Organic semiconductors

PH 673

Nanoscience and nanotechnology

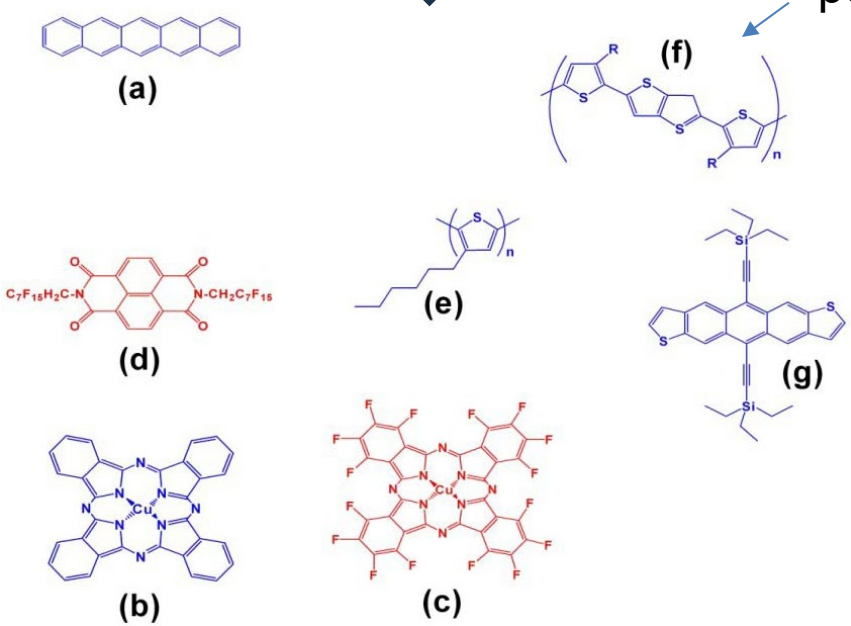
November 10, 2025

What is “organic” in “organic electronics”?

Active layers of are made of carbon-based molecules

“small” molecules

polymers



Why organic materials?

Traditional silicon technology

- High performance

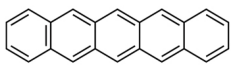
  BUT

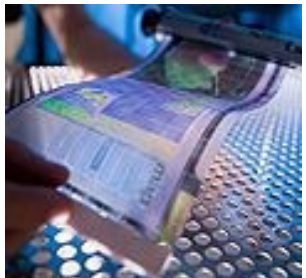
- Expensive fabrication and processing: high temperature, high pressure, special substrates
- Toxic byproducts of manufacturing
- Challenging to scale down to nanostructures

Organic materials

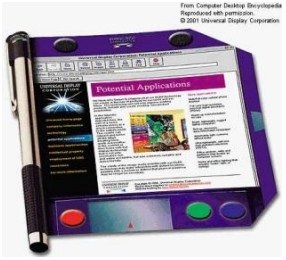
- Lower performance

  BUT
- Solution processable
- Low cost
- Flexible, lightweight substrates
- Tunable properties
- Scalable to single-molecule level



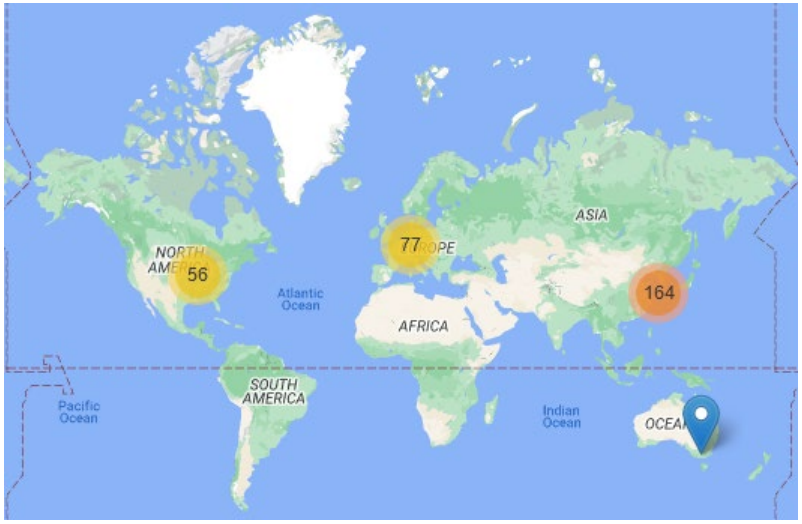


OLEDs: current status



www.oled.com

https://pid.samsungdisplay.com/en/digital-signage/transparent-displays



www.oled-info.com

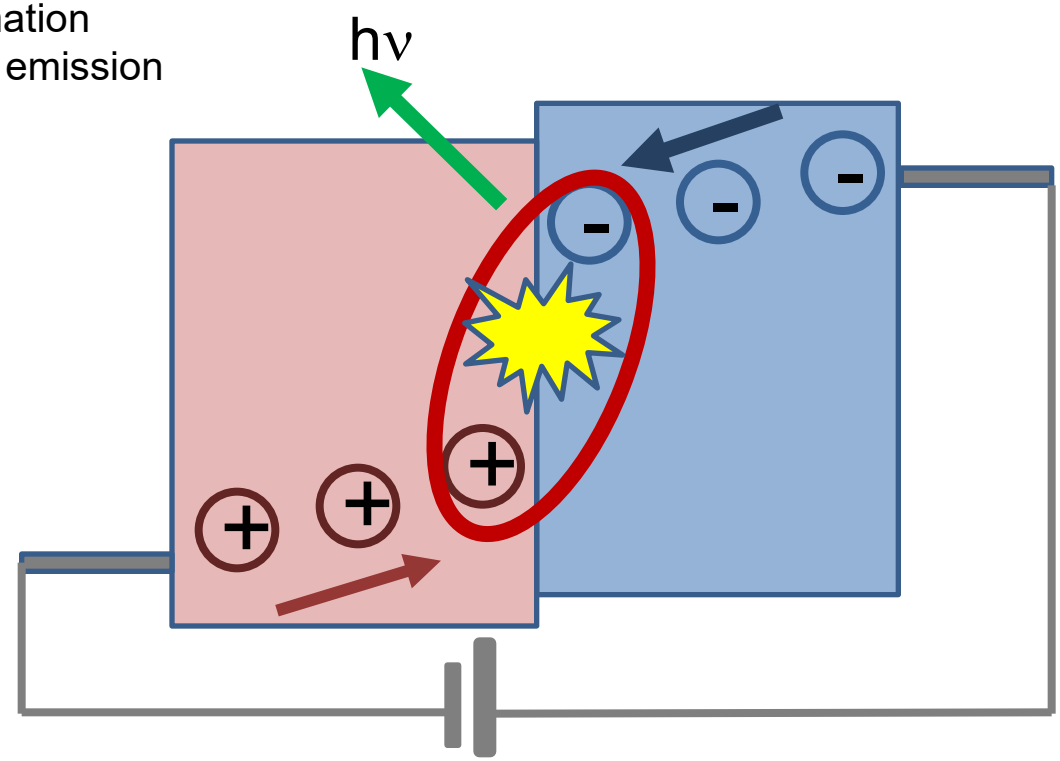
Current market ($38B in 2021, $73B in 2026):

- Displays (TVs, phones, watches, wearables, automotive)
- Lighting (low power consumption, brightness, color quality)

Samsung, LG, Sony, Apple, Nokia, Panasonic,…

How OLED works

1. Charge injection from electrodes
2. Charge (electron and hole) transport
3. Exciton (electron-hole) formation
4. Recombination with photon emission



- Need: molecules able to transport electrons and holes, as well as emit light of a particular frequency (wavelength)

Organic solar cells

Power conversion efficiency (% of solar energy converted into usable electricity):

Single-junction Si: ~25%

Multi-junction Si: ~45%

Organic solar cells:

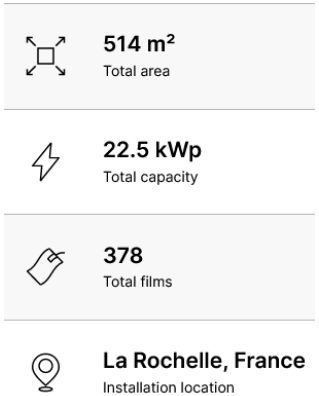
2000: 1%

2024: 20%

2025: 26% (organic-perovskites)

Potentially:

Cost effectiveness for commercialization: ~10-15%



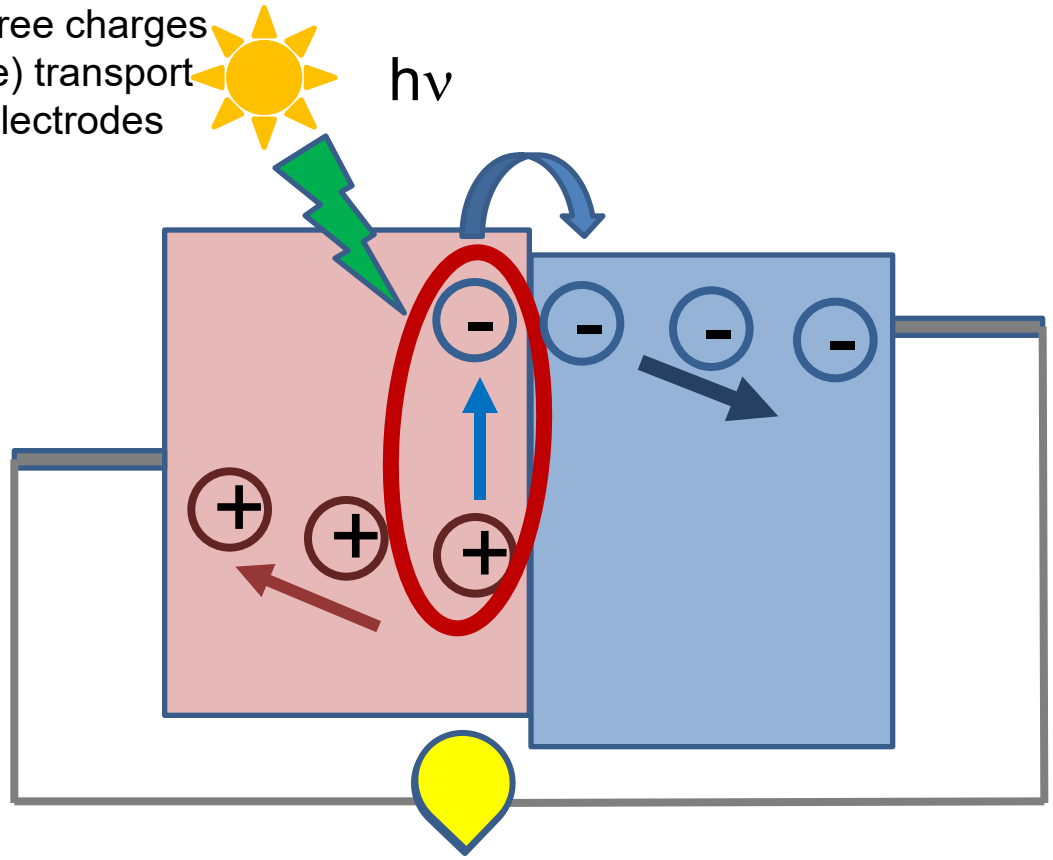
http://www.heliatek.com/

Combine Si with organic to boost to 35-38% in single junction !

Current market: $100M in 2021, $800M in 2030

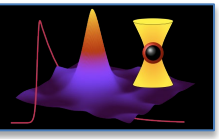
How solar cell works

1. Sunlight photon absorption
2. Exciton (electron-hole) formation
3. Exciton dissociation into free charges
4. Charge (electron and hole) transport
5. Charge collection at the electrodes



- Need: molecules able to absorb sunlight, separate the electron-hole pair, and transport electrons and holes

Applications overview

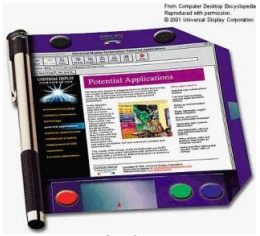


Blue EQE > 40%
UV EQE > 10%
Near-IR EQE 10%

2025:
Hall-effect μ>100 $cm^2/(Vs)$

Ren et al., *Adv. Sci.* **8**, 2002418 (2021)

OLEDs

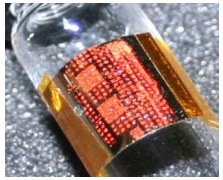


www.oled.com

Vasilopoulou et al., *Nat. Comm.* **12**, 4868 (2021)
Zhang et al., *Ang. Chem. Int. Ed.* **60**, 22241 (2021)
Shahalizad et al., *Adv. Funct. Mat.* **31**, 2007119 (2021)

Photodetectors

OTFTs

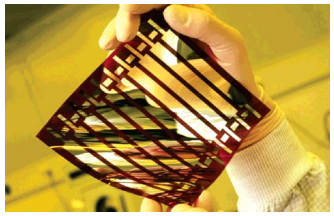


μ > 10 $cm^2/(Vs)$

Paterson et al., *Adv. Mat.* **30**, 1801079 (2018)

Photophysics +conductivity

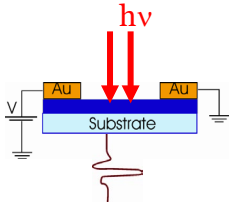
Solar cells



PCE ~ 20%

Gao et al., *Adv. Mat.* **34**, 2202089 (2022)

THz generation



Photorefractive devices

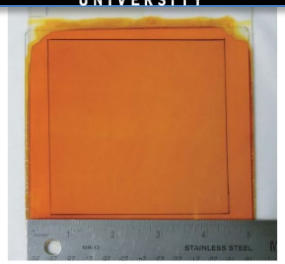
Blanche et al., *Materials* 1**4**, 5799 (2021)

Shin et al., *Adv. Sci.* **7**, 2001738 (2020)

Other applications: RFID tags, batteries, conductive ink, memory devices, sensors, smart cards, toys/games, …

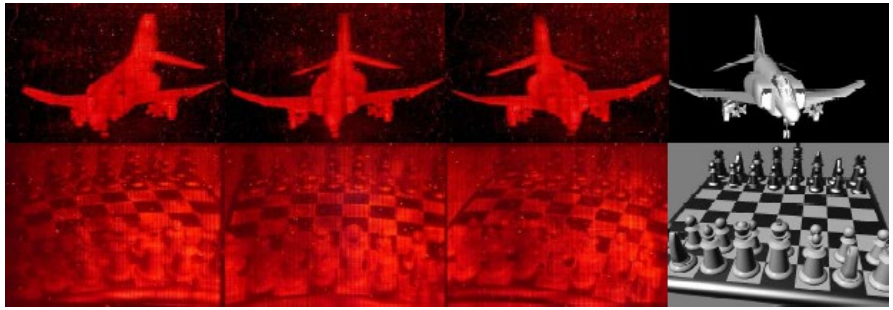
Need to understand: how molecules absorb, emit, and convert light into electric charge, conduct charge

3D Holographic Displays



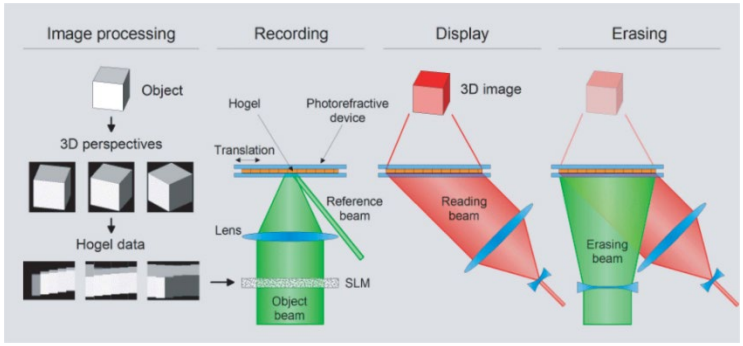
Photorefractive polymer film
100 μm thick

Figure 3 | Pictures of coloured holograms. **a**, Hologram of two model cars recorded on a 12-inch-diameter photorefractive device in HPO geometry. **b**, Hologram of a vase and flowers.



Tay et al., *Nature* **451**, 694 (2008)

P. Blanche et al., *Nature* **468**, 80 (2010)

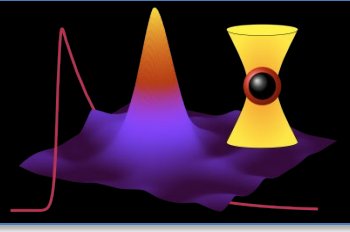


O. Ostroverkhova and W.E. Moerner, *Chem. Rev*. **104**, 3267 (2004)

Tutorial: O. Ostroverkhova, "Organic and polymeric photorefractive materials and devices," in *"Introduction to organic electronic and optoelectronic materials and devices"* (S. Sun and L. Dalton, Eds.), CRC Press, 2008; http://www.physics.oregonstate.edu/~ostroveo/research/resources/tutorials/Photorefractives tutorial/index.html

Optical properties

Light-matter interactions: two-level system



state 2 ——— E_2 $\quad \Psi_2(r,t) = \psi_2(r)\exp(-i\frac{E_2}{\hbar}t)$

state 1 ——— E_1 $\quad \Psi_1(r,t) = \psi_1(r)\exp(-i\frac{E_1}{\hbar}t)$

Transition rate:

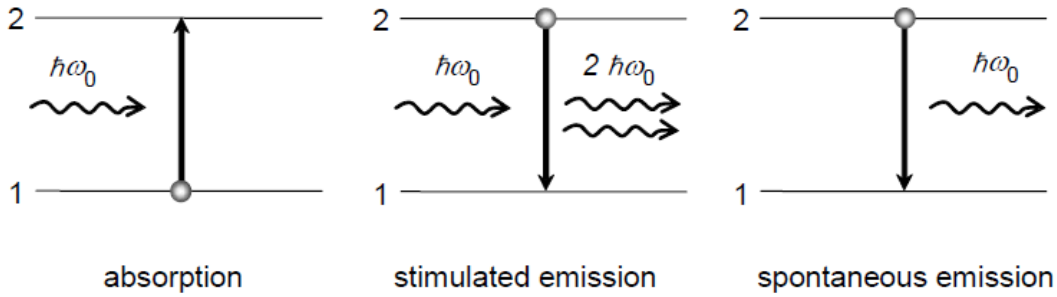
$$\Gamma_{12} = \frac{\pi}{\varepsilon_0 \hbar^2}|\mu_{12}|^2 W(\omega_0)$$

$$\Gamma_{12} = B_{12} W(\omega_0)$$

$$A = \frac{\hbar\omega^3}{\pi^2 c^3} B_{12}$$

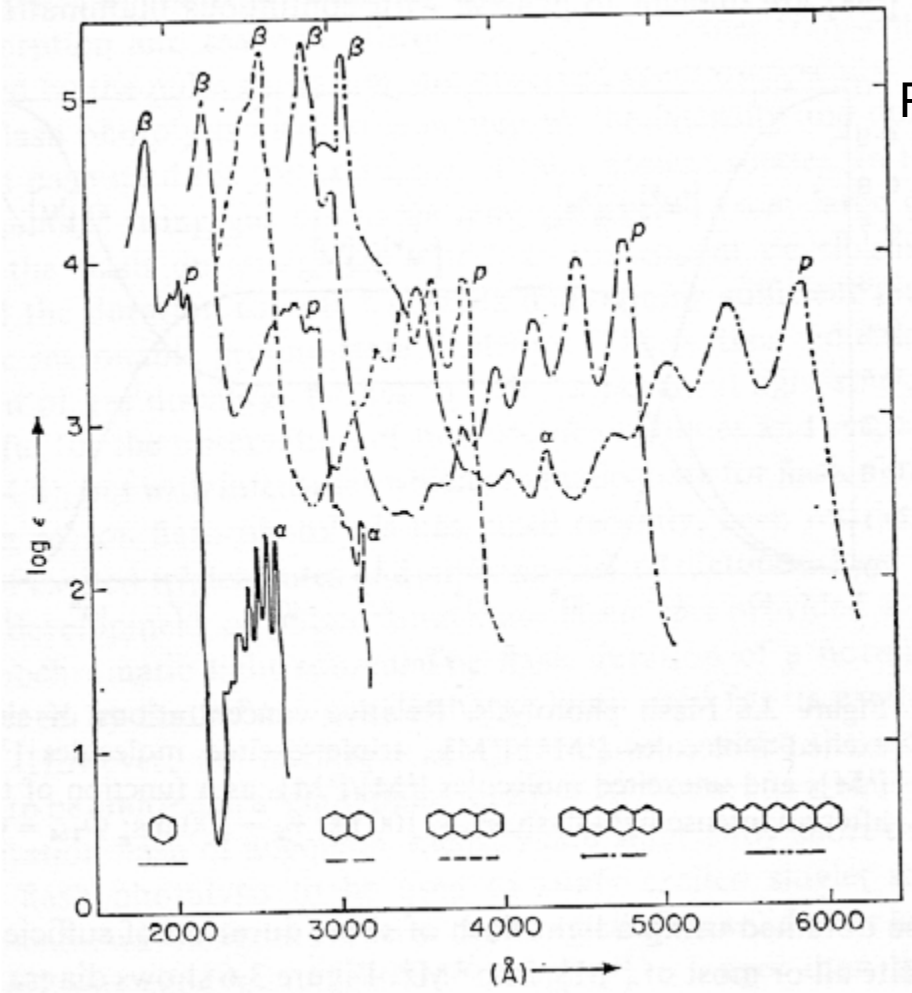
Transition dipole moment:

$$|\mu_{21}| = e\int \psi_1^* x \psi_2 dr$$



A, B – Einstein coefficients

Molecular absorption: particle-in-the box



For conjugated molecules:

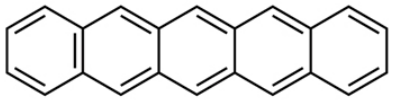
PFEO - perimeter free electron orbital model

$$E_n = \frac{n^2 h^2}{2ml^2}$$

l - perimeter

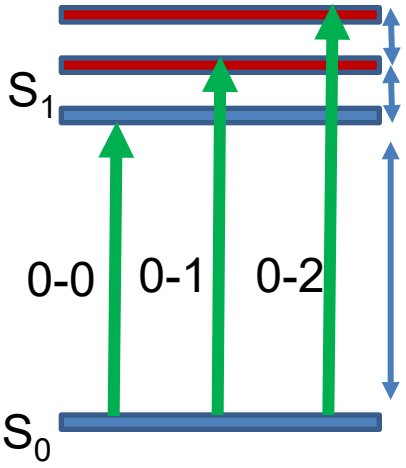
- Larger molecule – more red-shifted spectrum
- $E_{min} \sim 1/l$

Light absorption: molecule as a "box"

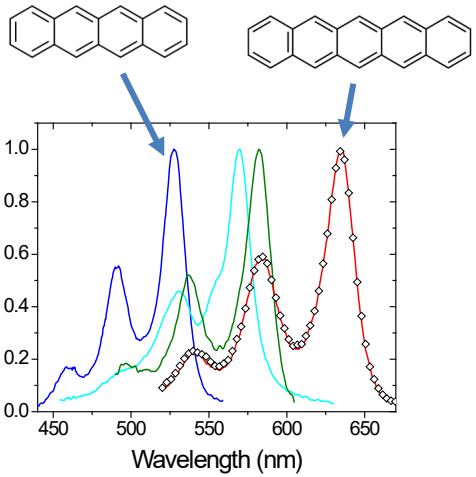


- Need molecules with conjugated core (alternating single/double bonds)
- Electron delocalized over the molecule
- Size of the conjugated core = size of the box
- Larger molecule = lower energies = longer wavelengths

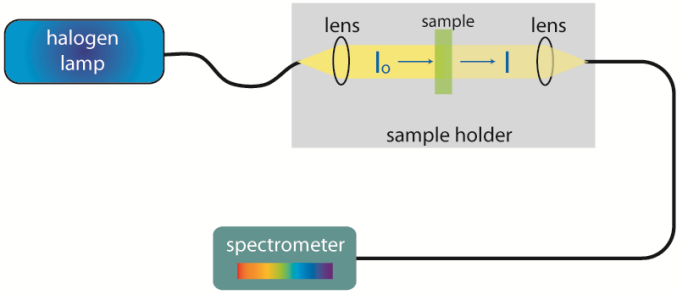
Total Energy = E_{el} + E_{vib} + E_{rot}



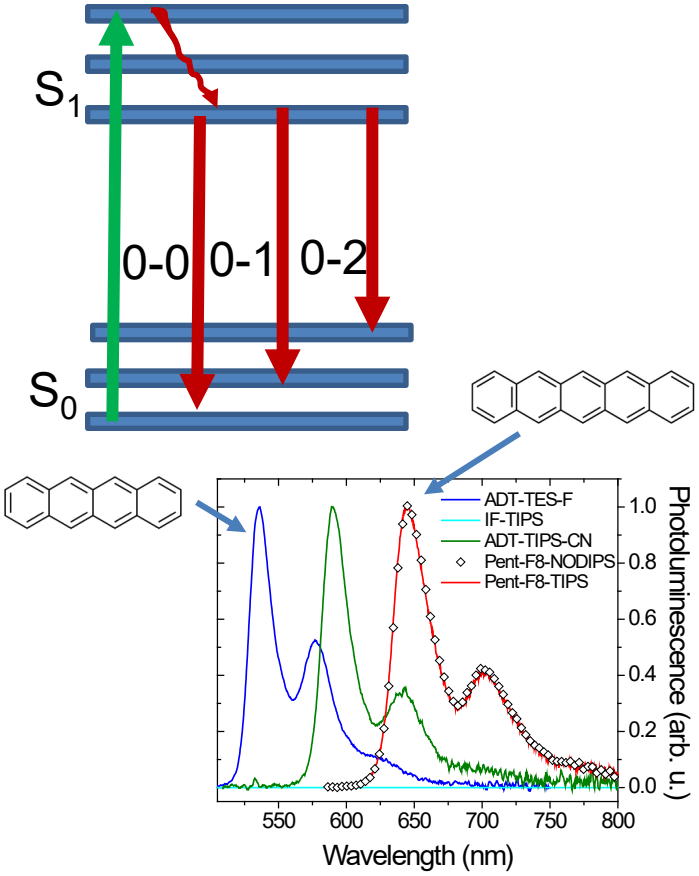
$E_{el} \sim 1/L^n$



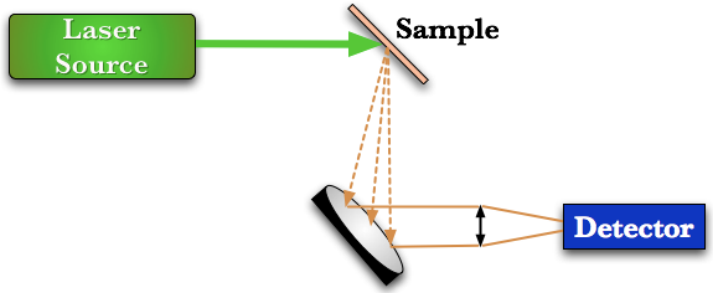
- Optical absorption spectroscopy



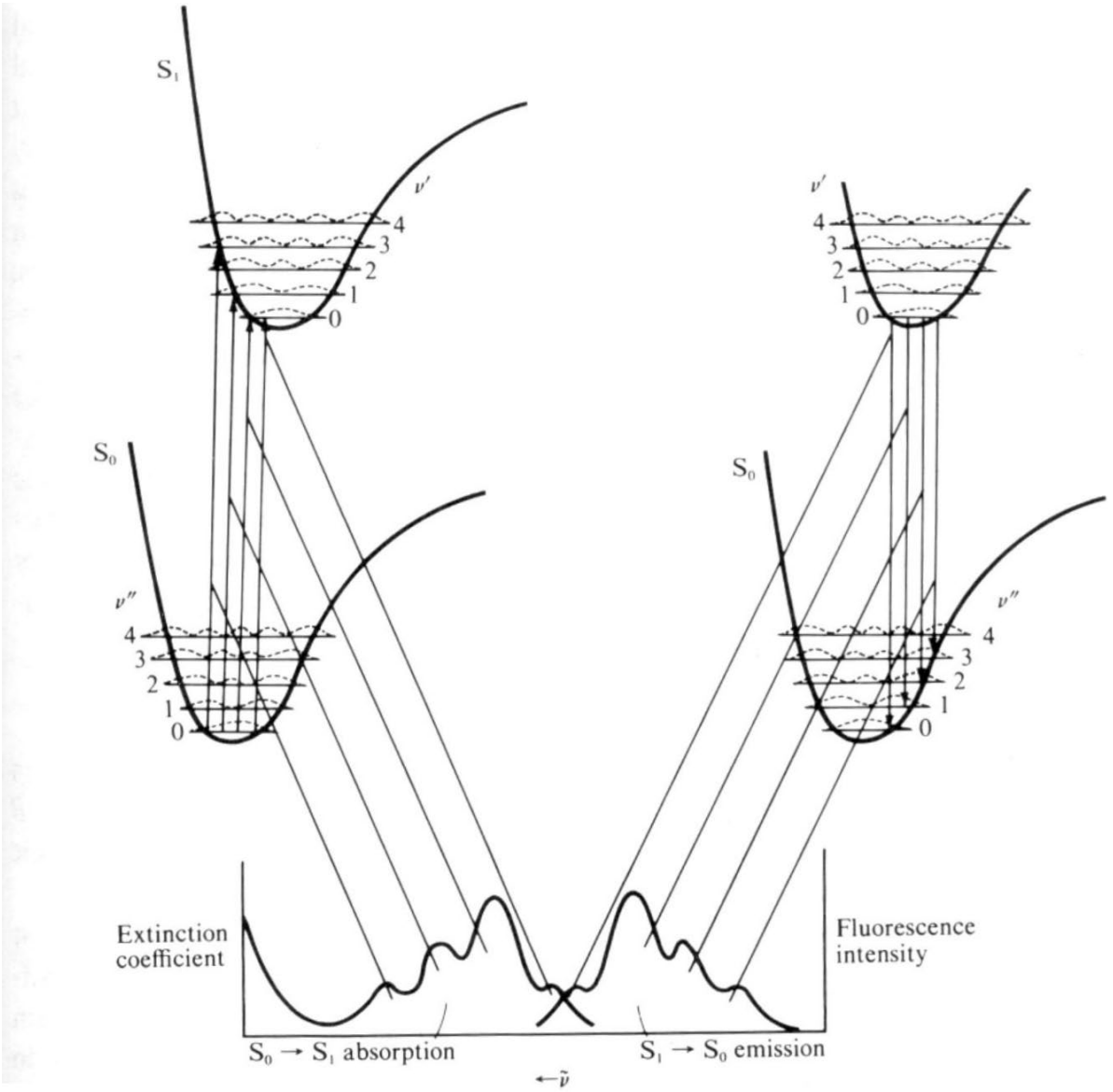
Light emission: mirror image of absorption



- Fluorescence (or photoluminescence) spectroscopy

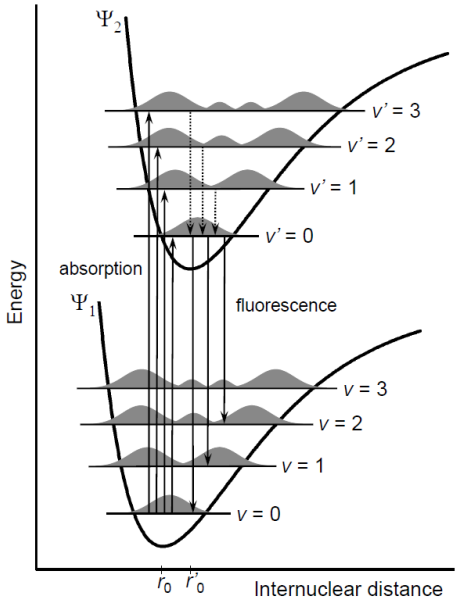


- Measure spectra and timing of each emission event



Simplified potential energy curves with vibrational probability functions showing how a mirror-image relationship can arise between the electronic absorption and emission bands. (From Kearwell and Wilkinson 1969, p. 108)

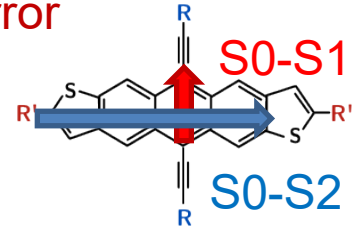
Absorption and fluorescence



$$\Psi(\mathbf{r},\mathbf{R}) = \psi(\mathbf{r})\,\chi(\mathbf{R})$$

Electronic part Nuclear part

- Absorption and emission ~ $|\mu_{12}|^2$
- Absorption and emission are mirror images
- Vibronic progression



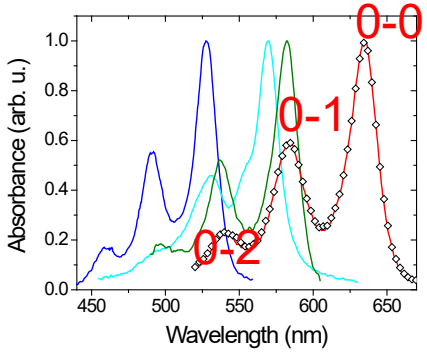
Transition dipole moment:

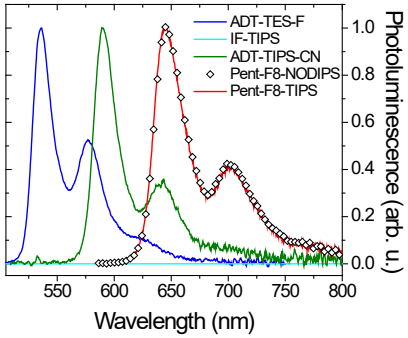
Absorption

$$\boldsymbol{\mu}_{12} = \int \chi^*_{2v'}\chi_{10}\,dR \int \psi^*_2 \boldsymbol{\mu}\,\psi_1\,dr$$

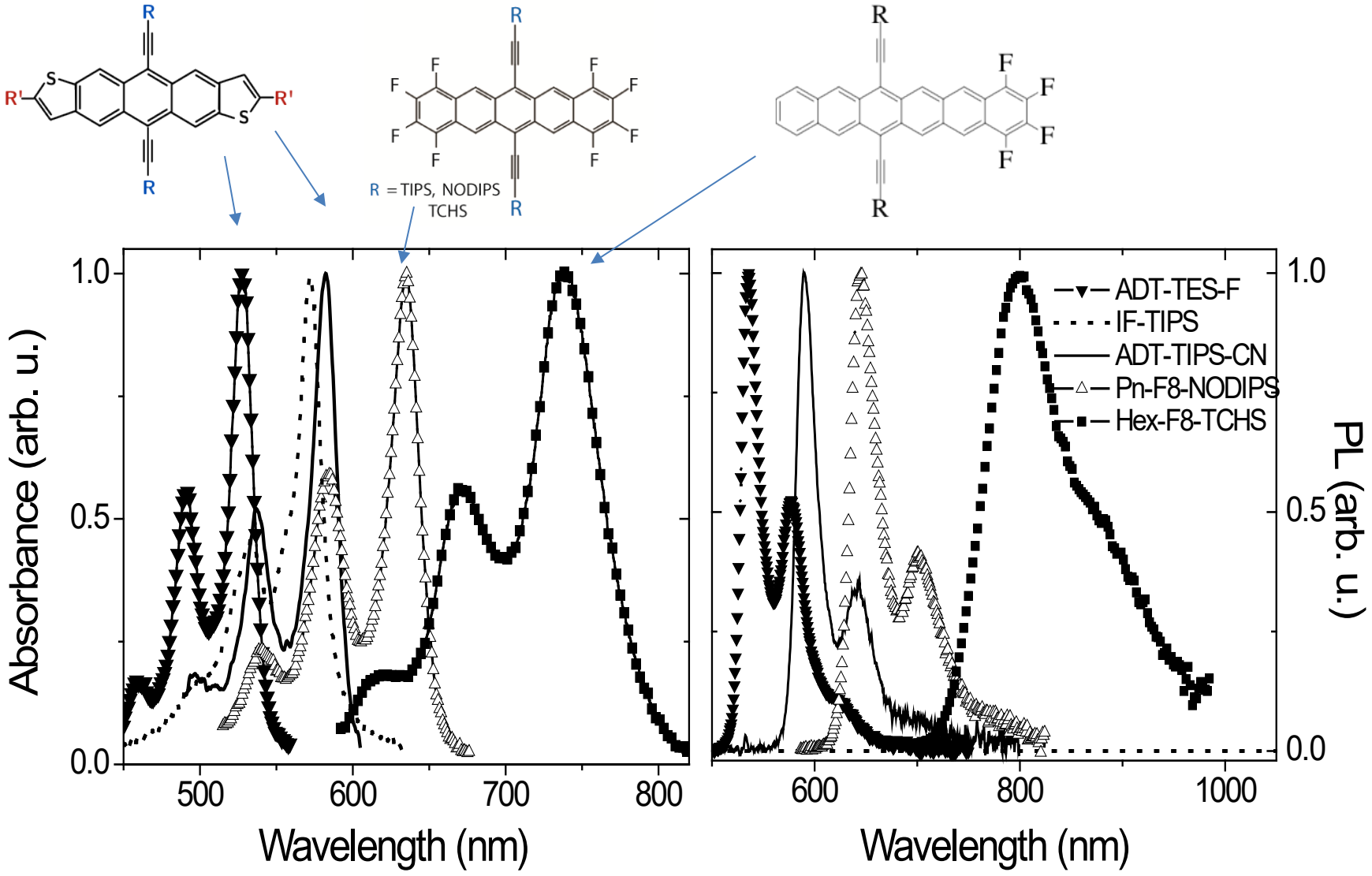
Emission

$$\boldsymbol{\mu}_{21} = \int \chi^*_{1v}\chi_{20}\,dR \int \psi^*_1 \boldsymbol{\mu}\,\psi_2\,dr$$





Optical properties: solutions

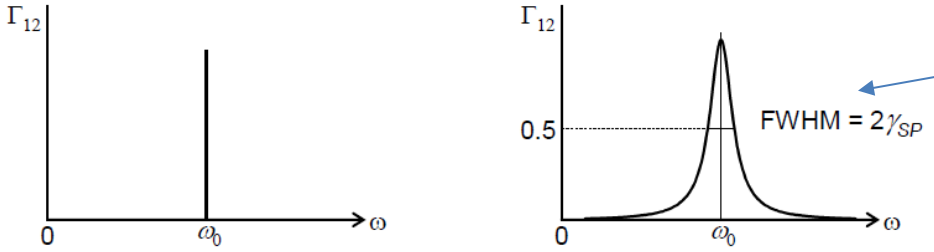


Linewidth

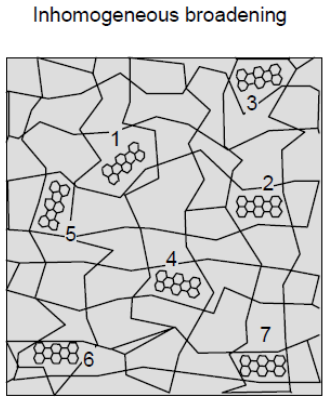
$$\Gamma_{12} = \frac{\pi}{2\hbar^2} E_0^2 |\mu_{12}|^2 \delta(\omega_0 - \omega)$$

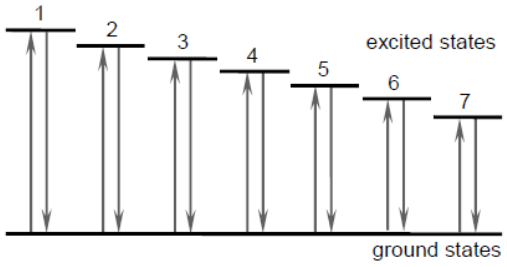
$$\Gamma_{12} = \frac{\pi}{2\hbar^2} E_0^2 |\mu_{12}|^2 \frac{\gamma_{SP}/\pi}{(\omega_0 - \omega)^2 + \gamma_{SP}^2}$$

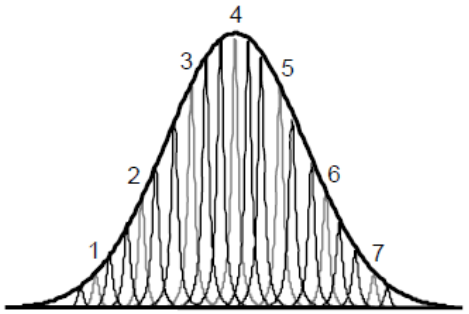
Lorentzian



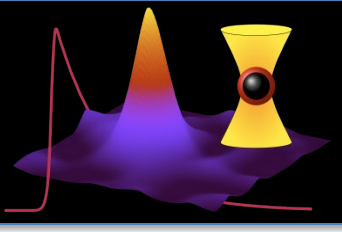
- Homogeneous broadening: Lorentzian (interactions with phonons)
- Inhomogeneous broadening: Gaussian (mechanical strain, electrostatic interactions)

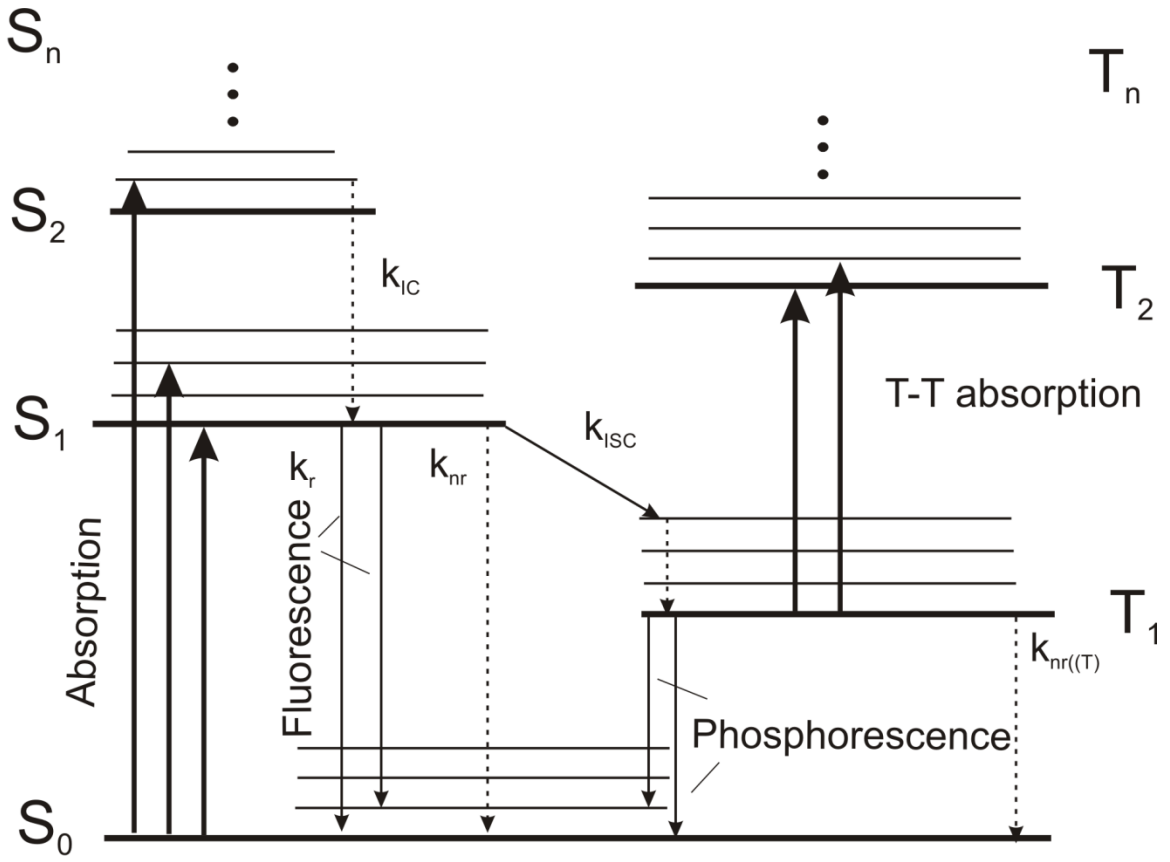






Jablonski diagram





Energy:
$E = E_e + E_{vib} + E_{rot}$

$$\psi_i = \psi_i(r)\chi_i(\sigma)$$

Spin

S_i – singlet states (spin S = 0)
T_i – triplet states (spin S = 1)

$$\boldsymbol{\mu}_{12} = \int \psi_2^*(r)\boldsymbol{\mu}\psi_1(r)dr \int \chi_2^*(\sigma)\chi_1(\sigma)d\sigma$$

Zero for S-T transitions (forbidden transitions)

Franck-Condon principle

$$\Psi(\mathbf{r},\mathbf{R}) = \psi(\mathbf{r})\,\chi(\mathbf{R})$$

Electronic part Nuclear part

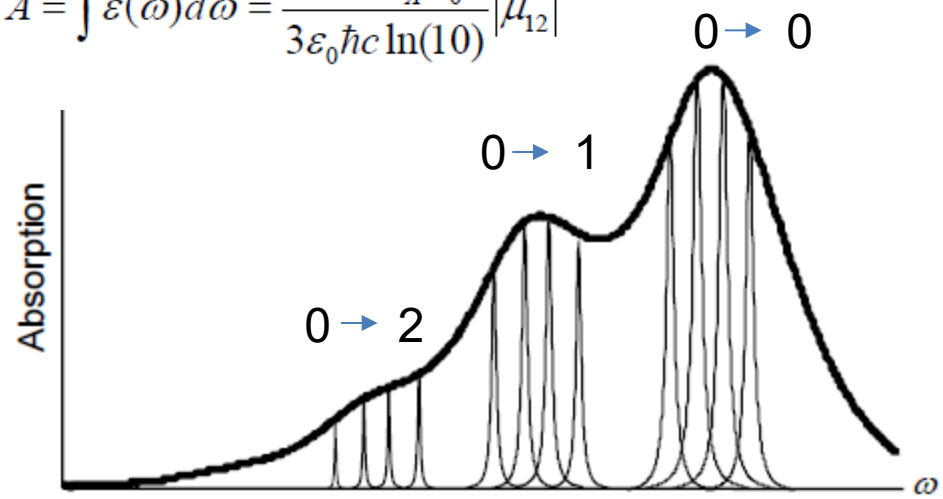
$$\boldsymbol{\mu}_{12} = \int \chi_2^* \chi_1 dR \int \psi_2^* \boldsymbol{\mu} \psi_1 dr$$

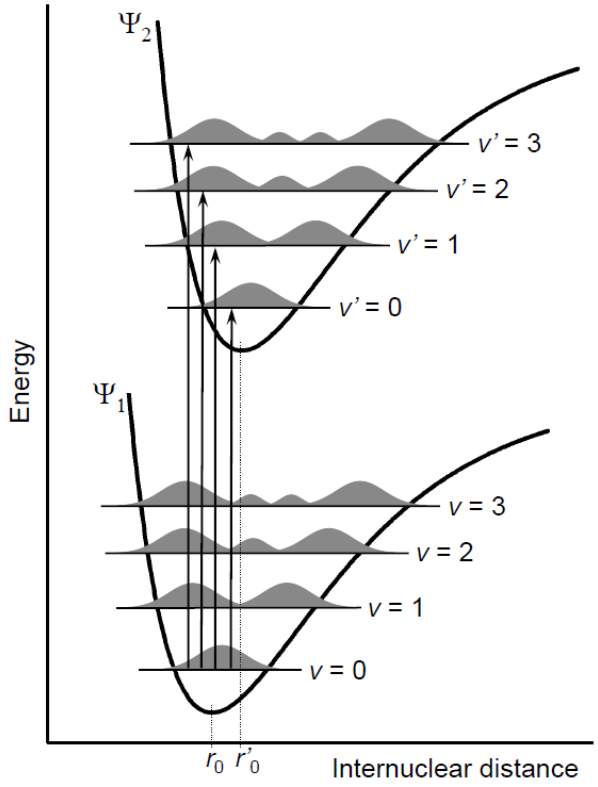
$$\rightarrow \quad S(\chi_2,\chi_1) = \left| \int \chi_2^* \chi_1 dR \right|^2$$

Frank-Condon factor

- Electronic transitions much faster than nuclear vibrations - most probable transition occurs between states with the same nuclear coordinates (vertical trans

$$A = \int \varepsilon(\omega) d\omega = \frac{2\pi^2 N_A \omega_0}{3\varepsilon_0 \hbar c \ln(10)} |\mu_{12}|^2$$

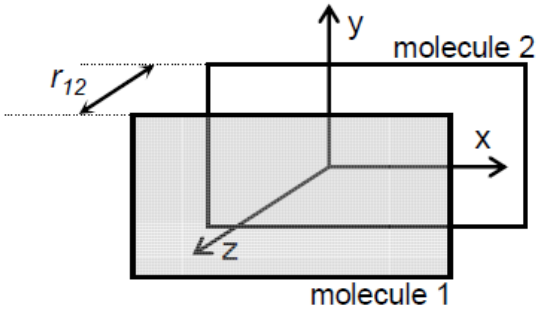




Two interacting molecules: dimer

$$\Psi_G = \psi_1 \psi_2$$ Ground state wavefunction

$$H = H_1 + H_2 + V_{12}$$ ← Intermolecular interaction



$$E_G = \iint \psi_1 \psi_2 H \psi_1 \psi_2 dr_1 dr_2 = E_1 + E_2 + \iint \psi_1 \psi_2 V_{12} \psi_1 \psi_2 dr_1 dr_2 = E_1 + E_2 + D_G$$

Ground state energy

- Shift in the ground state energy due to intermolecular interactions

$$\Psi_E = a\psi_1^u \psi_2 + b\psi_1 \psi_2^u$$ Excited state wavefunction

$$H\Psi_E = E_E \Psi_E \quad \text{or} \quad H\left(a\psi_1^u \psi_2 + b\psi_1 \psi_2^u\right) = E_E\left(a\psi_1^u \psi_2 + b\psi_1 \psi_2^u\right)$$

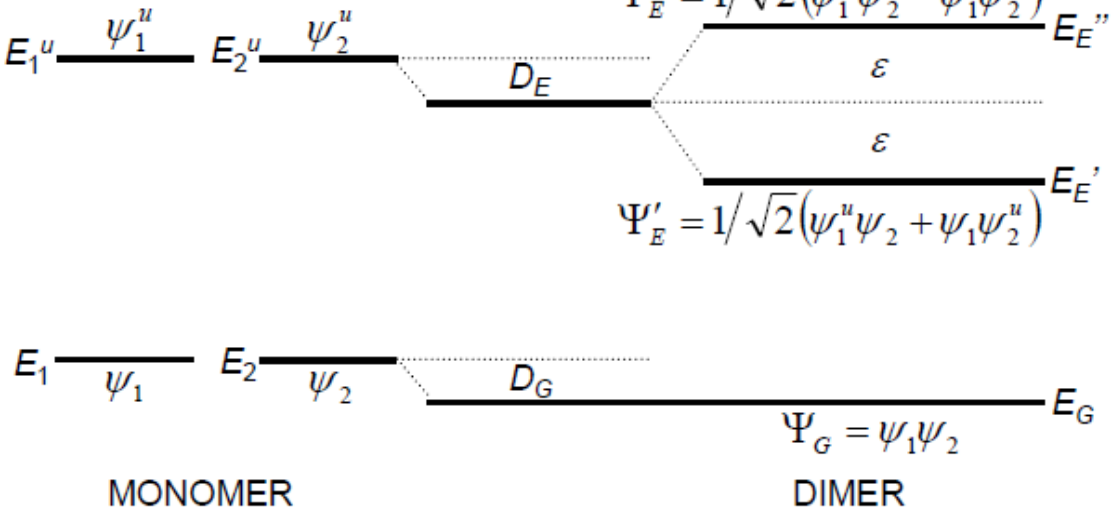
Excited state energy

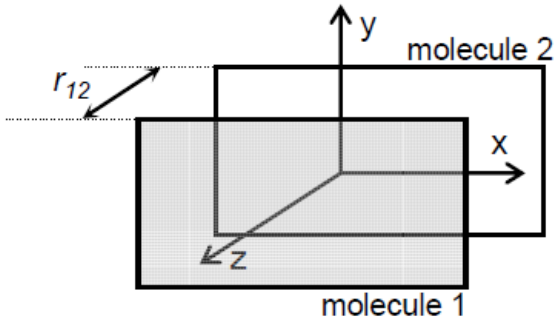
Two interacting molecules: dimer

$$E'_E = E_1^u + E_2 + D_E + \varepsilon$$

$$E''_E = E_1^u + E_2 + D_E - \varepsilon$$

$$V_{12} = \frac{e^2}{4\pi\varepsilon_0 r_{12}^3} \sum_{i,j} x_1^i x_2^j \quad \Rightarrow \quad \varepsilon = \frac{\mu_1 \mu_2}{4\pi\varepsilon_0 r_{12}^3}$$

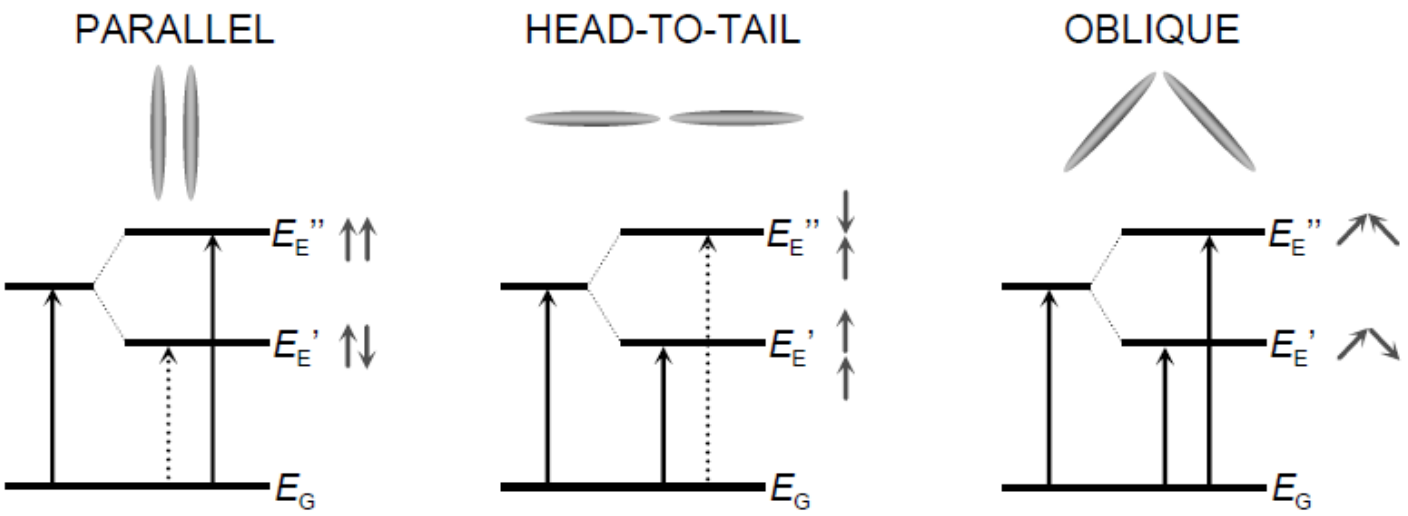




$$E_E - E_G = \Delta E = \Delta E_{monomer} + \Delta D \pm \varepsilon$$

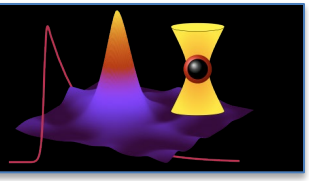
- Shift and splitting of the excited state energy and of energy of transitions due to intermolecular interactions

Two interacting molecules: dimer



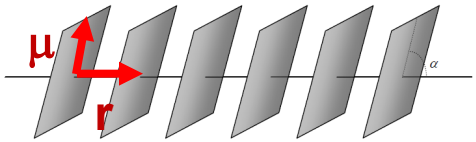
- Allowed or disallowed transitions depending on the orientation of molecular transition dipole moments

Many interacting molecules: aggregates



$$\Psi_G = \psi_1\psi_2\psi_3.....\psi_N = \prod_{n=1}^{N}\psi_n$$ ← Ground state

$$\Phi_a = \psi_1\psi_2\psi_3.....\psi_a^u.....\psi_N = \psi_a^u\prod_{\substack{n=1\\ n\neq a}}^{N}\psi_n$$ ← Excited state



$$\Psi_E^k = \sum_{a=1}^{N} C_{ak}\Phi_a$$

$$\varepsilon_{a,a+1} = \int \Phi_a V_{a,a+1}\Phi_{a+1}dr$$

Nearest-neighbor interactions

$$V_{12} = \frac{e^2}{4\pi\varepsilon_0 r_{12}^3}\sum_{i,j} x_1^i x_2^j$$

$$E_E^k = E_{E,a} + 2\left(\frac{N-1}{N}\right)\cos\left(\frac{2\pi k}{N}\right)\varepsilon_{a,a+1}$$

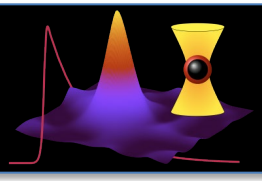
J_0

Energy: $$E_E^k = E_{E,a} + 2\left(\frac{N-1}{N}\right)\cos\left(\frac{2\pi k}{N}\right)\left(\frac{\mu^2}{4\pi\varepsilon_0 r^3}\right)(1-3\cos^2\alpha)$$

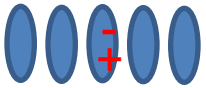
- Delocalized Frenkel excitons as a result of intermolecular coupling
- Properties depend on the transition dipole moment and the angle between μ and **r**
- J_0 can be <0 (J-aggregates) or >0 (H-aggregates)

→
- Shifts in the spectra
- Line broadening
- Intensity redistribution

Many interacting molecules: charge transfer excitons

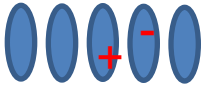


$$\Psi_G = \psi_1\psi_2\psi_3.....\psi_N = \prod_{n=1}^{N}\psi_n \quad \leftarrow \text{Ground state}$$



$$\Phi_a = \psi_1\psi_2\psi_3.....\psi_a^u.....\psi_N = \psi_a^u\prod_{\substack{n=1\\n\neq a}}^{N}\psi_n \quad \Leftarrow \text{Frenkel excitons (comprise neutral states)}$$

$$\Phi_{CT} = \psi_a^+\psi_{a+1}^- \prod_{\substack{n=1\\n\neq a,a+1}}^{N}\psi_n \quad \Leftarrow$$



CT excitons (comprise ionic states)

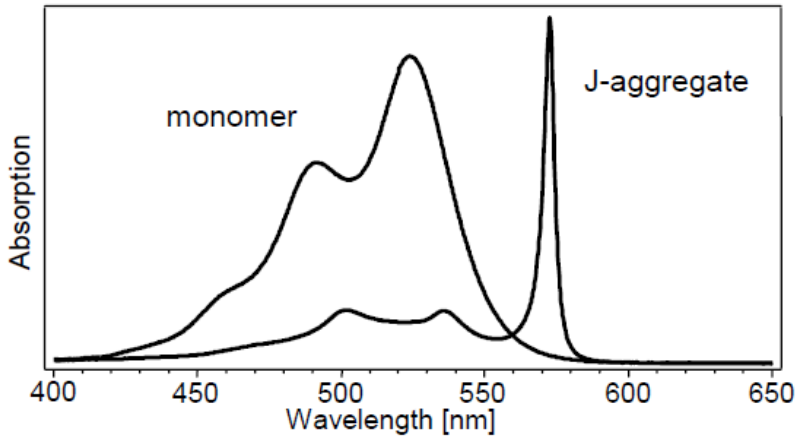
$$\Psi_E^k = \sum_{a=1}^{N} C_{ak}\Phi_a \quad (\text{or } \Phi_{CT})$$

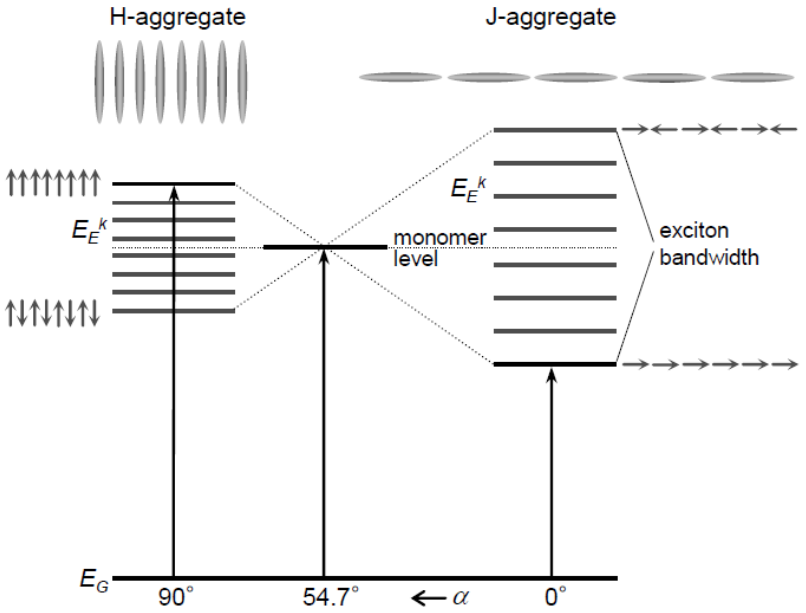
- Delocalized Frenkel and CT excitons also interact with each other
- Such interaction determines important properties: singlet fission, charge generation, emission, etc.
- Subject of debate
- Systematic studies in molecular crystals are needed

N. Hestand, F. Spano "Expanded theory of H- and J- molecular aggregates: the effects of vibronic coupling and intermolecular charge transfer", *Chemical Reviews* **118**, 7069-7163 (2018)

O. Ostroverkhova, "Organic Optoelectronic Materials: Mechanisms and Applications," *Chemical Reviews* **116**, 13279-13412 (2016)

H- and J-aggregates





J-aggregate:
- red-shifted absorption
- strong 0-0 PL emission, $I_{0\text{-}0}/I_{0\text{-}1}\sim L_{coh}$

H-aggregate:
- blue-shifted absorption
- forbidden 0-0 PL emission

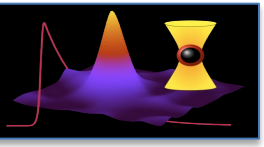
$$bandwidth = 4\left(\frac{N-1}{N}\right)\cos\left(\frac{2\pi k}{N}\right)\varepsilon_{a,a+1}$$

- For both, mirror symmetry is not expected anymore

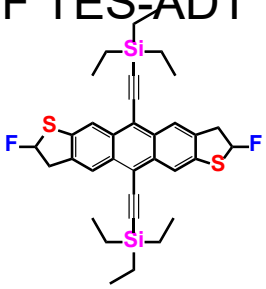
Realistic systems:
- not easy to assign
- can be a H-J mixture (e.g. π-stacked polymers)

F. Spano and C. Silva, *Annu. Rev. Phys. Chem.* **65**, 477 (2014)

Photophysics vs packing: single crystals



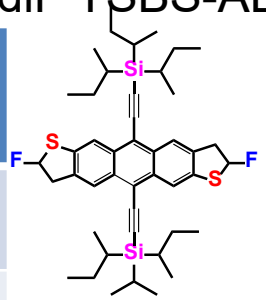
diF TES-ADT



High-performance organic semiconductors

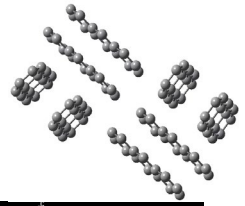
	a, Å	b, Å	c, Å	α, deg	β, deg	γ, deg
diF TES-ADT	7.1	7.2	16.6	97.5	91.4	107.5
diF TSBS-ADT	15.1	16.4	18.2	90	103	90

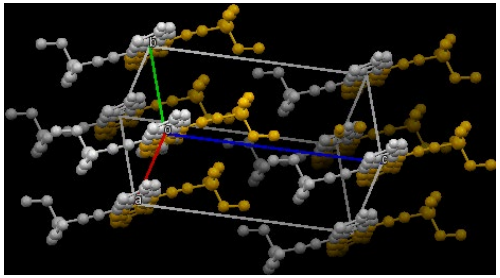
diF TSBS-ADT

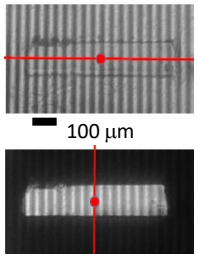


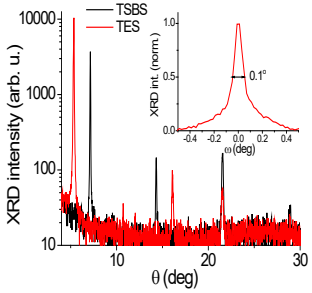
2D "brick-work"

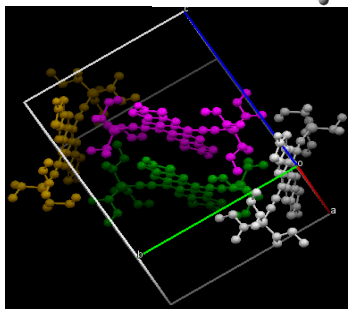
1D "sandwich-herringbone"



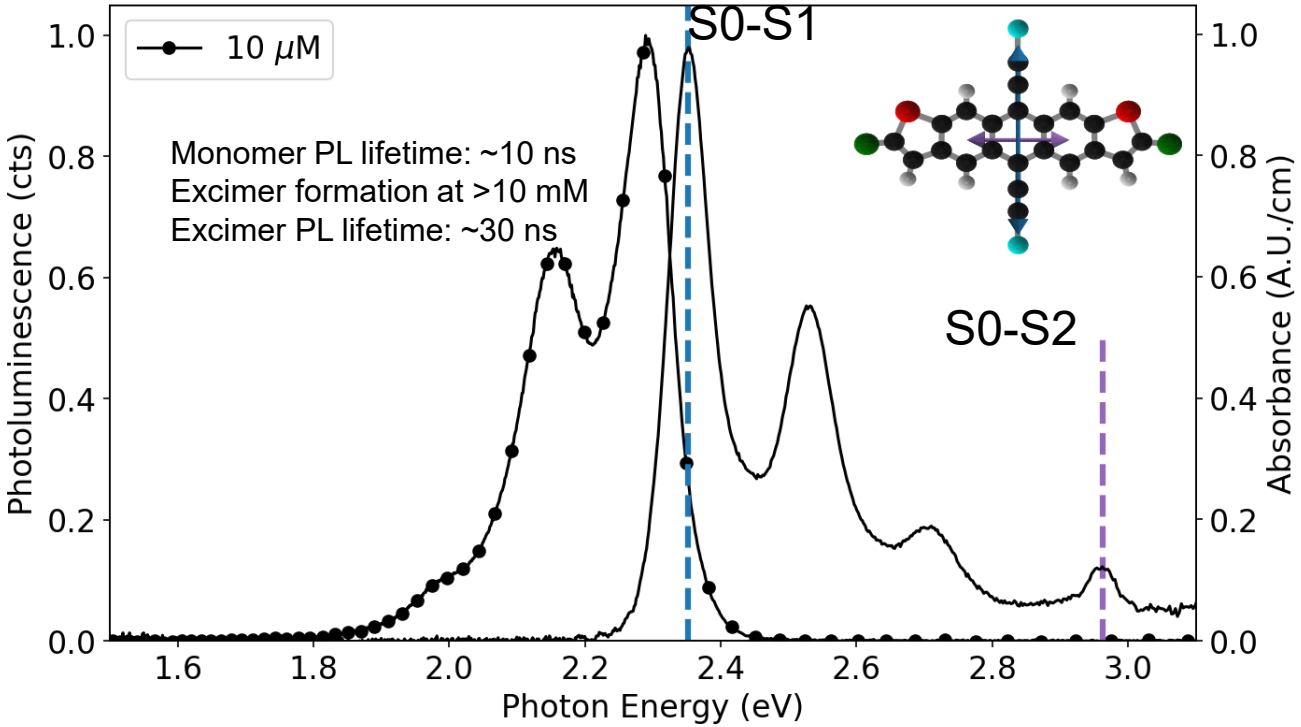


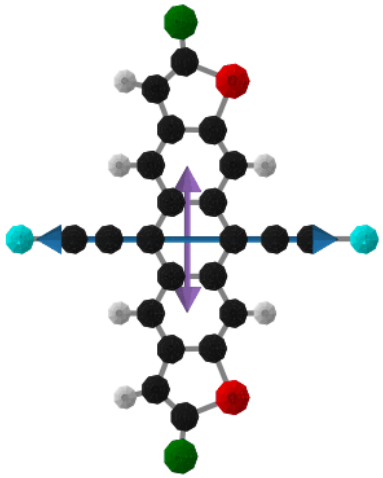






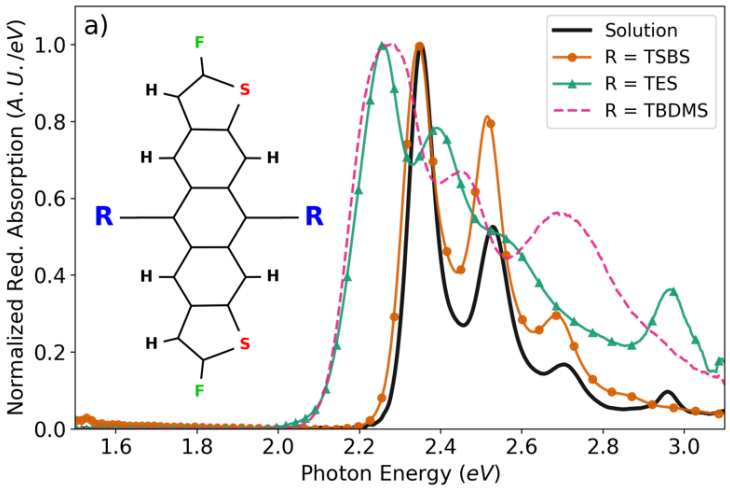
Isolated ADT molecules

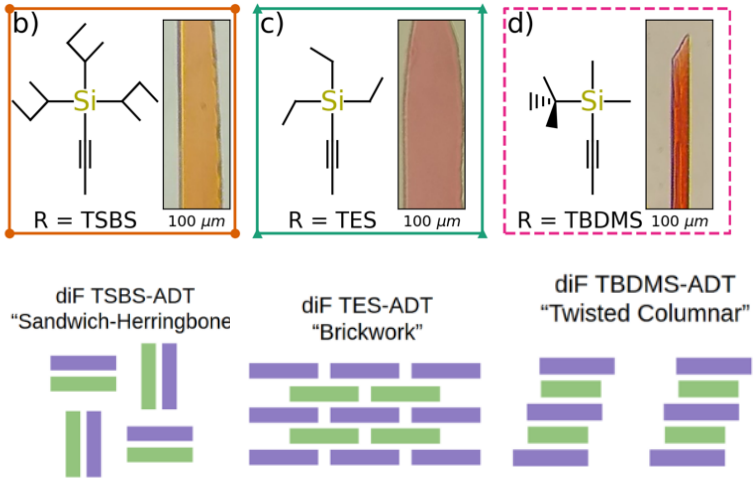


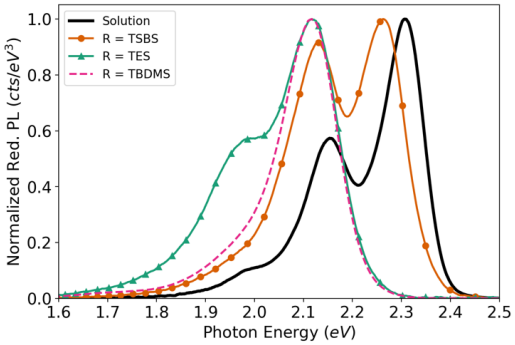


- Absorption and photoluminescence spectra behave as expected from “isolated” molecules

Molecular packing-dependent absorption and PL







- Absorption and PL shifts and oscillator strength redistribution due to intermolecular interactions in crystals
- Absorption strongly polarization-dependent
- Analyze polarization and temperature dependence, in conjunction with TD-DFT to understand intermolecular interactions

→

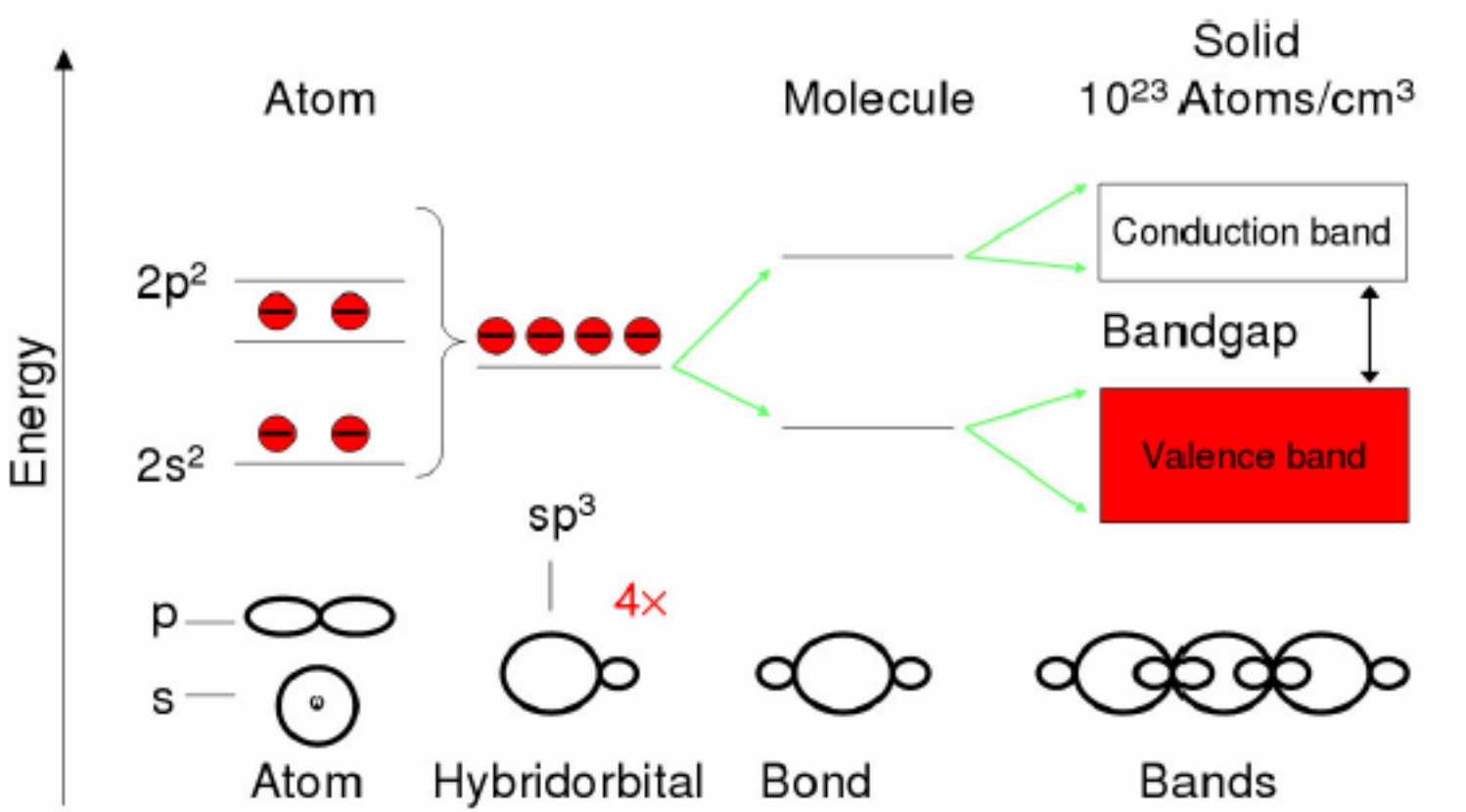
- Frenkel/CT exciton mixing
- Packing-dependent exciton nature

J. Van Schenck, G. Mayonado, J. E. Anthony, M. Graham, O. Ostroverkhova, "Molecular packing-dependent exciton dynamics in functionalized anthradithiophene derivatives: from solutions to crystals", *J. Chem. Phys.* **153**, 164715 (2020) (Featured Article)

Organic vs inorganic semiconductors: electronic properties

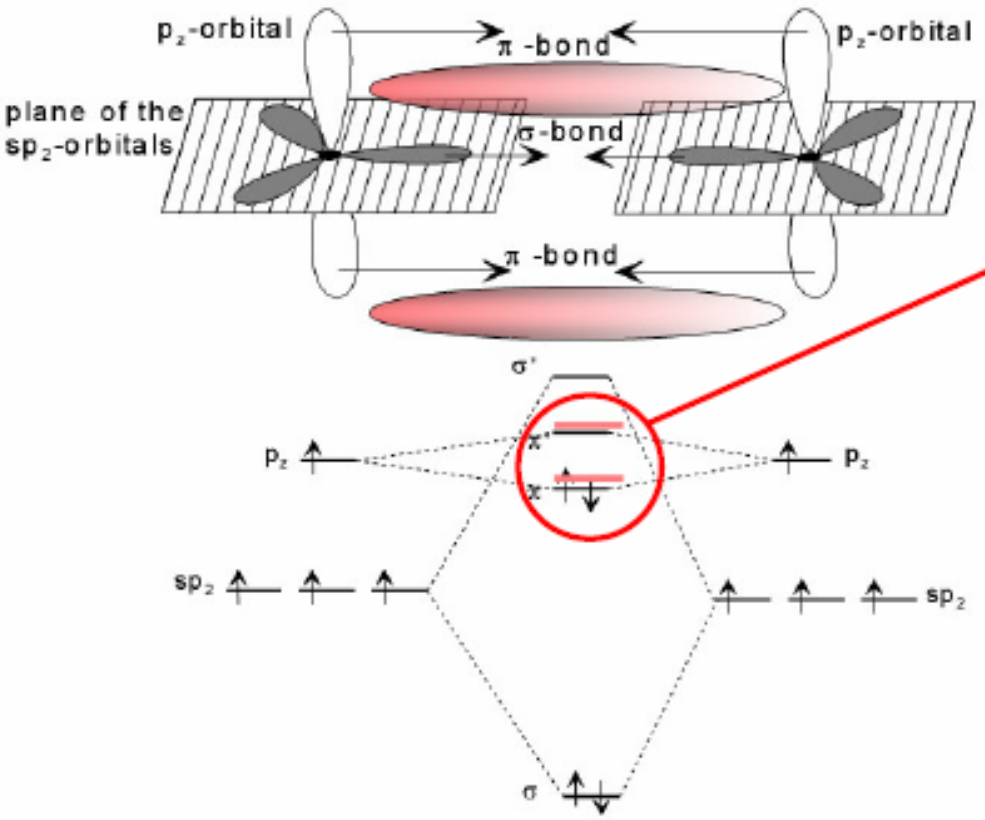
The carbon as fundamental element of organic materials

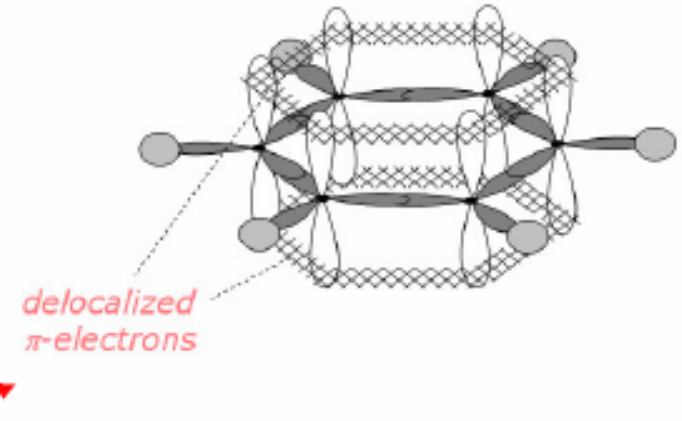
From atomic bonds to solid bands through intermolecular connectivity



The carbon as fundamental element of organic materials

Sp_2-hybridised Carbon:

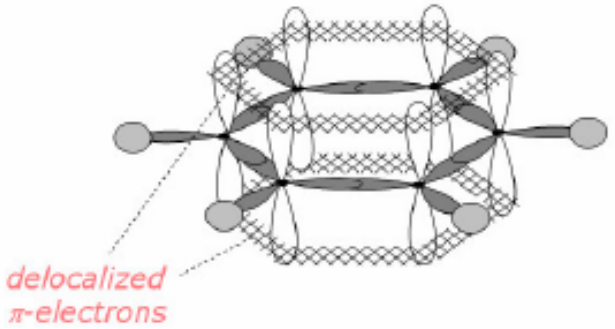


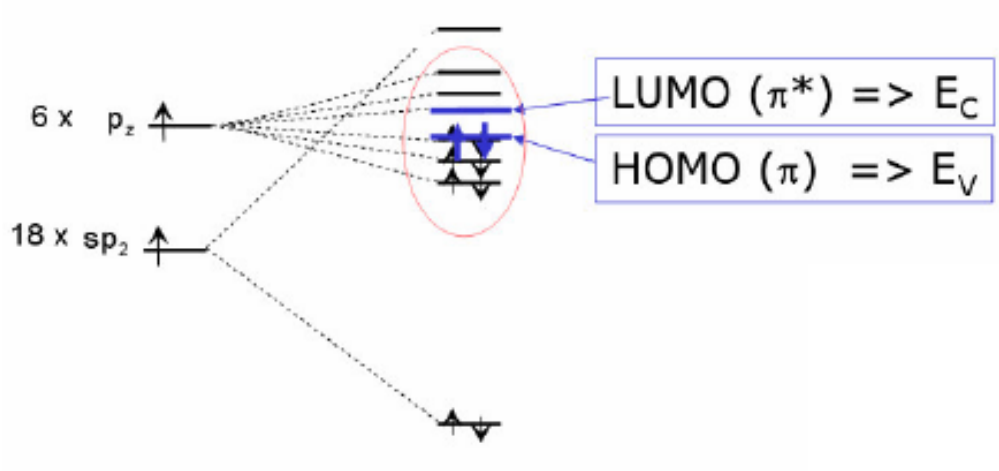


- Spatially extended electron system
- Low electronic binding energies
- Larger polarizability
- Good coupling between molecules in solid state
- Larger reactivity

The carbon as fundamental element of organic materials

- Saturated carbon – SP3 hybridization. Large energy gaps between filled and empty states.
- Unsaturated carbon – SP2 and SP hybridization. π states closer in energy, and more extended in space.
- Small π-π overlap between molecules create narrow bands, favoring electron moblity





- Spatially extended electron system
- Low electronic binding energies
- Larger polarizability
- Good coupling between molecules in solid state
- Larger reactivity

Non-covalent connectivity

How can neutral and non-polar molecular units form a crystal? Non-covalent interactions are responsible of crystal structure, governing the shape and size of the unit cell, as well as the functionality.

Types of interactions between two neutral molecules:

A) Both molecules have dipolar moment: **dipolar, H-bonding**

Aka Keesom interaction

$$V = \frac{-1}{4\pi\varepsilon_0}\frac{2p_1p_2}{r^3}$$

B) One molecule has dipolar moment, the other doesn't: **Induction**

Aka Debye interaction

$$V = \frac{-1}{(4\pi\varepsilon_0)^2}\frac{2p_1^2\alpha}{r^6}$$

C) None of the molecules has a dipolar moment: **van der Waals**

Aka London interaction

$$V = \frac{-1}{(4\pi\varepsilon_0)^2}\frac{A\alpha^2}{r^6}$$

The Nobel Prize in Physics 1910 was awarded to Johannes Diderik van der Waals *"for his work on the equation of state for gases and liquids"*.

Non-covalent connectivity

Real potential comes from addition of the attractive intermolecular forces and a general repulsive term accounting for steric molecular repulsion: this is repulsion between the nuclei and electron clouds of each molecule

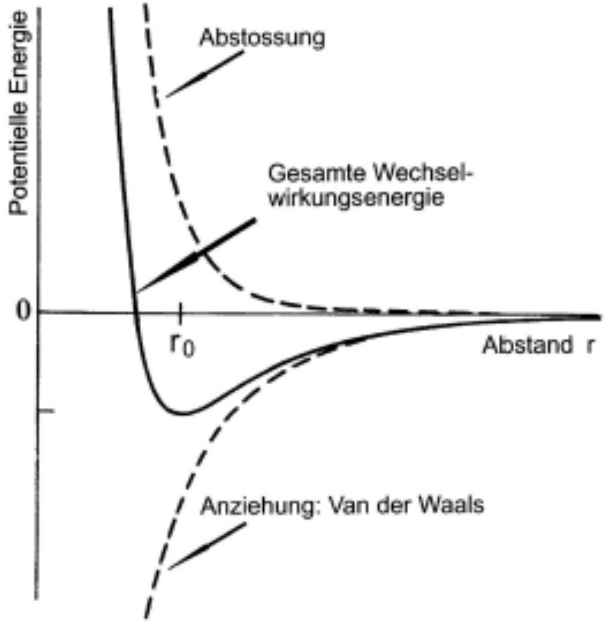
$$V_{rep.} = \frac{C}{r^{12}}$$

Lennard Jones potential:

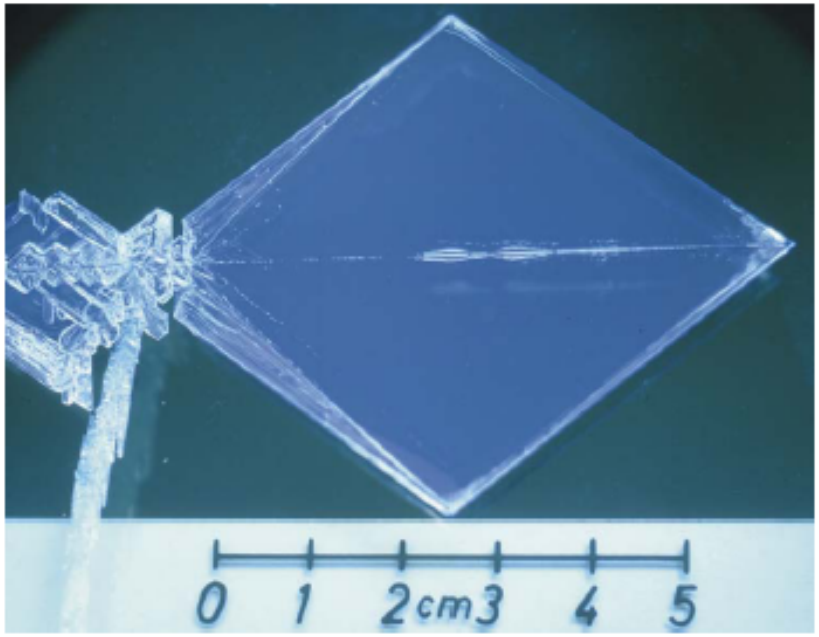
- Inter-molecular distance in the order of 0.3 nm
- Intermolecular bond energy weak, typically less than 10 kcal/mol (0.1 eV).

$$V = \frac{C}{r^{12}} - \frac{D}{r^{6}}$$

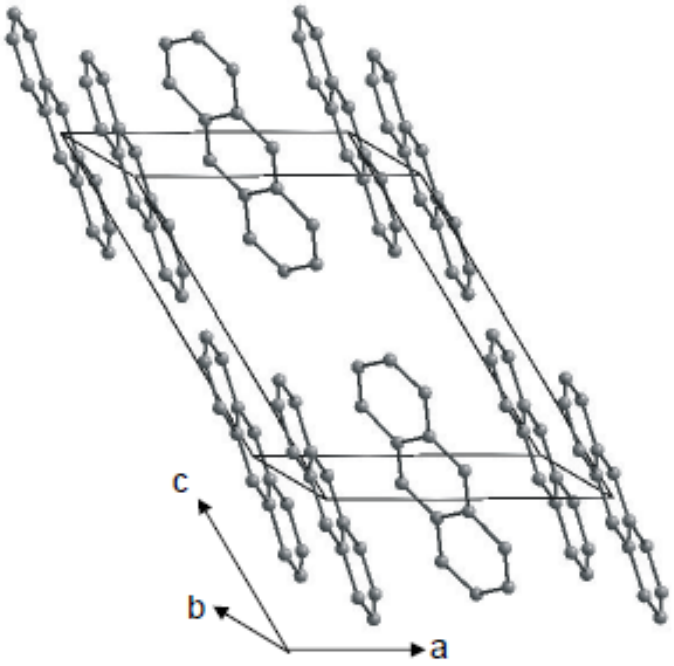
$V = 0$ für $r > r_0$, $V = \infty$ für r

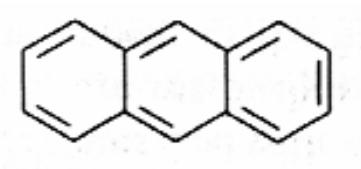


Molecular Crystals



Lattice Constants: a ~ 8.6 Å
b ~ 6.0 Å
c ~ 11.2 Å
β ~ 125°



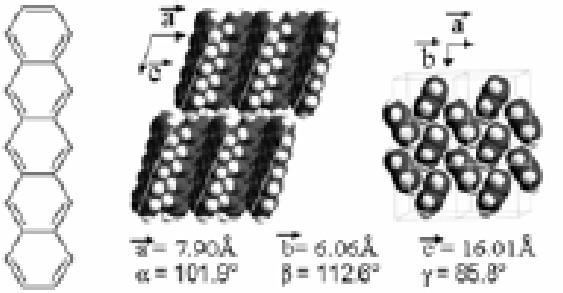


Anthracene
($C_{14}H_{10}$)

➔ van der Waals Bonding

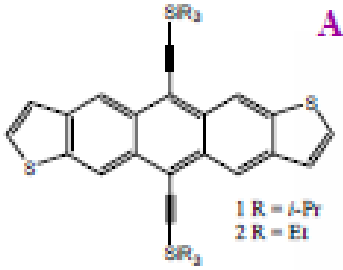
Organic Semiconductors for Thin Film Transistors

Pentacene: State of the Art Organic Semiconductor

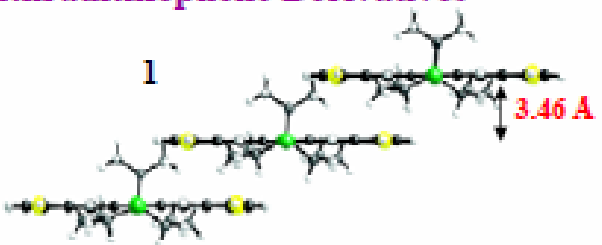


- On flat, inert oxide or polymeric dielectrics, pentacene molecules stand nearly vertical on the substrate
- Highest Hole Mobility in Organic Semiconductors: 3-5 cm^2/Vs

Enhanced π-Stacking Interactions in Anthradithiophene Derivatives



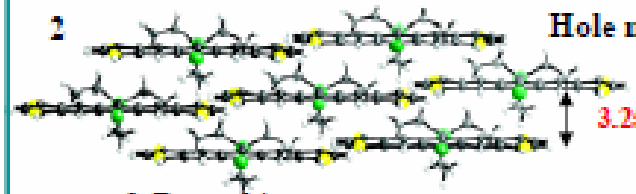
1



1-D slipped-stack arrangement

Hole mobility of $<10^{-4}$ cm^2/Vs

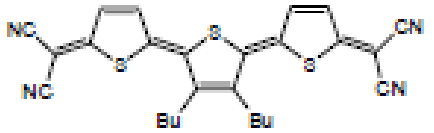
2

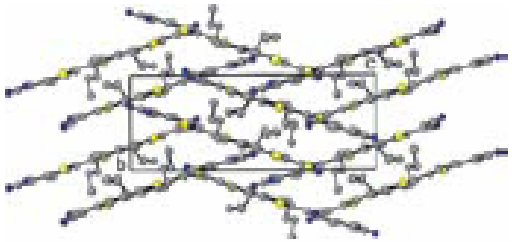


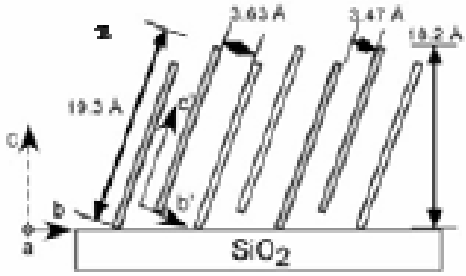
2-D stacking arrangement

Hole mobility of 1 cm^2/Vs

π–Stacking Quinoidal Terthiophene

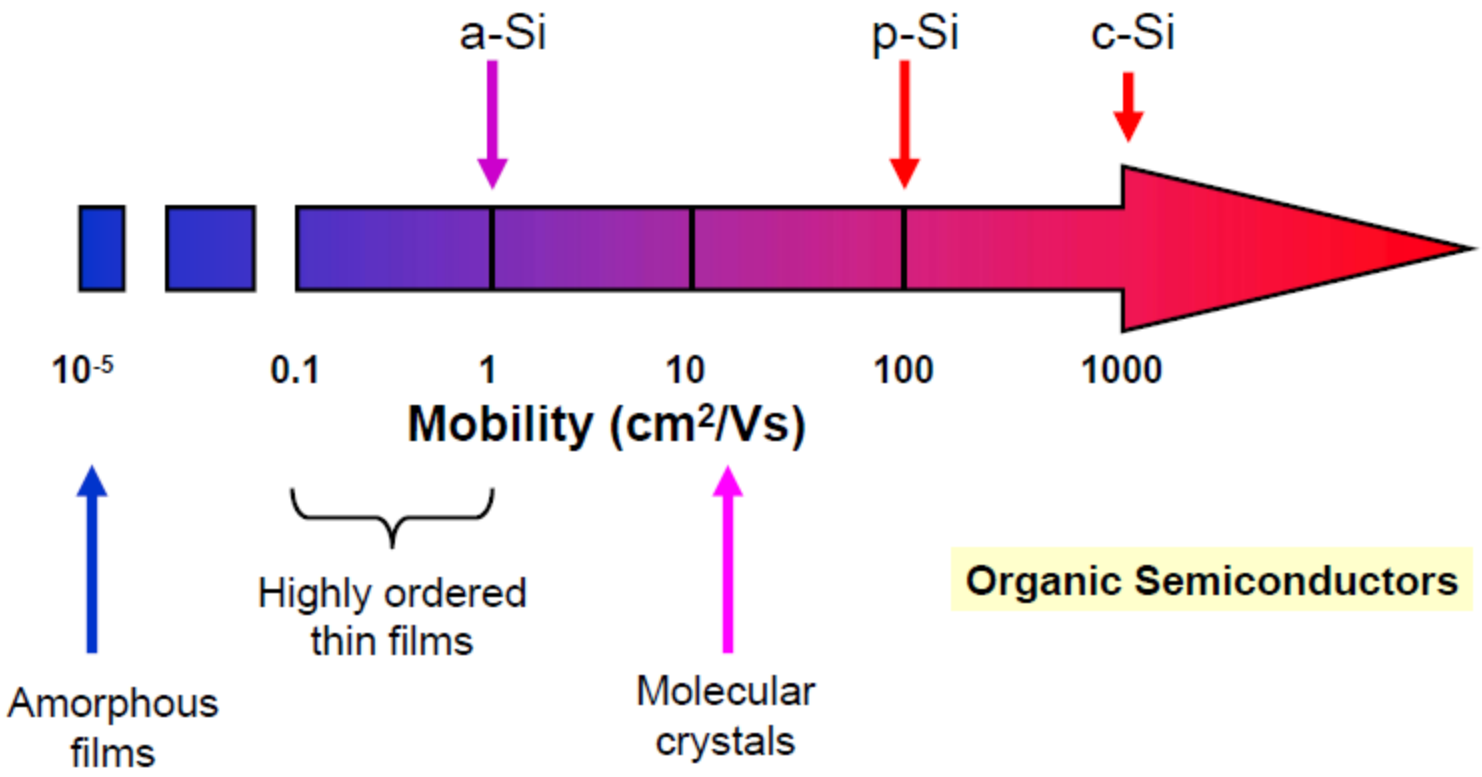




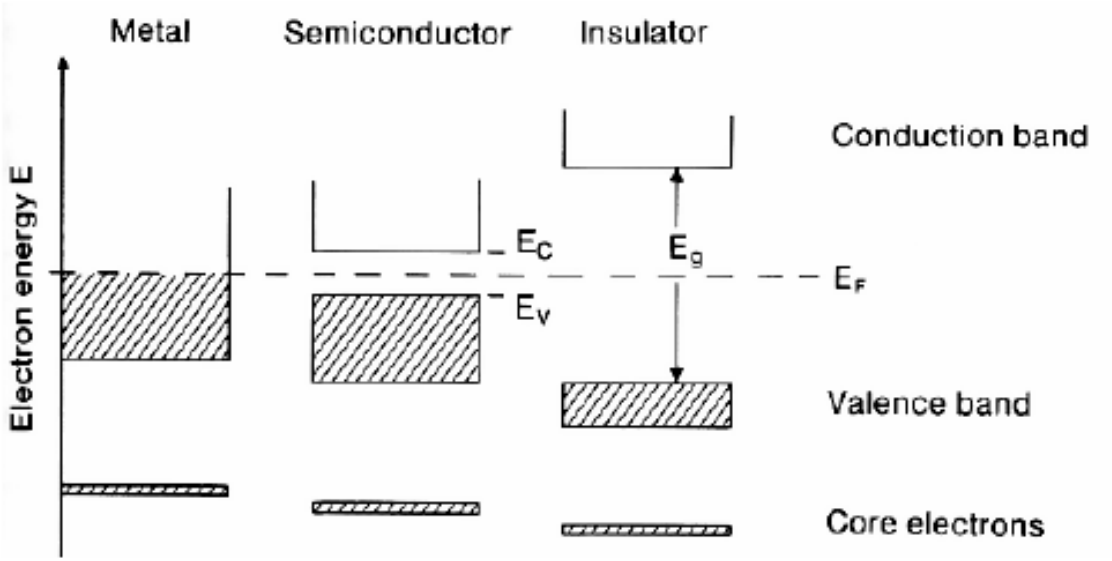


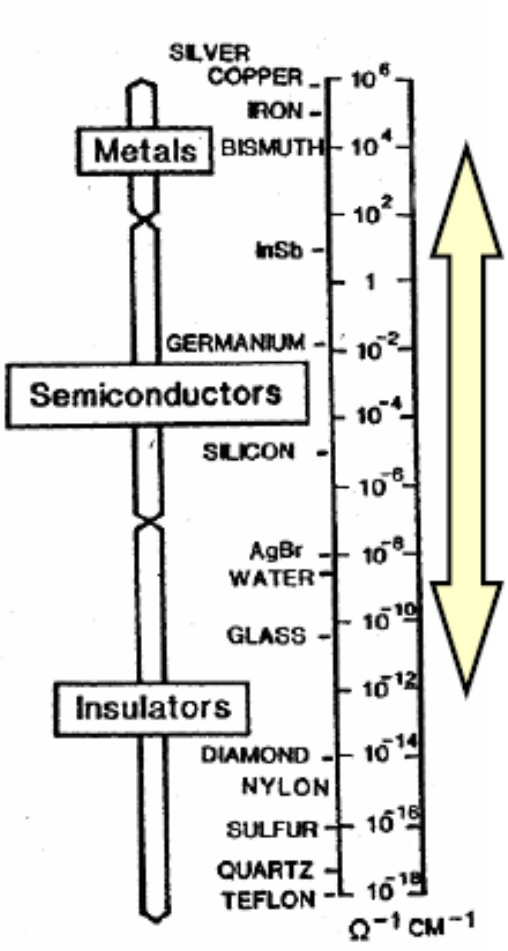
- High Electron Mobility: μ_e~0.2 cm^2/Vs
- Ambipolar Charge Transport

Charge Carrier Mobility



Electric Conductivity





Organic Conductors / Semiconductors:
$\sigma = 10^{-12} \ldots 10^{4}$ S/cm

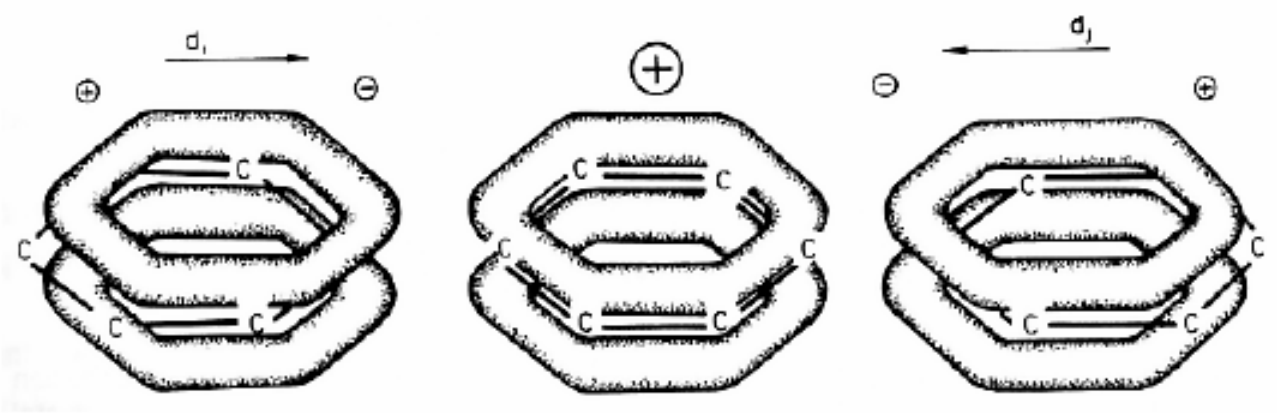
Charge Carriers in Organic Semiconductors

Molecular organic semiconductors

- Charge carriers in molecular organic semiconductors: molecule ions M^+ resp. M^-
- Gas phase: $M \rightarrow M^+ + e^-$ (ionisation energy I_g)
  $M + e^- \rightarrow M^-$ (electron affinity A_g)
- Crystal: Stabilisation of molecule ions in the solid state by polarisation energies P_e and P_h (cf. solvation energies in solutions)

  ➔ $A_c > A_g$ and $I_c < I_g$

Polarisation in the vicinity of a charged molecule

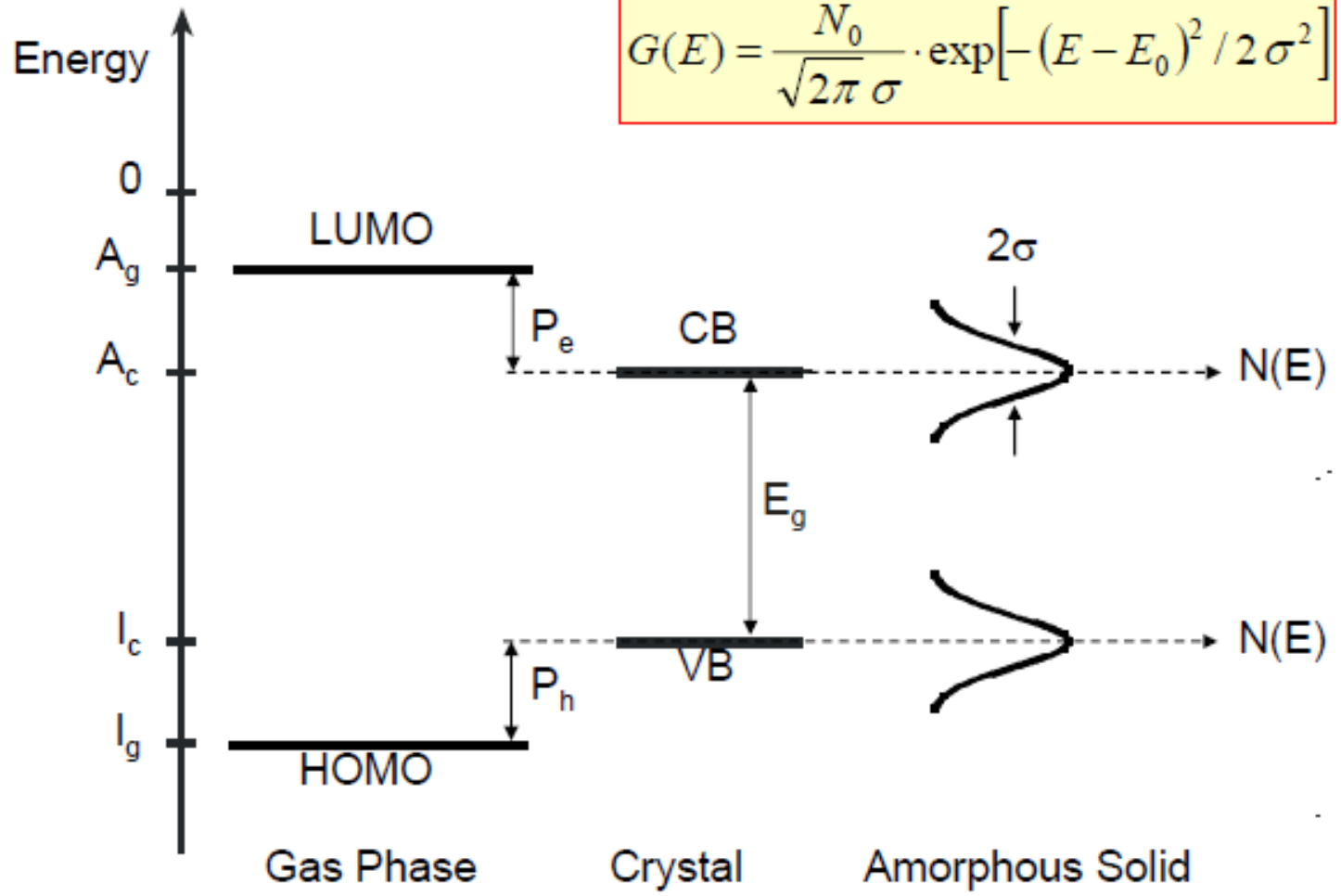


- Charge transport via transfer of pos./neg. charge from one molecule to the next.

Disorder Effects

- Variations of polarisation energies due to locally different molecular environment → distribution of energy levels (Gaussian type with typical width $\sigma \approx 100$ meV)

$$G(E) = \frac{N_0}{\sqrt{2\pi}\,\sigma} \cdot \exp\left[-(E - E_0)^2 / 2\sigma^2\right]$$



Polarisation Energy

- Origin of the polarisation energy: induced dipole moments on neighbouring molecules (plus higher order contributions)
- Simple Model:

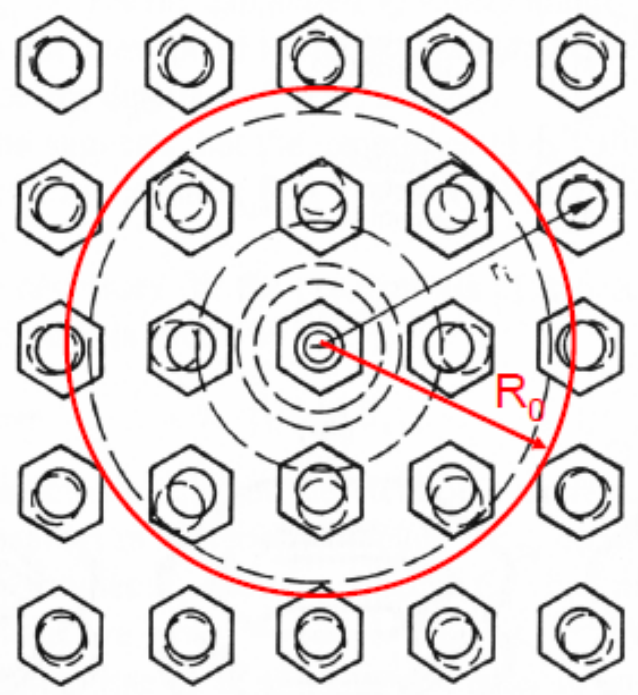
$$P = P' + \Delta P$$

$$r < R_0 : \text{discrete sum}$$

$$P' = \tfrac{1}{2} \sum_i \vec{F}_i(\vec{r}_i) \cdot \vec{\mu}_i$$

$$r > R_0 : \text{continuum}$$

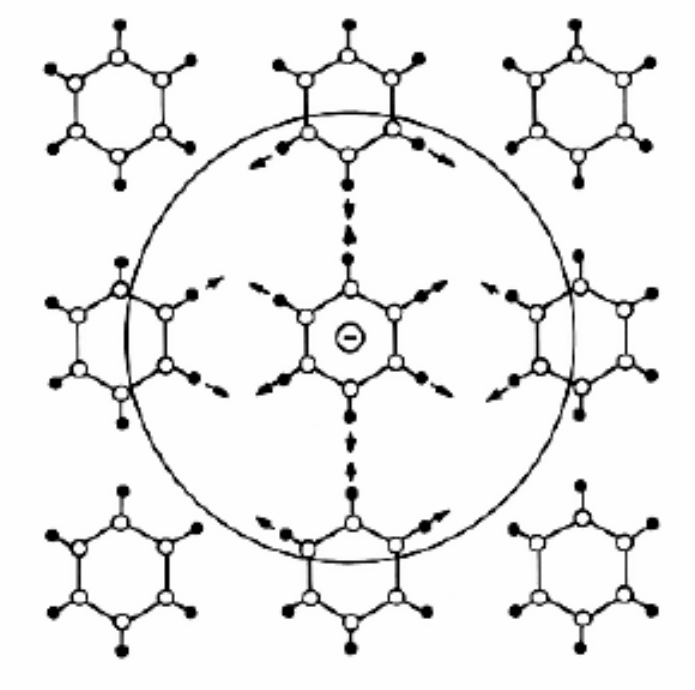
$$\Delta P = \frac{1}{4\pi\varepsilon_0} \cdot \frac{e^2}{2R_0} \cdot \left(1 - \frac{1}{\varepsilon}\right)$$



- Anthracene:
  P' = -1.26 eV, ΔP = -0.27 eV
- In general: $P_e \sim P_h = P = 1 \ldots 2$ eV
  → polarisation effect not negligible !

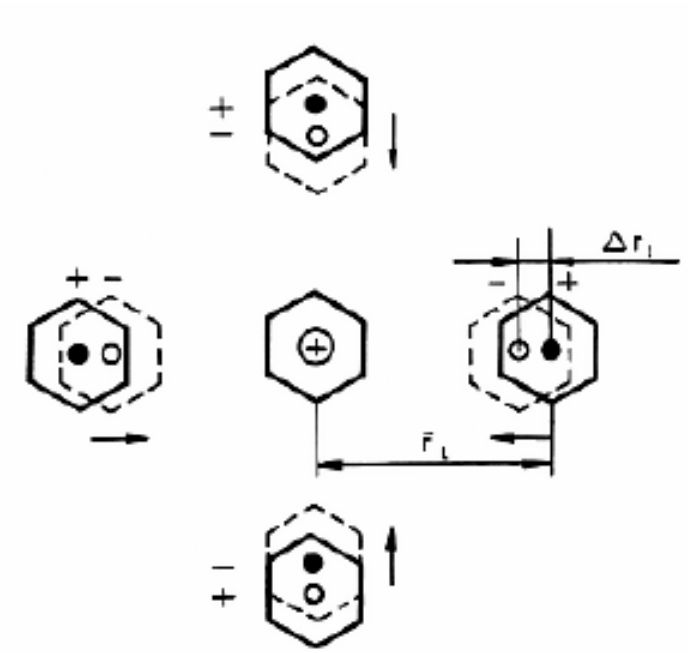
Polarons in Molecular Crystals

- Molecular polaron: interaction with **intra**molecular vibrations



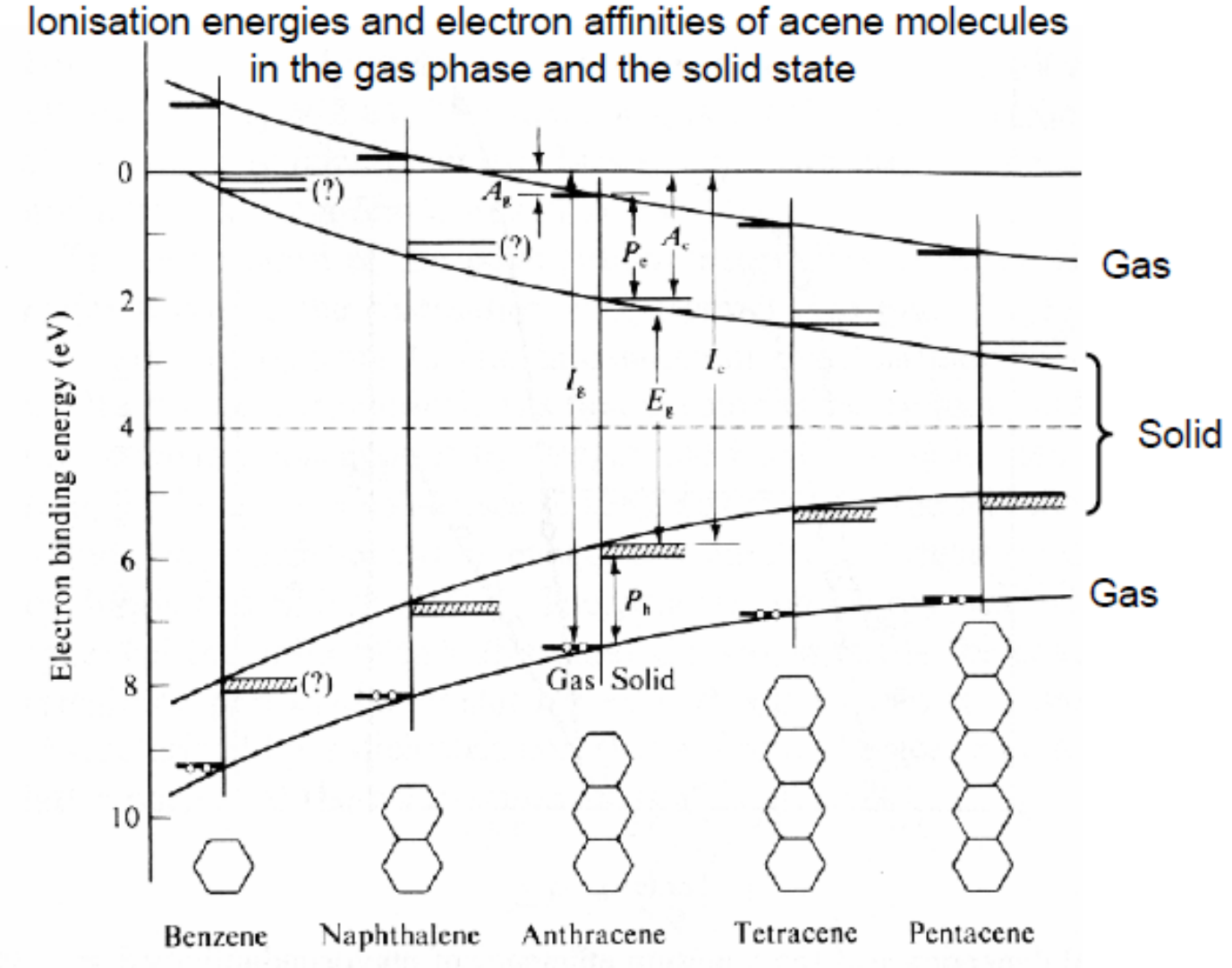
- Typical energies ~ 0.15eV

- Lattice polaron: interaction with **inter**molecular vibrations



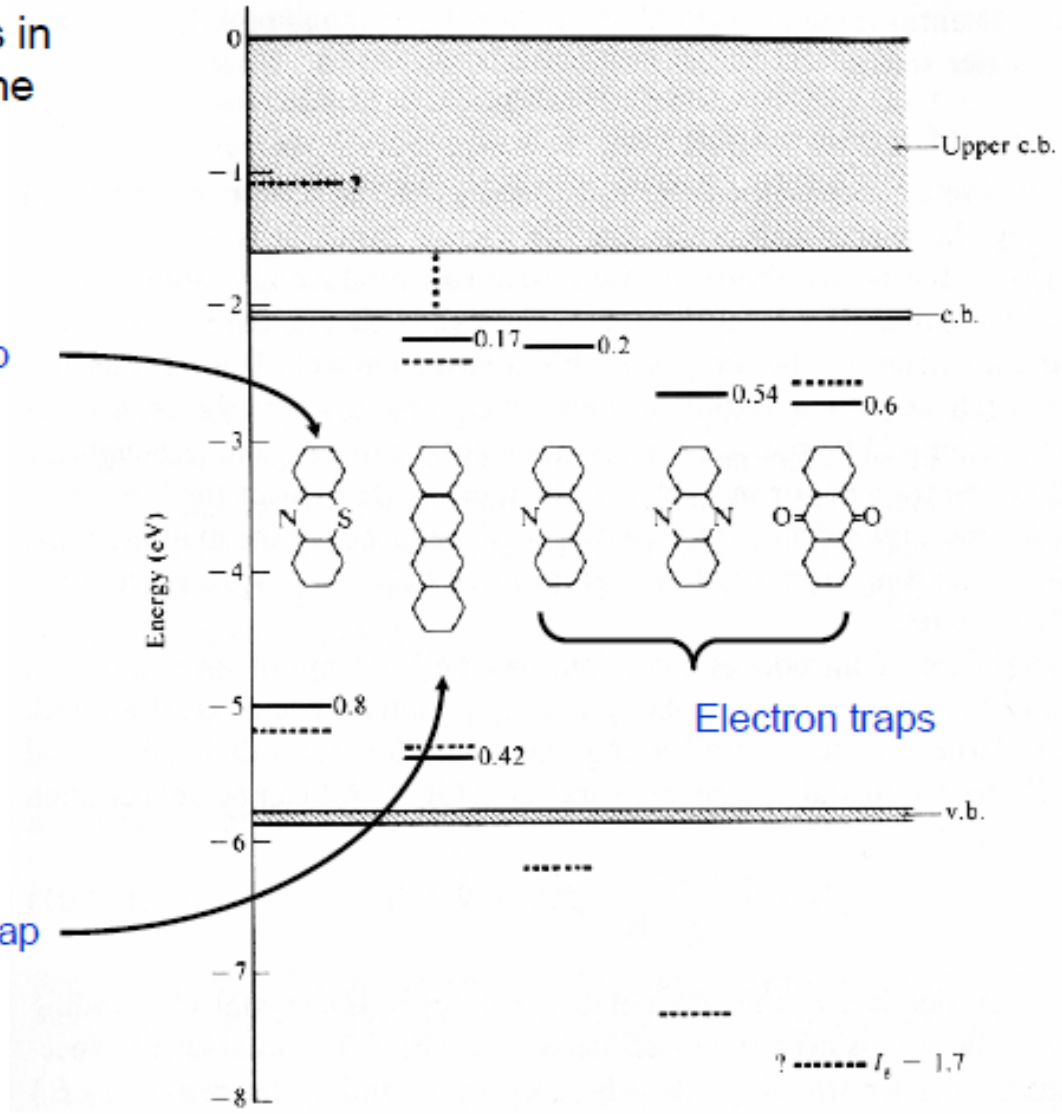
- Typical energies < 0.1eV

Polarisation Energies in Acenes



Charge Carrier Traps in Molecular Crystals

Impurities in anthracene



Hole trap

Exciton trap

Additionally:

- structural defects
- disorder

→ trap distribution (exponential / Gaussian)

Charge Carrier Mobility

Band Transport: energy bands $\mu \propto T^{-n} \qquad (n \approx 1.5)$

T = 300 K: $\mu \sim 1000\ cm^2/Vs$ (crystalline Si)

➔ **Phonon scattering**

(at low T: impurity scattering $\mu \propto T^{+n}$)

Hopping-Transport: localised carriers

T = 300 K: → $\mu << 1\ cm^2/Vs$ (amorphous materials)

$$\mu \propto \exp(-E_A/k_BT)$$

➔ **Phonon-assisted hopping**

Charge Carrier Density

Intrinsic carrier density: $n_i = N_0 \cdot \exp\left(-E_g / 2k_B T\right)$

T = 300 K

- Si: E_g = 1.12 eV; N_0 = 10^{19} cm^{-3} → **n_i = 10^{10} cm^{-3}**
  (Doping: n = 10^{15} … 10^{19} cm^{-3})

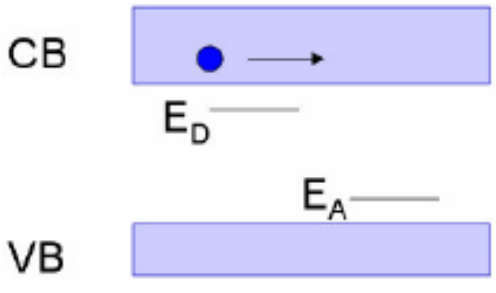
- Organic semiconductor
  with E_g = 2.5 eV; N_0 = 10^{21} cm^{-3} → **n_i = 1 cm^{-3}**

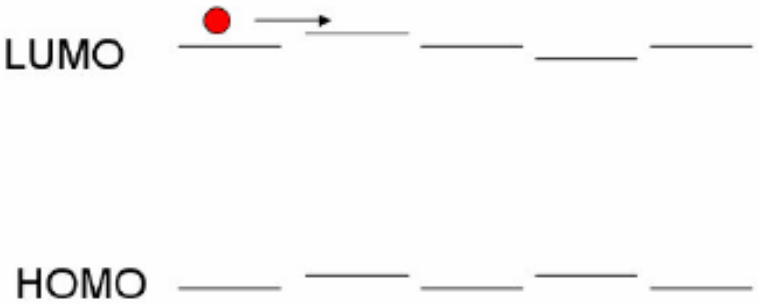
→ Peculiarities of organic semiconductors:
- Current carried by excess carriers → non-linear I-V characteristics
- Strongly field and temperature dependent mobility
- Anisotropic conductivity and mobility → tensors

Inorganic vs. Organic semiconductors

- broad bands
- small correlation energies (e-h ≈ 4meV)
- hydrogen model works

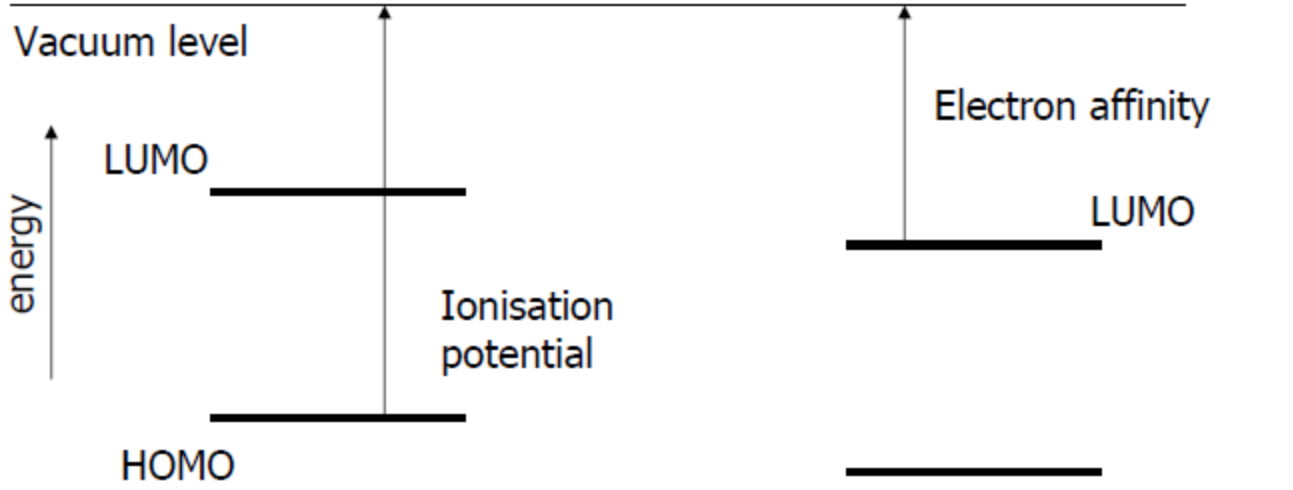
- hopping transport
- large correlation (e-h ≈ 1 eV)
- polaron effects important





Inorganic Semiconductor		Organic Semiconductor
Band	Transport Mechanism	Hopping
10^2-10^3	RT mobility (cm^2/Vs)	10^{-6}-1 (typ. 10^{-3})
10^{15}-10^{18} (doping controlled)	Charge carrier concentration	10^{10}-10^{16} (injection controlled)
$<<10^{15}$	Electr. Active impurit. (cm^{-3})	$\approx 10^{17}$

n- or p-type molecular semiconductors

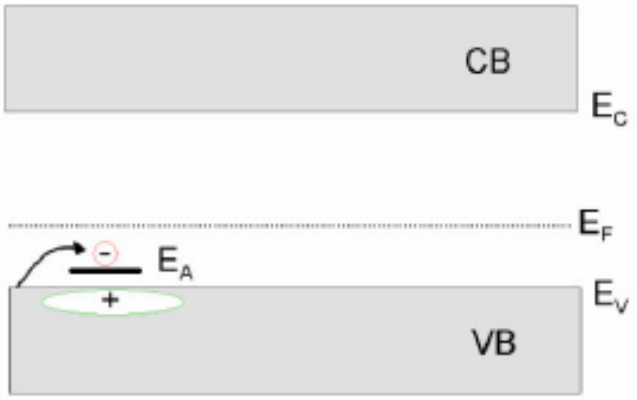


Molecular material with a low ionisation potential: electron donor ⇒ p-type semiconductor

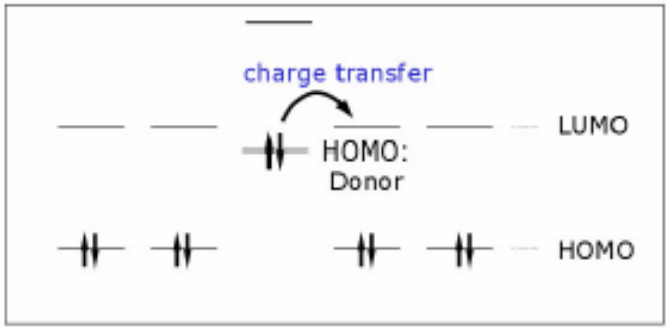
Molecular material with a high electron affinity: electron acceptor ⇒ n-type semiconductor

Doping organic semiconductors

Inorganic



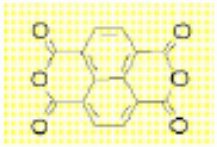
Organic



Organic dopants: electron transfer from high lying HOMO to matrix LUMO

Both n and p doping are possible in organic semiconductors by introducing charge donor or acceptor dopants into the molecular host matrix.

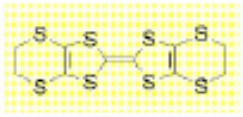
Charge donation of metal atoms (for example, alkaline elements) is very effective in modifying drastically (several orders of magnitude) the conductivity of organic materials.



Matrix:

Naphthalin-tetracarboxylic-dianhydride

(NTCDA)



Donor:

Bisethylendithio-tetrathiafulvalene

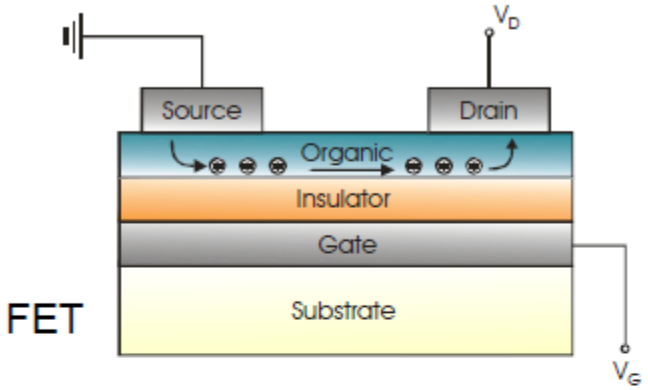
(BEDT-TTF)

Charge (photo)generation

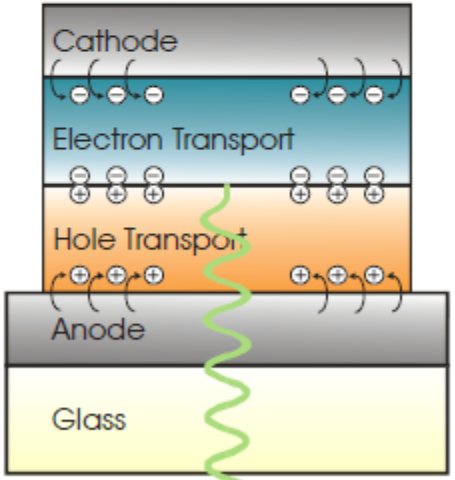
November 12, 2025

Charge Carrier Generation

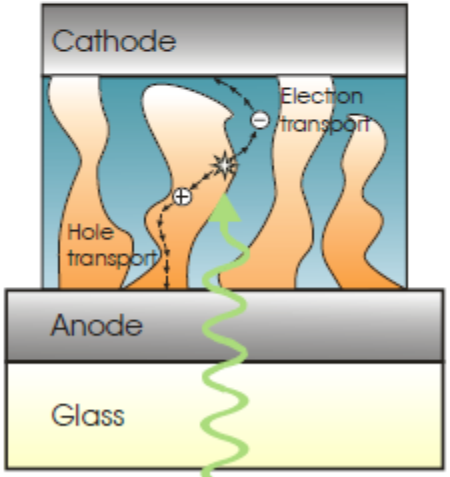
- Injection from contacts:
  → light-emitting diodes
- Field-effect doping:
  → field-effect transistors
- Photogeneration:
  → photodiodes and solar cells
- (Electro-)chemical doping



FET



LED

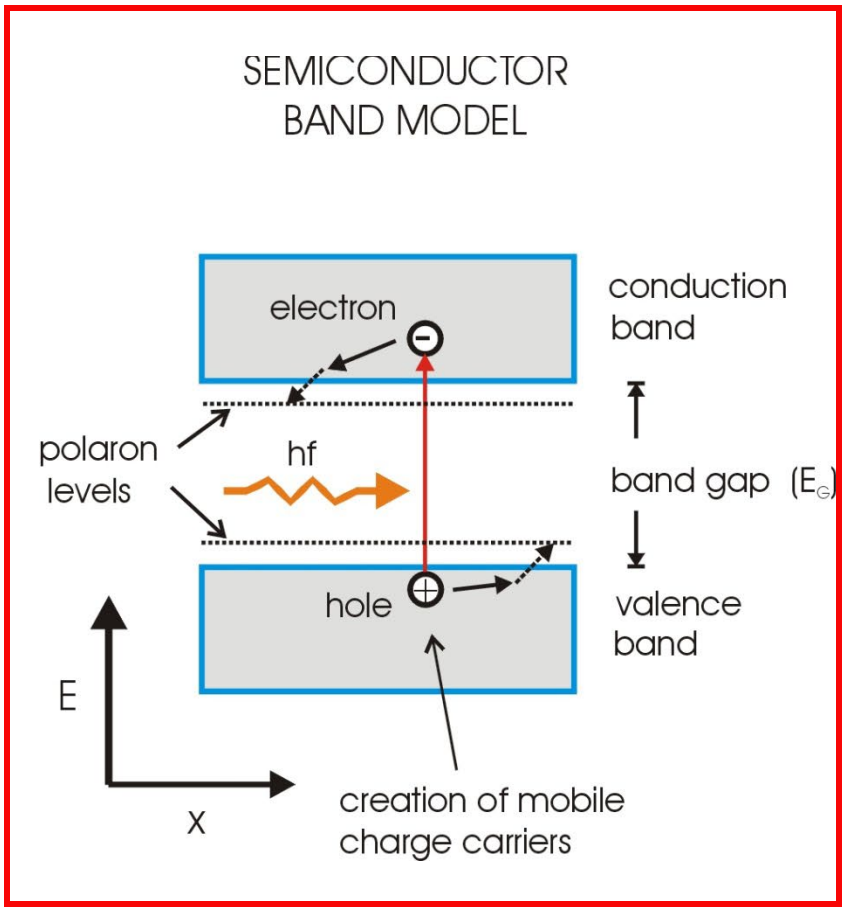


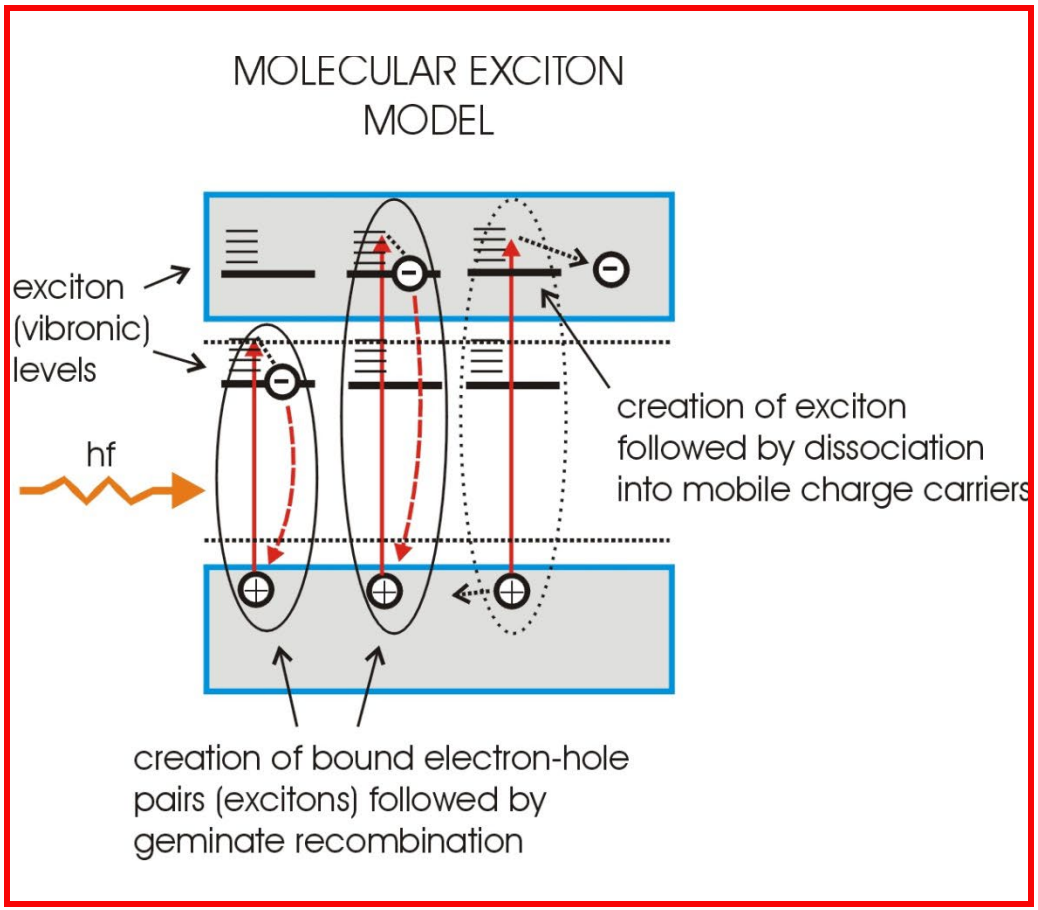
Solar cell

Light

Light

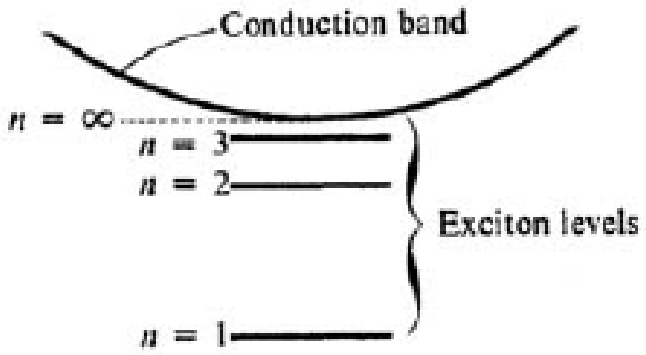
Photogeneration/transport





- Exciton binding energies ~0.1-0.5 eV: difficult to dissociate
- Use D-A systems to improve charge photogeneration

Wannier-Mott Excitons



Coulombic interaction between the hole and the electron is given by

$E_{EX} = -e^2/\epsilon r$

The exciton energy is then

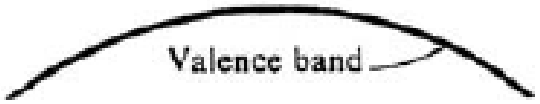
$E = E_{ION} - E_{EX}/n^2$, n = 1,2, ...

E_{ION} - energy required to ionize the molecule

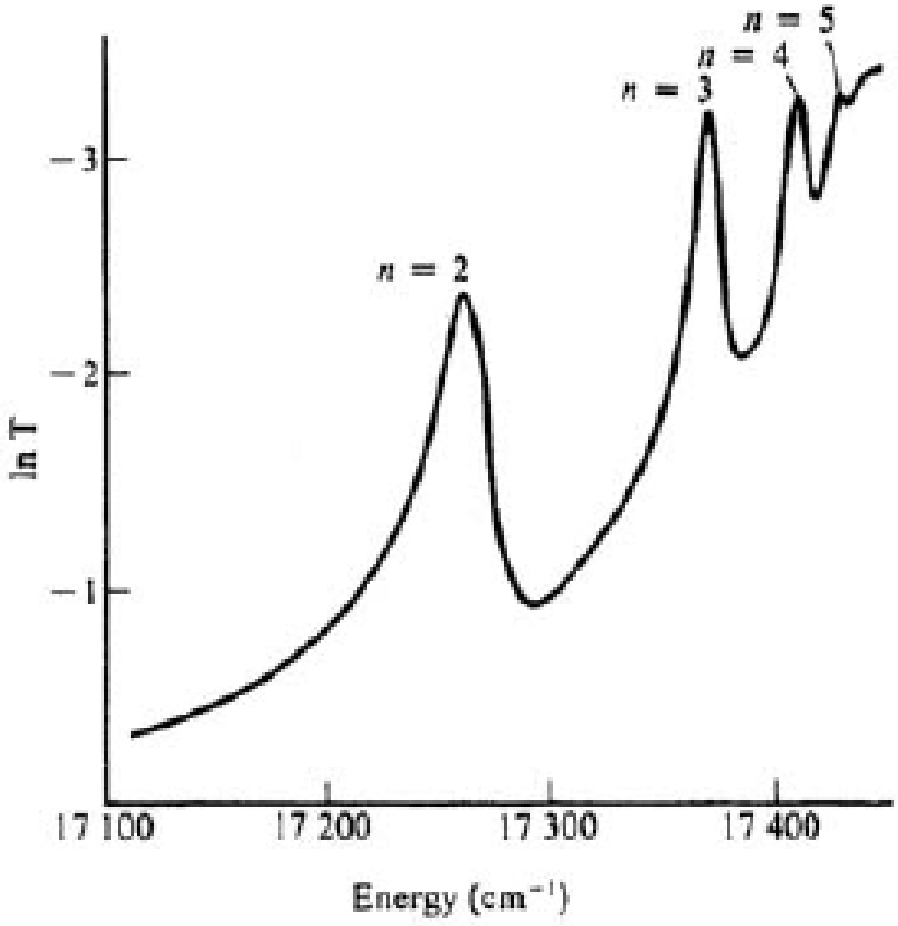
n - exciton energy level

$E_{EX} = 13.6\ eV\ \mu/m\epsilon$

μ- reduced mass = $m_e m_h / (m_e+m_h)$



An Example of Wannier-Mott Excitons



exciton progression
fits the expression

$\nu[cm^{-1}] = 17{,}508 - 800/n^2$

corresponding to
$\mu = 0.7$ and $\epsilon = 10$

Fig. I.D.28. The absorption spectrum of Cu_2O at 77 K, showing the exciton lines corresponding to several values of the quantum number n. (From Baumeister 1961)

Excitons

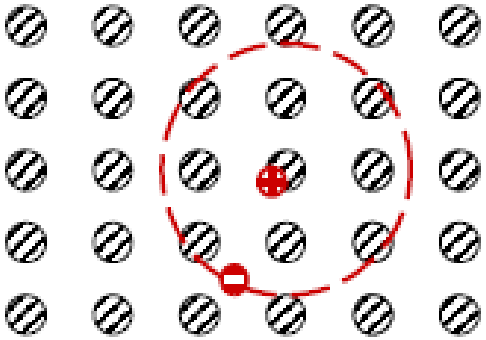
(bound electron-hole pairs)

treat excitons as chargeless particles capable of diffusion,

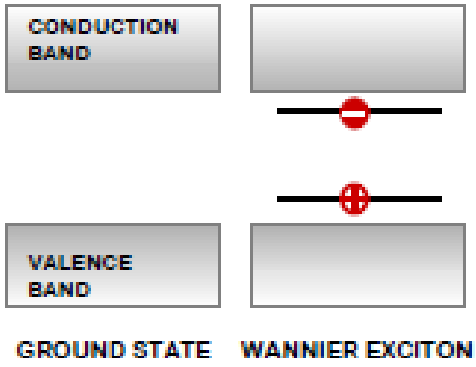
also view them as excited states of the molecule

Wannier exciton

(typical of inorganic semiconductors)



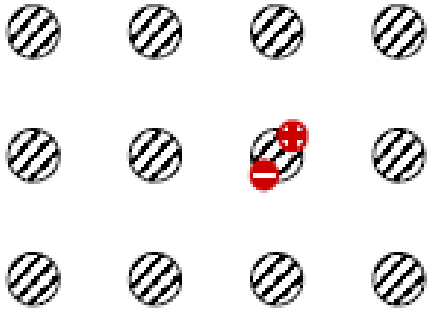
SEMICONDUCTOR PICTURE



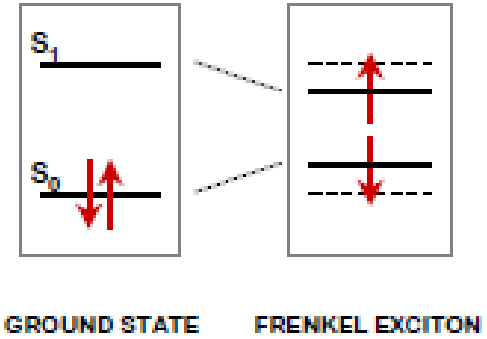
binding energy ~10meV
radius ~100Å

Frenkel exciton

(typical of organic materials)



MOLECULAR PICTURE

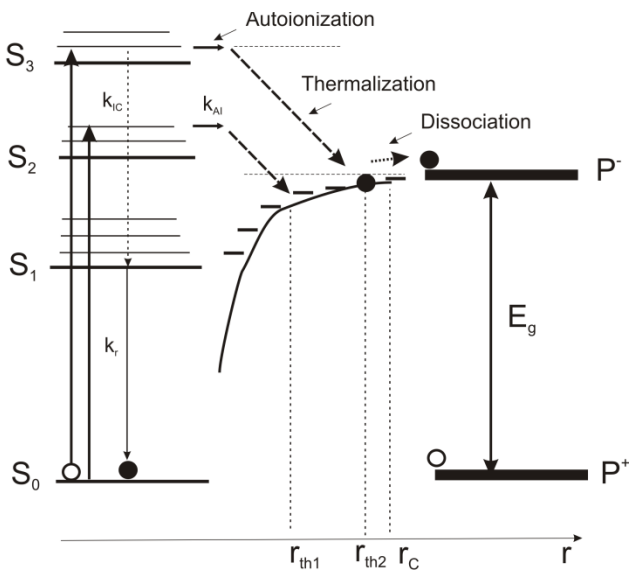


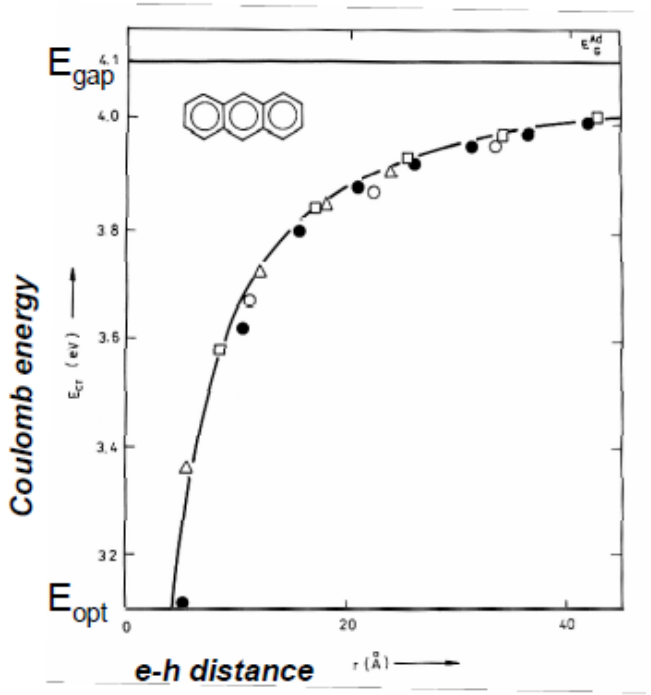
binding energy ~1eV
radius ~10Å

Charge Transfer (CT) Exciton

(typical of organic materials)

Charge Separation and Recombination





Polaron gap ~4.1eV

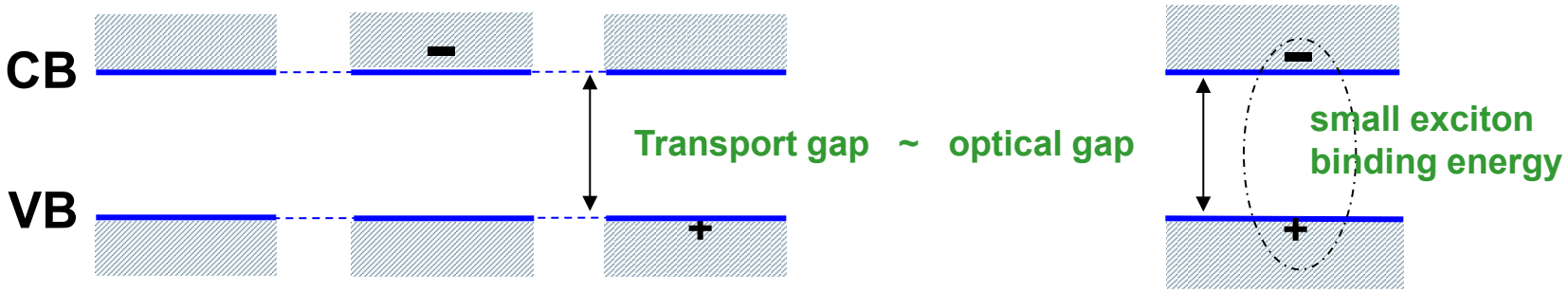
Optical gap ~3.1eV

Critical distance:
→ Coulomb radius

$$\frac{1}{4\pi\varepsilon\varepsilon_0}\cdot\frac{e^2}{r_C} = kT \quad (\varepsilon = 3,\ T = 300K)$$

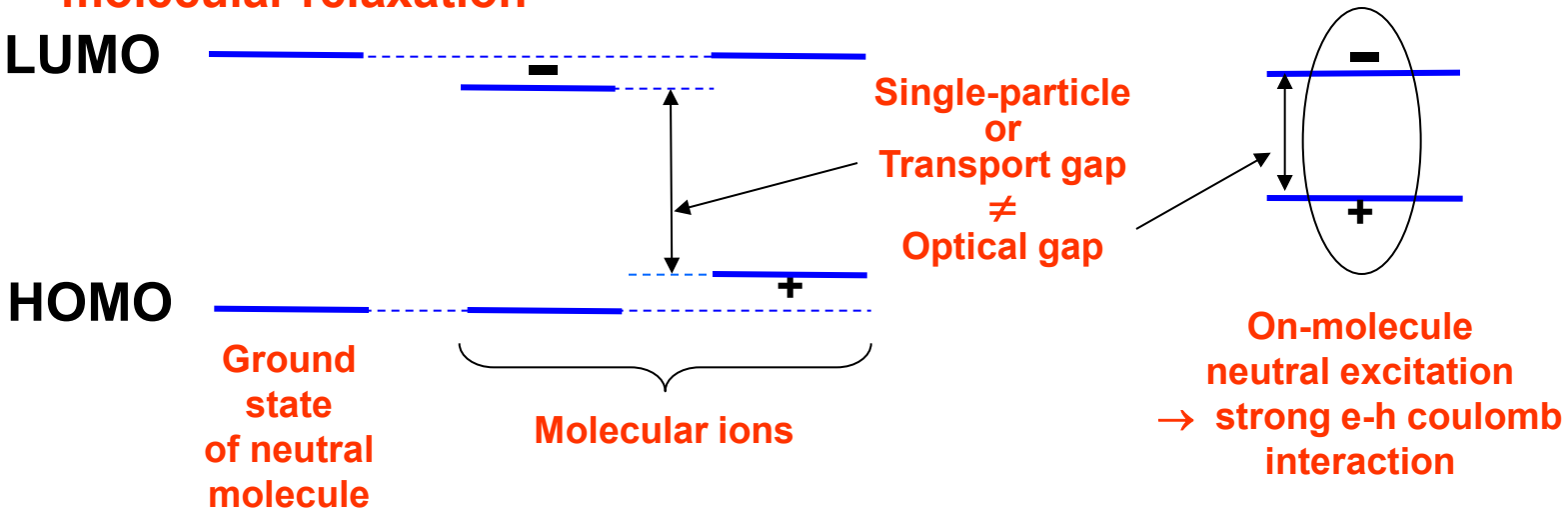
$$\Rightarrow r_C \approx 190\,\text{Å} \quad \text{"Coulomb radius"}$$

- **Inorganic semiconductor:** wide bands and delocalized states



Energy levels and transport: Bloch states and single-electron approximation

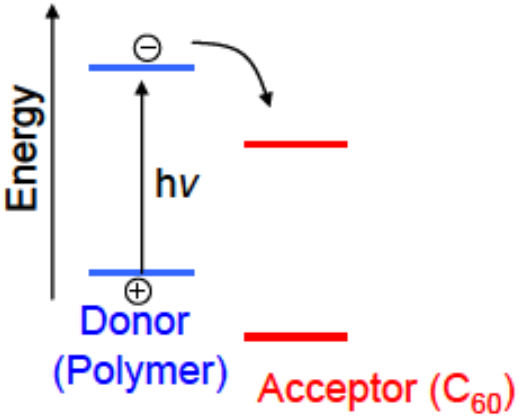
- **Organic molecular solid:** small transfer integral between molecules; charge carrier = molecular ions; electronic polarization + molecular relaxation



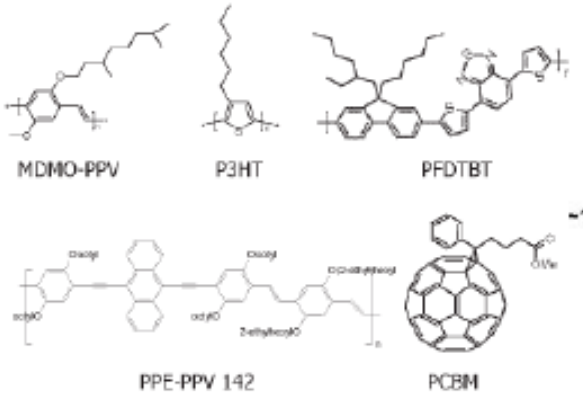
Transport gap – optical gap = exciton binding energy

Solar Cell Characteristics

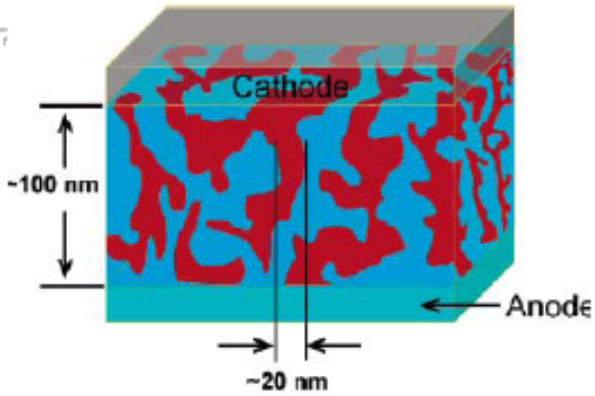
Mechanism



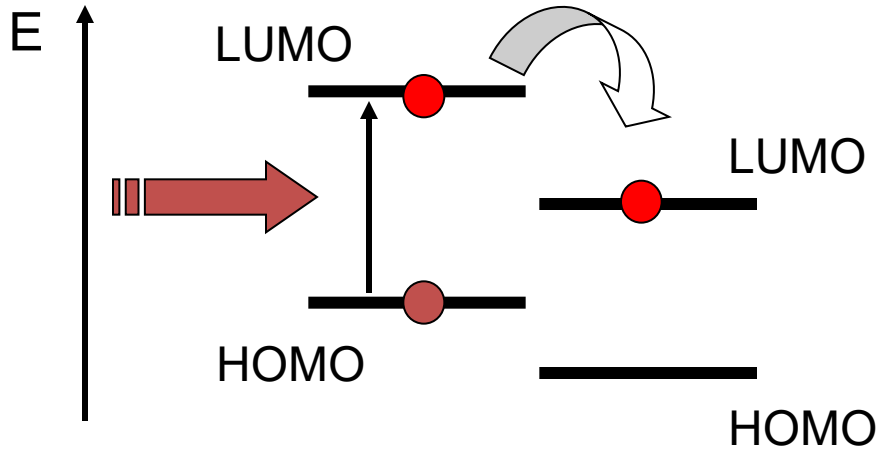
Typical Materials



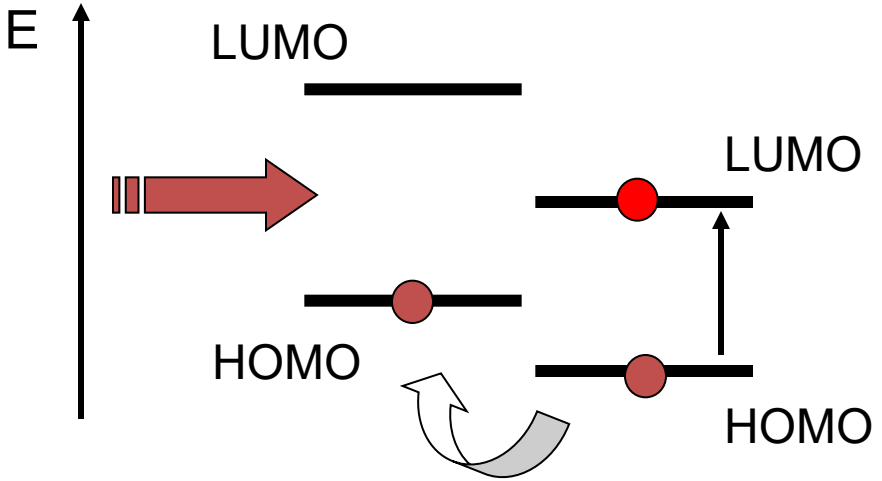
Nano-Morphology



Photoinduced Charge Transfer

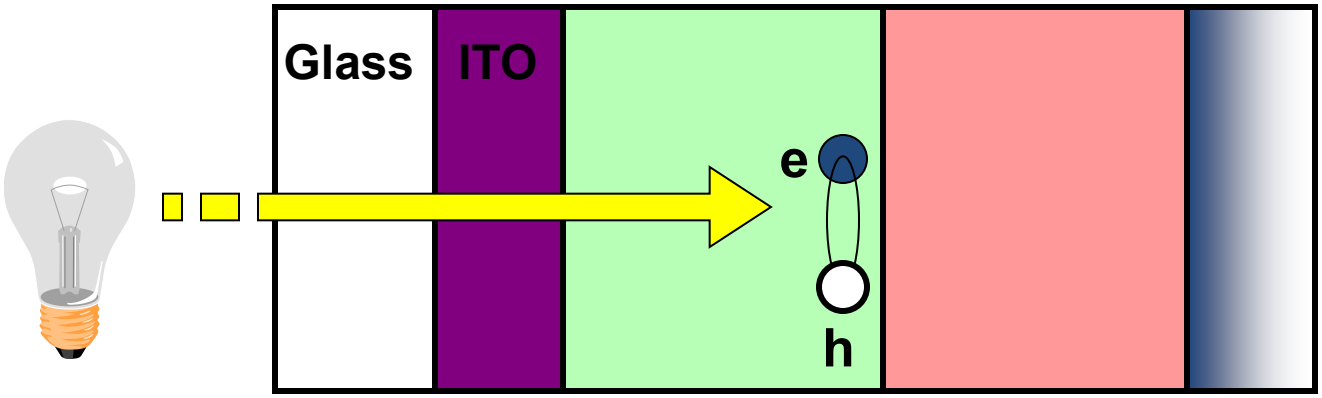


Photoinduced ELECTRON transfer

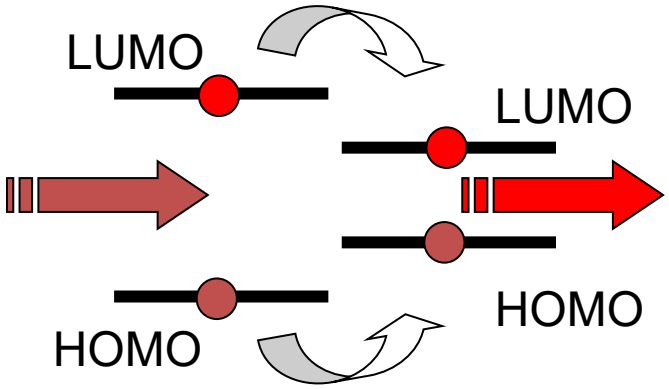


Photoinduced HOLE transfer

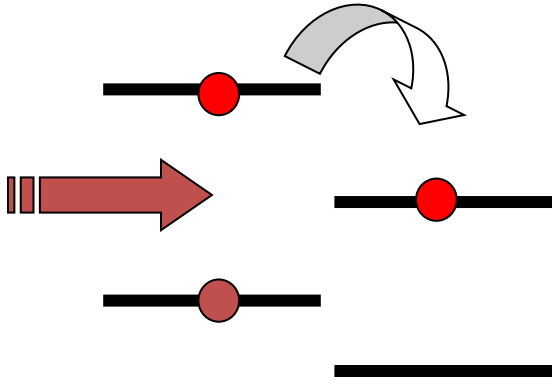
Charge and energy transfer in conjugated polymers



Organic Solar Cells



Energy transfer



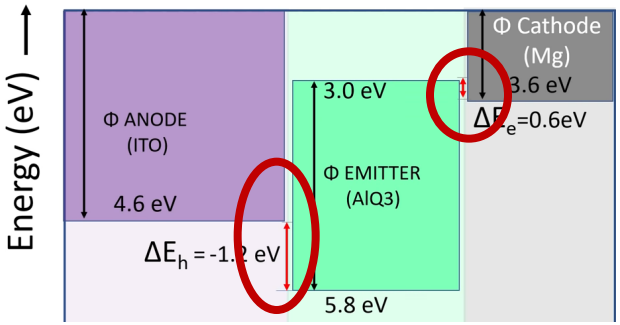
Charge transfer

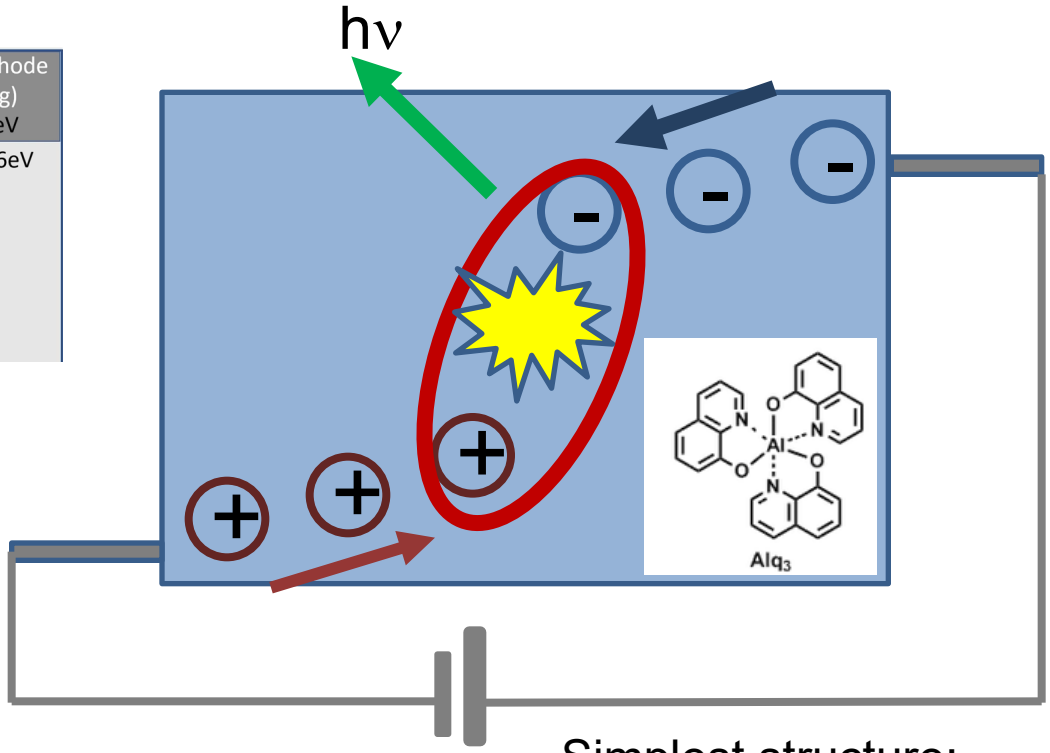
TABLE 1.1. *Comparison of Characteristic Features of Organic Molecular and Covalent (Atomic) Crystals*

Molecular crystal (e.g., anthracene-type crystal)	Covalent (atomic) crystal (e.g., silicon-type crystal)
Weak Van der Waals type of interaction (characteristic interaction energies $E_{VdW} = 10^{-3}$–10^{-2} eV)	Strong covalent-type interaction (characteristic interaction energies $E_{cov} = 2$–4 eV)
Marked tendency of charge carrier and exciton localization	Pronounced charge carrier delocalization
Self-energy of charge carriers and excitons determined by many-electron interaction (polarization) effects	Single-electron approximation valid
Charge carriers and excitons as polaron-type quasiparticles	Charge carriers as free holes and electrons
Low charge carrier mobilities ($\mu \approx 1$ cm^2/Vs) and small mean free path ($l \approx a_o$ = lattice constant) at room temperatures	High charge carrier mobilities and large mean free path [$l = (100-1000)a_o$]
Large effective mass of charge carriers $m_{eff} = (10^2$–$10^3)m_e$	Small effective mass of charge carriers $m_{eff} \leqslant m_e$
Hopping-type charge carrier transport dominant	Band-type charge carrier transport dominant
Excitons as molecular Frenkel-type quasiparticles	Excitons as Wannier-type quasiparticles
Low melting and sublimation temperatures, low mechanic strength, high compressibility	High melting and sublimation temperatures, high mechanical strength, low compressibility

OLEDs

Step 1: inject holes and electrons
(choose appropriate electrodes)



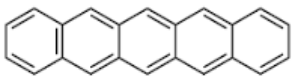


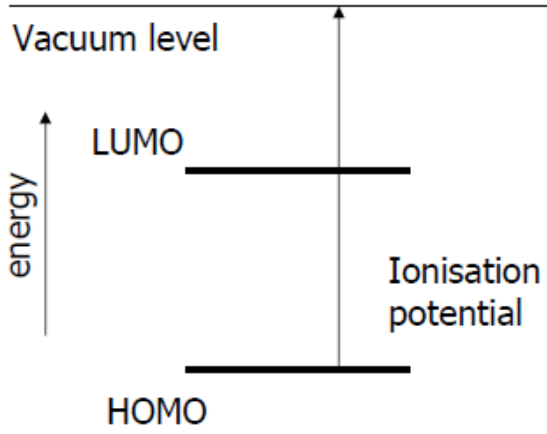
- Work function: how much energy is needed to release the charge
- Minimize energy barriers
- One of the electrodes (ITO) transparent

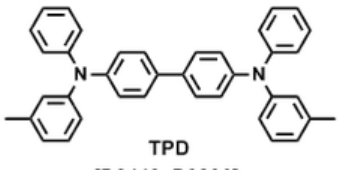
E.g. use FTO as a transparent Hole injector and Ytterbium (Φ = 2.6 eV) as an electron injector

Simplest structure: electrode/Alq3/electrode
Problem: Alq3 is better for electron than hole transport, and the hole injection barrier too high

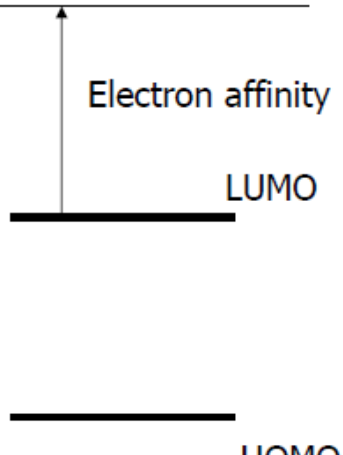
n- or p-type molecular semiconductors



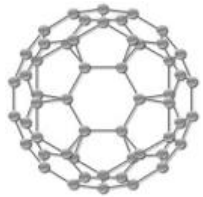


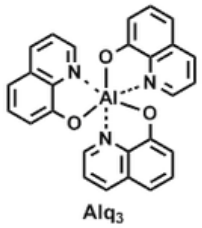


Molecular material with a
low ionisation potential:
electron donor ⇒
p-type semiconductor



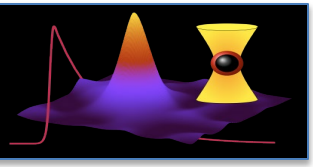
Molecular material with a
high electron affinity:
electron acceptor ⇒
n-type semiconductor

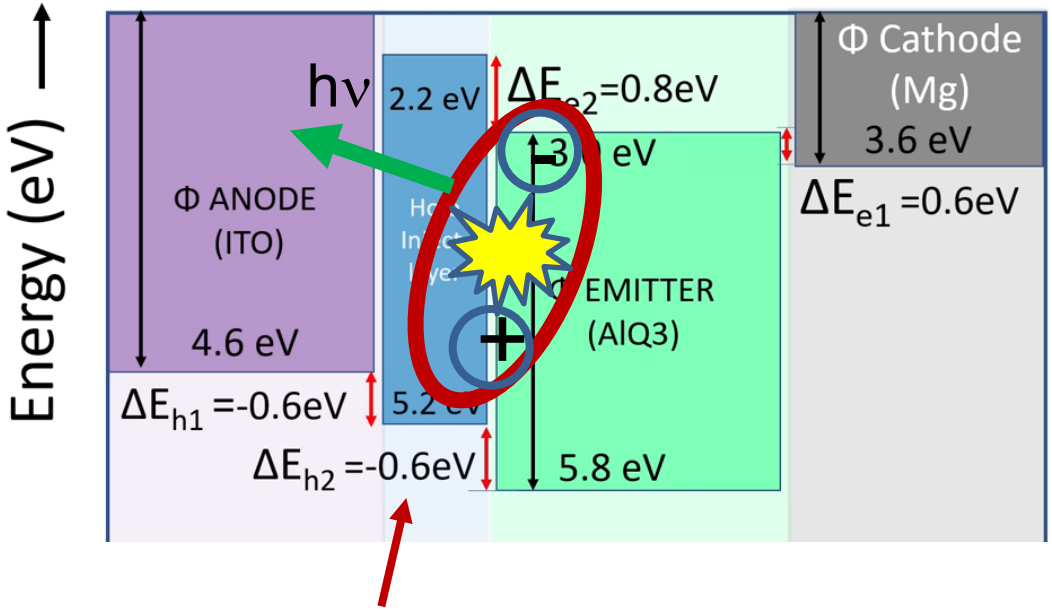


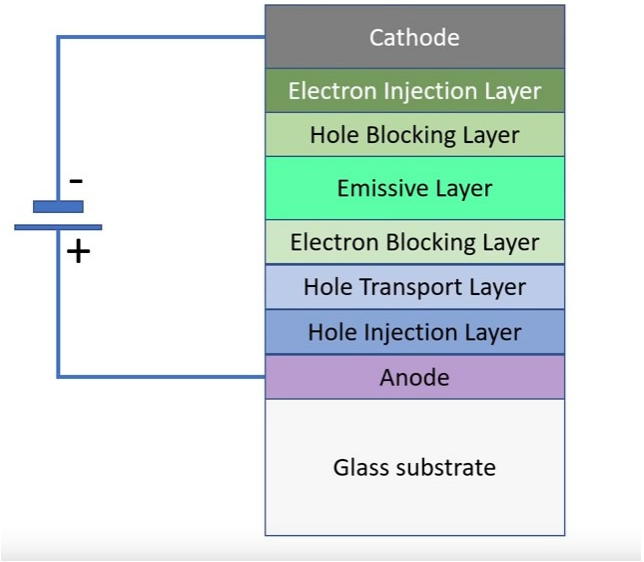


Depending on the molecular energy levels, some molecules transport holes and other transport electrons more efficiently

OLEDs





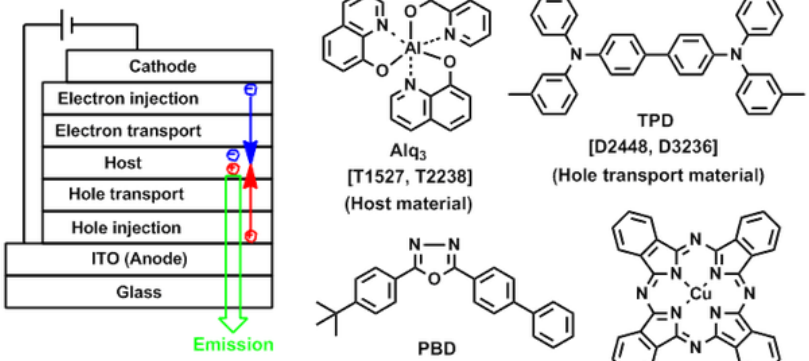


Insert a hole injection layer to help inject and transport holes (e.g. TPD)

More complicated structures

Example structure: glass/FTO/TPD (hole injection/transport)/Alq3 (electron injection/emitter)/Ytterbium

OLEDs



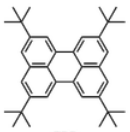
Alq_3
[T1527, T2238]
(Host material)

TPD
[D2448, D3236]
(Hole transport material)

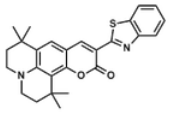
PBD
[B1767, B2696]
(Electron transport material)

CuPc
[P0655, P1628]
ion material)

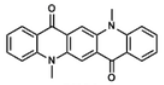
OLED Dopants



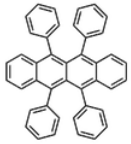
TBP
[T3053]



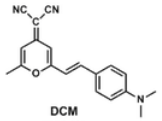
Coumarin 545T
[B4257]



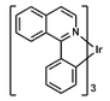
DMQA
[D2687, D3227]



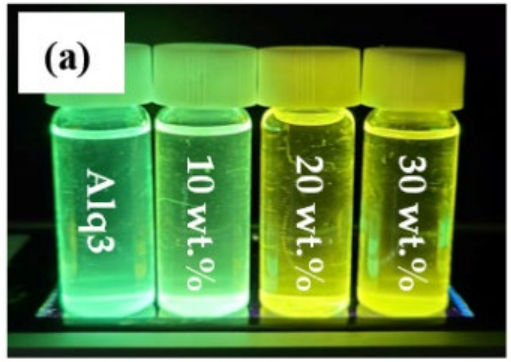
Rubrene
[T0561, T2233]

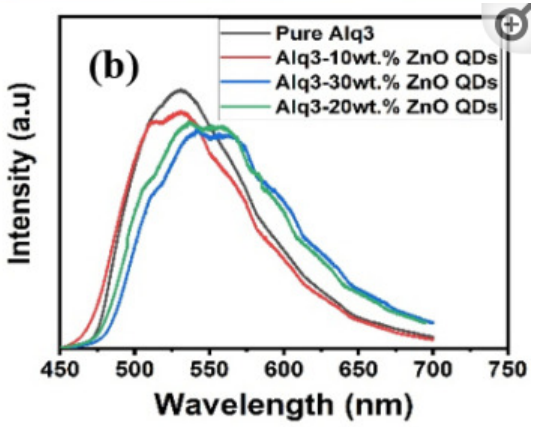


DCM
[D2849]



$Ir(piq)_3$
[T2685]





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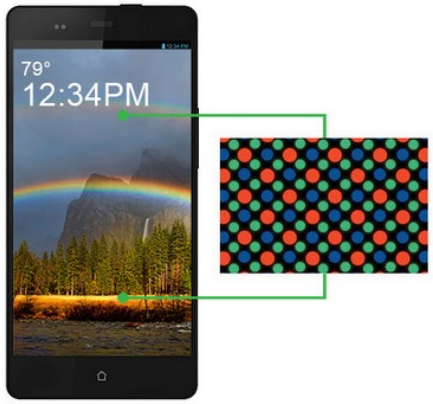
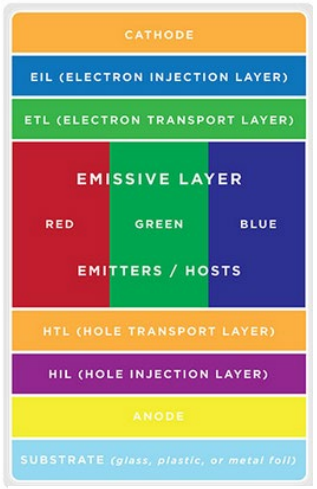
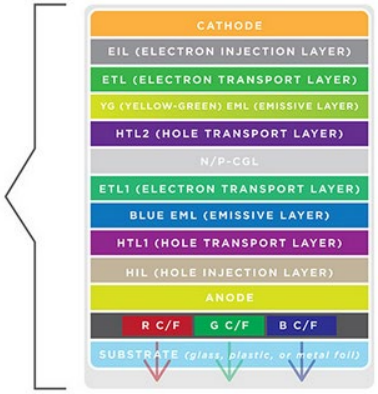
Multicolor OLEDs





Incorporate multiple emitters



https://oled.com/oleds/