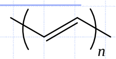
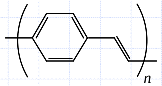
有機伝導体 Organic Conductors

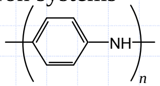
導伝性高分子：Polymers with conjugated π-electron systems



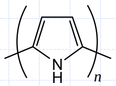
polyacetylene



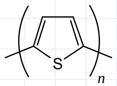
poly(phenylenevinylene)
PPV



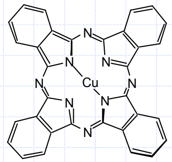
polyaniline



polypyrrole

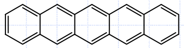


polythiophene



低分子
Small
Molecules

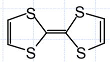
有機半導体
Organic
Semiconductors



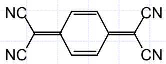
pentacene

phthalocyanine CuPc

電荷移動錯体
Charge-transfer
salts

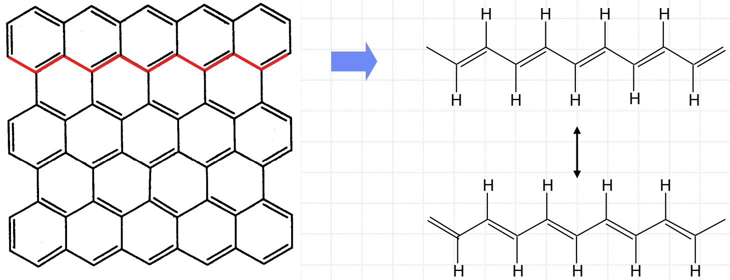


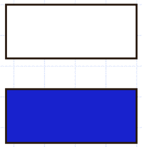
tetrathiafulvalene
TTF



tetracyanoquionodimethane
TCNQ

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





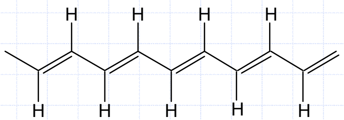
Electrically conducting because
the p-electrons can move.

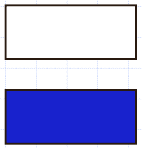
半導体
Semiconductor

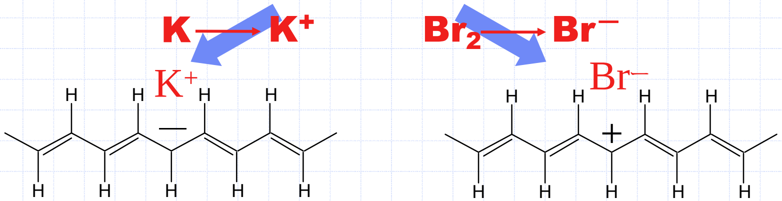
白川英樹　2000年 Nobel Prize
H. Shirakawa

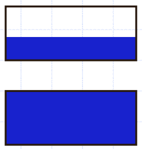
Doped Polyacetylene

10^{-5} S/cm

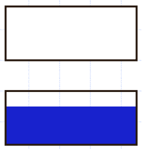








300 S/cm



Negative

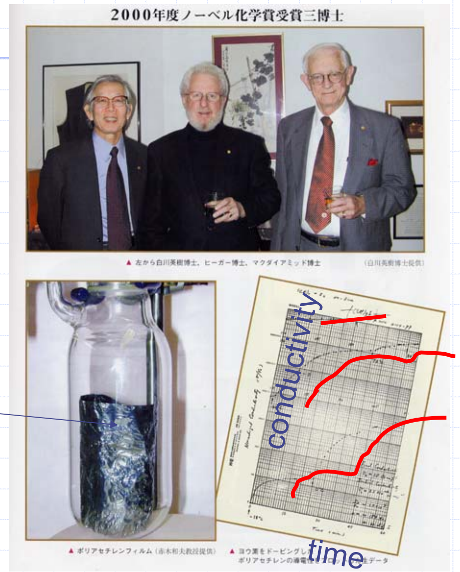
Positive

Electron dope（N型）

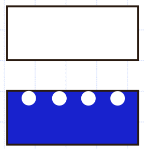
Hole dope（P型）

Doped Polyacetylene

白川英樹
A. J. Heeger
A. G. MacDiarmid
1974～1977

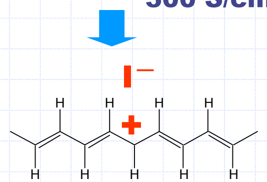


Polyacetylene
Film

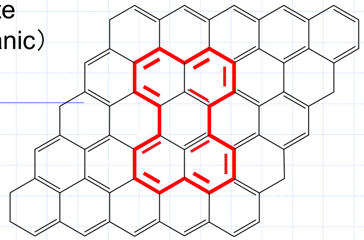


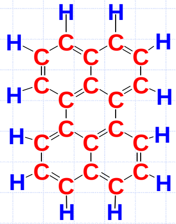
Iodine doped
Polyacetylene
Film

300 S/cm



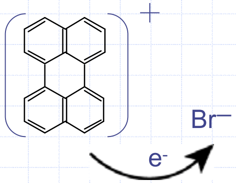
Graphite
(Inorganic)





perylene

First Electrically Conducting Organics



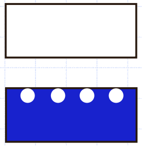
電荷移動

Charge-transfer complex
電荷移動錯体

Br doped Perylene shows high electric conductivity
First conducting charge-transfer salt
Akamatsu, Inokuchi, Matsunaga,

Nature, **173**, 168 (1954).

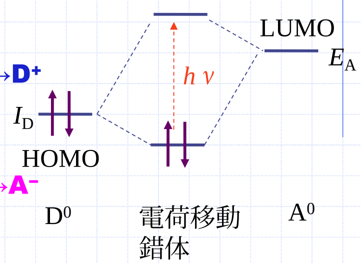
0.1 S/cm



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



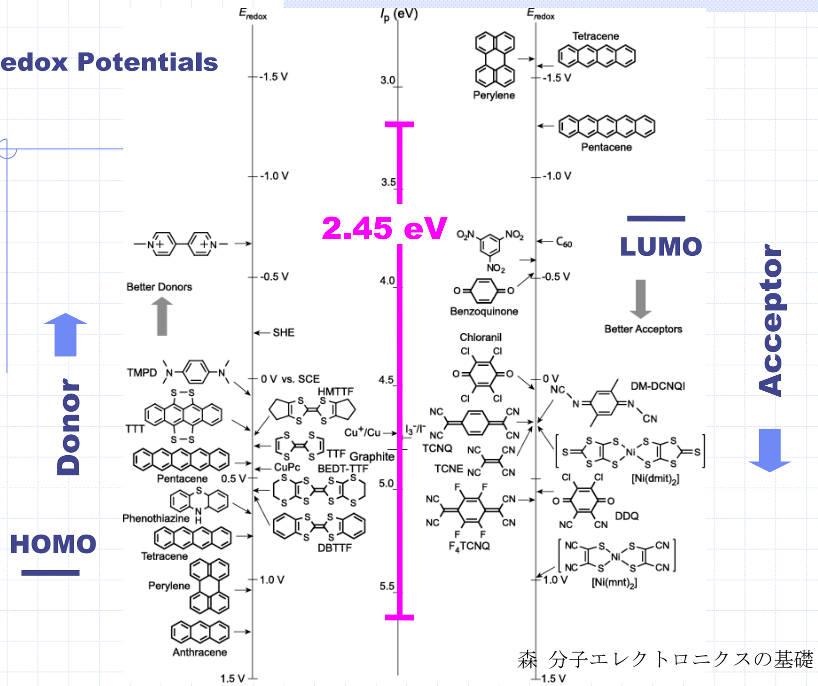
Completely $D^0A^0 \rightarrow D^+A^-$: Ionic charge-transfer complex

Nearly D^0A^0: Neutral charge-transfer complex
Small (quantum mechanical) mixing of the ionic state

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

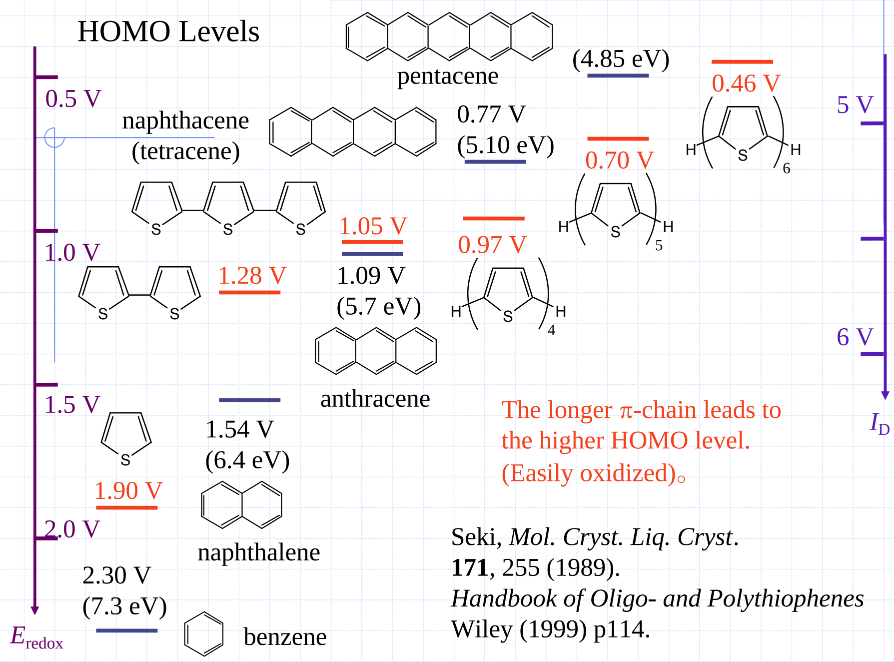
and the excitation corresponding to $D^0A^0 \rightarrow D^+A^-$
gives rise to charge-transfer absorption 電荷移動吸収 (visible to infrared)

Redox Potentials



森 分子エレクトロニクスの基礎 p322

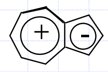
HOMO Levels



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

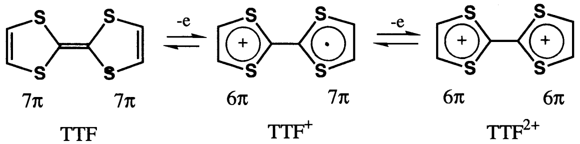
Seki, *Mol. Cryst. Liq. Cryst.* **171**, 255 (1989).
Handbook of Oligo- and Polythiophenes Wiley (1999) p114.

Good donors and acceptors



Azulene

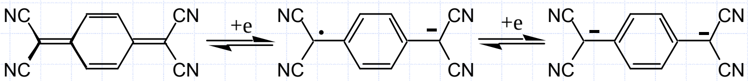
A good donor: Tetrathiafulvalene (TTF)



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.

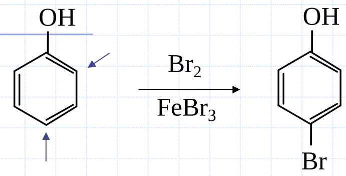
A good acceptor Tetracyanoquionodimethane (TCNQ)

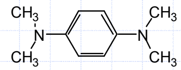


TCNQ TCNQ- TCNQ2-

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

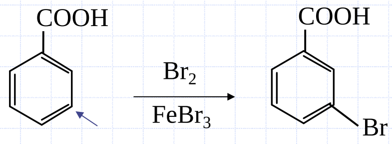
電子供与基：-OH、$-OCH_3$、$-NH_2$ → 電子供与体



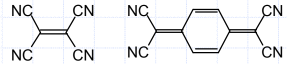


オルト、パラ配向

電子求引基：$-NO_2$、-CN、ハロゲン、-COOH、$-COOCH_3$、-CHO

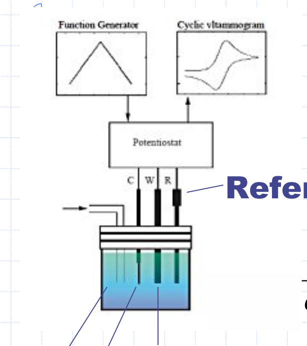


→ 電子受容体

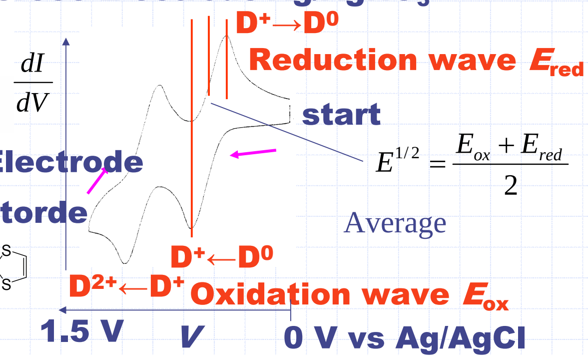


メタ配向

Cyclic voltammetry
Electrochemical Redox Potential



Referece Electrode Ag/AgNO$_3$

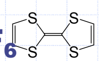


$$E^{1/2} = \frac{E_{ox} + E_{red}}{2}$$

Average

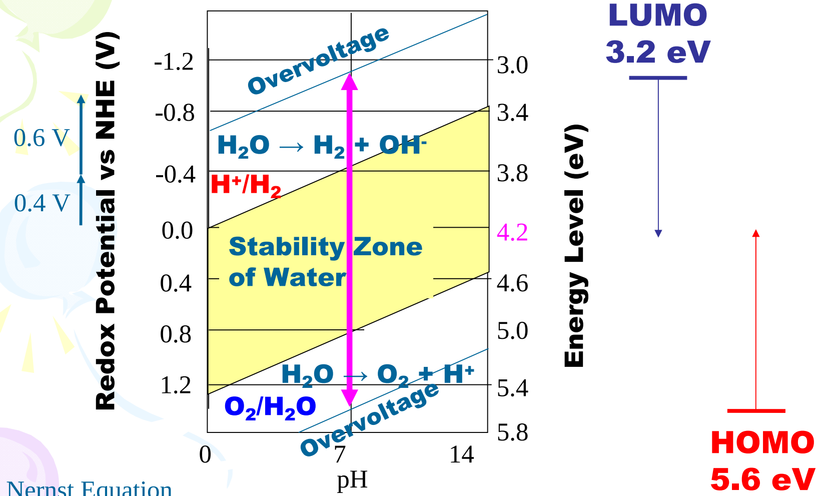
Working Electrode

Supporting Electorde

TTF + Bu_4NPF_6 
in PhCN

Stability Zone of Water

Schriver, Atkins, Inorganic Chemistry



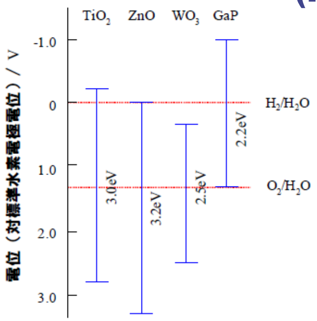
Nernst Equation

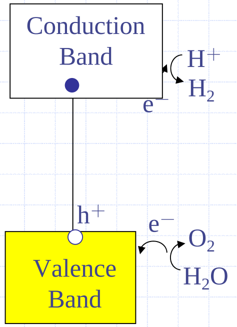
$$E = E^0 + \frac{RT}{F}\ln[H^+]$$

0.4 V

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

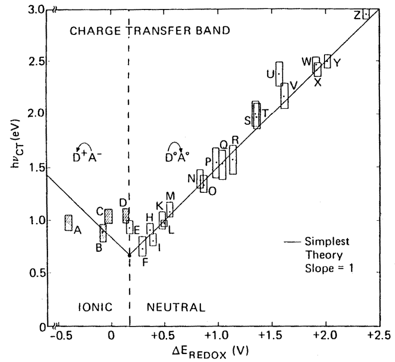
森 分子エレクトロニクスの基礎 p322

Charge-Transfer Absorption

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

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)

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

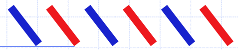


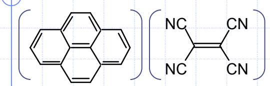
Mixed stack structure

Neutral and ionic：low conducting

Planer molecules make 1D stacks.

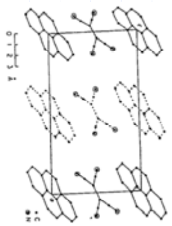
10^{-11} S/cm





pyrene tetracyanoethylene TCNE

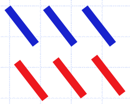
pyrene TCNE pyrene

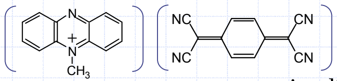


Segregate stack structure

Partial charge transfer：high conducting

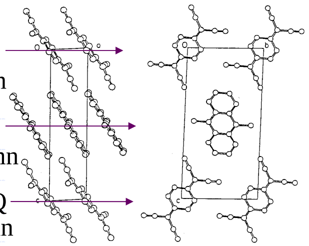
170 S/cm





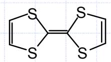
N-methylphenazinium (NMP) tetracyanoquinodimetane TCNQ

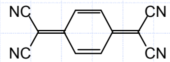
TCNQ column
NMP column
TCNQ column



(NMP)(TCNQ)：first 「Organic Metal」1966

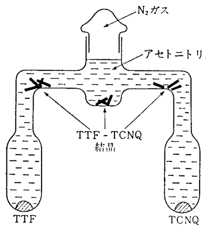
(TTF)(TCNQ)
1973
(TTF$^{0.59+}$)(TCNQ$^{0.59-}$)


tetrathiafulvalene TTF


tetracyanoquionodimethane TCNQ

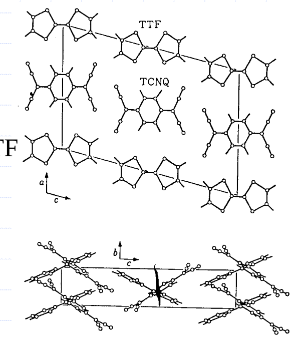
拡散法結晶成長

From acetonitril solutions of TTF and TCNQ



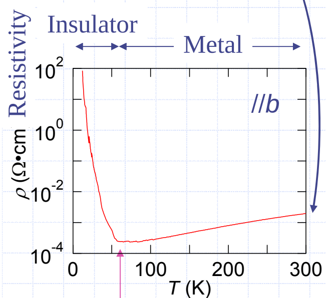
Segregated stacks

TTF



TCNQ TCNQ

600 S/cm

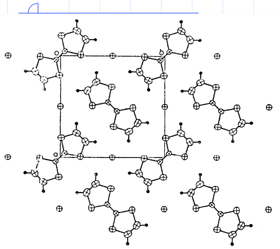


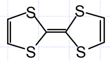
Metal-insulator transition at 54 K

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

Radical cation salt (Organic cation + Inorganic anion)

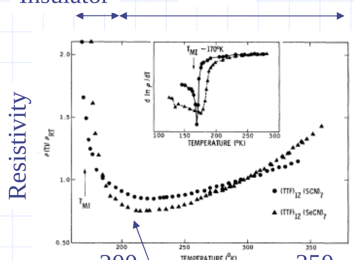
1D stacks





tetrathiafulvalene
TTF

500 S/cm

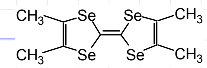


Metal-insulator transition at 200 K

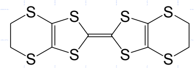
Planer molecules make 1D stacks.

Components of Organic Superconductors

Donors

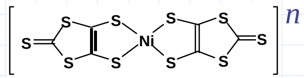


Tetramethyltetraselenafulvalene
TMTSF



Bis(ethylenedithio)tetrathiafulvalene
BEDT-TTF

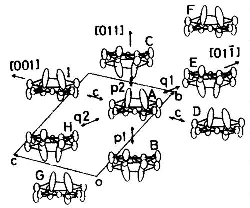
Acceptor

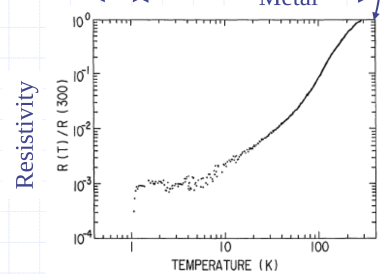


$[Ni(dmit)_2]^{n-}$

30 S/cm

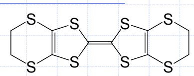
β-$(BEDT\text{-}TTF)_2I_3$ (1/2+, −)

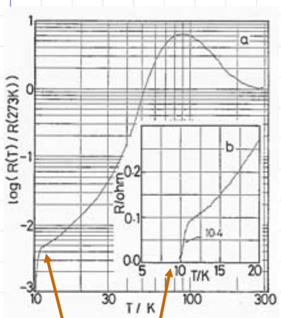




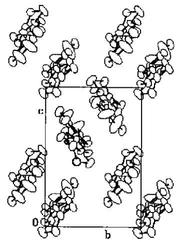
κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$

1/2+ + − −





Superconductivity at 10.4 K (1987)

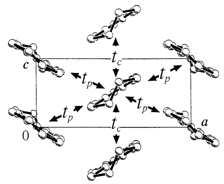


Electrochemical Crystal Growth

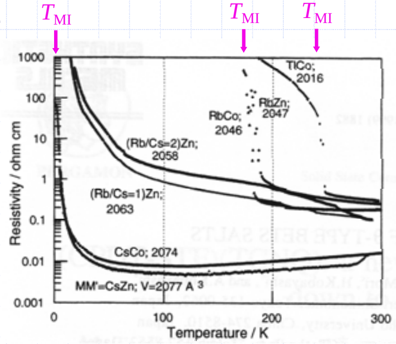
BEDT-TTF → BEDT-TTF⁺
$[Cu(NCS)_2]^-$
→ $(BEDT\text{-}TTF)_2Cu(NCS)_2$

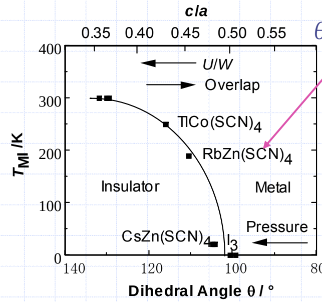
θ Phase ～ Herringbone

θ-$(BEDT\text{-}TTF)_2MM'(SCN)_4$



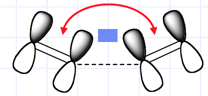
t_p: 101
t_c: 25 meV





θ-$(BEDT\text{-}TTF)_2MM'(SCN)_4$

Dihedral angle θ

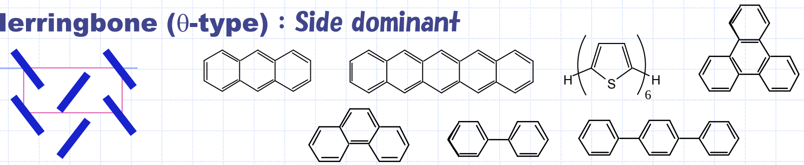


Large orbital overlap

Structures of Aromatic Compounds

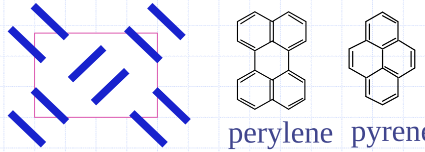
Acta Crystallogr. B **45**, 473 (1989).

Herringbone (θ-type) : *Side dominant*



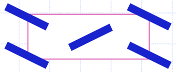
phenanthrene biphenyl terphenyl

Dimer (κ-type) : *Intermidiate*

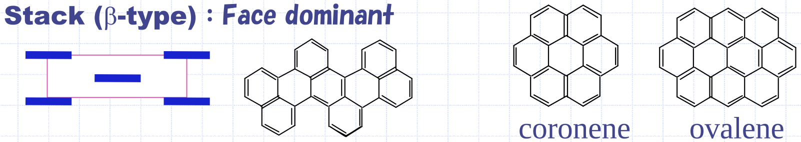


perylene pyrene

γ-Structure (θ-type) : *with large face*



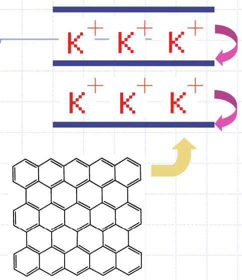
Stack (β-type) : *Face dominant*



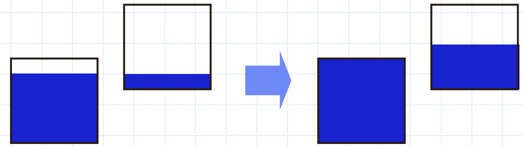
coronene ovalene

Large molecular plane induces parallel stacking structures.

Graphite Intercalation Compounds



Increase Conductivity



Dope

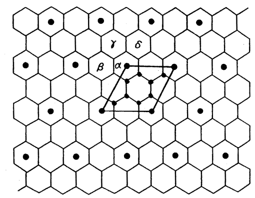


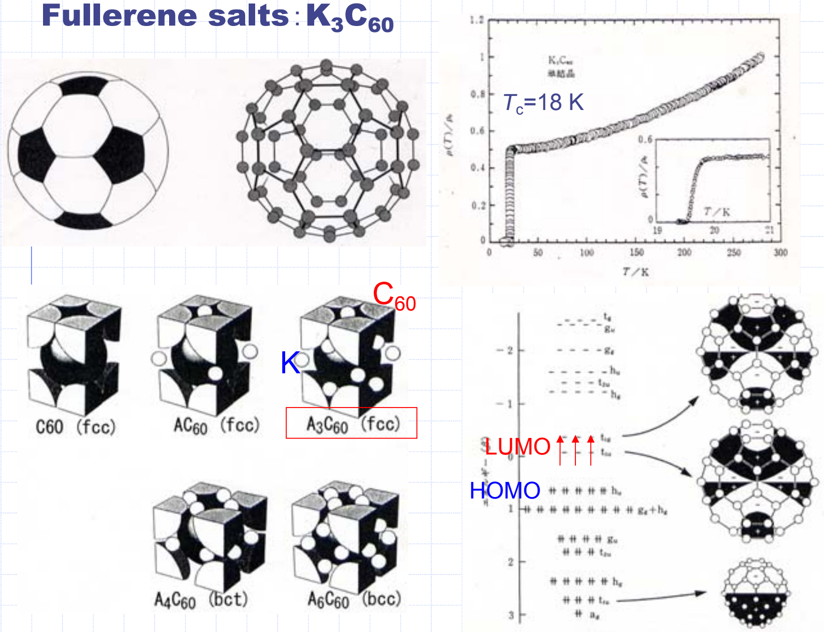
図6 グラファイト・カリウム C_8K 中のカリウム原子(●印)の配置

C_8K

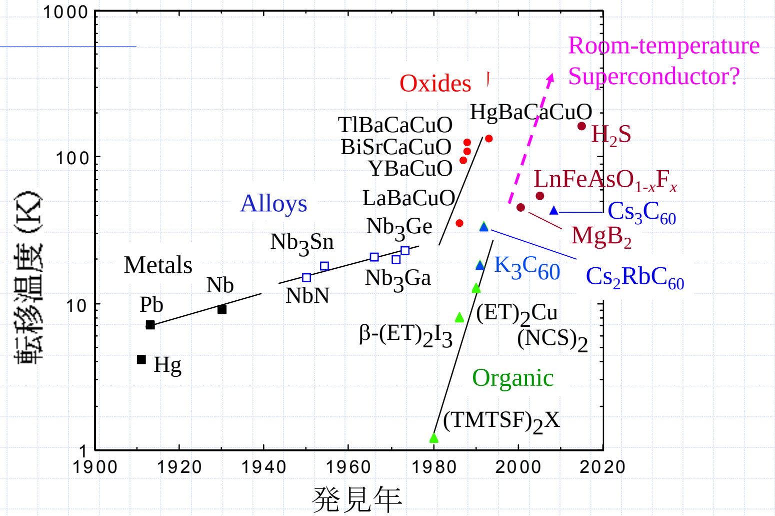
Superconductors

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

Fullerene salts : K_3C_{60}

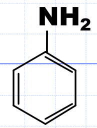


Transition Temperatures and Discovery of Superconductors



Polyaniline (PANI)

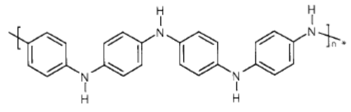
p-type



Electrochemical oxidation → Polyaniline

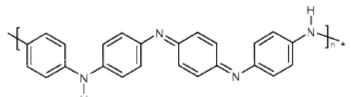
or $(NH_4)_2S_2O_8$

cf. Aniline black
black dye



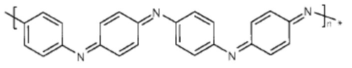
Leucoemeraldine

Coloeless insulator



Emeraldine

Blue or green (salt)

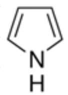


Pernigraniline

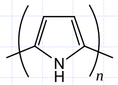
Blue/violet insulator

---

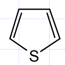
p-type



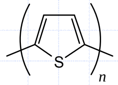
Electrochemical oxidation →



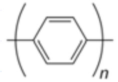
polypyrrole



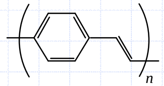
Electrochemical oxidation →



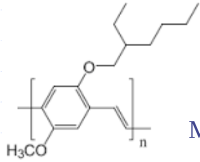
polythiophene



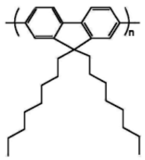
poly(parapenylene)



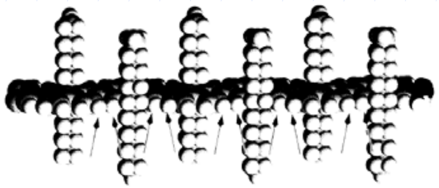
poly(phenylenevinylene)
PPV



MEH-PPV
Soluble



poly(dioctylfluorene)
Soluble



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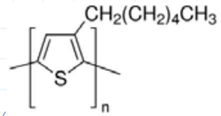
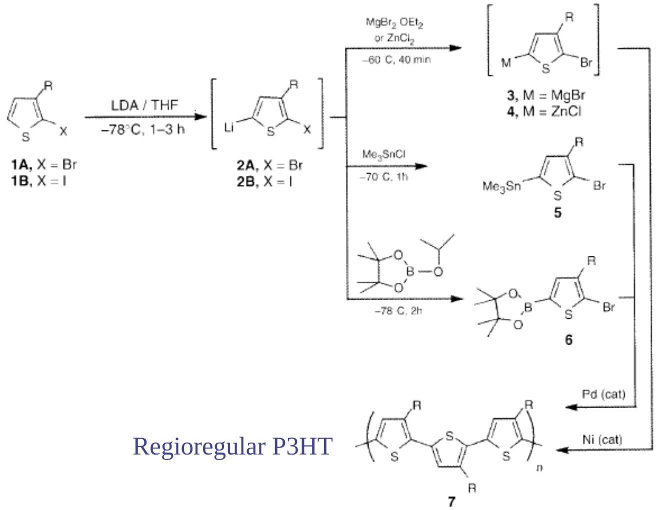
p-type



Regioregular
poly(3-hexylthiophene)
P3HT Soluble



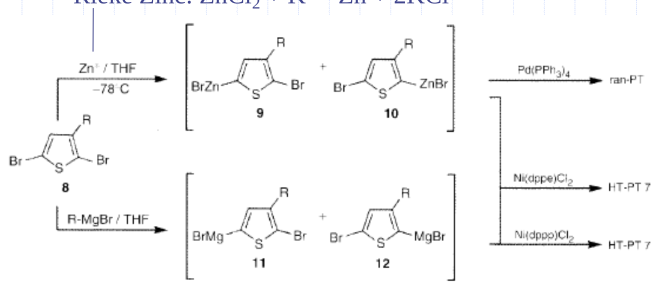
Tamao coupling

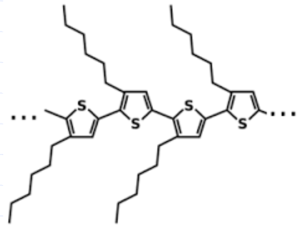
Stille coupling

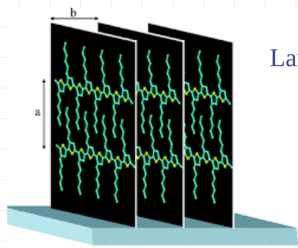
Suzuki coupling

Regioregular P3HT

Rieke Zinc: $ZnCl_2 + K \rightarrow Zn + 2KCl$



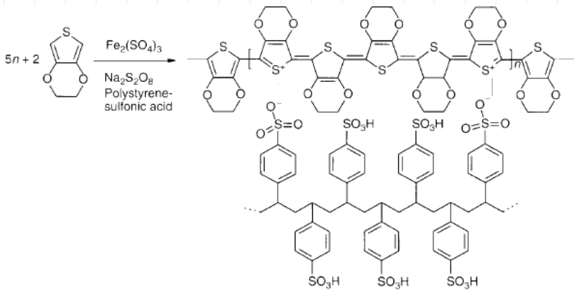




Lamella structure

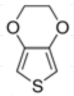
PEDOT/PSS

Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)



Bayer

Transparent and flexible conducting film from aquous solutions



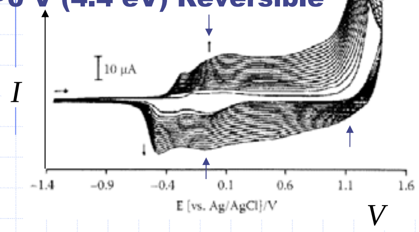
Electrochemical oxidation of EDOT

Monomer oxidation = Polymerization

~1.4 eV (5.8 eV) Irriversible

Polymer oxidation

~0 V (4.4 eV) Reversible



PEDOT/PSS Applications

1. Electrolyte Capacitor

→Reducing series resistance

2. Transparent conductor

3. Antistatic coating

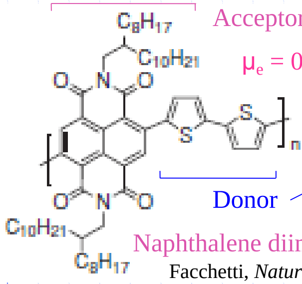
4. Hole injection layer in organic LED

5. Organic photovoltaics

6. Electrochromism

7. Organic transistors

Donor-Acceptor-Type Polymers



Acceptor

LUMO

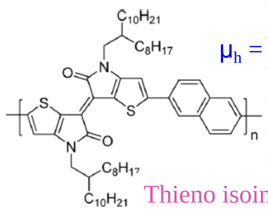
μ_e = 0.85 cm²/Vs

HOMO

Donor

Naphthalene diimide (NDI)

Facchetti, *Nature* 2009, **457**, 679.

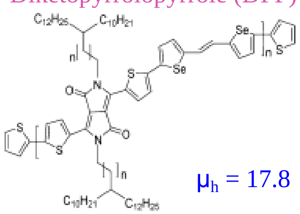


μ_h = 14.4

Thieno isoindigo

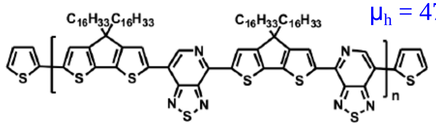
蔚山 *JACS* 2014, **136**, 9477.

Diketopyrrolopyrrole (DPP)



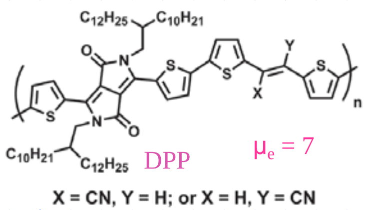
μ_h = 17.8

蔚山 *Chem. Mater*. 2015, **27**, 1732 .



μ_h = 47

Heeger, *Nano Lett*. 2014, **14**, 2764.

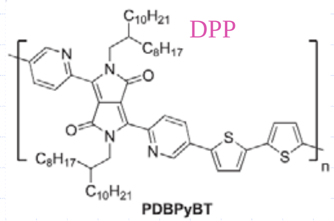


DPP

μ_e = 7

X = CN, Y = H; or X = H, Y = CN

慶尚 *Adv. Mater*. 2014, **26**, 7300.

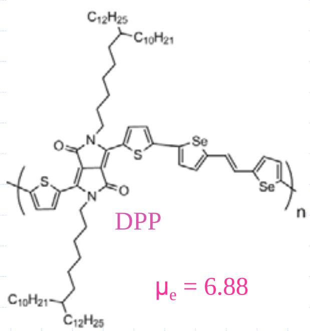


DPP

μ_e = 6.3

PDBPyBT

Waterloo *Adv. Mater*. 2014, **26**, 2636.

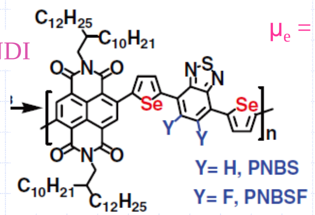


DPP

μ_e = 6.88

慶尚 *Chem. Mater*. 2016, **28**, 2287.

NDI



μ_e = 8.5

Y= H, PNBS

Y= F, PNBSF

北京 *Adv. Mater*. 2017, **29**, 1602410.