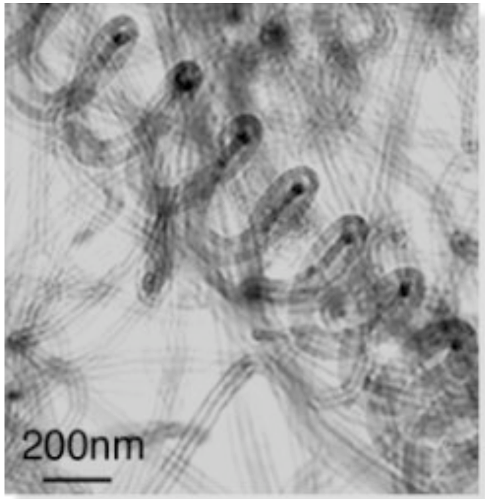
# Nanotechnology

3rd lecture

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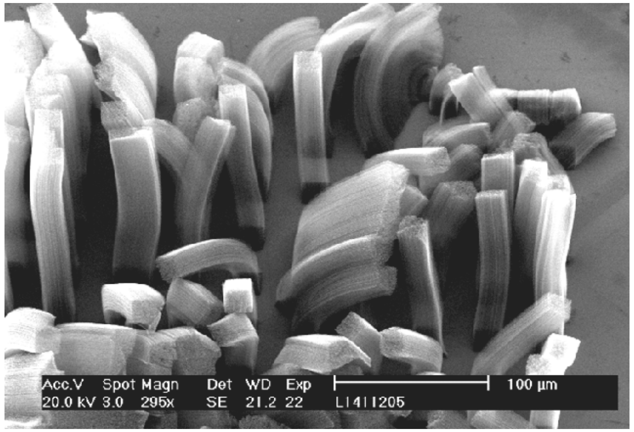
## Plan for today:

### *2.3. Solid State Devices*

Self-Assembled Monolayers

Nanogaps and Nanowires

### *2.4. Conclusions and Outlook*

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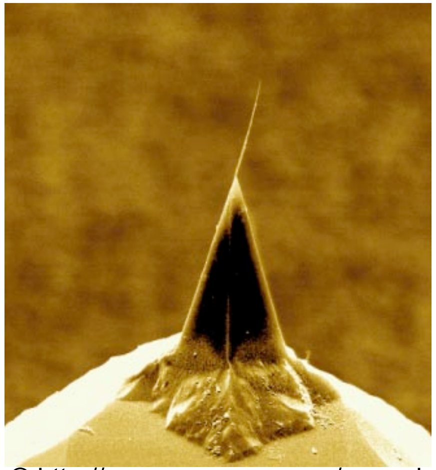

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### *3. Introduction to Carbon Nanotubes*

*3.1 Structure of Carbon Nanotubes*

*3.2 Synthesis of Carbon Nanotubes*

*3.3 Growth mechanisms of Carbon Nanotubes*

*3.4 Properties of Carbon Nanotubes*

*3.5 Carbon Nanotube based nano-objects*

*3.6 Applications of Carbon Nanotubes*

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## Last time we had:

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

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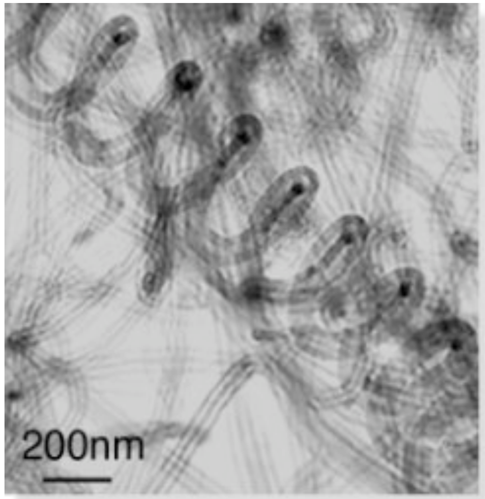


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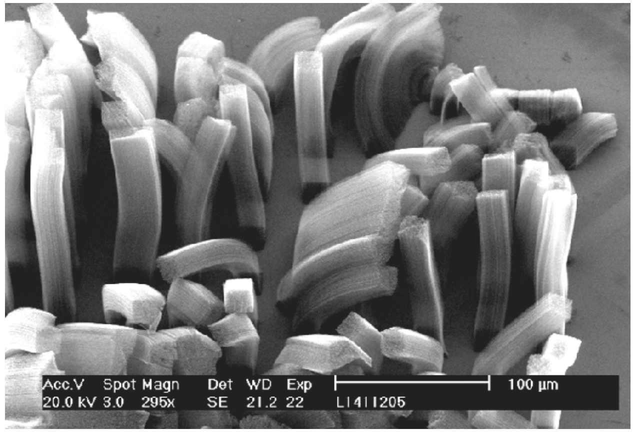


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## Plan for today:

***2.3. Solid State Devices***

Self-Assembled Monolayers

Nanogaps and Nanowires

***2.4. Conclusions and Outlook of the chapter Nanomaterials Synthesis and Applications: Molecule-Based Devices***

***3. Introduction to Carbon Nanotubes***

- ***3.1 Structure of Carbon Nanotubes***
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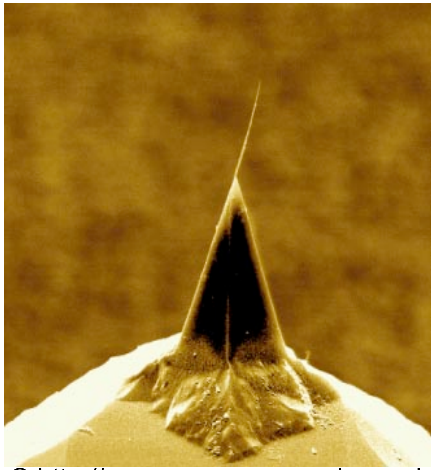

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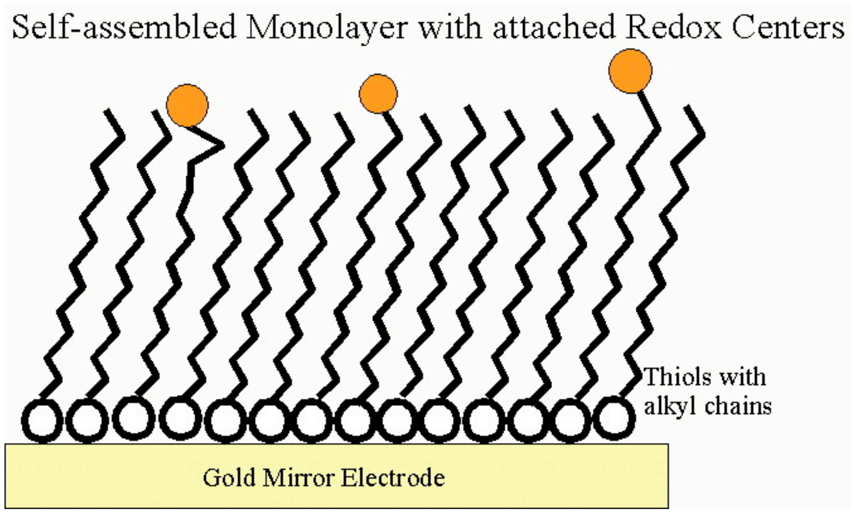
# Self-assembled monolayers

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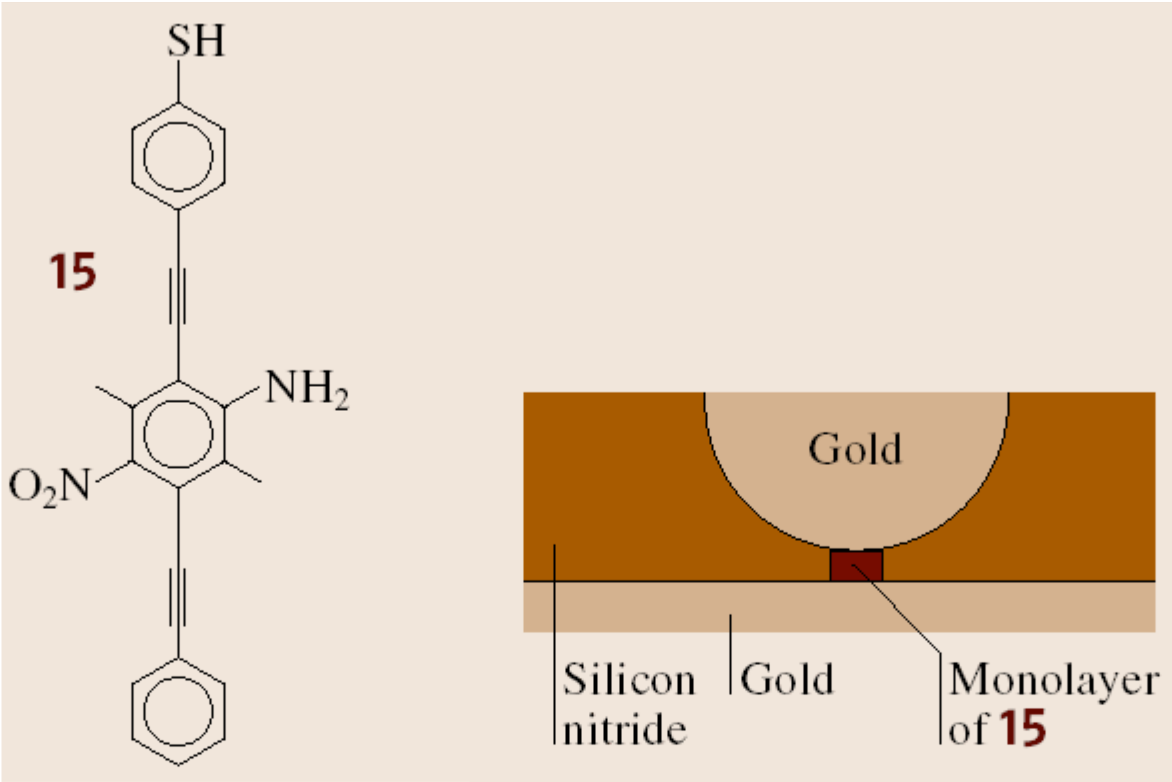
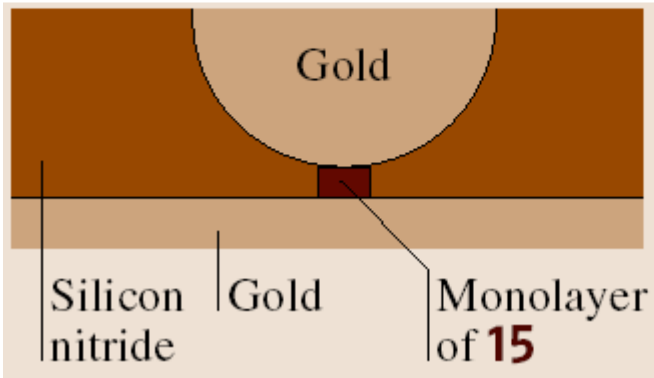
- The affinity of certain **sulfurated functional groups** for **gold** can be exploited to encourage the self-assembly of organic molecules on microscaled and nanoscaled electrodes.
- The thiol-gold bond is **believed to be a covalent bond**.

# Molecular device with self-assembled thiols

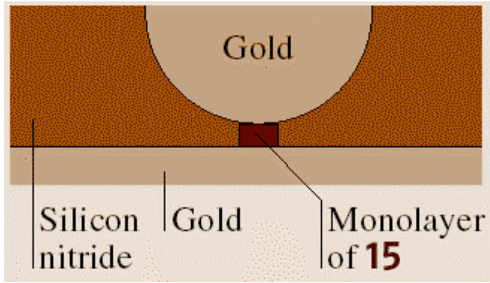


# Fabrication of this device with self-assembled thiols



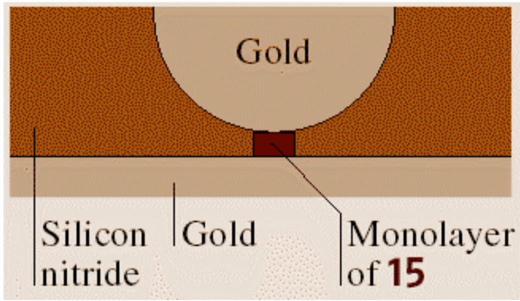

Take a silicon wafer, deposit 50nm silicon nitride by chemical vapour deposition, carve half sphere (diameter 30-50nm) with reactive ion etching, evaporate gold --> obtain bowl shaped electrode, etch silicon from other side, carve hole, immerse in solution of thiols, evaporate gold film.

# Properties of this molecular device




- The **contact area** is **less than 2000nm²** (approximately 1000 molecules)
- At the **application of voltage pulses** the **conductivity switches reversibly** between low and high values:
  - 30pA when 0.25V applied
  - if short voltage pulse of 5V is applied --> 150pA at 0.25V
- The **high conducting state** is **memorized** by the molecule-based device, and it is retained for more than 15min.
- The **low conducting mode is restored** after these 15 minutes **or stimulated** with a voltage pulse of −5 V.

# Properties of this molecular device

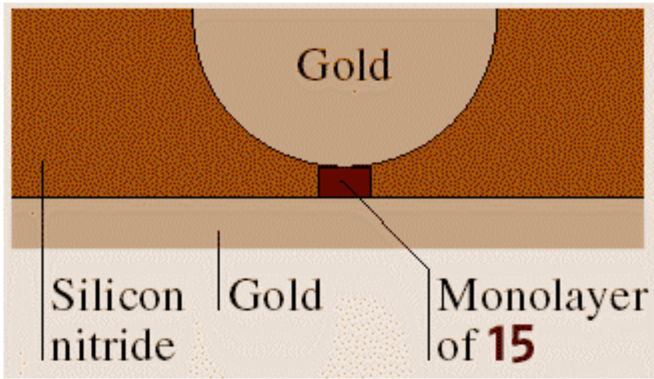



- The current output switches from a low to a high value, if a high voltage input is applied. It switches from a high to a low value, under the influence of a low voltage pulse.
- This behaviour offers the opportunity to **store and erase binary data** in analogy to a conventional **random access memory** (RAM) !
- A binary 1 can be stored in the molecule-based device applying a high voltage input, and it can be erased applying a low voltage input.

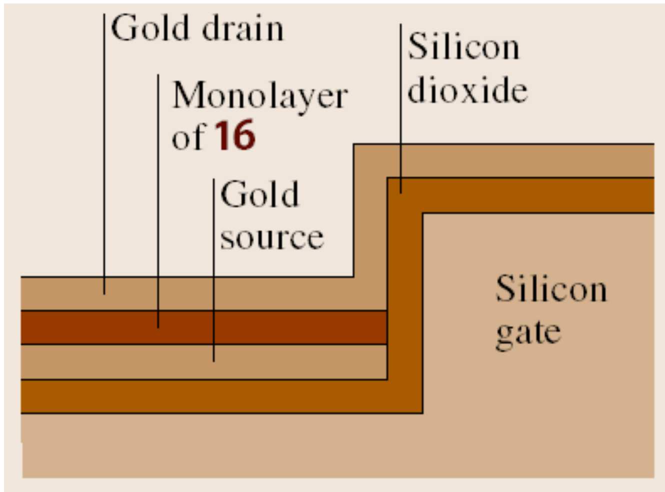
# RAM

- **Random access memory** (RAM) is the best known form of computer memory. RAM is considered "random access" because you can access any memory cell directly if you know the row and column that intersect at that cell.
- The opposite of RAM is **serial access memory** (SAM).

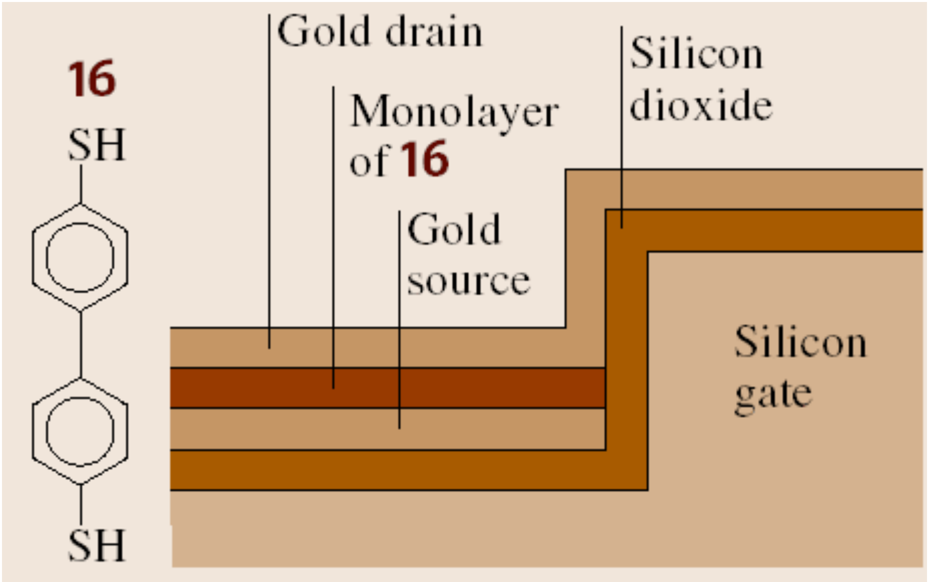
Up to now we had only one input and one output.




Now, we are going to look at three terminals and approach thereby the **molecule based transistor**!

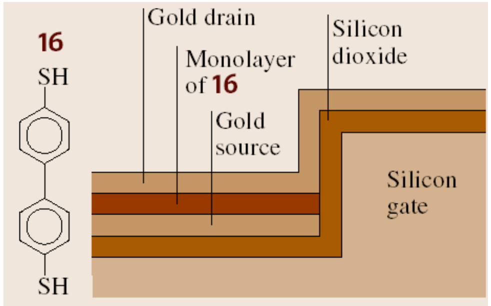


# Molecule based transistors



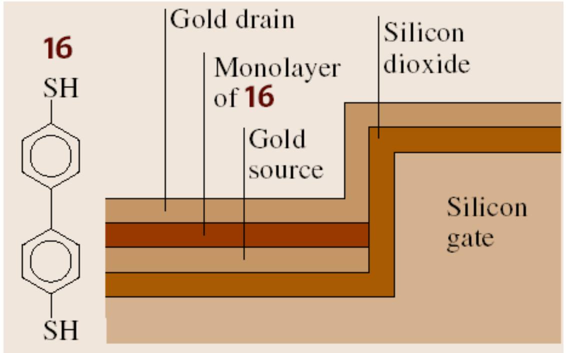

The **third electrode** gates the current flowing between the source and drain terminals.

# Fabrication of the molecule based transistor



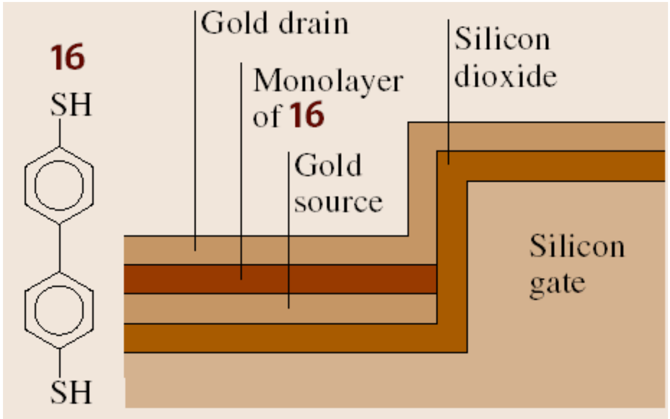

- Create **vertical step** in a doped silicon substrate by conventional lithography and anisotropic etching.
- Cover with **silicon dioxide** (thickness 30nm).
- Evaporate **gold** on lower step.
- Apply **bisthiols** (have thiols on both sides → high affinity for gold on both sides).
- Cover with **gold**.

# Properties of the molecule based transistor



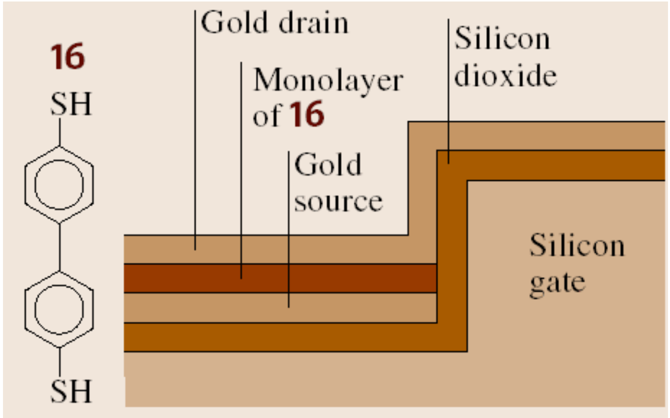

- Under the influence of the gate voltage, the **molecular components** embedded in this device **modulate the current flowing between the source and drain electrodes**.
- The **intensity** of the drain current **increases by five orders of magnitude** if the gate voltage is lowered below −0.2V

# Applications of the molecule based transistor




- Conventional transistors are the basic building blocks of digital circuits
- The **molecule-based transistor can be used to assemble real electronic circuits** incorporating molecular components.

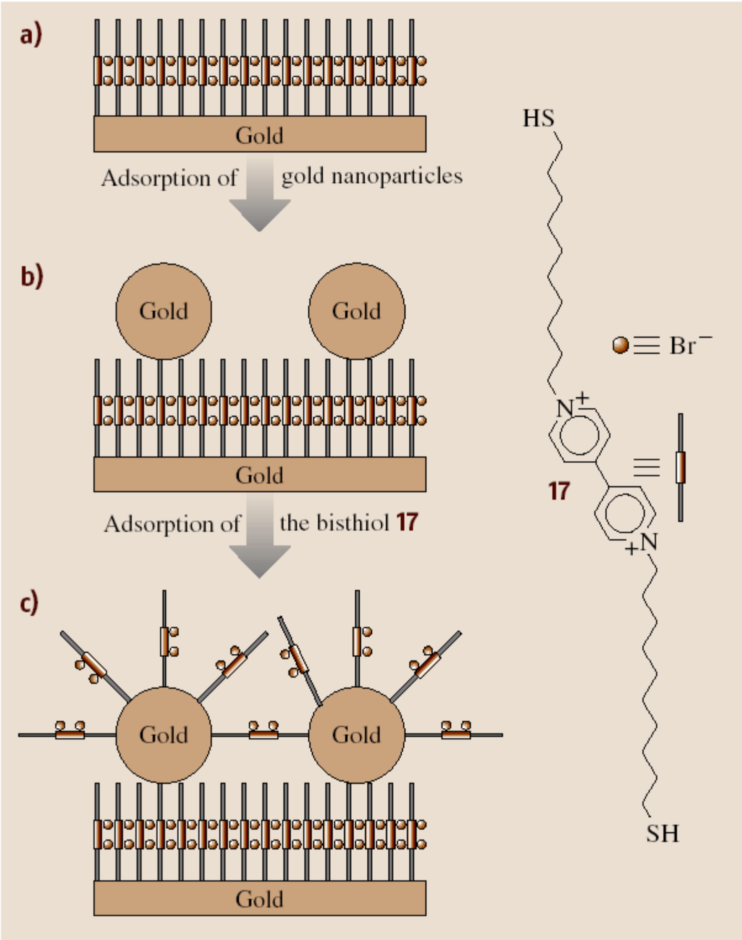
# Applications of the molecule based transistor




The connection of the drain terminals of two molecule-based transistors affords an **inverter**:

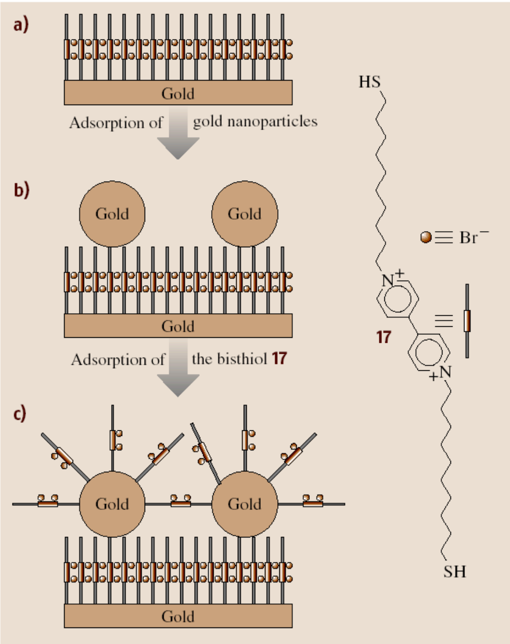
- An output voltage switches from a high (0V) to a low value (−2 V) when an input voltage varies from a low (2 V) to a high value (0 V) and vice versa.
- **NOT gate**!

# Nanocomposite materials: Thiol-gold nano-multilayer



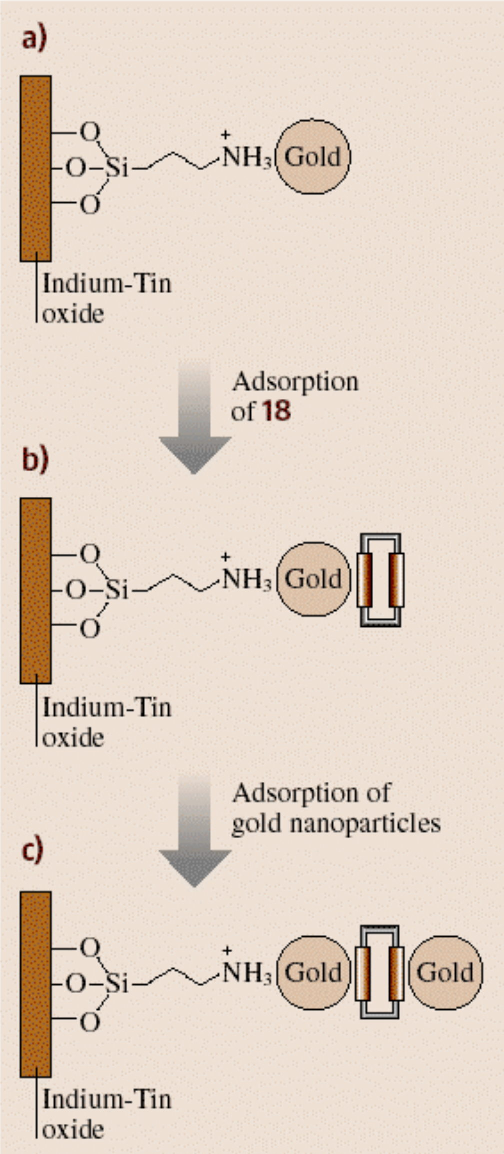

- Use the property of **thiols self assemble on gold** to fabricate nanocomposite materials.
- **Bisthiols** on gold, gold **nanoparticles** adsorb on the remaining thiol group, adsorption of **additional organic layer**, etc. etc.
- **Up to ten** alternating organic and inorganic **layers** can be deposited on the electrode surface.

# Properties of the thiol-gold nano-multilayer



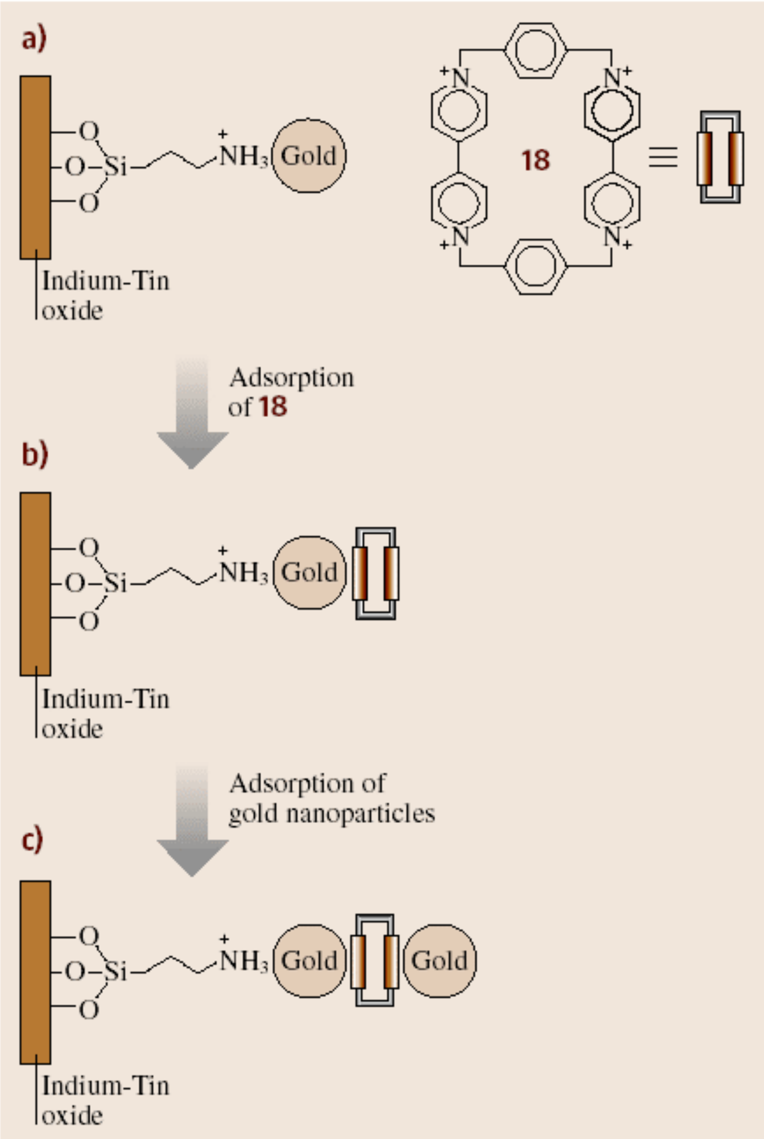

- The resulting assembly can mediate the **unidirectional electron transfer**.
- The electroactive multilayer allows the **flow of electrons in one direction only** in analogy to conventional diodes.
- The **current/voltage behaviour** is **probed by scanning tunnelling spectroscopy**.
- A change in the redox state of the bipyridinium components can be exploited to **reversibly gate the current flowing through this nanoscaled device**.

# Nano-multilayers on Indium-tin oxide



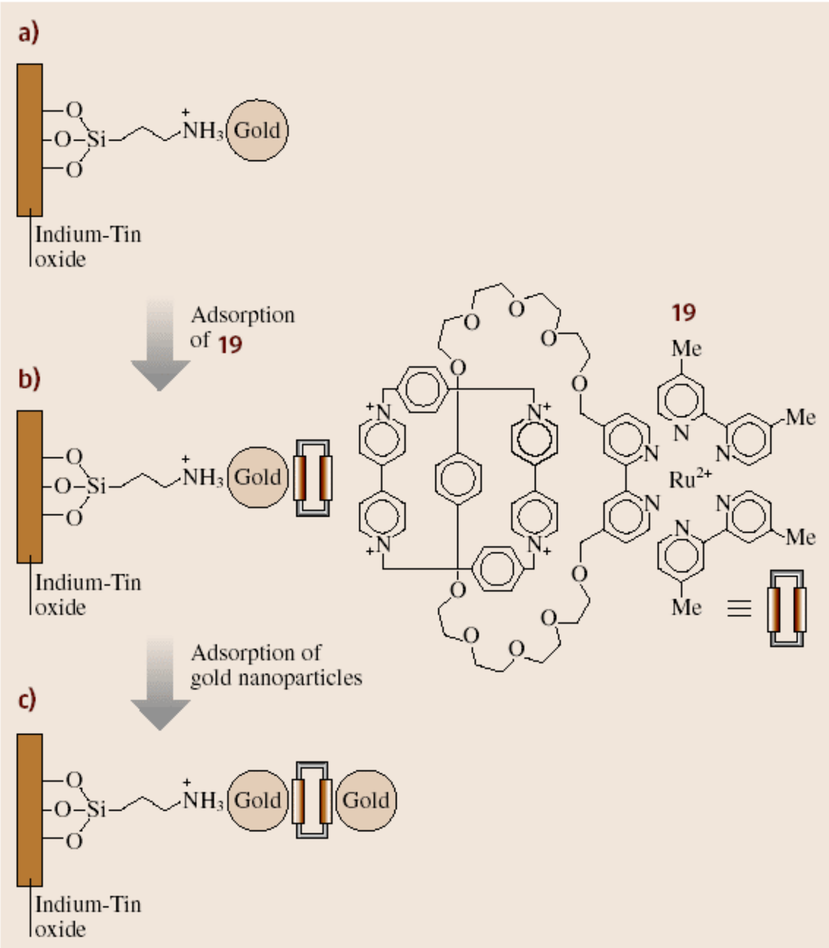

- The **indium-tin oxide** support is **functionalized** with 3-ammoniumpropylysilyl groups and then exposed to gold nanoparticles having a diameter of ca. 13nm.
- Alternating **layers of inorganic nanoparticles and organic building blocks** (e.g. bipyridinums, [2]catenanes) can be assembled **on indium-tin oxide** support.

# Nano-multilayers on Indium-tin oxide



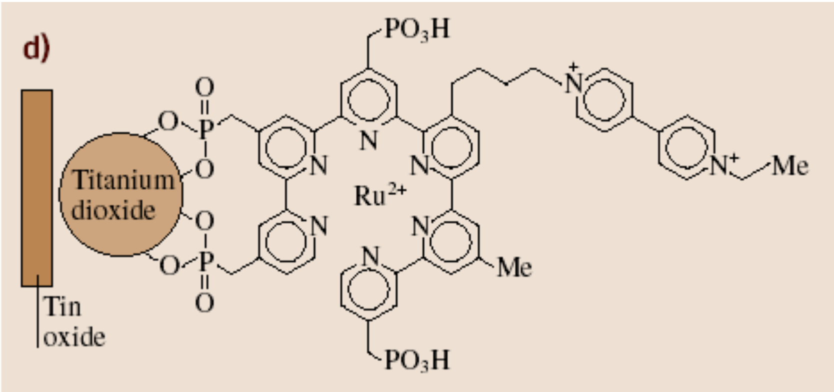

- The bipyridinium **cyclophane** produces an organic layer on the gold nanoparticles.
- The **ratio** between the number of tetracationic cyclophanes and that of the nanoparticles is ca. **100:1**.

# Nano-multilayers on Indium-tin oxide: a photoresponsive device




- In a closely related strategy, **[2]catenane** is absorbed onto the functionalized bulk, leading to similar composite arrays.
- Upon **irradiation** of the composite material at 440nm, **photo induced electron transfer** from the sensitizer to the appended acceptors occurs.
- The resulting **current switches between high and low values as the light source is turned on and off.**

# Another photoresponsive device




- Phosphonate groups can be used to anchor molecular building blocks to titanium dioxide nanoparticles.
- This nanocomposite array is used in a conventional electrochemical cell filled with an aqueous electrolyte containing triethanolamine.

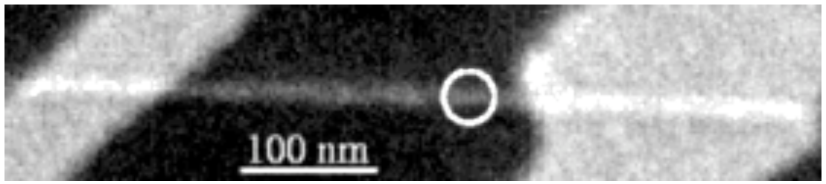
- Under a bias voltage of $-0.45$ V and **irradiation** at 532 nm, 95% of the excited ruthenium centers transfer electrons to the titanium dioxide nanoparticles.
- The photoinduced reduction of the bipyridinium dication is evident as a **characteristic band** in the absorption spectrum of the radical cation.
- This band persists for hours under open circuit conditions.
- But it fades in ca. 15s under a voltage bias of +1V, as the radical cation is oxidized back to the dicationic form.
- The state of the photogenerated form can be **read** optically, and **erased** electrically, applying a positive voltage pulse.

# Summary: Devices made with monomolecular layers

- The **electroactive and photoactive devices** presented above exploit the ability of **small collections of molecular components** to manipulate electrons and photons.
- Designed molecules were deposited on relatively large electrodes and can be addressed electrically and/or optically by controlling the voltage of the support and/or illuminating its surface.
- Now we move on to **monomolecular devices**.

# Nanogaps and Nanowires

- The transition from devices relying on collections of molecules to **unimolecular devices** requires the identification of practical methods to contact single molecules.
- A promising approach to unimolecular devices is the fabrication of nanometer-sized gaps in metallic features followed by the **insertion of individual molecules between the terminals of the gap**.

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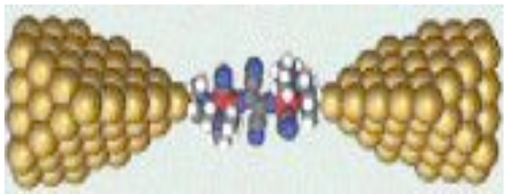

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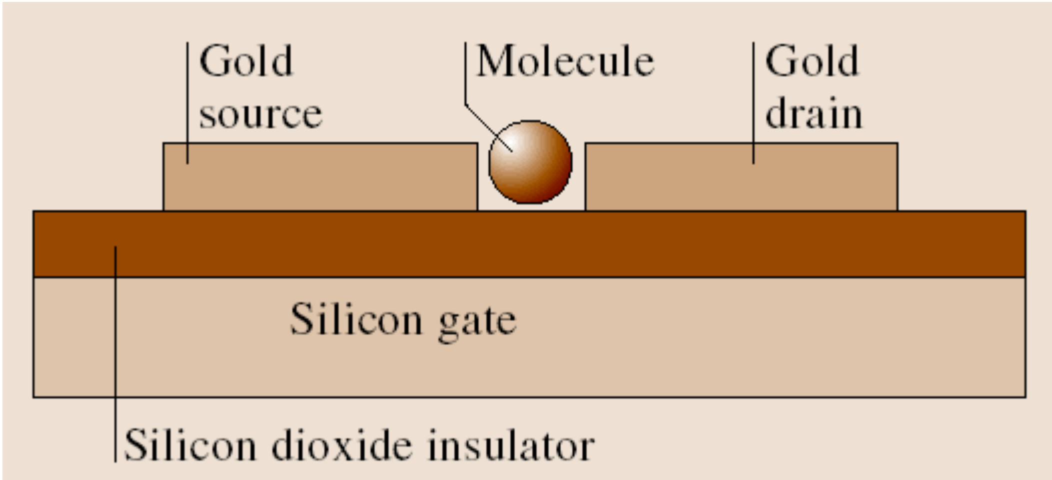
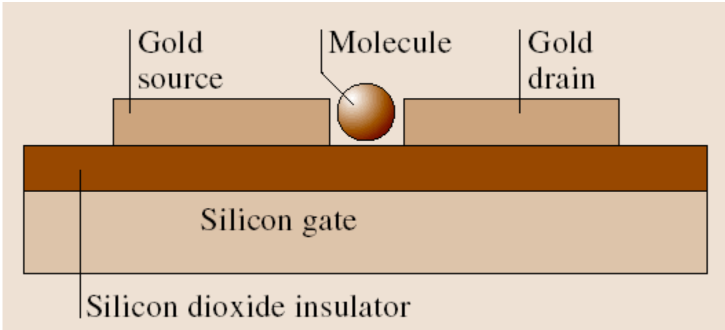
# Nanogaps and Nanowires



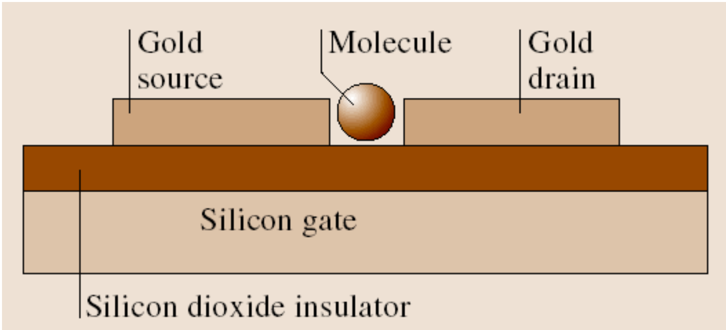

Nanoscaled transistors can be fabricated **inserting a single molecule** between source and drain electrodes mounted on a silicon/silicon dioxide support.

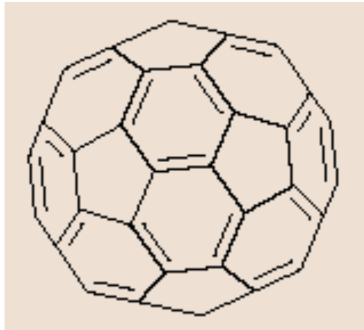
# Fabrication of single molecule transistor




- **Electron beam lithography** is used to pattern a gold wire on a doped silicon wafer covered by an insulating silicon dioxide layer.
- The **gold feature** is **broken by electromigration** to generate the **nanogap**.
- Lateral size of gap: **100nm**, thickness: **15nm**
- **Smallest nanogap: 1nm**
- **Insert single molecule** in gap

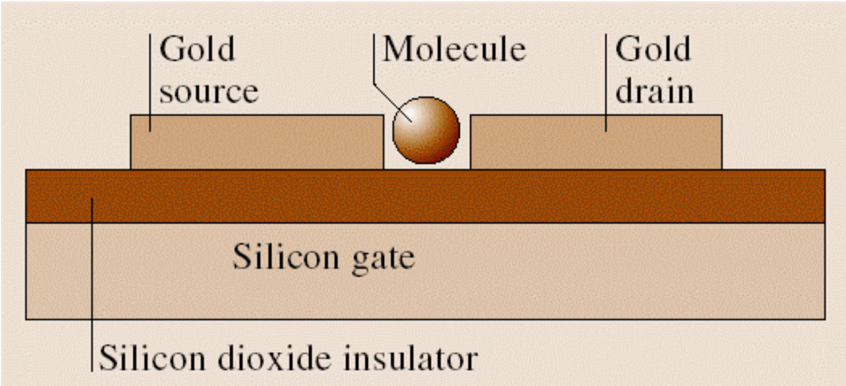
# C60 transistor

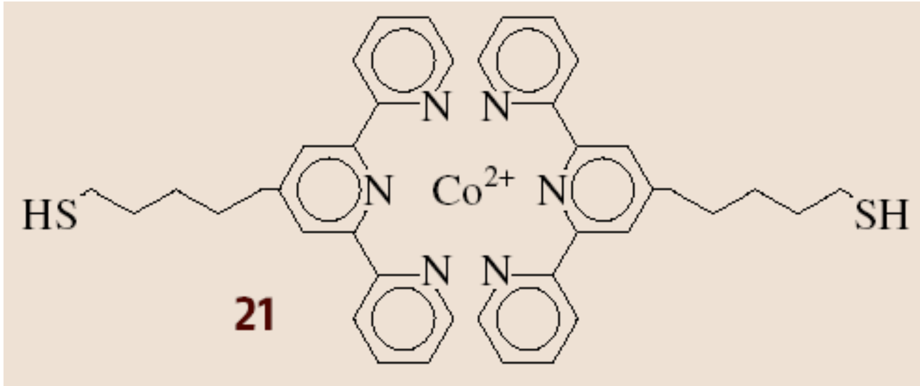


- The two gold terminals are drain and source, the silicon wafer is the gate. The molecule inserted is a **fullerene** ($C_{60}$, **0.7nm diameter**).
- The **junction conductance** (at 1.5K) is very small, **increases in steps at higher voltages**.
- This is a consequence of the finite energy required to oxidize/reduce the single $C_{60}$ positioned in the junction.

# Co(II) complex transistor

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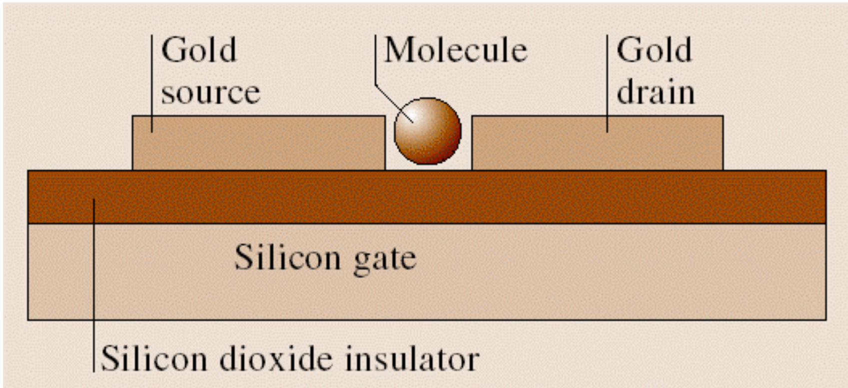
- The **gap** of this electrode-molecule-electrode junction is **1-2nm**, the **bisthiol** molecule is **0.24nm long**.
- As the source voltage is raised above this particular value, the **drain current increases in steps**, since finite energy is necessary to oxidize/reduce the cobalt center.
- The **conduction** of the electrode/molecule/electrode junction can be **tuned** adjusting the voltage of the silicon support.
- **The behaviour of this molecule-based nanoelectronic device is** equivalent to that of a conventional transistor: in both instances, the gate voltage regulates the current flowing from the source to the drain.

# Another method to produce nanogaps

- Take gold electrodes separated by a distance of about 20-80nm (made by **electron beam lithography**), perform **electrochemical deposition of gold** on the surfaces of both electrodes -- **get nanogap** separated by 1nm.
- The two **terminals of this nanogap** can be **“contacted” by organic nanowires** grown between them, e.g. polyaniline bridges.

# Polyaniline bridged nanogaps

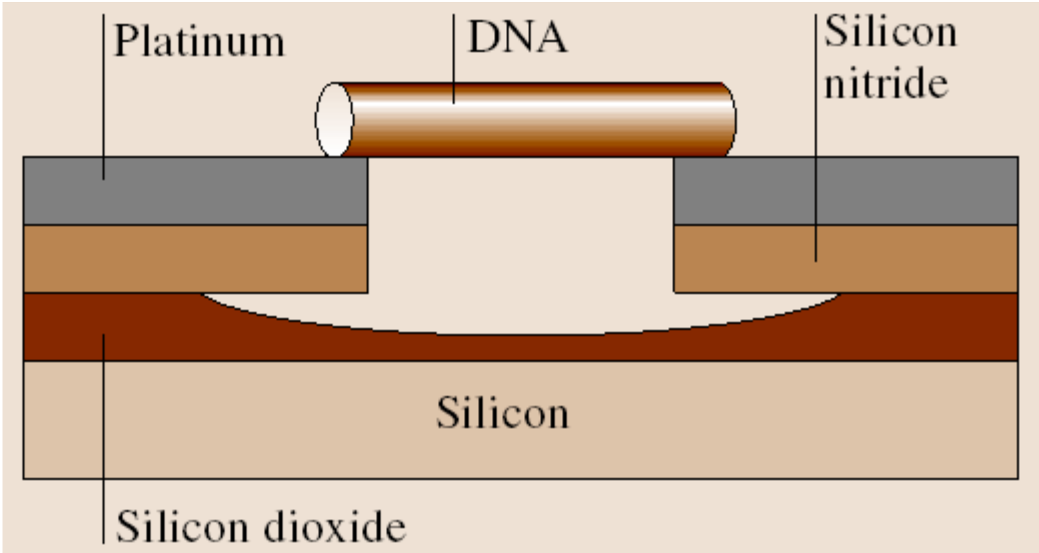



- Characteristics:
  - below 0.15V polyaniline is insulator, current less than 0.05A
  - above 0.15V current rises to 30nA (--> conductivity of10-100 S $cm^{-2}$ )
- The conductance of this nanoscaled junction switches on and off as a potential input is switched above and below a voltage threshold.

# Chemical sensing with nanojunctions

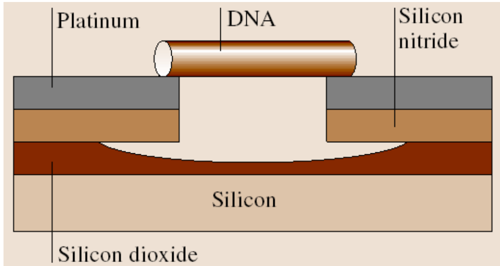
- The **influence of organic bridges on the junction conductance** can be exploited for **chemical sensing**: these bridges alter their conduction after exposure to dilute solutions of small organic molecules.
- **Organic analytes dock into the nanogaps** producing a marked decrease in the junction conductance.
- The **magnitude of the conductance** drop happens to be **proportional to the analyte–nanoelectrode binding strength**.

# DNA as an organic bridge in single molecule transistors



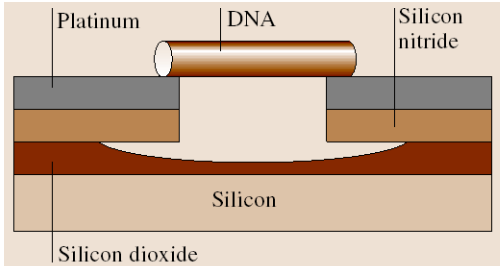

A DNA nanowire can bridge nanoelectrodes suspended above a silicon dioxide support.

# Fabrication of the DNA single molecule transistor.



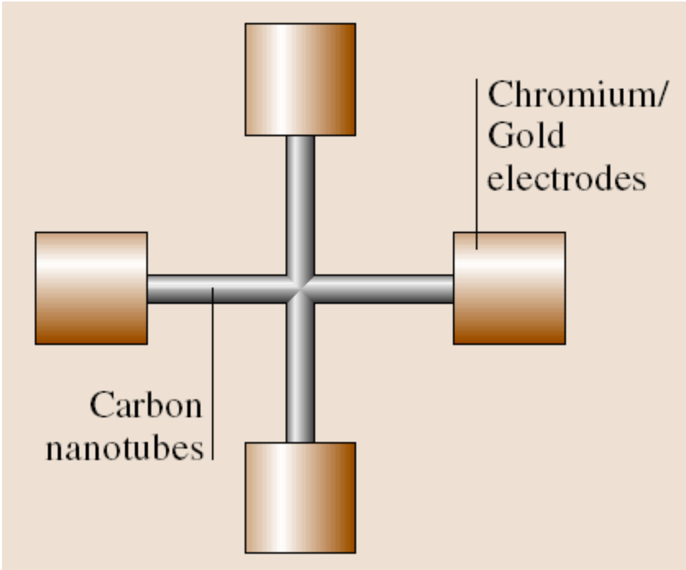

- **Pattern** a 30 nm wide slit in a silicon nitride overlayer covering a silicon/silicon dioxide support by electron beam evaporation.
- **Underetch** silicon dioxide layer
- **Sputter** on a **platinum** layer, chop - get gap of 8nm.
- Pour on dilute **DNA** double strand **solution**, apply **bias** of 5V to the electrodes → electrostatic forces encourage the **deposition of a single DNA wire on top of the nanogap**.

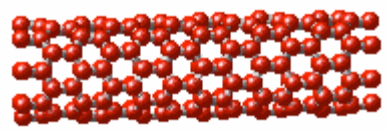
# Characteristics of DNA single molecule transistor.




- At **low voltage biases** DNA is an **insulator** → current of 1pA.
- **Above a certain voltage** threshold: current of up to **100nA**.
- Electron tunneling is extremely unlikely, since a gap of 8nm is large
- The off-set between the molecular conduction band and the Fermi levels of the electrodes is responsible for the insulating behaviour at low biases. Above a certain voltage threshold, the molecular band and one of the Fermi levels align facilitating the passage of electrons across the junction.

# Carbon nanotubes as bridges for nanogaps



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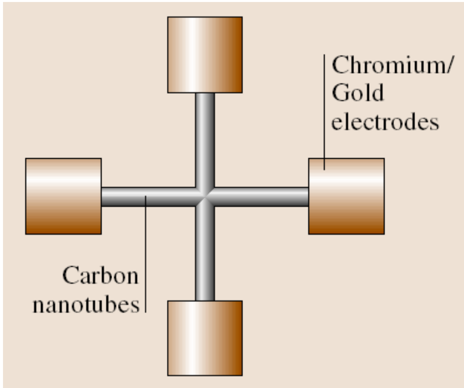
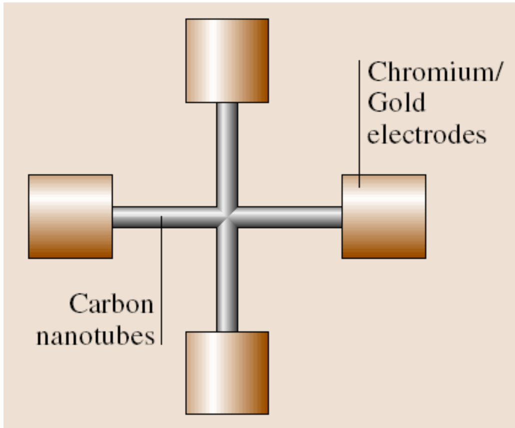
Nanoscaled **junctions** can be assembled on silicon / silicon dioxide supports crossing pairs of orthogonally arranged single-wall **carbon nanotubes** with chromium/gold electrical contacts at their ends.

# Assembly of nanoscaled cross junctions



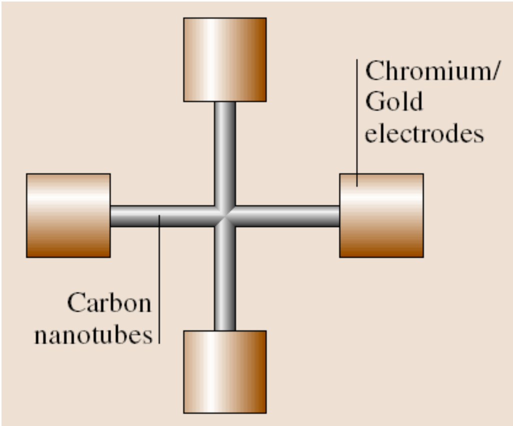

- **Pattern alignment marks** for the electrodes on silicon/silicon dioxide support by electron beam deposition.
- Expose substrate to **suspension of SWNT**.
- **Wash**.
- Locate SWNTs with tapping mode **AFM**.
- **Fabricate** chromium/gold **electrodes by e-beam lithography**.

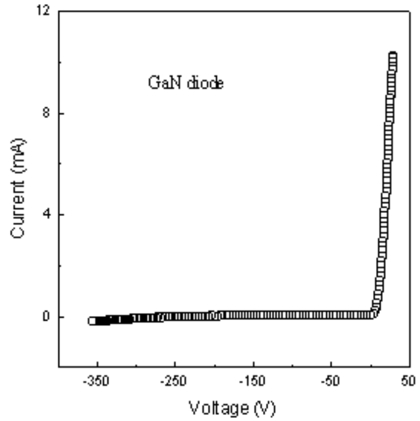
# Carbon nanotubes: electronic properties




Carbon nanotubes can be either **metallic or semiconducting**.

# Carbon nanotubes: electronic properties

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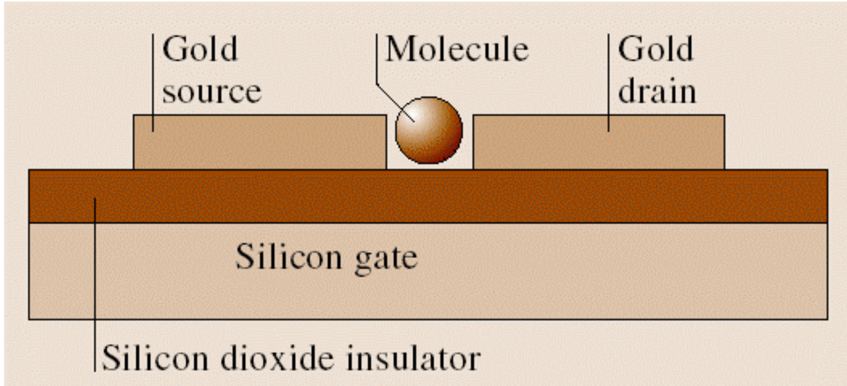
There are **three types of cross junctions** (CJs):

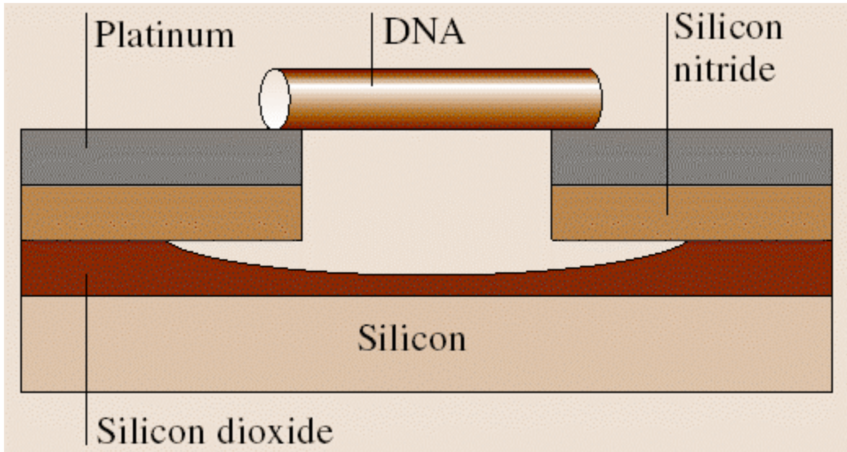
- The CJ formed by **two metallic SWNTs** shows **high conductance and Ohmic behaviour.**
- The CJ formed by **two semiconducting SWNTs** also shows **high conductance and Ohmic behaviour.**
- The CJ formed by **one metallic and one semiconducting carbon nanotube** shows **rectifying behaviour**: The metallic nanotube depletes the semi-conducting one at the junction region producing a nanoscaled **Schottky barrier** with a pronounced rectifying behaviour.

# Problem

This is all nice and interesting, but there is a **problem** in the transistors mentioned above:

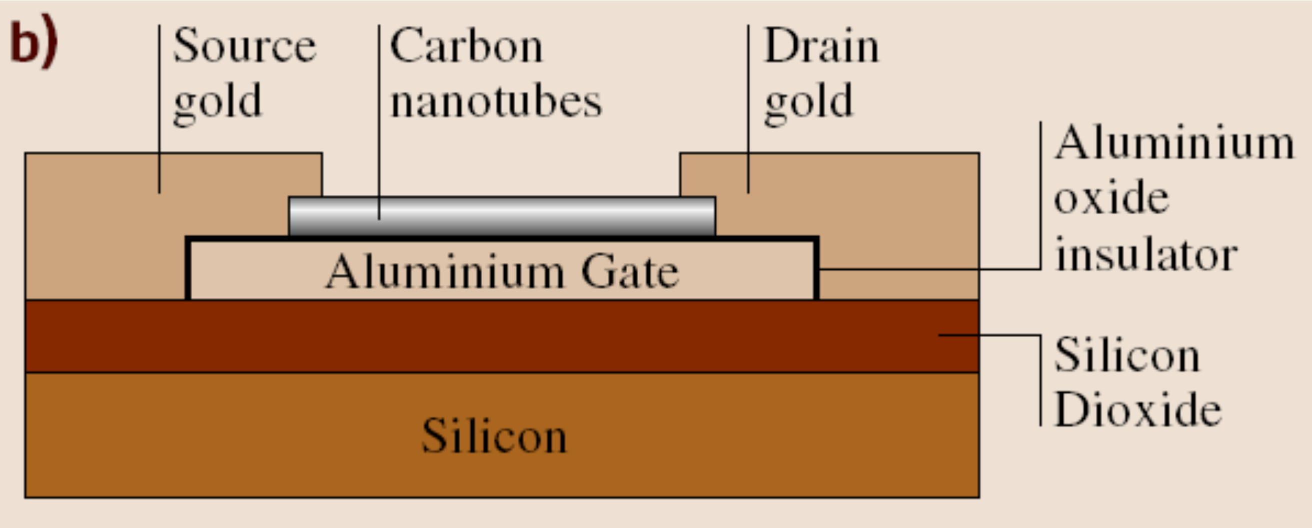
The **silicon gate extends under the entire chip** → only one single molecule transistor is possible per chip, **no coupling** of individual transistors is **possible**.



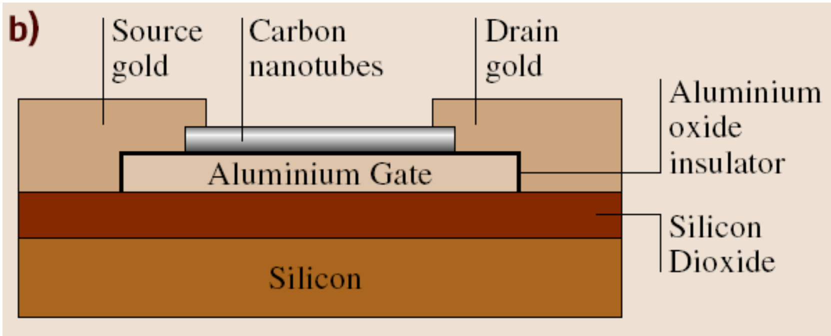
# Solution

Separate the gate:



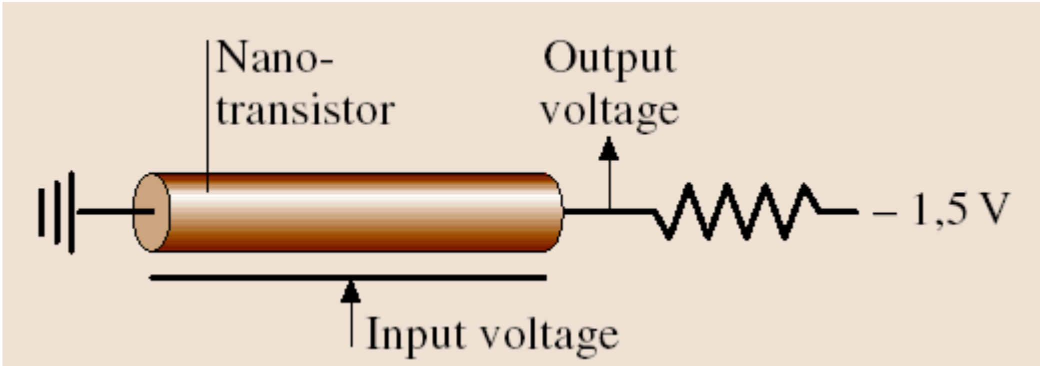

- Multiple nanoscaled transistors can be fabricated on the same chip and operated independently.
- This unique feature offers the **possibility of fabricating nanoscaled digital circuits by interconnecting** the terminals of independent nanotube transistors.

# SWNT transistor with separated gate



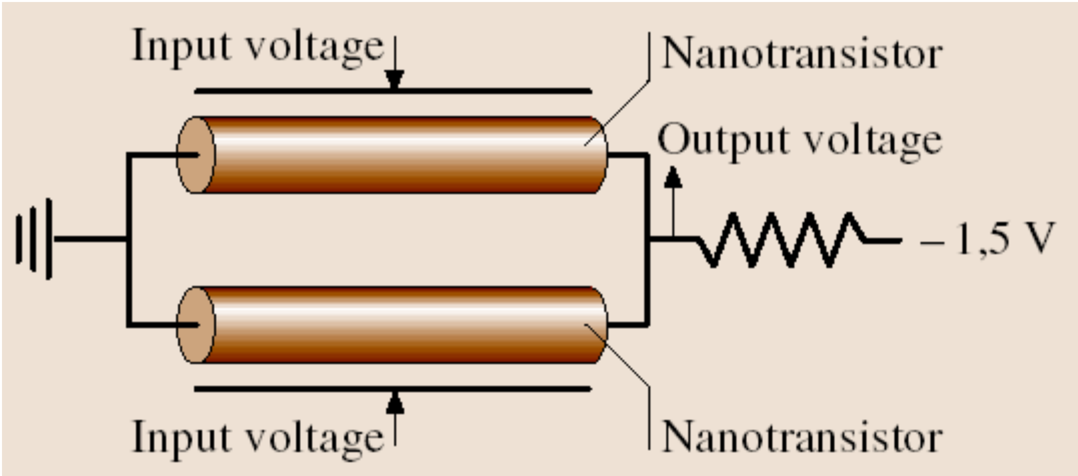

- **Pattern** an **aluminum finger** on a silicon/silicon dioxide substrate by e-beam lithography. Then expose to **air**: aluminum oxidizes, building an insulating **$Al_2O_3$ layer**.
- With the **AFM**, select SWNTs positioned on the aluminum finger, register coordinates, **evaporate gold contacts** by e-beam lithography.
- The final assembly is a **nanoscaled three-terminal device equivalent to a conventional field effect transistor**.
- At a source to drain bias of ca. −1.3V, the drain current jumps from ca. 0 to ca. 50nA when the gate voltage is lowered from -1.0 to -1.3V.

# NOT gate built from SWNT transistors



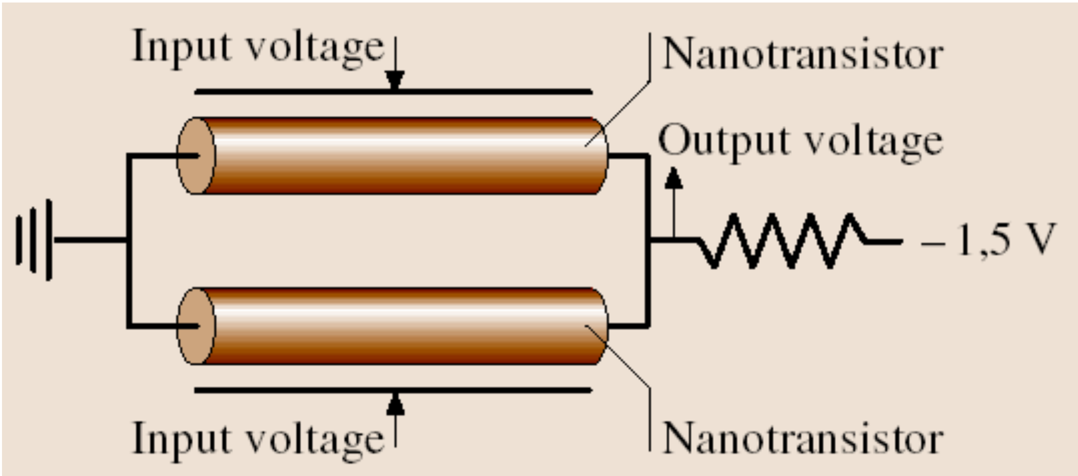

- A voltage input applied to the gate modulates the nanotube conductance altering the voltage output probed at the drain terminal. In particular, **a voltage input** of **−1.5V** lowers the nanotube resistance (26MΩ) below that of the bias resistor (100MΩ). As a result, the **voltage output** drops to **0V**.
- When the **voltage** input is **raised to 0V**, the nanotube resistance increases above that of the bias resistor and the **voltage output** becomes **−1.5V**.

# NOR gate built from SWNT transistors



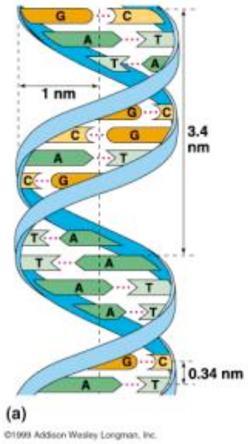

- The **source terminals** of two independent nanotube transistors fabricated on the same chip are **connected** by a gold wire **and grounded**.
- Similarly, the two **drain terminals** are **connected** by another gold wire and **contacted to** an off-chip **bias resistor**.

# NOR gate built from SWNT transistors




- When the resistance of at least one of the two nanotubes is below that of the resistor, the output is 0V.
- When both nanotubes are in a nonconducting mode, the output voltage is -1.5V.
- The signal transduction behaviour translates in to a NOR operation.

# Conclusions and Outlook (1)



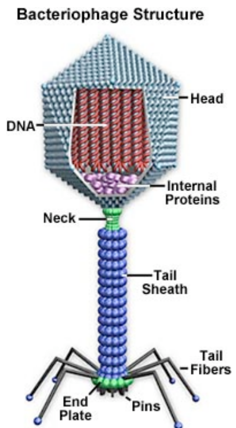
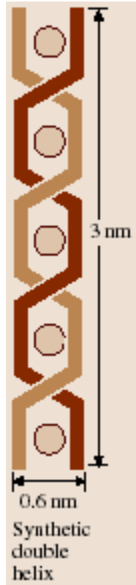



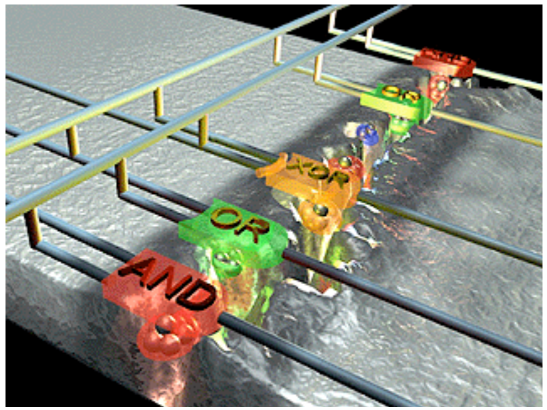

Figure 1

- **Nature** builds nanostructured biomolecules relying on a **highly modular approach**.

  The power of **chemical synthesis** offers the opportunity of mimicking nature’s modular approach to nanostructured materials.

- **Man-made** electroactive and photoactive **molecules** which are able to reproduce **AND, NOT, and OR** operations **as well as simple combinations** of these basic logic functions are already **a reality**.

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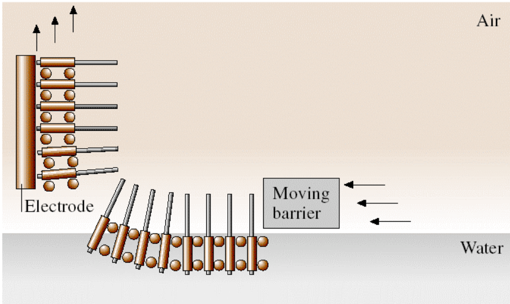
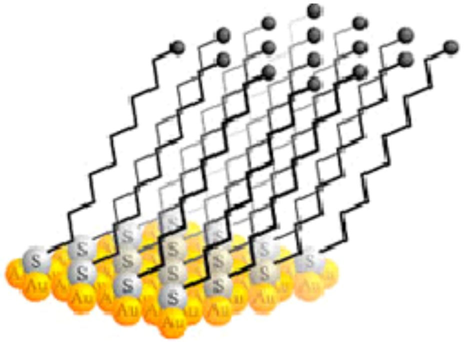
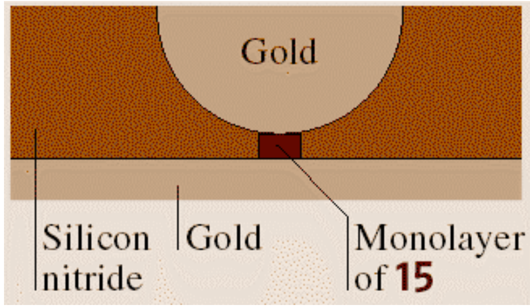
# Conclusions and Outlook (2)

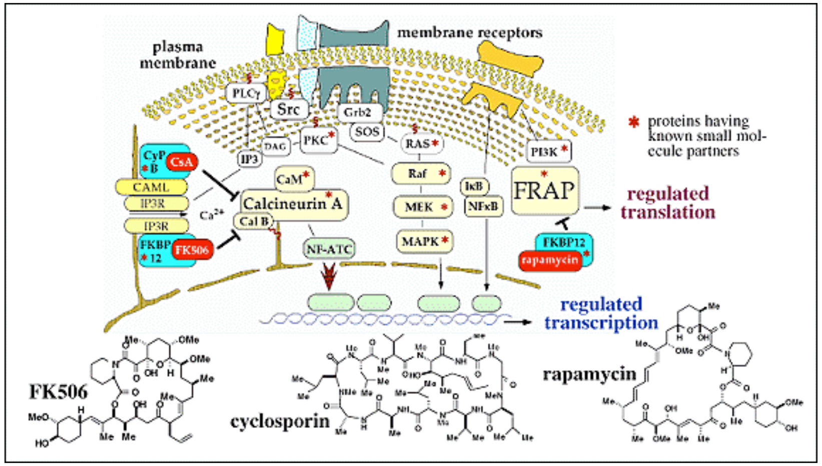





- Deposition of functional molecules on the surfaces of appropriate electrodes following either the Langmuir–Blodgett methodology or self-assembly processes.
- Remarkable examples of molecule-based materials and devices now available demonstrate the great potential and promise for this research area.

# Conclusions and Outlook

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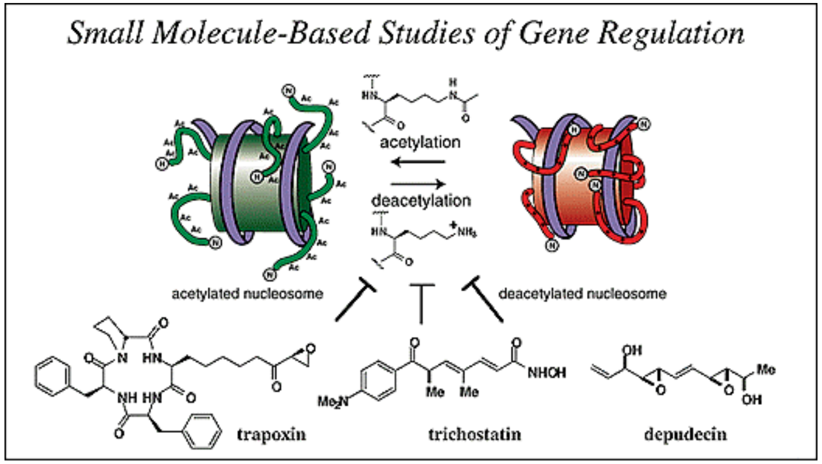


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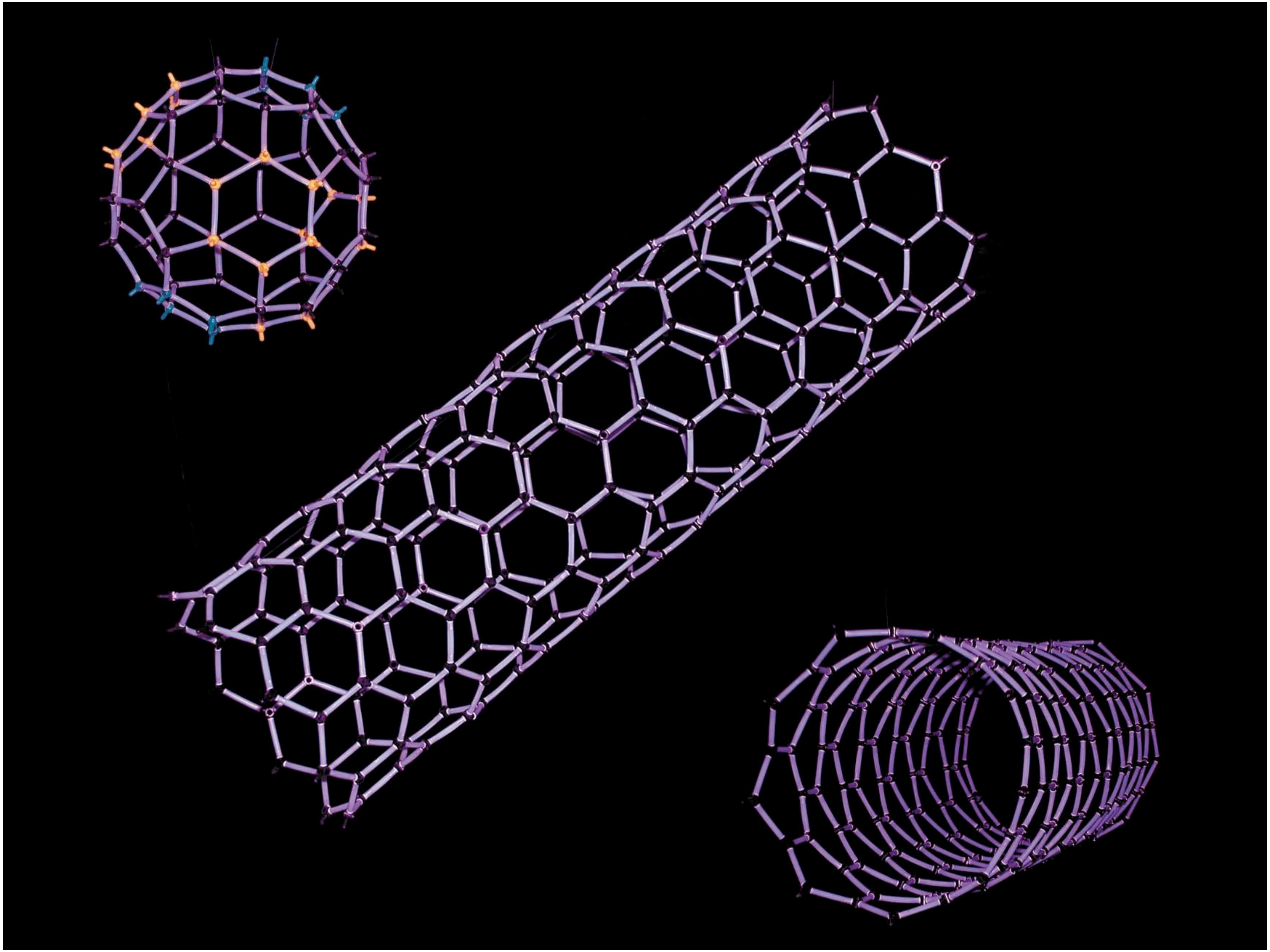
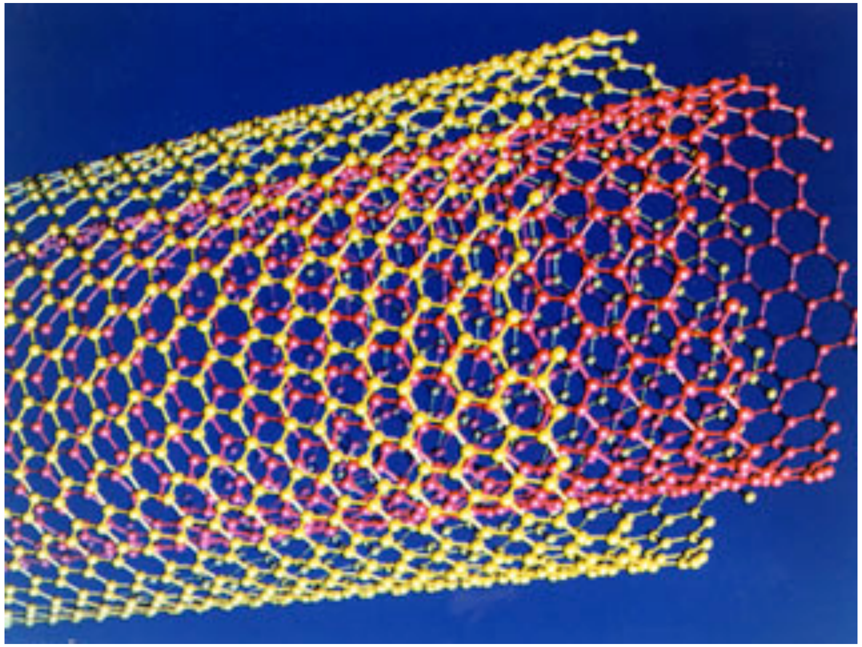
- **Nature** is replete with examples of extremely sophisticated molecule-based devices, and will continue to illuminate our path, **teaching us** not only **how to synthesize nanostructured molecules** but also **how to use them**.
- From tiny bacteria to higher animals, **we** are all a **collection of molecule-based devices**.

# Introduction to Carbon Nanotubes





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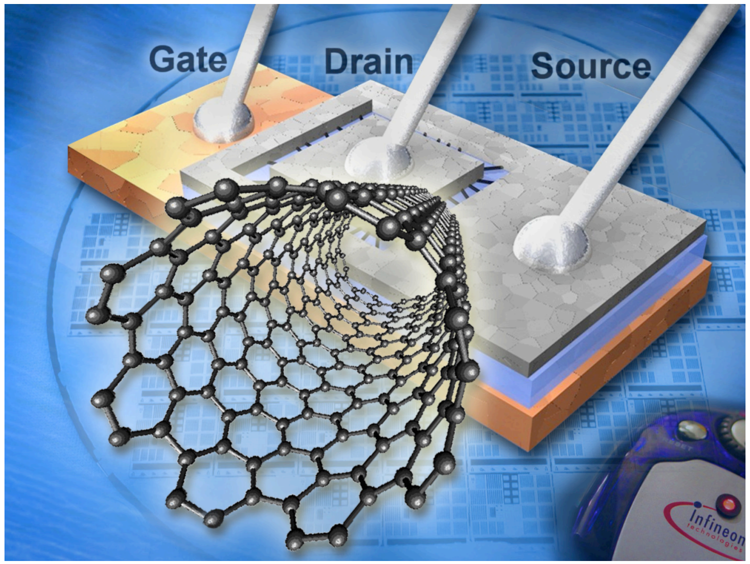


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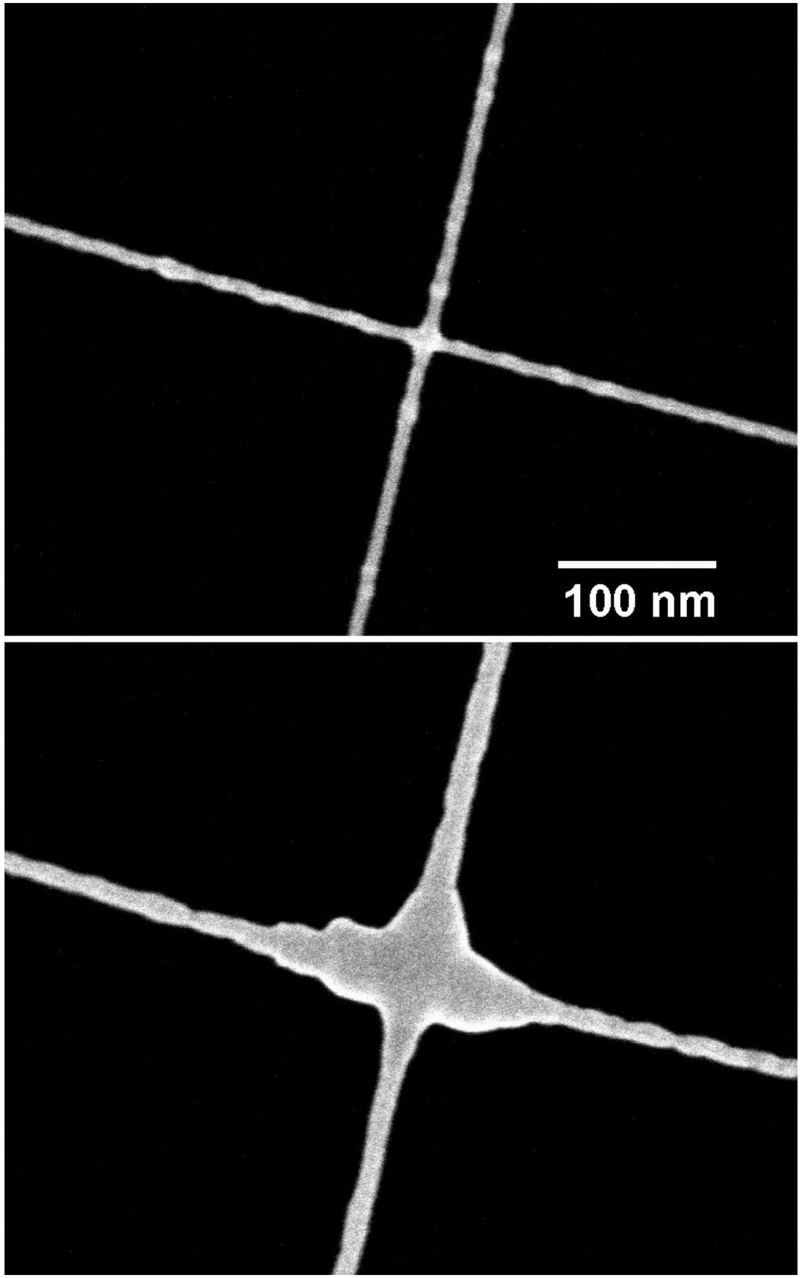
Carbon_Nanotubes_HiRes_1.jpg

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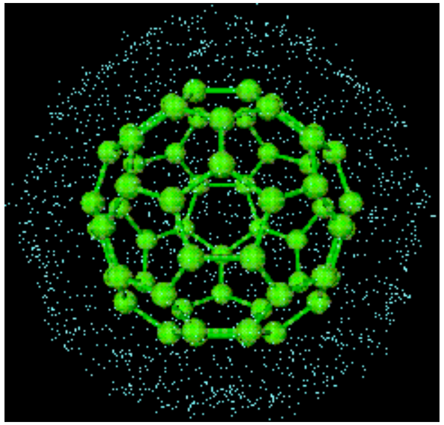
# Fullerenes ($C_{60}$, $C_{70}$, etc.)



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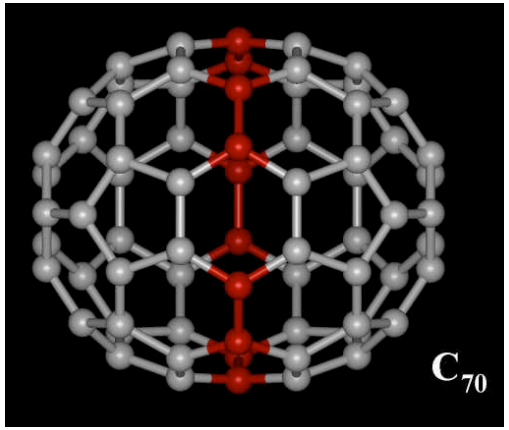


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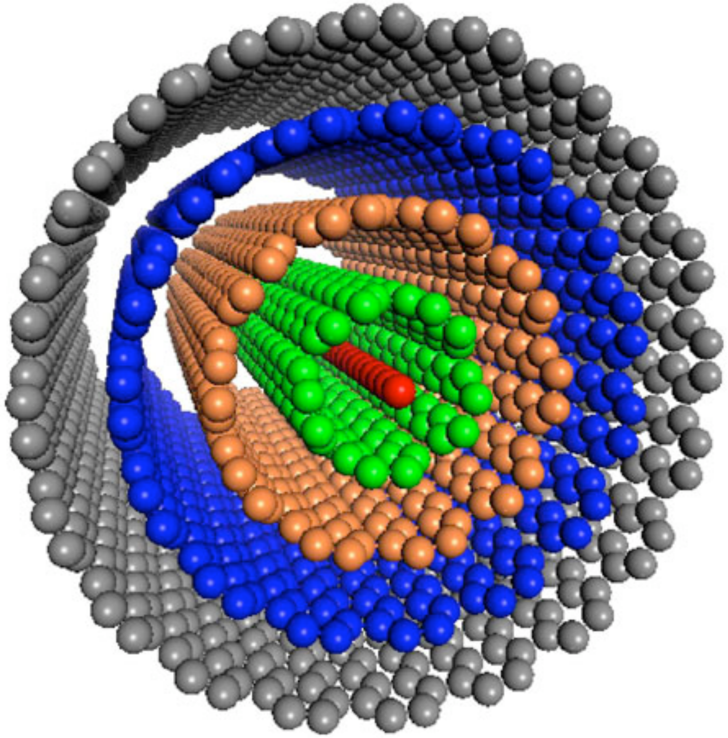
~pmslhome/Fullerene/C70.jpg

- Fullerenes, or buckminsterfullerenes in full, are **molecules composed entirely of carbon**, taking the form of a hollow sphere, ellisoid, tube, or ring.
- They are sometimes called buckyballs or buckytubes, depending on the shape.
- **Discovered** in **1985**, **Nobel Prize** in **1996**.
- **Few** related **applications** have actually yet reached the market.

# Carbon Nanotubes

The world already dreams of **space elevators** tethered by the strongest of cables, **hydrogen-powered vehicles**, **artificial muscles**, and so on – feasts that would be **made possible by the emerging carbon nanotube science**.



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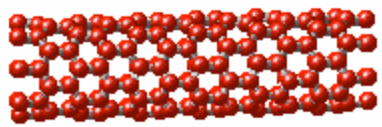
# Carbon Nanotubes - History

- Carbon filaments prepared by *Hughes and Chambers* in **1889** were probably the **first patent** ever deposited in the field.
- The worldwide enthusiasm came unexpectedly in **1991**, after the catalyst-free formation of nearly perfect concentric multiwall carbon nanotubes (c-**MWNTs**) was reported as by-products of the formation of fullerenes by the electric-arc technique.
- The real breakthrough occurred **1993**, with the discovery – again unexpected – of single-wall carbon nanotubes (**SWNTs**) by *Iijima* et al. and *Bethune* et al.

# Carbon Nanotubes - today



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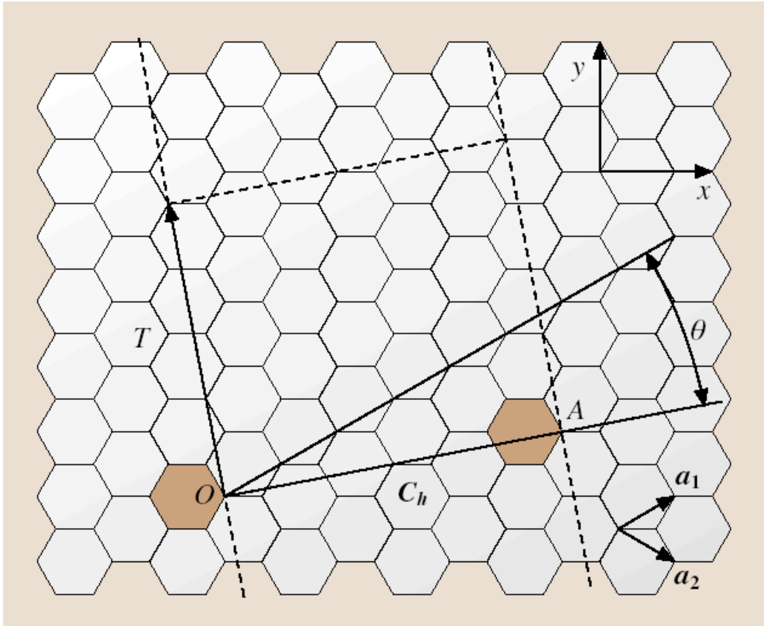
About **five papers a day** with carbon nanotubes as the main topic are currently published by research teams from around the world.

# Structure of carbon nanotubes

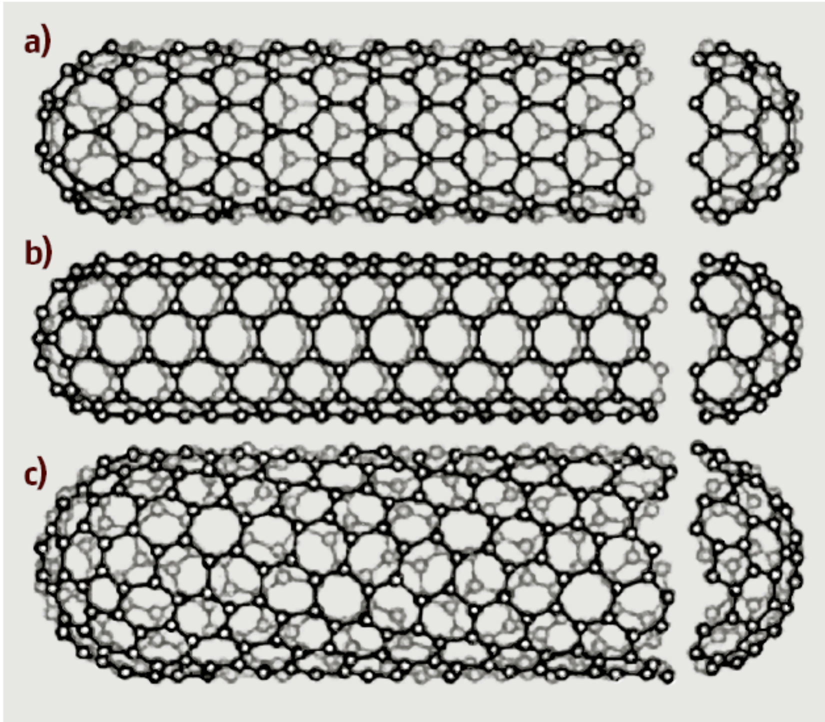
# Graphene sheets

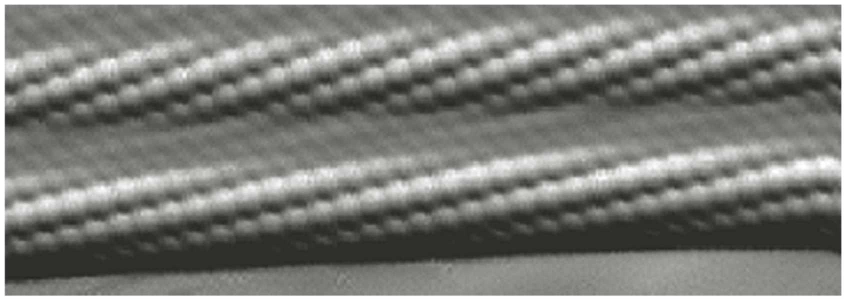



A **graphene sheet** is a polyaromatic mono-atomic layer made of an hexagonal display of **sp$^2$ hybridized carbon atoms** that genuine graphite is built up with.

# Single-Wall Nanotubes

**Roll** a perfect graphene **sheet** into a cylinder, and close the tips by two caps, each **cap** being a hemi-fullerene with the appropriate diameter.

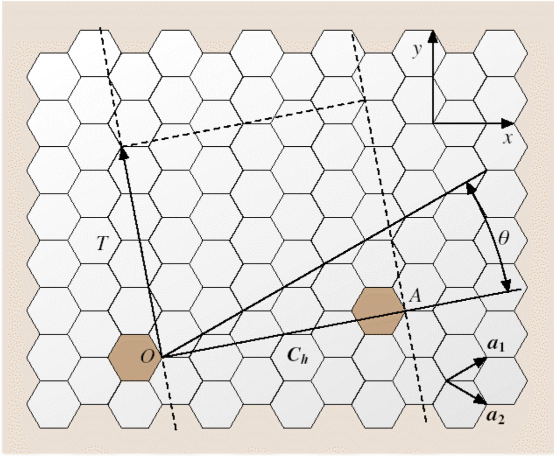


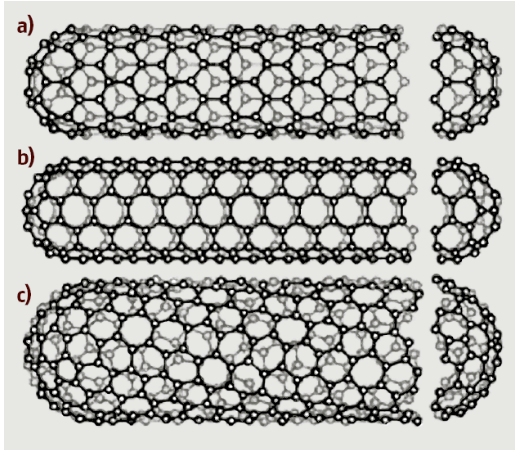



- **Maximum diameter** of SWNT: **2.5nm**

  (below this value, flattened two-layer sheets are energetically more favourable).
- **Minimum diameter**: **0.4nm**
- **Suitable energetic compromise** for diameter: **1.4nm**
- **Length**: up to micrometers or even **millimeters**!
- SWNTs are unique examples of **single molecules with high aspect ratio**.

# Consequences from structure



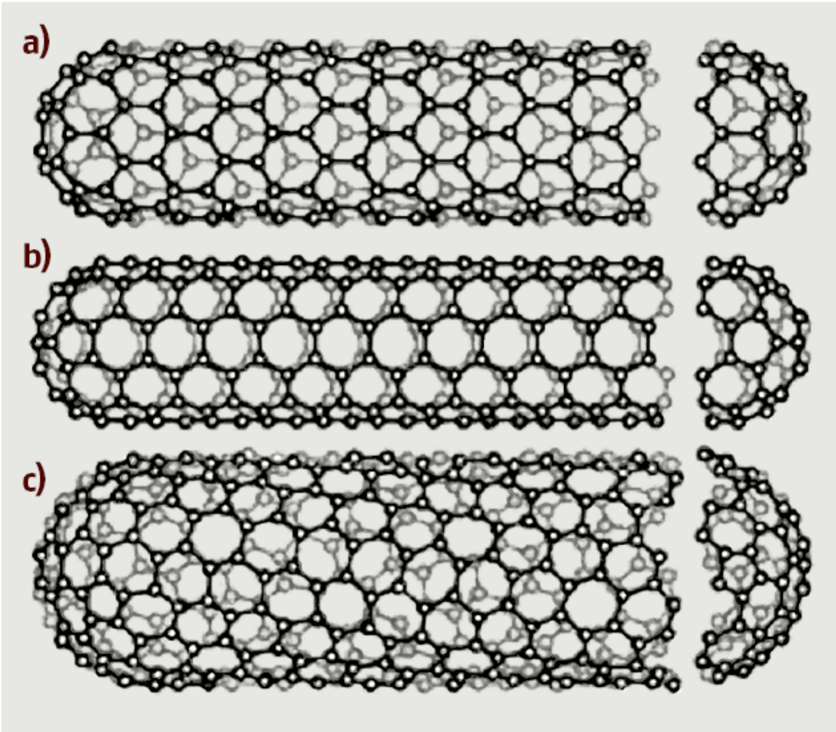




1. All carbon atoms are involved in **hexagonal** aromatic rings only and are therefore in equivalent position, except at the nanotube tips where 6×5 = 30 atoms at each tip are involved in **pentagonal** rings (considering that adjacent pentagons are unlikely).
2. The **chemical reactivity** of SWNTs is **highly favored at the tube tips**, at the very location of the pentagonal rings.
3. **No pure $sp^2$ hybridization anymore**, since C=C bond angles are no longer planar.

# $sp^2$ vs. $sp^3$ hybridisation

- The hybridization of carbon atoms are no longer pure $sp^2$ but get some percentage of the **$sp^3$ character**, in a proportion that **increases as the tube radius of curvature decreases**.
- **In $C_{60}$ molecules** (highest radius of curvature), the **$sp^3$ proportion is about 30%**.

# SWNT structures




Zig-zag type

Armchair type

Helical type