Nano-Science of Organic (Super)conductors

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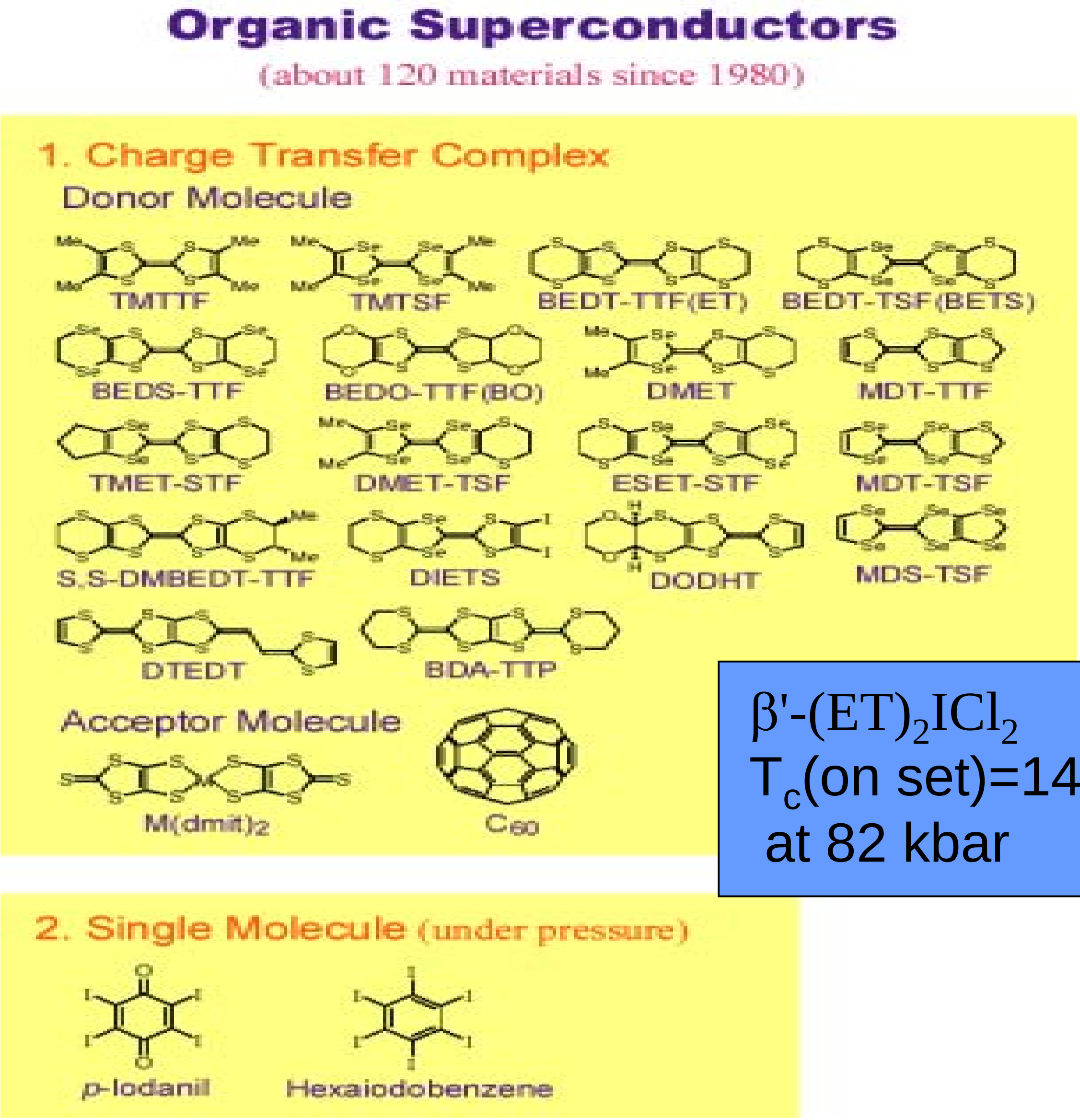
July 26, 2002



Organic Superconductors

(about 120 materials since 1980)

1. Charge Transfer Complex

Donor Molecule

Acceptor Molecule

2. Single Molecule (under pressure)

β'-$(ET)_2ICl_2$

T_c(on set)=14.2K

at 82 kbar

Design of Organic (Super)conductors & Study of Their Physical Properties

1. Introduction

- Carrier Generation & Carrier Path
- On-site Coulomb Repulsion vs. Bandwidth (Mott Criterion)
- Metal-Insulator or Metal-Superconductor Transition
- Dimensionality ● Molecular Design

2. Preparation & Measurements

- Crystal & Electronic (Band) Structures
- Conductivity, Magnetic Susceptibility

3. 10K Class Superconductors

- Electron Correlation ● Anisotropic Spin Lattice

4. κ-$(ET)_2Cu_2(CN)_3$

- Ground State

  Spin-Liquid (Ambient Pressure) vs Superconductor (Uniaxial Strain)

5. Conclusion

- Superconductivity is Mediated by Magnetic Interactions (non BCS)

Organic Superconductor

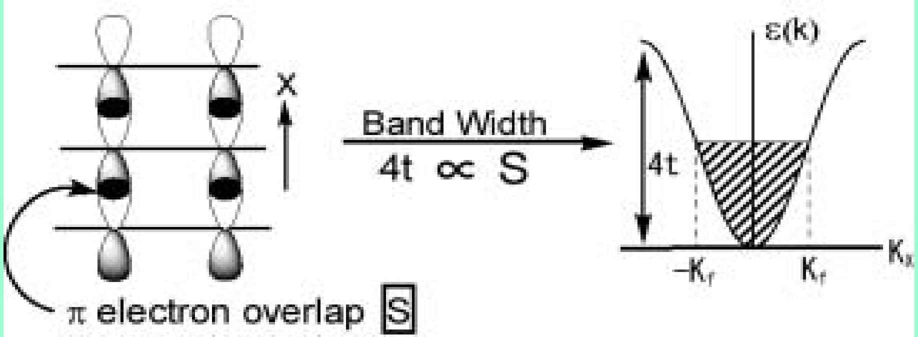
Starting Point ①　　　　Organic Metal

Requirement　i. **Generation of Carrier**
　　　　　　ii. **Generation of Conduction Path**

1: Charge Transfer Interaction

$$D + A \longrightarrow D^{\gamma+} \cdots A^{\gamma-}$$

2:Uniform Segregated Column



$$D^{1+}A^{1-}$$

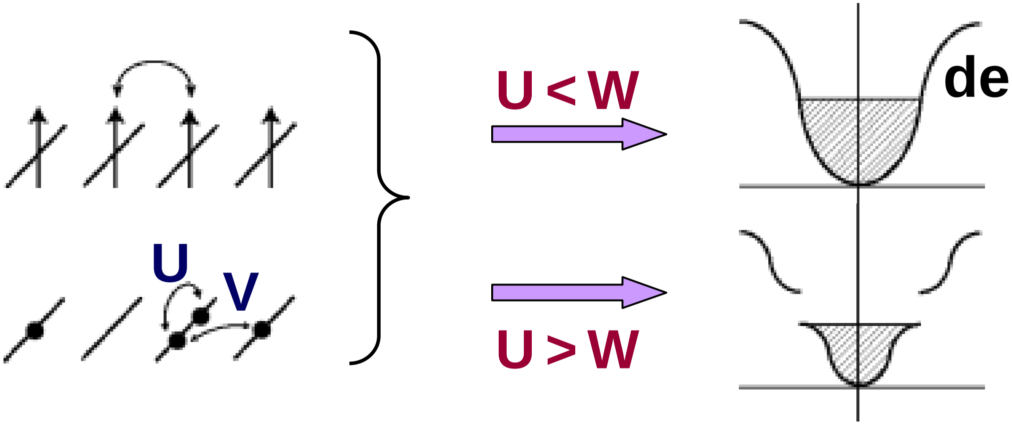
Metal for Inorganic

Insulator for Organic

Mott Insulator

3:**Mott Criterion**

Organic Material → Bandwidth ($W = 4t$) $\lesssim U$

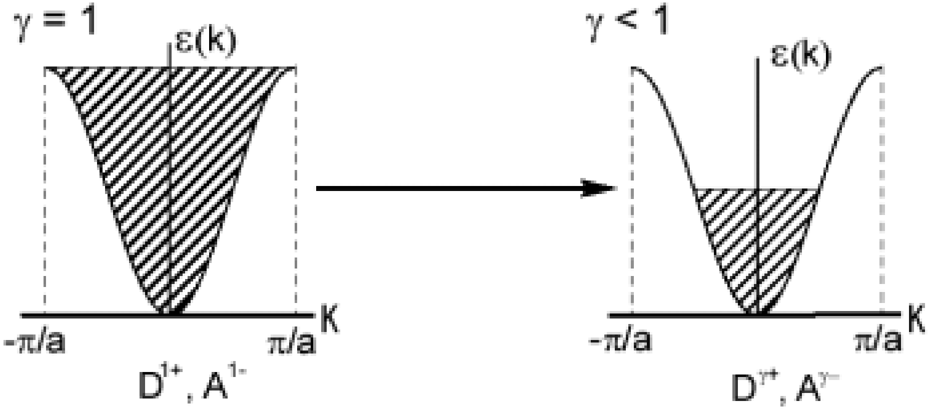


delocalized (itinerant) e

localized (electron correlated system)

To overcome Mott criterion

Fully Ionic



Partially Ionic

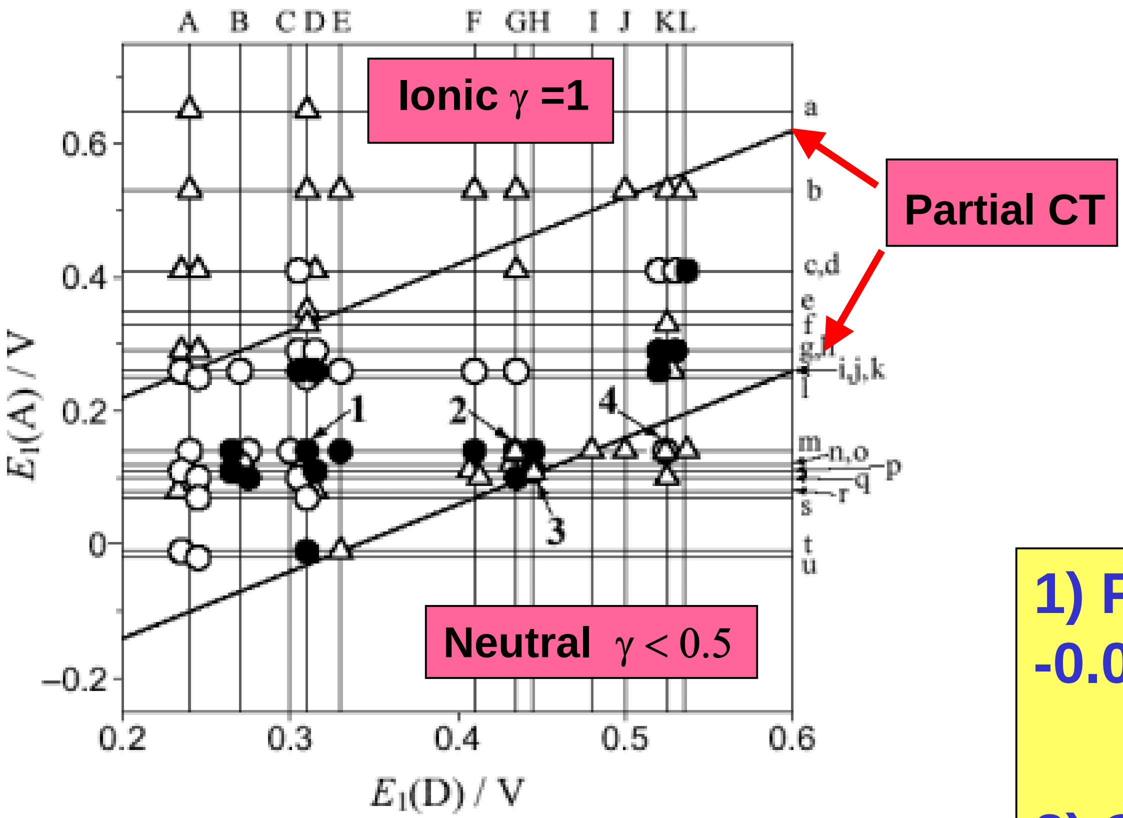
Uniform Segregated Column with Partial CT

McConnell-Hofman-Metzger Equation

Proc. Natl. Acad. Sci., USA, 53, 46(1965)

$$E_c(\gamma)/N = [(I_P - E_A)\gamma - M\gamma^2]$$

TTF•TCNQ Q-1D System



Ionic γ =1

Partial CT

Neutral $\gamma < 0.5$

Donor
A:TTT
B:TMTTF
D:TTF
G:TMTSF
H:TSF
K:BEDT-TTF

Acceptor
b:F_4TCNQ
e:2,5-I_2
i:F
m:TCNQ
p:2,5-Et_2

△: Insulator
○: Highly conducting
●: Metal

Ionic region: Mott insulator, spin-Peierls
Partial CT region: Organic Metal
Neutral region: non-linear optics

Saito, Ferraris, BCSJ, 1980

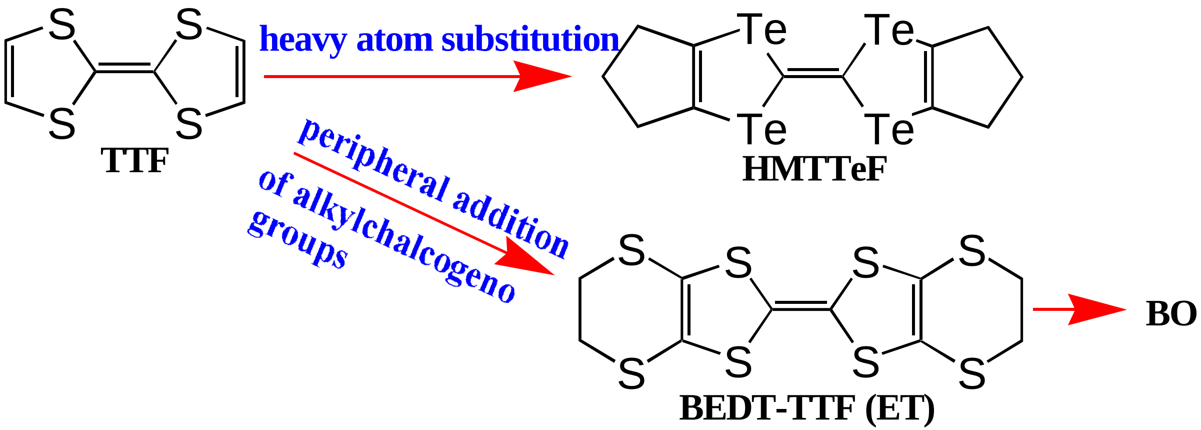
1) Partial CT state
$-0.02 \leq \Delta E(DA) \leq +0.34$
$0.5 \leq \gamma < 1$

2) Complex Isomerism
TMTSF•TCNQ (2)
TSF•Et_2TCNQ (3)
ET•TCNQ (4)
└→ 2D nature of ET

Modification of Dimensionality & Self-Assembling Ability

1) Increase of Dimensionality (self-assembling ability) : t↑ U↓

○ γ becomes wide for 'metallic regime'
○ Mott criterion becomes moderate
○ One-D Fermi → Two-D Fermi → stable metal towards any disorder··· BO system



TTF

heavy atom substitution

HMTTeF

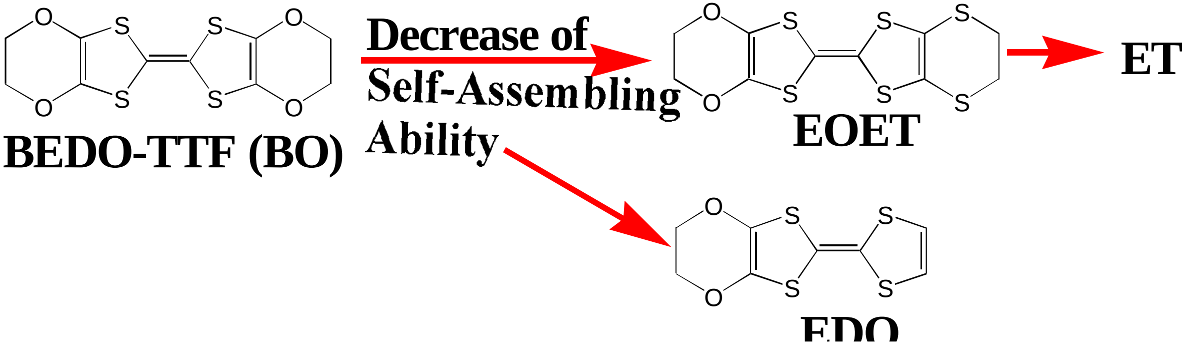
peripheral addition of alkylchalcogeno groups

BEDT-TTF (ET)

→ BO

2) Decrease of Self-Assembling Ability: t↓ U↑

○ Induce Phase Instability : New MI Phase Transition



BEDO-TTF (BO)

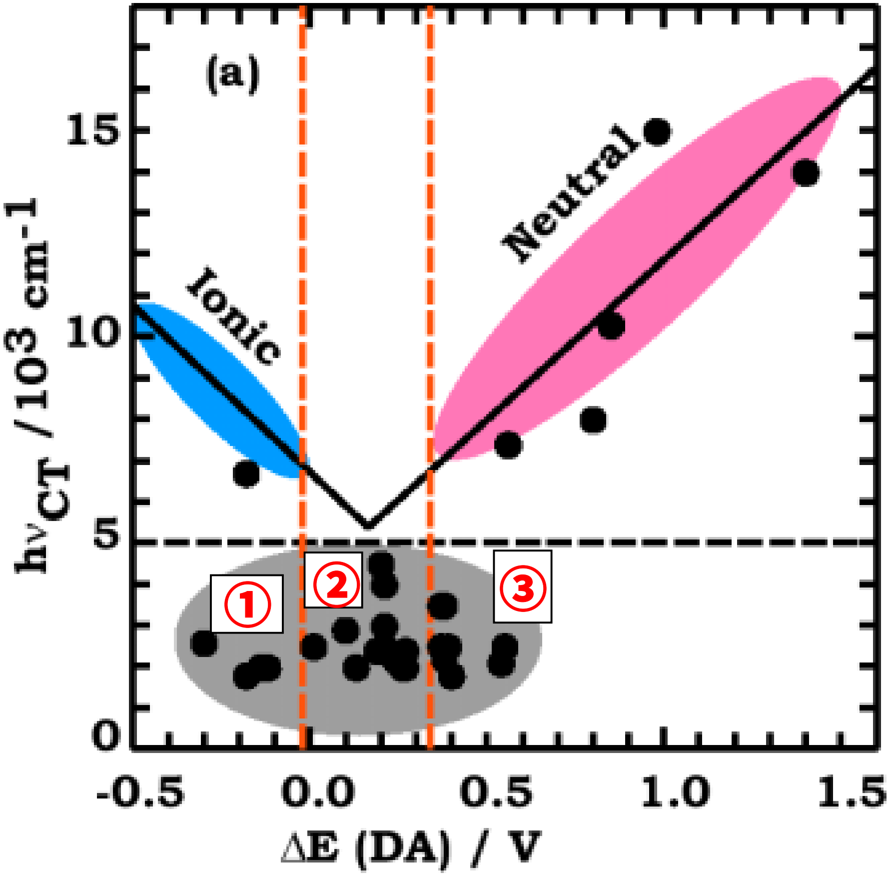
Decrease of Self-Assembling Ability

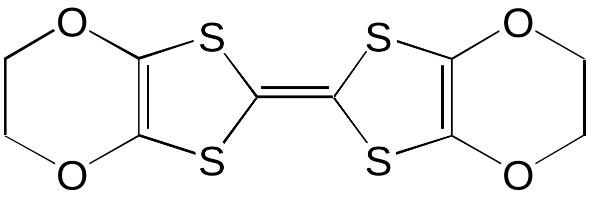
EOET

→ ET

EDO

BEDO-TTF System : Strong Self-Assembling Ability





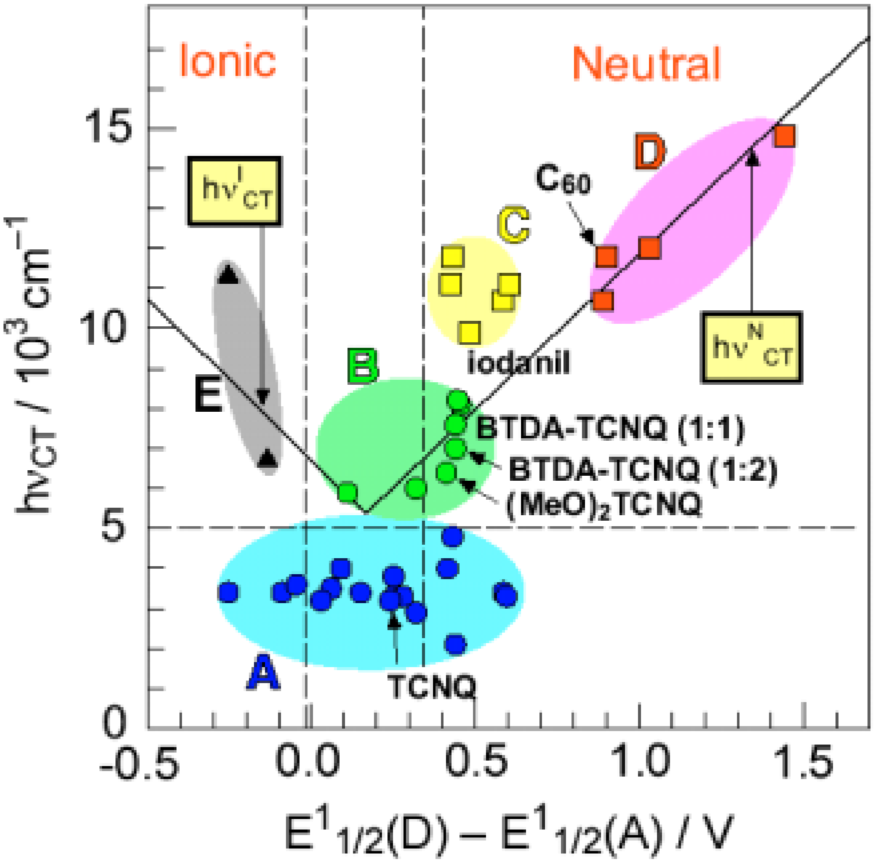
BEDO-TTF (BO)

- **Wide ΔE(DA) for Metal**
- **Stable 2D Metal**
- **Strong against Disorder (Pellet, LB & RDP Films)**

JACS, 118, 8604(1996)

① D:A≠1:1 (D>A) ② $1>\gamma\geq 0.5$ **for TTF•TCNQ** ③ **$0.5\geq\gamma\geq 0.3$**

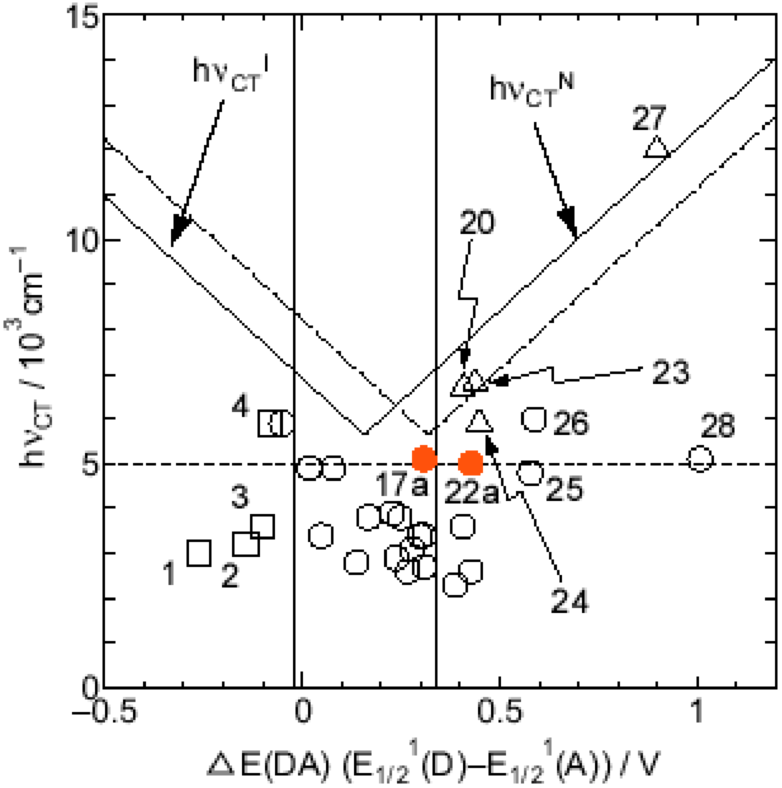
EOET DA Complexes

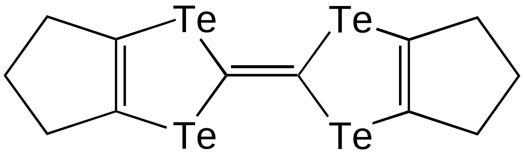


Group
A: Partial CT & Segregated
B: Partial CT & Alternating
C: Clathrate
D: Neutral & Alternating
E: Ionic

G.Saito et al., J. Mater. Chem., 12, 1640(2002)

HMTTeF System





HMTTeF

wide ΔE(DA)
highly conductive 10^4 Scm^{-1}

17a: HMTTeF•Et$_2$TCNQ•(THF)$_{0.1-0.5}$

22a:HMTTeF•BTDA-TCNQ(THF)$_{0.1-0.5}$

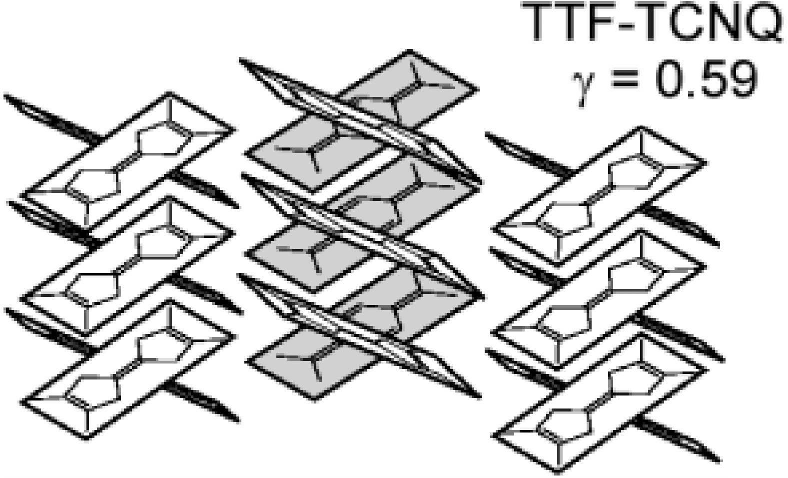
1. Metallic (near RT)
2. Alternating DA Stack

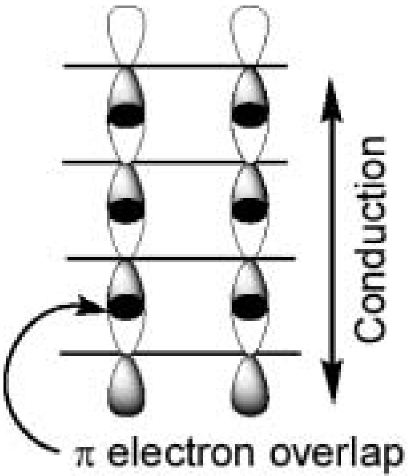
S.S.Pac, G.Saito, J. Solid. State Chem., 168, 486(2002)

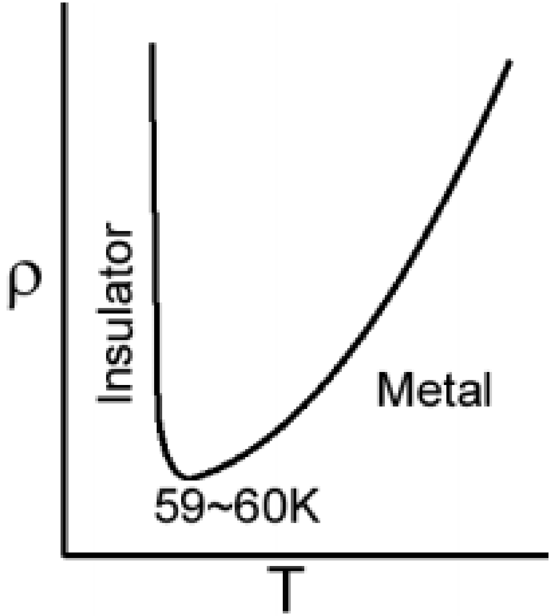
Organic Superconductor Starting Point ②

Suppress the M-I Transition of Low-dimensional Metal

1973~







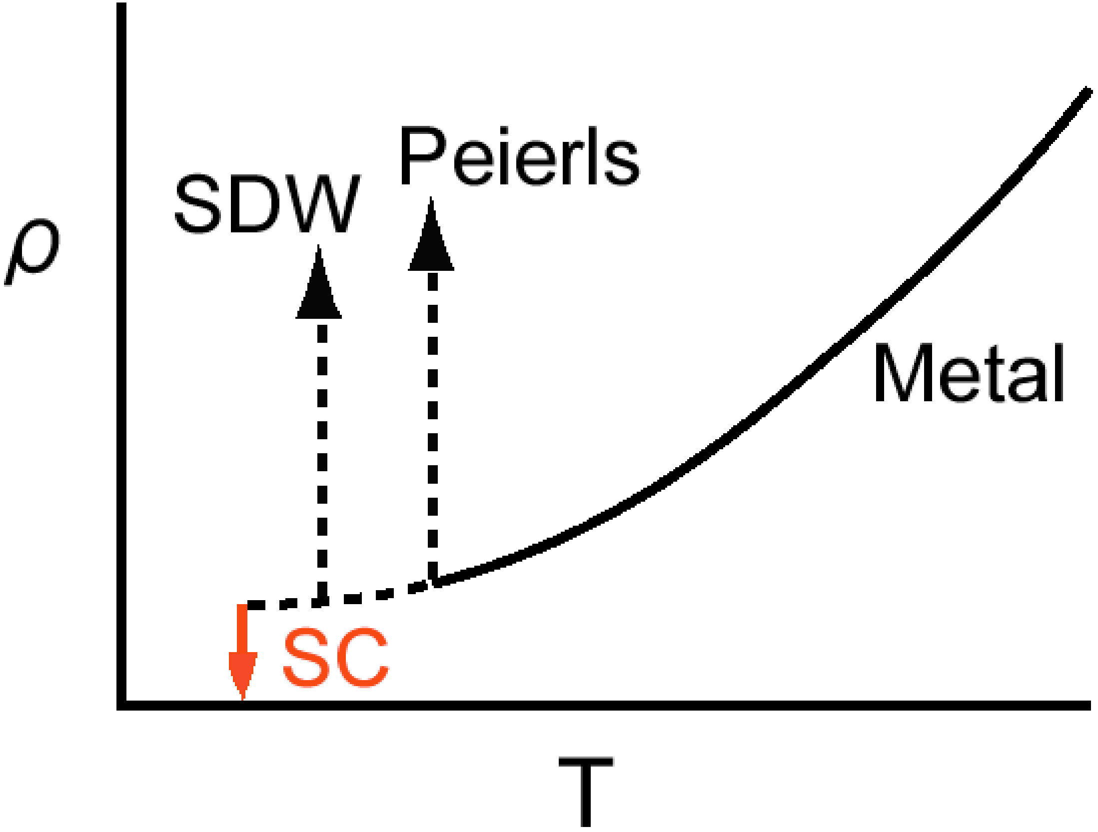
Ferraris,Cowan et al.

One-dimensional Metal

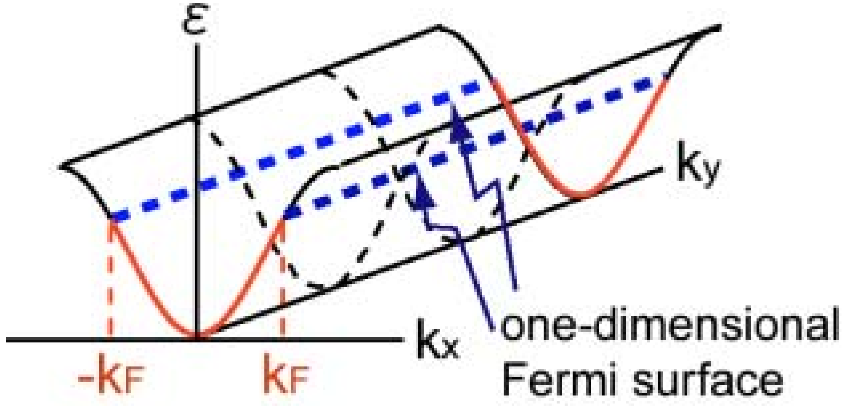
Three Low-temperature Phases of Low-dimensional Metal

1. Peierls (electron-phonon)
2. SDW (spin-spin)
3. SC (Cooper pair)

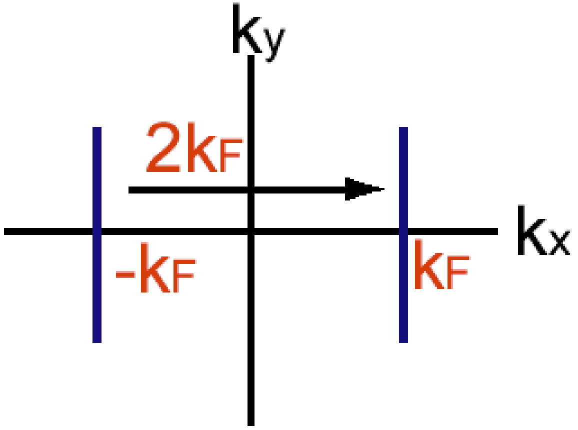
Organic Metal → Peierls Insulator



How to Suppress the Peierls Transition (in k space)

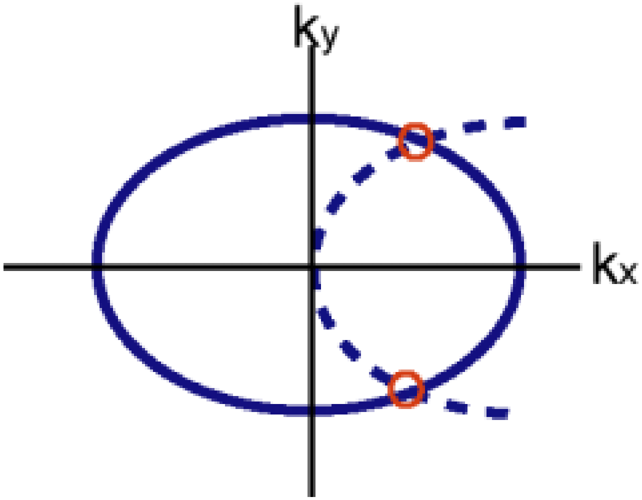


one-dimensional Fermi surface



avoid $2k_F$ nesting
increase dimensionality

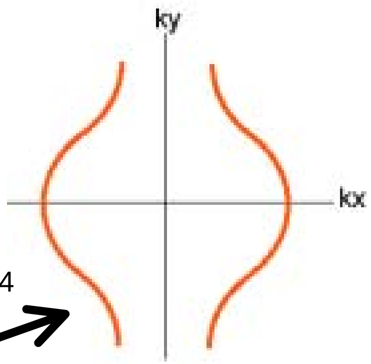
two-dimensional Fermi surface

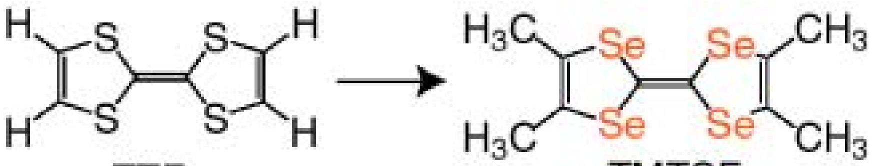


How to Suppress the Peierls Transition (in real space)

1. S → Se 1980 Bechgaard, Jerome

One-dimensional $(\mathrm{TMTSF}^{0.5+})_2X$, $X=ClO_4$

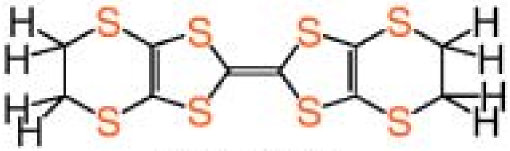




TTF

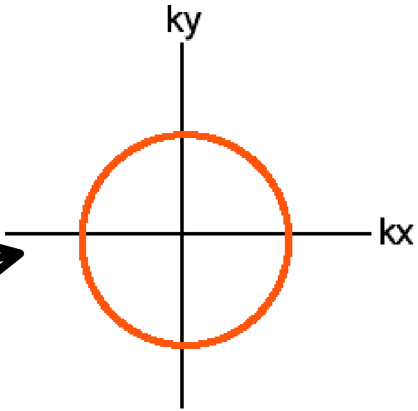
TMTSF

2. S → S + S



BEDT-TTF

1982 Two-dimensional Metal
no MI Transition
Saito, Enoki, Toriumi, Inokuchi



3. C_{60} $(M^+)_3C_{60}^{3-}$, M=K, ⋯

1991 Three-dimensional Metal
Hebard, Haddon et al.

Design of Functional Molecular Materials

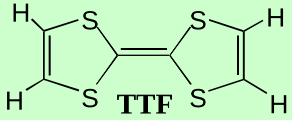
Structure (Molecule, Crystal, Electronic, Band)
vs Function

Weak Intermolecular ↓ Interaction

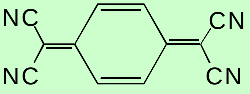
CT (π-π, n-π), Hydrogen Bond(CH･･O) , vdW(S･･S, Se･･Se, Te･･Te) , Coulomb(Madelung、on-site off-site electron correlation)

CT：
e Donor＋e Acceptor (or Anion)

1) $TTF^{\delta+}TCNQ^{\delta-}$ (δ=0.59)



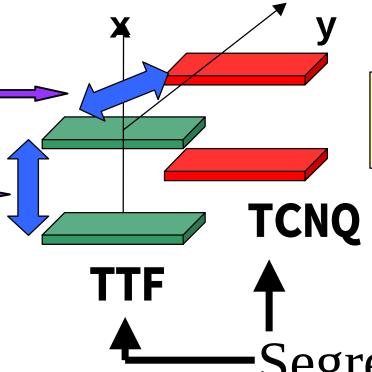
TTF



TCNQ

CT_1 Control Ionicity δ

CT_2 Control Band, Fermi surface, ζ

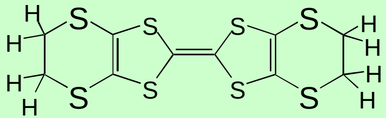


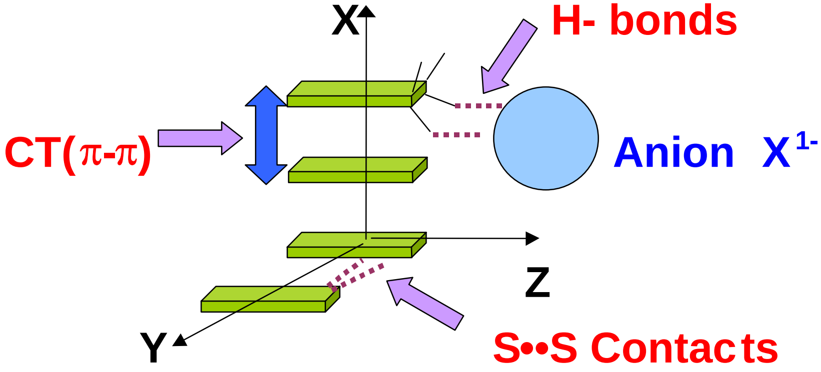
Segregated Column

t_x >> t_y, t_z → 1D metal

2) (BEDT-TTF$^{\delta+}$)$_2$X

δ=0.5　1 hole／dimer

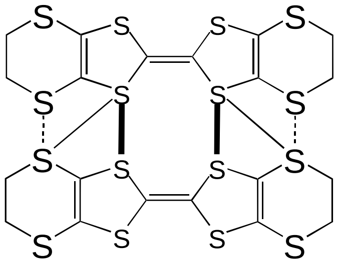




S‥S Contacts

(S$_{in}$‥S$_{in}$):(S$_{in}$‥S$_{out}$):(S$_{out}$‥S$_{out}$)
= 10 : 3.6 : 1

For ET salts: no S$_{in}$‥S$_{in}$ contact



$t_x \sim t_y >> t_z$

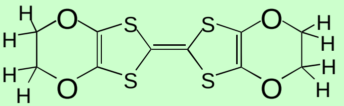
2 Dimensional

◎face-to-face (π– π) & side-by-side (S‥S) compete
◎Hydrogen bond (CH-X) modifies electronic structure

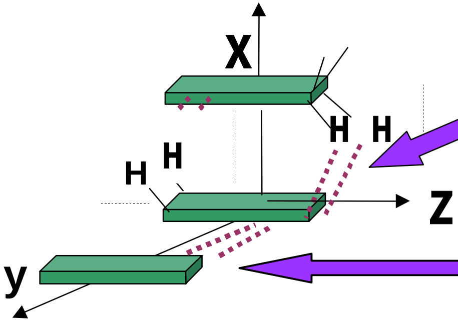
varied ethylene conformation

Polymorphism (α , α ', β , β ', β ", θ , κ • • •)

4) (BEDO-TTF)$_2$X Self-assembling Ability



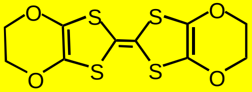
BEDO-TTF(BO)

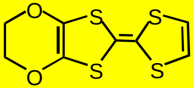


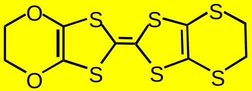
CH$_2$··O Hydrogen Bond

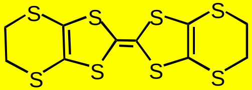
Short S$_{in}$…S$_{in}$ contact

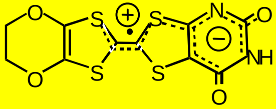
t_y(60°) ~ t_y(0°) >> t_x → 2D Metal (stable towards any disorder)

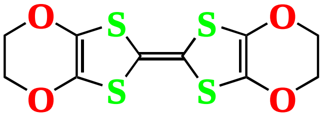

Metallic LB films, Metallic transparent films(self-assembling)


New Metal-Insulator Transition (molecular deformation)


Two-leg Spin-ladder (molecular symmetry C$_{2v}$)

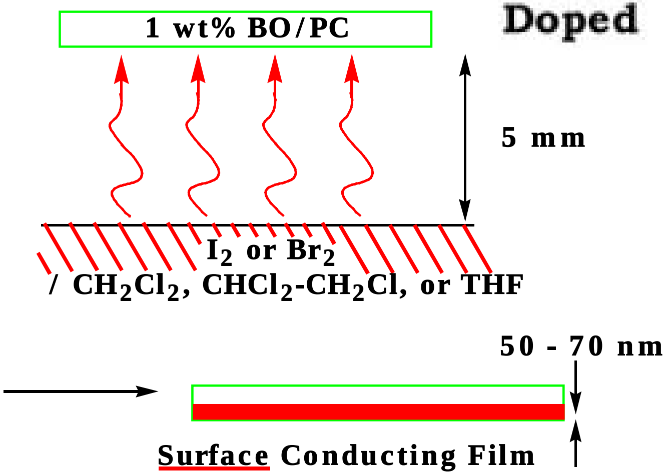

Spin-liquid vs Superconductor(e-correlation U/W, t'/t)


Molecular Electronics (mean free path vs e-correlation)



BEDO-TTF (BO)

·Film Preparation



1 wt% BO/PC

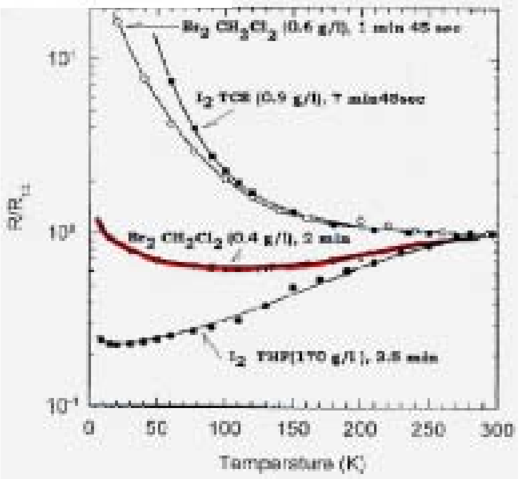
5 mm

I_2 or Br_2 / CH_2Cl_2, $CHCl_2$-CH_2Cl, or THF

50 - 70 nm

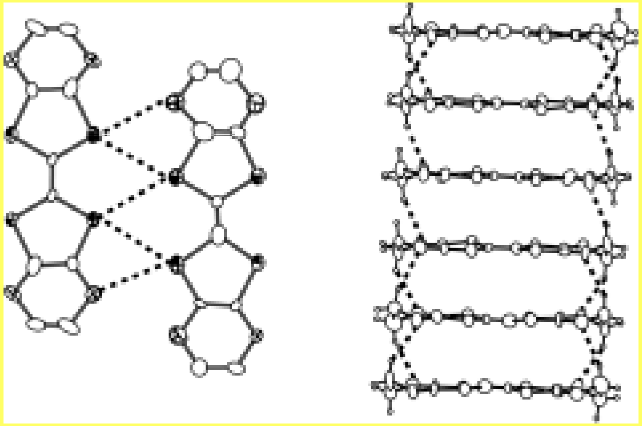
Surface Conducting Film

1×10^3 Ω/□ (≈ 10^{-3}-10^{-2} Ωcm)

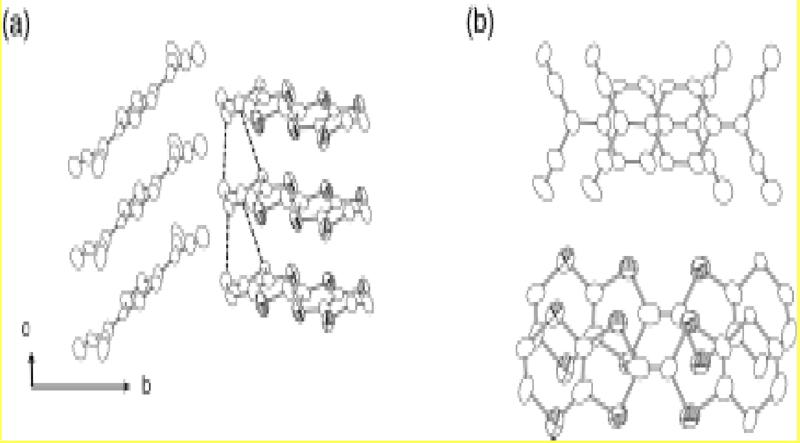


JMC 10, 893-910(2000) $M(dto)_2$, 10, 911-919(2000) TNBP, 11, 364-373(2001) DHCP, JACS 122, 4436-4442(2000) degree of CT, Synth. Metals, 120, 721, 739, 863 (2001) plasmons, design, MCLC, 376, 113-120(2002) $MM'(ox)_3$, JSSC, 168, 450-456(2002) $M(isoq)_2(NCS)_4$

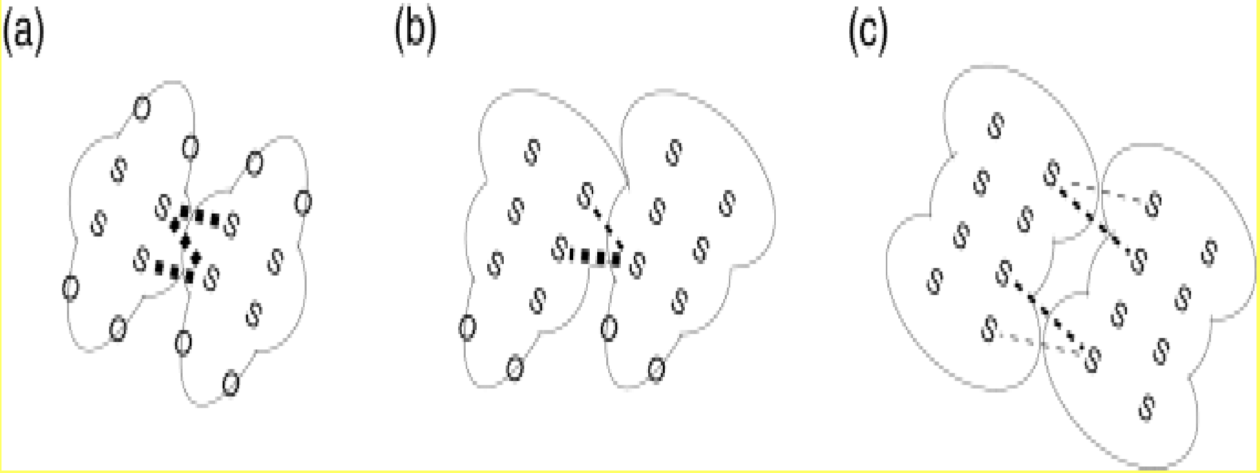
Stacking of BO molecules



Stacking of EOET molecules



Geometry & Symmetry effect on side-by-side atomic contacts

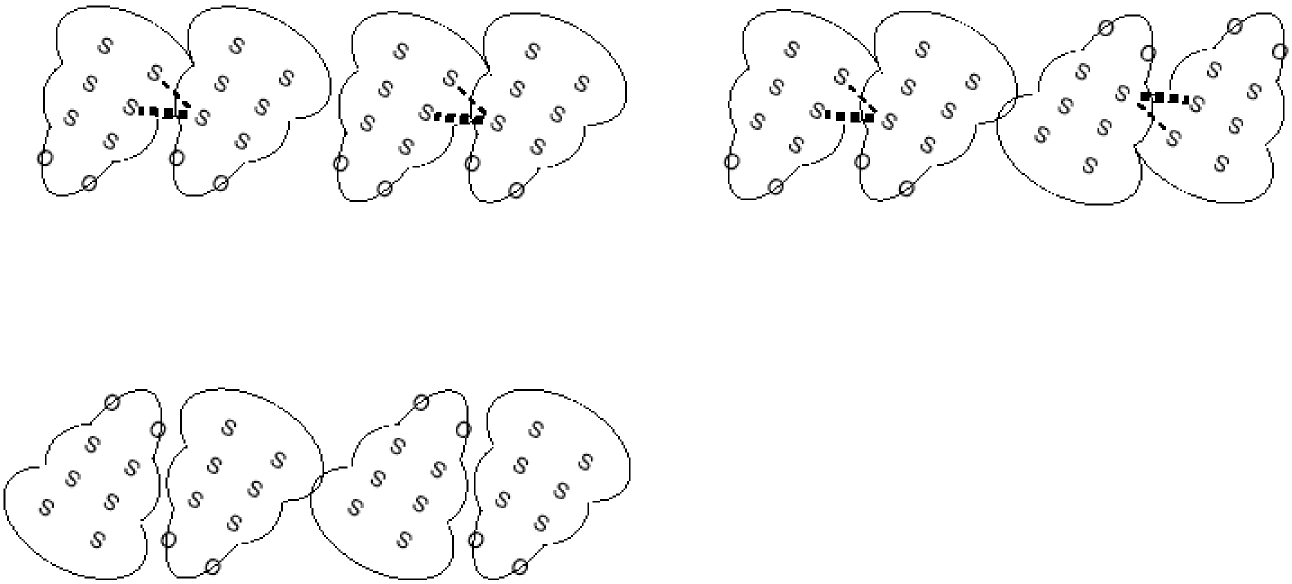


BO EOET(head-to-head) ET

Design of Two-Leg Spin-Ladder based on EOET

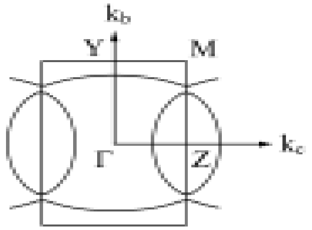
G. Saito et. al.

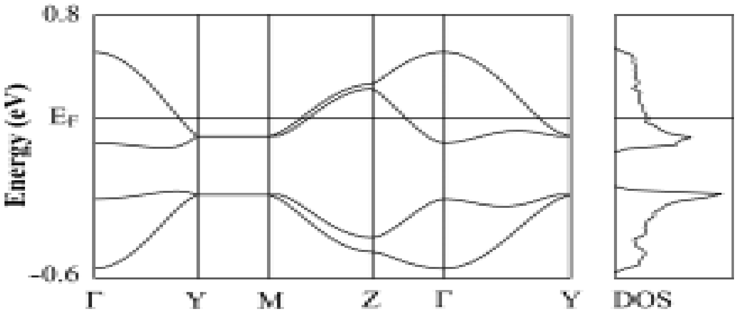
Figure 04



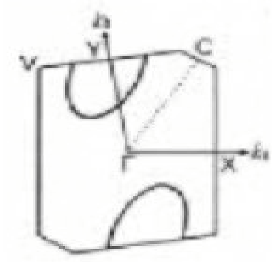
Energy Dispersion, Fermi Surface, DOS

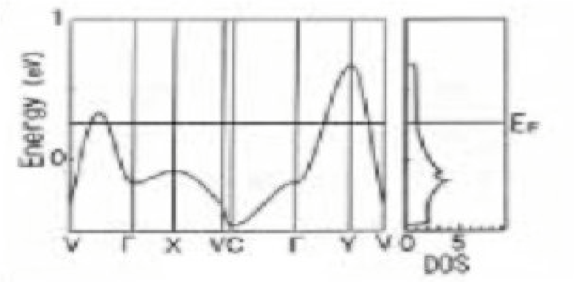
κ-$(ET)_2Cu(NCS)_2$





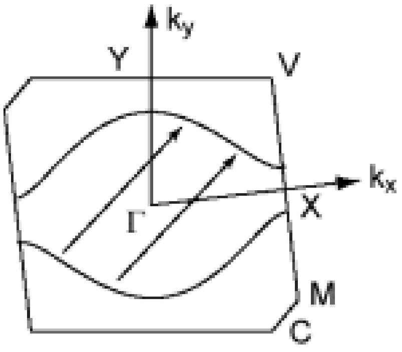
$(BO)_{2.4}I_3$



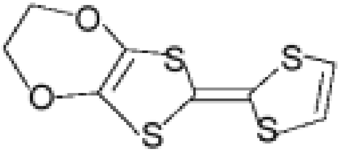


2D → 1D

$(EDO)_2PF_6$



ionized



neutral

New Metal-Insulator Transition triggered by molecular deformation

Ota, Yamochi, Saito
J. Mater. Chem., 12, 2600(2002)

Summary(1)

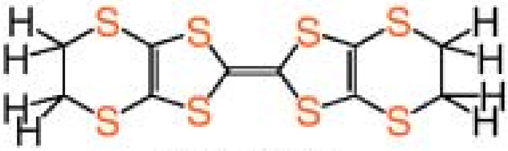
1. **Uniform Segregated Column with Partial CT controllable by Self-assembling Ability & (I_P-E_A)**

2. **Dimensionality controllable by physical (pressure) & chemical "heavy atom substitution" "peripheral addition of alkylchalcogeno groups" methods (size, symmetry, degeneracy)**

1D	**TTF**	↓	**Stability**
1~2D	**ET**		**&**
	EOET		**Self-Assembling Ability**
2D	**BO**		

Preparation & Characterizations of 10 K Class Superconductors

	Tc/K	
	H	D
κ-$(ET)_2Cu(NCS)_2$	10.4	11.2
$Cu[N(CN)_2]Br$	11.8	11.2
$Cu[N(CN)_2]Cl$	12.8	13.1 (at 0.3kbar)
$Cu(CN)[N(CN)_2]$	11.2	12.3



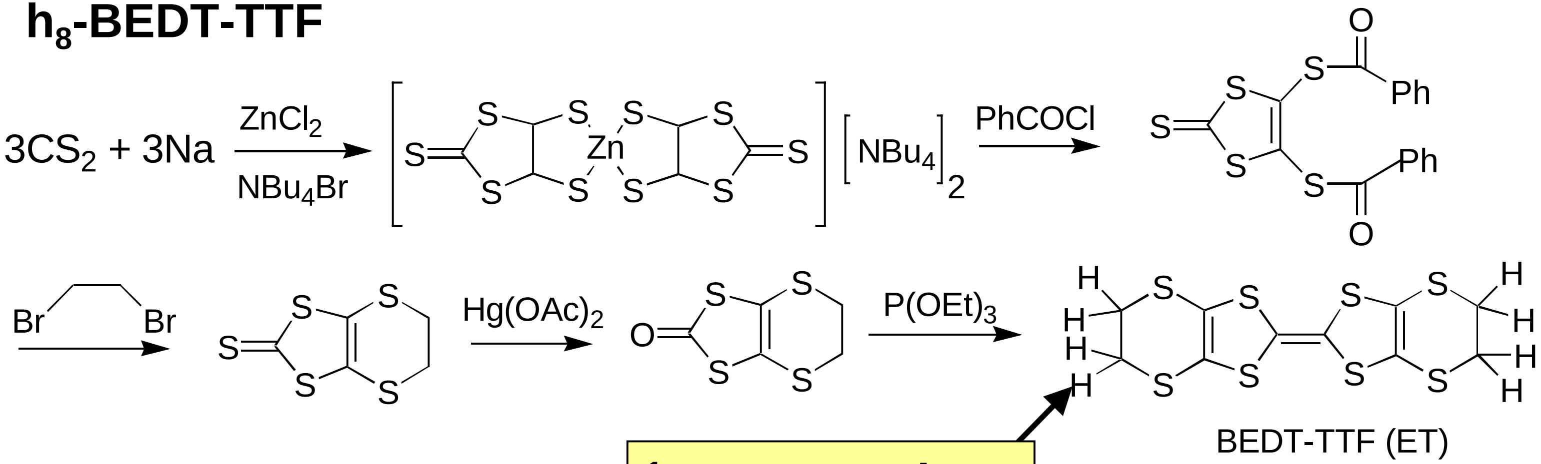
BEDT-TTF

H-Salt

H → D-Salt

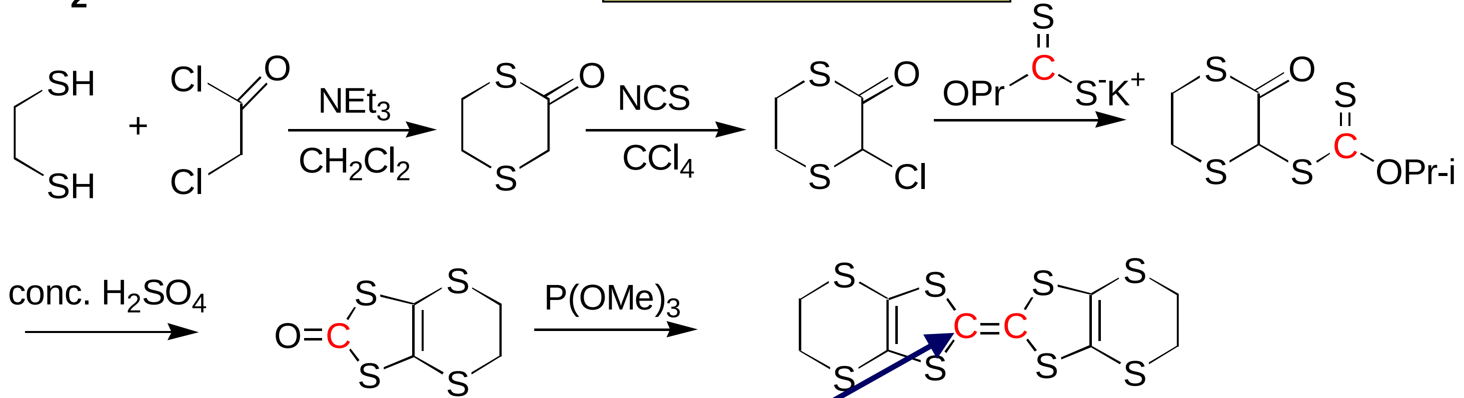
Synthesis of BEDT-TTF (ET)

h_8-BEDT-TTF



^{1}H-NMR Probe

$^{13}C_2$-BEDT-TTF



^{13}C-NMR Probe

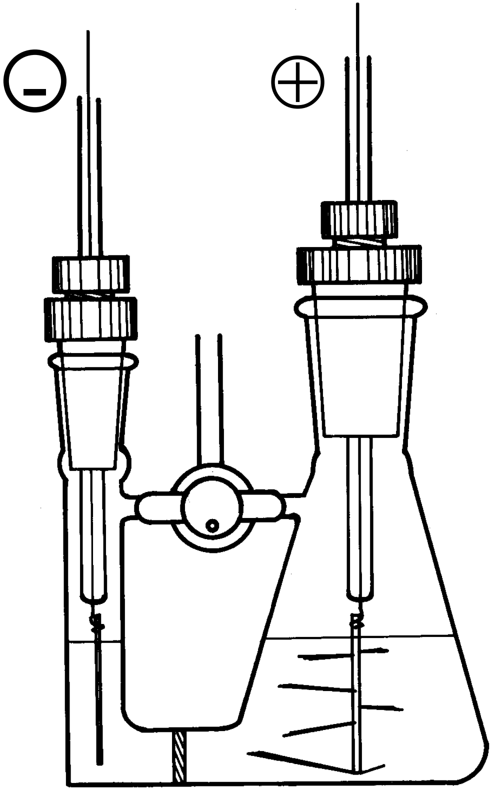
$^{13}C_2$-BEDT-TTF (ET)

Long Symmetric Linear Anion ?

NCS - Cu - SCN
~ 15 Å

vs

I - I - I$^{\ominus}$
10.1 Å
β-$(ET)_2I_3$ Tc = 8K

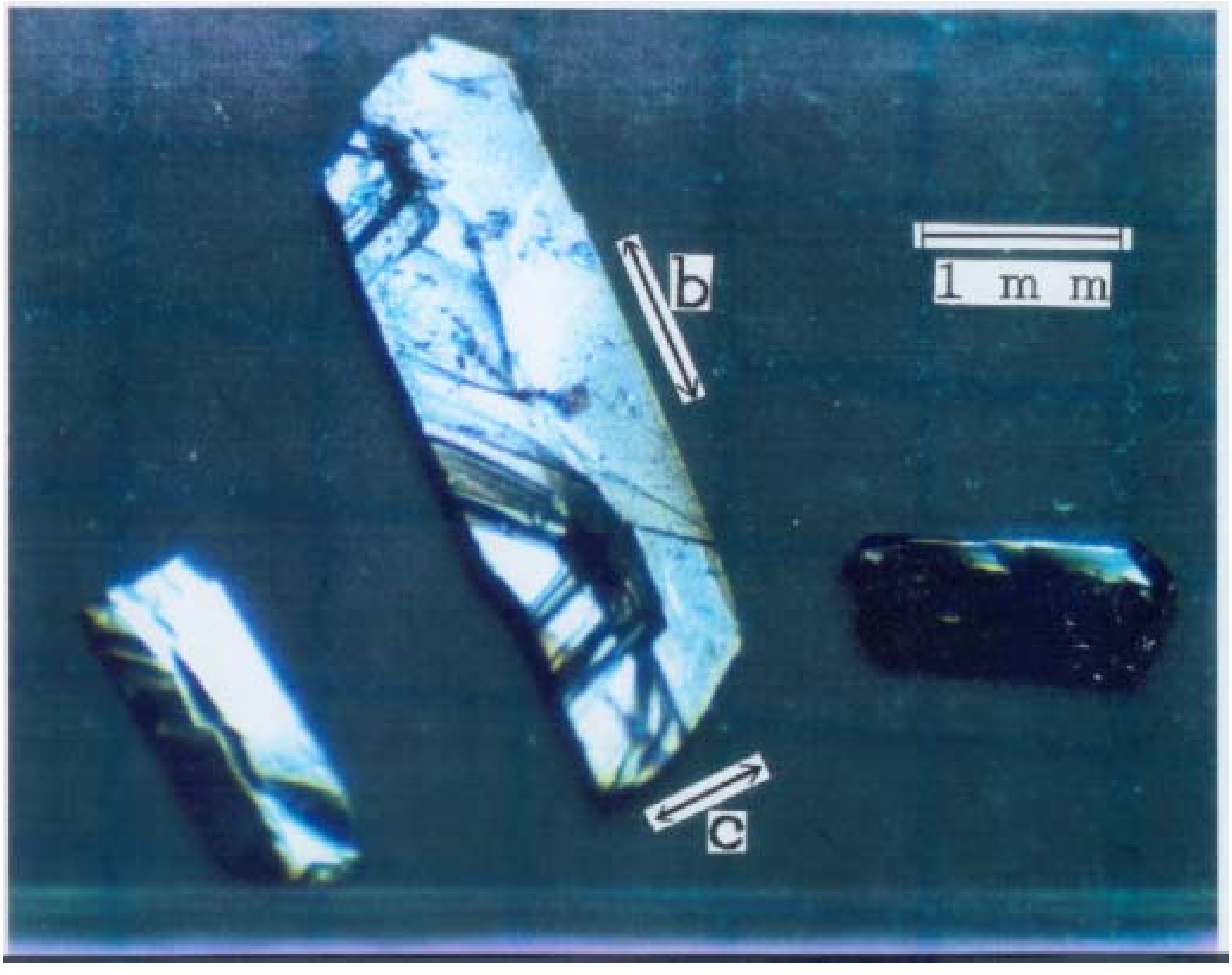


Electrocrystallization

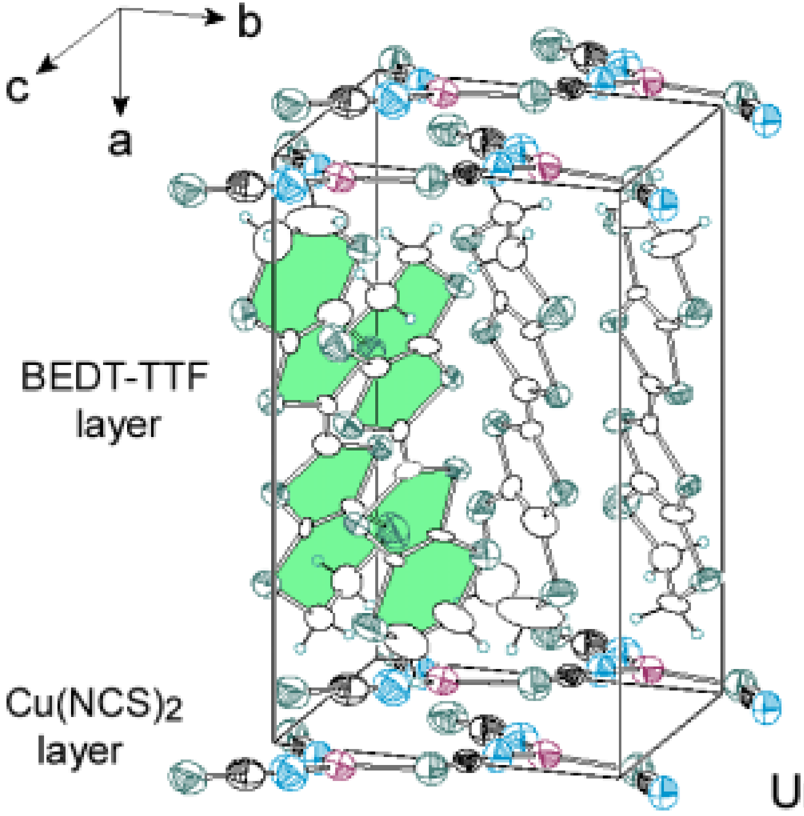
1. Supporting Electrolyte
   $CuSCN + KSCN + 18$ -crown-6 ether
   70 mg 130 mg 200 mg
   K^+ , $SCN^{\ominus}$, CuSCN
2. Donor BEDT-TTF $\longrightarrow$ BEDT-TTF$^{\oplus}$
3. Solv 1,1,2-trichloroethane or benzonitrile
4. Current 0.5 ~ 4 μA, ~2 weeks

$(BEDT\text{-}TTF)_2Cu(NCS)_2$
1988 Urayama, Saito *et al*.

κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ bc-plane: 2D conducting

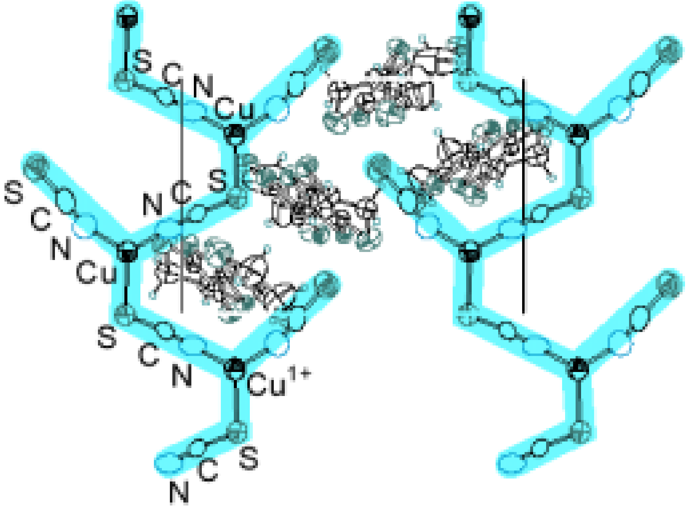


κ-(BEDT-TTF)$_2$Cu(NCS)$_2$



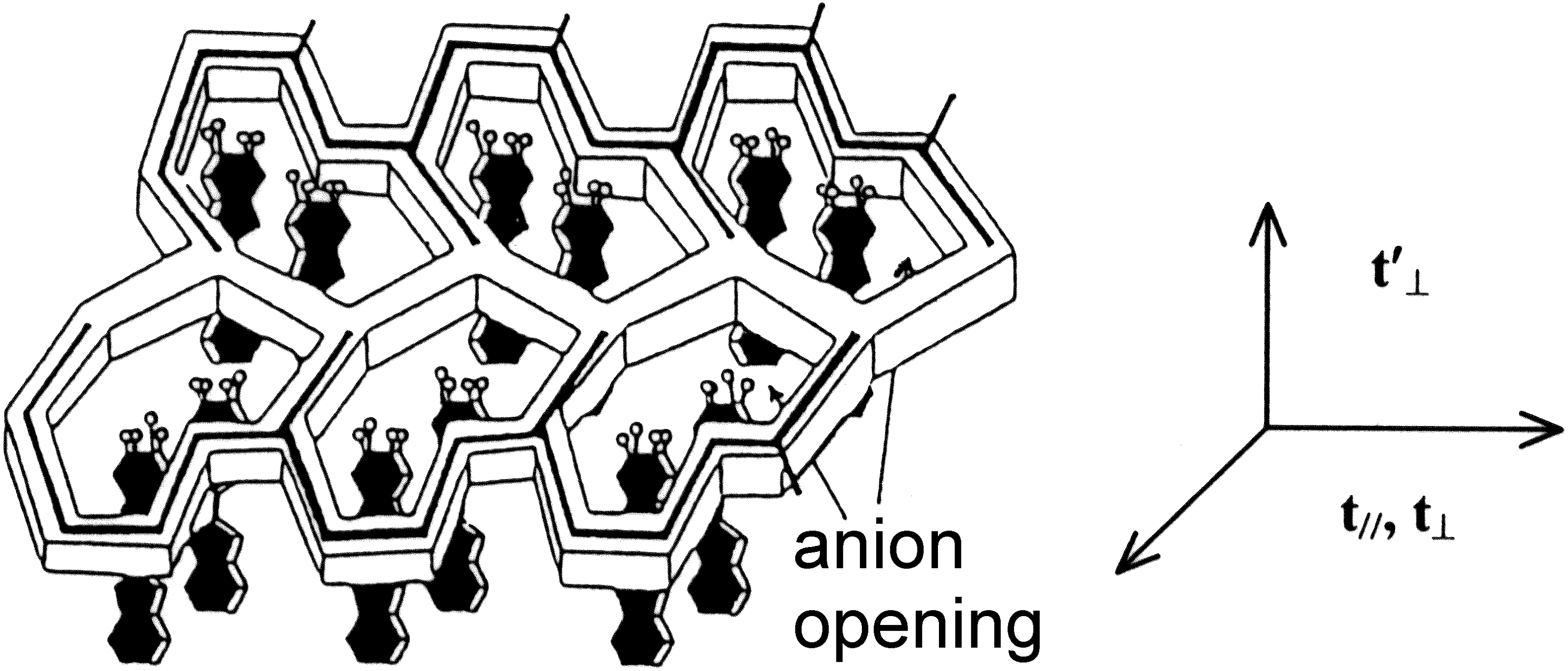
[dextro rotatory form]

monoclinic $P2_1$



Urayama, Saito *et al.*, Chem. Lett., 1988, 55

κ-(BEDT-TTF)$_2$X, X:polymerized anion

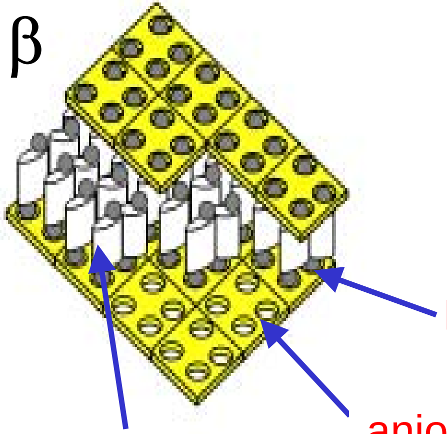


1. Pattern → donor packing pattern
2. Basal Plane Size → $t_{//}$, $t_\perp$, DOS
3. Thickness → $t'_\perp$

G.Saito et al., Mol. Cryst. Liq. Cryst.

Patterns of Anion Opening & Donor Packing

β

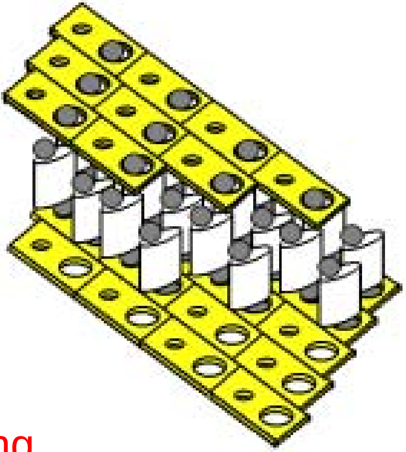


H atom

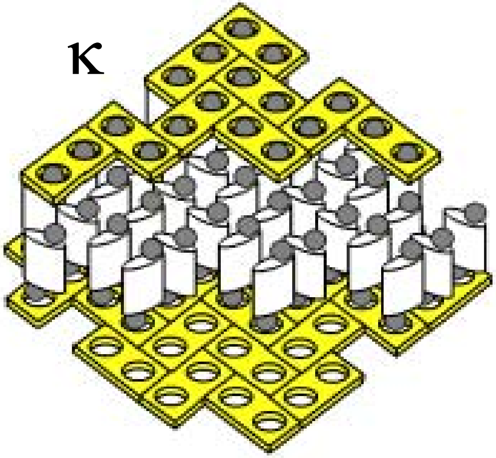
anion opening

ET molecule

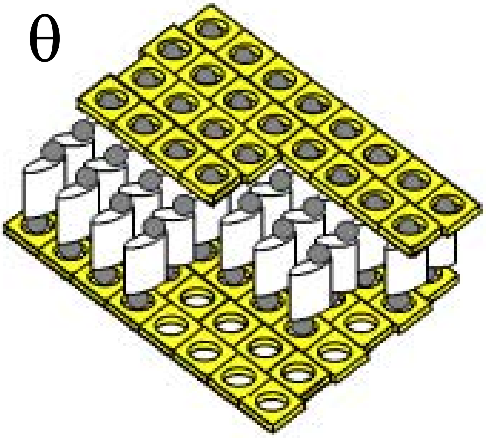
α



κ



θ



H.Yamochi et al., JACS, 115, 11319(1993)

Design of High T_c ET Superconductors

1. Big anion → Packing density of ET↓ → $t_{//}$↓ → DOS↑ → T_c↑

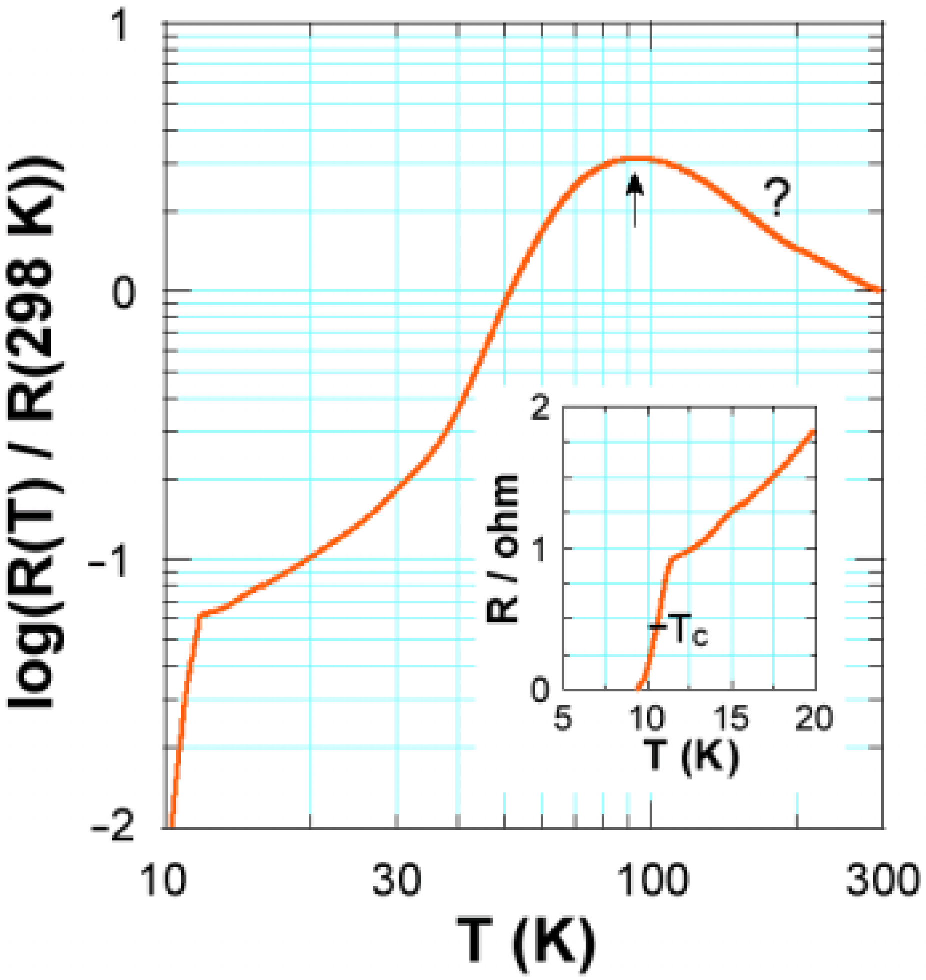
2. Thin anion → Inter-donor-layer $t'_{\perp}$↑ → 3D nature↑ → T_c↑

3. 2D polymerized anion + donor-anion interaction↑ →
   3D structural nature↑ → thermal contraction↓ →
   keep DOS large → T_c↑

↓

Use big and thin anion which forms thin 2D anion layer
and provides both
loose donor packing and strong anion•••donor atomic contacts

κ-(BEDT-TTF)$_2$Cu(NCS)$_2$



4 probe Au wire Au paste

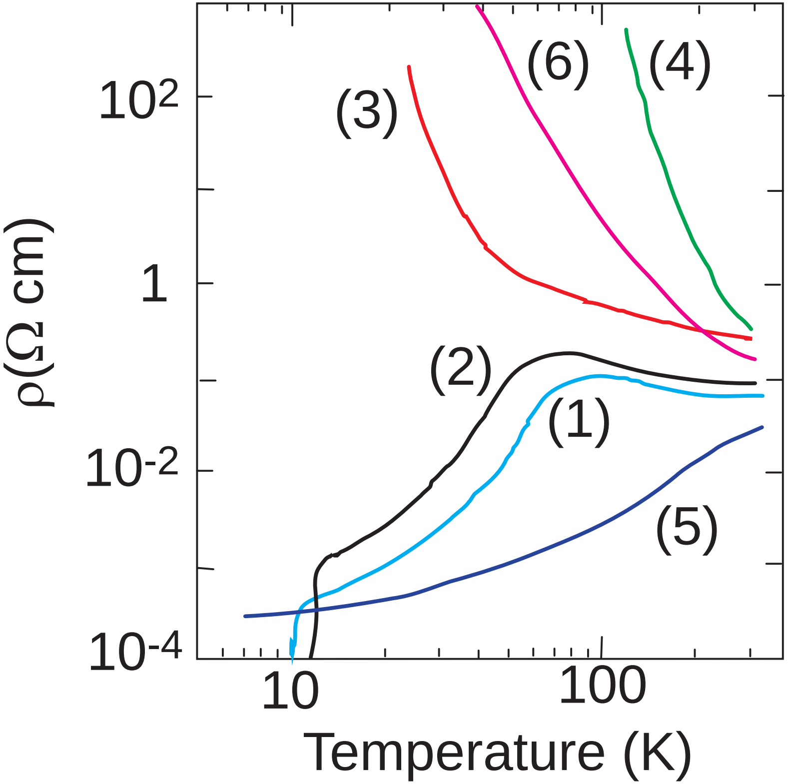
σ_{RT}(//b) = 10 ~ 40 S cm^{-1}

$\sigma_{a^*} : \sigma_b : \sigma_c$ = 1/600 : 1 : 1.2

T$_c$ on set : 11.0 K
off set : 9.8 K
mid-point : 10.4 K

Pressure ↑ → T$_c$ ↓
(−3.0 K/kbar)

Resistivity for ET Salts



10K Class Superconductor

(1) κ-$(ET)_2Cu(NCS)_2$

(2) κ-$(ET)_2Cu[N(CN)_2]Br$

(3) κ-$(ET)_2Cu[N(CN)_2]Cl$

Mott Insulator at Ambient

Superconductor at 0.3kbar

Electron Correlated Insulator

(4) θ-$(ET)_2Cu_2(CN)[N(CN)_2]_2$

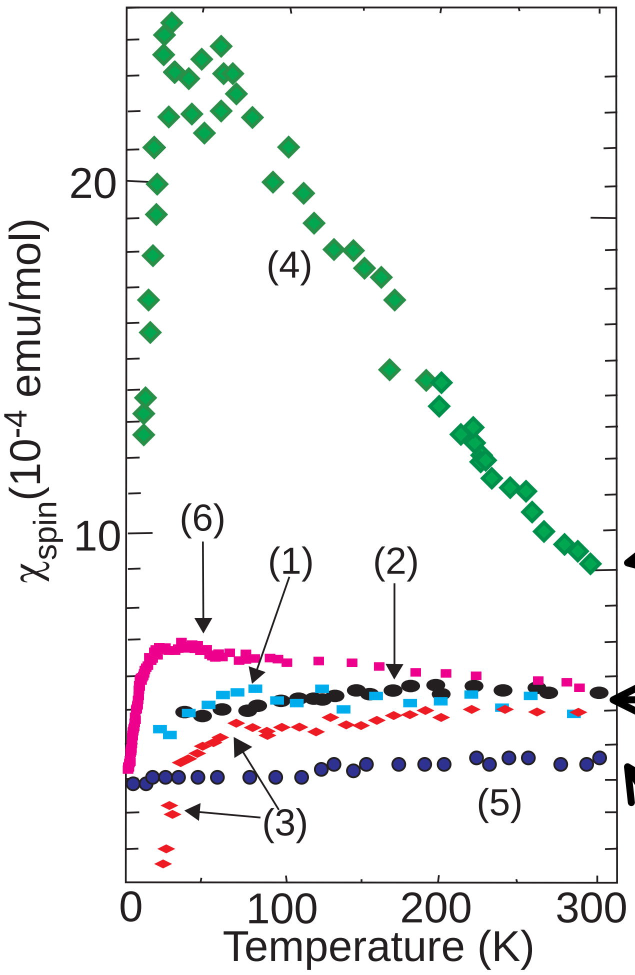
2D Metal with low Tc

(5) β-$(ET)_2AuI_2$

What about

(6) κ-$(ET)_2Cu_2(CN)_3 \longrightarrow$ Mott Insulator

EPR Magnetic Susceptibility χ_{spin}



For a metal $\chi_{spin} = \chi^0_{spin}/(1-D(\varepsilon_F)U_{eff})$

χ^0_{spin} : Pauli Paramagnetism

$D(\varepsilon_F)$:Density of States at Fermi level

U_{eff} : effective U

Insulator:(4)

10K Super (Poor Metal)
(1), (2), (3) & (6)?

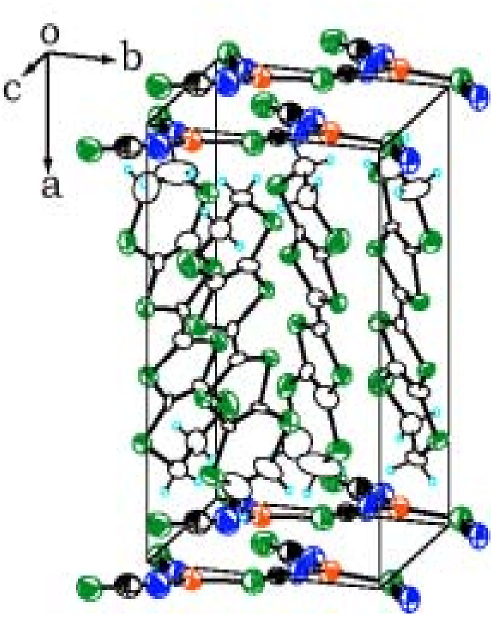
Good Metal: (5) β-$(ET)_2AuI_2$

U Increase

κ -Type 10 K Superconductor κ-$(ET)_2X$

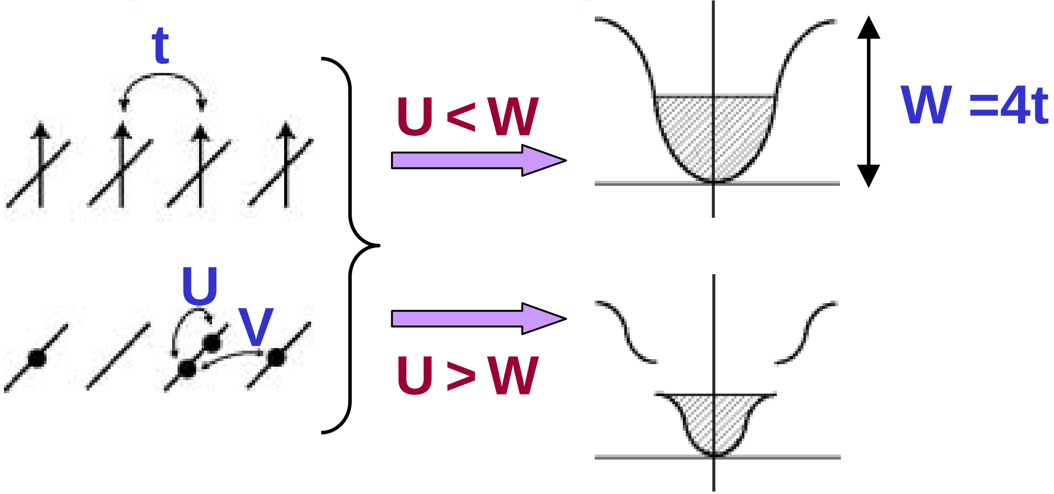
X: polymerized anion

$Cu_2(CN)_3$, $Cu(NCS)_2$
$Cu[N(CN)_2]Y$
(Y: Cl, Br, I)
$Cu(CN)[N(CN)_2]$



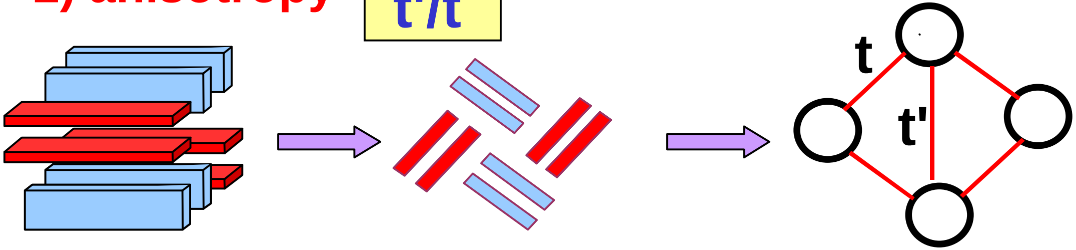
1) delocalization vs. localization (electron correlation)

U/W



2) anisotropy

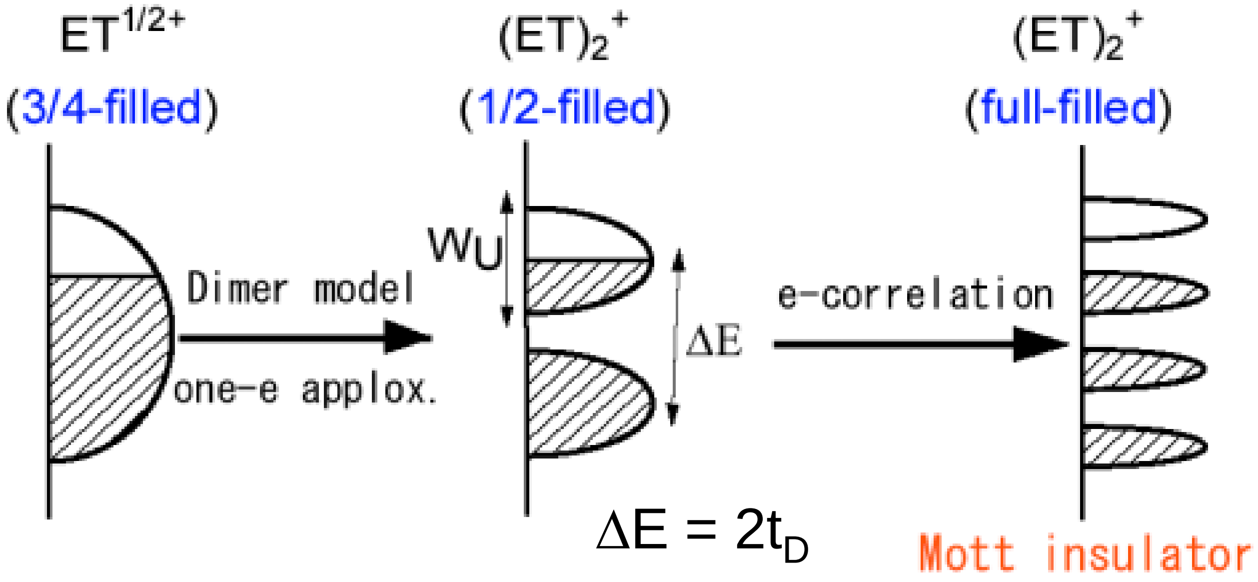
t'/t



Electron correlation

Mott criterion for dimerized system: $W_u/\Delta E$ vs W_u

W_u: upper Hubbard band width, ΔE: dimerization energy

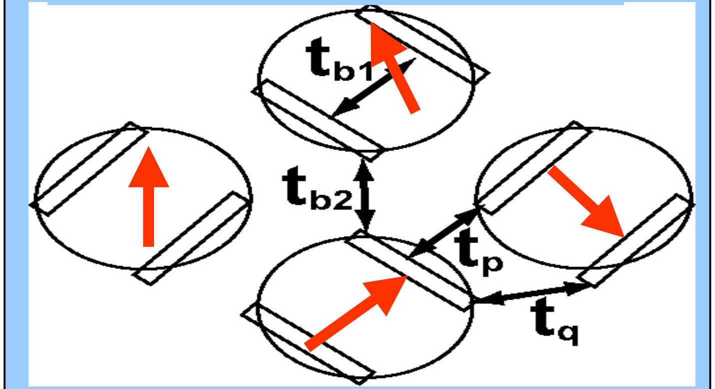


$\Delta E = 2t_D$

Anisotropy *κ-(ET)$_2$X*= *anisotropic triangular lattice*

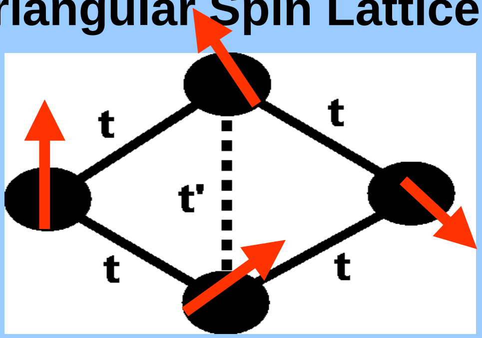
ET molecule = +0.5 ⟶ ET dimer has 1 spin

Donor Packing Pattern

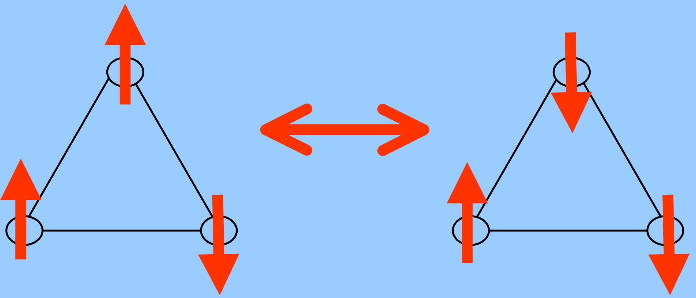


dimer model

Triangular Spin Lattice



Large geometrical frustration between local spins when $t'/t \sim 1$

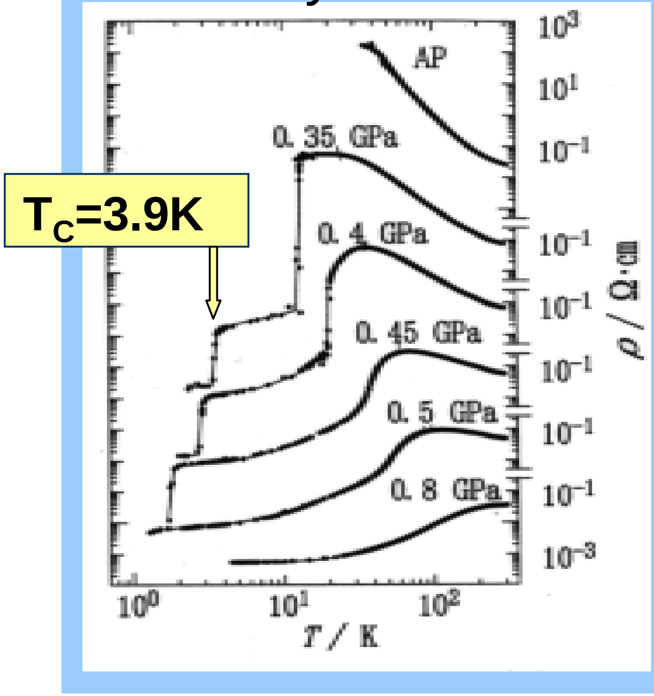


Ground state?

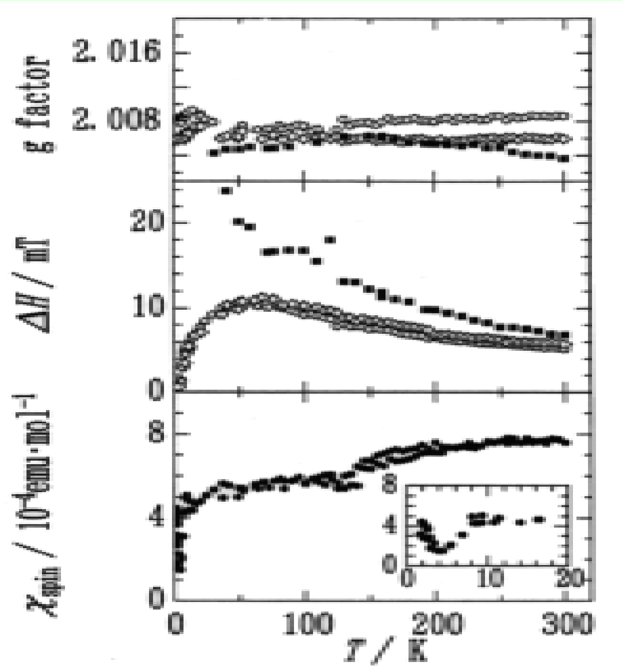
- **Antiferromagnet**
- **Spin liquid insulator (RVB)**

κ-$(ET)_2Cu_2(CN)_3$ Uniform triangular lattice → Ground state ?

Resistivity


T_C=3.9K

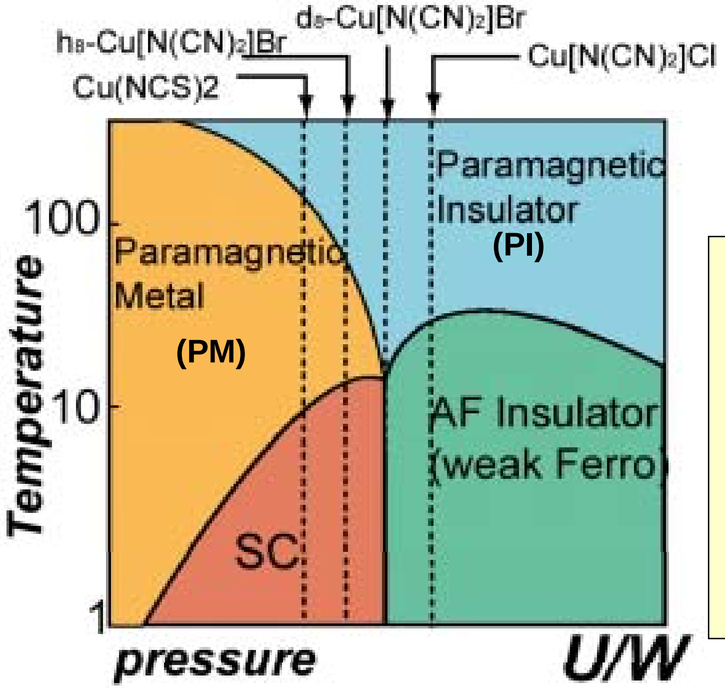
EPR



X	t'/t	ground state	Tc (K)	Pc(kbar)
$Cu_2(CN)_3$	1.06	???	3.9	0.4
$Cu[N(CN)_2]Cl$	0.75	Antiferro	12.8	0.3
d8-$Cu[N(CN)_2]Br$	0.68	Antiferro		Rapid cool

T. Komatsu et al. JPSJ (1996), McKenzie, Comm. Cond. Mat. Phys. (1998)

κ-(ET)$_2$X   T - P phase diagram



K.Kanoda 1997

Spin-canting
Antiferromagnet (AF)
T=27 K

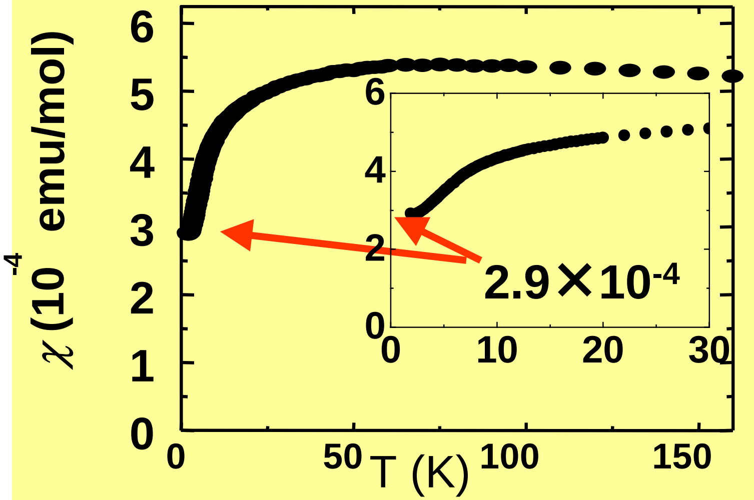
Only includes U/W

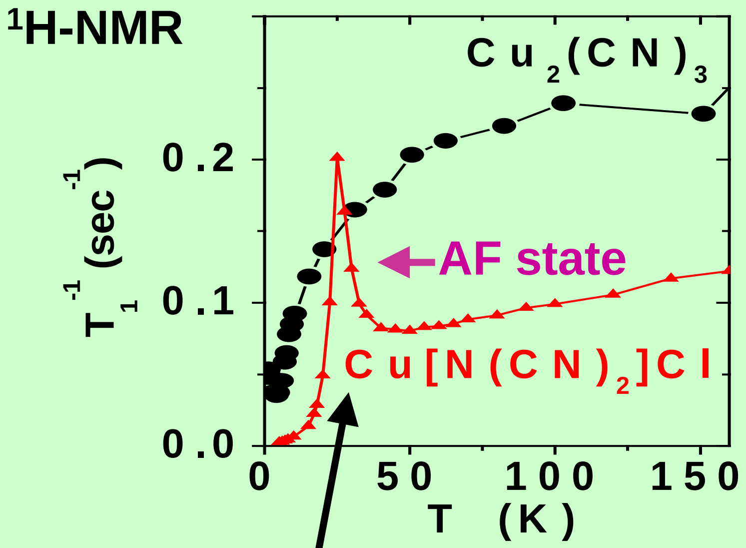
This phase diagram is not applicable to

- **X=Cu(CN)[N(CN)]$_2$ (only PM and T$_C$=11.2 K)**
- **X=Cu$_2$(CN)$_3$ (no AF but shows SC under pressure)**

Ground State of a Mott Insulator κ-$(ET)_2Cu_2(CN)_3$

Magnetic Susceptibility (SQUID)





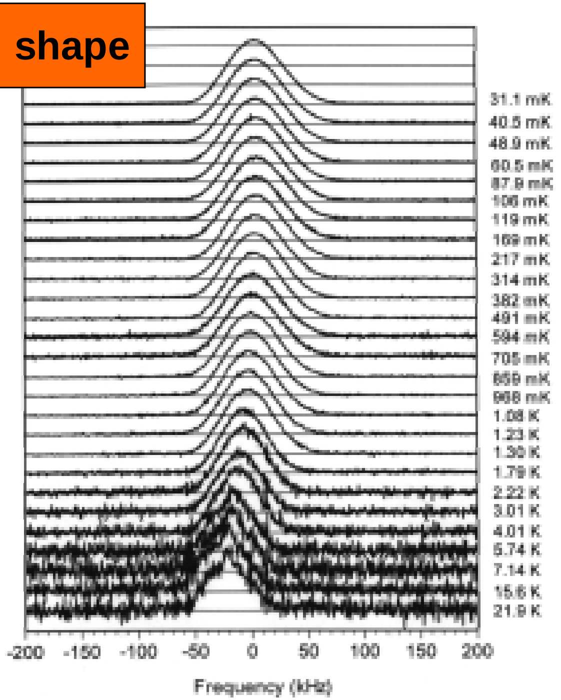
- ^{1}H-NMR ~ 31 mK
- SQUID ~ 1.9 K, 0.32 T
- EPR ~ 1.4 K
- μSR 1.5 K - 20 mK

	t'/t	G state
$Cu[N(CN)_2]Cl$	0.75	AF
(AF neighbors to SC state)		
$Cu_2(CN)_3$	1.06	

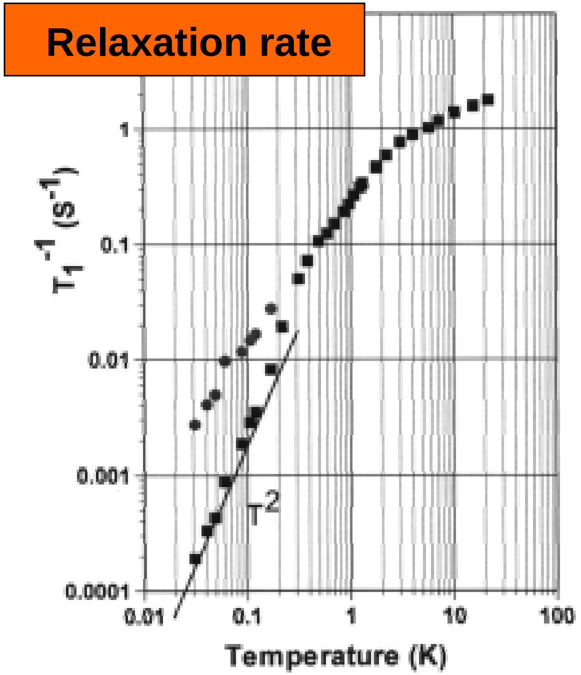
No Magnetic Order → Spin-Liquid State

Very resent results ^{1}H-NMR
(single crystal, f_0=76.700 MHz, H_0=1.7967T⊥2D layer)

Signal shape



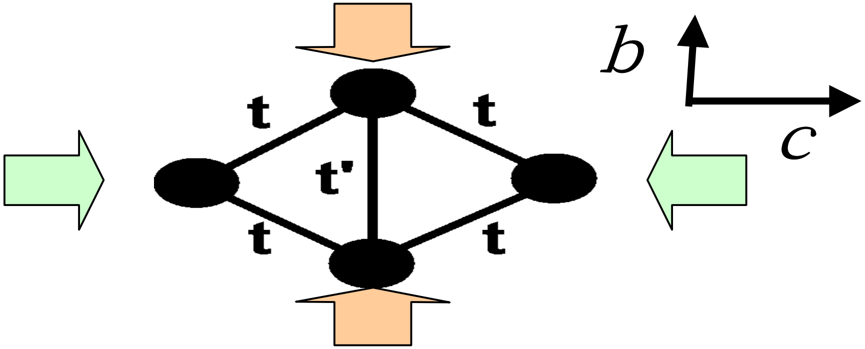
Relaxation rate

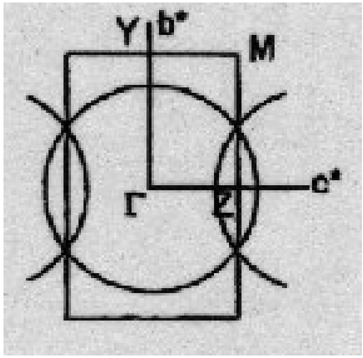


No Magnetic Order down to 30mK → spin-liquid state

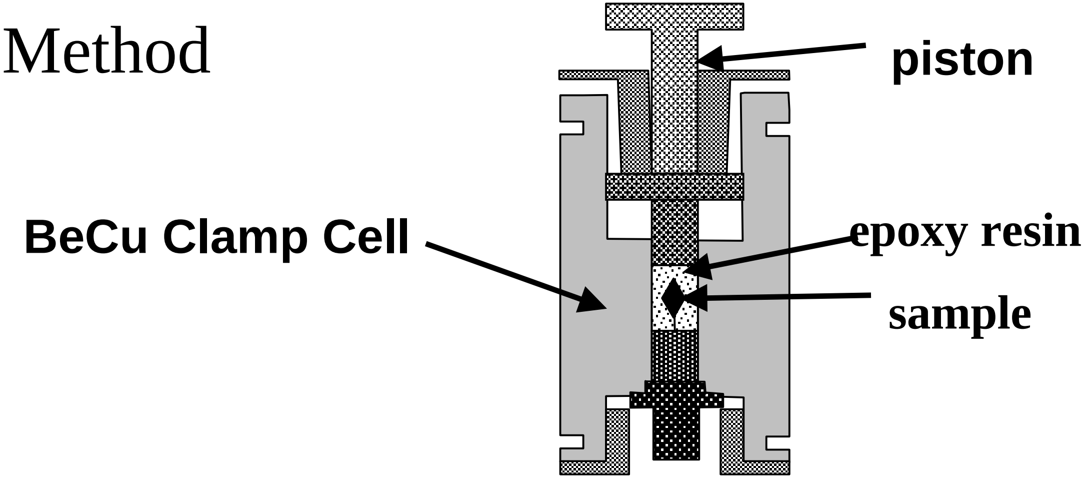
Main signal (■) $T_1^{-1} \sim T^2$ → Gapless

Control of Triangular Anisotropy *t'/t* by Uniaxial Strain





Maesato Method



piston

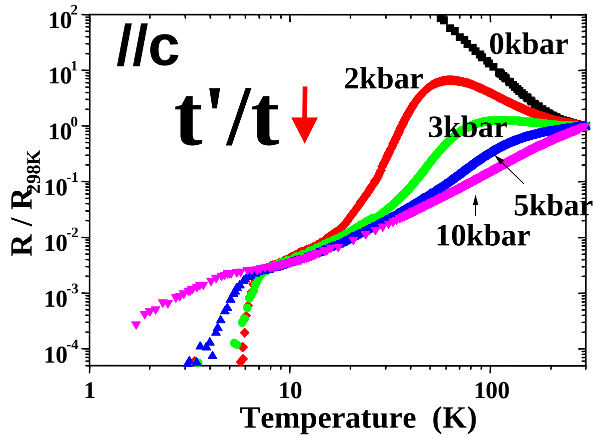
BeCu Clamp Cell

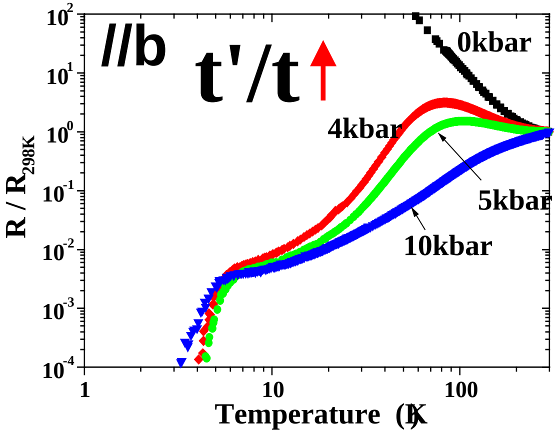
epoxy resin

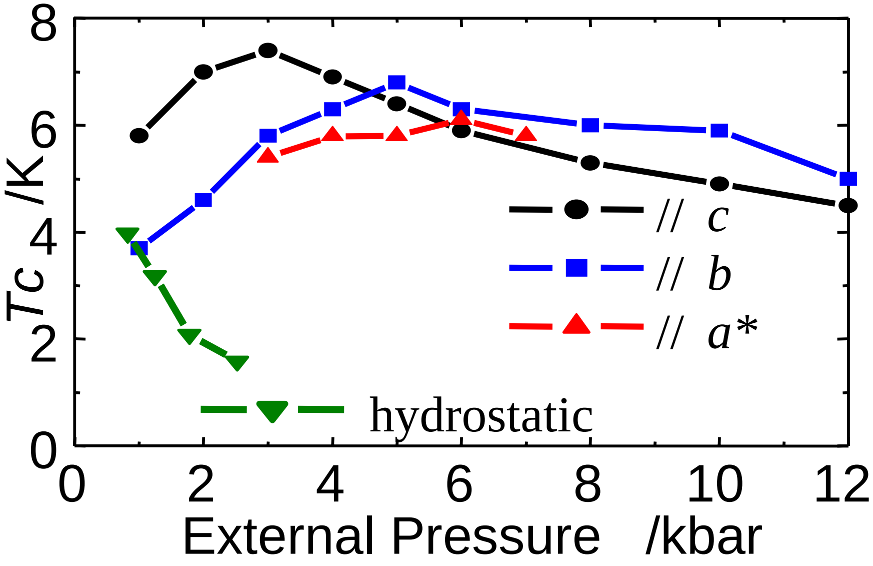
sample

Apply Stress Uniaxially without Poisson Effect

κ-(ET)$_2$Cu$_2$(CN)$_3$ Uniaxial Strain vs Hydrostatic Pressure



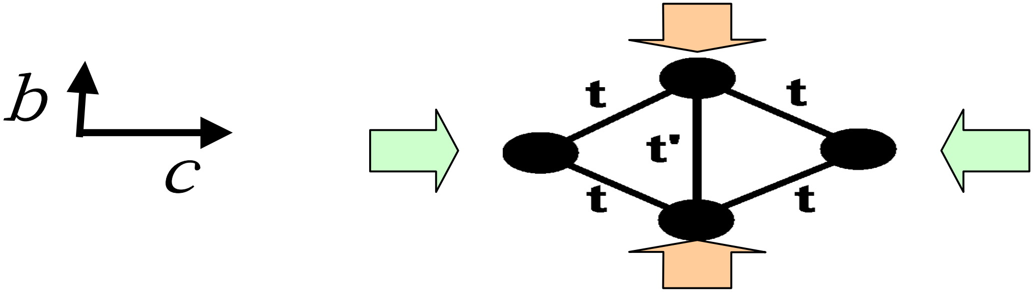


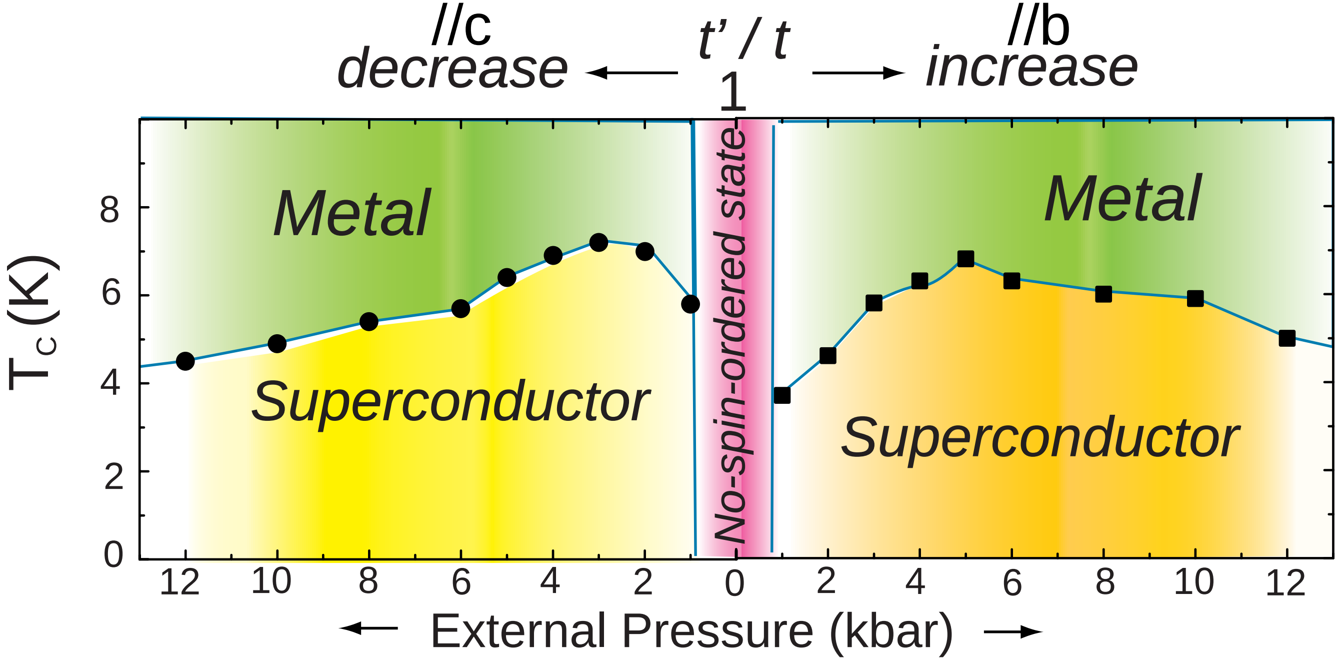


T_C under Uniaxial Strain

- **Increase in weak pressure in every direction**
- **Anisotropic (//c > //b > //a*)**
- **Higher than under hydrostatic pressure**

Uniaxial Strain on κ-$(ET)_2Cu_2(CN)_3$





Summary(2)

1. Ground state of a Mott insulator κ-(ET)$_2$Cu$_2$(CN)$_3$ is Spin-Liquid Sate

2. Anisotropy t'/t is critical for ground state of κ-(ET)$_2$X: spin-ordered AF vs. spin-disordered (spin-liquid) states

3. Uniaxial Strain vs ~~Hydrostatic~~
for Anisotropic Electronic State

A release of spin frustration in a spin-liquid state induces a superconducting state

→ Magnetic mediation

Molecular Design of Single Component Conductors

NATO

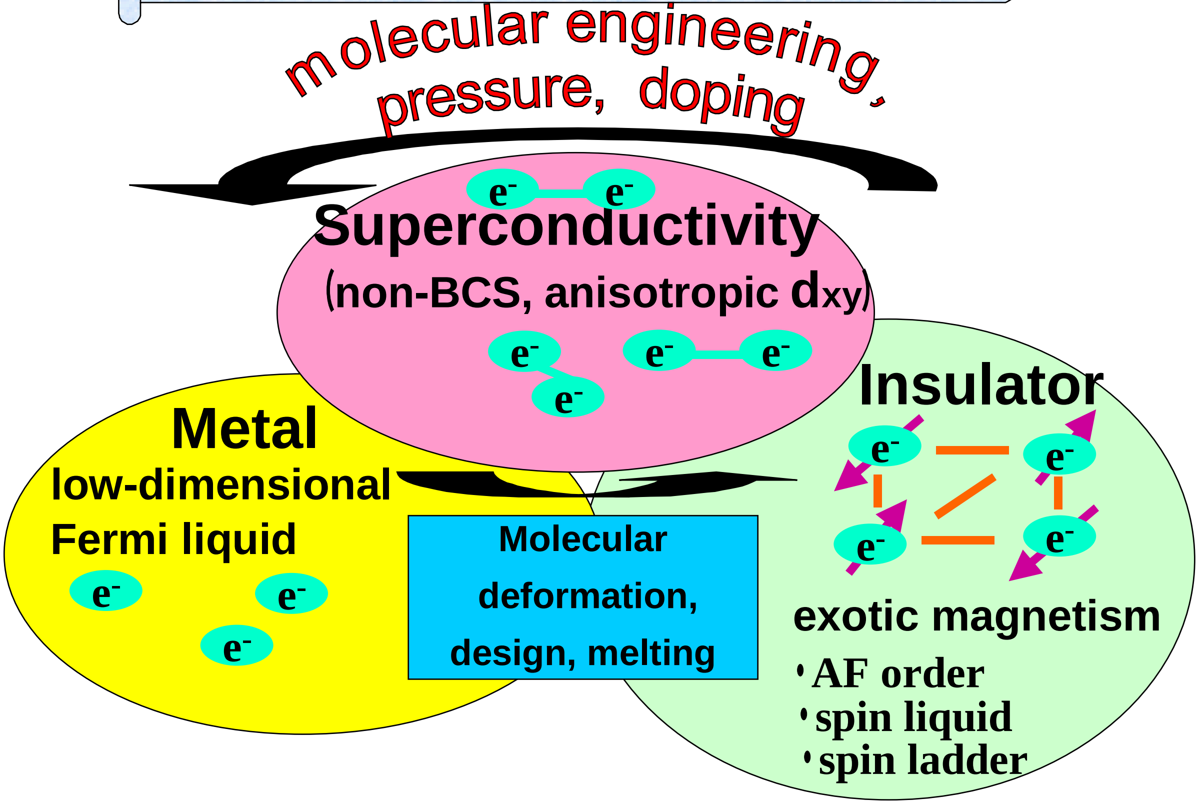
1. Introduction
   Examples of Single Component Conductors
   a. Super under Pressure
   b. Organometallic complexes
   c. Neutral Closed Shell Compounds
   d. Neutral Open Shell Compounds
   e. Zwitter ionic (Betainic) Radicals

2. On-Site Coulomb Repulsion
   vs Mean-Free Path of Molecular Wire

3. Fused Mesomeric Betainic Radicals

4. Hydrogen Bond & Self-Complementarity

Many electrons in nano-scale stage made of soft & anisotropic media



molecular engineering, pressure, doping

Superconductivity

(non-BCS, anisotropic d_{xy})

Metal

low-dimensional Fermi liquid

Molecular deformation, design, melting

Insulator

exotic magnetism

- AF order
- spin liquid
- spin ladder