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RADICAL CATION SALTS of TTF DONORS with the Ta 2 OF 10 2-DIANION

Cécile Mézière, Magali Allain, Nabil Mroweh, Pascale Auban Senzier, Enric Canadell, Narcis Avarvari

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Cécile Mézière¹, Magali Allain¹, Nabil Mroweh², Pascale Auban Senzier³, Enric Canadell⁴, Narcis Avarvari¹

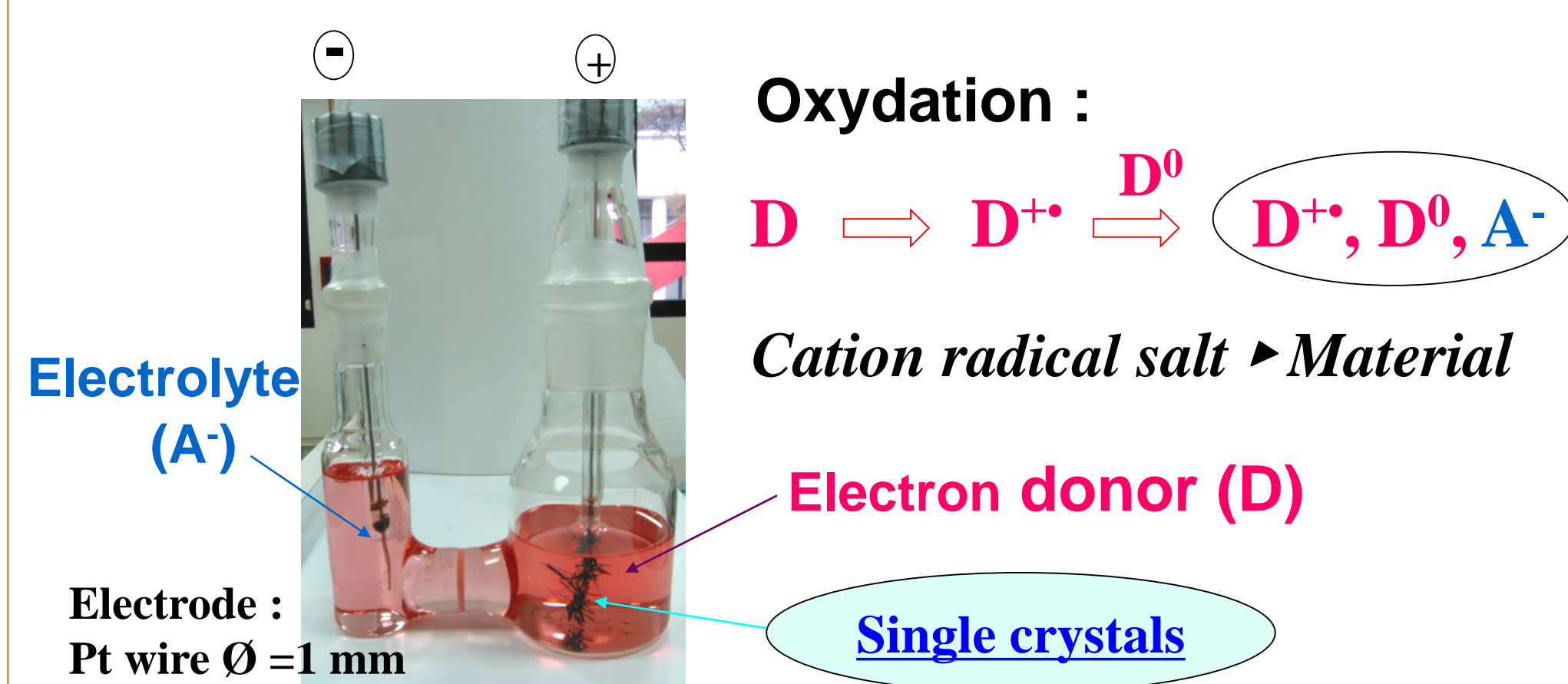
¹Laboratoire MOLTECH-Anjou, UMR 6200 CNRS-Université d'Angers, Faculté des Sciences, 2 bd Lavoisier, 49045 ANGERS Cedex, France

²Laboratoire de Chimie et Biologie des Métaux - CEA, 17 rue des Martyrs, 38 054 Grenoble, France

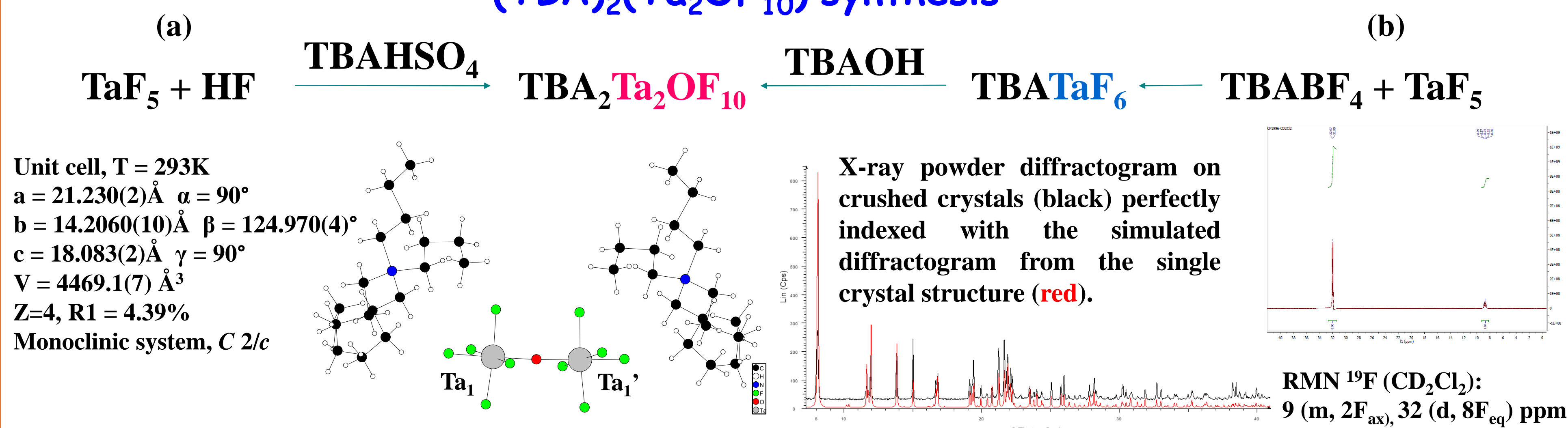
³Laboratoire de Physique des Solides, UMR8502 CNRS-Université Paris Sud, Bât. 510, 1 rue Nicolas Appert, 91405 Orsay Cedex, France

⁴Institut de Ciència de Materials de Barcelona (CSIC), Campus de la UAB, E-08193 Bellaterra, Spain

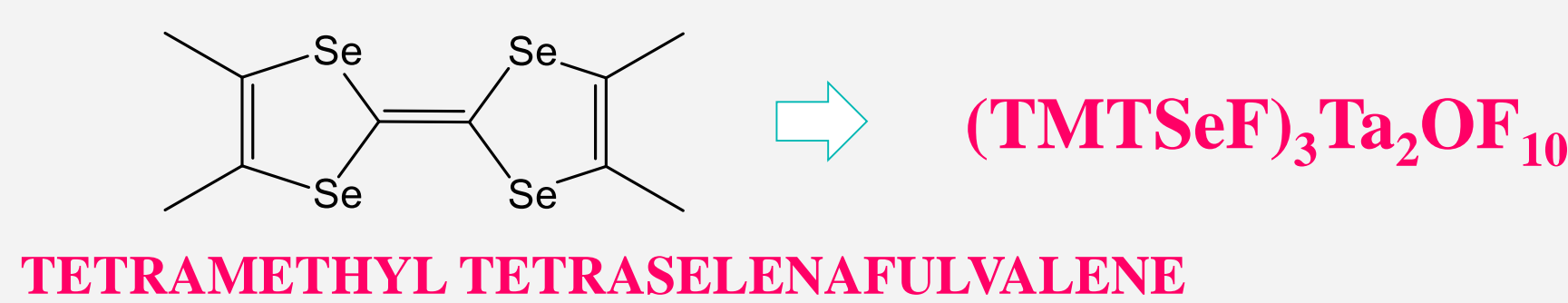
Electrocrystallization set up [2]



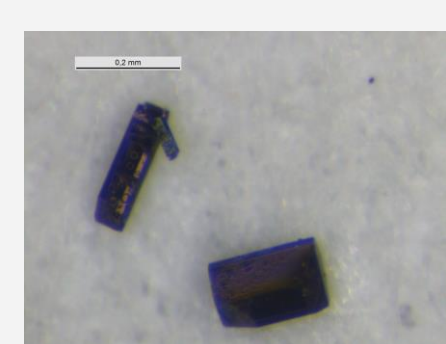
(TBA)₂(Ta₂OF₁₀) synthesis



X = Se

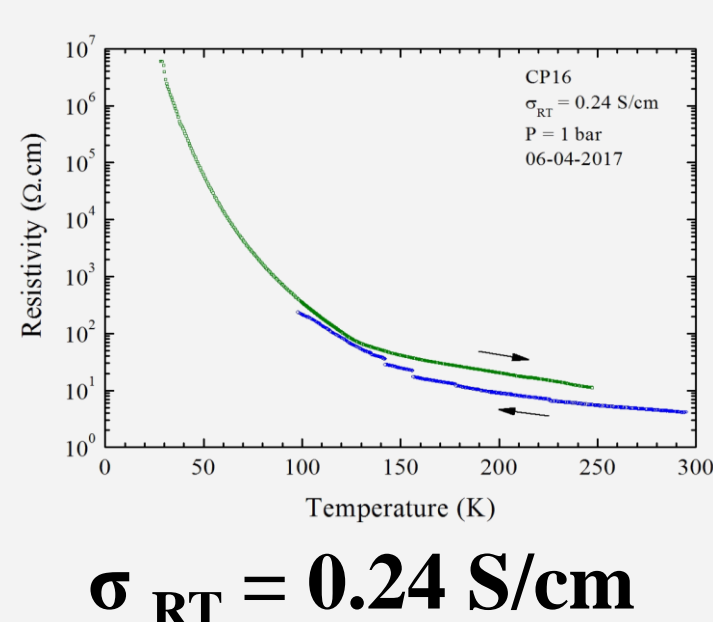
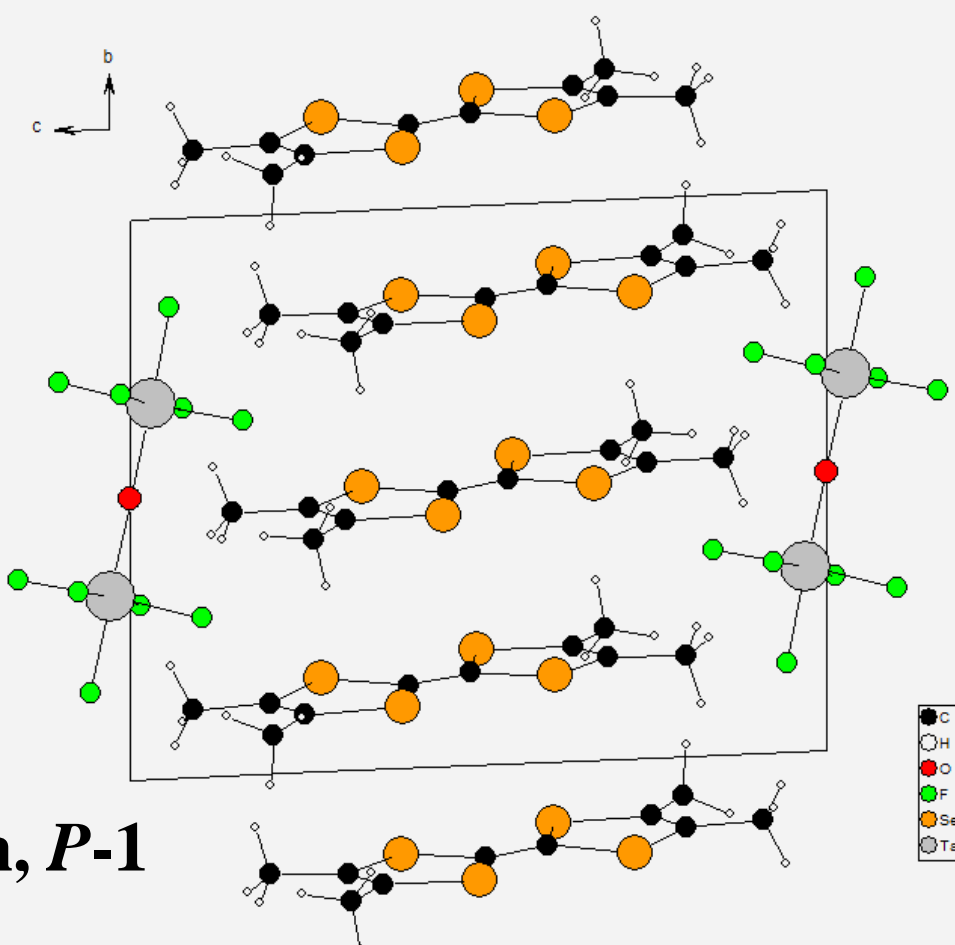


This phase was first reported (*Synth. Met.* 1991, 42, 1939) as (TMTSeF)₂Ta₂F₁₁



Prisms

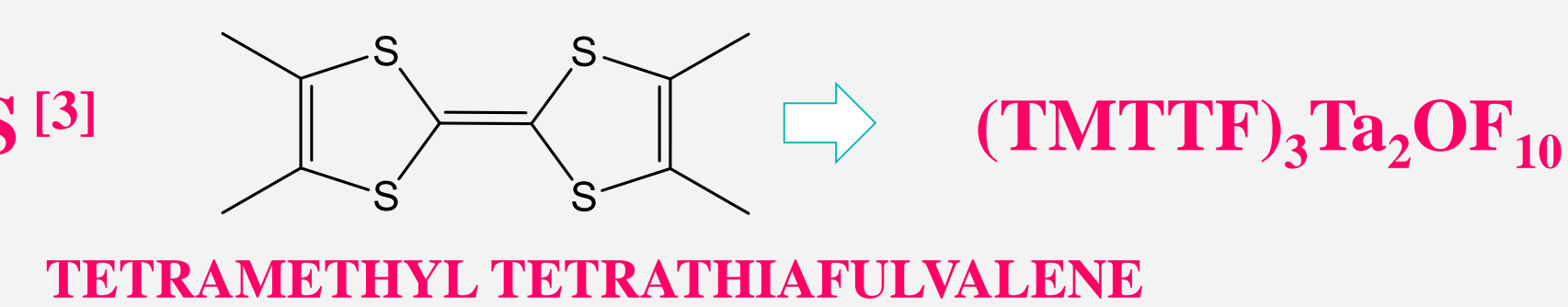
Unit cell, T = 293K
 $a = 7.8356(9) \text{ \AA}$ $\alpha = 90.28(1)^\circ$
 $b = 10.993(1) \text{ \AA}$ $\beta = 80.09(1)^\circ$
 $c = 13.558(2) \text{ \AA}$ $\gamma = 77.836(8)^\circ$
 $V = 1123.6(2) \text{ \AA}^3$
 $Z=1$, R1 = 2.87%, Triclinic system, P-1



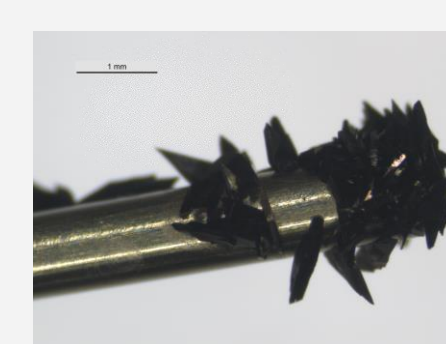
D = TMTXF

Solvent: CH₂Cl₂
 T = 20°C, I = 1 μA

X = S [3]

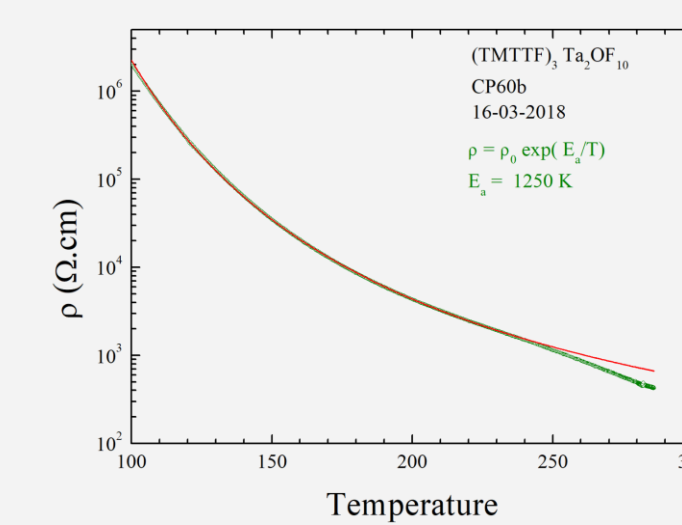
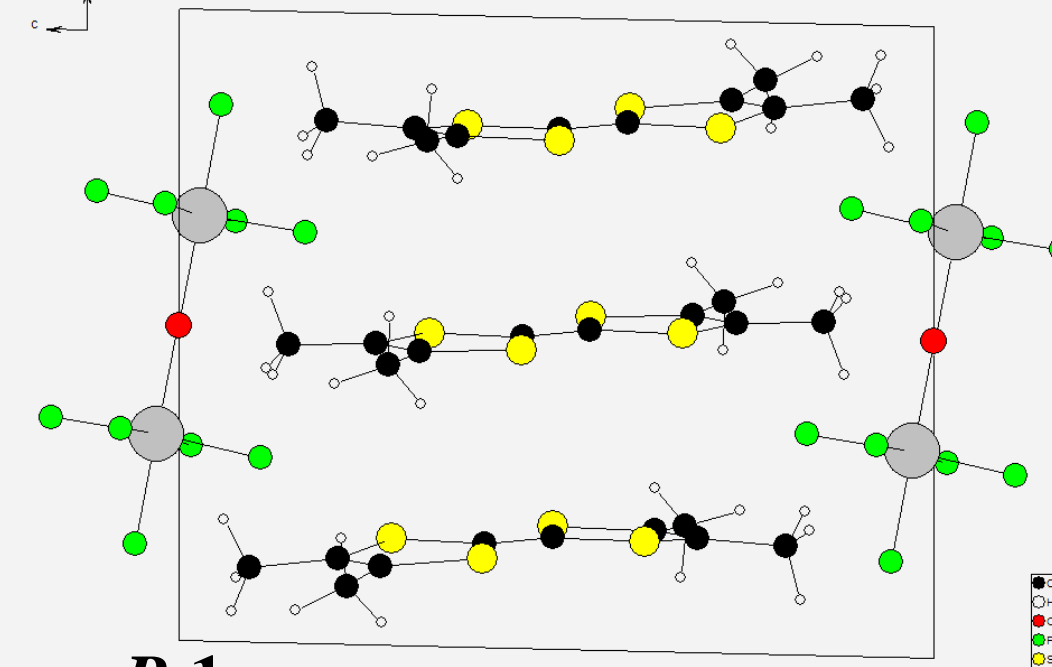


Mentioned in [4] concerning the preparation of (TMTTF)₂TaF₆:
 "Occasionally, another poly-type 3:1 salt, (TMTTF)₃(TaF₅)₂O, was formed."



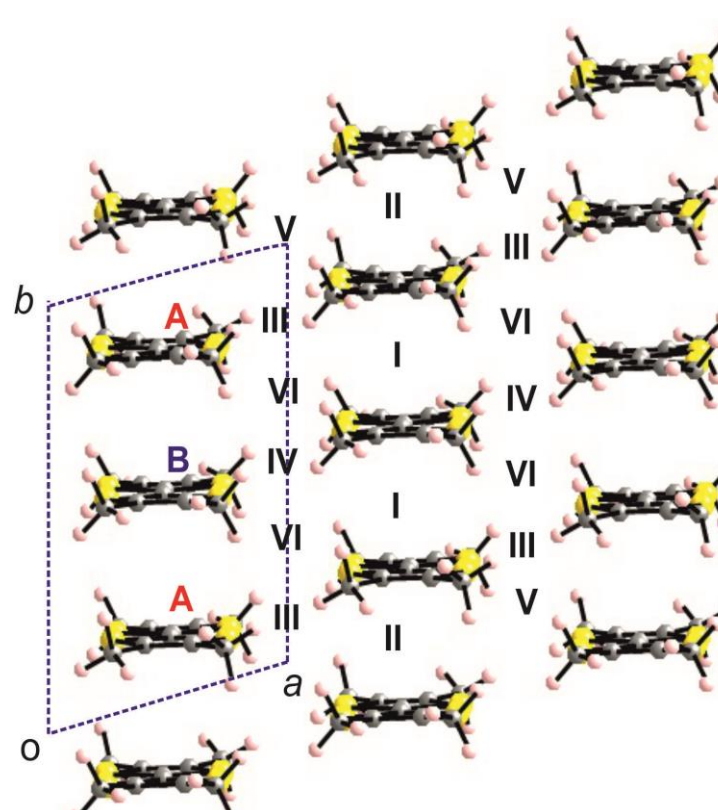
Thick plates

Unit cell, T = 293K
 $a = 7.8130(1) \text{ \AA}$ $\alpha = 86.153(7)^\circ$
 $b = 10.960(1) \text{ \AA}$ $\beta = 78.048(4)^\circ$
 $c = 13.091(1) \text{ \AA}$ $\gamma = 77.49(1)^\circ$
 $V = 1070.4(2) \text{ \AA}^3$
 $Z=1$, R1 = 3.67%, Triclinic system, P-1



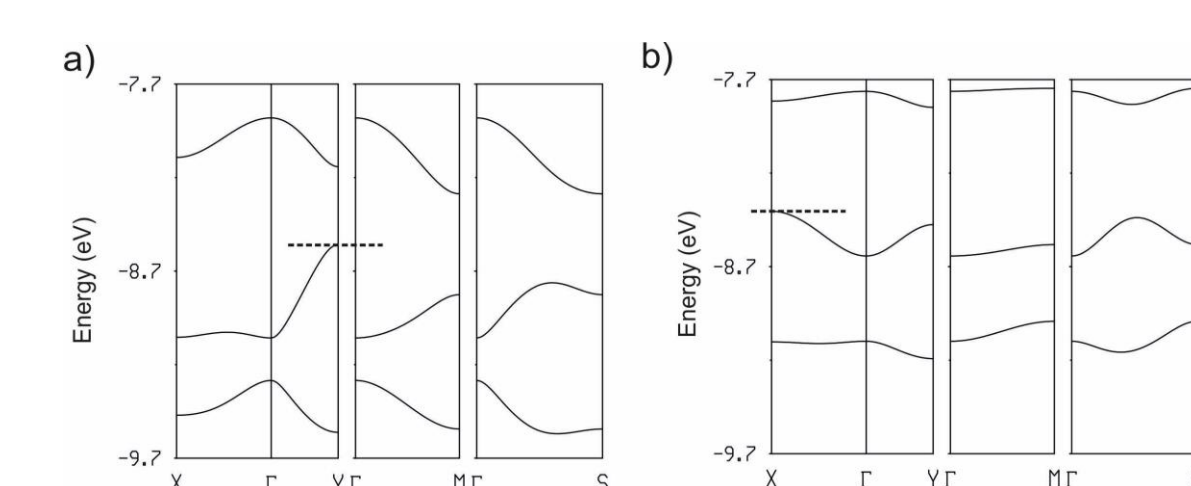
Uniform stacking of oxidized TMTXF molecules / Semi-conducting materials

Electronic structures: The donor layer of each salt is built from centrosymmetric A-B-A trimers of donor molecules. The intermolecular interaction I is by far the strongest and suggests a 1D conductivity. For the TMTTF salt all other interactions are considerably weaker. In TMTSeF salt interaction II is substantial and this difference is mostly at the origin of the pseudo-1D behavior of TMTSeF salt as well as the 100 times less conductivity properties of TMTTF salt.



Interaction (type)	(TMTSeF) ₃ Ta ₂ OF ₁₀	(TMTTF) ₃ Ta ₂ OF ₁₀
I (A-B)	0.7561	0.7368
II (A-A)	0.3458	0.0105
III (A-A)	0.0261	0.0360
IV (B-B)	0.0349	0.0295
V (A-A)	0.0696	0.1302
VI (A-B)	0.0118	0.0205

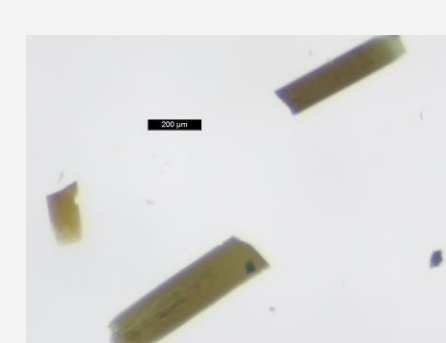
Abs. values of the $|\beta_{\text{HOMO-HOMO}}|$ intermolecular interaction energies (eV) for the different donor...donor interactions.



Calc. band structure for the donor layers of (TMTSeF)₃Ta₂OF₁₀ (a) and (TMTTF)₃Ta₂OF₁₀ (b) where the dashed line refers to the Fermi level.

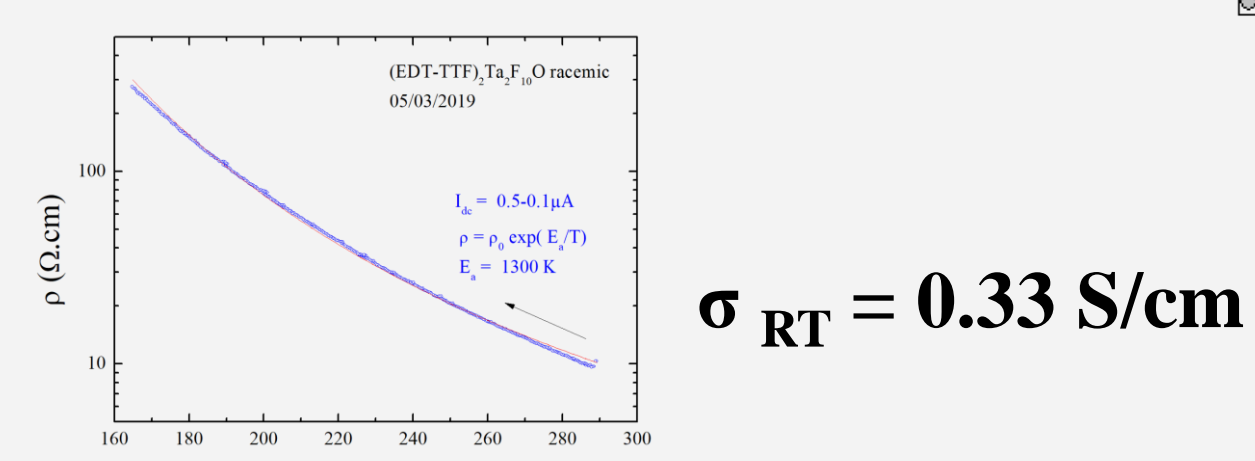
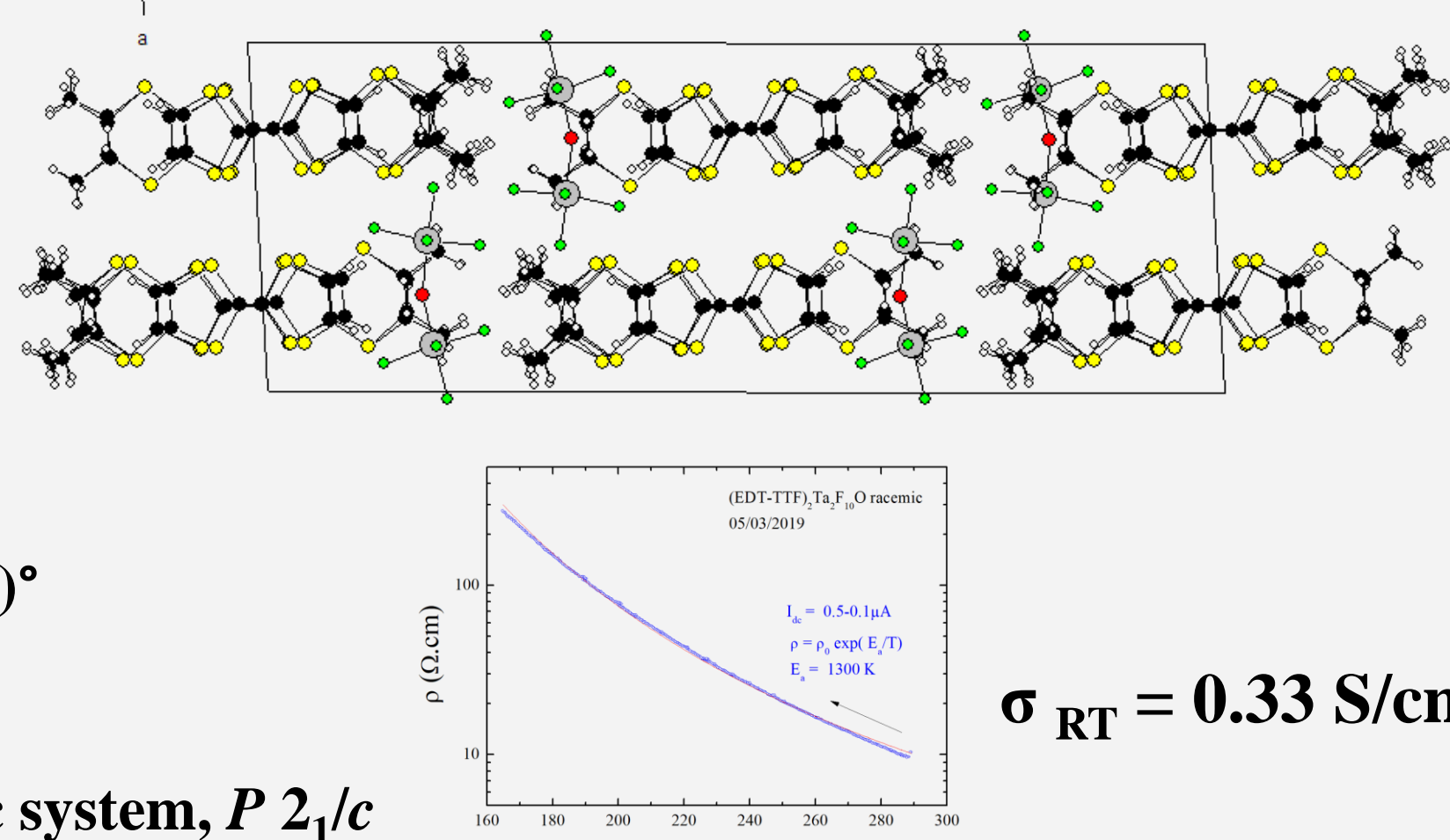
(RAC)-(DM-EDT-TTF)₃Ta₂OF₁₀

Solvent: CHCl₃
 T = 20°C, I = 0.5 μA



Thin plates

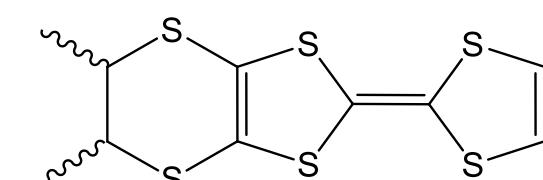
Unit cell, T = 150K
 $a = 12.5633(6) \text{ \AA}$ $\alpha = 90^\circ$
 $b = 10.7252(9) \text{ \AA}$ $\beta = 93.226(5)^\circ$
 $c = 34.292(2) \text{ \AA}$ $\gamma = 90^\circ$
 $V = 4613.3(5) \text{ \AA}^3$
 $Z=4$, R1 = 9.52%, Monoclinic system, P 2₁/c



The enantiopure is about 3 times more conductive

D = DM-EDT-TTF

DIMETHYL ETHYLENEDITHIO TETRATHIAFULVALENE

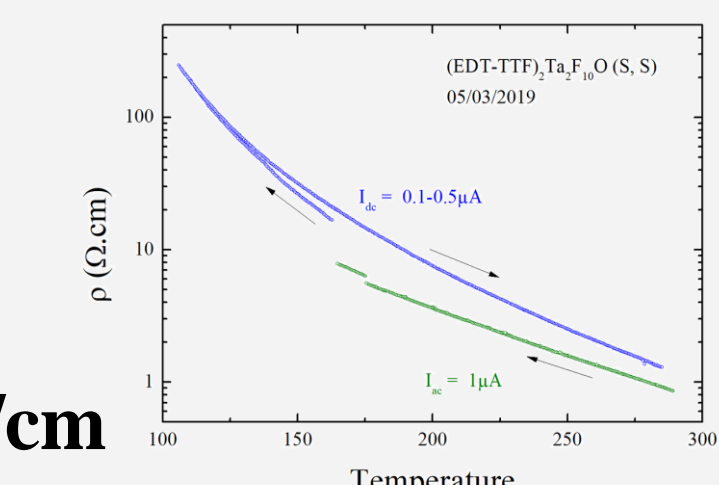
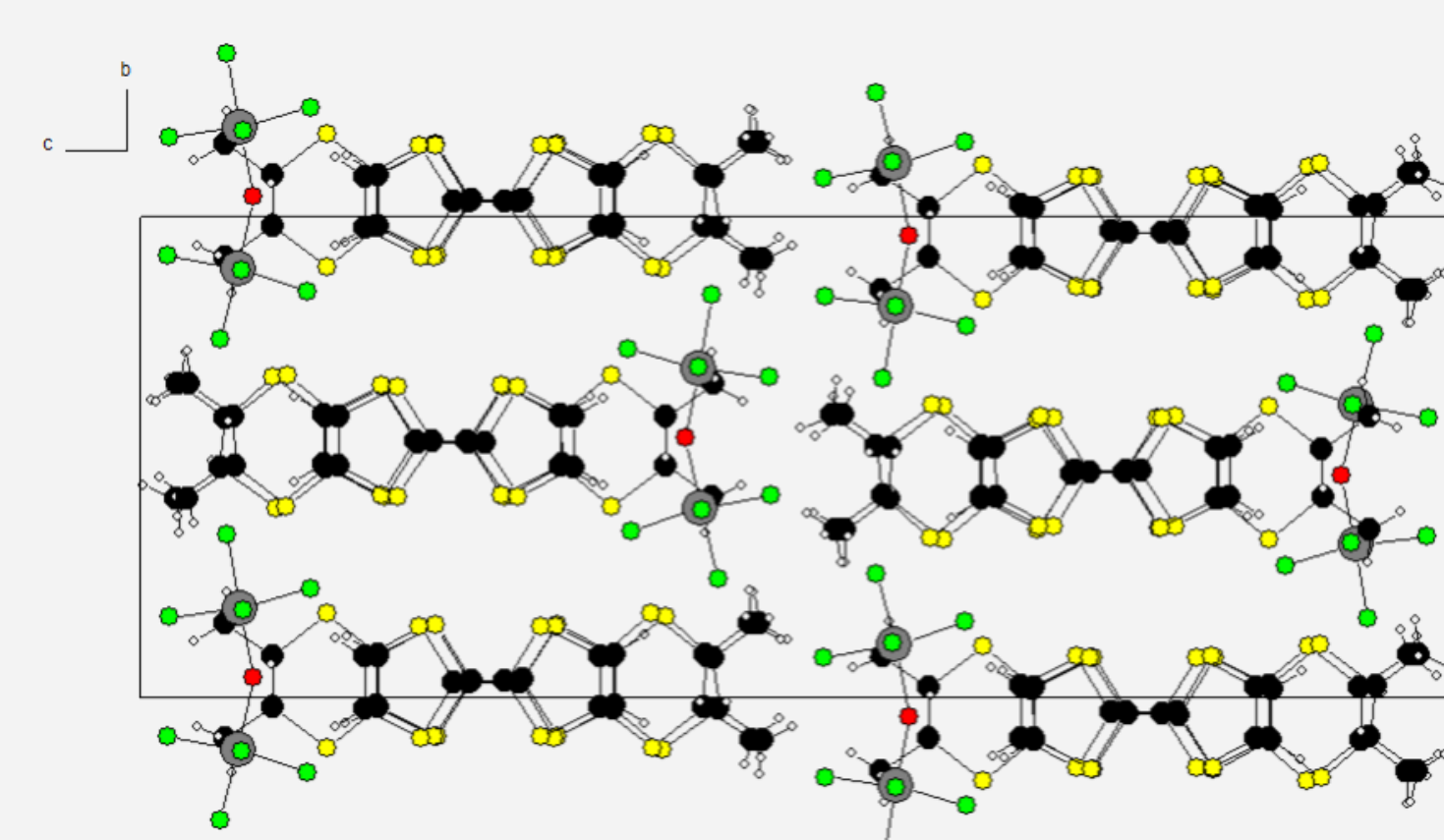


(S,S)-(DM-EDT-TTF)₃Ta₂OF₁₀



Needles

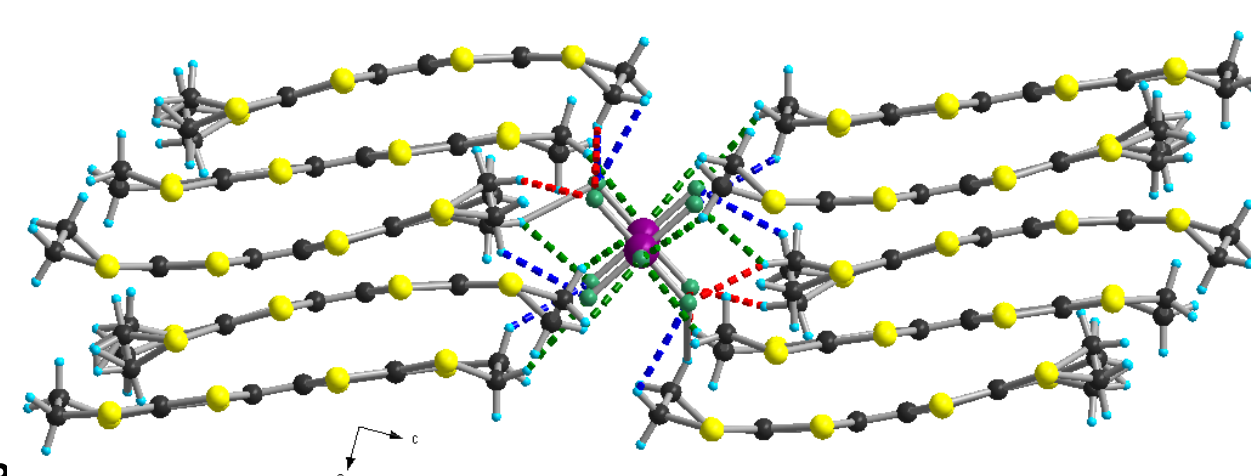
Unit cell, T = 293K
 $a = 10.8773(2) \text{ \AA}$ $\alpha = 90^\circ$
 $b = 12.6267(2) \text{ \AA}$ $\beta = 90^\circ$
 $c = 34.4236(8) \text{ \AA}$ $\gamma = 90^\circ$
 $V = 4727.9(2) \text{ \AA}^3$
 $Z=4$, R1 = 4.38%, Orthorhombic system, P 2₁2₁2₁



σ_{RT} = 1.1 S/cm

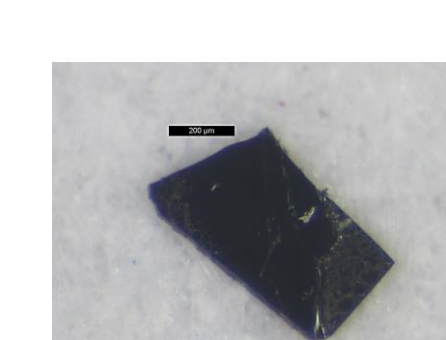
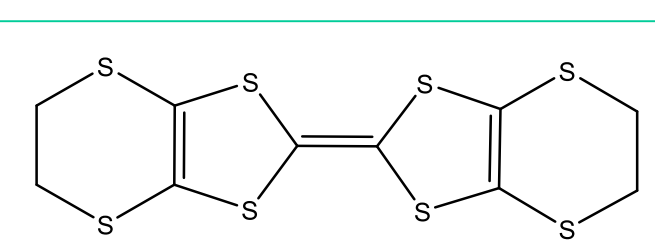
Solvent: CH₂Cl₂
 T = 20°C, I = 0.5 μA

Unit cell, T = 293K
 $a = 12.615(1) \text{ \AA}$ $\alpha = 90^\circ$
 $b = 11.984(1) \text{ \AA}$ $\beta = 90.234(9)^\circ$
 $c = 16.747(1) \text{ \AA}$ $\gamma = 90^\circ$
 $V = 2531.8(3) \text{ \AA}^3$
 $Z=2$, R1 = 6.50%, Monoclinic system, P 2₁/a

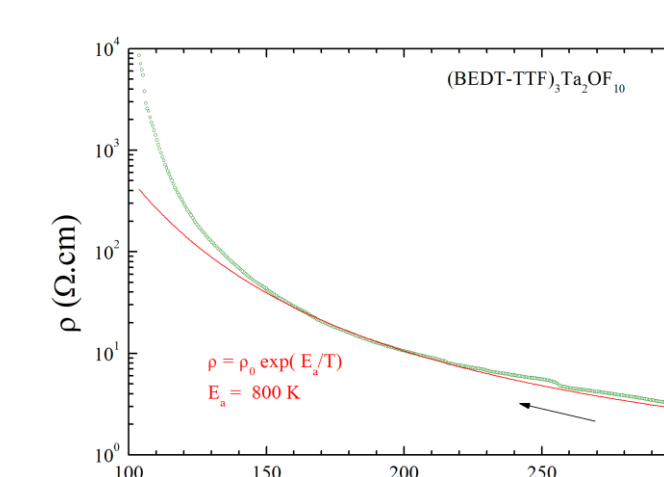
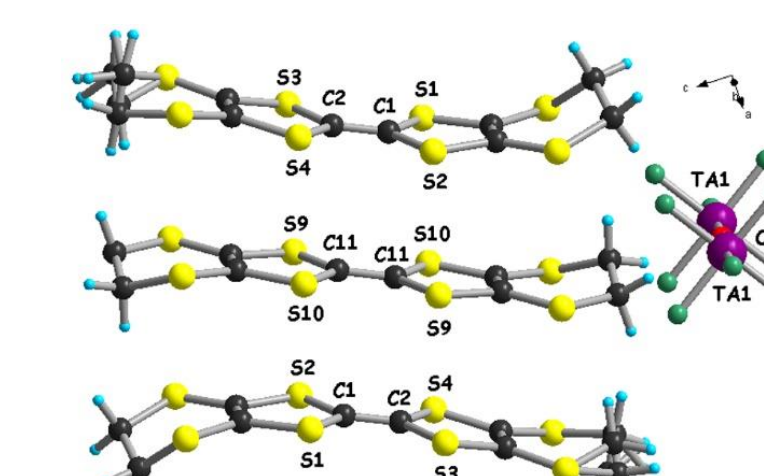


D = BEDT-TTF

BIS ETHYLENEDITHIO TETRATHIAFULVALENE



Plates



Compared to the previous salts presenting the same 3:1 stoichiometry, i.e. (TMTXF)₃Ta₂F₁₀O, the anions are rotated by 90° with respect to the donors like in DM-EDT-TTF. Again, fluorine atoms engage in intermolecular hydrogen bonding with hydrogen atoms of the ethylene groups.

The crystalline parameters correspond to those of a phase apparently wrongly described as (BEDT-TTF)₃Ta₂F₁₁ more than 30 years ago [5] with the donor packing and their arrangement with respect to the anions being the same.

There is a band gap separating the empty and filled bands and (BEDT-TTF)₃Ta₂F₁₀O is a regular semiconductor.

[1] N. Mroweh, C. Mézière, M. Allain, P. Auban-Senzier, E. Canadell, N. Avarvari, *Chem. Sci.*, 2020, 11 (37), 10078

[2] P. Batail, K. Boubekeur, M. Fourmigué, J.C. Gabriel, *Chem. Mater.*, 1998, 10, 3005

[3] J.M. Fabre, L. Giral, A. Gouasmia, H.J. Cristau, Y. Ribeill, *Bull. Soc. Chim. Fr.*, 1987, N°5, 823

[4] F. Iwase, K. Sugiura, K. Furukawa, T. Nakamura, *J. Phys. Soc. JPN*, 2009, 78, 10, 104717-1

[5] J. V. Acrivos, H. P. Hughes, S. S. P. Parkin, *J. Chem. Phys.*, 1987, 86, 1780; J. V. Acrivos, *Mol. Cryst. Liq. Cryst.*, 1996, 284, 411.