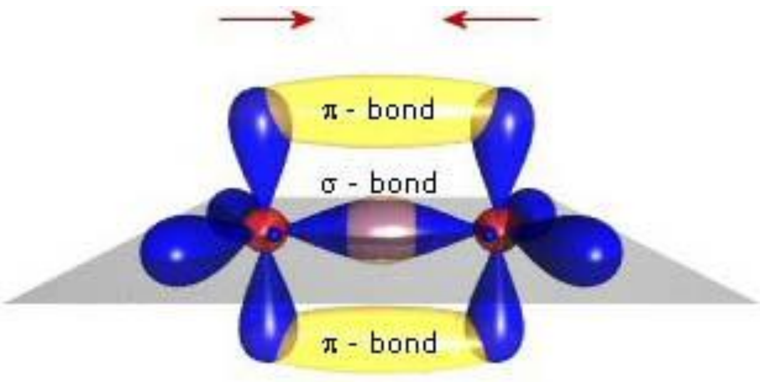
Carbon Atom

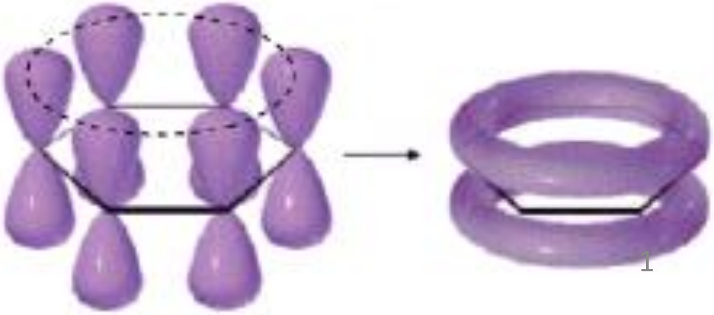
Each carbon atom usues two single bonds to bond itself with a hydrogen atom and with a carbon atom and a double bond to bond otself with one more carbon atom Non può esserci un legame doppio tra tutti gli atomi di carbonio adiacenti, ma questi legami si presenteranno alternati

Single and double bonds alternation→ conjugation

Conjugation length → length of a molecular chain with a perfect alternation between single and double bonds

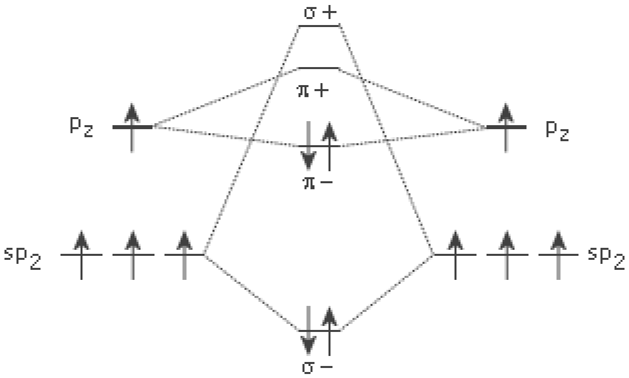


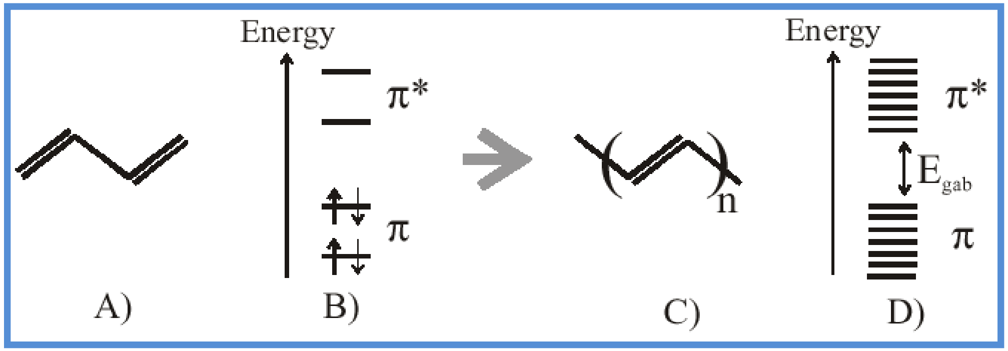
Benzene



The amount of σ o π bond in one molecule determins the bad gap amplitude, whereas, the number of atoms determines the energetic distance between these new states

Molecules with few atoms are characterized by discrete states, when the number of atomes is big enough sugh dscrete states ar so energetically close that can be considered as and energetic band





Band Gap in organic conjugated polymers

N atoms will form N/2 π bonds, i.e. there will be N π molecular orbitals (N/2 bonding and N/2 antibonding)

Considering the Pauli exclusion principle, only two electrons can occupy the single orbital

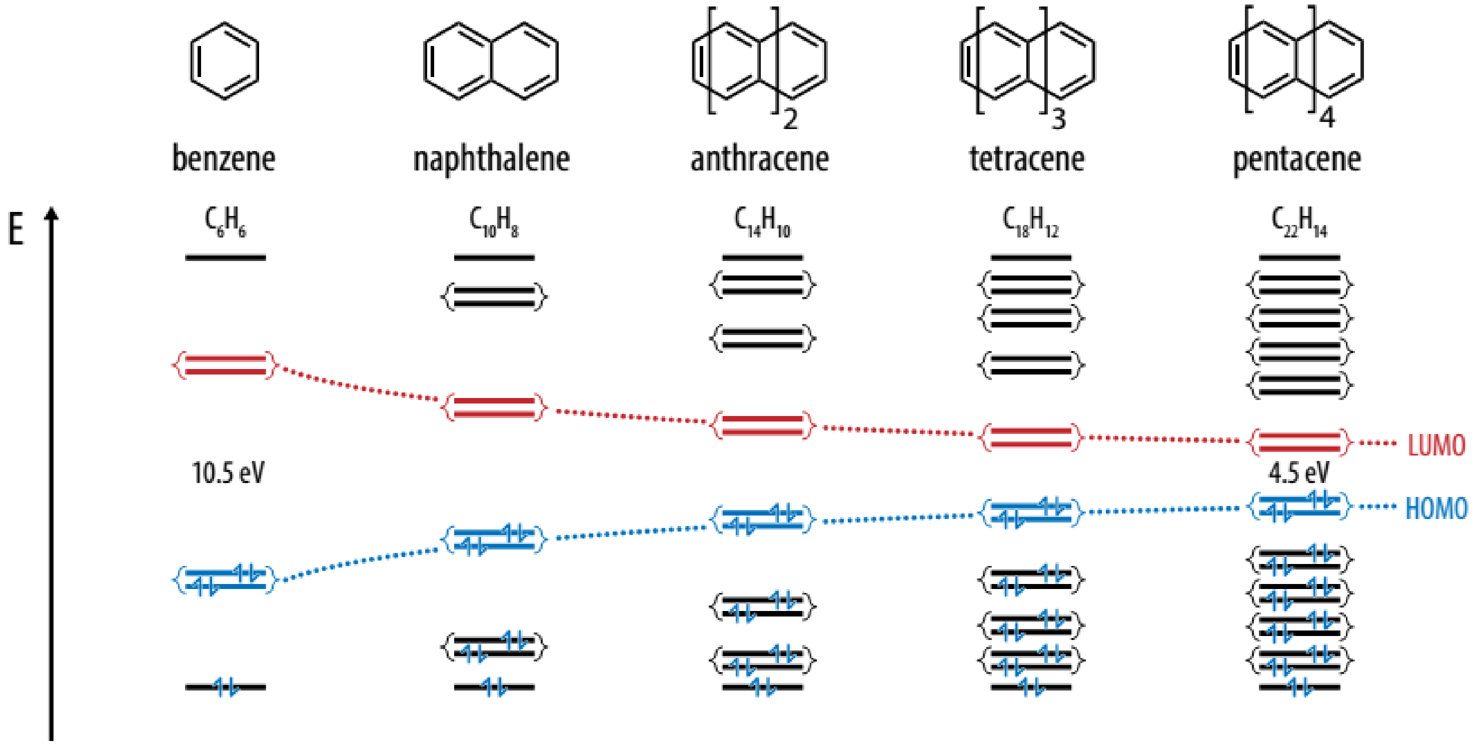
Ithe number of occupied states n will be N/2

$$E(HOMO) = \frac{\left(\frac{N}{2}\right)^2 h^2}{8m(Nd)^2} \qquad E(LUMO) = \frac{\left(\frac{N}{2}+1\right)^2 h^2}{8m(Nd)^2}$$

$$E_G = E(LUMO) - E(HOMO) = \frac{(N+1)h^2}{8m(Nd)^2}$$

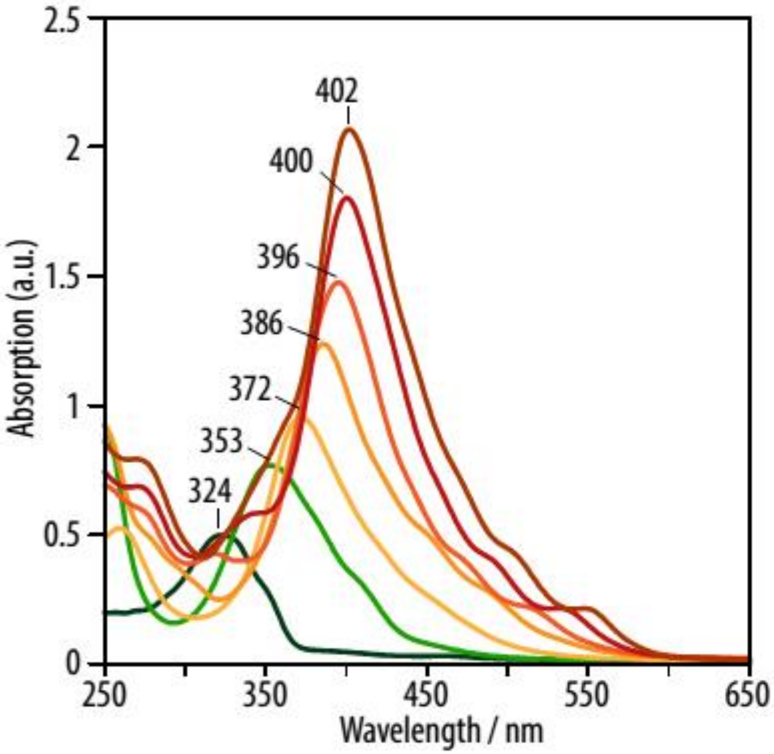
the band gap decreases when the molecule conjugation length (Nd) increases

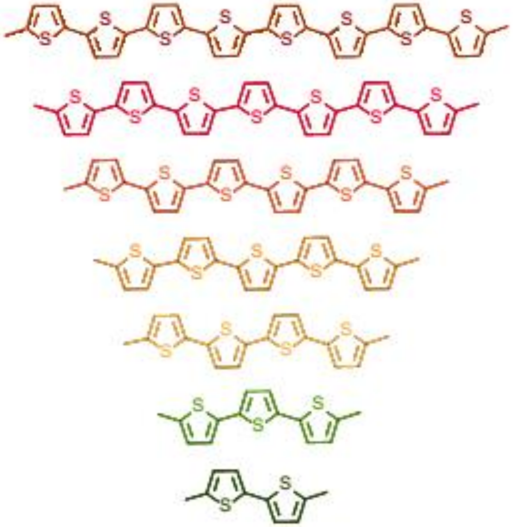
Band Gap in organic conjugated polymers



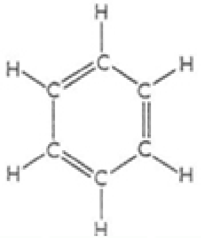
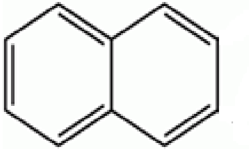
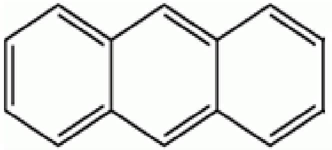
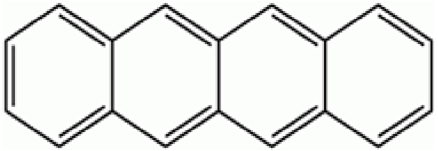
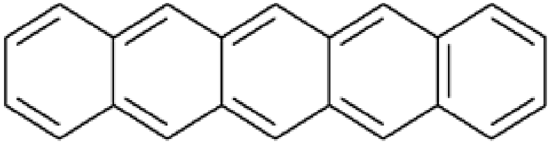
The higher the conjugation length the smaller the band gap

Band gap

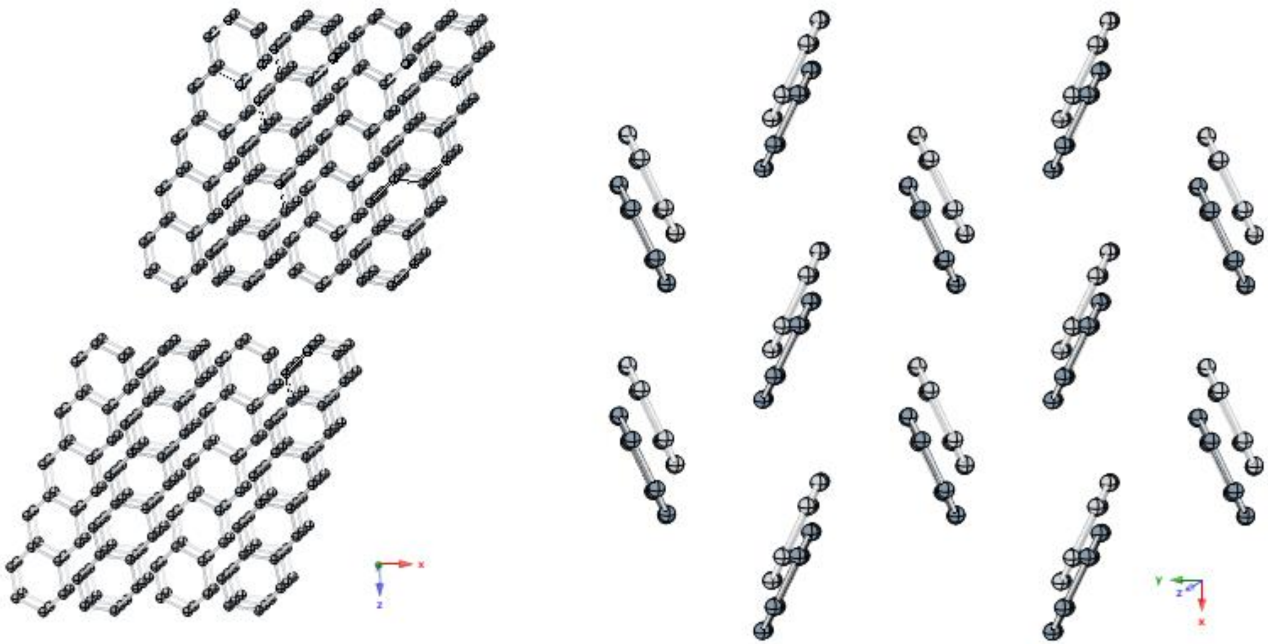

2.5
2
1.5
1
0.5
0
Absorption (a.u.)
250
350
450
550
650
Wavelength / nm
402
400
396
386
372
353
324



Band Gap in organic conjugated polymers

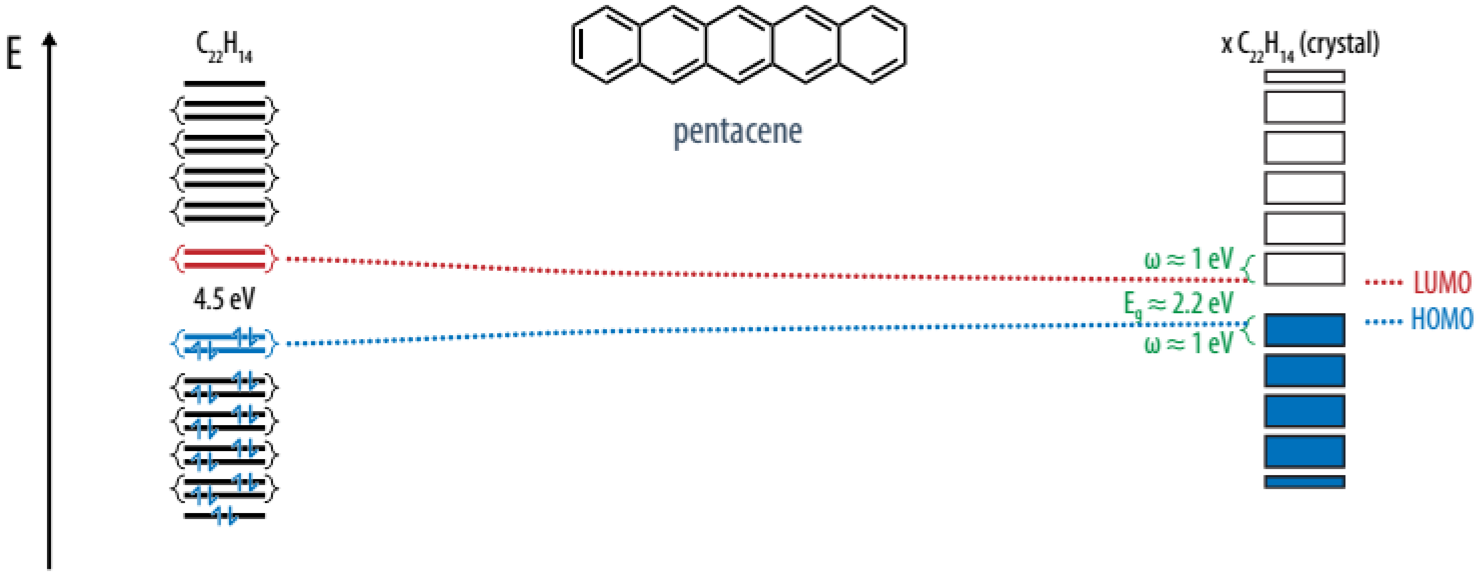
		Band Gap
Benzene		6.0 eV
Naphtalene		4.3 eV
Anthracene		3.3 eV
Tetracene		2.6 eV
Pentacene		2.1 eV

Band gap



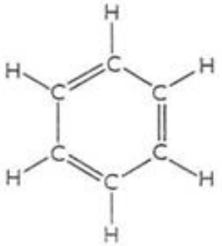
In a film there is a multitude of molecules which interact, the way these molecules assemble in the film determines the electronic properties of the film

- Molecular packing → structural properties
  pi-stacking
- Domains dimensions → morphological properties

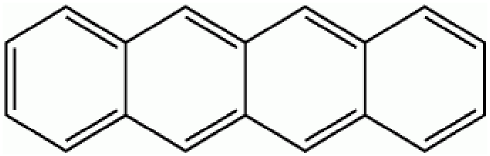


- This is the reason why the band gap of a film is much smaller than the band gap of a single molecule
- Creation of additional energetic levels, bonding and antibonding , creation of small bands (ca. 1eV)
- Extended energetic bands where charge carriers can move, similarly to inorganic materials

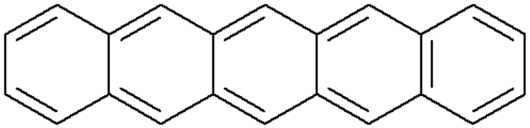
Benzene
Aromatic small molecules



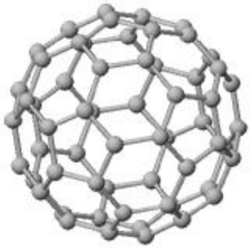
Tetracene



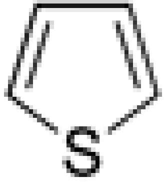
Pentacene



Fullerene, C60

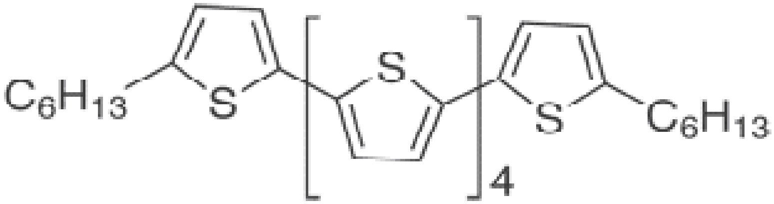


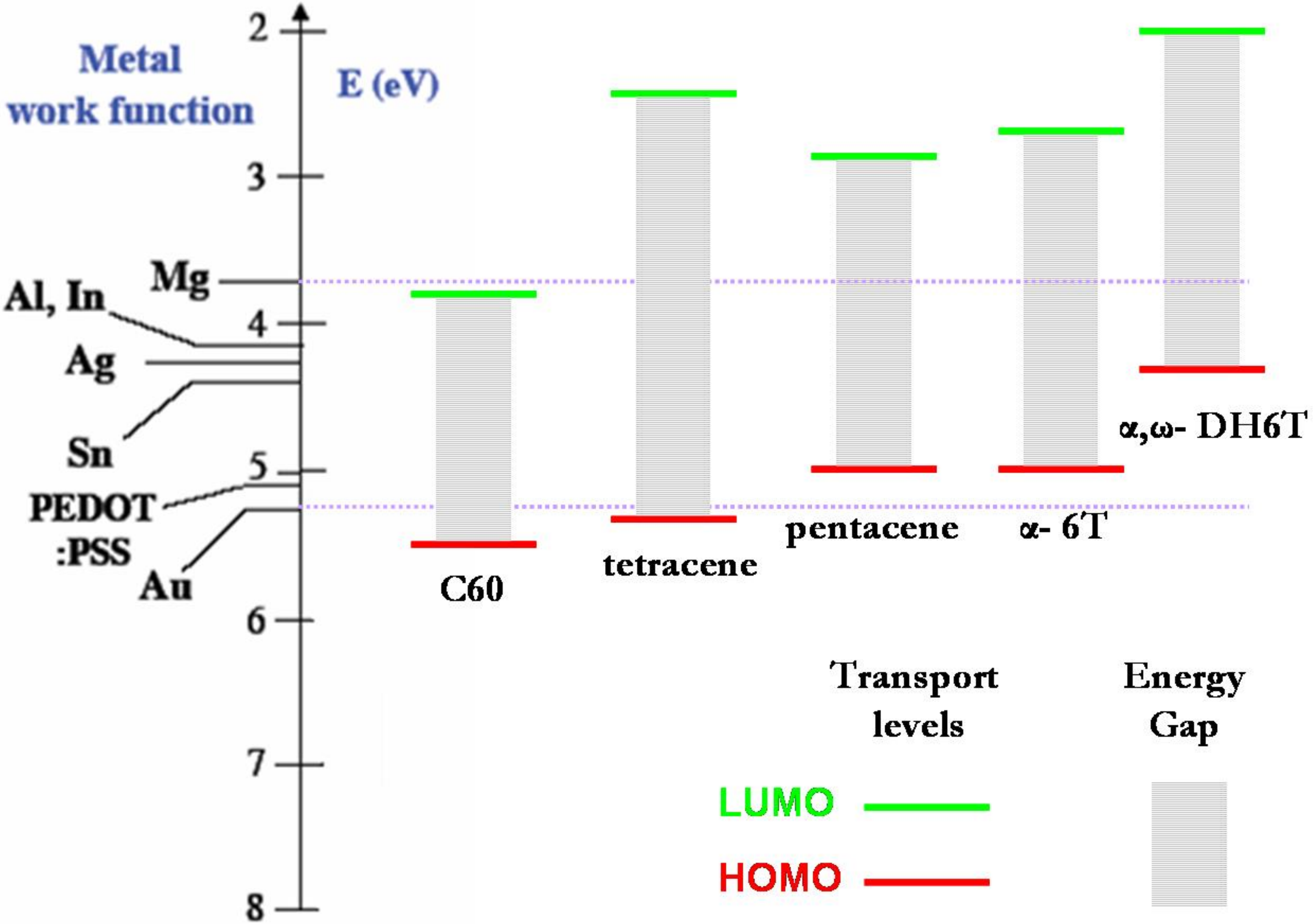
Thiophene
Heterocyclic oligomers



Sexithiophene (4T, 5T, 6T, 8T)

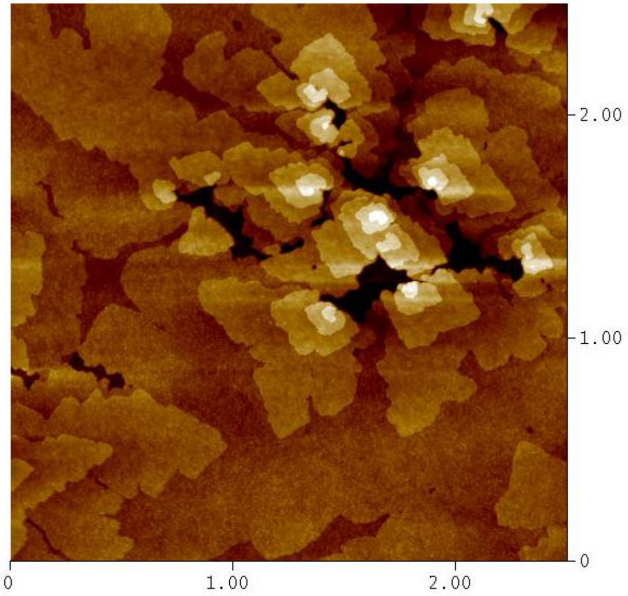
Dihexyl-sexithiophene (DH6T)

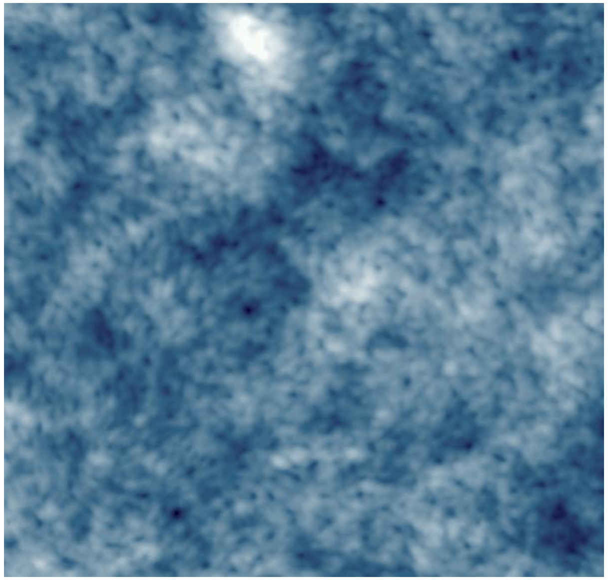


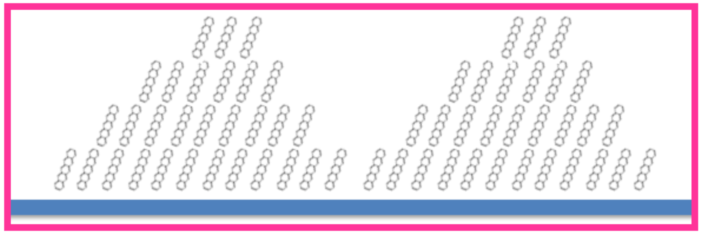

Metal work function
E (eV)
2
3
4
5
6
7
8
Mg
Al, In
Ag
Sn
PEDOT :PSS
Au
C60
tetracene
pentacene
α- 6T
α,ω- DH6T
Transport levels
Energy Gap
LUMO
HOMO

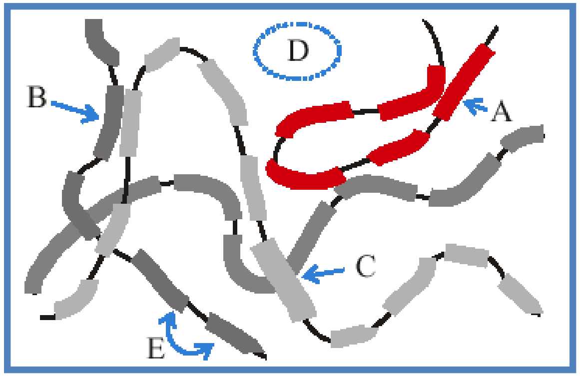
Oligomers

Polymers









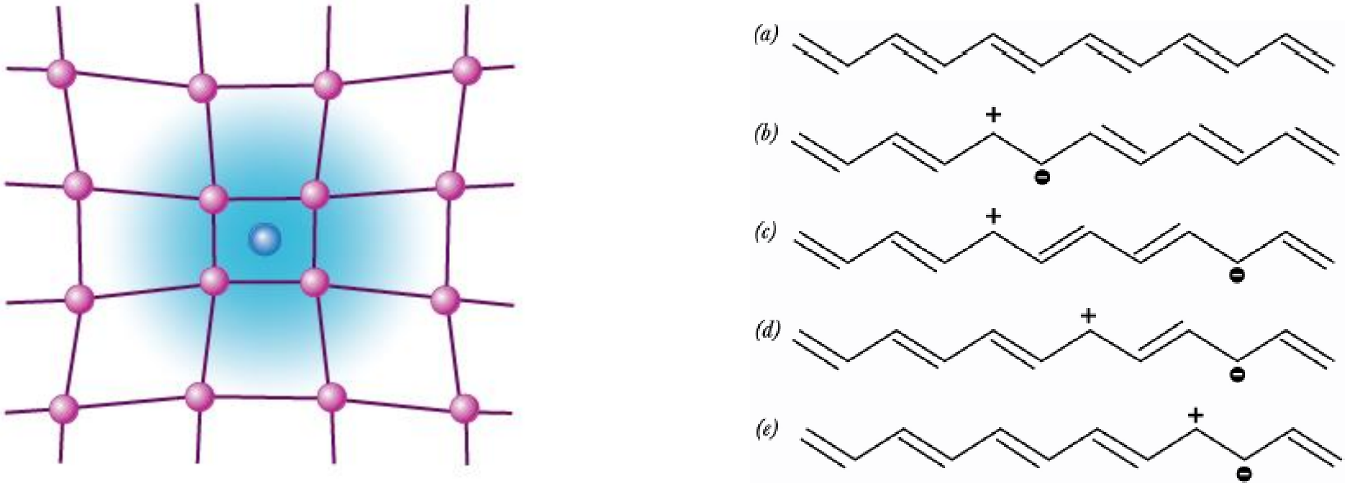
Organic conductors and semiconductors

The polaron

We already said that cnojugation is rquire in order to have charge transport in organic molecues

A charge moving in a conjugated molecule, interact with the molecule itself, creating a deformation of the molecule.

Such deformation is called **POLARON**



Formation of a polar and its transport across a molecule

The polaron

In other words, in a nojugated molecule, a charge moving is self-trapped within the molecule due to the induced deformation of the surroundinig

This process leads to a localized energetic state within the band gap of the material, i.e. between HOMO and LUMO

The polaron can be seen as a new charge, a free charge moving in a conjugated system but with a high mass

m eff (polaron) >> m eff (free electron)

mobility (polaron) << mobility (free electron)

Mobility, conductivity, in a conjugated molecule is generally small

The polaron

Actually, in all the systems where a charge is moving will exist a polaron, also if we consider a free electron moving in a period crystal structure

In inorganic crystal such effect is present but so small that can be not taken into account

In the conjugated molecules, we have covalent bonds which are relatively weak, Van der Waals interactions, therefore, the electric field created by a moving charge can deform such bond, i.e. can deform the molecule

Therefore, the polaronic effect is much more evident

Imagine to have a ball moving on a sheet, blanket

The polaron

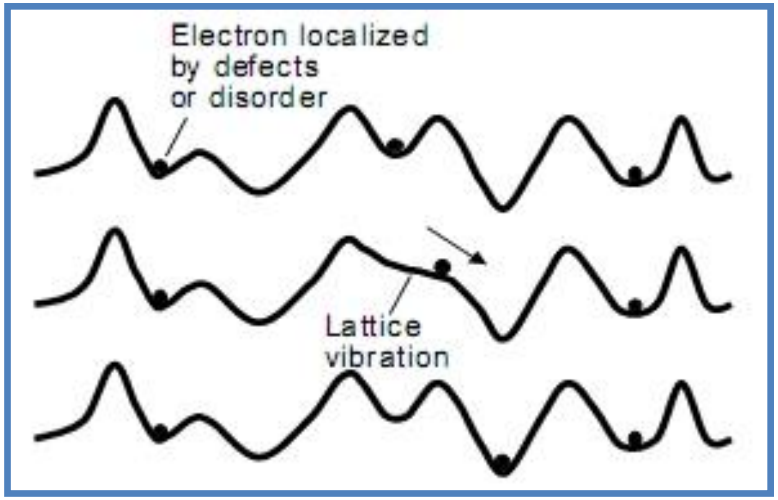
The molecule could be considered as the sheet and the ball as a charge carrier

The way the ball deforms the sheet could be different, depending on the mass of the ball, but also on the way this sheet is stretched

If the charge interaction radius is bigger than the atomic distance, we speek about **LARGE POLARONS** → band like transport

If the charge interaction radius is smaller than the atomic distance, we speek about **SMALL POLARONS** → thermally activated transport - hopping

The polaron



Hopping

A charge carrier (polaron) moving in a molecule is self-trapped, there is a localized state. In order to move from one state to another, we have to spend some energy in order to allow it to make an energetic jump, i.e. hop from one state to another

This hops are allowed as long as in the molecule there is conjugation

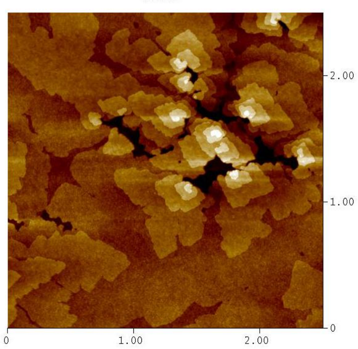
In a film we have also to consider the charge transfer between different molecule

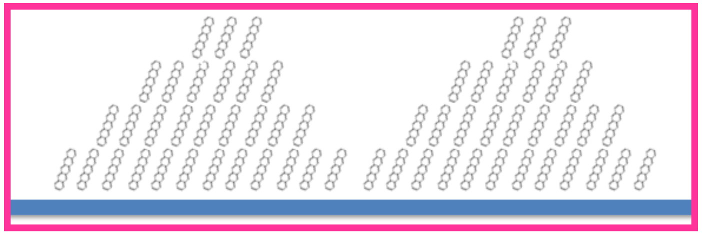
The polaron

In a film we generally have

- Hopping transport when small polarons are present
- Band like transport when large polarons are present

Oligomers





Polymers