Nanotechnology

2nd lecture

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Hello!
I now hold this lecture for the forth time.

My way of giving lectures will be shaped by YOUR feedback.

Please do tell me
* what you like
* what you don´t like
* if it is too superficial
* if it is too detailed
* if you like that I present the text, too, on the powerpoint slides
  (I do this because some of you might know written English better than spoken English, and you could always read what I mean)
* any other points of interest.

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Last time we had:

- **Introduction to Nanotechnology**
- **Part A Nanostructures, Micro/Nanofabrication, and Micro/Nanodevices**
  - **2. Nanomaterials Synthesis and Applications: Molecule-Based Devices.**
    - **2.1. *Chemical Approaches to Nanostructured Materials***
      - From Molecular Building Blocks to Nanostructures

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Plan for today:

Nanoscaled Biomolecules: Nucleic Acids and Proteins
Chemical Synthesis of Artificial Nanostructures
From Structural Control to Designed Properties and Functions

2.2. Molecular Switches and Logic Gates

From Macroscopic to Molecular Switches
Digital Processing and Molecular Logic Gates
Molecular AND, NOT, and OR Gates
Combinational Logic at the Molecular Level
Intermolecular Communication

2.3. Solid State Devices

From Functional Solutions to Electroactive and Photoactive Solids
Langmuir–Blodgett Films
Self-Assembled Monolayers
Nanogaps and Nanowires

2.4. Conclusions and Outlook

Chemical approaches to nanostructured materials

- The **top-down** approach to engineered building blocks is extremely **powerfu**l and can deliver effectively and reproducibly microscaled objects.
- This strategy becomes increasingly **challenging, however**, as the dimensions of the target structures approach the **nanoscale**.

From molecular building blocks to nanostructures

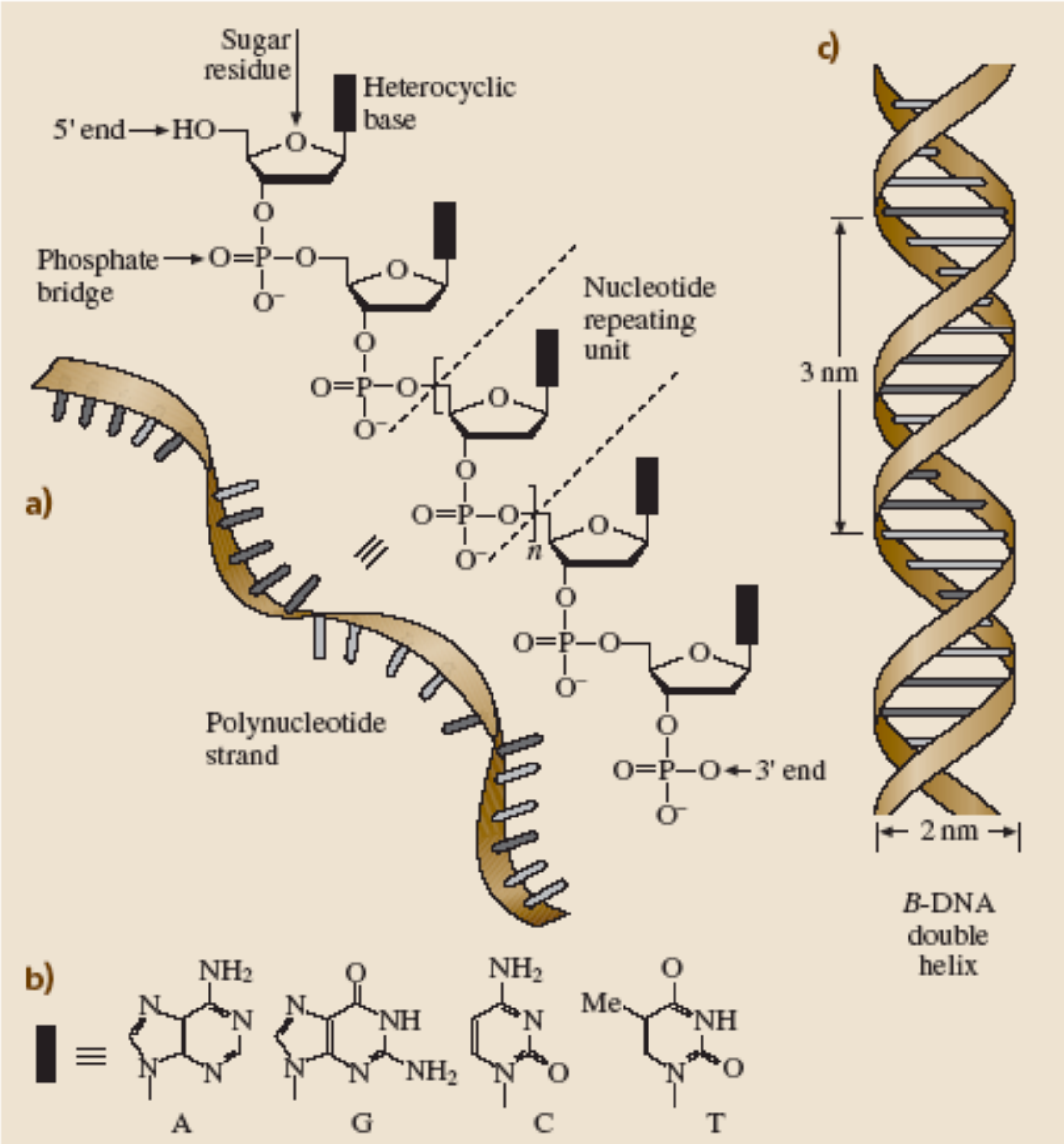
- **Nature** efficiently builds **nanostructures** by relying on **chemical approaches**.
- Tiny molecular **building blocks** are assembled with a remarkable degree of structural control in a variety of nanoscaled materials with defined **shapes, properties, and functions**.

Nanoscaled biomolecules: nucleic acids (1)

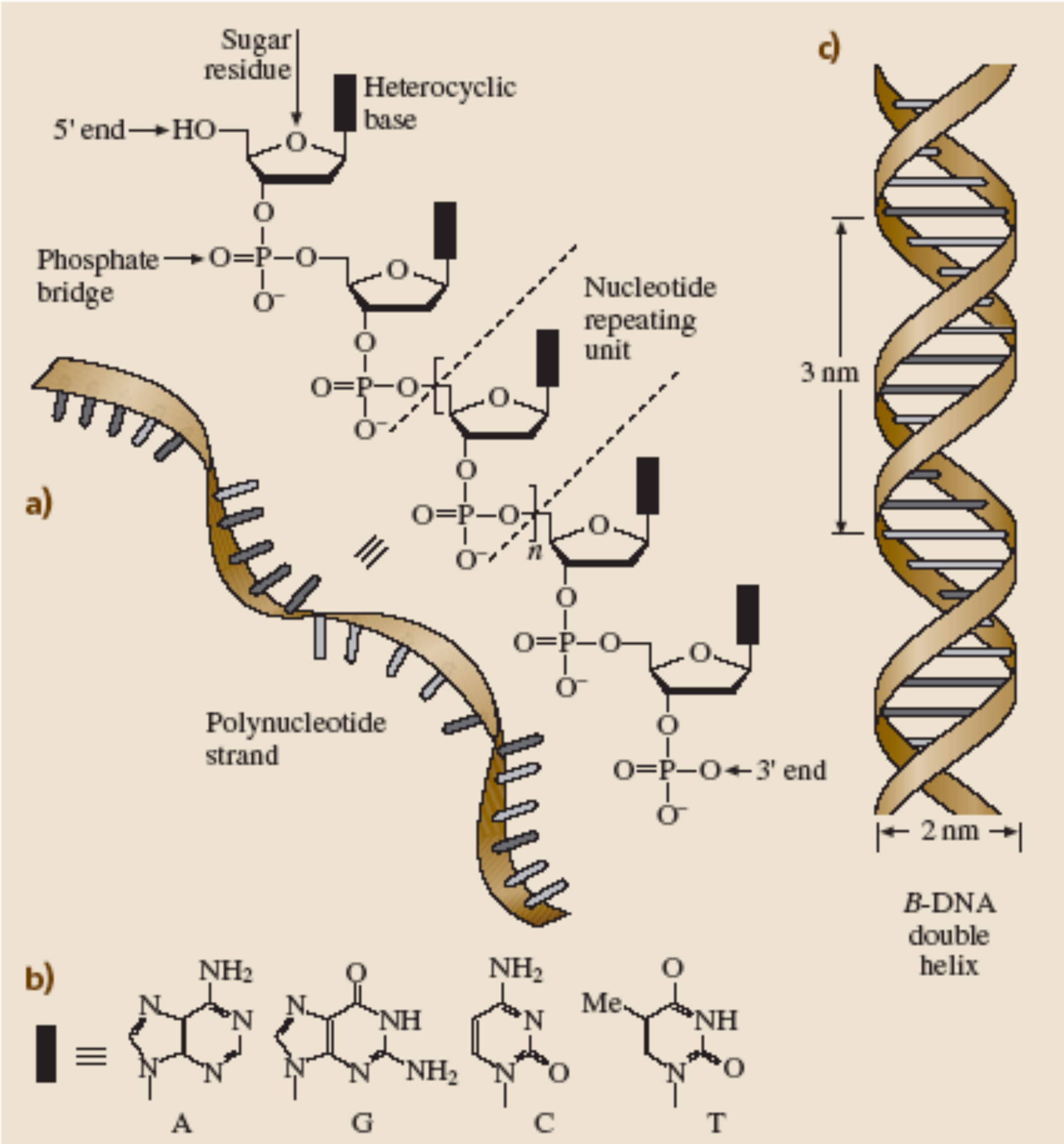
- Nanoscaled macromolecules play a fundamental role in **biological processes**.
- **Nucleic acids** ensure the transmission and expression of genetic information.
- Nature can build a huge number of closely related nanostructures relying only on **4 building blocks** (A, C, T, G).

Nanoscaled biomolecules: nucleic acids (2)

- e.g.: 100 nucleotide repeating units →
- 4^{100} polynucleotide sequences possible
- **Precise structural control @ the nanometer level**



A polynucleotide strand (a) incorporates alternate phosphate and sugar residues joined by covalent bonds. Each sugar carries one of four heterocyclic bases.



(b) noncovalent interactions between complementary bases in two independent polynucleotide strands encourage the formation of nanoscaled double helices (c).

Nanoscaled biomolecules: proteins (1)

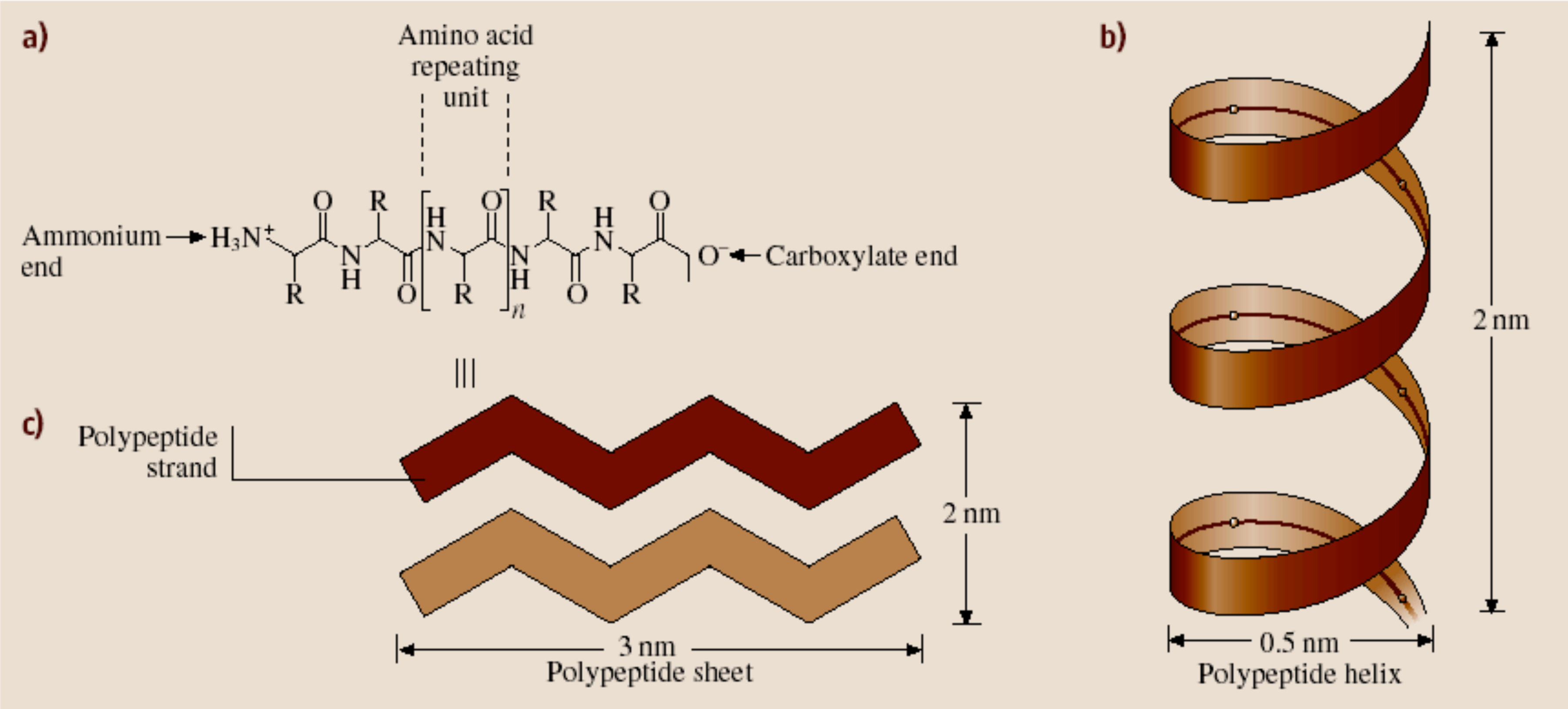
- **Proteins** are also built joining simple molecular **building blocks**, the **amino acids**, by strong covalent bonds.
- 20 different amino acids, backbone of robust [C-N] and [C-C] bonds.
- Genetic code.

Nanoscaled biomolecules: proteins (2)

- e.g.: polymer with 100 amino acids →
- 20^{100} polypeptide sequences possible
- Nature can assemble an enormous number of different biomolecules relying on the same fabrication strategy and a relatively small number of building blocks.

Nanoscaled biomolecules: proteins (3)

- Secondary and tertiary structure of the protein
- α–helices: tubular nanostructures, 0.5nm wide, 2nm long
- β–sheets: 2 to 15 parallel or antiparallel polypeptide chains form nanoscaled sheets, average dimension $3*2nm^2$



A polypeptide strand (**a**) incorporates amino acid residues differing in their side chains and joined by covalent bonds. Hydrogen bonding interactions curl a single polypeptide strand into a helical arrangement (α-helix) (**b**) or lock pairs of strands into nanoscaled sheets (β-sheets) (**c**).

Chemical synthesis of artificial nanostructures (1/3)

- Modern **chemical synthesis** has evolved considerably over the past few decades.
- Experimental procedures to join molecular components with **structural control at the picometer level** are available.

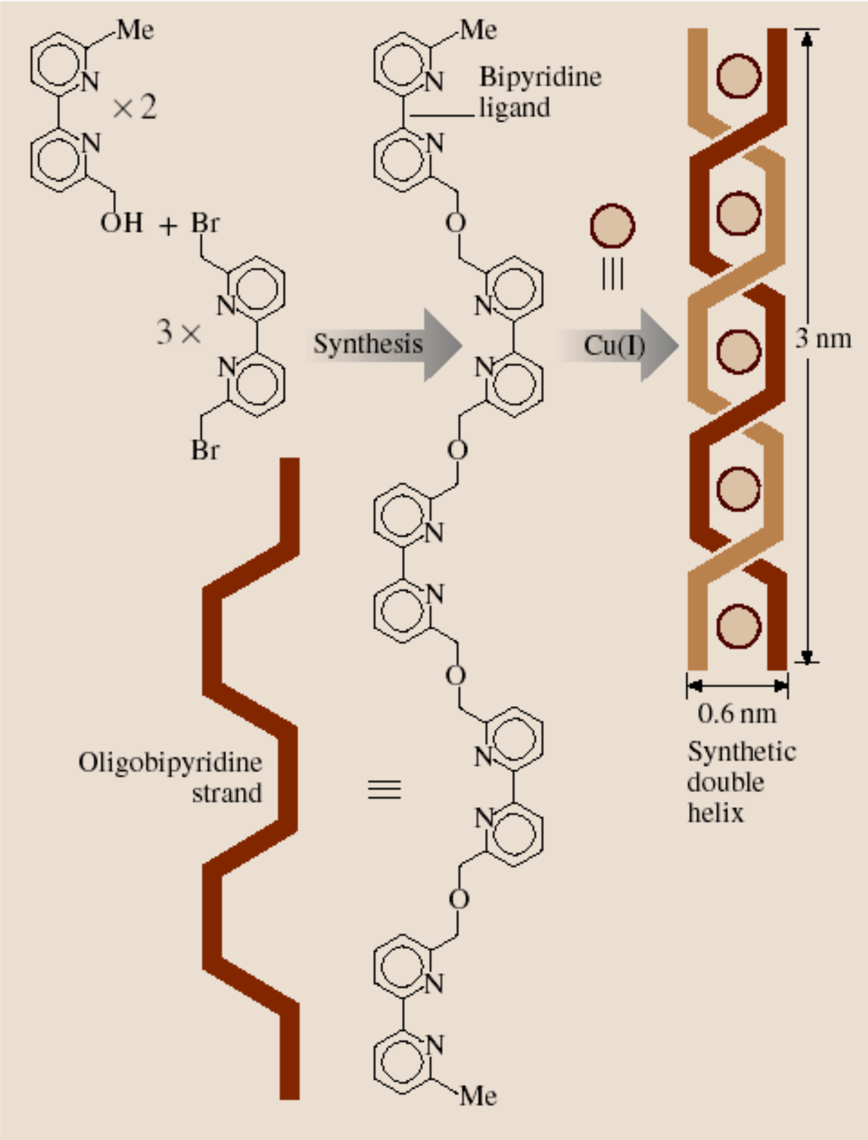
Chemical synthesis of artificial nanostructures (2/3)

Furthermore, the tremendous progress of **crystallographic and spectroscopic techniques** has provided efficient and reliable tools to **probe** directly the **structural features** of artificial inorganic and organic compounds.

Chemical synthesis of artificial nanostructures (3/3)

- Mimicking Nature: **bipyridines** as small building blocks, covalent bonds, secondary structure via noncovalent actions – **double helical arrangement**, wrapping around Cu centers.

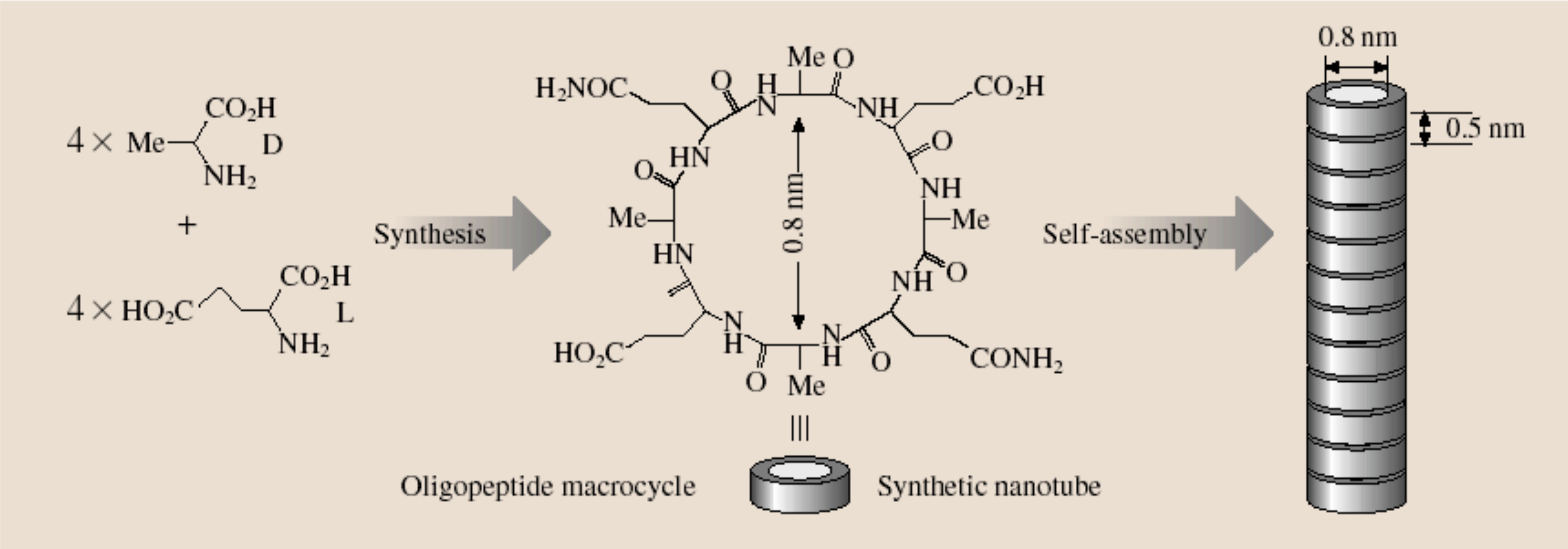
- diameter 0.6nm, length 3nm.



An oligobipyridine strand can be synthesized joining five bipyridine subunits by covalent bonds. The tetrahedral coordination of pairs of bipyridine ligands by Cu(I) ions encourages the assembly of two oligobipyridine strands into a **double helical arrangement**.

Chemical synthesis of artificial nanostructures (4)

- Mimicking Nature: using **amino acids** as the small building blocks → make „macrocycles“ with a covalent backbone.
- Result: **nanotube** with 0.8nm inner diameter, walls maintained in position via 8 hydrogen bonds per macrocycle.



Cyclic oligopeptides can be synthesized joining eight amino acid residues by covalent bonds. The resulting macrocycles self-assemble into nanoscaled tube-like arrays.

Chemical synthesis of certain structures is nice, but what about their function? Can we control this?

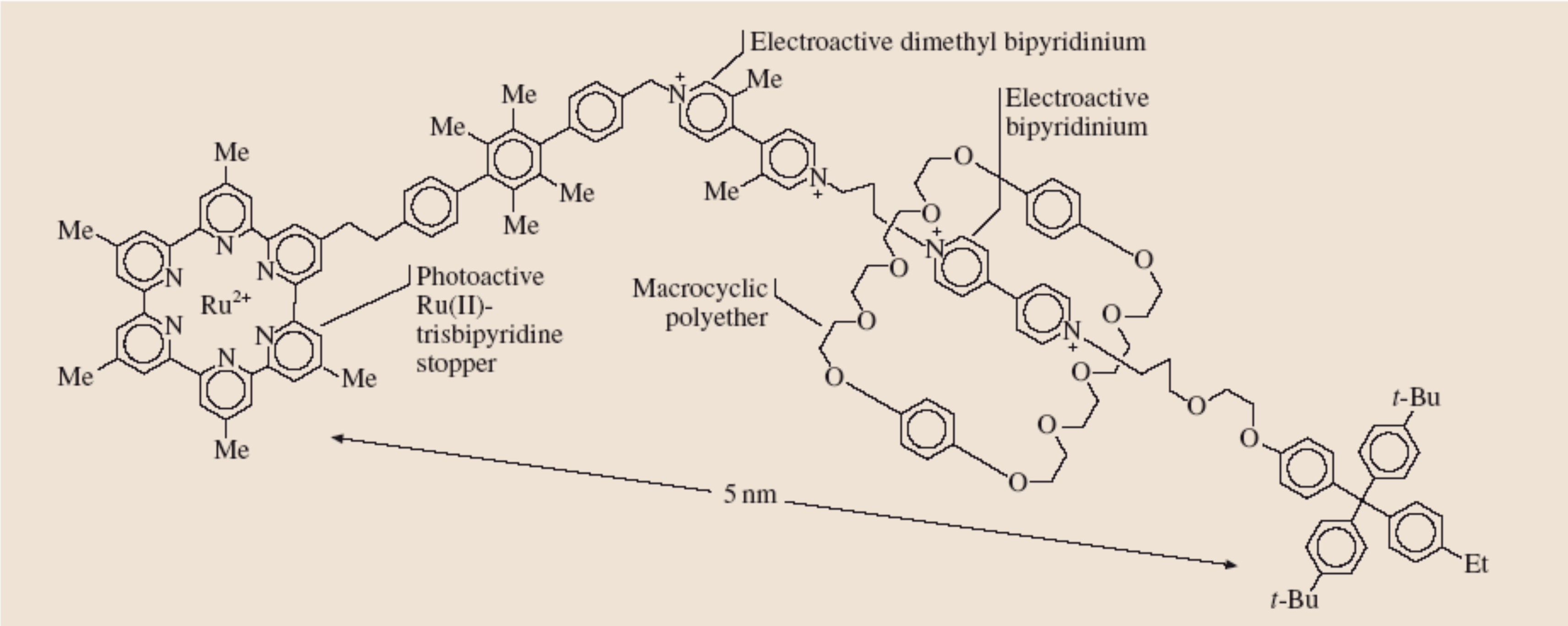
From structural control to designed properties and functions

- The high degree of structural control is accompanied by the possibility of **designing specific properties into the target nanostructures**.
- **Creating functional machines!** Electroactive, photoactive.

From structural control to designed properties and functions

- Studies show: organic and inorganic compounds can exchange electrons with macroscopic electrodes. It is possible to tune the absorption and emission of photons at a molecular level.
- → **Engineer** chromophoric and fluorophoric functional **groups with defined absorption and emission properties**!

From structural control to designed properties and functions: the molecular motor



From structural control to designed properties and functions: the molecular motor

- Material: [2]rotaxane, synthesis requires 12 synthetic steps
- electrocactive unit
- Light-induced start of shuttle → shuttle walks along chain. Shuttle walks back after diffusion of the molecular oxygen in the solution.

Molecular switches and logic gates

Logic gates

- A logic gate is the elementary building block of a digital circuit. Most logic gates have two inputs and one output.
- Using combinations of logic gates, complex operations can be performed.
- A digital integrated circuit consists of an array of logic gates

From macroscopic to molecular switches (1)

- The **major challenge** in the quest for nanoswitches, is the **identification of reliable design criteria and operating principles** for these innovative and fascinating devices.
- Certain **organic molecules adjust** their structural and electronic **properties when stimulated** with chemical, electrical, or optical inputs.

From macroscopic to molecular switches (2)

- Overall, these nanostructures **transduce input stimulations into detectable outputs** and, appropriately, are called **molecular switches**.
- The chemical system returns to the original state when the input signal is turned off.
- The output of a molecular switch can be a chemical, electrical, and/or optical signal that varies in intensity with the interconversion process.

Digital processing and molecular logic gates

- The three basic **AND, NOT, and OR** operators combine binary inputs into binary outputs following precise logic protocols.
- NOT operator: 0→1, 1→0 (inverter)
- OR operator: (1,1)→1, (0,1)→1, (1,0)→1, (0,0)→0
- AND operator: (1,1)→1, (0,1)→0, (1,0)→0, (0,0)→0

Digital processing and molecular logic gates

- The output of one gate can be connected to one of the inputs of another operator.
- **NAND** gate: connecting the output of an AND gate with the input of a NOT gate
- **NOR** gate: connecting the output of an OR gate with the input of a NOT gate.
- The NAND and NOR operations are termed universal functions because any conceivable logic operation can be implemented relying only on one of these two gates

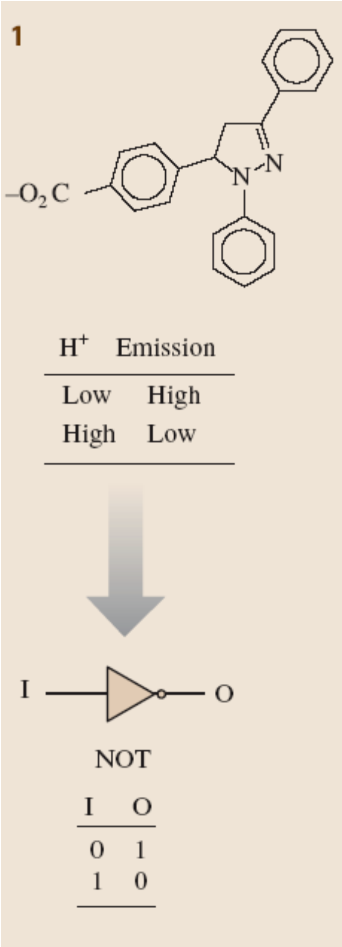
Digital processing and molecular logic gates

- The logic gates of conventional microprocessors are assembled interconnecting transistors, and their input and output signals are electrical.
- But the concepts of binary logic can be extended to chemical, mechanical, optical, pneumatic, or any other type of signal.

Digital processing and molecular logic gates

AND, NOT and OR operations can be reproduced **with fluorescent molecules**, in which the flurescence quantum yield depends on the concentration of (an) certain ion(s).

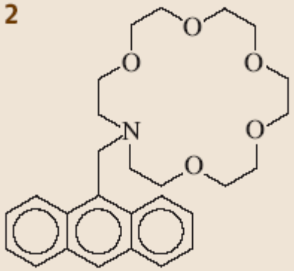
Molecular **NOT** gate



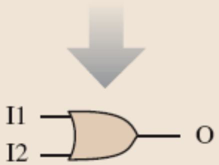
The fluorescence intensity of this pyrazoline derivative is high when the concentration of H^+ is low, and vice versa.

Molecular **OR** gate

2



Na^+	K^+	Emission
Low	Low	Low
Low	High	High
High	Low	High
High	High	High



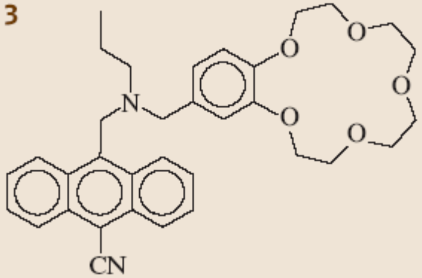
OR

I1	I2	O
0	0	0
0	1	1
1	0	1
1	1	1

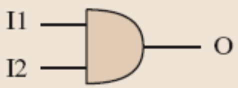
The fluorescence intensity of this anthracene derivative is high when the concentration of Na^+ and/or K^+ is high. The emission is low when both concentrations are low.

Molecular **AND** gate

3



H^+	Na^+	Emission
Low	Low	Low
Low	High	Low
High	Low	Low
High	High	High



AND

I1	I2	O
0	0	0
0	1	0
1	0	0
1	1	1

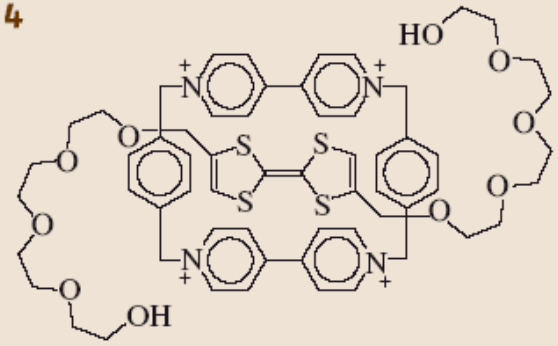
The fluorescence intensity of the anthracene is high only when the concentrations of H^+ and Na^+ are high. The emission is low in the other three cases.

Combinatorial logic at the molecular level

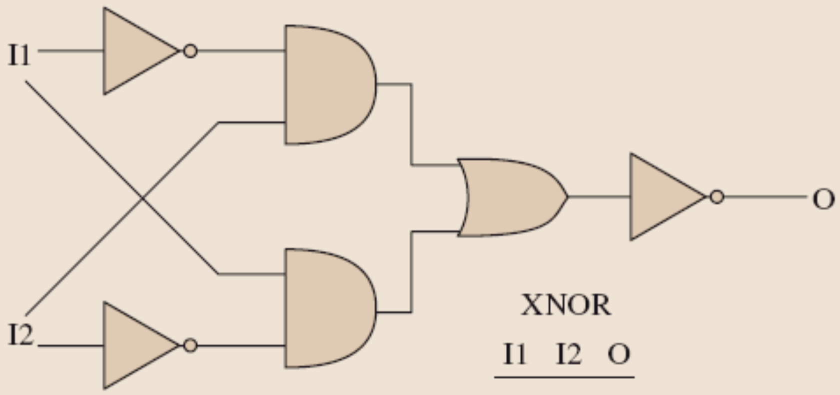
- The molecular AND, NOT, and OR gates have stimulated the design of related chemical systems able to execute the three basic logic operations and simple combinations of them.
- The implementation of logic operations at the molecular level is not limited to the use of chemical inputs. For example, electrical signals and reversible redox processes can be exploited to modulate the output of a molecular switch.

XNOR gate

4



TTF	BIPY	Absorbance
Low	Low	High
Low	High	Low
High	Low	Low
High	High	High



XNOR

I1	I2	O
0	0	1
0	1	0
1	0	0
1	1	1

The charge-transfer absorbance of this complex is high when the voltage input addressing the tetrathiafulvalene (TTF) unit is low and that stimulating the bipyridinium (BIPY) units is high and vice versa. If a positive logic convention is applied to the TTF input and to the absorbance output (low = 0, high = 1) while a negative logic convention is applied to the BIPY input (low = 0, high = 1), the signal transduction translates into the truth table of a XNOR circuit.

Intermolecular communication

The logic function of a given circuit can be adjusted altering the number and type of basic gates and their interconnection protocol.

Intermolecular communication

- However, the connection of the input and output terminals of independent molecular AND, NOT, and OR operators would offer the **possibility of assembling any combinational logic circuit from three basic building blocks**.
- **Modular approach** → very powerful.
- **Problem: which wires to use**.

Solid state devices

From functional solutions to electro-active and photoactive solids

- The **molecular switches**, as presented before, are operated exclusively in solution and remain **far from potential applications** in information technology at this stage.
- The **integration of liquid components** and volatile organic solvents in practical digital devices is **hard to envisage**.

From functional solutions to electro-active and photoactive solids

- The development of miniaturized molecule-based devices requires the identification of methods to **transfer** the **switching mechanisms** developed in solution **to the solid state**.
- **Nanometer-thick organic films on** the surfaces of micro-scaled or nano-scaled **electrodes** are what we want to build.

From functional solutions to electro-active and photoactive solids

Two main approaches for the **deposition of organized molecular arrays on inorganic supports** have emerged so far:

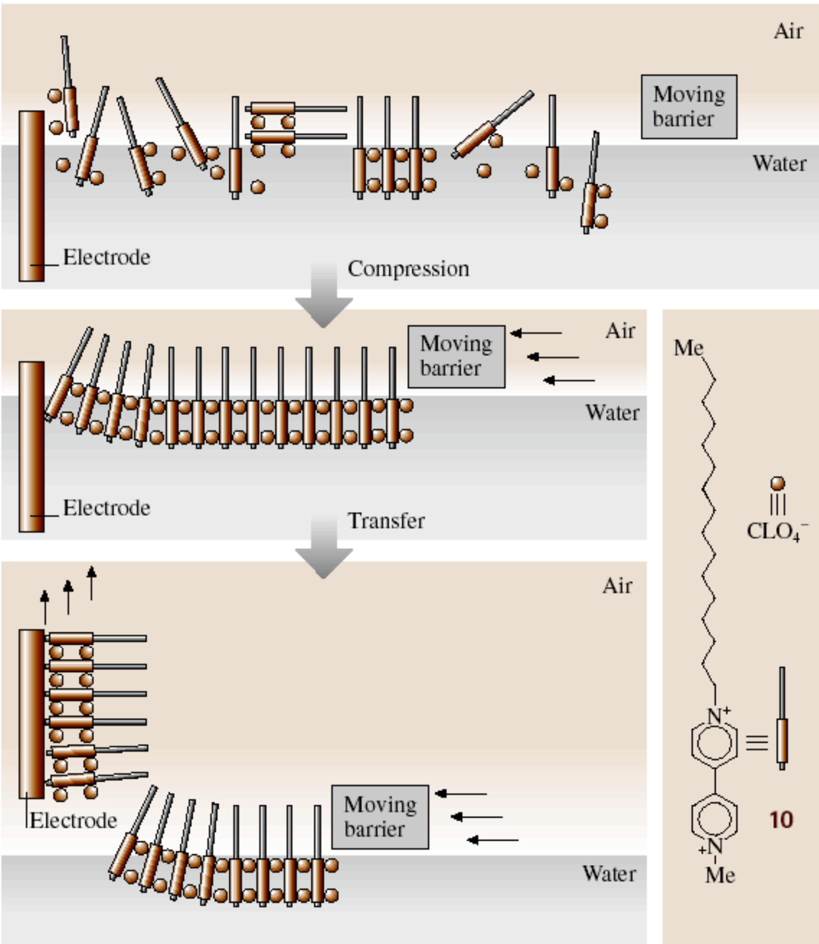
- In one instance, amphiphilic molecular building blocks are compressed into organized monolayers at air/water interfaces. The resulting films can be transferred on supporting solids employing the **Langmuir–Blodgett technique**.
- Alternatively, certain molecules can be designed to adsorb spontaneously on the surfaces of compatible solids from liquid or vapor phases. The result is the **self-assembly of organic layers** on inorganic supports.

Solid state devices

Langmuir–Blodgett Films

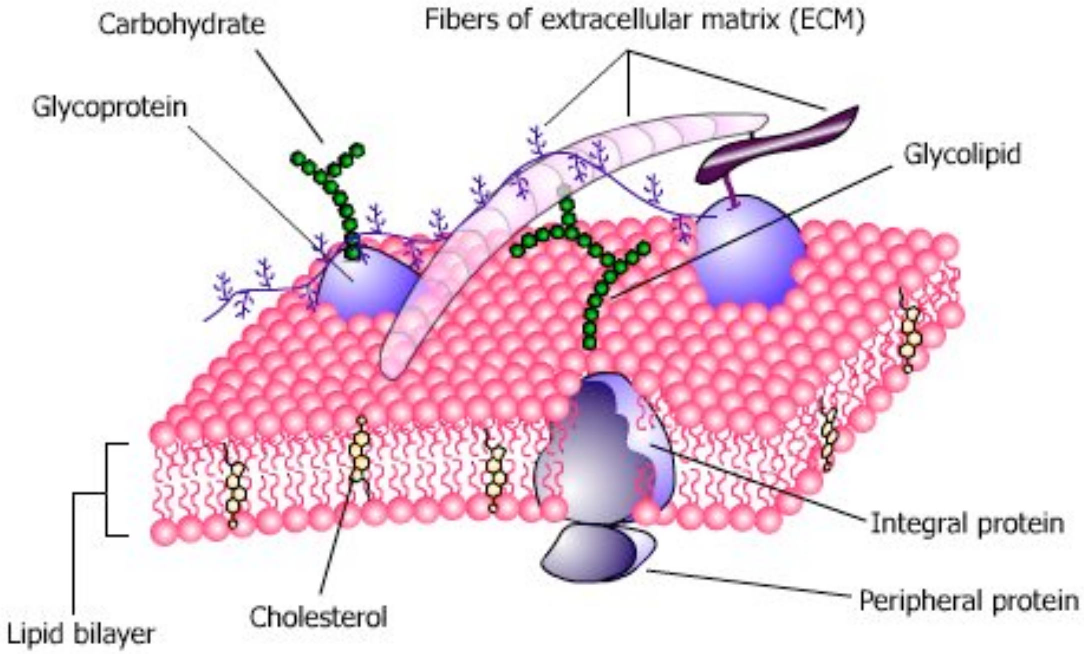
- A LB-film is a packed monolayer at the air/water interface.
- **Hydrophilic** (hydros = water; philic = loving) molecules dissolve well in water (a polar solvent), whereas **hydrophobic** (waterminding) molecules dissolve best in an apolar solvent.
- Molecules that consist of both a hydrophobic and a **hydrophilic** part are called **amphiphiles** (amphi = both) and are the building blocks for Langmuir–Blodgett Films.

Langmuir–Blodgett Films



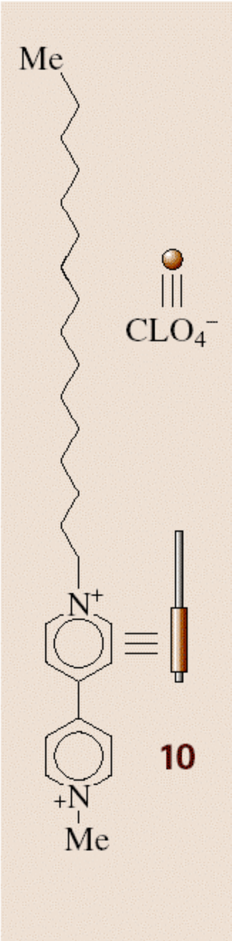
- The **compression** of the amphiphilic dication with a **moving barrier** results in the formation of a **packed monolayer** at the air/water interface.
- The **lifting of the electrode** pre-immersed in the aqueous subphase encourages the **transfer** of part of the monolayer **on the solid support electrodes.**

Inset: lipid bilayer of cells



- The lipid bilayer is the outer membrane of many biological cells.
- It is comprised of a special type of lipid. The membrane contains numerous proteins and sugars.

Amphiphile used for LB-films

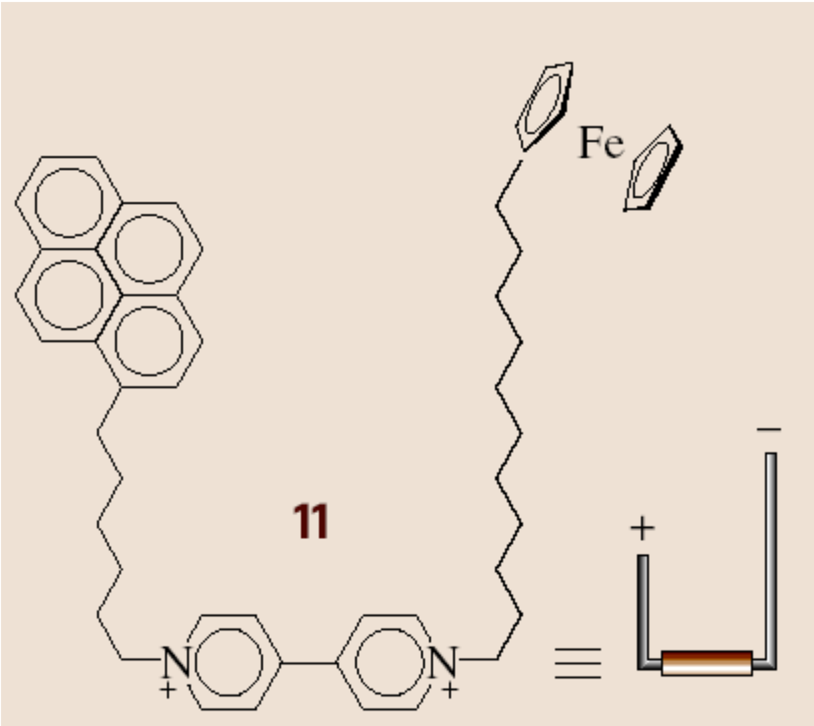


- This amphiphile has a hydrophobic hexadecyl tail (top) attached to a hydrophilic bipyridinium dication (bottom).
- It dissolves in chloroform and methanol.

Formation of an LB-Film

- **Disorganized amphiphiles** are floating on the water surface, after the organic solvent has evaporated.
- The molecular building blocks are **compressed** into a **monolayer** with the aid of a **moving barrier** and build an organized monolayer at the air/water interface.
- The **slow lifting** of the solid support drags the monolayer away from the aqueous subphase.
- The result is a surface coverage of ca. $\mathbf{4\times10^{10} mol*cm^{-2}}$, and a **molecular area** of ca.$\mathbf{40Å^{2.}}$
- This film can become the functional components of molecule-based devices.

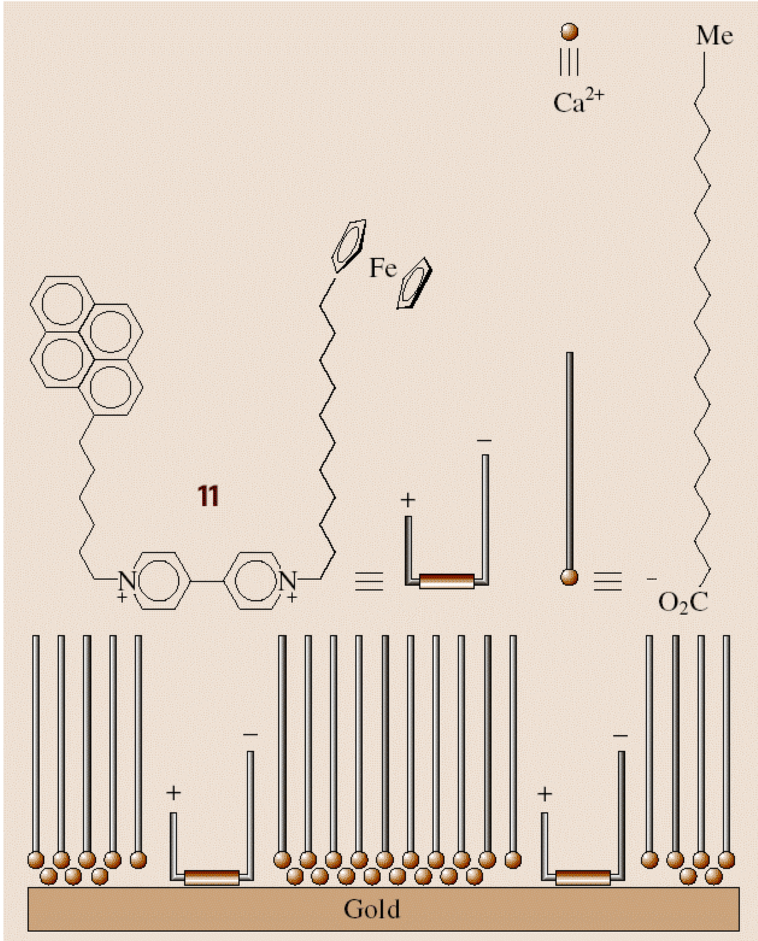
Building block of molecule based devices



This **electroactive and photoactive amphiphile** contains hydrophobic ferrocene and pyrene tails and a hydrophilic bipyridinium head.

LB-film of amphiphiles and arachidic acid

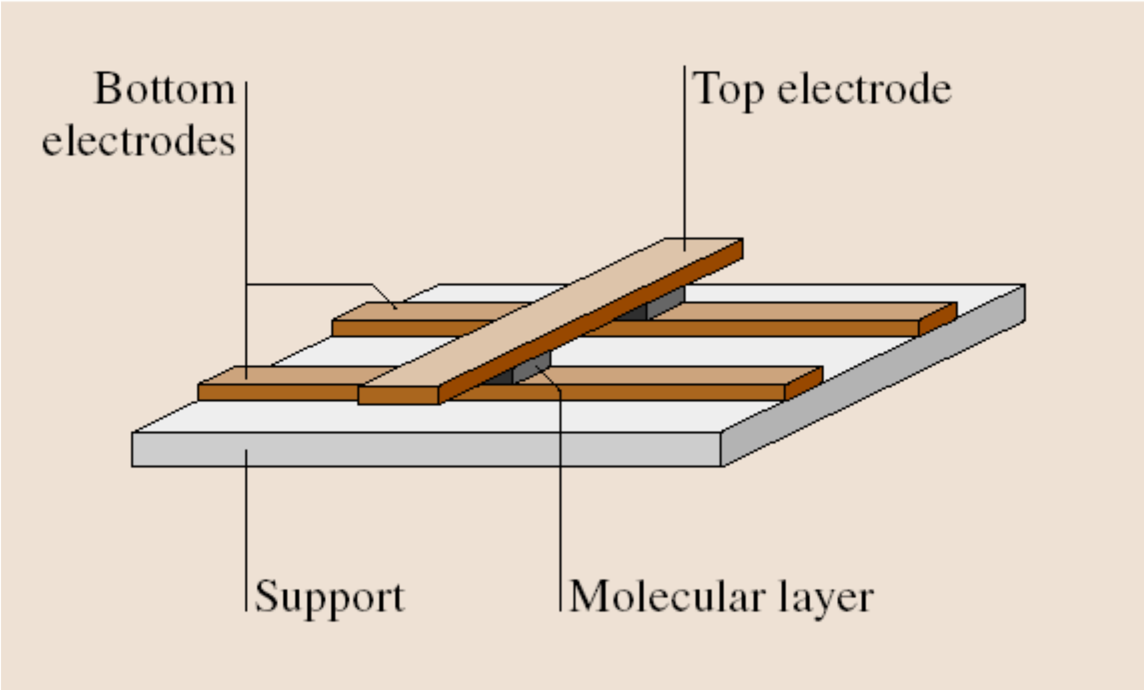
- A mixed monolayer of these **amphiphiles and arachidic acid**, which is transferred with the LB technique to the surface of a transparent **gold electrode**.
- The coated electrode can be integrated in a conventional **electrochemical cell**.



Fabricate molecule based devices

- A **unidirectional flow of electrons** across this monolayer/electrode junction is established **under the influence of light**.
- The ability to transfer electroactive monolayers from air/water interfaces to electrode surfaces can be exploited to fabricate molecule-based electronic devices.

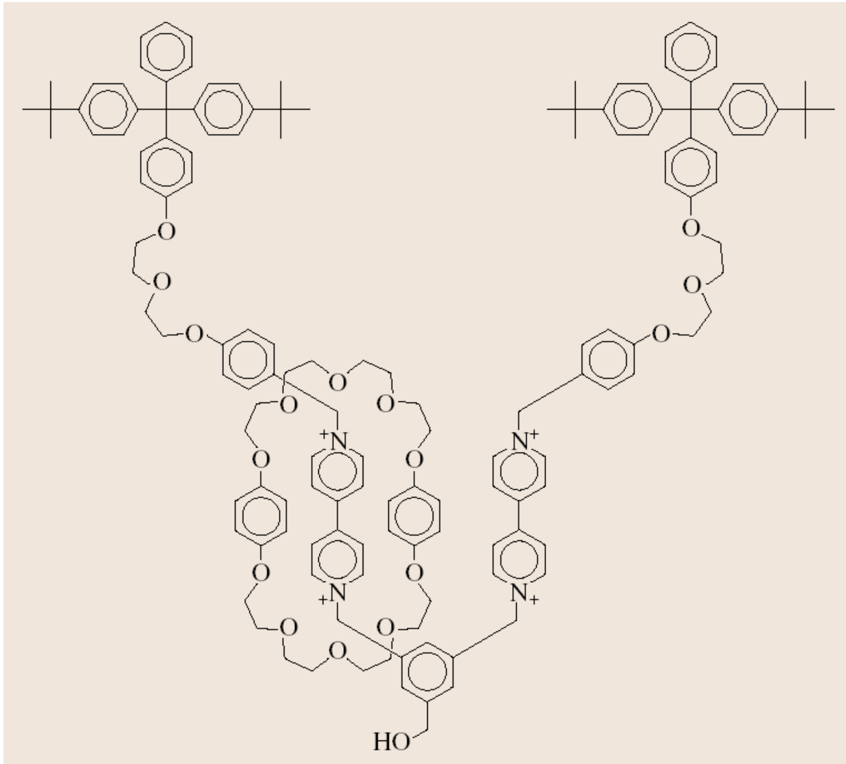
Electrode / molecular monolayer / electrode junction



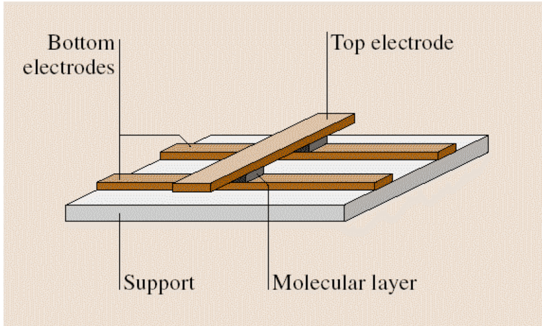
Arrays of interconnected **electrode / monolayer / electrode tunneling junctions** can be assembled combining the Langmuir–Blodgett technique with electron beam evaporation.

[2]rotaxane as building block

- Monolayers of the **[2]rotaxane** (**amphiphilic** character) are transferred with the LM-technique to aluminum / aluminum oxide electrodes of a patterned silicon chip.
- The **molecular area** is ca. **130Å^2**.
- The **current/voltage signature** of these electrode / monolayer / electrode junctions can be **recorded grounding the top electrode and scanning the potential of the bottom electrode**.



Characteristics of [2]rotaxane based device

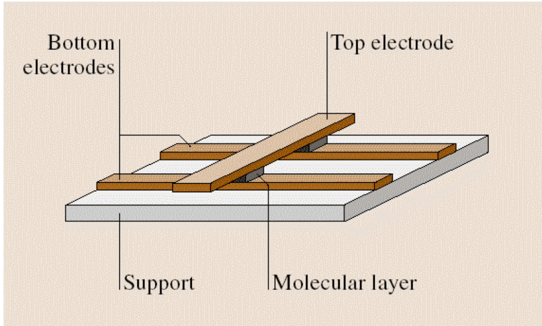


- If the applied **potential** is **below −0.7V**: bipyridinium-centered LUMOs mediate the **tunnelling** of electrons leads to a current enhancement.
- Also, modest increase in current when **potential above 0.7V** (**tunneling** due to participation of the phenoxy-centered HOMOs in the tunneling process.
- After a single **positive voltage pulse**, however, **no current** can be detected **anymore** if the potential is returned to negative values.
- This positive potential scan suppresses **irreversibly** the conducting ability of the electrode/molecule/electrode junction.

LUMOs, HOMOs

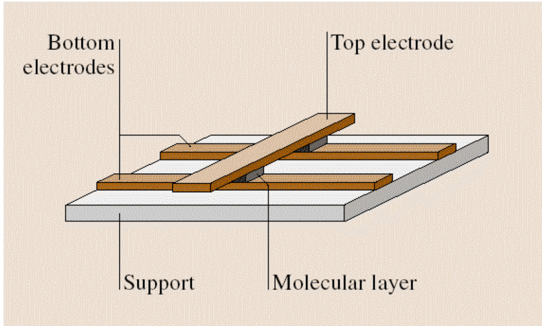
- HOMO and LUMO are acronyms for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively.
- The energy level difference of the two (HOMO-LUMO) can sometimes serve as a measure of the excitability of the molecule: the smaller the energy, the easier it will be excited.

Simple logic operations with the [2]rotaxane device



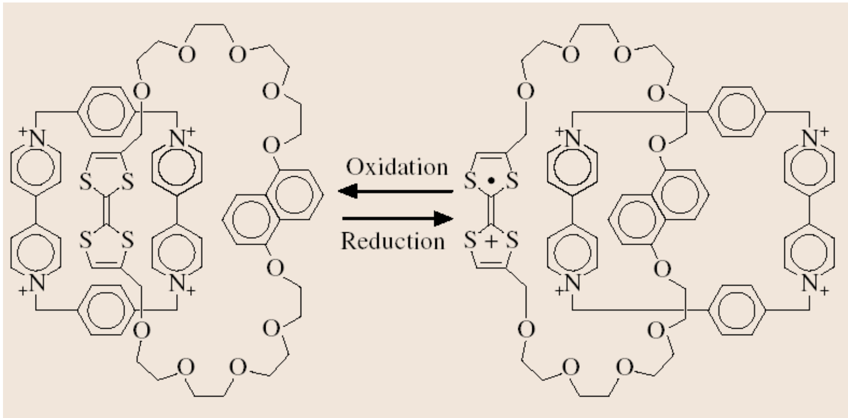
- The **two bottom electrodes** can be **stimulated** with voltage inputs while **measuring** a **current** output at the common top electrode.
- When at least one of the two inputs is high (0 V), the output is low (< 0.7nA). When both inputs are low (−2V), the output is high (ca. 4nA).

Simple logic operations with the [2]rotaxane device



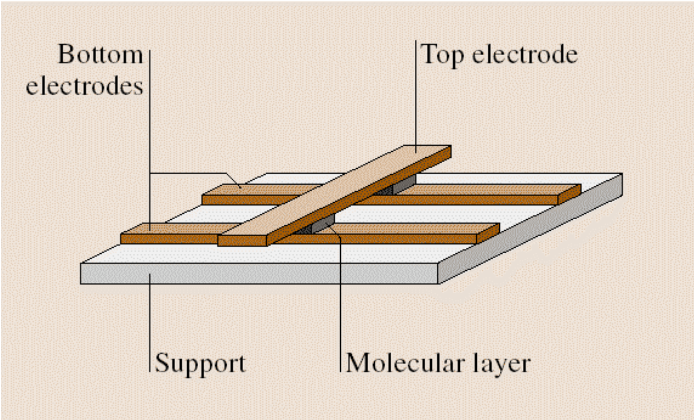
If a negative logic convention is applied to the voltage inputs (low = 1, high = 0) and a positive logic convention is applied to the current output (low = 0, high = 1), the signal transduction behaviour translates into the truth table of an **AND** gate.

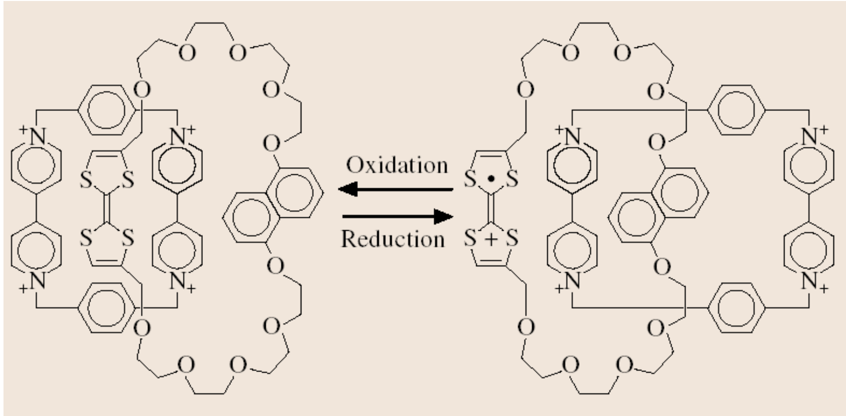
[2]catenane as building block



- Organic solutions of the hexafluorophosphate salt of this [2]catenane and six equivalents of the sodium salt of dimyristoylphosphatidic acid can be co-spread on the water surface of a Langmuir trough.
- The **molecular area** is ca. **125Å^2**.
- **Monolayers** are transferred to the surfaces of the bottom n-doped silicon/silicon dioxide electrodes of a patterned silicon chip.
- Subsequent assembly of a top titanium/aluminum electrode affords **electrode/monolayer/electrode arrays**.

Characteristics of [2]catenane based device



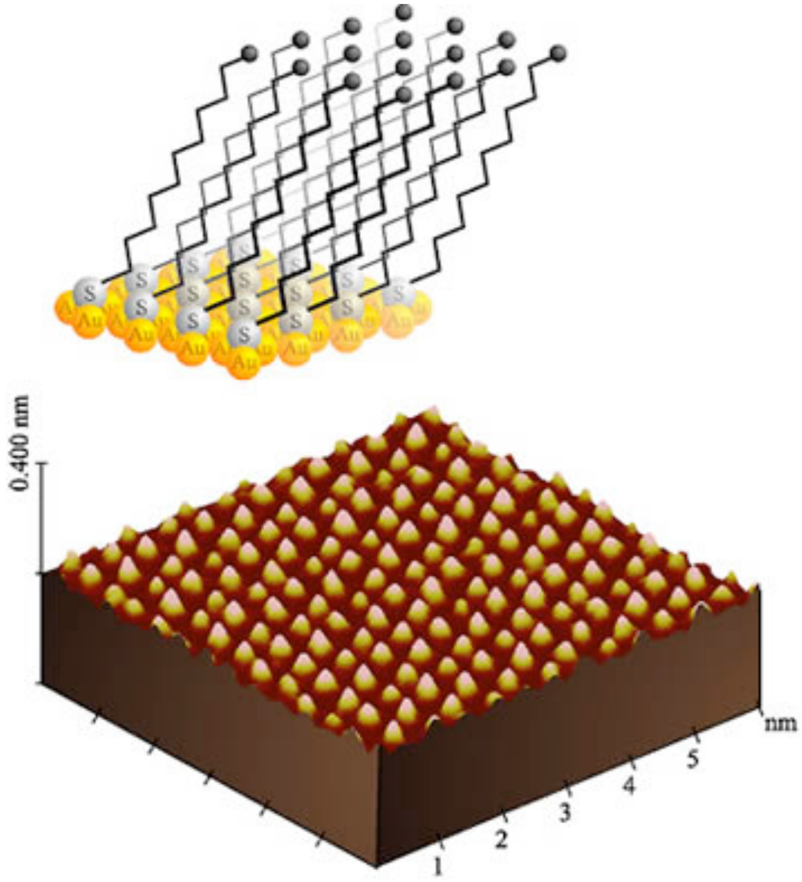


- Alternating positive and negative voltage pulses can **switch reversibly** the junction resistance between high and low values.
- This intriguing behavior is a result of the redox and dynamic properties of the [2]catenane.
- The voltage pulses applied to the bottom electrode of the electrode/monolayer/junction oxidize and reduce the tetrathiafulvalene unit inducing the interconversion between the oxidized and reduced forms.
- The difference in the stereoelectronic properties of these two states translates into **distinct current/voltage signatures**.

Solid state devices

Self-assembled monolayers

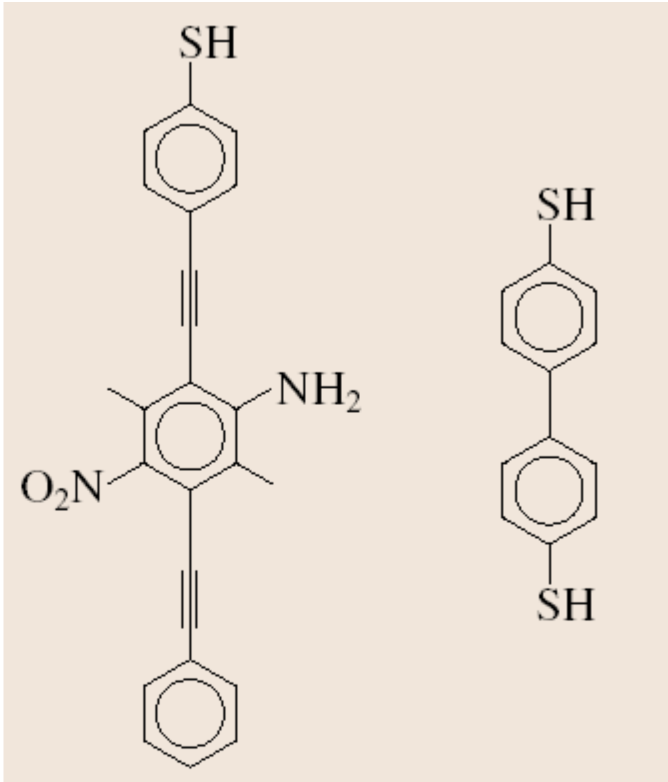
- LB-films are one way to produce molecular monolayers.
- An alternative strategy to coat electrodes with **molecular layers** relies on the ability of certain compounds to **adsorb spontaneously** on solid supports from liquid or vapor phases.



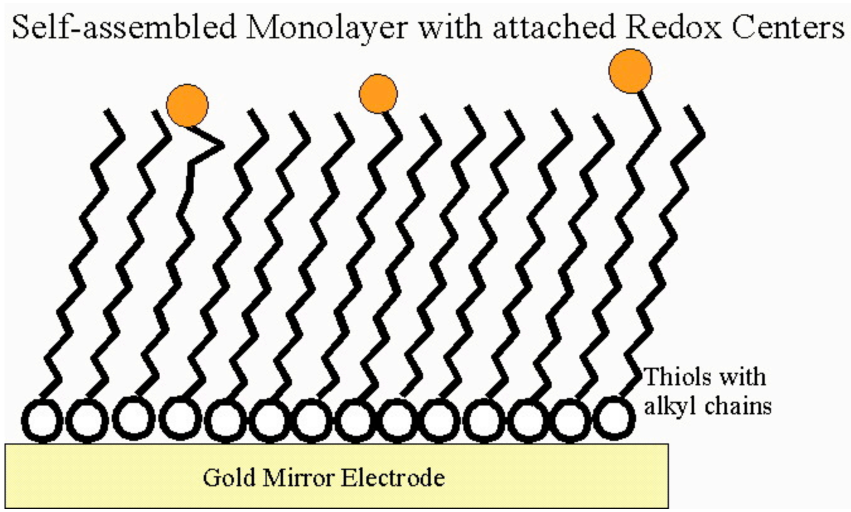
STMによるウンデカンチオール自己組織化単分子膜の観察

Thiols

- **Thiols** (formerly known as **mercaptans**) are compounds which contain the thiol group –SH attached to a carbon atom.



Self-assembled monolayers



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- The affinity of certain **sulfurated functional groups** for **gold** can be exploited to encourage the self-assembly of organic molecules on microscaled and nanoscaled electrodes.
- The thiol-gold bond is **believed to be a covalent bond**.

That´s it for today.

Plan for the next lecture

Hier noch was einfügen, sams und ??

3.1 Structure of Carbon Nanotubes

- 3.1.1 Single-Wall Nanotubes
- 3.1.2 Multiwall Nanotubes

3.2 Synthesis of Carbon Nanotubes

- 3.2.1 Solid Carbon Source-Based Production Techniques for Carbon Nanotubes
- 3.2.2 Gaseous Carbon Source-Based Production Techniques for Carbon Nanotubes
- 3.2.3 Miscellaneous Techniques
- 3.2.4 Synthesis of Aligned Carbon Nanotubes

3.3 Growth Mechanisms of Carbon Nanotubes

- 3.3.1 Catalyst-Free Growth
- 3.3.2 Catalytically Activated Growth