Organic and Printed Electronics

LESSON 4 – ORGANIC SEMICONDUCTORS FOR LAE

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Objectives and content

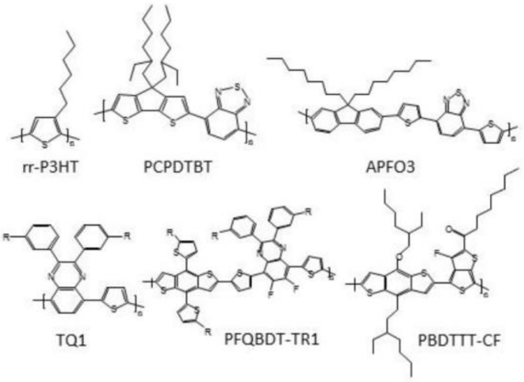
Objectives

- To introduce the basic concepts, terminology and physics of organic and disordered semiconductors from the ground up.
- To introduce core concepts to enable understanding of the basic mechanisms of operation of organic electronic and optoelectronic devices.

Content

- Energy levels in semiconductors for large area systems
- Optoelectronic Properties
- Charge Transport

Some Example Organic Semiconductors

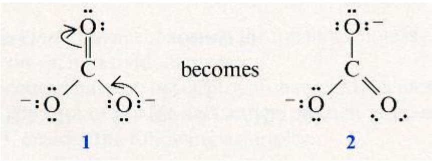


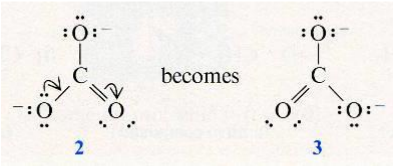
What is a common feature of these?

Some quick chemistry: Lewis Structure and Resonance

- Assuming we know bonding structure, we can assign electrons by making each individual atom form a noble gas configuration

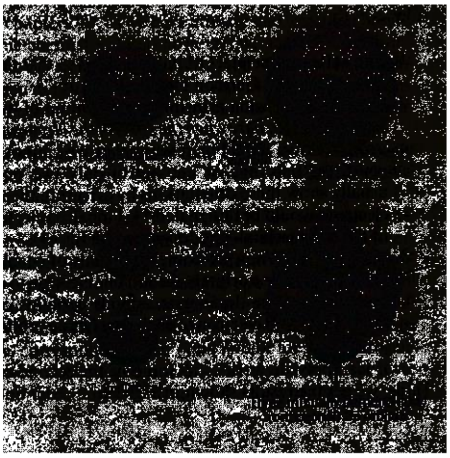
- Problem with Lewis Structures: In reality, we can write multiple different versions of the same molecule by only changing positions of electrons, e.g., CO_3^{2-}.





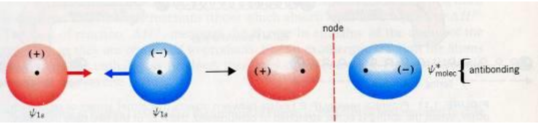
Some quick chemistry: Orbitals

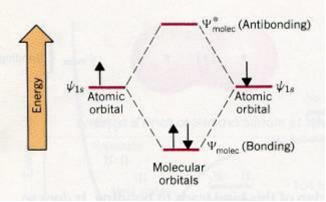
- As you may remember from basic chemistry, we know that electrons actually exist in orbitals.



Some quick chemistry: Molecular Orbitals

- Consider formation of H_2
- As the 2 H atoms approach each other, their 1s wavefunctions interact. The in-phase interaction cause a reinforcement of the probability function (called a bonding orbital), while the out-of-phase interactions cause interference (called an antibonding orbital). Just like atomic orbitals, each orbital contains only 2 electrons

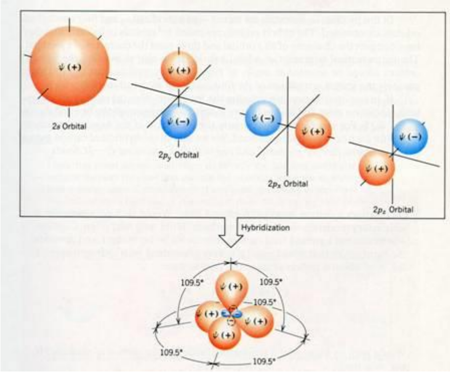




- The bonding orbitals are in the ground state; in the excited state, the antibonding orbitals may be occupied.

Some quick chemistry: Hybridization

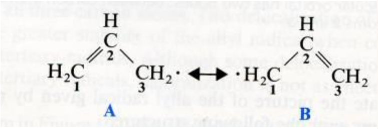
- We know that methane has a tetravalent tetrahedral structure. The asymmetry between 2s and 2p cannot explain this.
- In fact, the wave functions for 2s and 2p combine to form a hybrid (sp^3)

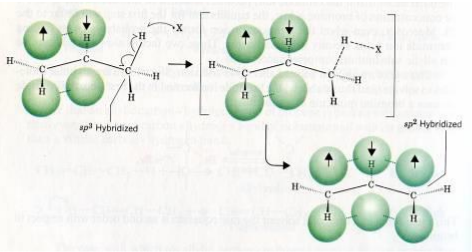


- Other hybrids such as sp^2, etc., also exist.

Some quick chemistry: Conjugation

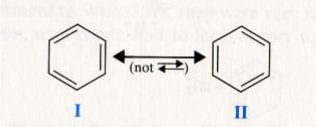
- The particular situation in which a double-bond sits adjacent to a p-orbital on an atom is called conjugation.
- Conjugation is the basis of electronic transport in organic systems; since the double bond is delocalized, i.e., it can switch with the adjacent single bond.



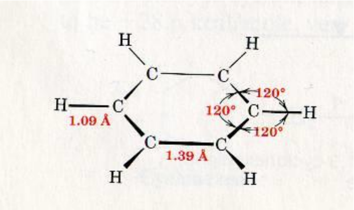


Some quick chemistry: Aromatic Compounds

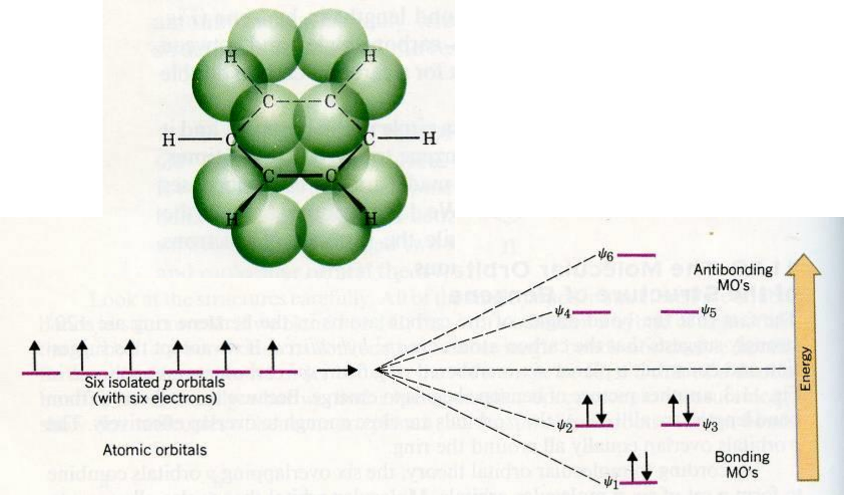
- The most basic aromatic structure is the benzene molecule



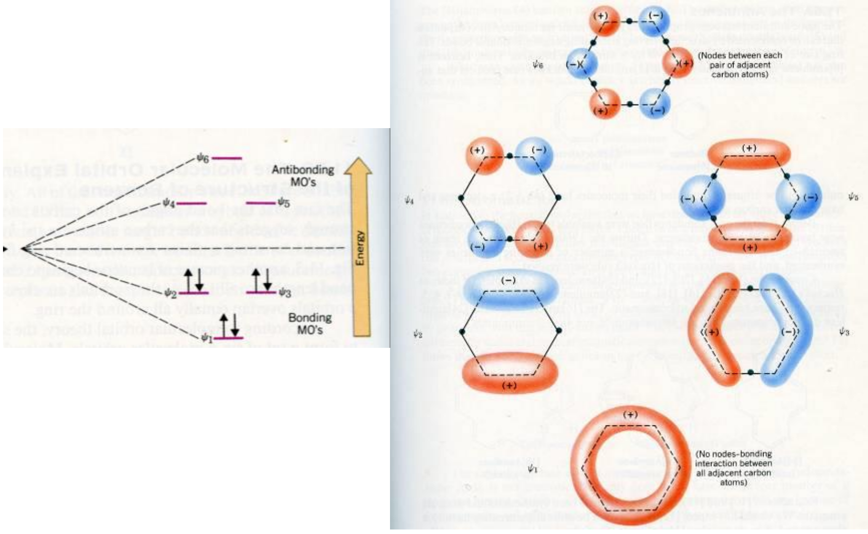
- Note that all bonds are neither single nor double. They are in between the two. This has been verified spectroscopically, with bond lengths and angles matching the above predictions.



Some quick chemistry: Orbital Structure of Benzene

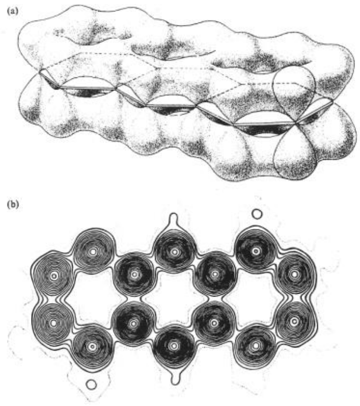


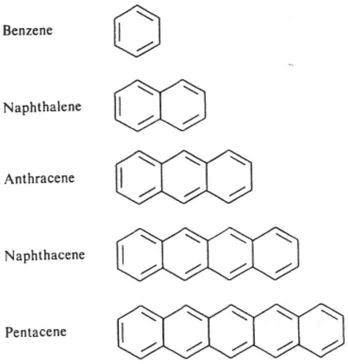
Some quick chemistry: MO Structure of Benzene



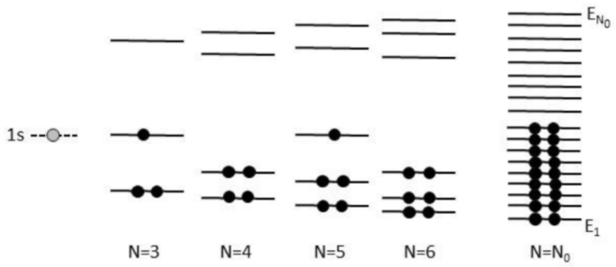
Conjugation as the basis of conduction

- Due to π-p conjugation, electrons are delocalized above and below the nuclear plane of conjugated systems.





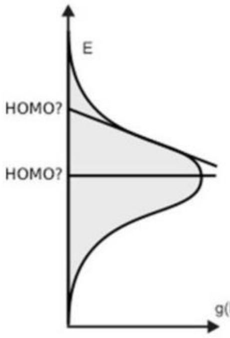
Appearance of an energy gap: from 1 to N



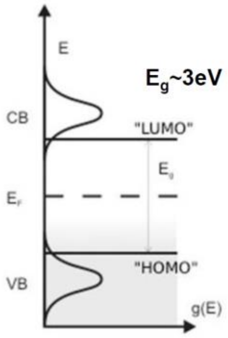
Evolution of the molecular orbital energies for a linear chain of N interacting singly-occupied 1s orbitals (hydrogen atoms)

The **gap in energy** separating the highest occupied molecular orbital (**HOMO**) and the lowest unoccupied molecular orbital (**LUMO**), Ψ_+ and Ψ_-, respectively for the H_2 molecule, represent the **minimum energy** needed to create an **excited state**.

Electrostatics of organic semiconductors



the most common ways to evaluate the frontier orbital energy edges



A schematic view of the density of states around the Fermi level.

The **density of states (DOS)** enumerates the number of possible states as a function of energy.

At 0 K, the electrons occupy the lowest possible energy states, and for a metal the energy up to which all the levels are filled is called the **Fermi level**.

valence band edges-> HOMO
conduction band edge-> LUMO

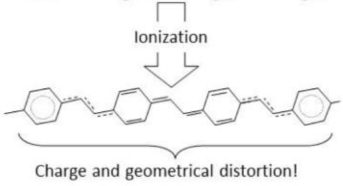
Crystalline materials -> well defined bands & unambiguous definition of ionization potential and electron affinity

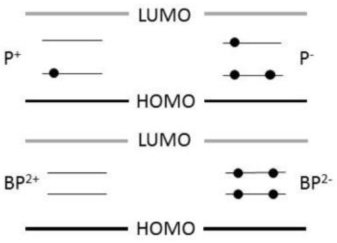
Disordered materials -> ill defined band edges and their positions are difficult to measure

Preview: Charge movement

Peierls instability -> position & electronic density distortion -> can travel along the chain (with some energy)

The combination of a charge with an accompanying potential well is a quasi-particle called a **polaron**, which is inherently localized in space

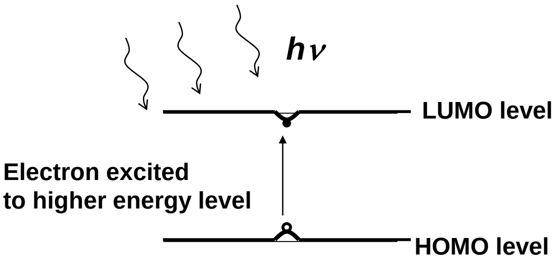




segment of a poly(p-phenylenevinylene) chain undergoing bond alternation upon ionization

polaronic species (P – singly charged and BP – doubly charged) appearing in the HOMO-LUMO gap upon ionization

Interactions with light



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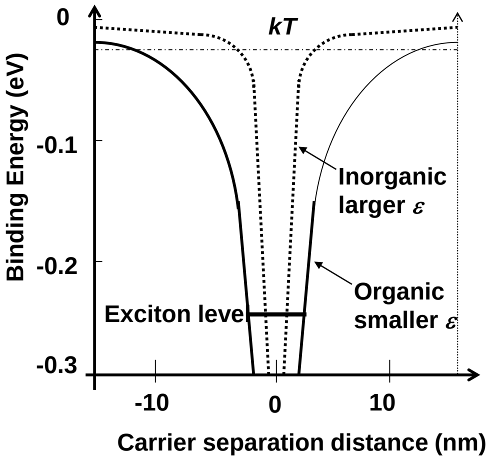
LUMO level

Electron excited to higher energy level

HOMO level

- Absorbed photons do NOT always form Free electrons and holes
- Absorbed photon creates an *exciton*

Exciton binding



- More localisation of electron in organic semiconductor
- Smaller ε in organic semiconductor - larger force of attraction
- The exciton binding energy needs to be overcome for its dissociation

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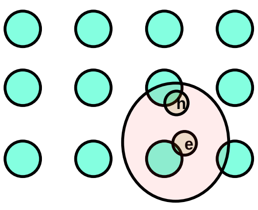
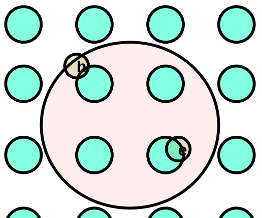
Excitons

- ❑ **Neutral species**
- ❑ **Only energy carriers**



Frenkel Exciton

- Highly localised
- Common in molecular solids
  - In organic semiconductors

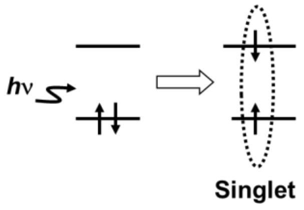


Wannier-Mott Exciton

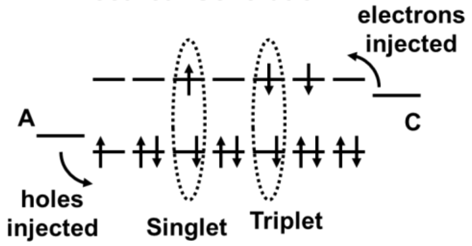
- **Extended**
- **Common in crystals**

Singlets and Triplets

- Photo Generation



- Electrical Generation



- Molecule absorbs photon
- Electron unchanged
- Only singlets formed

- Electrons/holes injected
- Electron spins random
- Singlets and triplets formed

By themselves triplets cannot undergo radiative recombination

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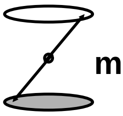
Singlets and Triplets

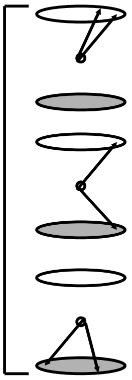
Under Particle Exchange:

S=0



$m_s=0$ $\frac{1}{\sqrt{2}}\{\uparrow(1)\downarrow(2)-\uparrow(2)\downarrow(1)\}$ **Anti-symmetric**

S=1



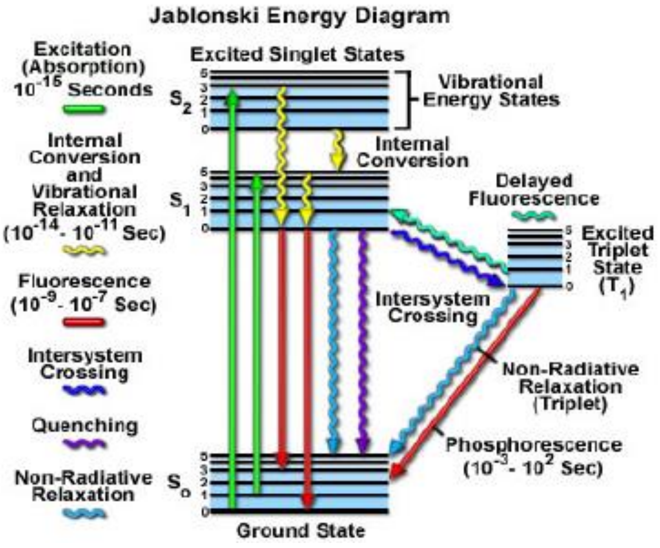
$m_s=+1$ $\frac{1}{\sqrt{2}}\{\uparrow(1)\uparrow(2)\}$

$m_s=0$ $\frac{1}{\sqrt{2}}\{\uparrow(1)\downarrow(2)+\uparrow(2)\downarrow(1)\}$

$m_s=-1$ $\frac{1}{\sqrt{2}}\{\downarrow(1)\downarrow(2)\}$

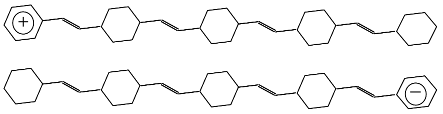
Symmetric

Relaxation

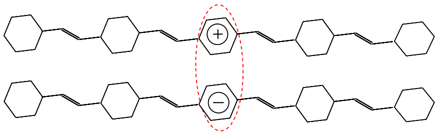


Preview: How might an OLED work?

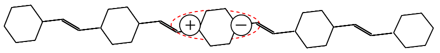
1. Unbound electron-hole pair on neighbouring chains:



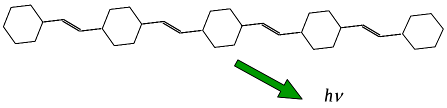
2. Electron-hole pair is captured to form a weakly bound ‘charge-transfer’ exciton:



3. Inter-conversion to a strongly bound exciton:



4. Singlet exciton decays radiatively:

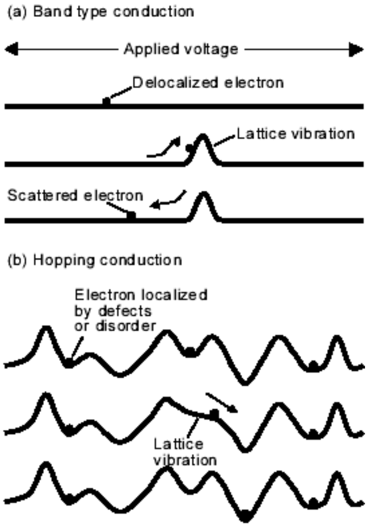


Transport of charges

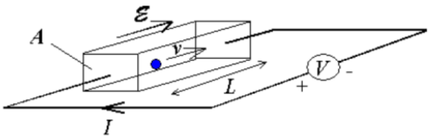
2 generic types of transport

- Band transport – mobility generally decreases with T due to increased scattering
- Hopping transport – mobility generally increases with T

- Which one do you expect in LAE?



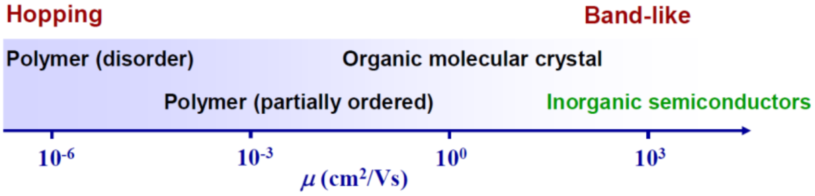
Mobility… what does it mean?



$$v = \mu \cdot E$$

Drift velocity v [m/s]
Mobility μ [m²/Vs]
Electrical field strength E=V/L [V/m]

- **μ describes how fast are carriers under an E-field**
- **μ is strongly dependent on electronic structure (order) of materials**

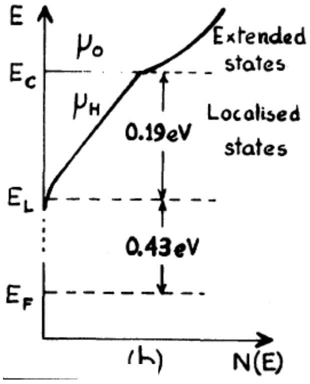


The multiple trapping and release model

- **The MTR model takes account of the fact that most amorphous systems have large number of trap states within the bandgap. In fact, the overall states are partitioned into:**
  - **Extended States: States at and above the band edges, corresponding to the valence and conduction bands in crystalline semiconductors**
  - **Localized States: States that exist within the bandgap and periodically trap and release carriers from the extended states**
- **The consequence of these localized states is a reduction in conductivity, since the number of free carriers is less than the expected number. Equivalently, we can say that the mobility is lowered if we assume the carrier concentration is fixed**

History: MTR

- **The MTR model was originally developed to describe behavior in amorphous silicon and other disordered systems. Typically, these systems showed exponential band tails, as shown below:**



Basic equation framework

- **Consider conductivity:** $\sigma = n_f \, q\mu_0$.
  - **Where n_f is the number of free carriers (i.e., in extended states)**
- **If we want to write this in terms of the total expected carriers, we have:**
  - **Where θ_s is the fraction of carriers that are free**
- **If we choose to embed this within the mobility, we can write the reduced mobility as:**

$$\sigma = n_{\mathrm{tot}} \, q\theta\mu_0$$

$$\mu = \theta\mu_0$$

Temperature dependence of MTR mobility

- **Depending on the temperature, carriers spend time either moving within the extended states or trapped in the localized states.**
- **If we assume only a single localized state at energy E, the mobility is:**

$$\mu_D = \mu_0 \alpha \exp[-(E_c - E)/kT].$$

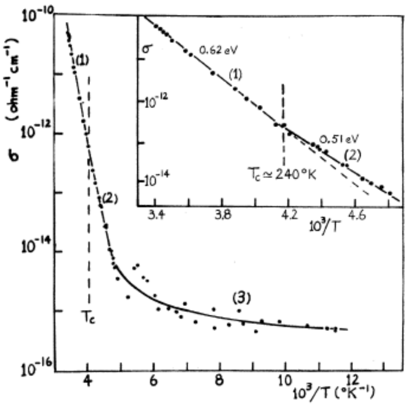
- **Correspondingly, the transport of carriers in the extended states can be modeled as brownian motion from state to state, resulting in the mobility:**

$$\mu_0 \simeq (ea^2/6kT)\nu_{e1}$$

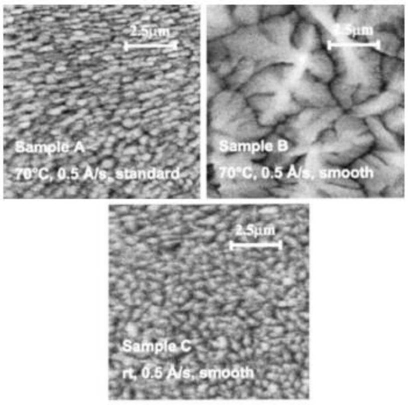
  - **where ν_{e1} is the electronic frequency, typically 10^{15} Hz**

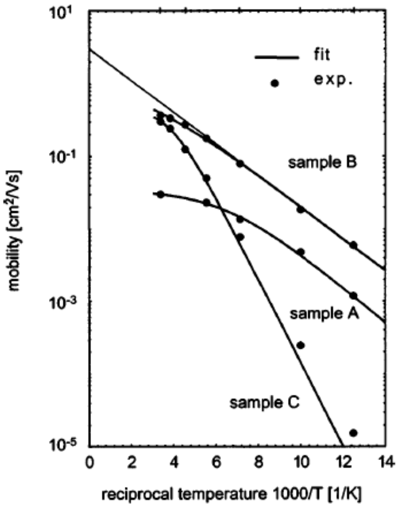
T dependence of MTR conductivity

- **The MTR effect results in a temperature gradient in (1).**
- **As the temperature is reduced (2), carriers are unable release from the localized states; instead they hop between localized states (called phonon-assisted hopping), resulting in a change in slope**
- **At still lower temperatures (3), carriers aren't even excited into the localized states, and it is believed that carriers hop through states near the Fermi level.**



Effect of film quality on MTR





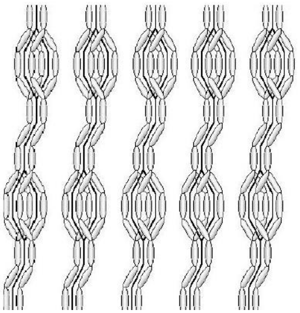
Classes of organic semiconductors

- **Organic semiconductors may be classified based on whether they are polymers or small molecules**
  - **<u>Polymers</u>: Typically soluble. Performance is usually mediocre due to poor transport between strands**
  - **<u>Oligomers</u>: Typically insoluble. Performance is usually improved due to good crystallinity**

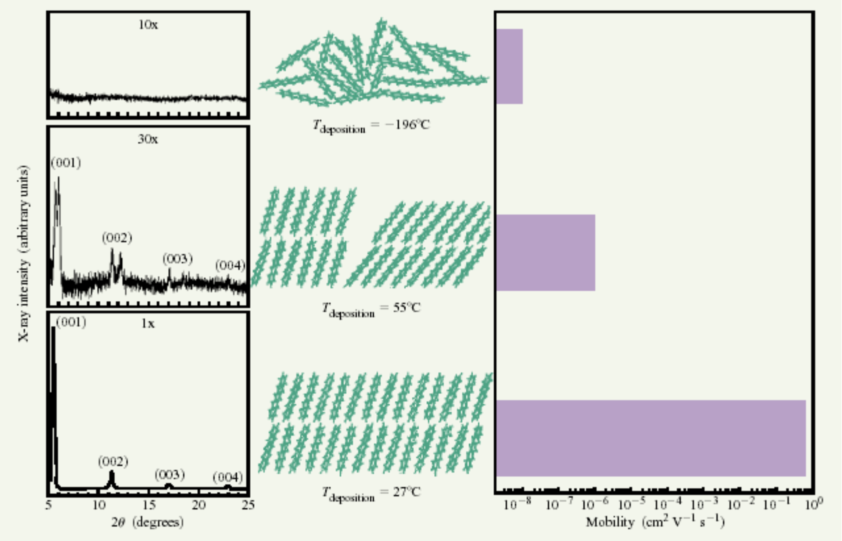
Note that insolubility and crystallinity usually go hand-in-hand; the same properties that make materials resistant to solvents often make them pack well, resulting in good electronic conduction in semiconductors.

Pi-stacking: The key to good transport

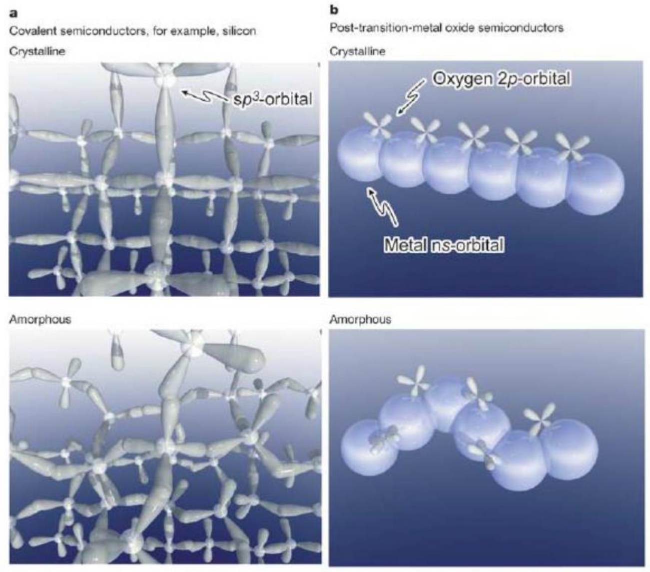
- **As discussed previously, crystallinity is crucial to achieving good transport properties.**
- **Unlike inorganic semiconductors, organic semiconductors have no covalent bonding between molecules; instead, bonding is by overlap of pi-orbitals, often called pi-stacking**
- **Pi-stacking allows for hopping of carriers between molecules.**



Channel ordering effects on transport



Other LAE Semiconductor Examples: Transition Metal Oxides



Comparison

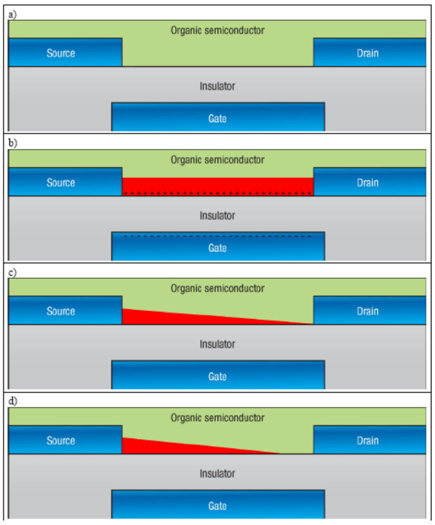
Properties	Oxides	Organics
Printability	+	+
Environmental stability	+	-
Conductivity of charge carriers	+	-
Processing Temperature	-	+
Cost	+	-
Availability in large quantity	+	-
Precursor snthesizing (*e.g.* p-type amorphous oxides)	-	+
Ink formulation	-	+

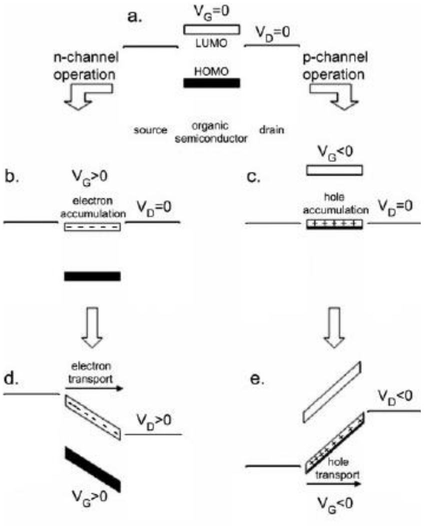
Questions to consider

- Can organic materials be considered conductors?
- What is a typical characteristic of an organic semi-conducting molecule?
- What is a HOMO ? LUMO ?
- Will the band widths resulting from the inter-monomer molecular orbital interactions in a linear polymer chain increase or decrease with the number N of monomers in the chain?
- What is required for an ohmic contact to be formed between a conductor and an organic material?
- Charge carrier mobilities in organic semiconductors are usually low, why?
- Will increased film order increase or decrease charge mobility?
- Will materials impurities tend to increase or decrease charge mobility?
- How will temperature increase affect mobility?
- How are optical absorption and photoluminescence related in an organic material ?

ORGANIC THIN FILM TRANSISTORS

Qualitative operation of organic TFTs



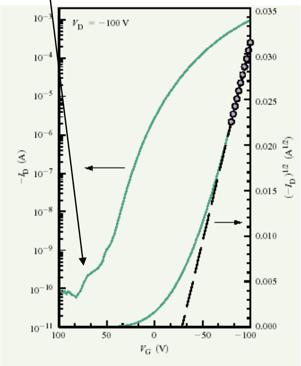


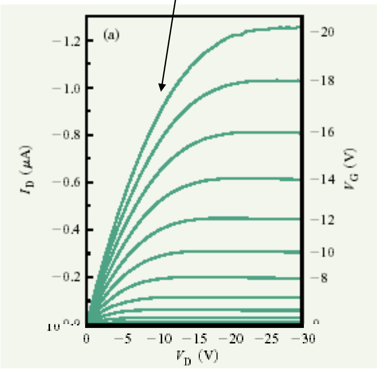
Typical I-V curves in organic TETs

Note the GIDL-like behavior under reverse gate bias, and note the slow turn-on

Also note the non-exponential behavior of subthreshold

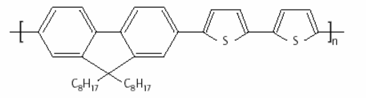
Note the deviation from square law behavior, and note the series resistance



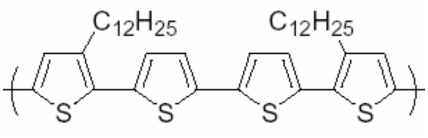


Typical p-type polymer semiconductors

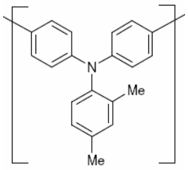
- **All organic semiconductors are conjugated systems, where electronic conduction occurs due to resonance**
- **Room temperature carrier concentrations are typically extremely low, making these semi-insulating**



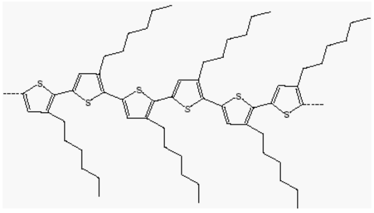
F8T2



PQT



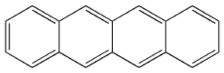
Poly Aryl Amine



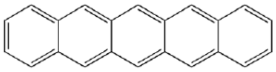
Poly hexyl thiophenes

P-type oligomer semiconductors

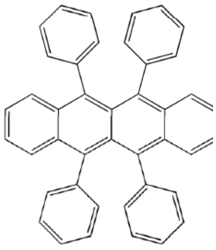
- **Insoluble (must be evaporated)**



Tetracene

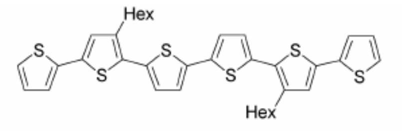


Pentacene

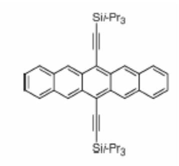


Rubrene

- **Soluble (printable)**



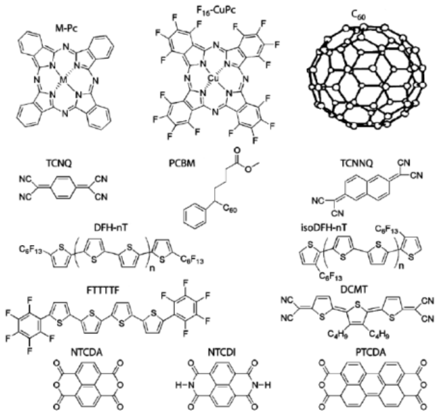
DH6T



Silylethynylated Pentacene

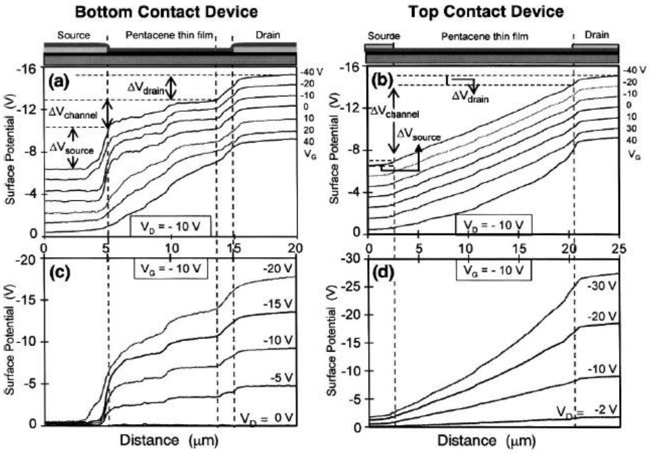
N-type organic semiconductors

- **N-type organic semiconductors are relatively rare; they tend to be less stable, and it is generally more difficult to achieve contacts to organic LUMO levels**



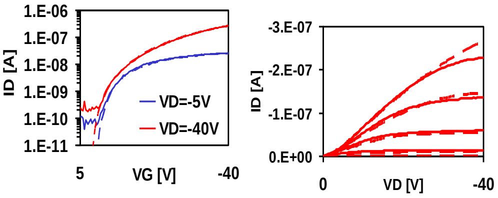
Contact effects in organic TFTs

- **Most organic TFTs have non-ohmic contacts. Scanning potentiometry measurements attest to highly non-ideal contacts.**



Modeling of organic TFTs

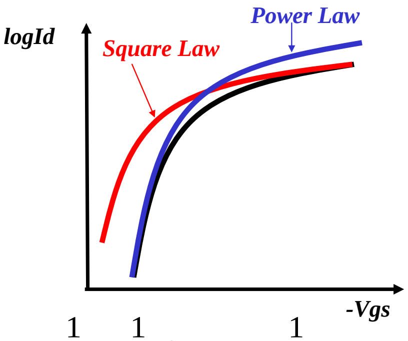
- **The complications of MTR-based transport coupled with non-ideal contacts results in the need for substantial modification of standard square-law MOSFET theory.**

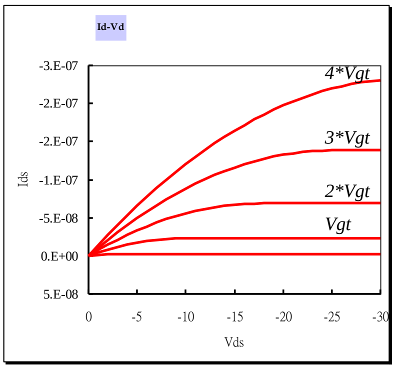


- **Square-law device**
- **Contact resistance** $R_S = f(V_G,V_D)$
- **Field-dependent μ** $\mu=\mu_o(V_G/V_{AA})^{\gamma_o}$
- **Barrier Modification** $\Delta V_T=\exp(-L/l_{eff})$
- **Contact barrier** $R_B=\exp(\Phi_B/kT)/V_G$

Mobility in OTFTs

- Remember, OTFTs have field-dependent mobilities due to MTR





$$\frac{1}{\mu}=\frac{1}{\mu_0}+\frac{1}{KMU\cdot\left(V_{gs}-V_t\right)^{\gamma}}$$

So what does modeling tell us

- Must pick applications where f_T requirements are <<1MHz
  - Displays
  - Some RFID applications

- Power constraints may be important
  - High field requirement due to MTR
  - Lots of power dissipation due to large capacitances

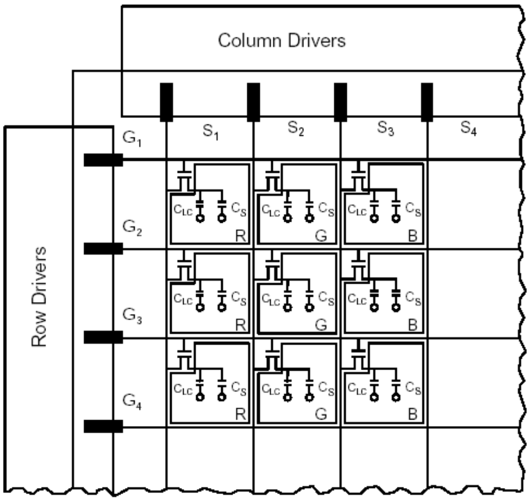
- Lifetime / stability must be considered
  - Environmental degradation
  - Bias stress effects

Application Example 1: AMLCD Pixels

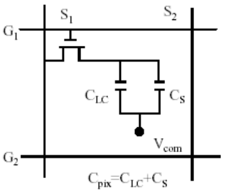
- <u>Reasons to consider</u>
  - Large area application, so exploits economic advantages
  - Performance requirements are very reasonable; switching speed is <100kHz, and 10V supply voltage *maybe* acceptable (*caveat: Power)*

- <u>Concerns</u>
  - Need very low leakage
  - The eye picks up on variation, so need very good stability and reproducibility
  - Manufacturing using printing just isn't there yet – low resolution, low-speed displays probably make the most sense in the short term

AMLCD Schematic



Transient Response Issues



•TFT On-Resistance

$$R_{TFT-ON} \bullet C_{pix} << \frac{T_f\ (\text{frame time})}{N\ (\text{number of rows})}$$

For less than 1% charging error: $R_{on} \bullet C_{pix} \le \frac{T_f}{5N}$

•TFT Off-Resistance

$$R_{TFT-Off} \bullet C_{pix} >> \frac{T_f(N-1)}{N}$$

For less than 1% discharge: $R_{off} \bullet C_{pix} \ge 100 T_f$ $\Rightarrow \frac{R_{off}}{R_{on}} \ge 500N$

For XGA (1024x768) display: $\frac{R_{off}}{R_{on}} > 0.38 \times 10^6$

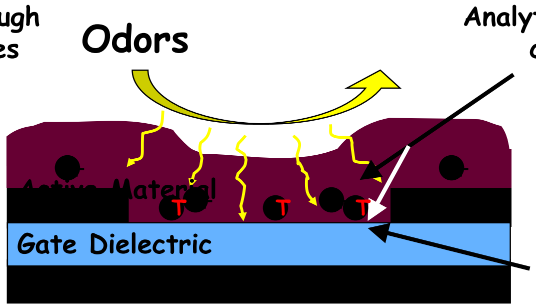
For $C_{pix} = 0.5\,pF$, and $V_{LC} = 5V, \Rightarrow I_{on} > 1.15\,\mu A$; and $I_{off} < 1.5\,pA$

- **The on-current requirements are reasonable to achieve; however, the on-off ratio requirements are currently well beyond what has been achieved in a fully-printed OTFT**

Application Example 2: Sensors

- **Reasons to consider**
  - **Can exploit sensitivity of OTFTs to achieve novel sensors**
  - **In many cases, form factor requirements of sensors make plastic-based circuits very attractive**
- **Concerns**
  - **Need very stable operation for reliable transduction**
  - **Specificity, sensitivity, etc. are concerns**

OTFTs as sensors



Absorbed through grain boundaries and reactive molecular sites

Film expands

Analyte changes charge conduction

Analyte donates carriers or activates existing donors

Analyte introduces traps interface charge