

Nanoscience technology and advanced materials
PHYS 6014

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Lecture 3

Summary of last lecture's basics

What is the top-down and what is the bottom up approach? What drives the bottom-up process?

What is the definition of surface energy and what is “magic numbers”

Describe the nucleation and growth process of a nanoparticle.

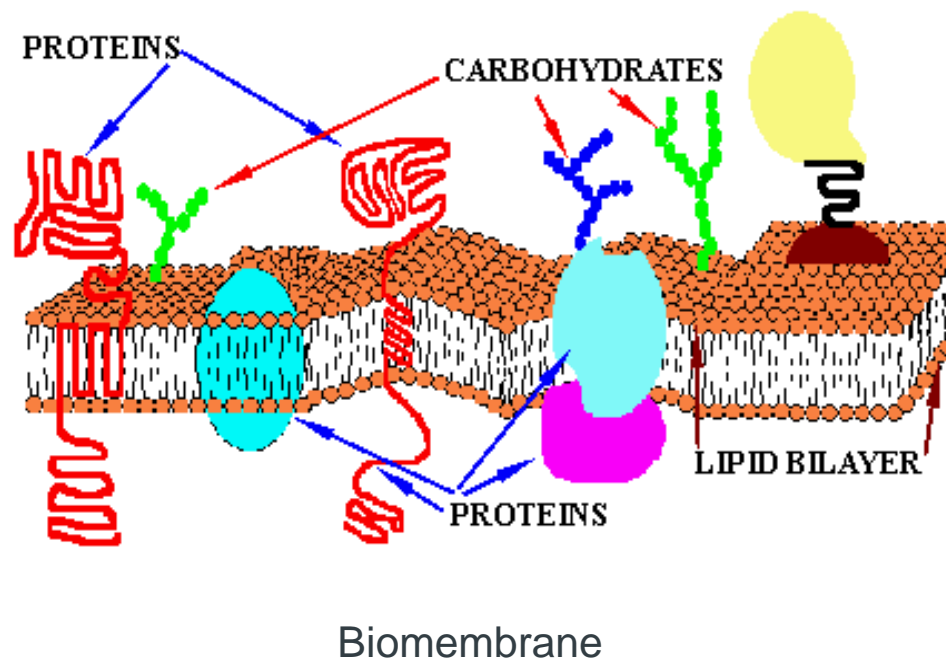
Nanoparticle functionalization strategies. What are the differences between them?

Examples of nanocrystal synthesis based on thermal decomposition, galvanic Replacement reaction and seeding procedures.

Self-Assembly

Self-assembly is a process in which components, either separate or linked, spontaneously form ordered aggregates.

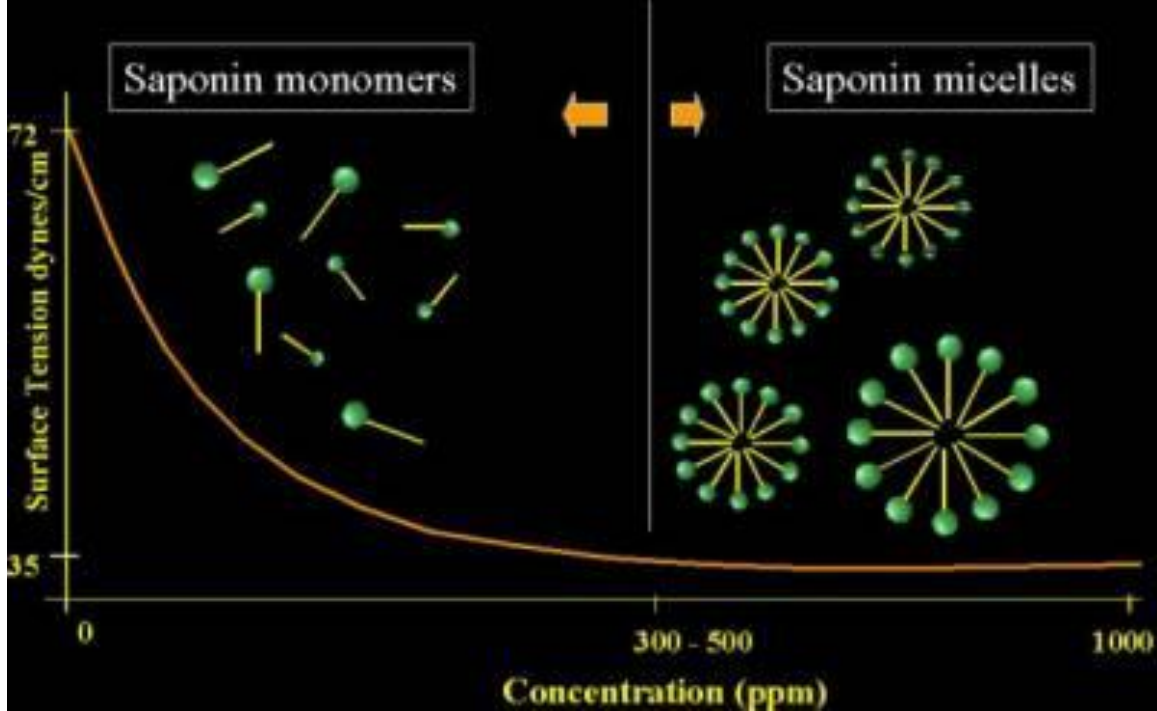
Self-assembly can occur with components having sizes from the molecular to the macroscopic, provided that appropriate conditions are met.



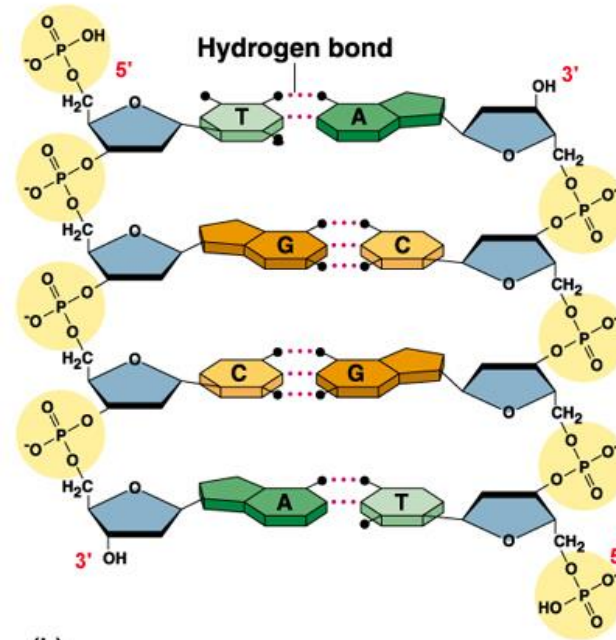
- **Components**
 - A self-assembling system consists of a group of molecules or segments of a macromolecule that interact with one another.
- **Interactions**
 - Self-assembly occurs when molecules interact with one another through a balance of attractive and repulsive interactions.
 - These interactions are generally weak (that is, comparable to thermal energies) and non-covalent.
- **Reversibility (or Adjustability)**
 - For self-assembly to generate ordered structures, the association either must be reversible or must allow the components to adjust their positions within an aggregate once it has formed.
- **Environment**
 - The self-assembly of molecules normally is carried out in solution or at an interface to allow the required motion of the components.

Some self-assembly interactions

1. The hydrophobic effect
2. Hydrogen bonding
3. π -stacking
4. Van der Waals interactions
5. Ionic bonds
6. Electrostatic interactions
7. Reversible covalent S-S bonds in protein folding



$$\Delta G = \Delta H - T\Delta S$$

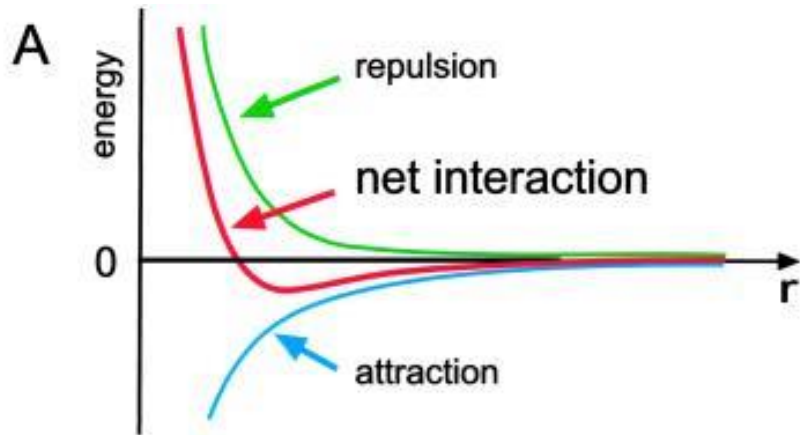


(b)

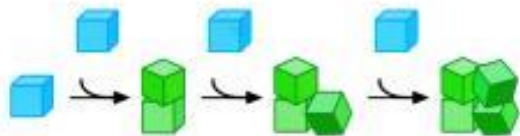
(c)

Conditions for Self-Assembly

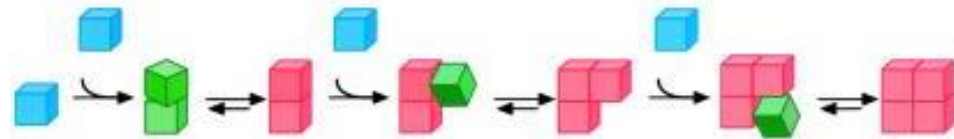
Components that can equilibrate, or adjust their positions once in contact, can form ordered crystals if the ordered form is the lowest-energy form



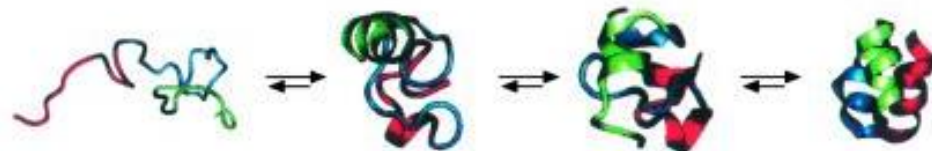
B Irreversibility gives glasses.



C Reversibility gives crystals ...



D ... and ordered macromolecules.



What could be achieved by controlling the self assembly process ?

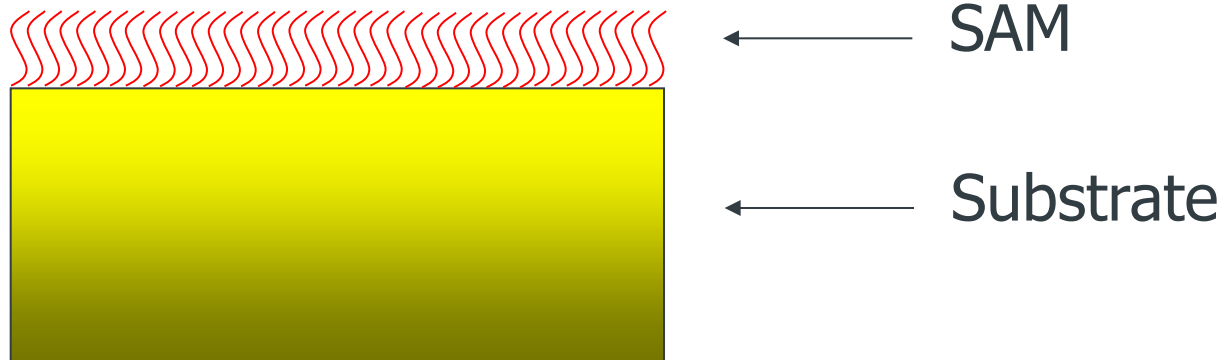
Development of :

- *Nanowires* and as a result faster integrated circuits
- Ultra small *electronic devices*
- *Diagnostic methods* in biology and genetics
- Highly sensitive and selective *chemical detectors*

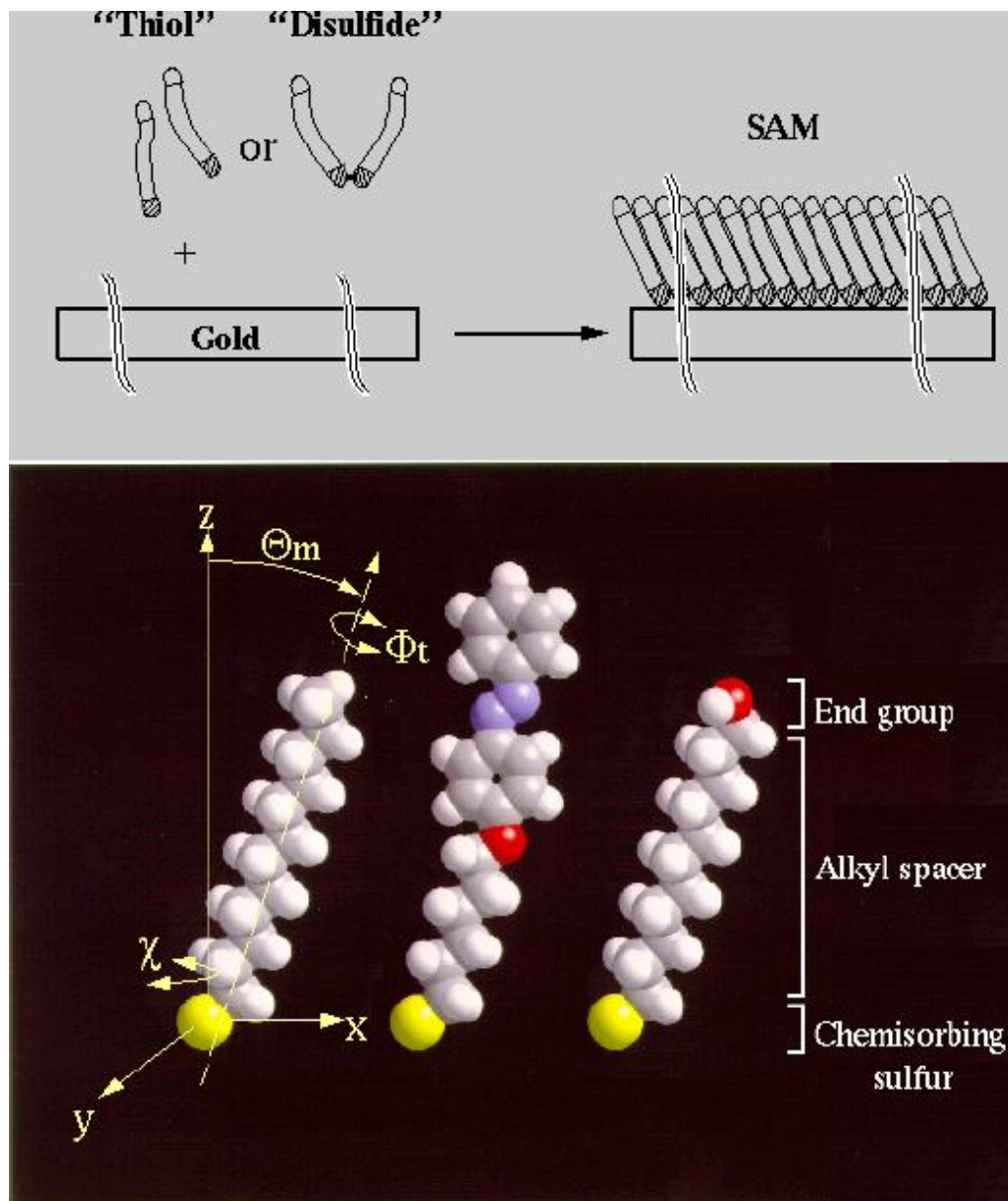
- **Self-Assembled Monolayers**
- **Block Copolymers**
- **Ionically Self-Assembled Monolayers**
- **DNA-based Assembly**
- **Nanoparticles assemblies**

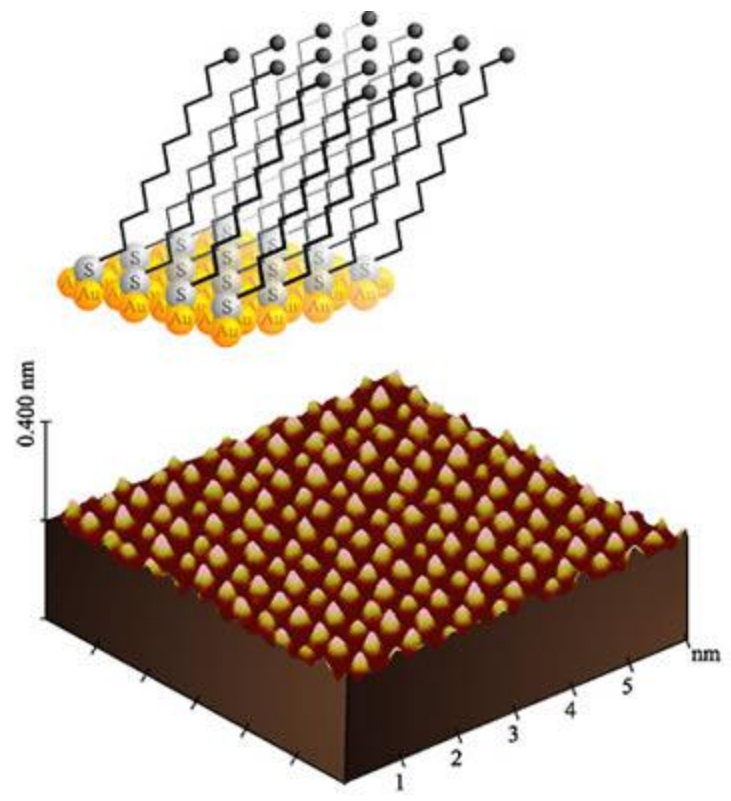
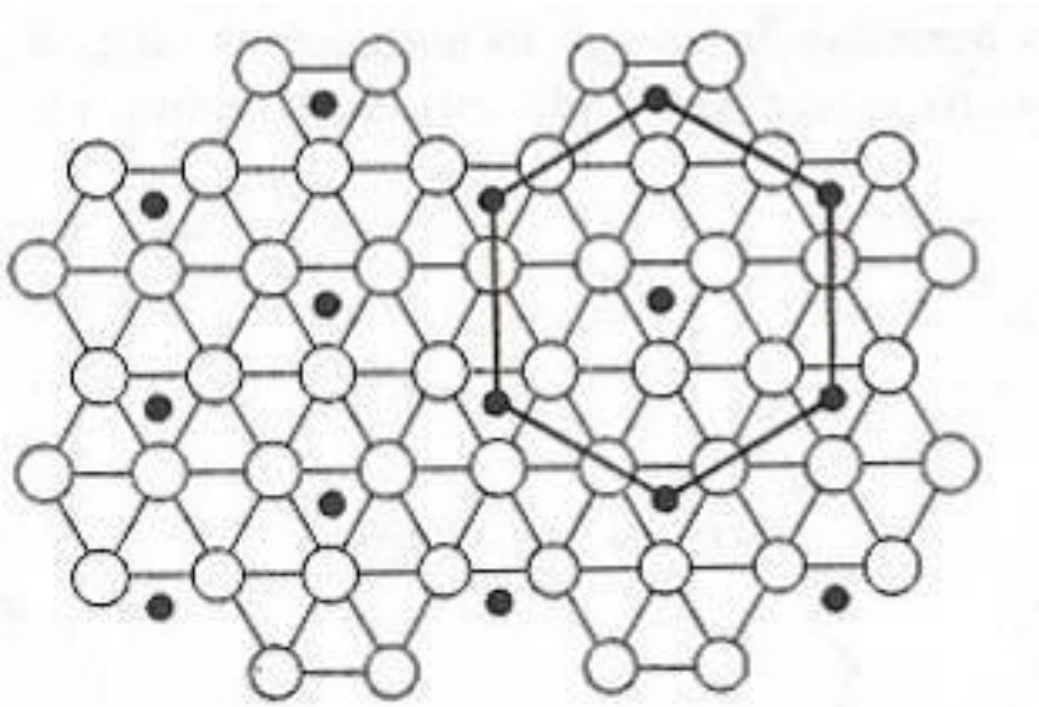
Self-Assembled Monolayers

- “Self-assembly” refers to the deposition of an organized layer onto a substrate with a high-degree of control and/or ordering.
- One common example are “Self-Assembled Monolayers” (SAMs): organic molecules that deposits from solution onto a substrate with a thickness of a single molecule and a well-defined orientation.



Example:

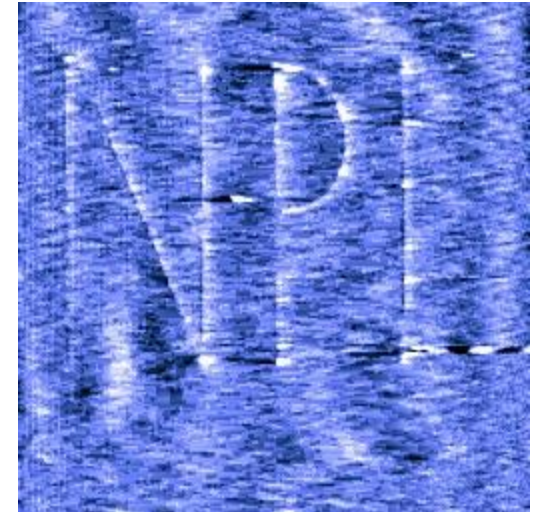
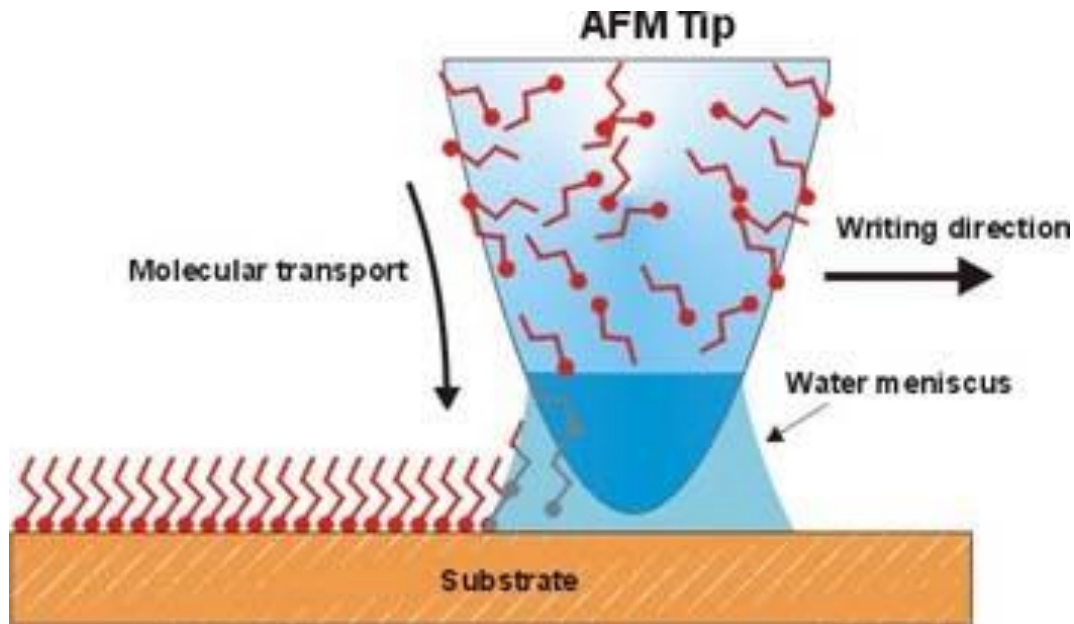




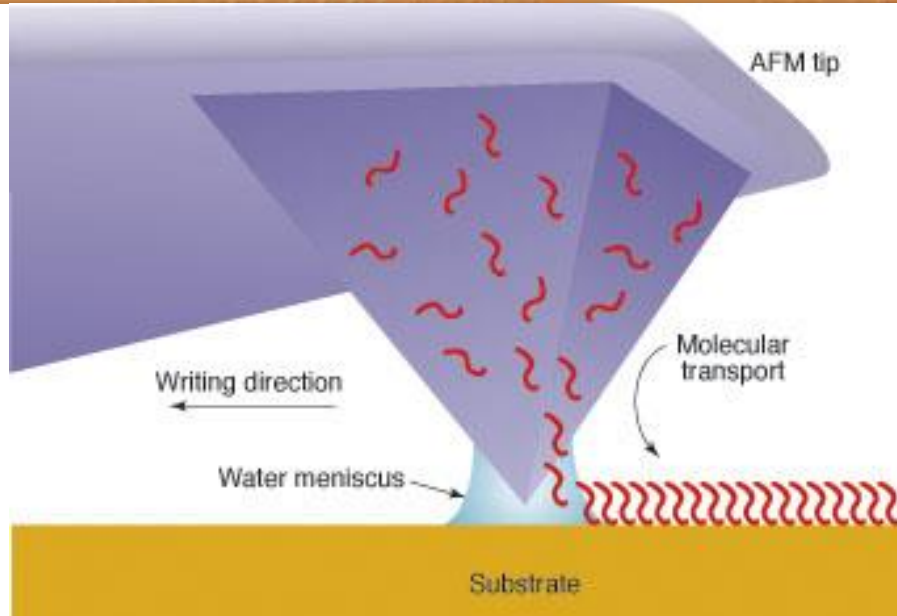
Postulated adsorption pattern of a thiol on Au (111)

Thiol molecules form an hexagonal lattice

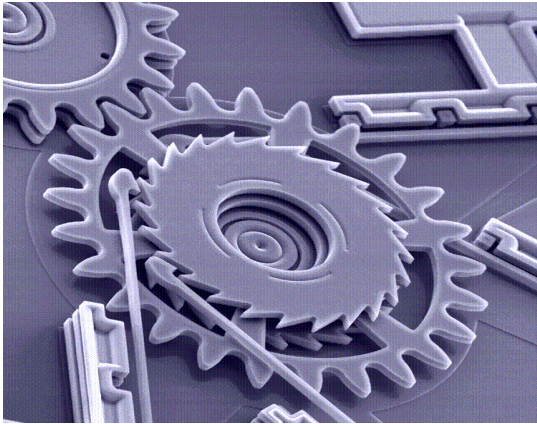
More control can be introduced by changing the binding groups, or the length or structure of the organic chain



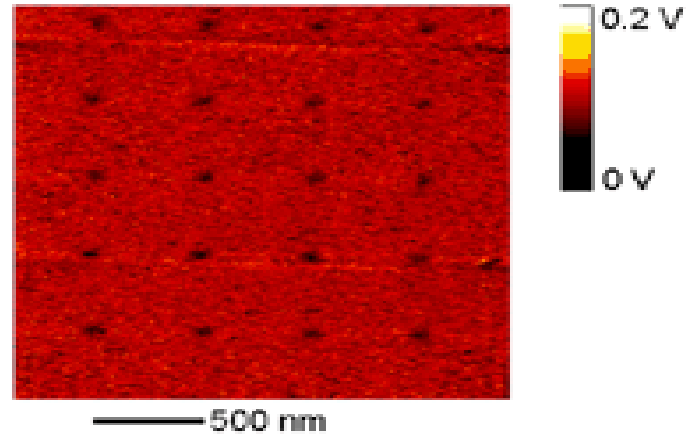
Particles written on a gold surface



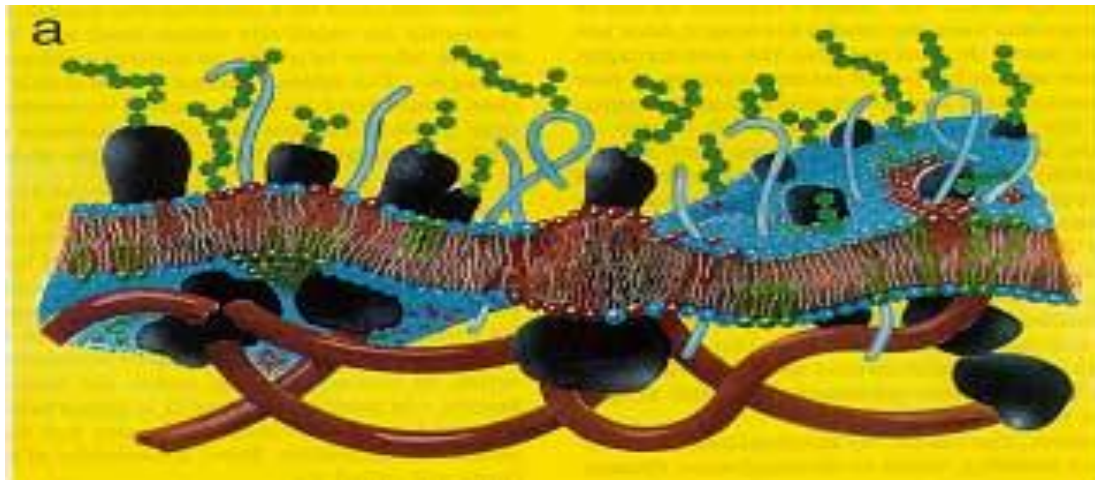
Some applications of SAMs



Anti-stiction (anti-static friction) coatings in MEMS



Lithography



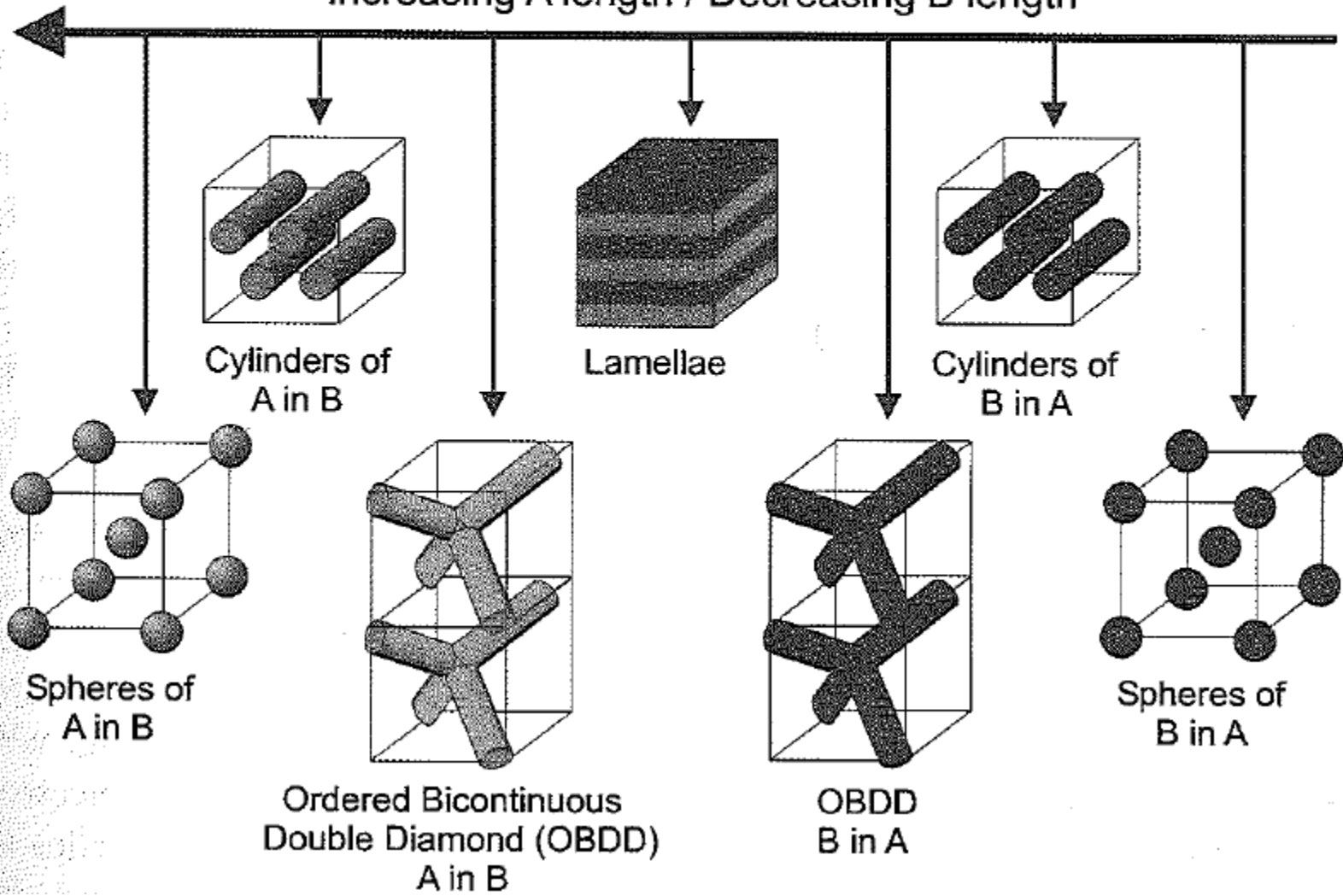
Biomimetic membranes

- **Self-Assembled Monolayers**
- **Block Copolymers**
- **Ionically Self-Assembled Monolayers**
- **DNA-based Assembly**
- **Nanoparticles assemblies**



Microphase separation

Increasing A length / Decreasing B length

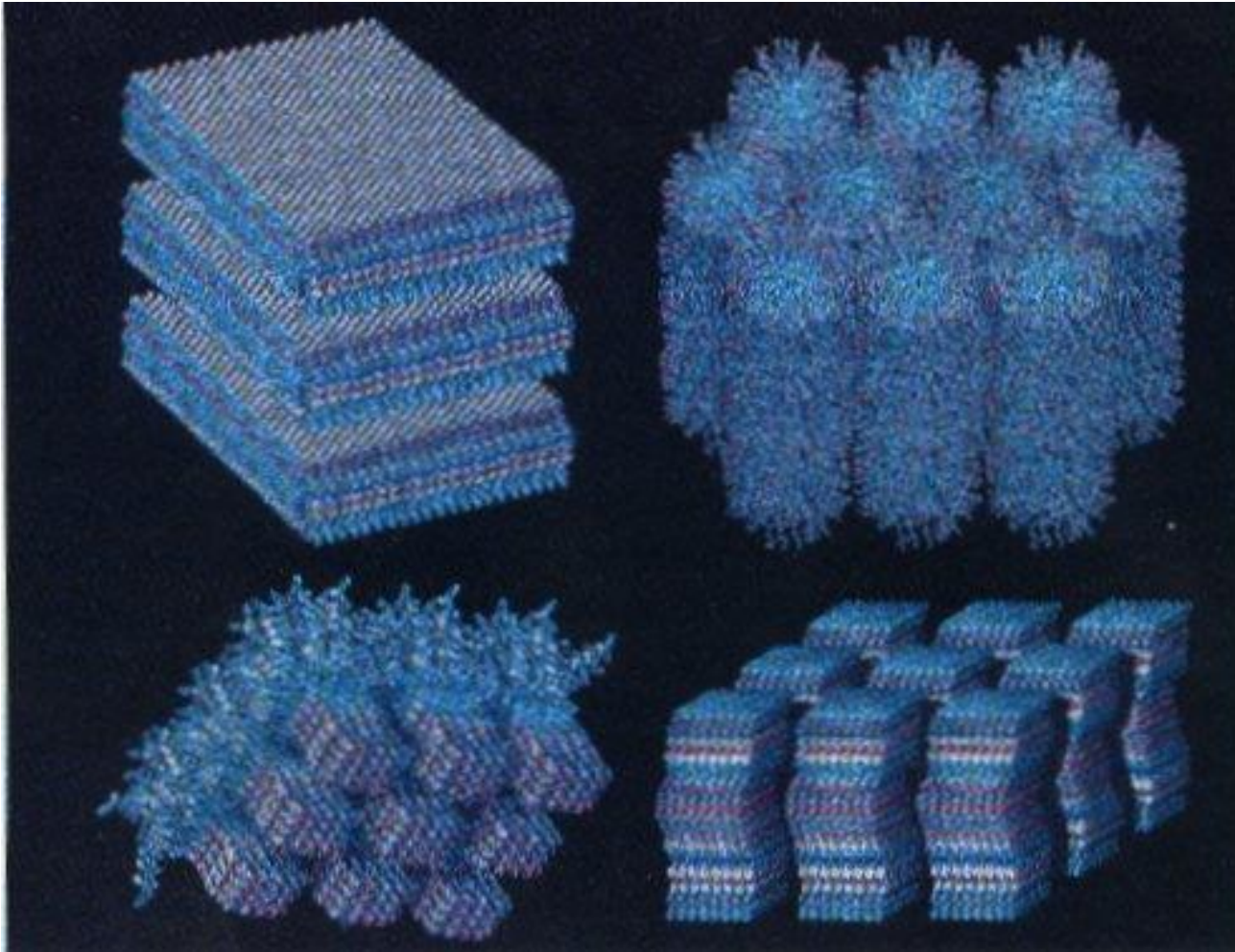


Self-assembly of block copolymers can be directed by:

- a) Electric fields
- b) Mechanical forces
- c) Solvent polarity
- d) Chemical attachment to surfaces
- e) Epitaxial self-assembly on nanopatterned substrates

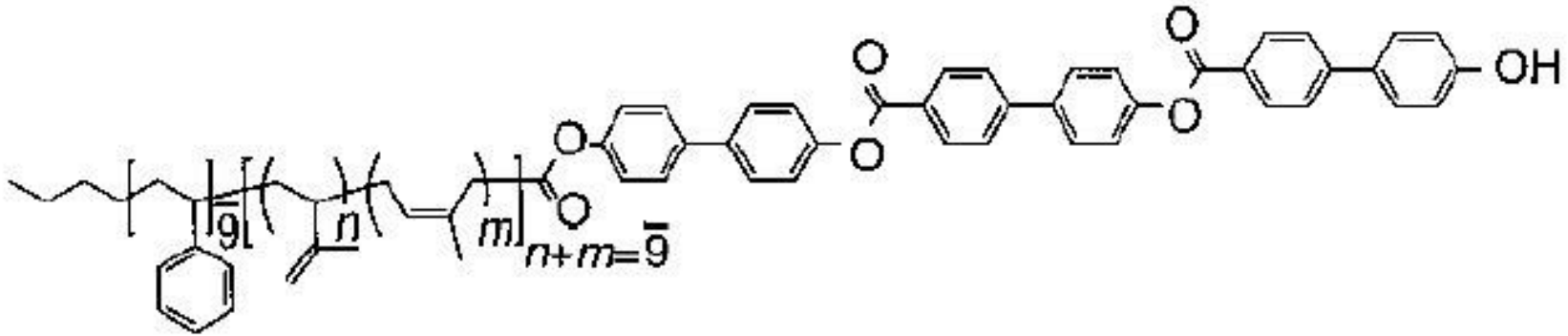
A broader use of copolymers

- a) lithographic masks,
- b) porous membranes,
- c) scaffolds for biomaterials
- d) templates for organizing nanocrystals

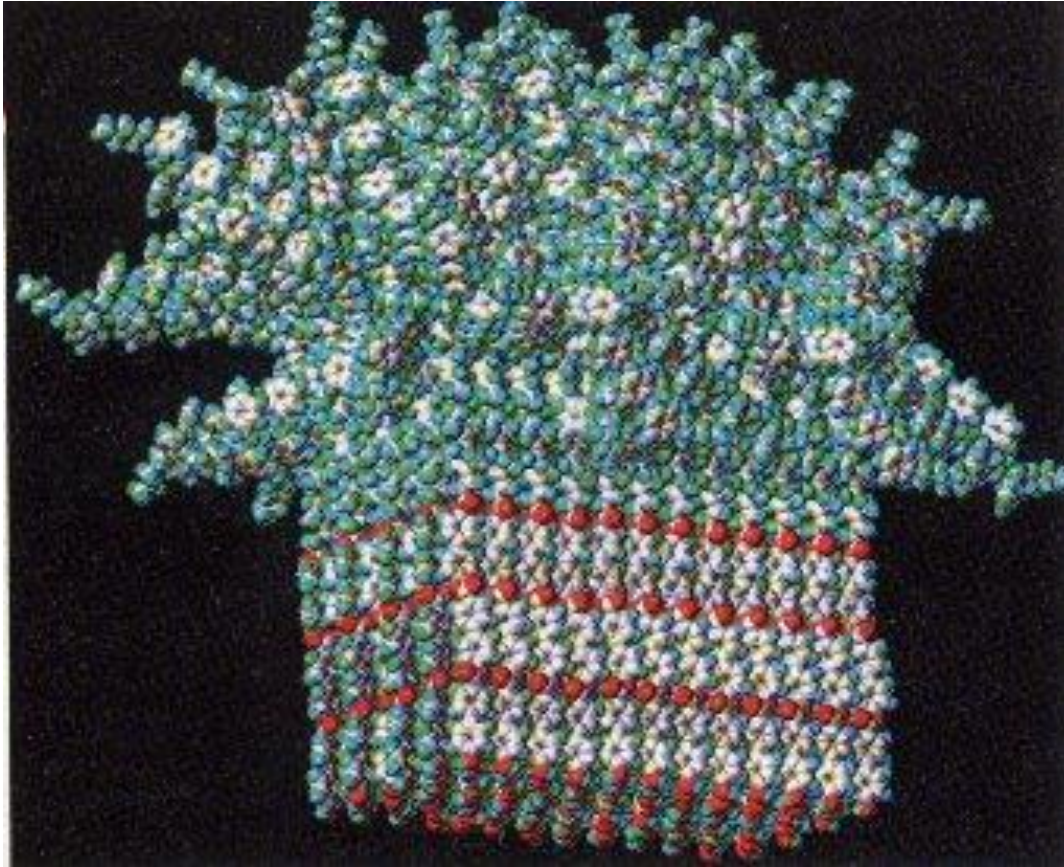


Regularly sized and shaped nanostructures may tile into superlattices of varying geometries and symmetries.

Example: triblock copolymer

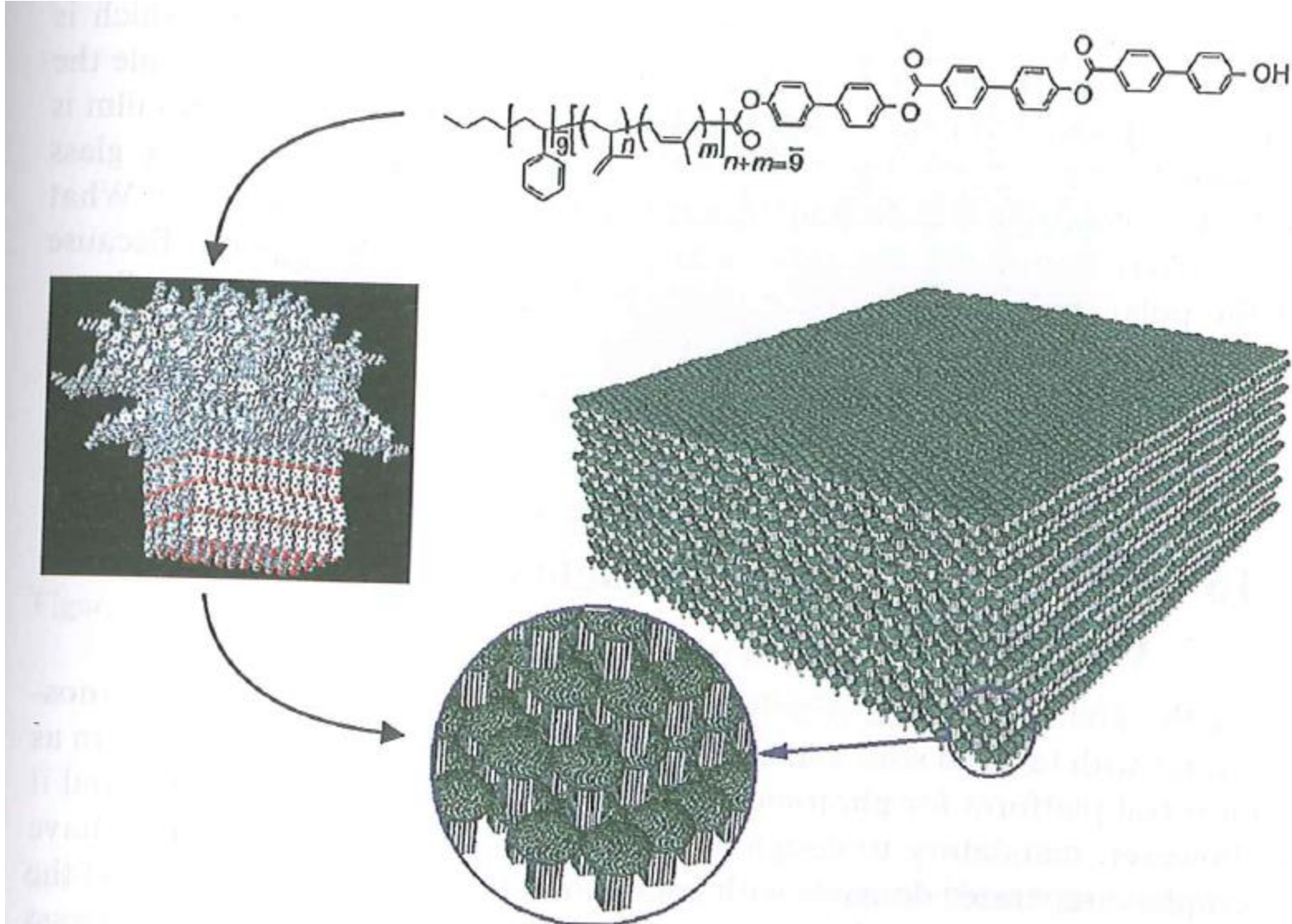


- The diphenyl block (right) is rigid and of well-defined length. Can lead to well-ordered crystalline structure.
- The two left-most blocks are flexible and have variation in composition and length. Tends towards disordered, amorphous structure.



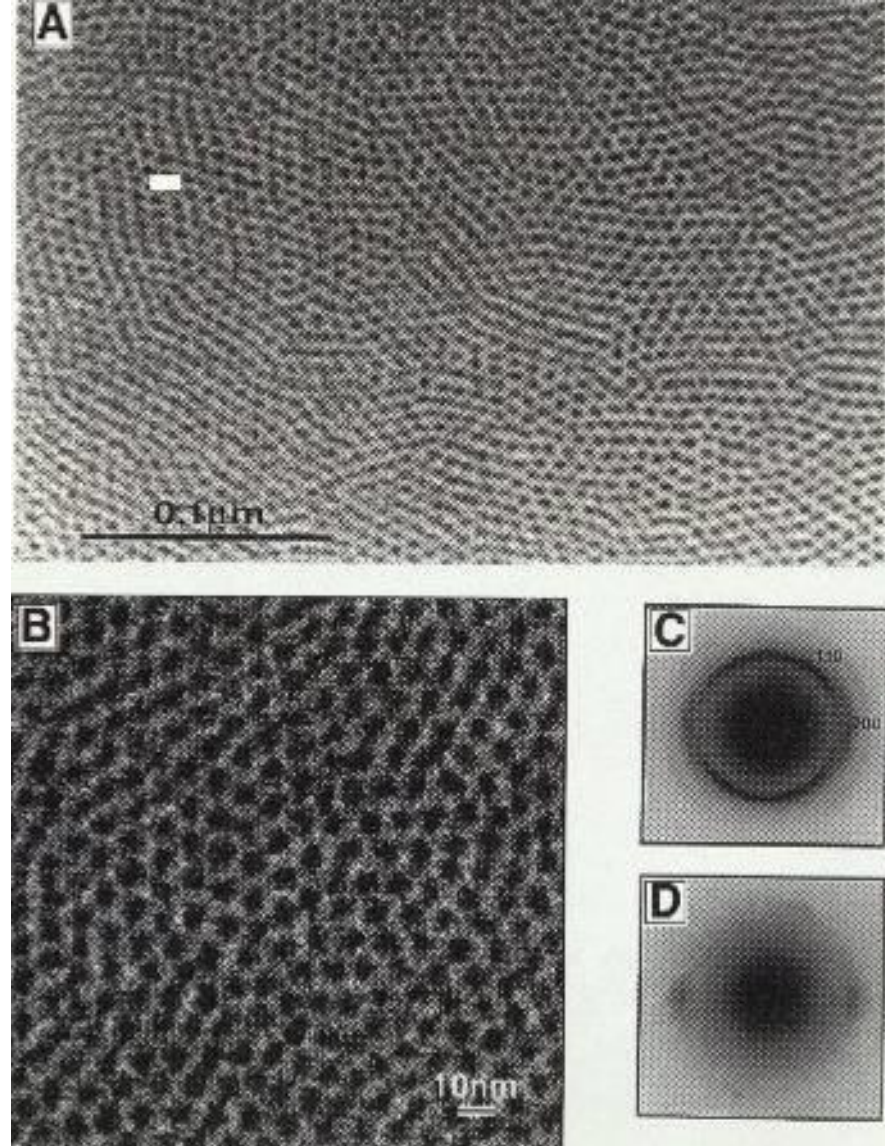
- Molecular model of the supramolecular unit composed of 100 triblock molecules
- Rod segment packing in the mushroom stem is based on electron diffraction data and its rectangular shape on the observation of an oblique superlattice of nanostructures.

A super lattice of the triblock copolymer



TEM images of Triblock Copolymer

- TEM images of a film formed by the triblock molecules, revealing regularly sized and shaped aggregates that self-organize into superlattice domains.
- Wide-angle (C) and small-angle (D) ED patterns are observed.



Give a definition for self-assembly. Discuss the different types of self-assembly interactions

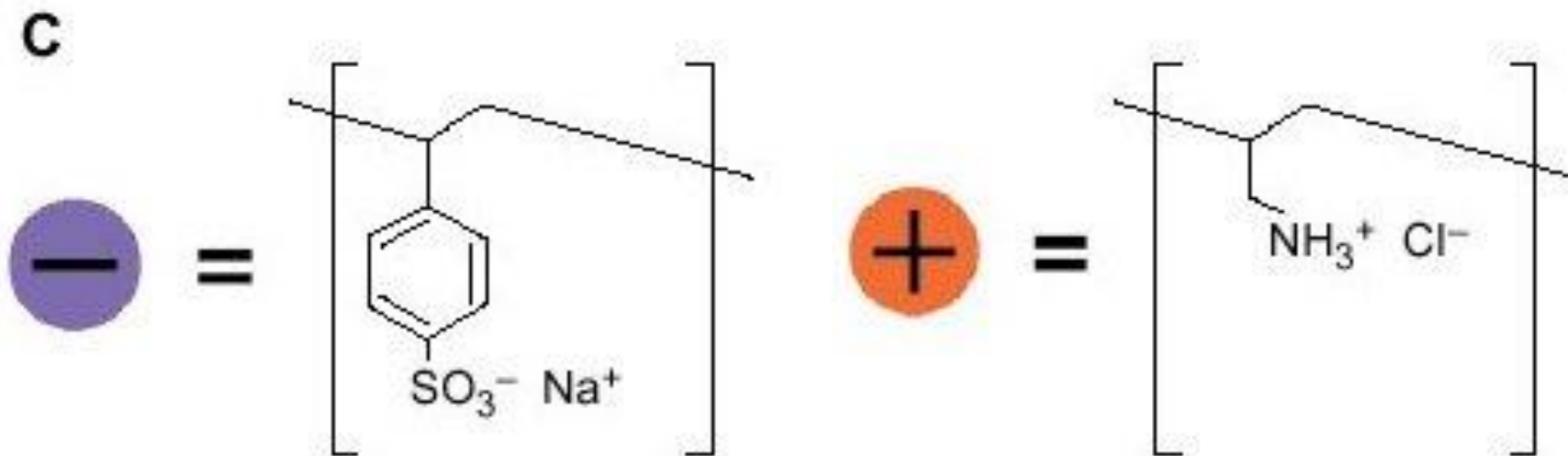
Answer:

Self-assembly is a process in which components, either separate or linked, spontaneously form ordered aggregates. Self-assembly can occur with components having sizes from the molecular to the macroscopic, provided that appropriate conditions are met.

Some types of self assembly interactions are:

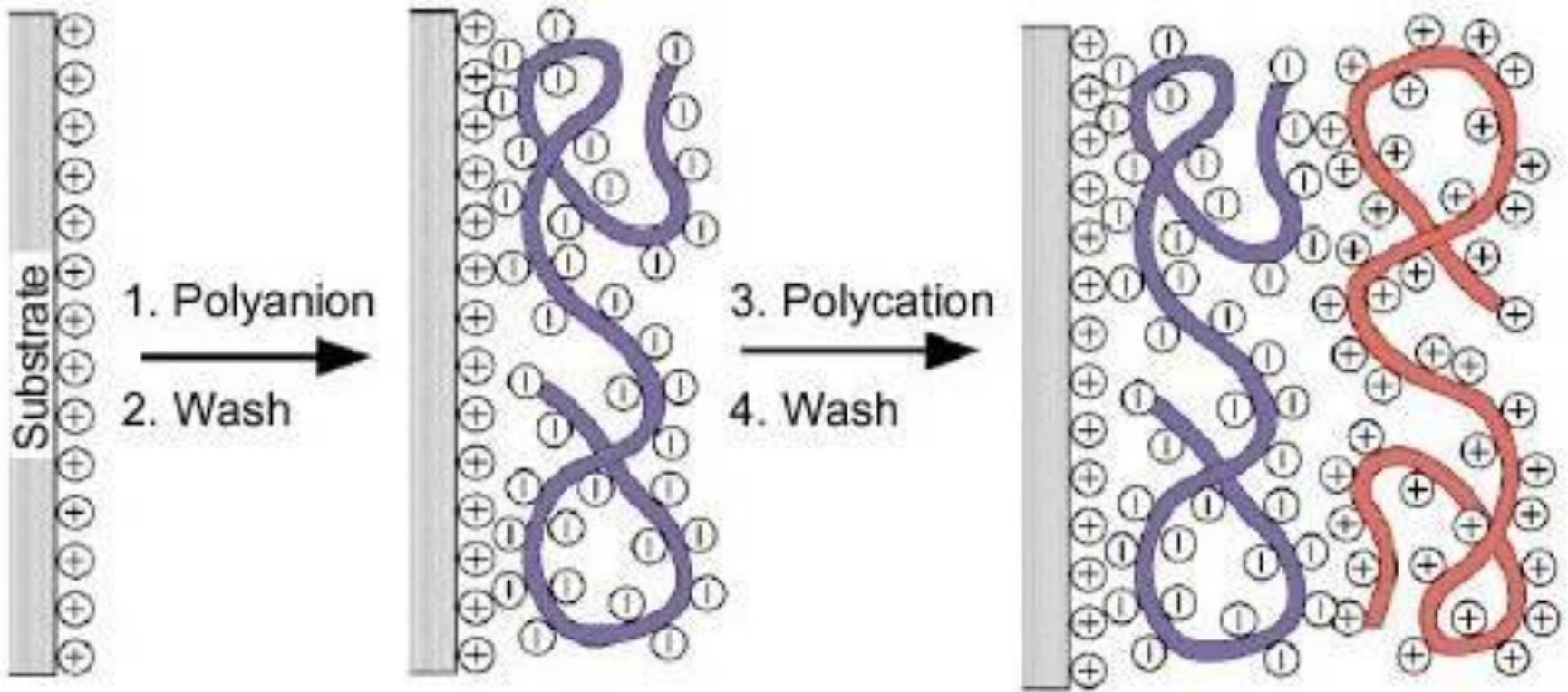
- 1) The hydrophobic effect (for example in micelles)
- 2) Hydrogen bonding (for example in DNA)
- 3) π -stacking (for example in DNA)
- 4) Van der Waals interactions (for example between long carbon chains in organic molecules)
- 5) Ionic bonds (for example in salts)
- 6) Electrostatic interactions (for example between nanoparticles)
- 7) Reversible covalent S-S bonds (for example in protein folding)

- **Self-Assembled Monolayers**
- **Block Copolymers**
- **Ionically Self-Assembled Monolayers**
- **DNA-based Assembly**
- **Nanoparticles assemblies**



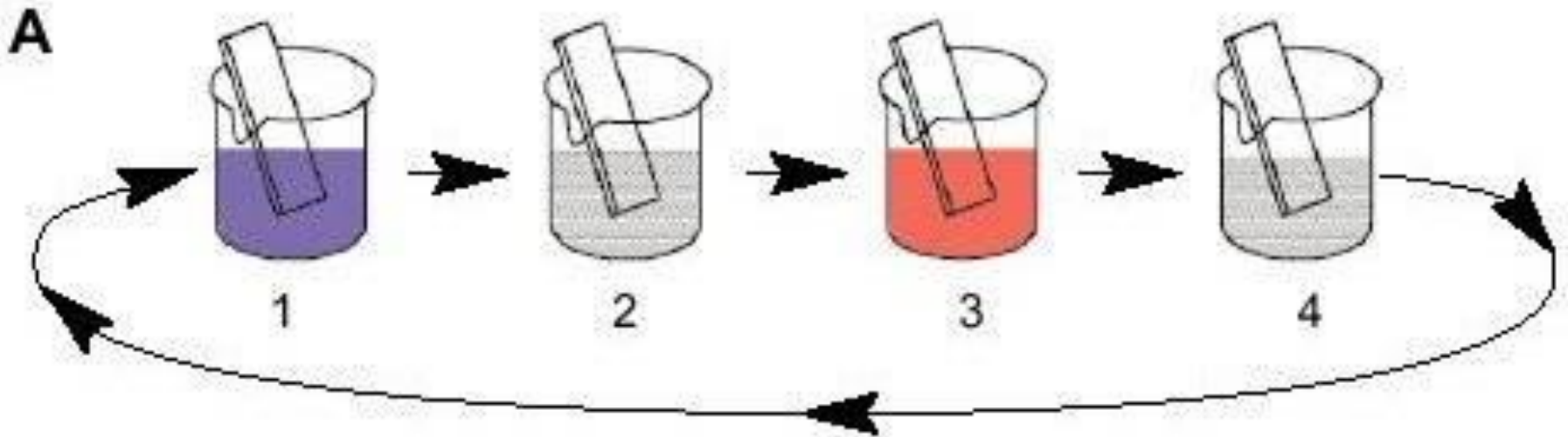
Different monomers will exhibit different ionic properties

For example, the sodium salt of poly(styrene sulfonate) will be negatively charged, while poly(allylamine hydrochloride) will be positively charged.



These ionic properties enable the controlled successive stacking of single layers of each polyion

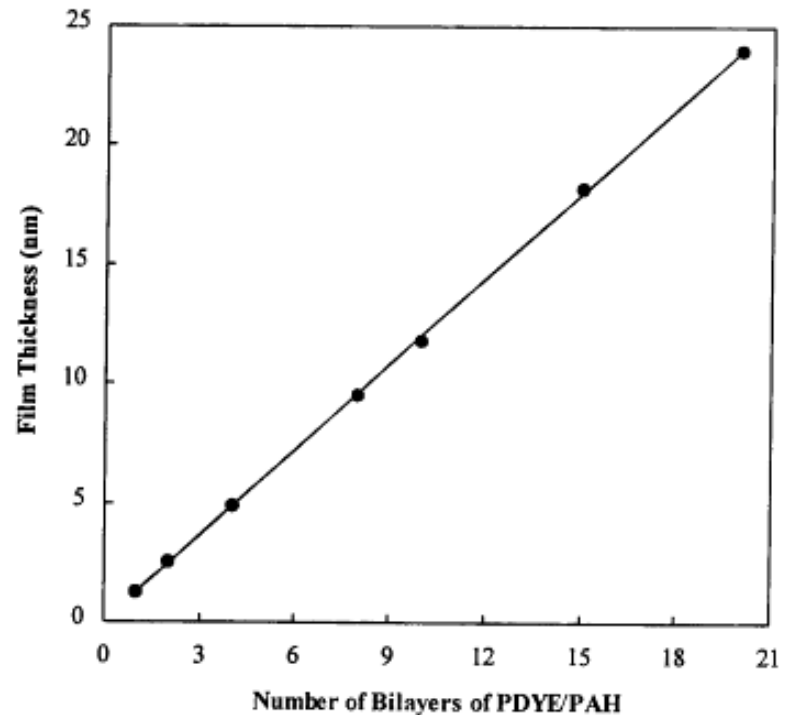
Synthesis of polyionic multilayer structures



- Steps 1 and 3 represent the adsorption of a polyanion and polycation, respectively, and steps 2 and 4 are washing steps.
- The four steps are the basic buildup sequence for the simplest film architecture, $(a/b)_n$.
- The construction of more complex film architectures requires only additional beakers and a different deposition sequence.
- Layers of controlled thickness can be deposited with typical deposition time of one minute per layer.

Reproducible Layer Thickness

- Total film thickness (measured by variable angle ellipsometry) as a function of number of deposited bilayers yields excellent linearity with number of deposited bilayers.
- Thickness of 1.2 nm per bilayer in example shown.

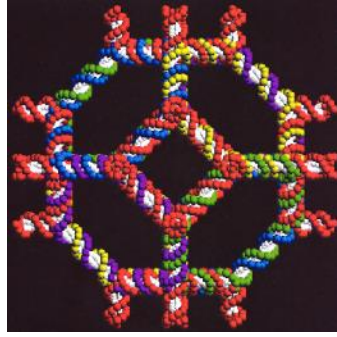
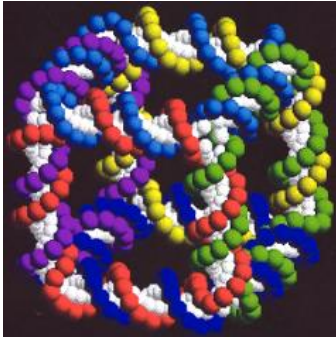


- **Self-Assembled Monolayers**
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- **Nanoparticles Assemblies**

Why use DNA for nanostructure assembly ?

➤ Extremely specific and reversible binding.

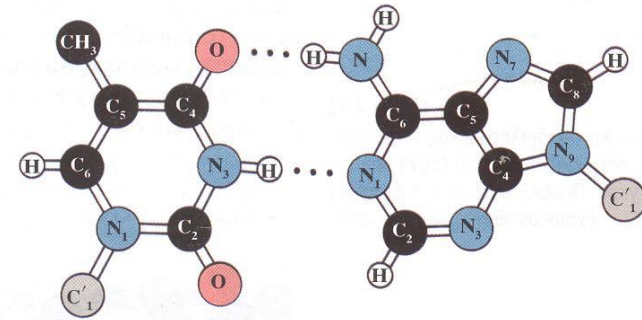
➤ Controllable structural versatility.



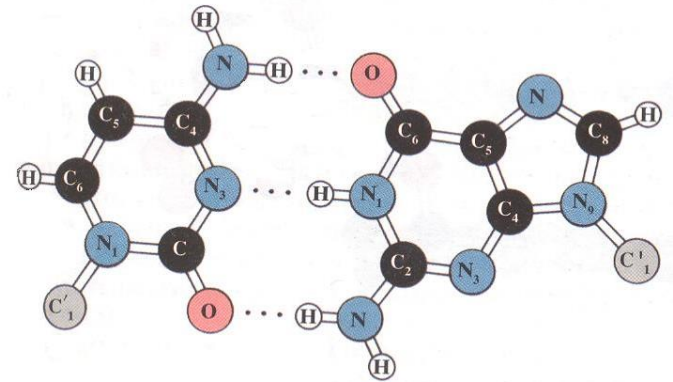
(N.Seeman et. al., *Fifth Foresight Conference: DNA Nanotechnology*)

➤ Easily modifiable with different functional groups.

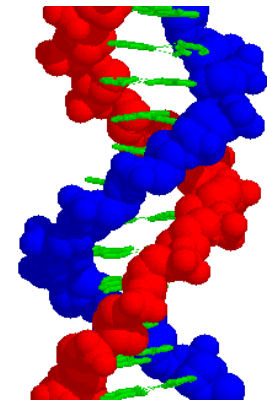
(Thiols, amines, carboxylic acids)

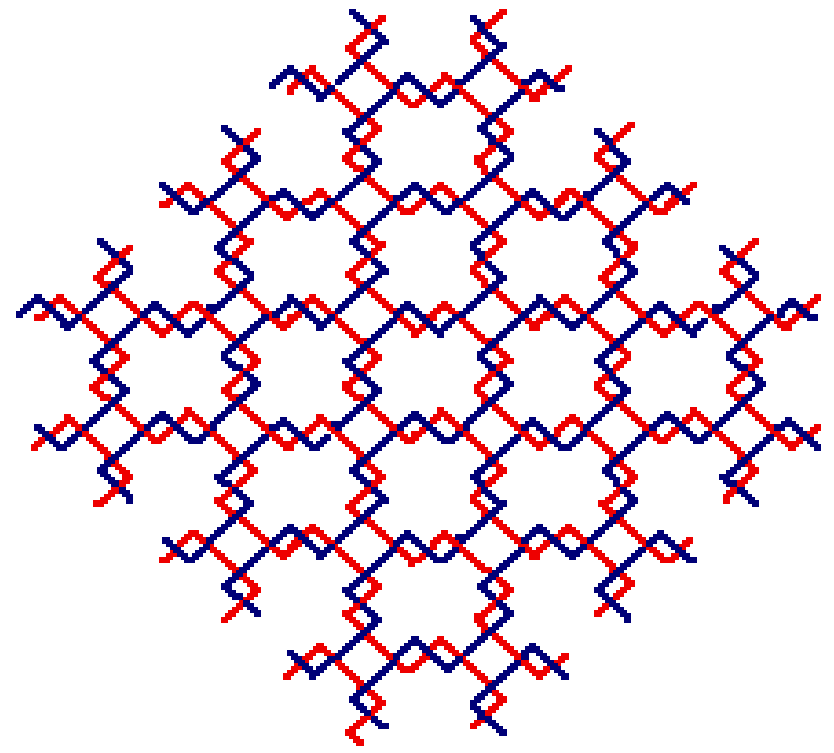
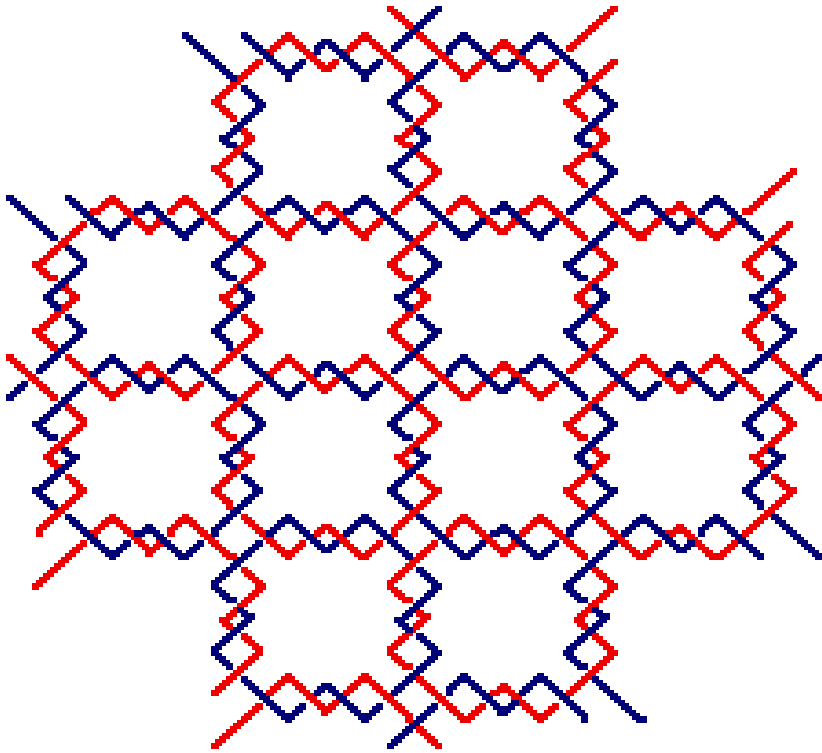


Adenine and Thymine



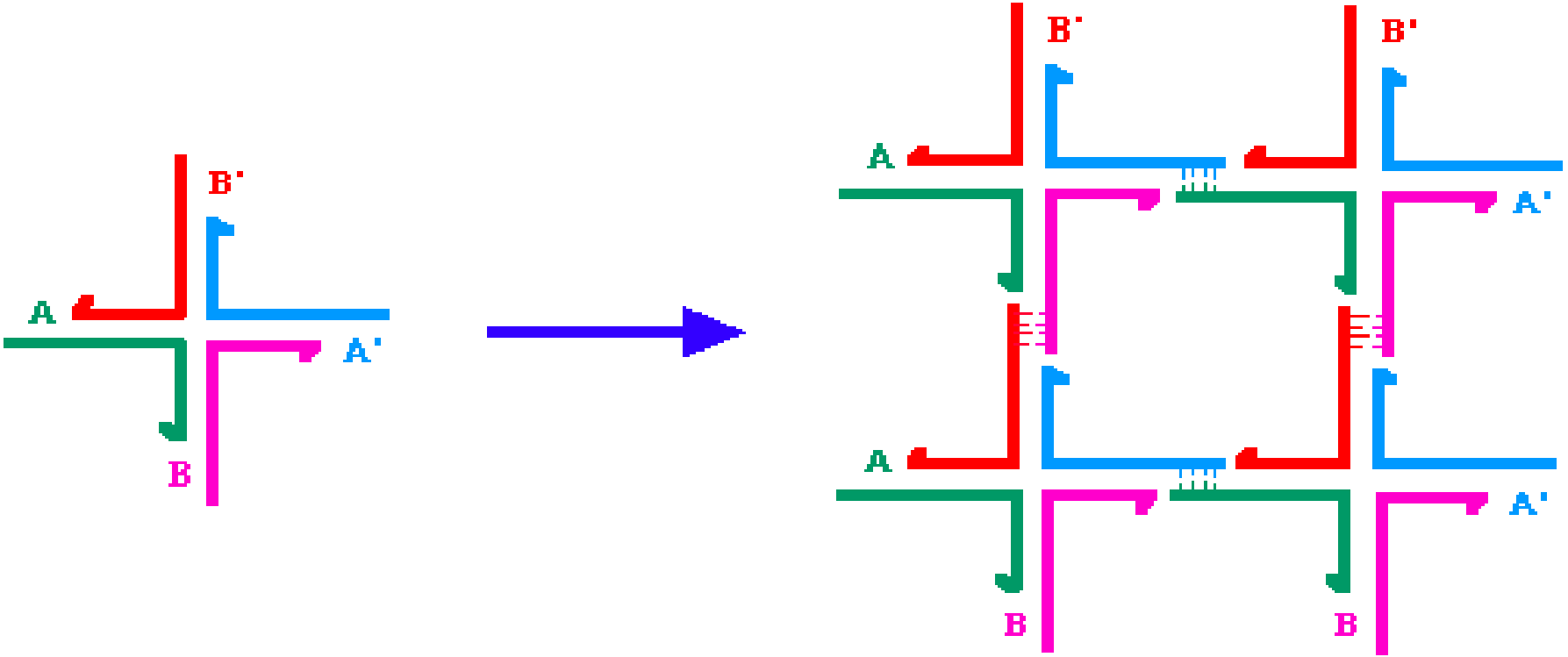
Guanine and Cytosine



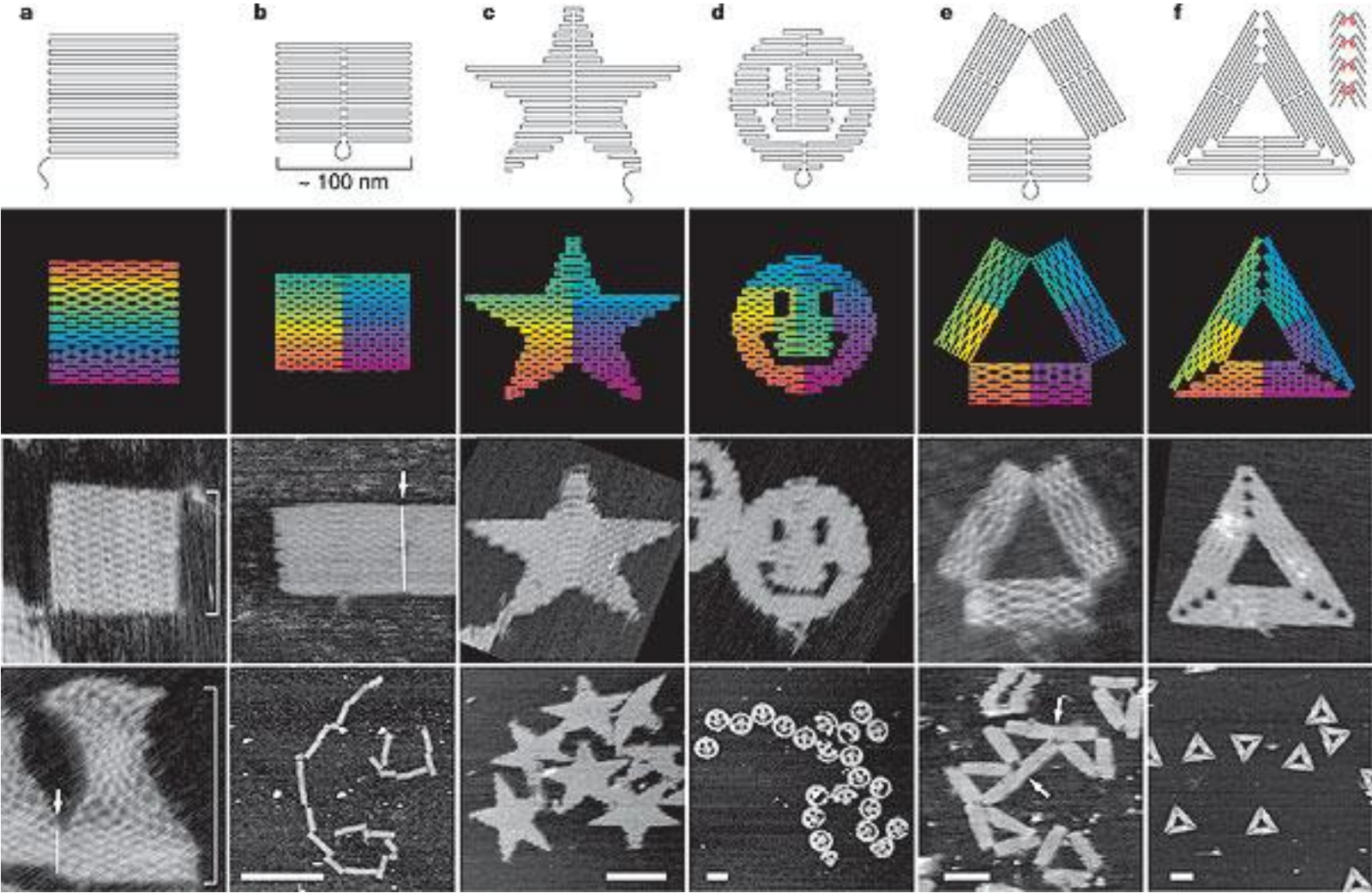


Various geometrical shapes can be constructed from DNA assemblies

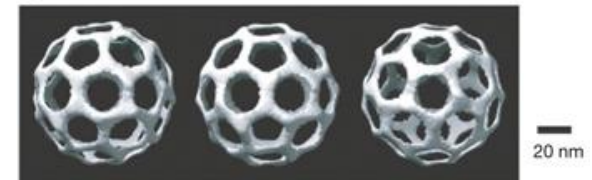
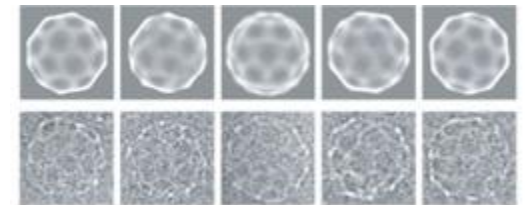
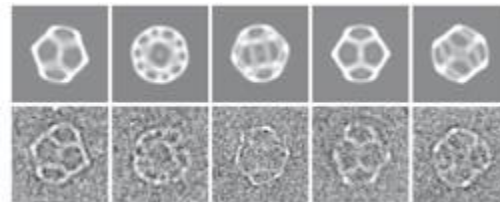
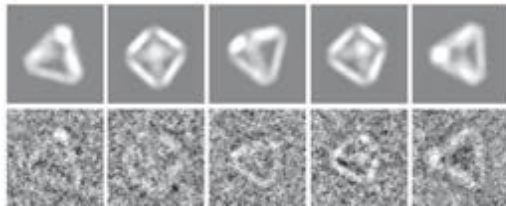
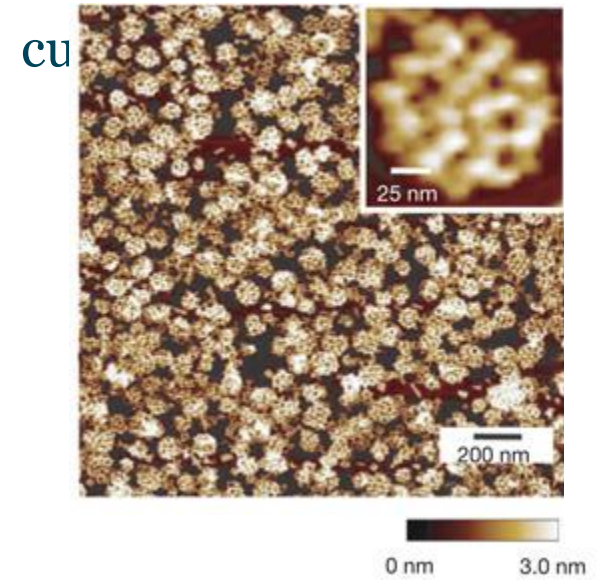
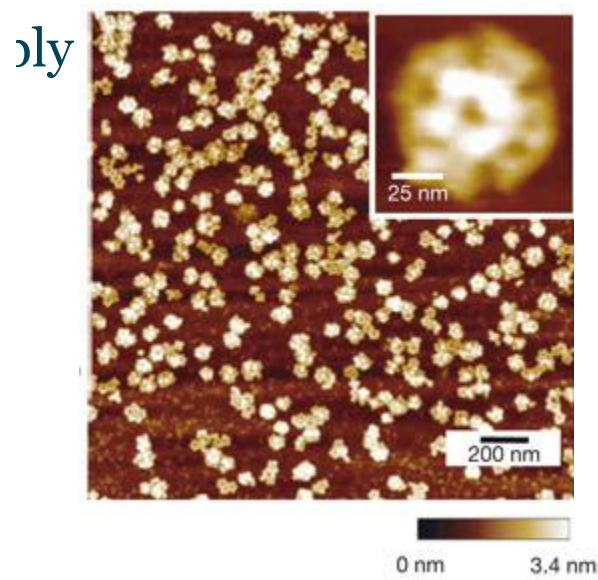
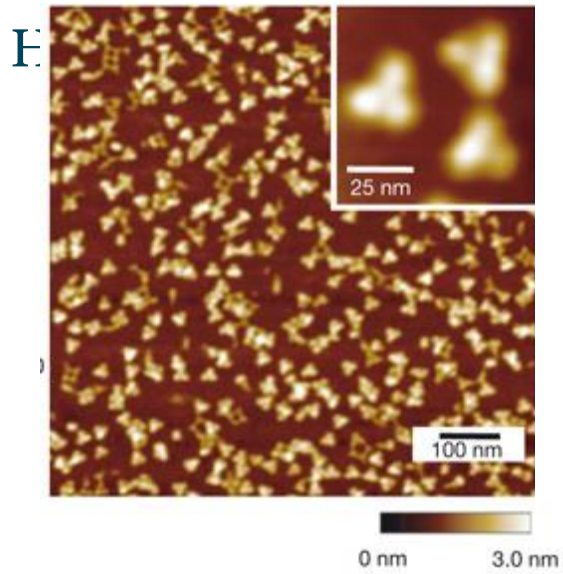
Example: Branched Junction Assembly



Folding DNA to Create Nanoscale Shapes and Patterns



P. W. K. Rothmund, Nature 440, 297 (2006)



- **Self-Assembled Monolayers**
- **Block Copolymers**
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- **DNA-based Assembly**
- **Nanoparticles assemblies**

Assembly strategies

DNA driven assembly

Small molecules interactions

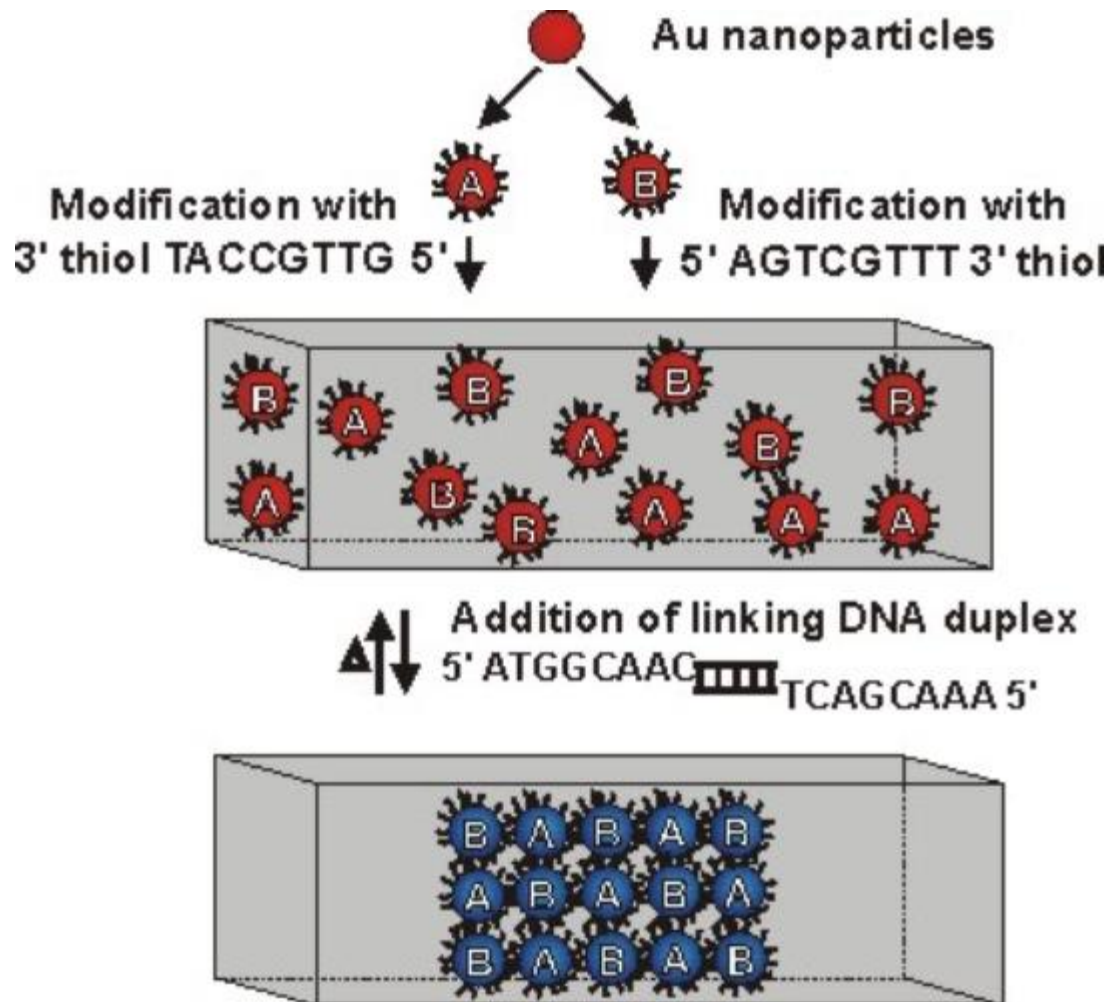
Electrostatic interactions

Other biological interactions

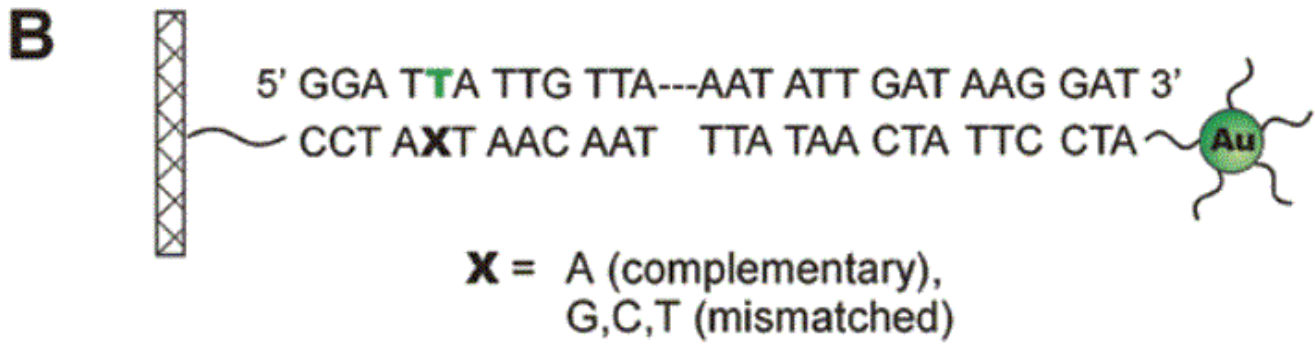
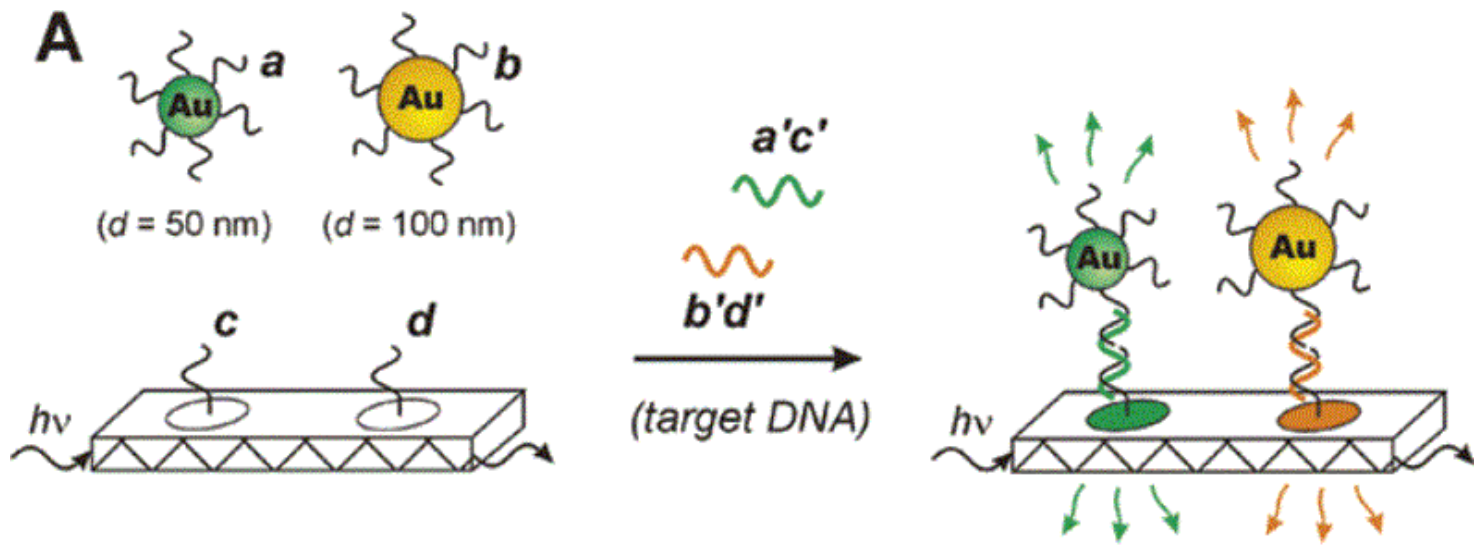
Polarity

Inorganic fusion

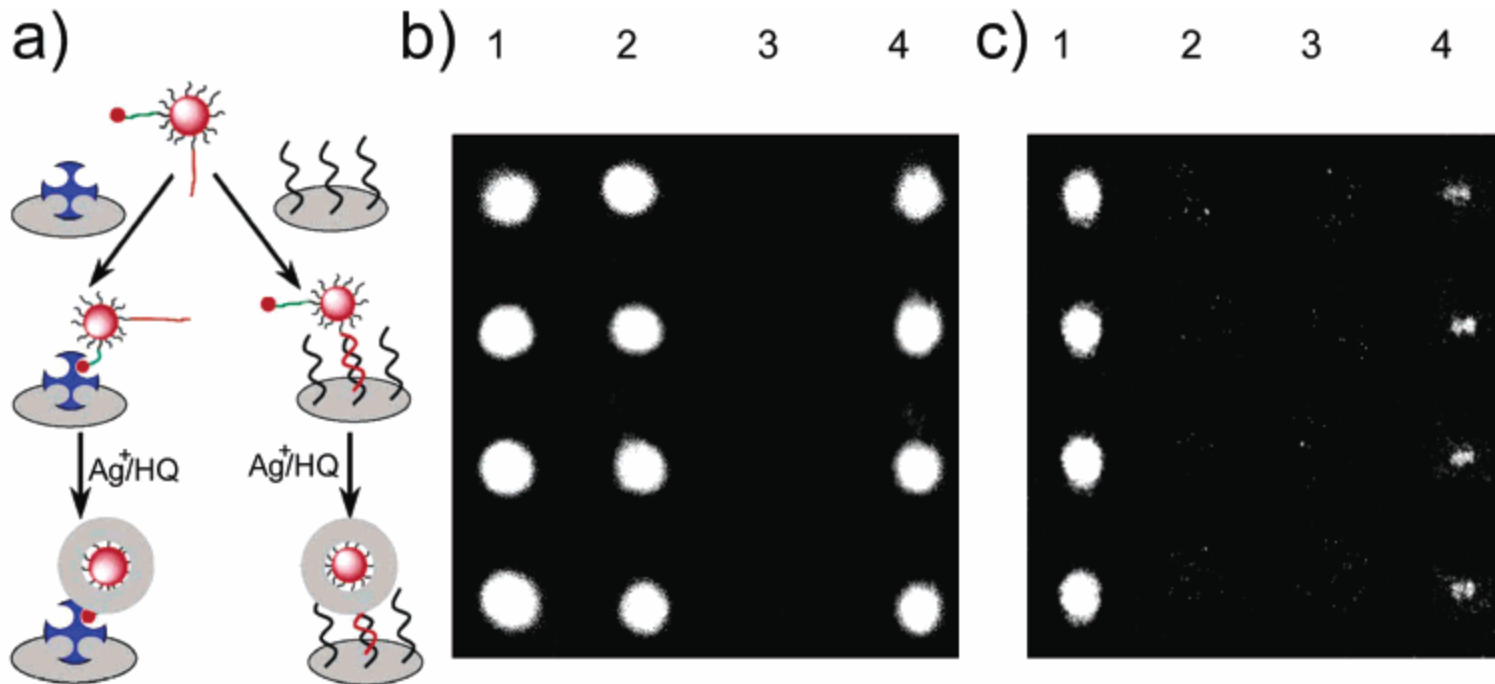
Various applications of DNA-nanoparticle conjugates



➤ Scanometric DNA array detection with nanoparticle probes.



Microarrays



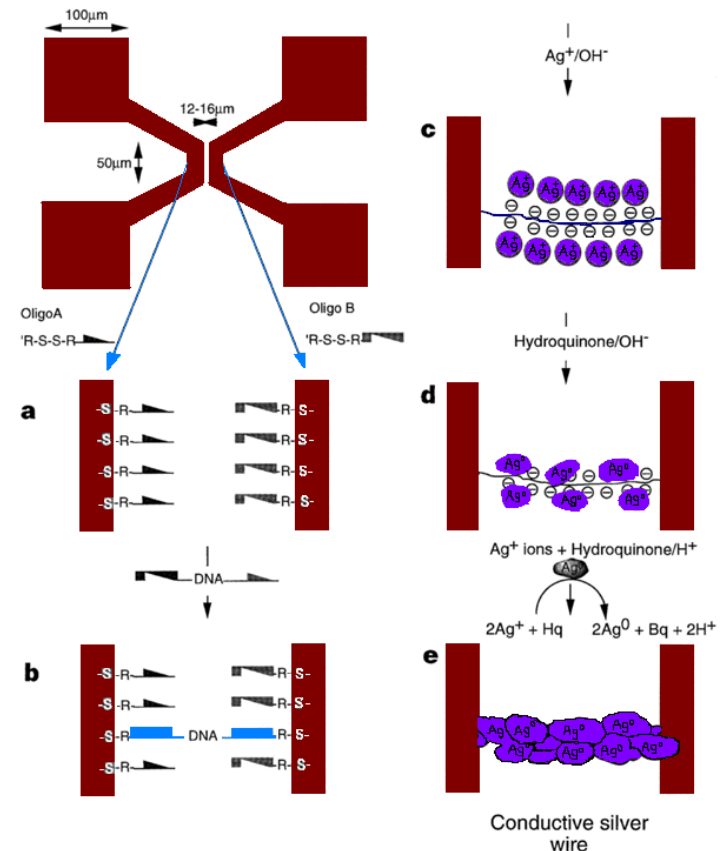
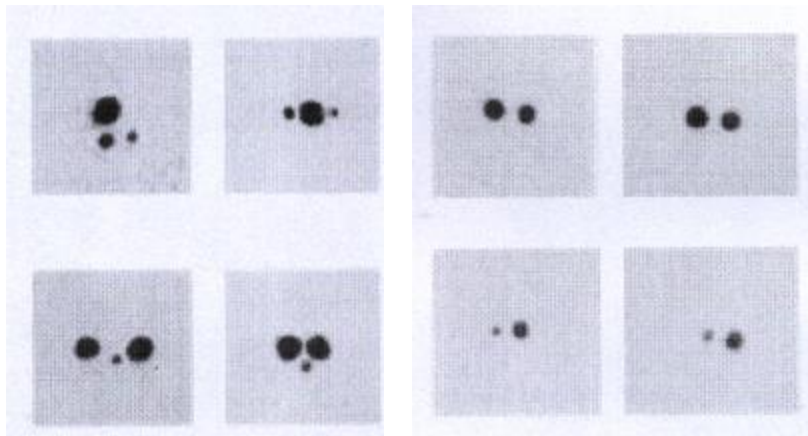
Bioconjugate Chem. 2005, 16, 497–500

Schematic representation of DNA and protein microarrays labeled with bifunctional gold nanoparticles followed by silver enhancement (a). Light scattering images of protein microarray (b) and DNA microarray (c) after silver enhancement. In b, avidin was spotted on column 1, 2, and 4, while protein A was spotted as a nonspecific control on column 3; in c, perfectly matched DNA was spotted on column 1, three-base-mismatched DNA was spotted on column 2, two-base-mismatched DNA was spotted on column 3, and one-base-mismatched DNA was spotted on column 4

Various applications of DNA-nanoparticle conjugates

- DNA -template for building Ag microwires between Au microelectrodes.

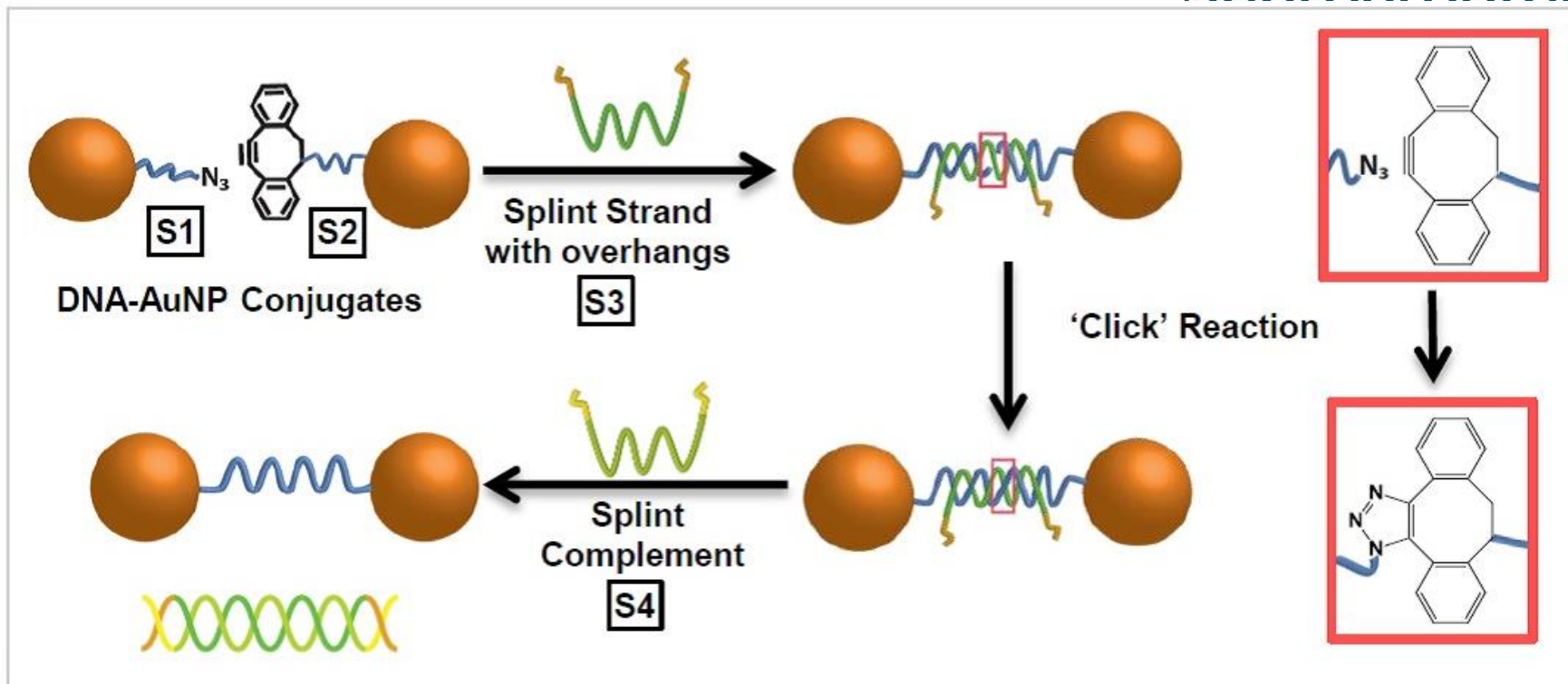
(Braun et. al., *Nature* 1998, 391,775)



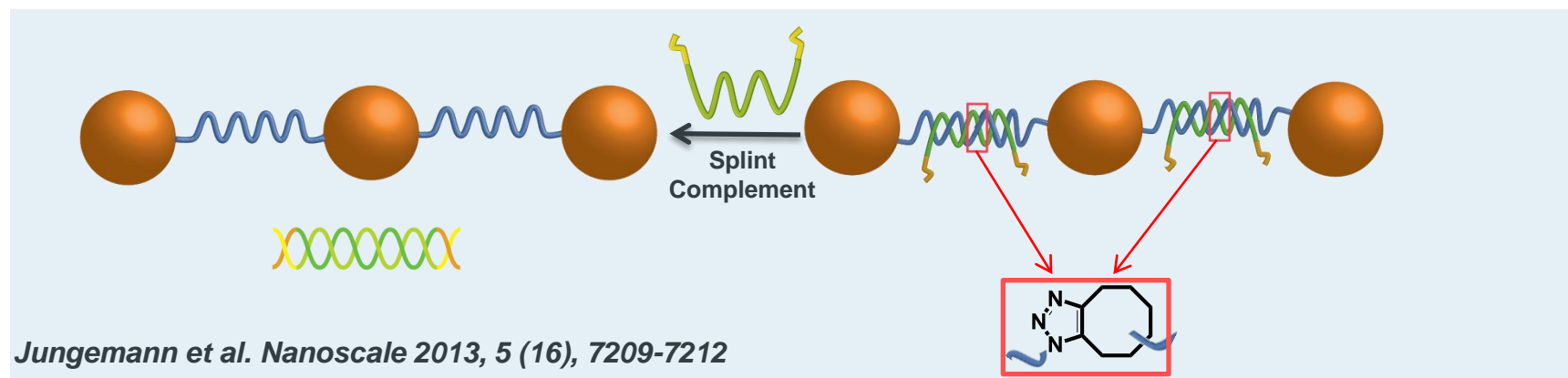
- DNA-based assembly of gold nanocrystals.

(Alivisatos et.al., *Angew.Chem.Int.Ed.*, 1999, 38, 1808)

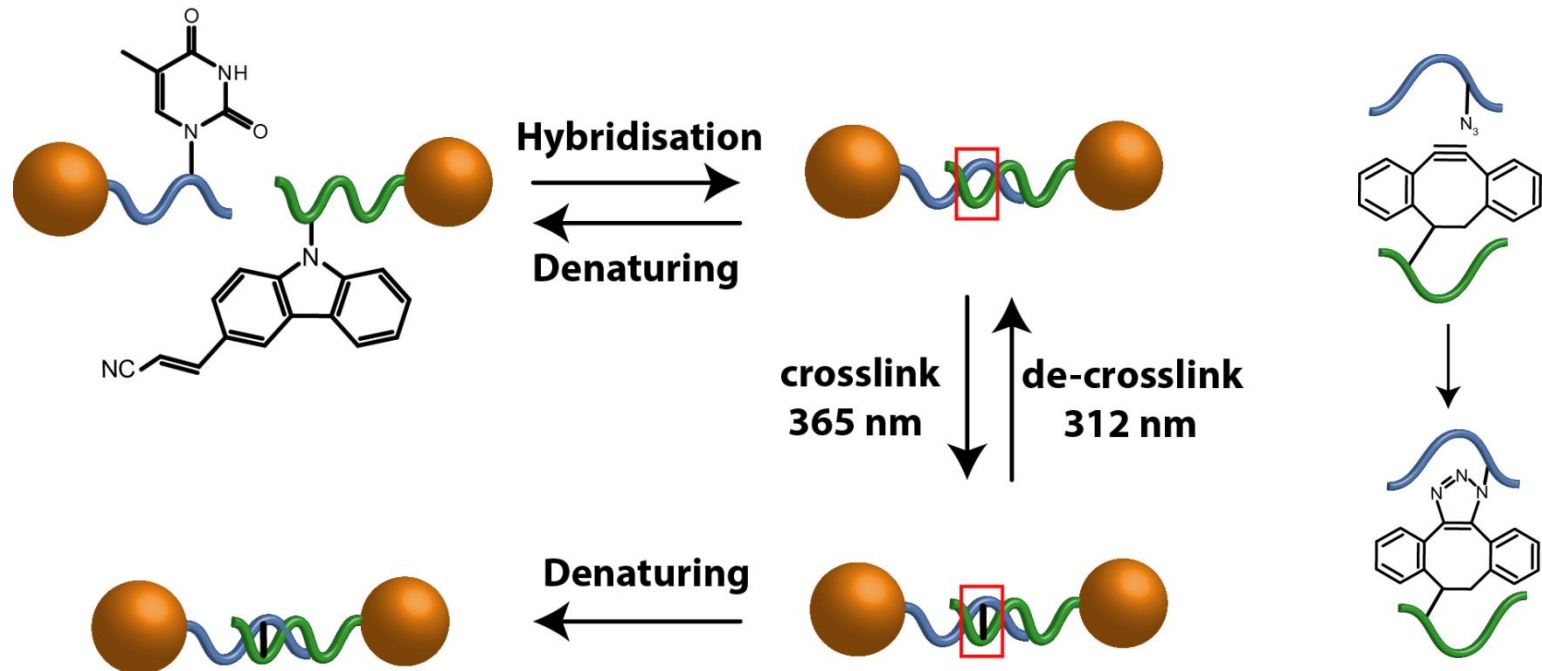
Chemical ligation of DNA-gold nanoparticles



or

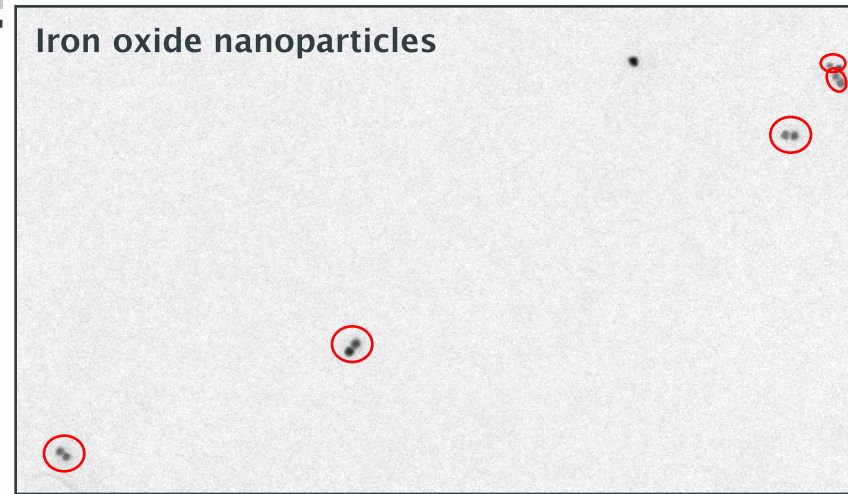
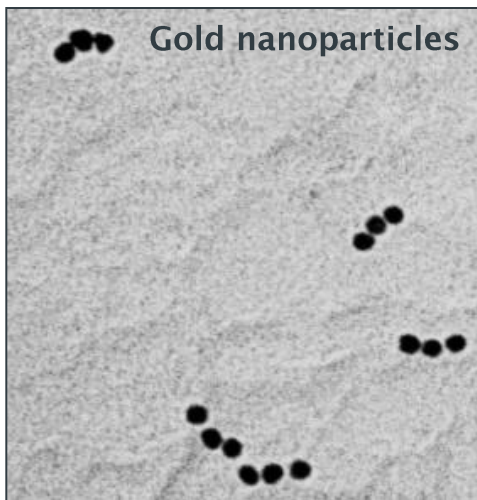
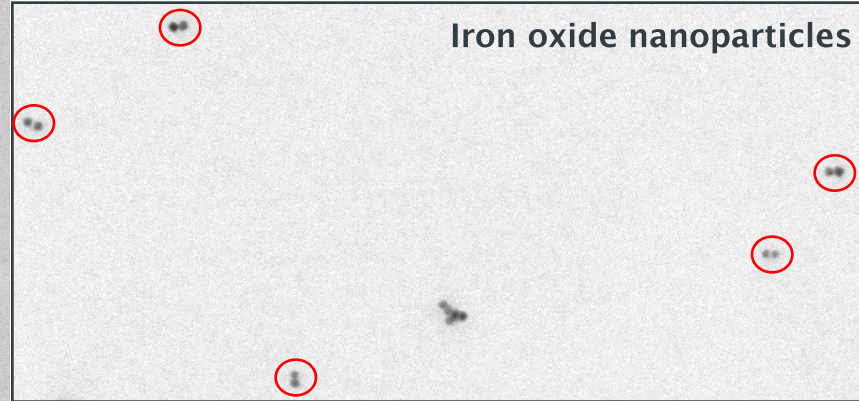
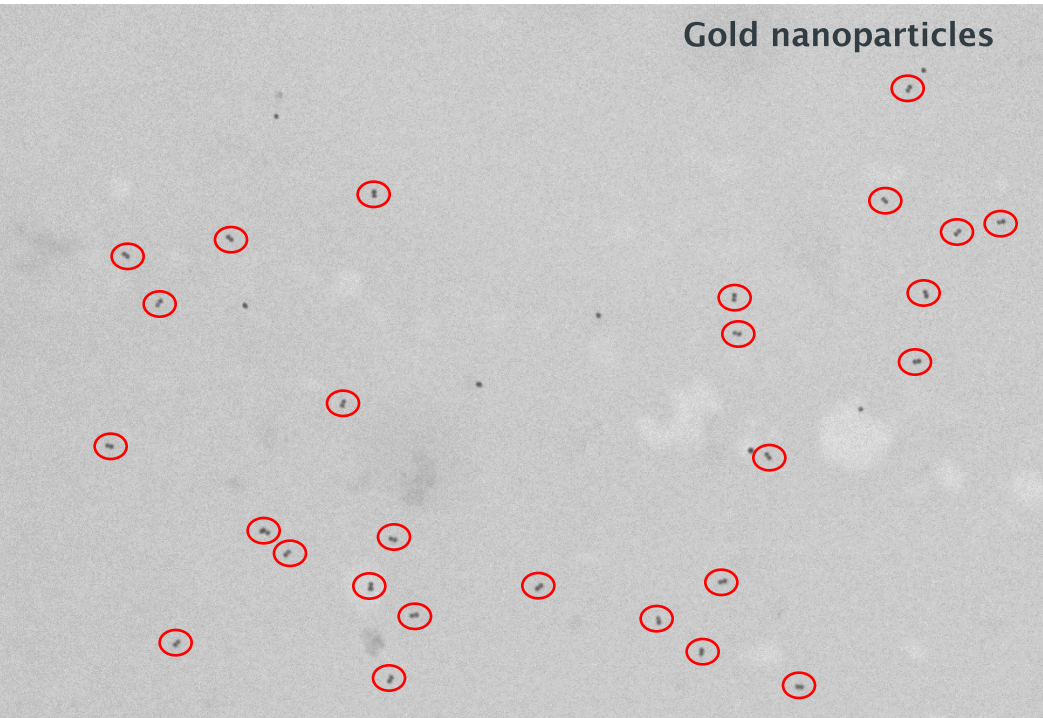


DNA-mediated Assembly of AuNPs -Cross-linking via cyanovinyl carbazole-



- Cyanovinyl carbazole base substituent can be photo cross-linked with an adjacent Thymine base.

TEM images of programmed nanoparticle assemblies

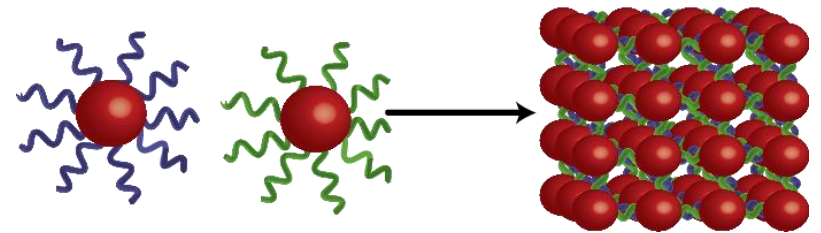
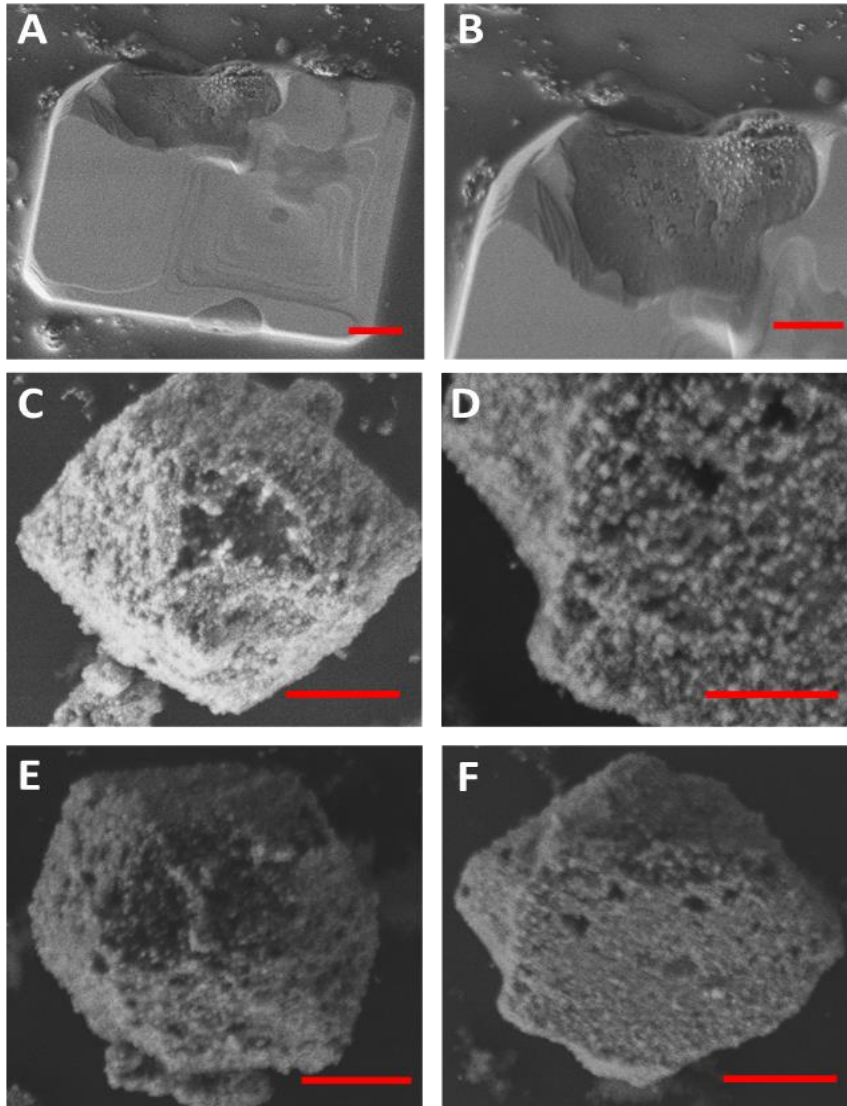


500 nm

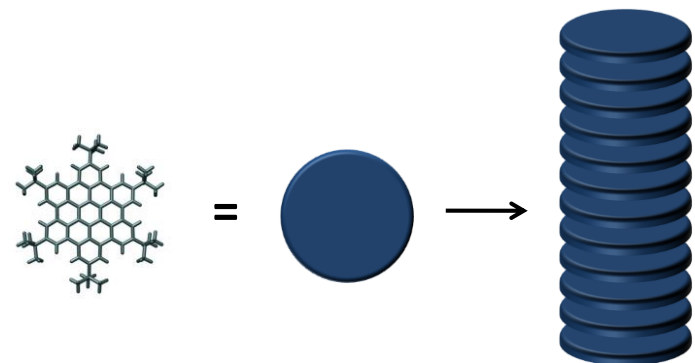
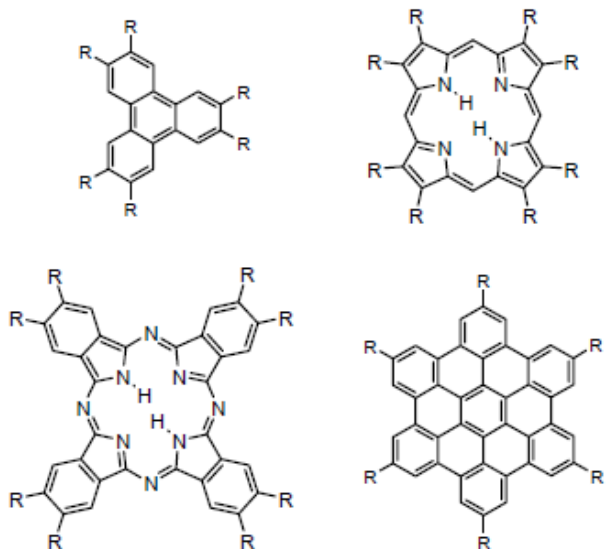
500 nm

50 nm

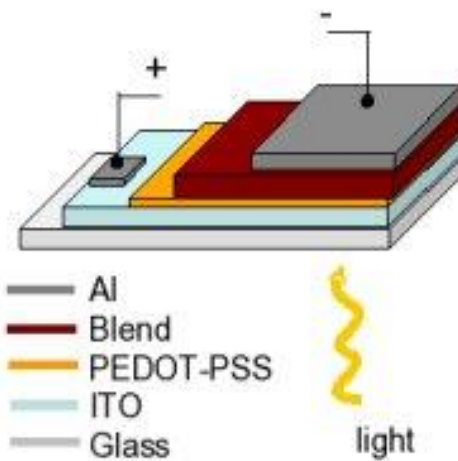
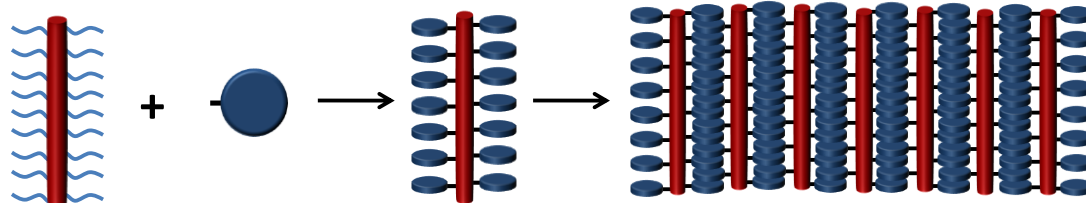
500 nm

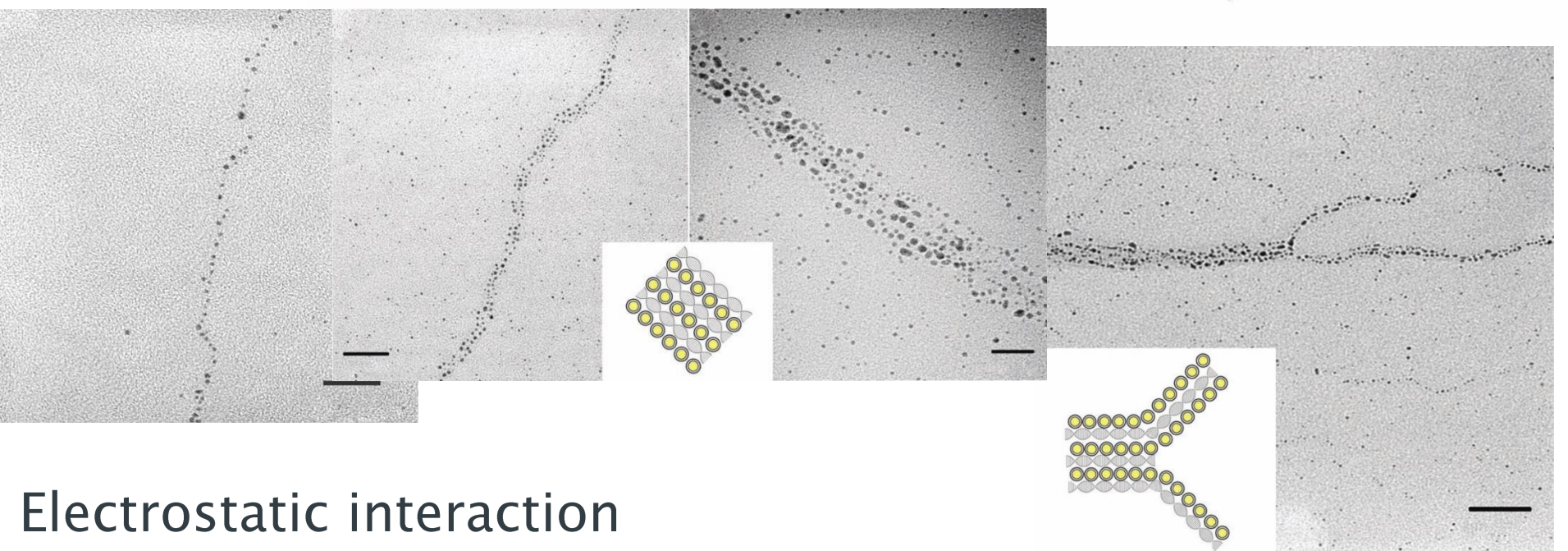
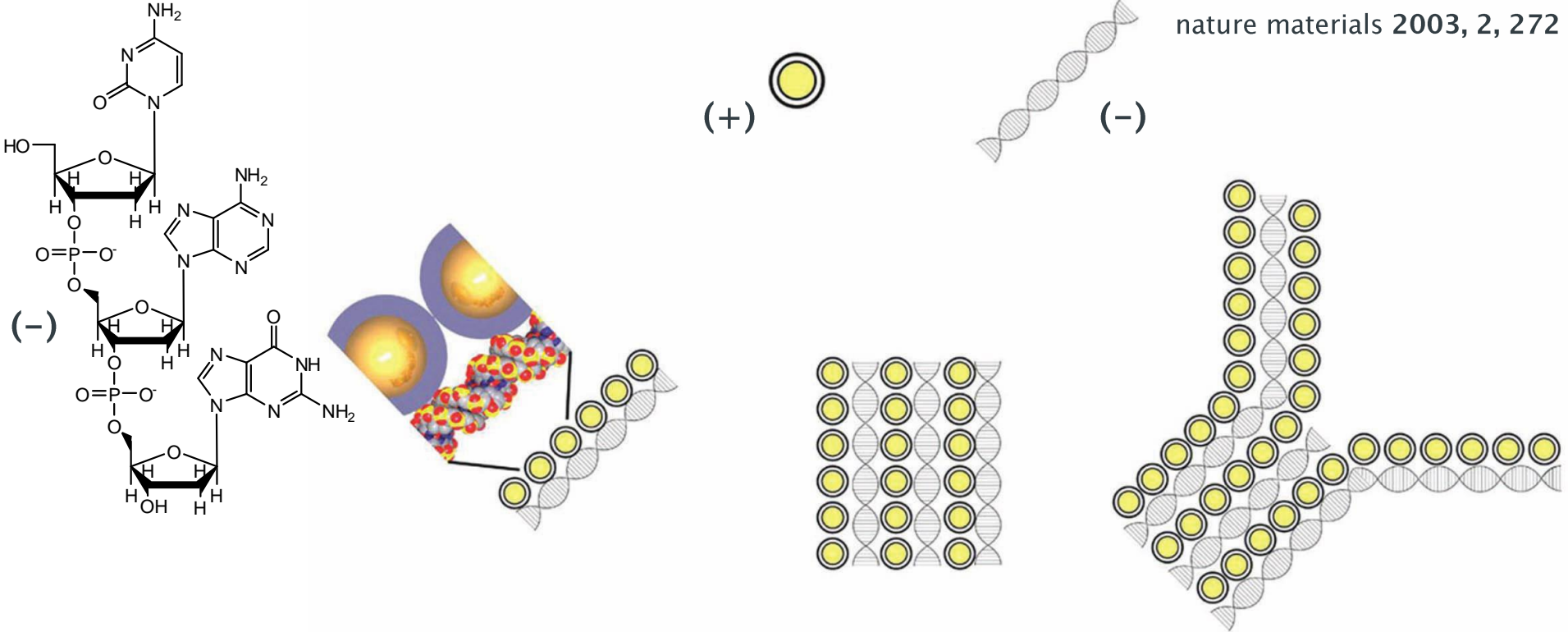


Polycyclic aromatic hydrocarbons

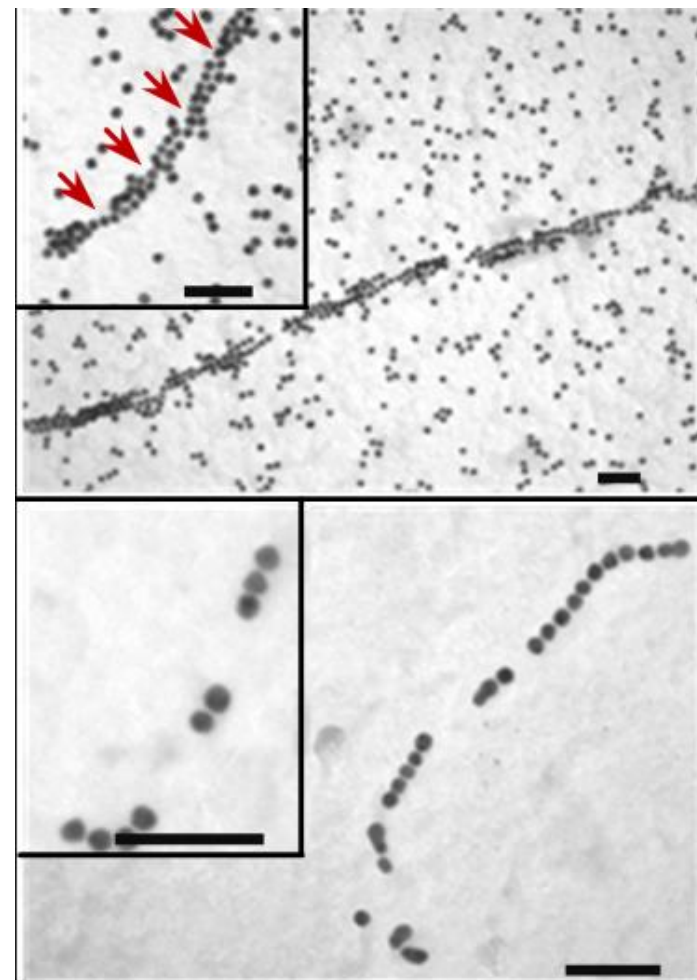
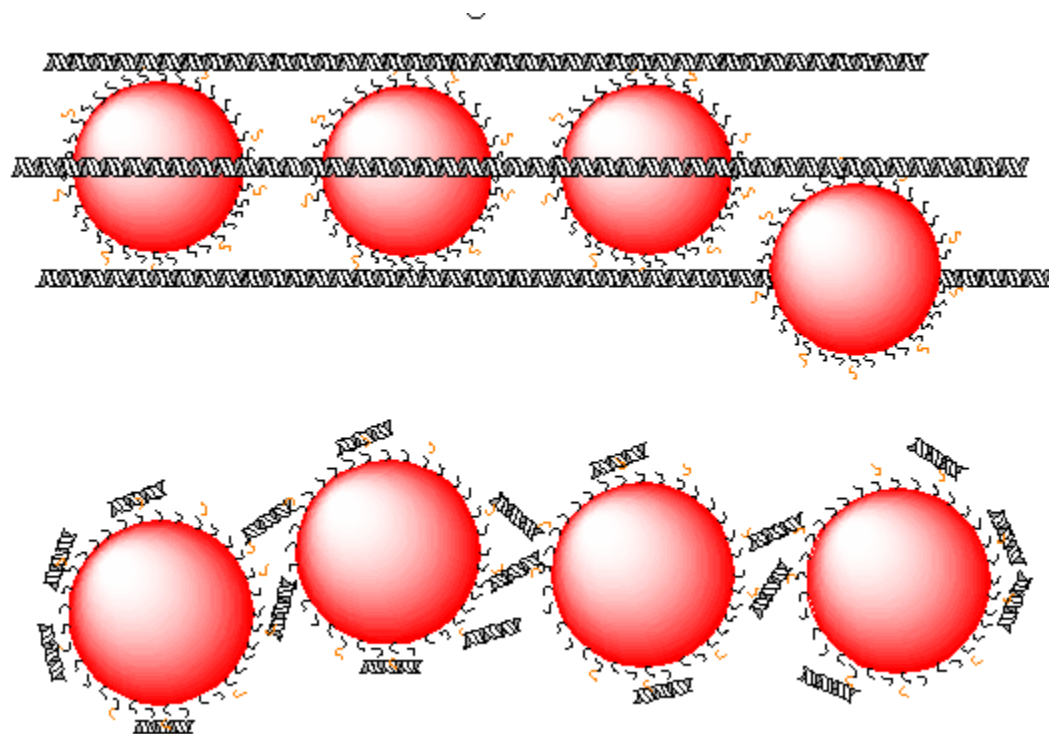


Solar cells

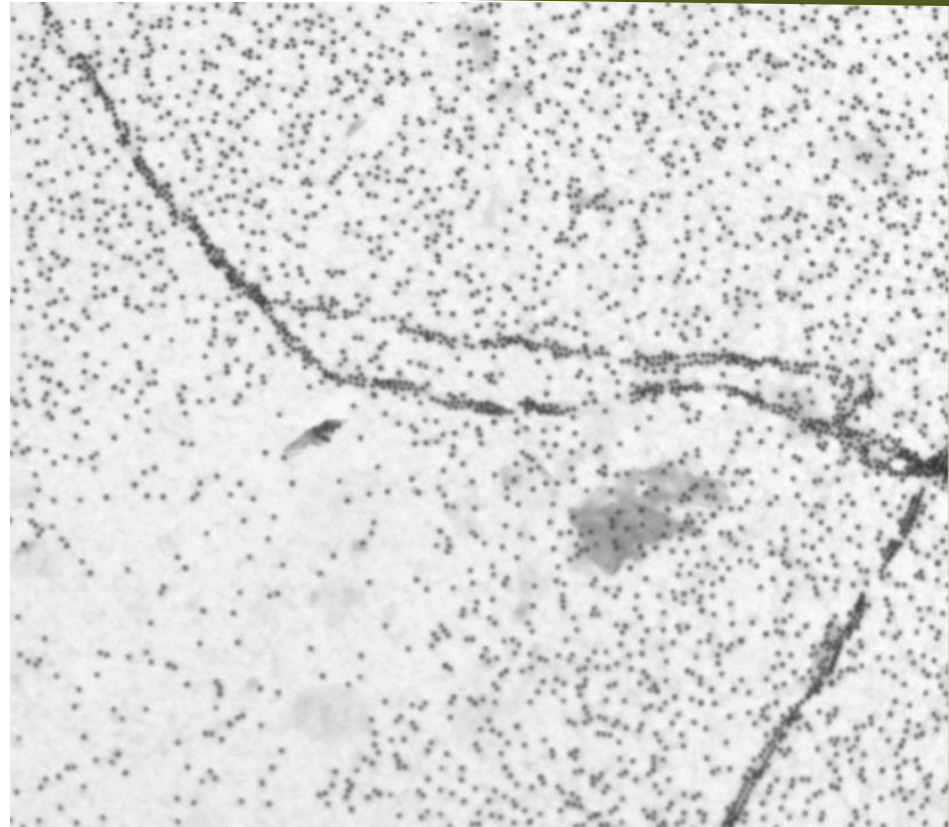
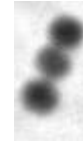
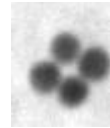
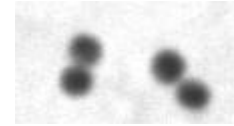
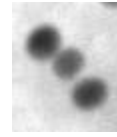
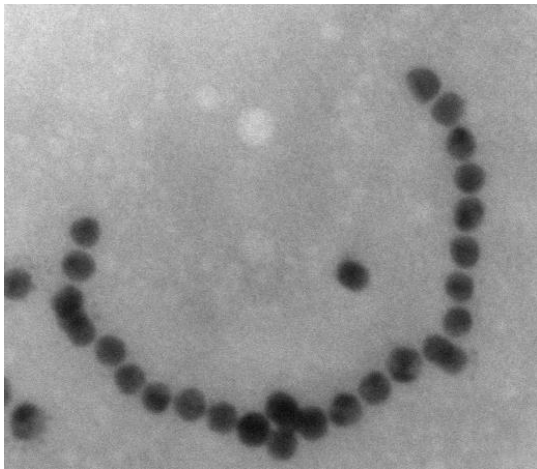
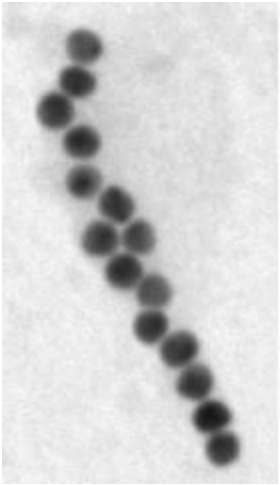




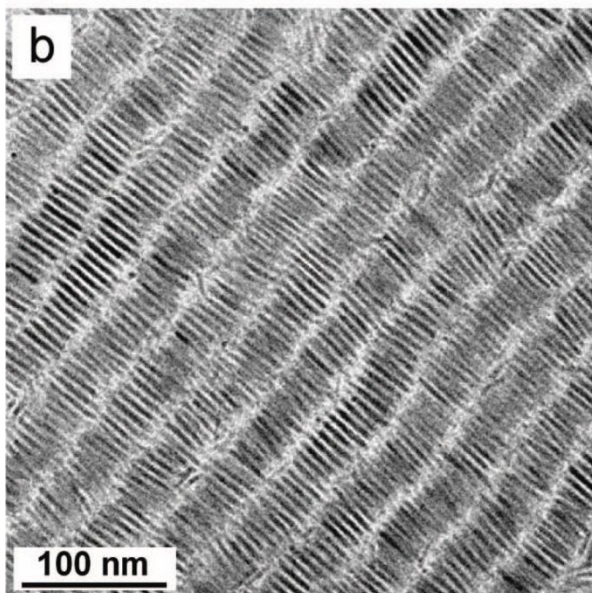
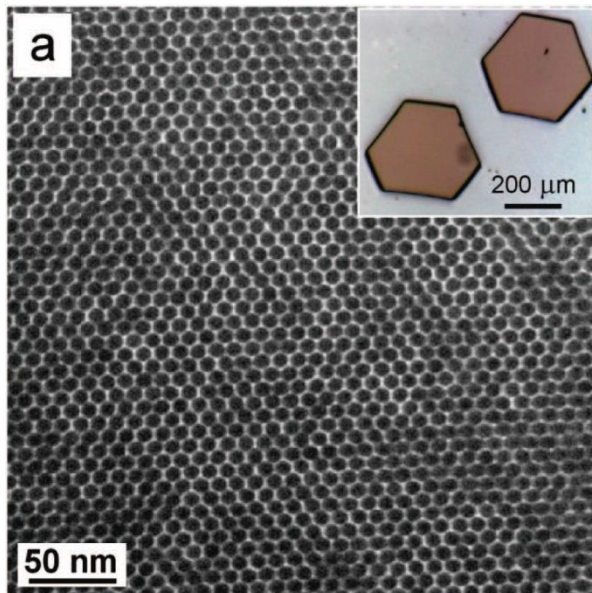
DNA nanoparticle-assemblies



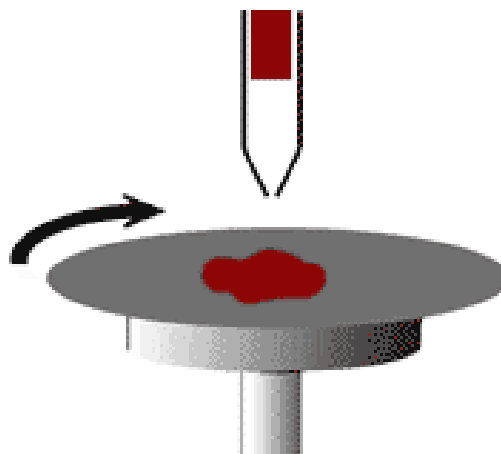
Oligonucleotide-peptide interactions



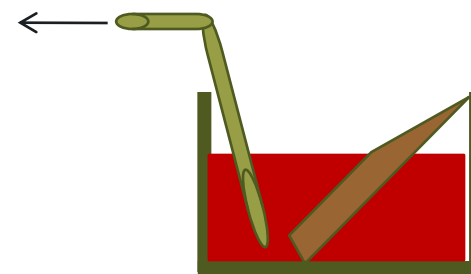
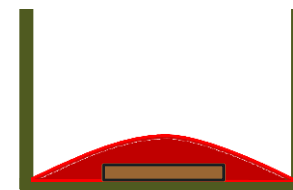
Some other strategies to assemble nanocrystals



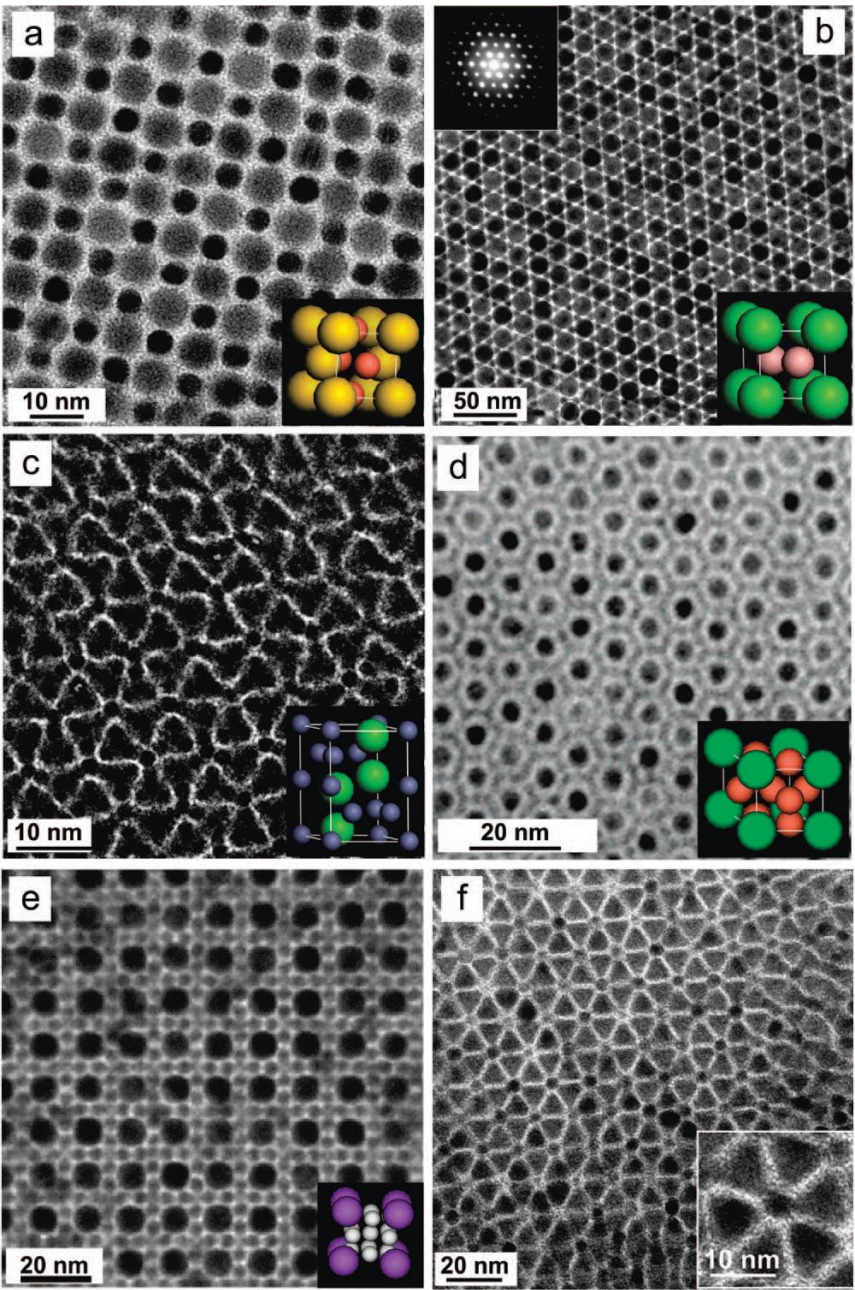
Spin coating or drop-casting



evaporation



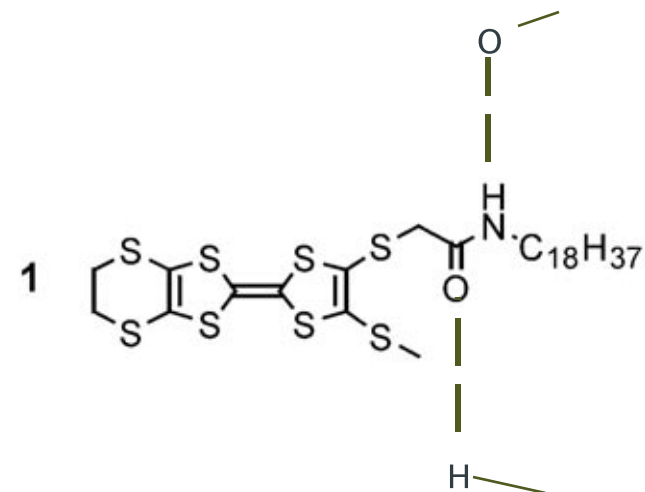
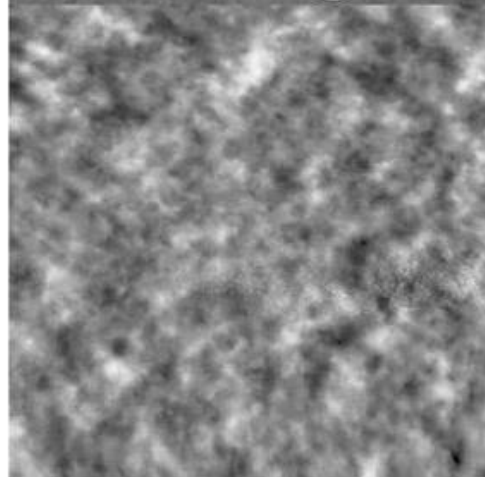
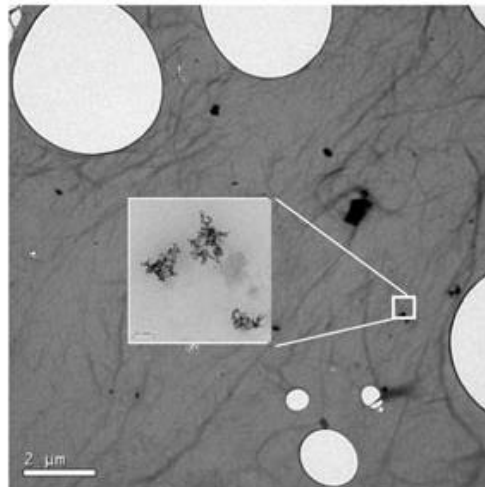
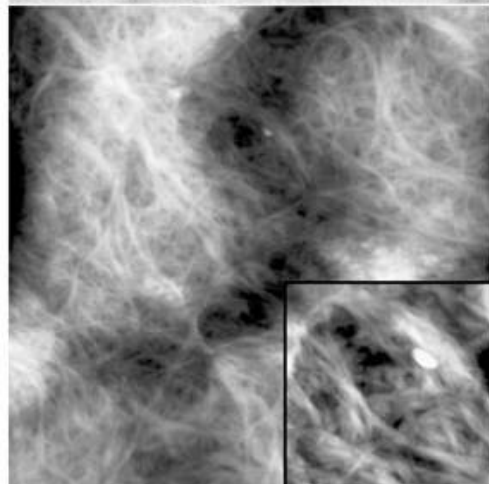
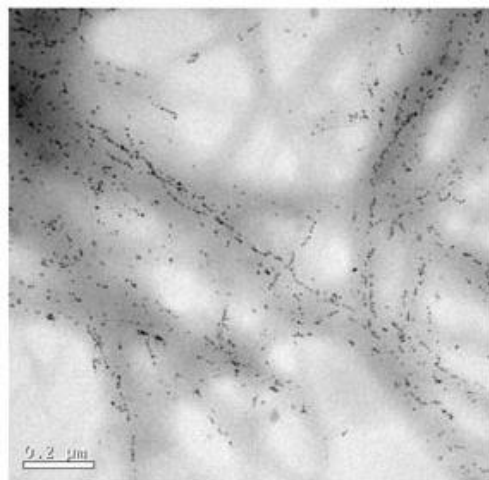
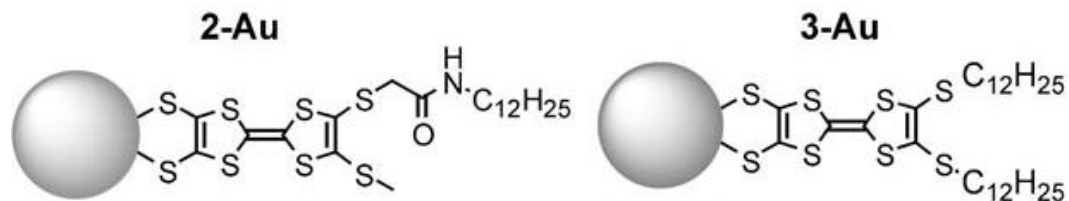
Gradual solvent removal



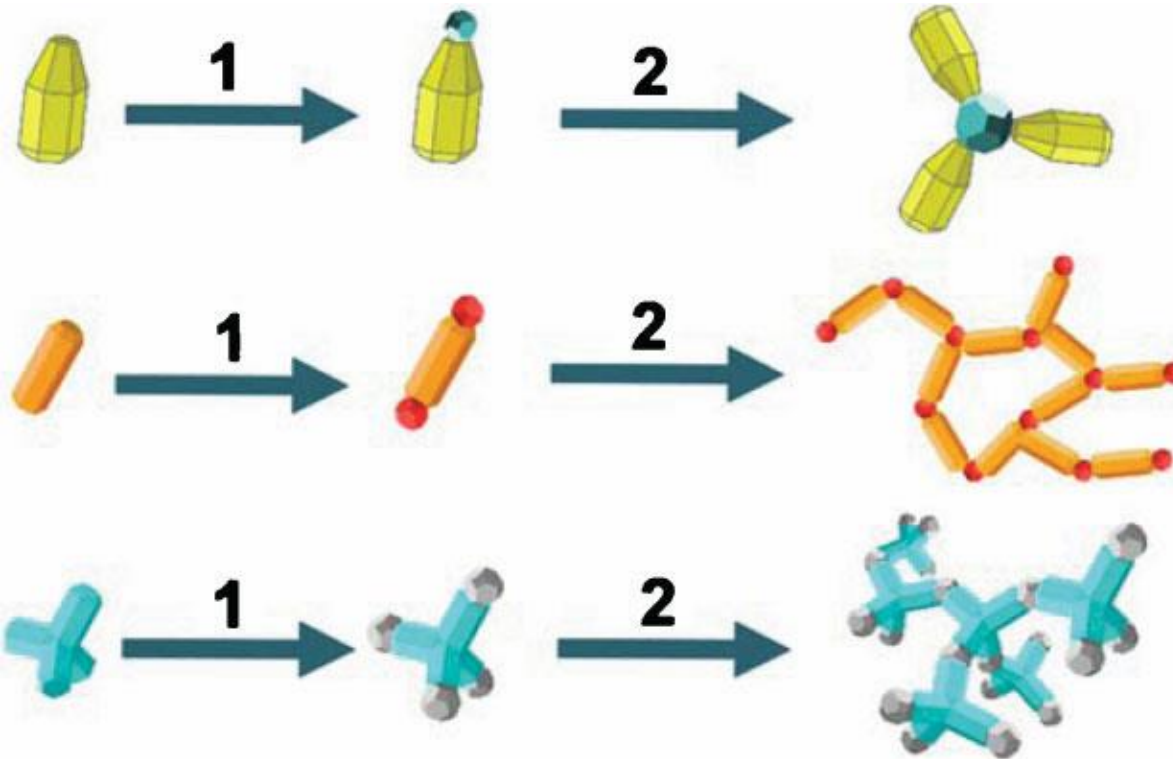
Some factors that define the structure:
a) Size of particles
b) Concentration
c) Type of capping ligands

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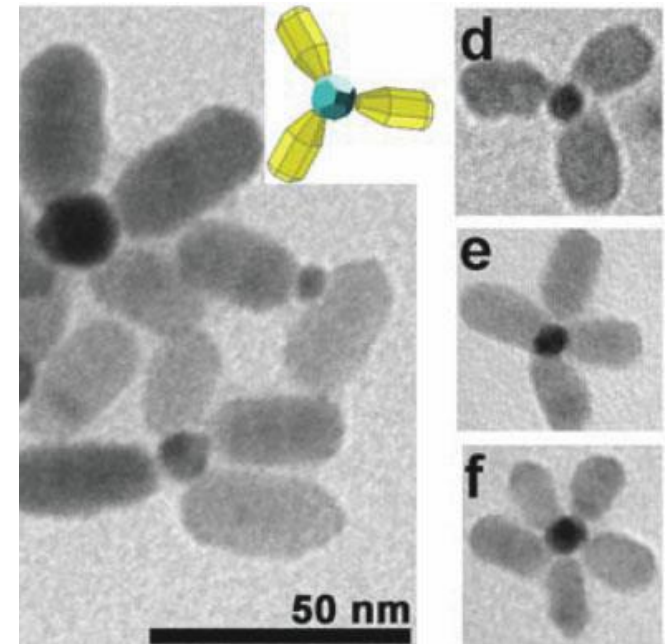
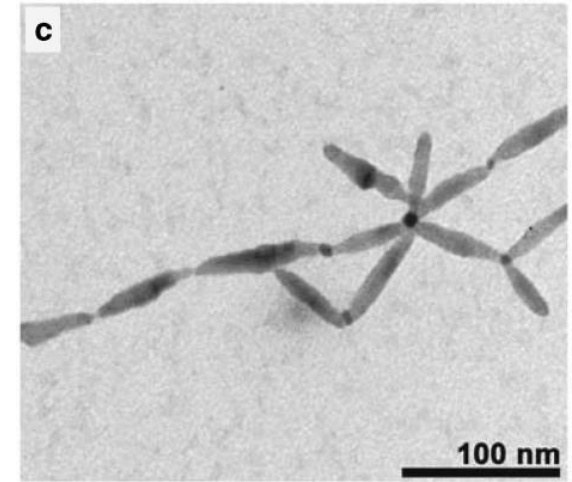
Small molecule interactions



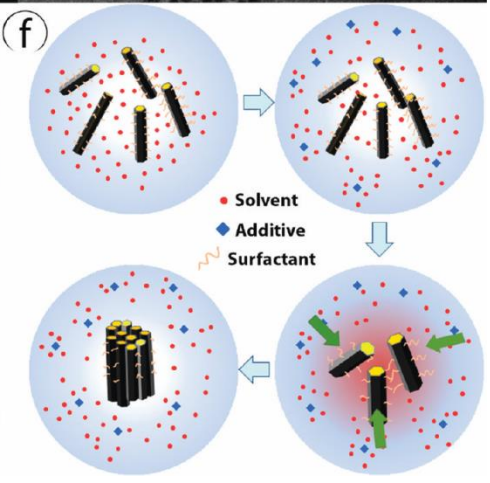
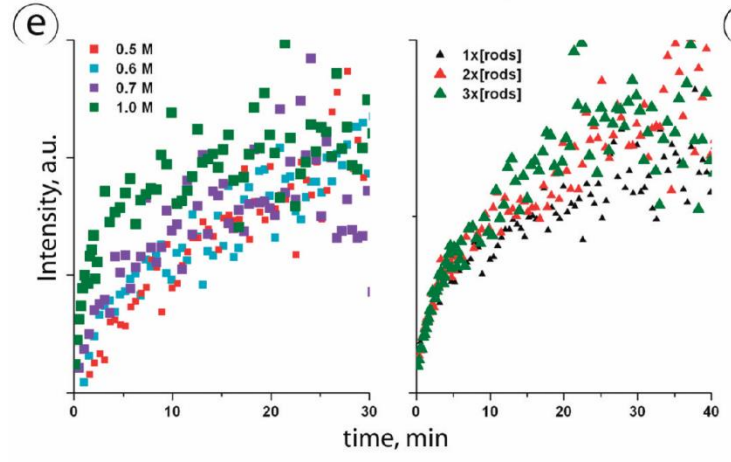
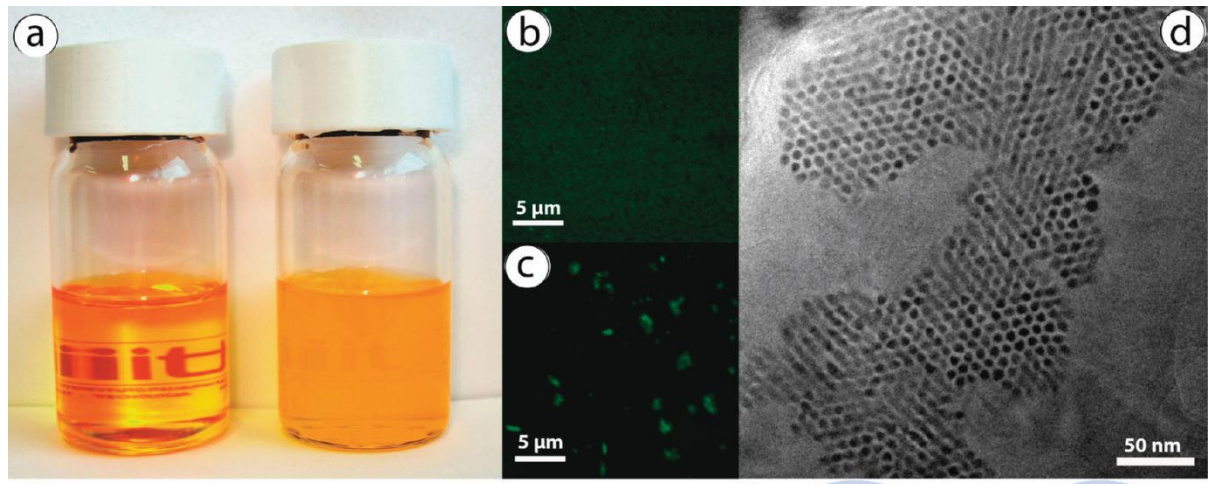
Nano-welding

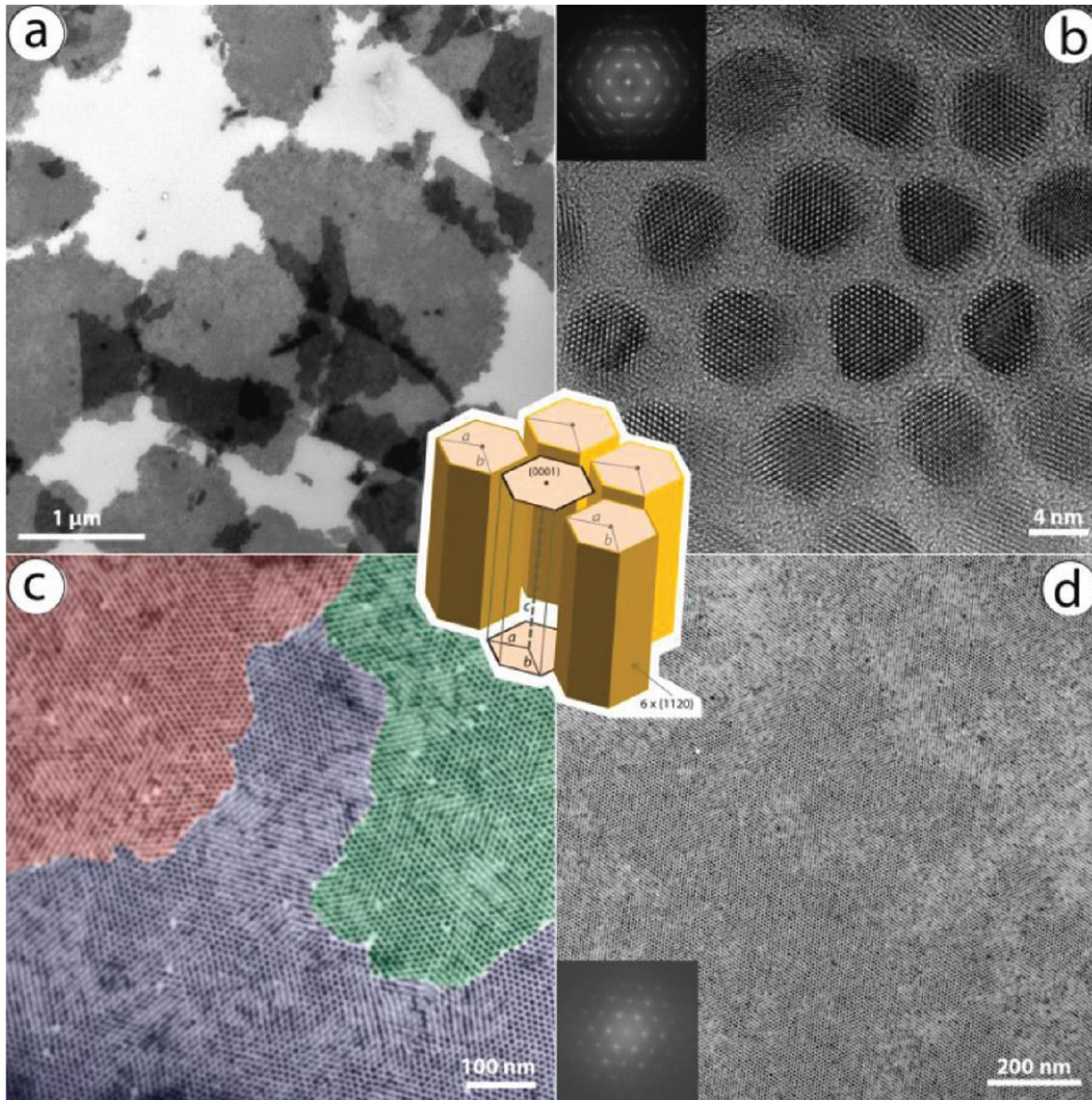


1. Precursors for gold nanocrystals: AuCl_3 , TOAB, DDA
2. Iodine solution : 0.1% I_2 (w/v) molar ratio NCs: I_2 = 1:15



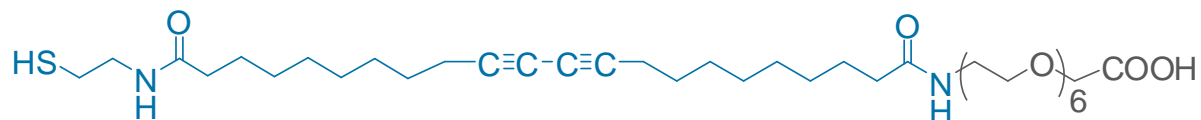
Depletion forces



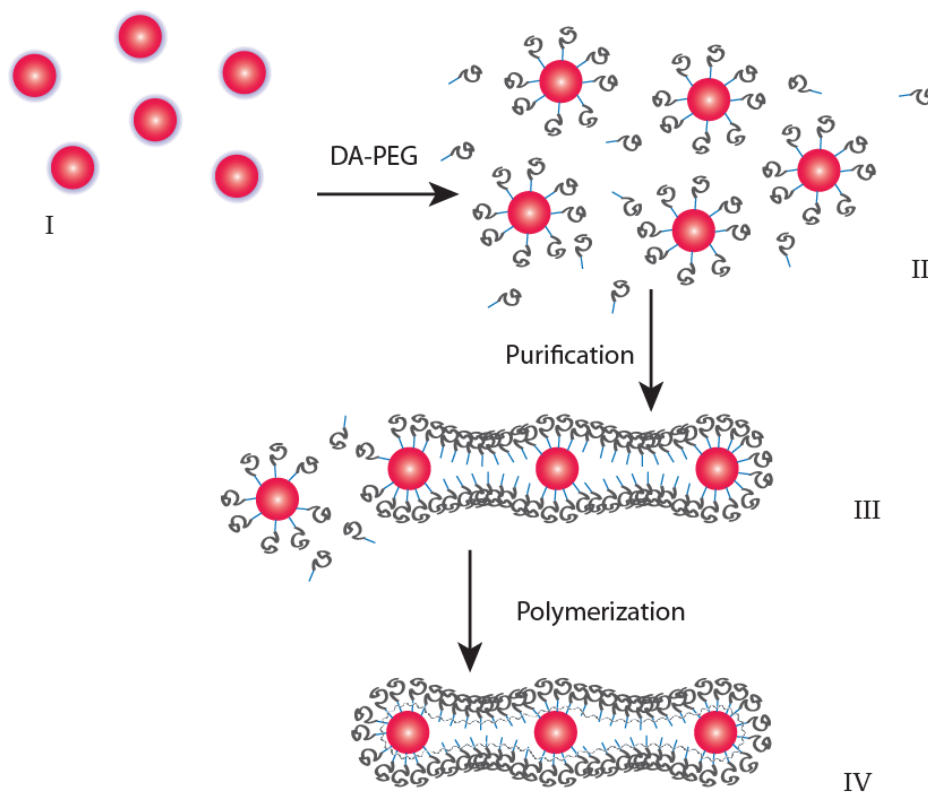


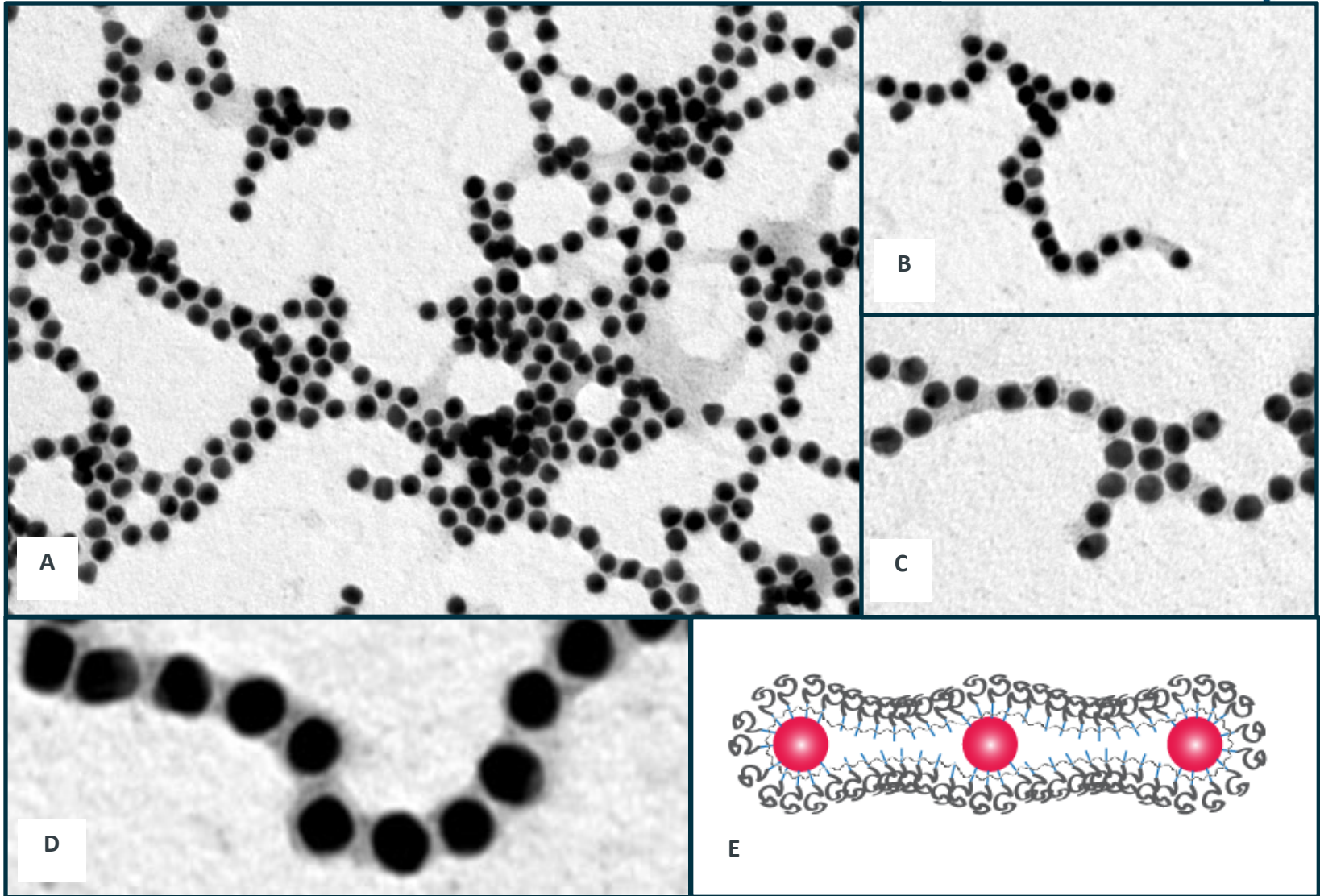
Self-assembly of colloidal nanoparticles

A



B





What is self-assembly? What are the principles of molecular self-assembly?
Give examples of self-assembly interactions.

What is SAMs ? Discuss examples and applications.

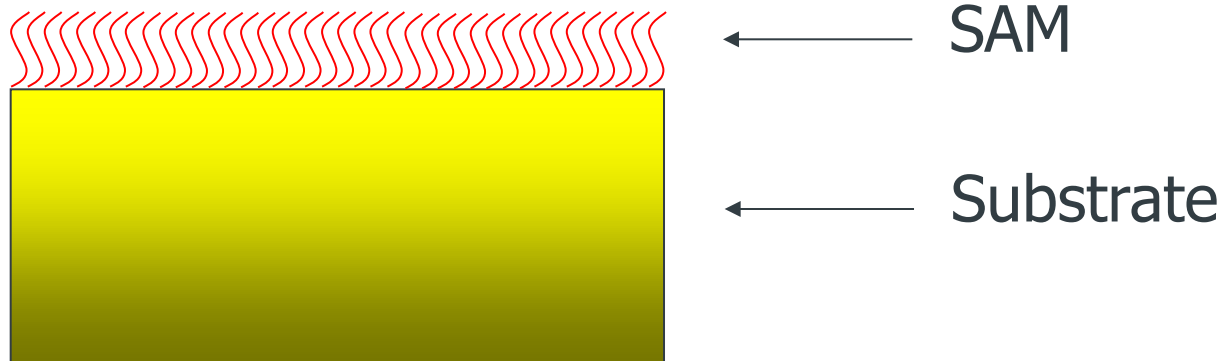
What is a block copolymer? Give two examples of block copolymers and discuss their self-assembly properties.

Give examples of DNA self-assembly.

Discuss strategies of nanoparticle self assembly and their applications

What is SAMs ? Discuss examples and applications.

“Self-Assembled Monolayers” (SAMs): organic molecules that are deposited from solution onto a substrate with a thickness of a single molecule and a well-defined orientation.

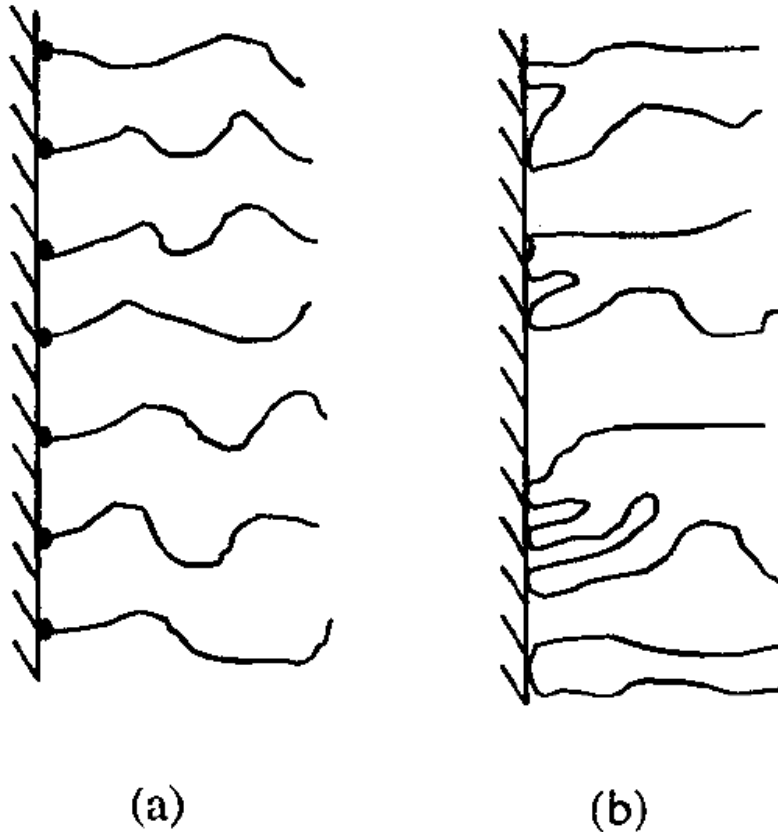


The pattern of SAMs on a surface can be controlled by changing the structural characteristics of the organic molecules. SAMs are employed to several applications. An example is their use as anti-stiction coatings in micro-devices.

In situations where two surfaces with areas below the micrometer range come into close proximity they may adhere together. At this scale, forces become significant. The phenomenon of two such surfaces being adhered together in this manner is called stiction. Stiction may be related to hydrogen bonding or residual contamination. SAMs are used to protect the microparts of the devices coming together.

Name two ways that a surfactant can interact with the nanoparticle surface

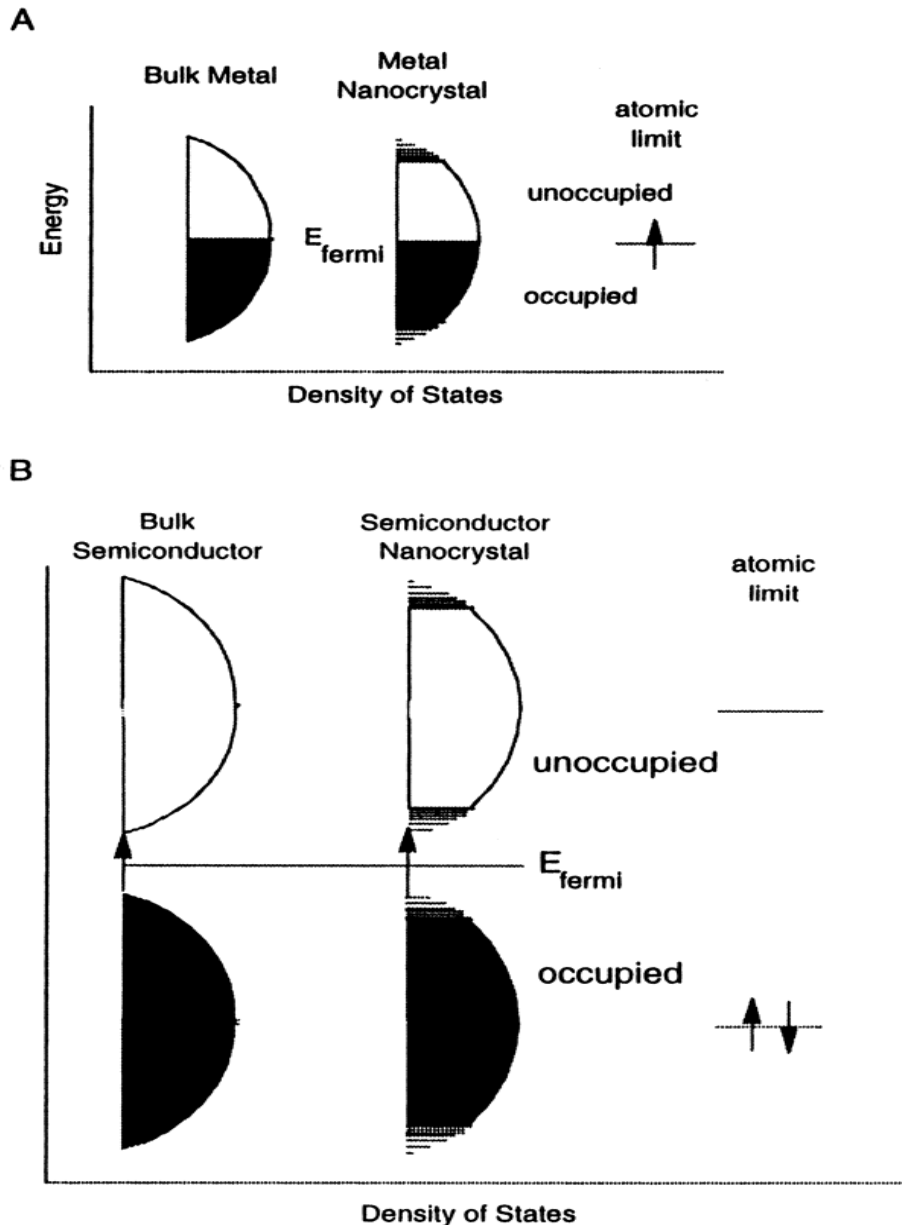
Answer:



- a) Chemisorption – An anchored ligand which covalently binds to the surface of the nanoparticle (i.e. a thiol–gold bond or a amine–silver bond)
- b) Adsorption– the ligand is adsorb at the surface of the nanocrystal (i.e. hydrophobic, van der Waals interactions)

**What is the difference between metal and semiconductor nanoparticles?
Draw a graph and explain.**

Answer:



In any material, there will be a size below which there is substantial variation of fundamental electrical and optical properties with size, which will be seen when the energy level spacing exceeds the temperature. For a given temperature, this occurs at a very large size in semiconductors, as compared to metals. This can be understood by considering that the bands of a solid are centered about atomic energy levels, with the width of the band related to the strength of the nearest neighbor interactions. As a function of increasing size, the center of a band develops first and the edges develop last. Thus, in metals, where the Fermi level lies in the center of a band, the relevant energy level spacing is still very small, and at temperatures above a few kelvin, the electrical and optical properties more closely resemble those of a continuum, even in relatively small sizes (tens or hundreds of atoms). In semiconductors, however, the Fermi level lies between two bands, so that the edges of the bands dominate the low-energy optical and electrical behavior. Optical excitations across the gap depend strongly on the size, even for crystallites as large as 10 000 atoms.