Size, shape, functional groups, symmetry etc. are suitable for production of the larger assembly.

Self-assembly

- Examples: DNA, protein folding, viral assembly.
- Benefit of self-assembly: if biological processes (e.g. DNA replication) required breaking covalent bonds the energy loss would be enormous and synthesis of biological molecules would be more complex and time-consuming.
- In biomolecules the building blocks are coded with the right information to form larger assemblies themselves and any mistakes are corrected during the assembly process.
- Errors in coding cause errors in assembly → diseases such as BSE, Alzheimer, Parkinson (protein misfolding into toxic fibres), cystic fibrosis (loss of function of the protein), Lafora disease (error in DNA coding).

Self-assembly

Examples: self-assembly via metal coordination. Labile and highly directional with strict geometry → predictable.



Ligand

Metal

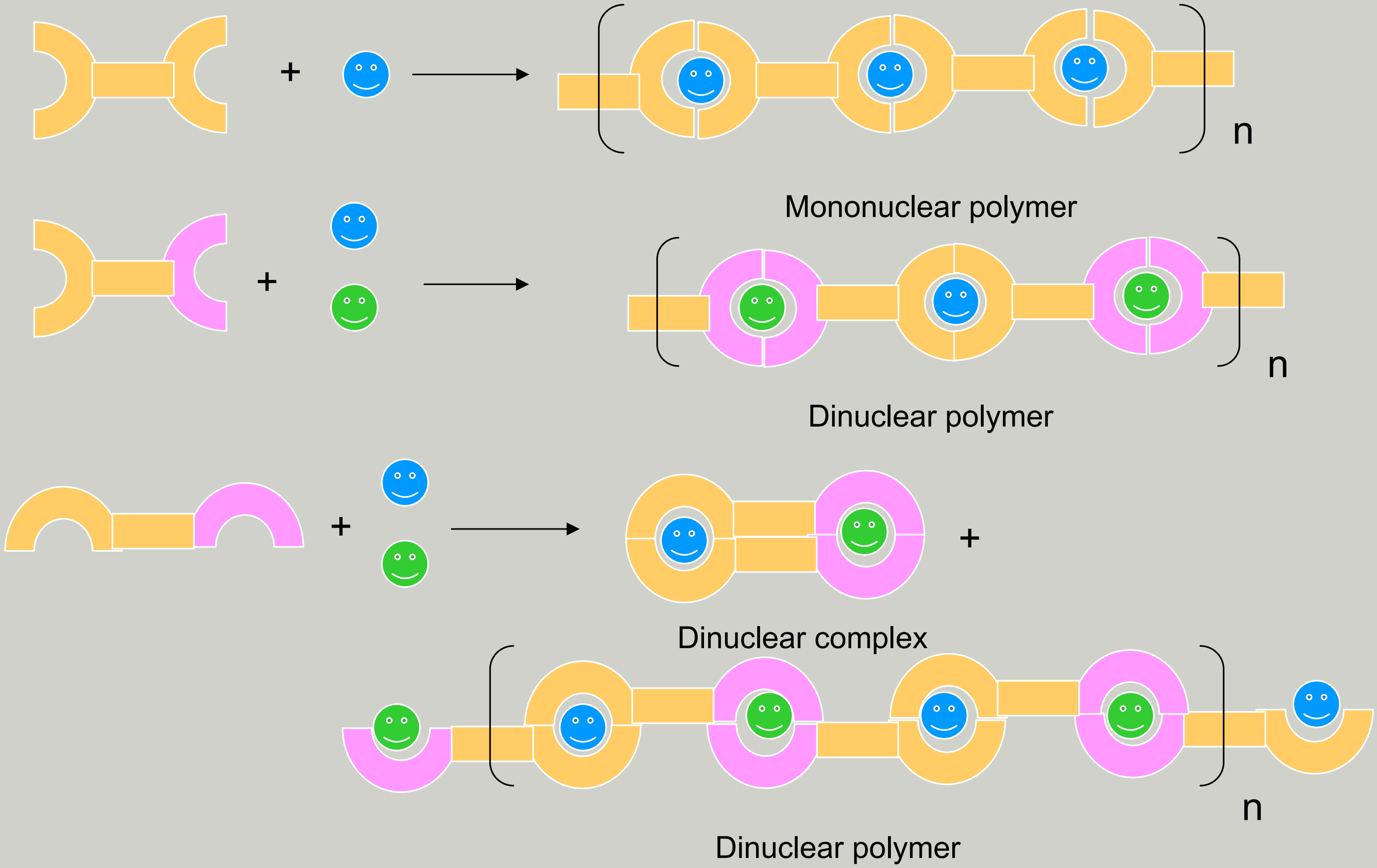
Mononuclear 1:2 complex

Mixture of mononuclear 1:2 complexes

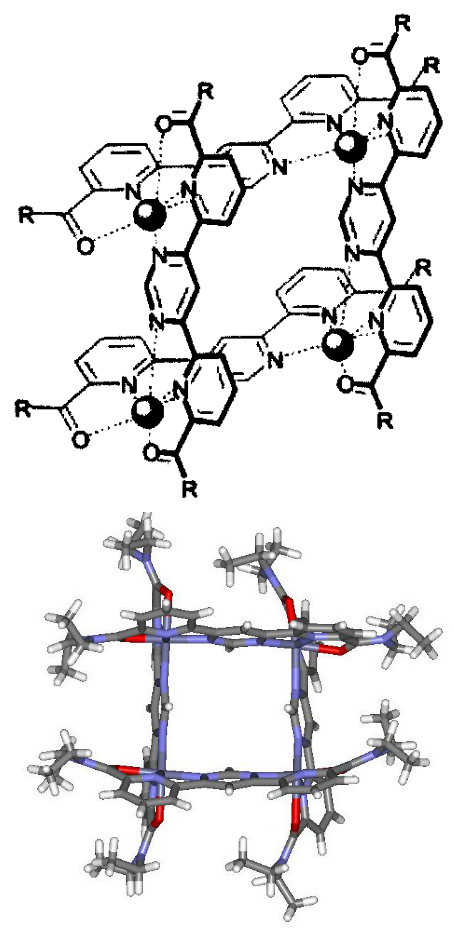
Mixture of mononuclear

1:2 and 1:1:1 complexes

Self-assembly via metal coordination

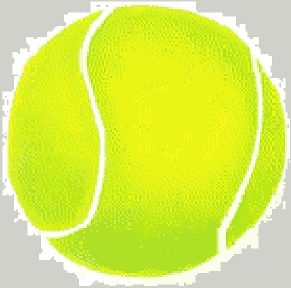


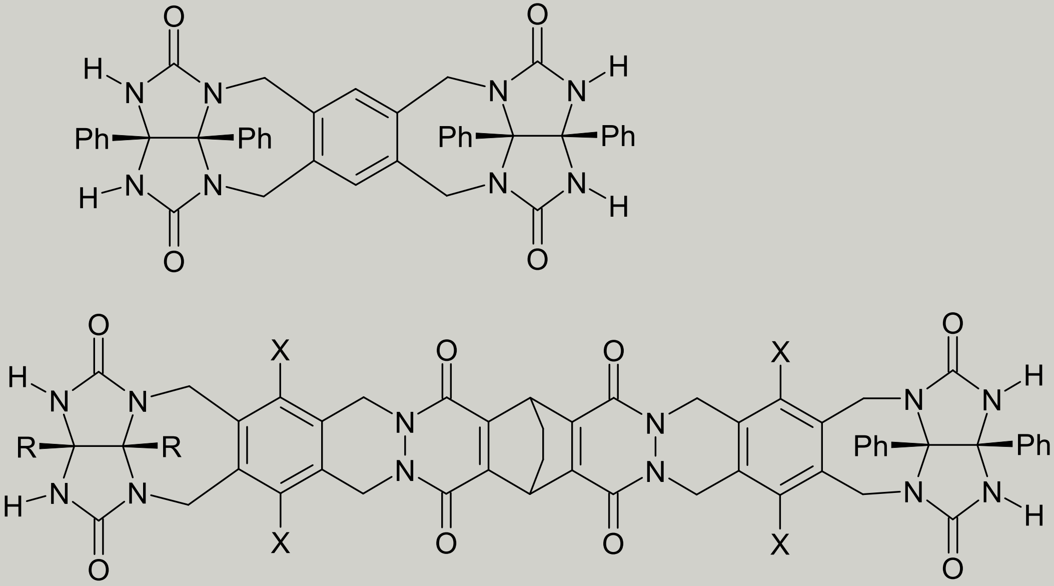
Self-assembly via metal coordination



Self-assembly via hydrogen bonding

- Also directional and hence somewhat predictable.
- Example 1. “Tennis balls” based on self-complementary, intrinsically curved hydrogen bonding compounds.

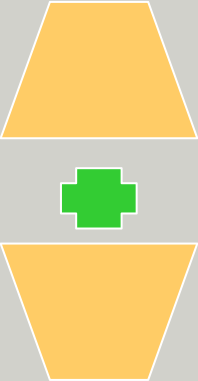


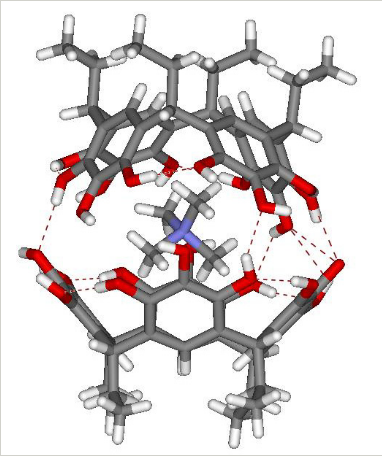


Self-assembly via hydrogen bonding

Example 2. Self-assembling capsules

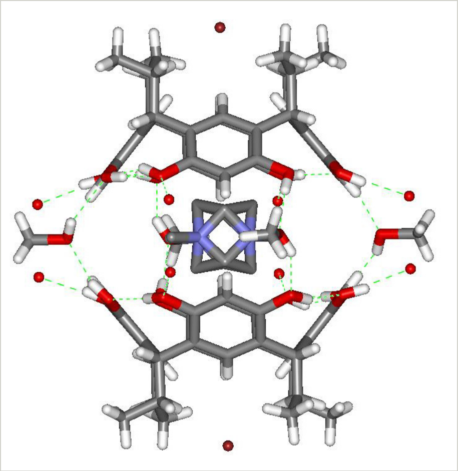
- Building blocks may be either self-complementary and directly hydrogen bonded or connected via separate spacer molecules (hydrogen bonding is mediated by a spacer).





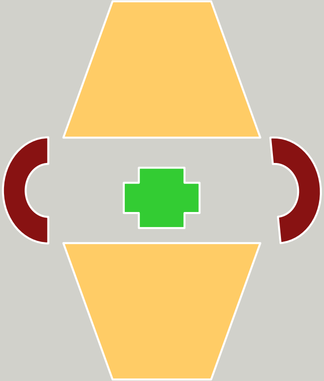
Directly hydrogen bonded

A. Åhman, M. Nissinen, M. Luostarinen and K. Rissanen, Supramol.Chem. 2004.



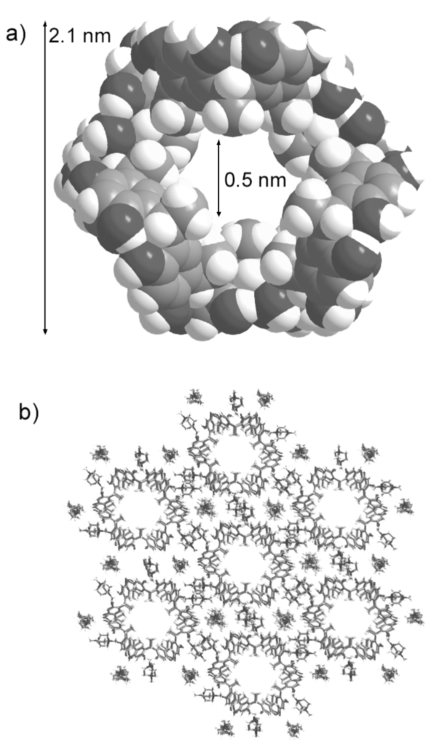
Solvent mediated

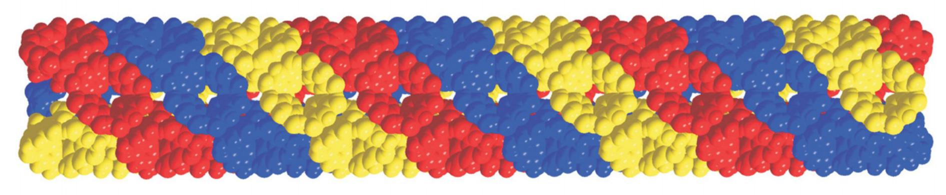
H. Mansikkamäki, M. Nissinen and K. Rissanen, Chem. Commun. 2002.

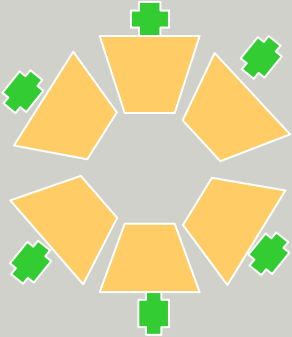


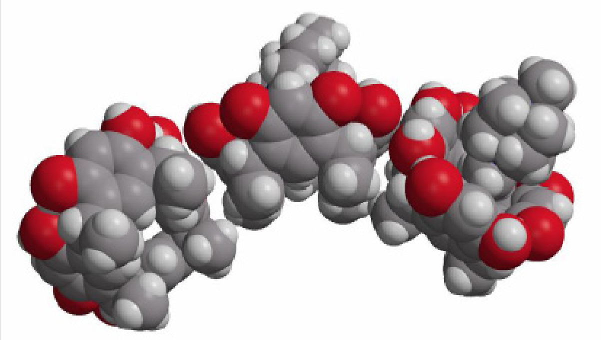
Self-assembly via other weak interactions

- $\pi \cdots \pi$ interaction governed assembly of resorcinarene into a nanotube.





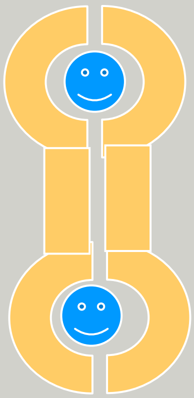




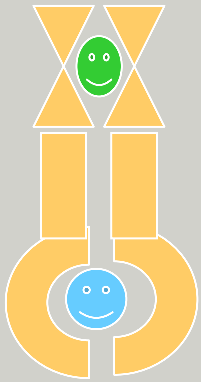
H. Mansikkamäki, M. Nissinen and K. Rissanen, Angew. Chem. Int. Ed. (2004).

Self-assembly

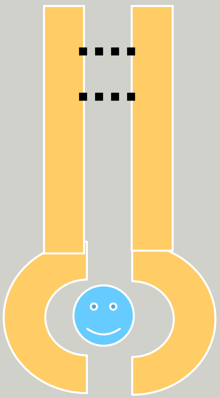
- Note, that in most cases self-assembling systems are a combination of multiple different types of interactions (e.g. H-bonding, metal coordination or H-bonding and π-interactions).
- Self-assembly process is dominated by the most stabilising interactions in descending hierarchy → the strongest interactions form first and are then supported by the weaker ones.



Single-interaction assembly



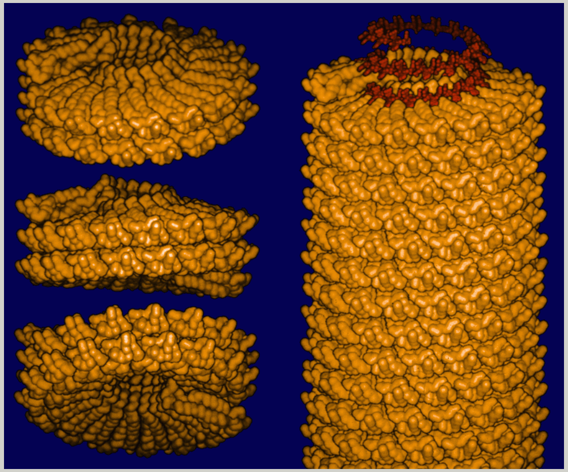
Unimediated multiple interaction assembly



Multimediated multiple interaction assembly

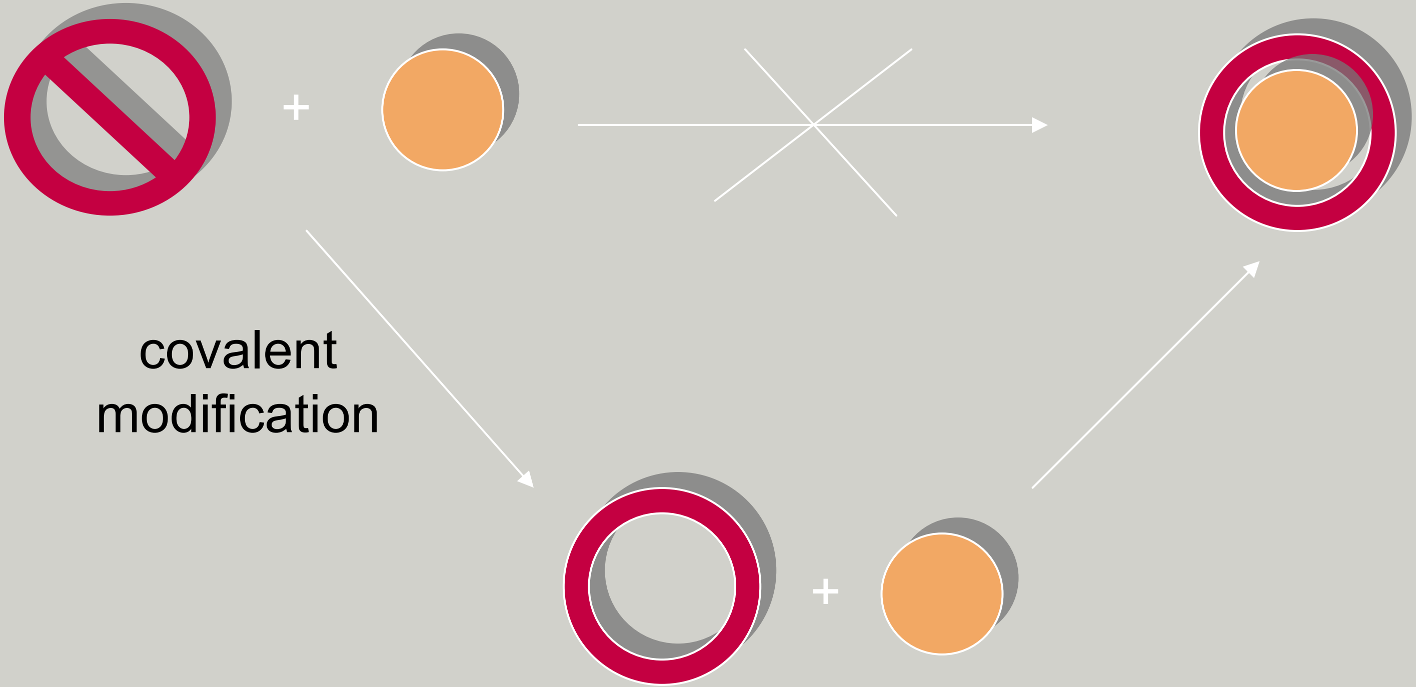
Self-assembly

- Self-organisation: The term incorporates both the interactions between the self-assembled species and the integration of interactions leading to collective behaviour.
- Strict self-assembly: The assembly forms spontaneously when components are mixed together in correct ratio and suitable conditions and the formation is reversible and presents the thermodynamic minimum for the system, e.g. the formation of tobacco mosaic virus, DNA.



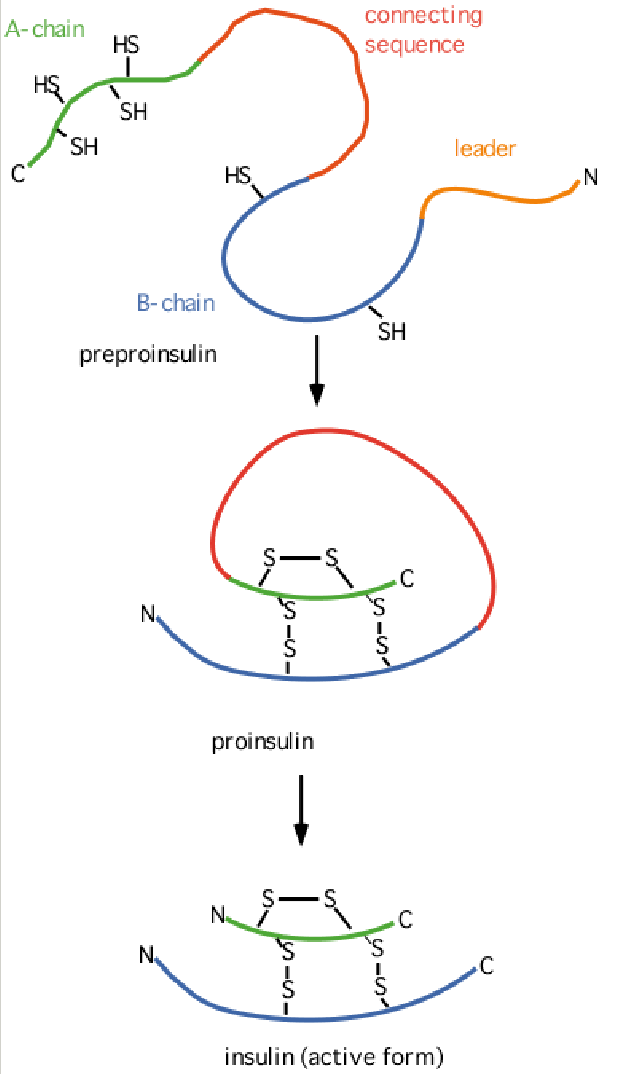
Self-assembly

- Molecular self-assembly: Concerns the change of covalent bond(s).
- The process is irreversible and the product does not need to be the thermodynamic minimum structure.



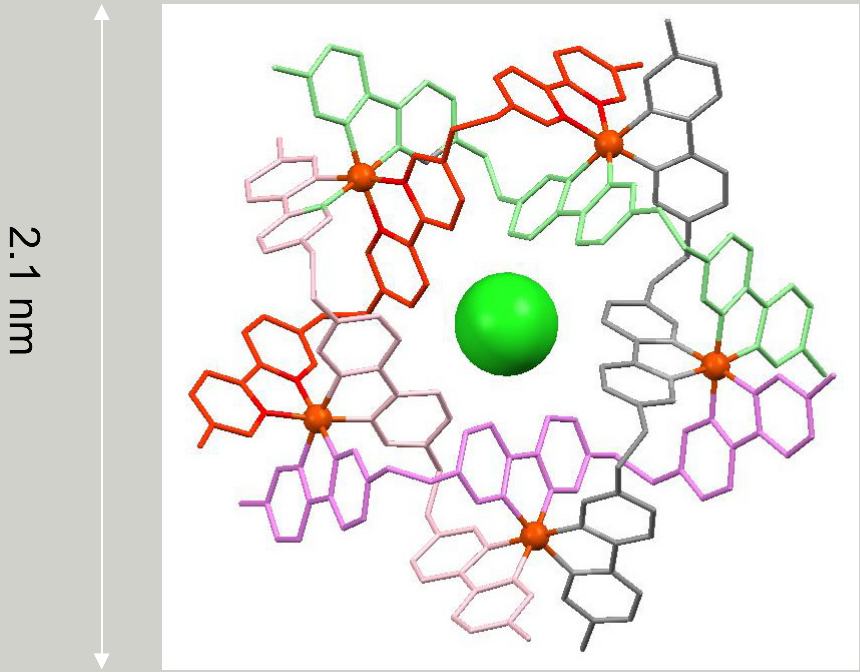
Self-assembly

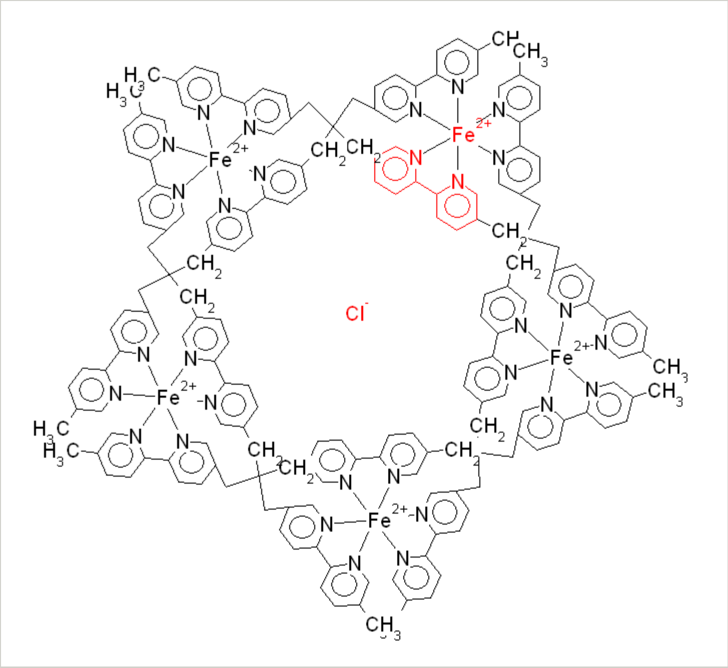
- Example: Biosynthesis of insulin – self-assembly followed by covalent modification



Self-assembly

- In addition to pre-programmed functionalities self-assembly can be achieved via templates.





J.-M. Lehn et al. Angew. Chem. Int. Ed. 1996.

Self-assembly

- Emergent self-assembly arises from unpredictable structures or properties over time.

http://www.lboro.ac.uk/

Self-assembly - applications

- The most common applications of self-assembly are the synthesis of molecular machines (catenanes, rotaxanes) and other supra/nanochemical assemblies (directed self-assembly and self-assembly with post-modification).
- Self-assembled monolayers (SAM).

Molecular devices

- Nanomanipulation: moving atoms or molecules one by one by AFM, STM or by using optical or magnetic tweezers or glass microfibres.
- Nanomanipulation is not practical in making large quantities of functional nanomaterials → directed or templated chemical methods work better.
- Molecular machine: multicomponent system in which the reversible movement of the components can be controlled by an external stimulus (photons, electrons, chemical compounds).
- Examples of supramolecular devices: switches, rectifiers, motors.
- Problem: how the devices communicate with outside world → photoactivity, redox-activity.

Supramolecular photochemistry

- Light-induced processes are very important in biological systems (e.g. photosynthesis)
- Light-absorbing components are readily available and can be utilised in various physical states and media
- Light-induced processes include charge separation, catalysis, energy migration, changes in optical properties, redox modifications, regulation of binding properties, sensor and switcher applications etc.
- In supramolecular chemistry re-emission of radiation is of interest in sensing and signalling, while chemical reactions induced by light are of interest in molecular switches and photocatalysis

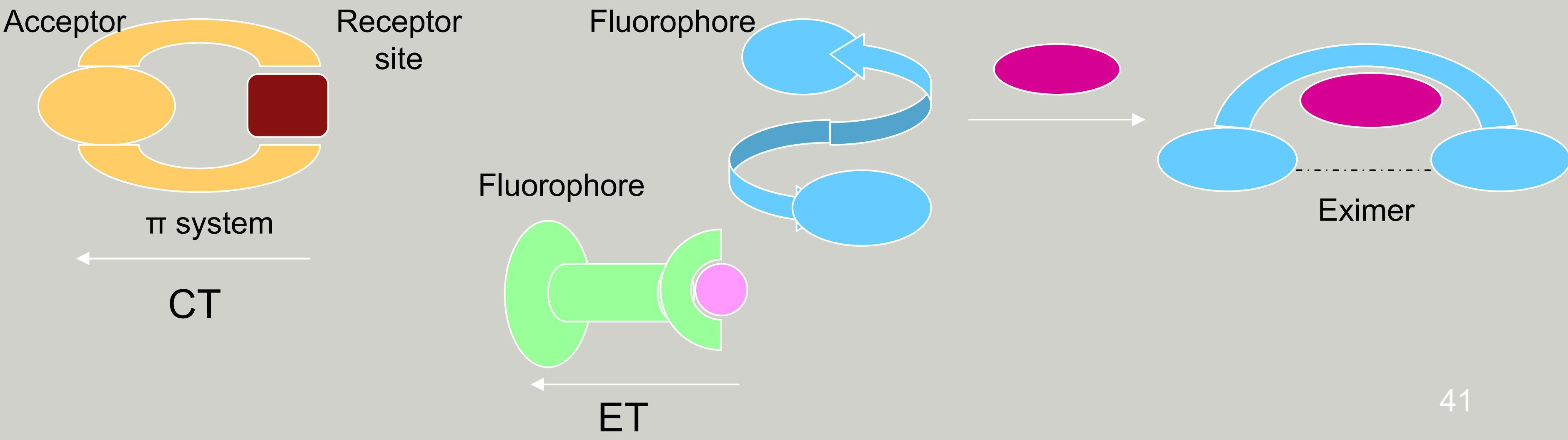
1. Photochemical devices

- Basic requirements: particular region of the molecule is excitable by electromagnetic radiation, which changes the electronic interactions between the components.

  a) Charge transfer (CT)

  b) Energy transfer (ET)

  c) Eximer / exciplex formation (i.e. formation of a dimer or complex between an excited state and a ground state)

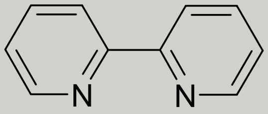


Photochemical devices

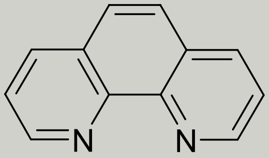
- Idea: a series of molecules are linked together to a supramolecular array and a signal is transferred as an intercomponent process → machines, switches, sensors and molecular electronics.
- Typical components: transition metal centers [Ru(II), Os(II) and Re(I)] coordinated to aromatic nitrogen donor ligands, such as 2,2'-bipyridine (bpy), 1,10-phenantroline (phen) or terpyridines (terpy).

  a) absorb and re-emit light due to π-π* transitions.

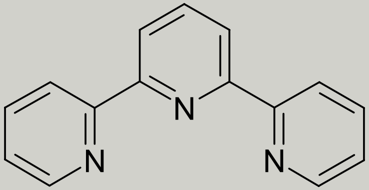
  b) metal-to-ligand charge transfer (MLCT) occurs.



bpy

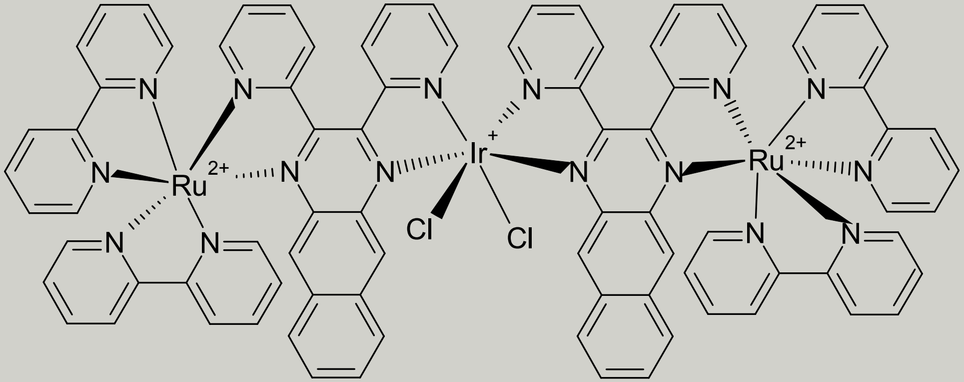


phen



terpy

Photochemical devices



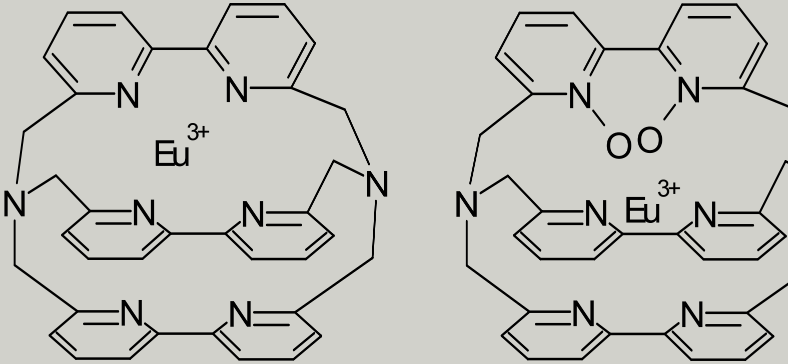
photosensitiser

electron storage
and reaction center

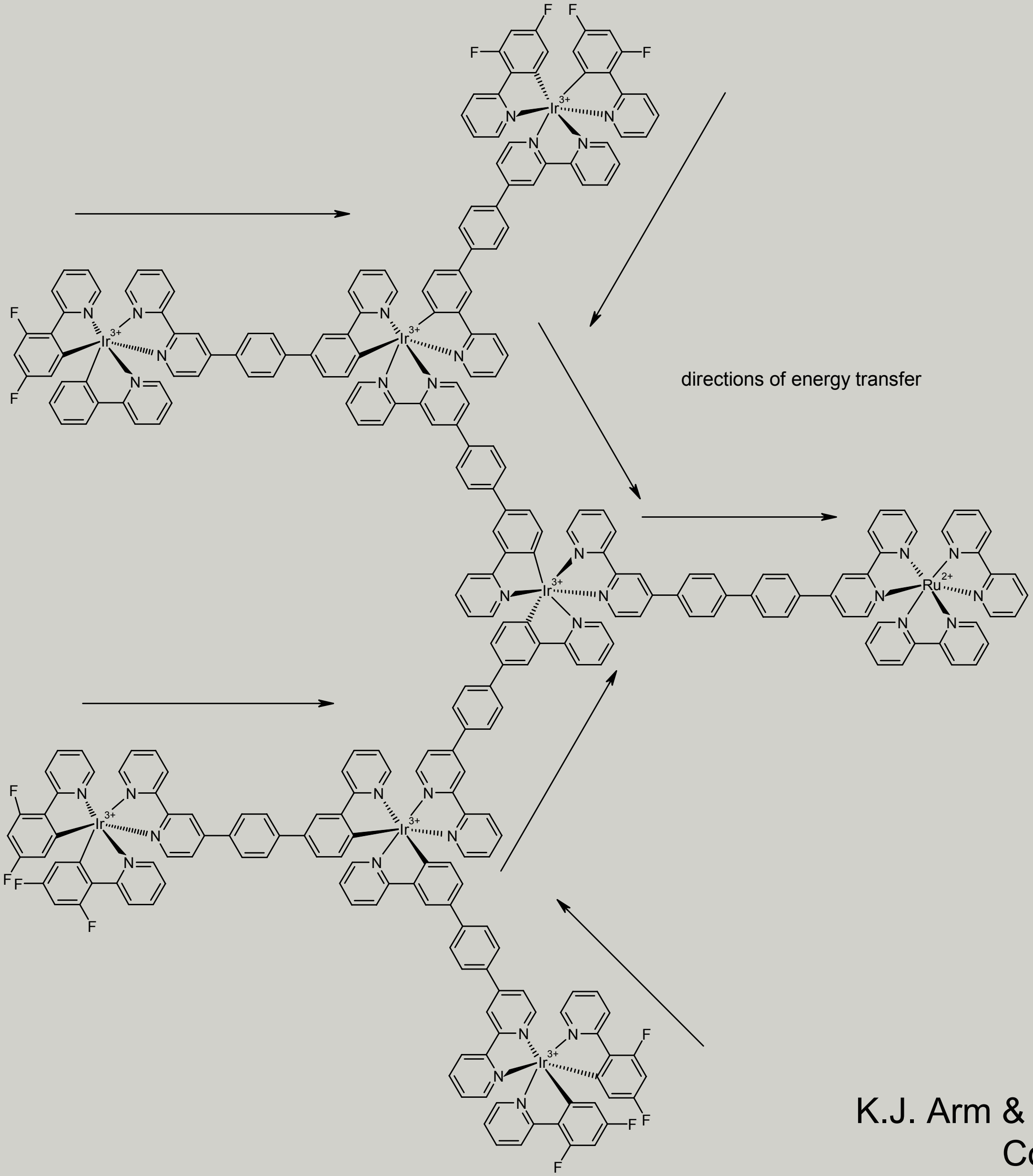
photosensitiser

Photochemical device designed to mimic the photosynthesis (utilization of solar energy.

Two examples of light conversion device.



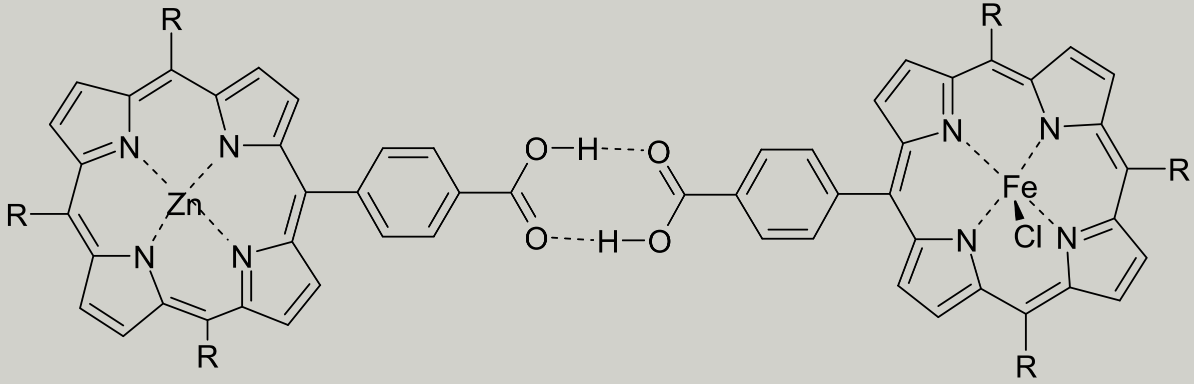
Photochemical devices



K.J. Arm & J.A.G. Williams, Chem. Commun. 2005.

Photochemical devices

- The most typical photochemical devices are strongly bonded (covalent or coordination bonds), but also some non-covalently bonded porphyrin based devices are known
- The non-covalent bond must form an effective conduit for electron transfer process → complementary binding via multiple interactions (e.g. H-bonding or π-interactions).

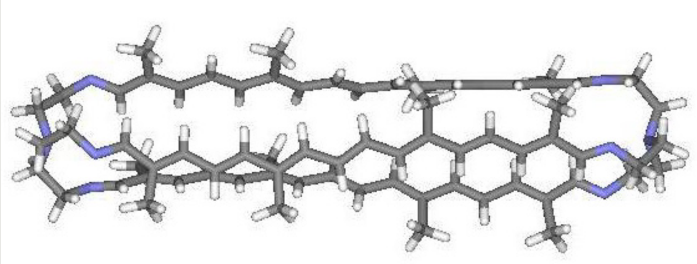


2. Molecular wires and rectifiers

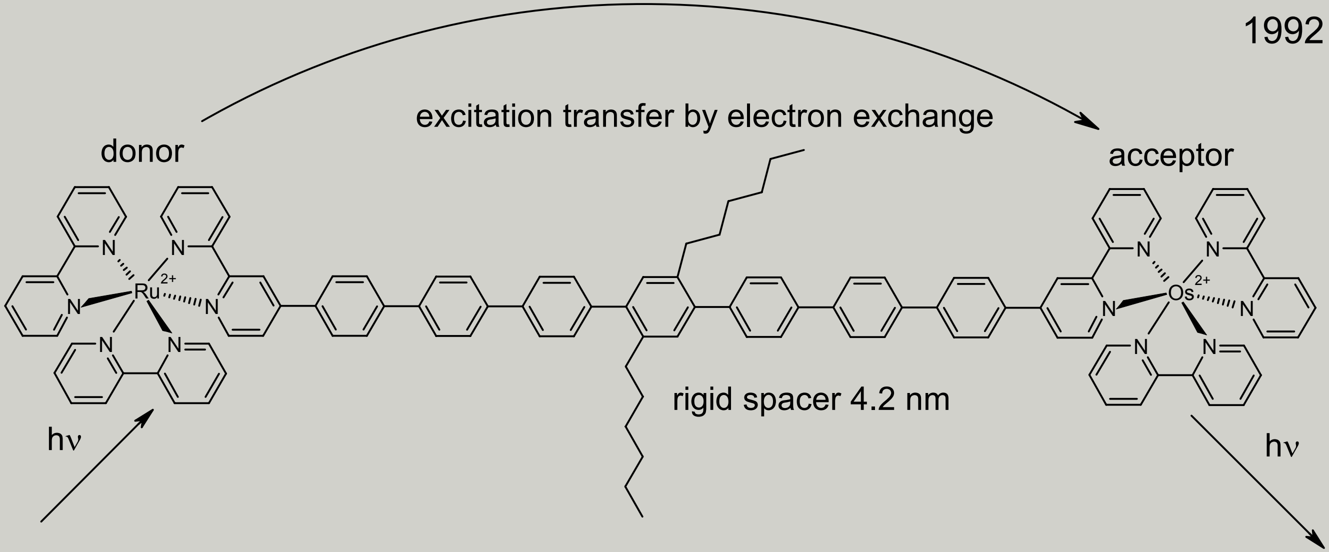
- Molecular wires: long, rod-like compounds or groups, typically containing conjugated π systems → ability to transfer electrons or energy between the donor and the acceptor.

  → Dexter electron-exchange mechanism

  → Direct-current (DC) electron conductivity

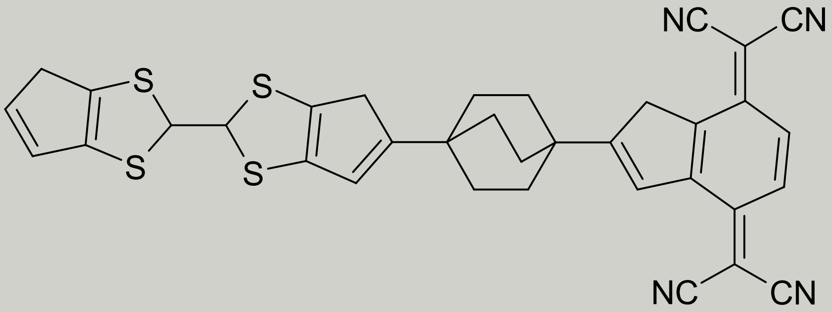


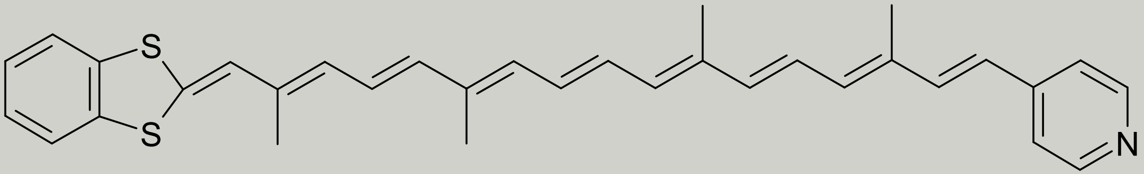
J.-M. Lehn et al. Helv. Chim. Acta 1992



Molecular wires and rectifiers

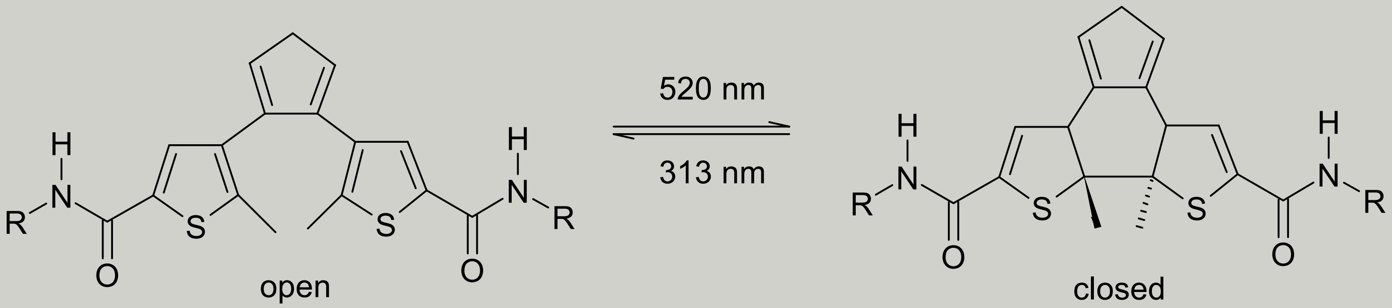
- Rectifier: a device that allows the electron flow only to one direction → conversion of alternating current (AC) into direct current (DC).
- Conventional rectifier is made of a contact between a *p*-type (electron poor) and *n*-type (electron rich) semiconductor → molecular rectifier should have the same properties, i.e. electron donor and acceptor separated by an insulator.





3. Molecular switches

- Switch: a compound which can be transformed (for example conformationally or chemically) from one state to another, so that a function of a molecule is either on or off. The transform can be caused, for example, by light or binding of a guest molecule.
- Example: 1,2-dithienylethene, which undergoes a reversible ring closure upon irradiation with UV and visible light.



R = $C_{12}H_{25}$

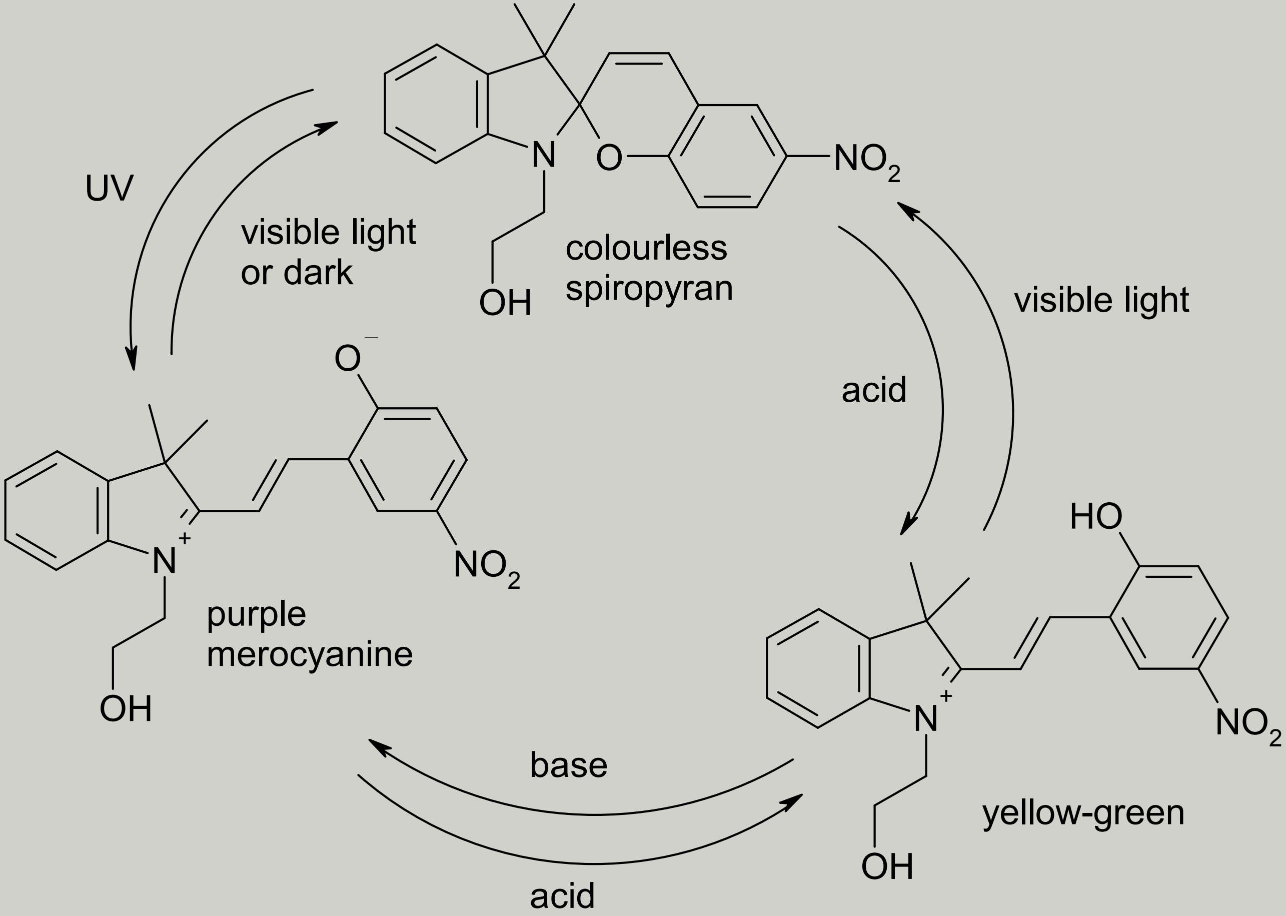
Molecular switches

Three state molecular switch:

1) UV light
2) Visible light
3) Acid

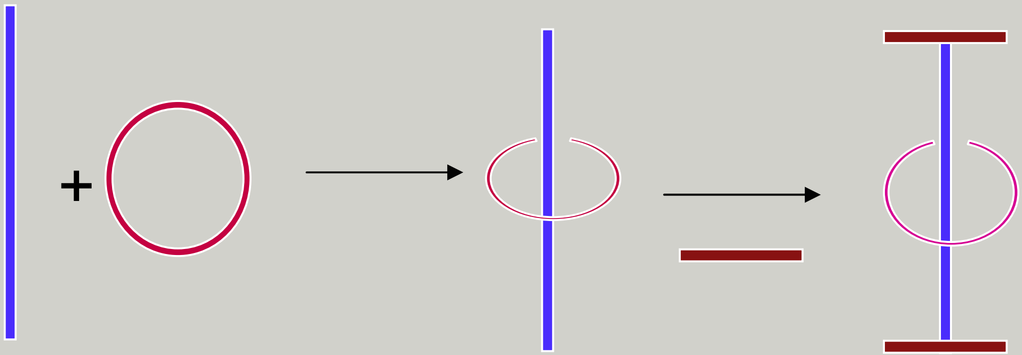
→ absorbance at 401 nm

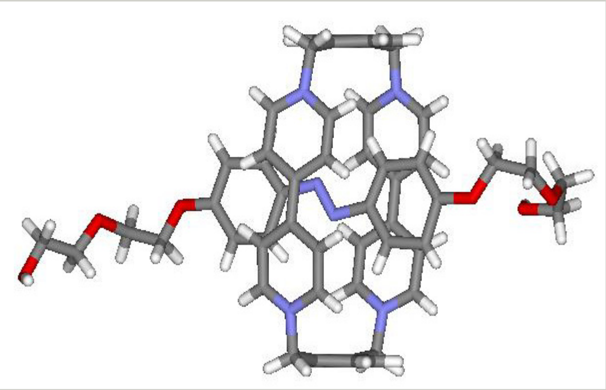
→ absorbance at 563 nm

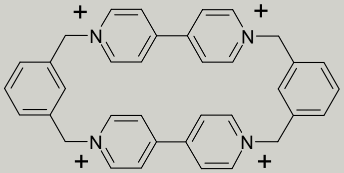


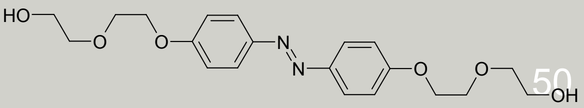
Molecular switches: rotaxanes

- Rotaxanes: a compound consisting of a linear molecule with bulky end groups threaded through a macrocyclic ring.
- Pseudorotaxanes: ”rotaxanes without stoppers”, i.e. linear part can slip through the cyclic part of the molecule. Frequently precursors for rotaxanes.





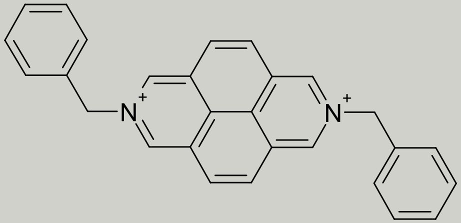




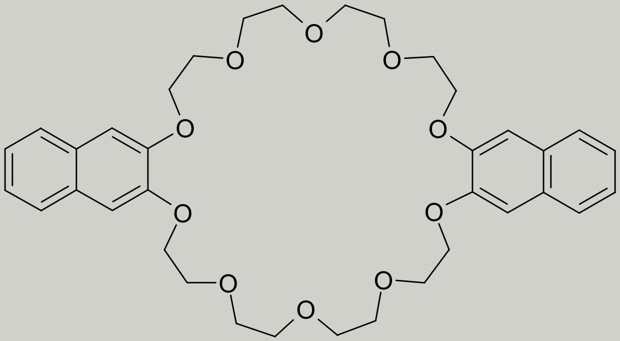
Pseudorotaxane: J.F. Stoddart et al. Chem. Eur. J. (1999).

Molecular switches: rotaxanes

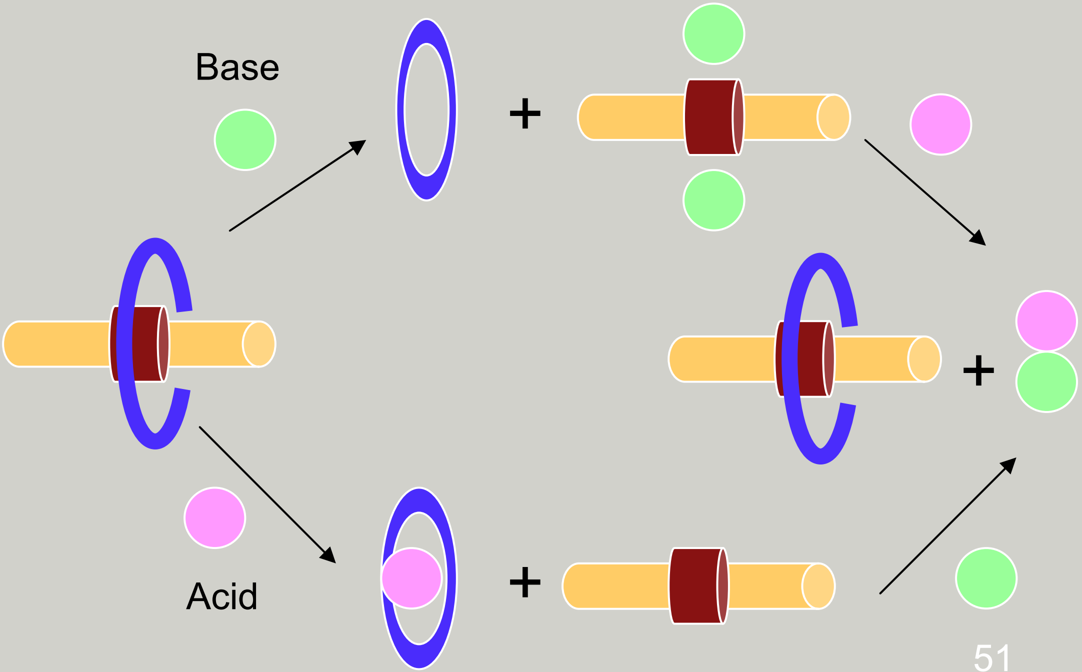
- Logic gates: switches that use binary notation, i.e. output is either 1 or 0.
- The simplest form YES/NOT gate, more complicated AND/OR/XOR (exclusive OR) gates.
- Example: pseudorotaxane based XOR gate



electron acceptor 2,7-diazapyrenium



electron donating aromatic corwn ether

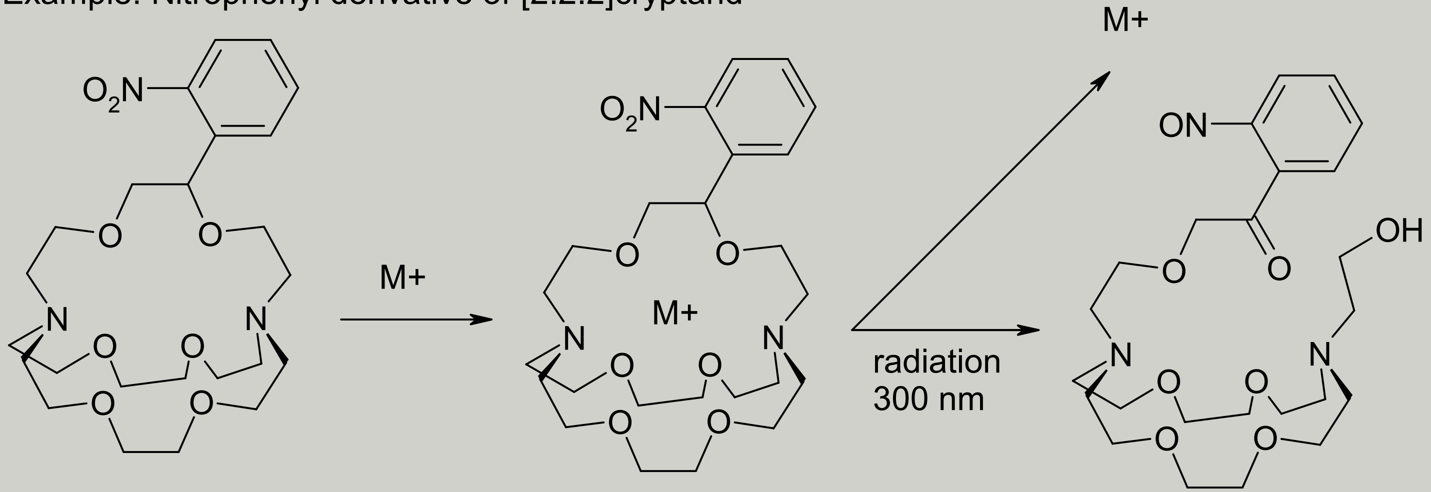


J. Stoddart et al. J. Am. Chem. Soc. 1997

Molecular switches

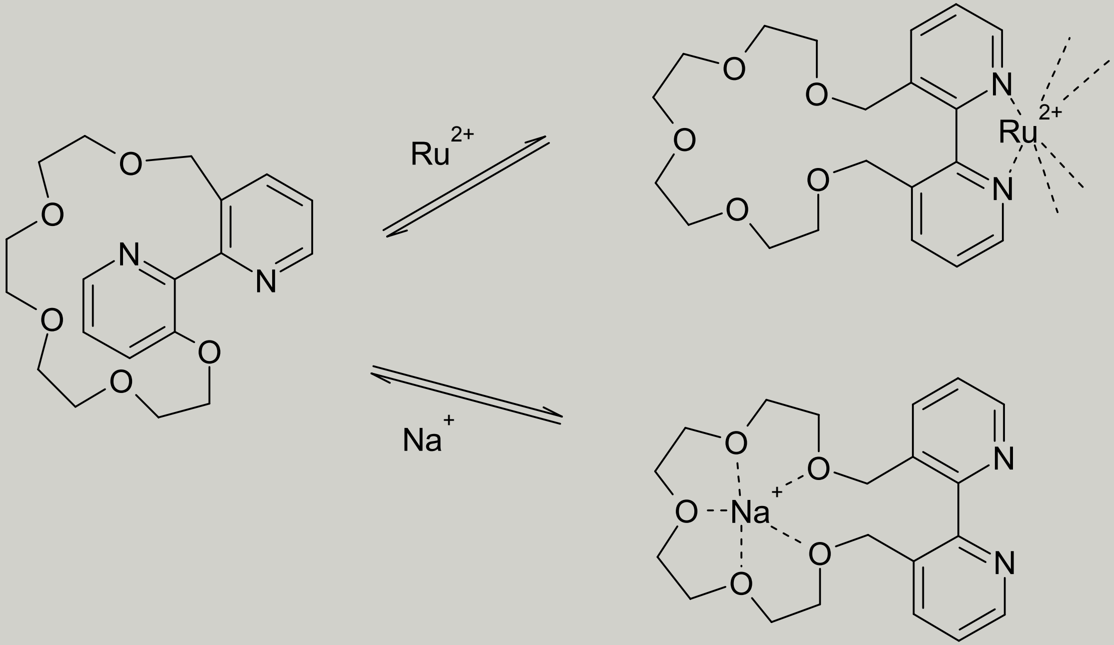
- Photoionic signal: photochemical switching between strongly cation binding host and more weakly binding host causes a light-triggered pulse of released cations

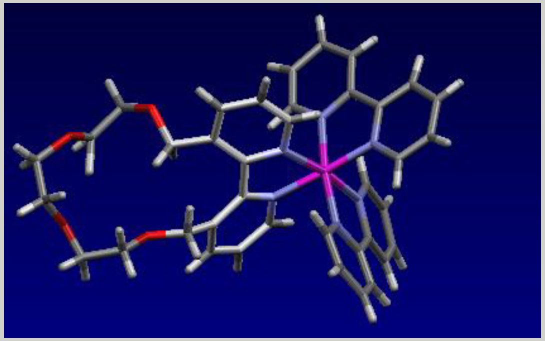
Example: Nitrophenyl derivative of [2.2.2]cryptand



Molecular switches

- Allosteric switches: system which involves conformation coupling between two or more binding sites, i.e. binding at one site induces a conformational change that influences the binding ability of another binding site





S. Dutta et al., Eur. J. Inorg. Chem. (2003) 2812.

4. Molecular muscles

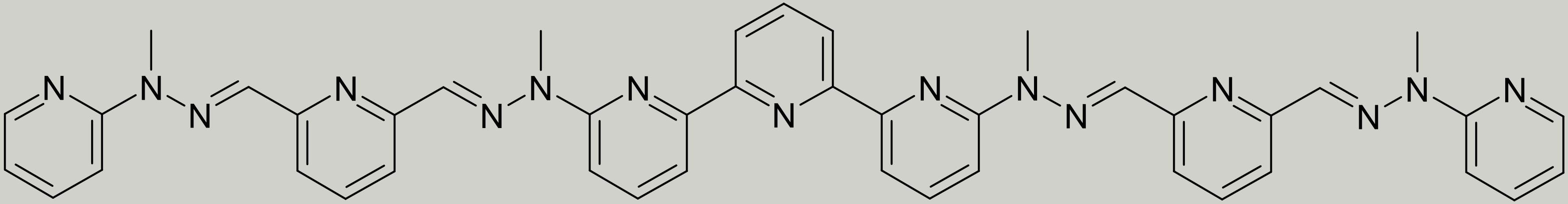
- Electroactive polymers (EAP) could mimic the function of muscles.

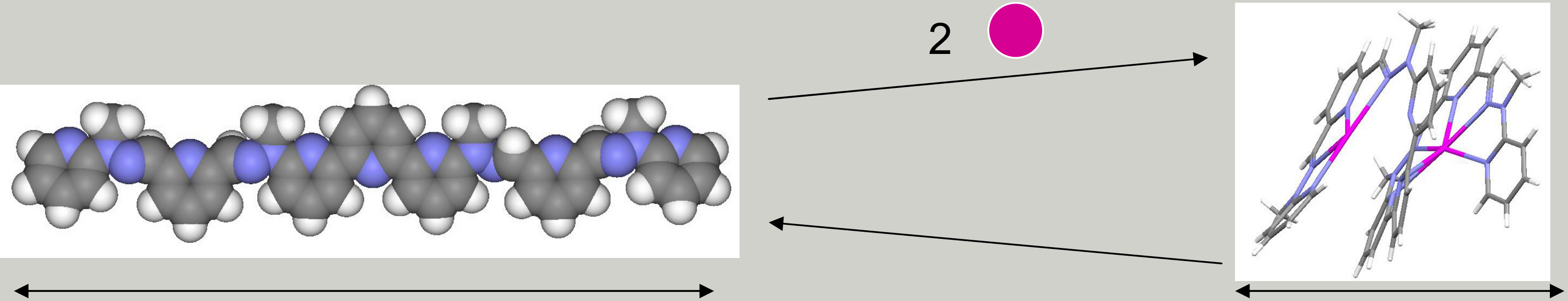
  a) ionic EAPs: ionic polymers, gels, ionic polymer composites, conductive polymers, which bend due to the movement of free ions. Disadvantage: need to be wet and encased between two flexible coatings which require continuous supply of electricity.

  b) electronic EAPs: ferroelectric polymers, dielectric elastomers, electroactive graft elastomers, which are stimulated by an electric field.

Molecular muscles

- Non-polymeric molecular muscle





Folding by adding Pb^{2+}

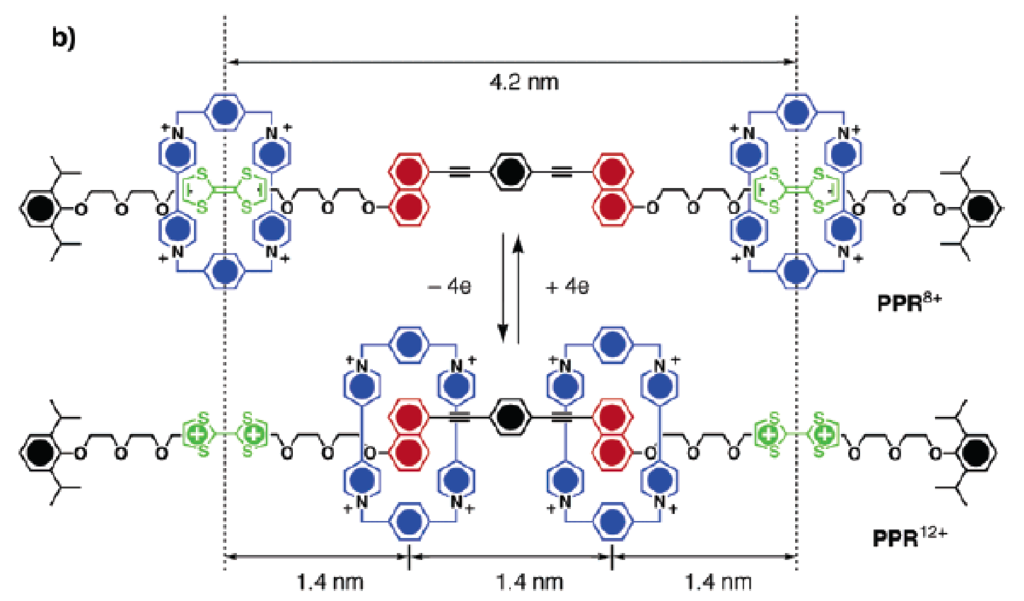
2 ●

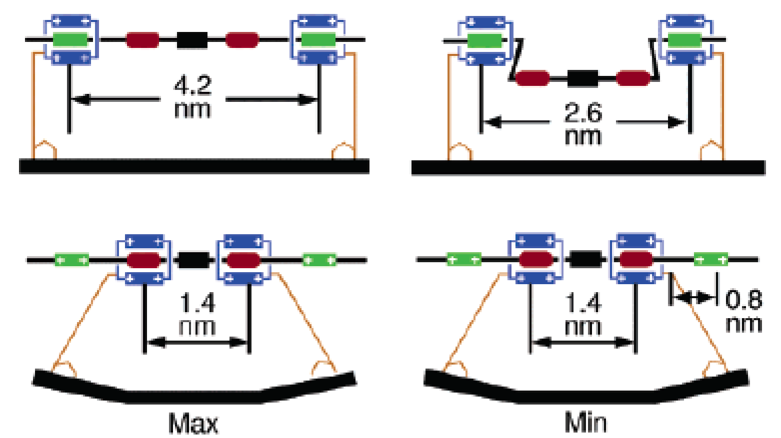
4 nm

Unfolding by removal of Pb^{2+} by tren

0.72 nm

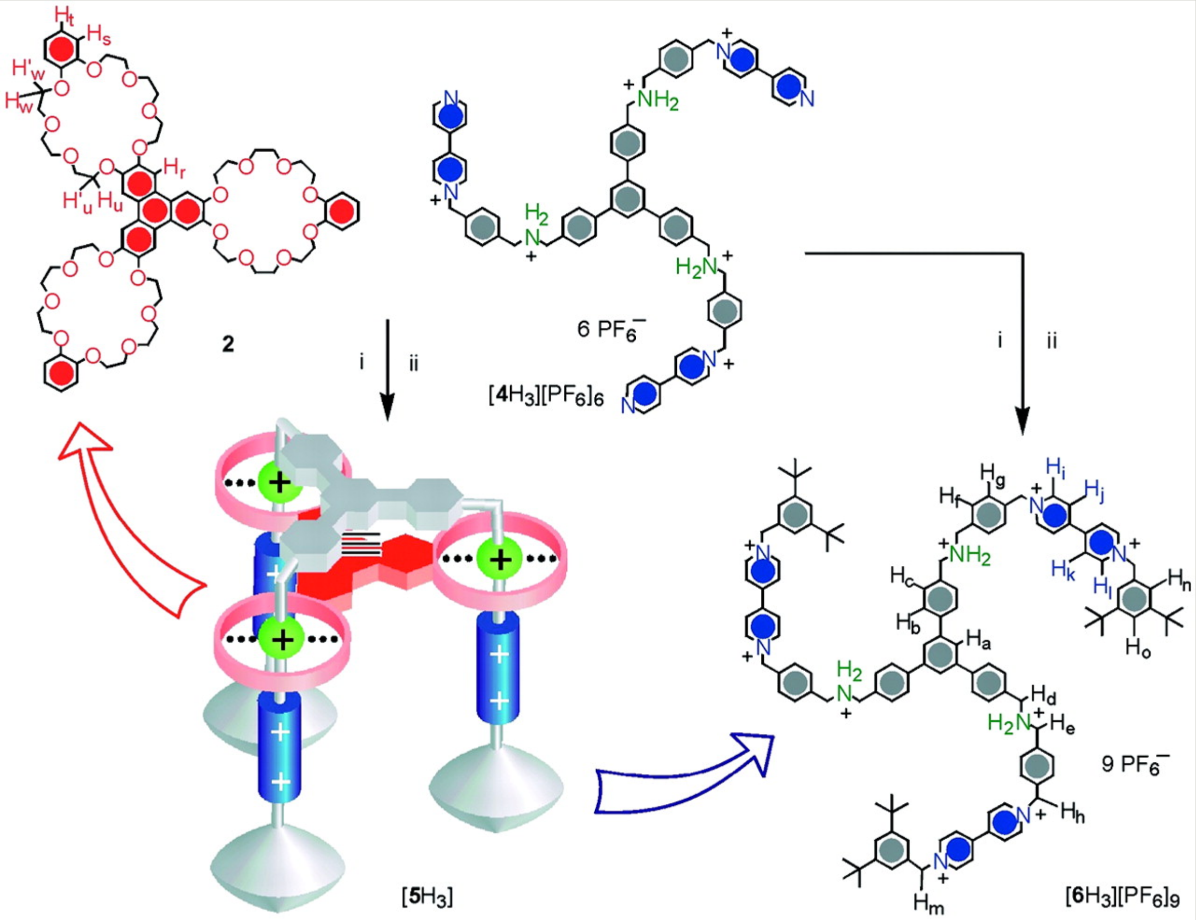
Molecular Muscles





J. Fraser Stoddart et al. J. Am. Chem. Soc., 2005

5. Molecular elevators

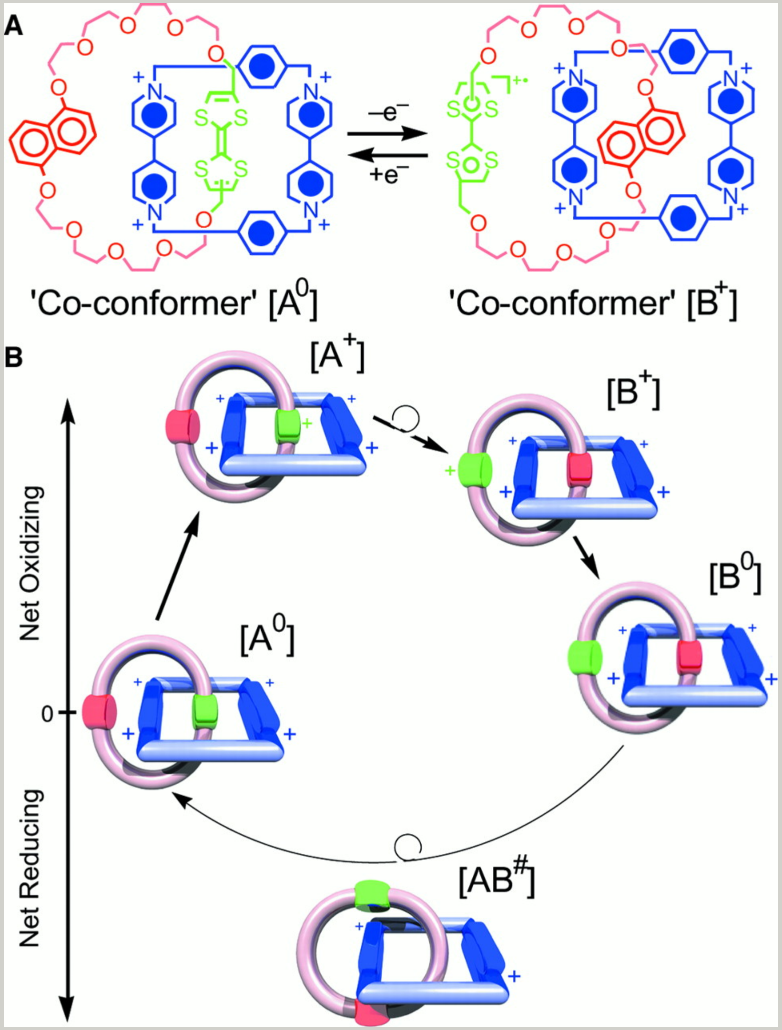


J. D. Badjic et al., Science 303,
1845 -1849 (2004)

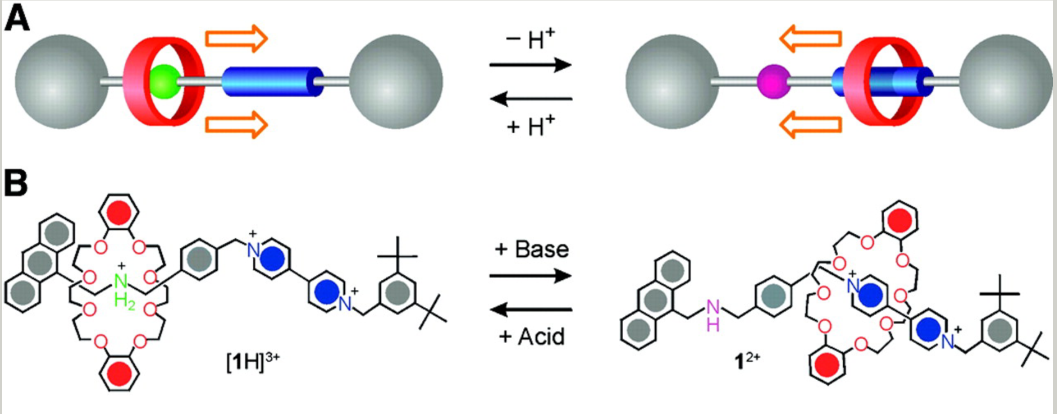
Published by AAAS

Science AAAS

6. Molecular shuttles



C. P. Collier et al., Science 289, 1172 -1175 (2000)



J. D. Badjic et al., Science 303, 1845 -1849 (2004)

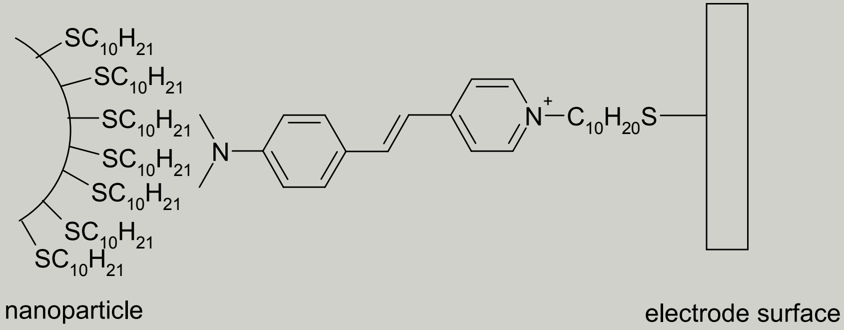
Published by AAAS

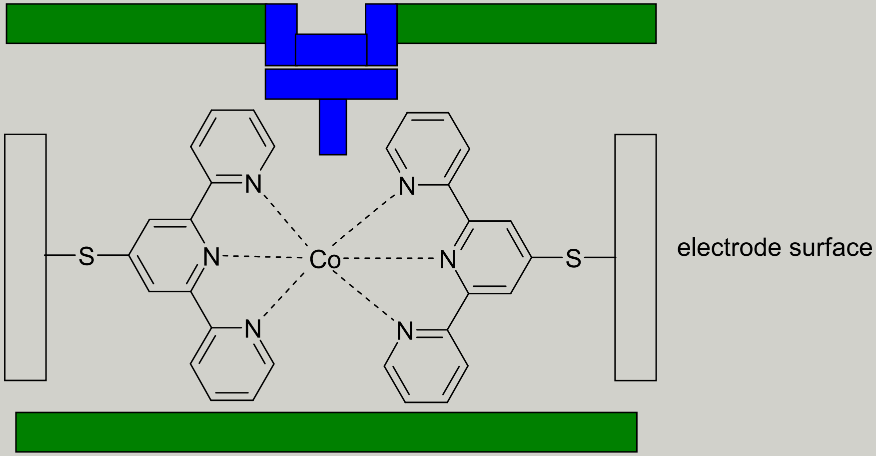
Molecular devices

- Previous examples are mainly of academic interest, while applications outside laboratory are still scarce.
- Some examples of a single molecule electronic devices exist:

a) Passive single molecule rectifier linking a thiol-coated gold tip to Au electrode.

b) Active single molecule transistor based on a thiol-terminated cobalt terpyridyl complex.





Molecular devices

Groundbreaking scientists in the field of molecular machines:

J.-M. Lehn, Univ. Strasbourg, France, Nobel prize in chemistry 1987 (together with D.J. Cram and C.J. Pedersen)

J.F. Stoddart, UCLA, USA

J.-P. Sauvage, Univ. Strasbourg, France

D.A. Leigh, Univ. Edinburgh

Polymer supported sensors

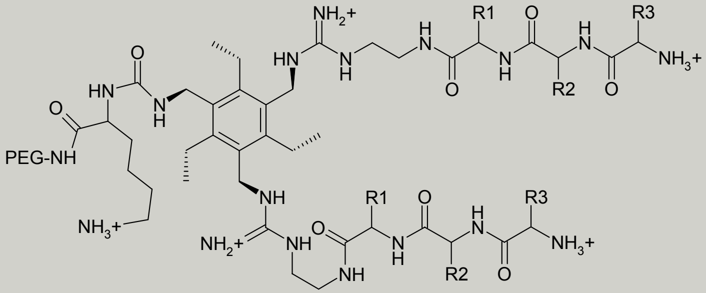
- Conductive polymers, polymer composites, dye-doped polymer matrixes, surface acoustic wave sensors (SAW).
- Examples:

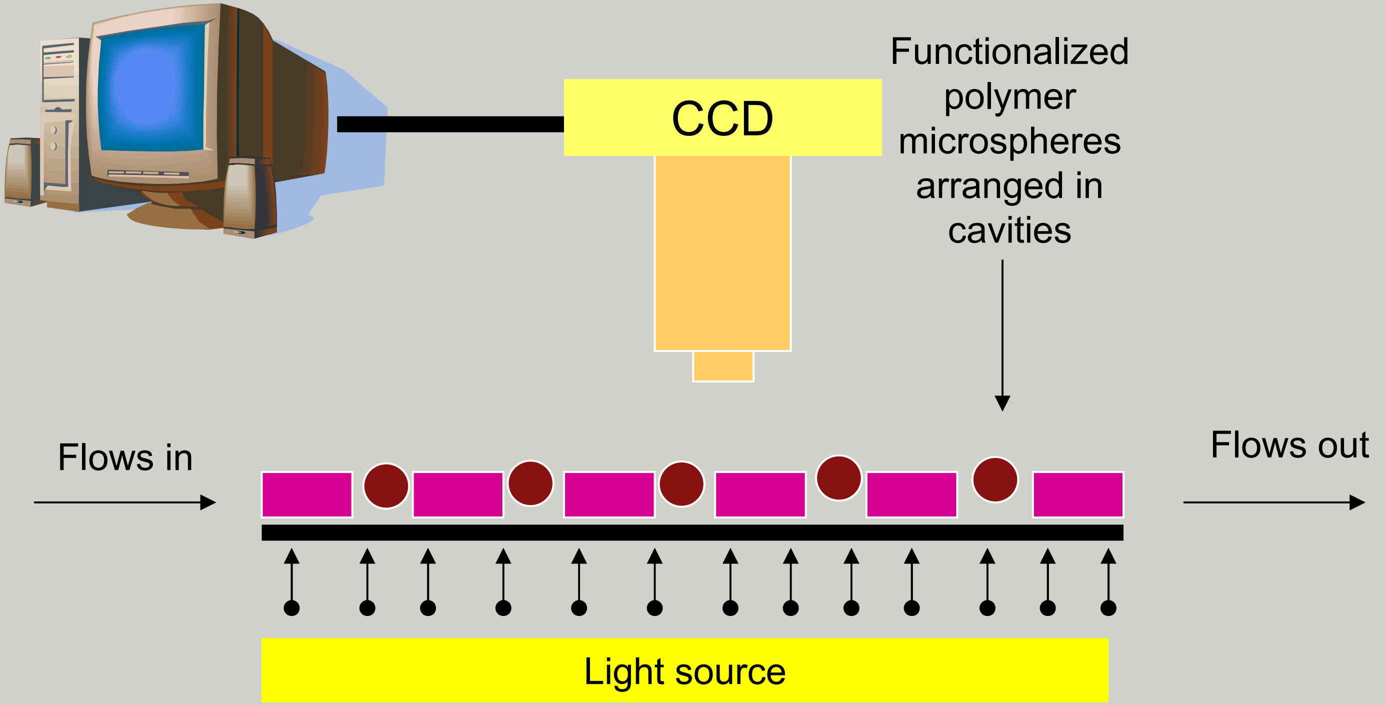
a) electronic nose

b) latex agglutination tests (LAT) for clinical analyses: over 60 in commercial use. Disadvantage: multiple analyte detection is not possible

c) multianalyte chip-based sensor array based on indicator displacement assay (IDA) (electronic tongue)

Polymer supported sensors





CCD

Functionalized polymer microspheres arranged in cavities

Flows in

Flows out

Light source

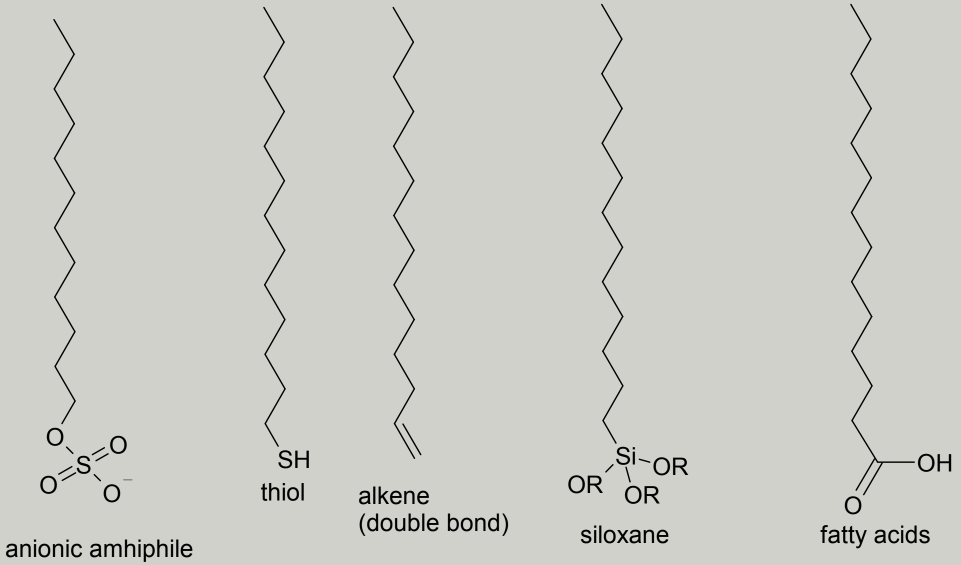
Self-assembled monolayers (SAM)

- Self-assembly can also be used to form ordered two dimensional monolayers by chemisorption of suitably functionalized molecules onto substrate layers.
- Typical structure of monolayer forming molecules:

  a) amphiphiles with a long alkyl chain and polar head group

  b) long chain molecules with functional group capable of surface binding at one end (thiols, siloxanes, fatty acids double bonds)
- Some applications: anti-corrosion and wear protection

Self-assembled monolayers (SAM)



- Preparation of SAMs:

  a) immerse a clean substrate with a reactive surface into a solution of a coating molecules, which slowly assemble to a ordered, close-packed monolayer

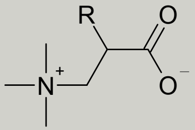
  b) assembly of amphiphilic molecules (surfactans) at fluid interfaces

Self-assembled monolayers (SAM)

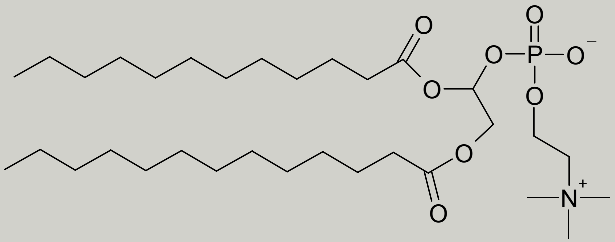
- Surfactants or amphiphiles: molecules with two distinct regions with very different solubilities, i.e. hydrophilic (water-soluble) and lipophilic (hydrophobic; soluble to organic solvents).
- Lipophilic part is typically long aliphatic chain, fluorocarbon chain or aromatic group
- Classification based on the hydrophilic part:

a) Anionic (sulphonate, carboxylate, phosphonate)
b) Cationic (ammonium)
c) Amphoteric (zwitterions)
d) Nonionic (fatty acids)

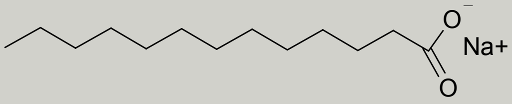
- Examples: soaps, phospholipids, fatty acids



betaine



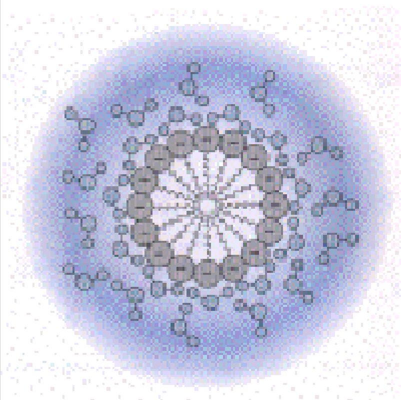
phospholipids

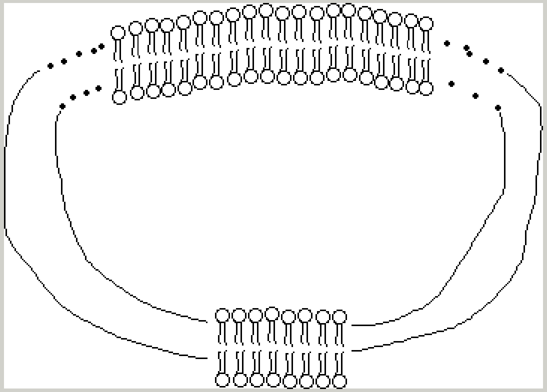


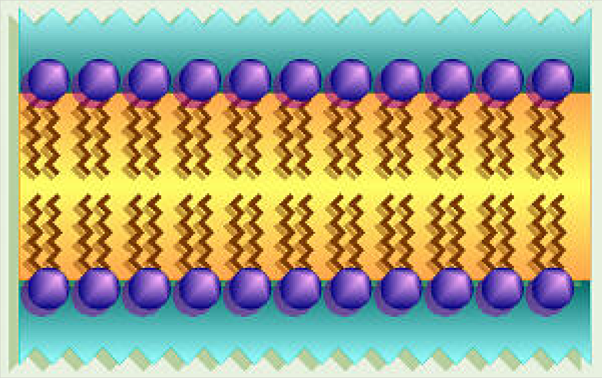
soap (carboxylate)

Self-assembled monolayers (SAM)

- Due to amphiphilic nature of the molecule they aggregate on the water-air interface as monolayers → Langmuir-Blodgett films.
- Amphiphiles can also organize themselves to micelles, bilayers and vesicles depending on the conditions and concentration.

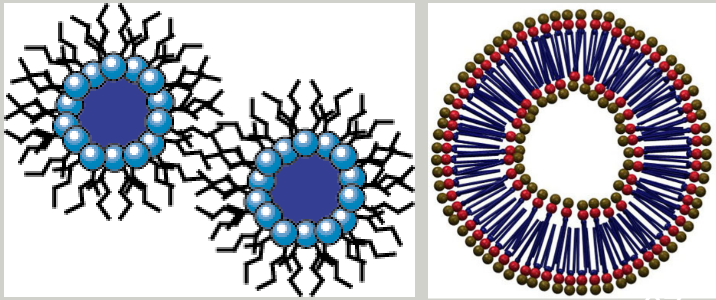






Self-assembled monolayers (SAM)

- Critical micelle concentration: the concentration at which micelle formation begins. Depends at the nature of the organic group.
- Bilayers: extended, sheet-like micelles, for example phospholipid bilayers in biological cells.
- Vesicle: Bilayer encloses an inner aqueous phase from outer phase.
- Artificial phosholipid vesicles (liposomes) are used to transport vaccines, drugs and enzymes to target cells or organs and used as model systems for studying biological ion transport across membranes

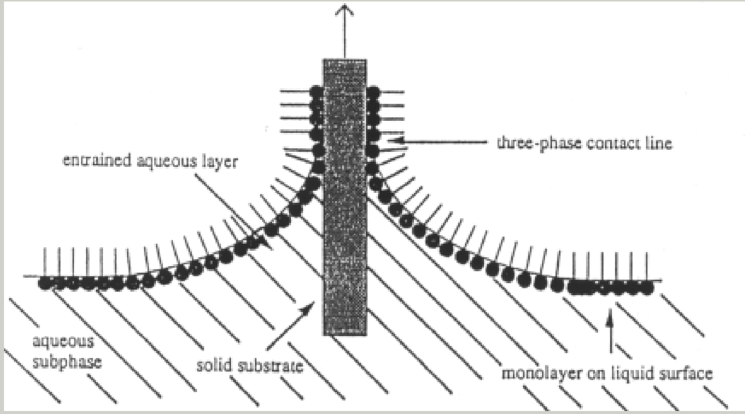


Self-assembled monolayers (SAM): Langmuir-Blodgett films

- 1774 Benjamin Franklin observed experimentally the formation of a monolayer by dropping oil to water, but did not realize it was a monolayer.
- A hundred years later Lord Rayleigh speculated the formation of a monolayer and Agnes Pockles constructed a basis for surface balance in her kitchen sink (Nature, 1891).
- The idea was then adopted by Irwing Langmuir to form and transfer monolayers of fatty acids, esters and alcohols onto solid substrates.
- Katherine Blodgett: also multilayer films may be formed and transferred onto solid substrate.

Self-assembled monolayers (SAM): Langmuir-Blodgett films

- Idea: a solid substrate is repetitively dipped through a mechanically compressed monolayer spread at the water-air interface → solid material is assembled to the surface.
- Molecules used must have more than 12 carbon atoms in the chain, since shorter chains form micelles and other types of assemblies.
- Too long chains may crystallize on the surface.

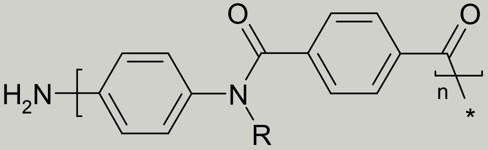


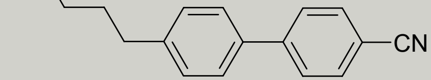
Liquid crystals

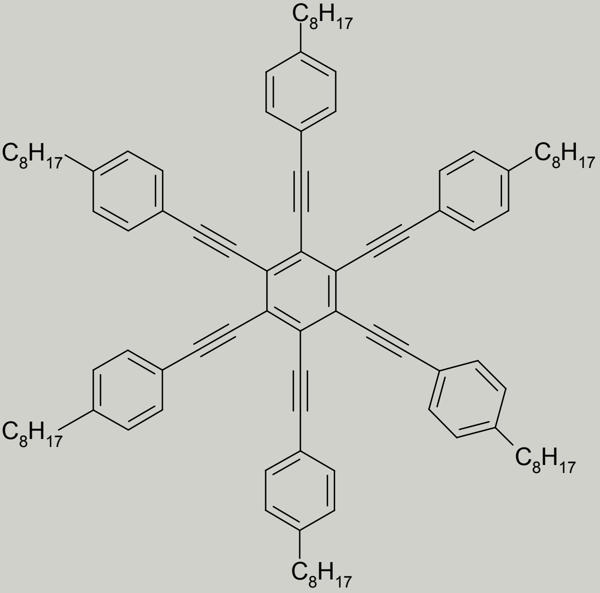
- Liquid crystals: materials, which exhibit fast kinetics (deformability, dynamics) of liquids but also have some degree of long-range crystal-like ordering → intermediate phase between liquid and solid.
- Various applications is precise temperature measurement, measuring direction or orientation dependent properties, as stationary phases in the chromatographic techniques and in high-tech materials (LCDs etc).
- Benefits of liquid crystals: cheap, nontoxic, in LCDs flat and compact size.
- Mesophases are characterised by polarised optical hot-stage microscopy, differential scanning calorimetry or small angle X-ray scattering.

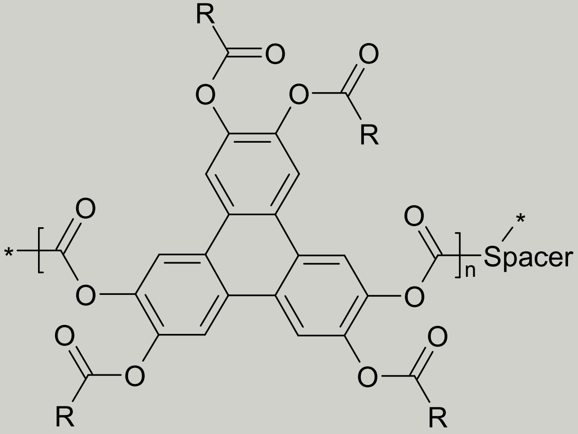
Liquid crystals

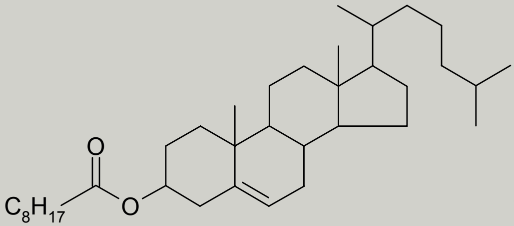
- Mesogens: liquid crystal forming molecules which are anisotropic in shape, i.e. rod-like *calamitic* (ca. 25 Å long and cylindrical) or disk-like *discotic* (flat and circular). Also polymers and aggregates are suitable.









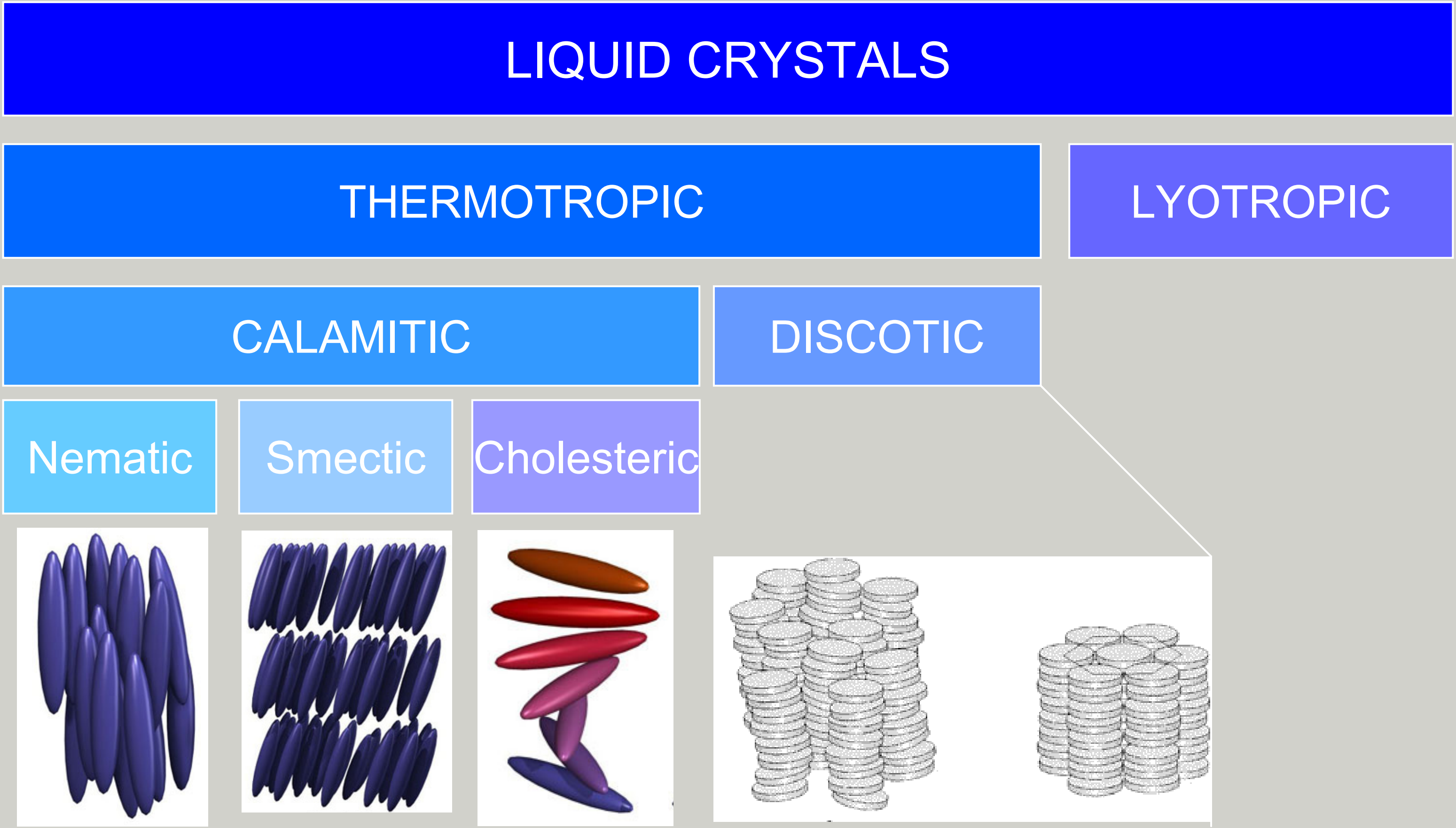


Liquid crystals

- Anisotropic shape, intermolecular interactions and viscosity of the liquid cause mesogens to line up in various ordered ways → fluid material with macroscopic domains of aligned molecules.

- Liquid crystalline behaviour is highly temperature dependent → occurs above the melting point but yet at so low temperatures that the molecular motion is slow and the energies of intermolecular interactions are strong compared with thermal energies.

Liquid crystals



LIQUID CRYSTALS

THERMOTROPIC

LYOTROPIC

CALAMITIC

DISCOTIC

Nematic

Smectic

Cholesteric

Liquid crystals

- **Thermotropic substances**: substances that form mesophases as a function of temperature and which arise from gradual melting of crystalline solid.
- Categories: a) **calamitic** b) **discotic** depending on the shape of the molecules.
- Subcatogories of the calamitic phases:

1) **Nematic** phase: high degree of long-range orientational order, but no long-range translational order, i.e. mesogens point at the same direction but are disordered with respect to slippage along rod axis. Most common in applications.
2) **Smectic** phase: two-dimensionally ordered layer arrangement in which thickness of the layer ≈ length of the molecular rod.
3) **Cholesteric** phase: helical nematic phase with a helical pitch of 200-2000 nm.

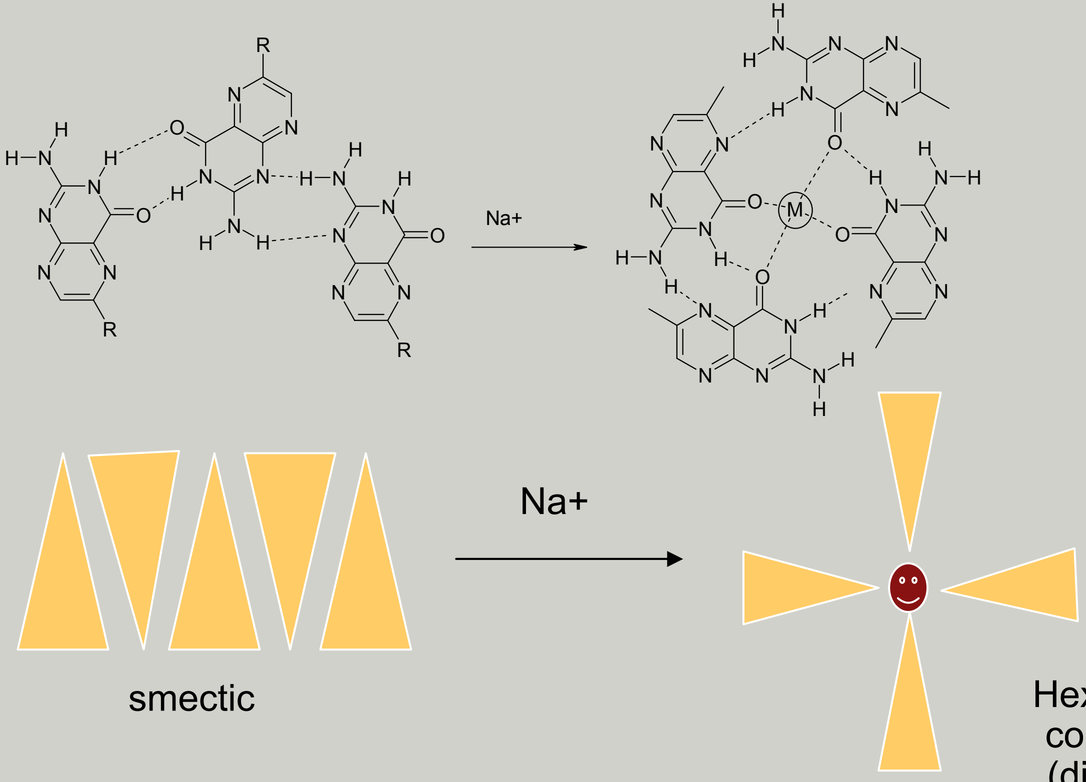
Liquid crystals

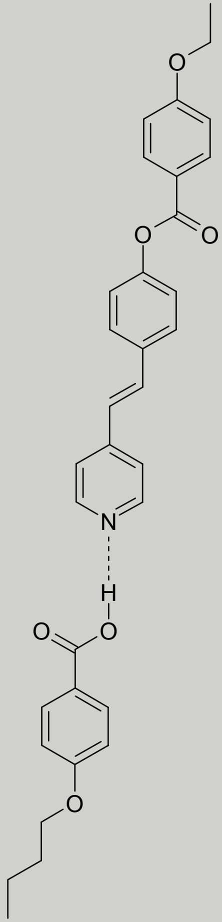
- Subcatogories of the discotic phases:
  a) nematic
  b) columnar phases

- Columnar phases which are hollow in the middle are called tubular mesophases
- **Lyotropic** substances require the influence of a solvent or medium → solid lattice is broken down by dissolving and lyotropic liquid crystals are formed by two or more components (amphiphile and water or other solvent)
- Lyotropic phases are either **lamellar bilayers, micelles** or **cylindral**.

Liquid crystals

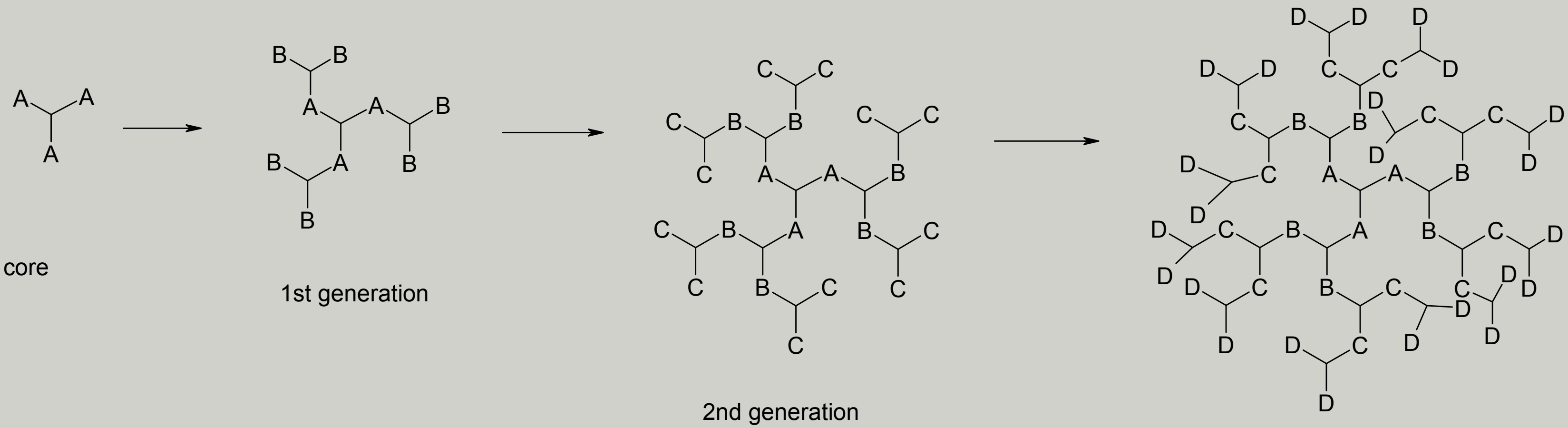
- Supramolecular liquid crystals: mesophase is formed by specific weak interactions (in particular hydrogen bonding or ionic interactions).





Dendrimers

- Dendrimers (cascade molecules): macromolecules with a highly branched, 3-D architecture that has grown from a central core in a tree-like fashion. May be classified as a special kind of polymer.
- Dendron (dendrite): building block (branch) of a dendrimer.
- The repeat is called “generation”.



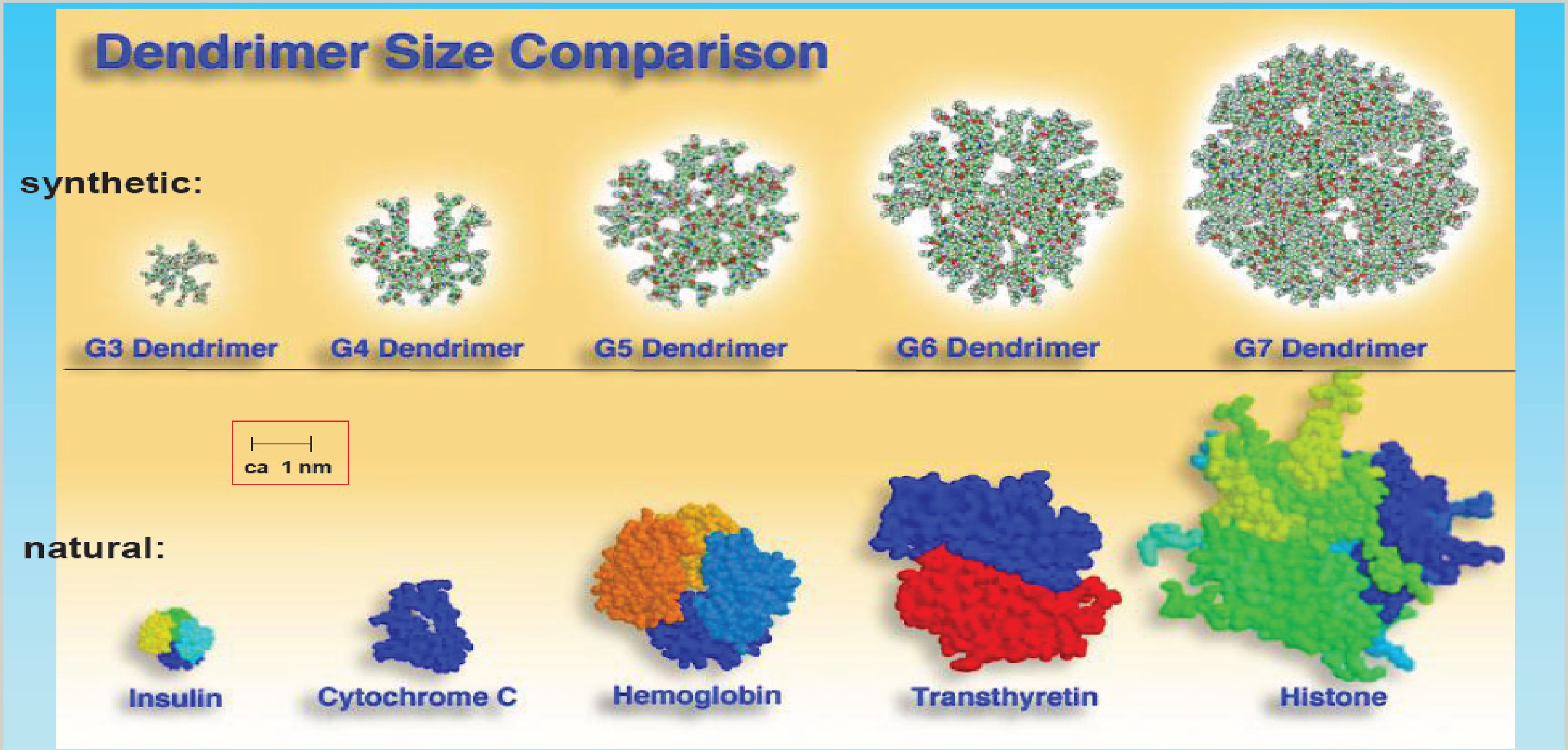
core

1st generation

2nd generation

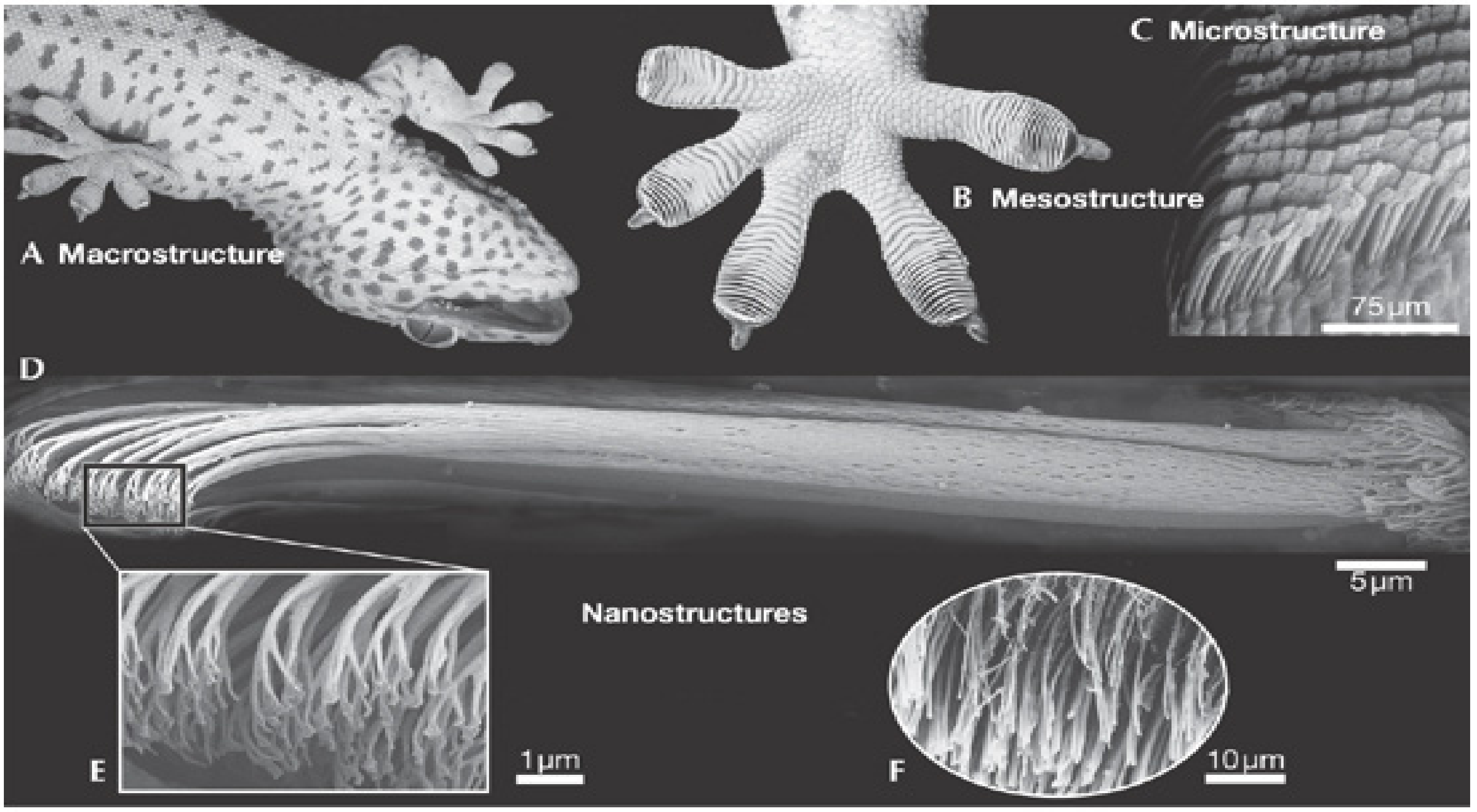
3rd generation

Dendrimers



Quelle: http://nano.med.umich.edu/images/sizes.jpg
(„Center for Biologic Nanotechnology“, University of Michigan)

Dendrimers



A.Rinaldi, EMBO reports, 2007

Dendrimers

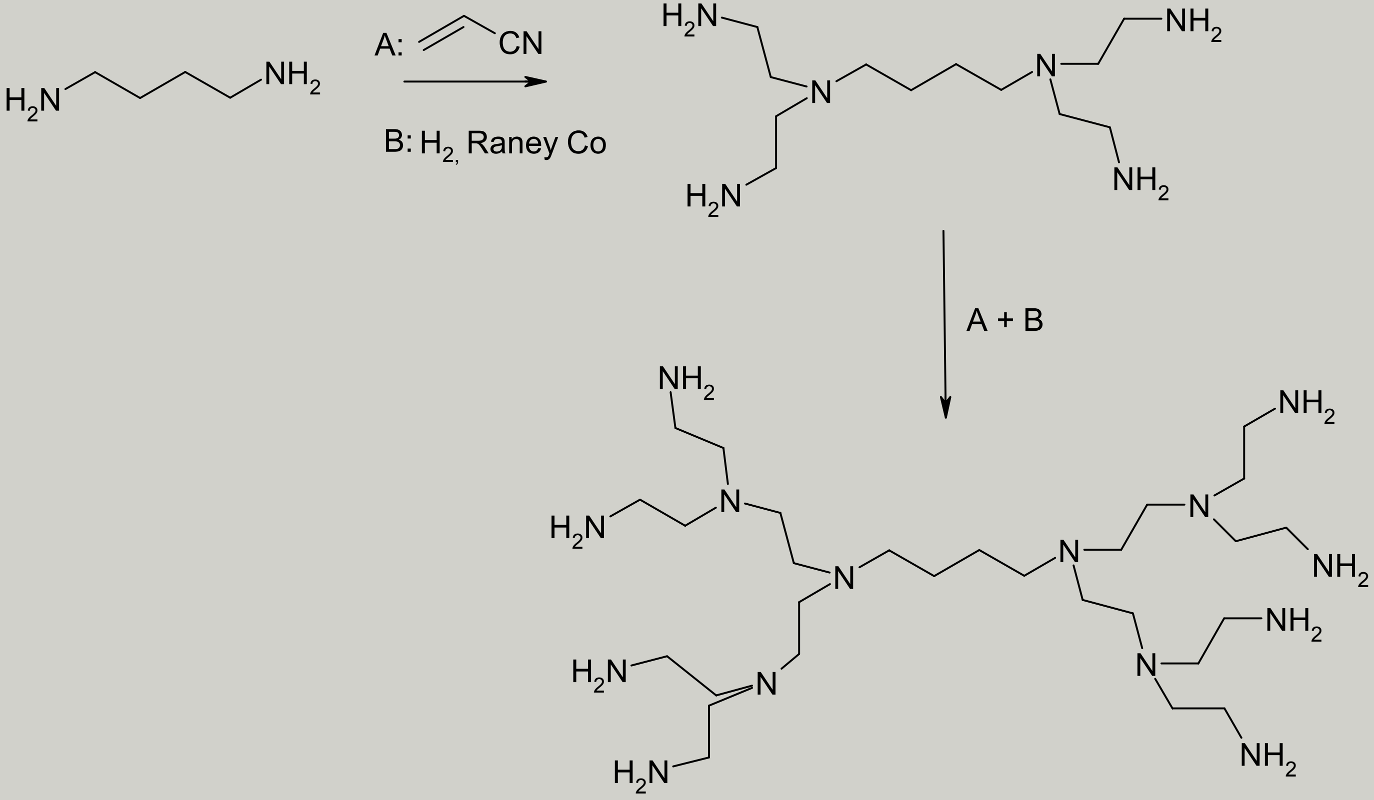
- Dendrimers can be used or they have potential

  1) as host molecules (dendritic core region is porous while densely packed outer layer provides a shield for the inner region)
  2) as reaction vessels / reactors (e.g. catalysis)
  3) in medicine: diagnostics, transport
  4) as functional materials (e.g. nanoporous super-absorber, chromatography)
  5) as molecular devices (e.g. light-harvesting technology)

Dendrimers

- Preparation of dendrimers:

  1. **Divergent synthesis** (from inside to outside): generations are added in an iterative manner

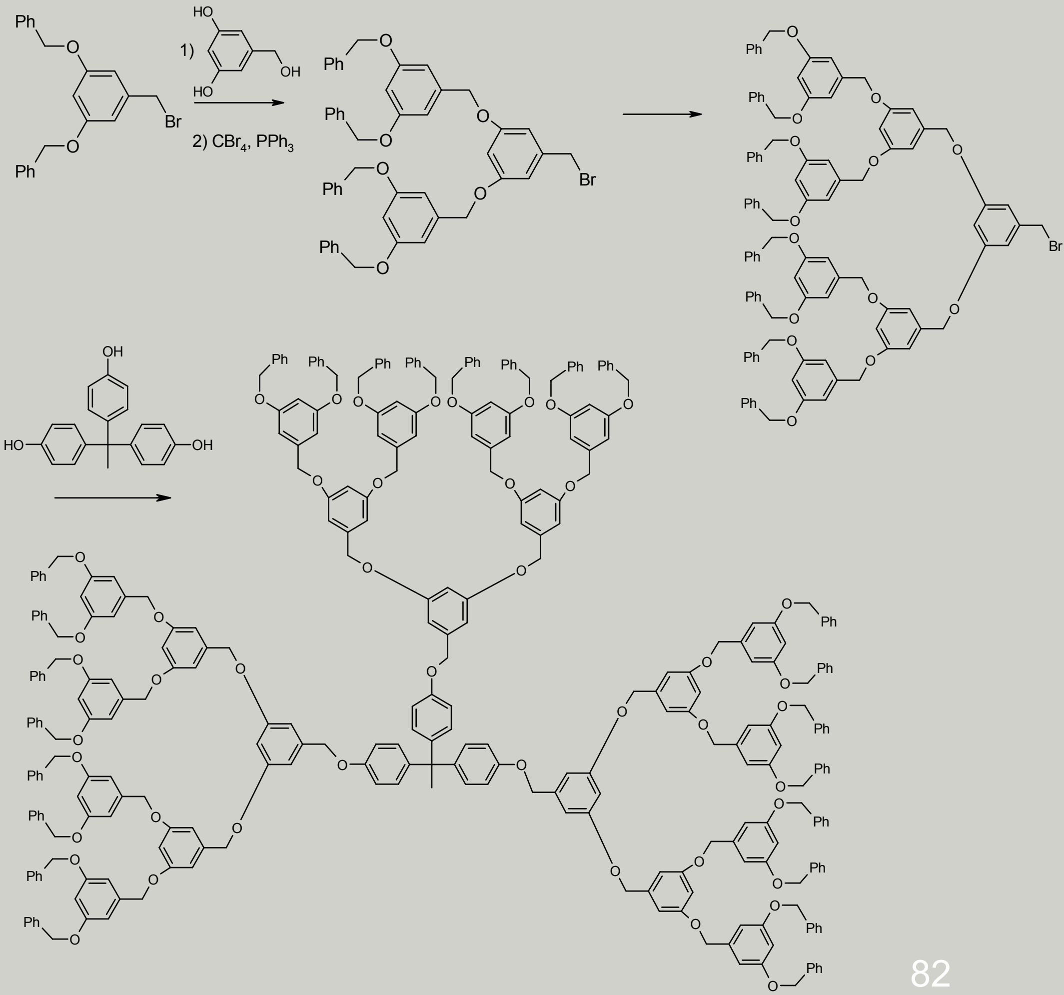


Dendrimers

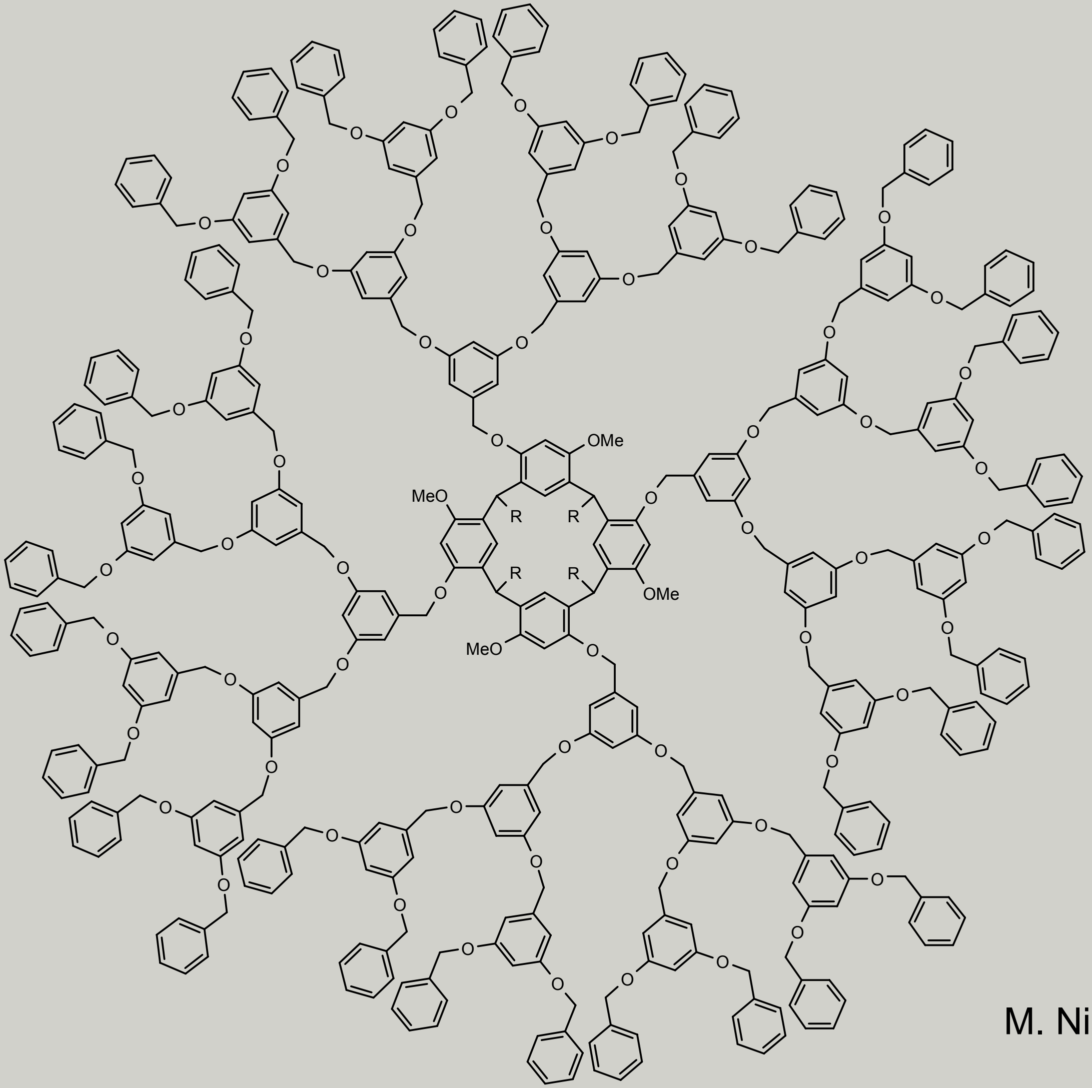
2. **Convergent synthesis**:

branches of dendrimer are synthesised separately and in the final step of the synthesis attached to the central core.

Benefits: less defects and higher purity



Dendrimers



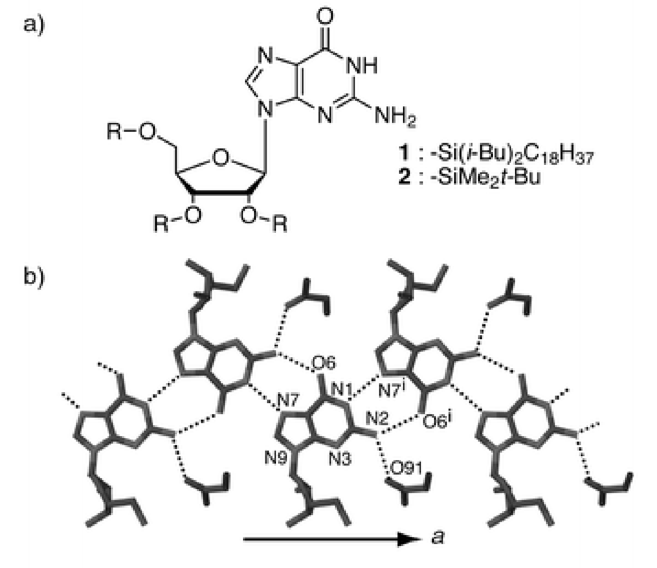
M. Nissinen & K. Rissanen et al. J. Incl. Phenomena, 2007

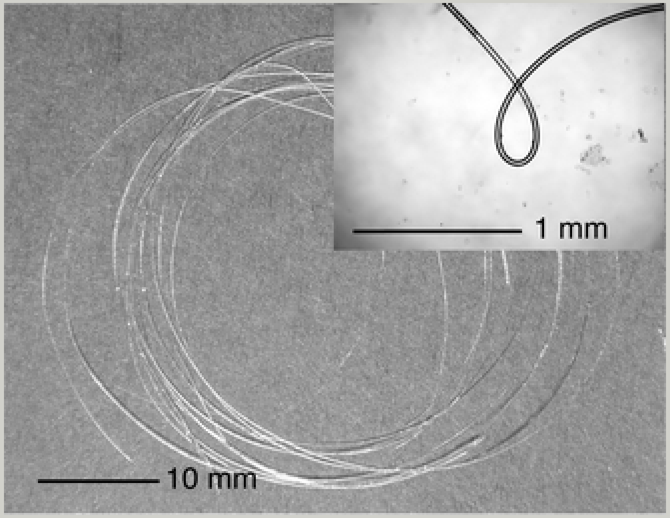
Dendrimers

- Benefits of dendrimers compared to traditional polymers
  - * structurally exact skeleton from identical molecules
  - * easier to characterise
  - * possibility to make cavities (porous inner core)
  - * formation of unimolecular micelles
  - * defined supramolecular chemistry
  - * multiplication of functional groups
  - * multiplication of luminescence effects
  - * multiplication of switching effects
  - * accurate building blocks for example for nanotechnology

Fibres and gels

- Fibre: compound (typically a polymer) that possess a continuous filament or a discrete elongated piece of material, such as nylon, polyester etc.
- Supramolecular fibre: long chain of small molecules linked via weak interactions.

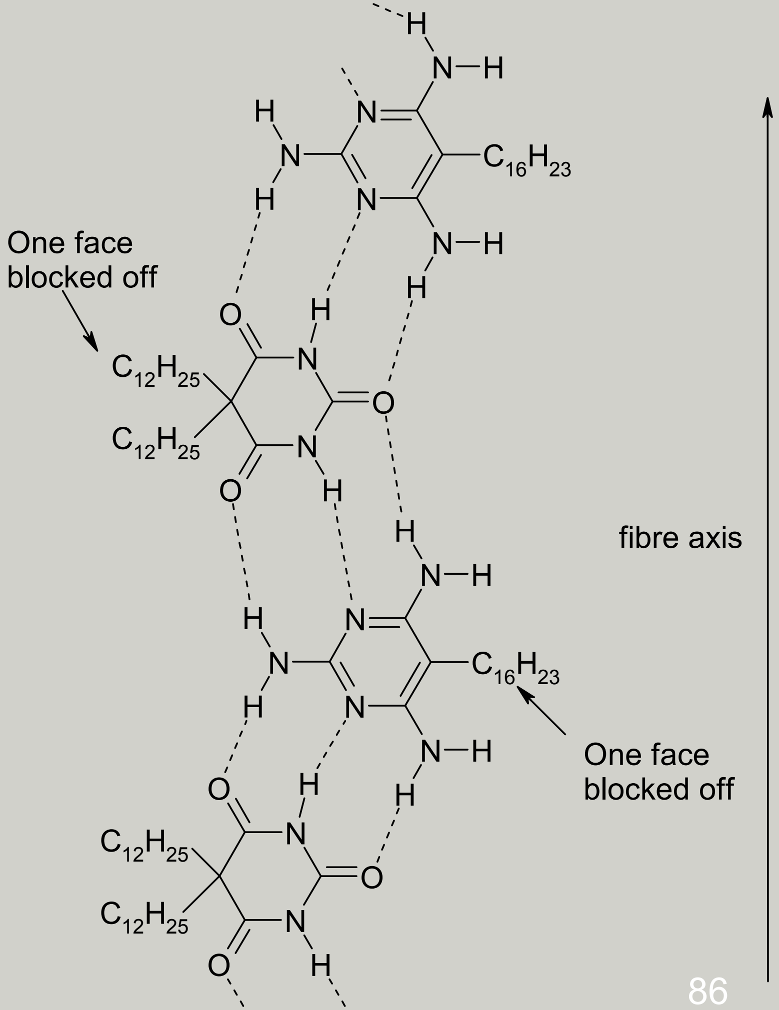




I. Yoshikawa et al. Chem. Commun., 2001

Supramolecular gels

- Supramolecular gel: self-assembly of small low molecular weight gelators (LMWG) to form extended fibres that interlink via weak interactions to a continuous 3-D entangled porous network and trap solvents or gases
  - Hydrogel: gel traps water
  - Organogel: gel traps solvent
  - Aerogel: gel traps gas



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