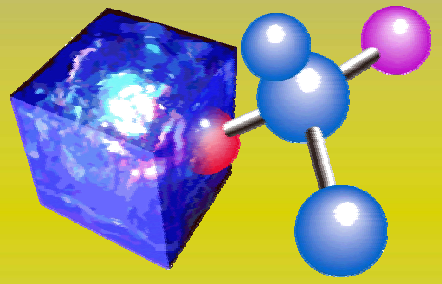
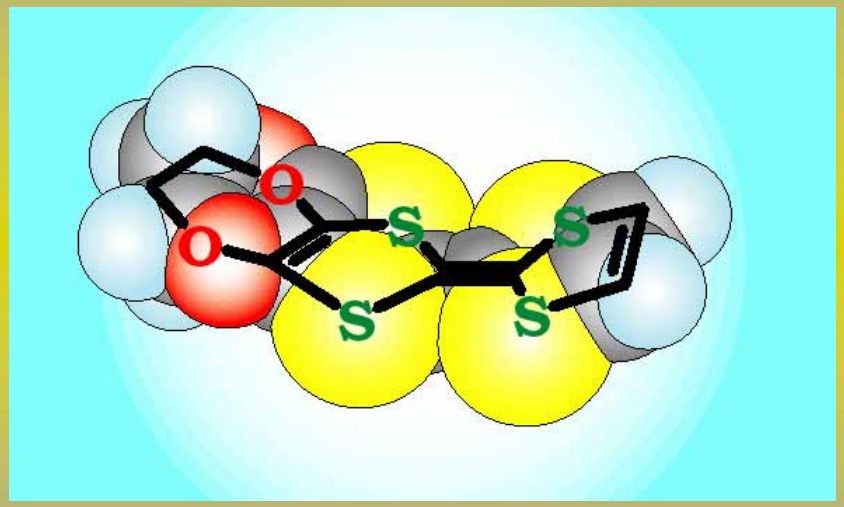
有機導電体における分子自由度



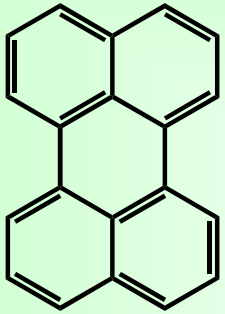
低温物質科学
研究センター
矢持 秀起



- 分子性導体の歴史
- $(EDO\text{-}TTF)_2PF_6$の多重不安定性
  超高速・高効率光誘起相転移
- 分子の化学修飾と錯体の物性変化

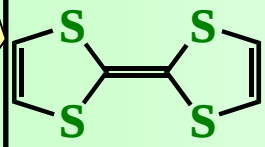
Molecular Conductor — Summarized History

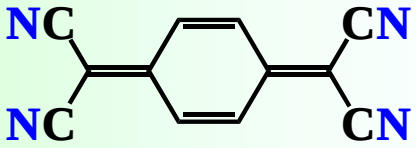
1954 Organic Semiconductor



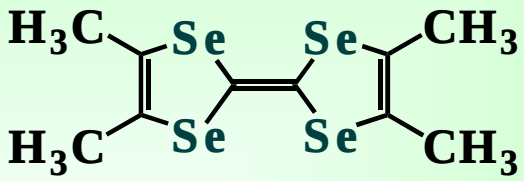
• Br_2

1960s 1D Organic Metals

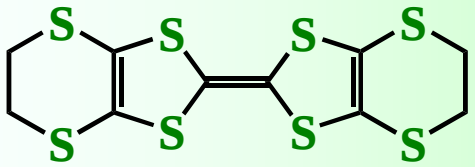




1980s: Organic Superconductors



Q1D Superconductors
max. *T*c = 1.4 K (AP)



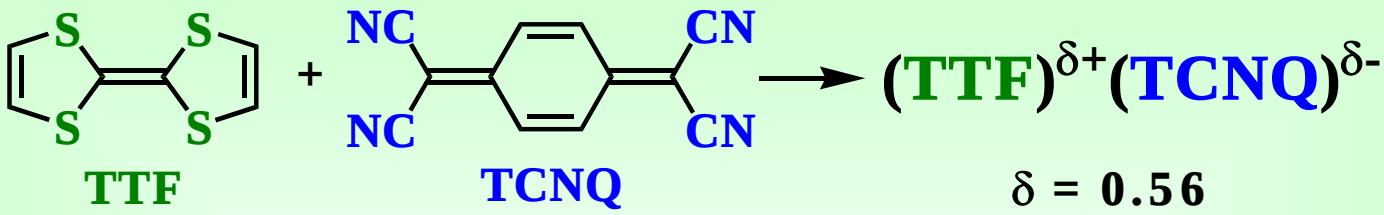
2D Superconductors
max. *T*c = 12.3 K (AP)

1990s: 3D Molecular Superconductors

max. *T*c = 33 K (AP)

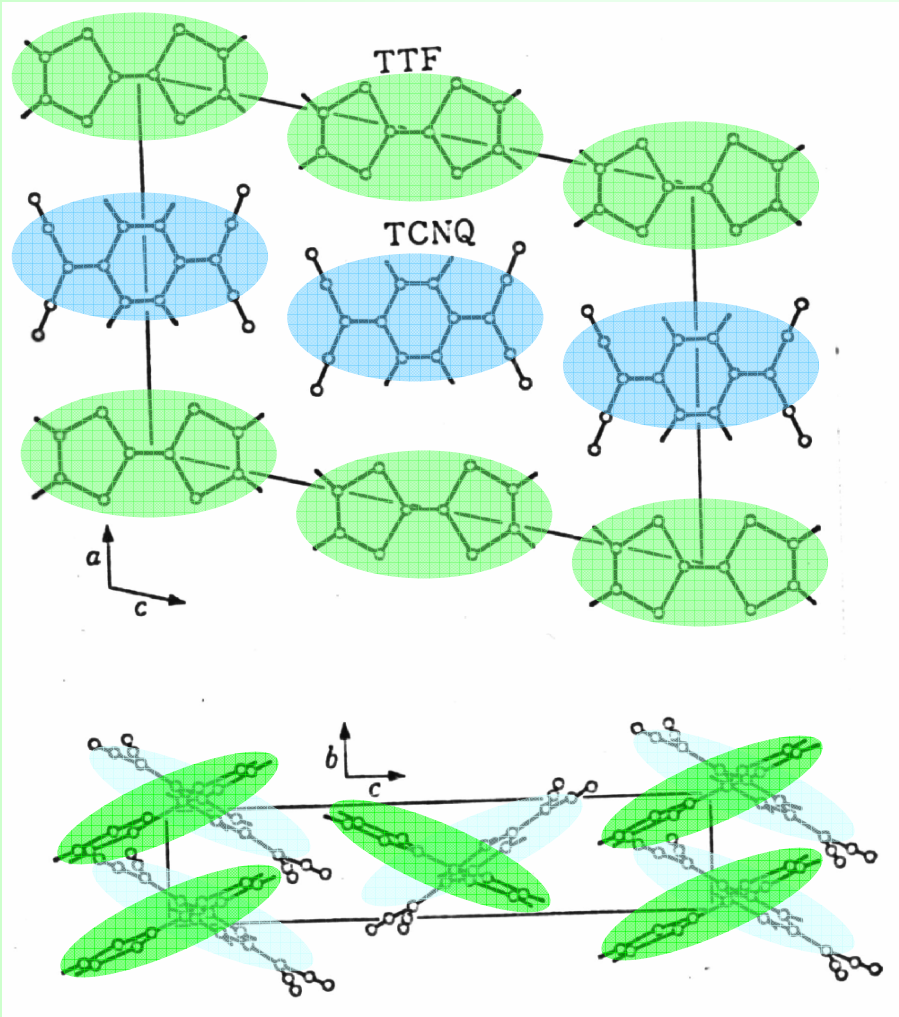
Increment of Dimensionality

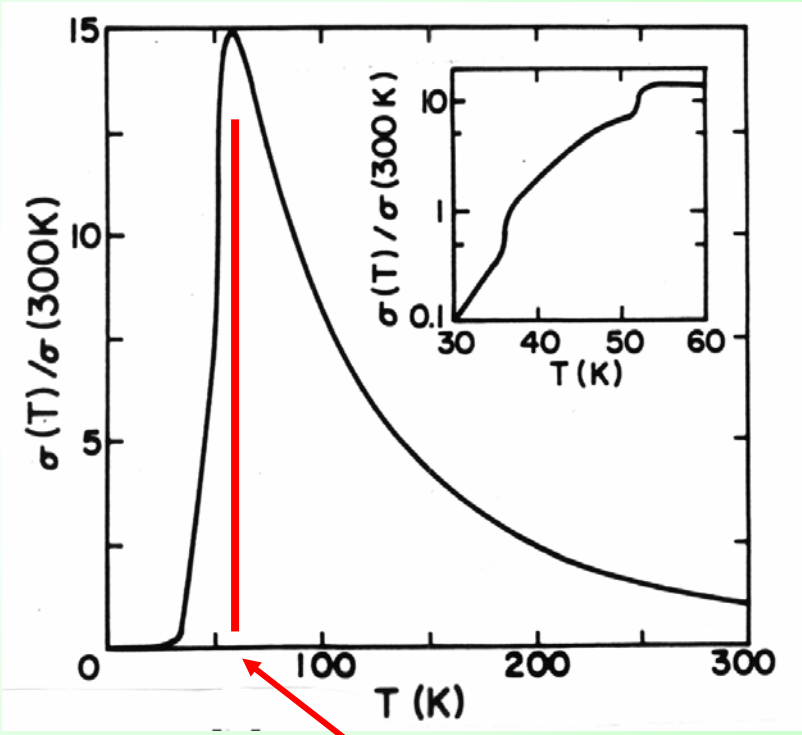
TTF•TCNQ - The First Organic Metal



TTF TCNQ

$\delta = 0.56$





38 K **54 K**

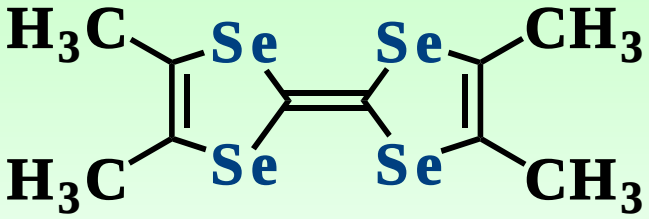
Peierls gap **Peierls gap**

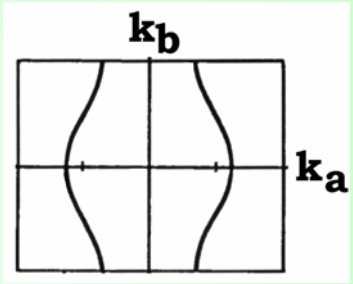
In TTF chain **in TCNQ chain**

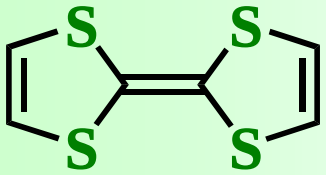
Semiconductor **Metal**

Increasing the Dimensionality

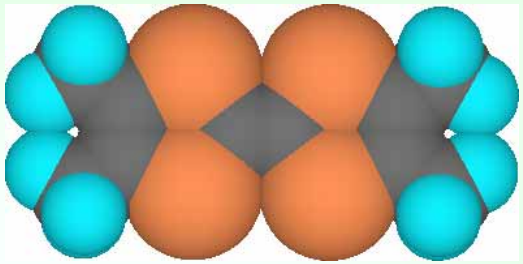
Increment of side-by-side intermolecular interaction



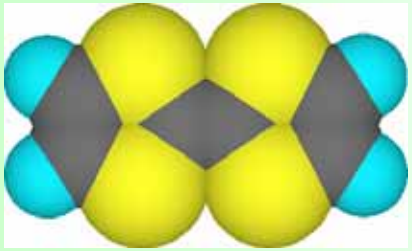




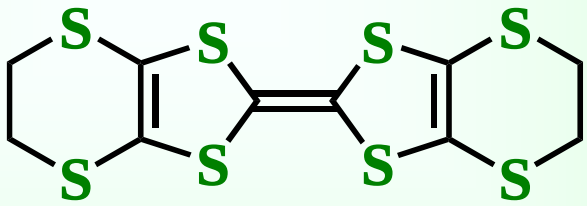
Atom Size

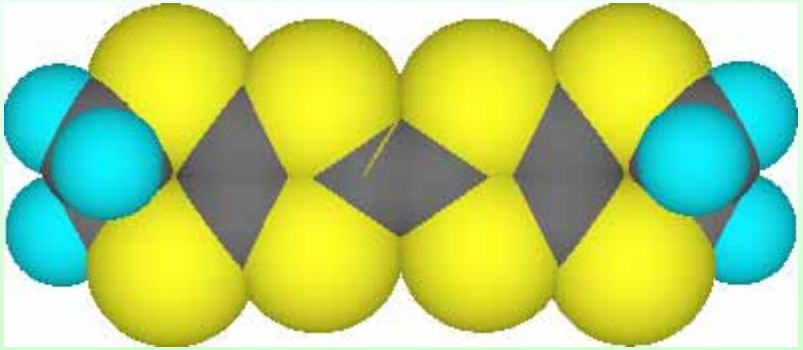


TMTSF



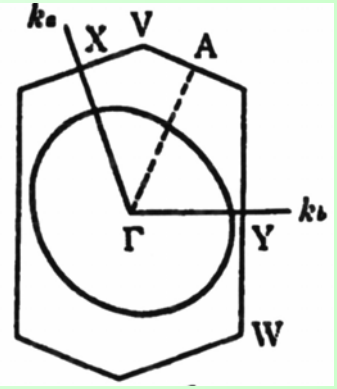
Number of Atoms





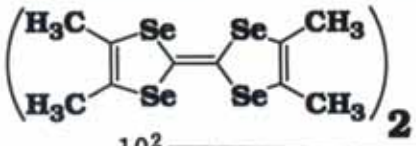
TTF

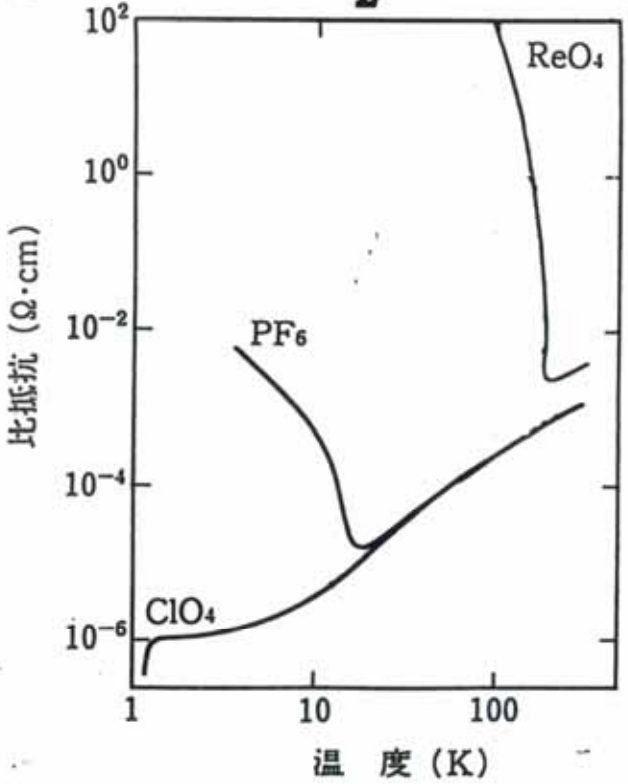
BEDT-TTF (ET)



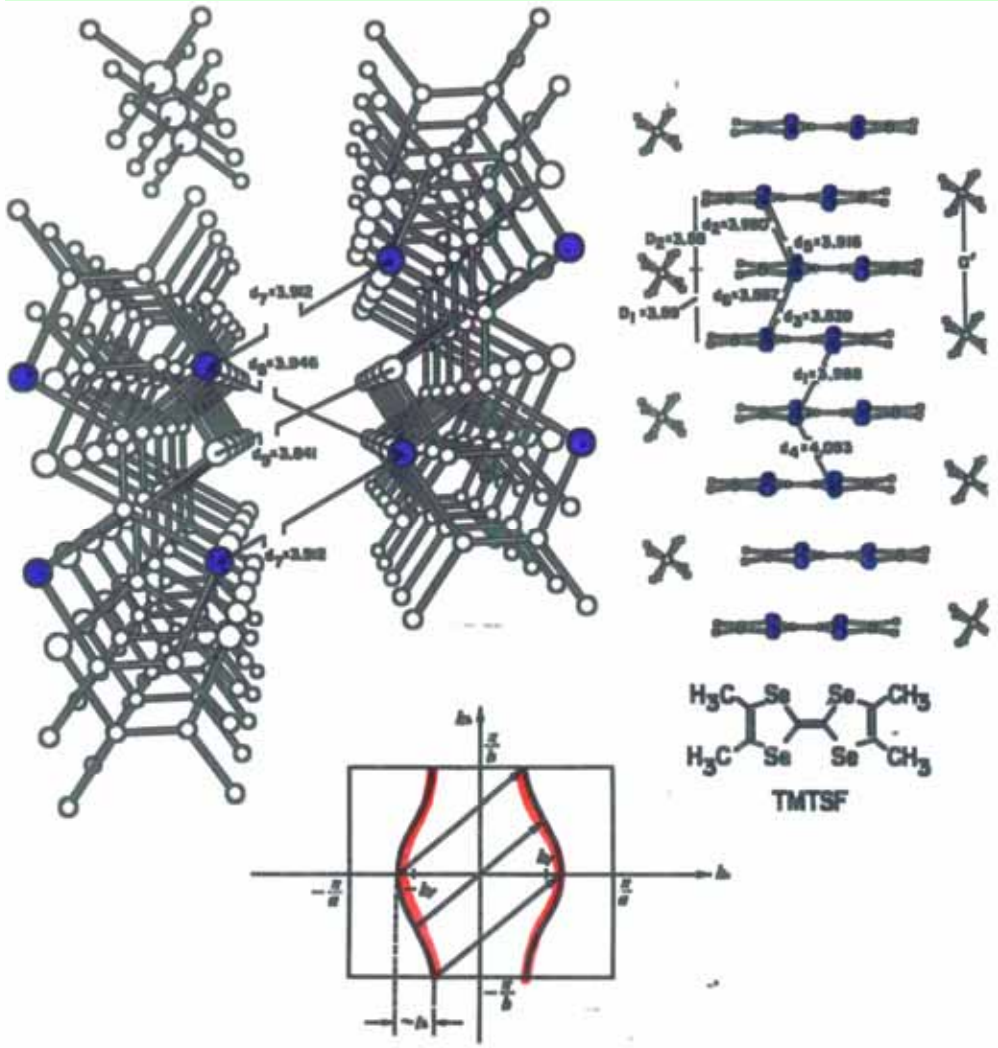
TMTSF Superconductors

TMTSF (Super)conductors

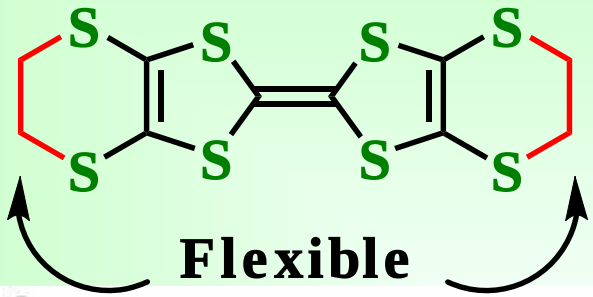


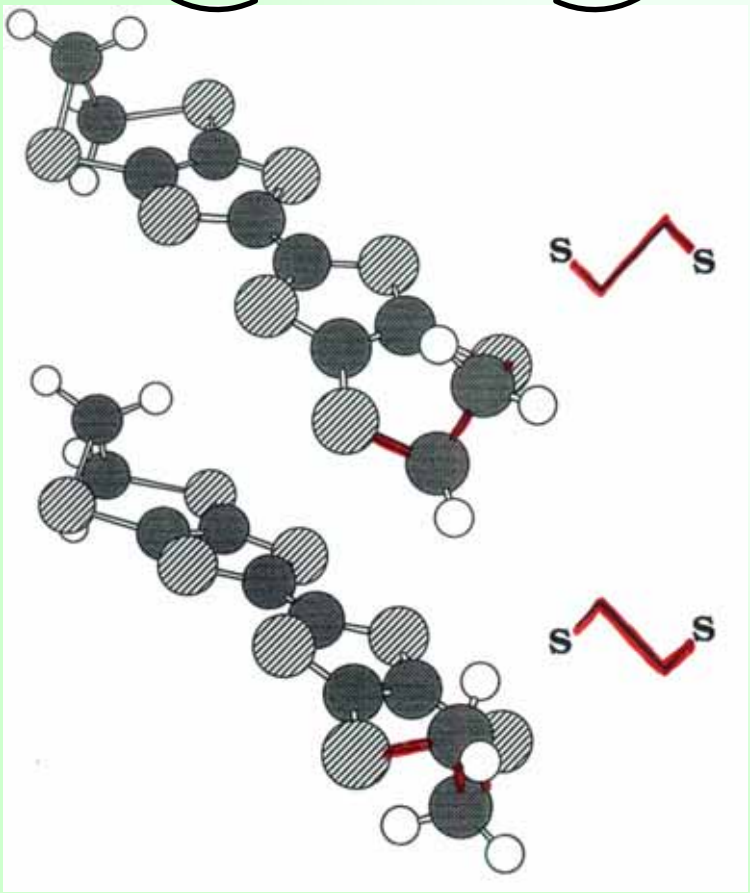


Compound	T_c(K)	Pressure (Kbar)
PF_6^-	0.9	10-12
ClO_4^-	1.2	none
ReO_4^-	1.3 - 1.5	12
FSO_3^-	2.5	>6



BEDT-TTF Superconductors



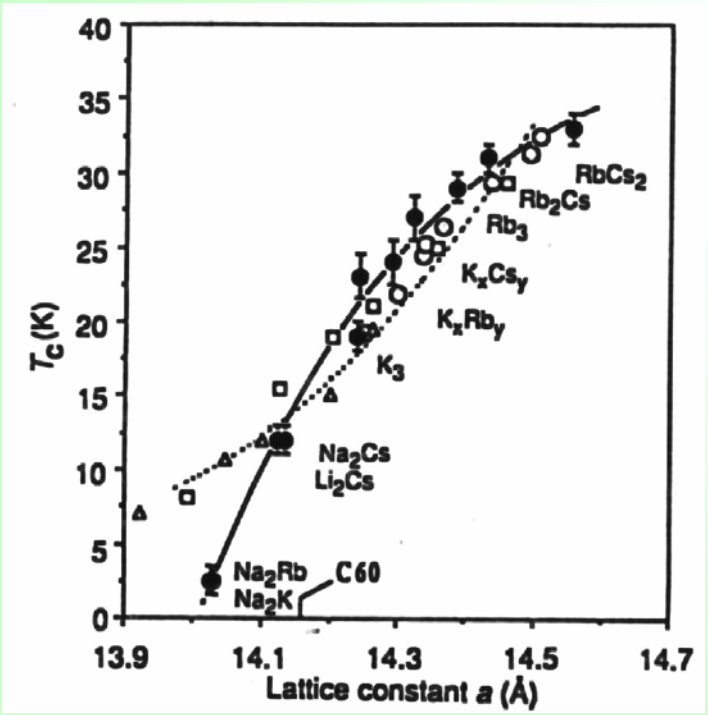


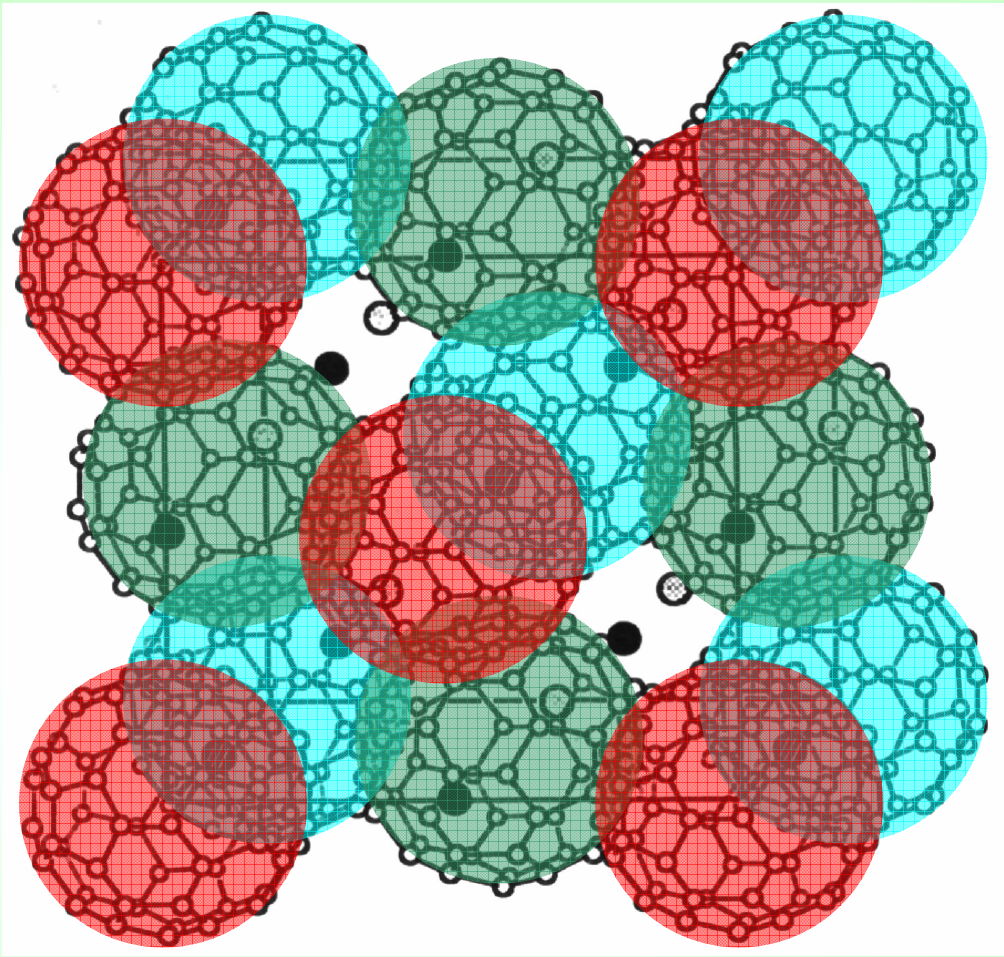
BEDT-TTF(ET)
Ambient Pressure Superconductors
(Planar Anion Layers)

Tc	*Complex*	
11.8 K	κ-$(ET)_2Cu[N(CN)_2]Br$	
11.2 K	κ-$(ET)_2Cu(CN)[N(CN)_2]$	
11.1 K	κ_H-$(ET)_2Ag(CF_3)_4(TCE)$	(11.1 & 9.4 K)
10.5 K	κ_H-$(ET)_2Au(CF_3)_4(TCE)$	
10.4 K	κ-$(ET)_2Cu(NCS)_2$	
10.2 K	κ_H-$(ET)_2Ag(CF_3)_4(CHCl_2-CH_2Br)$	
9.2 K	κ_H-$(ET)_2Cu(CF_3)_4(TCE)_x$ $(x < 1)$	
8.5 K	β''-$(ET)_4[(H_2O)Fe(ox)_3](PhCN)$	
8.1 K	β_H-$(ET)_2I_3$	
5.2 K	κ_L-$(ET)_2Cu(CF_3)_4(CHBr_2-CH_2Br)$	
5.0 K	κ-$(ET)_2Ag(CN)_2H_2O$	
5.0 K	β-$(ET)_2AuI_2$	
4.9 K	κ_L-$(ET)_2Cu(CF_3)_4(CHCl_2-CH_2Br)$	
4.8 K	κ_L-$(ET)_2Ag(CF_3)_4(CHBr_2-CH_2Br)$	
4.5 K	κ_L-$(ET)_2Ag(CF_3)_4(CHBrCl-CH_2Br)$	
4.1 K	κ_L-$(ET)_2Ag(CF_3)_4(CHCl_2-CH_2Br)$	
4.0 K	κ_L-$(ET)_2Cu(CF_3)_4(TCE)$	
3.8 K	κ_L-$(ET)_2Ag(CF_3)_4(CHBrCl-CH_2Cl)$	
3.8 K	κ'-$(ET)_2Cu_2(CN)_3$	
3.6 K	κ-$(ET)_2I_3$	
3.6 K	θ-$(ET)_2I_3$	
2.7 K	β-$(ET)_2IBr_2$	
2.6 K	κ_L-$(ET)_2Ag(CF_3)_4(TCE)$	
2.1 K	κ_L-$(ET)_2Au(CF_3)_4(TCE)$	
1.5 K	$\beta_L(ET)_2I_3$	
0.8 K	α-$(ET)_2NH_4Hg(SCN)_4$	
0.3 K	α-$(ET)_2KHg(SCN)_4$	

& much more at present

3-dimensional Superconductors





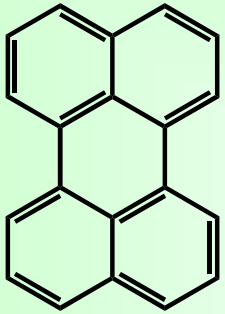
Alkali metals are in the interstitial sites among C_{60}'s.

Max T_c = 33 K ($RbCs_2C_{60}$)

Summarized History

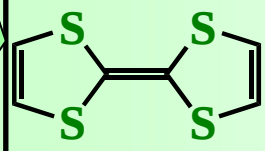
Increment of Dimensionality

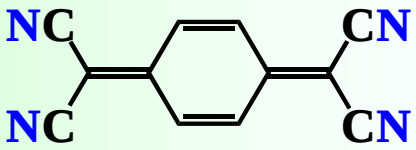
1954 Organic Semiconductor



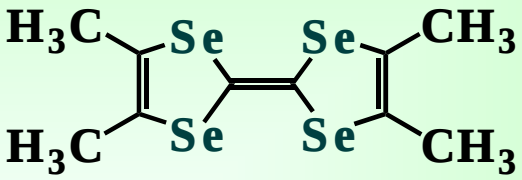
• Br_2

1960s 1D Organic Metals

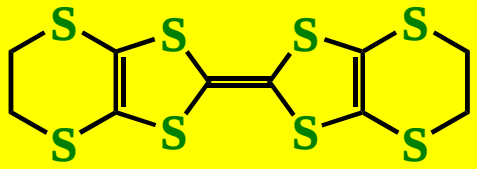




1980s: Organic Superconductors



Q1D Superconductors
max. *T*c = 1.4 K (AP)

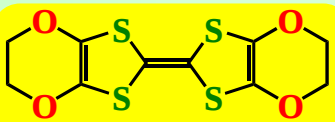


2D Superconductors
max. *T*c = 12.3 K (AP)

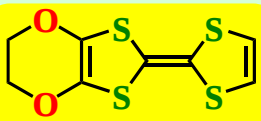
Molecular Degree of Freedom

Lattice point ≠ Simply a point

- √ Size
- √ Shape
- √ Functionality



BEDO-TTF (BO)

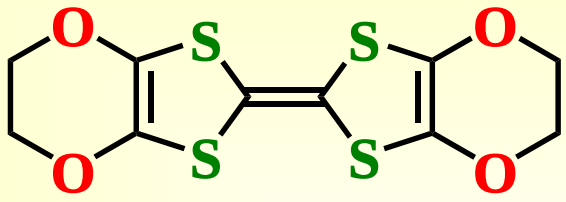


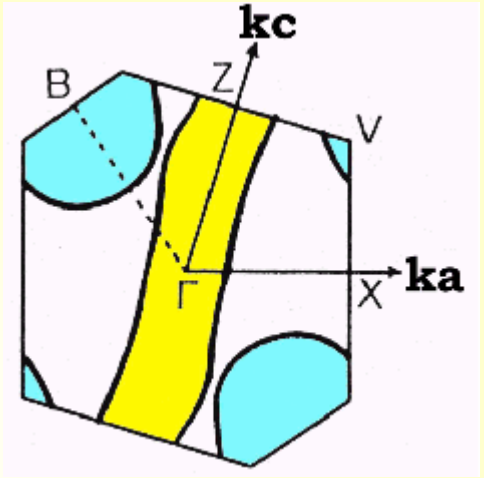
EDO-TTF

1990s: 3D Molecular Superconductors

max. *T*c = 33 K (AP)

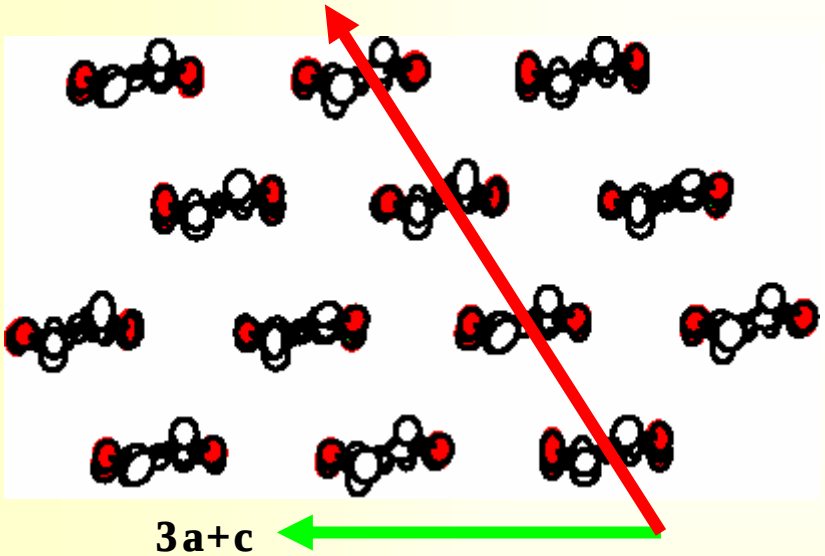
BEDO-TTF(BO) Salt



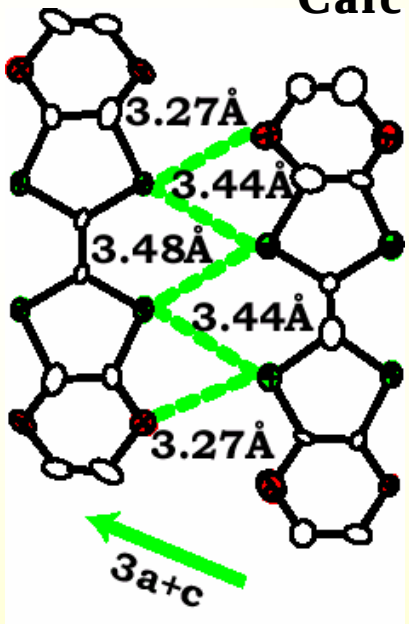


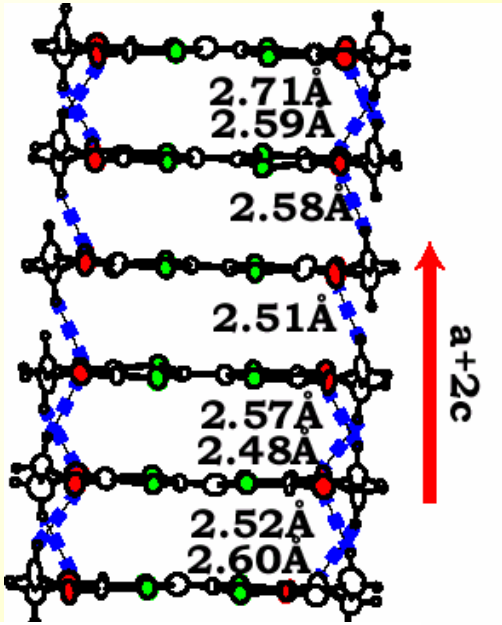
Calculated Fermi Surface

Self-assembling Packing Pattern



2D Layered Structure
→ 2D Electronic Structure





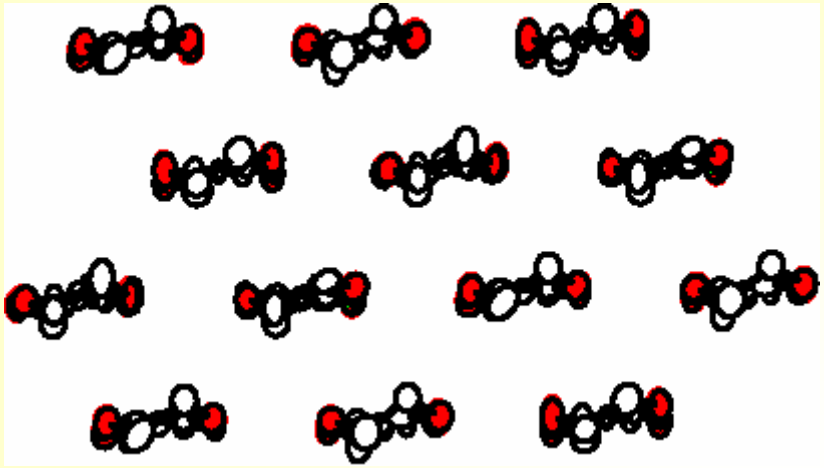
Side-by-side Heteroatomic Contacts

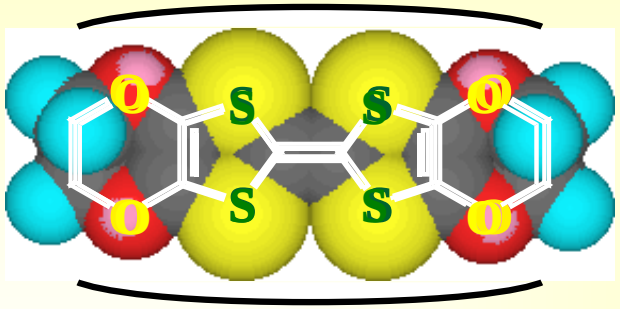
vdW
S•••S = 3.60 Å
S•••O = 3.32 Å

Weak Hydrogen Bond Network

vdW
H•••O = 2.72 Å

Partial Suppression of Self-assembling Nature of BO





Flat Side Surface

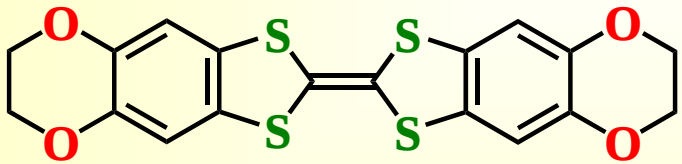
-OCH_2CH_2O-

→ Stable Metal

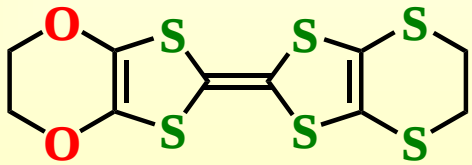
NO PHASE TRANSITION

obstruction

Introduction of Bulky Substituent

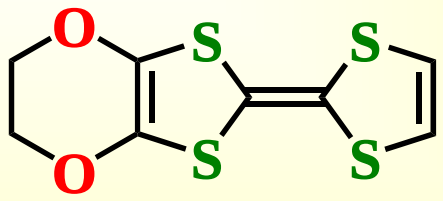


BEDO-DBTTF



EOET

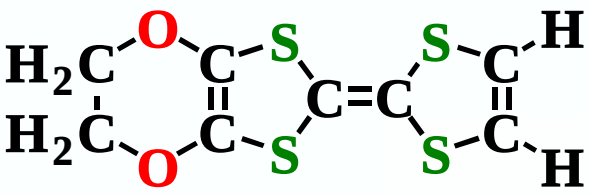
Removal of an EDO Group



EDO-TTF

EDO-TTF Complexes

At 2001 (when we started): Synthesis of donor
A few kinds of complexes: No description of composition
Conductivity: No description or ≤ 2×10^{-4} Scm^{-1}



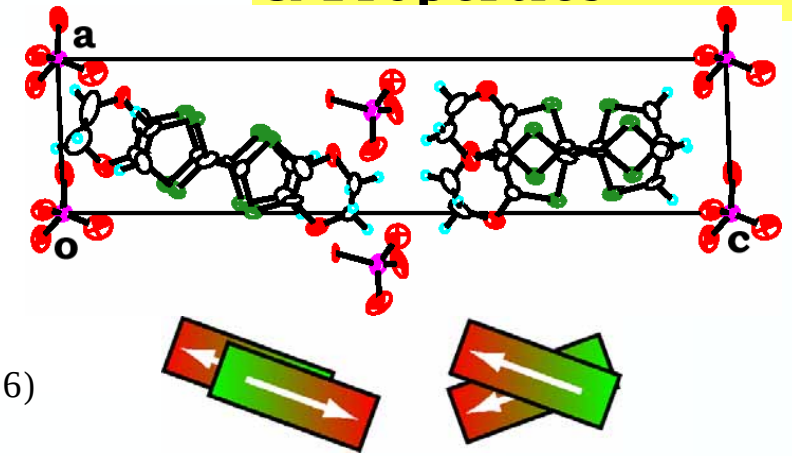
EDO-TTF

+ TCNQ deriv. → **No Metal**
No Self-assembling

A. Ota, et al., *Mol. Cryst. Liq. Cryst.*, **376**, 177-182 (2002)

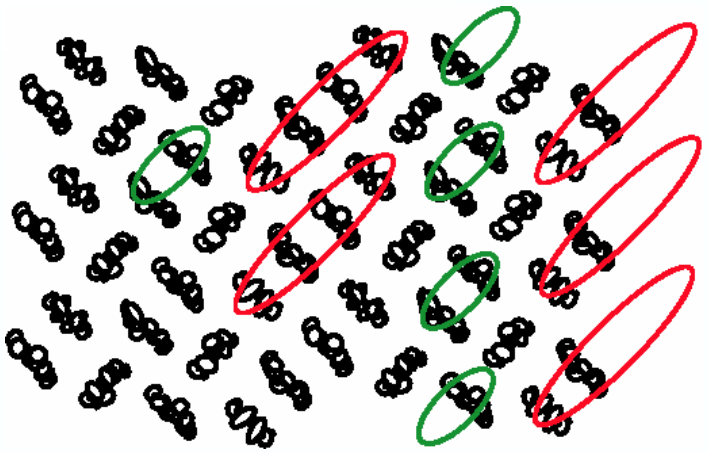
+ Inorg. Anions → **Variety of Structure & Properties**

2:1 ReO_4, $GaCl_4$
σ_{RT} = 130, 54 Scm^{-1}
Activated behaviors ≤ 250 K
Different typed columns



A. Ota et al., *J. Low Temp. Phys.*, **142**(3/4), 425 (2006)

5:3 BF_4
σ_{RT} = 1 Scm^{-1} (Ea = 62 meV)
4:0.85:4(H_2O) Sb_2F_{11}
σ_{RT} = 2 Scm^{-1} (Ea = 55 meV)
Multimer & monomer



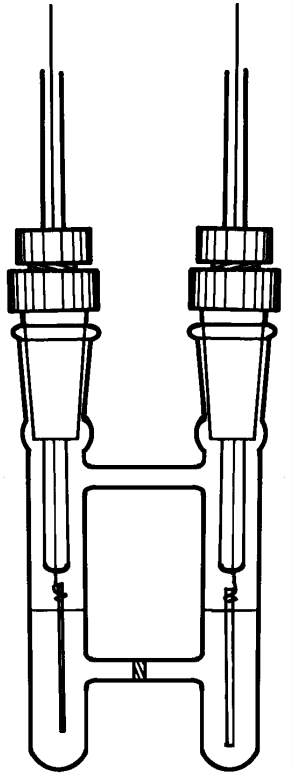
A. Ota et al., in "Multifunctional Conducting Molecular Materials", eds. G. Saito et al., RSC Publishing, Cambridge, UK. (2007), pp. 115-118.

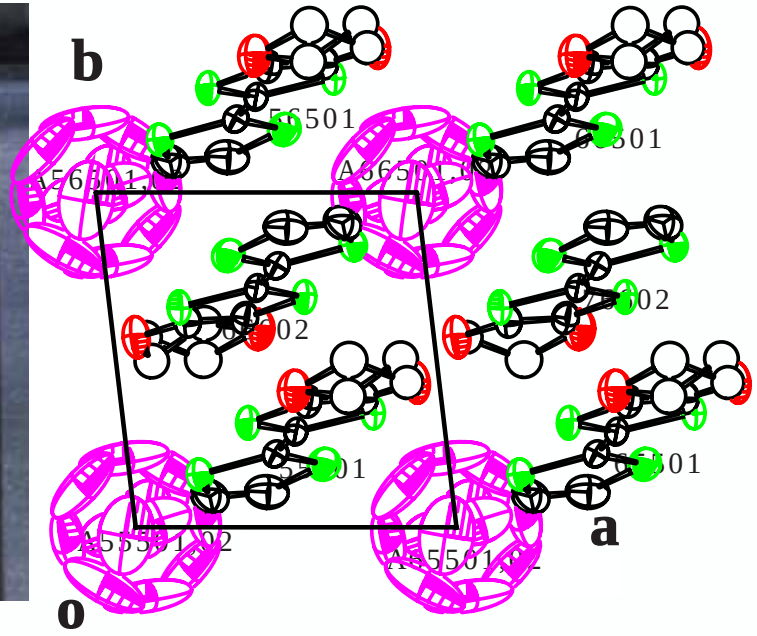
EDO-TTF — Preparation of PF_6 Complex

Electrooxidation (Electrocrystallization)

EDO-TTF + $(Bu_4N)PF_6$ / EtOH → $(EDO\text{-}TTF)_2PF_6$

11.6 mg 68.1 mg 18 mL 0.5 μA 12 days black elongated plates

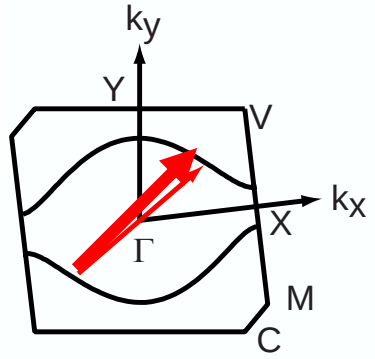




Triclinic P $\bar{1}$
a = 7.197(0.9) Å
b = 7.343(0.6)
c = 11.948(1)
α = 93.454(7)°
β = 75.158(6)
γ = 97.405(7)
V = 605.0(1) Å^3
Z = 1
R = 5.6 %

EDO-TTF was added to (+) side only, while ca. half amount of $(Bu_4N)PF_6$ was added to each chamber.

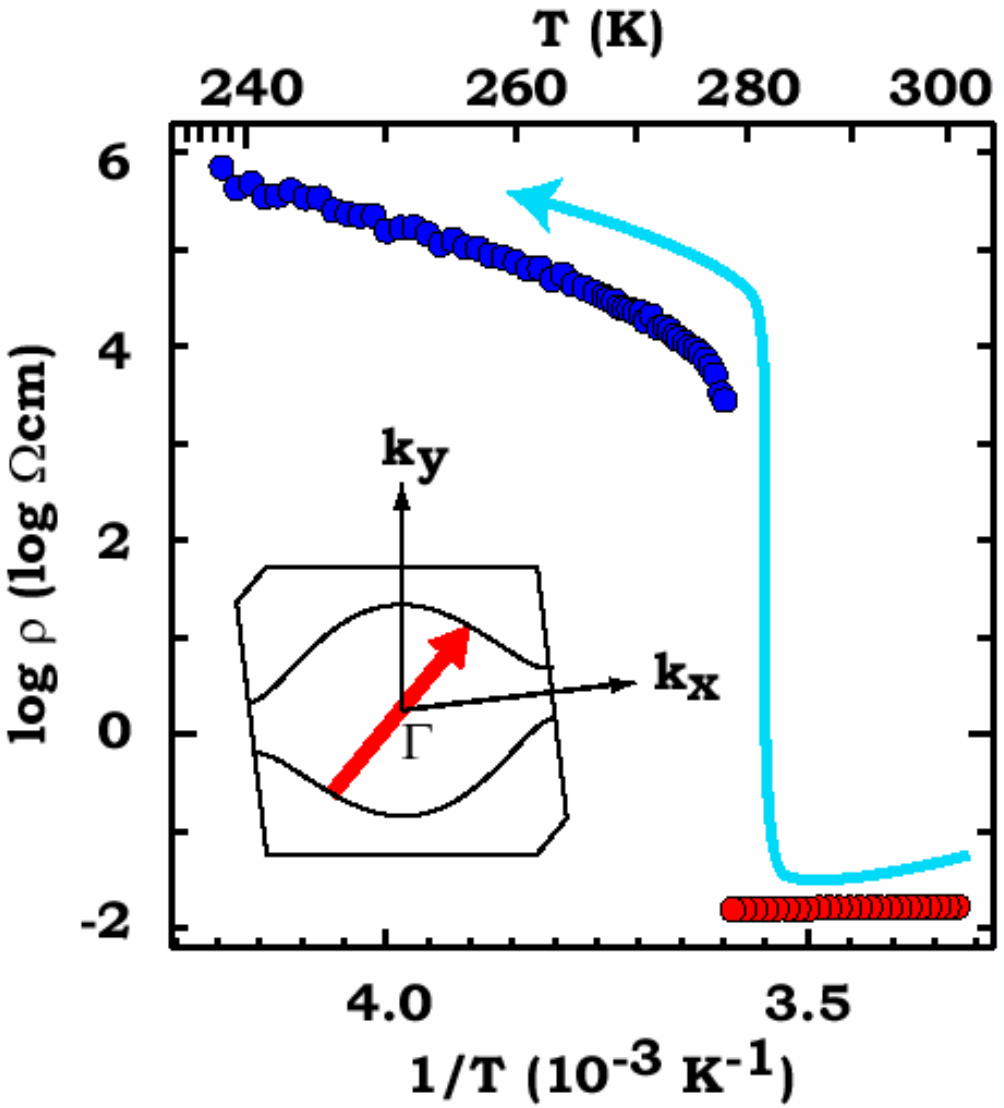
Head-to-Tail Stacking along b-axis.
Disordered Ethylene.
Isotropic Rotation of PF_6^-.



Almost Uniform 1D Intermolecular Overlap Integrals.

A. Ota et al., *J. Mater. Chem.*, **12**, 2600 (2002)

Thermally Induced MI Transition of $(EDO\text{-}TTF)_2PF_6$

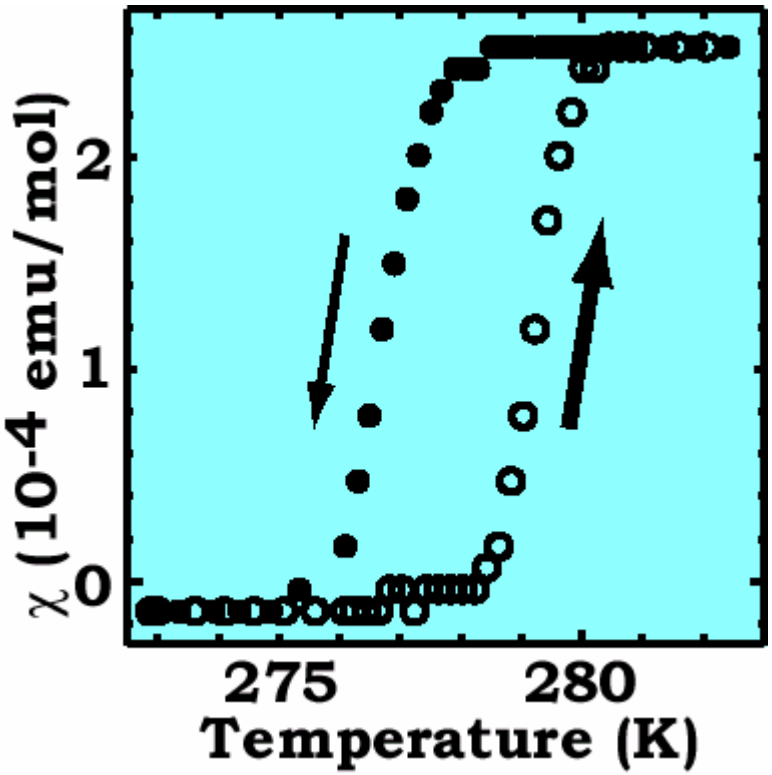


$T_{MI} \approx 280$ K

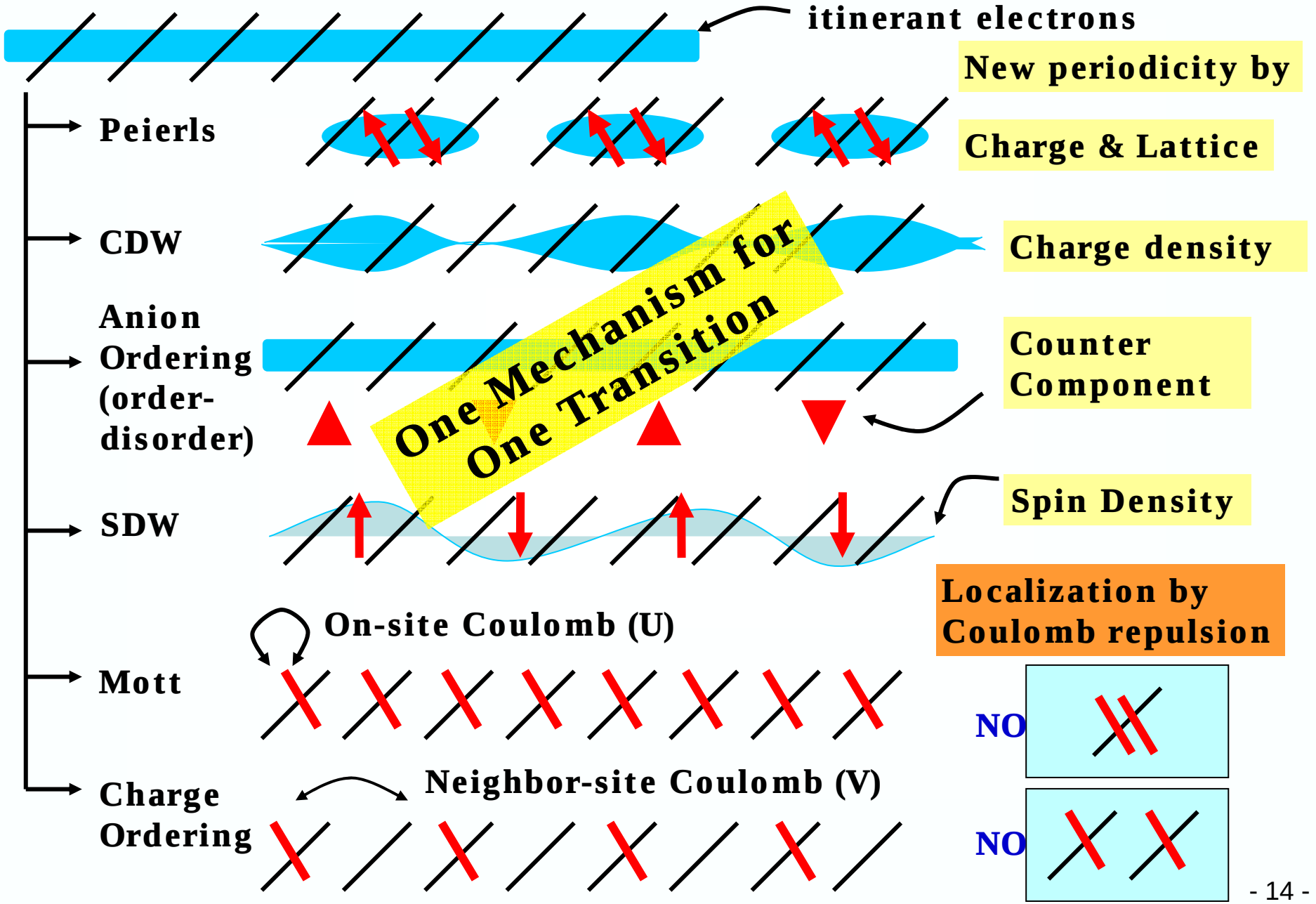
ρ jump: ca. 5 order

Paramag. ↔ Non-mag.

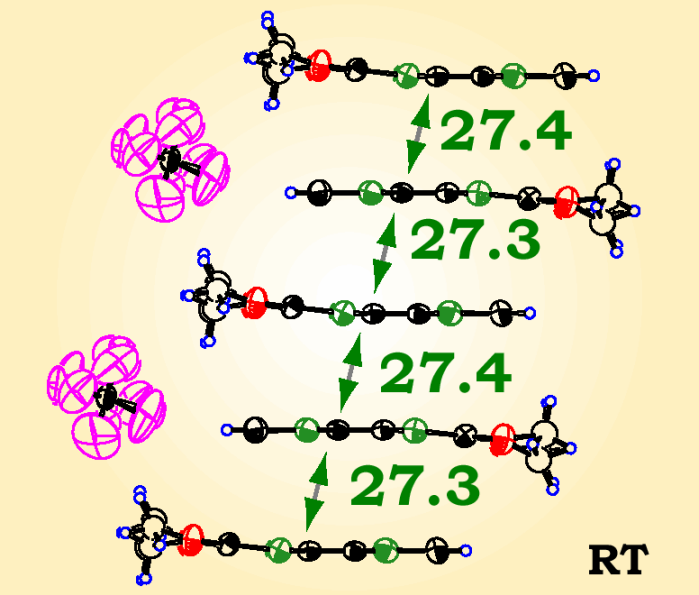
First-order Transition

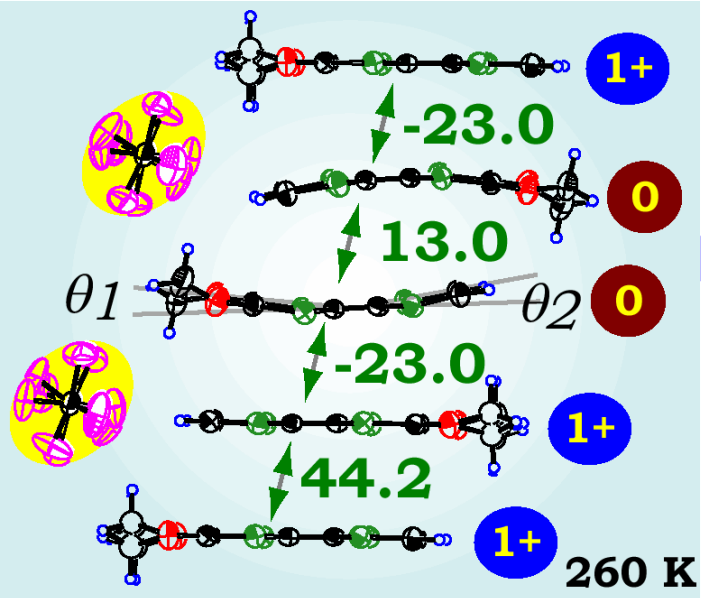


How Metal-Insulator Transitions Occur



$(EDO\text{-}TTF)_2PF_6$ — Above and Below T_{MI} (280 K)





(Overlap Integral × 10^3)

Distinct Molecular Deformation

θ_1, θ_2: 6.0°, 0.3°

planar: 0.8°, 2.1°
bent: 11.1°, 7.9°

Overlap Integral	from Bond Length	PF_6 Rotation
Uniform	0.5+	Isotropic
⇕	⇕	⇕
Alternate	1+/0	Uniaxial
↙	↙	↙
Peierls	Charge Ordering	Order-Disorder

Molecular Deformation is regarded as the Origin to Mix Metal-Insulator Transition Mechanisms (Multi-instability).

$(EDO\text{-}TTF)_2PF_6$ – Other Properties –

Raman Spectra: **4.2 K → Coexistence of 0.9+, 0.1+ Donors**

O. Drozdova et al., *Synthetic Metals*, **133-134**, 277-279 (2003).

Accurate Structure Analysis with MEM method:

285 K → +0.6(1)

260 K → F: +0.8(1) , B: +0.2(1)

S. Aoyagi et al., *Angew. Chem. Int. Ed.*, **43**(28), 3670-3673 (2004) .

Reflection Spectra: **Significant Temperature Dependence**

O. Drozdova et al., *Phys. Rev.*, **B70**(7), 075107-1-8 (2004) .

Calorimetry: **Transition Entropy**

→ Unharmonicity of PF_6 Rotation in RT Phase

K. Saito et al., *Chem. Phys. Lett.*, **401**(1-3), 76-79 (2005).

Uni-axial Strain: **along c* → T_{MI}↑ (> 60 K/4 kbar)**

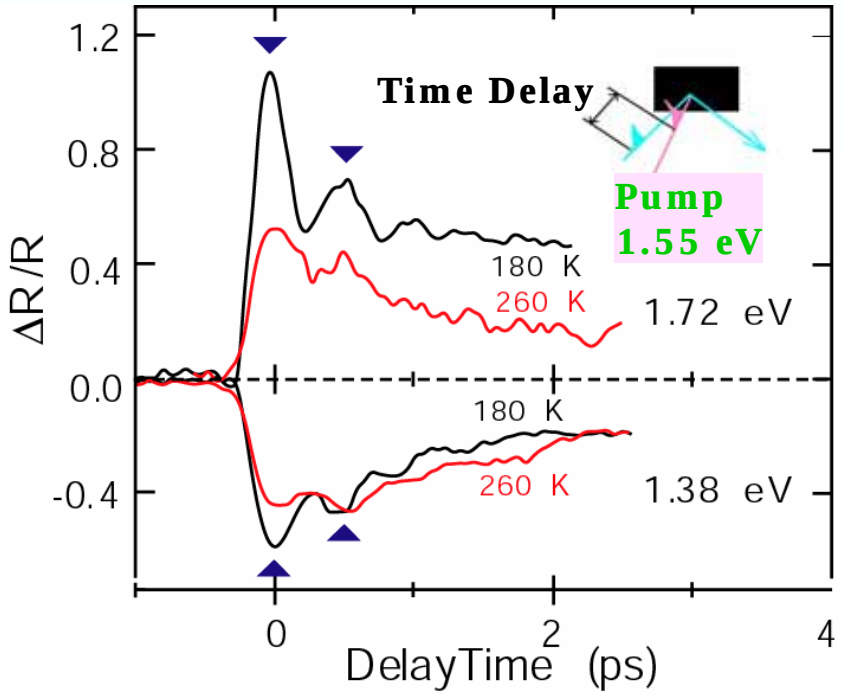
M. Sakata et al., *Synthetic Metals*, **153**(1-3), 393-396 (2005).

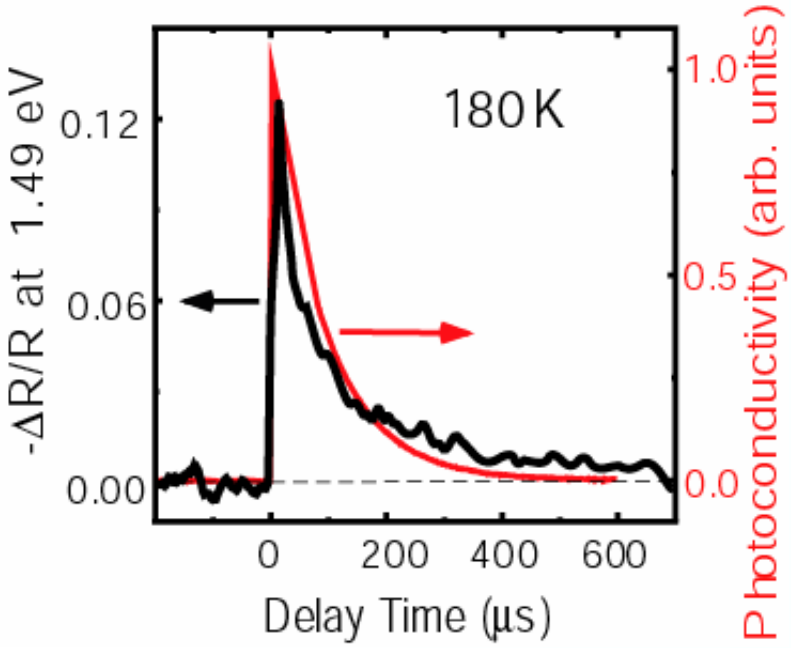
Photo-induced Phase Transition:

Ultra-fast Highly Efficient, ~ 0.1 ps, 50 - 500 donors/photon

M. Chollet et al., *Science*, **307**, 86-89 (2005).

Photo-induced Phase Transition (PIPT)





Completes in ca. 1.5 ps

1 photon / 50-500 molecules

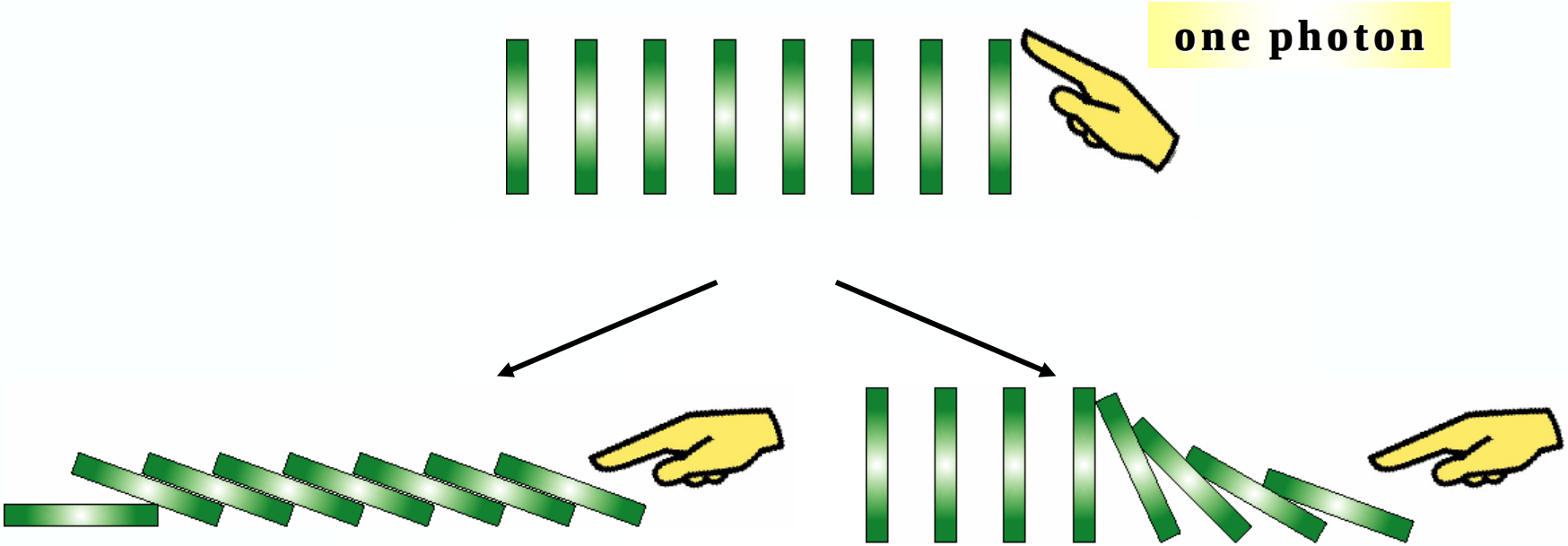
PIPT to Highly Conducting Metastable State

vibration: ca. 0.5 ps/cycle at 180 K

Strong Electron-Lattice Interaction

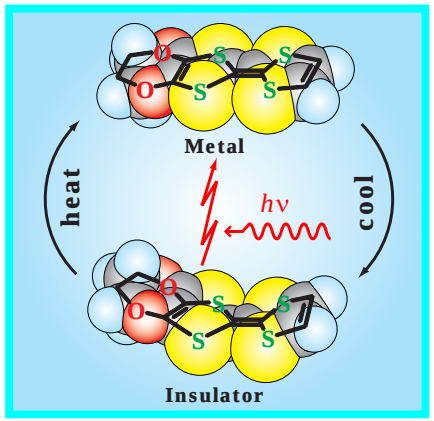
M. Chollet et al., *Science*, **307**, 86-89 (2005)

PIPT — Comparison with other systems



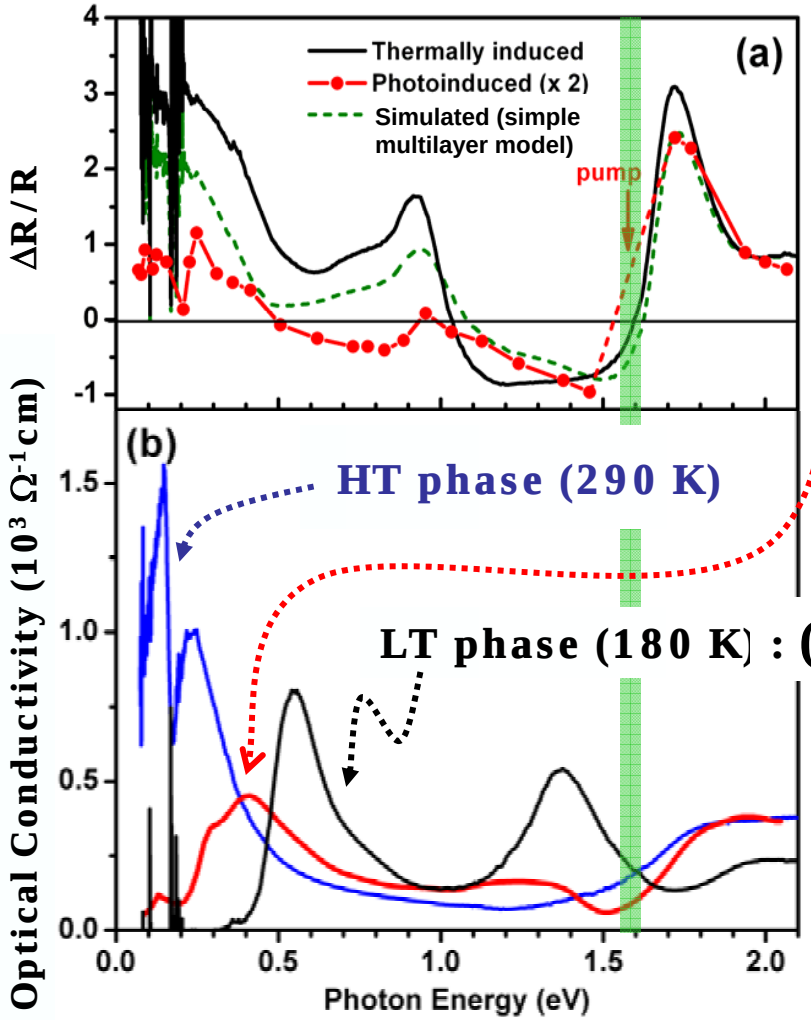
Our system
50 – 500 molecules
within ca. 0.1 ps

RbTCNQ (Ins. - Metal)
< 10 molecules, ca. 0.1 ps
TTF-Chloranil (Neutral - Ionic)
280-2,800 molecules, ~1 ns



Ultra-fast & Highly Efficient PIPT
Controllable Initialization
Development of Phase Transition
→ Dynamics of Non-equilibrium State

PI Metastable State ≠ RT Metallic Phase



Wide Range Optical Conductivity Spectra

0.1 ps after pump
one peak at low energy

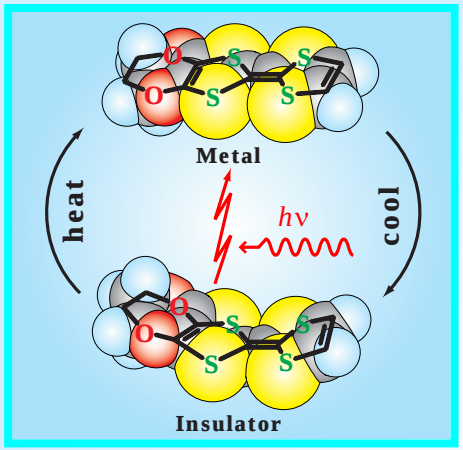
Theoretical Calculation
H: t, U, V, γ (e-ph coupling
ə anion potential modulation)
time dependent model

: (0110)

PIPT state: (1010) Charge Disp.
≠ RT Metallic (½ ½ ½ ½) Phase
Lattice potential:
fluctuated in this time scale

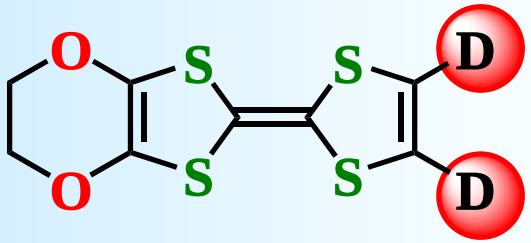
K. Onda, S. Ogihara, K. Yonemitsu, N. Maeshima, T. Ishikawa, Y. Okimoto, X.F. Shao, Y. Nakano, H. Yamochi, G. Saito, S. Koshihara, ***Phys. Rev. Lett.***, 101(6), 067403-1-4 (2008)

After $(EDO\text{-}TTF)_2PF_6$ – Isotope Effect



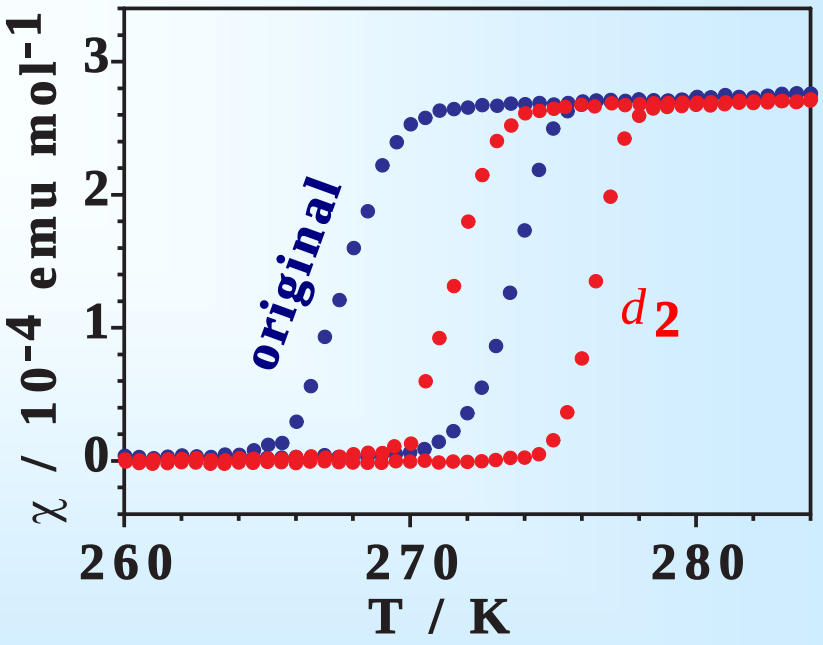
Electron-Phonon (Electron-Molecular Vibration) Coupling

Isotope substitution
→ Lattice (Molecular) Vibrations



EDO-TTF-d_2

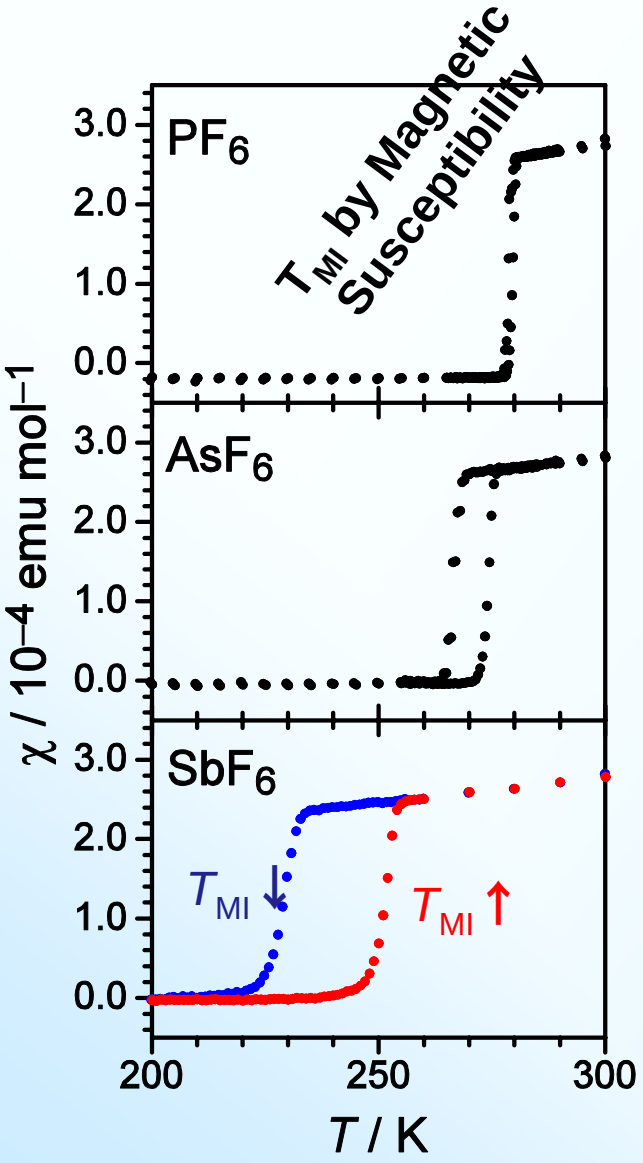
- **Modulation of π-system (conduction path) vibrations**
- **For PF_6 & AsF_6 complexes**
  $d_0 \rightarrow d_2$: $\Delta T_{MI} \approx 3$ K



$(EDO\text{-}TTF\text{-}d_x)_2AsF_6$

After $(EDO\text{-}TTF)_2PF_6$ – Anion Size Effect

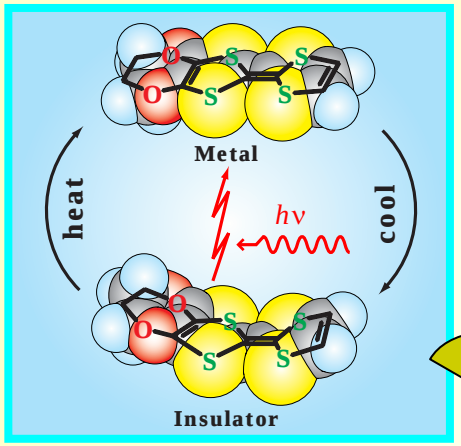
Isostructural $(EDO\text{-}TTF)_2XF_6$ (X = P, As Sb)



	Size	T_{MI} (K)	ΔT_{MI} (K)
PF_6		279.0	1.0
AsF_6		270.8	5.5
SbF_6		242	14

スライド内容 一部削除
ここで観測された、転移温度とヒステリシス幅の陰イオン依存性については、現在、その詳細を解析中です。

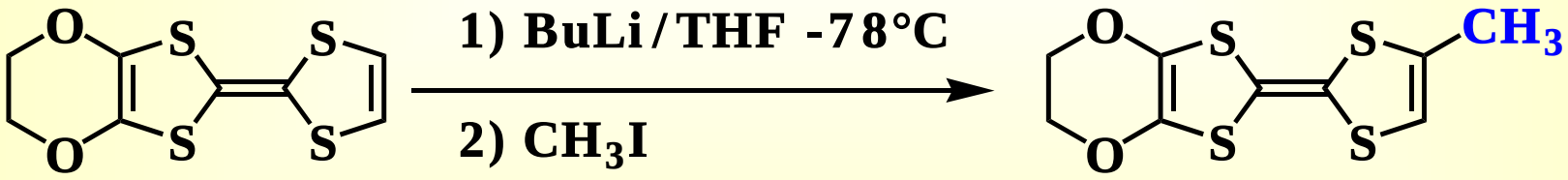
Molecular Design Based on EDO-TTF



Distinct Molecular Deformation
Multi-instability of Itinerant Electrons

To Find Further Peculiar Systems
Similar π-electron system
Similar Molecular Size
Lower Symmetry

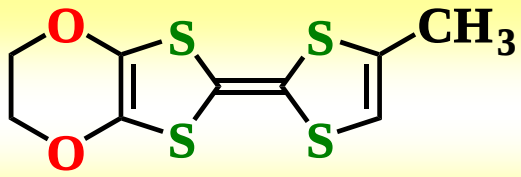
EDO-TTF having Small Sized Substituent



EDO-TTF

MeEDO-TTF
(43 % yield)

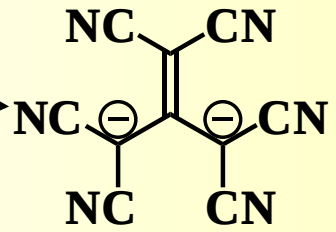
cf. 17 % yield: A. Miyazaki et al., (2001)



MeEDO-TTF

Complexes

Anion	D : A	σ_{rt} (S cm^{-1}) Compressed Pellets
BF_4	2 : 1	26 (Metal)
ClO_4	2 : 1	24 (Metal)
PF_6	2 : 1	3 (Semi.)
AsF_6	2 : 1	15 (MI at 240 K)
SbF_6	2 : 1	6 (MI at 250 K)
HCTMM	4 : 1	6 (Semi.)

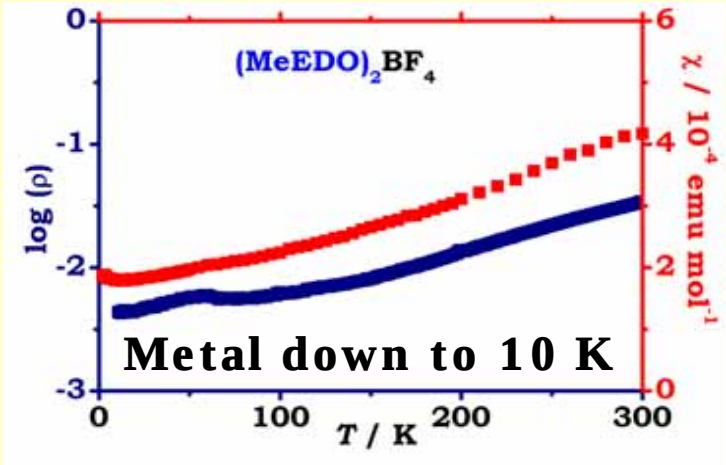


X.F. Shao et al., *J. Mater. Chem.*, **18**, 2131-2140 (2008)

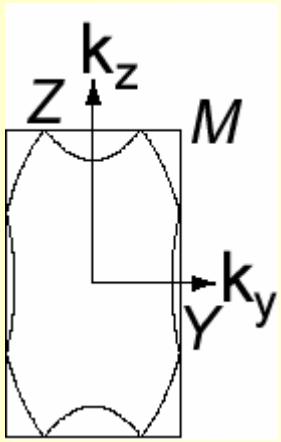
2:1 PF_6	σ_{rt} (S cm^{-1})
Black powder	3 (Semi.)
Dark green plates	29 (MI at 200 K)
Black plates	0.07 ↔ 4 (Semi.-Semi. at 303 K)

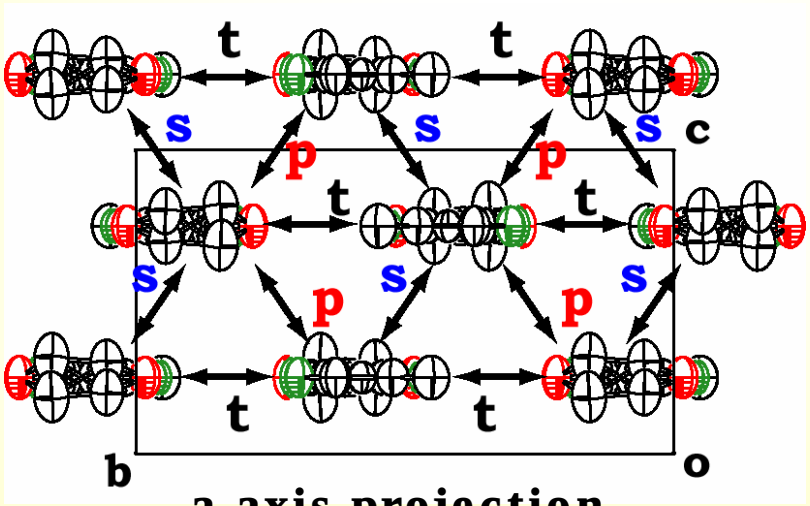
Crystal Structure of $(MeEDO\text{-}TTF)_2X$ ($X = BF_4$, ClO_4)

For $X = BF_4$

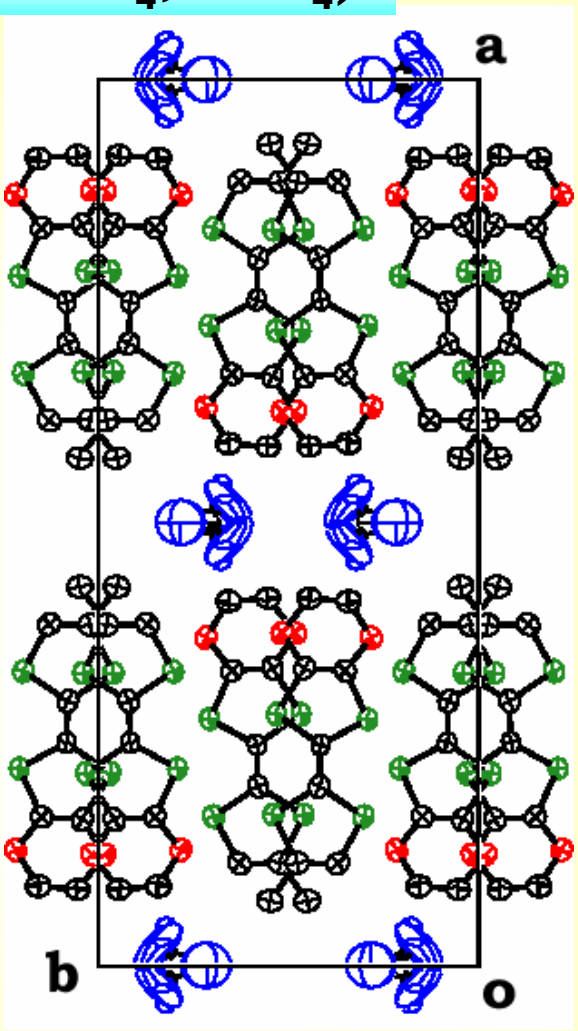


Orthorhombic
Cmcm
a = 28.752(2) Å
b = 12.369(1)
c = 6.969(1)
V = 2478.4(4) Å^3
Z = 4
R = 5.7 %
($I_o > 2\sigma(I_o)$)
GooF = 1.044





a-axis projection



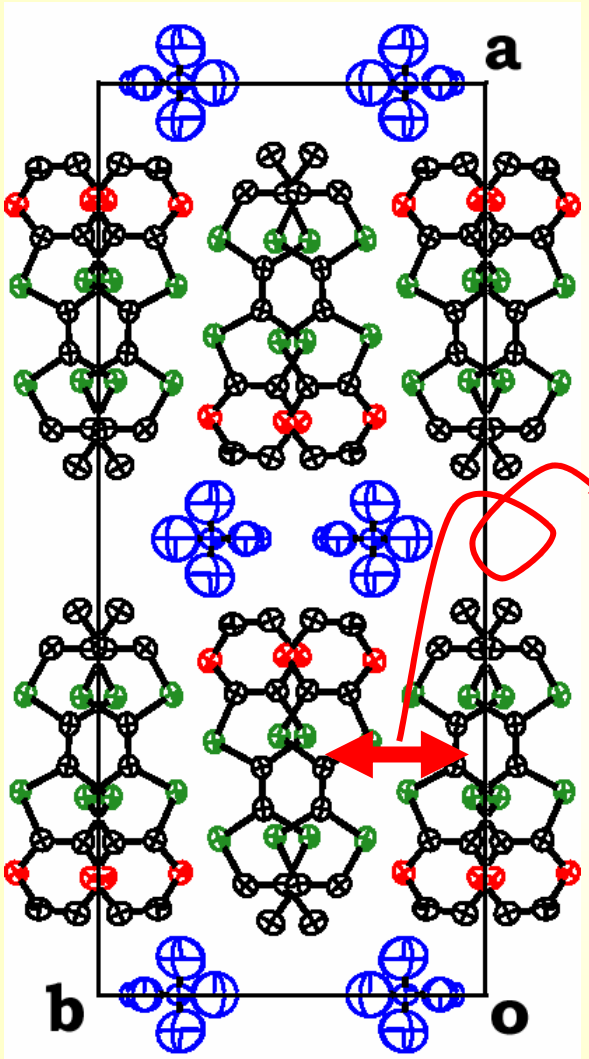
c-axis projection

2D Fermi Surface with weak intermol. interactions

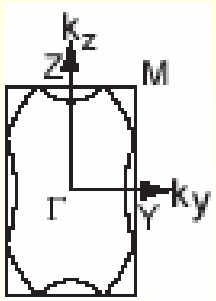
t = 11.7, p = 8.4, s = -5.1 × 10^{-3}

Donor: Head-to-Head (parallel)
Anion: Disordered

$(MeEDO\text{-}TTF)_2PF_6$: Semiconductor-Semiconductor

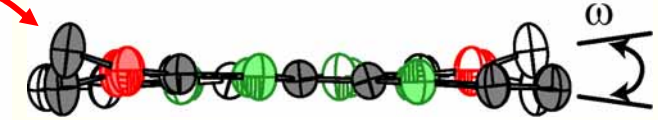


H-phase



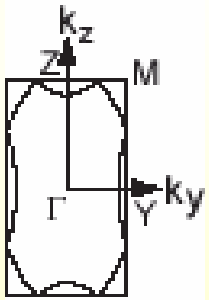
Nearly Localized Charge-order

ω = 0°

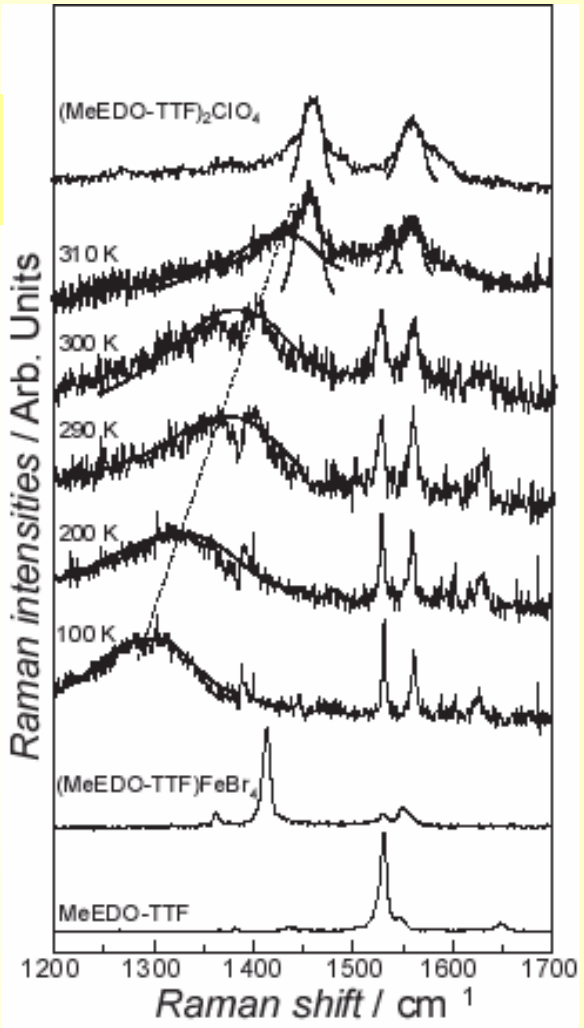


ω ≈ 4°

L-phase



Definitive Charge-order



Black Plate H-phase isostructural with metallic BF_4 & ClO_4

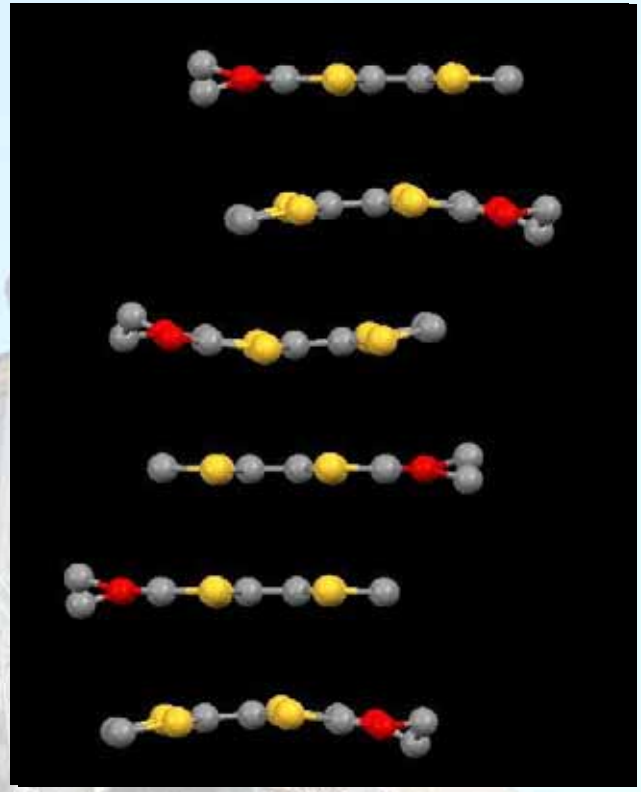
V / t

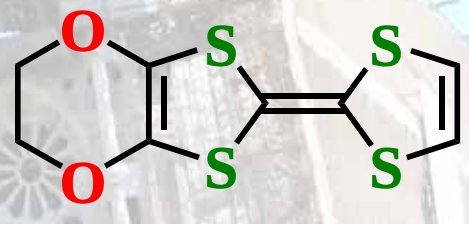
Area of Conducting Layer (Å²)

Stable	BF_4	ClO_4	PF_6	Semi-
metal	86.19	86.41	88.07	conductor

有機導電体における分子自由度

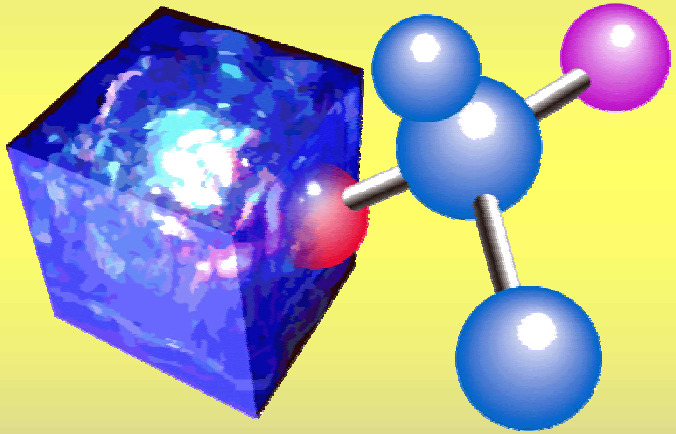
- 格子点 ≠ 点
  - 形状・大きさ・機能性
  - 形状変化が可能
- 新たな機能性物質
  - 多重不安定性
    - 外場敏感相転移物質
    - 光誘起相転移物質
      - → 開始時刻の制御
      - → 非平衡状態の研究

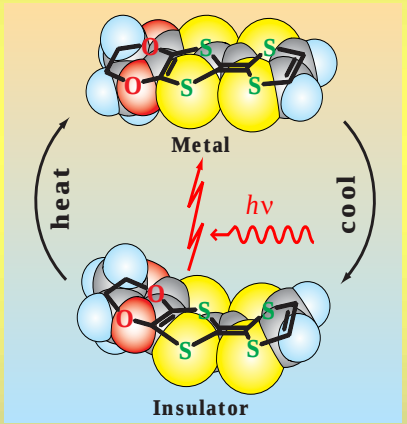




低温物質科学研究センター

Research Center for Low Temperature and Materials Sciences





分子性材料開拓・解析研究分野

Division of Molecular Materials Science