Propriétés Structurales et Electroniques dans les Conducteurs Organiques

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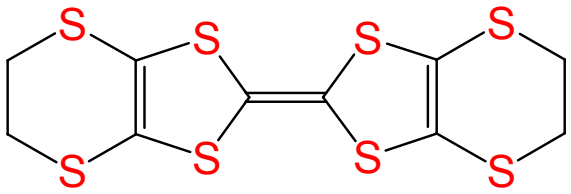
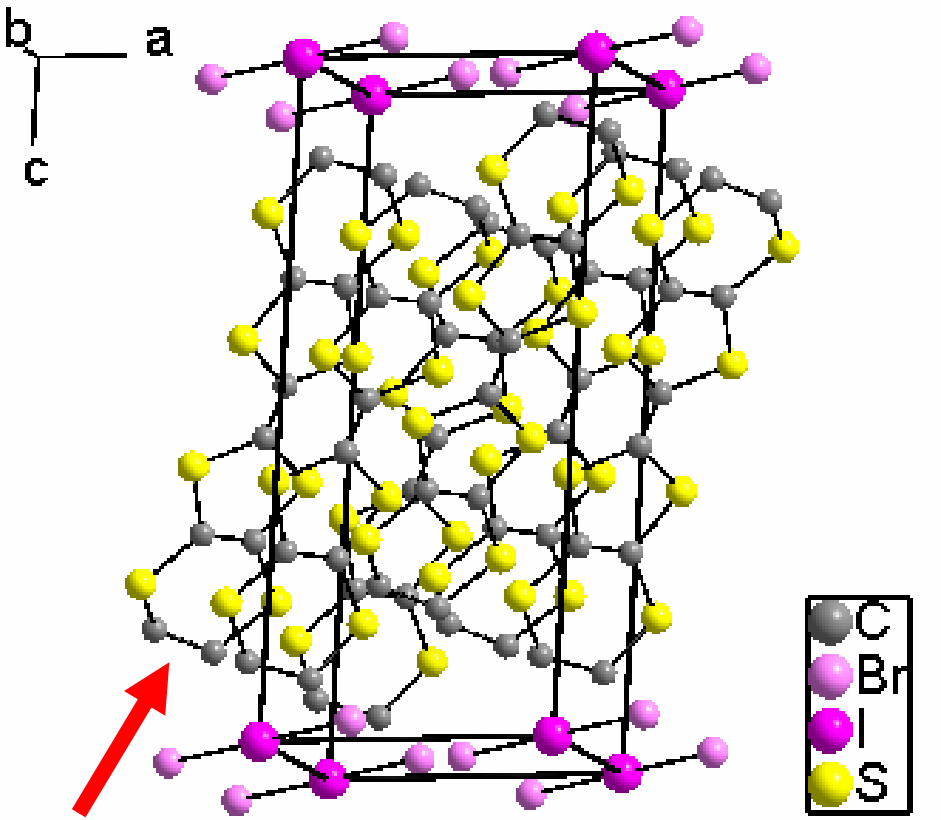
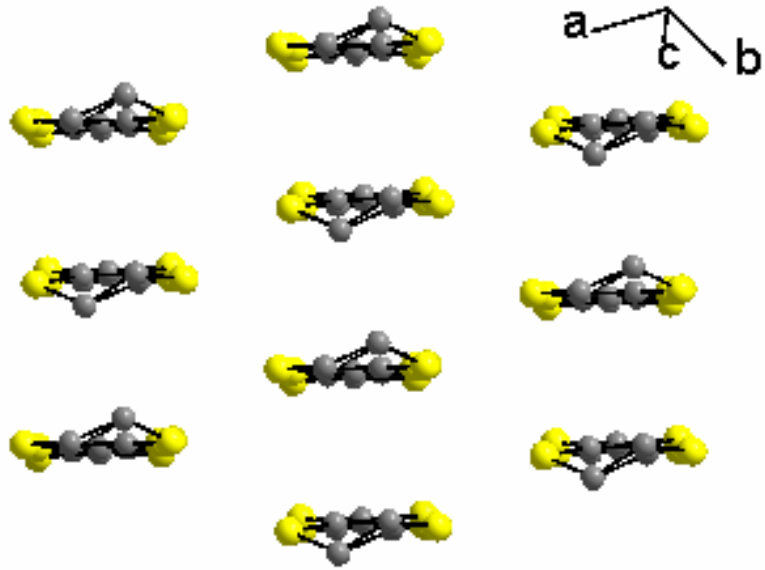
2D STRUCTURES OF BEDT-TTF SALTS



BEDT-TTF

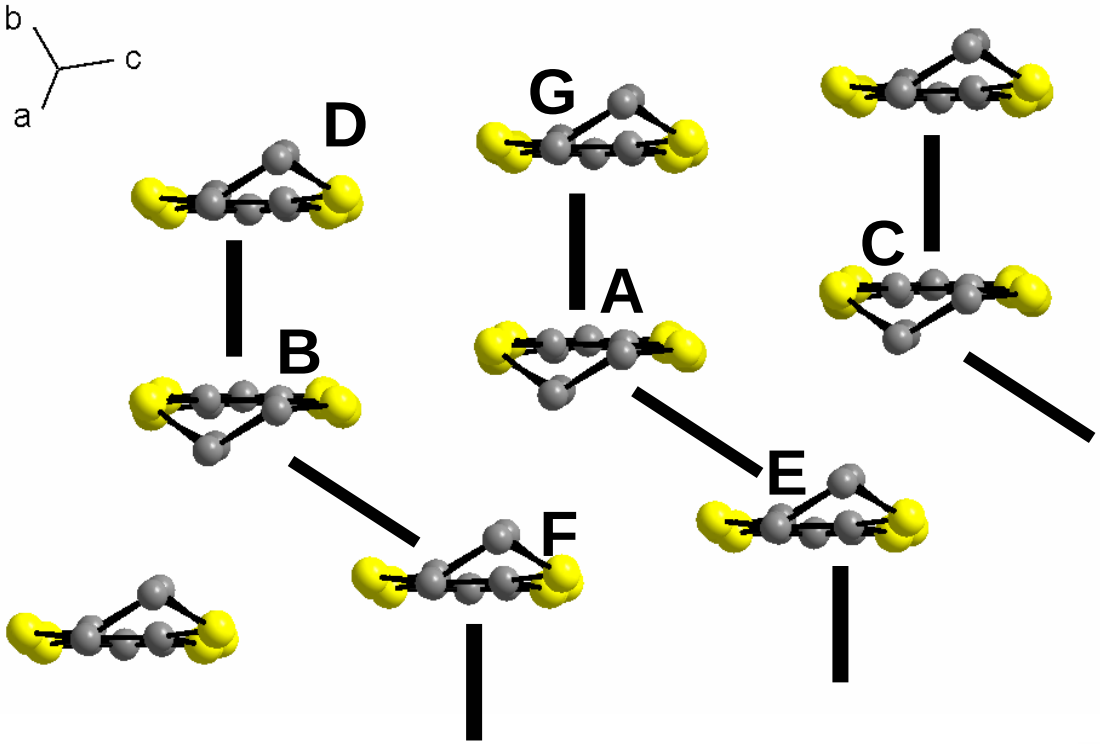




Layered structures

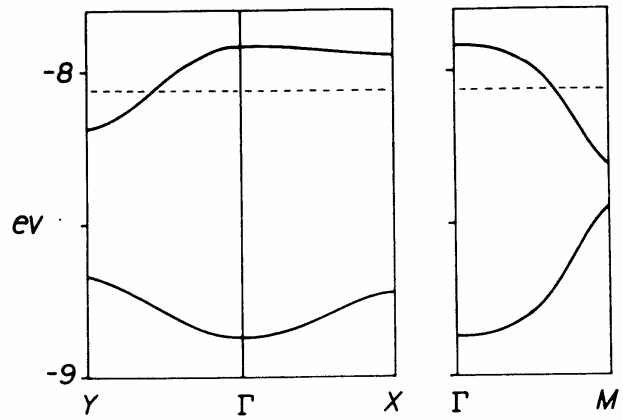
α, β, κ, λ, θ phases

1D or 2D ? β-(BEDT-TTF)$_2$(ICl$_2$)

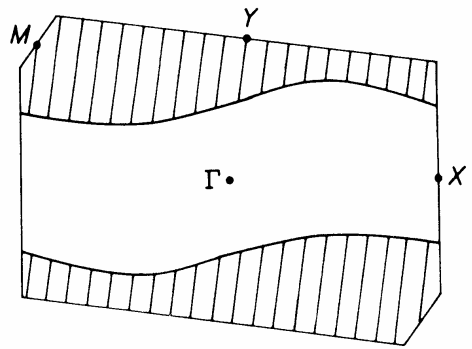


2 molecules per unit cell :
2 bands

2 donor molecules for 1 anion :
$\frac{3}{4}$ filled system

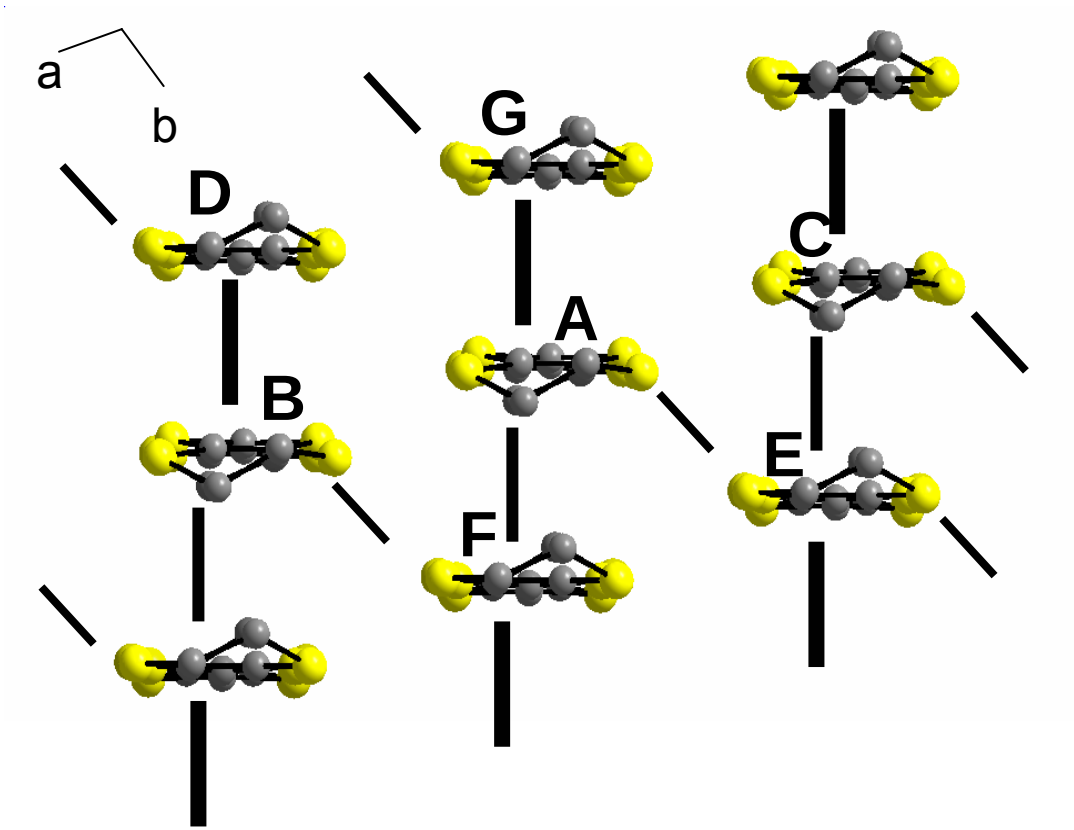


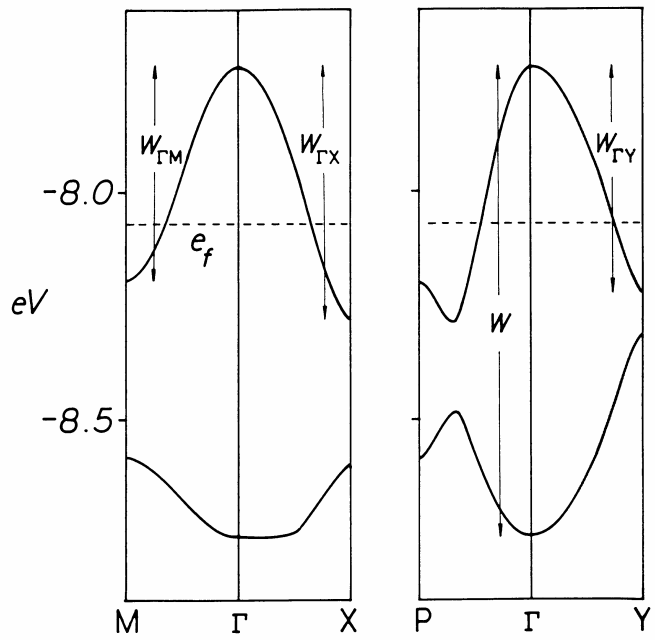
Pairs A-G interacting along b :

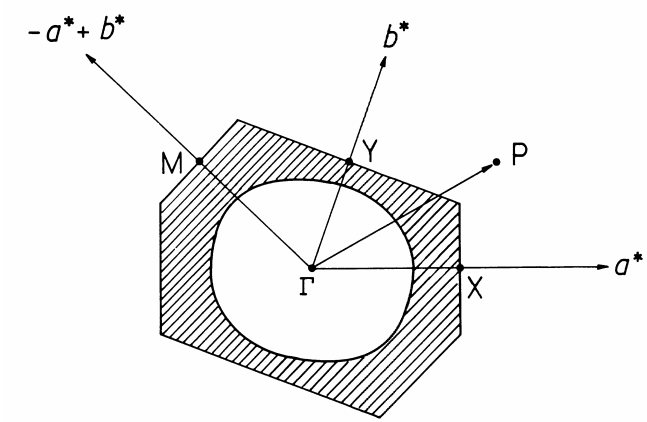


1D structure and open Fermi surface :
Metal-insulator transition

β-(BEDT-TTF)$_2$(IBr$_2$)







A-G pairs interacting along *a*+*b* and along *b*

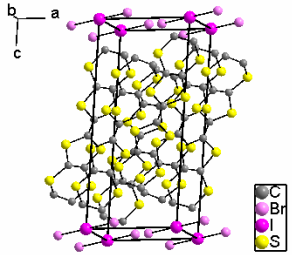
2D electronic structure with closed Fermi surface

Superconducting transition at 3 K

R. P. Shibaeva, E. B. Yagubskii, *Chem. Rev.* **2004**, *104*, 5347 and refs therein

RECURRENT TRENDS vs. EVOLUTIONS

Organic/inorganic segregation



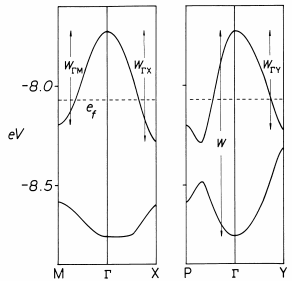
→ Control of the interface : Hydrogen / halogen bonding

Mixed valence systems ($\rho = \frac{1}{2}$)

$(BEDT\text{-}TTF)_2(IBr_2)$

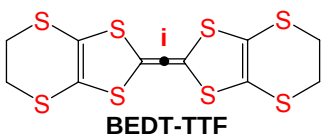
→ Non stoichiometric systems : Polymeric anions

Dimerized chains
$\frac{1}{2}$-filled systems



→ Non-dimerized chains
$\frac{1}{4}$-filled systems

Symmetric molecules
Centro-symmetric crystals



→ Non-symmetric molecules
Chiral molecules and salts

RECURRENT TRENDS vs. EVOLUTIONS

Organic/inorganic segregation	→	**Control of the interface : Hydrogen / halogen bonding**
Mixed valence systems ($\rho = \frac{1}{2}$)		Non stoichiometric systems : Polymeric anions
Dimerized chains $\frac{1}{2}$-filled systems		Non-dimerized chains $\frac{1}{4}$-filled systems
Symmetric molecules Centro-symmetric crystals		Non-symmetric molecules Chiral molecules and salts

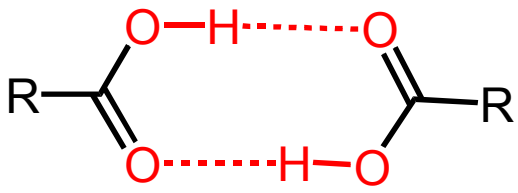
CONTROL OF THE SOLID STATE STRUCTURES

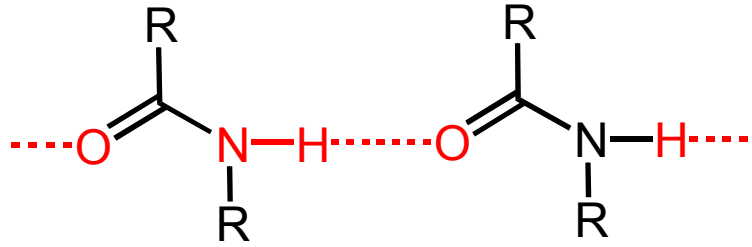
Hydrogen bonding

Electrostatic, attractive, directional interaction

Hydrogen bond motifs

Cooperativity

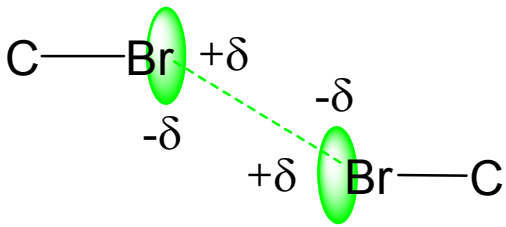


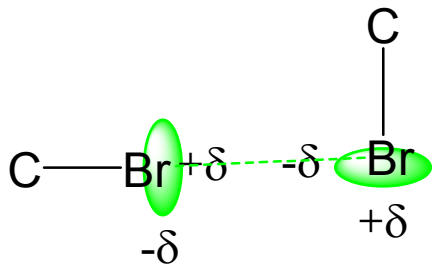


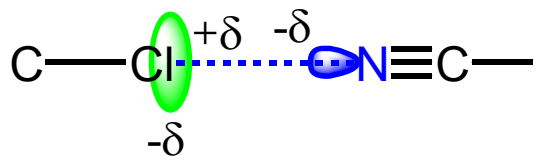
Halogen bonding:

X···X distances shorter than the van der Waals radii

Anisotropic electron density (polar flattening)

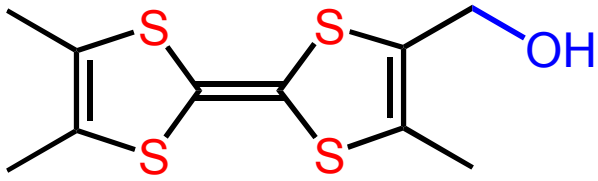






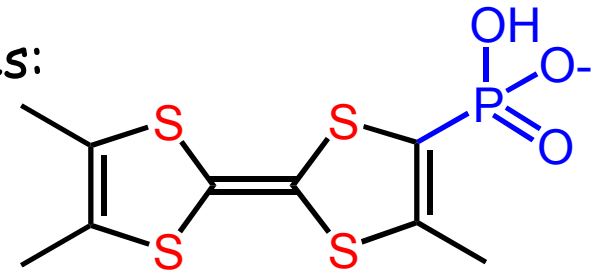
TTF's FOR HYDROGEN BONDING

Alcohols



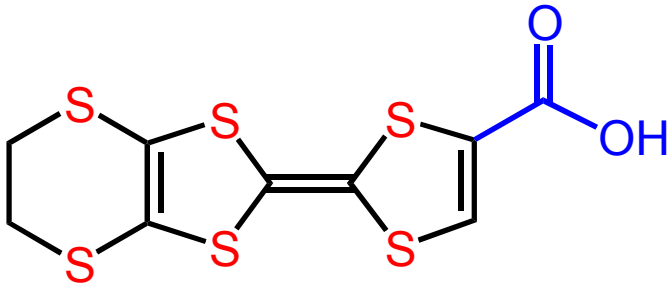
$Me_3TTF\text{-}CH_2OH$

Phosphonates:



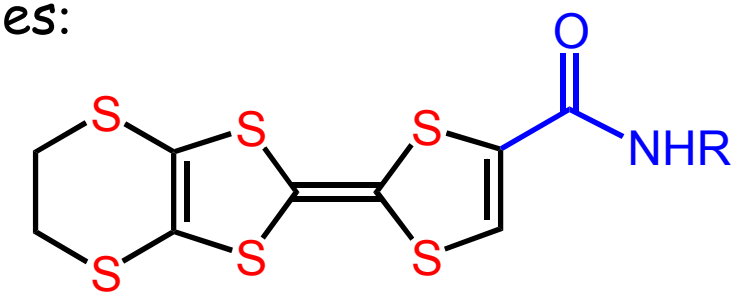
$Me_3TTF\text{-}PO_3H^-$

Acids:



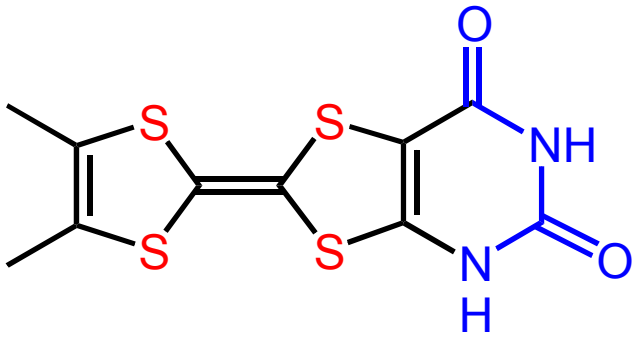
EDT-TTF-CO_2H

Amides:

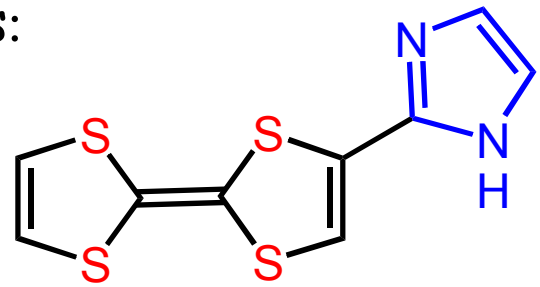


EDT-TTF-CONHR

Uracils:



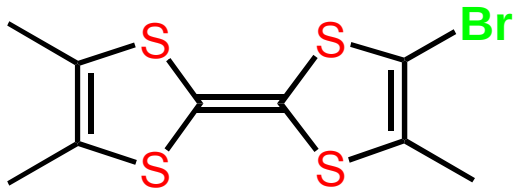
Imidazoles:



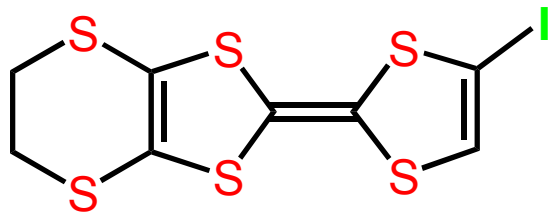
M. Fourmigué, P. Batail, *Chem. Rev.* **2004**, *104*, 5379.

TTF's FOR HALOGEN BONDING

Monohalogenated

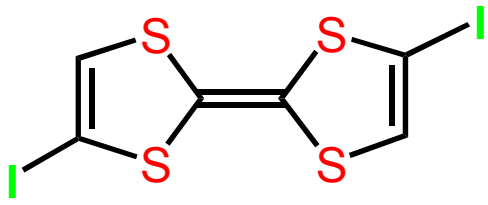


$Me_3TTF\text{-}Br$

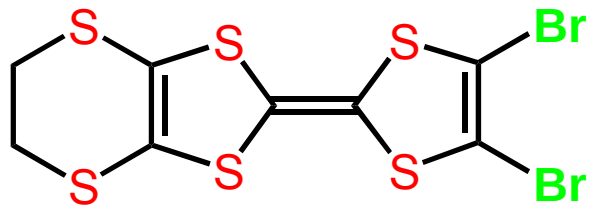


EDT-TTF-I

Di-halogenated:

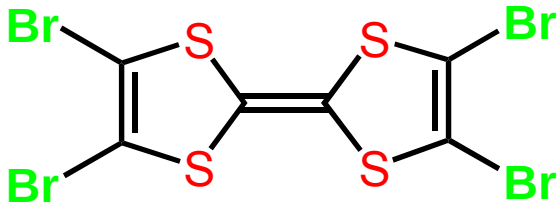


cis-trans-$TTF\text{-}I_2$

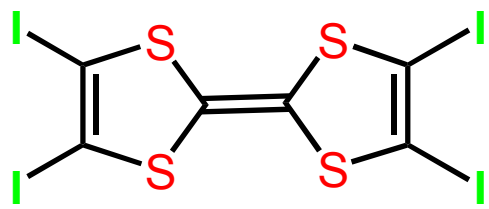


EDT-TTF-Br_2

Tetra-halogenated:



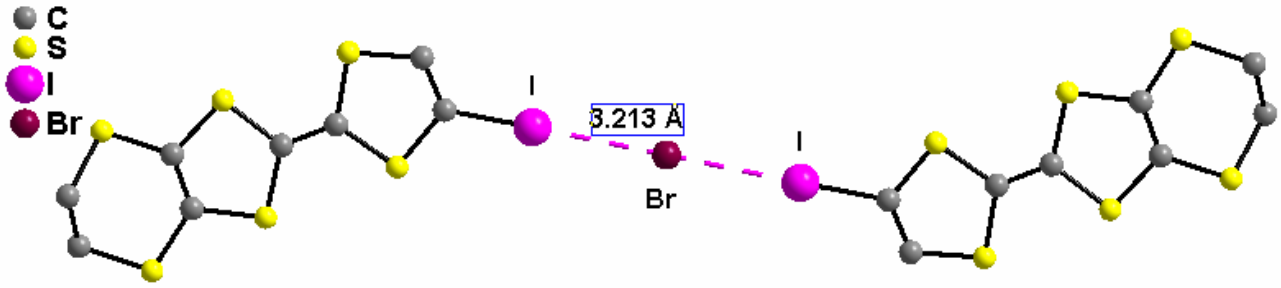
$TTF\text{-}Br_4$



$TTF\text{-}I_4$

M. Fourmigué, P. Batail, *Chem. Rev.* **2004**, *104*, 5379.

ACTIVATION OF HALOGEN BONDING

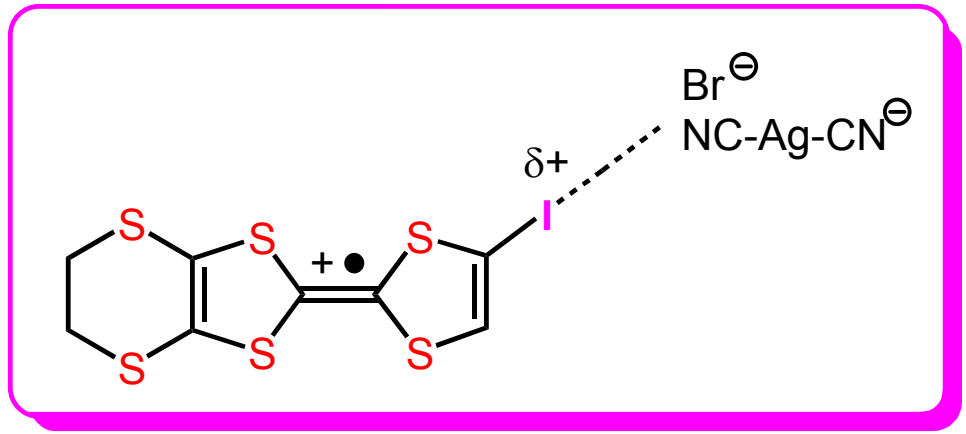


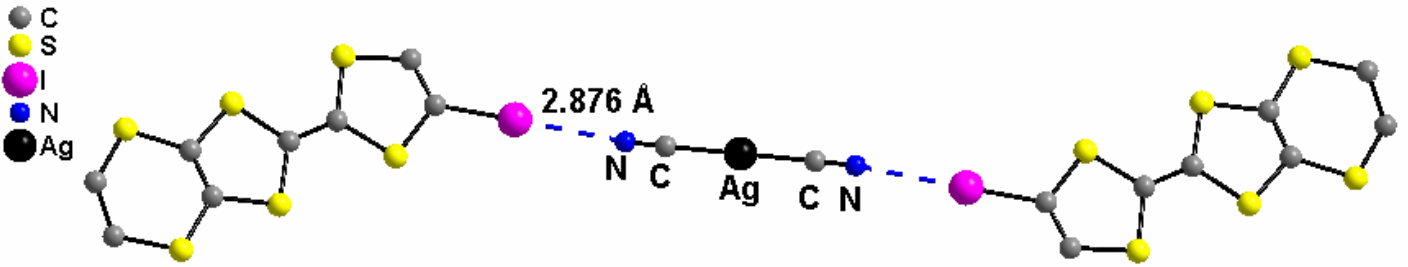
I ••• Br

Σr_{vdW} = 3.85 Å, exp: 3.21 Å

I ••• N(≡C)

Σr_{vdW} = 3.55 Å, exp: 2.88 Å





T. Imakubo, H. Sawa, R. Kato, *Synth. Metals* **1995**, *73*, 117.

ACTIVATION OF HALOGEN BONDING

$(EDO\text{-}TTF\text{-}I_2)_2[Ni(mnt)_2]$:

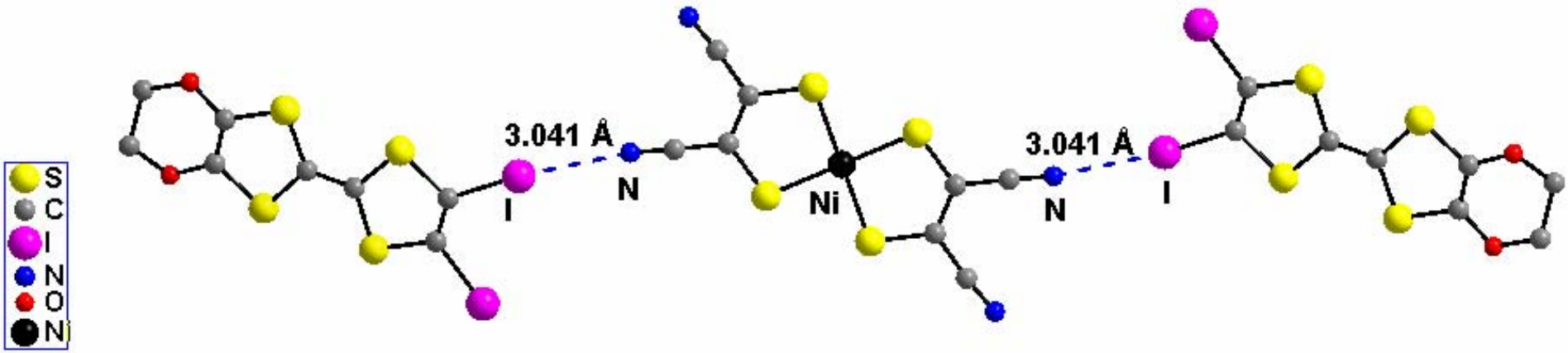
I ••• N(≡C)

Σr_{vdW} = 3.55 Å, exp: 3.041 Å

Mixed-valence metallic salt

Segregated stacks of EDO-TTF-I_2 and $Ni(mnt)_2$

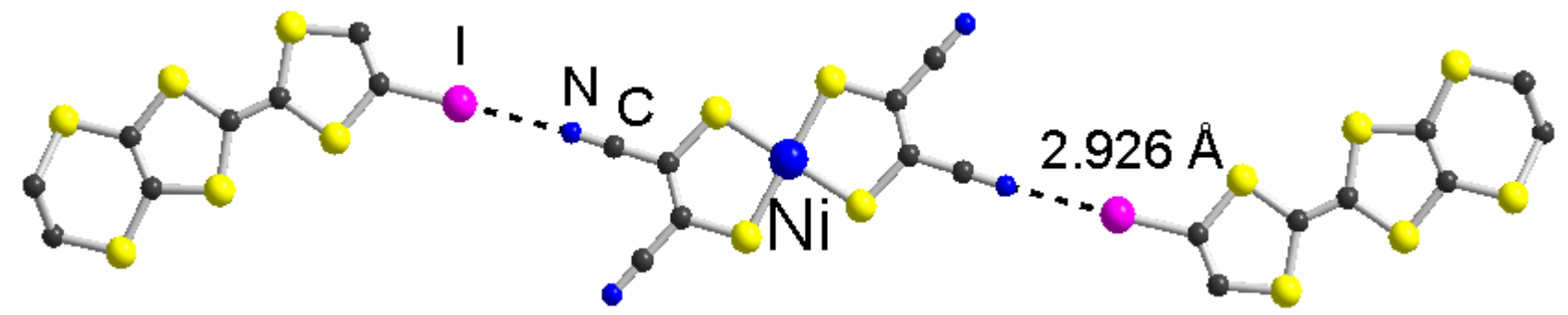
Conducting EDO-TTF-I_2 stacks halogen-bonded to 1D ferromagnetic $Ni(mnt)_2$ chains



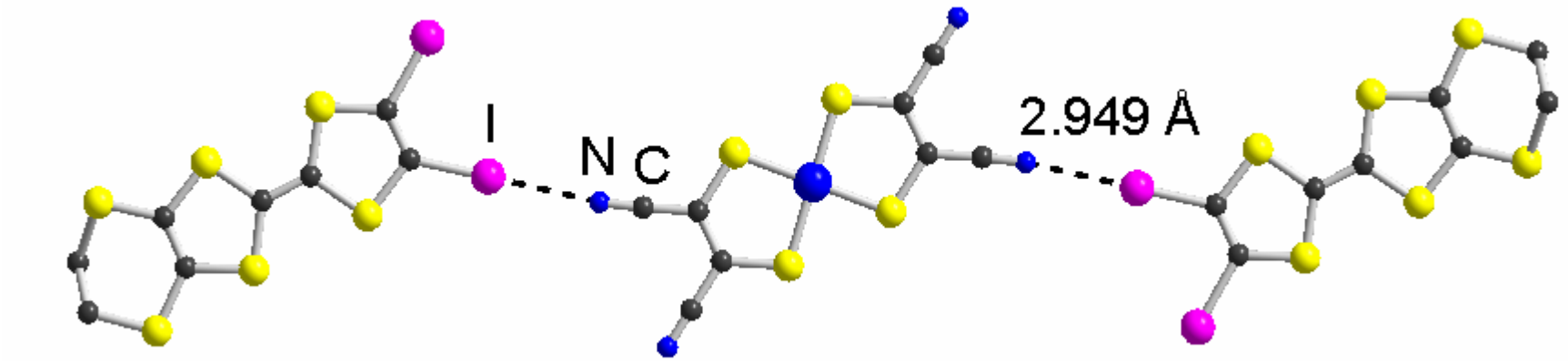
J. Nishijo, E. Ogura, J. Yamaura, A. Miyazaki, T. Enoki, T. Takano, Y. Kuwatani, M. Iyoda, *Solid State Commun.* **2000**, *116*, 661.

ACTIVATION OF HALOGEN BONDING

$(EDT\text{-}TTF\text{-}I)_2[Ni(mnt)_2]$: I ••• N(≡C): 2.926 Å ($\Sigma r_{vdW}$ = 3.55 Å)



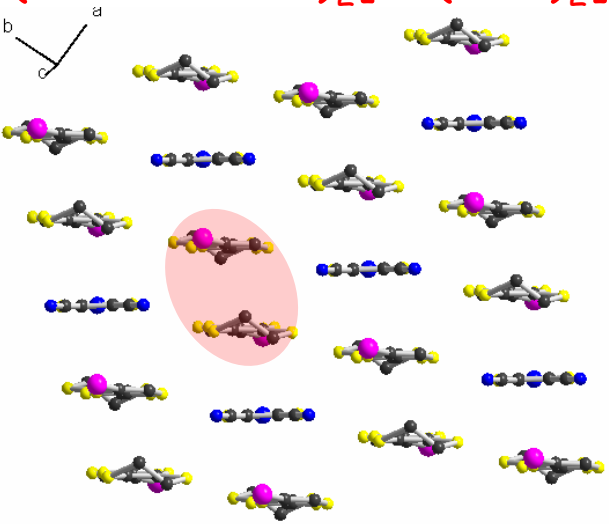
$(EDT\text{-}TTF\text{-}I_2)_2[Ni(mnt)_2]$: I ••• N(≡C) 2.949Å ($\Sigma r_{vdW}$ = 3.55 Å)



T. Devic, B. Domercq, P. Auban, P. Molinié, M. Fourmigué *Eur. J. Inorg. Chem.* **2002**, 2844

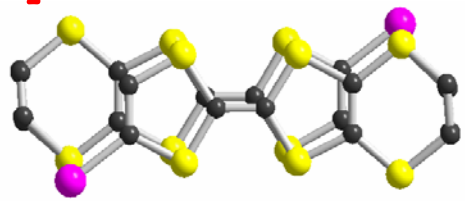
ACTIVATION OF HALOGEN BONDING

$(EDT\text{-}TTF\text{-}I)_2[Ni(mnt)_2]$:



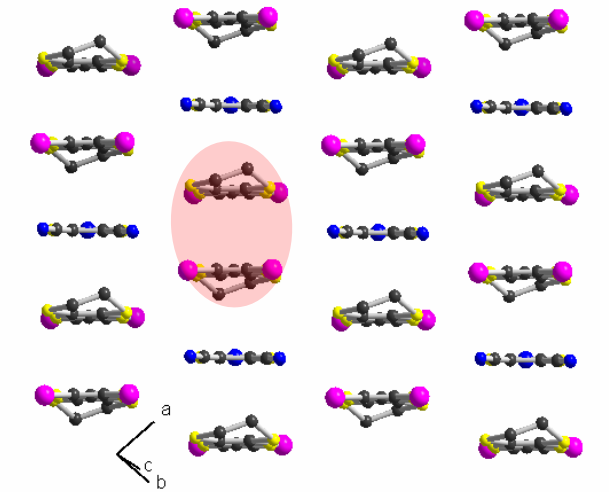
- Eclipsed overlap of $(EDT\text{-}TTF\text{-}I)^+$, $\rho = 1$

$(EDT\text{-}TTF\text{-}I^+)_2[Ni(mnt)_2^{2-}]$:



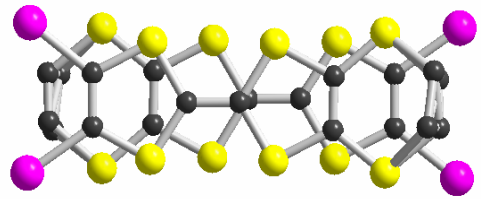
Diamagnetic Insulator

$(EDT\text{-}TTF\text{-}I_2)_2[Ni(mnt)_2]$:



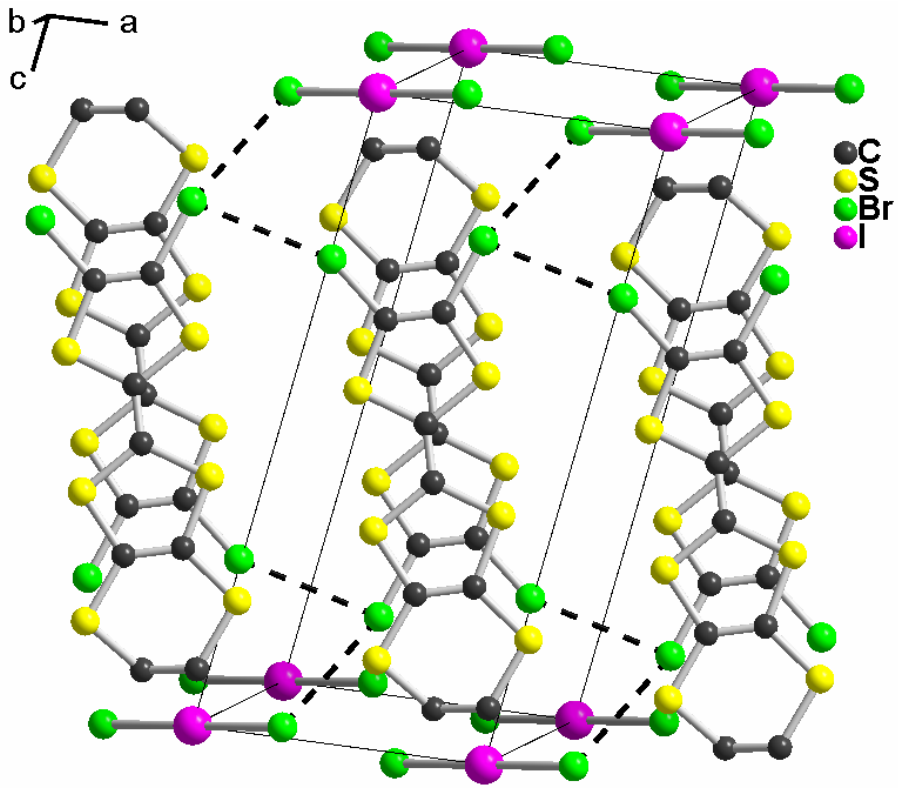
- Slipped overlap of $(EDT\text{-}TTF\text{-}I_2)^{0.5+}$, $\rho = 0.5$

$(EDT\text{-}TTF\text{-}I_2)_2^+[Ni(mnt)_2^{1-}]$:



Curie law for two S=1/2 spins

Br···Br INTERACTIONS IN $(EDT\text{-}TTFBr_2)_2(IBr_2)$



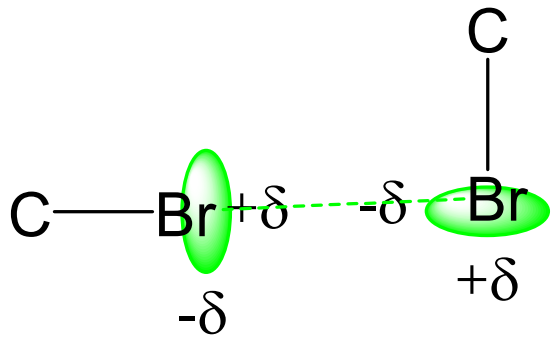
Short Br···Br distances (vdW: 3.7 Å)

- Donor ··· donor: 3.456(1) Å

θ_1 = 96.7(1)°, θ_2 = 152.0(1)

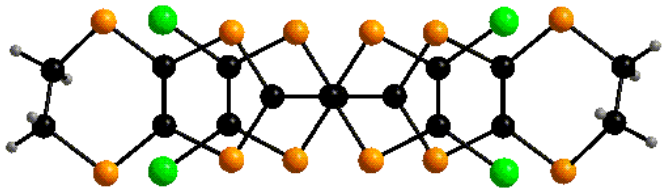
- Donor···anion: 3.422(1) Å

θ_1 = 109.37(3), θ_2 = 164.6(1)



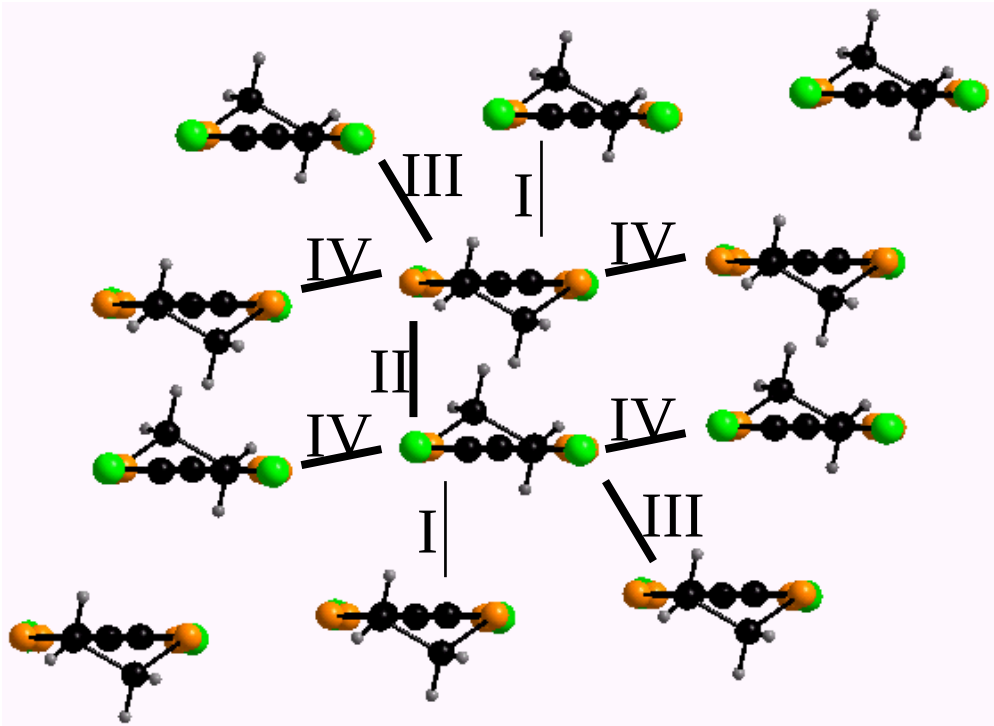
Br···Br INTERACTIONS IN $(EDT\text{-}TTFBr_2)_2(IBr_2)$

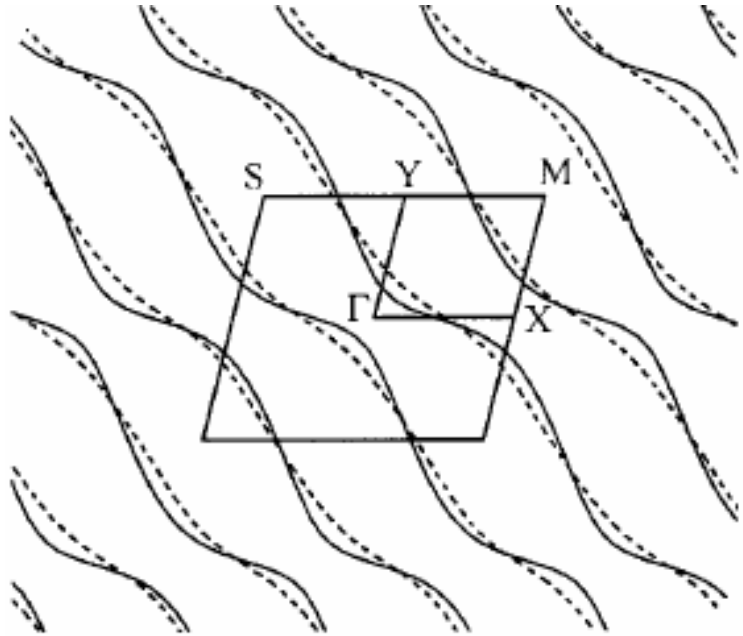
Intra-dimer interaction (β_{II}):



β_I = 0.04 eV
β_{II} = 0.44 eV
β_{III} = 0.26 eV
β_{IV} = 0.12 eV

Semi-conducting behavior with σ_{RT} = 1 S cm^{-1}

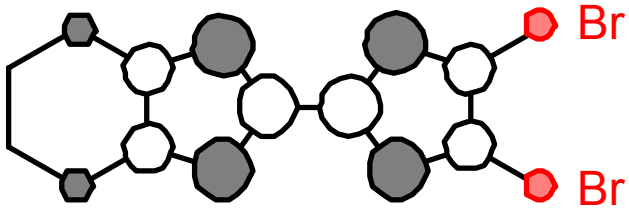


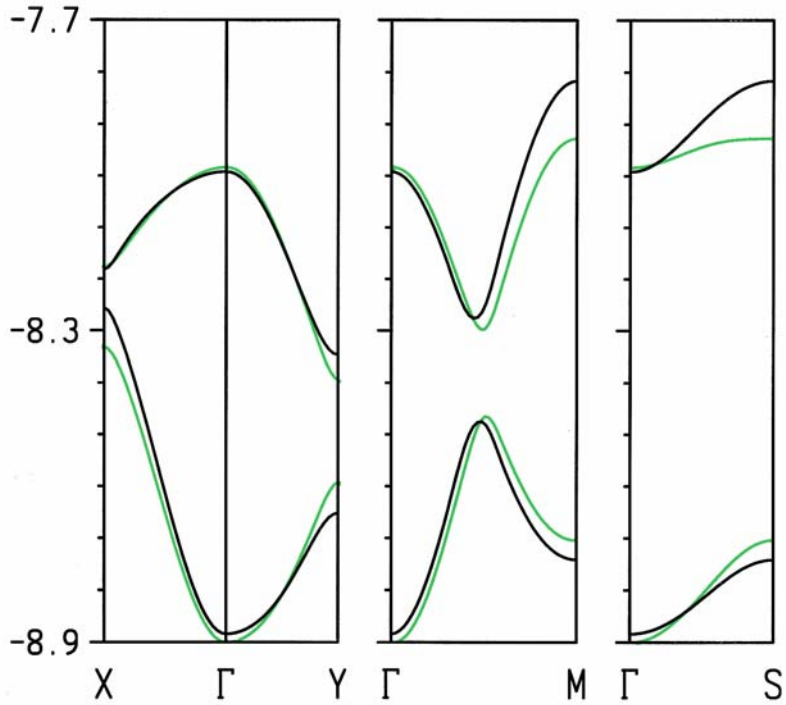


Fermi surface for:
$(EDT\text{-}TTFBr_2)_2(IBr)_2$ (full line) and
$(EDT\text{-}TTFI_2)_2I_3$ (dotted line)

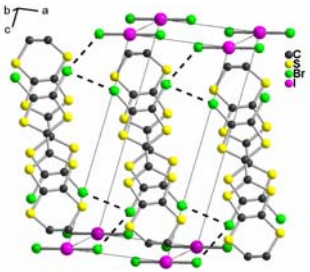
Br···Br INTERACTIONS IN $(EDT\text{-}TTFBr_2)_2(IBr_2)$

Br atoms take part in the HOMO:





Two-fold role of the Br atoms:



- Short Br···Br contacts
- Participation in the HOMO and to the band dispersion

In green:
band dispersion with H

B. Domercq, T. Devic, M. Fourmigué, P. Auban, E. Canadell, *J. Mater. Chem.* **2001**, *11*, 1570

CONCLUSIONS ON INTERFACE CONTROL

- Hydrogen- or halogen bonding interactions coexist with delocalized band structures for metallic conductivity

- Hydrogen- or halogen bonding interactions are enhanced in such salts because of their (in part) electrostatic nature

- Halogen atoms contribute to the band dispersion

RECURRENT TRENDS vs. EVOLUTIONS

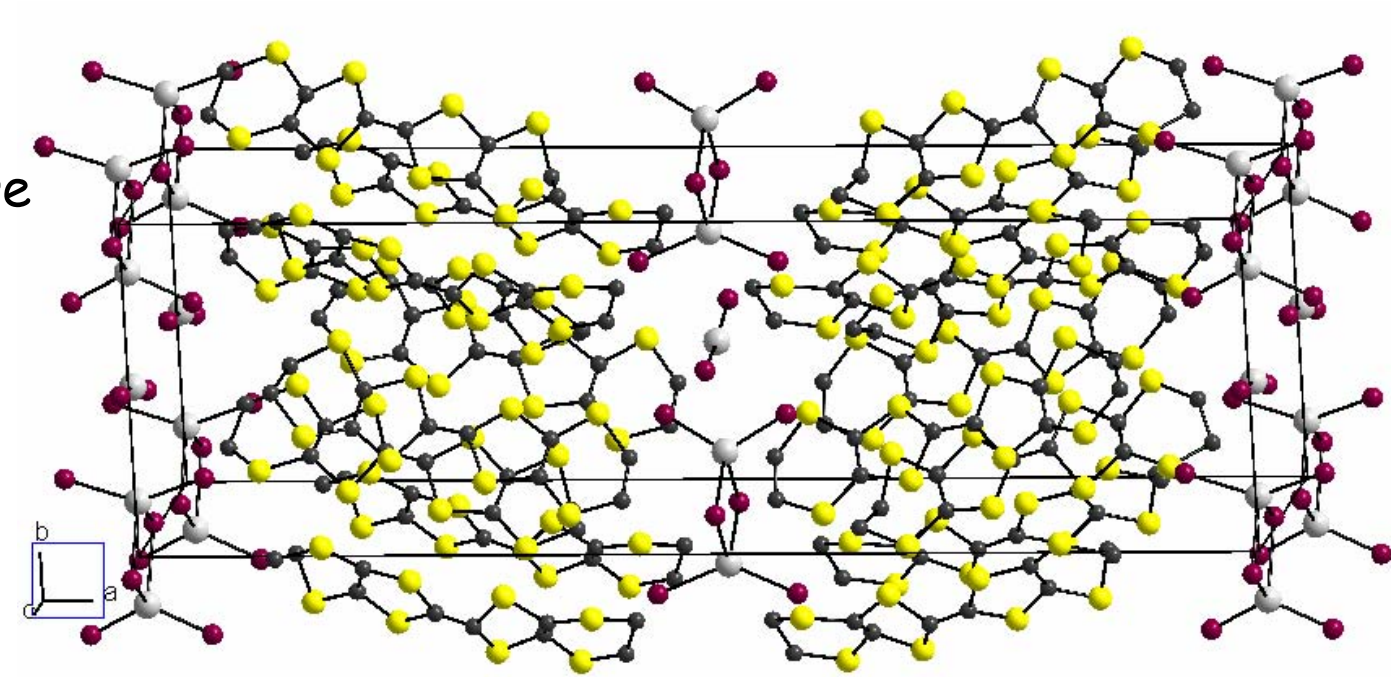
Organic/inorganic segregation		Control of the interface : Hydrogen / halogen bonding
Mixed valence systems ($\rho = \frac{1}{2}$)	→	**Non stoichiometric systems : Polymeric anions**
Dimerized chains $\frac{1}{2}$-filled systems		Non-dimerized chains $\frac{1}{4}$-filled systems
Symmetric molecules Centro-symmetric crystals		Non-symmetric molecules Chiral molecules and salts

NON-STOICHIOMETRY

- High Tc superconductors are doped Mott insulators
- Can we dope molecular systems ?

Unusual band filling could be the answer
Cf: T. Mori, *Chem. Rev.* **2004**, *104*, 4947.

κ-$[ET]_4[Hg_{3-\delta}Br_8]$,
($\delta \approx 0.11$)
is a ambient-pressure superconductor with a donor charge equal to $0.5 + \delta/2$



O. A. Dyachenko,
V. V. Gritsenko, G. V. Shilov, R. N. Lyubovskaya, R. B. Lyubovskii, *Synth. Met.* **1994**, *62*, 193

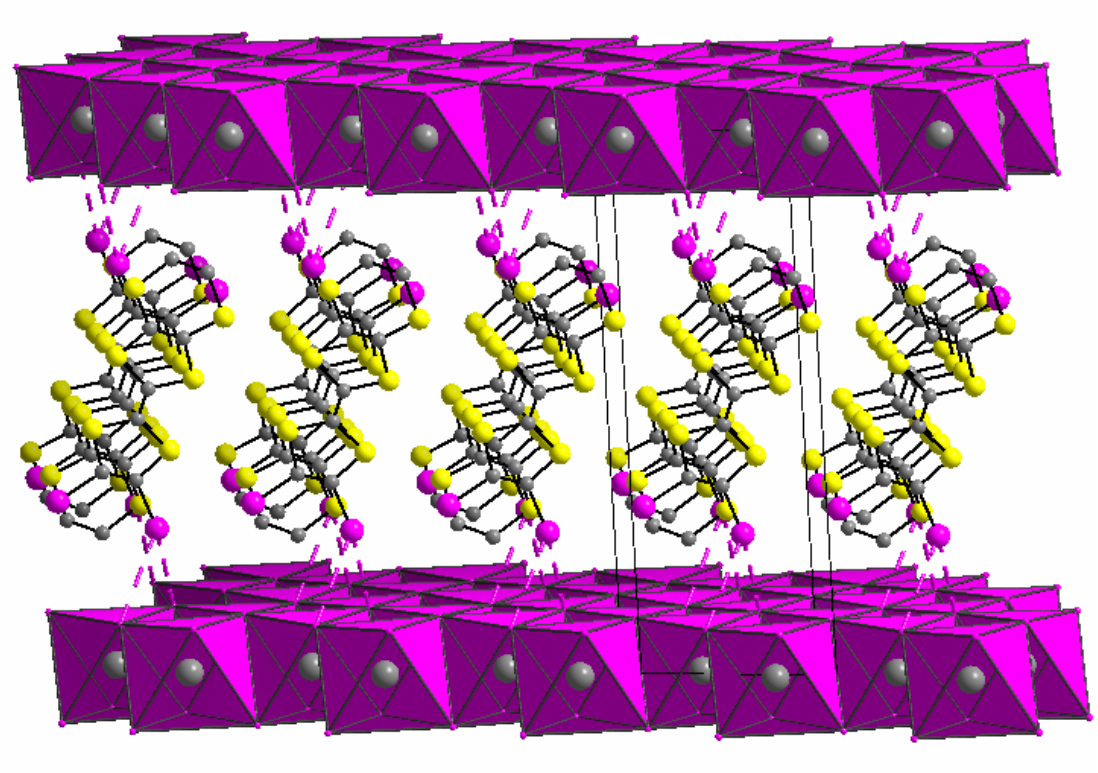
POLYMERIC IODOPLUMBATES

$(EDT\text{-}TTF\text{-}I_2)_2[Pb_{5/2}I_6]$:

I_{donor}••• I_{anion} 3.81, 4.09 Å
(van der Waals gap:
4.95 Å in PbI_2)

Polyanion with PbI_2 structure

Pb vacancies $[Pb_{5/2}\ \square_{1/2}\ I_6]^{-1}$
to give $\rho = 0.5$



T. Devic, M. Evain, Y. Moelo, E. Canadell, P. Auban-Senzier, M. Fourmigué, P. Batail, *J. Am. Chem. Soc.* **2003**, *125*, 3295.

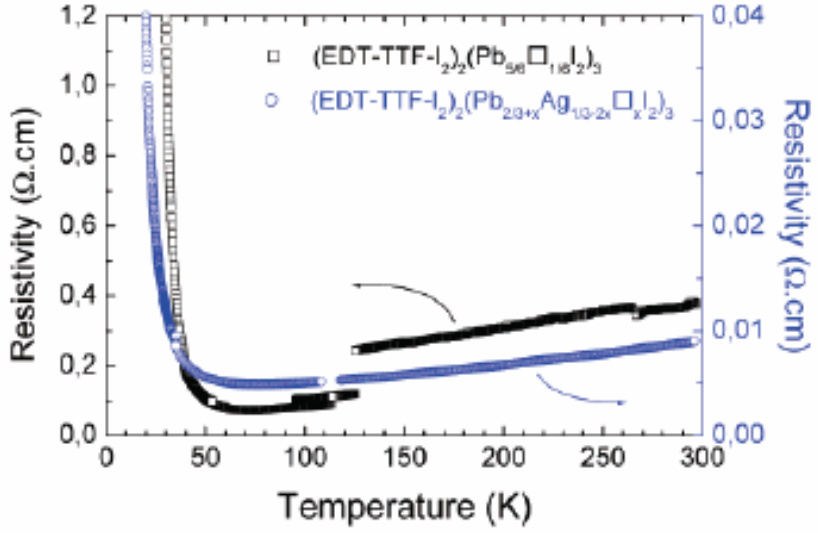
POLYMERIC IODOPLUMBATES

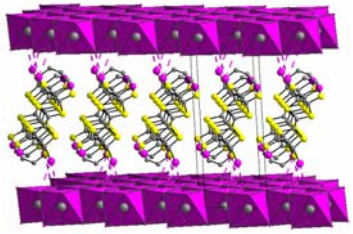
$(EDT\text{-}TTF\text{-}I_2)_2[Pb_{5/2}I_6]$:

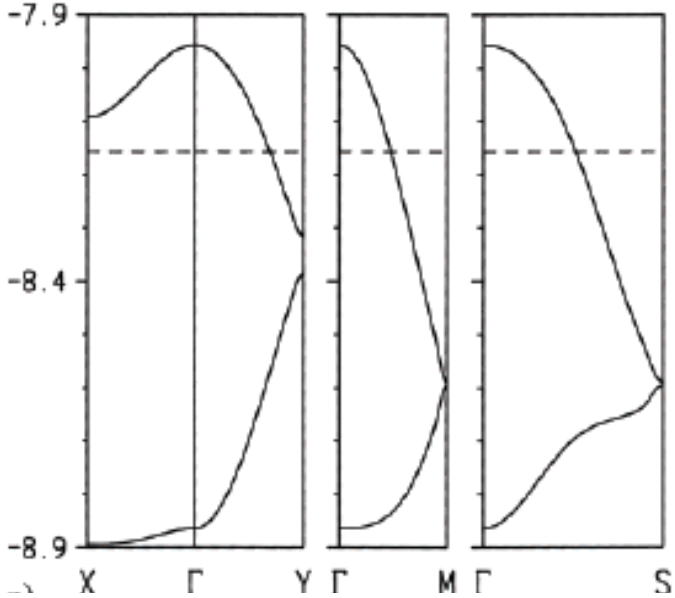
a mixed-valence metallic salt with weak dimerisation

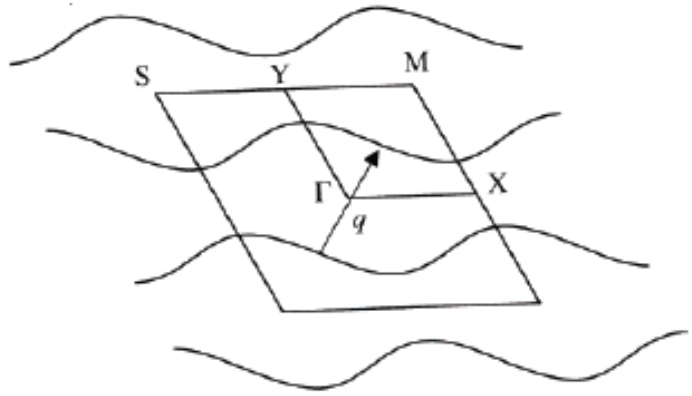
σ_{RT} = 2.5 S cm^{-1}

with T_{MI} = 70 K associated with CDW



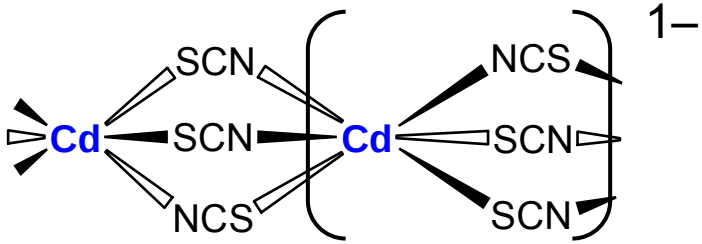


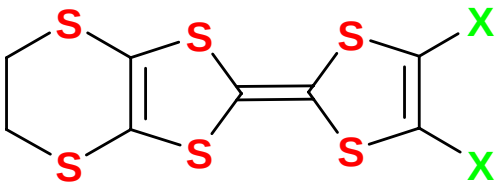




POLYMERIC ANIONS

- Cadmium thiocyanates form 1D infinite anionic chains in a variety of salts





X = Br **EDT-TTFBr_2**
X = I **EDT-TTFI_2**

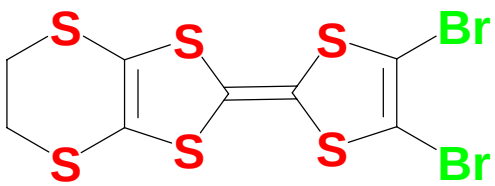
Two salts with either CH_3CN or TCE inclusion

- $[EDT\text{-}TTF\text{-}I_2]_4[Cd_3(NCS)_8]\cdot CH_3CN\cdot H_2O$ $\rho = 0.5$ $\sigma_{RT} = 0.67$ S cm^{-1}

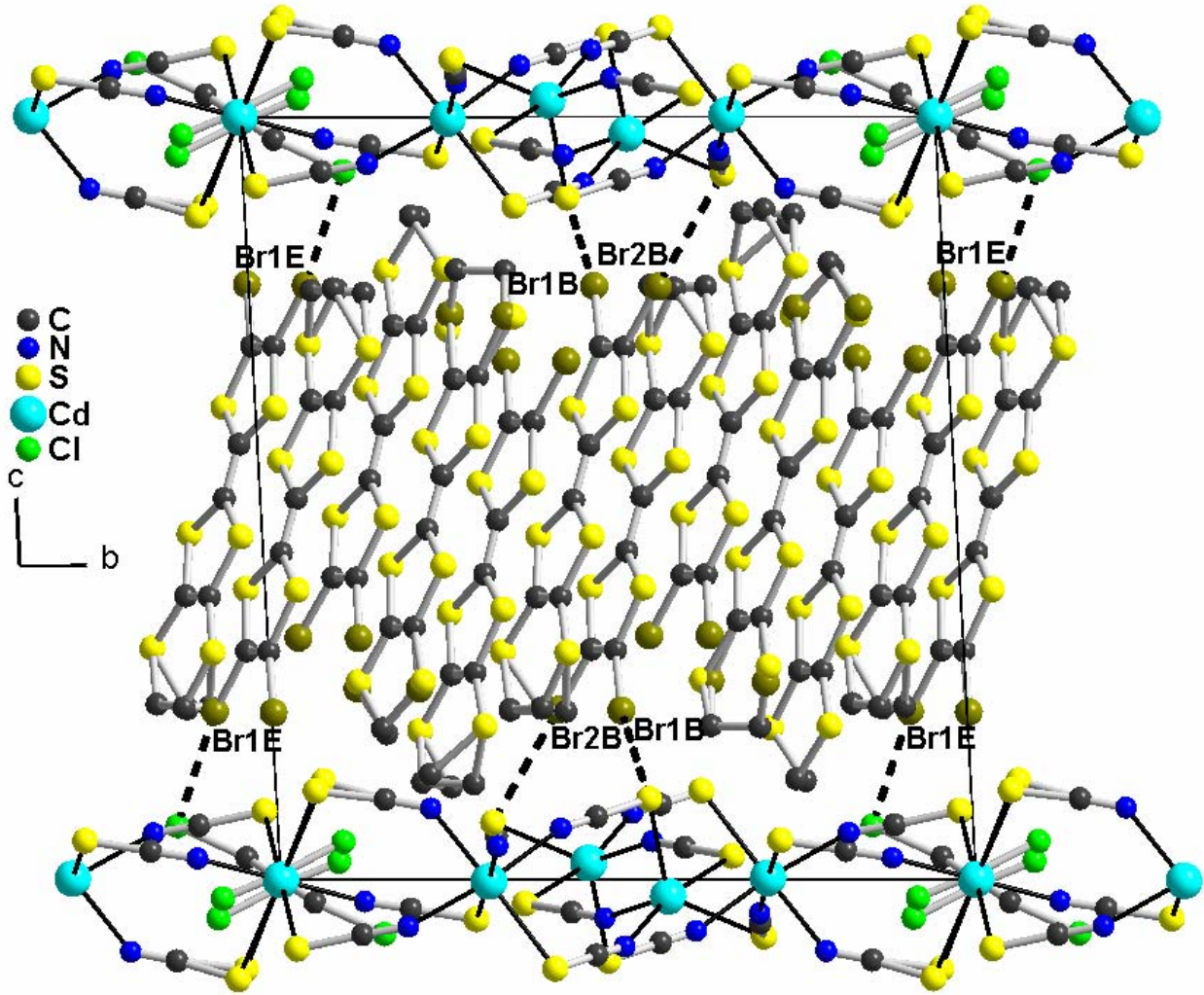
- $[EDT\text{-}TTF\text{-}Br_2]_{10}[Cd_5(SCN)_{14}]\cdot 2TCE$ **$\rho = 0.4$ $\sigma_{RT} = 33$ S cm^{-1}**

With TCE inclusion:

- Organic/inorganic segregation



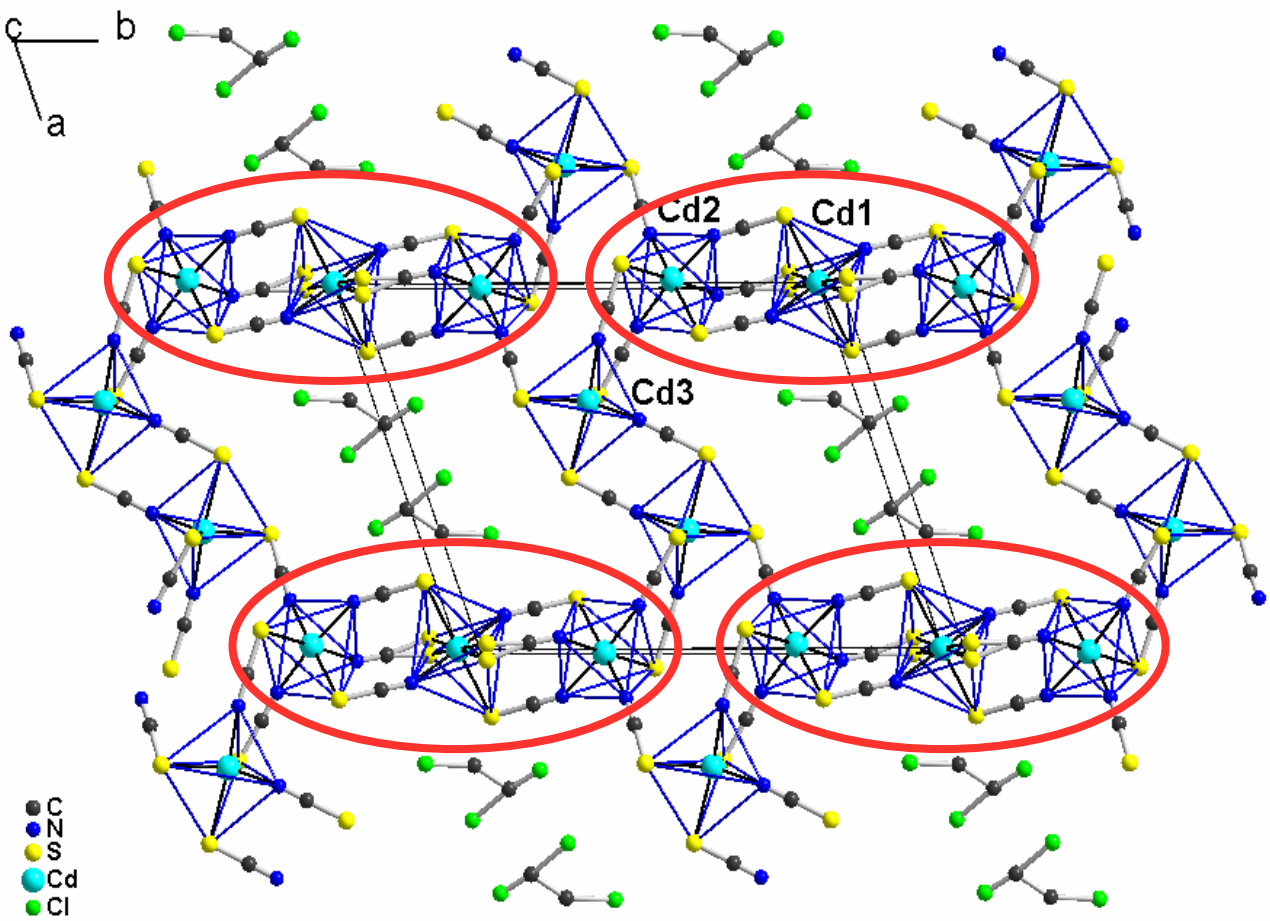
EDT-TTFBr_2



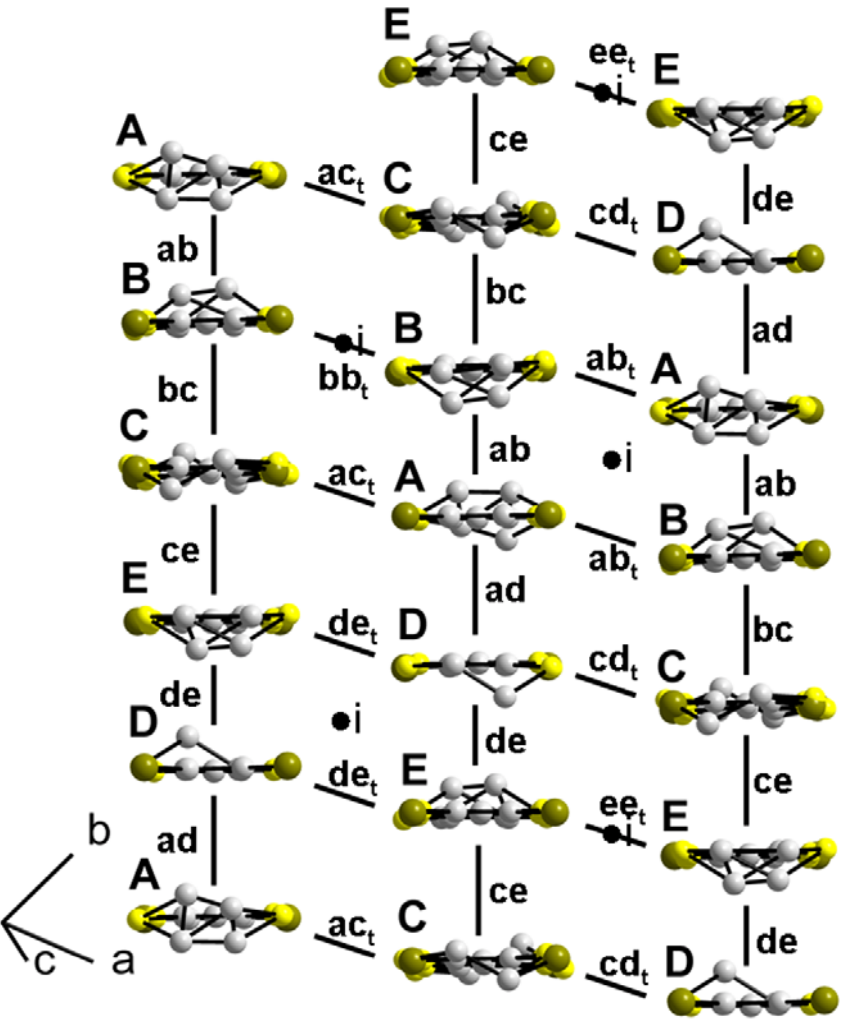
With TCE inclusion:

- Organic/inorganic segregation

- Reconstruction of the 1D $[Cd(SCN)_3)]$ chains into layered porous structures, with trimeric moieties reminiscent of the starting chains



Electronic Interactions



- Intrachain:

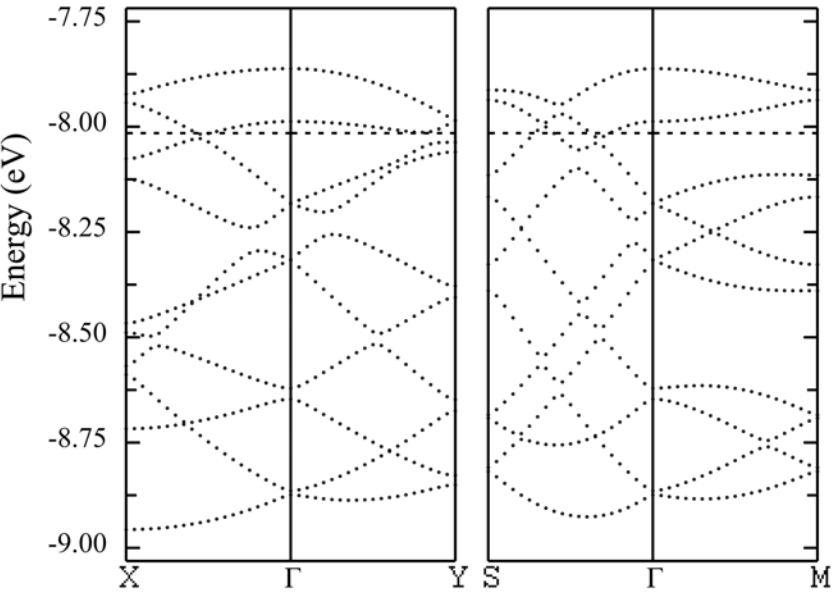
β_{intra} = 0.377, 0.380, 0.364, 0.408, 0.393 eV;

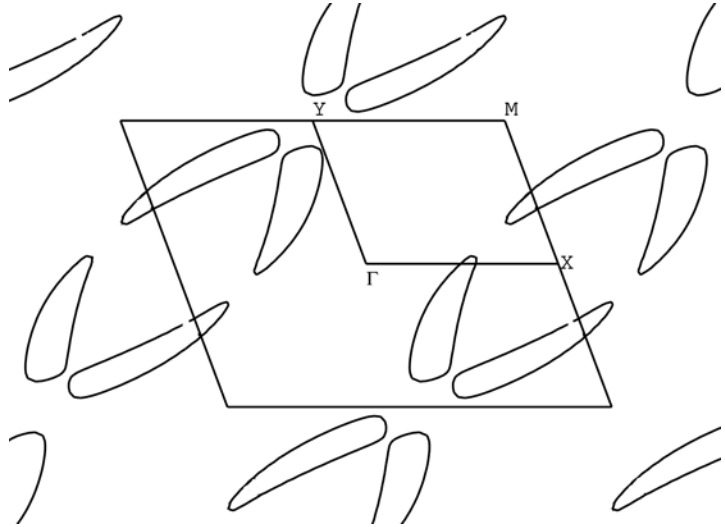
- Interchain:

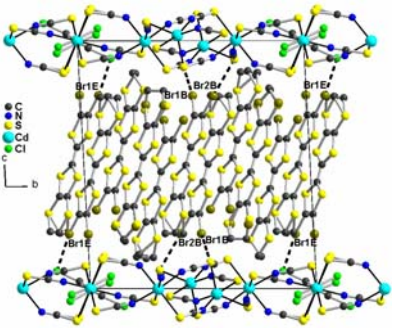
β_{inter} = 0.049, 0.064, 0.059, 0.047, 0.032, 0.034 eV

1D structures

Band Structure

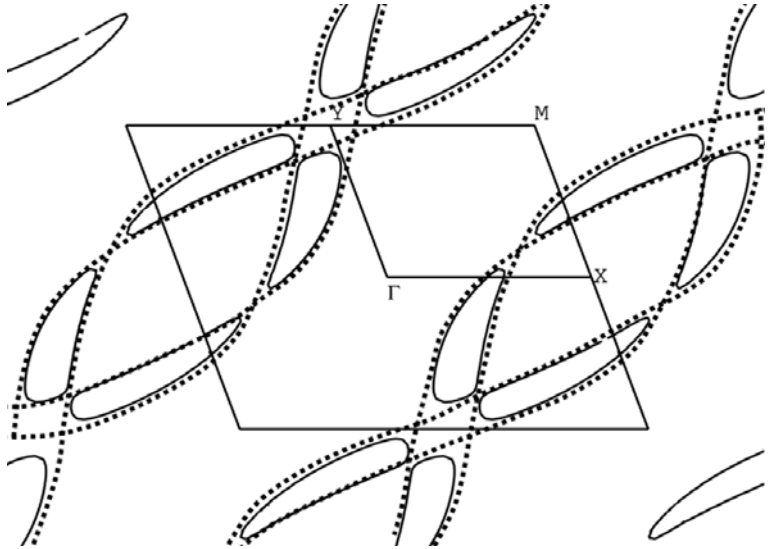






ρ= 0.4 σ_{RT} = 33 S cm^{-1}

E_{act} = 370 K = 0.03 eV



Fourmigué, M; Auban-Senzier, P. *Inorg. Chem.* **2008**, *47*, 9979.

RECURRENT TRENDS vs. EVOLUTIONS

Organic/inorganic segregation		Control of the interface : Hydrogen / halogen bonding
Mixed valence systems ($\rho = \frac{1}{2}$)		Non stoichiometric systems : Polymeric anions
Dimerized chains $\frac{1}{2}$-filled systems	→	**Non-dimerized chains** **$\frac{1}{4}$-filled systems**
Symmetric molecules Centro-symmetric crystals		Non-symmetric molecules Chiral molecules and salts

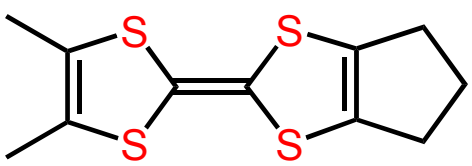
NON-DIMERIZED SYSTEMS

- Donor chains in Bechgaard salts are slightly dimerized, hence the conduction band splits into two bands and the upper band is half filled

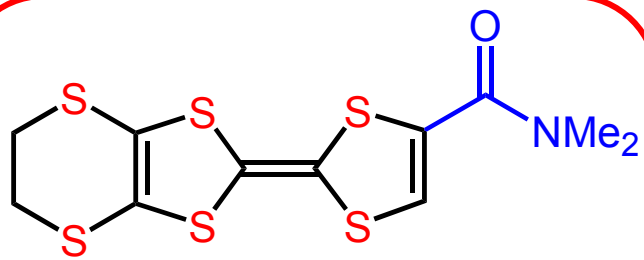
- Electronic localization is associated with $\frac{1}{4}$ and $\frac{1}{2}$-Umklapp electron scattering processes

- A non-dimerized, quarter-filled system is expected to be a Mott insulator with $\frac{1}{4}$ -Umklapp scattering only

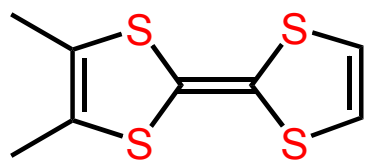
- Few experimental realizations in:



(**DMtTTF**)$_2$ClO$_4$
(**DMtTTF**)$_2$ReO$_4$
Delhaès, 1983; Kikuchi, 1985



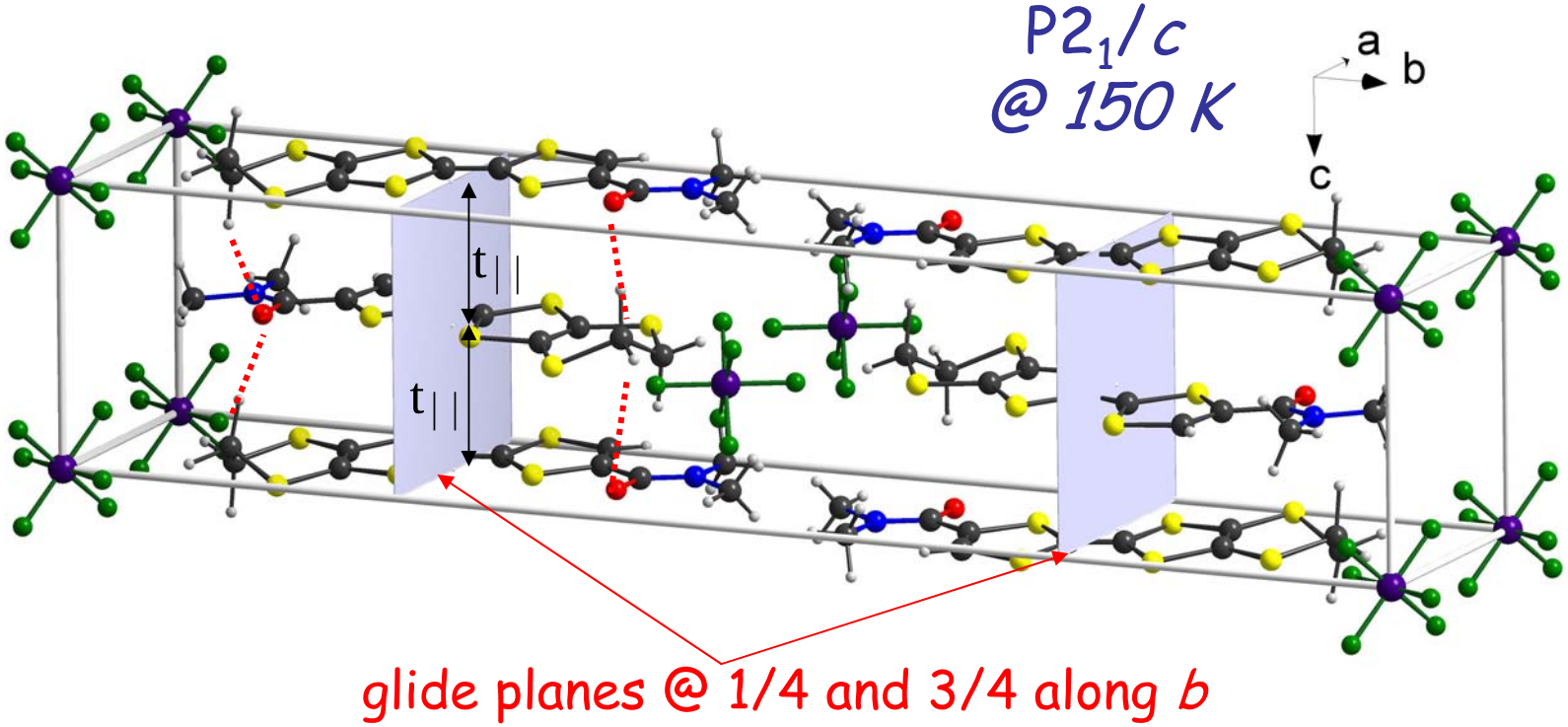
(**EDT-TTF-CONMe$_2$**)$_2$AsF$_6$
(**EDT-TTF-CONMe$_2$**)$_2$Br
Batail, 2003



(***o*-DMTTF**)$_2$Br
(***o*-DMTTF**)$_2$I
Fourmigué, Coulon, 2008

A QUARTER-FILLED SYSTEM: $[EDT\text{-}TTF\text{-}CONMe_2]_2AsF_6$

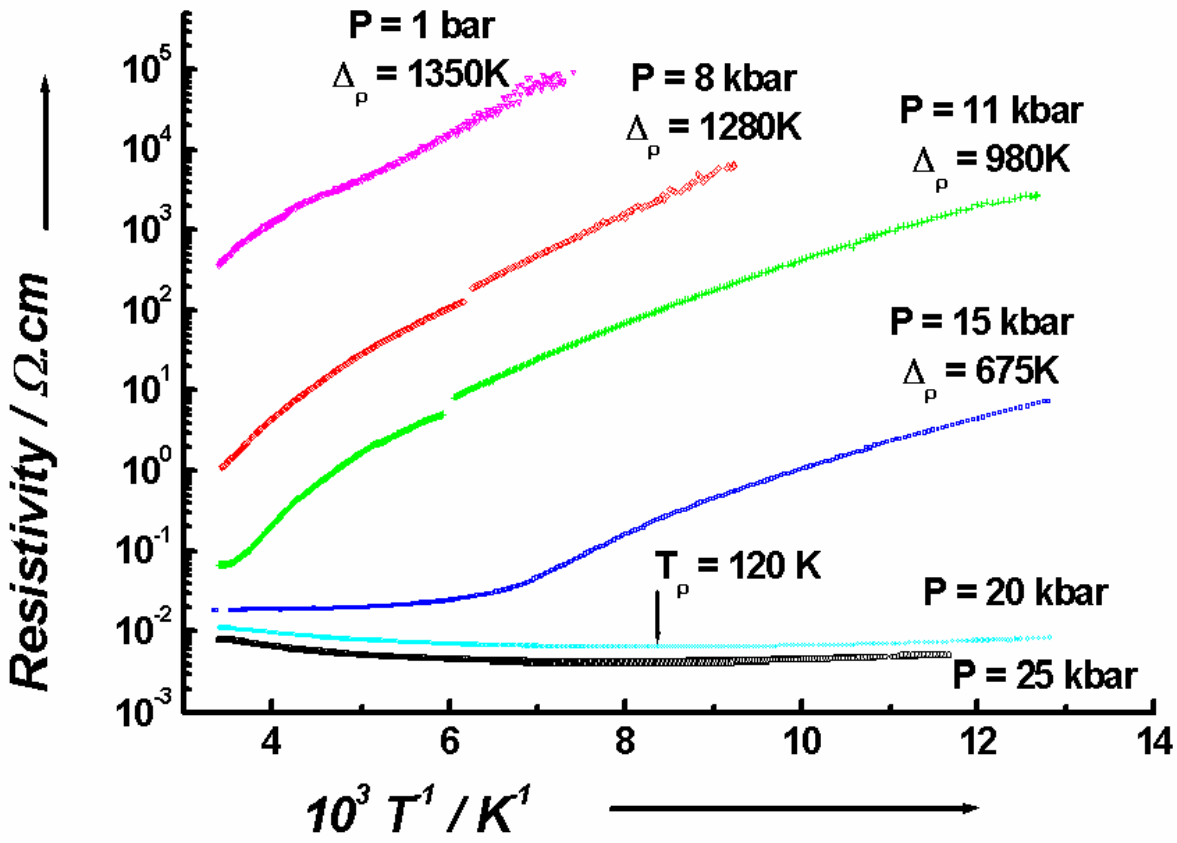
- C–H•••O hydrogen bonds rigidify the stacks along *c*
- In both HT Pnma and LT $P2_1/c$ forms, molecules within a stack are related to each other via a glide plane, hence the uniform stacks



K. Heuzé, M. Fourmigué, P. Batail, C. Coulon, R. Clérac, E. Canadell, P. Auban-Senzier, S. Ravy, D. Jérome, *Adv. Mater.* **2003**, *15*, 1251.

A QUARTER-FILLED SYSTEM: $[EDT\text{-}TTF\text{-}CONMe_2]_2AsF_6$

- Mott insulator, becomes metallic above 15 kbar
- Mott gap mostly controlled by the on-site and nearest neighbor interactions



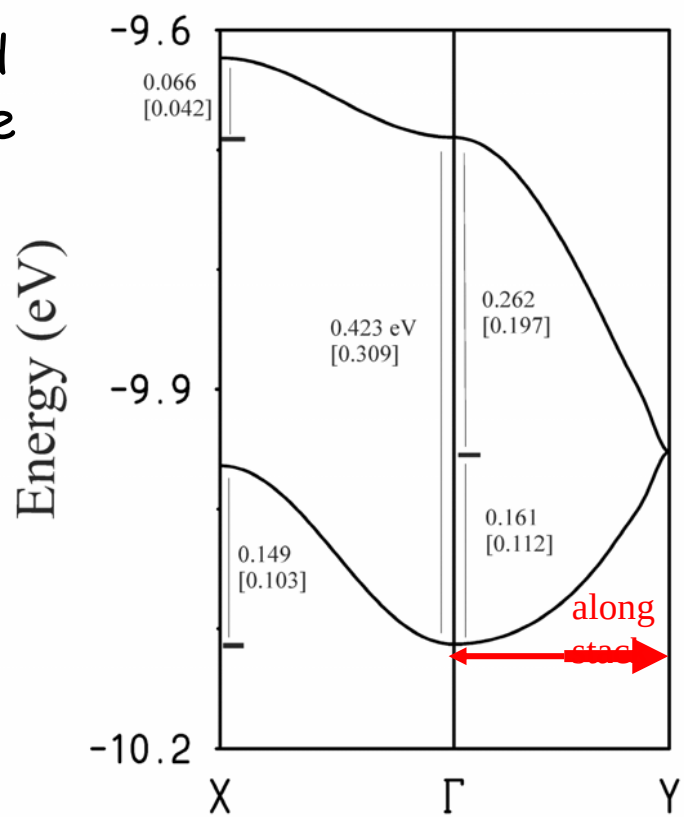
CHEMICAL vs. PHYSICAL PRESSURE: Br^- *vs.* AsF_6^-

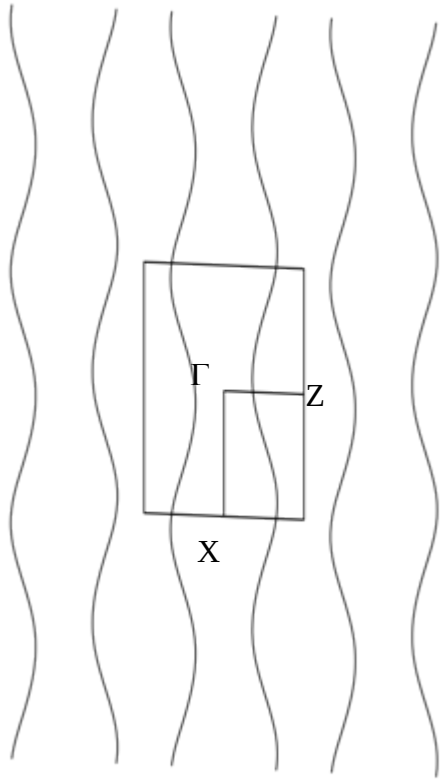
- Unit cell volume @ 295 K: Br^-: 1511.9(3) Å^3 AsF_6^-: 1664.0(2) Å^3

$$V(AsF_6^-) = V(Br^-) + 76\ Å^3$$

- Transfer integrals and band dispersion increase in the Br- salt, when compared with the AsF_6^- salt [values]

- Both salts are pseudo 1D systems with sizeable $t_\perp$





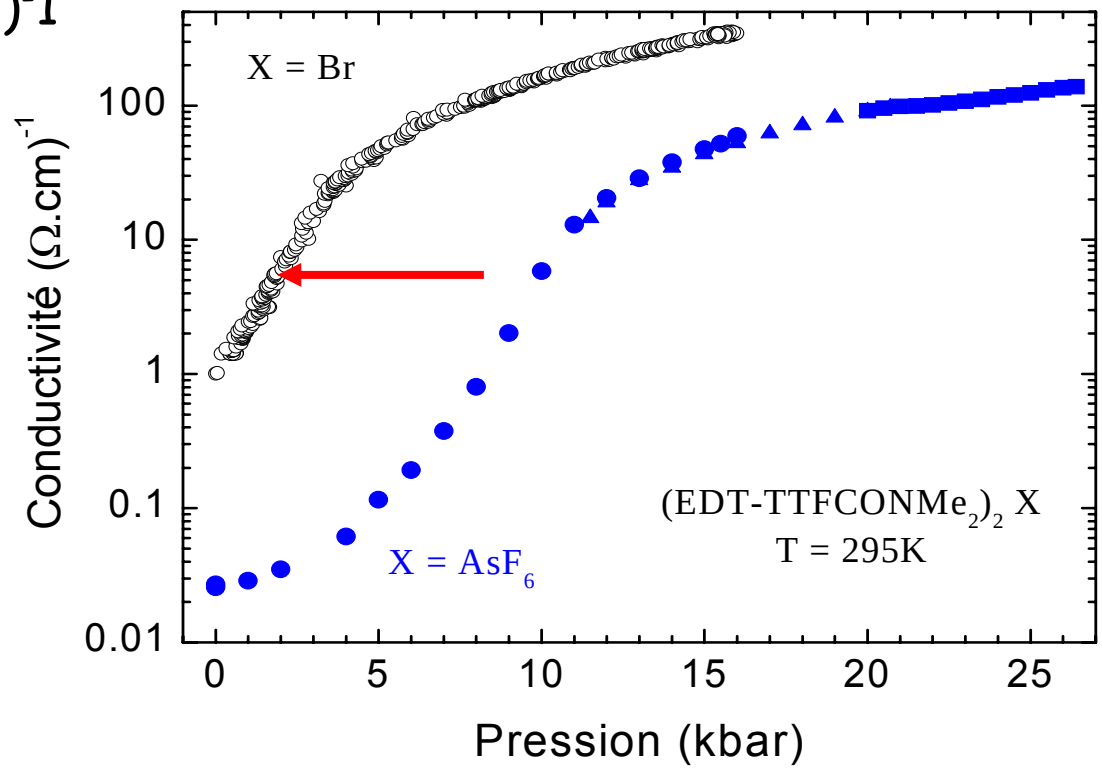
CHEMICAL vs. PHYSICAL PRESSURE: Br^- *vs.* AsF_6^-

- X = AsF_6^- σ(1bar) = 0.03 $(\Omega.cm)^{-1}$
- X = Br^- σ(1bar) = 1 $(\Omega.cm)^{-1}$

- Metallic behavior above

  15 kbar (AsF_6^-)

  7 kbar (Br^-)



$AsF_6^- \longrightarrow Br^-$ = – 8 kbar

CHARGE ORDERING AND WIGNER CRYSTALLIZATION

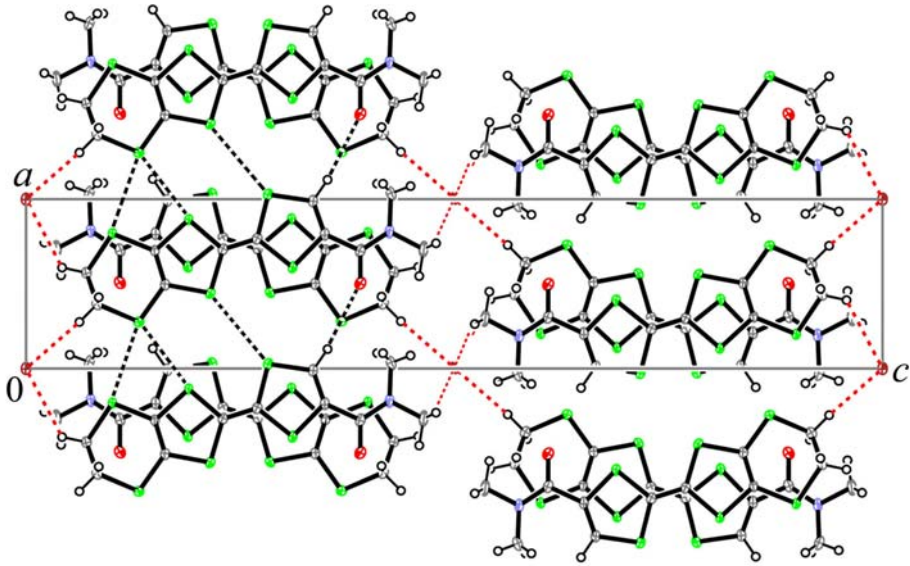
- Dielectric constant
(Pasquier, Auban-Senzier – Orsay)

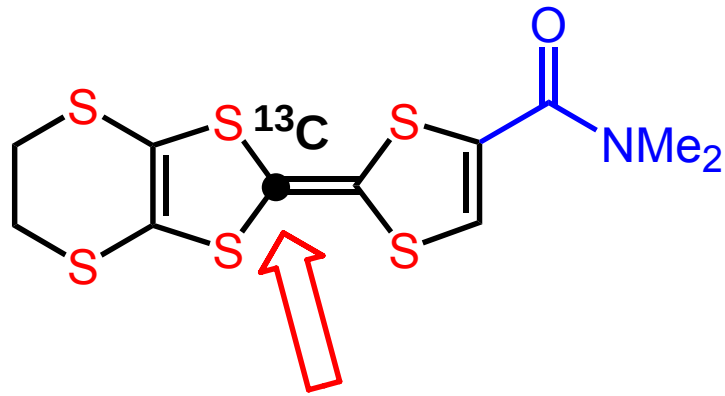
- ^{13}C Solid state NMR
(Brown – UCLA)

- IR reflectivity and Raman
(T. Yamamoto - IMS and Osaka Univ.)

- ^{13}C –marked molecule
(C. Mézière – Orsay)

- X-ray diffraction
L. Zorina – Angers, P. Fertey - SOLEIL
P. Foury, J.-P. Pouget - Orsay

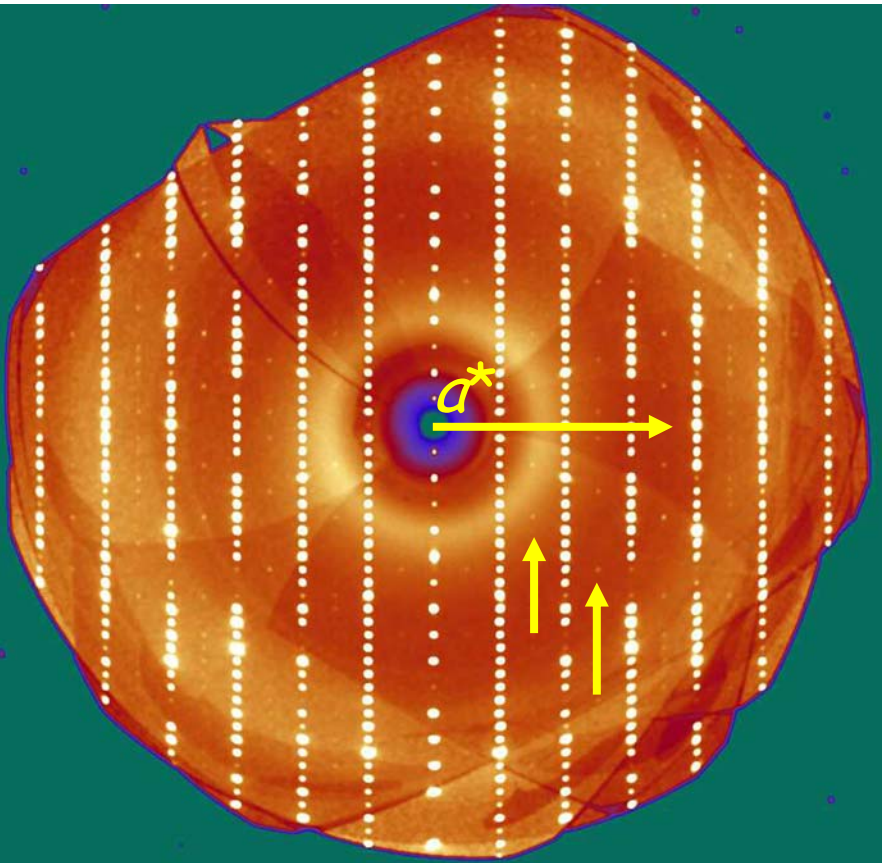


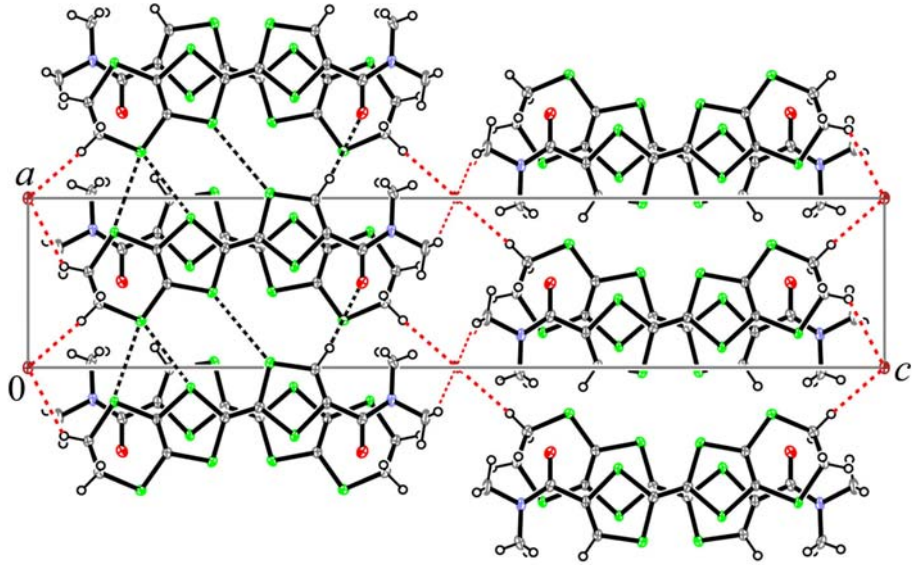


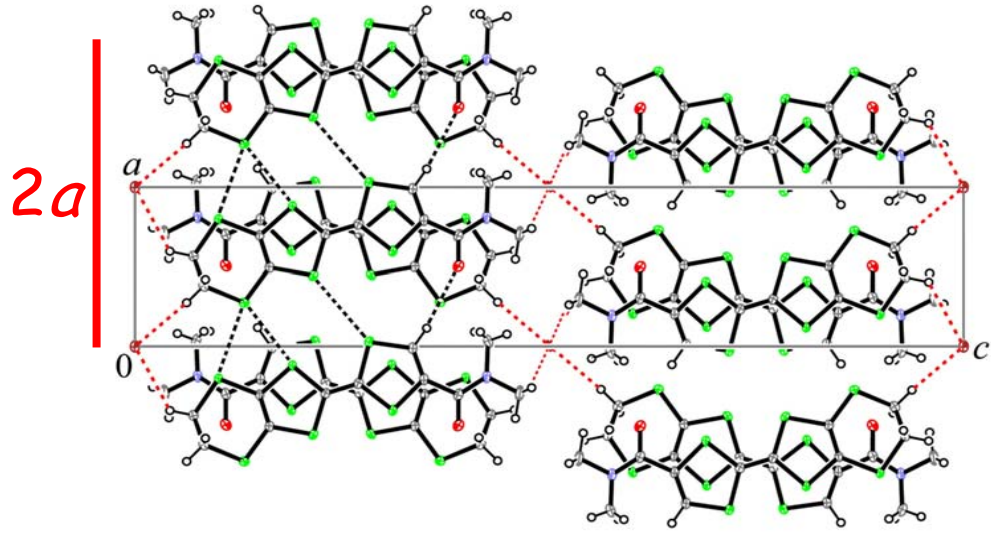
CHARGE ORDERING AND WIGNER CRYSTALLIZATION

- Pnmb at 300 K with one independent molecule does not allow for CO

- Doubling along *a* observed already at 300K





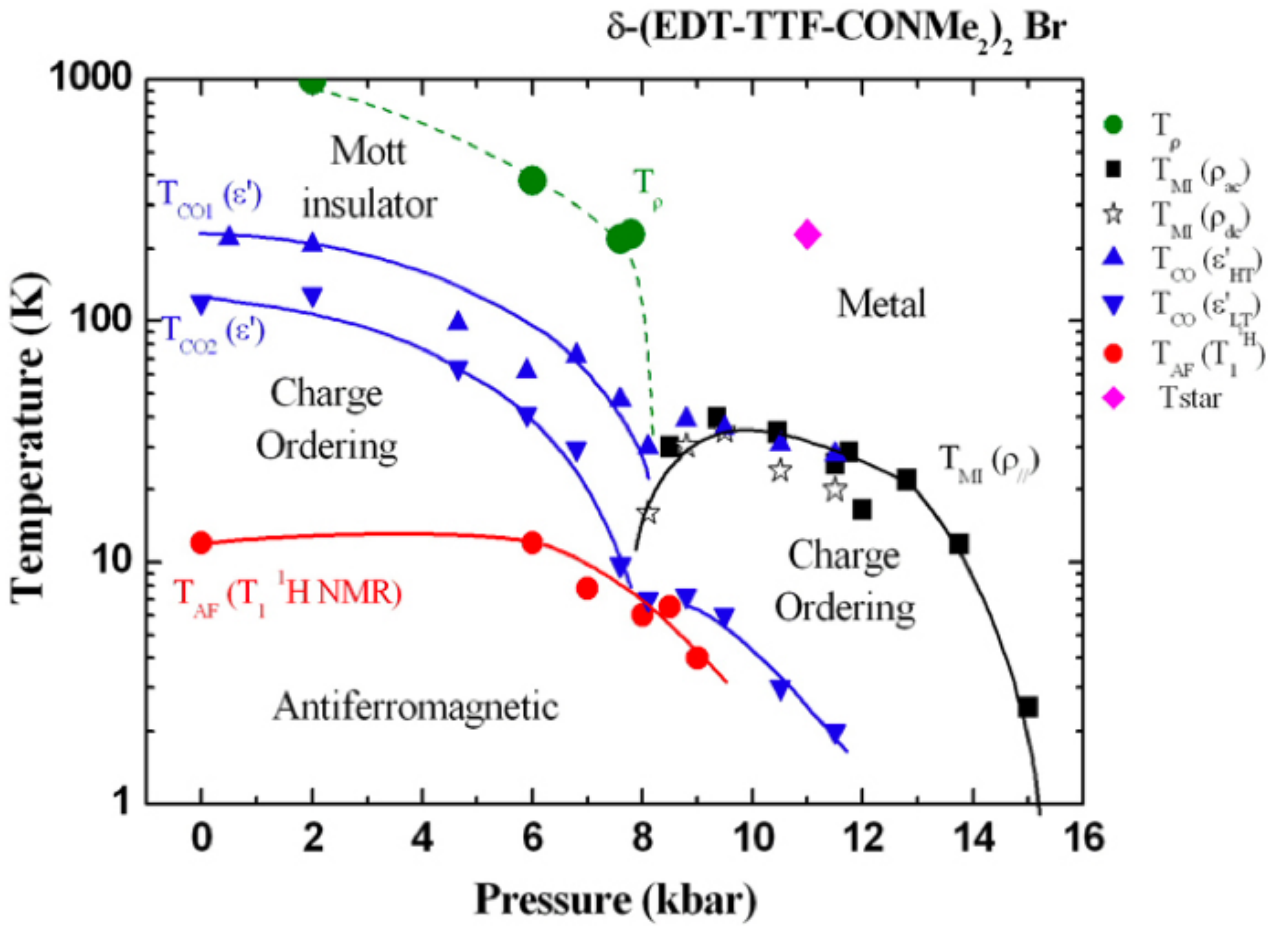


COMPLETE PHASE DIAGRAM

- Complex phase diagram

P. Auban-Senzier,
C. Pasquier
D. Jérome

- ANR CHIRASYM – Projet NT05-2 42710 Conducteurs organiques à symétrie contrôlée



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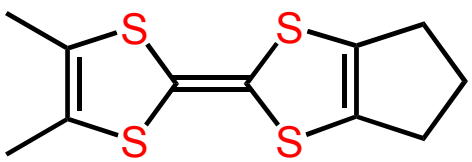
- Few experimental realizations in:



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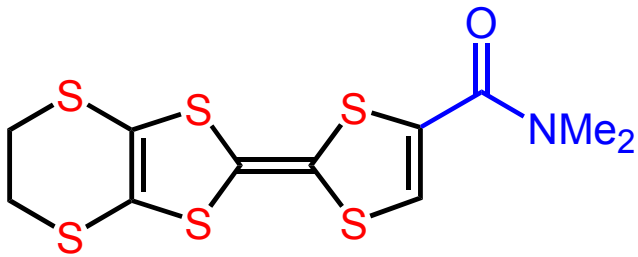

(**EDT-TTF-CONMe$_2$**)$_2$AsF$_6$
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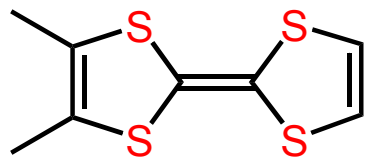
Batail, 2003



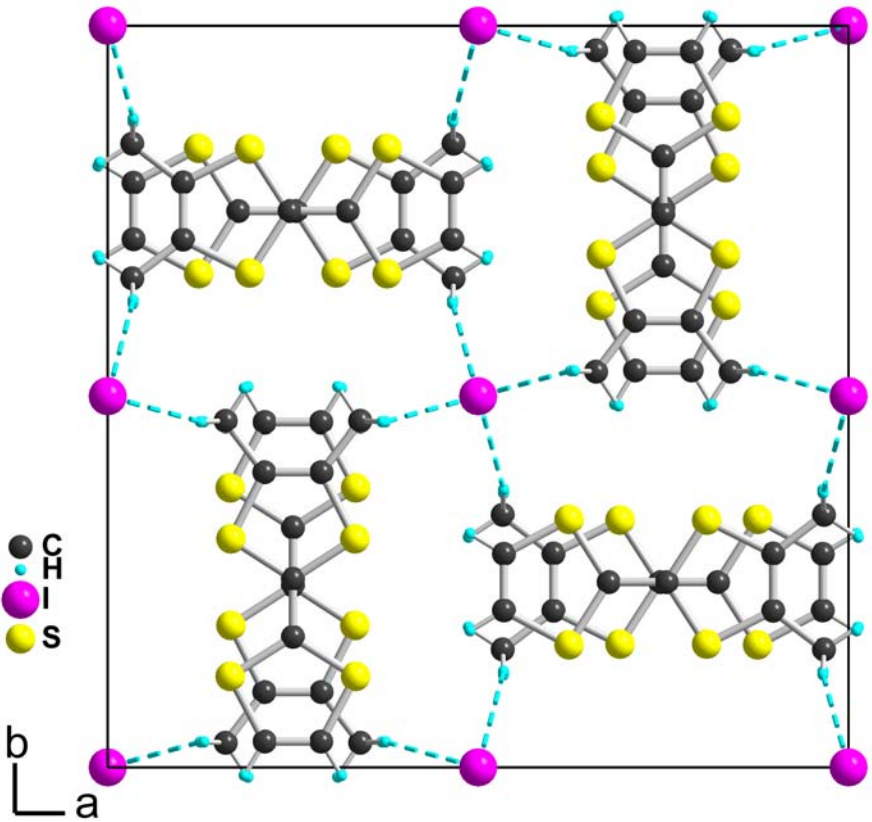
(***o*-DMTTF**)$_2$Br
(***o*-DMTTF**)$_2$I

Fourmigué, Coulon, 2008

Tetragonal halide salts

Electrocrystallization with Cl^-, Br^-, I^-, affords 2:1 salts, tetragonal system space group I-42d

Anion	I^-	Br^-	Cl^-
a (Å)	17.4031(2)	17.0920(3), -1.8%	16.9376(6), -2.7%
c (Å)	7.0978(1)	7.0582(2), -0.6%	7.0400(3), -0.8%
V ($Å^3$)	2149.70(5)	2061.96(8), -4.1%	2019.6(1), -6.0%



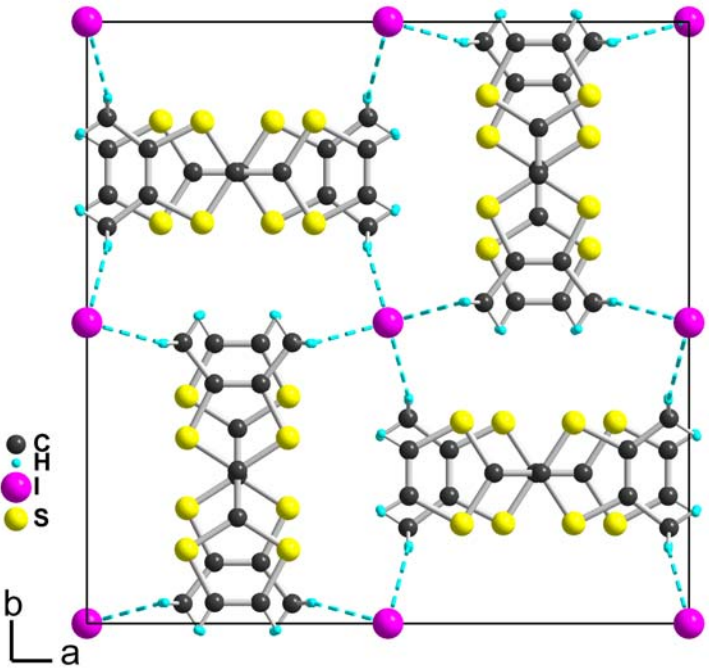
1) Strict 2:1 stoichiometry contrasts with TTF halide salts

2) Isomorphous series

Evolution with anion size:

Lateral expansion *vs.* stacking direction

Tetragonal halide salts



1) o-Me_2TTF molecules on the 2-fold axis of the I-42d space group

Uniform stacks by symmetry

Helical structure

Strict $\frac{1}{4}$ filling on the bands

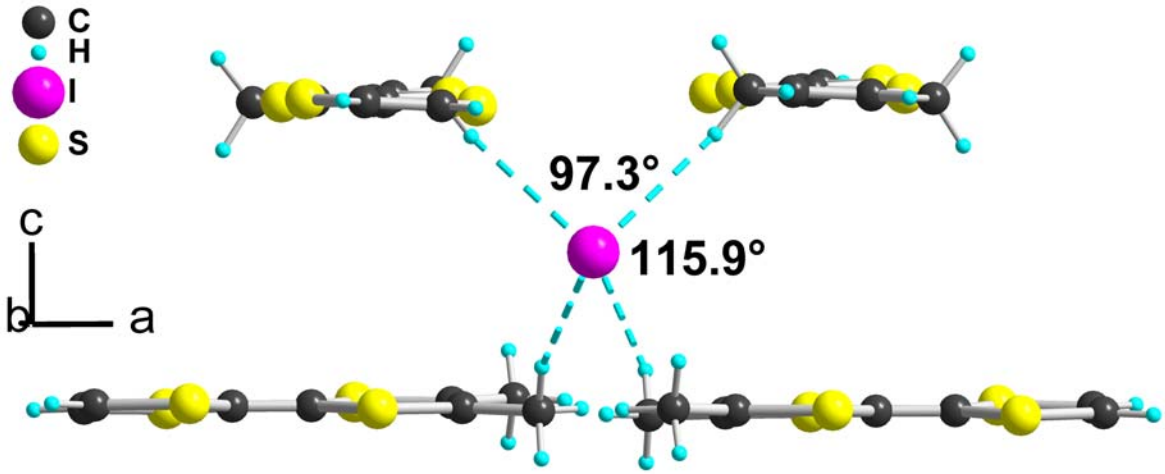
2) Stacks perpendicular to each other

Strong 1D character

M. Fourmigué, E. W. Reinheimer, K. R. Dunbar, P. Auban-Senzier, C. Pasquier, C. Coulon
Dalton Trans., **2008** 4652.

C—H···Hal Hydrogen Bonding

The CH_3 groups are engaged in C—H···Hal^- hydrogen bonds in a distorted tetrahedral environment

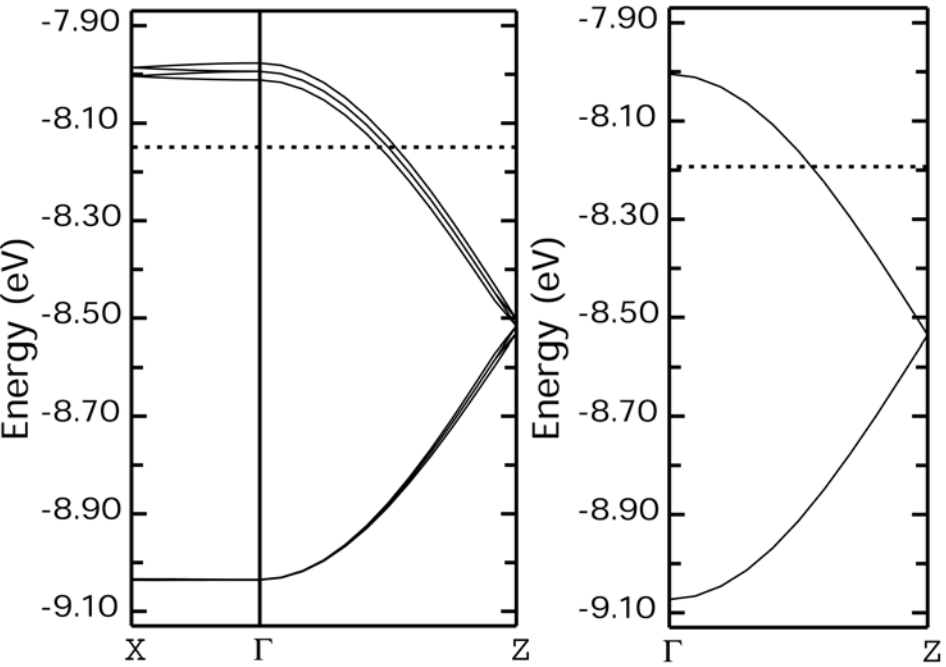


Anion	I^-	Br^-	Cl^-
H···Hal (Å)	3.008	2.912, -3.2%	2.861, -4.9%
C-H···Hal (°)	164.2	163.5	163.7
H···Hal^-···H (°)	97.3, 115.9	94.6, 117.4	94.4, 117.5

Note: hydrogen activation upon oxidation usually stronger for sp_2 rather than sp_3 H atoms

See: M. Fourmigué, P. Batail, *Chem. Rev.* **2004**, *104*, 5379

Band structure



- 1D calculations give a $\frac{3}{4}$ filled system without gap
- 3D calculations give avoided crossings at the Z point
- Very strong anisotropy (compared with TMTTF salts)

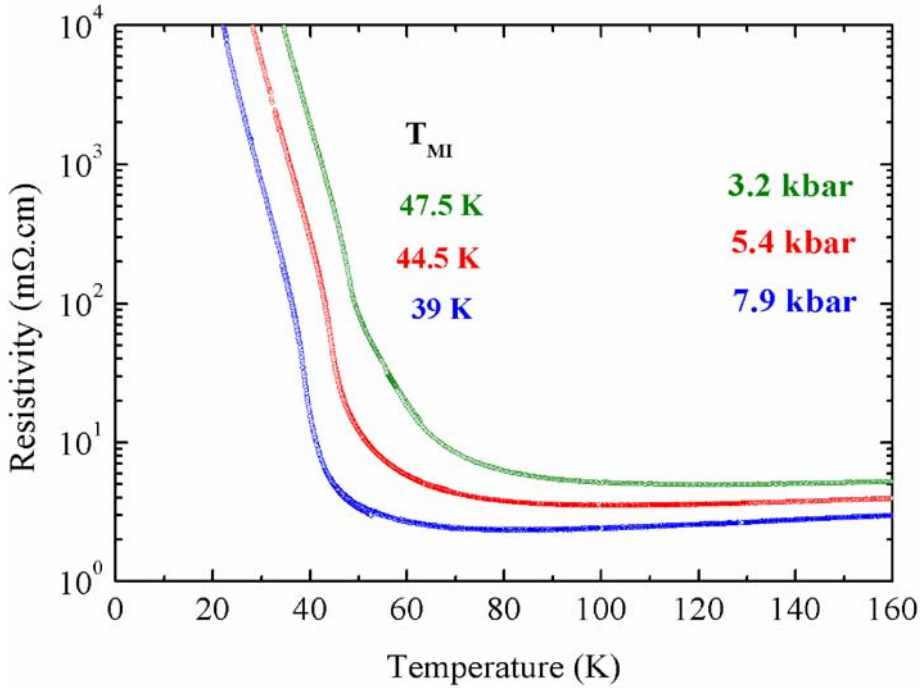
Anion	H_{intra} (eV)	H_{inter1} (eV)	H_{inter2} (eV)	H_{intra}/H_{inter2}
I^-	0.427	0.011	0.007	39
Br^-	0.466	0.015	0.002	31
Cl^-	0.461	0.017	0.003	27

Conductivity properties of the Br^- Salt

Longitudinal conductivity:

- σ_{RT} = 150 S cm^{-1}
- Metallic behavior down to T_{MI} = 50K
- Application of pressure:

σ_{RT}: only +15% per kbar
(half of TMTTF salts, role of C—H···Hal$^-$)
MI transition to 39 K at 7.9 kbar



Transverse conductivity:

- $\sigma_\perp$ = 0.25 S cm^{-1} at room temperature
- MI transition at the same temperature than in longitudinal configuration.
- Anisotropy ratio $\sigma_{//} / \sigma_\perp \approx 400$!!

In TMTTF salts:
$\sigma_{//} / \sigma_{\perp 1}$ = 100 and $\sigma_{//} / \sigma_{\perp 2} = 10^4$

RECURRENT TRENDS vs. EVOLUTIONS

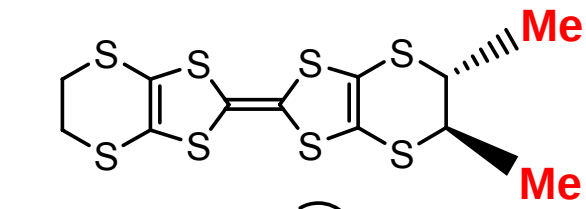
Organic/inorganic segregation		Control of the interface : Hydrogen / halogen bonding
Mixed valence systems ($\rho = \frac{1}{2}$)		Non stoichiometric systems : Polymeric anions
Dimerized chains $\frac{1}{2}$-filled systems		Non-dimerized chains $\frac{1}{4}$-filled systems
Symmetric molecules Centro-symmetric crystals		Non-symmetric molecules Chiral molecules and salts

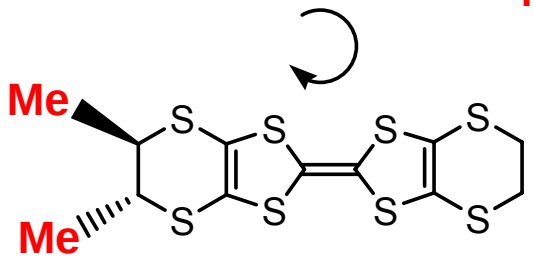
CHIRAL CONDUCTORS

Why ?

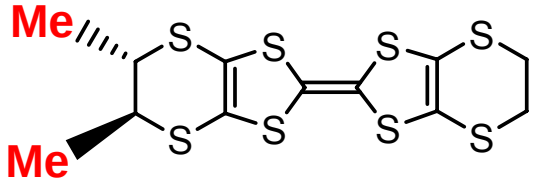
- Enantiopure molecules are expected to exhibit less disorder than the racemic mixture in the crystalline state

- Many chiral TTFs described





(*R*,*R*)-DMBEDT-TTF



(*S*,*S*)-DMBEDT-TTF

but lack of complete series of (R), (S) and (±) conducting salts of the same precursor for useful comparisons

Amabilino, DB; Veciana, J, *Supramol. Chiral.* **2006**, *265*, 253
Griffiths J-P, Nie H, Brown RJ, Day P, Wallis JD *Org Biomol Chem* **2005**, *3*, 2155

CHIRAL CONDUCTORS

Why ?

- Recent reports by Rikken et al. on electrical magneto-chiral anisotropy (eMChA) effects

$$R^{D/L}(\mathbf{I},\mathbf{B}) = R_0\{1 + \beta B^2 + \chi^{D/L}\mathbf{I}\cdot\mathbf{B}\}$$

eMChA effect (very weak)

Chiral SWNT: Krstić, Rikken et al. *J. Chem. Phys.* **2002**, *117*, 11315

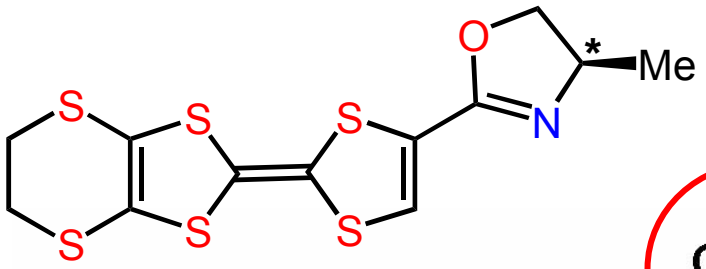
- Can we prepare chiral conductors based on TTF derivatives ?

Two strategies:

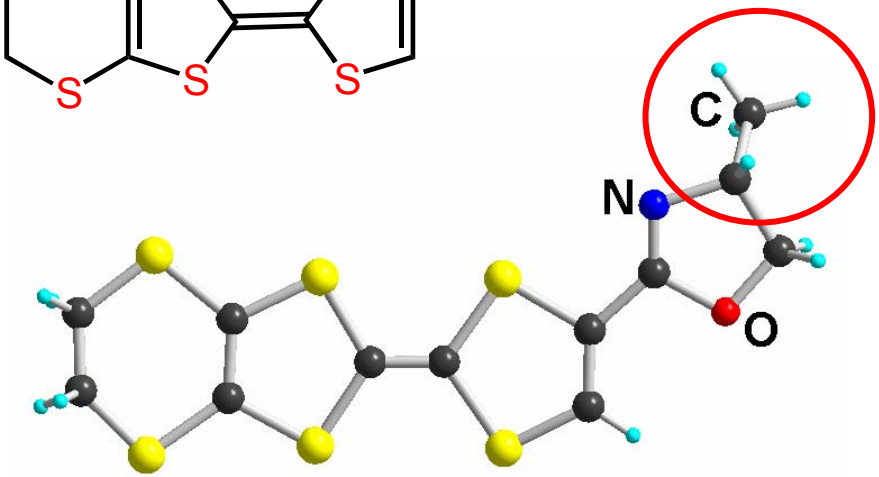
chiral donor molecules

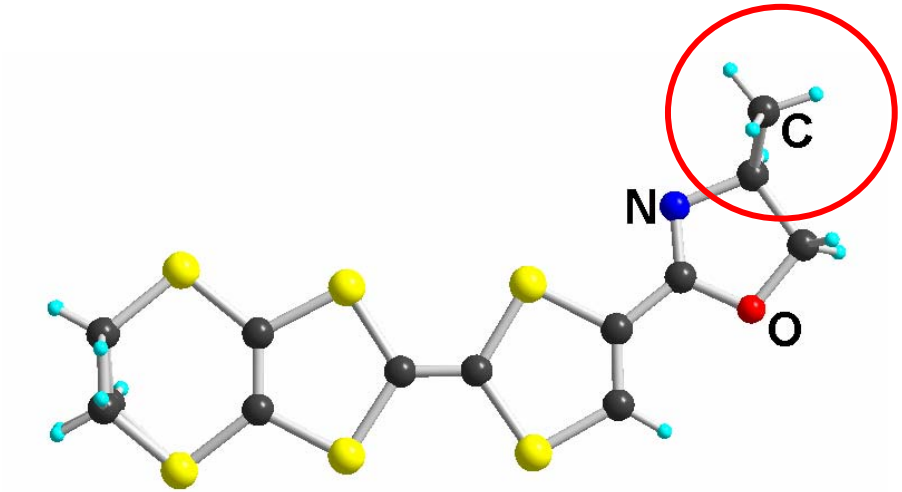
chiral counter ions

TETRATHIAFULVALENE OXAZOLINES



Prepared in the racemic and pure *R* and *S* forms without separation





(R)-EDT-TTF-OxaMe, S. G. $P2_1$

a = 6.3686(10), b = 7.667(2), c = 16.419(3) Å
β = 99.60(2)°, V = 790.4(3) $Å^3$

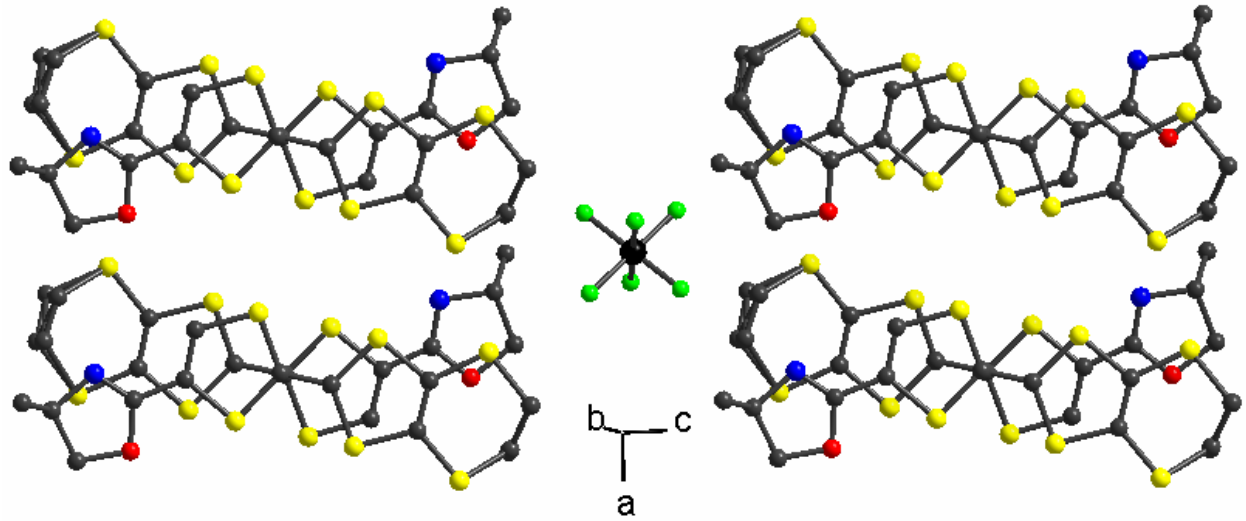
(S)-EDT-TTF-OxaMe, S. G. $P2_1$

a = 6.3167(5), b = 7.7578(7),c = 16.243(1) Å
b = 99.96(1)°, V = 784.0(1) $Å^3$

C. Réthoré, M. Fourmigué, N. Avarvari, *Chem. Commun.* **2004**, 1384
C. Réthoré, M. Fourmigué, N. Avarvari, *Tetrahedron* **2005**, *61*, 10935

TETRATHIAFULVALENE OXAZOLINES

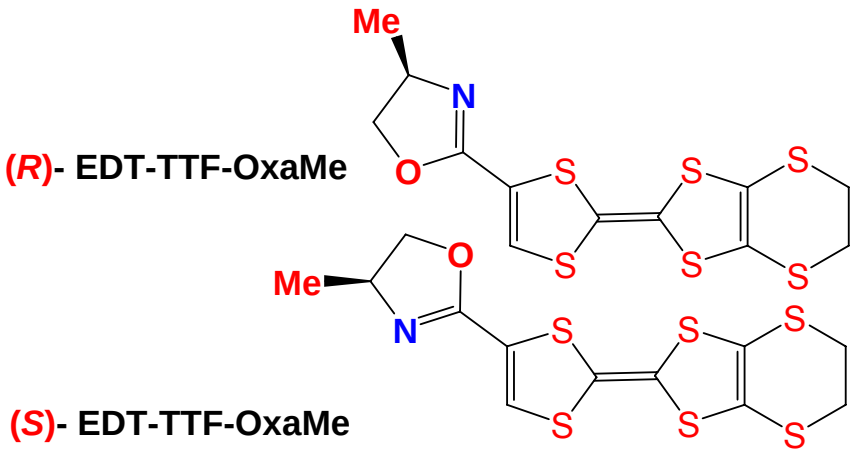
Electrocrystallization with AsF_6^- anion affords three salts with the *R*, *S* and racemic EDT-TTF oxazolines

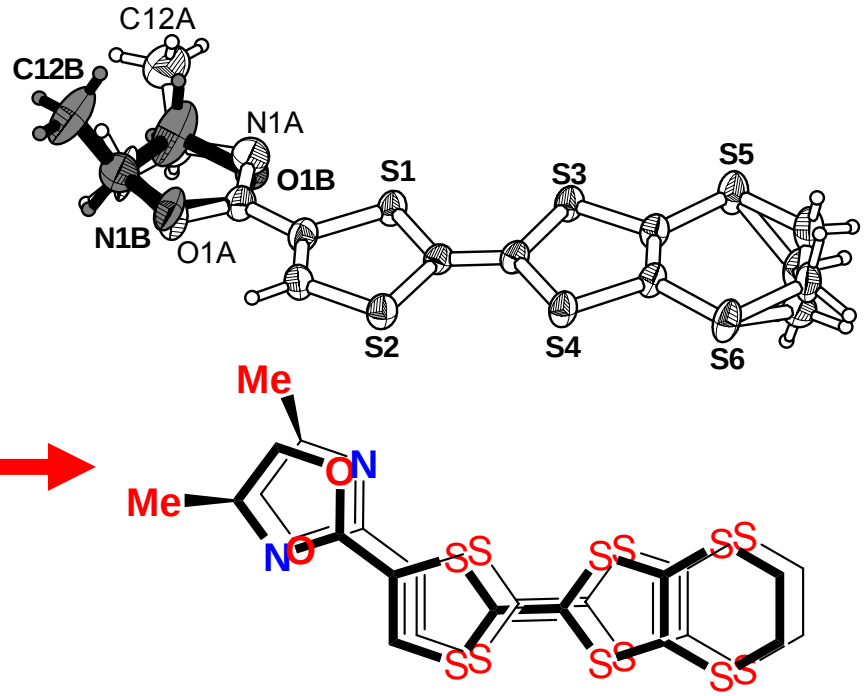


	SG	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)
rac	P-1	6.4102(3)	7.5058(4)	17.9870(4)	83.523(4)	86.529(3)	85.458(4)	856.03(6)
(R)	P1	6.3918(7)	7.5020(9)	17.941(2)	83.197(14)	86.638(14)	85.548(14)	850.60(17)
(S)	P1	6.3962(7)	7.4884(9)	17.940(2)	83.130(14)	86.579(14)	85.520(14)	849.41(17)

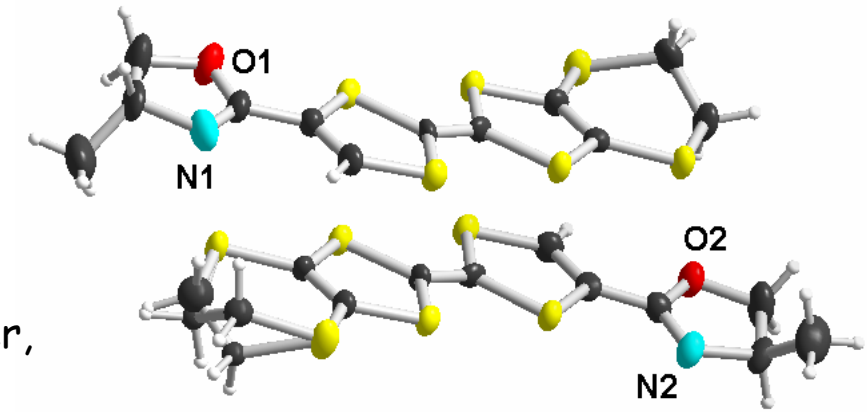
TETRATHIAFULVALENE OXAZOLINES

- Disorder in the racemic mixture:





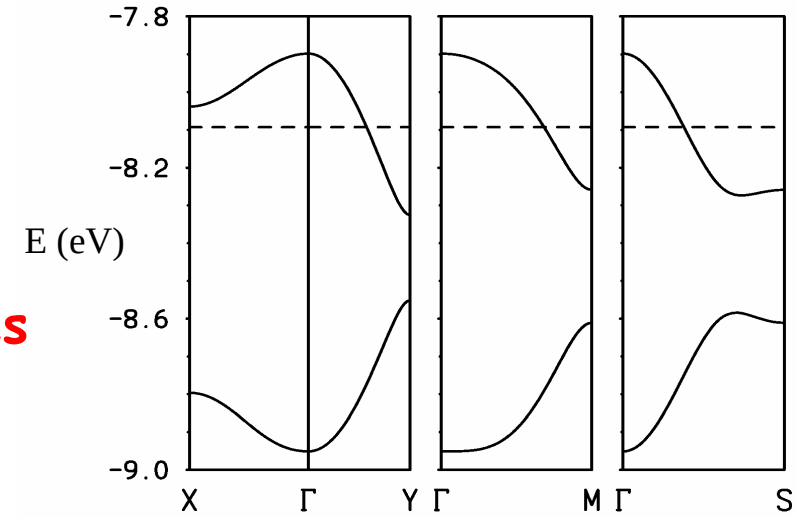
- Two crystallographically independent molecules in the enantiopure salts:



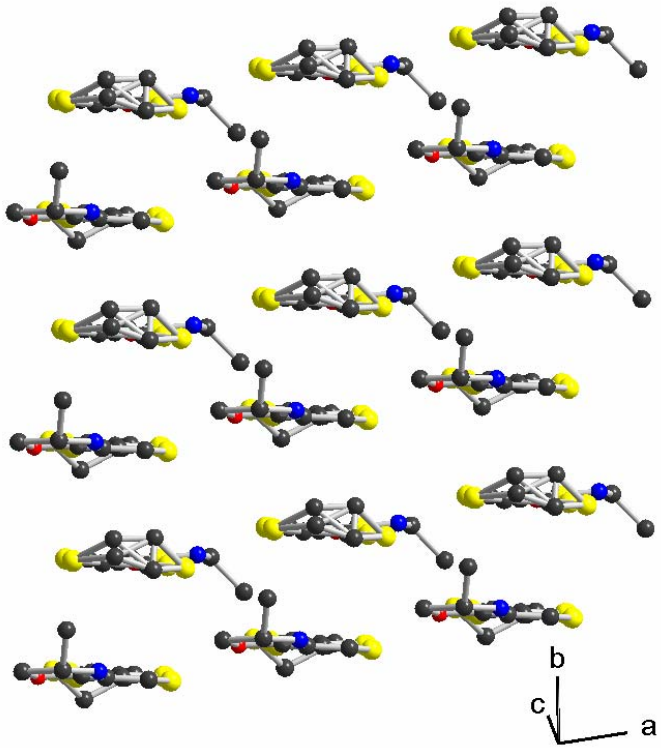
C. Réthoré, N. Avarvari, E. Canadell, P.Auban-Senzier, M. Fourmigué *J. Am. Chem. Soc.* **2005**, *127*, 5748

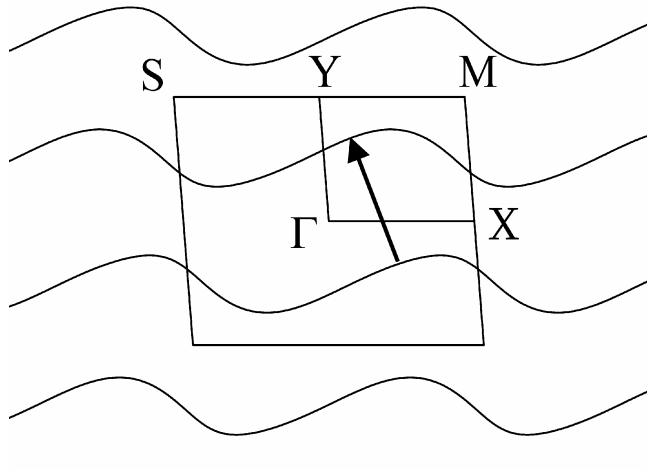
TETRATHIAFULVALENE OXAZOLINES

Intermolecular interactions:
β intrastack: 0.529/0.337 eV
β interstack: 0.086/0.034 eV



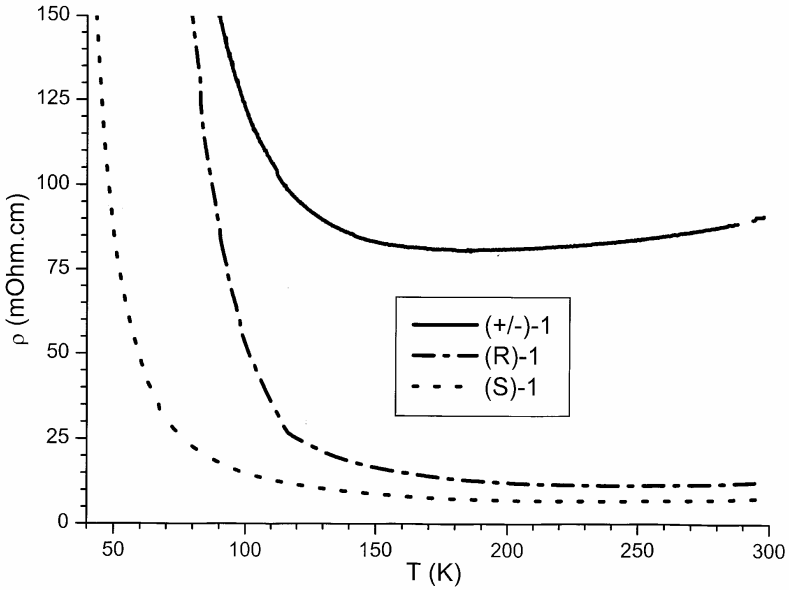
1D electronic structures



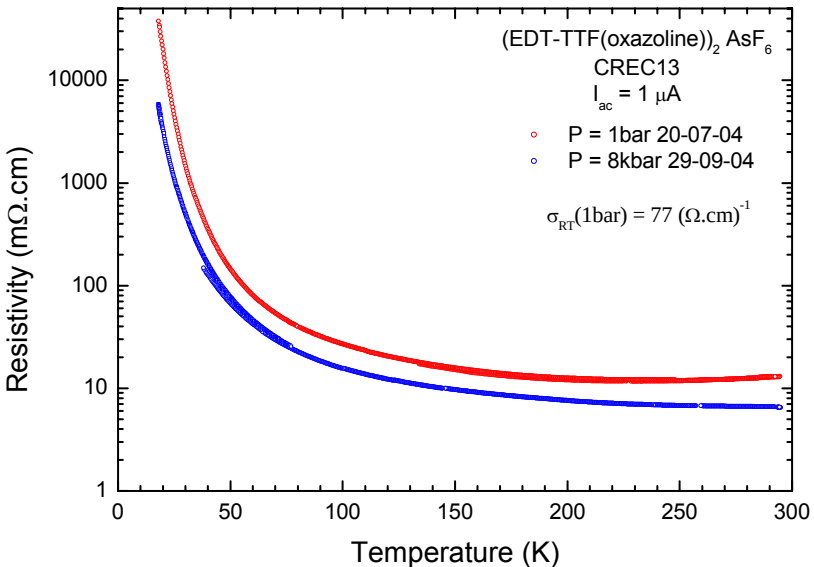


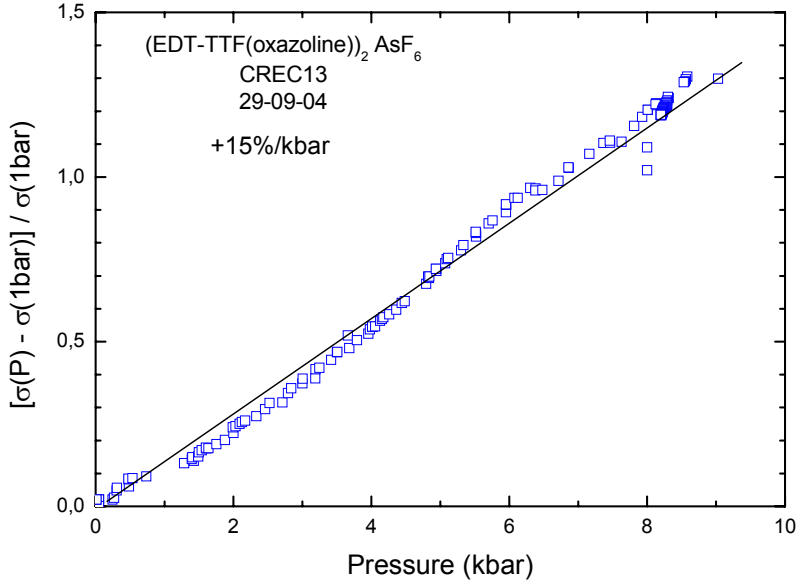
TETRATHIAFULVALENE OXAZOLINES

The absence of disorder
in the enantiopur salts
decreases the resistivity by 10



Pressure dependence: +15% per kbar





CONCLUSIONS & PERSPECTIVES

Control of the interface :
Hydrogen/halogen bonding → Halogen contribute to dispersion
Spin density ?

Non stoichiometric systems :
Polymeric anions → Efficient but relies on serendipity

Non-dimerized chains
¼-filled systems → Very rare systems with rich physics

Non-symmetric molecules
Chiral molecules and salts → Chiral centers favor disorder
Toward planar or axial chirality
Search for helicoidal structures

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