

# LINZ LECTURES

**Lecture 1. The Development of Organic Conductors:  
Metals, Superconductors and Semiconductors**

**Lecture 2A. Introduction and Synthesis of Important  
Conjugated Polymers**

**Lecture 2B. Solid State Polymerization**

**Lecture 3. Fullerene Chemistry**

**Lecture 3B. Molecular Engineering**

# The Development of Organic Conductors: Metals, Superconductors and Semiconductors

Lessons from History

# Organic Electronics (MOLECULAR) Materials

**Design**



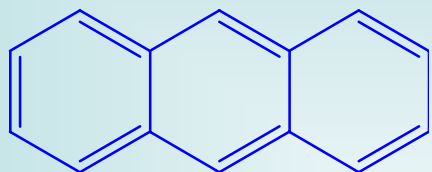
Ensemble



Properties

# Organic Conductors, Early History

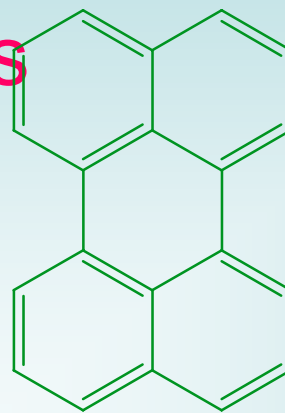
## Charge Carrier Generation: Electron Donors



Pochettino, A., *Accad. Lincei Rend.*,  
**1906**, 15, 171

Photogeneration of  
electron-hole pairs

Donors



Perylene (Per)

*facile hole  
generation  
through oxidation*

$$\text{Per}(\text{I}_2)_3 \quad \sigma_{\text{RT}} = 0.5 \text{ S/cm}$$

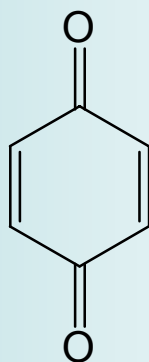
Akamatu, H.; Inokuchi, H.; Matsunaga, Y.  
*Nature*, **1954**, 173, 168

Labes, M. M., et al *Proc. Int. Conf. Semicon.  
Phys. Prague* **1960**, p 850

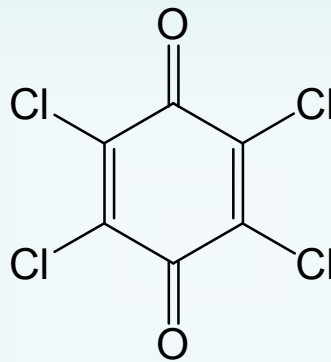
$\text{Per}(\text{I}_2)_4 \quad \sigma_{\text{RT}} = 30 - 50 \text{ S/cm}$  (metal to  
ca 270K)

Labes, M. M., et al *J. Chem. Soc. Chem. Commun.*  
**1979**, 329

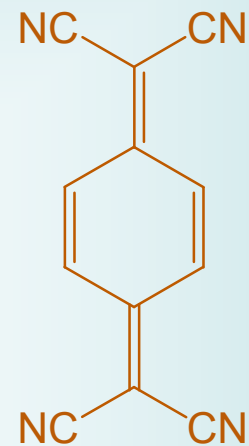
# Charge Generation: Electron Acceptors, Acceptor Repertoire



Quinone



Chloranil



TCNQ

Facile electron generation through reduction

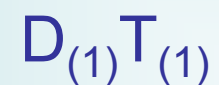
Acker, D. S.; Blomstrom, D. C., *J. Am. Chem. Soc.*, **1962**, *84*,  
3370

1962 - 1965 Preparation of many TCNQ<sup>(-•)</sup>  
M<sup>(+)</sup> organic conductors

## Types of TCNQ Salts or Charge-Transfer (C-T) Complexes

Simple

Complex



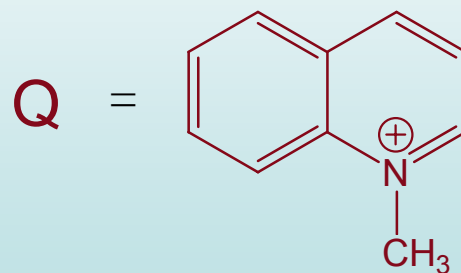
$D_nT_m$

$$\sigma_{RT} = 10^{-12} - 10^{-6}$$

$$\sigma_{RT} = 10 - 100$$

e.g.  $Li TCNQ$

e.g.  $Q TCNQ_2$



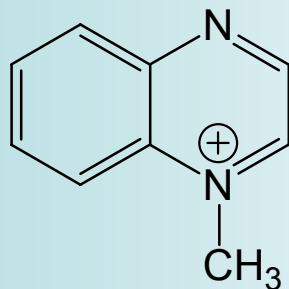
# Conductivities of Simple and Complex TCNQ Salts

(S<sub>cm</sub><sup>-1</sup>)

Cation

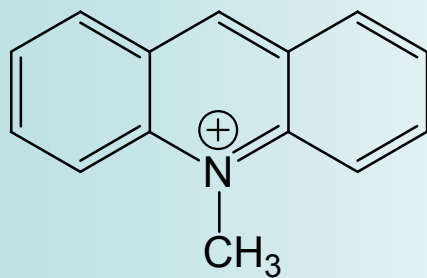
Simple

Complex



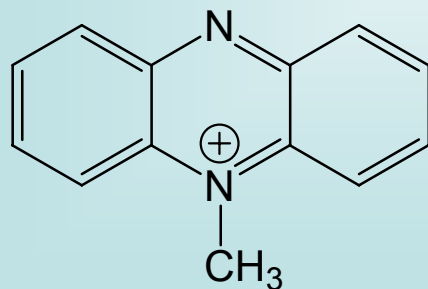
$10^{-8}$

$\approx 10^2$



$10^{-14}$

$\approx 10^{-1}$

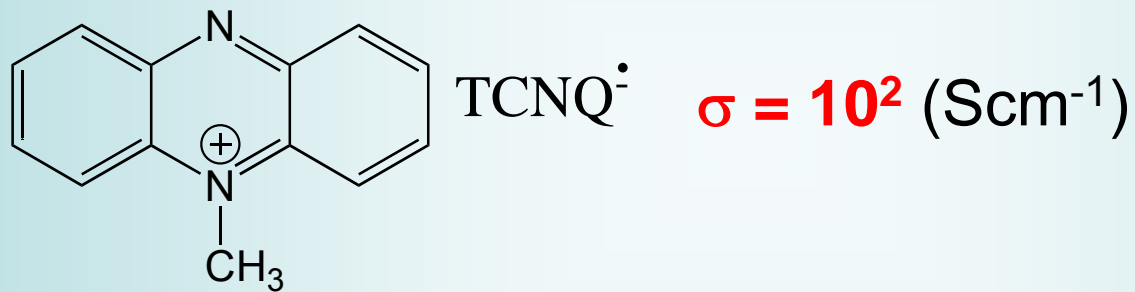


$10^2$

$\approx 10^{-1}$



# The Special Case



NMP TCNQ

Temperature dependence of the conductivity possibly metallic (I. Schegolev and also A.J. Heeger)

**SCIENTIFIC  
AMERICAN**

FEBRUARY 1965

VOLUME 212

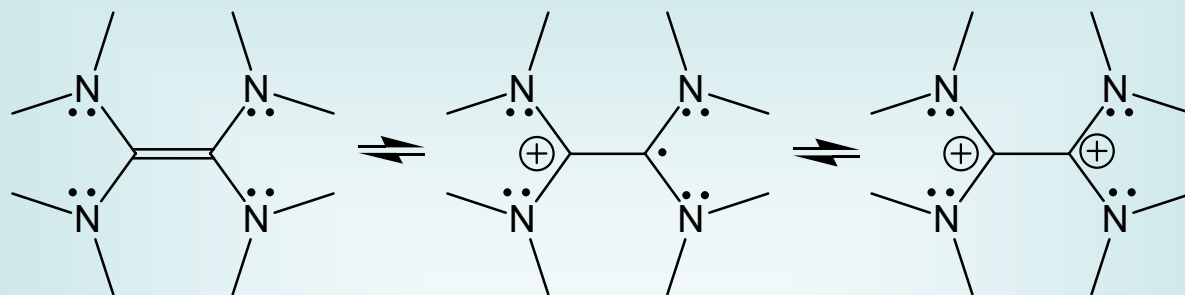
NUMBER 2

**SUPERCONDUCTIVITY AT ROOM TEMPERATURE**

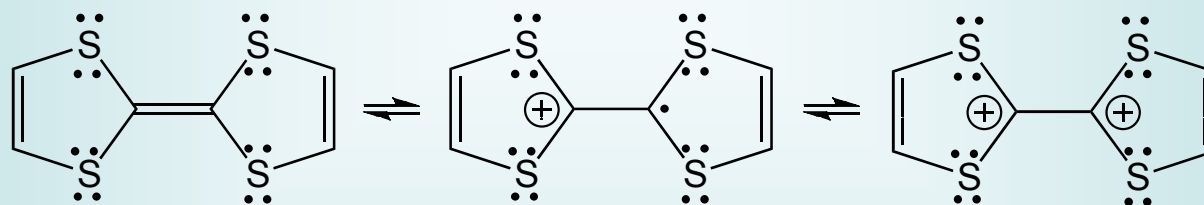
**IT HAS NOT YET BEEN ACHIEVED, BUT THEORETICAL  
STUDIES SUGGEST THAT IT IS POSSIBLE TO SYNTHESIZE  
ORGANIC MATERIALS THAT, LIKE CERTAIN METALS  
AT LOW TEMPERATURES, CONDUCT ELECTRICITY  
WITHOUT RESISTANCE**

BY W. A. LITTLE

# The Birth of TTF



TDAE

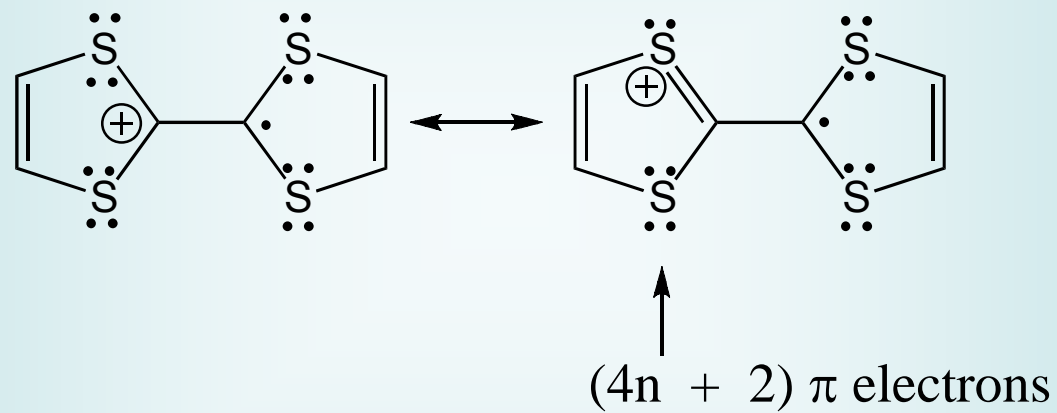


TTF

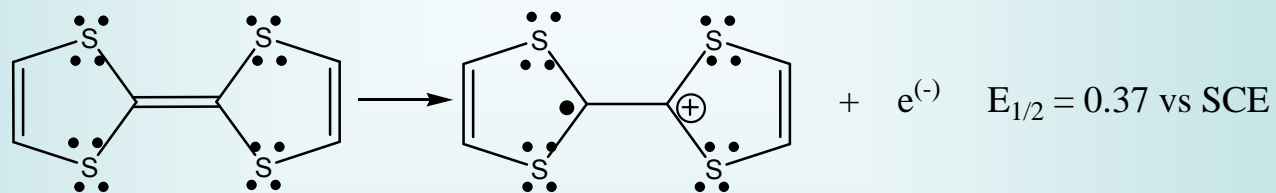
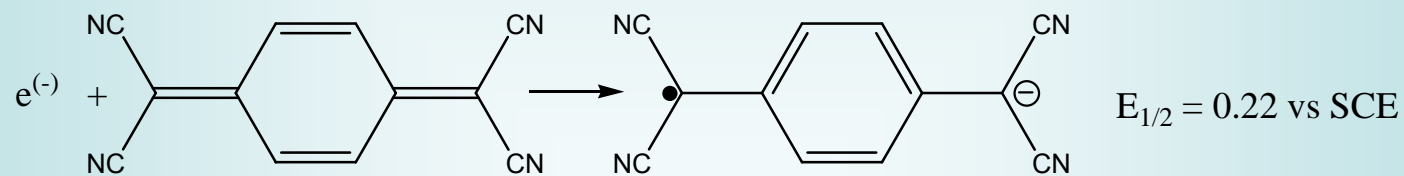
Wudl, F.; Smith, G. M.; Hufnagel, E. J. *Chem. Commun.* **1970**, 1453–1454.

Wudl, F.; Wobschall, D.; Hufnagel, E. J. *J. Am. Chem. Soc.* **1972**, *94*, 670–670

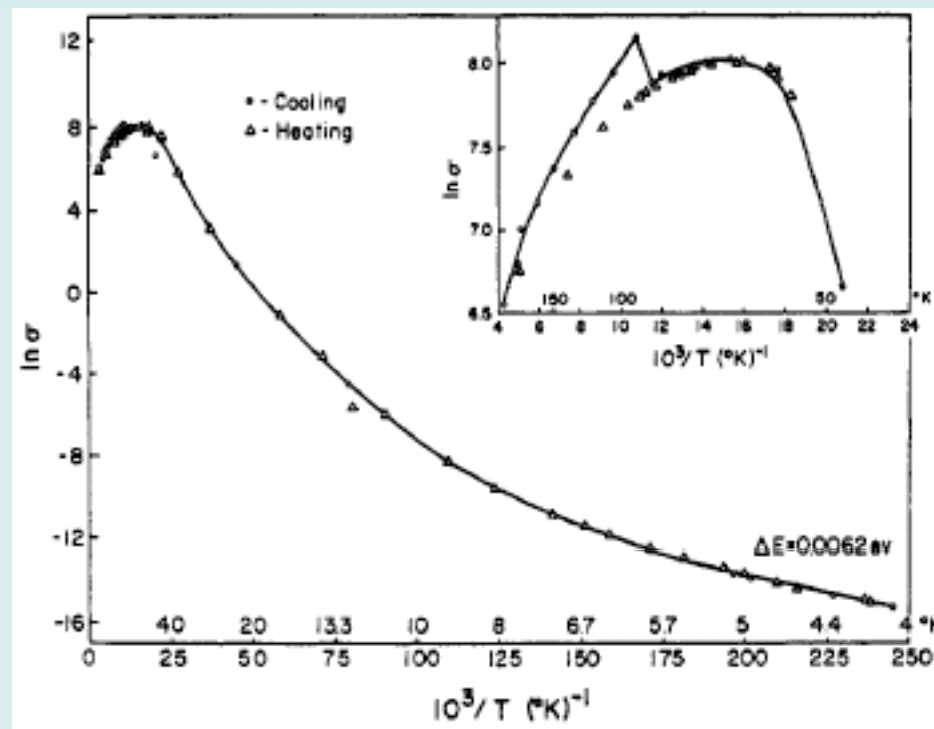
# An Important Design Feature



# The Marriage of TTF & TCNQ



# TTF-TCNQ, The First Organic Metal



$$R = \rho l/A$$

$$\sigma = 1/R$$

$$\sigma = N\mu e$$

$\sigma$  = Conductivity

$N$  = Avogadro's number

$\mu$  = mobility

$e$  = electron charge

J. Ferraris, D. O. Cowan, V. Walatka, Jr., J. H. Perlstein *J. Am. Chem. Soc.*  
**1973**, 95, 948.

# The "Giant Conductivity Peak" Phenomenon

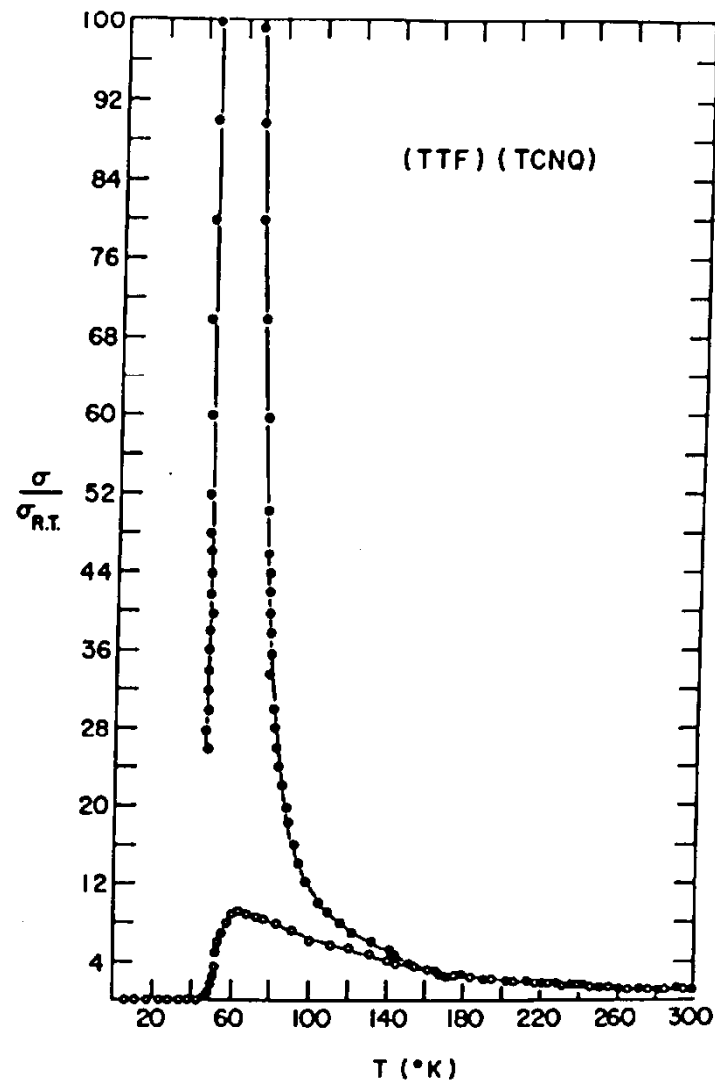


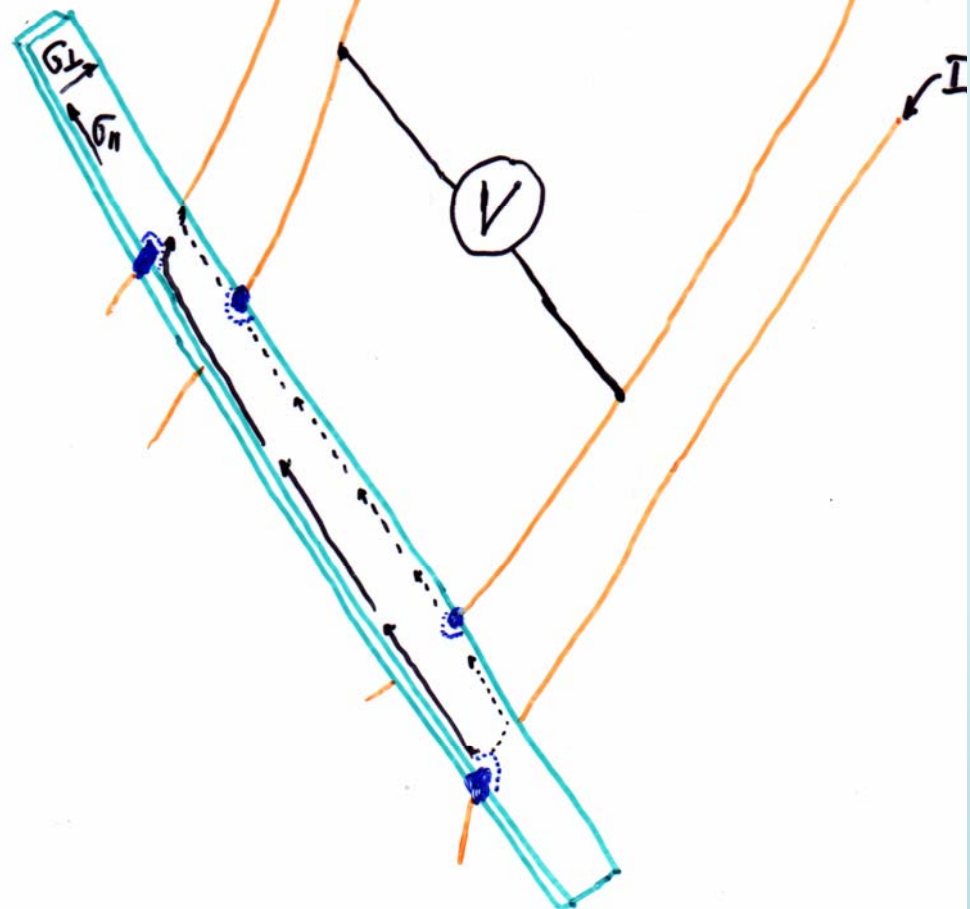
FIG. 3. Temperature dependence of the conductivity of (TTF) (TCNQ) single crystal (—●—●—) and of (TTF) (TCNQ) typical crystals (—○—○—).

Coleman, et al, *Sol. State Commun.*  
**1973**, 12, 1125 - 1132



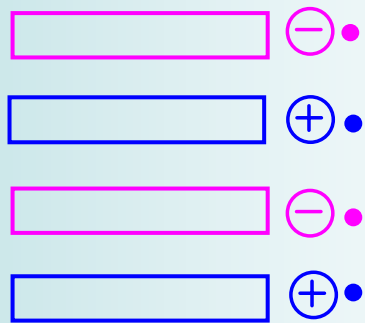


$$\sigma_{||} \sim 10^3 \sigma_{\perp}$$
$$\frac{\sigma_{||}}{\sigma_{\perp}} = f(T)$$

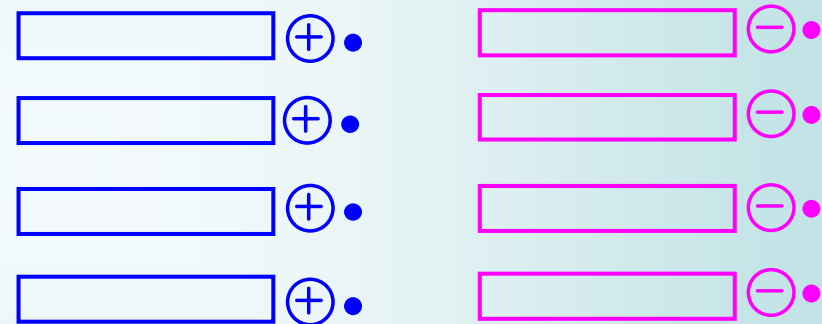


# Two Possibilities of Flat Molecule Ensembles

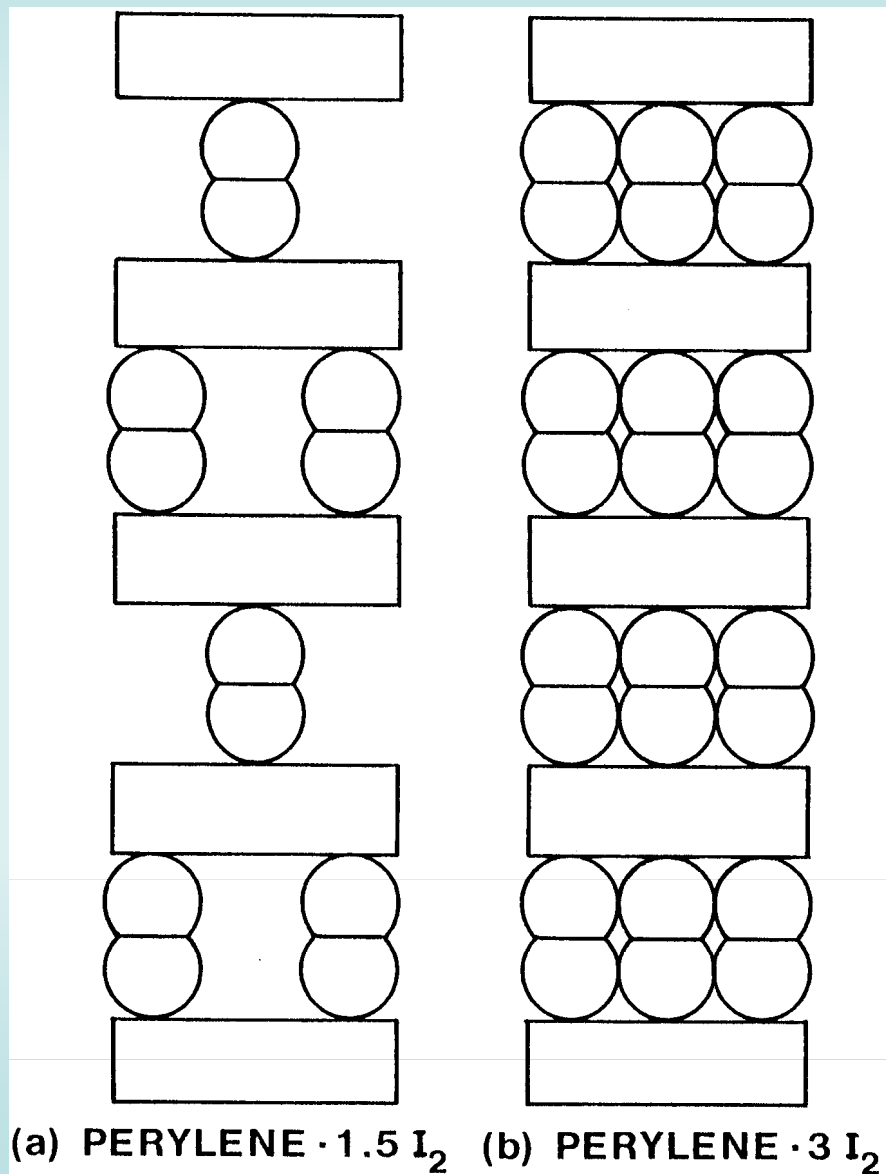
Alternating Stack



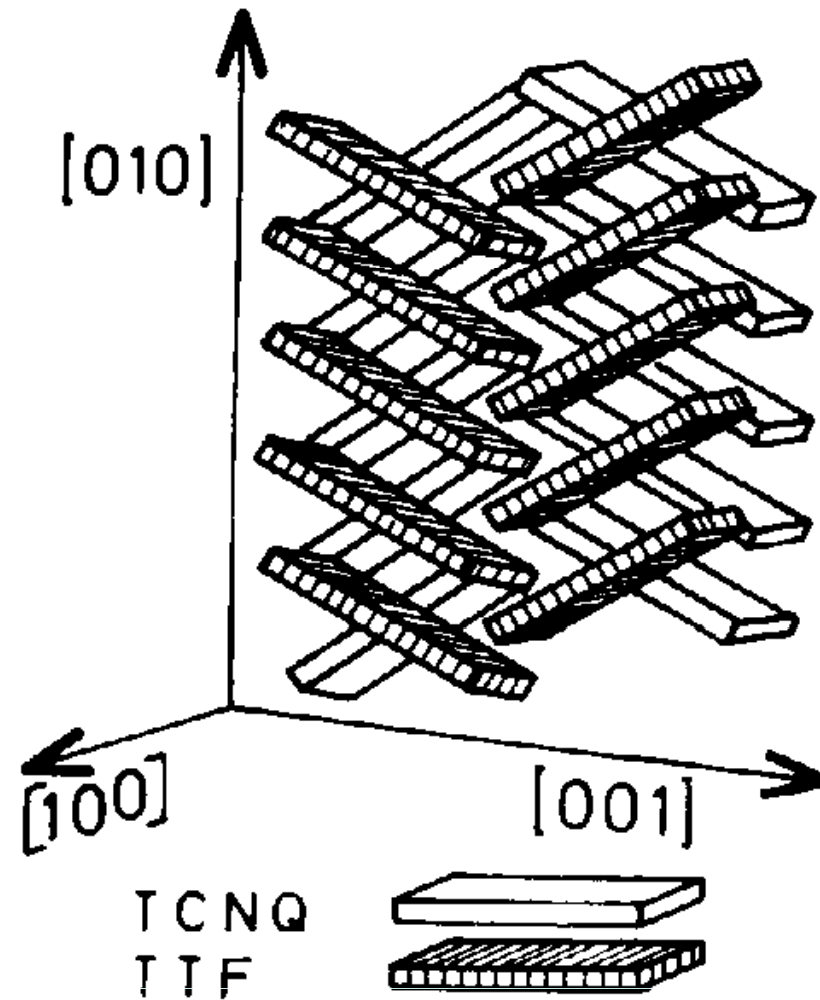
Segregated Stack



# Proposed Structure of Perylene Iodides

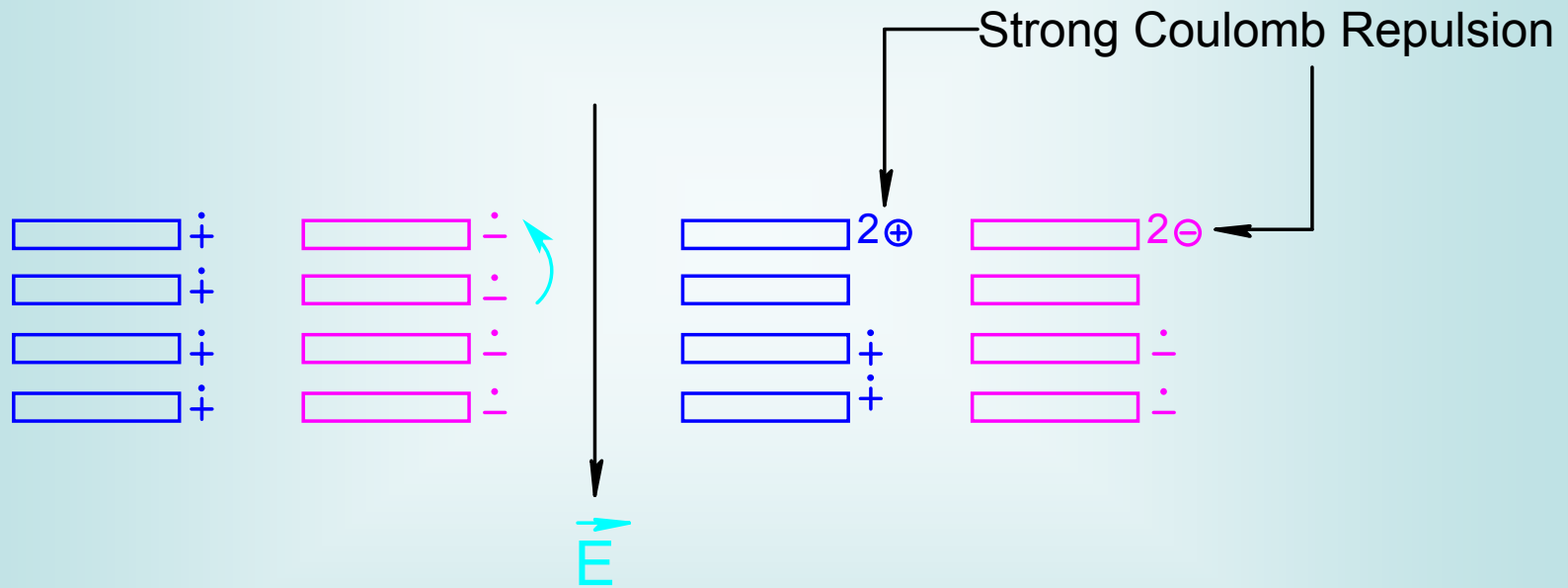


# The Structure of TTF-TCNQ

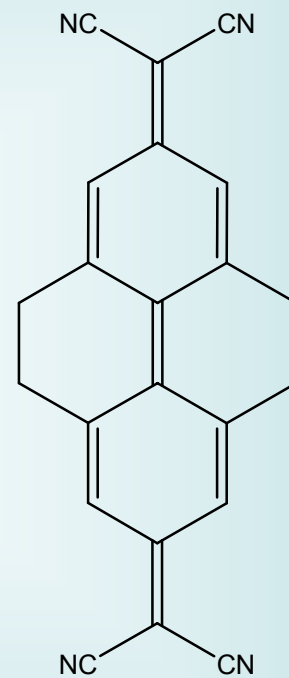
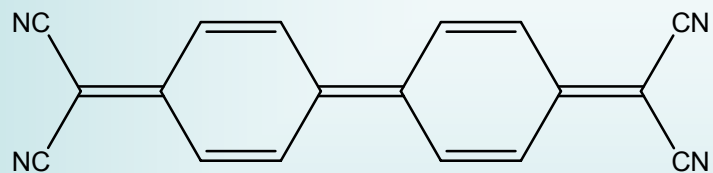
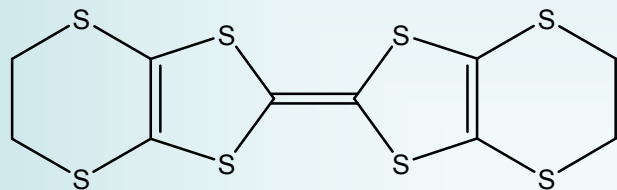


Geene R.L.; Street G.B., *Proceedings of the NATO-ASI on Chemistry and Physics of One-Dimensional Metals, Boizano, Italy, August 1976*. (Edited by KELLER Hi.). Plenum Press, New York (1977)

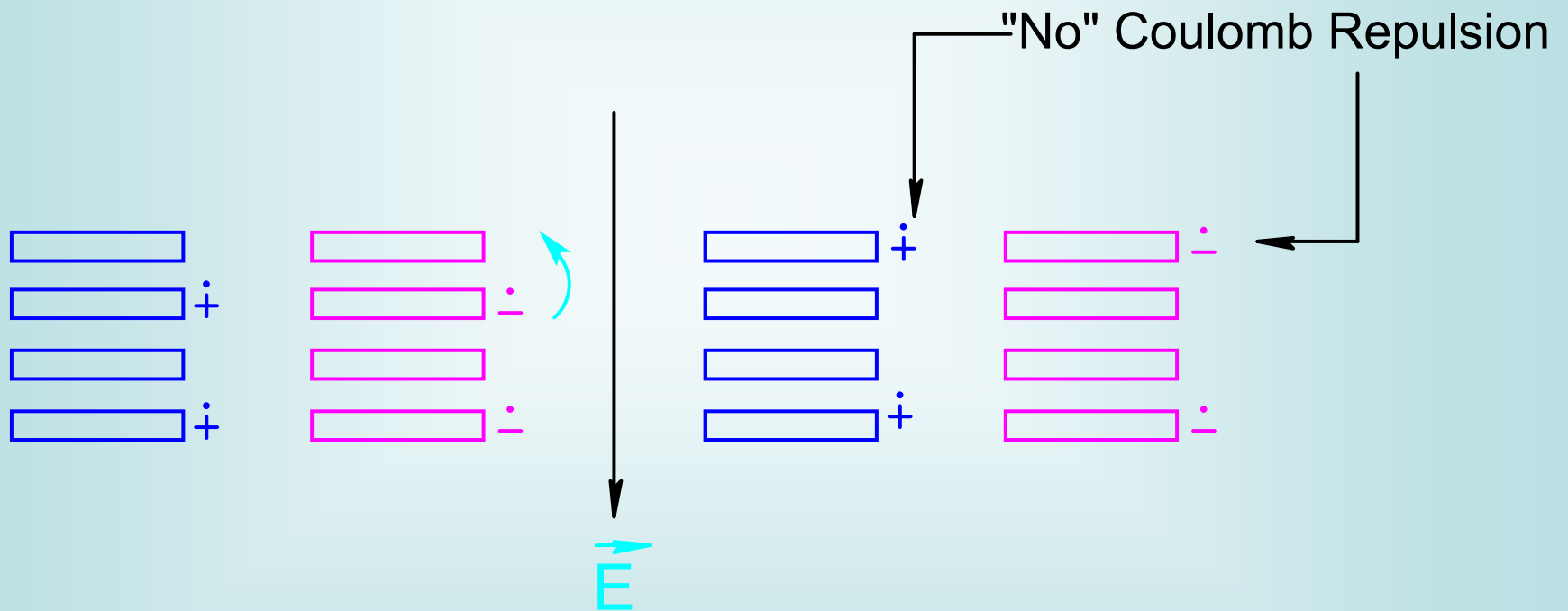
# A Problem with Transport in a $\frac{1}{2}$ Filled Stack (Band)



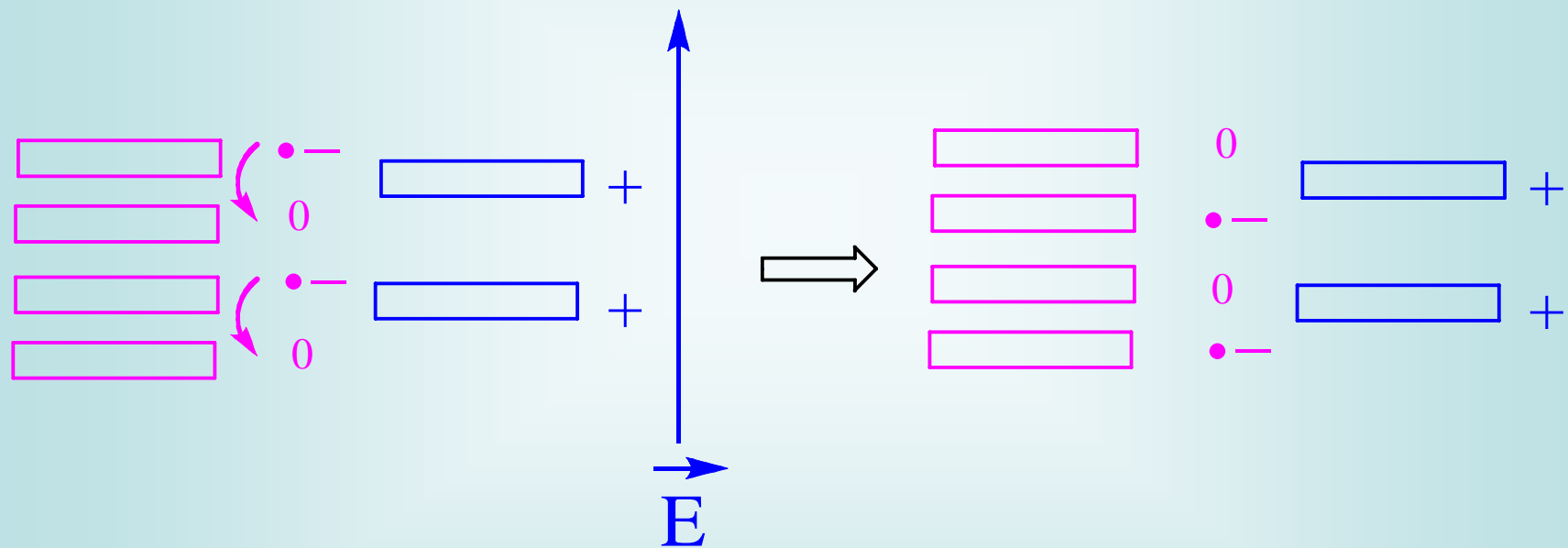
# Responding to Physicists Recipes



# Soos-Torrance Model (Mixed Valence)



# Facile Conductivity in Complex Salts of TCNQ

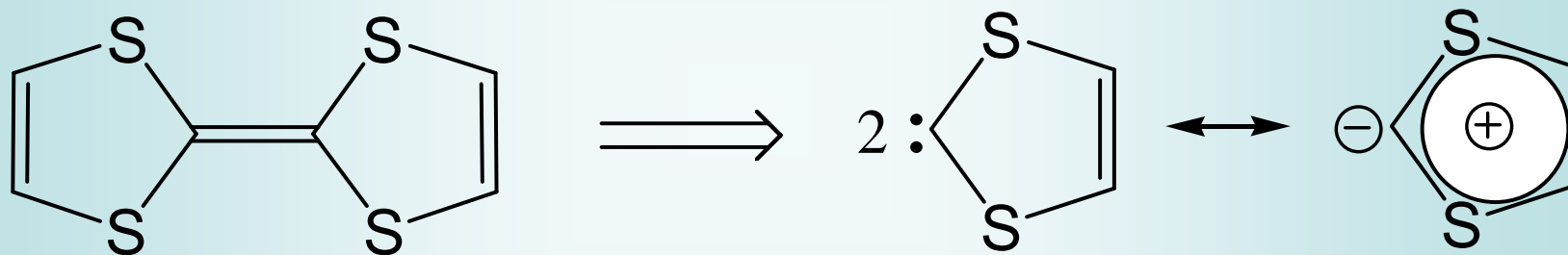




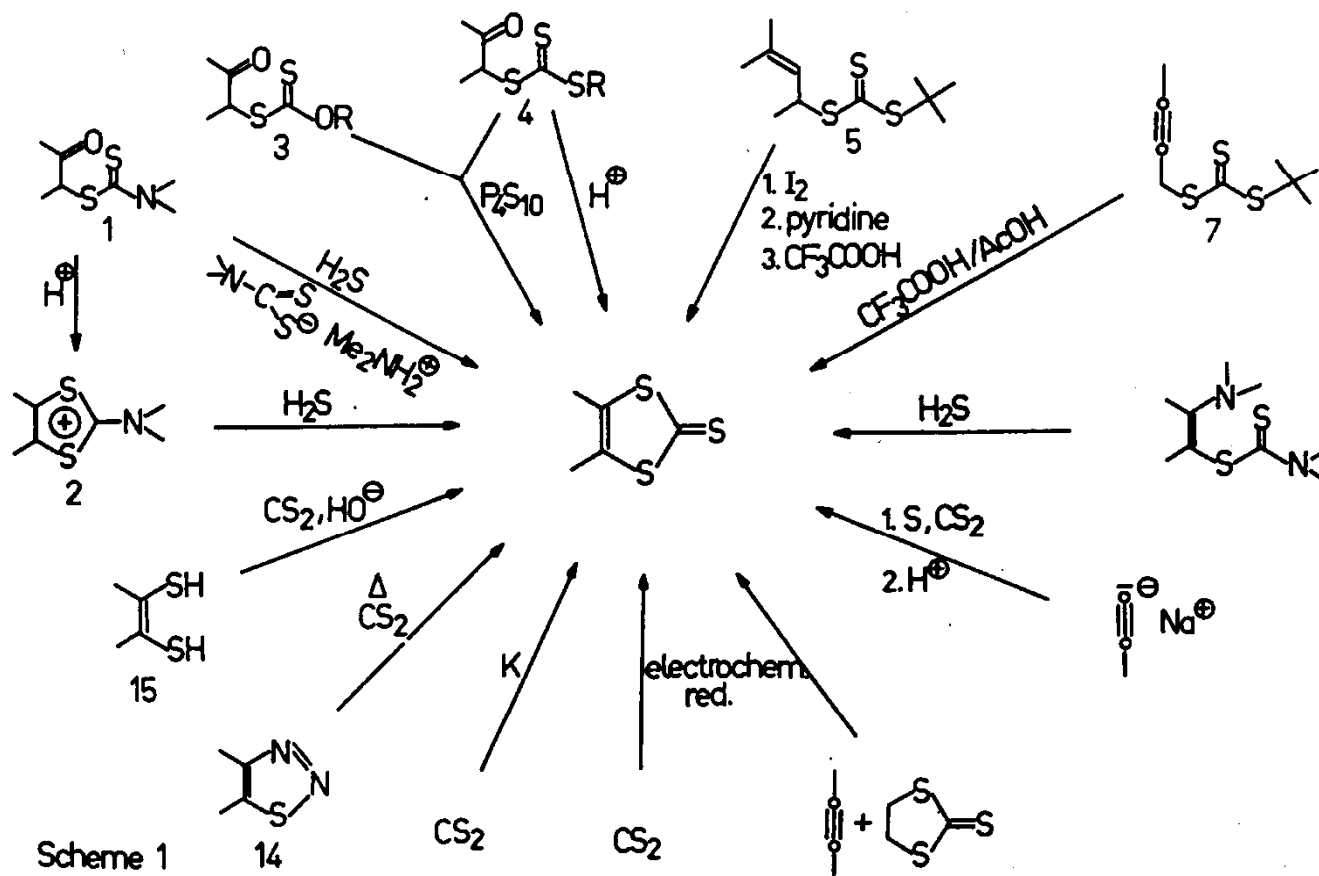
# Chemical Interlude

# Synthesis of TTF and Derivatives

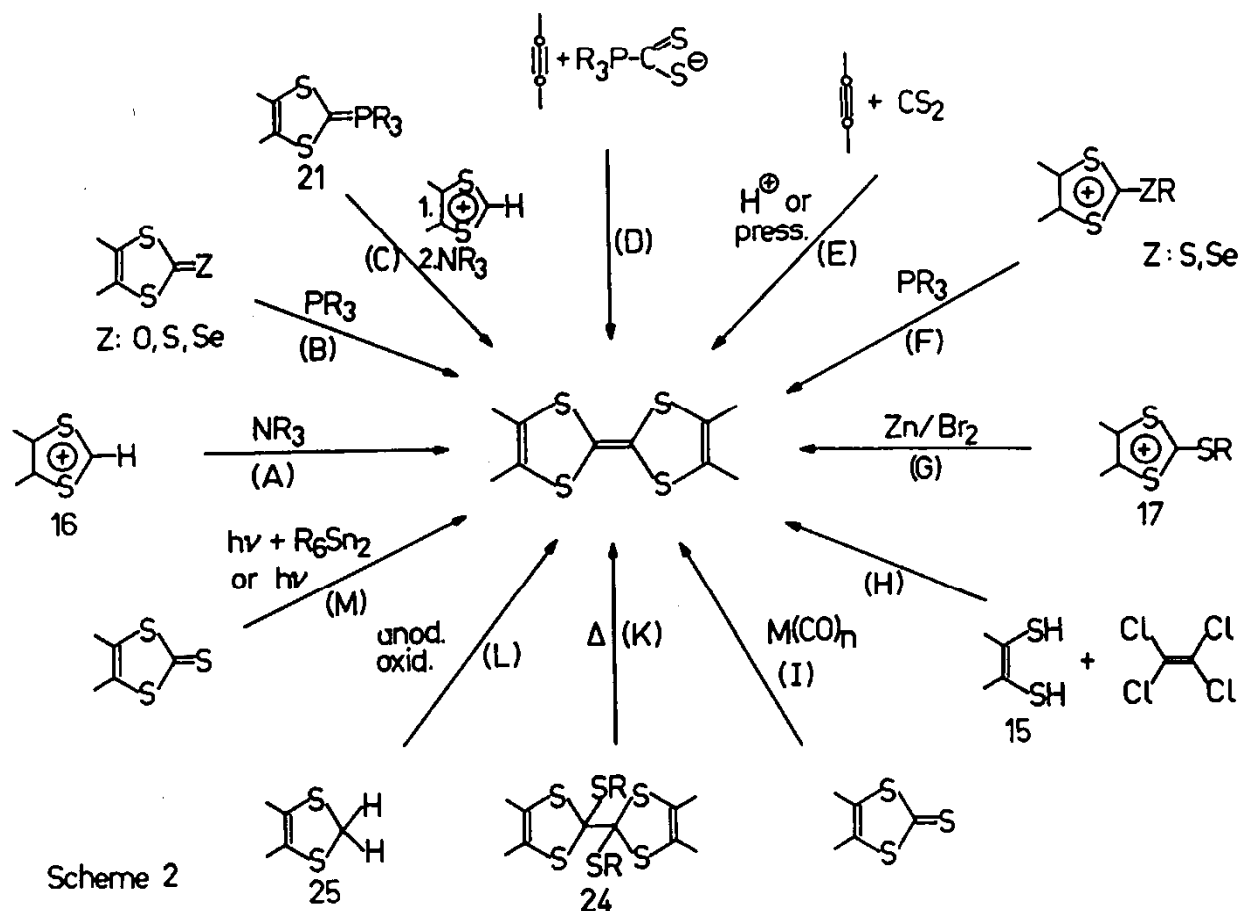
## Strategy



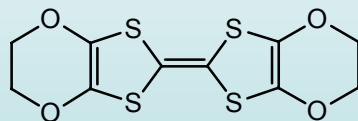
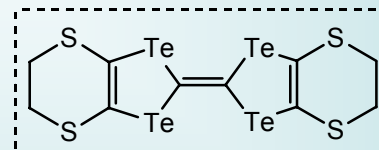
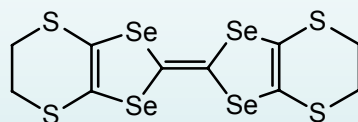
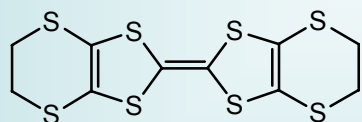
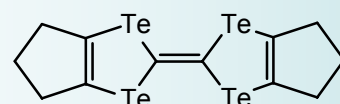
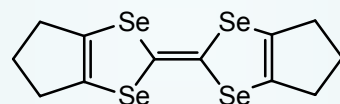
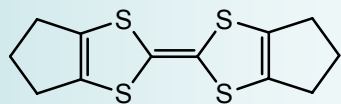
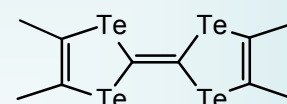
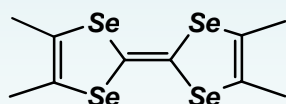
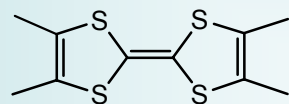
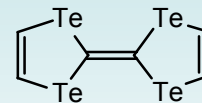
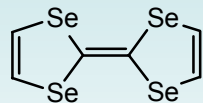
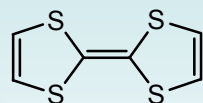
# Synthesis of 1,3-Dithiole-2-thiones



# Synthesis of TTFs

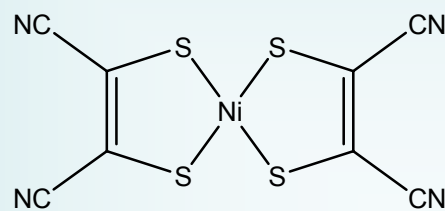
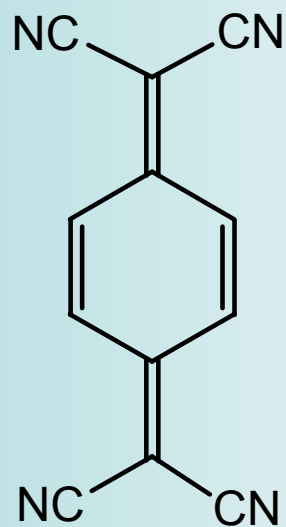


# The Most Popular and Unusual Tetrachalcogen Fulvalenes

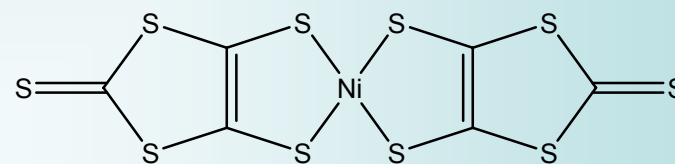


**S**, **Se** = Superconducting; [ ] = not yet prepared

# The Most Popular Acceptors



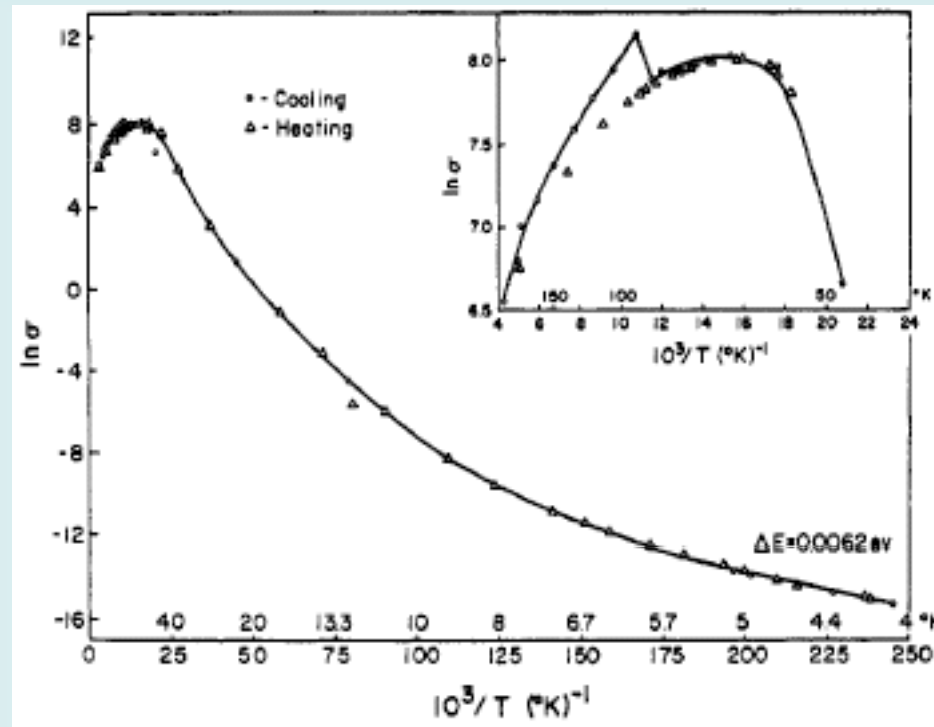
mnt



dmit

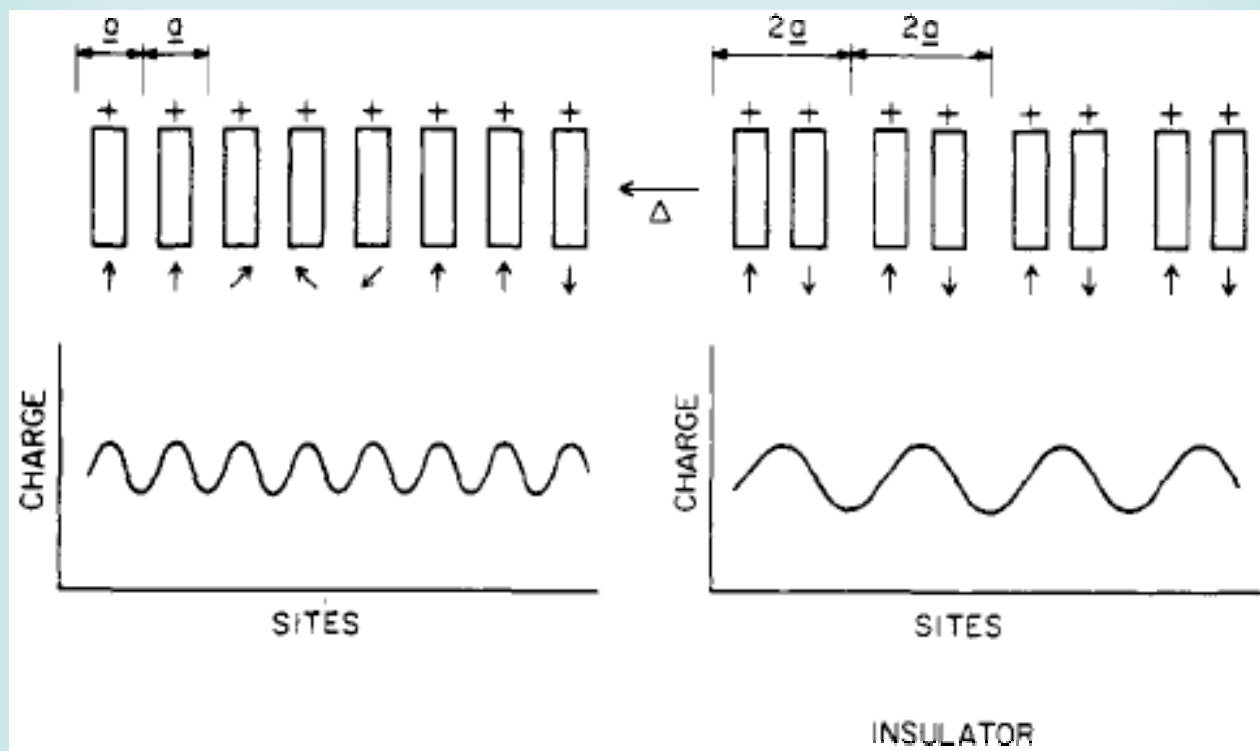
Metal Dithiolenes

# TTF-TCNQ, The First Organic Metal?



**Why the loss in conductivity?**

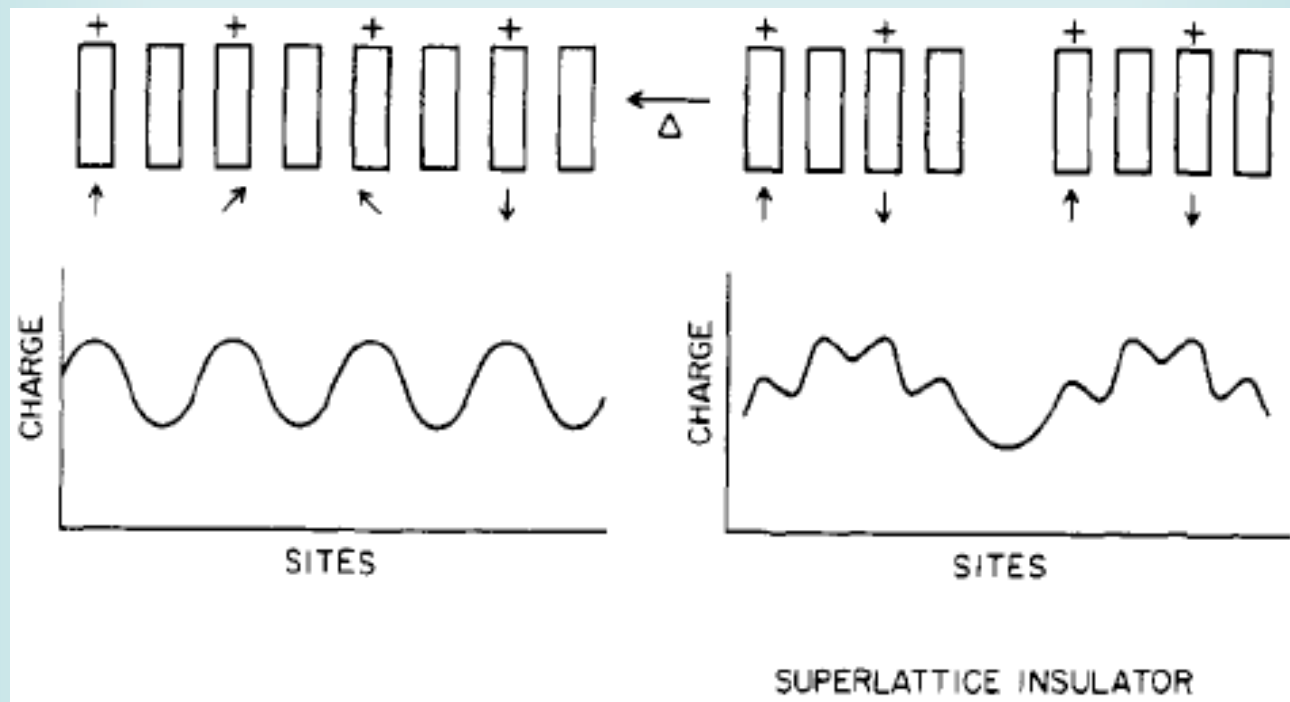
# The Peierls Distortion



Peierls Distorted State

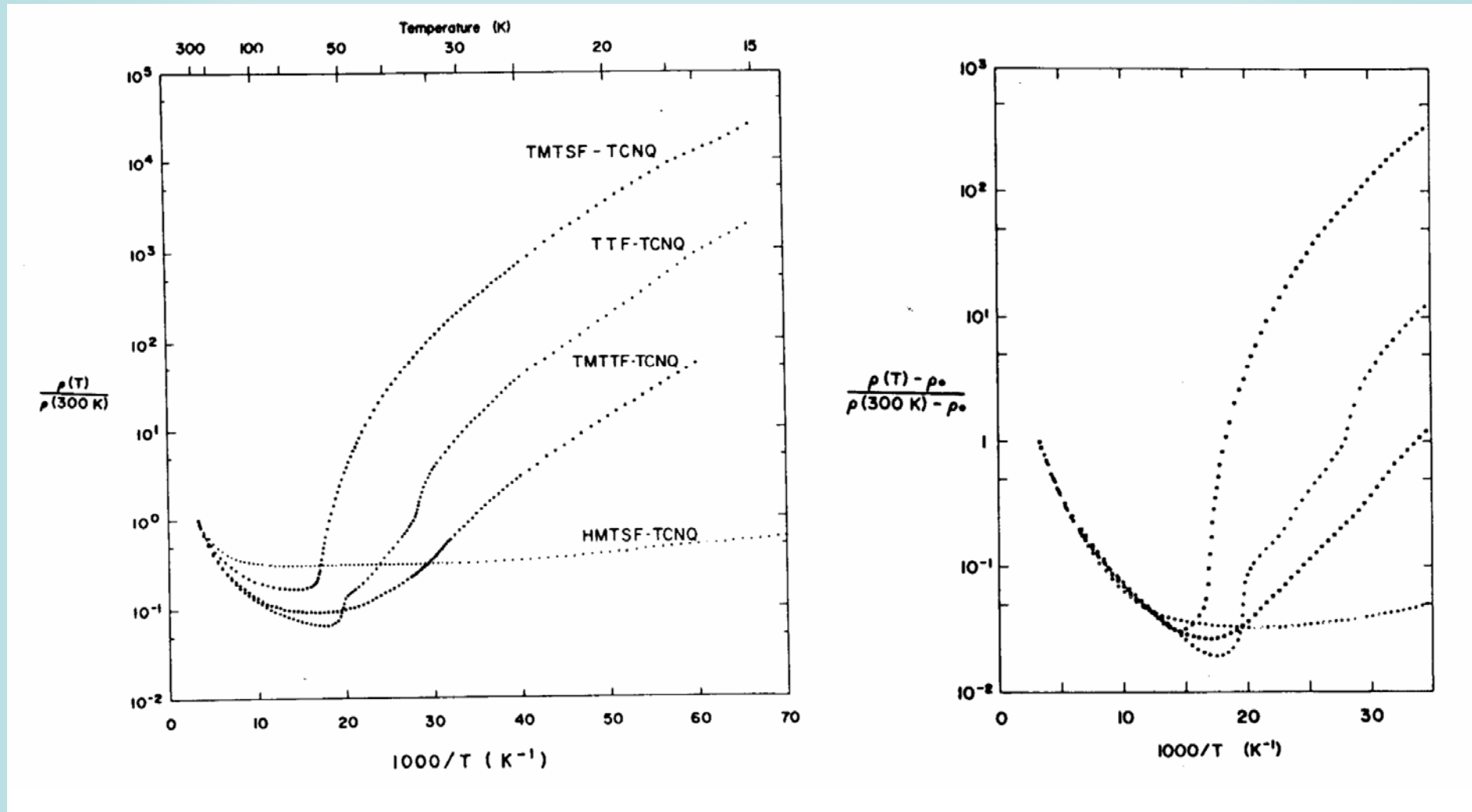


# The Peierls Distortion in More Complex Cases



Peierls Distorted State

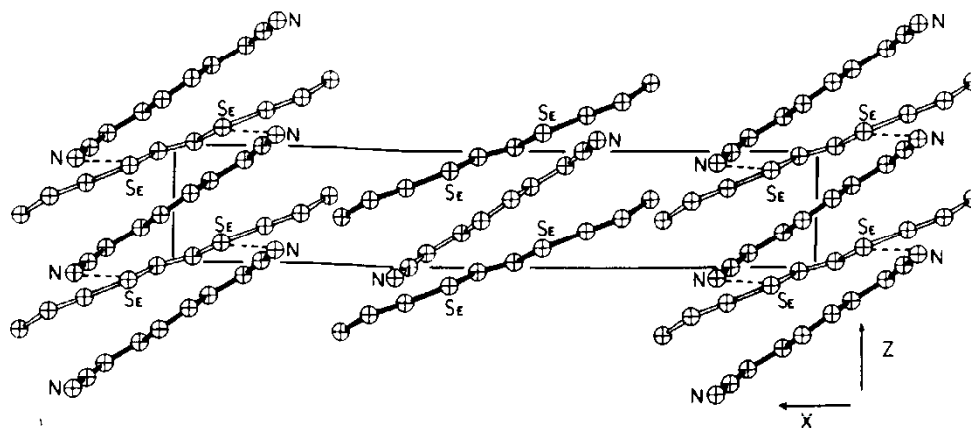
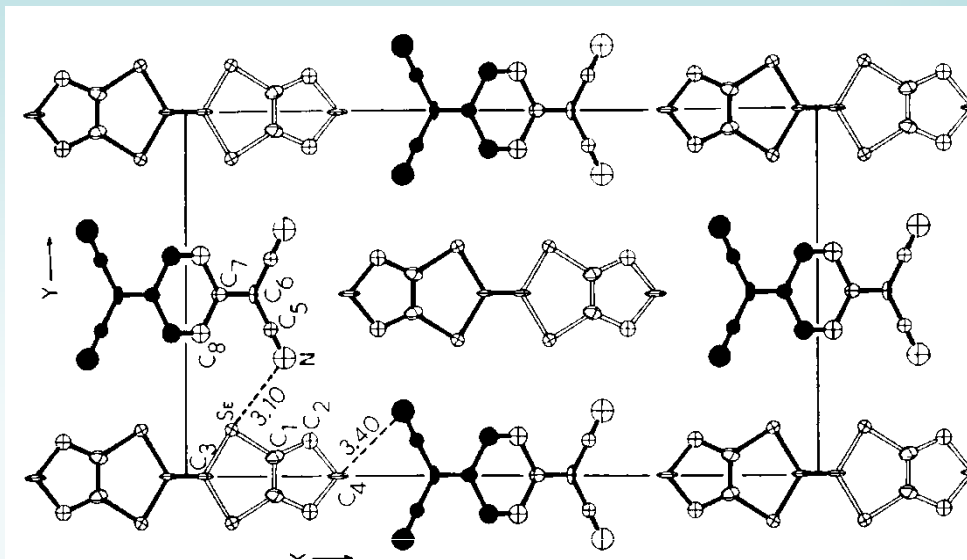
# Comparative Temperature-Dependent Resistivities



Bloch, A.N.; Carruthers, T.F.; Poehler, T.O.; Cowan, D.O. in "Chemistry and Physics of One-Dimensional Metals, Keller, H.J., Ed; Plenum, NY 1977; pp 47 -85

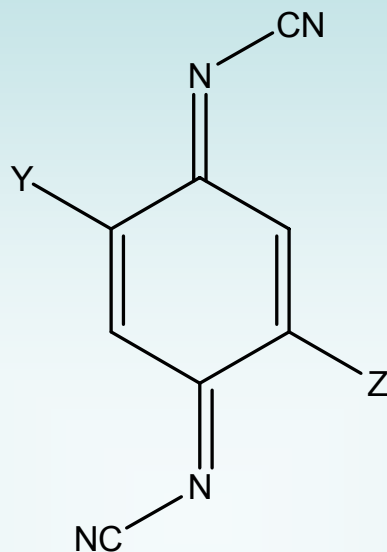
# Dealing with the Peierls Catastrophe: Increase in Dimensionality and Disorder

## HMTSF-TCNQ



Bloch, A.N.; Carruthers, T.F.; Poehler, T.O.; Cowan, D.O. in "Chemistry and Physics of One-Dimensional Metals, Keller, H.J., Ed; Plenum, NY 1977; pp 47 -85

# The DCNQI Story: A Truly 3-D Molecular Metal



Y = Z = Me

Y = Br, Z = I

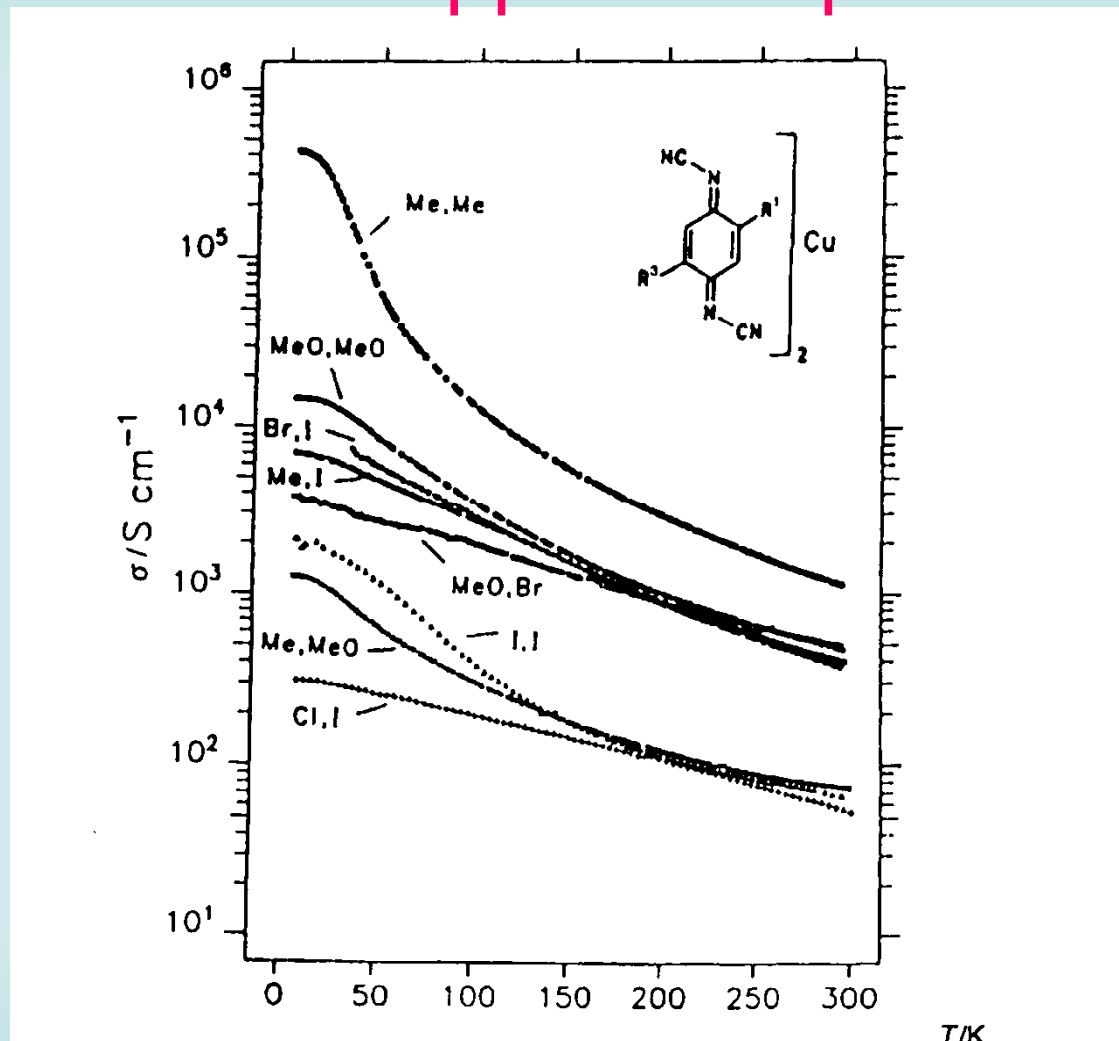
Y = Z = I

Y = Cl, Z = I

Y = Z = MeO

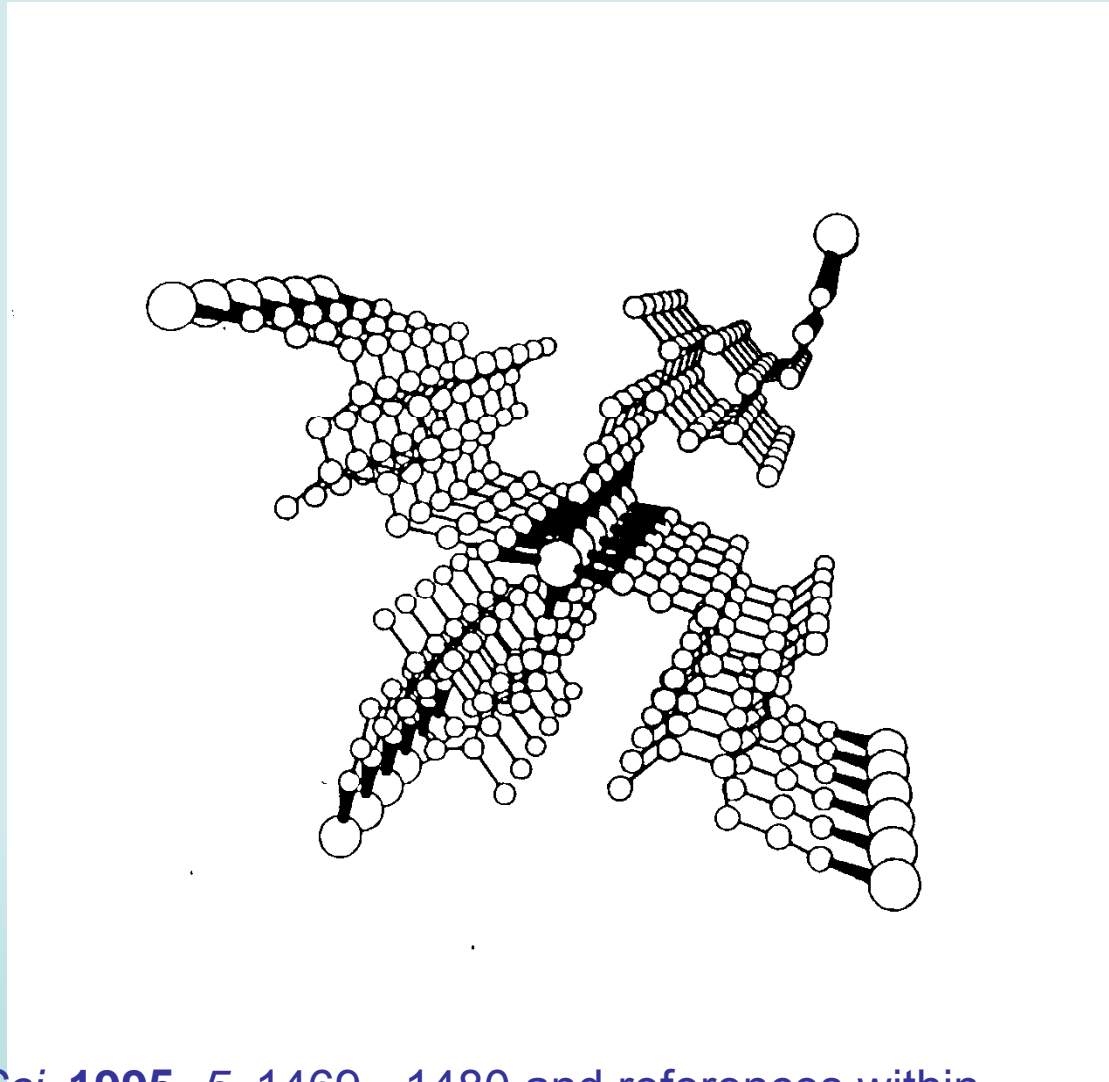
Etc, etc

# Temperature Dependence of the Conductivity Of the Copper Complexes



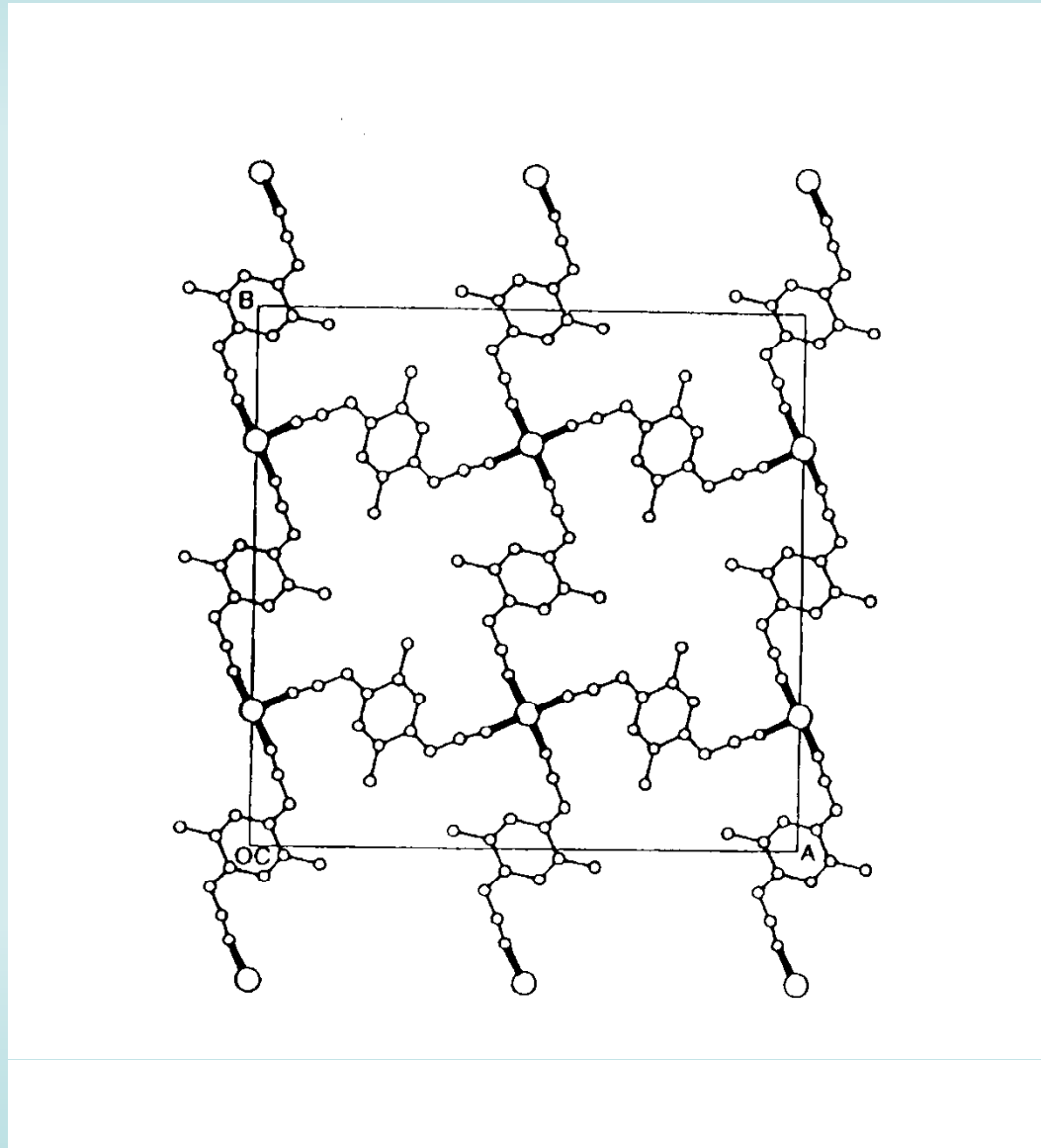
Hünig, S. *J. Mat. Sci.* **1995**, 5, 1469 - 1480 and references within

# Copper-Mediated 3-Dimensionality



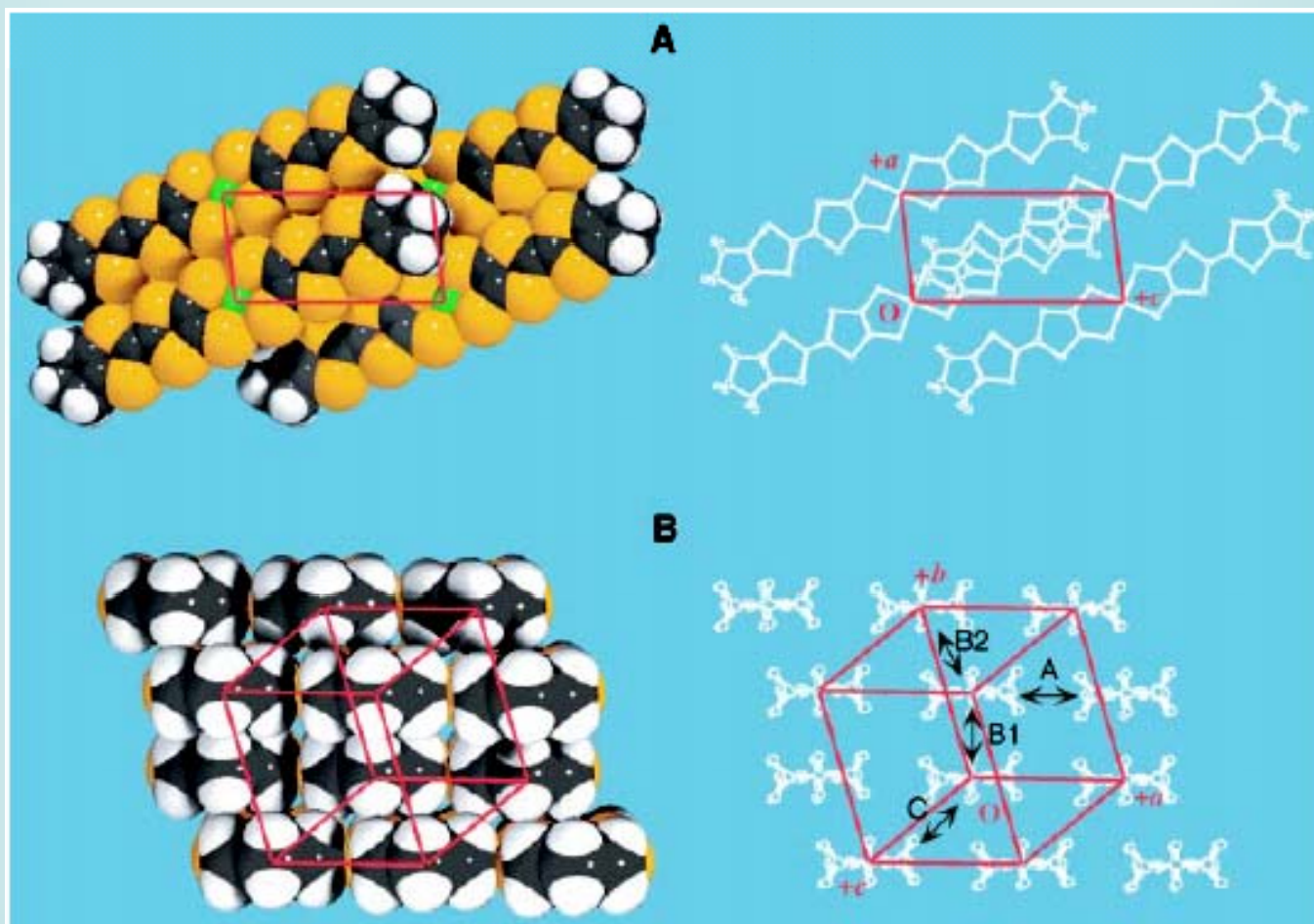
Hünig, S. *J. Mat. Sci.* **1995**, *5*, 1469 - 1480 and references within

# View of a Single Layer



Hünig, S. *J. Mat. Sci.* **1995**, 5, 1469 - 1480 and references within

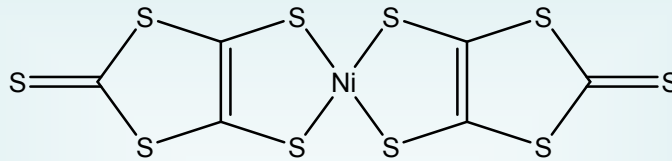
# A Molecular Metal Designer's Dream: The Single Component Metal



Hisashi Tanaka, Yoshinori Okano, Hayao Kobayashi, Wakako Suzuki, Akiko Kobayashi\*  
*Science*, **2001**, 291, 285.



# The Key Building Block

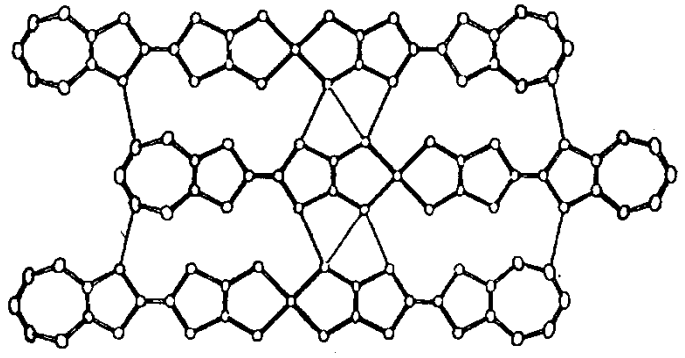
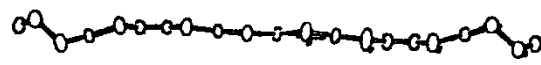
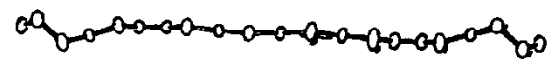


dmit

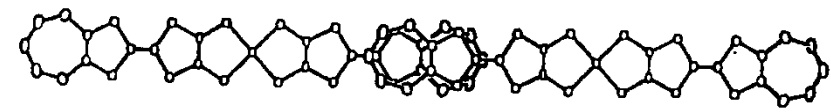
Metal Dithiolenes



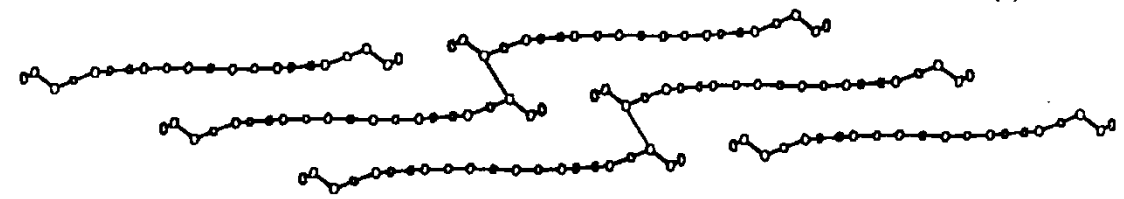
(a)



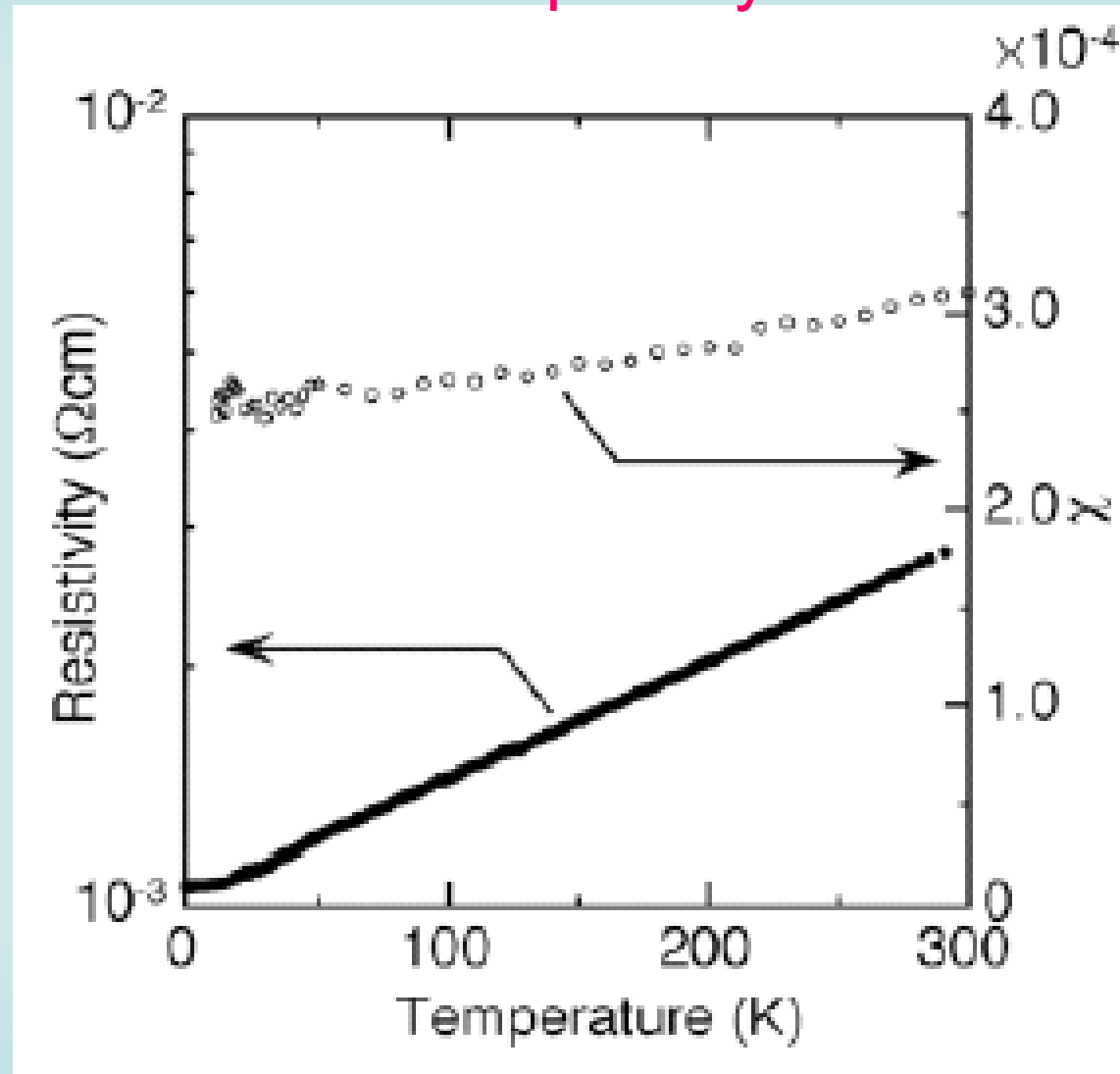
(b)



(c)

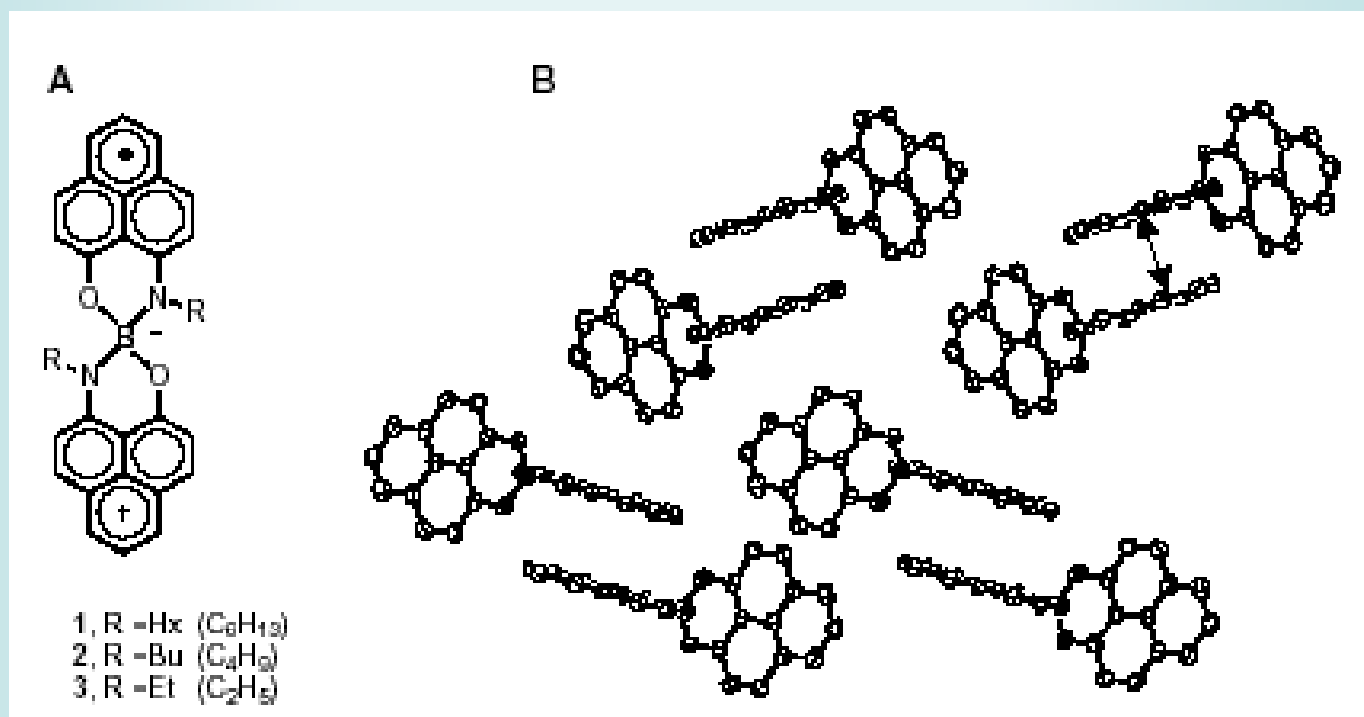


# Temperature Dependence of the Resistivity & Magnetic Susceptibility



Hisashi Tanaka,<sup>1</sup> Yoshinori Okano,<sup>1</sup> Hayao Kobayashi, Wakako Suzuki, Akiko Kobayashi\*  
*Science*, **2001**, 291, 285.

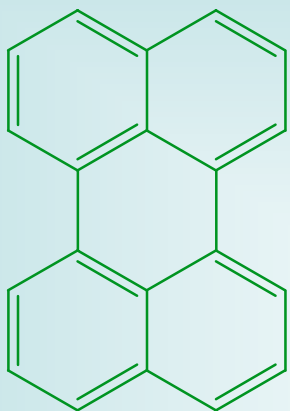
# Another Single-Component Conductor



M. E. Itkis, X. Chi, A. W. Cordes, R. C. Haddon, *Science*, **2002**, 291, 1443.

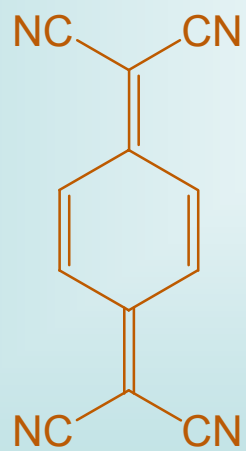
# Take Home Messages from this Lesson

1.



Perylene (Per)

facile oxidation = *p*-doping



TCNQ

facile reduction = *n*-doping

Can Organic Metals be Superconductors?

**SCIENTIFIC  
AMERICAN**

FEBRUARY 1965

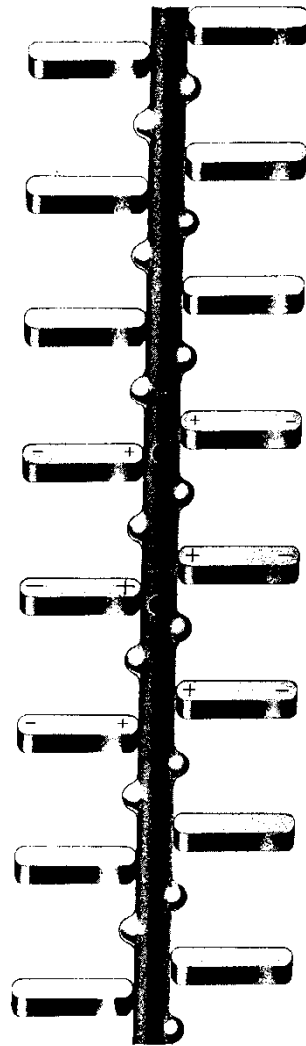
VOLUME 212

NUMBER 2

**SUPERCONDUCTIVITY AT ROOM TEMPERATURE**

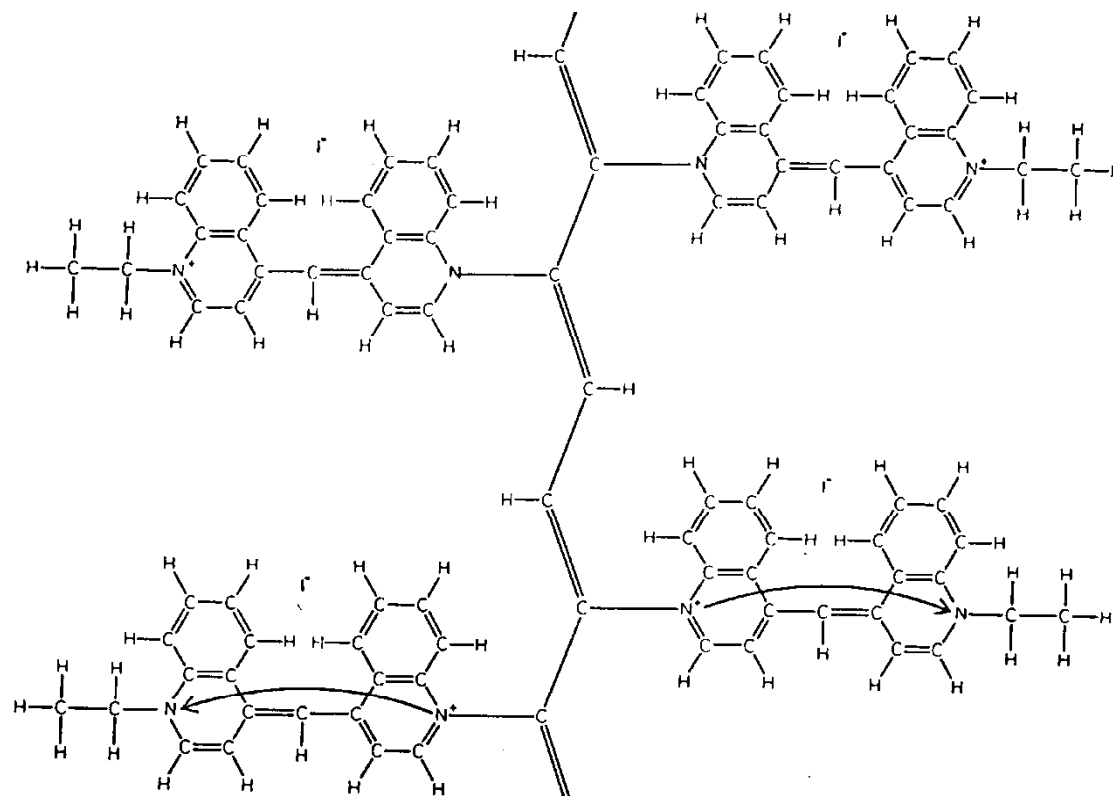
**IT HAS NOT YET BEEN ACHIEVED, BUT THEORETICAL  
STUDIES SUGGEST THAT IT IS POSSIBLE TO SYNTHESIZE  
ORGANIC MATERIALS THAT, LIKE CERTAIN METALS  
AT LOW TEMPERATURES, CONDUCT ELECTRICITY  
WITHOUT RESISTANCE**

BY W. A. LITTLE



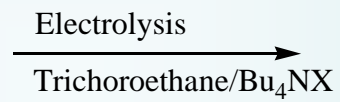
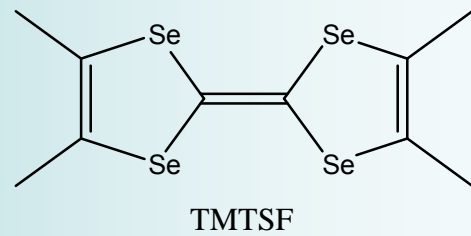
ELECTRON PAIRS are conducted along the spine of a hypothetical superconducting molecule by an attractive mechanism similar to that in a superconducting metal. As an electron passes each side chain its electric field polarizes the side-chain molecule and induces a positive charge at the end nearer the spine. A second electron is attracted to this region of positive charge and is thereby indirectly attracted to the first electron.





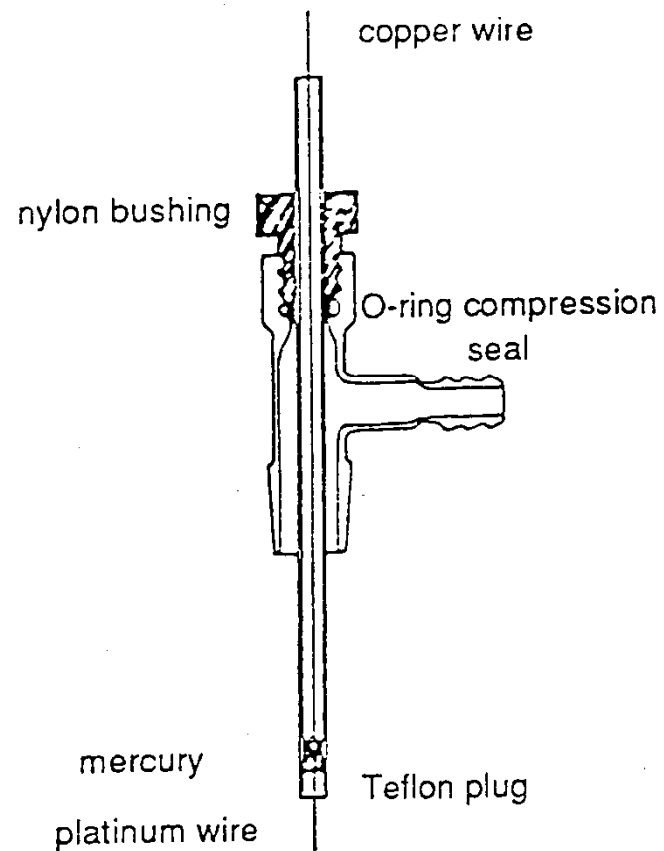
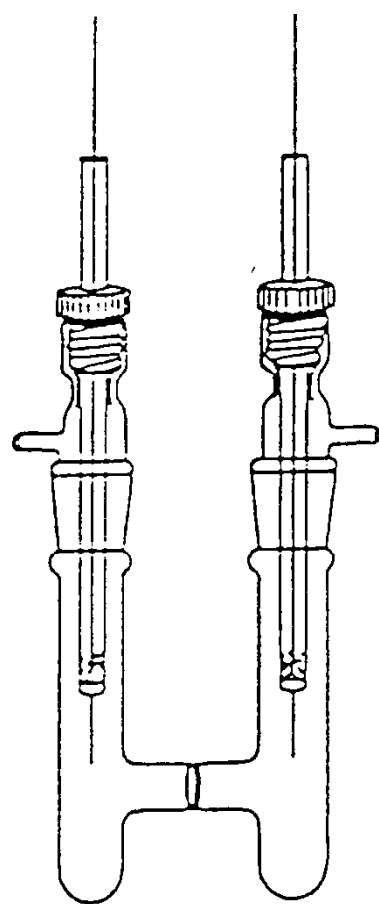
**HYPOTHETICAL SUPERCONDUCTING MOLECULE** is built around a “spine” of carbon atoms connected by alternating single and double bonds. Periodically along the spine a side chain consisting of the common dye diethyl-cyanine iodide extends outward. These side-chain molecules are highly polarizable; that is, an electron can move freely from a nitrogen site close to one end of the molecule to another nitrogen site close to the other end. A colored *N* designates the nitrogen atom that contains the resonating electron in the two possible conditions of polarization. Electrons can also move freely along the spine itself.

# The First Organic Superconductors



$\text{TMTSF}_2\text{X}$   
Bechgaard Salts

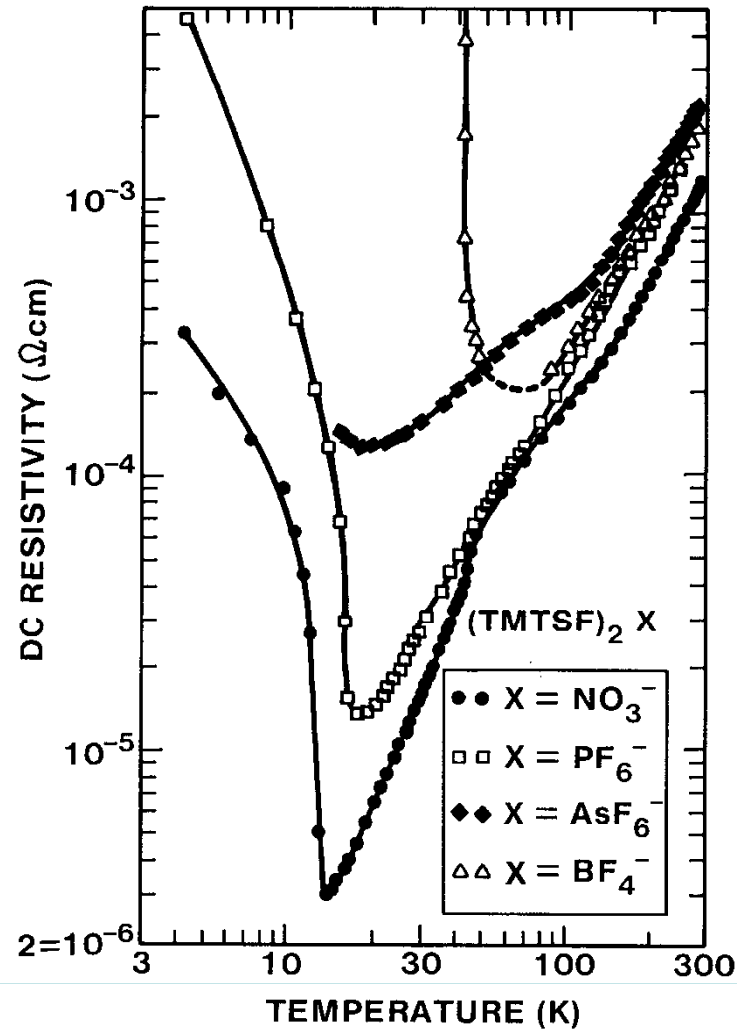
# Electrochemical Synthesis Apparatus



# Actual Electrosynthesis



D.C. RESISTIVITY vs TEMPERATURE FOR TYPICAL SAMPLES OF  $(\text{TMTSF})_2\text{X}$ . NOTE THE LOGARITHMIC TEMPERATURE AND RESISTIVITY SCALES.



From Bechgaard, K and Jerome, D., *Scientific American*, 1984(?)

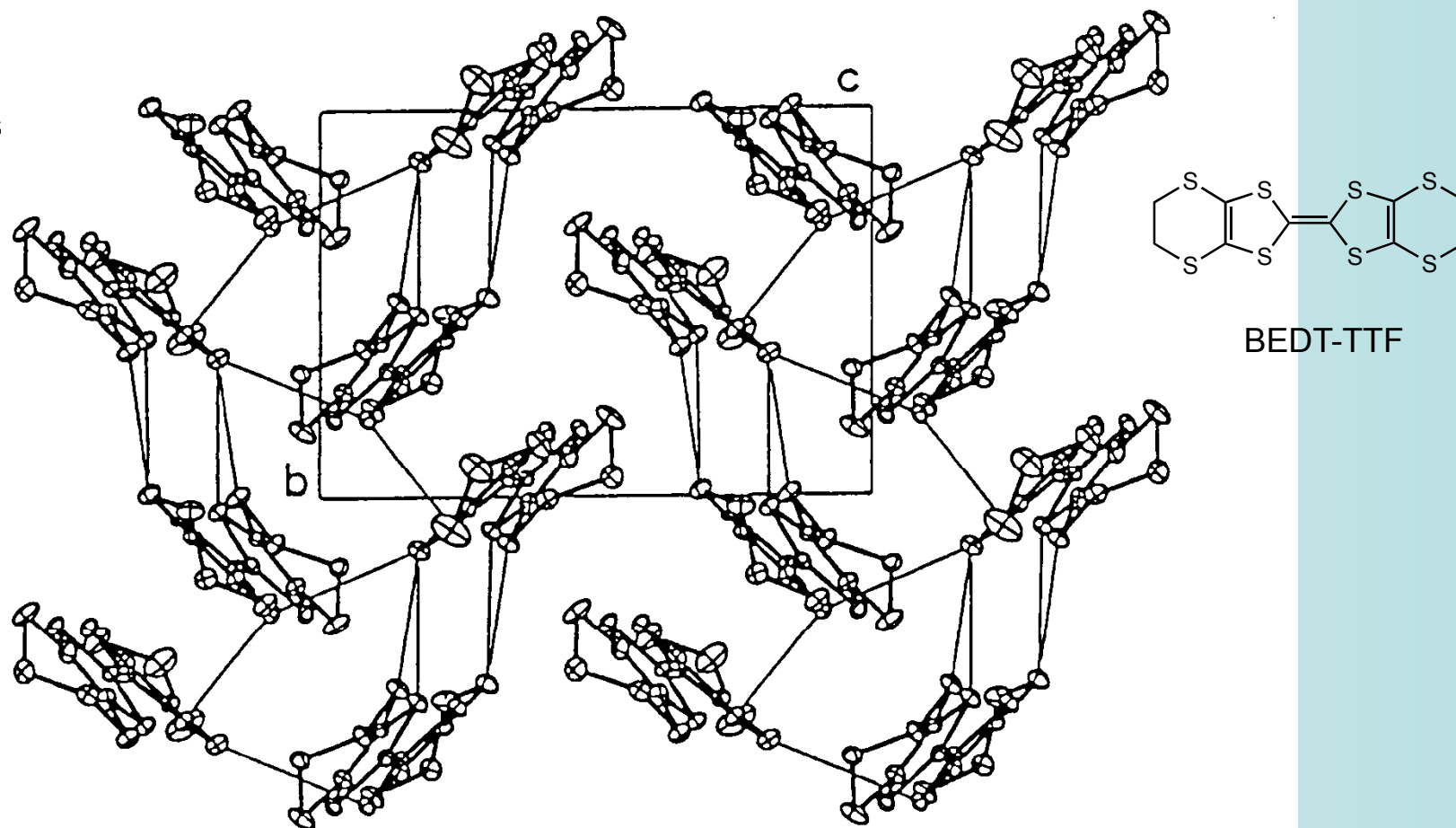
# Summary of Requirements for Organic Metals and Superconductors

Planar  $\pi$ -donors and/or acceptors

Segregated **stacks** of  $\pi$ -donors and/or acceptors

Partial charging of **stacks** of  $\pi$ -donors and/or acceptors

# The End of the Stack Tyranny: the Kappa Phase



**Figure 2.7** Structure of  $\kappa$ -(BEDT-TTF)<sub>2</sub>[Cu(NCS)<sub>2</sub>] at 118 K. S...S contacts shorter than 3.6 Å are indicated by thin lines. (From Ref. 43.)

# A Polymeric Anionic Layer

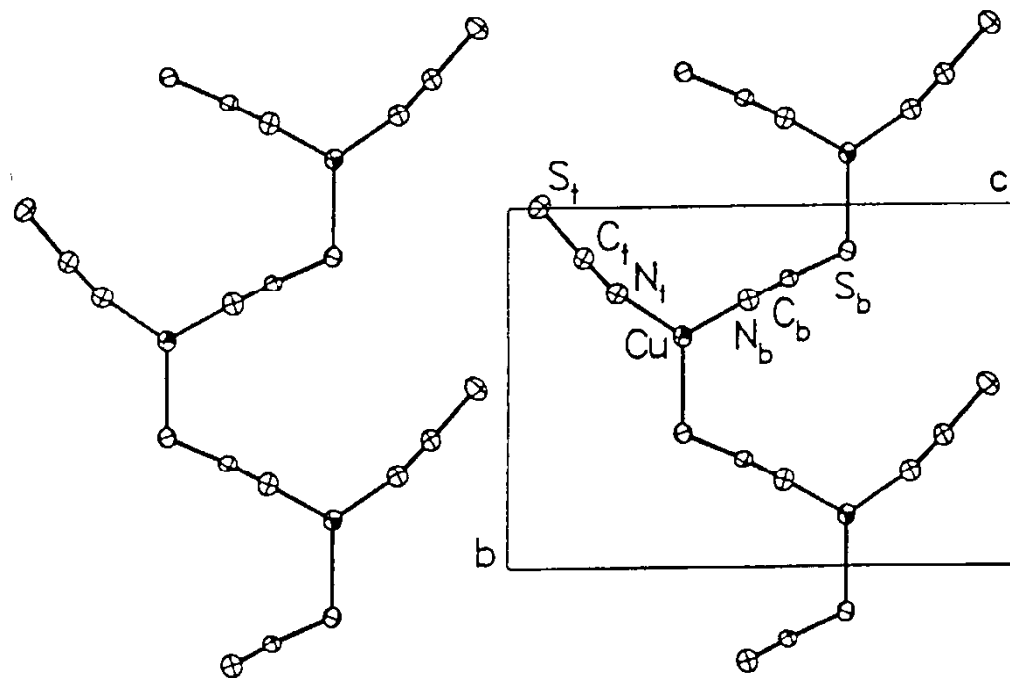


Figure 2.8 Polymeric  $[\text{Cu}(\text{NCS})_2]^-$  anion in  $\kappa\text{-(BEDT-TTF)}_2^+[\text{Cu}(\text{NCS})_2]^-$ . (From Ref. 43.)



## Other Organic Superconductors and Materials

### **Buckminsterfullerene-Derived Solids**

BEDT-TTF, etc superconductivity WITH magnetism

Molecular ferri- and ferromagnetism

# Take Home Messages from this Lesson

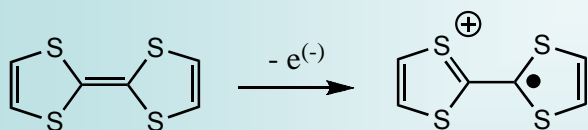
2.

Need charge AND unpaired Spin to observe high conductivity

# Summary

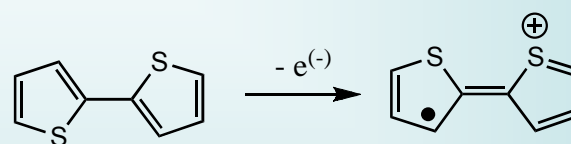
Organic materials based on molecular solids, while showing conductivities as high as those of some traditional metals, also exhibit other very unusual properties.

The lessons learned from organic metals apply directly to conducting polymers



C-T from TTF

VS



*p*-Doping of PT

*The End*

Thanks!