Organic Semiconductors & Devices

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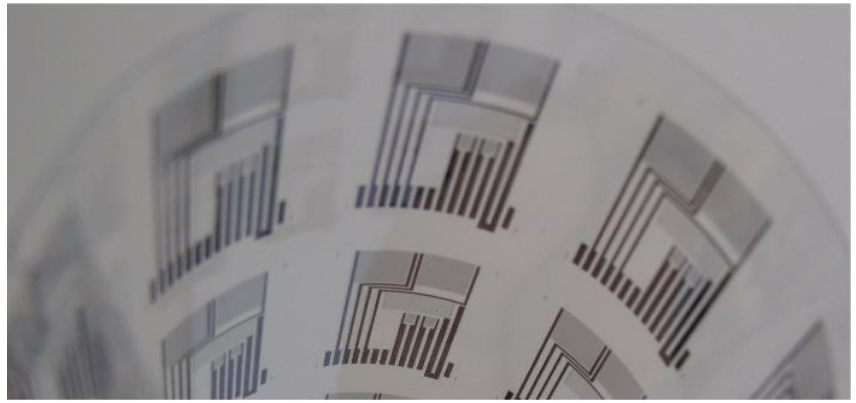
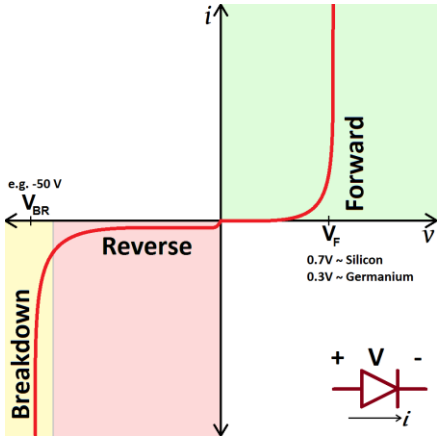
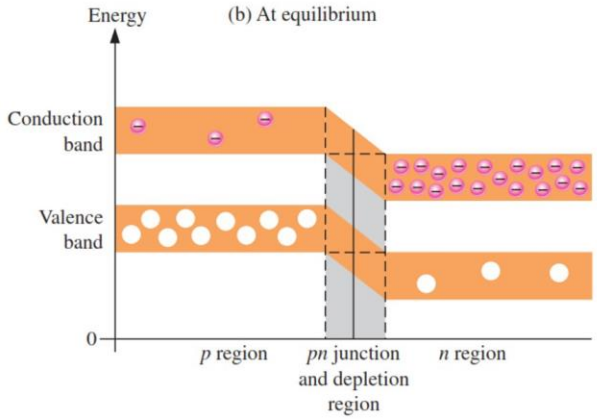
Flexible and Conformable Devices



How to predict any device





- Equilibrium
  - Energy levels
  - DoS (Eg, N)
  - Charge carriers
- Operation
  - Electric Field
  - Mobility

Organic Semiconductors

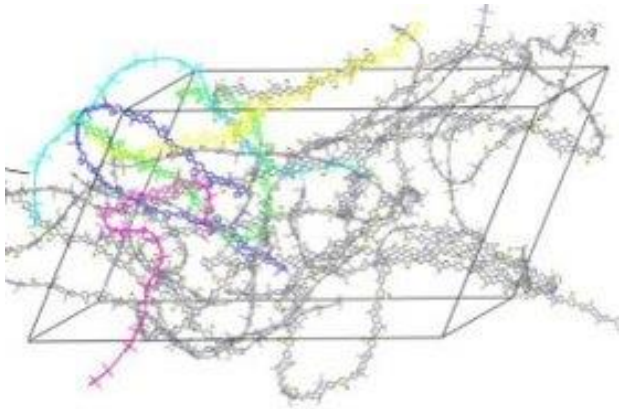
There are no energy bands

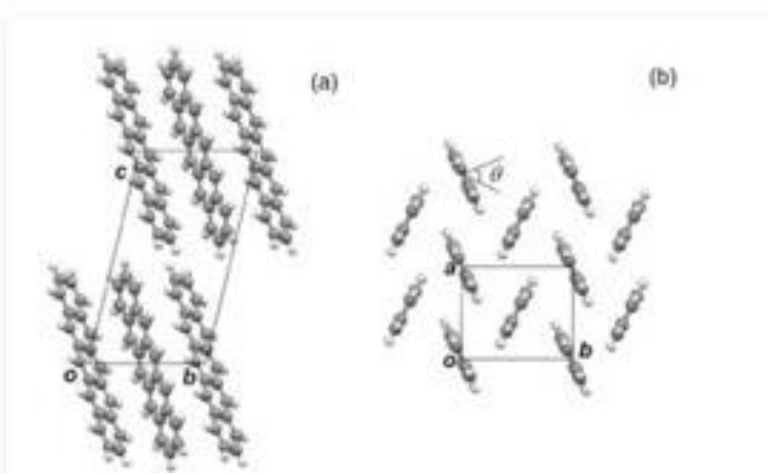
There are no charge carriers

Fermi level at interfaces don't line up

Organic Materials

- Molecular or polymer solids: molecular or long chain
- Amorphous thinfilms: Positional disorder, order not longer than 10nm
- Strong covalent bonds, weak intermolecular interactions





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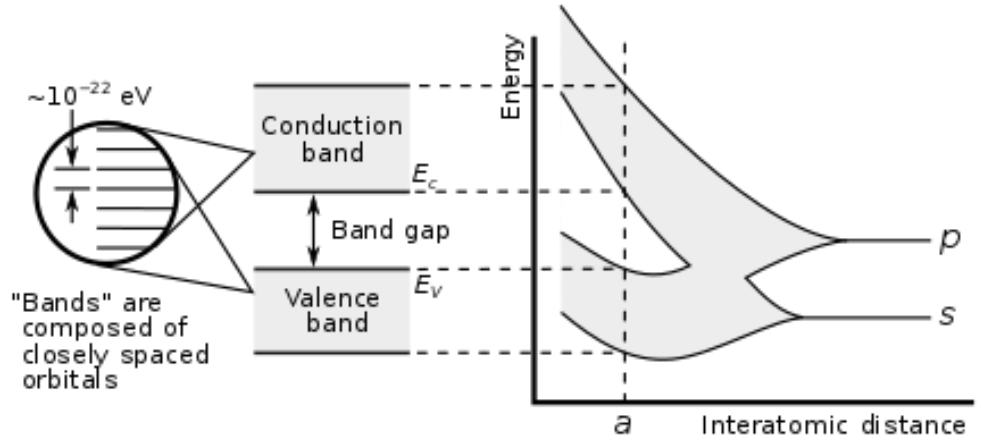
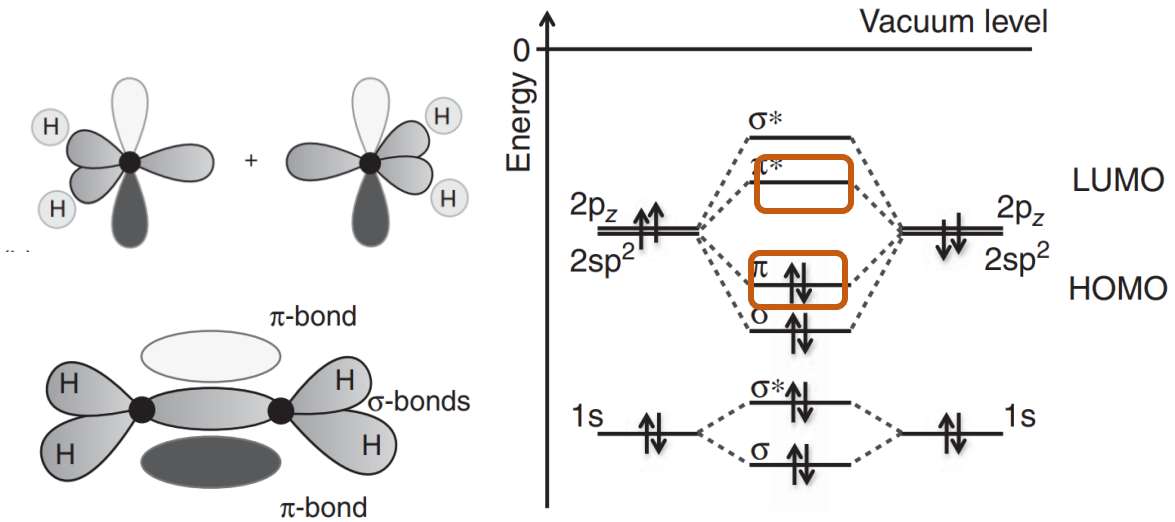
Energy Levels



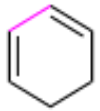


- As distance between atoms reduces, energy levels split
- 2N electrons occupy N energy levels

- Molecular orbitals form from atomic orbitals
- Strong covalent bonds
- Weak intermolecular interactions; molecular orbitals don't split further
- Highest Occupied & Lowest Unoccupied Molecular Orbital

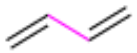
Kohler, Bassler, "Electronic Processes in Organic Semiconductors"

Conjugation



1,3-Cyclohexadiene
(Conjugated)

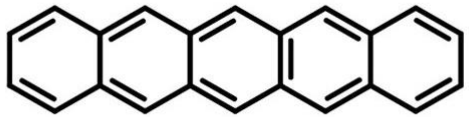
1,4-Cyclohexadiene
(Non-Conjugated)



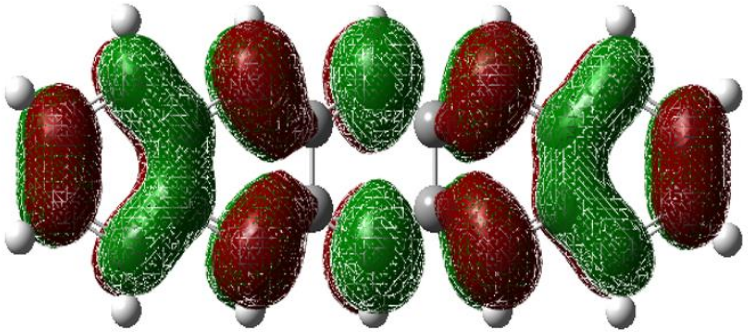
1,3-Butadiene
(Conjugated)

1,4-Pentadiene
(Non-Conjugated)

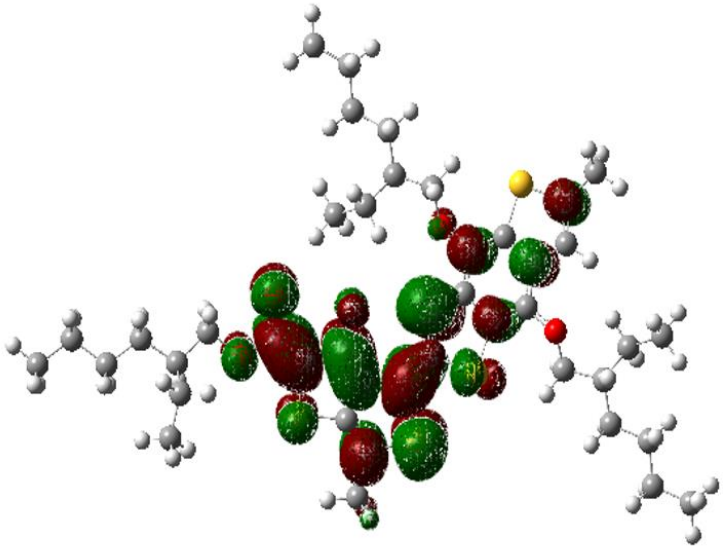
Pentacene



Conjugation --> Delocalization



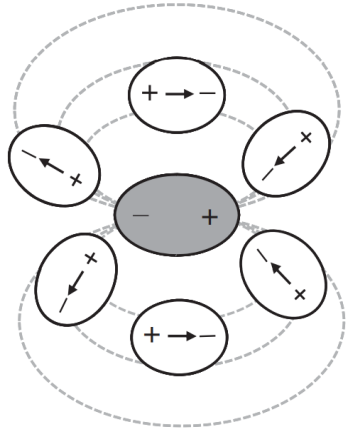
LUMO of pentacene delocalized over molecule



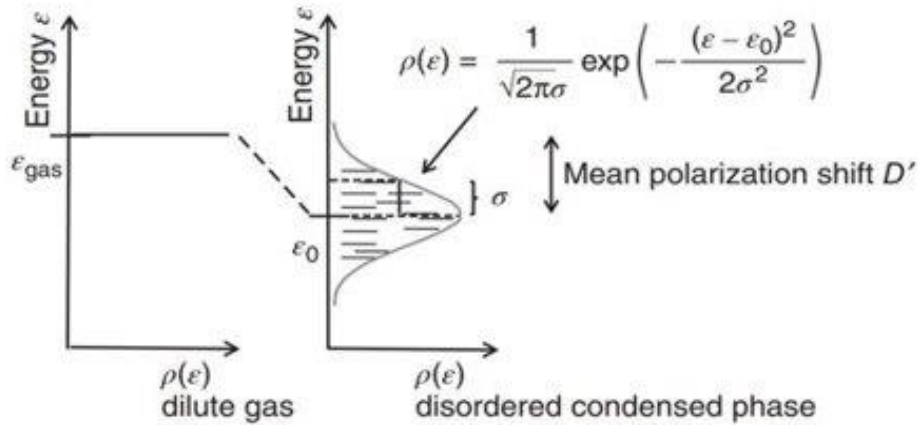
LUMO delocalized over conjugated backbone but not non-conjugated side chains

Density of States

- Molecular distances are large: no further splitting
- Solid state: shift in energy levels
- Amorphous materials:
  - Environment of each molecule is different
  - Shift in energy is different for each molecule



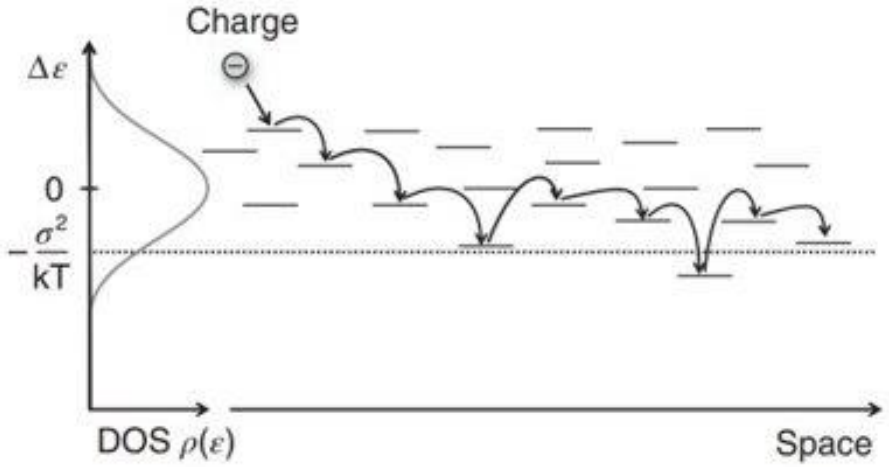
Environment of each molecule is different; unpredictable



Energy levels throughout the solid are shifted by a random amount; considered to form a gaussian distribution

Charge Transport

- Charge hopping to neighbouring sites
- Neighbouring sites are accessible
- Orbital transfer—a connected pathway for electrons

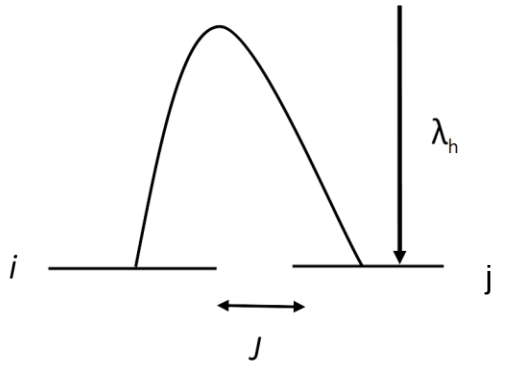


Hops depend on

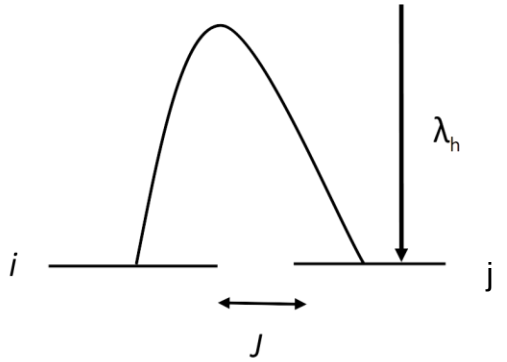
Site energy level

Physical site proximity

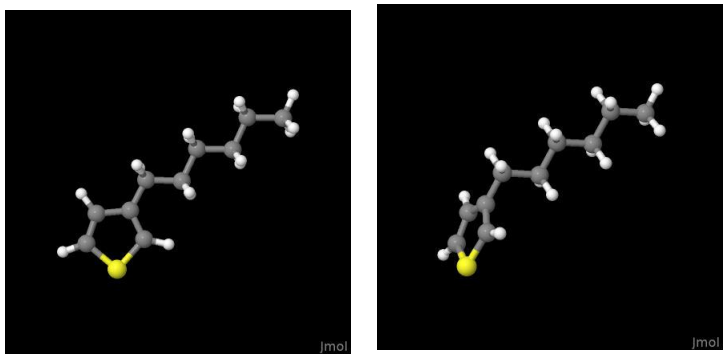
Activation energy



Charge Transport



- Addition of charge to a neutral molecule causes bonds to rearrange; consumes reorganisation energy (λ)
- Reorganisation energy is activation barrier to every charge hop



Addition of charge changes configuration

- 'J' is charge transfer integral: Intermolecular electronic coupling
- Is the overlap of orbitals feasible?

$$k_{ij} = \frac{J^2}{\hbar}\sqrt{\frac{\pi}{\lambda\, kT}}\exp\left(-\frac{(\lambda + E_i - E_j)^2}{4\,\lambda\, kT}\right)$$

Mobility

- Charge transport is sequence of hops, each taking time (t= 1/k_{ij})
- Random walk follows path of several electrons, get average displacement (r)
- Intermolecular distance is a gaussian distribution around ideal molecular spacing
- In electric field, average displacement is according to its direction, but hops are in random direction too, depending on which neighbours allow feasible energy levels and orbital overlap

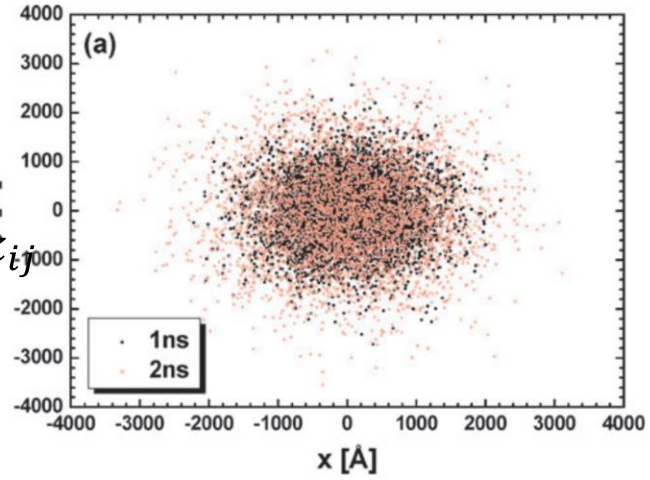
$$D = \frac{1}{2n}\frac{\langle r^2 \rangle}{t}$$

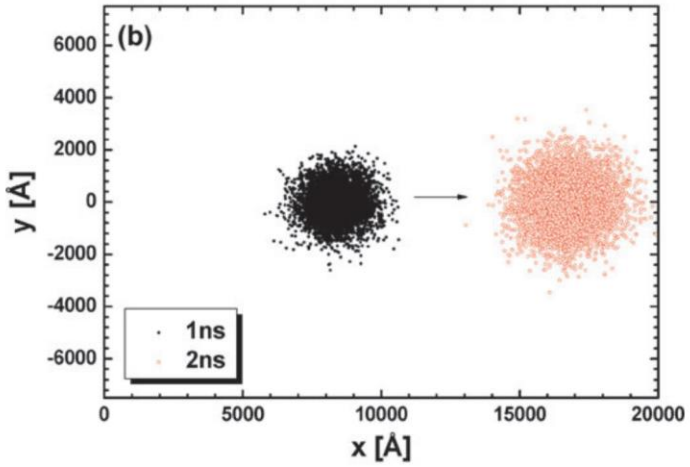
$$= \frac{1}{2n}\langle r^2 \rangle \sum k_{ij}$$

$$\mu = \frac{q}{kT} D$$

$$\mu = \frac{v}{E}$$

$$= \left\langle \frac{r}{t} \right\rangle \frac{1}{E}$$



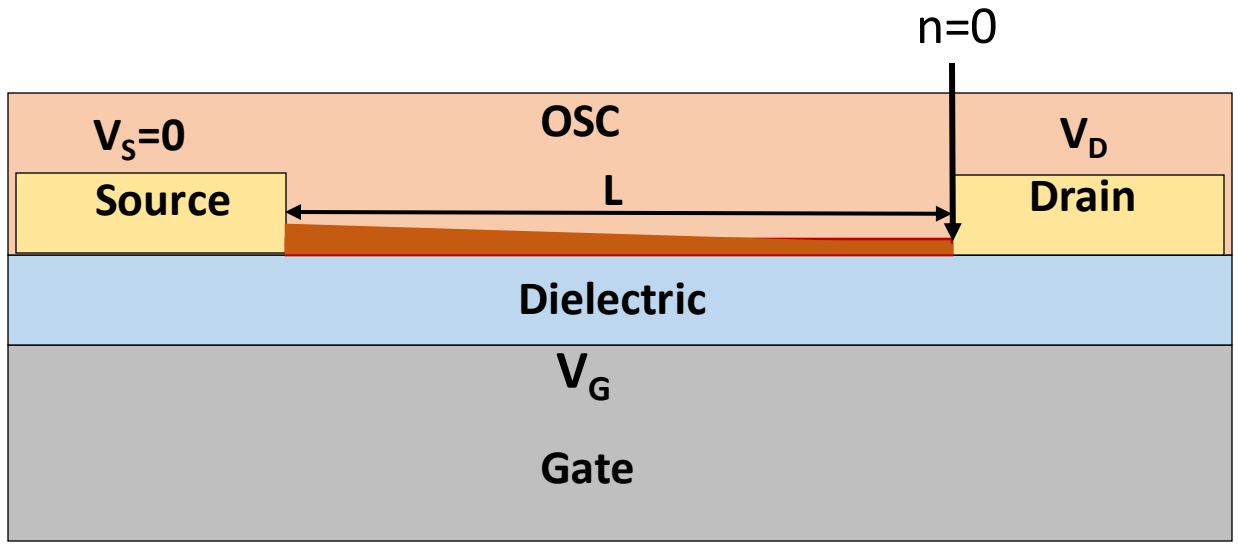


Chem. Soc. Rev., 2010, 39, 423–434

Organic Field Effect Transistors

Low charge carrier density:

- Thin Film Transistors
- Accumulation mode



$$n = C(V_G - V_T)$$

$$n = C(V_G - V_T - V_D/2)$$

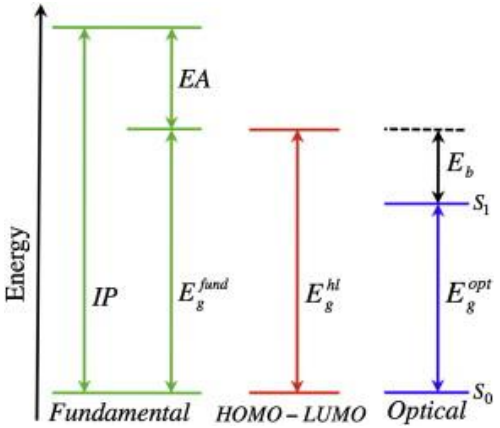
Linear $$I_D = \mu C \left(V_G - V_T - \frac{V_D}{2}\right) V_D \frac{W}{L}$$

Saturation $$I_D = \mu C \left(\frac{V_G - V_T}{2}\right) \frac{W}{L} (V_G - V_T)$$

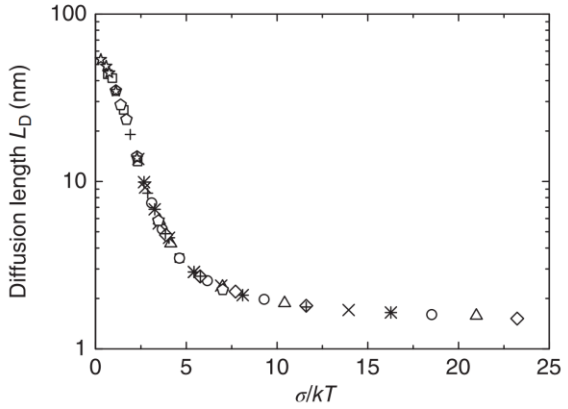
$$\mu_{Sat} = \left(\frac{\partial \sqrt{I_D}}{V_G}\right)^2 \frac{2L}{CW}$$

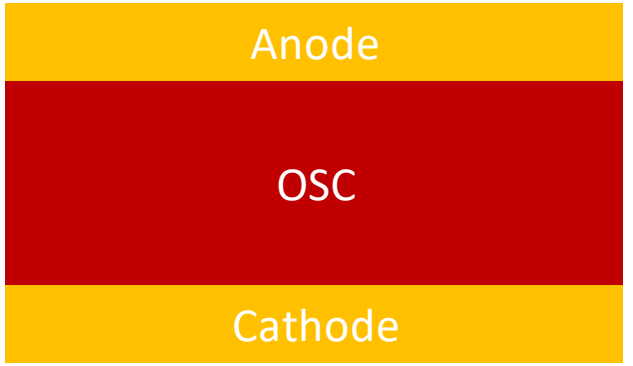
Simplest Solar Cell

Binding Energy



- Exciton formation
  - Binding Energy: electron and hole are bound together on a molecule
- Exciton Diffusion
  - Excitation transfers have a small diffusion length
  - Exciton recombines before reaching electrodes: inefficient device

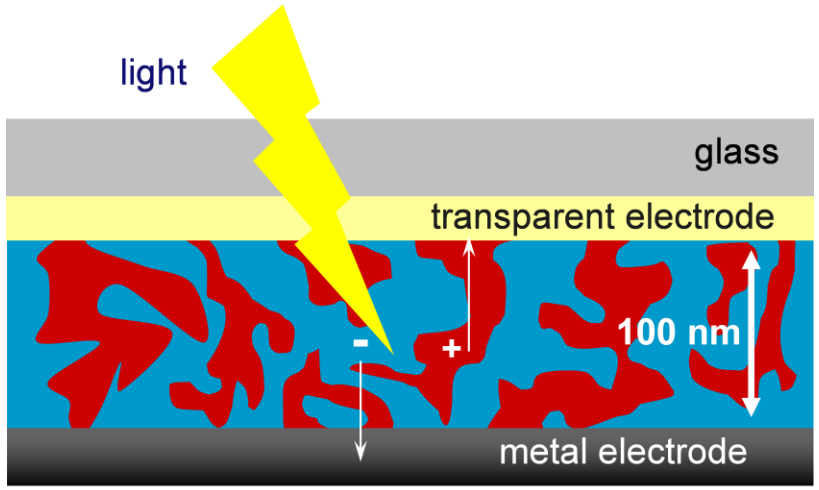


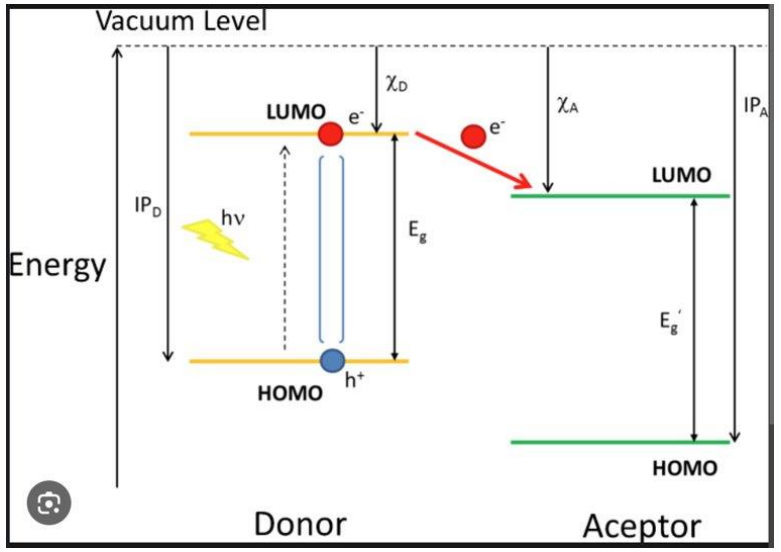


Organic Diode

Bulk Heterojunction Organic Solar Cells

- Molecular junctions
- Energy difference at DA interface separates exciton
- Electron and hole transport to electrodes via network of acceptor and donors





Summary

- Amorphous solids
- Energy levels
- Polarons transport- *k*
- Mobility
- Organic transistors
- Exciton transport
- BHJ cells