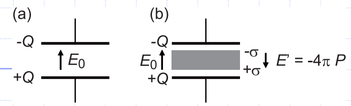
Dielectrics in a capacitor



Capacitors:

$Q = CV$ $q = \varepsilon E$ $E = V/d$

$C = \varepsilon S/d$ $Q = qS$

ε_0 = 0.088 pF/cm

Insert dielectrics with keeping q

Actual field Original electric field

$E = E_0 - 4\pi P$ $\varepsilon_0 E = D - P$ $q' = q - \sigma$

$\rightarrow D = E + 4\pi P$ cgs $D = \varepsilon_0 E + P$ MKS

$D = \varepsilon E$ dielectric const. $D = \varepsilon_0 \varepsilon_r E$ $\rightarrow$

E* decreases $1/\varepsilon$ of *D e.g. Si (ε = 11.9) → 1/11.9 water → 1/80

Insert dielectrics with keeping V → C is × ε

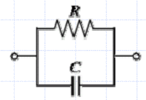
In particular, $\sigma = q$ perfect polarization → $E = 0$ and $\varepsilon = \infty$

→ Metal (E = 0 in a metal)

Always $P > 0$ → $\varepsilon > 1$

Displacement current when charging a capacitor

$$I = \frac{dQ}{dt} = \frac{dCV}{dt} = i\omega CV \quad \text{using} \quad V = Ve^{i\omega t}$$



Conductance of the dielectric, $G = 1/R$, is added,

$$I = GV + i\omega CV = (G + i\omega C)V$$

In the Maxwell equation

$$\nabla \times H = \frac{1}{c}\frac{\partial D}{\partial t} + \frac{4\pi}{c} j \quad \text{cgs (for MKS: } 4\pi \rightarrow 1,\ c \rightarrow 1)$$

Insert $D = \varepsilon E$ and $E = Ee^{i\omega t}$

$$\nabla \times H = \frac{1}{c}\varepsilon\frac{\partial E}{\partial t} + \frac{4\pi}{c}\sigma E = \frac{1}{c}\left(\varepsilon + \frac{4\pi i \sigma}{\omega}\right)\frac{\partial E}{\partial t}$$

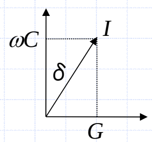
Inside ( ) is replaced by $\varepsilon^* = \varepsilon' + i\varepsilon''$

$$\varepsilon^* = \varepsilon + \frac{4\pi i \sigma}{\omega}$$

Imaginary part of the complex dielectric constant is conductivity.

$$I = GV + i\omega CV = (G + i\omega C)V$$

where $\tan\delta = \dfrac{G}{\omega C} = \dfrac{\varepsilon''}{\varepsilon'}$



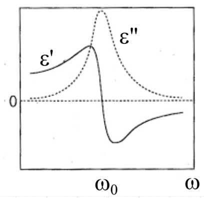
$\tan\delta = \varepsilon'' = 0$ **No dielectric loss (no conductance)**

To obtain ω dependence of ε, in the eq. of motion of an electron

$$\frac{d^2x}{dt^2} + 2\gamma\frac{dx}{dt} + \omega_0^2 x = \frac{e}{m}E$$

$P = Nex = \varepsilon_0(\varepsilon_r^* - 1)E$, **and** $E = Ee^{i\omega t}$ **are inserted.**

$$\varepsilon_r^* = 1 + \frac{Ne^2/\varepsilon_0 m}{\omega_0^2 - \omega^2 + i2\omega\gamma}$$



ω_0 **: characteristic frequency**

Polarization P due to the dipole relaxes accoring to $\dfrac{dP}{dt} = \dfrac{P_b}{\tau} - \dfrac{P}{\tau}$

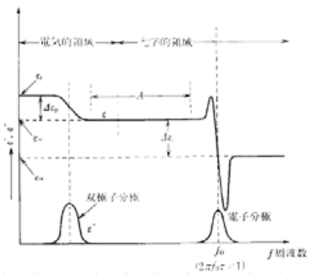
Inserting $P = P_b e^{i\omega t}$ **affords**

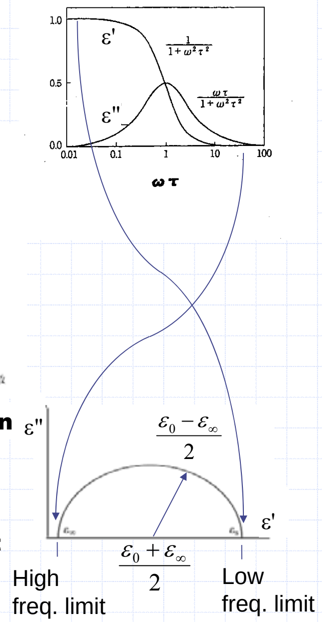
$$\varepsilon_r^* = \varepsilon_{r\infty} + \frac{\varepsilon_{r0} - \varepsilon_{r\infty}}{1 + i\omega\tau}$$

In summary

ε'→

ε"→





Deleting ω and τ from the above equation

$$\left(\varepsilon' - \frac{\varepsilon_0 + \varepsilon_\infty}{2}\right)^2 + \varepsilon''^2 = \left(\frac{\varepsilon_0 - \varepsilon_\infty}{2}\right)^2$$

Cole Cole plot

Maxwell equation $\nabla \times E = \frac{\mu}{c}\frac{\partial H}{\partial t}$ **affords**

$$\nabla^2 E = \frac{\varepsilon\mu}{c^2}\frac{\partial^2 E}{\partial t^2} + \frac{4\pi\sigma\mu}{c^2}\frac{\partial E}{\partial t}$$

Inserting $E = E_0 e^{i(qr-\omega t)}$ **gives**

$$q^2 = \mu\frac{\omega^2}{c^2}\left(\varepsilon + i\frac{4\pi\sigma}{\omega}\right)$$

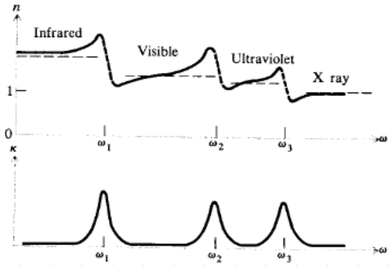
Light velocity $v = \omega/q$ **, reflactive index** $n = c/v$ **in a medium, and complex reflactive index** $n^* = n + ik$ **give** $|n^*|^2 = \varepsilon^*$

Reflactive index

ε'→

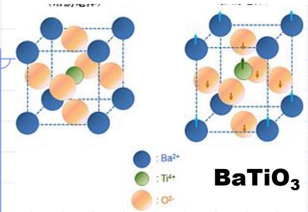
Absorption coefficient

$\alpha = \frac{2\omega}{c}k$ ε"→

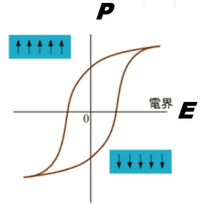


Fowler, *Introduction to Modern Optics*

Ferroelectrics: spontaneous polarization in a direction
(E = 0 leads to $P \neq 0$)



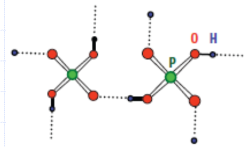
$BaTiO_3$ perovskite



Displacement type | **Order-disorder type** | **Antiferroelectric**

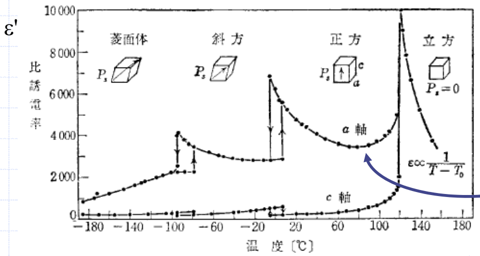
0 0 0 0 0 → ↑↑↑↑↑ ← ←↑↓→↑   ↑↓↑↓↑
0 0 0 0 0 → ↑↑↑↑↑ ← ↓→↑↓←   ↓↑↓↑↓
0 0 0 0 0 → ↑↑↑↑↑ ← ↑↓→↑←   ↑↓↑↓↑

$T > T_c$ **$BaTiO_3$**   **$T < T_c$**   **$T > T_c$** **KD_2PO_4**

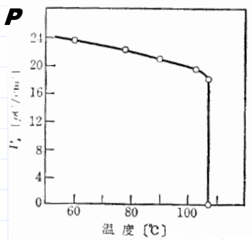


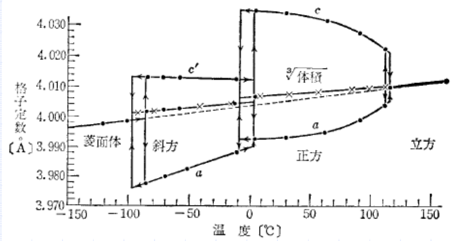
$BaTiO_3$

ε'



P





Free energy F is expanded by P (because $P \sim 0$ at $T \sim T_c$)

$$F = aP^2 + bP^4 +$$

P at F minimum is obtained by differenciating F by P.

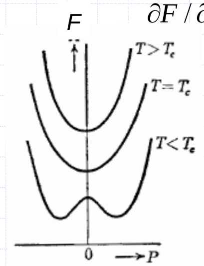
$$\partial F / \partial P = 2aP + 4bP^3 = 0$$

$$P = \sqrt{\frac{-a}{2b}}, 0$$

Assuming $a = a_0(T - T_c)$,

$T > T_c$ $P = 0$

$T < T_c$ $P = \sqrt{\frac{-a}{2b}} = \sqrt{\frac{a_0(T_c - T)}{b}}$



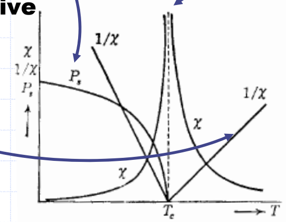
Energy in a field E is

$$F = aP^2 + bP^4 + \varepsilon_0 PE$$

differenciated by P to give

$$\varepsilon' = \frac{P}{E} = \frac{\varepsilon_0}{2a_0(T - T_c)}$$

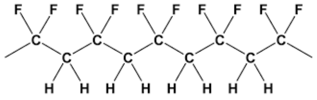
Curie law



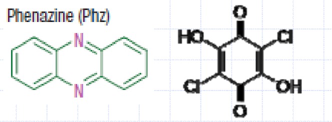
2nd order transition

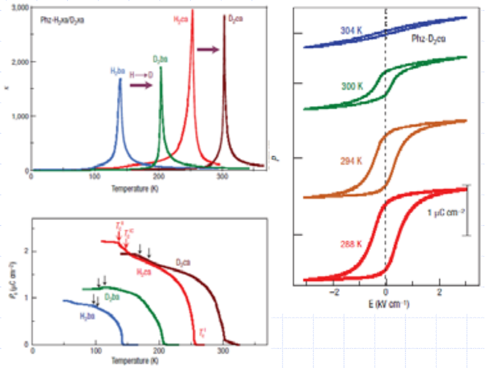
Organic ferroelectrics

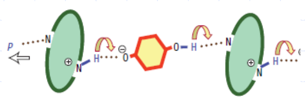
ポリフッ化ビニリデン
PVDF (Polyvynilydenedifluoride)



Polyvinylidene fluoride (PVDF)

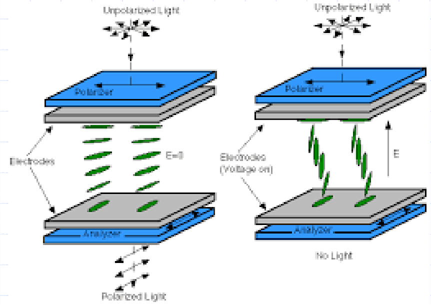






Nature Mater. **7**, 357 (2008).

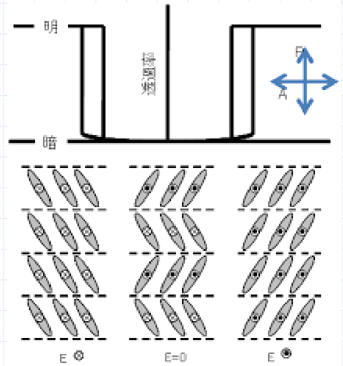
Liquid crystal display Swisted Nematic

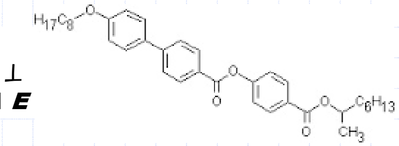


E **off** **Light on** ***E*** **on** **Light off**

In a rod-like molecule
Largely different ε in // and ⊥
→ Parallel alignment in a field *E*

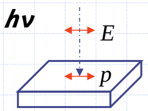
Antiferroelectric liquid crystal





MHPOBC

Optical Properties of Metals（Plasmon）



Eq. of motion vibrated by an electric field *E*:

$$m\frac{dp}{dt} = -eE - \frac{p}{m\tau} \qquad p = p(\omega)e^{i\omega t}$$

These lead to $-i\omega p(\omega) = -eE(\omega) - \dfrac{p(\omega)}{\tau}$

then $j(\omega) = -enp(\omega)/m = \dfrac{ne^2\tau}{m}\dfrac{E}{1-i\omega\tau}$

Using $\sigma_0 = \dfrac{ne^2\tau}{m}$ → $\sigma(\omega) = \dfrac{\sigma_0}{1-i\omega\tau}$

or $\mathrm{Re}\,\sigma = \dfrac{\sigma_0}{1+\omega^2\tau^2} \qquad \mathrm{Im}\,\sigma = \dfrac{\sigma_0\omega\tau}{1+\omega^2\tau^2}$

Dielectric constant of a metal $\varepsilon \to \varepsilon + \dfrac{4\pi i\sigma}{\omega}$

$$\varepsilon' = \varepsilon - \frac{4\pi\sigma_0\tau}{1+\omega^2\tau^2} \qquad \varepsilon'' = \frac{4\pi\sigma_0}{\omega(1+\omega^2\tau^2)}$$

At low frequency: ωτ<<1→ real =0 $\varepsilon \sim i\dfrac{4\pi\sigma}{\omega}$

Refractive index $n^* = \sqrt{\varepsilon} = n + ik$ **leads to** $n \sim k = \sqrt{\dfrac{\mathrm{Im}\,\varepsilon}{2}} = \sqrt{\dfrac{2\pi\sigma_0}{\omega}}$

Reflectivity $R = \left|\dfrac{1-n^*}{1+n^*}\right|^2 = \dfrac{(n-1)^2+k^2}{(n+1)^2+k^2}$ **is *R* ~ 1**

Light cannot enter, and is reflected: metallic luster.

At high frequency: ωτ>>1 → real part:

$$\varepsilon' = \varepsilon - \frac{4\pi\sigma_0}{\omega^2\tau} = \varepsilon - \frac{4\pi ne^2}{\omega^2 m} = \varepsilon\left(1 - \frac{\omega_p^2}{\omega^2}\right)$$

Plasma frequency $\omega_p^2 = \dfrac{4\pi ne^2}{m}$

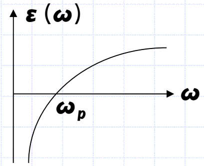
$\omega < \omega_p$ $\varepsilon < 0$ $n = 0$ → $R = 1$ **Total reflection**

Light cannot enter, and is reflected: metallic luster.
ω_p **near ultraviolet in ordinary metals**

$\omega > \omega_p$ $\varepsilon > 0$ $k = 0$

→ **Absorption** $\alpha = \dfrac{2\omega}{c}k$ → 0

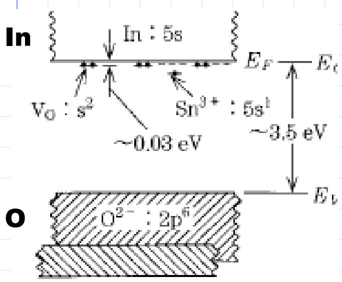
→ **Metals are transparent for UV light.**

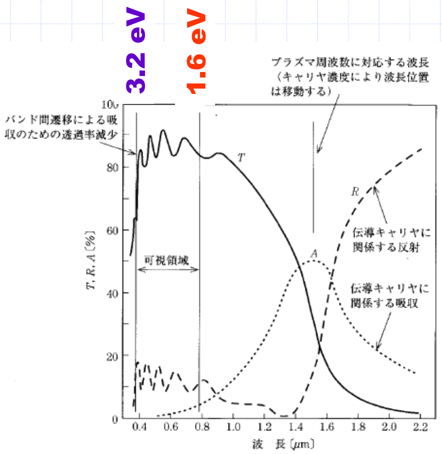


Transparent conductors   Doped wide-gap semiconductors

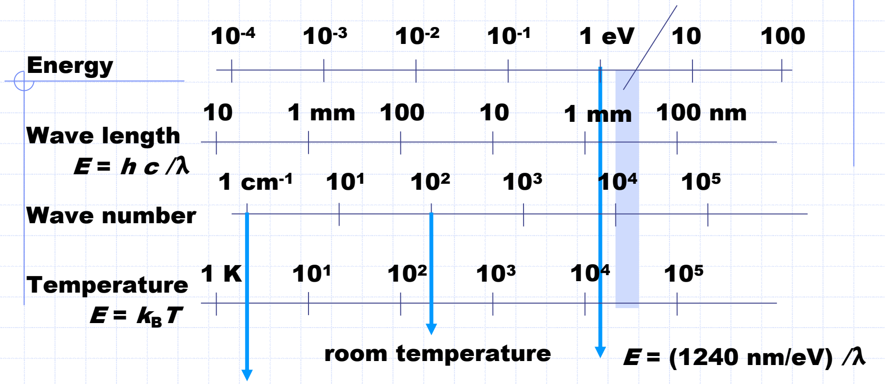
Liquid crystal display
LED display
Solar cell

ITO In_2O_3 In^{3+} (+Sn^{4+})





Energy units conversion



E = (1240 nm/eV) $/\lambda$

1 cm^{-1}～1 K ～1 T
Magntic field
$E = k_B T$ $E = \mu_B H$

1 eV = 1.24 μm $eV = hc/\lambda$
= 8065 cm^{-1}
= 11605 K $E = k_B T$
= 0.96x10^5 J/mol or C/mol
eN_A Faraday const. =1 mol charge

1 eV ～ 1 μm ～10^4 cm^{-1}
～10^4 K ～ 100 kJ/mol

Various transparent conductors

In_2O_3 several %Sn doped → ITO (Indium tin oxide)

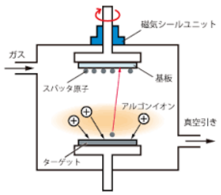
In (3+) → Sn (4+) Electron doped cf. Si(4+) → As(5+)

Oxygen defficient → In^0 from charge nuetrality
→ Electron doped

Electron doped in most oxides

Films from magnetron sputtering

2 x 10^{-4} Ωcm, E_g ~ 3.3 eV



SnO_2 Rutile、oxygen defficiency

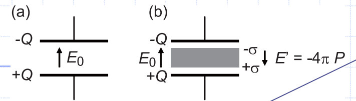
ZnO Wurzite、oxygen defficiency

$Ti_{1-x}Nb_xO_2$ Rutile

$SrTiO_3$ Perovskite、oxygen difficiency

$12CaO \cdot 7Al_2O_3$ Partly reduced, electron doped (Electrolyde)

Dielectrics in a capacitor   Magnets



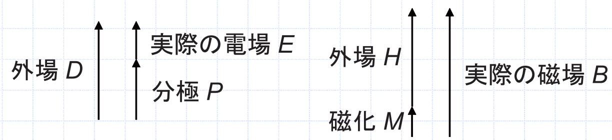
$B = H + 4\pi M$
$= \chi H$

$E = E_0 - 4\pi P$
→ $D = E + 4\pi P$
$= \varepsilon E$ always $P > 0$
Si ε = 11.9   → ∞ E = 0 Metal
Actual E is 1/11.9 of D.

		weak	strong
$M > 0$	increases H	paramag.	ferromag.
$M < 0$	cancels H	diamag.	supercon.

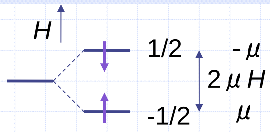
P and M have opposite signs.
ordinary χ ~ 10^{-4}
Actual B ~H

(a) 誘電体   (b) 磁性体



$D = E + 4\pi P$ $B = H + 4\pi M$ cgs
$D = \varepsilon_0 E + P$ $B = \mu_0 H + M$ MKS

Curie Paramagnetism



Magnetic moment from unpaired electons

$\mu = \gamma \hbar \mathbf{S} = -g\mu_B \mathbf{S}$

Zeemann splitting due to the magnetic field $\mathbf{H}$

$E = -g\mu_B \mathbf{HS} = -\mu \mathbf{H}$

Split to two for $S = 1/2$. In thermal equilibrium:

$$\frac{N_\uparrow}{N} = \frac{e^{\mu H/k_BT}}{e^{\mu H/k_BT} + e^{-\mu H/k_BT}} \qquad \frac{N_\downarrow}{N} = \frac{e^{-\mu H/k_BT}}{e^{\mu H/k_BT} + e^{-\mu H/k_BT}}$$

lead to

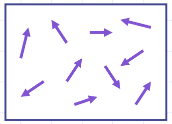
$$M = \mu_B(N_\uparrow - N_\downarrow) = N\mu \tanh\frac{\mu H}{k_BT} \approx N\mu\left(\frac{\mu H}{k_BT}\right) \leftarrow \frac{\mu H}{k_BT} \ll 1 \quad \text{so}$$

$$\chi = \frac{M}{H} = \frac{N\mu^2}{k_BT} = \frac{C}{T}$$

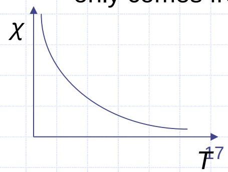
Curie constant

Except for S=1/2 $C = \frac{NS(S+1)g^2\mu_B^2}{3k_B}$ only comes from S.

χ is inversely proportional to T.

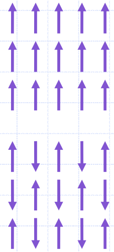


Random spins
Aligned under magnetic field.
More aligned at low T.



Magnetic Order

Ferromagnetism : all parallel
The whole material is a magnet.



J>0
$S_i // S_j$ is stable

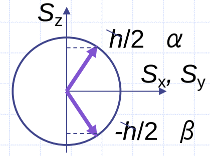
Antiferromagnetism :
alternately opposite directions

J<0
Antiparallel S_i and S_j

Spin Hamiltoniam

$$\hat{H} = -\sum_{i,j} 2J_{ij}\bar{S}_i\bar{S}_j - g\mu_B H\sum_i \bar{S}_i$$

Interaction   Zeemann splitting

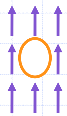


S_i is a vector like (S_x, S_y, S_z): (Heisenberg model).
When spin is always directed in one direction (z) due to the large magnetic anisotropy coming from the crystal field, we only consider S_z.
(Ising model)

When S_i=1/2, S_j=1/2, (Interaction)=−J/2
When S_i=1/2, S_j=−1/2, (Interaction)=J/2
] Energy difference J

Note: (Interaction) is defined as $-\sum_{i,j} J_{ij}\bar{S}_i\bar{S}_j$ in old literatures.
J is twice larger.

Molecular Field (Mean Field) Approximation



Focusing on S_i, and use average sum for Σj

$$\hat{H} = \sum_i S_i\left(-\sum_j 2J_{ij}S_j - g\mu_B H\right) = -g\mu_B(H_{eff} + H)\sum_i S_i$$

$$H_{eff} = \frac{1}{g\mu_B}\sum_j 2J_{ij}\langle S_j\rangle$$

Interaction with S_j is replaced by a field (effective or internal field)(有効 or 内部磁場) generated on S_i.

S_j changes every moment, but Sj is approximated by the average <S_j>
(分子場近似 or 平均場近似 Molecular Field or Mean Field Approximation)

Statistical distribution similar to the Curie paramagnetism gives

$$M = \frac{N\mu^2 H}{k_BT} \xrightarrow{H \to H_{eff}+H} M = \chi_0(H_{eff}+H)$$

where $M = Ng\mu_B\langle S\rangle$ leads to

$$H_{eff} = \frac{\sum_j 2J_{ij}\langle S_j\rangle}{N(g\mu_B)^2} M = aM$$

分子磁場係数

Put this in the above eq. to give

$M = \chi_0(aM+H)$

$$M\left[(1-\chi_0 a)\right] = \chi_0 H \quad \rightarrow \quad \chi = \frac{M}{H} = \frac{\chi_0}{1-\chi_0 a} = \frac{C}{T-\theta}$$

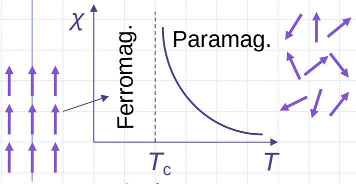
Curie-Weiss則

$$\theta = \frac{1}{k_B}\sum_j 2J_{ij} = \frac{2zJ}{k_B}$$

← Coordination number z for nearest neighbor J's

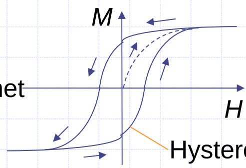
Weiss temperature

J>0→ θ >0 Ferromagnetism

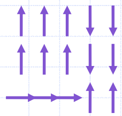


Curie temperature

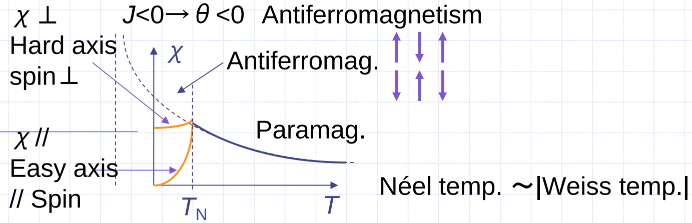
$T \to T_c$: $\chi \to \infty$
$T < T_c$: $M \neq 0$ for H=0
Spontaneous Magnetism → Magnet
T_c Fe 1043 K Ni 627 K



Magnetization of Ferromagnet



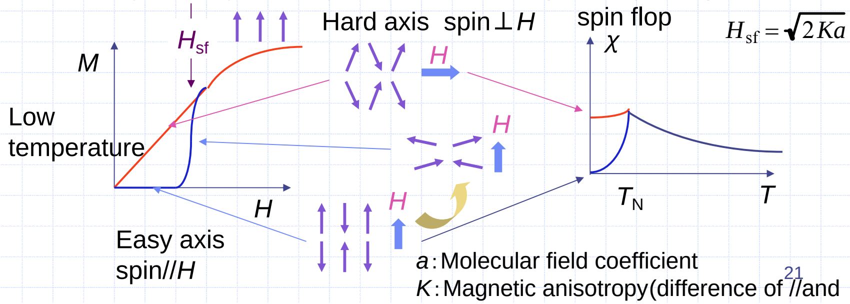
Usual ferromagnet has randomly oriented magnetic domains (磁区), but magnetic field aligns the spin orientation to make a bulk magnet.



Easy axis of antiferromagnets

Spins in antiferromagnet are oriented in a particular direction due to
1) Dipole interaction 2) crystal field

Increasing H along the easy axis leads to abrupt change to spin ⊥ H at H_{sf}.

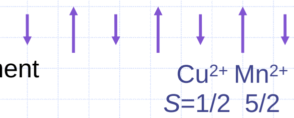


a : Molecular field coefficient
K : Magnetic anisotropy(difference of // and ⊥)

Ferrimagnetism

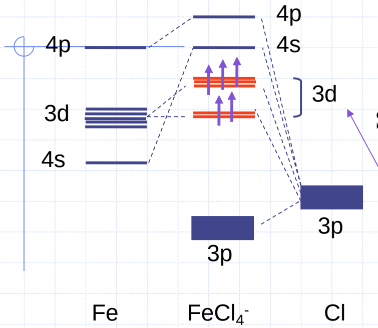
Alternating spins with different S
(e.g. different metals) lead to remaining moment
even for antiparallel order for J<0.

Ferrite Fe_3O_4 has Fe^{3+} and Fe^{2+}.
Most molecular magnets.



Magnetism

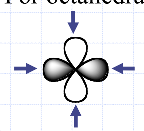
Molecular orbital of transition metal compounds



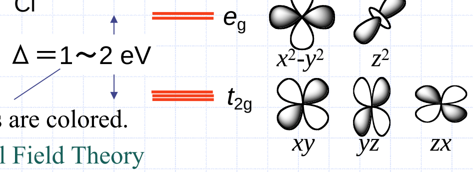
Ligand orbital: bonding
Transition metal d-orbitals: antibonding
s, p levels are further antibonding
All valence electron enters in the d levels

Splitting of the d levels (Coordination Splitting)

For octahedral



Two e_g orbitals directed to the ligands are lifted, and more antibonding.

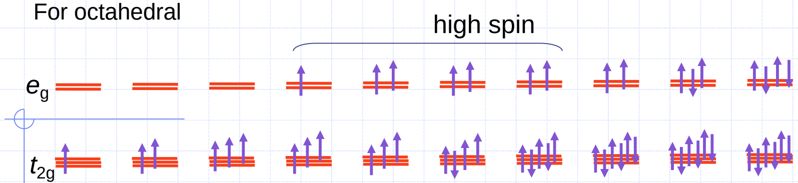


Absorb visible light
→Transition metal compounds are colored.

Ligand Field Theory or Crystal Field Theory
Molecular Field Theory of
Transition Metal Compounds

Three t_{2g} orbitals have nodes in the direction of the ligands, and are nonbonding.

For octahedral

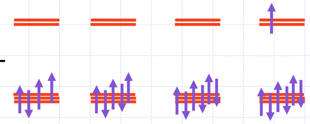


	d1	d2	d3	d4	d5	d6	d7	d8	d9	d10
S=	1/2	1	3/2	2	5/2	2	3/2	1	1/2	0
	Ti^{3+}	Ti^{2+}	Cr^{3+}	Cr^{2+}	Fe^{3+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
	V^{4+}	V^{3+}	Mn^{4+}	Mn^{3+}	Mn^{2+}	Co^{3+}	Ni^{3+}			Cu^{+}
				Ti^0	V^0	Cr^0	Mn^0	Fe^0	Co^0	Ni^0
				4	5	6	7	8	9	10

For d = 4∼7, when crystal field > Hund rule, low spin state achieved

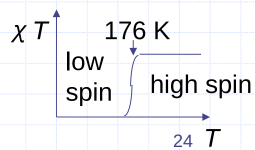
Transition from high spin to low spin by changing T
Spin crossover

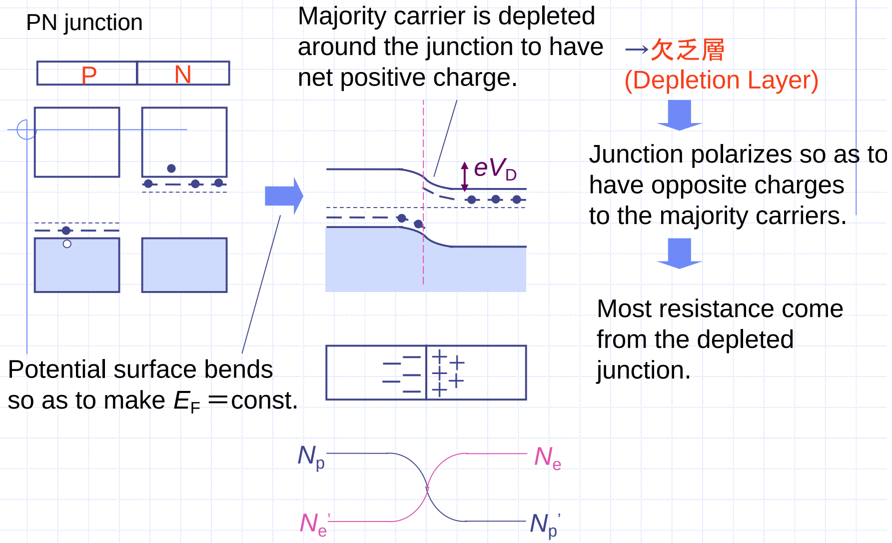
Low spin d^6 is nonmagnetic

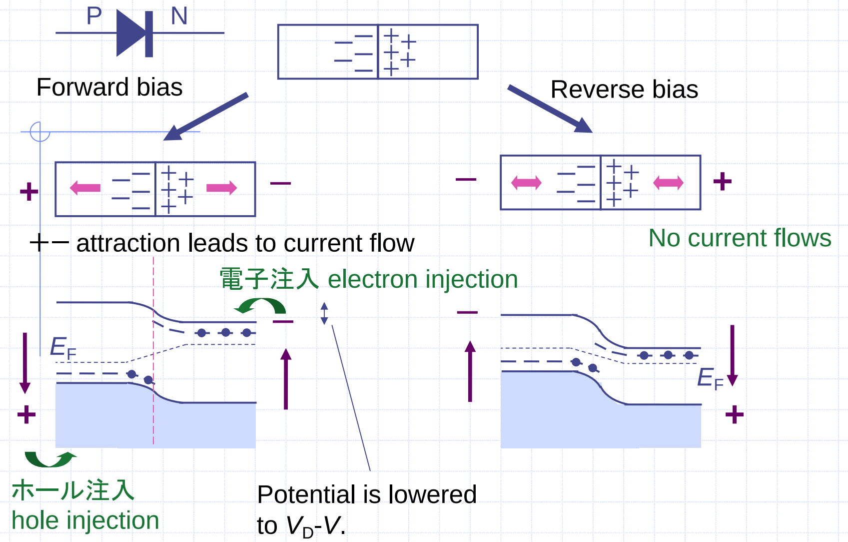


	d4	d5	d6	d7
S=	1	1/2	0	1/2

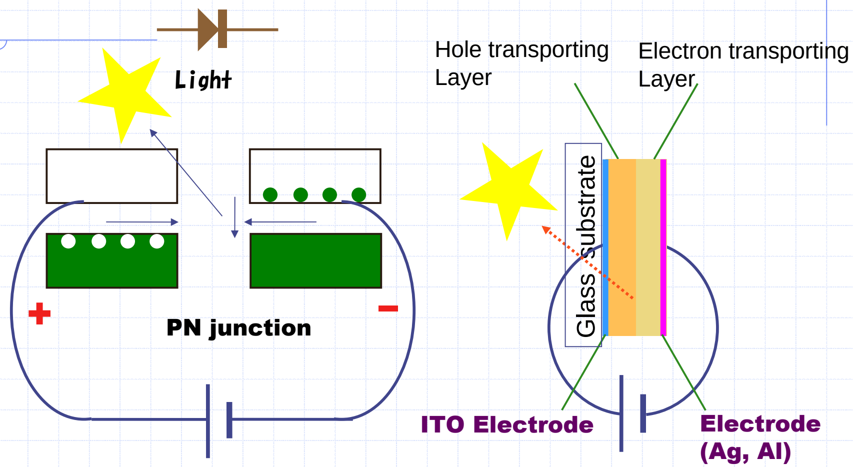
$[Fe^{II}(phen)_2(NCS)_2]$







有機発光ダイオード Light Emitting Diode (LED)
有機EL (Electroluminescence)



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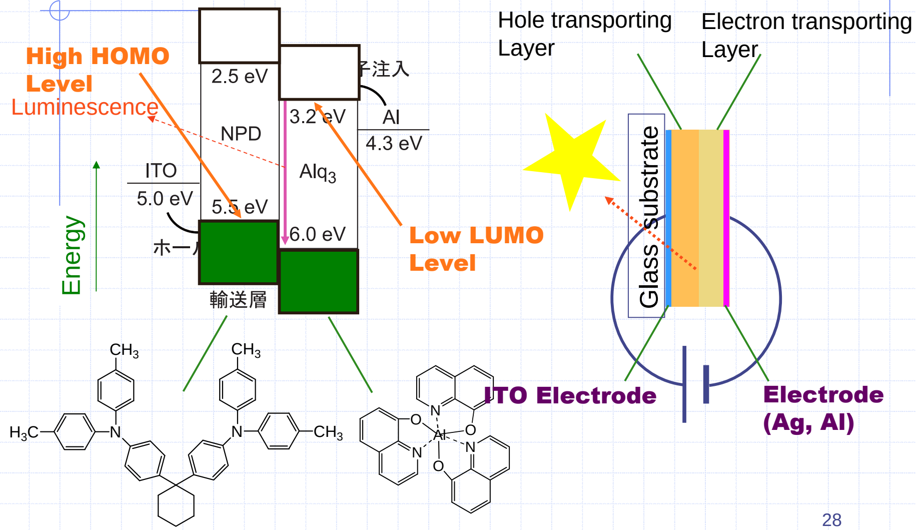
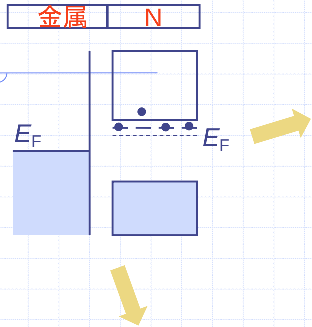
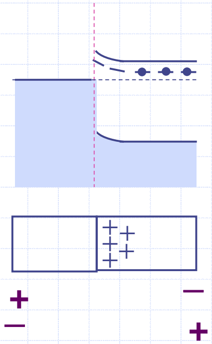


Metal-semiconductor junction



Metal E_F < E_F in N-type



Adjust E_F

Depletion layer

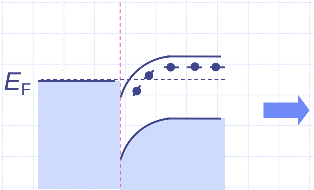
Shottokey Diode

Forward

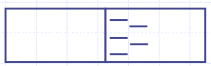
Reverse

Shottokey Barrier

Meta E_F > E_F in N-type : Ohmic contact



Accumulation layer in majority carrier

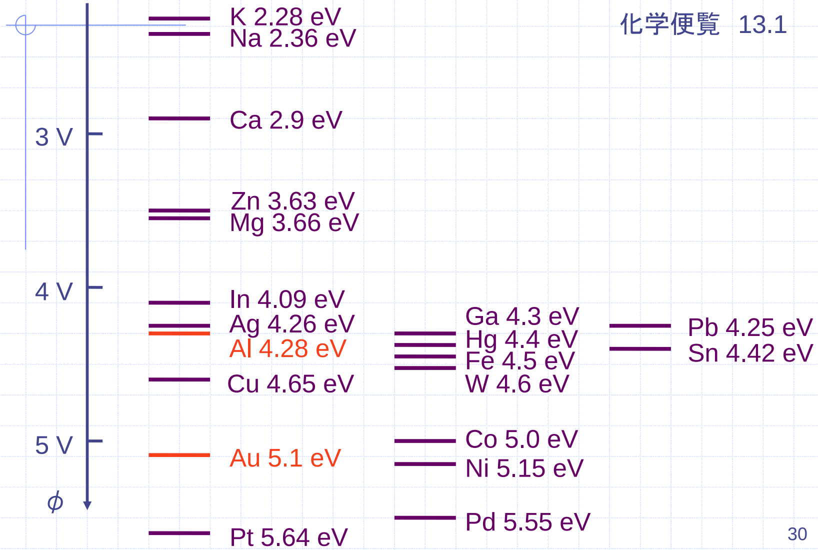


Current flow for both biases.

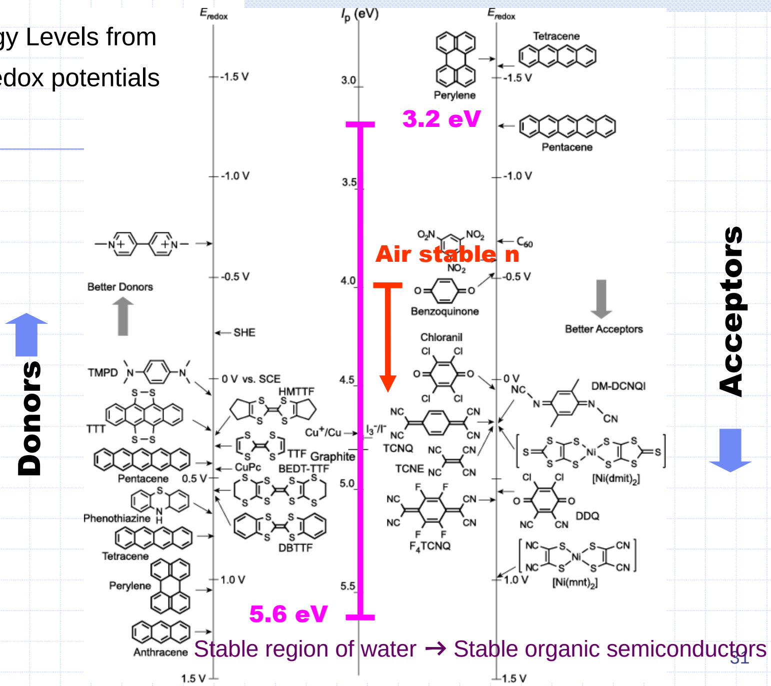
Work function of Metals (Position of E_F)

cf. Ionization potential for semiconductors

化学便覧 13.1

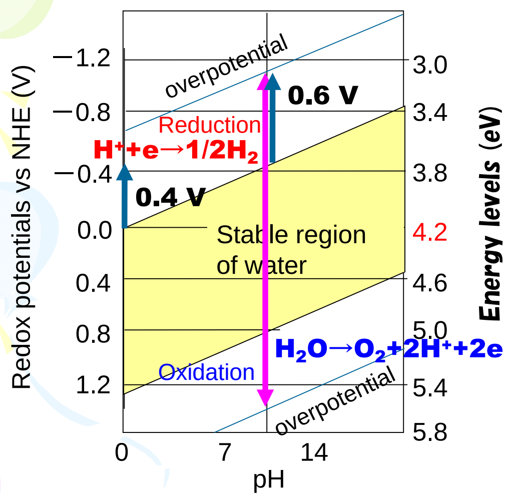


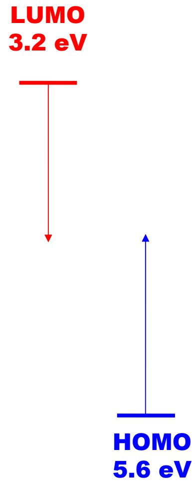
Energy Levels from Redox potentials



Stable region of water → Stable organic semiconductors

Stable region of water

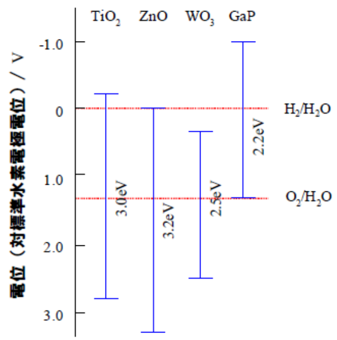


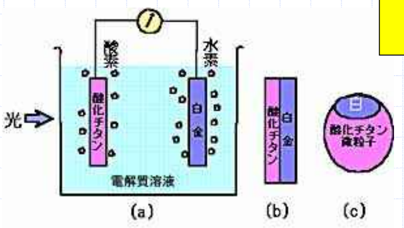


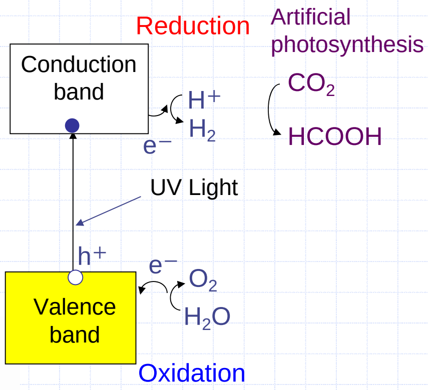
Atkins, Inorganic Chemistry

Photocatalysis : TiO_2 irradiation decomposes water to H_2 and O_2

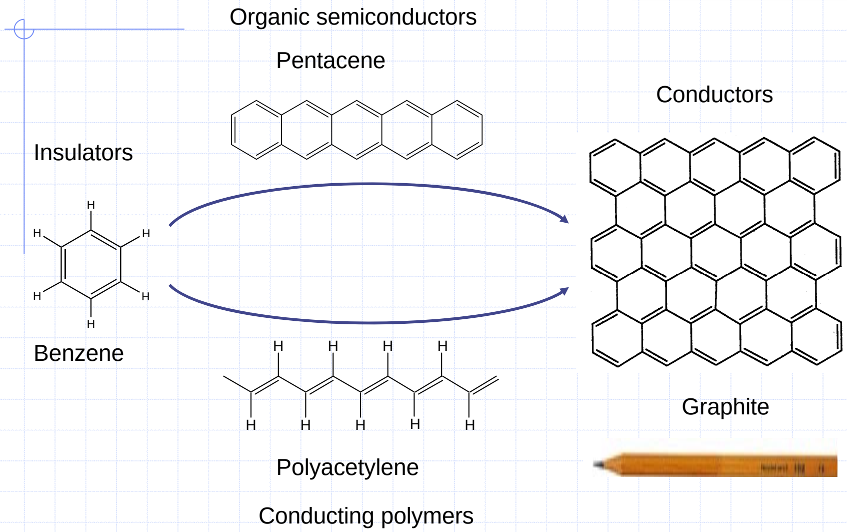
(Honda-Fujishima effect)



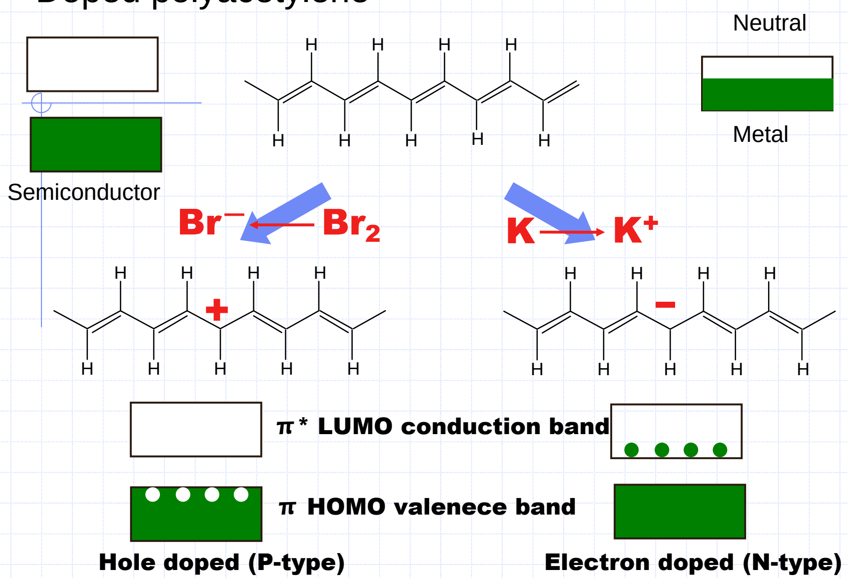




How organic materials conduct electricity?

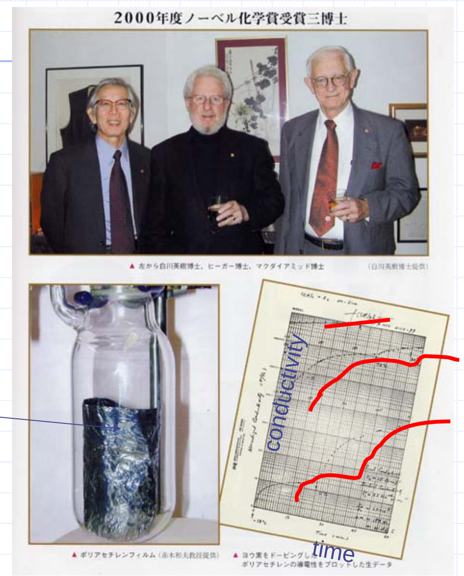


Doped polyacetylene

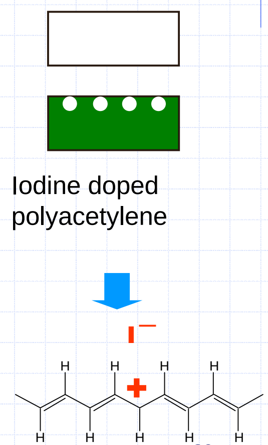


Discovery of conducting polymers

H. Shirakawa
A. J. Heeger
A. G. MacDiarmid
1974～1977

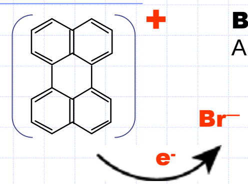


Polyacetylene film

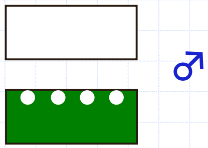


First conducting organics：charge-transfer complex

Perylene

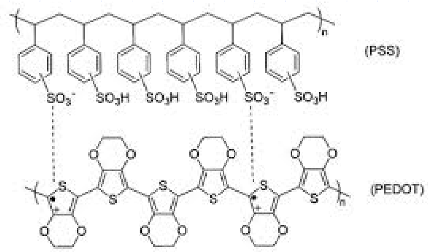


Bromine doped perylene is highly conducting.
Akamatsu, Inokuchi, Matsunaga, *Nature*, 1954.



Polyacetylene → Polythiophene

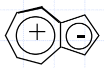
PEDOT:PSS
poly(ethylenedioxythiophene)：polystyrene sulphonate)



Conductivity σ ~ 300 S/cm
S = Ω^{-1} Siemens

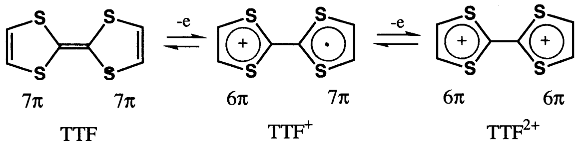
Water solution

Good donors and acceptors



Azulene

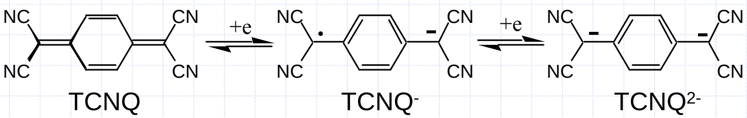
A good donor: Tetrathiafulvalene (TTF)



0.38 V

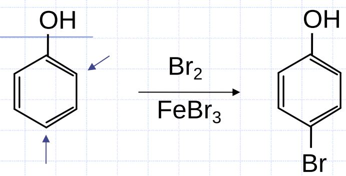
This 7π system easily gives up one electron to form a 6π system.
(C→1π、S→2π)
Electron donating groups such as $-NH_2$, $-OCH_3$ strengthen donor ability.

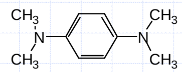
A good acceptor Tetracyanoquionodimethane (TCNQ)



Reduction restores from the quinoid structure to an aromatic 6π system.
− emerges on the foot of two electron withdrawing groups (CN).
Electron withdrawing groups such as -CN、$-NO_2$ strengthen acceptor ability.

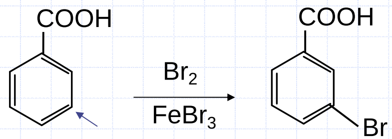
Electron donating：-OH、$-OCH_3$、$-NH_2$ → Electron Donors



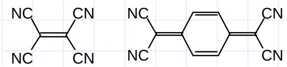


ortho, para

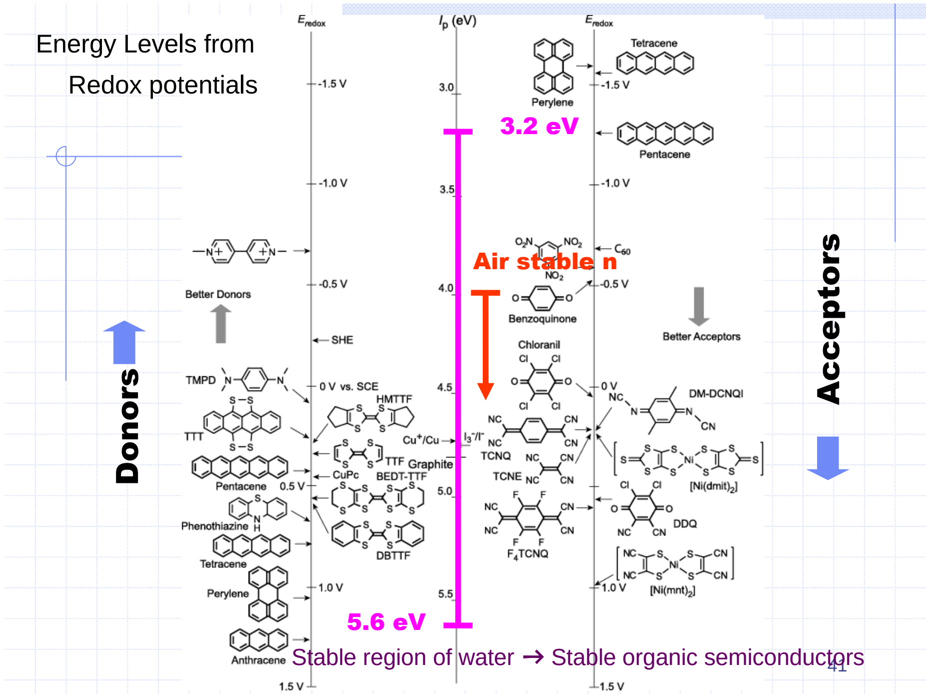
Electron withdrawing：$-NO_2$、-CN、halogene、-COOH、$-COOCH_3$、-CHO



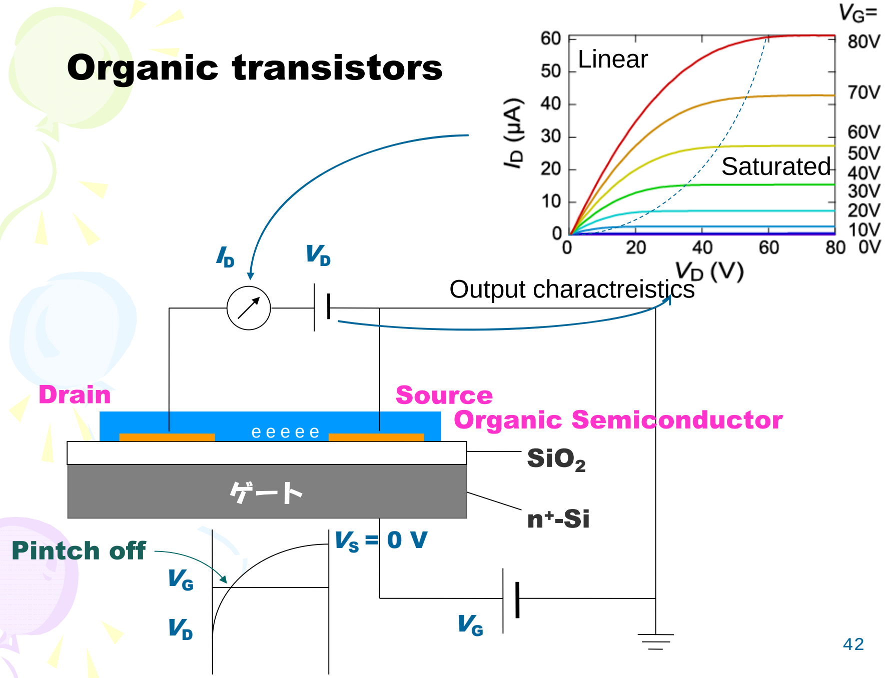
→ Electron Acceptors



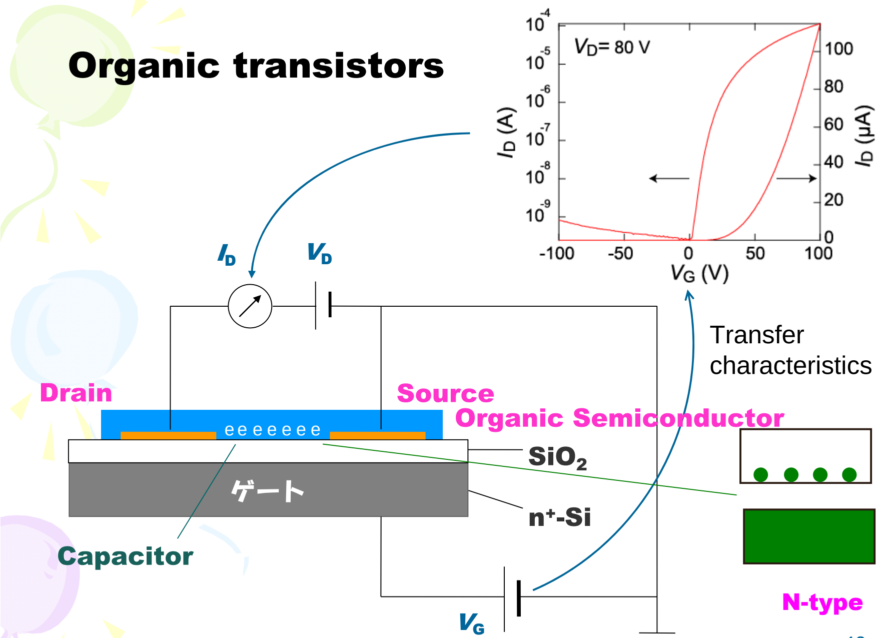
meta



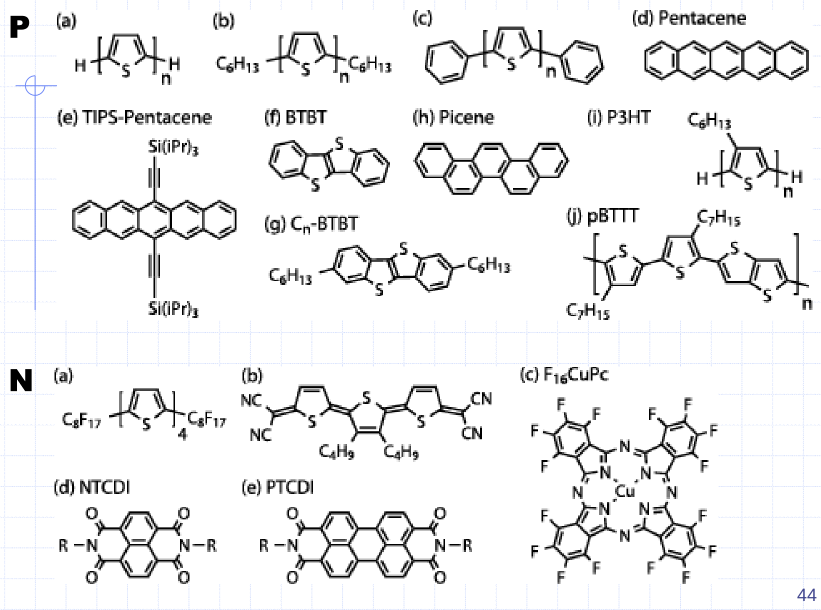
Organic transistors

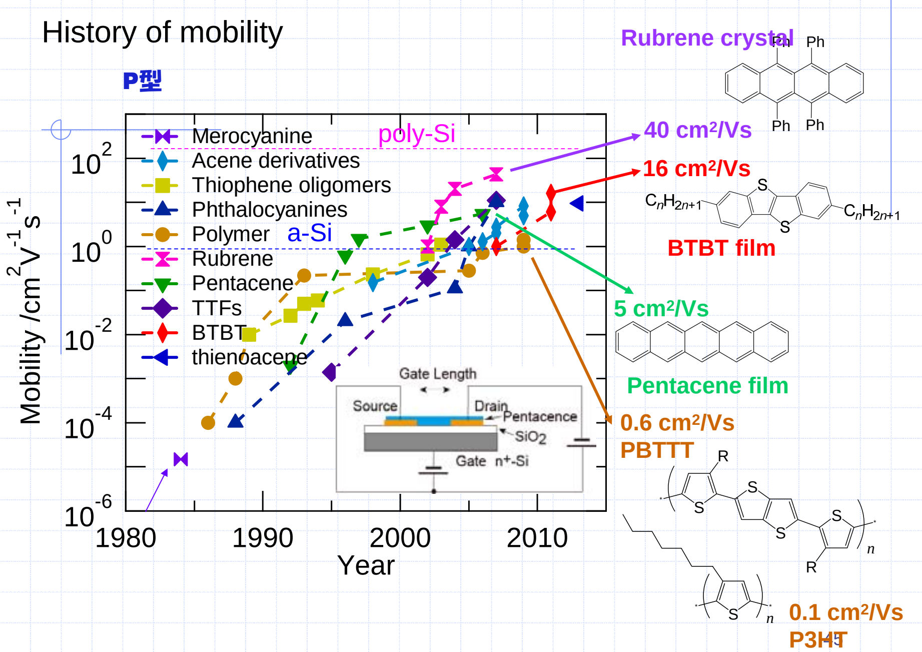


Organic transistors

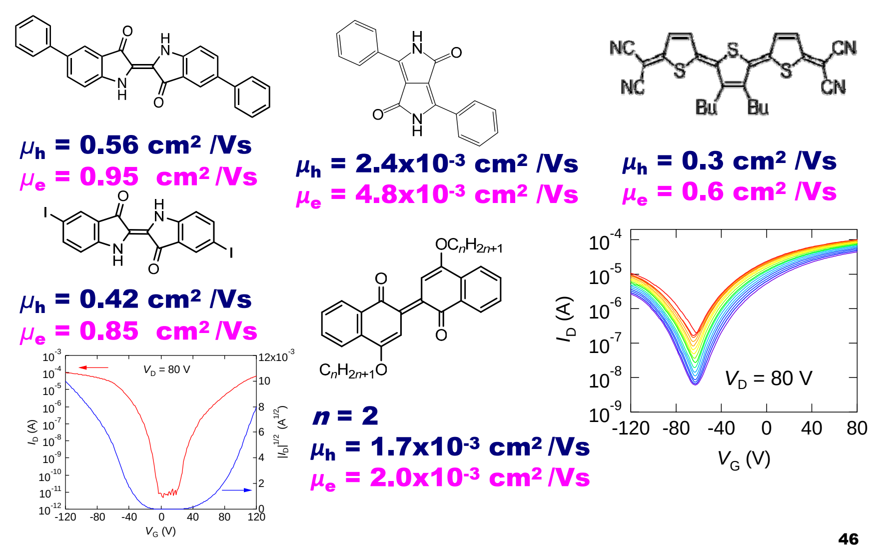


Organic transitor materials

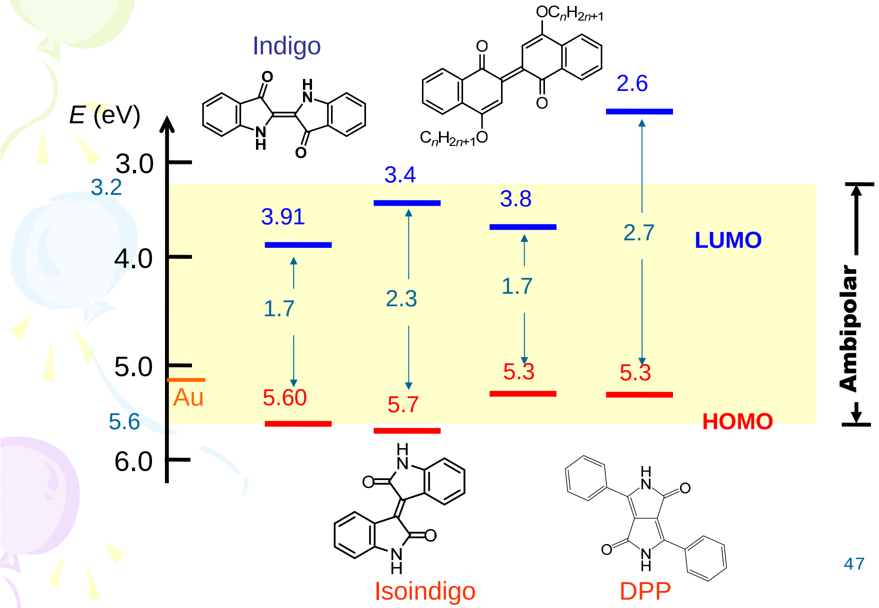




Ambipolar transistors (Both P and N)



HOMO/LUMO Levels

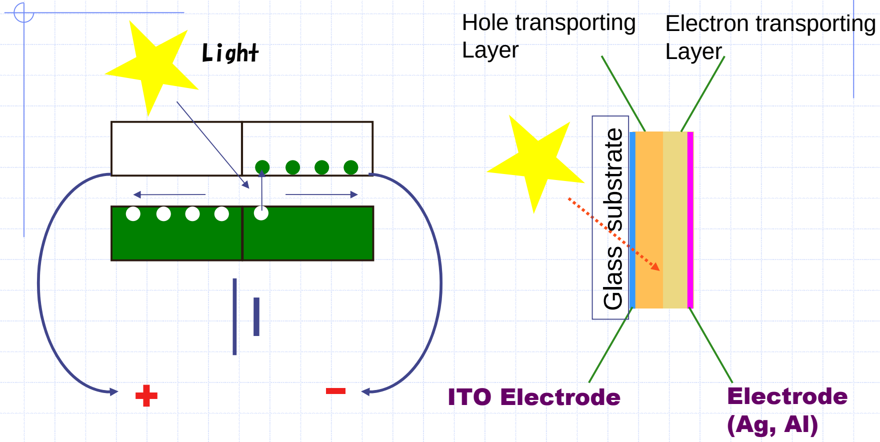


Conductivity $\sigma = \dfrac{ne^2\tau}{m} = ne\mu$ **Mobility**

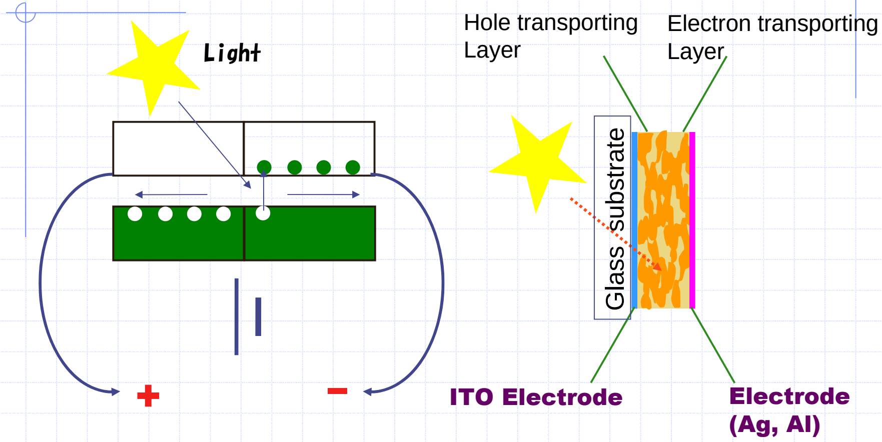
Typical volume of organic molecule : 400 Å³
→ 1 electron / molecule → *n* = 1.25 x 10²¹ cm³

Mobility 1 cm²/Vs → σ = 200 S/cm

Organic solar cells are opposite of organic LED
Electricity ← Light

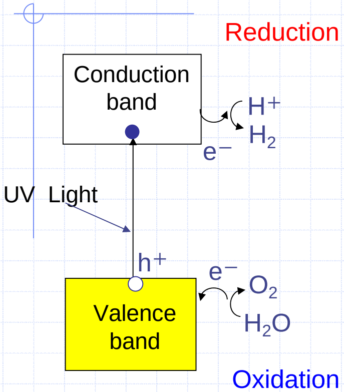


Organic solar cells are opposite of organic LED
Electricity ← Light



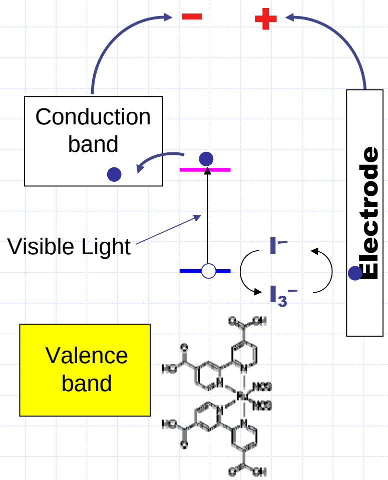
Scramble → Bulk heterojunction
Efficiency～10%

Photocatalyst



TiO_2

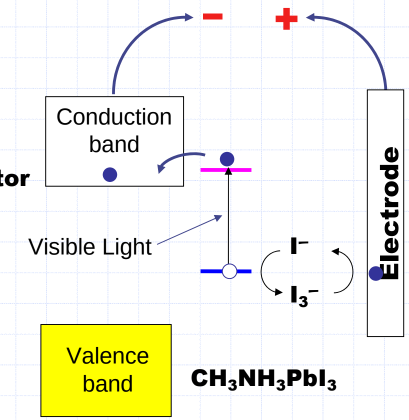
Dye sensitized solar cell



TiO_2 **Dye**
Effeciency 10%+α

Perovskite dye sensitized solar cell

Efficiency
Si film 15%
Si crystal 25%
Compound semiconductor >30%
Organic film 10%
Dye sensitized 10%+α
Perovskite 20%



$CH_3NH_3PbI_3$

TiO_2 **Dye**
Efficiency 20%