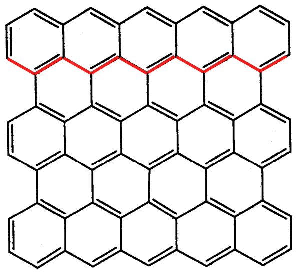
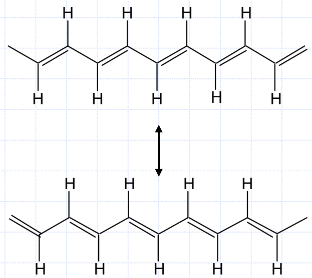
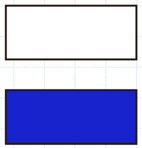
One chain truncated from graphite (terminated by hydrogenes)
→ Polyacetylene



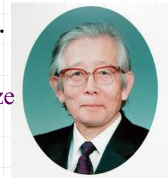




Electrically conducting because the p-electrons can move.

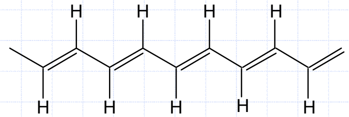
半導体 Semiconductor

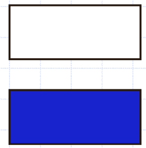
白川英樹 2000年 Nobel Prize H. Shirakawa

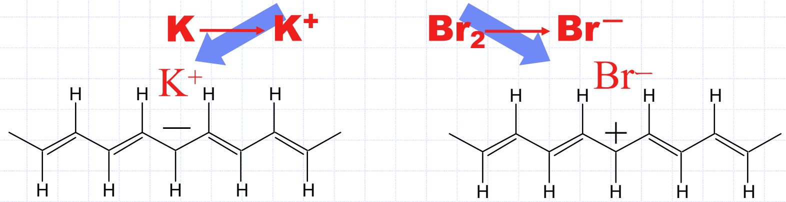


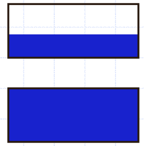
Doped Polyacetylene

10-5 S/cm

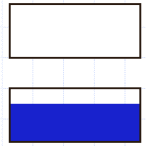








300 S/cm



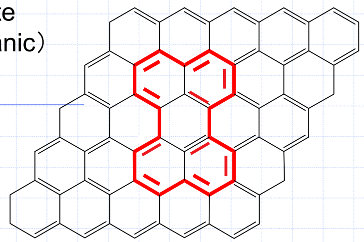
Negative

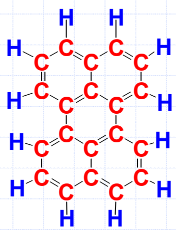
Positive

Electron dope (N型)

Hole dope (P型)

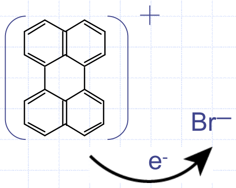
Graphite (Inorganic)





First Electrically Conducting Organics

perylene

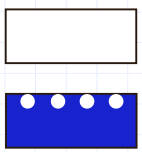


Charge-transfer complex
電荷移動錯体

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

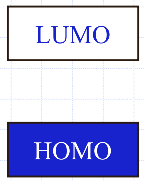
Electron donor 電子供与体

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

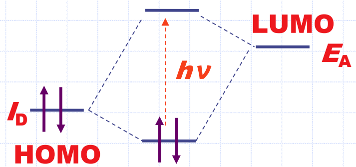
Lowest Uncuppied Molecular Orbital



conduction band

valence band

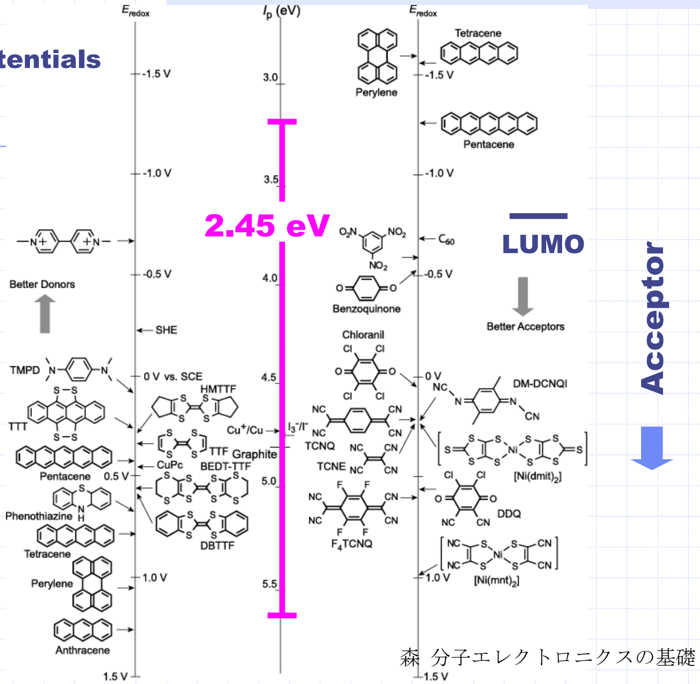
Highest Occupied Molecular Orbital



D^0 **$D^{\delta+}A^{\delta-}$** **A^0**

Charge-transfer complex

Redox Potentials



森 分子エレクトロニクスの基礎 p322

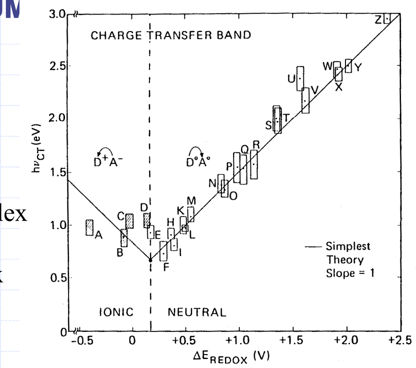
Charge transfer absorption (vis～near ir)

Mixing colorless neutral donor and acceptor solutions → organe~yellow solution

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

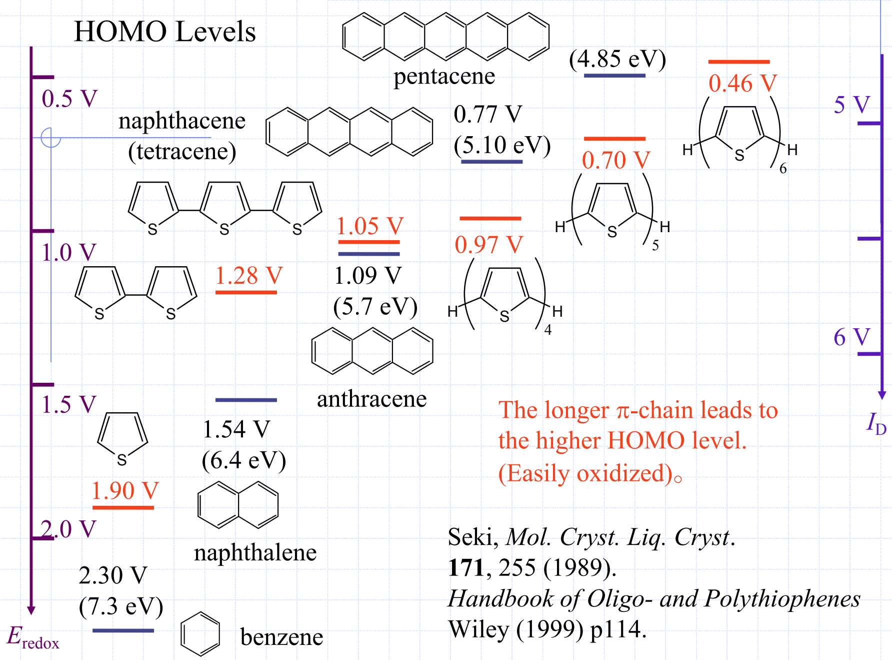
I_D : donor ionization energy
E_A : acceptor electron affinity
$E(D^+A^-)$: Electrostatic enrgy in D^+A^-

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



$>$0.1 V　D^0A^0 is stabler than D^+A^-
Neutral charge-transfer complex
$<$ 0.1 V　D^+A^- is stabler than D^0A^0
Ionic charge-transfer complex

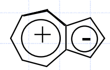
HOMO Levels



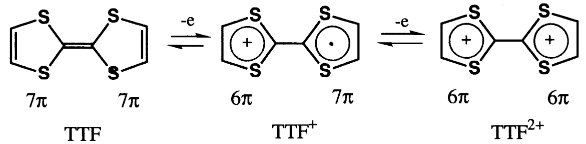
The longer π-chain leads to the higher HOMO level. (Easily oxidized)。

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

Good donors and acceptors



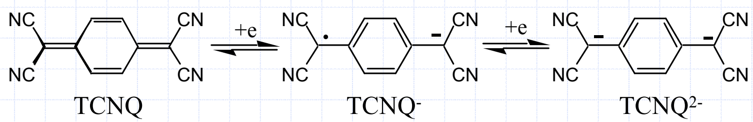
A good donor:　Tetrathiafulvalene (TTF)



0.38 V

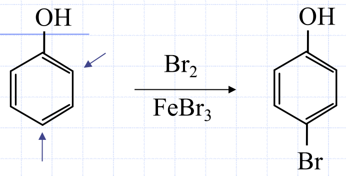
This 7π system easily gives up one electron to form a 6π system.
(C→1π、S→2π)
Electron donating groups such as $-NH_2$, $-OCH_3$ strengthen donor ability.

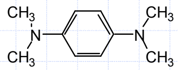
A good acceptor　Tetracyanoquionodimethane (TCNQ)



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.

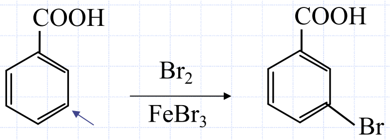
El donating：-OH、-OCH$_3$、-NH$_2$ → Donor



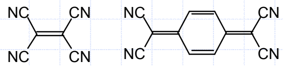


ortho, para

Elc withdrawing：-NO$_2$、-CN、halogene、-COOH、-COOCH$_3$、-CHO

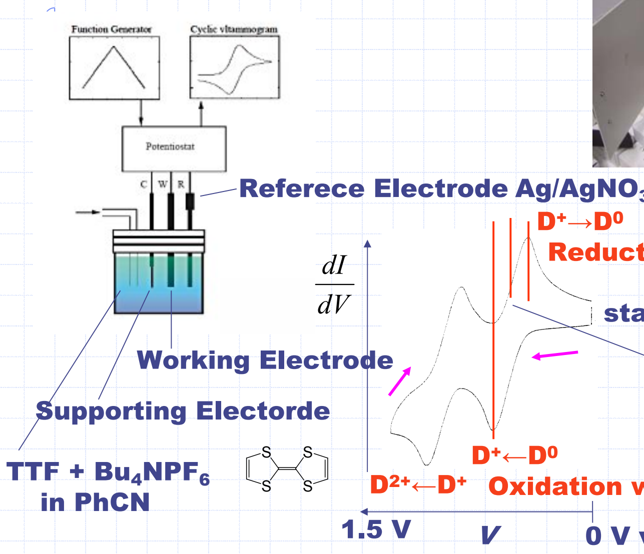


→ Acceptor



meta

Cyclic voltammetry
Electrochemical Redox Potential



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

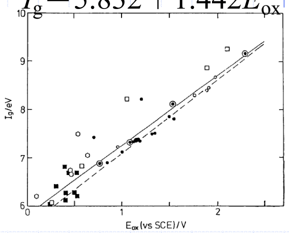
Average

Conversion of redox potentials to ionization energy

	I_g/eV[a]	Ref.	I_s/eV[b] UPS	Yield	Ref.	E_{ox}/V (vs SCE)
Benzene	9.17	69	7.3		118	2.30
Naphthalene	8.12*	69	6.4		43	1.54
Anthracene	7.36*	69	X5.6$_7$		24	1.09
Naphthacene	6.89*	69	5.10		43	0.77
Pentacene	6.58*	69	4.85		90	
Phenanthrene	7.86	73	X6.0$_8$		25	1.50
Chrysene	7.51	73	5.8		43	1.35
Benz[a]anthracene	7.38	73	5.64		90	1.18
Triphenylene	7.81	75	6.2		91	1.55
Dibenz[a,h]anthracene	7.35	43	5.55		91	1.19
Picene	7.5	73	5.7		91	1.33
Pyrene	7.37	75	X5.5$_8$		25	1.16
Benz[a]pyrene	7.12	73	5.4		124	1.27
Perylene	6.90*	43	X5.1$_2$		18	0.85
Benzo[ghi]perylene	7.12*	73	X5.2$_6$		25	1.01
Coronene	7.25*	75	5.52		90	1.23

Slop～1.5 ← solvation

$I_g = 5.832 + 1.442 E_{ox}$



Seki, *Mol. Cryst. Liq. Cryst*. **171**, 255 (1989).

Electrochemical reference electrodes (cyclic voltammetry)

Standard calomel Hg$_2$Cl$_2$ vs. SCE = 0.24 V NHE

vs. Ag/AgCl = 0.22 V NHE

Ferrocene = 0.38 V vs. SCE

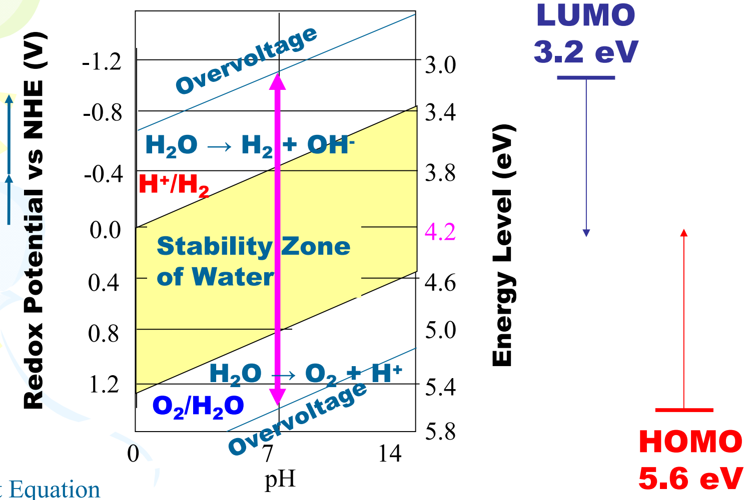
E = E_{redox}(vs. SCE) + 4.4 V

= E_{redox}(vs. Ferrocene) + 4.8 V

Tang, *J. Am. Chem. Soc*. **130**, 6064 (2008); H. Meng, *Chem. Mater*. **15**, 1778 (2003); De Leewd, *Synth. Met*. **87**, 53 (1997); Tang, *J. Am. Chem. Soc*. **131**, 5264 (2009).

Stability Zone of Water

Schriver, Atkins, Inorganic Chemistry



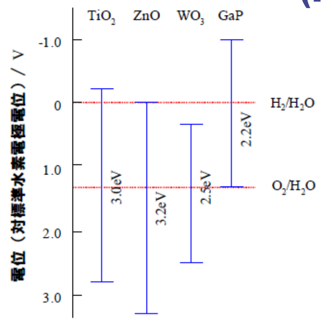
Nernst Equation

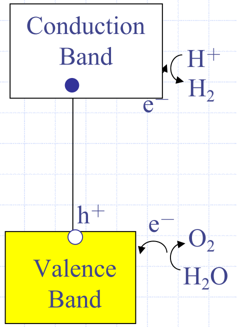
$$E = E^0 + \frac{RT}{F}\ln[H^+]$$

0.4 V

Photocatalyst

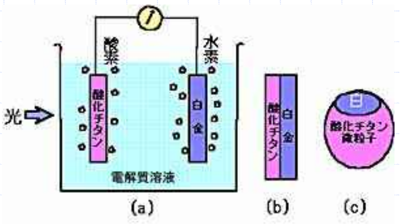
(Honda·Fujishima Effect)





Reduction

Oxidation



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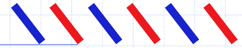
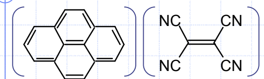
Planer molecules make 1D stacks.

Mixed stack structure

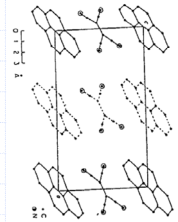
Neutral and ionic：low conducting **10^{-11} S/cm**





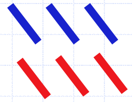
pyrene tetracyanoethylene TCNE

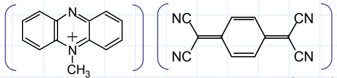
pyrene TCNE pyrene



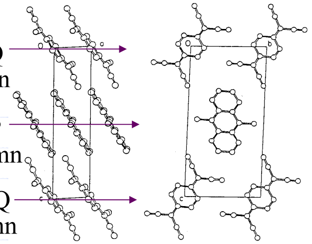
Segregate stack structure

Partial charge transfer：high conducting **170 S/cm**





N-methylphenazinium (NMP) tetracyanoquinodimetane TCNQ



TCNQ column

NMP column

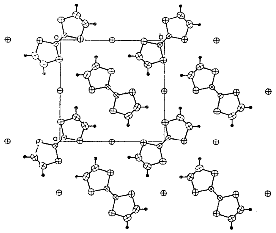
TCNQ column

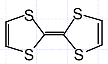
(NMP)(TCNQ)：first 「Organic Metal」 1966

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

Radical cation salt (Organic cation + Inorganic anion)

1D stacks



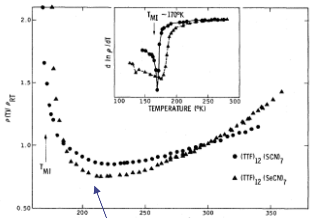


tetrathiafulvalene TTF

500 S/cm

Insulator Metal

Resistivity



200 350

Temperature (K)

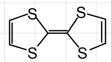
Metal-insulator transition at 200 K

Planer molecules make 1D stacks.

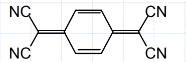
(TTF)(TCNQ)

1973

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



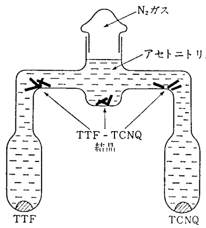
tetrathiafulvalene TTF



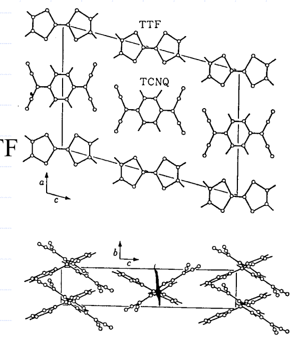
tetracyanoquionodimethane TCNQ

Diffusion method

From acetonitril solutions of TTF and TCNQ



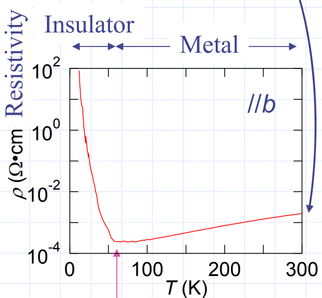
Segregated stacks



TTF

TCNQ TCNQ

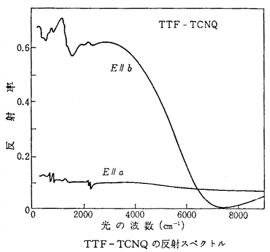
600 S/cm



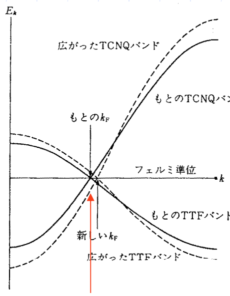
Metal-insulator transition at 54 K

(TTF)(TCNQ)

Reflectance
One-dimensional metal

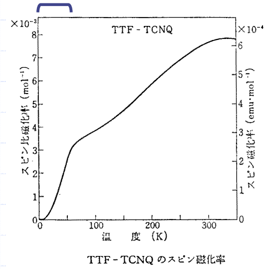


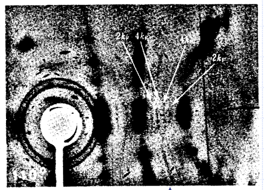
Energy band



Nonmagnetic below54 K

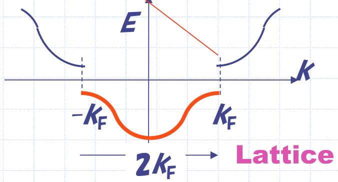
Spin susceptibility





X-ray : periodicity at $2k_F$

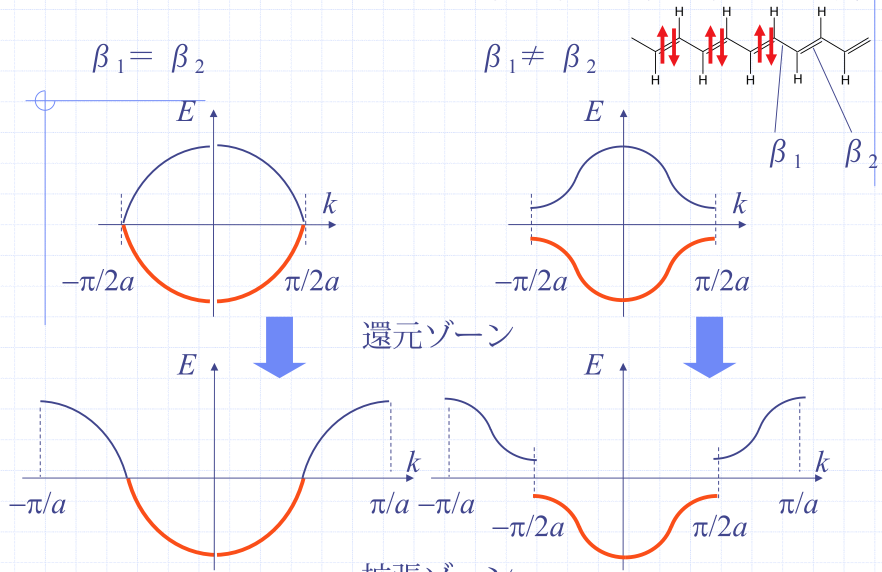
Cross TTF HOMO band and TCNQ LUMO band
at $k_F = 0.1475b^* = 0.295\pi/b = (0.59/2)(\pi/b)$



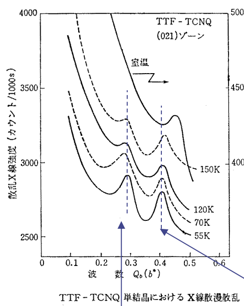
Nonmagnetic insulator
(Peierls transistion)

Lattice periodicity $2k_F$

一重結合と二重結合のβは異な



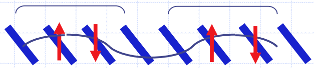
(TTF)(TCNQ)



$2k_F = 0.295b^*$

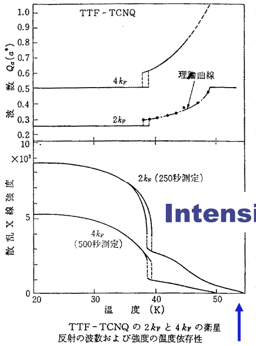
$4k_F = 0.59b^*$

$D^{1/2+}$ **1/2e/mol**



Charge density with $1/2k_F$ wavelength
Charge density wave (CDW)

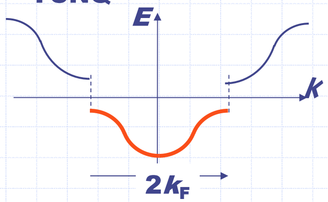
k_F : T dependent



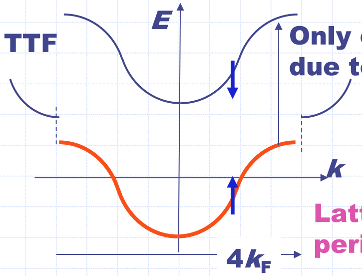
Intensity

54 K

TCNQ



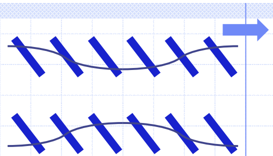
TTF



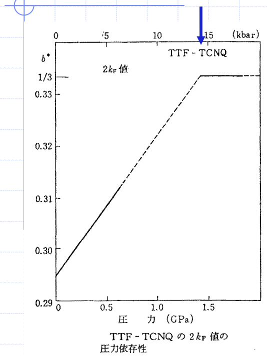
Only one electron due to U

Lattice periodicity $4k_F$

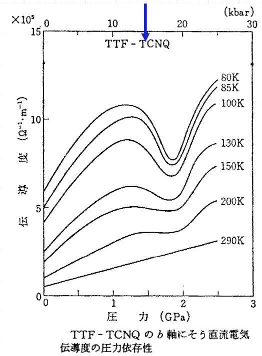
(TTF)(TCNQ)



$2k_F$ changes under pressure
Lock in at 1/3 above15 kbar

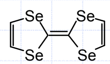


Low-T conductivity drop
above 15 kbar

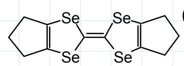


Collective motion
of CDW
(Frölich mode)

To reduce the Peierl transition T, enhance the interchain contacts bySe

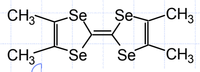


(TTF)(TCNQ) 54 K
(TSF)(TCNQ) 29 K

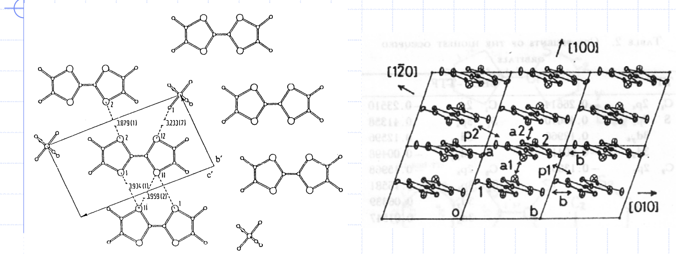


(HMTTF)(TCNQ) 50 K
(HMTSF)(TCNQ) 24 K
scarecely increase

$(TMTSF)_2PF_6$: First organic superconductor



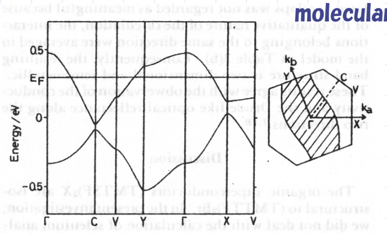
Quasi 1D: open Fermi surface
but 1/10 interchain interaction



Transfer integral (meV)

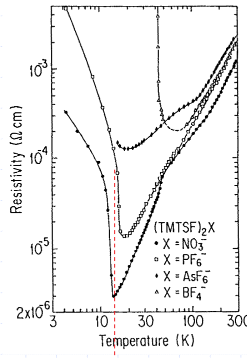
	HOMO
a1	200
a2	230
b	35
p1	20
p2	7

calculated from molecular orbitals



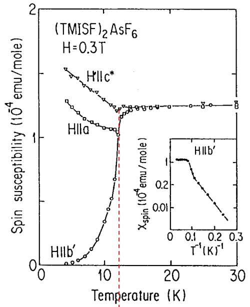
$(TMTSF)_2PF_6$: First organic superconductor

Resistivity



Metal-insulator transition at 12 K

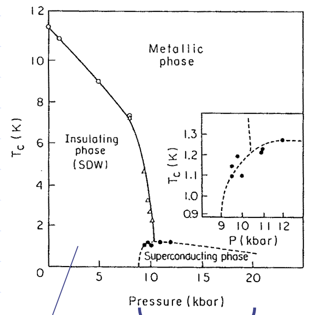
Static magnetic susceptibility



Anisotropic susceptibility below 12 K

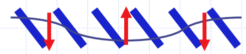
Antiferromagnetism
Spin density wave (SDW)

Phase diagram under pressure



Superconductivity at T_c~1 K

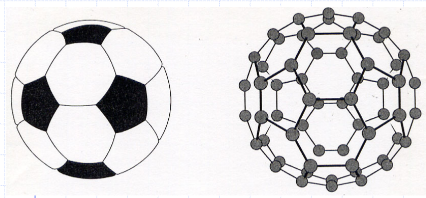
Antiferromagnetis (SDW) insulator

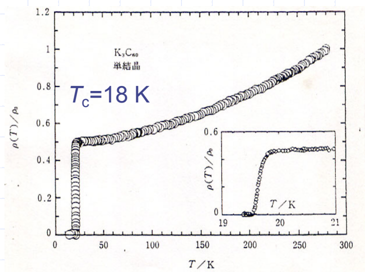


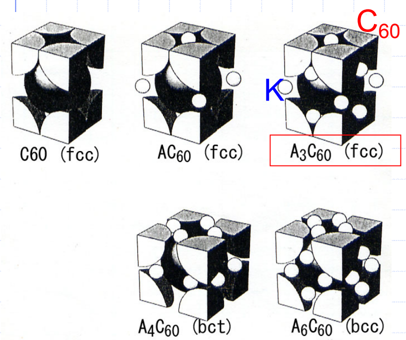
Origin of metal-insulator transition and the experimental determination

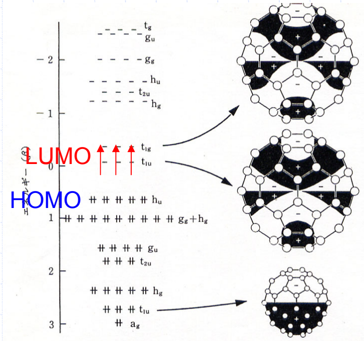
	Resistivity	Static susceptibility by SQUID	Spin susceptibility by ESR	X-ray diffraction
Charge density wave (Peierls transition)	ρ Insulator Metal T_{MI} T	χ nonmagnetic insulator T	χ_s the same ΔH continuous $\chi \propto \dfrac{1}{k_B T(3+e^{E_g/k_BT})}$	$2k_F$ periodicity $> T_{MI}$ diffuse $< T_{MI}$ spot
Spin density wave	ρ Insulator Metal T_{MI} T	antiferromagnetic insulator χ $\chi_\perp$ $\chi_{//}$ T_{MI} T	ΔH diverge Intensity drops to 0 T	Nothing
Mott insulator・Charge order	ρ Insulator Metal T_{MI} T	χ paramagnetic insulator T_{MI} T	χ_s the same ΔH continuous SDW or spin-Peierls at lower T	Mott: nothing Charge order: extraperiodicity
Spin-Peierls transition	ρ Insulator at all T T	χ nonmagnetic T	χ_s the same ΔH continuous $\chi \propto \dfrac{1}{k_B T(3+e^{E_g/k_BT})}$	$2k_F$ periodiciry

Fullerene salts: K_3C_{60}

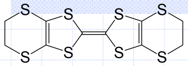






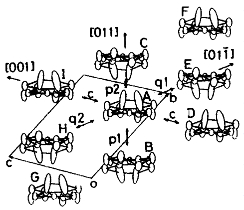


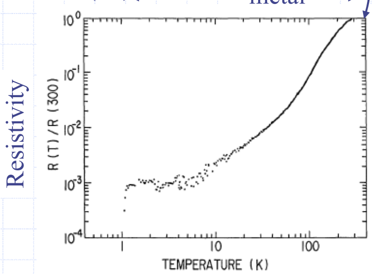
β-$(BEDT\text{-}TTF)_2I_3$



BEDT-TTF (T_c=1.5 K) First ambient-pressure superconductor

30 S/cm





Transfer integrals

β (meV)

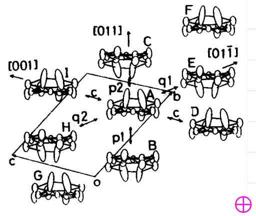
方向	HOMO
p1	245
p2	84
c	50
q1	127
q2	68

Intercahin～p2

From MO calc.

2D metal

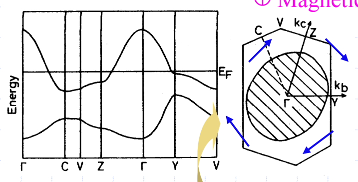
Shubnikov- de Haas Oscillation in β -$(BEDT\text{-}TTF)_2I_3$



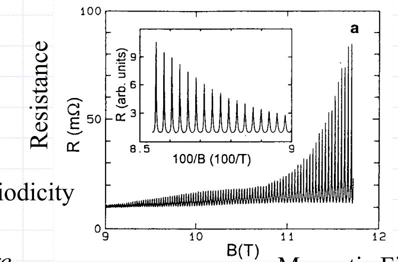
Oscillation of electrons rotating around the Fermi surface is observed at low T (< 1 K) and under strong magnetic field (> 10 T).

Shubnikov-de Haas oscillation

⊕ Magnetic Field



100 mK



Hatched Area

Periodicity

Fermi surface is 50% of the 1st Brillouin zone.

$$\Delta\left(\frac{1}{B}\right) = \frac{2\pi e}{\hbar S_k}$$

Magnetic Field

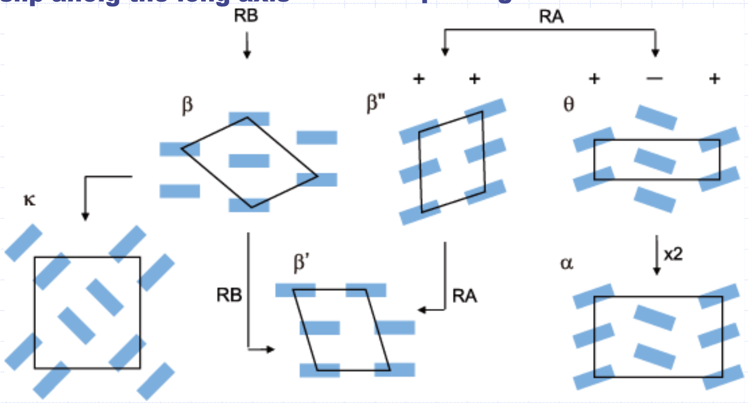
Kang, et al. *Phys. Rev. Lett.* **62**, 2559 (1989).

Various structures of BEDT-TTF

Mori, *Bull. Chem. Soc. Jpn*. **71**, 2509 (1998); **72**, 179 (1999); **72**, 2011 (1999).

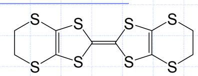
Ring over bond: slip anolg the long axis

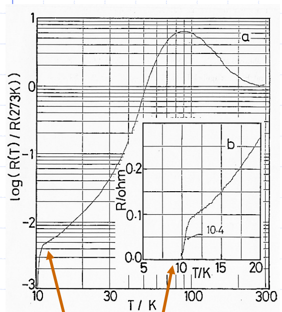
"Ring over atom" : slip along the short axis



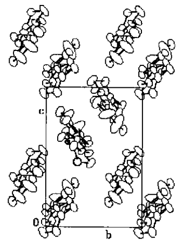
κ -$(BEDT\text{-}TTF)_2Cu(NCS)_2$

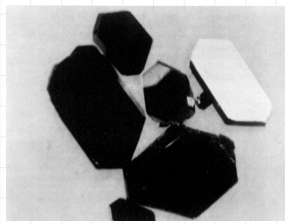
1/2+



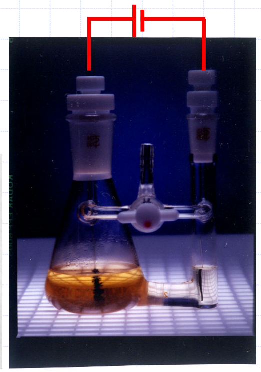


Superconductivity at 10.4 K (1987)





Electrochemical Crystal Growth



BEDT-TTF → BEDT-TTF$^+$

$[Cu(NCS)_2]^-$

→ $(BEDT\text{-}TTF)_2Cu(NCS)_2$

κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

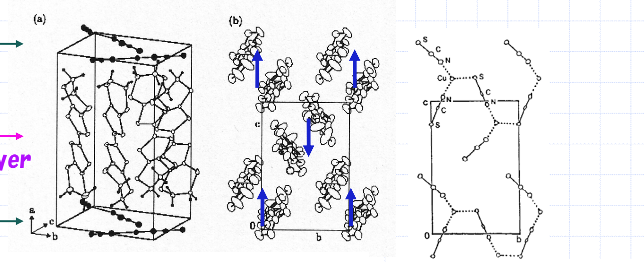
First organic superconductor above 10 K (T_c=10.4 K)

Urayama et al. *Chem. Lett.* **1988**, 55; **1988**, 463.

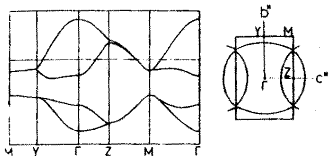
Cu(NCS)$_2$ Anion layer

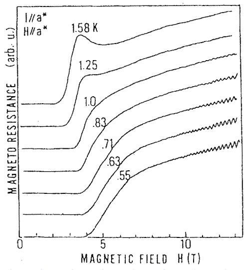
BEDT-TTF Conducting layer

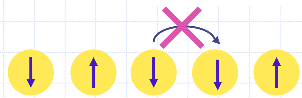
Cu(NCS)$_2$ Anion layer



Ideal 2D







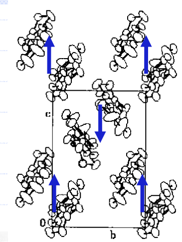
Dimer Mott Insulator

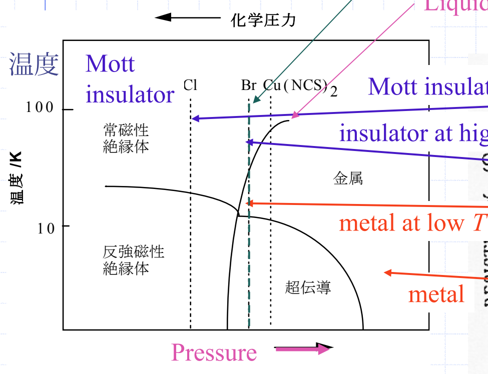
Metal-insulator transition in κ phase organic superconductors

κ-(BEDT-TTF)$_2$Cu[C(CN)$_2$]Cl
κ-(BEDT-TTF)$_2$Cu[C(CN)$_2$]Br
κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

Thermal contraction shifts the boundary right

Critical (end) point like Liquid-gas boundary





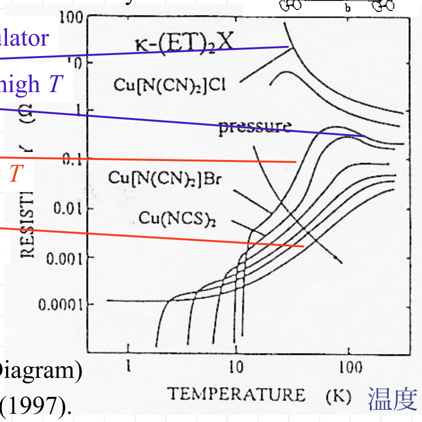
Mott insulator

insulator at high T

metal at low T

metal

Resistivity



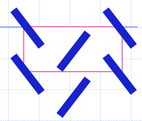
Universal phase diagram κ phase (Kanoda Diagram)

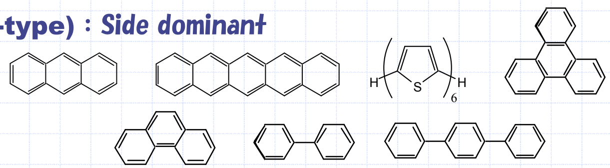
K. Kanoda, *Hyperfine Interact*. **104**, 235 (1997).

Structures of Aromatic Compounds

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

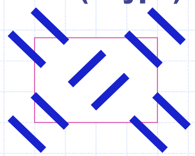
Herringbone (θ-type) : *Side dominant*

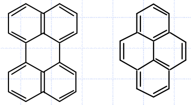




phenanthrene biphenyl terphenyl

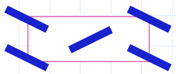
Dimer (κ-type) : *Intermidiate*



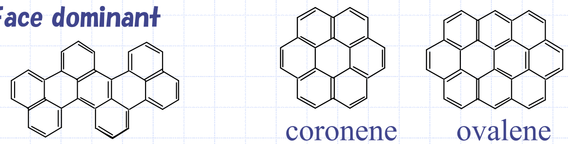


perylene pyrene

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



Stack (β-type) : *Face dominant*



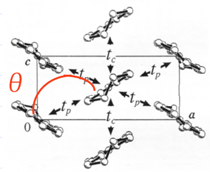
coronene ovalene

Large molecular plane induces parallel stacking structures.

θ 相統一的相図

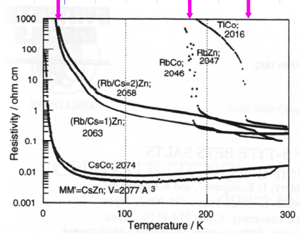
H. Mori et al. *Phys. Rev*. B **57**, 12023 (1998).

二面角 θ

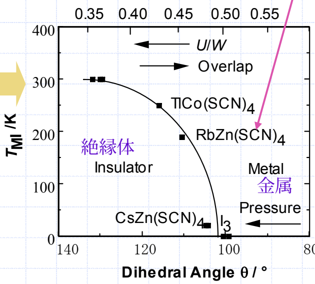


θ-(BEDT-TTF)$_2$MM'(SCN)$_4$

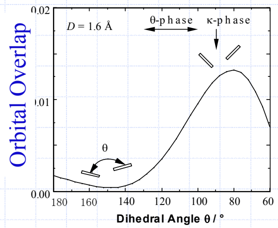
T_{MI} T_{MI} T_{MI}

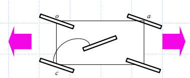


θ-(BEDT-TTF)$_2$MM'(SCN)$_4$

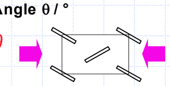


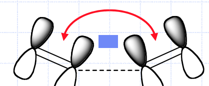
Orbital Overlap





二面角 θ



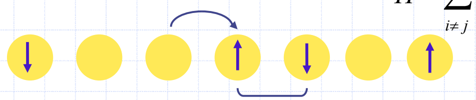


Orbital overlap 大↑

Charge order in non half-filled bands

Only half filled is insulating in the Hubbard model
→ Artifact of on-site U?

$$H = \sum_{i \neq j} t_{ij} a_i^{\dagger} a_j + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \underline{\sum_{i \neq j} n_i n_j}$$



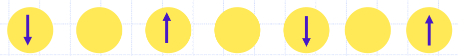
extended Hubbard model

***V* loss**

Adjacent-site electron leads to by *V* (off-site Coulomb repulsion) higher energy

At 1/4-filled, alternate arrangement is stable.

Charge order insulator

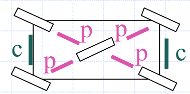


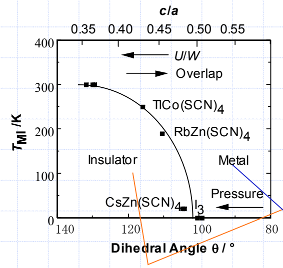
2-fold periodicity

(= $4k_F$ CDW in a one-dimensional system)

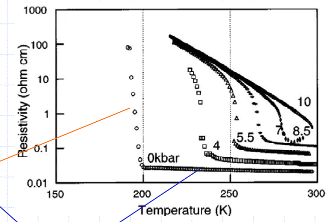
(cf. no new periodicity in a Mott insulator)

θ相電荷整列
θ相：uniform 2次元格子
電荷整列 ← 絶縁化

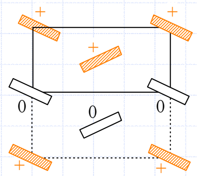




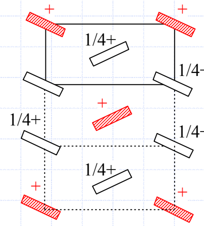
θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$



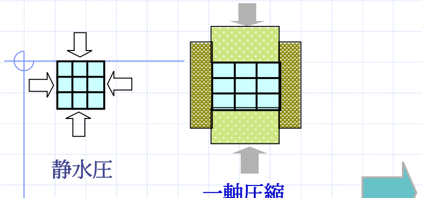
低温絶縁相：電荷整列
Horizontal stripe



「金属」相：3倍non-stripe
電荷整列 →
平坦電気抵抗
NMR, ラマン, X線
T_{MI}1次転移



一軸圧縮法→統一的相図検証



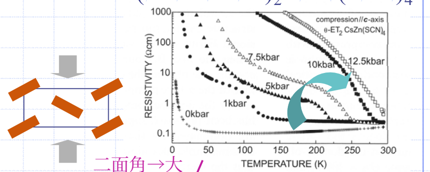
静水圧
一軸圧縮

Sub t le control different from hydrostatic.
Organics are susceptible to pressure.

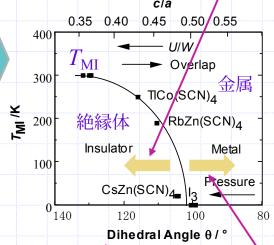
Superconducting only under uniaxial strain

α-(BEDT-TTF)$_2$KHg(SCN)$_4$
α-(BEDT-TTF)$_2$I$_3$
θ-(DIETS)$_2$Au(CN)$_4$

θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$

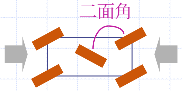


二面角→大

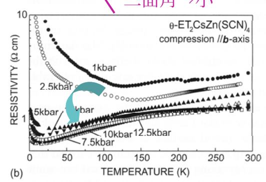


θ相統一的相図
θ-(BEDT-TTF)$_2$A

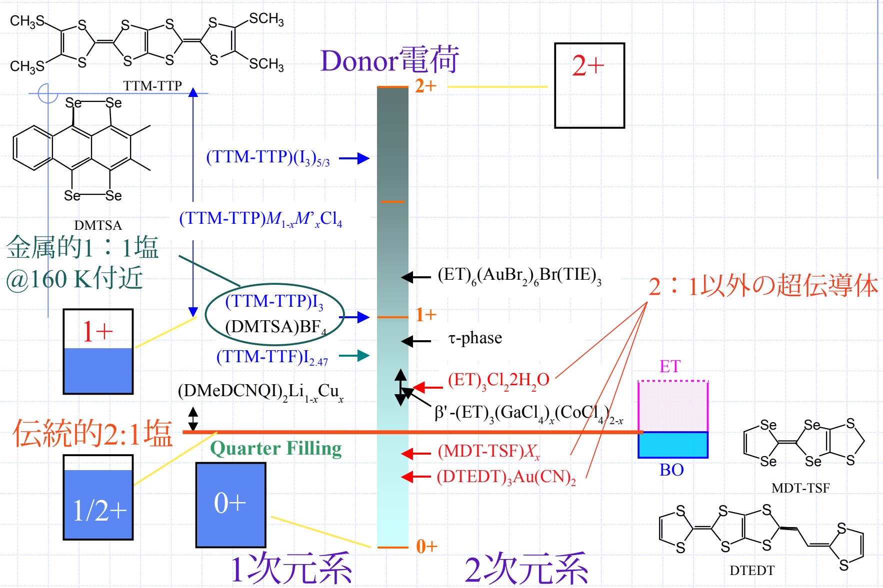
二面角



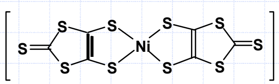
二面角　二面角→小



2：1組成以外有機伝導体　　T. Mori, *Chem. Rev.* 104, 4947 (2004).



$[M(dmit)_2]$: Only anionic organic superconductor

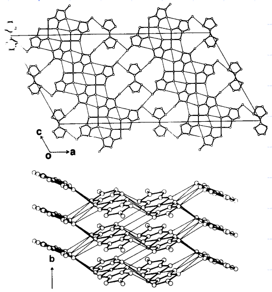


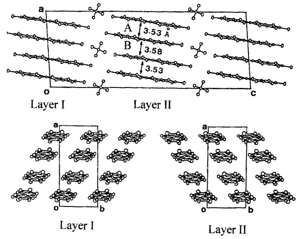
R. Kato, *Chem. Rev.* **104**, 5319 (2004).

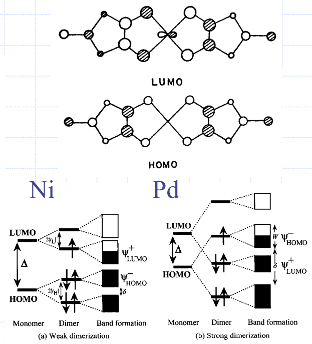
n=0〜2− M=Ni, Pd

$(TTF)[Ni(dmit)_2]_2^{1/2-}$
T_c=1.62 K (7 kbar)

$((CH_3)_4N)[Ni(dmit)_2]_2^{1/2-}$
T_c= 5 K (7 kbar)





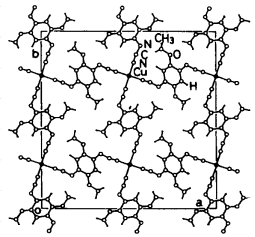


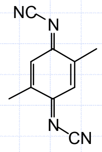
(EDT-TTF)$[Ni(dmit)_2]$(1.3 K) is ambient, others are high-pressure superconductors。
1D band. HOMO and LUMO have close energy levels, so that the dimerization (particularly in Pd complexes) leads to crossing HOMO and LUMO bands.

$Cu(DMDCNQI)_2$ Organic conductor coordinated to metals

R. Kato, *Bull. Chem. Soc. Jpn*. **73**, 515 (2000).
S. Hünig, *Chem. Rev.* **104**, 5535 (2004).

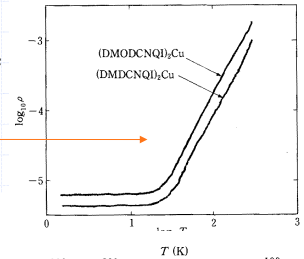
1D stack
N of CN coordinate to Cu



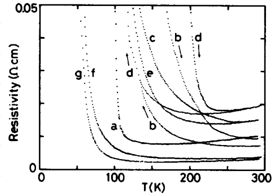


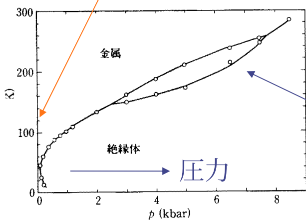
N,N'-dicyano-quinonediimine

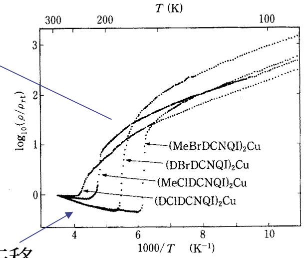
$Cu^{1.3+}$ mediates interchain interaction to make metallic @LT



Cu→Li, Na, Ag
→Peierls転移





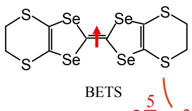


Halogen substituted
DCNQI: 金属-半導体転移

Beyon band theory (1) πd system

T. Mori, *J. Phys. Soc. Jpn*. **71**, 826 (2002).

Estimate *J* from *t*

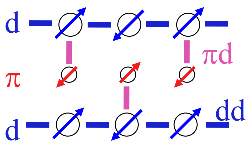


$FeBr_4^-$ **Magnetic anion**
***S* = 5/2**

$J_{\pi d}$= - $\frac{2\Sigma t_{\pi d}^2}{5\Delta}$ (5)

J_d= - $\frac{2\Sigma t_d^2}{25U}$ (25)

Magnetic structure κ-$(BETS)_2FeBr_4$



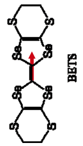
$$k_BT_N=\frac{35}{6}[J_d+\frac{\chi_q}{2k_BC_\pi}J_{\pi d}^2]=(dd)+(\pi d)$$

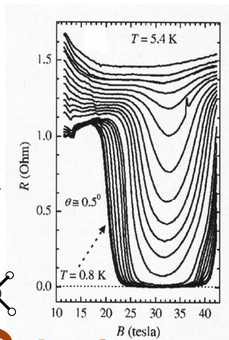
〜2.5 K

dd πd

Antiferromagnetic transision *T*

λ-$(BETS)_2FeCl_4$





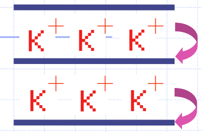
$J_{\pi d}$ < 0

+ =0

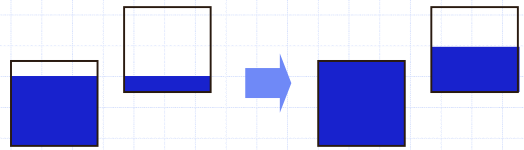
External field **Internal field**

Center field of field induced superconductivity

Graphite Intercalation Compounds



Increase Conductivity



Dope

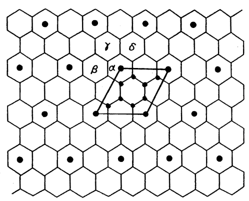


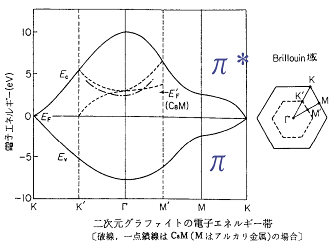
図6 グラファイト・カリウム C₈K 中のカリウム原子(●印)の配置

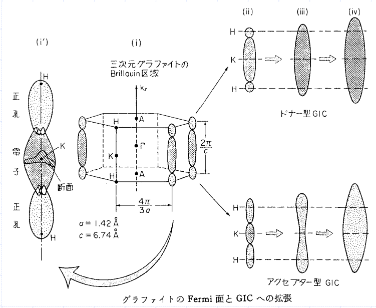
C_8K

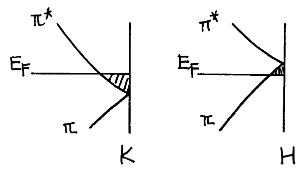
Superconductors
C_8K T_c = 0.39-0.55 K
C_8Rb T_c = 0.03-0.15 K
C_8Cs T_c = 0.02-0.14 K

Energy band of graphite

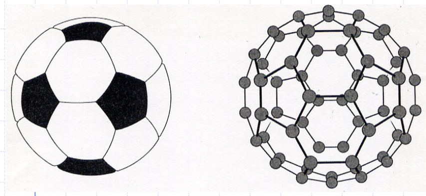
2D semimetal

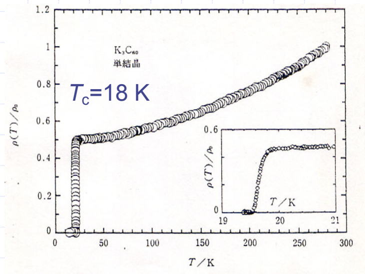


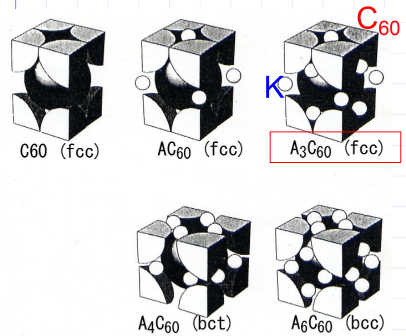


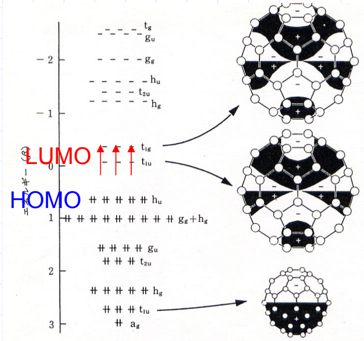


Fullerene salts：K_3C_{60}









Transition Temperatures and Discovery of Superconductors