5 Molecules for molecular electronics

Main classes in use:

1. Hydrocarbon-based molecules
2. All-carbon systems:
   graphene, fullerenes, carbon nanotubes
3. Anchoring groups
4. Summary: Functionalities

From: Rainer Waser, Nanoelectronics and Information Technology, 3rd edition, Wiley-VCH Verlag GmbH & Co, Weinheim 2012

Required functionalities

For digital electronics:

- Conducting wires: low resistance, high ampacity.
- Insulators: high resistivity, high breakdown voltage.
- Switches: high on/off resistance ratio, reliable switching, small leakage current in off position.
- Storage elements: long storage time, low loss.

For logic circuits:

- Diodes: high forward/backward current ratio.
- Amplifiers: high gain.

For composite devices:

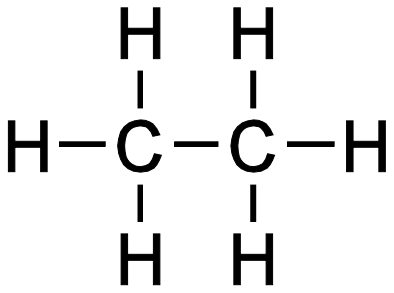
- Anchoring groups: reliable contact between functional molecular unit and electrode.

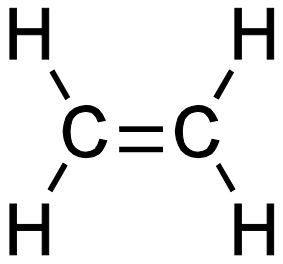
Required functionalities

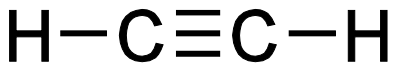
Further requirements

- Mechanical stiffness, rodlike molecules
- Reproducible binding position and conformation: Selforganization
- Switches: reproducible change of conformation upon switching.

5.1 Hydrocarbons

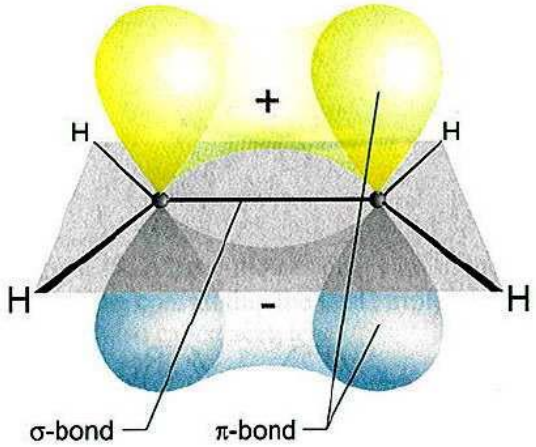


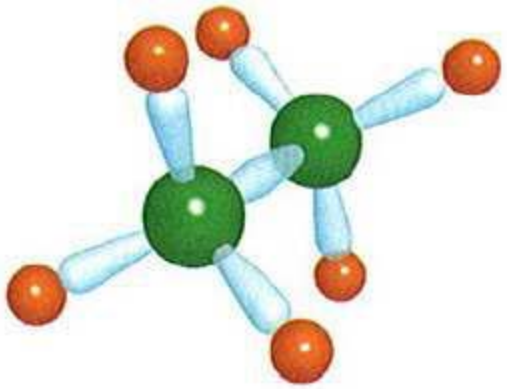


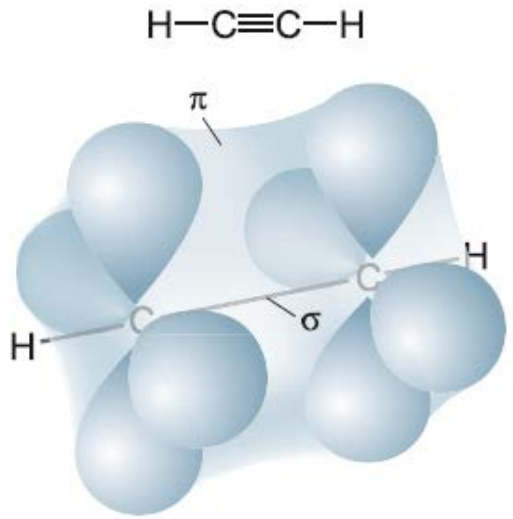


Ethane

Ethyne (Acetylene)



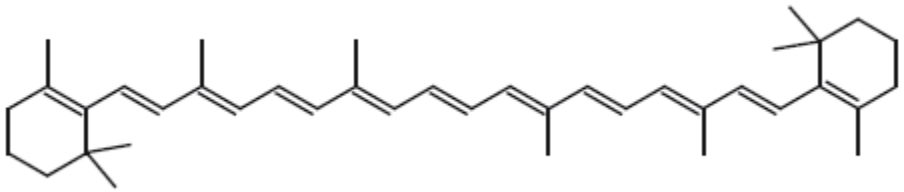




Conjugation

- Delocalized electronic state due to π system
- Insulating or conducting depending on bonding scheme:
- Signature:

- alternation of double and single bond or triple and single bond: conjugated = conducting
- other sequences („broken conjugation“) : insulators



β-carotin: long conjugated bone

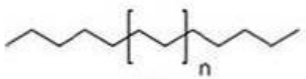
penta-1,4-diene

penta-1,3-diene

penta-1,2-diene

Examples of insulators and conductors

Insulators



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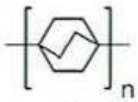

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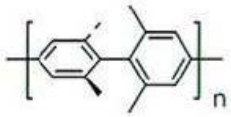

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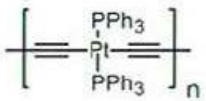

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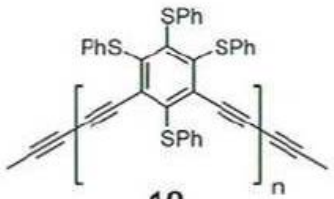

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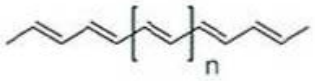
Conductors



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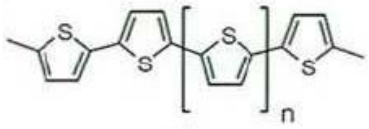

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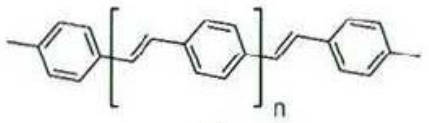

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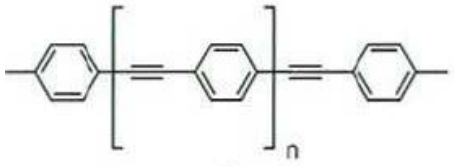

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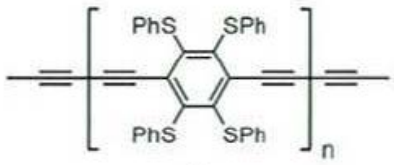

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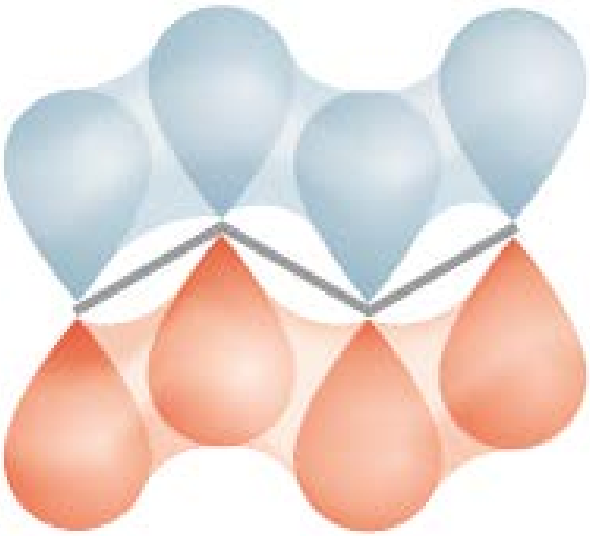
Conjugated (aromatic) Hydrocarbons

Linear: Polyenes

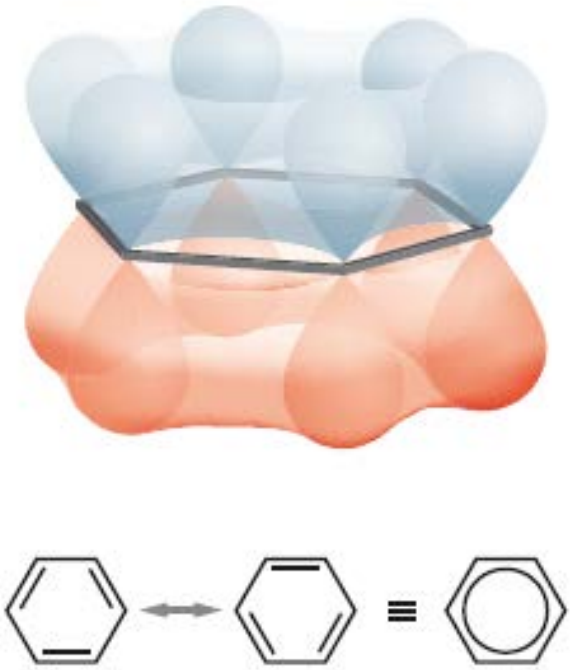
Cyclic: phenylene

(a)



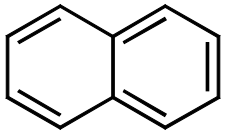
Tetratriene

(b)

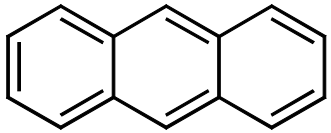


Benzene

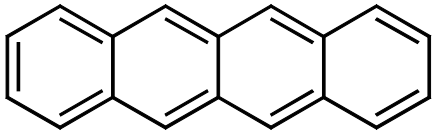
Polycyclic aromatic molecules



Naphtalene

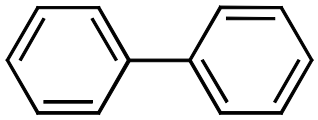


Anthracene

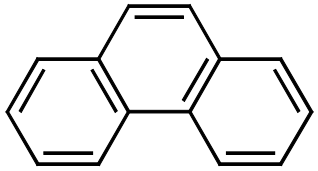


Tetracene

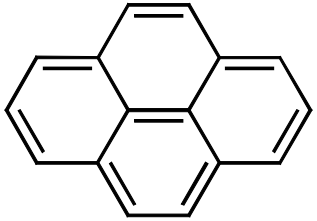
Cyclopentadiene anion



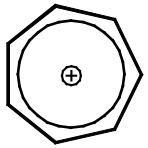
Biphenyl



Phenanthrene



Pyrene

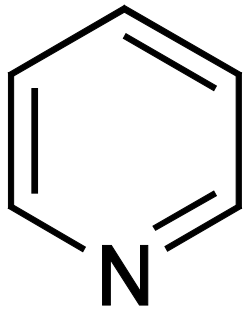


Cycloheptatriene cation

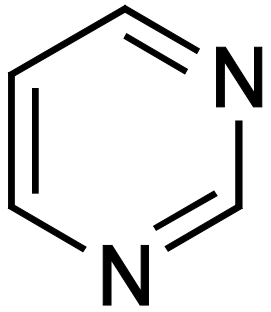
Degree of conjugation depends on coupling position because of quantum interference properties (meta/para/ortho position)

Heterocycles: electron pushing or pulling aromates

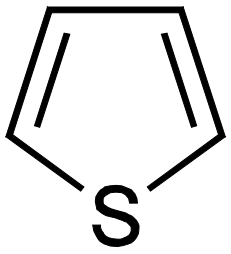
5-rings or 6 rings of hydrocarbons in which 1 or 2 C's are replaced by another atom.
Most common replacement atoms: N, S, O



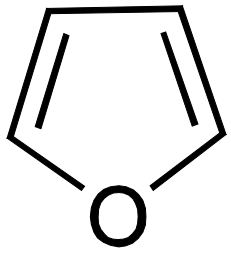
Pyridine



Pyrimidine

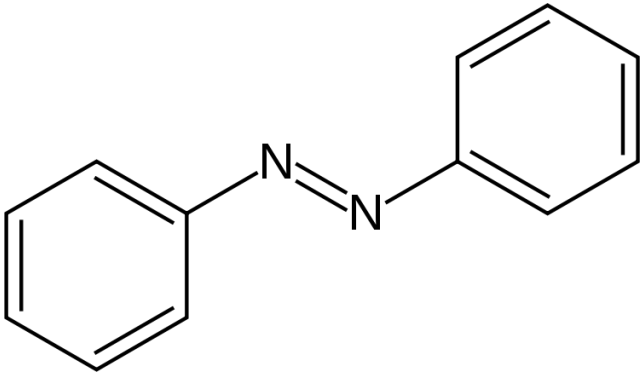


Thiophene

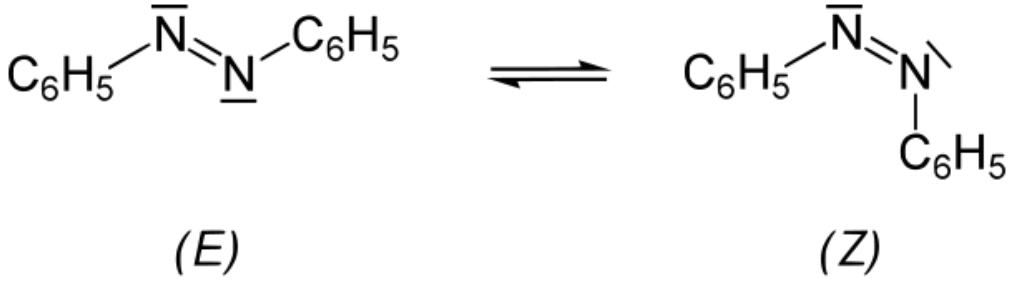


Furane

5.1.1 Molecular Switches

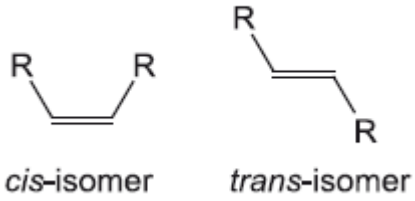


Azobenzene

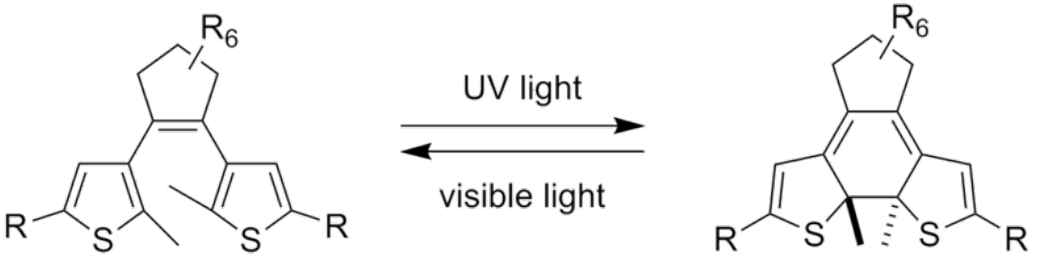


(E) (Z)

Cis/trans isomerization: Pronounced conformational change



cis-isomer *trans*-isomer



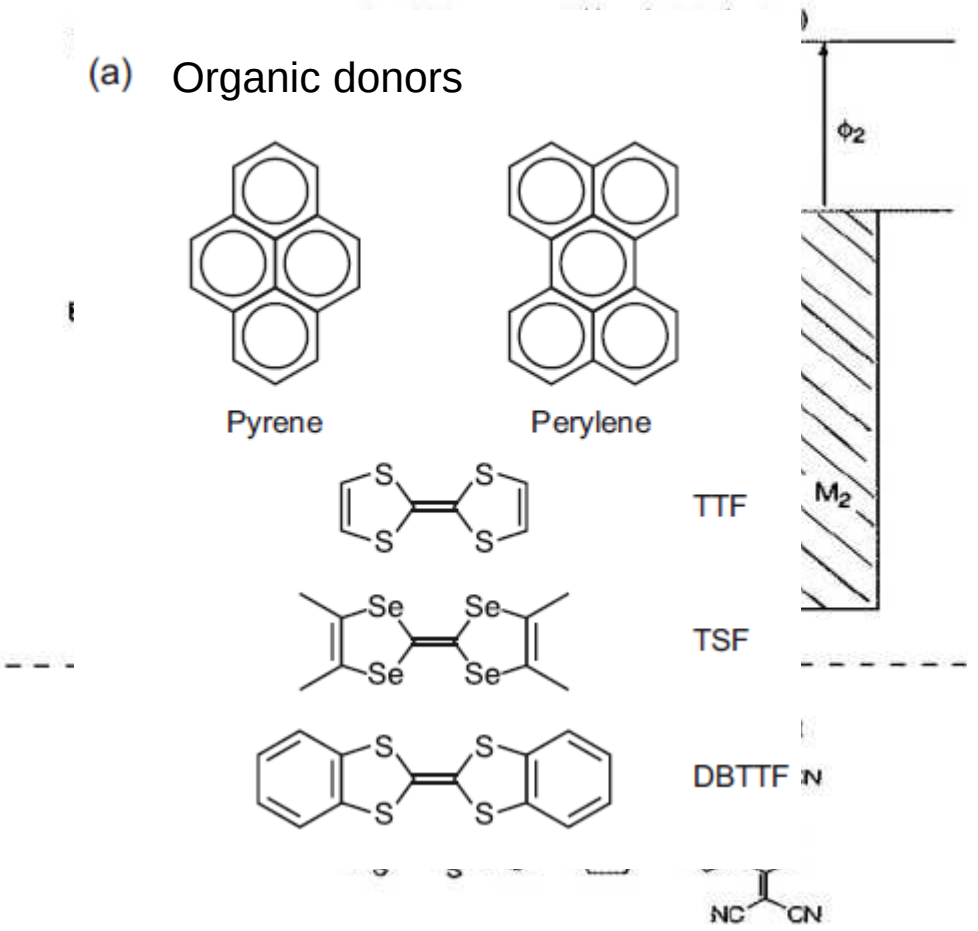
open form
(generally colorless)

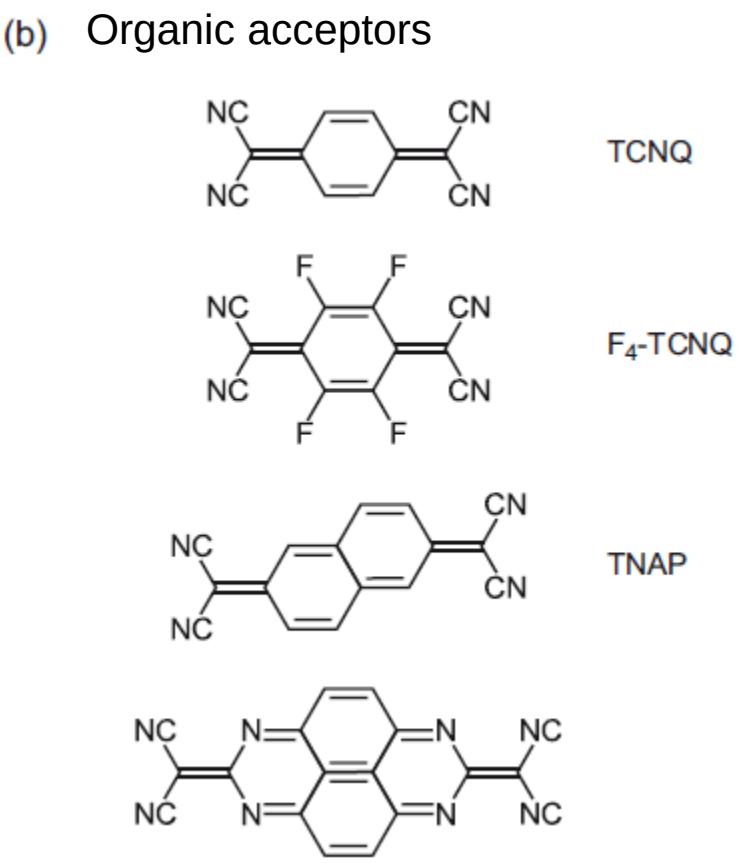
closed form
(generally colored)

Diarylethene

Ring opening/closure switches
Small conformational change

5.1.2 Molecular diodes

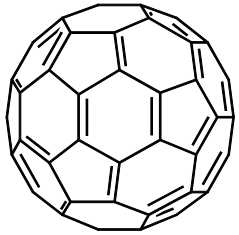




A. Aviram & M. Ratner, 1974

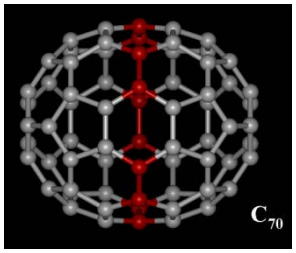
5.2 All carbon materials

Fullerenes

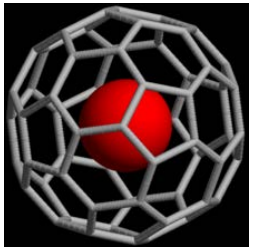


C_{60}

- 12 pentagons, 20 hexagons
- conjugated



- bigger/smaller fullerenes: C40, C70, C82,
  usually obtained by adding/removing pentagons or hexagons

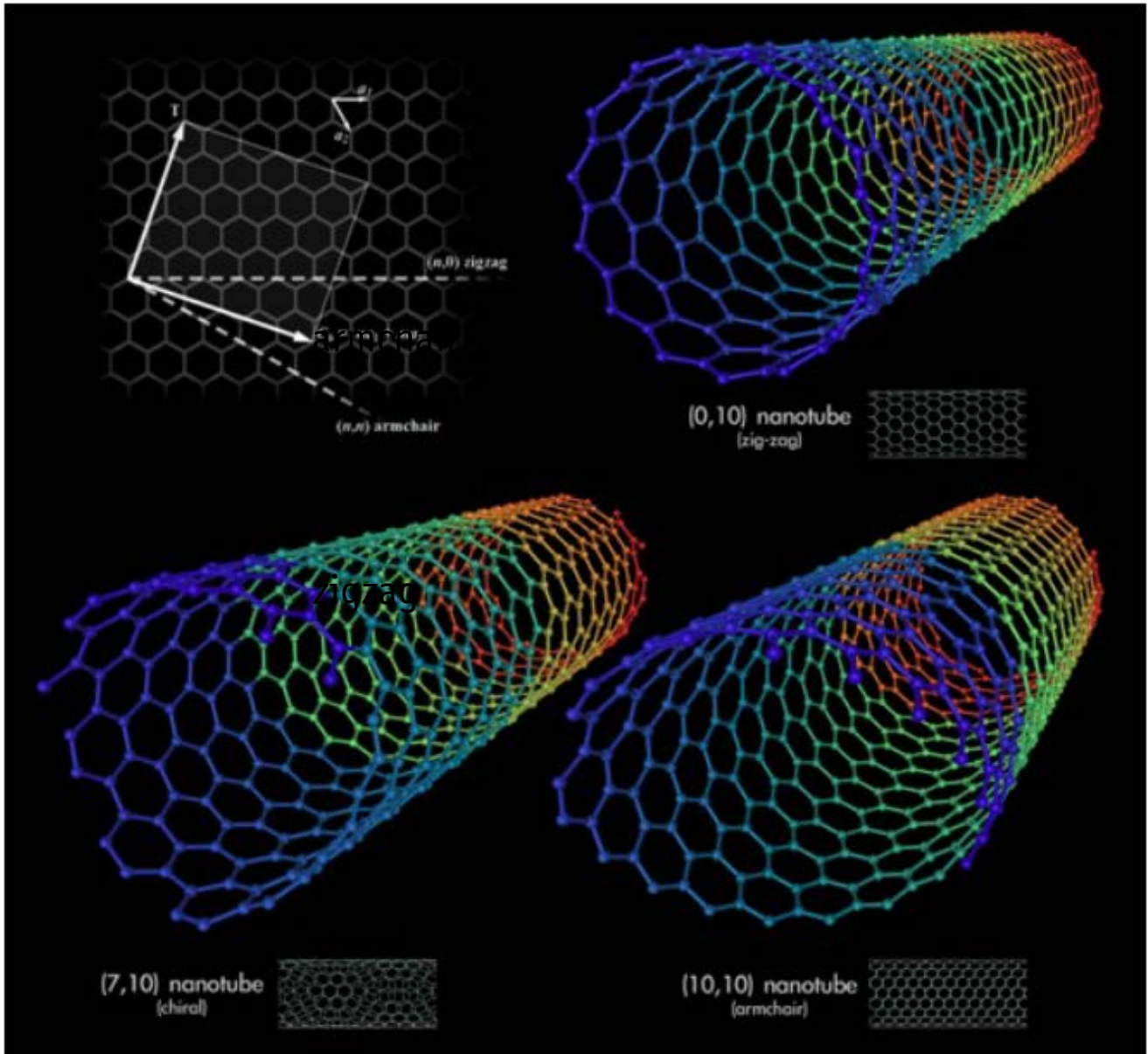


- doped and functionalized fullerenes, e.g. endohedral

5.2 All carbon materials

Carbon Nanotubes

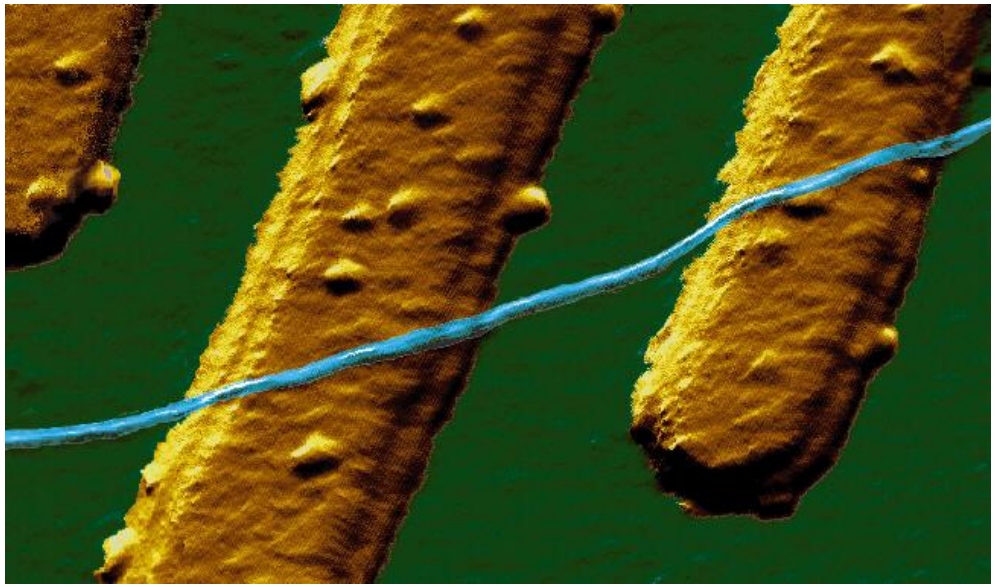
- conjugated
- various chiralities and electronic properties
- 1 dimensional conductors
- Mostly capped by fullerene-like dome

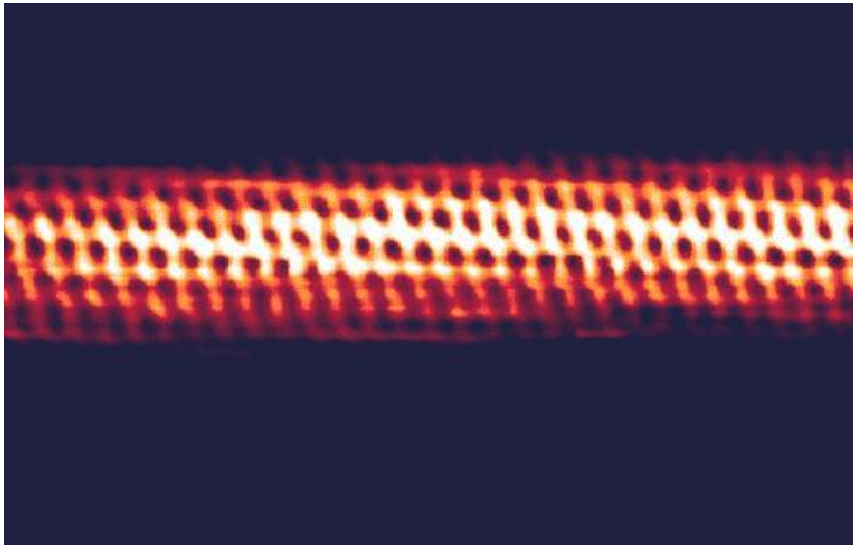


5.2 All carbon materials

Carbon Nanotubes

- conjugated
- various chiralities and electronic properties
- 1 dimensional conductors (quantum wires)

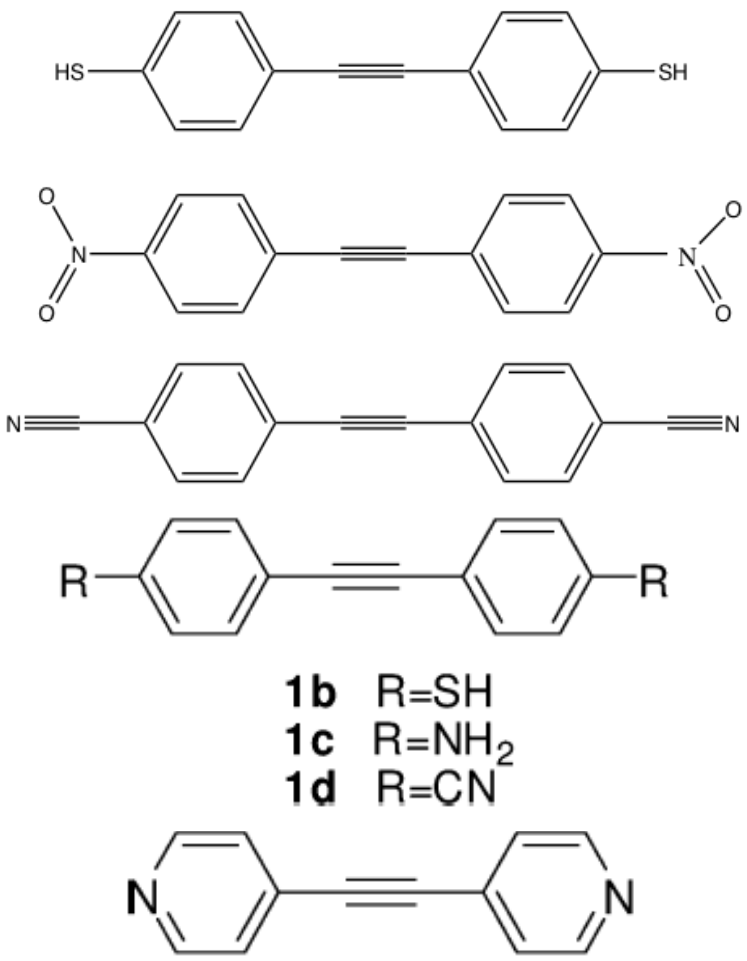




Source: TU Delft,

5.3 Anchoring groups

Goal: "Good" contacts between metals (mostly gold) and „kernel" of the molecule
Problem: direct Au-C bonds are difficult to achieve (but possible now)
Solution: Anchoring group



Thiol: Sulfur-Au bond (H cleaves off)
Most common system in ME (= **1b**), mostly HOMO transport

Nitro: weak electronic coupling,
mostly LUMO transport, often physisorbed

Cyano (Nitrile) = **1d,** rather weak coupling,
often physisorbed, mostly LUMO

1c: Amine: binds selectively
to undercoordinated Au atoms, mostly HOMO

Pyridine: rather good coupling, LUMO

5.4 Functionalities and suitable molecules

- Conducting wires: polyenes and alkynes
- Insulators: alkanes
- Switches: cis/trans conformation (azobenzene), ring-opening-ring-closure: diarylethenes
- Storage elements: all kinds of molecules with at least two states (conformations, redox states, spin states, and vibrational states)
- Diodes:
- Amplifiers: all molecules whose electronic levels can be tuned by a gate electrode might act as amplifiers. No amplification demonstrated yet.
- Anchoring groups: thiols, amines, nitros, cyanos or heterocycles with the substituent atoms serving as linkers to the metal electrodes