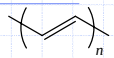
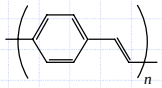
有機伝導体 Organic Conductors

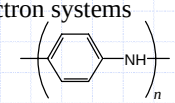
導伝性高分子 :Polymers with conjugated π-electron systems



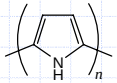
polyacetylene



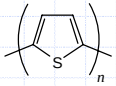
poly(phenylenevinylene)
PPV



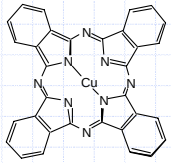
polyaniline



polypyrrole



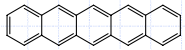
polythiophene



phthalocyanine CuPc

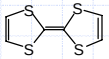
低分子
Small
Molecules

有機半導体
Organic
Semiconductors

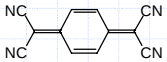


pentacene

電荷移動錯体
Charge-transfer
salts

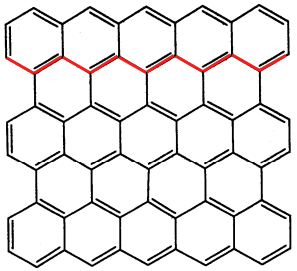


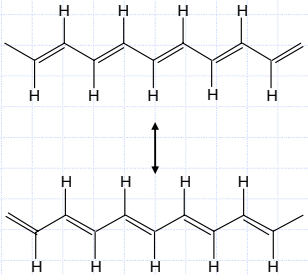
tetrathiafulvalene
TTF



tetracyanoquionodimethane
TCNQ

One chain truncated from graphite (terminated by hydrogenes) → Polyacetylene



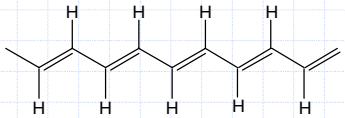


Electrically conducting because the p-electrons can move.

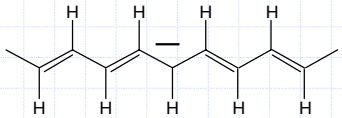
半導体 Semiconductor

白川英樹 H. Shirakawa 2000年 Nobel Prize

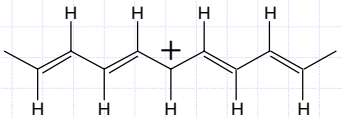
Doped Polyacetylene



K^+



Br^-



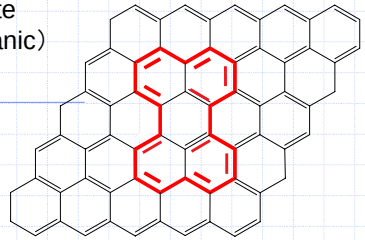
Negative

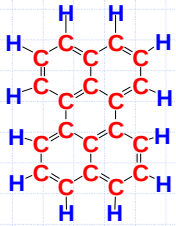
Electron dope (N型)

Positive

Hole dope (P型)

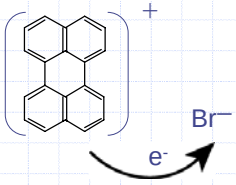
Graphite (Inorganic)





perylene

First Electrically Conducting Organics



電荷移動

Br doped Perylene shows as high electric conductivity as 0.1 Scm^{-1}.
First conducting charge-transfer salt
Akamatsu, Inokuchi, Matsunaga,
Nature, **173**, 168 (1954).

Charge-transfer complex 電荷移動錯体

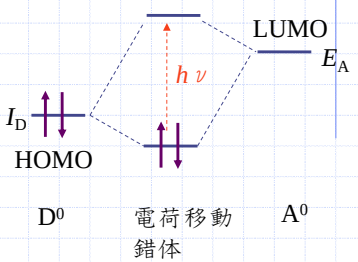
Charge-transfer complex電荷移動錯体

Electron donor 電子供与体

Compounds easily oxidized to $D^0 \rightarrow D^+$ with high HOMO levels

Electron acceptor 電子受容体

Compounds easily reduced to $A^0 \rightarrow A^-$ with low LUMO levels



Completely $D^0A^0 \rightarrow D^+A^-$: Ionic charge-transfer complex

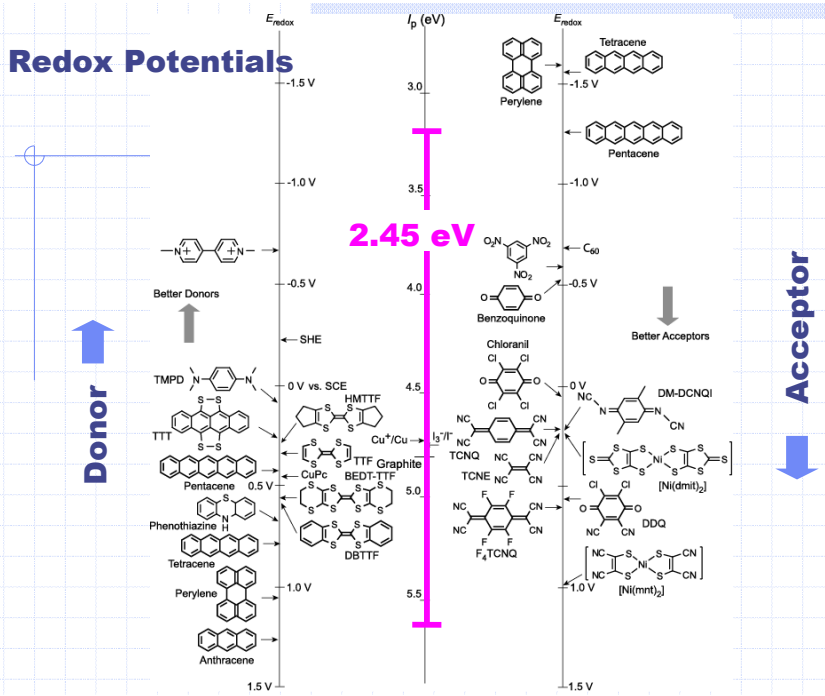
Nearly D^0A^0: Neutral charge-transfer complex

Small (quantum mechanical) mixing of the ionic state

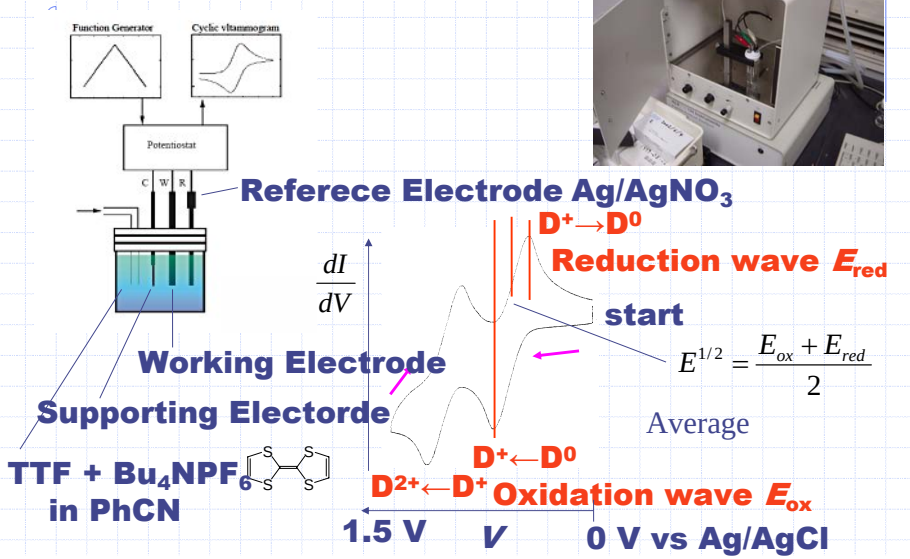
$$\phi = \phi(D^0A^0) + c\,\phi(D^+A^-)$$

and the excitation corresponding to $D^0A^0 \rightarrow D^+A^-$ gives rise to charge-transfer absorption 電荷移動吸収 (visible to infrared)

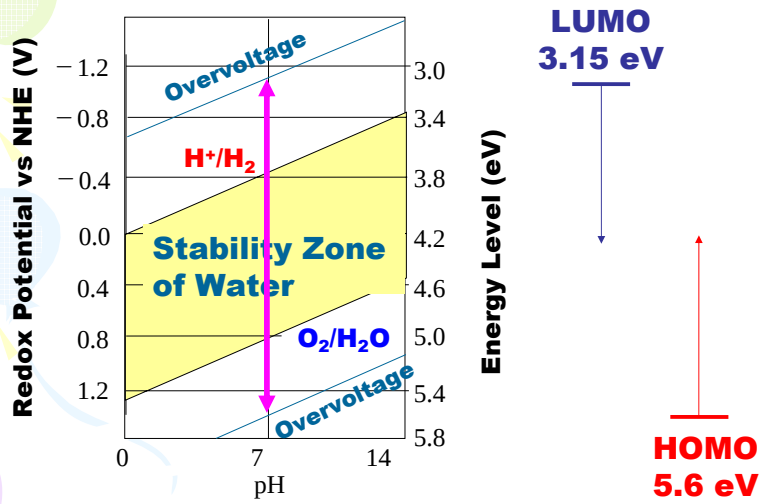
Redox Potentials



Cyclic voltammetry
Electrochemical Redox Potential



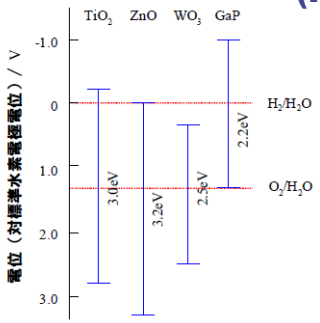
Stability Zone of Water

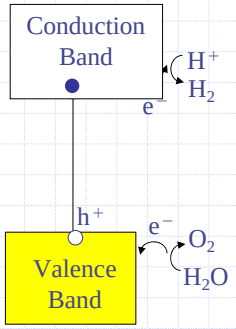


Schriver, Atkins, Inorganic Chemistry

Photocatalyst

(Honda·Fujishima Effect)





Reduction

Oxidation

Electrochemical Redox Potential (cyclic voltammetry)
Standard Calomer Electrode Hg_2Cl_2 vs. SCE = 0.24 V NHE
vs. Ag/AgCl = 0.22 V NHE
Ferrocene＝0.38 V vs. SCE
Energy Level ＝ E_{redox}(vs. SCE) + 4.4 V
＝ E_{redox}(vs. Ferrocene) + 4.8 V

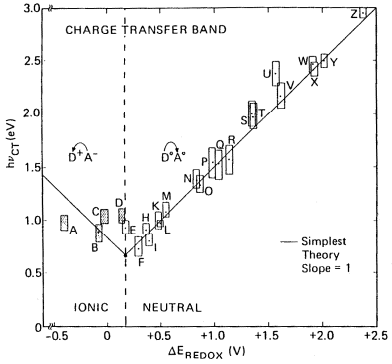
森 分子エレクトロニクスの基礎 p322

(Mixing solutions of colorless neutral donor and acceptor gives an orange to yellow solution.)

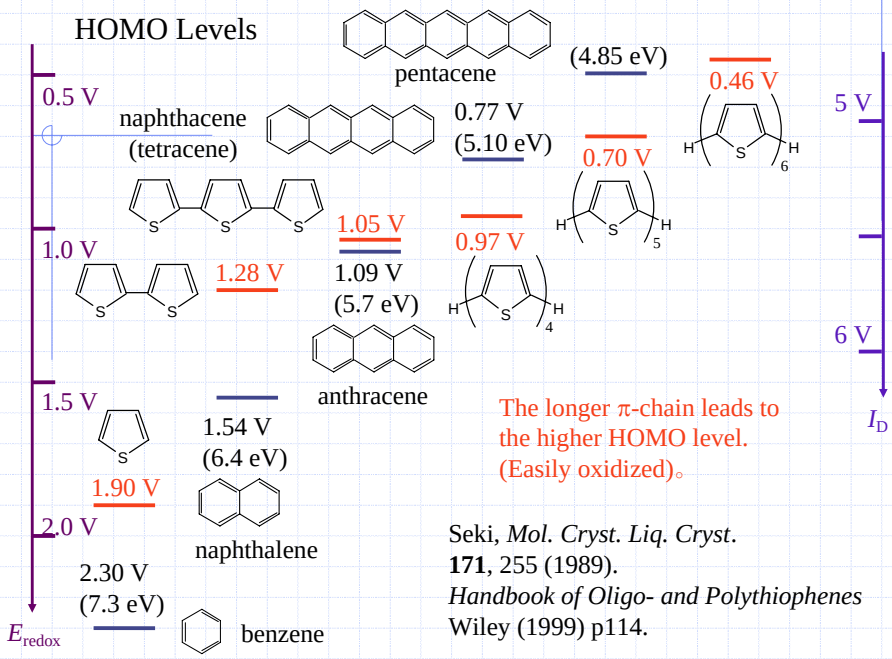
$h\nu = I_D - E_A - E(D^+A^-)$

I_D ：Ionization energy of the donor
E_A ：electron affinity od the acceptor
$E(D^+A^-)$ ： Coulomb attraction of D^+ and A^- (Madelung energy)

$h\nu = I_D - E_A - E(D^+A^-) \sim E_{redox}(HOMO) - E_{redox}(LUMO)$



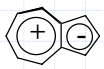
HOMO Levels



The longer π-chain leads to the higher HOMO level. (Easily oxidized)。

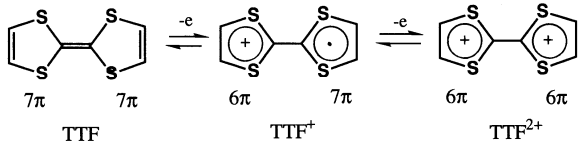
Seki, *Mol. Cryst. Liq. Cryst.* **171**, 255 (1989).
Handbook of Oligo- and Polythiophenes Wiley (1999) p114.

Good donors and acceptors



Azulene

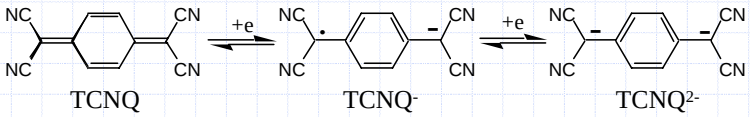
A good donor: Tetrathiafulvalene (TTF)



0.38 V

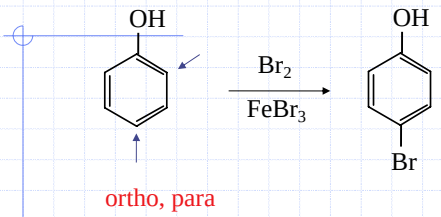
This 7 π system easily gives up one electron to form a 6 π system.
(C→1 π 、S→2 π)
Electron donating groups such as $-NH_2$, $-OCH_3$ strengthen donor ability.

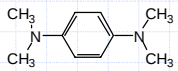
A good acceptor Tetracyanoquionodimethane (TCNQ)



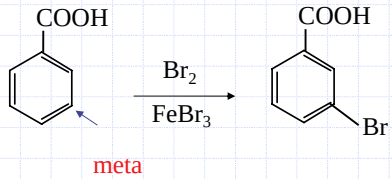
Reduction restores from the quinoid structure to an aromatic 6 π system.
－ emerges on the foot of two electron withdrawing groups (CN).
Electron withdrawing groups such as -CN、$-NO_2$ strengthen acceptor ability.

Electron donating：-OH、-OCH_3、-NH_2 → Electron Dnor

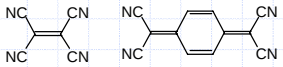


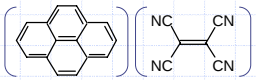


Electron withdrawing：-NO_2、-CN、Halogen、-COOH、-$COOCH_3$、-CHO



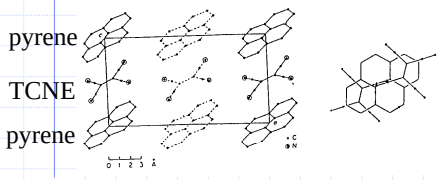
→ Electron Acceptor





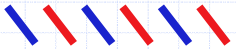
pyrene　tetracyanoethylene TCNE

Mixed stack in a neutral complex



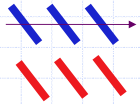
Mixed stack structure

Neutral and ionic：low conducting



Segregate stack structure

Partial charge transfer：high conducting

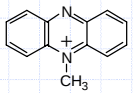


High conducting

// stack

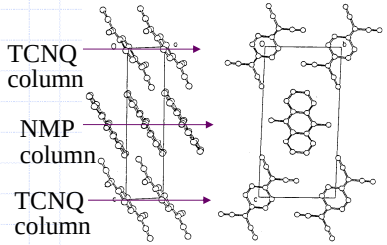
(NMP)(TCNQ)：first 「Organic Metal」1966

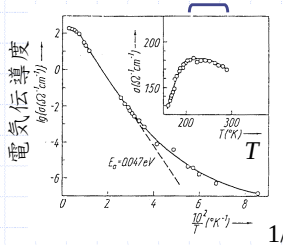
Metal at 200 K～rt



N-methylphenazinium (NMP)

Segregated

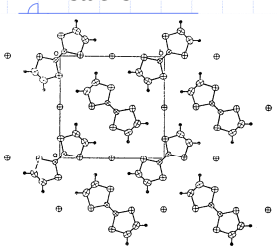




(TTF)X_x：Typical 1D Metal　(X＝Cl, Br, I, SCN, x～0.71)

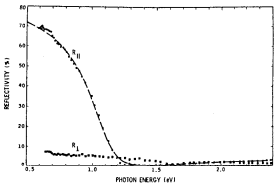
Peierls transition ← non magnetic insulator below 200 K

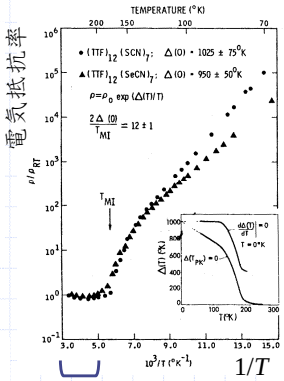
1D stacks



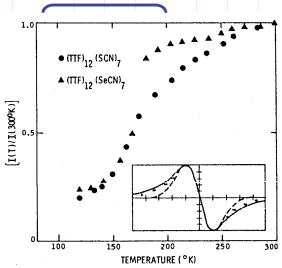
反射率：

Strongly 1D

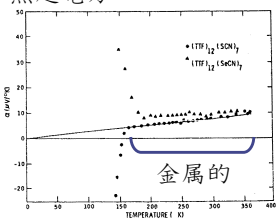




Metallic above 200 K



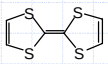
熱起電力



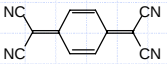
(TTF)(TCNQ)

1973

$(TTF^{0.59+})(TCNQ^{0.59-})$



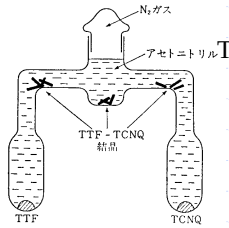
tetrathiafulvalene TTF



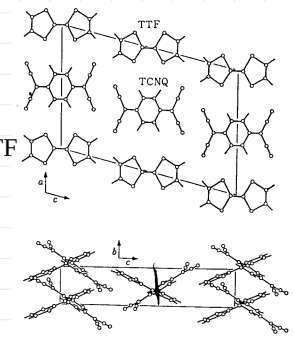
tetracyanoquionodimethane TCNQ

拡散法結晶成長

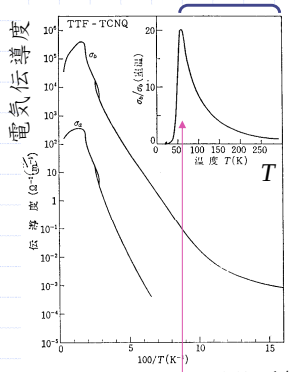
From acetonitril solutions of TTF and TCNQ



分離積層型



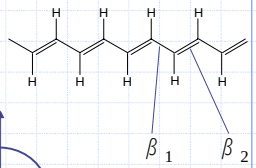
Metal at 54 K～rt

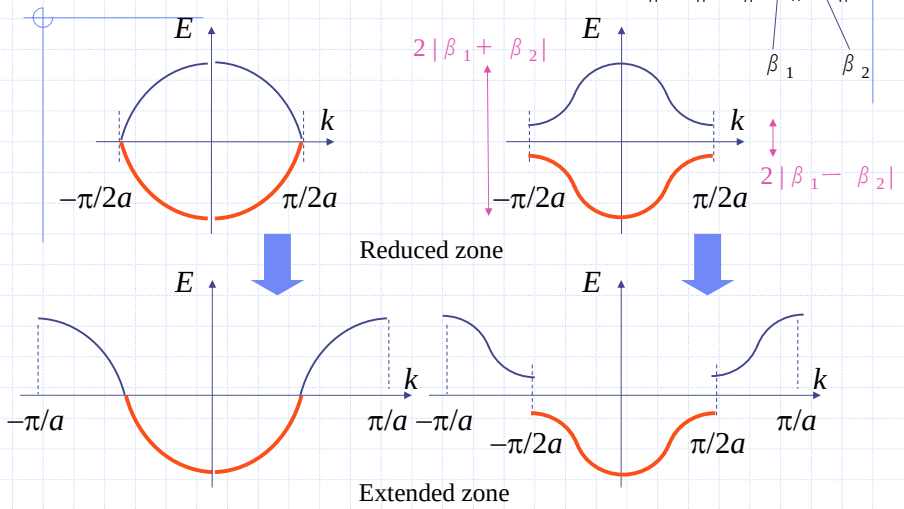


TTF - TCNQ の直流電気伝導度の温度依存性

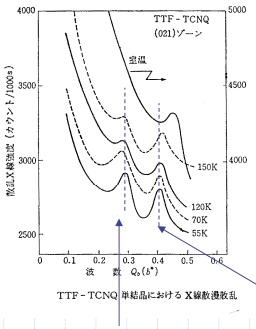
Metal-insulator transition at 54 K

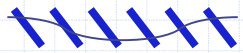
Different β for single and double bonds





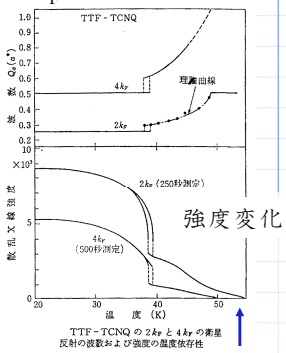
(TTF)(TCNQ)





Charge has periodicity with wavelength $1/2k_F$
(電荷密度波)
Charge density wave (CDW)

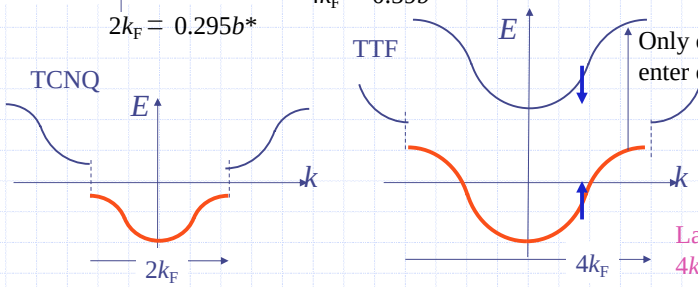
k_F：若干温度変化



54 K

$2k_F = 0.295b^*$

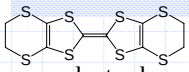
$4k_F = 0.59b^*$



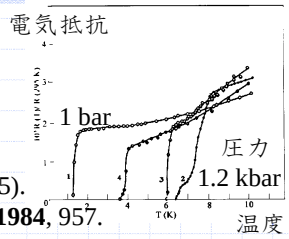
Only one electron can enter owing to U.

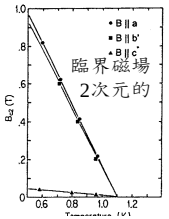
Lattice periodicity: $4k_F$

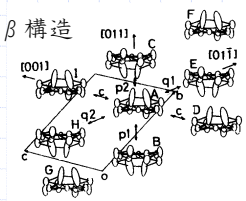
β-(BEDT-TTF)$_2$I$_3$

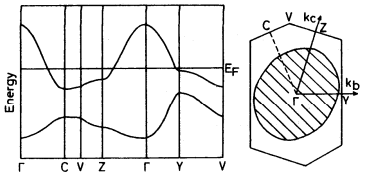


First ambient pressure superconductor based on BEDT-TTF (T_c=1.5 K)。
Yagubskii et al. *JETP Lett.* 39, 12 (1984).
Small pressure increases T_c to 8 K. Murata *JPSJ* **54**, 1236 (1985). Laukhin *JETP Lett.* **41**, 81 (1985).
First 2D close Fermi surface: Mori et al. *Chem. Lett.* **1984**, 957.





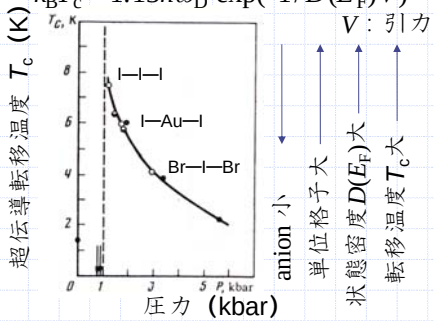




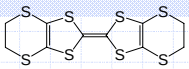
Linear anions AuI_2, IBr_2 other than I_3 make β 型超伝導体 (I_2Br: asymmetry → ×)

$$k_B T_c = 1.13 h\omega_D \exp(-1/D(E_F)V)$$

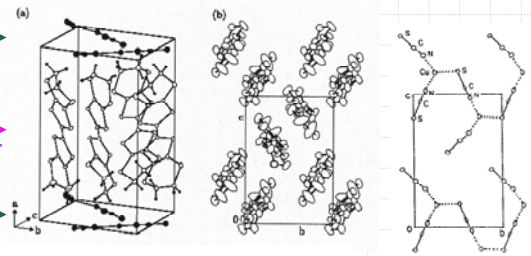
V：引力



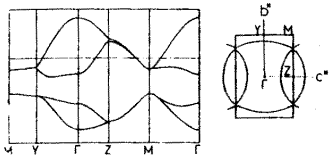
κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

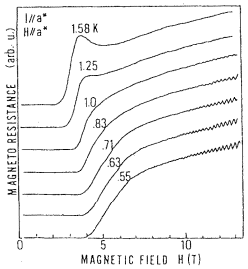


First organic superconductor with exceeding T_c= 10 K (T_c=10.4 K)
Urayama et al. *Chem. Lett.* **1988**, 55; **1988**, 463.



Ideal 2D system





Closed 2D Fermi surface was firstly proved from the observation of Shubnikov de-Haas oscillation.
Oshima et al. *Phy. Rev.* B **38**, 938 (1988).

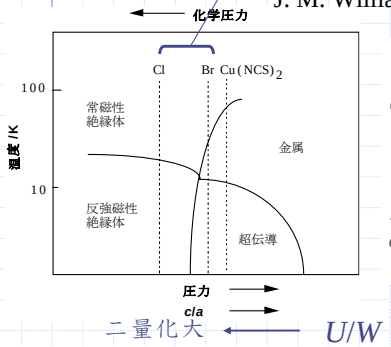
κ 相統一的相図(鹿野田diagram)

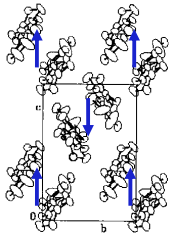
K. Kanoda, *Hyperfine Interact*. **104**, 235 (1997).

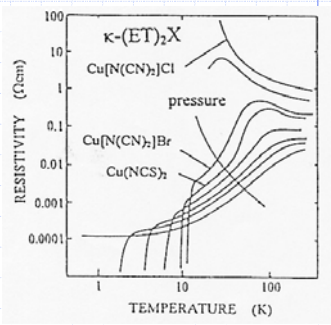
κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br T_c=11.6 K

κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl T_c=12.8 K (0.3 kbar)

J. M. Williams et al. *Inog. Chem*. **29**, 3; **29**, 2555(1990).

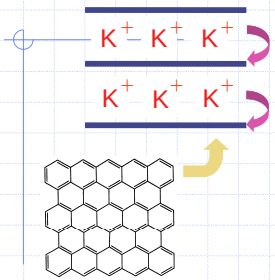




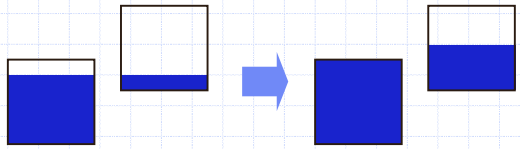


Insulating phase of the κ-phase is a Mott (antiferromagnetic at LT) insulating phase because strong dimerization makes the 1/4-filled band to effectively half filled. Superconductivity appears close to the Mott insulating phase similarly to the copper oxides, suggesting Cooper pair formation related to antiferromagnetic correlation.

Graphite 層間化合物



Increase the conductivity



ドープ

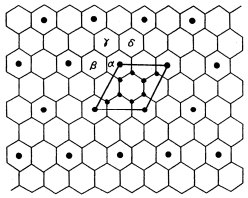


図6 グラファイト・カリウム C_8K 中のカリウム原子(●印)の配置

C_8K

Superconducting at very low T

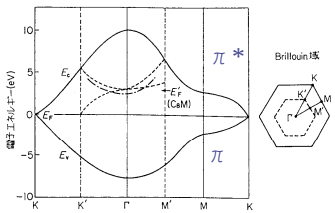
C_8K T_c = 0.39-0.55 K

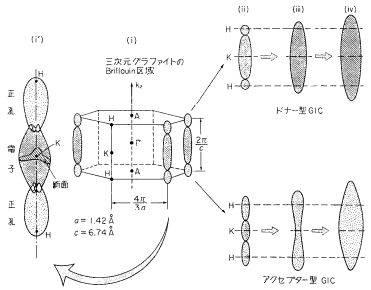
C_8Rb T_c = 0.03-0.15 K

C_8Cs T_c = 0.02-0.14 K

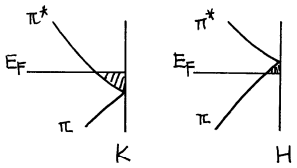
Energy band of graphite

2次元半金属



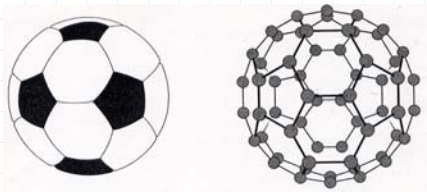


グラファイトの Fermi 面と GIC への拡張

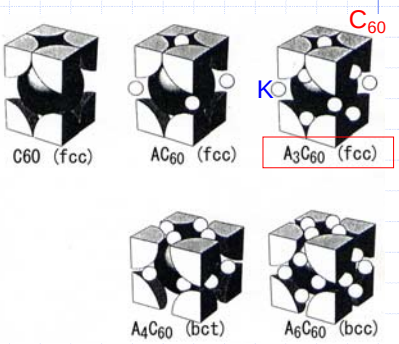


3次元的分子性超伝導体：K_3C_{60}

Fullerene

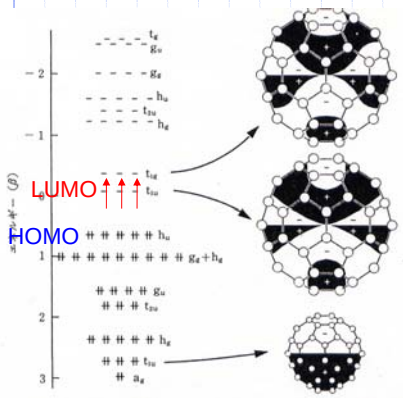


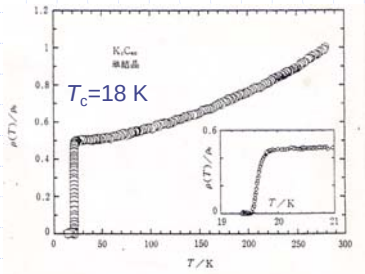
C_{60}



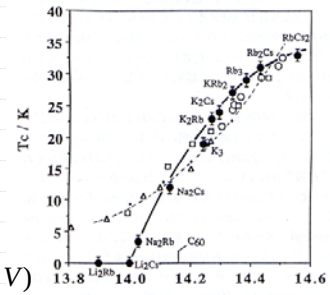
Buckminster Fuller制作Dome

K_3C_{60}分子軌道&超伝導





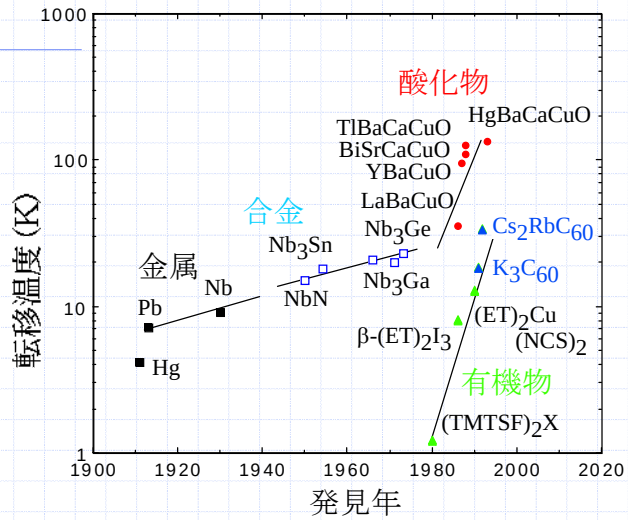
cf. Tc=33K (Cs_2RbC_{60})



弱結合BCS

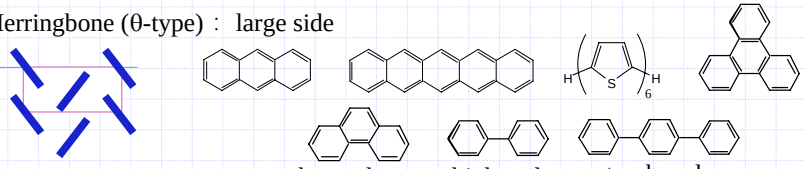
$$k_B T_c = 1.13 h\omega_D \exp(-1/D(E_F)V)$$

超伝導物質の転移温度と発見年



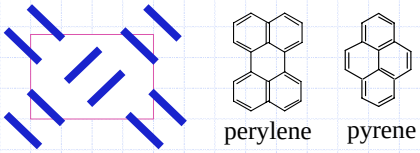
Structures of Organic Semiconductors *Acta Crystallogr*. B **45**, 473 (1989).

Herringbone (θ-type)： large side



phenanthrene　biphenyl　terphenyl

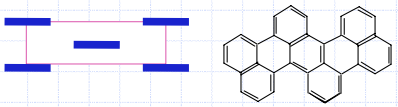
Dimer (κ-type)： intermediate

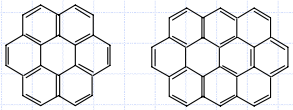


perylene　pyrene

γ-構造(θ-type)： large plane

Stack (β-type)： large plane





coronene　ovalene

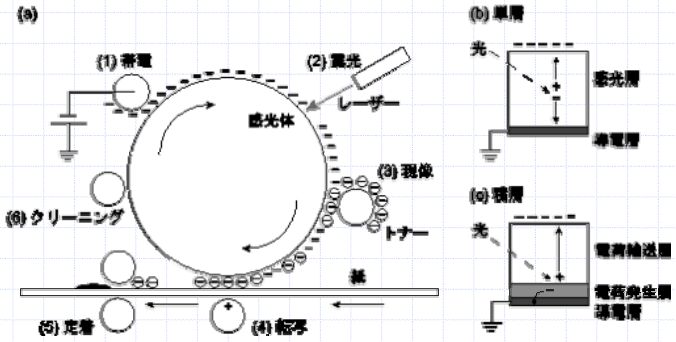
Large plane reduce the tilting angle.

Organic Semiconductors

Photoconductivity

Electrophotography　C. F. Carlson (1938)

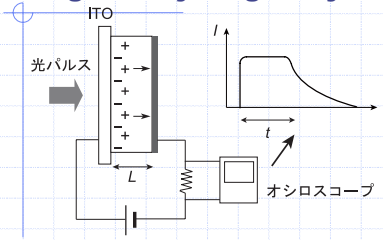
Copy, Laser Printer



Photoconductivity

Time of Flight (TOF)

High Purity Single Crystals



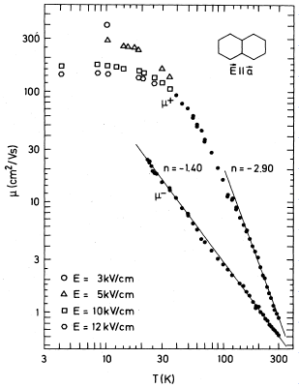


Table TOF Mobility Anisotropy (cm²/Vs)

	Hole *a*/*b*/*c*	Electron *a*/*b*/*c*
Naphthalene	0.94/1.48/0.32	0.62/0.64/0.44
Anthlacene	1.13/2.07/0.73	1.73/1.05/0.39
Perylene	Activated	2.37/5.53/0.78
Terphenyl	0.6/-/0.80	0.34/1.2/0.25

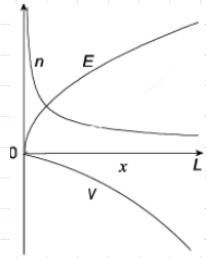
N. Karl, *Landort-Börnstein Numerical Data and Functional Relationships in Science and Technology*, New Series Group III 17a-i (1985).

Space-Charge-Limited Current (SCLC)

Carrier injection to an insulating material

$J = en\mu E$ ➡ $\frac{\partial E}{\partial x} = \frac{en}{\varepsilon} = \frac{J}{\varepsilon\mu E}$

Integrate ➡ $E = \left(\frac{2J}{\varepsilon\mu}\right)^{1/2} x^{1/2}$



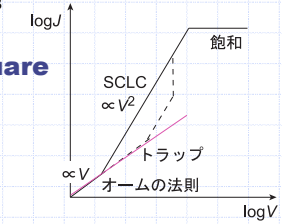
***n* is assumulated around the electrode** $x = 0$

***E* is steep around** $x = 0$

Integrate up to *L* with respect to *x*, to give *V*

$$V = \int_0^L E dx = \left(\frac{8J}{9\varepsilon\mu}\right)^{1/2} L^{3/2} \Rightarrow J = \frac{9}{8}\varepsilon\mu\frac{V^2}{L^3}$$

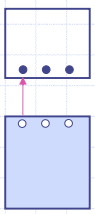
Current is proportional to voltage square
non Ohmic
Mobility μ is obtained

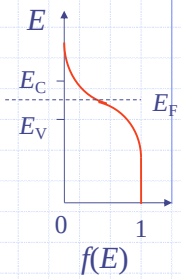


Because $E_C - E_F >> k_B T$,
the Fermi distribution reduces to

$$f(E) = \frac{1}{e^{\frac{E_i-\mu}{k_B T}} + 1} \rightarrow e^{-\frac{E_i-\mu}{k_B T}}$$

the Boltzmann distribution.





Electron number

$$N_e = \int D(E) f(E) dE = N_e^0 e^{-\frac{E_C - E_F}{k_B T}}$$

Hole number

$$N_p = N_p^0 e^{\frac{E_V - E_F}{k_B T}}$$

lead to

$$N_e \cdot N_p = N_e^0 N_p^0 e^{\frac{E_V - E_F}{k_B T} - \frac{E_C - E_F}{k_B T}} = N_e^0 N_p^0 e^{-\frac{E_g}{k_B T}}$$

$E_g = E_C - E_V$

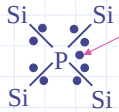
At given T and E_g, a decrease of hole # pushes up E_F, and increases electron #.
$N_e = N_p$ in the intrinsic semiconductor, so if $N_e^0 = N_p^0$
(the same electron and hole mass)

$$E_F - E_V = E_C - E_F \rightarrow E_F = \left(\frac{E_C + E_V}{2}\right)$$

Fermi level is located at the center of the energy gap.

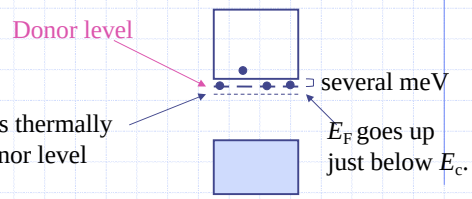
Doping

Impurity P, As in Si
5 electrons : donor



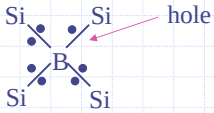
Extra one electron is thermally excited from the donor level and moves around.
→ to increase σ by several orders.

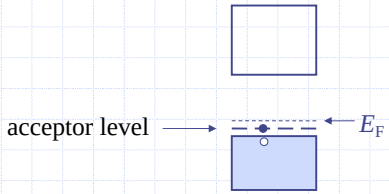
Majority carrier $N_e >> N_p$ minority carrier



N型半導体
Negative

Impurity B, Al in
3 electrons : acceptor

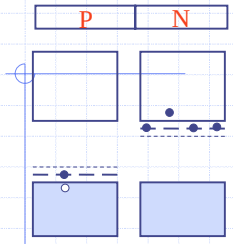




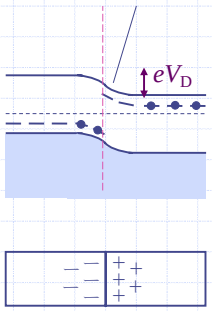
Majority carrier $N_p >> N_e$ minority carrier

P型半導体
Positive

PN junction



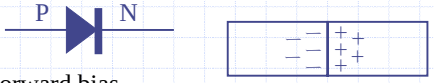
Majority carrier is depleted around the junction to have net positive charge. → 欠乏層 (Depletion Layer)



Junction polarizes so as to have opposite charges to the majority carriers.

Most resistance come from the depleted junction.

Potential surface bends so as to make E_F = const.



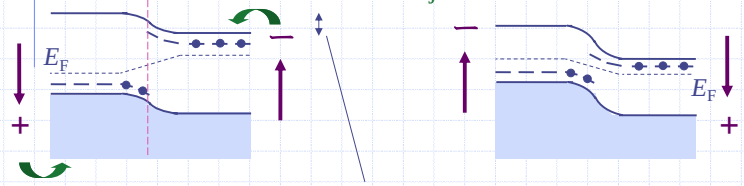
Forward bias

Reverse bias

+− attraction leads to current flow

No current flows

電子注入 electron injection



ホール注入
hole injection

Potential is lowered to V_D-V.

Majority carrier in N $\quad N_e = N_e^0 e^{-\frac{E_C - E_F}{k_B T}}$

Minority carrier in P $\quad N_e' = N_e^0 e^{-\frac{E_C - E_F + eV_D}{k_B T}} \rightarrow N_e' = N_e e^{-\frac{eV_D}{k_B T}}$

Under bias V, this leads to $\quad N_e' = N_e e^{-\frac{e(V_D - V)}{k_B T}}$

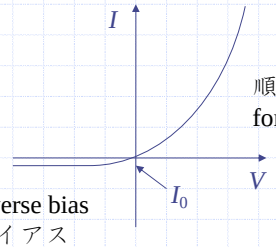
Majority carrier transport from N to P (electron diffusion current) $\propto N_e$

Minority carrier transport from P to N (electron generation current) $\propto N_e'$

Total current $I \propto N_e' - N_e = I_0 (e^{eV/k_B V} - 1)$

(The same equation for holes)

($I_0 = N_e e^{-eV_D/k_B T}$ does not depend on V.)



順方向
forward bias

reverse bias
バイアス

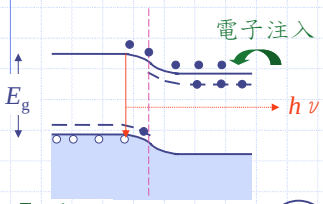
Current flows only for forward bias。(Diode)

Diodes for specialized uses

Light Emitting Diode

Recombination of injected carriers at forward bias generates light.

電子注入 electron injection



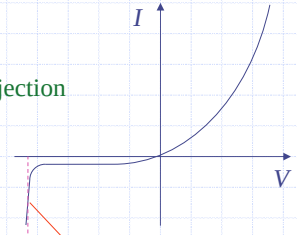
ホール注入
hole injection

EL：Electroluminescence

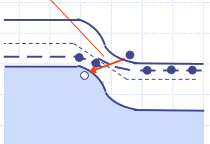
$h\nu$ depends on E_g.

Zener Diode

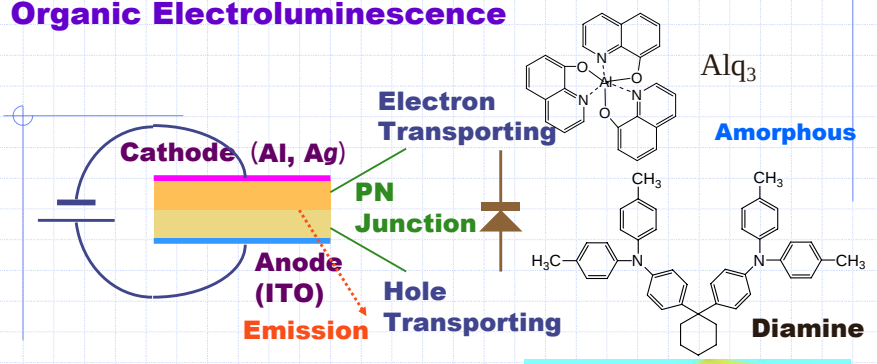
Standard voltage at the reverse bias.

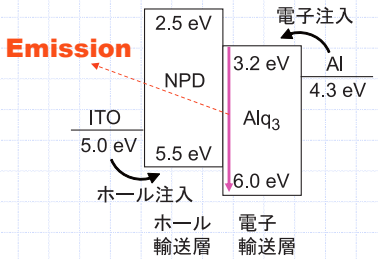


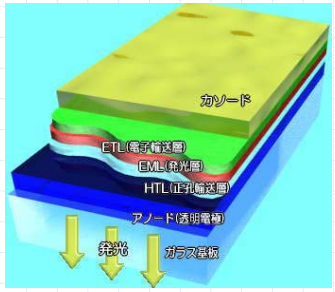
Zener Breakdown



Organic Electroluminescence

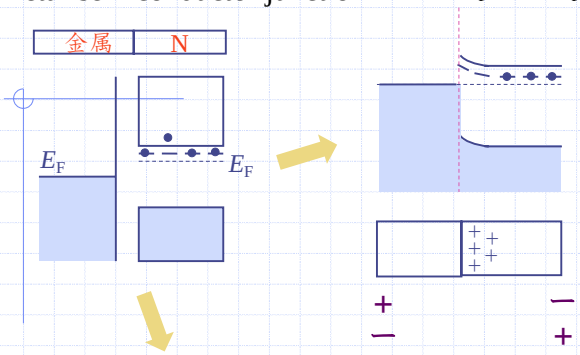






Metal-semiconductor junction

Metal E_F < E_F in N型半導体



Adjust E_F

Depletion layer

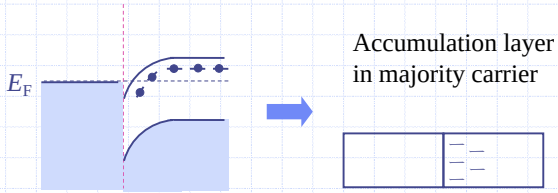
Shottokey Diode

Forward

Reverse

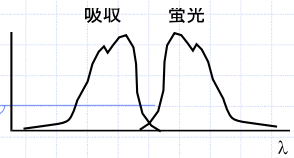
Shottokey Barrier

Meta E_F > E_F in N型半導体：Ohmic contact



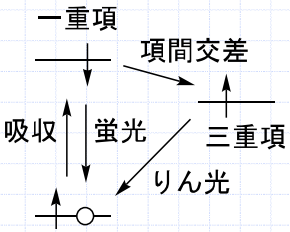
Accumulation layer in majority carrier

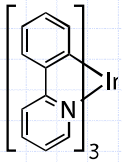
Current flow for both biases.



Fluorescence Quantum Yield

Benzene	0.07	Naphthalene	0.23	Anthracene	0.36
Tetracene	0.21	Pylene	0.65	Perylene	0.94
Rubrene	~1.0	Fluorene	0.80		
biphenyl	0.18	Terphenyl	0.93	PPV	0.08
TPD	0.35	Alq_3	0.25	Sexithiophene	0.40





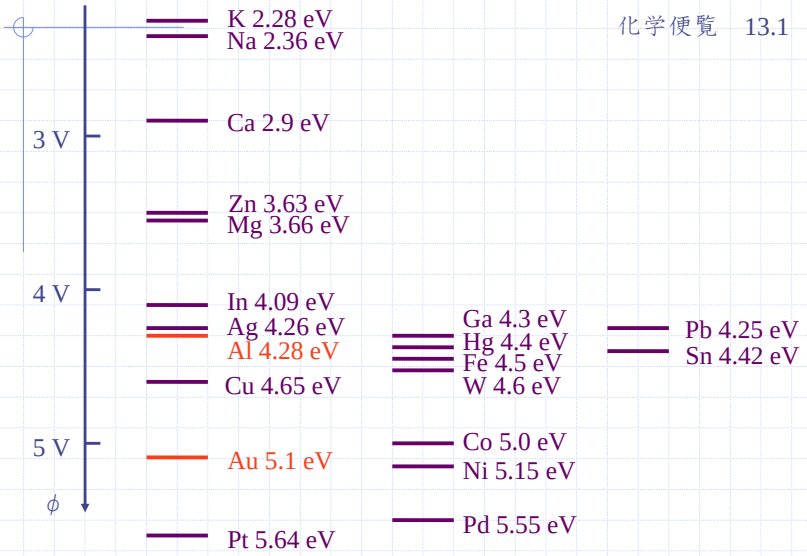
Fluorescence from singlet 25%

Phosphorescence from triplet 75%

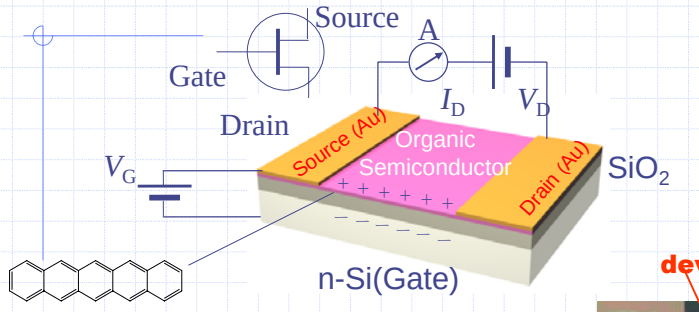
Work function of Metals (Position of E_F)

cf. Ionization potential for semiconductors

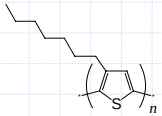
化学便覧 13.1



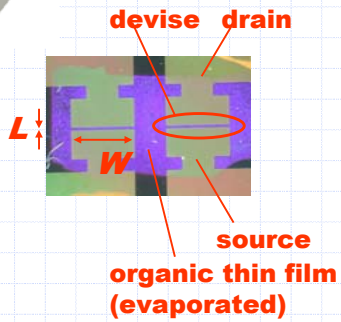
Organic Transistors



Pentacene



Polythiophene
(P3HT)



Organic Transistors
(Gradual Channel Approximation)

Charge on the semiconductor

$Q = C(V_G - V_T)$

$V(x)$ **depends on** x

$Q(x) = C(V_G - V_T - V(x))$

ne **corresponds to** $Q(x)$ **in** $\sigma = ne\mu$

Electric filed is $E_x = -dV(x)/dx$

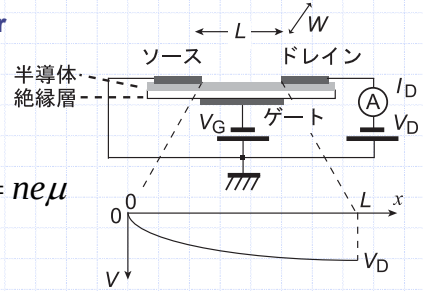
$I_D = WQ(x)\mu(-dV(x)/dx)$

Inserting $Q(x)$ **and integrate**

$$\int_0^L I_D dx = \int_0^{V_D} WC\mu(V_G - V_T - V(x))dV$$

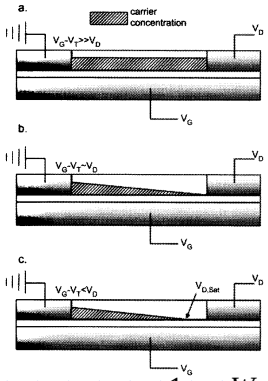
I_D **is constant**

$$I_D = C\mu\frac{W}{L}[(V_G - V_T)V_D - \frac{1}{2}V_D^2]$$



Thin-Film Transistors

$$I_D = \frac{W\mu C}{L}((V_G - V_T)V_D - \frac{1}{2}V_D^2)$$



Linear

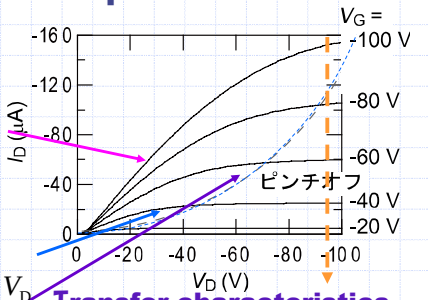
Pinch off

$V_G - V_T = V_D$

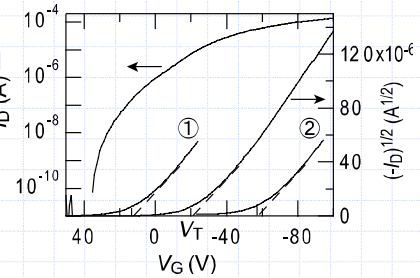
Saturated

$$I_D = \frac{1}{2}C\mu\frac{W}{L}(V_G - V_T)^2$$

Output characteristics

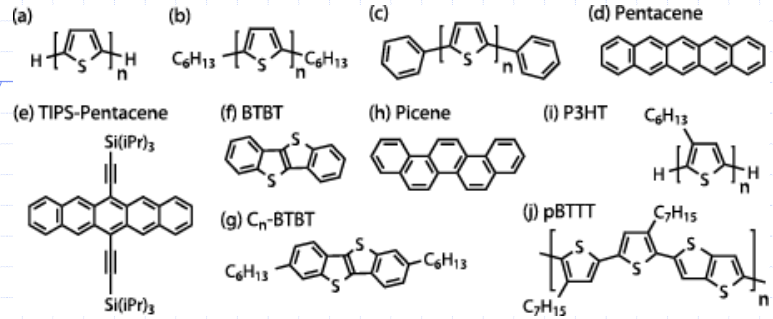


Transfer characteristics

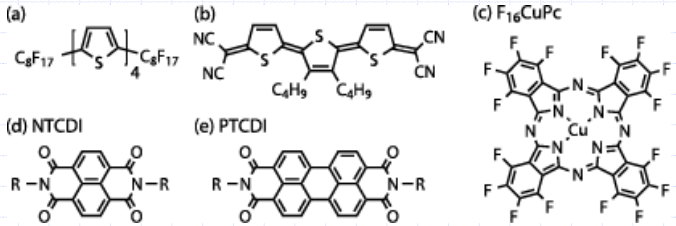


Organic Transistor Materials

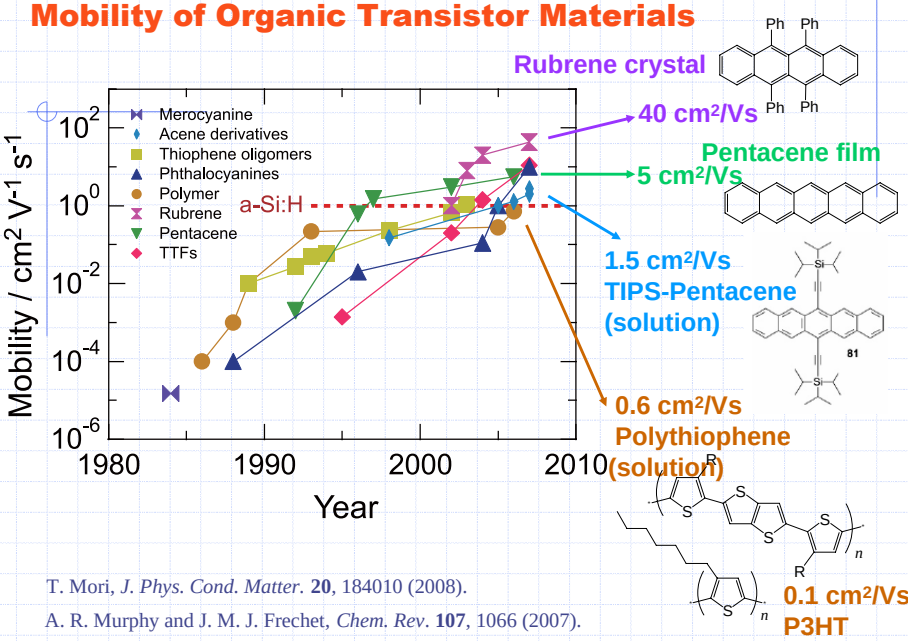
P



N



Mobility of Organic Transistor Materials

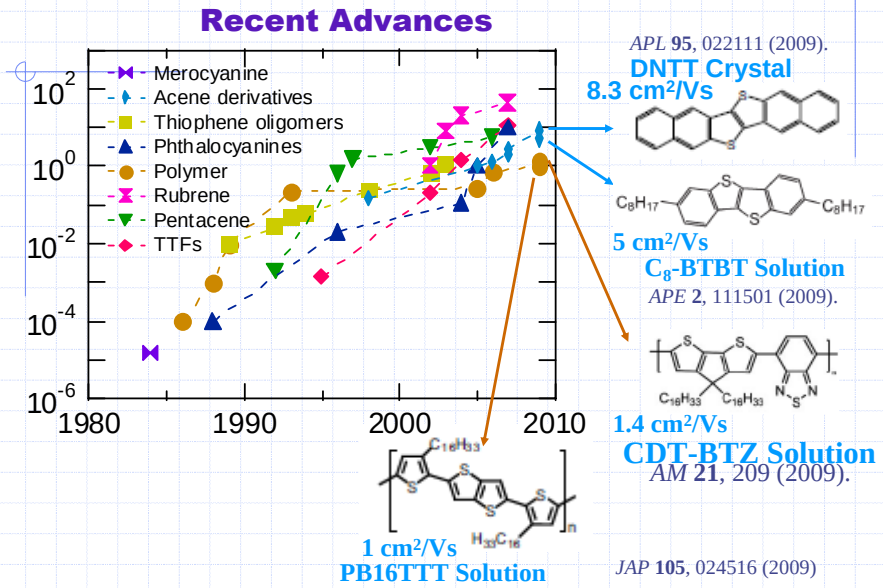


T. Mori, *J. Phys. Cond. Matter.* **20**, 184010 (2008).

A. R. Murphy and J. M. J. Frechet, *Chem. Rev.* **107**, 1066 (2007).

Mobility of Organic Transistor Materials

Recent Advances



Organic Electroluminescence Display

SONY

SONY 11-inch 2007

Mobile

Car Autdio

Light emitting
→ High Contrast

1987 Kodak Tang

Organic Transistors

(1) Flexible Displays
→ Electric Paper

NHK

SONY

(2) Flexible Scanner

(3) Flexible Sensor

Artificial Skin

Organic Transistors

(4) Low Cost → RF ID Tags

Print Electronics

← **Inkjet Printing**

Large Area
Flexible
Low Cost

→

"Painted" IC