PHAS0058

Physics of Advanced Materials

Lecture 1: Organic semiconductors - physics

In this lecture...

- What are organic semiconductors?
- Origin of semiconductvity in organic materials:
  - hybridisation of orbitals
  - π-conjugation
- Bound states:
  - polarons
  - excitons
- Energy transitions and PL spectra
- Physics of charge transfer

What are organic semiconductors?

Types of OSCs
- single molecules
- polymers:
  - plastics
  - rubbers
  - foams
  - foils
  - ...

organic = carbon-based
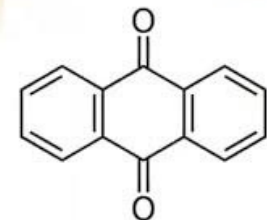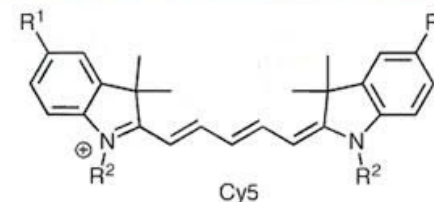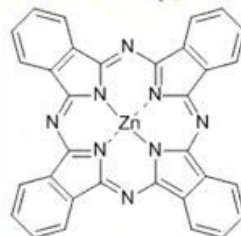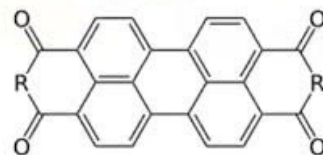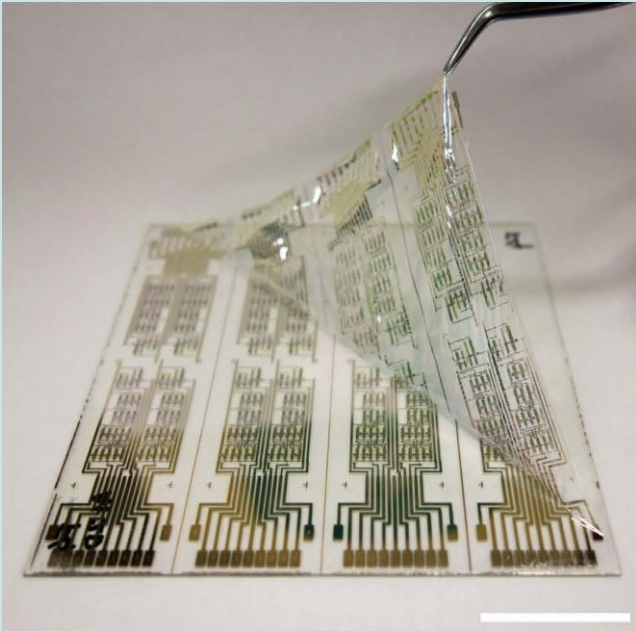
Why organic semiconductors?
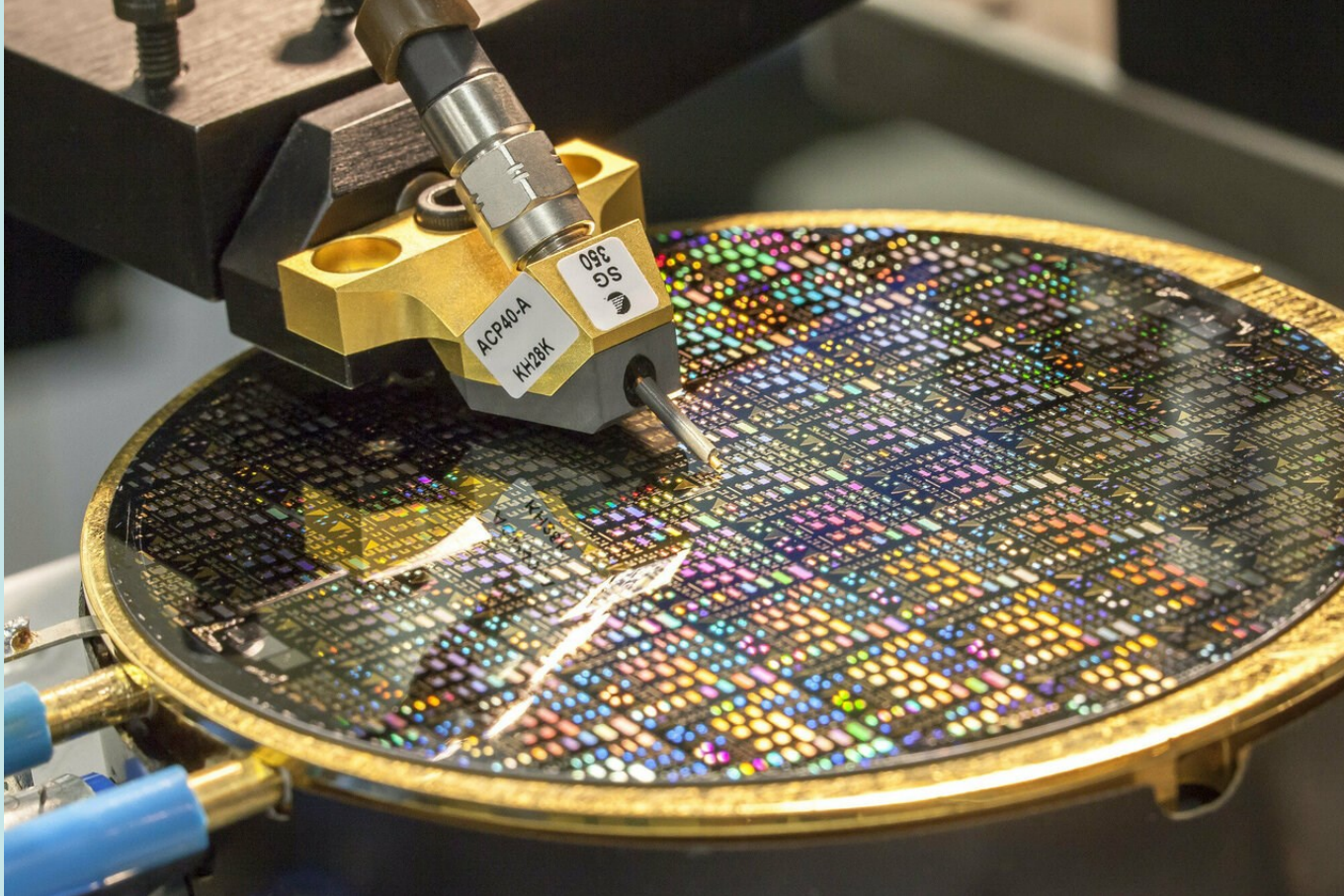
Silicon – material of choice:
+ abundant
+ high-quality

but also:
- not luminescent
- costly to purify and handle
- not ideal for large-area applications

Properties of organic electronics
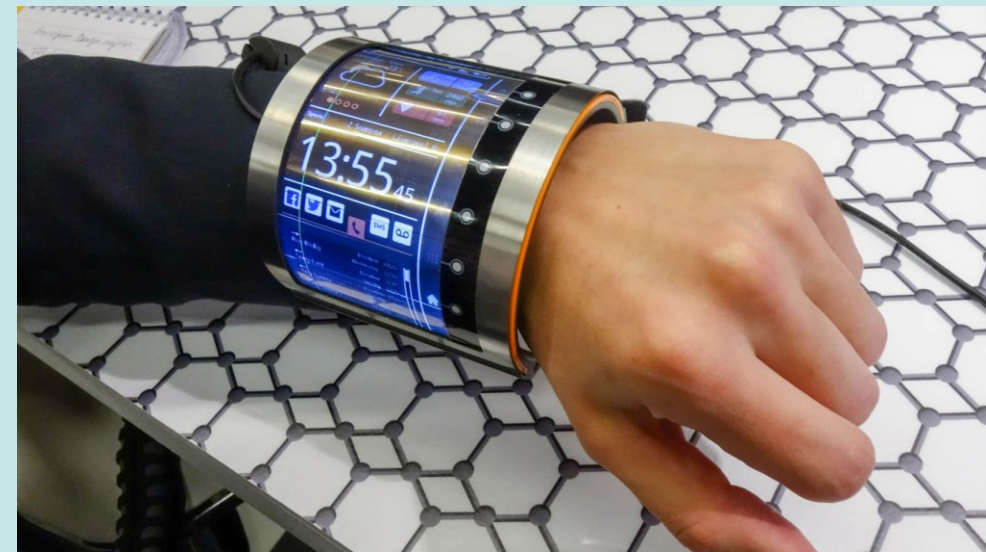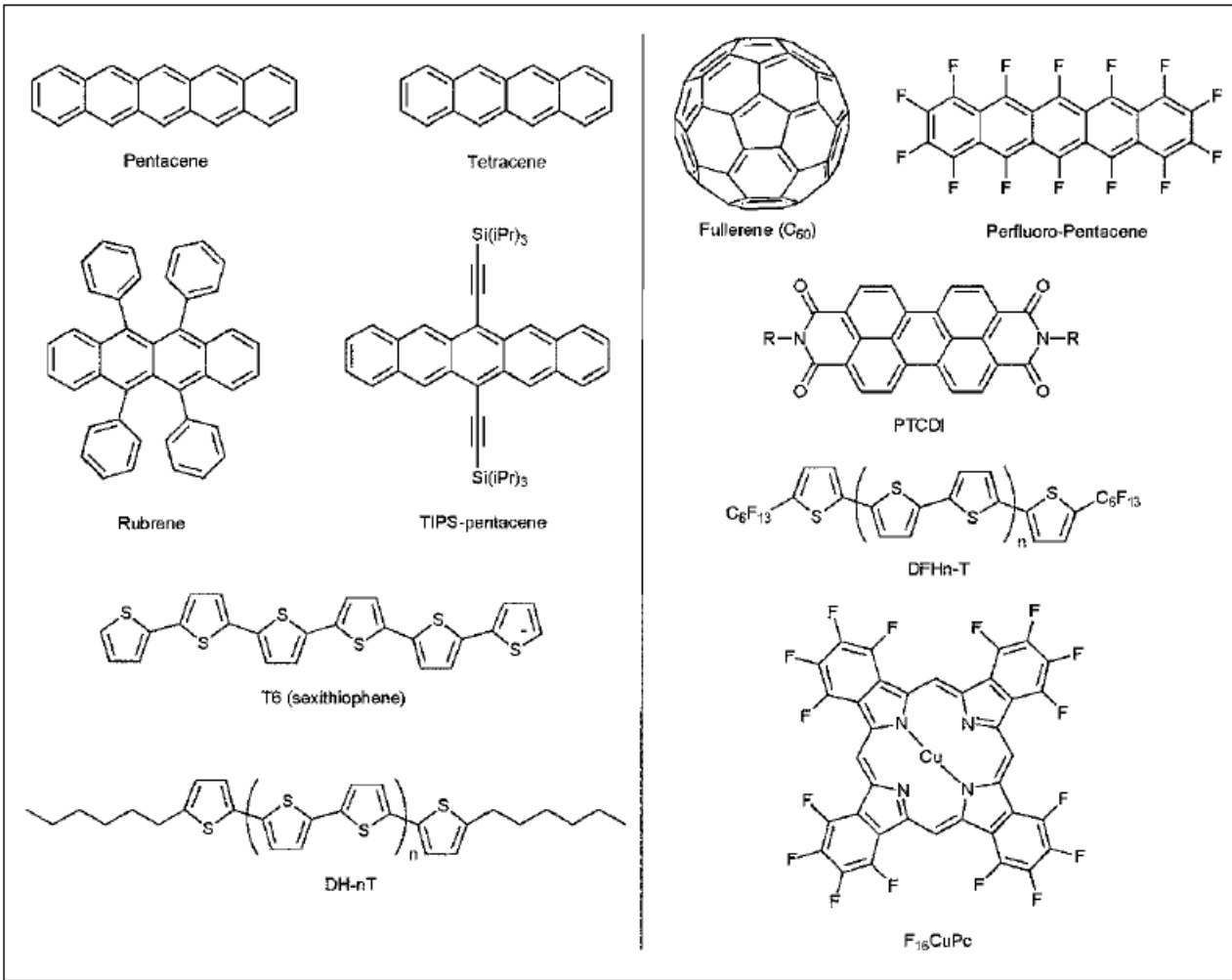

advantages:
- solution processing
    - price (low temp & pressure)
    - substrate choice (flexibility)
    - area size
    - printing (roll-to-roll)
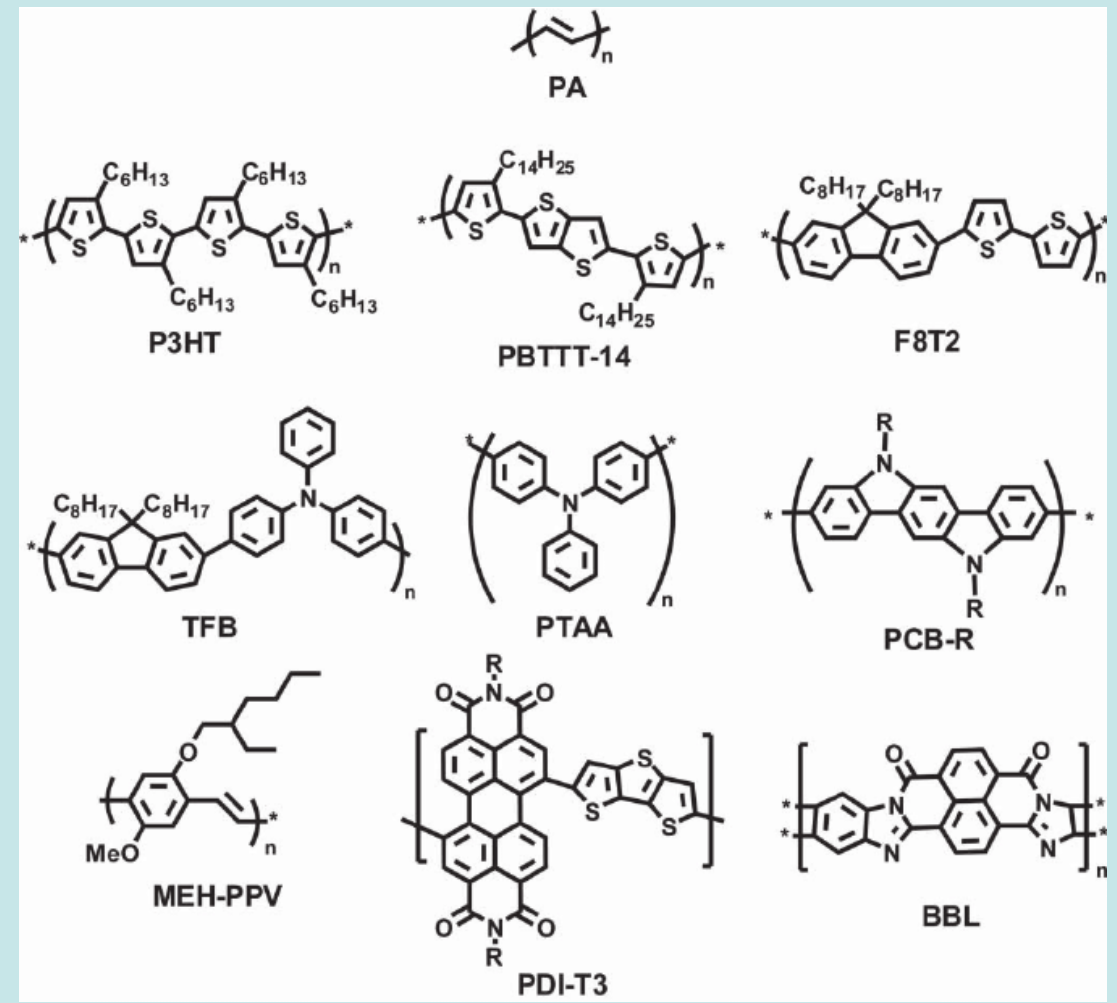- biocompatibility
- molecular design

disadvantages:
- slower than silicon
- sensitive to water, UV, oxygen...
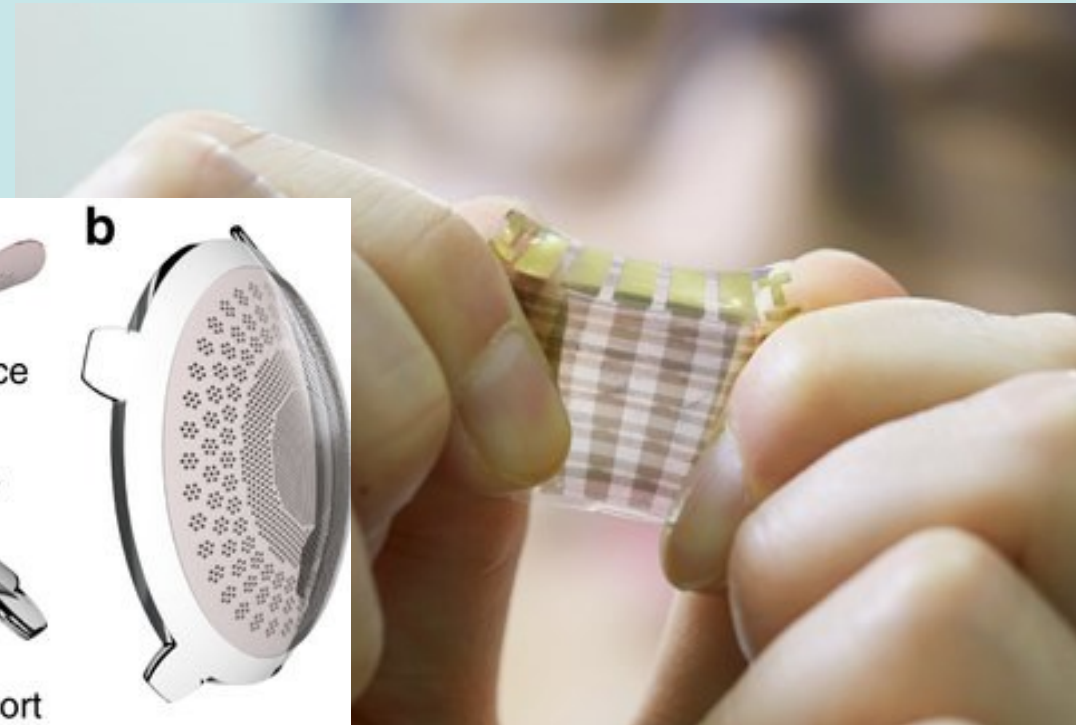
Example materials

molecular

polymers

Already available:

- Rollable TVs: https://www.lg.com/global/lg-signature/rollable-oled-tv-r

- Flexible, compostable PVs

- Retinal chips

- Smart fabrics

- ...

Images: https://www.researchgate.net/figure/Foldable-and-photovoltaic-wide-field-retinal-prosthesis-a-3D-model-of-the-fabricated_fig1_323641091
https://www.sait.samsung.co.kr/saithome/research/organic.do

a PDMS–photovoltaic interface

Dome-shaped PDMS support

b
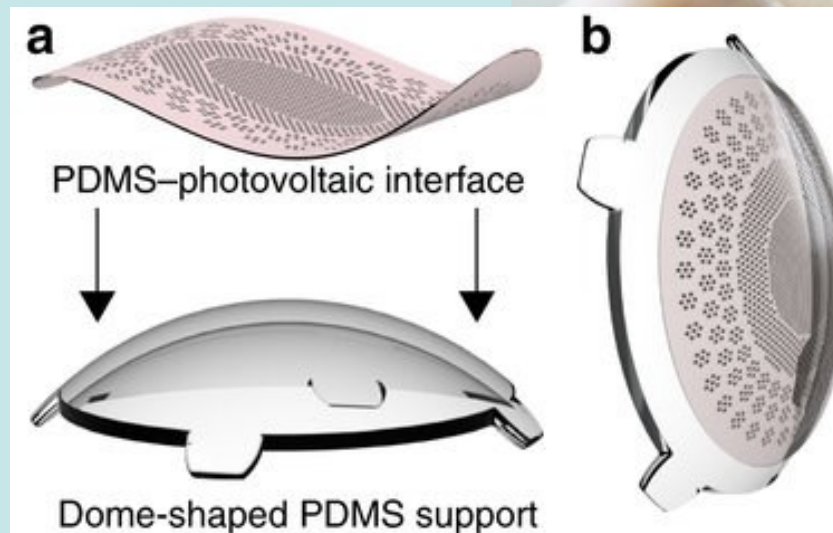
Semiconductivity of organic materials

How can polymers and molecules become semiconductive?

Hybridisation

sp$_2$ hybridisation

2s   2p$_X$ 2p$_Y$ 2p$_Z$

unhybridized *p* orbitals

sp^3 Hybridization   *sp^2* Hybridization   *sp* Hybridization

2p$_z$

sp^2

sp2 hybridisation

p orbital

sp^2 orbital   *sp^2* orbital

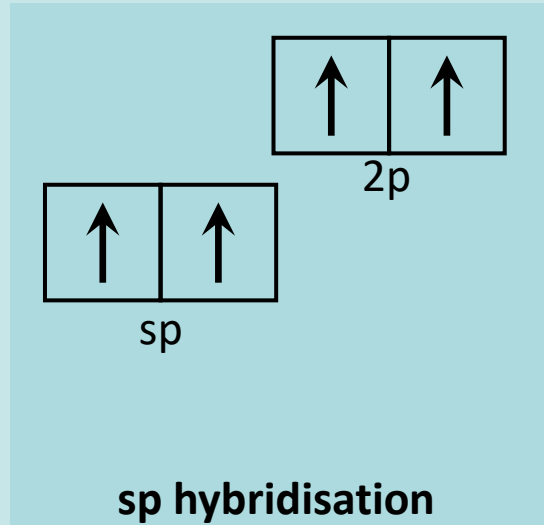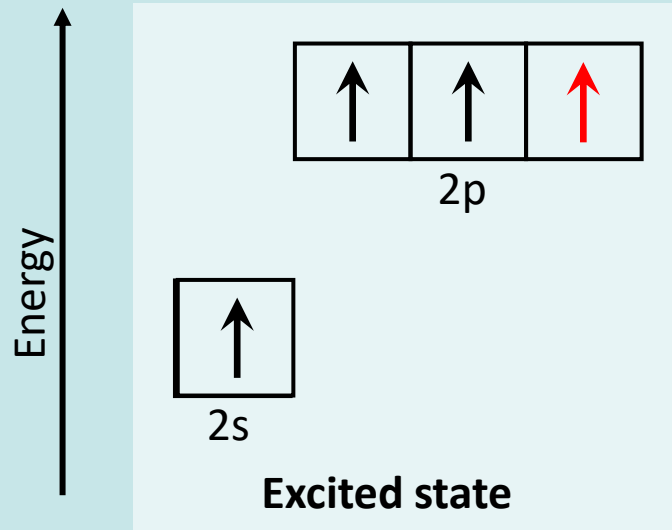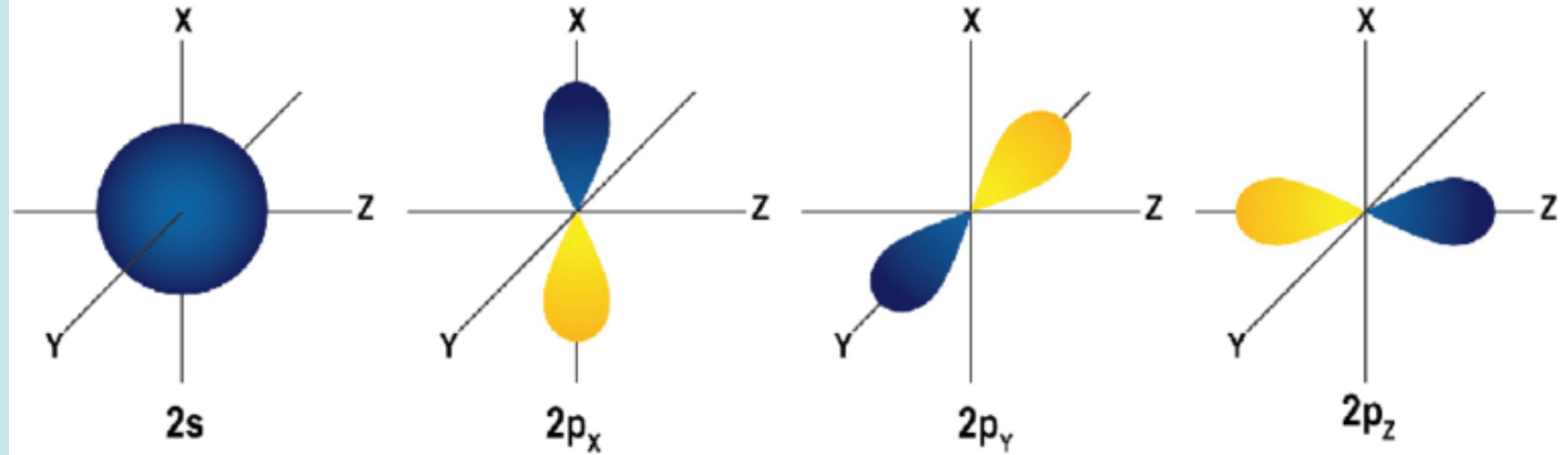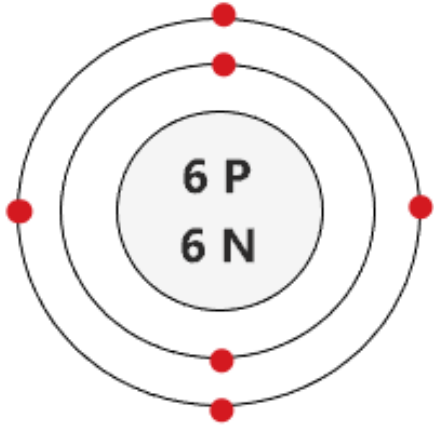*sp^2* orbital
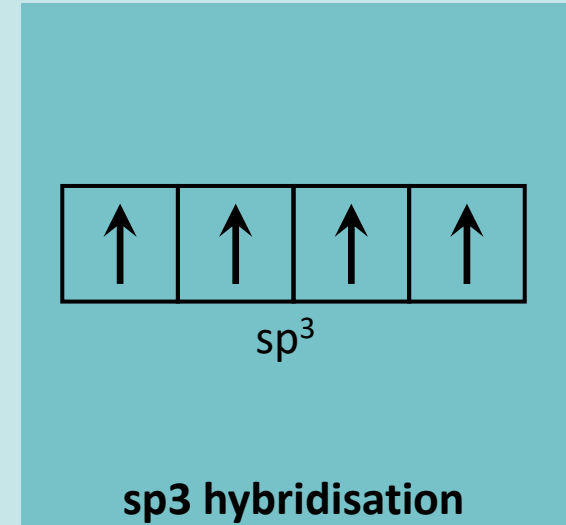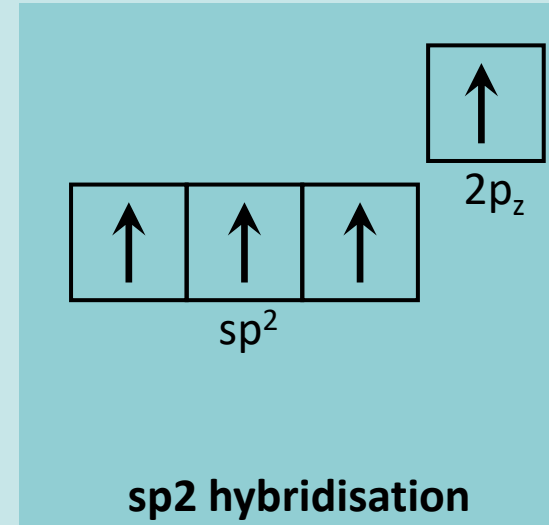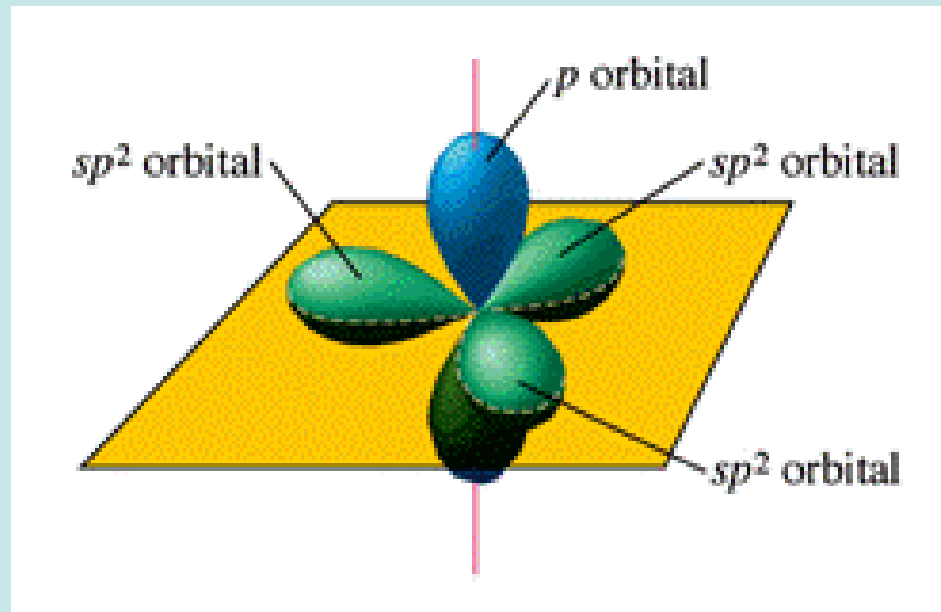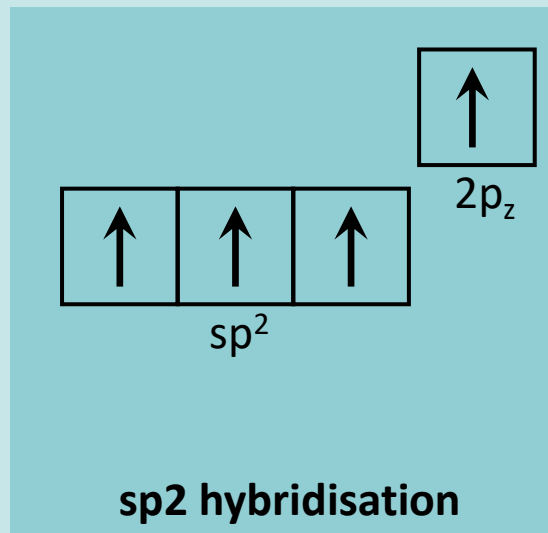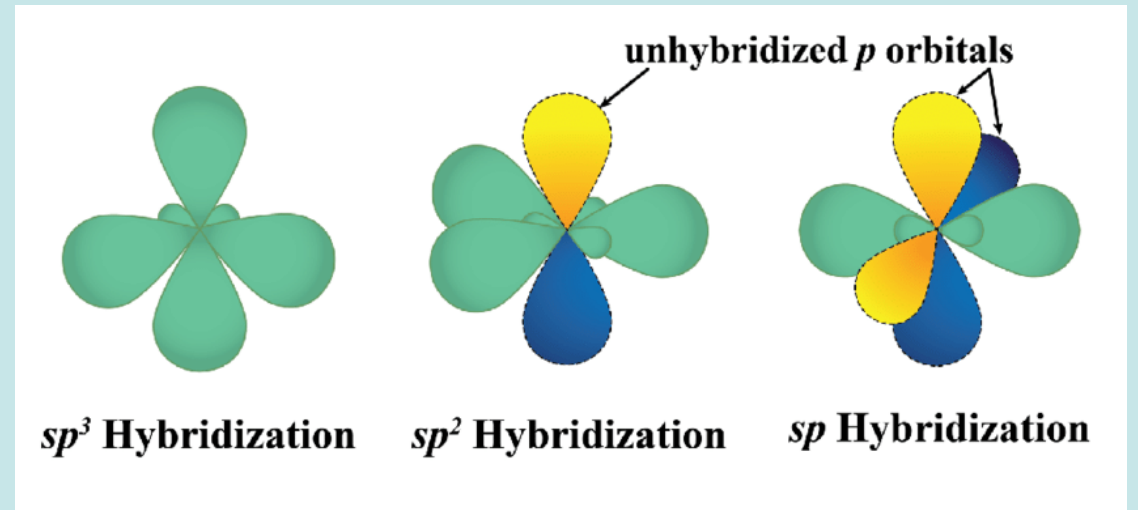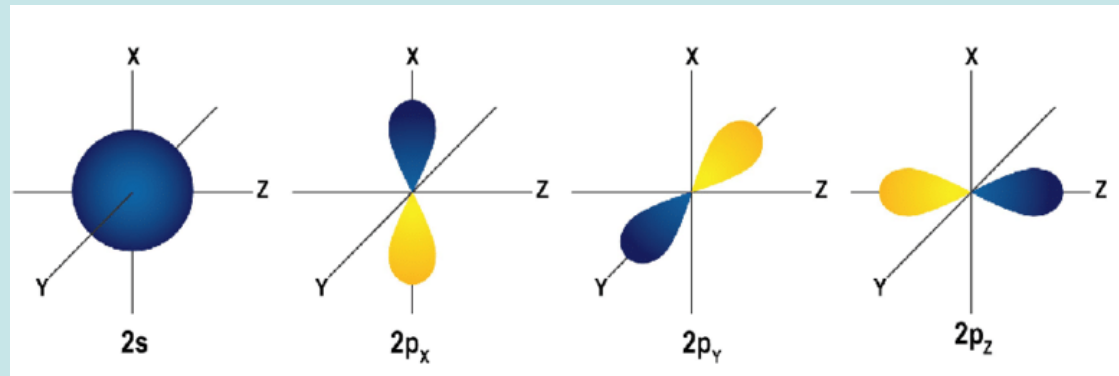
Bonding between C atoms

σ-bonds:
- overlap of hybridised orbitals
- along the chain
- strong
- highly directional
- forms stable carbon structures

π-bonds:
- overlap of $2p_z$ orbitals
- weak
- restricts rotation (planarise)
- forms stable carbon structures
- delocalised in conjugated molecules

sp^2 hybrid orbital
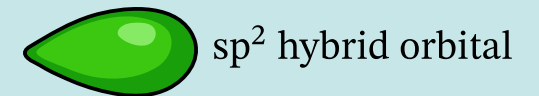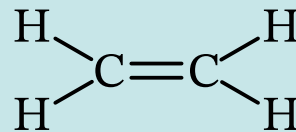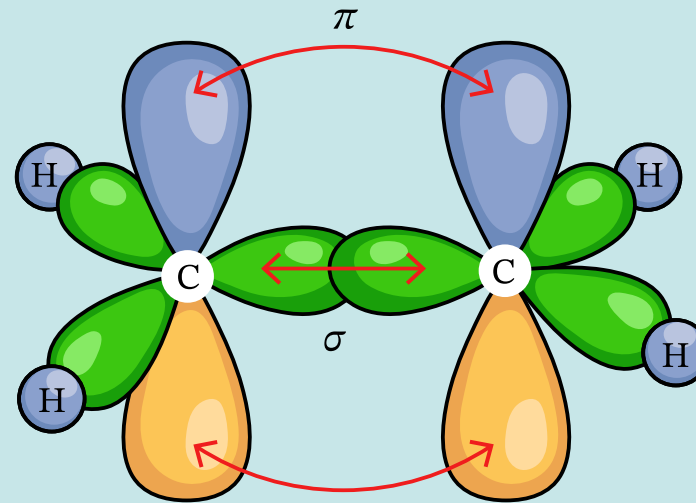
Nonhybridized p orbital

Hydrogen atom 1s orbital

Conjugation
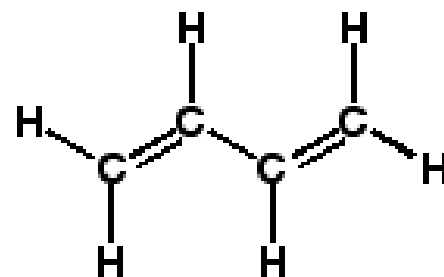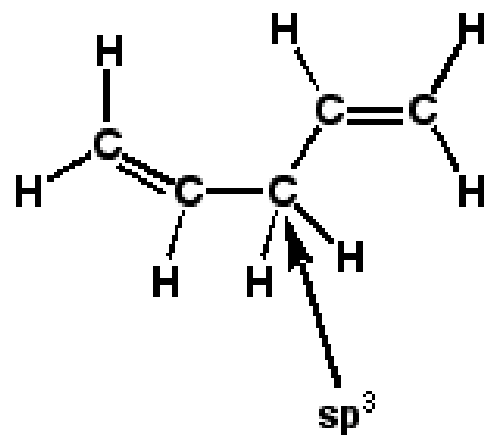
All carbon atoms sp^2

sp^3
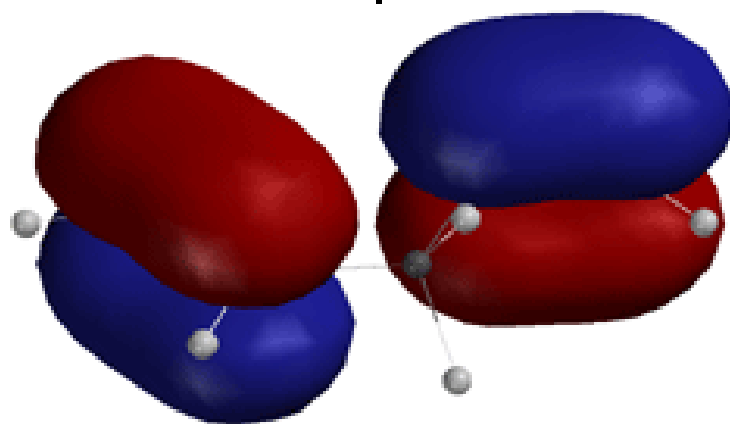
Non-conjugated π system
(π bonds do not interact)
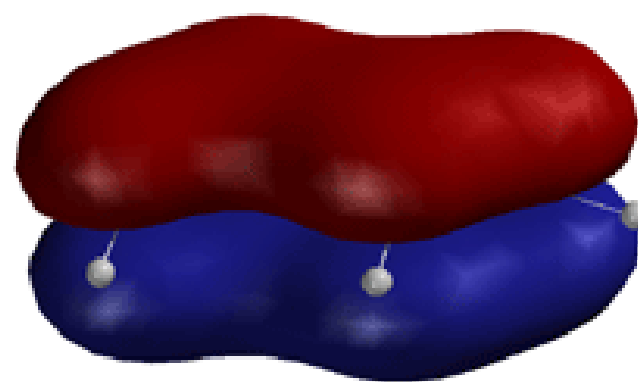
Conjugated π system
(Electron density
delocalized over all
four carbon atoms)

CONJUGATION

delocalisation of π/π*-states over many carbon atoms

π-bonding

conjugation length
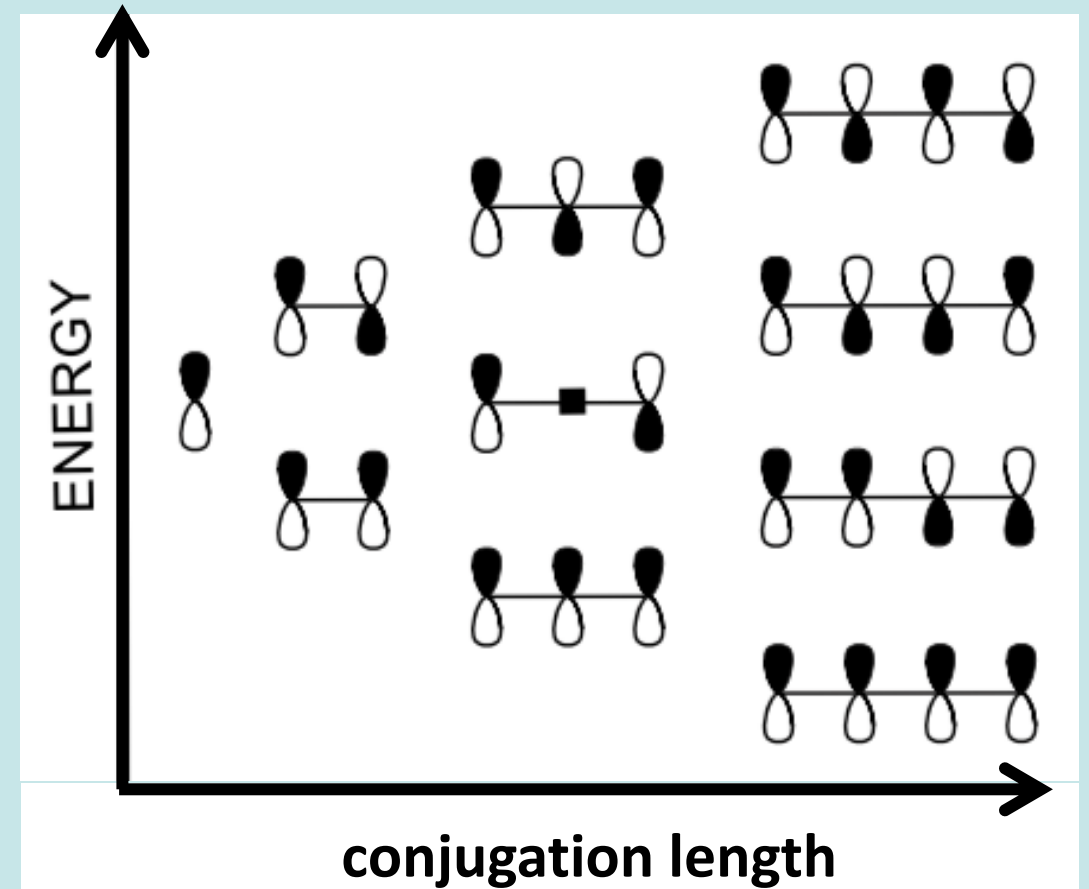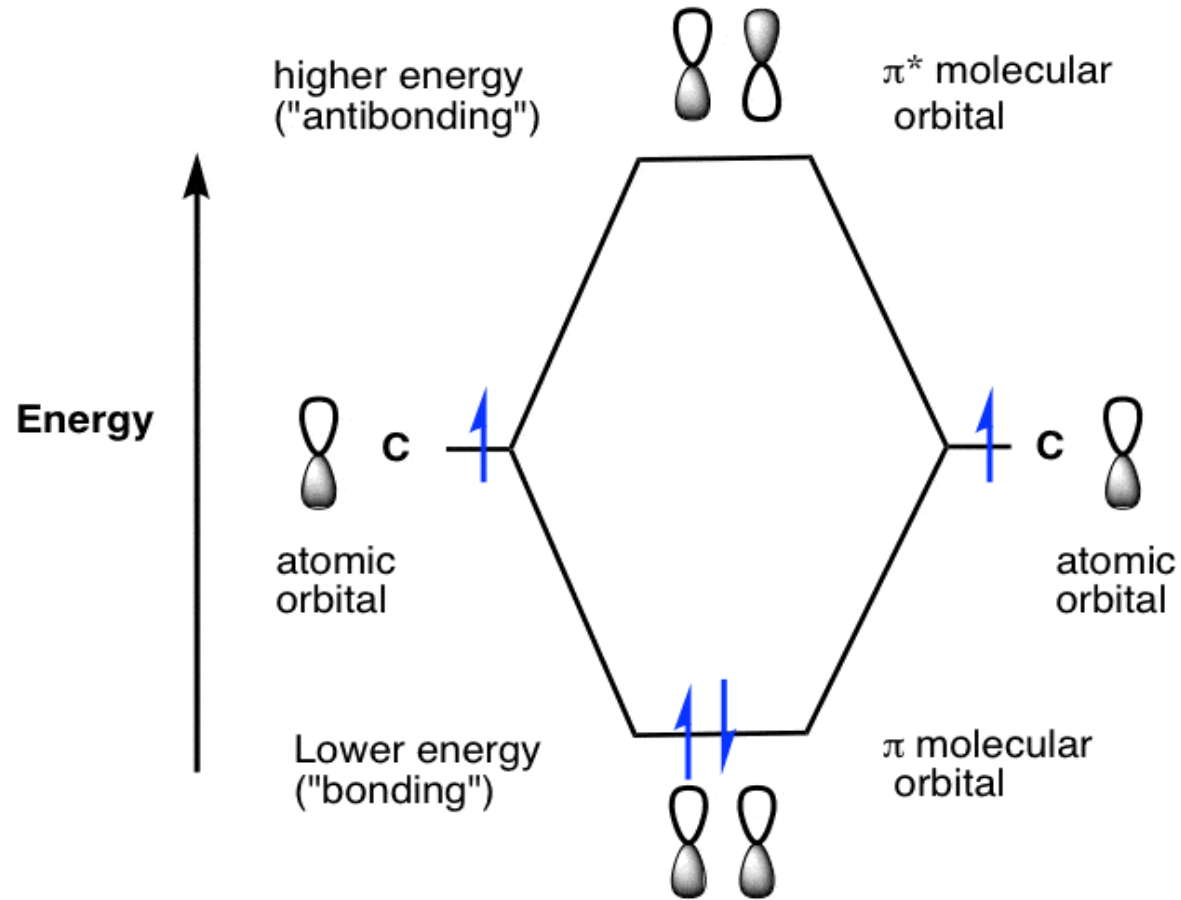
conjugation = delocalisation of π/ π* orbitals over many carbon atoms

HOMO/LUMO
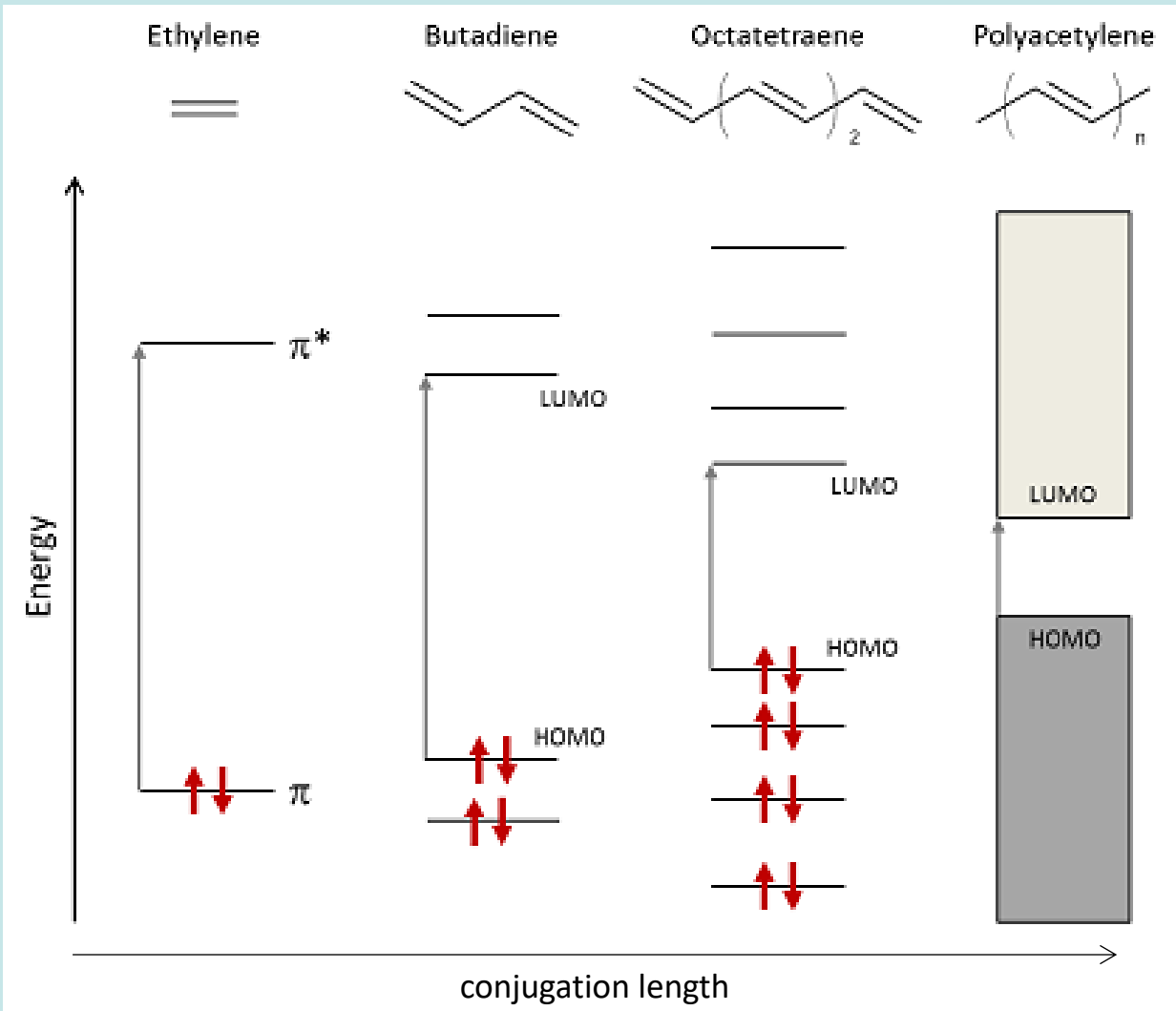
alternating single and double bonds usually indicate conjugation

LUMO – lowest unoccupied molecular orbital

HOMO – highest occupied molecular orbital

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Image from Optoelectronics group at Cavendish Laboratory

π-π stacking
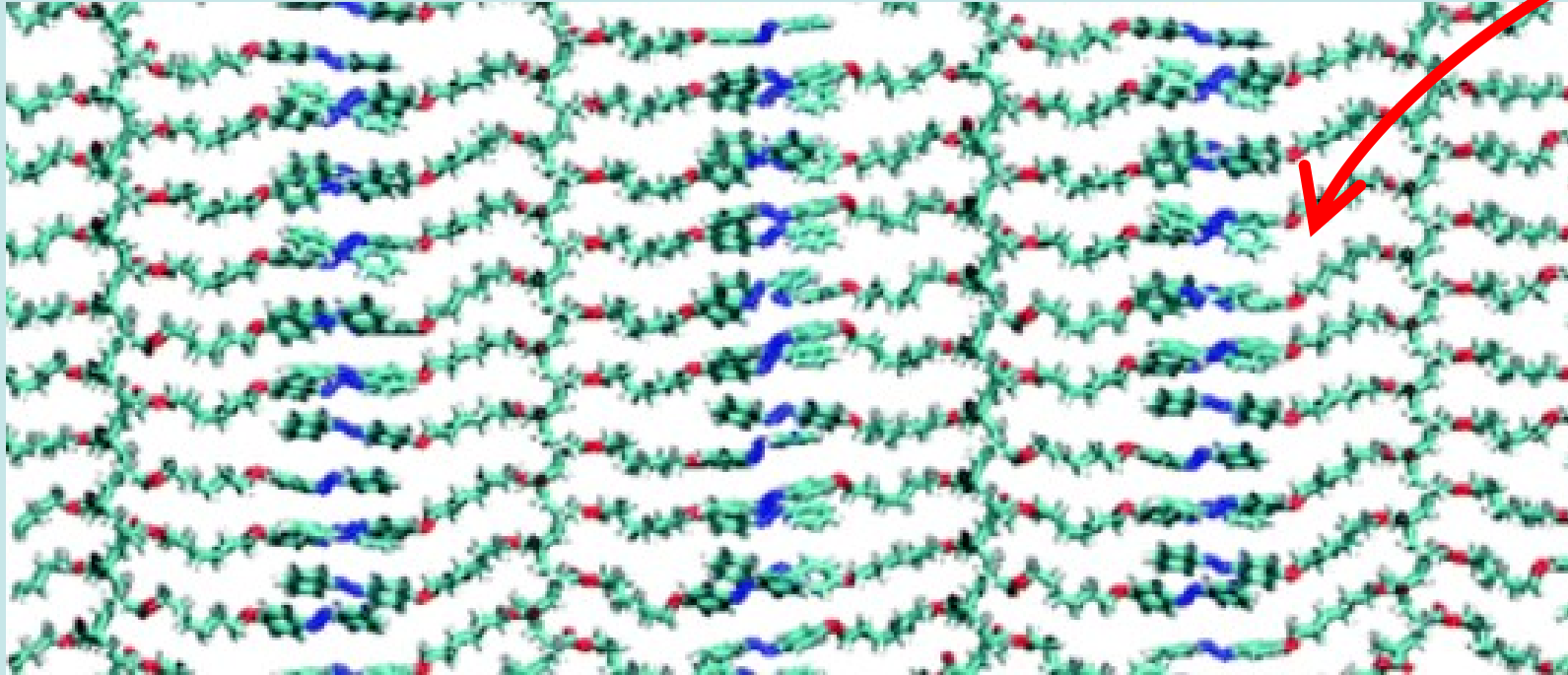
overlap of π orbitals of neighbouring molecules

delocalization

- efficient charge transport
- lower optical bandgap

Structure vs. conjugation length

The size of the bandgap depends on both the number of monomers n and the effective conjugation length

- more planar molecules have lower energy gap (longer conjugation length)
- planarity may be affected by:
  - chemical defects
  - topological defects
  - interaction between molecules (e.g. sidechains)

Polarons

Peierl's transition (aka. dimerization)

Undimerised:
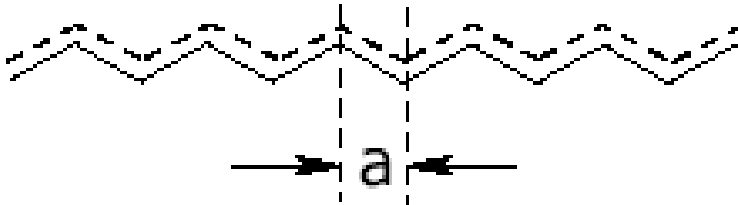
Peierl's transition

Dimerised:

Result:

- **alternated short and long bonds**

- longer period = lower energy

- result: chain of dimers

- different phases available
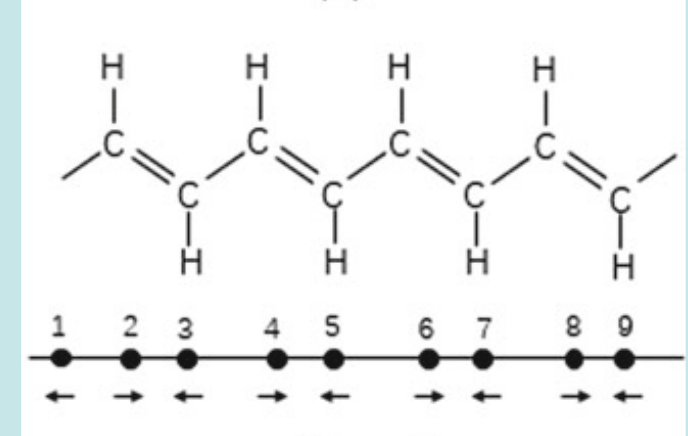
Types of dimerization (phases)
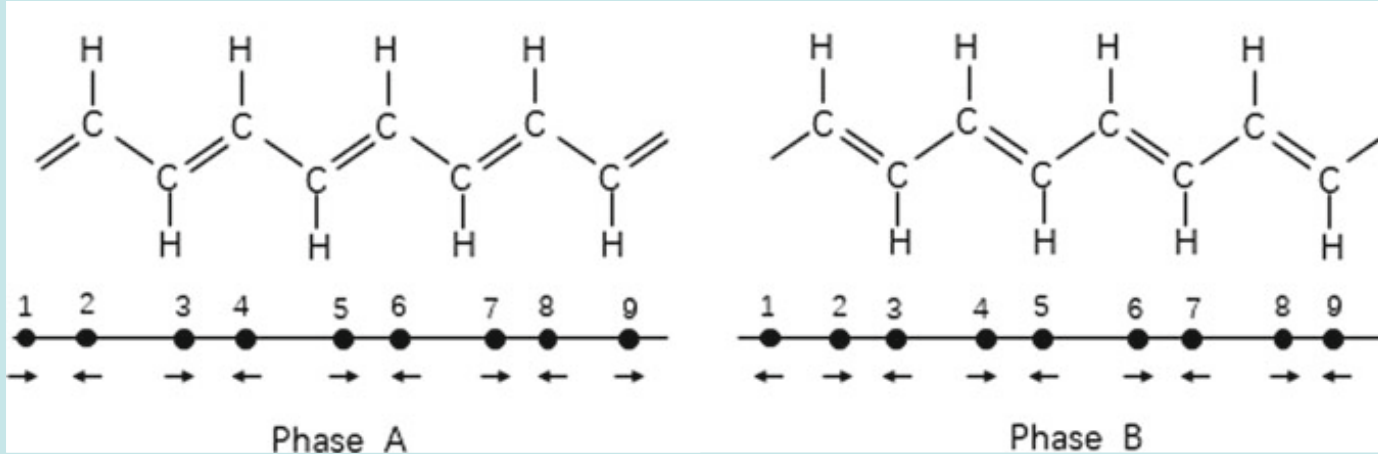
trans-polyacetylene

degenerate
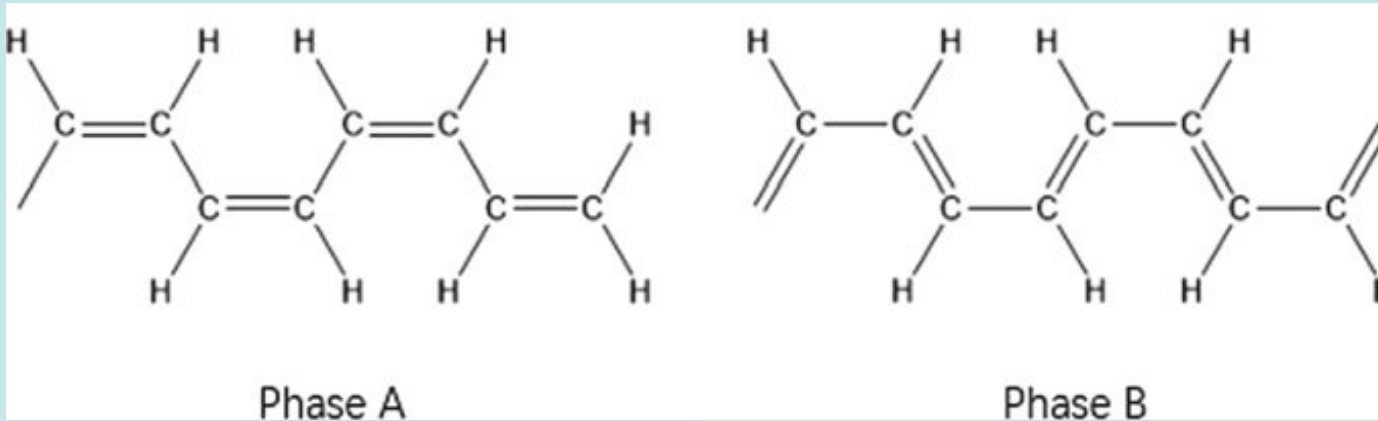
cis-polyacetylene

non-degenerate

NB. For inorganic semiconductors *degenerate* indicates instead a semiconductor doped so heavily that the Fermi Energy is inside the conduction or valence band. Here: degenerate means having the same energy (like in Quantum Mechanics).

Dimerisation in other polymers
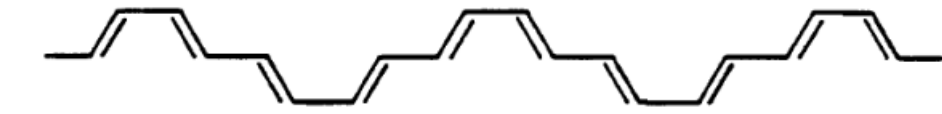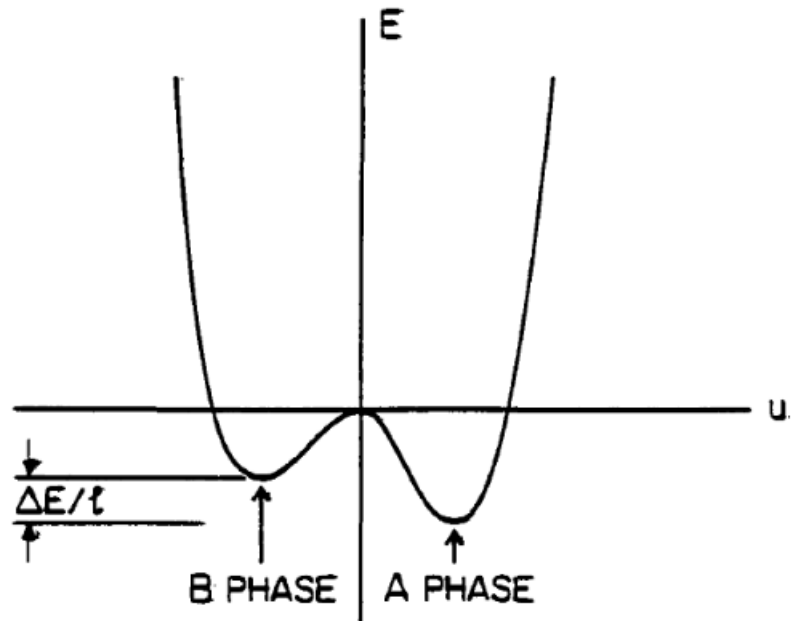
polythiophene
non-degenerate
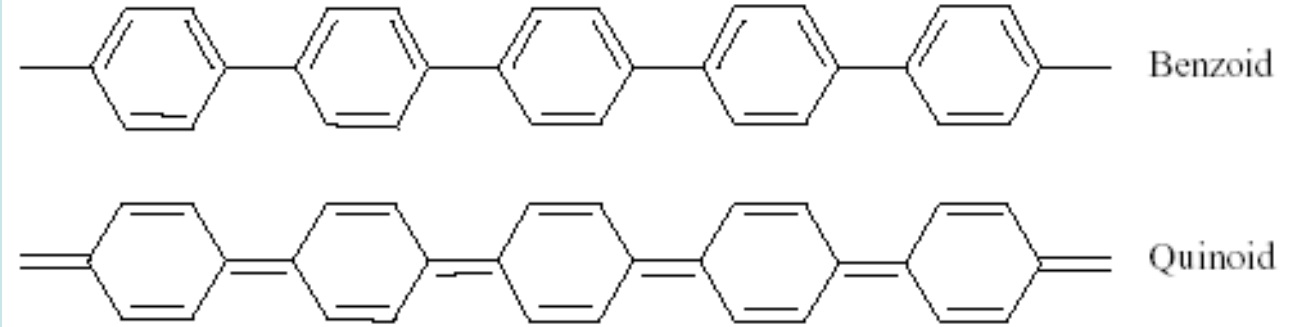
pera-terphenyl
non-degenerate

Solitons

Phase A   Phase B   Phase A   Phase B

Phase B
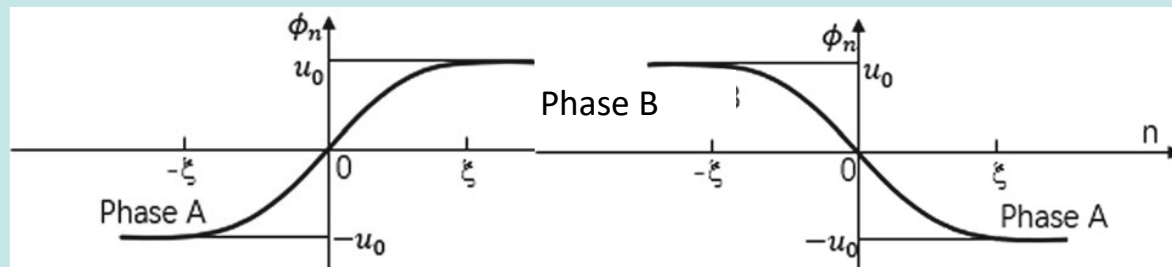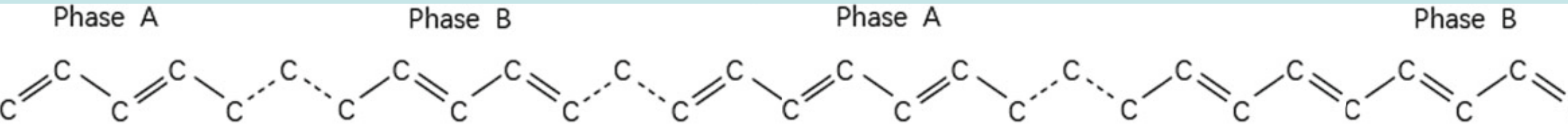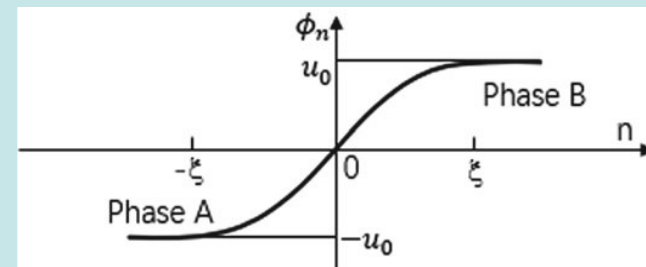
positive wall   negative wall   positive wall

SOLITON   ANTI-SOLITON   SOLITON
S $\bar{S}$ S

order parameter for the physical displacement of n-th atom (u_n): $\phi_n = (-1)^n u_n$

State distribution in solitons
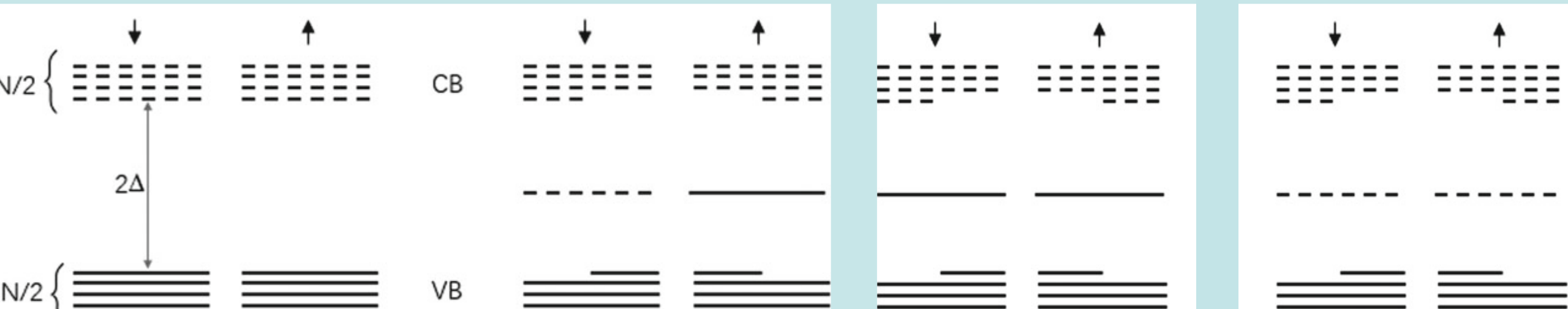
typical dimer

neutral SOLITON $q = 0$

negative SOLITON $q = -e$

positive SOLITON $q = +e$

filled state

empty state
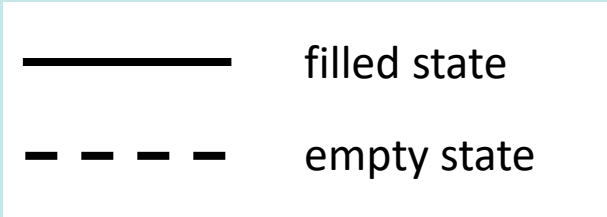
spin $s = \pm\frac{1}{2}$

spin $s = 0$

spin $s = 0$

$S - \bar{S}$ configurations

S	$\bar{S}$	total charge	interaction
+e	-e	0	annihilation
-e	+e		
+e	+e	**+2e**	large separation
-e	-e	-2e	
+e	0	+e	bound state (polaron)
0	+e		
-e	0	**-e**	
0	-e		

Soliton   Phase B   Anti-soliton

Phase A   Phase A
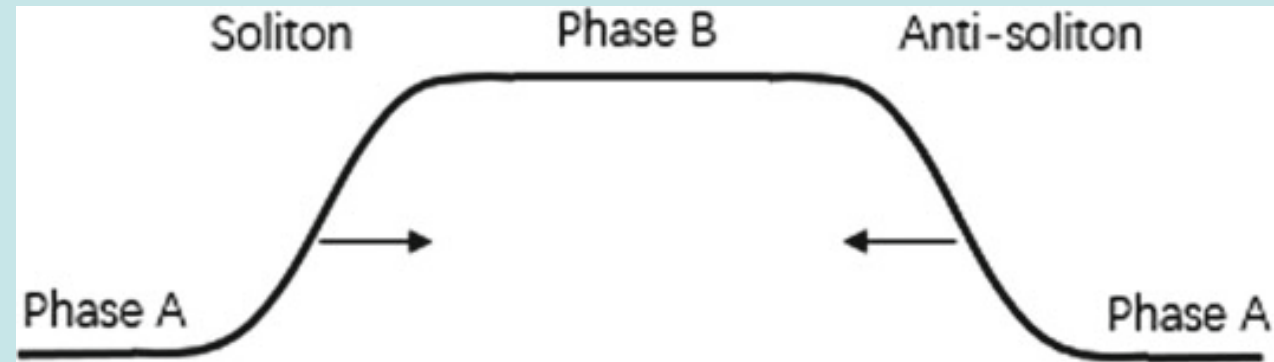
Polarons

- quasiparticle
- bound state of an S-$\bar{S}$ pair
- created by structural deformation
- moving with the structural deformation
- spin ±1/2 (like in e/h)
- carries charge and spin
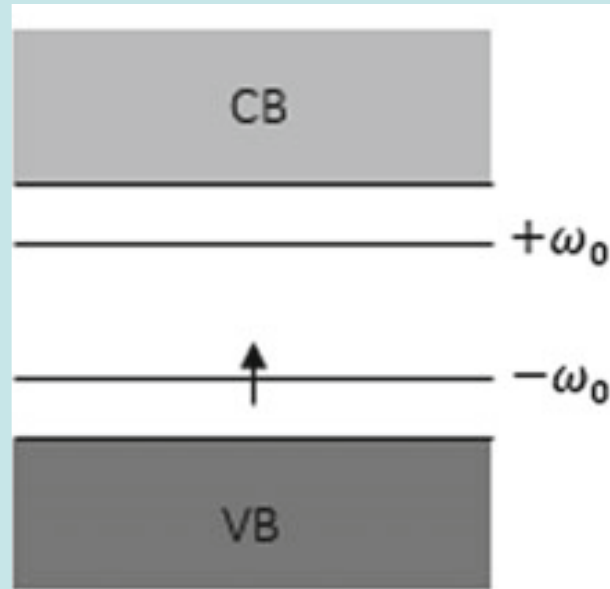
positive POLARON
$$q = +e$$
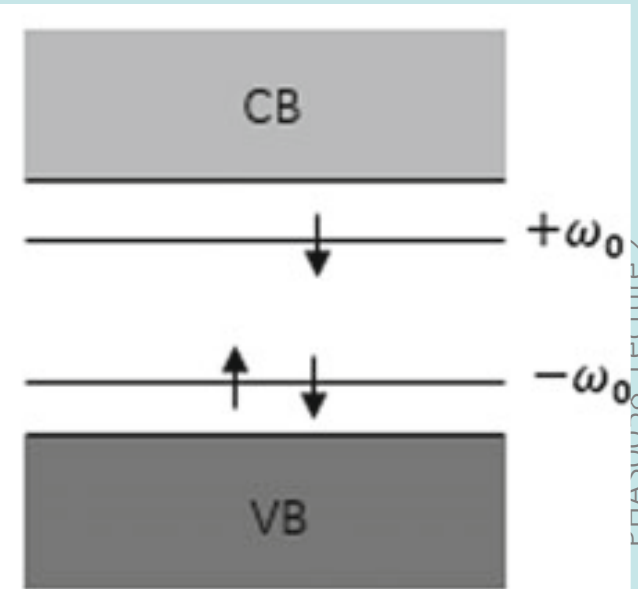
negative POLARON
$$q = -e$$

Excitons

Excitons

- quasiparticle
- bound excited state of electron and hole
- held together by Coulomb interaction of e-h

Wannier exciton

- weak coupling
- binding energy ~10 meV
- large distance between e/h (~10 nm)
- typical in inorganic semiconductors

Frenkel exciton

- strong coupling between e/h
- binding energy 0.2-1 eV
- small distance between e/h (~1 nm) (comparable with lattice spacing)
- typical for organic semiconductors

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Singlet-triplet splitting

- ground state is usually a singlet
- triplet population is 3 times larger
- introduces further energy level splitting

S_1 ————————— ↕ Exchange energy ————————— T_1

S_0 —————————

↑↓ - ↓↑

↑↑   M=1

↓↓   M=-1

↑↓ + ↓↑   M=0
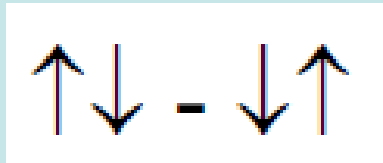
singlet

S=0
(opposing spin)
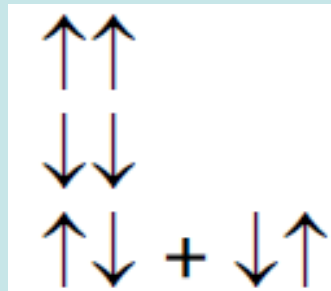
triplet

S=1
(same spin)
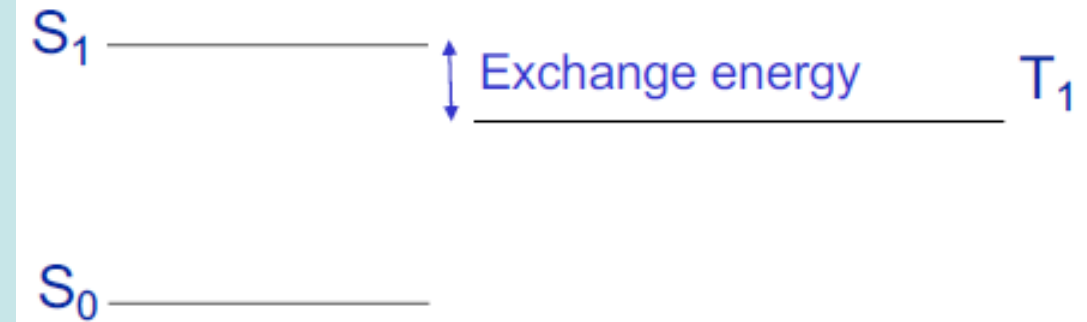
- exchange energy usually contains a polaronic contribution
- spin-orbit coupling can enable triplets emission (e.g. heavy atom)

Transitions

Spin transitions

excited singlet states, S_1

excited triplet states, T_1

ground state, S_0

fluorescence

phosphorescence

spin-allowed ->
fast and efficient

spin-forbidden ->
slow and inefficient
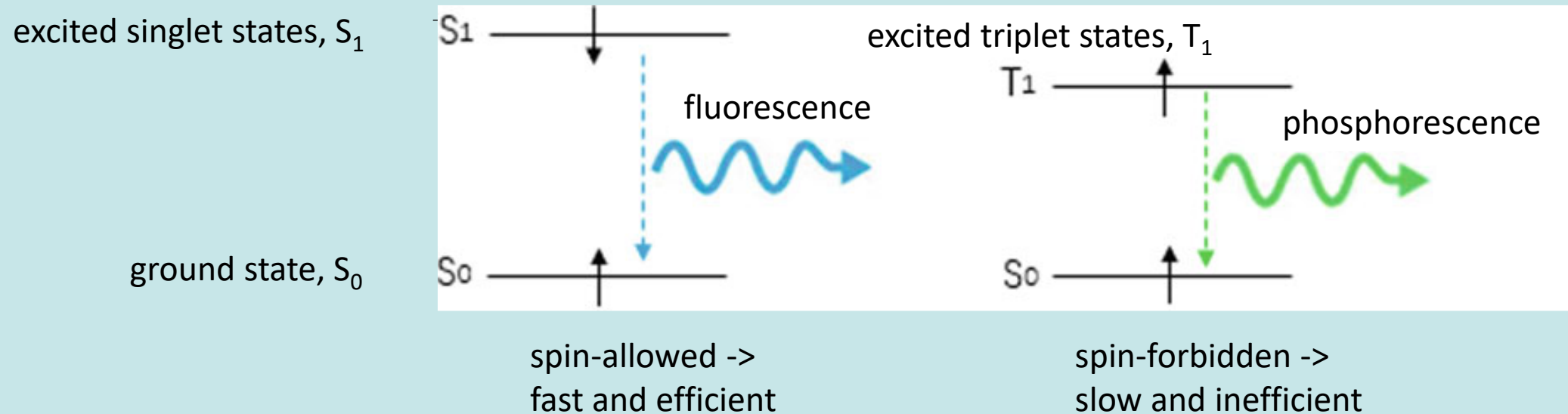
- optical transitions only allowed within manifolds
- non-radiative transitions between manifolds are frequent (Intersystem Crossing)
- each state additionally split into a manifold of vibrational states

Simplified scheme – Jablonski diagram
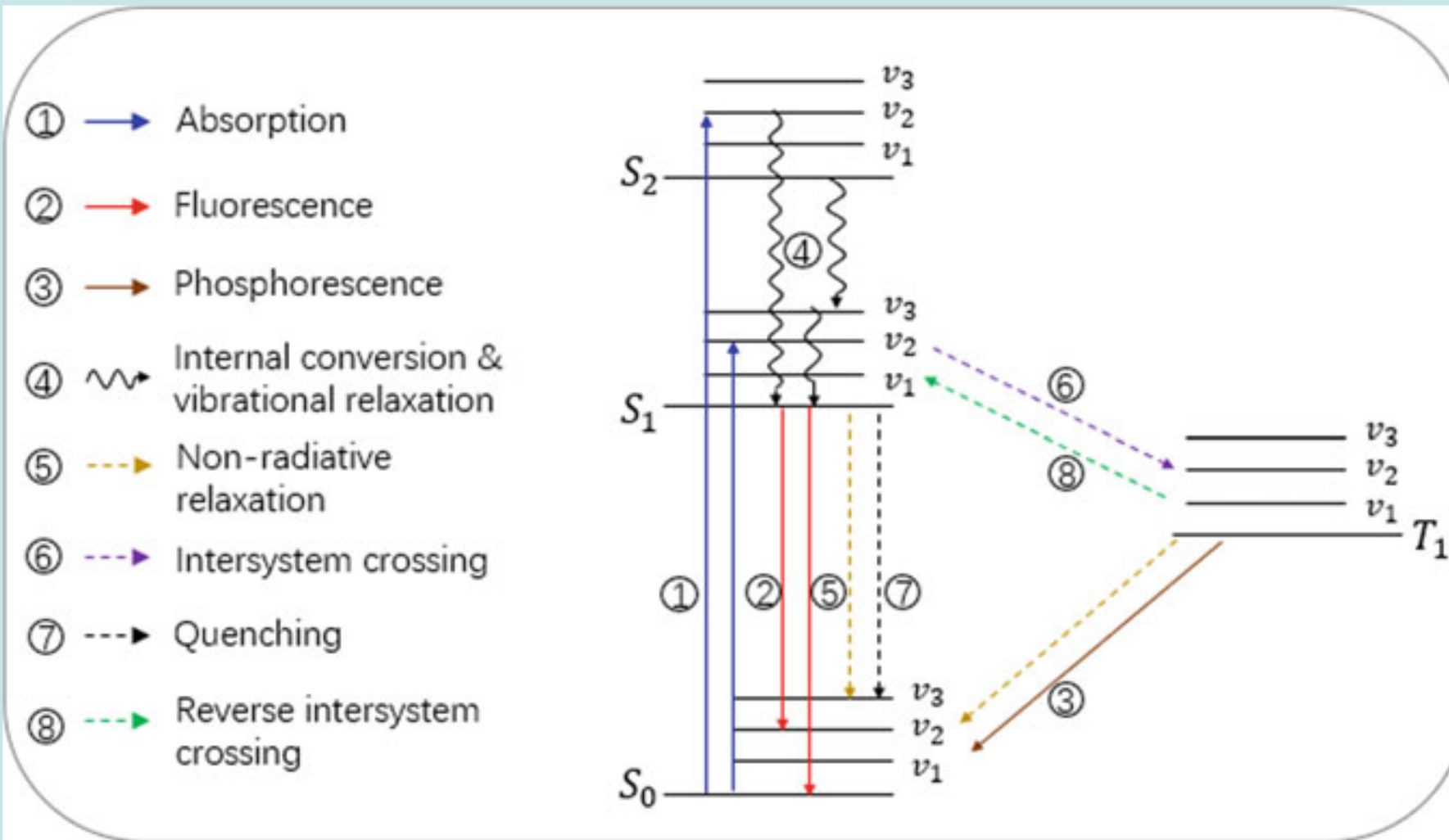
Timescales:
- absorption: fs or less
- internal conversion: 10^{-14}-10^{-11} s
- vibrational relaxation: $<10^{-12}$ s
- fluorescence (after) few ns
- phosphorescence: 10^{-3}-10^{2} s

Lifetimes:
- singlet S1: 10^{-9}-10^{-7} s

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Spectroscopy of OSc

Transition rates

Dr Monika Szumilo

$$dN = kNdt$$

$$k = k_r + k_{nr}$$

$$k_{nr} = \sum_i k_{nri}$$

$$N = N_0 e^{-kt} = N_0 e^{-\frac{t}{\tau}}$$

- N - population of the excited state
- dN - no. of excited states decaying in a time interval dt
- k – decay rate
- k_r = radiative decay
- k_{nr} – non-radiative decay
- i – individual non-radiative channels
- τ – decay time (lifetime) of the excited state
- N_0 – initial population (at t=0)
- L - luminescence

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$$L = k_r N = k_r N_0 e^{-kt} = k_r N_0 e^{-\frac{t}{\tau}}$$

Dr Monika Szumilo

$$L = k_r N = k_r N_0 e^{-kt} = k_r N_0 e^{-\frac{t}{\tau}}$$

$$\eta = PLQY = \frac{emitted\ photons}{absorbed\ photons} = \frac{emitted\ photons}{generated\ singlets}$$

$$\eta = \frac{k_r}{k_r + k_{nr}}$$

to maximise PLQE:
reduce k_{nr} and increase k_r

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Stokes Shift
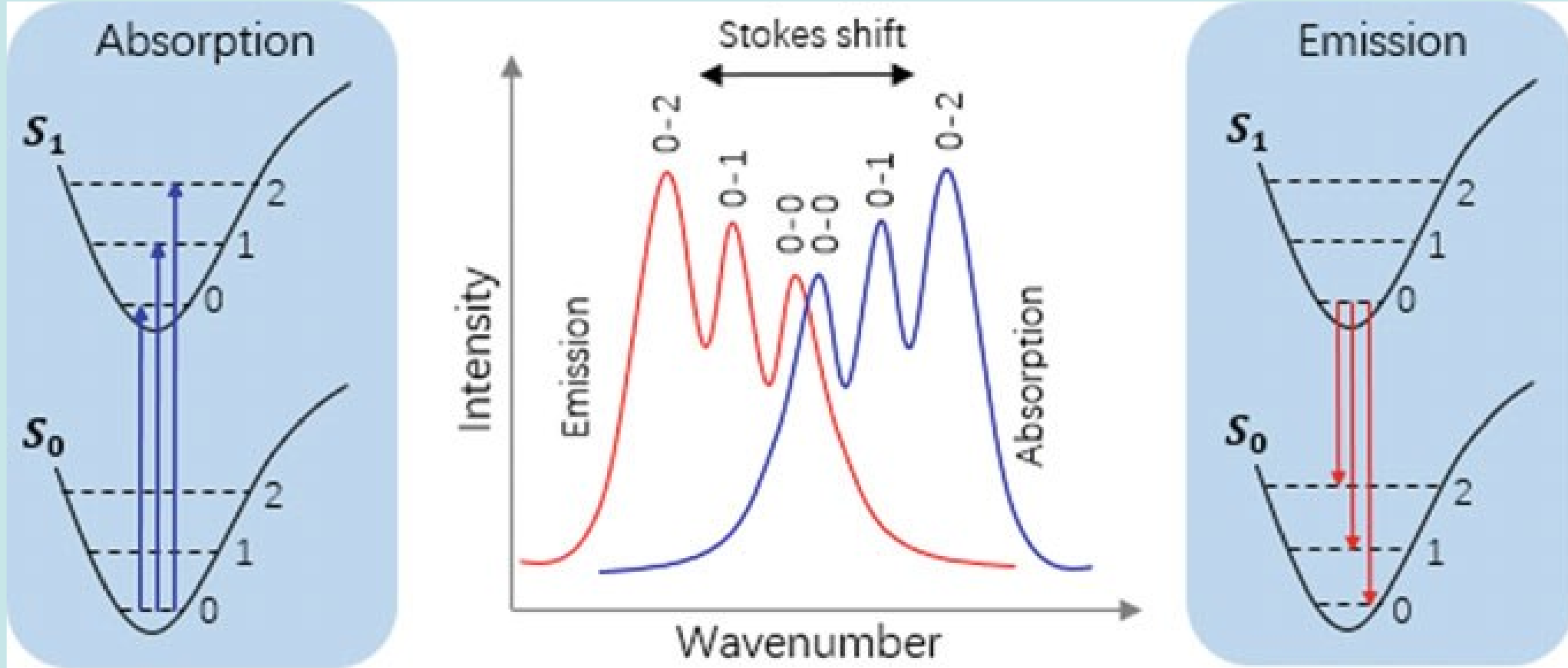
Temperature dependence

as temperature increases:
 - average twist angle along the chain increases
- conjugation decreases
- energy gap increases
- absorption and emission are blue-shifted

M. G. Harrison et al., Phys. Rev. B **55** p7831-7849 (1997) Thermochromism of MEH-PPV in solid state
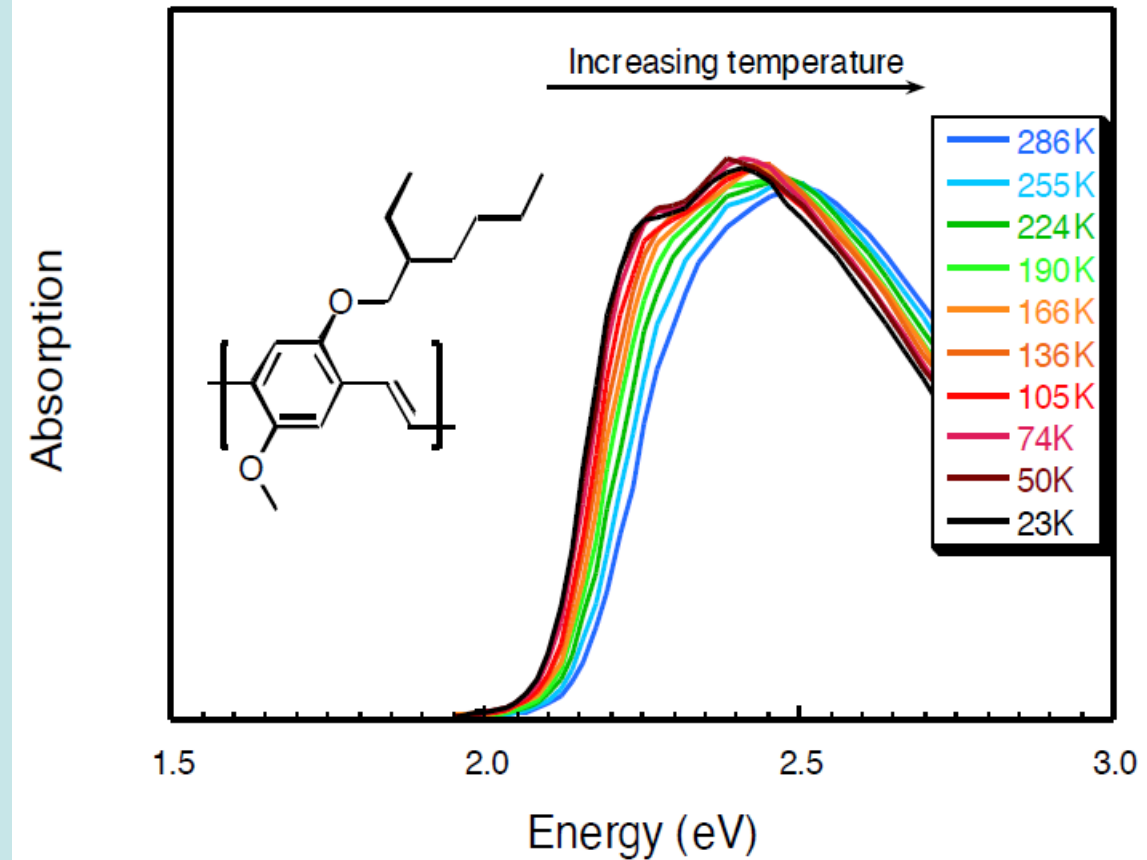
Transfer of charges

Transition vs. transfer

transition: within the same atom/molecule

transfer: between molecules (donor and acceptor)

Förster Transfer

- dipole-dipole energy transfer
- non-radiative, only for spin-allowed transitions
- requires spectral overlap of emission (donor) and absorption (acceptor) spectrum
- long-range: 10 nm
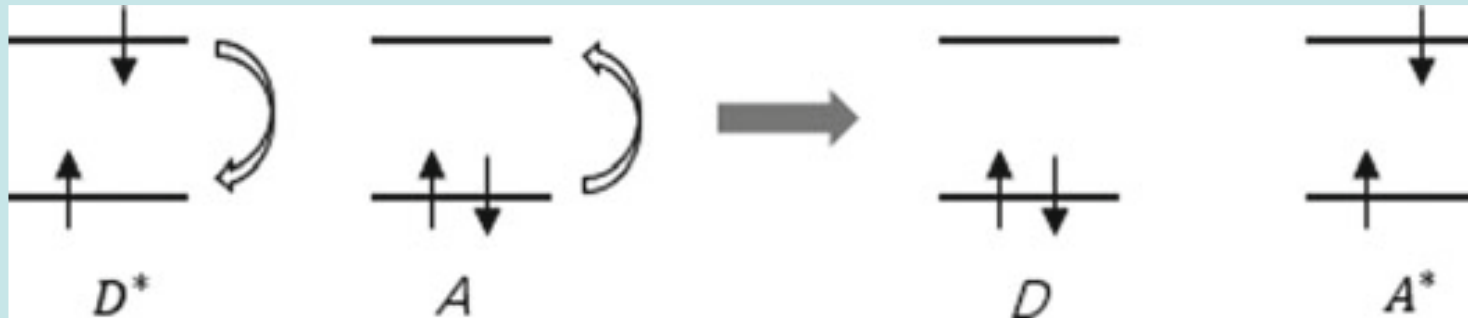
$$k_{ET} \sim \frac{1}{\tau_d}\left(\frac{r_0}{r}\right)^6$$

k - transfer rate
r – distance between donor and acceptor
τ_d – lifetime of the excited state of donor
r_0 – Förster radius

Dexter Transfer

- diffusion – direct charge transfer between excitons
- tunnelling of electrons, i.e. two charges moving between molecules
- two exchanges do not need to be simultaneous
- net transfer of excitation energy
- spin is unimportant
- short-range: 2nm

$$k_{ET} \sim e^{-\frac{2r}{L}}$$

k - transfer rate
r – distance between donor and acceptor
L – van der Waals radii

Marcus Charge-Transfer theory

$$k = \frac{J^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(\lambda + G_0)^2}{4\lambda k_B T}\right)$$

- k - charge-transfer rate
- J – transfer integral
- λ – reorganisation energy
- ΔG_0 – change of total Gibbs free energy

for crystals ΔG_0=0 and the equation becomes:

$$k = \frac{J^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{\lambda}{4 k_B T}\right)$$

- usually unipolar (one charge preferred over the other)
- often directional (molecule/chain orientation governing conjugation)

Charge transfer summary

Aspect	Markus Charge Transfer	Förster Transfer (FRET)	Dexter Transfer
Mechanism	Electron/hole hopping	Dipole-dipole interaction	Electron exchange
Nature of Transfer	Charge transfer	Energy transfer	Energy transfer via charge exchange
Range	Medium (~nm range)	Long (1–10 nm)	Short (<2 nm)
Dependence	Free energy, V, λ	Spectral overlap, distance	Wavefunction overlap

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Properties vs. applications

property	meaning	important for:
mobility	how easily can charge move through the material?	OFET
recombination	how easy is to separate an exciton?	PV
luminescence	how efficient is radiative recombination?	OLED

Summary

- Organic = carbon-based

- hybridization to π/ π* orbitals results in creation of a band gap

- HOMO/LUMO affected by conjugation length

- intra- and inter-molecular alignment important

- limited free charge transport (excitons and polarons)

Next week:

Organic Light Emitting Diodes (OLEDs)

Self-study:
Basic semiconducting devices (on Moodle)