Organic Electronic Materials

Electronic structure of conjugated polymers

Semiconductor materials

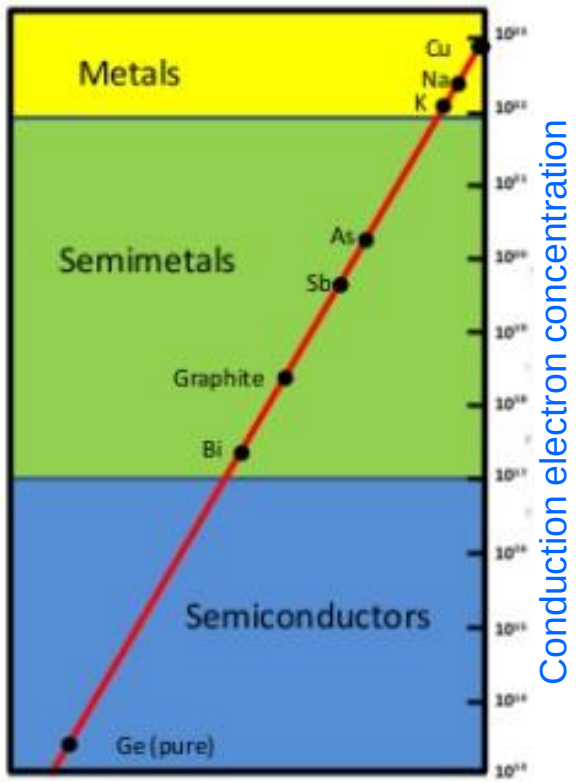
Electrical Conductivity of Materials

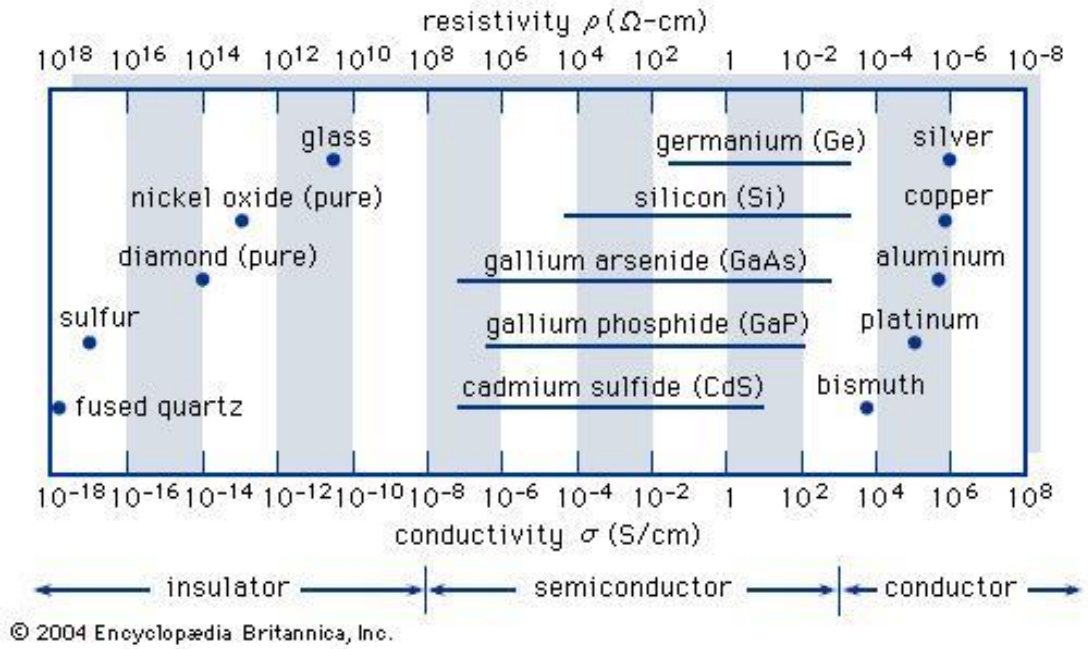
Metals: $\sigma > 10^5$ $(\Omega\ cm)^{-1}$ or S

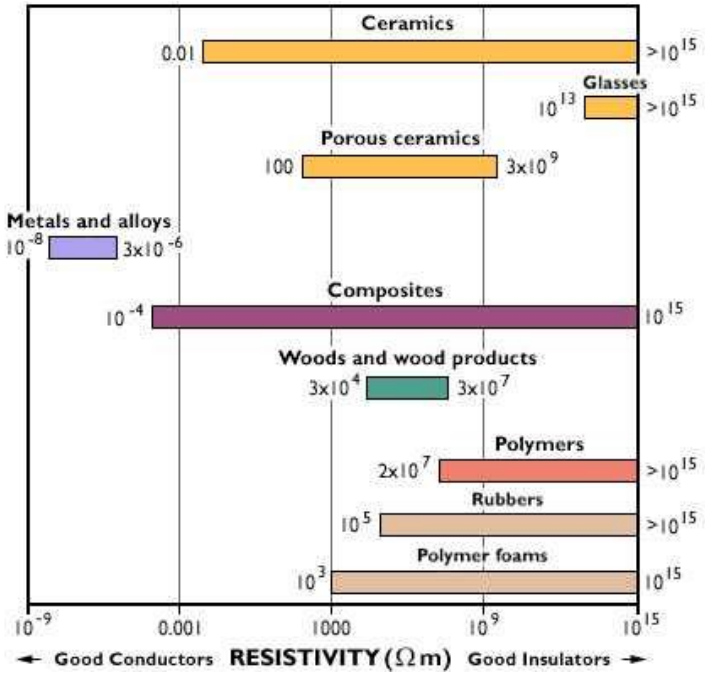
Semiconductors: $10^{-6} < \sigma < 10^5$ $(\Omega\ cm)^{-1}$

Insulator: $\sigma < 10^{-6}$ $(\Omega\ cm)^{-1}$

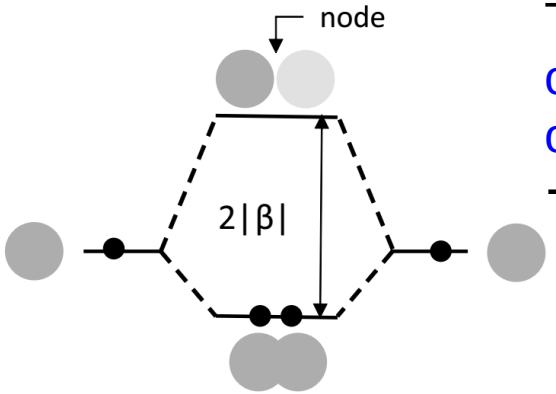
Transistors, switches, diodes, photovoltaic cells, detectors, thermistors, …







Semiconductors are materials which have an electrical conductivity between the conductors and the insulators



Energy level diagram of two hydrogen atoms interacting to form a H2 molecule.

The 1s orbital overlap cause two new molecular orbitals to form: on bonding (Ψ_+), where the electrons from the respective 1s orbitals go, and one antibonding (Ψ_-) that becomes unoccupied.
→ Energy gap: $|2\beta|$

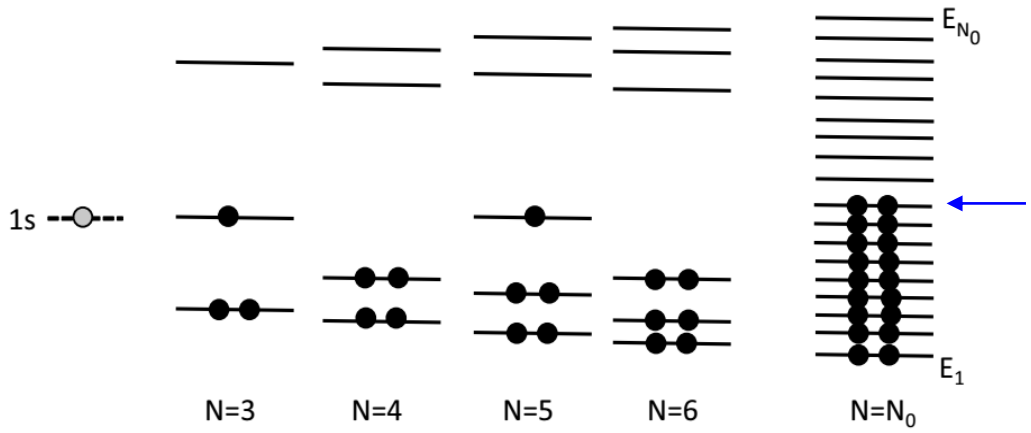
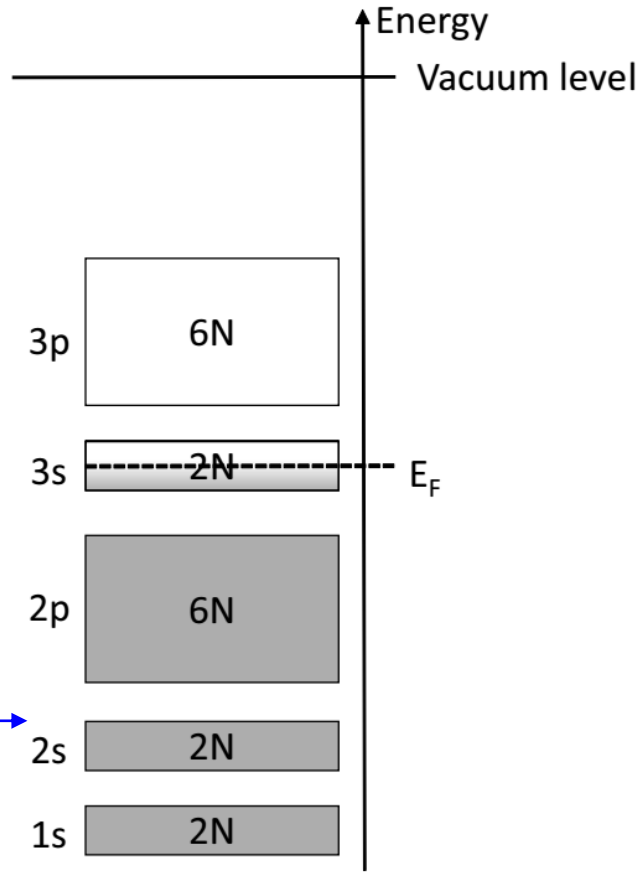


Figure 2.8 Evolution of the molecular orbital energies for a linear chain of N interacting singly occupied 1s orbitals (hydrogen atoms).



- The energy scale is referenced to the vacuum level.
- The Fermi energy, E_F, defines the highest occupied electronic state at T = 0 K and is here positioned in the middle of the 3s band, that is, Na metal. (Na, total electron number = 11)

Vacuum level: an electron that has been emitted from the material but has zero kinetic energy

Energy diagrams of Na atom & Na solid

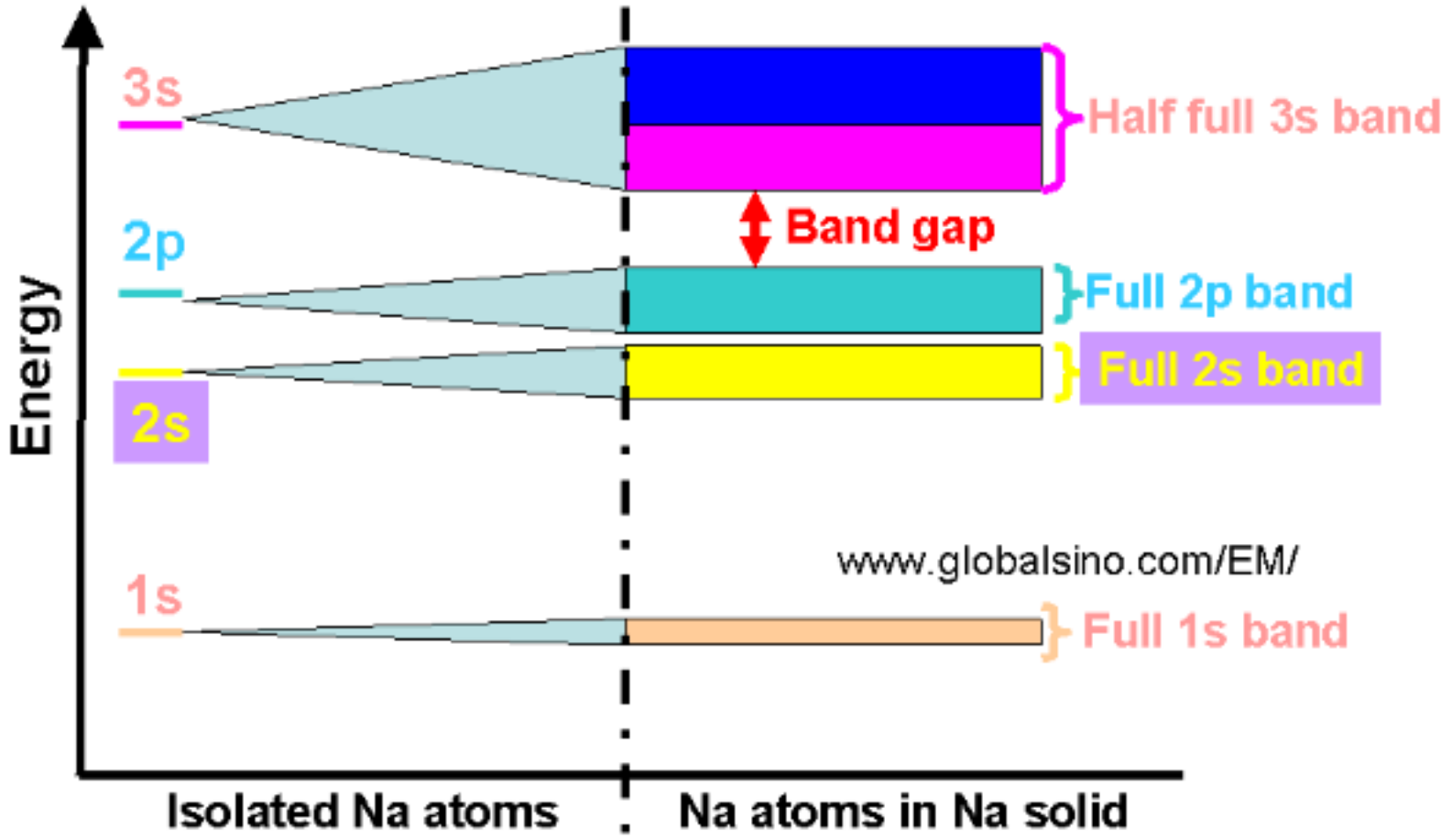
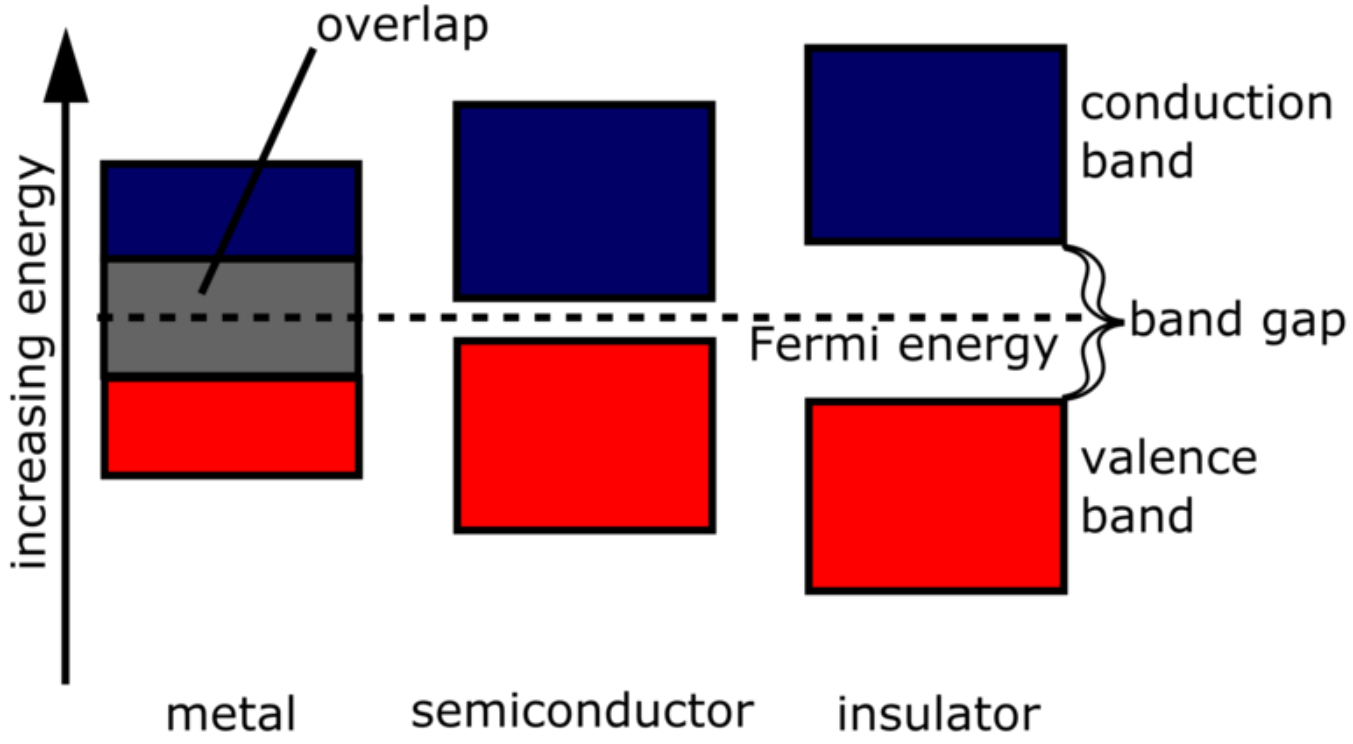


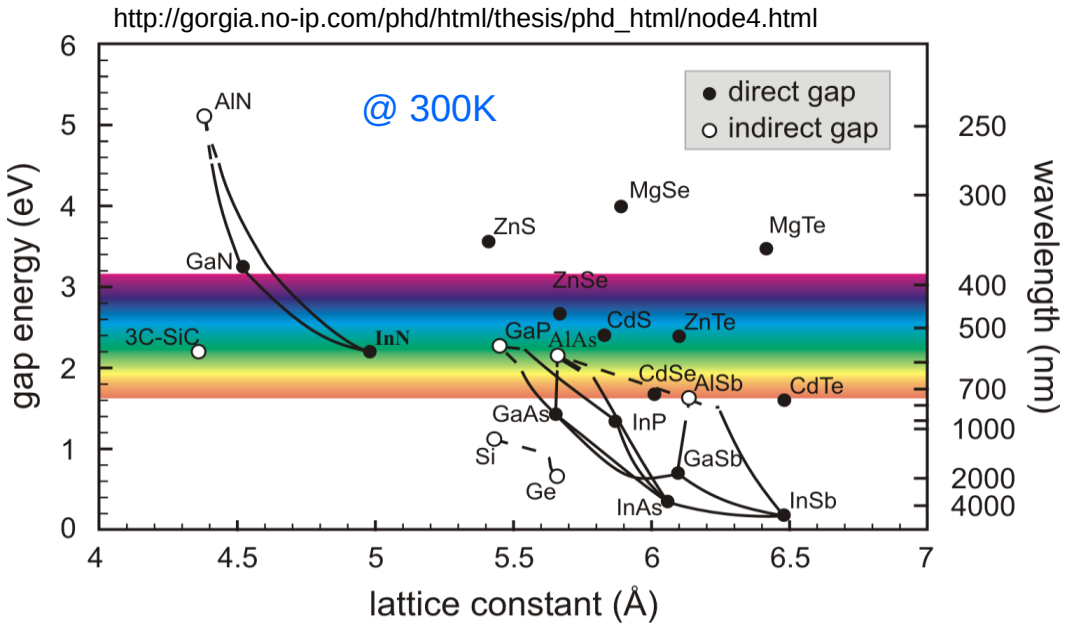
Figure 3789. Difference of energies between an isolated Na atom and a Na solid.

Band Gap & Semiconductor

- The intrinsic conductivity & carrier concentrations
  - Controlled by E_g/k_BT ← ratio of the band gap to the temperature
  - E_g/k_BT ↑ : the concentration of intrinsic carriers & the conductivity will be low

Inorganic semiconductors: 1 ~ 2 eV





Si: 1.17 @ 0K, 1.11 eV @ 300K
Ge: 0.774 @ 0K, 0.66 eV @ 300K

Intrinsic materials

- Perfect semiconductor crystal with no impurities or lattice defects
- No charge carriers at 0k
  - Valence band : filled with electrons
  - Conduction band: empty
- High T
  - E-h pairs (EHPs): only charge carriers
  - Valence band electrons are excited thermally → conduction band

  Cf. Breaking of covalent bonds: E_g is required to break covalent bonds
- $n = p = n_i$

  n: concentration of conduction band electrons (electrons/cm^3)

  p: concentration of valence band holes (holes/cm^3)
- Recombination : annihilating the e-h pair

  When an electron in the conduction band makes a transition (direct or indirect) to an empty state (hole) in the valence band
- At the equilibrium

$$r_i = g_i$$

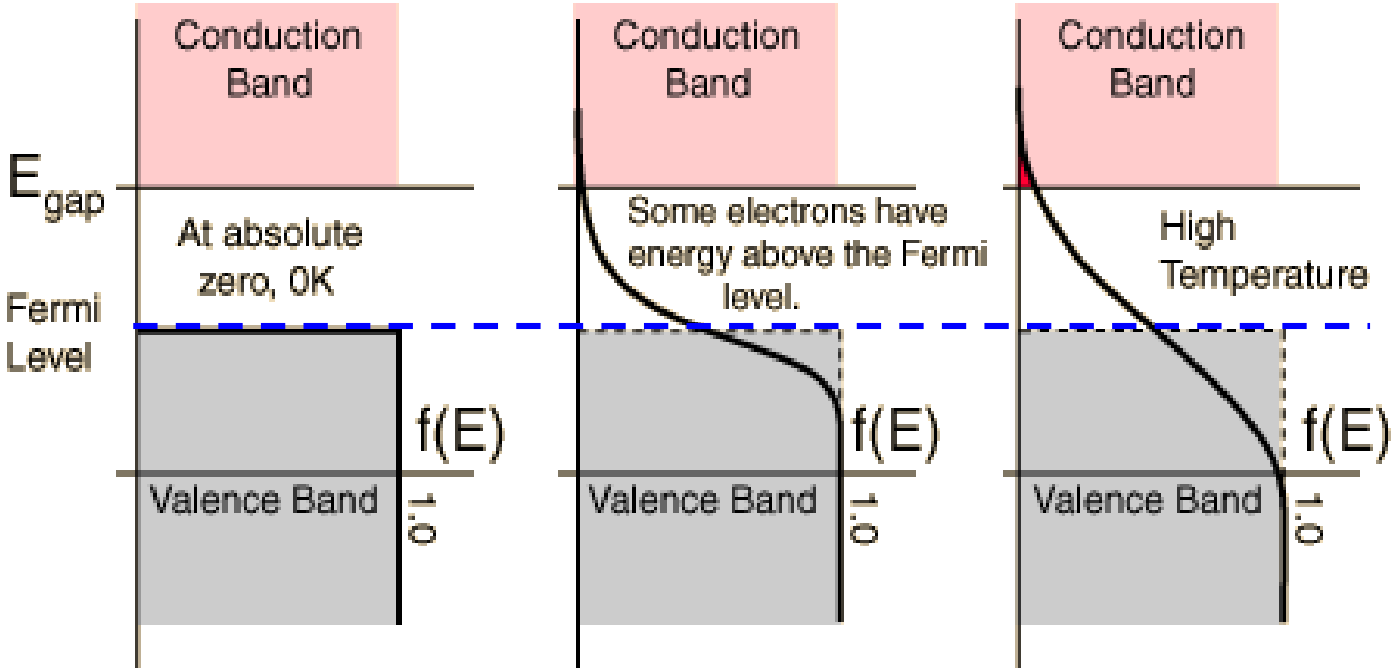
Fermi level

In the intrinsic semiconductor, $n = p$

If $m_h = m_e$ $\quad \mu = \frac{1}{2} E_g$

Fermi level is in the middle of the forbidden gap

Chemical potential



Intrinsic semiconductor에서 Fermi level μ는 energy gap의 중앙에 위치. 에너지 ε=μ 이면 f=1/2 이다.

- No electrons can be above the valence band at 0K, since none have energy above the Fermi level and there are no available energy states in the band gap.
- At high temperatures, some electrons can reach the conduction band and contribute to electric current.

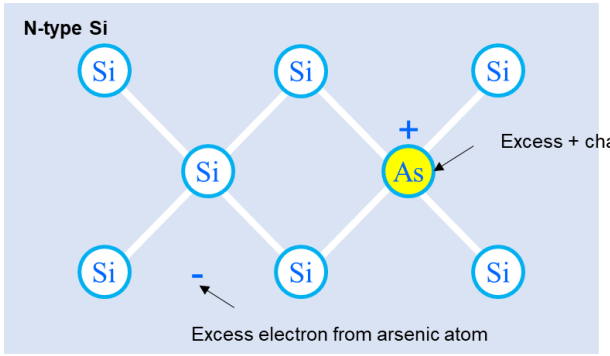
Extrinsic material (Impurity conductivity)

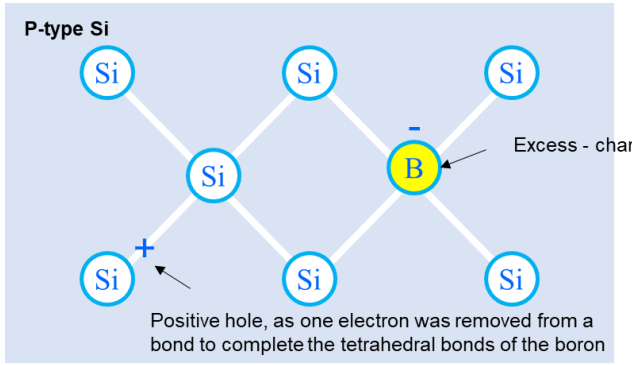
- Addition of boron to Si
  - 1 boron atom to 10^5 silicon atoms → the conductivity increases by a factor of 10^3 at RT
- Stoichiometric deficiency → 반도체에서 불순물로 작용
  defect semiconductor
- Impurities → Doped semiconductors
- Si, Ge: 4 covalent bonds

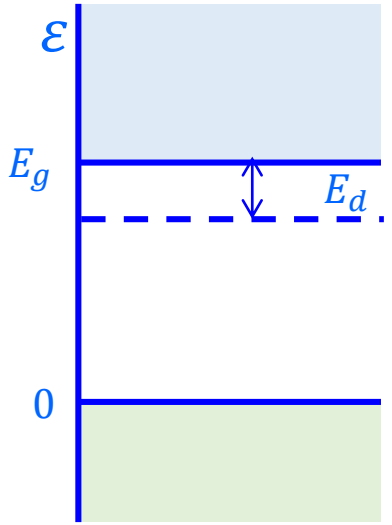
Create carriers in semiconductors by doping

III	IV	V
B	C	
Al	Si	P
Ga	Ge	As
In		Sb

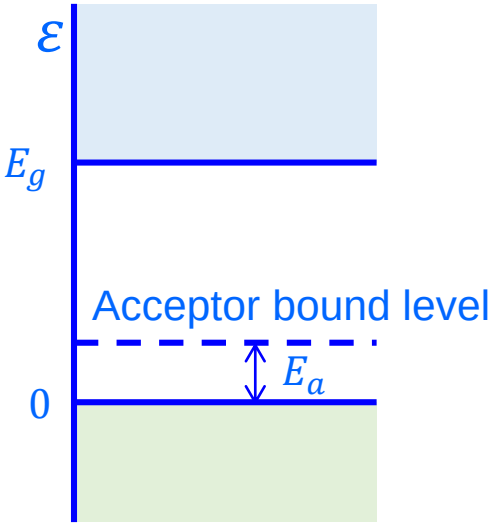
- Doping with P, As: one valence electron from the impurity atom left → Donor
- Doping with Al, Ga → Acceptor





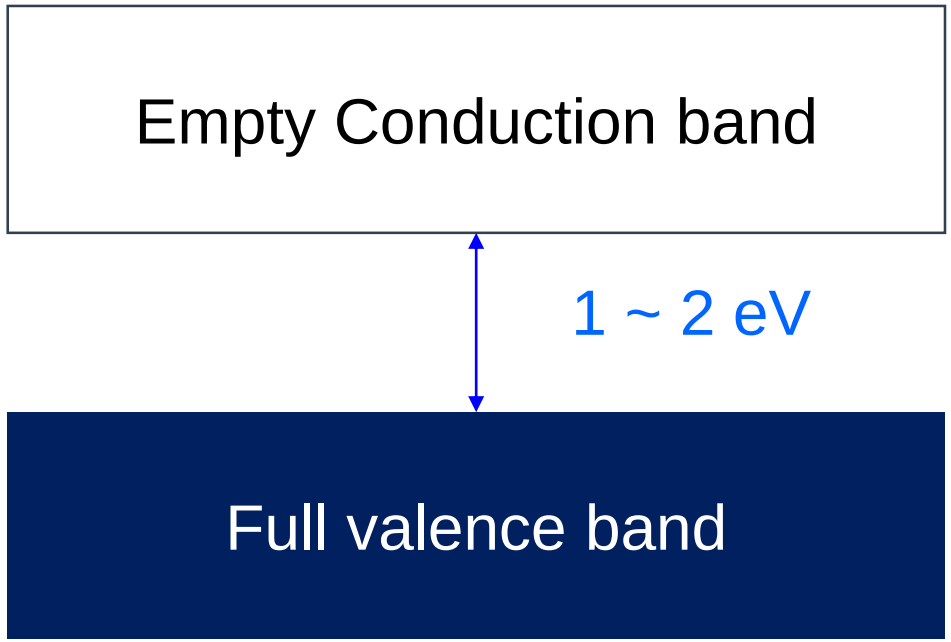


N-type

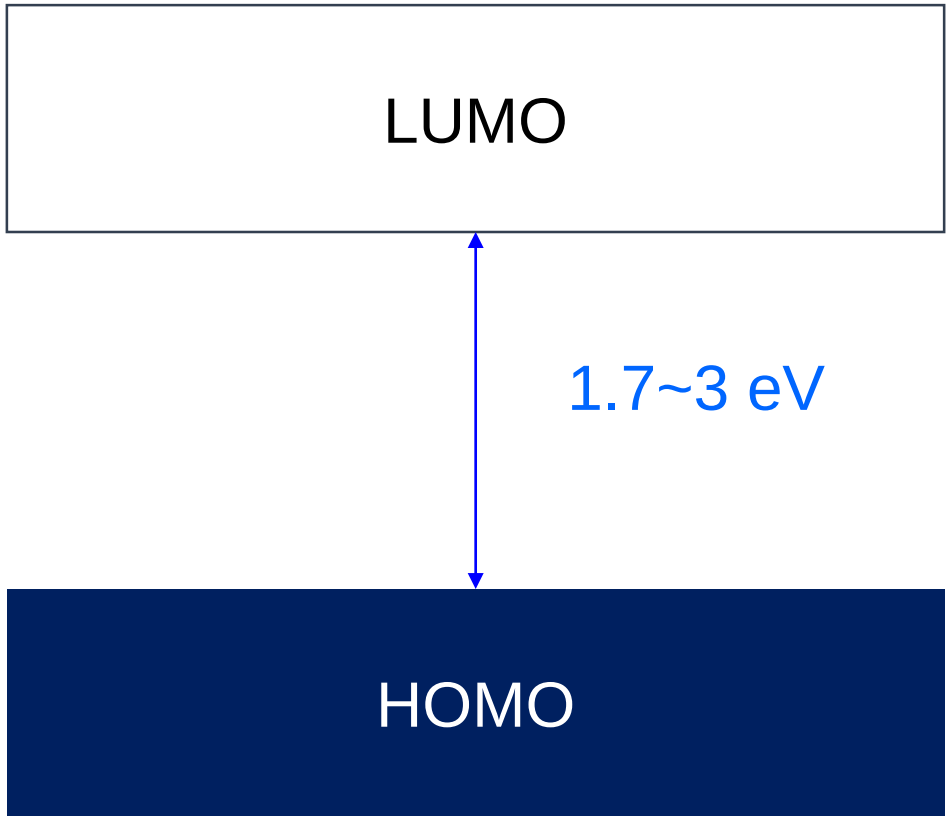


P-type

Inorganic semiconductors



Organic semiconductors



From Chemical Bonds to Bands

Time-dependent Schrodinger eq.

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi \qquad H = -\left(\frac{\hbar^2}{2m}\right)\nabla^2 + V(r)$$

Ψ is related to the probability of finding the electron at a particular point/time
ρ is related to $\Psi\Psi'$

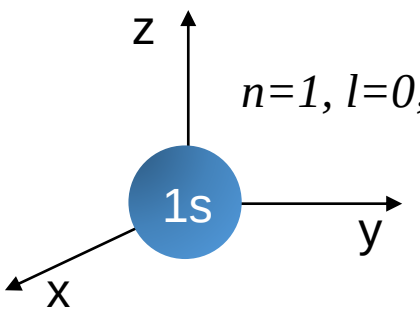
⟶ Solution: quantum numbers *(n, l, m)*

⟶ Energy and shape of orbit or 'cloud' of e^-/p^+

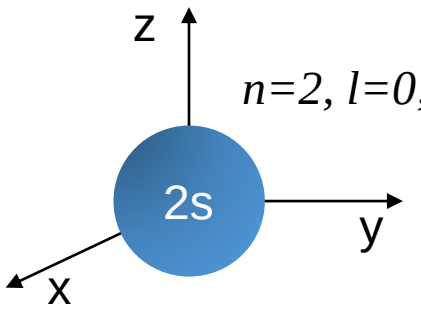
- l=0 : "s" ("s" stands for sharp) orbital.
- l = 1, the orbital is called a "p" (principal) orbital
- l = 2, the orbital is called a "d" (diffuse) orbital
- l = 3, the orbital is called an "f" (fundamental) orbital.

n: energy of electron
l: angular momentum of the electron in its orbit around the nucleus
2l+1 solutions → 2(2l+1) maximum # of electrons of this energy
m: magnetic quantum number

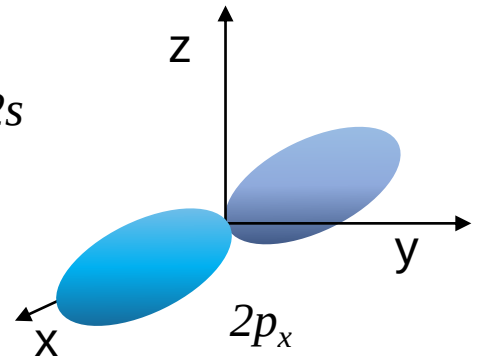
the total wave function of the electrons on an atom can be written as a linear combination of individual atomic orbitals.

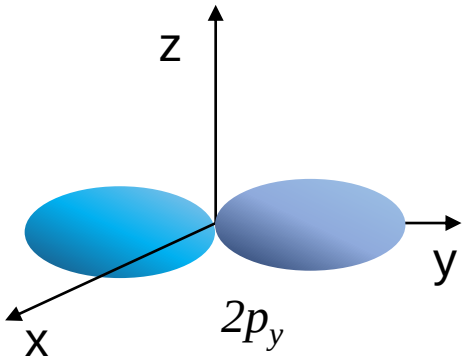


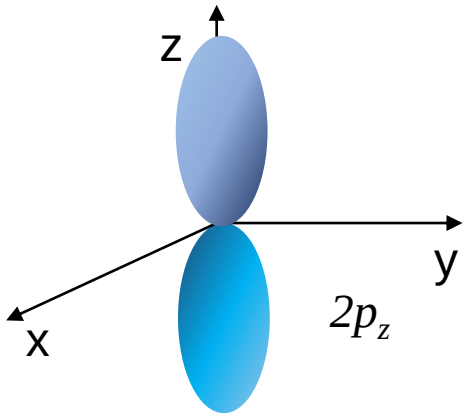
n=1, l=0; 1s



n=2, l=0; 2s



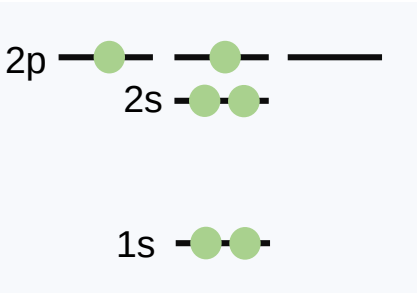




n=2, l=1; $2p_x$, $2p_y$, $2p_z$

2s orbital has a spherical nodal plane (not shown)

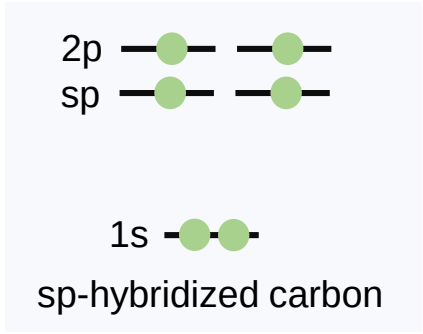
Hybrid atomic orbitals for understanding how carbon atoms bond to form molecules/polymers



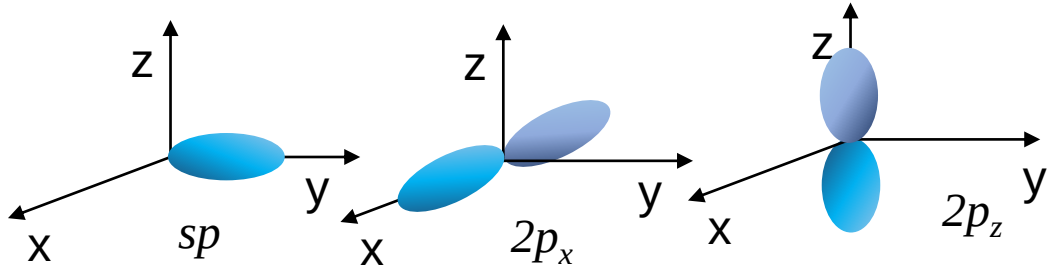
the carbon atom

$1s^2 2s^2 2p^2$

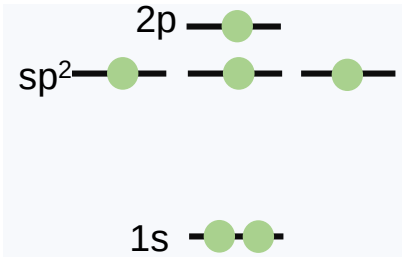
Ground state of C



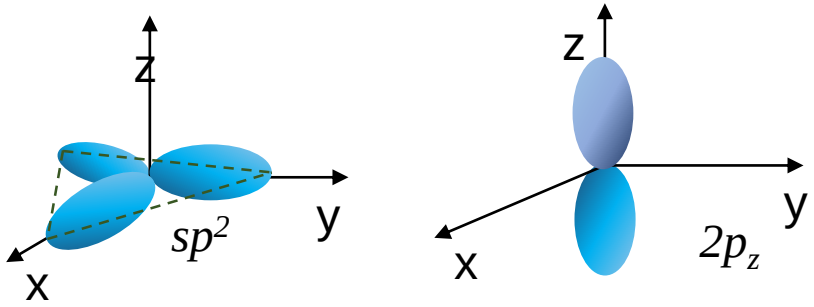
sp-hybridized carbon



- Linear combination of equal weight between the 2s orbital and a $2p_y$ orbital
- $2p_x$ and $2p_z$, retain their original shape



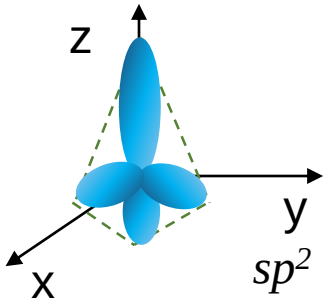
sp^2-hybridized carbon



- a linear combination between the 2s and the $2p_x$ and $2p_y$ orbitals occur, with the $2p_z$ orbital unchanged.



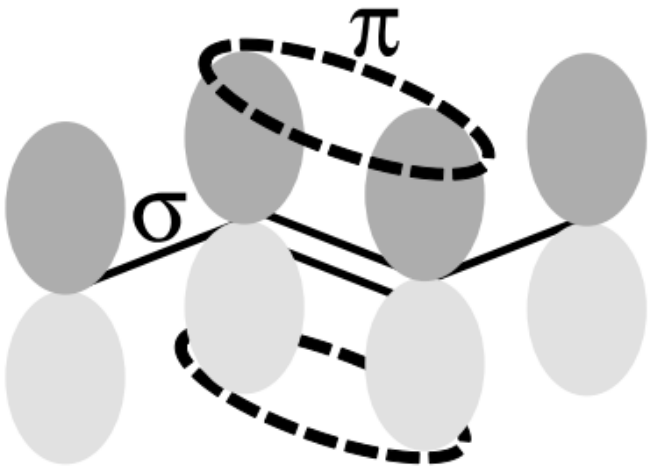
sp^2-hybridized carbon



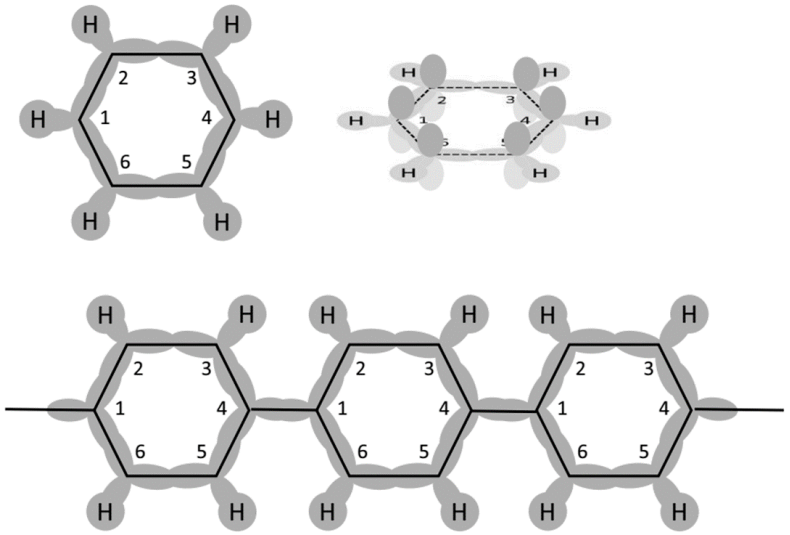
- All orbitals participate in the linear combination

occupied n = 2 orbitals can reorganize themselves to minimize the overall energy by promoting one of the two 2s electrons into a 2p orbital → forming linear combinations of the original n = 2 orbitals.

→ covalent bonding: two atoms forming bonds share (valence) electrons



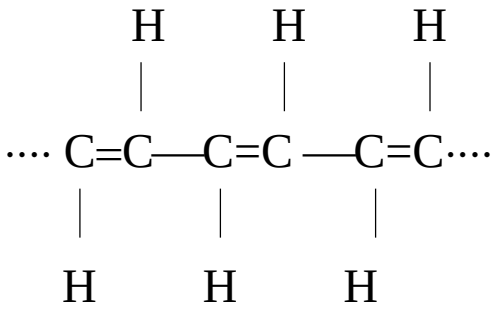
Sketch of p_z-p_z overlap forming a p bond. The sp^2 lobes forming the bandshakes bonds that define the molecular geometry are not shown



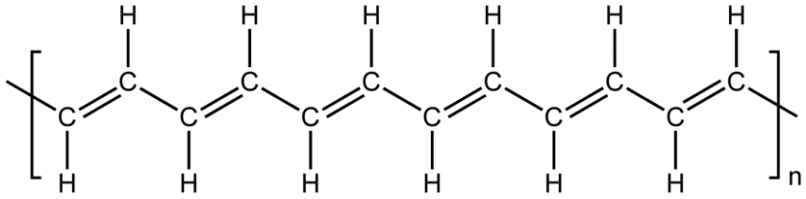
Benzene ring formed by σ-bonding sp2 orbitals (top left) and pz π-bonding orbitals (top right). Benzene rings repeatedly bonding at the 1 and 4 positions, forming a linear polymer chain: poly(p-phenylene) (bottom)

- a σ and a π bond working together: double bond
- Double bond length is shorter than sp3 case due to the additional screening effect of π bond

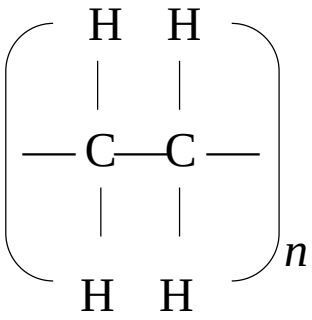
- C : basic ingredient of organic materials
- Conjugation : basic ingredient of organic semiconductors
  - A chain of carbon atoms with alternating single & double bonds



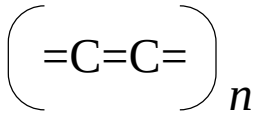
- ✓Opening a band gap (splitting of the energy levels)
- ✓Delocalization of charge in the splitting levels



Polyacetylene

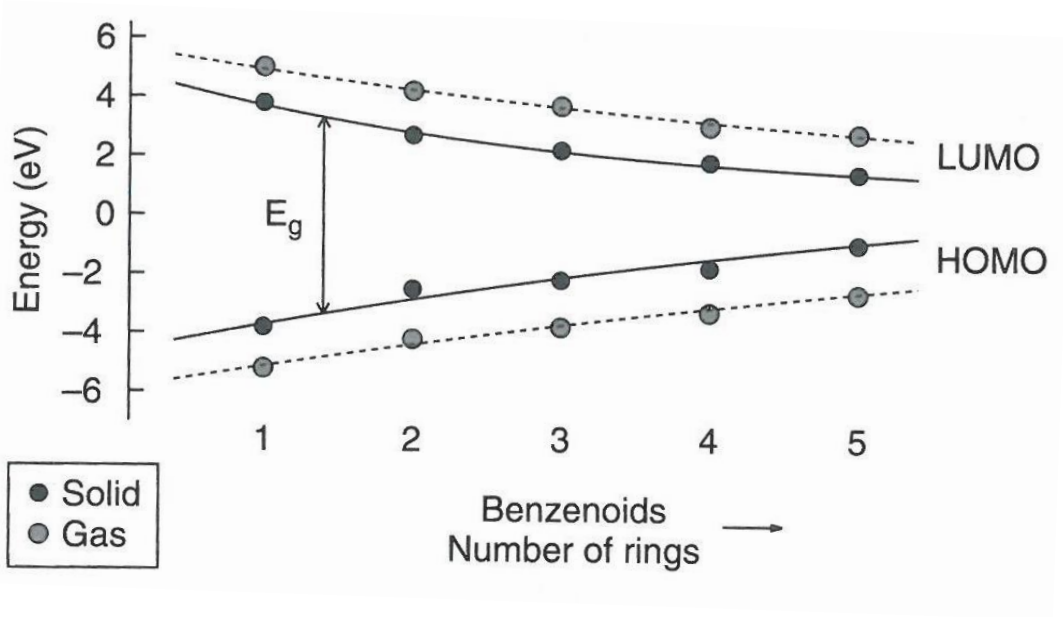


Nonconjugated Polyacetylene

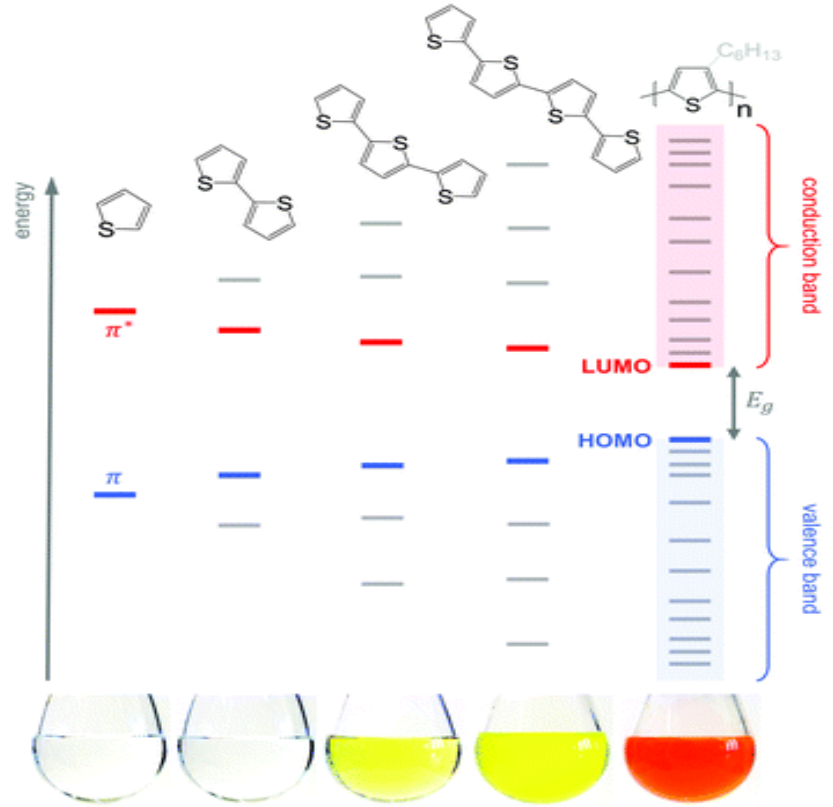


Polyyallene

- Conjugation length : designate the length or average length of uninterrupted chain
  - The bandgap is further narrowed in the solid state form by van der Waals interaction between molecular orbits on near molecules



Band gap Eg as a function of molecular size in benzenoids. For increasing conjugation length, from benzene to pentacene, the gap narrows. This effect is caused by incased dislocation of the charges and is further amplified when the molecules are close to each other in solids.



Evolution of the HOMO and LUMO levels as well as Eg with increasing number of thiophene repeat units, resulting in valence and conduction

History of conjugated polymer

- Trans-polyacetylene in 1977: chemically doped polyacetylene

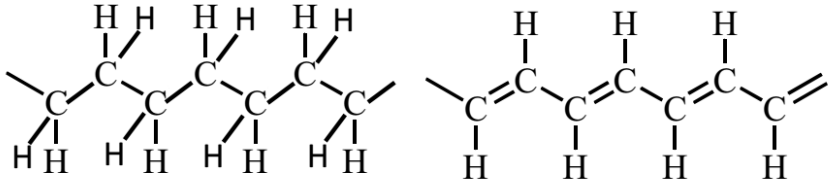
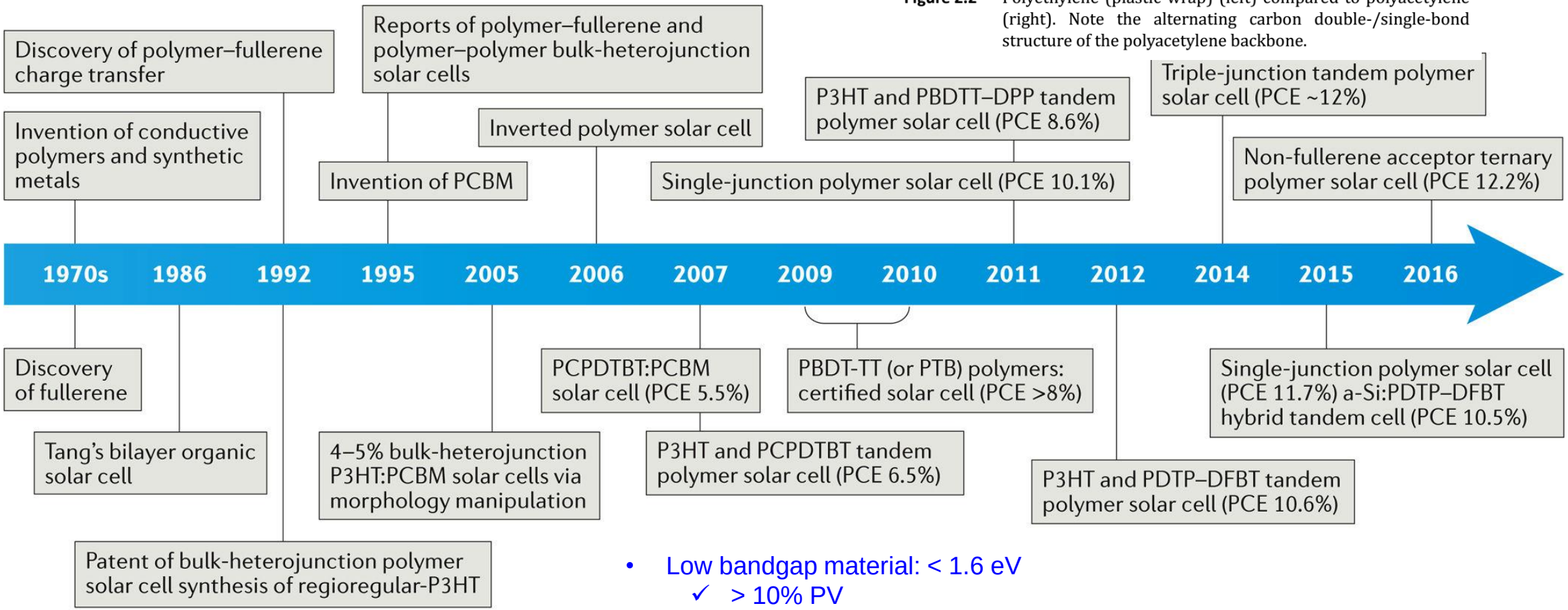


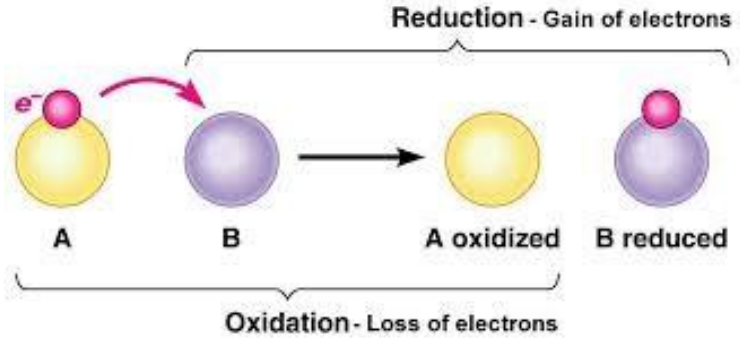
Figure 2.2 Polyethylene (plastic wrap) (left) compared to polyacetylene (right). Note the alternating carbon double-/single-bond structure of the polyacetylene backbone.



- Low bandgap material: < 1.6 eV
  - ✓ > 10% PV
  - ✓ Photodetector with up to 1450 nm response, >10^{12} cm $Hz^{1/2}$/W detectivity
  - ✓ FETs with ambipoler mobilities of ~10 $cm^2/V{\cdot}s$

Nature Review Materials 2, Article number: 17043 (2017)

Doping process in polymer



N-doping: partial reduction of polymer chain (gain of electron)

Per functional unit: $-[P]- + y\,e + y\,M^+ \rightarrow -[(P^{y-})\,M_y^+]-$

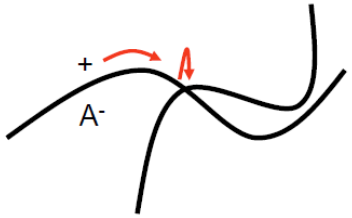
$-[P]_x - + xy\,e + xy\,M^+ \rightarrow -[(P^{y-})\,M_y^+]_x-$ AsF_5, Br_2, I_2, etc

P-doping: partial oxidation of polymer chain (loss of electron)

Per functional unit: $-[P]- + y\,A^- \rightarrow -[(P^{y+})\,A_y^-]- + y\,e$

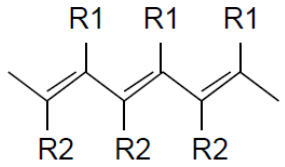
$-[P]_x- + xy\,A^- \rightarrow -[(P^{y+})\,A_y^-]_x + xy\,e$

	Charge transport:	Ionic transport
p-doping	Polaron (+.)	A^-
	Bipolaron (++)	A^-, A^-
n-doping	Soliton (0,+, -)	



Intra and inter chain charge transport

Let's draw on the board a generic case !



R2 = neutral group
R2 = anionic group (A^-)

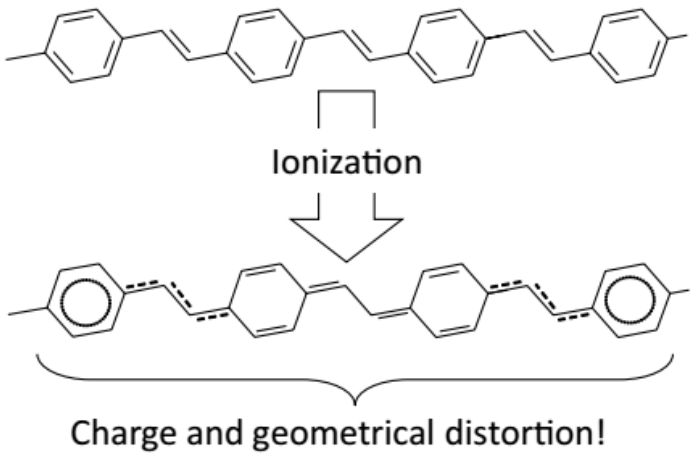
- Doping process: involve ionic transport
  can be described in terms of diffusion/reaction eqs.

- Significant doping levels (until 10 mole %)
- There is a charge transfer between the incorporated dopant atom and the polymer chain = the lattice is partially oxidized or reduced

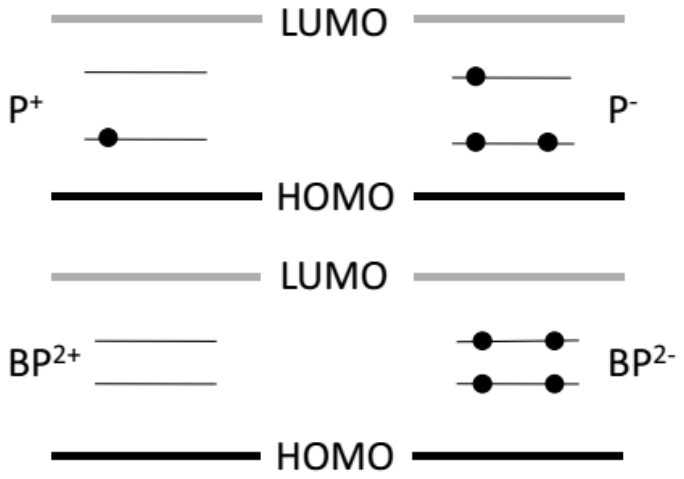
Charge injection and transport

- Conjugated polymers have a nonconstant charge distribution
- Peirels's theory: a system needs to dimerize to become stable when it has a nonconstant charge distribution
  - → Dimerization into alternating carbon single and double bonds causes a positional and electronic perturbation along the chain
  - → adding charge (reducing) or subtracting charge (oxidizing) to or from π-conjugated materials causes both positional and electronic distortions
  - → Distortion generates potential well ⇒ **polaron:** the combination of a charge with an accompanying well

Bipolaron: electronic states occupied by two electrons (or holes) (two polarons of equal charge interacting)

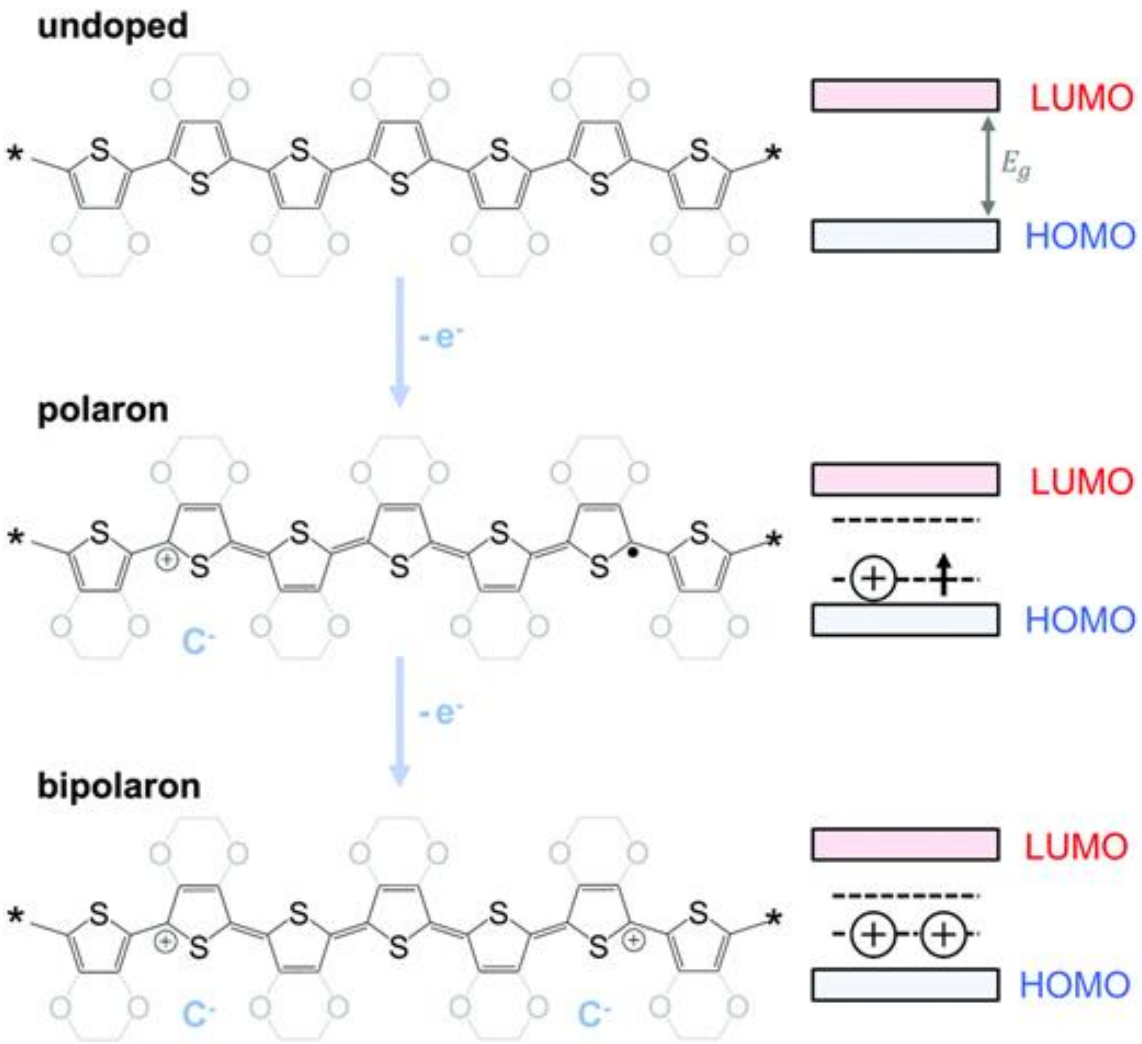


Segment of a poly(p-phenylenevinylene) chain undergoing bond alternation upon ionization.

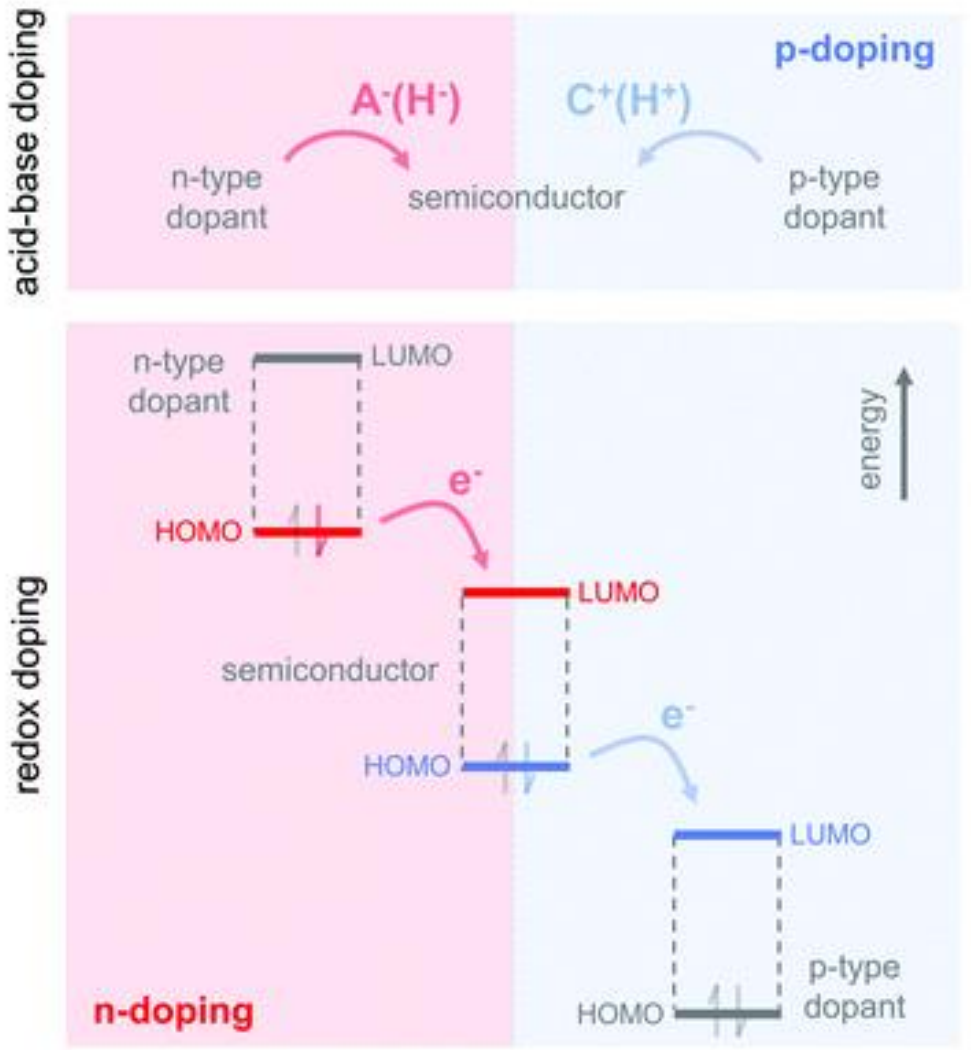


Polaronic species (P: singly charged; BP: doubly charged) appearing in the HOMO–LUMO gap upon ionization.

- IP: energy cost of removing an electron from the HOMO
- EA: energy gain from adding an electron to LUMO
- λ (relaxation E): energy gain from the reorganization into polaronic species

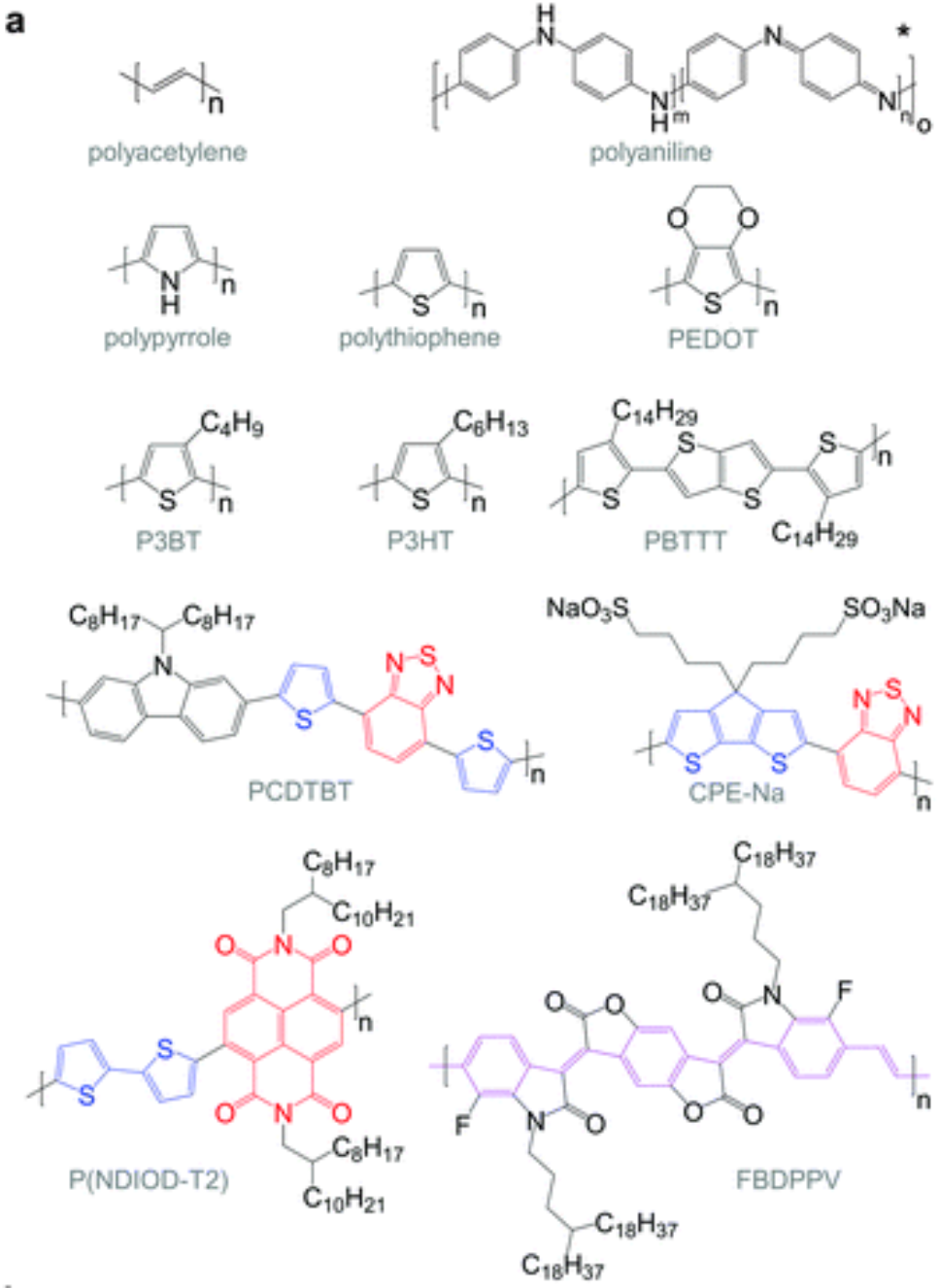


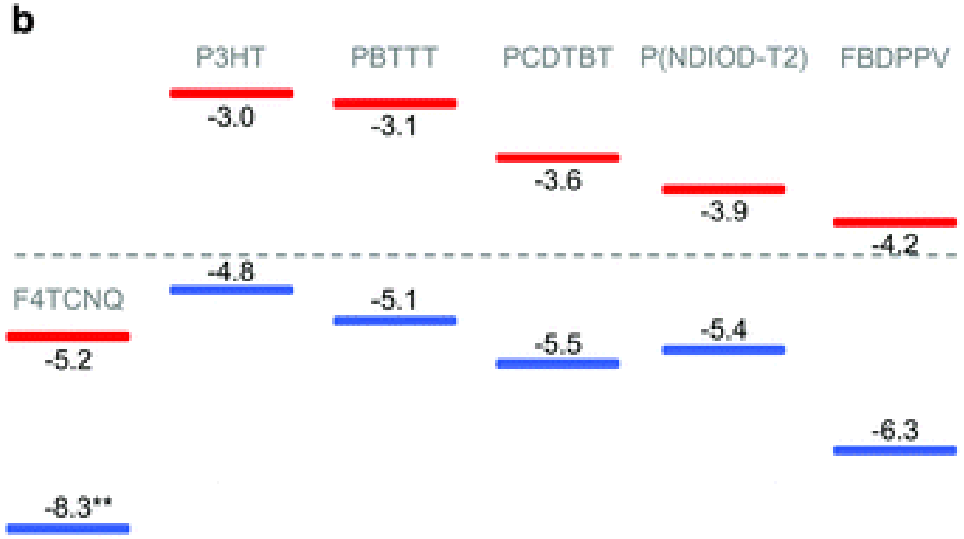
Schematic for p-doing of polythiophene and PETOD and the corresponding band structure. Electron transfer ($-e^-$) to the undoped polymer (top) leads to the formation of a polaron (middle) and finally a bipolaron state (bottom); counterions (C^-) ensure charge neutrality



Basic principle of acid-base doping, which involves the transfer of an anion (A^-, eg, H^-) or cation (C^+, e.g, H^+) to the semiconductor (top); and redox doping, which involves the transfer of an electron to the LUMO or from the HOMO of the semiconductor in the case of n- and p- doping, respectively (bottom)

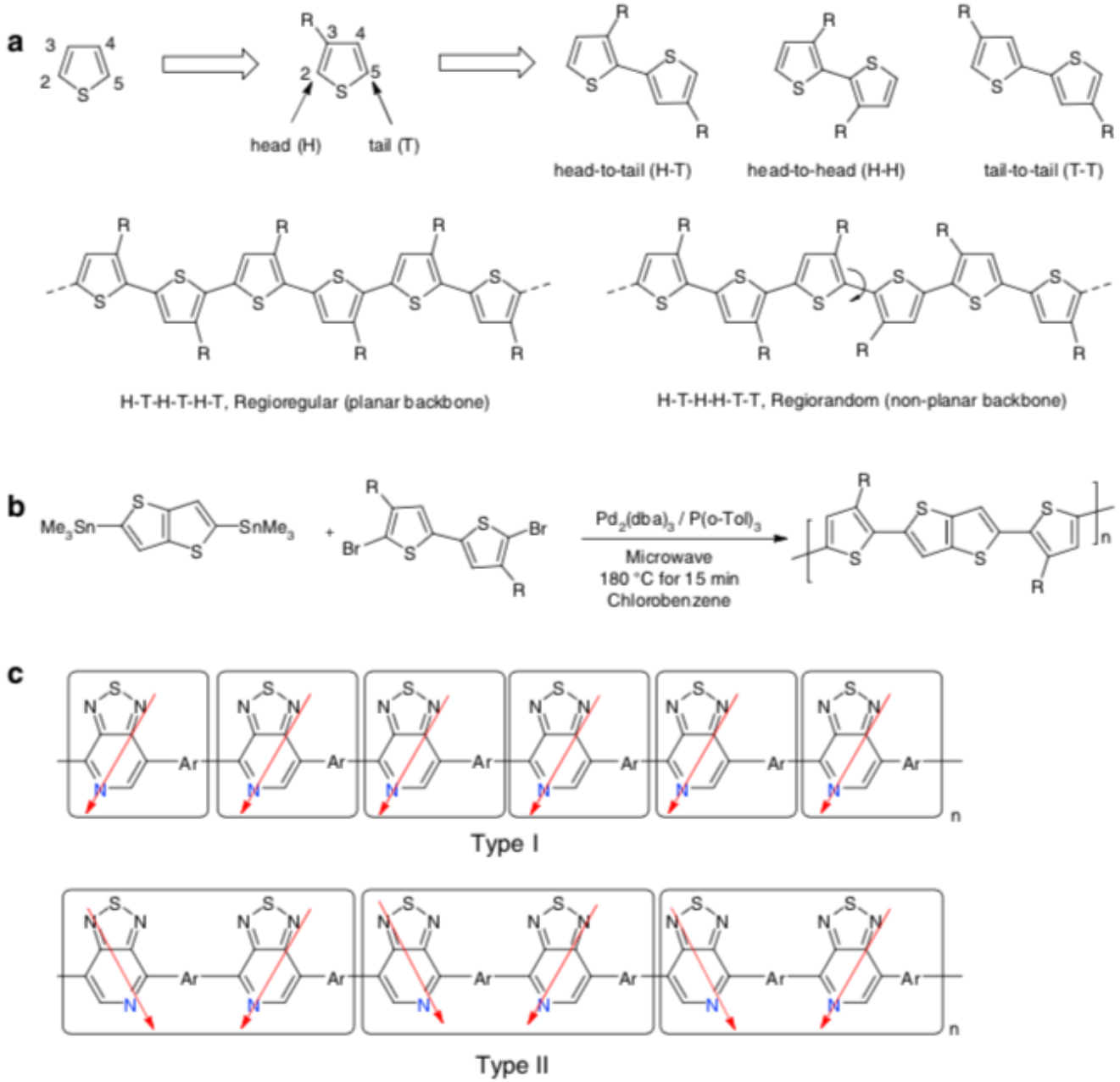
Conjugated polymers



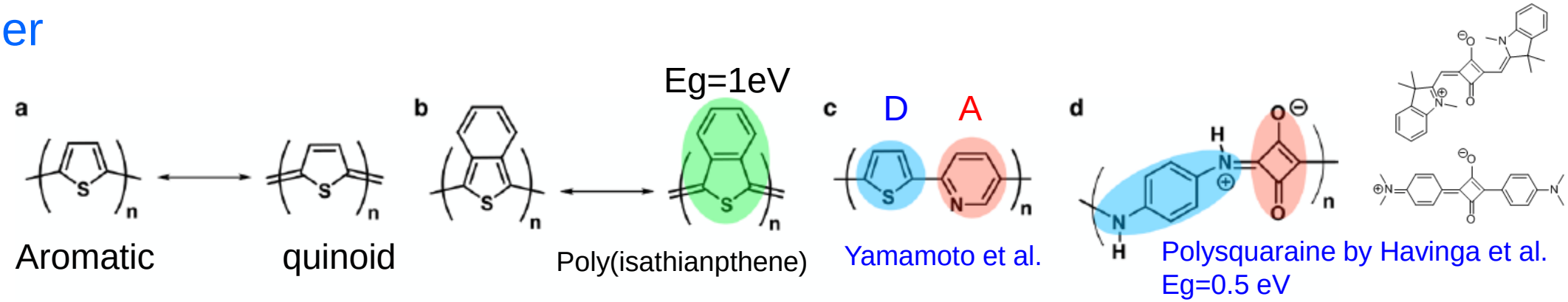


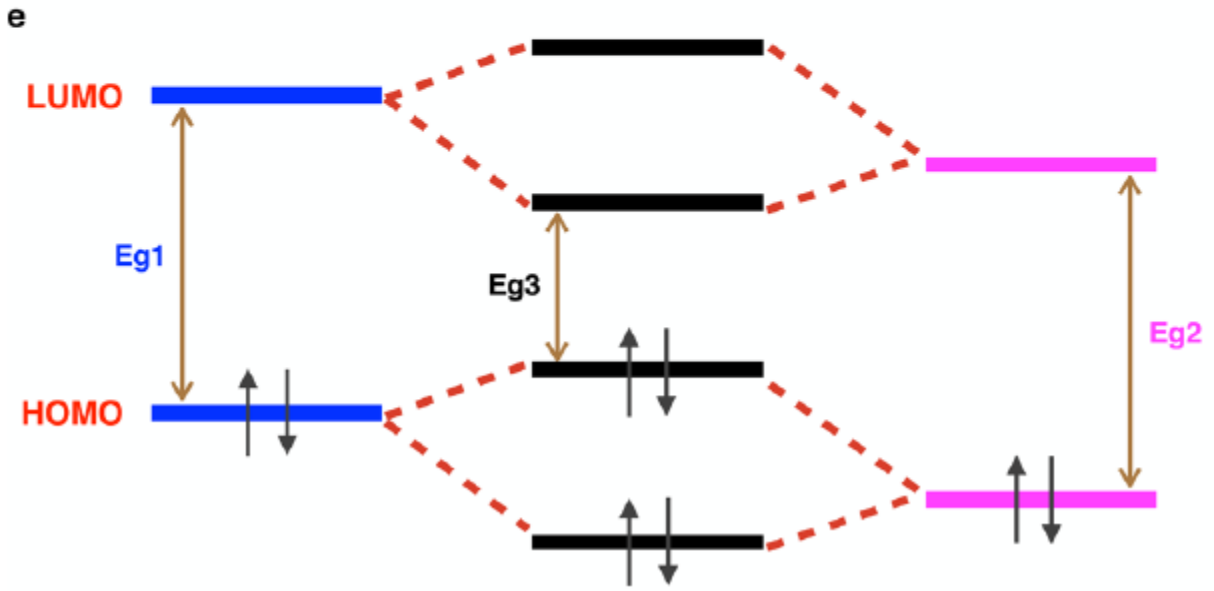
Chemical structures of conjugated polymers. For the donor-acceptor architectures, donor (blue) and acceptor (red) moieties are indicated in blue and red, respectively. The PPV-backbone in FBDPPV is indicated in purple; *leucoemeraldine (m=1, n=0), emeraldine base (m=n=0.5), pernigraniline (m=0, n=1); (b) HOMO and LUMO levels lf P3HT, PBTTT, PCDTBT, P(NDIOD-T2) and FBDPPV, ad well as the oxidizing agent F4TCNQ; ** not to scale

Regioregular (RR) & Regiorandom

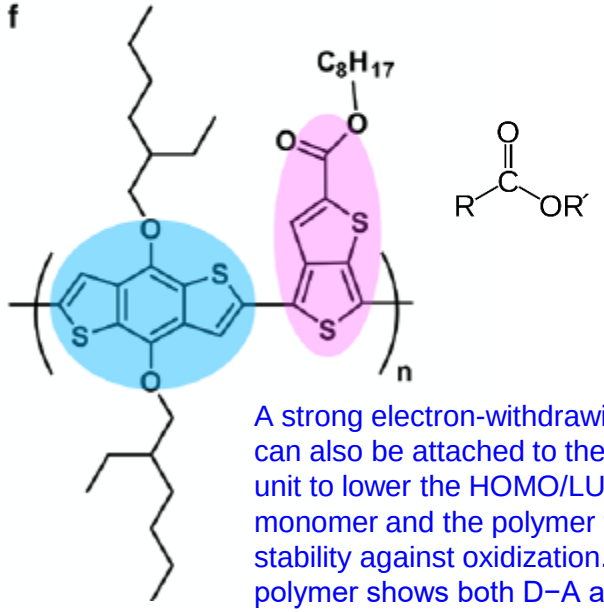


DA polymer





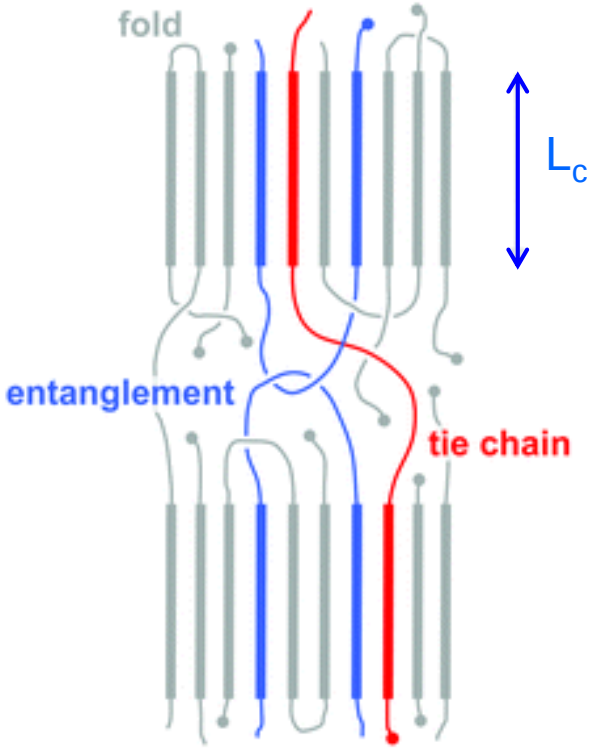
Interaction HOMOs and LUMOS → creating new energy levels: higher HOMO, lower LUMO



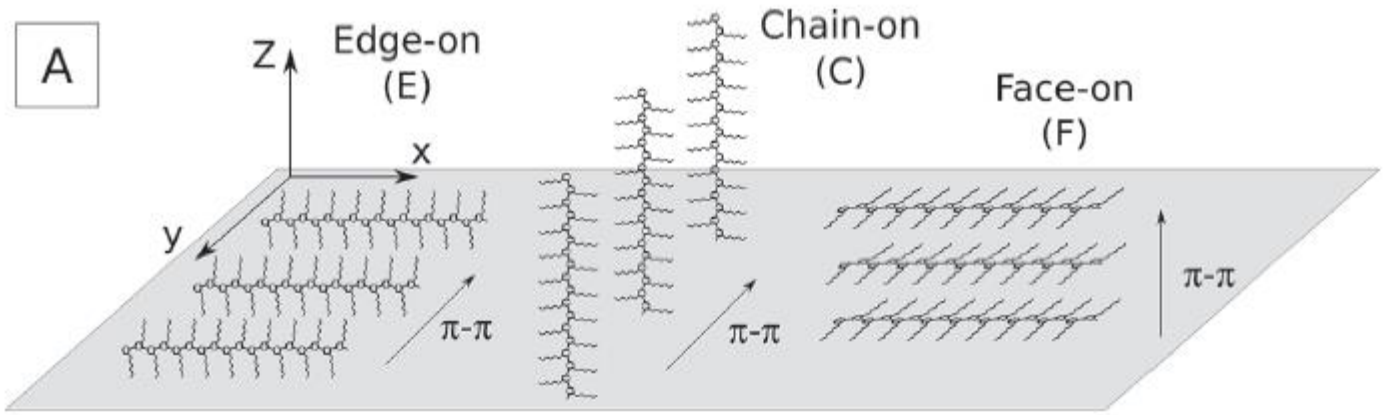
A strong electron-withdrawing ester group can also be attached to the thienothiophene unit to lower the HOMO/LUMO level of the monomer and the polymer to improve the stability against oxidization. As a result, the polymer shows both D−A and quinoid characteristics.

Figure 1. Strategies to make low-bandgap polymers. (a) Aromatic (left) and quinoid (right) resonance structures of polythiophene. (b) **Stabilization** of the quinoid resonance structure (green color). (c) Donor−acceptor copolymer made by Yamamoto (blue part is donor and red part is acceptor). (d) Donor−acceptor copolymer made by Havinga. (e) Simplified mechanism of bandgap lowering by donor−acceptor interaction. (f) Modern synthetic approach that **combines both methods** (purple part is electron-accepting and can stabilize the quinoid resonance structure).

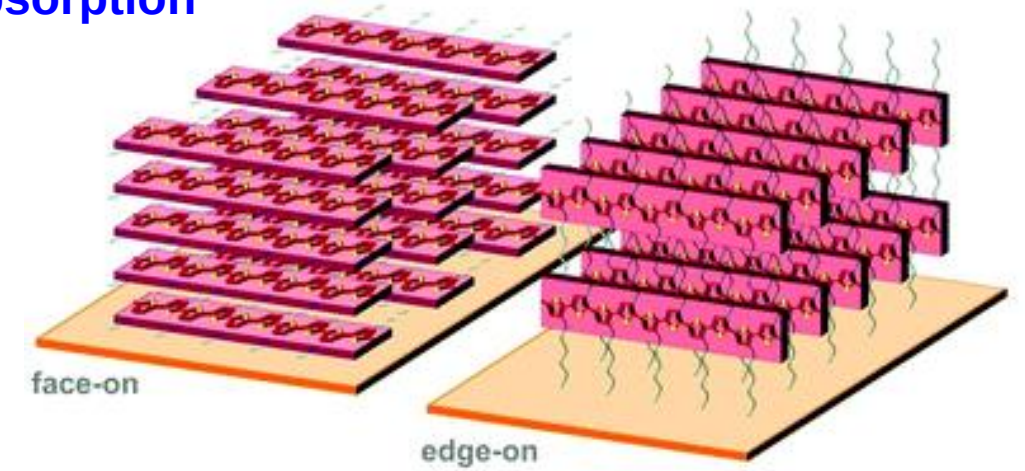
Conjugated Polymer crystal



Schematic nanostructure of a semi-crystalline polymer, indicating a chain fold that re-enters the same crystallite (with lamellar thickness L_c), a tie chain that bridges two adjacent crystallites, and a chain entanglement that is trapped in the amorphous region between two crystallites.



Jsc, Voc, absorption



Face-on (left) and edge-on (right) orientation of P3HT crystallite with the π-stacking direction lying out-of-plane and in-plane, respectively.