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Radical cation salts of TTF donors with the Ta₂OF₁₀ Anion

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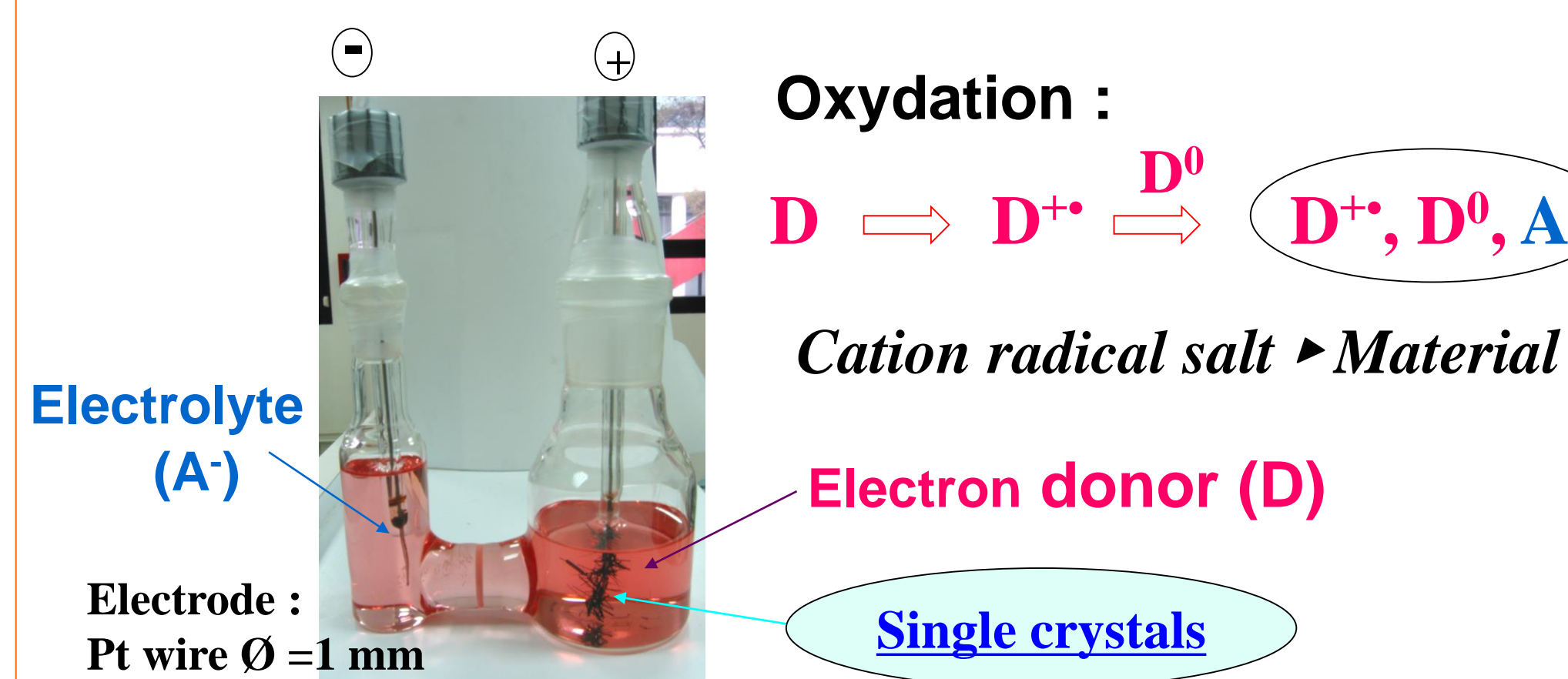
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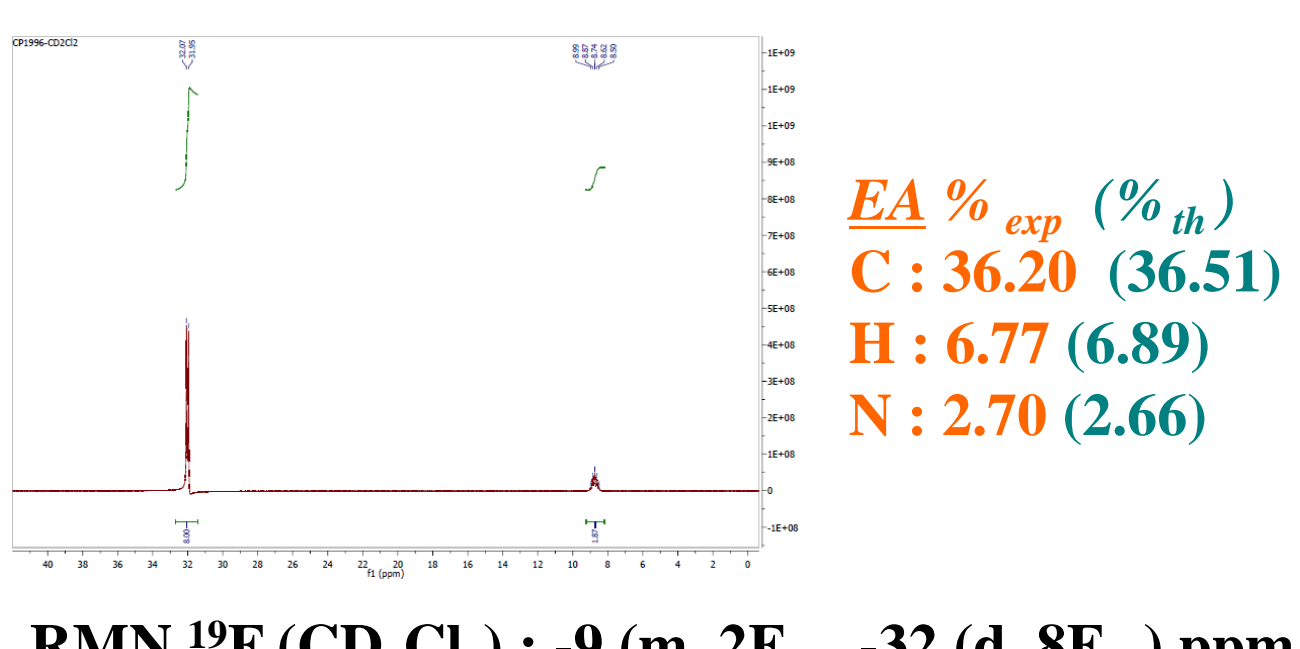
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³Institut de Ciència de Materials de Barcelona (CSIC), Campus de la UAB, E-08193 Bellaterra, Spain

Electrocrystallization set up [1]

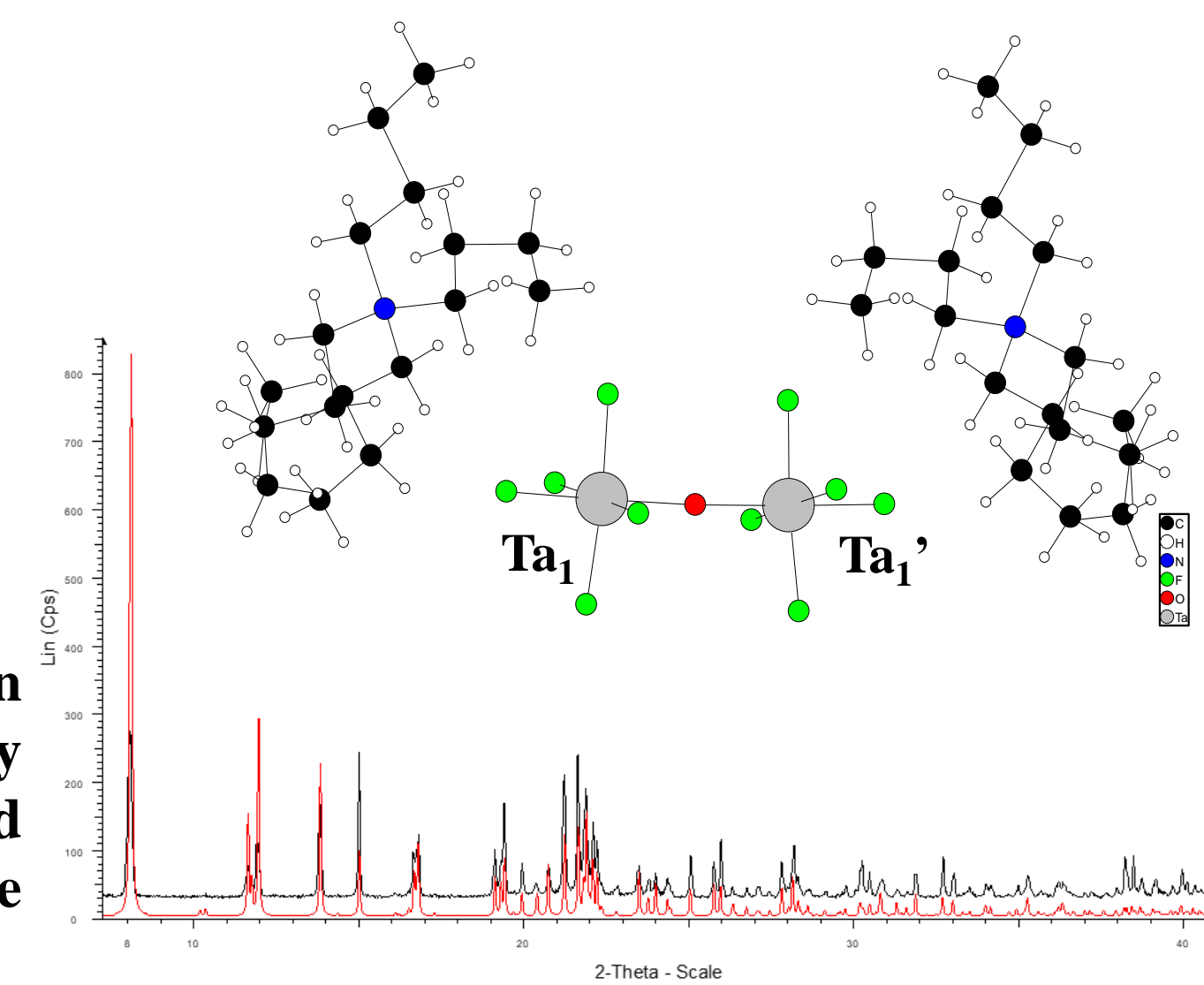


(TBA)₂(Ta₂OF₁₀) synthesis

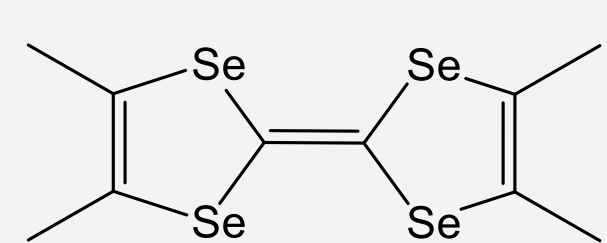


Unit cell, T = 293K
a = 21.230(2) Å $\alpha = 90^\circ$
b = 14.2060(10) Å $\beta = 124.970(4)^\circ$
c = 18.083(2) Å $\gamma = 90^\circ$
V = 4469.1(7) Å³
Z=4, R1 = 4.39%
Monoclinic system, C 2/c

X-ray powder diffractogram on crushed crystals (black) perfectly indexed with the simulated diffractogram from the single crystal structure (red).



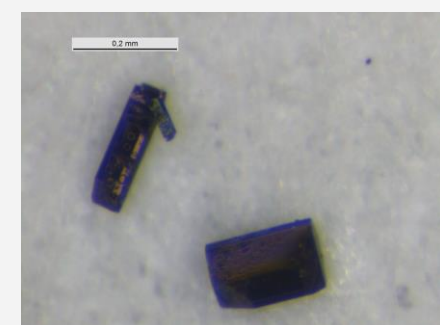
D = TMTSeF



(TMTSeF)₃Ta₂OF₁₀

TETRAMETHYL TETRASELEFULVALENE

Solvent: CH₂Cl₂
T = 20°C, I = 1 μA

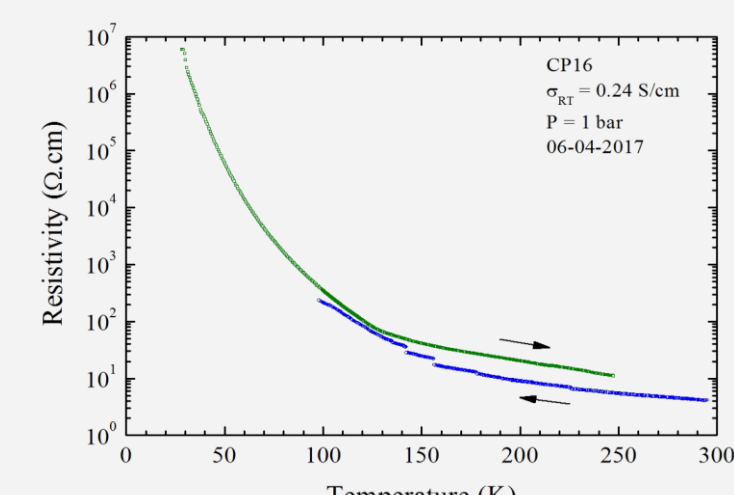
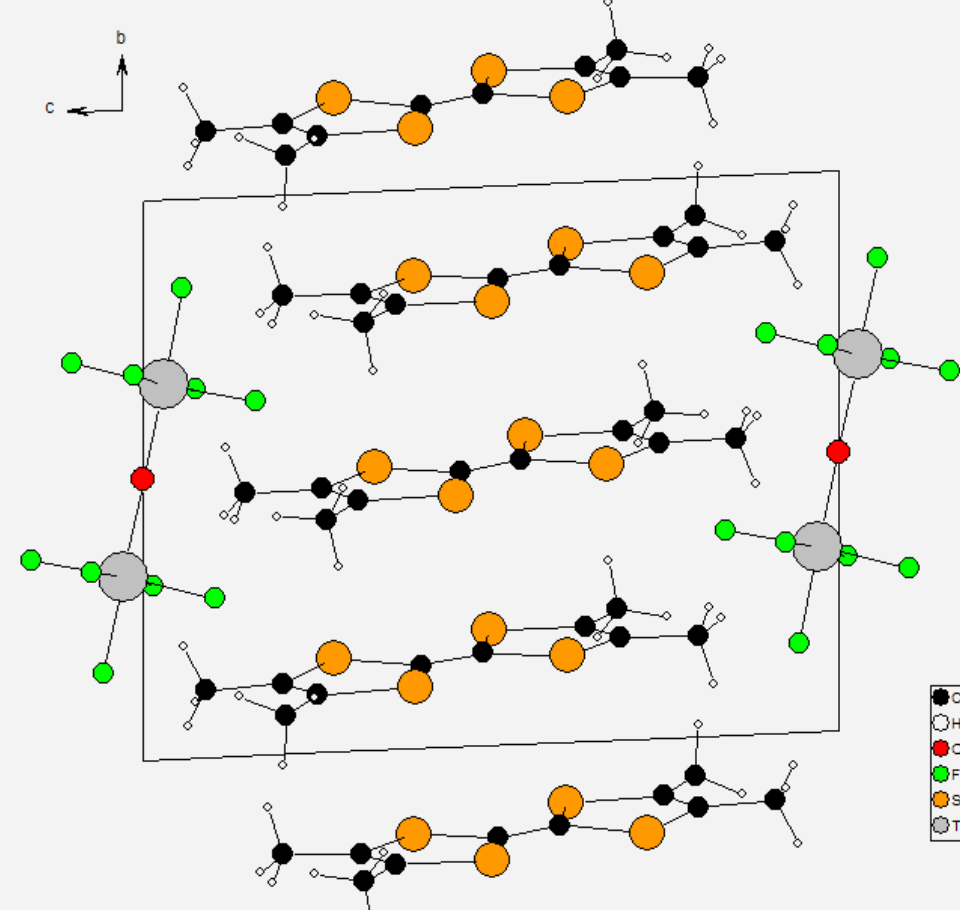


Prisms

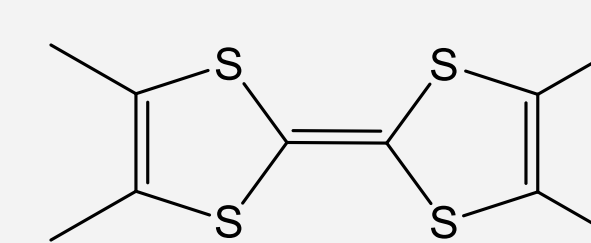
Unit cell, T = 293K
a = 7.8356(9) Å $\alpha = 90.28(1)^\circ$
b = 10.993(1) Å $\beta = 80.09(1)^\circ$
c = 13.558(2) Å $\gamma = 77.836(8)^\circ$
V = 1123.6(2) Å³
Z=1, R1 = 2.87%
Triclinic system, P-1

$\sigma_{RT} = 0.24$ S/cm

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



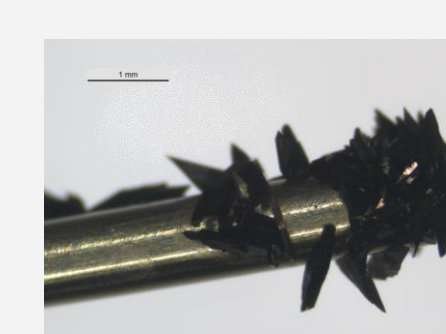
D = TMTTF [2]



(TMTTF)₃Ta₂OF₁₀

TETRAMETHYL TETRATHIAFULVALENE

Solvent: CH₂Cl₂
T = 20°C, I = 1 μA

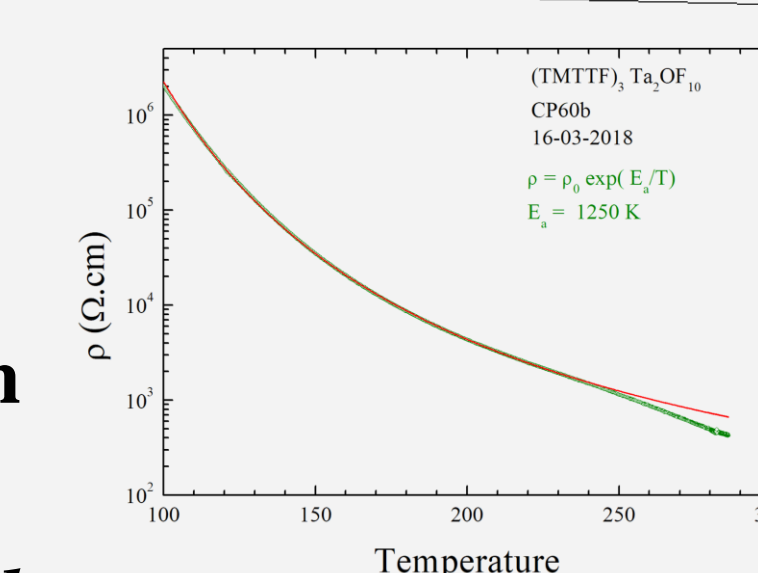
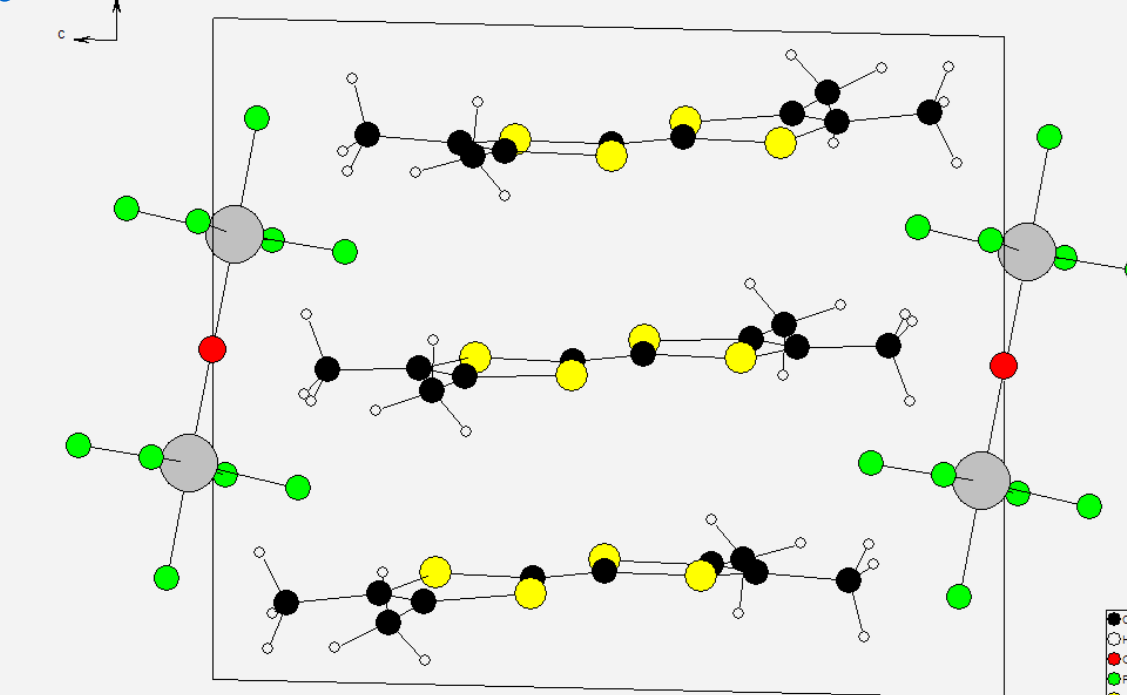


Thick plates

Unit cell, T = 293K
a = 7.8130(1) Å $\alpha = 86.153(7)^\circ$
b = 10.960(1) Å $\beta = 78.048(4)^\circ$
c = 13.091(1) Å $\gamma = 77.49(1)^\circ$
V = 1070.4(2) Å³
Z=1, R1 = 3.67%
Triclinic system, P-1

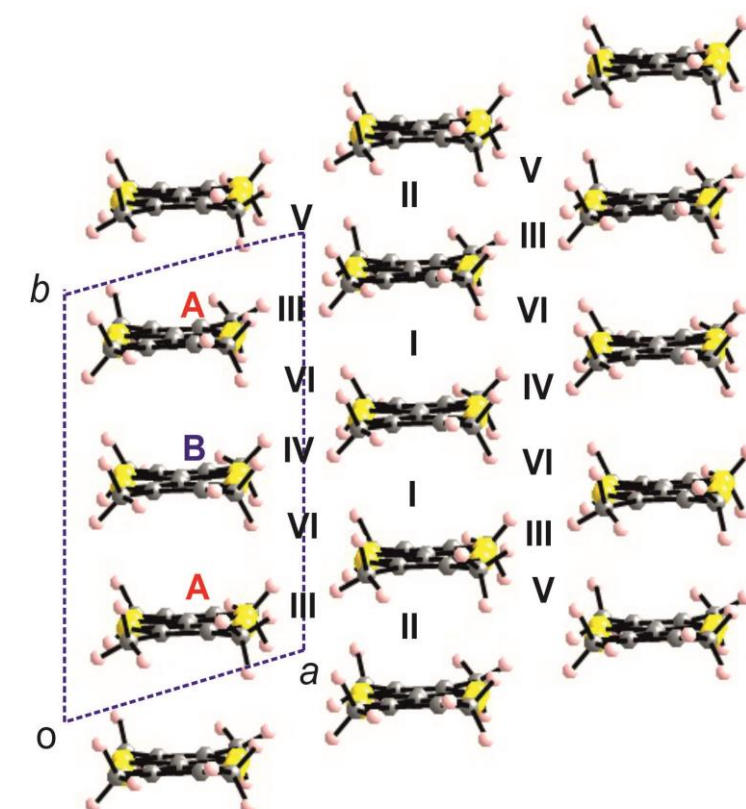
$\sigma_{RT} = 0.0025$ S/cm

Mentioned in [3] concerning the preparation of (TMTTF)₂TaF₆: "Occasionally, another polytype 3:1 salt, (TMTTF)₃(TaF₃)₂O, was formed."



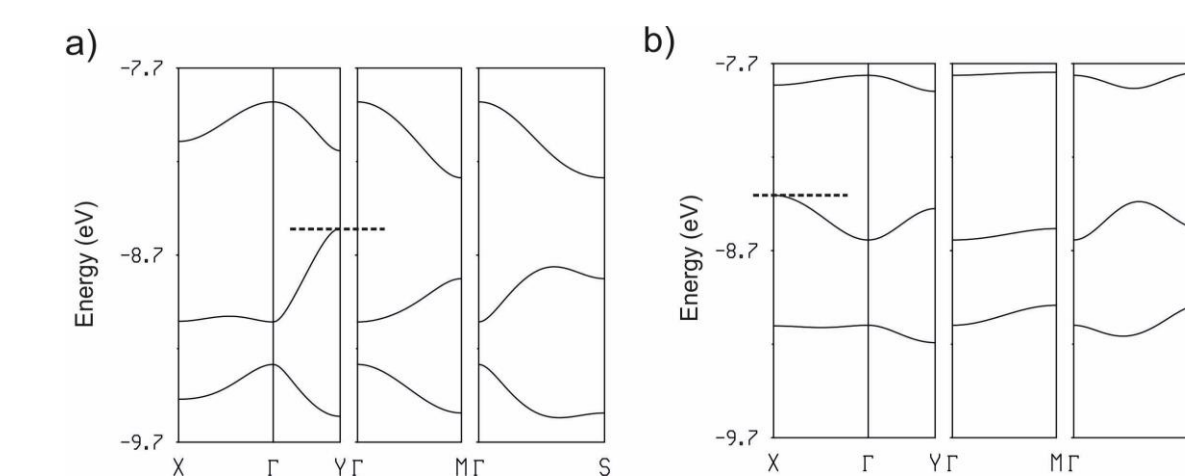
Uniform stacking of oxidized TMTXF molecules / Semi-conducting materials

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 stronger 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 10 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

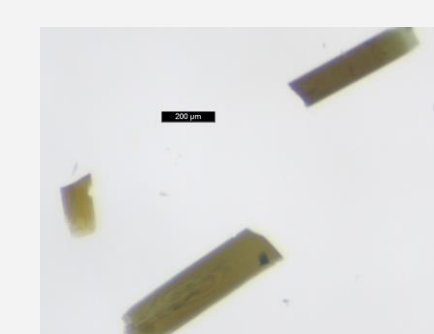
Abs. values of the $|\beta_{HOMO-HOMO}|$ intermolecular interaction energies (eV) for the different donor...donor interactions.



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

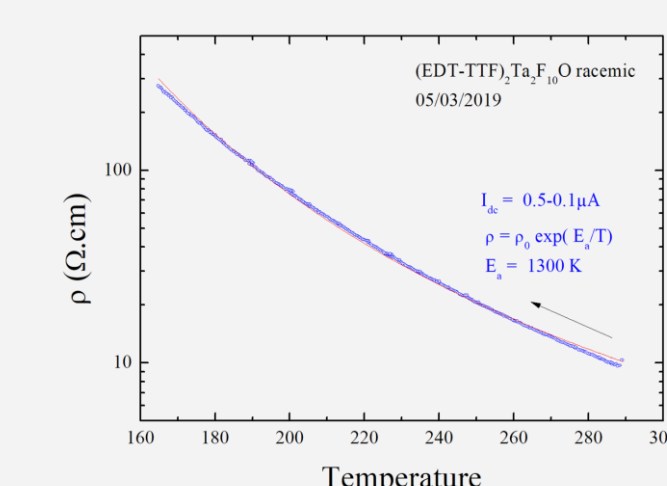
(RAC)-(DM-EDT-TTF)₃Ta₂OF₁₀

Solvent: CHCl₃
T = 20°C, I = 0.5 μA



Thin plates

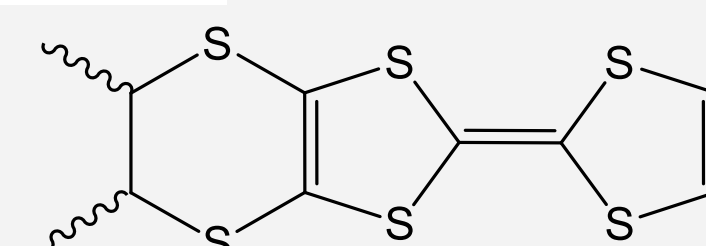
Unit cell, T = 150K
a = 12.5633(6) Å $\alpha = 90^\circ$
b = 10.7252(9) Å $\beta = 93.226(5)^\circ$
c = 34.292(2) Å $\gamma = 90^\circ$
V = 4613.3(5) Å³
Z=4, R1 = 9.52%
Monoclinic system, P 2₁/c



$\sigma_{RT} = 0.33$ S/cm

The enantiopure is about 3 times more conductive

D = DM-EDT-TTF



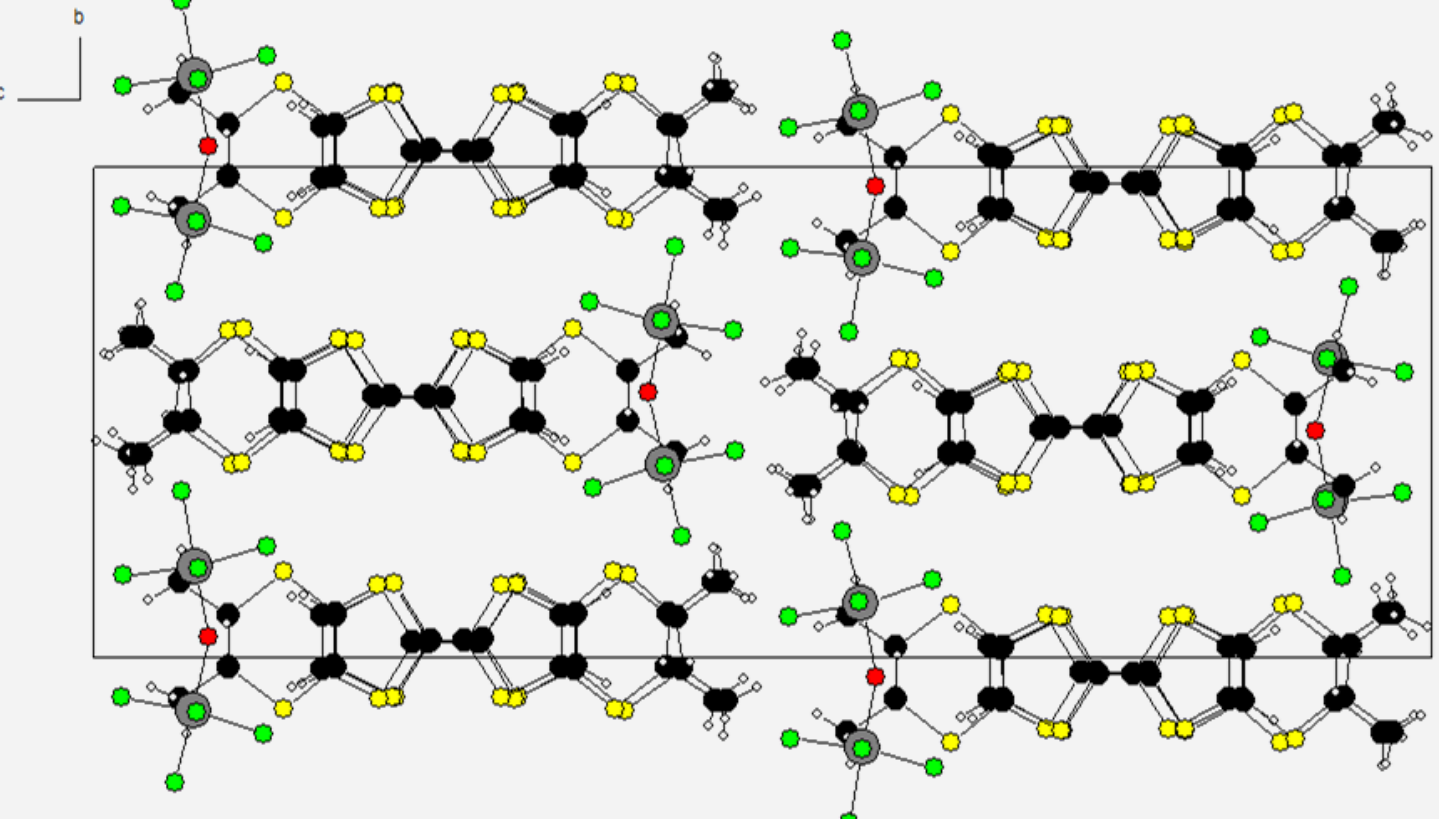
DIMETHYL ETHYLENEDITHIO TETRATHIAFULVALENE



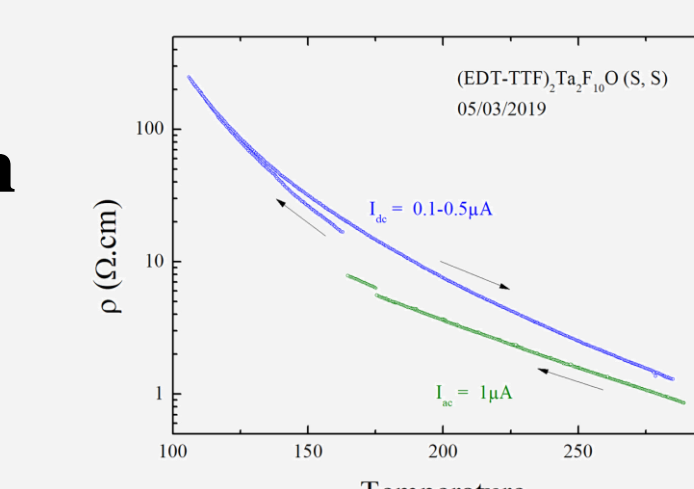
Needles

Unit cell, T = 293K
a = 10.8773(2) Å $\alpha = 90^\circ$
b = 12.6267(2) Å $\beta = 90^\circ$
c = 34.4236(8) Å $\gamma = 90^\circ$
V = 4727.9(2) Å³
Z=4, R1 = 4.38%
Orthorhombic system, P 2₁2₁2₁

(S,S)-(DM-EDT-TTF)₃Ta₂OF₁₀



$\sigma_{RT} = 1.1$ S/cm



Synthesis of new conducting (chiral) TTF radical cation salts based on the unexplored $Ta_2OF_{10}^{2-}$;

Investigation of the electrical magnetochiral anisotropy (eMChA) effect on the chiral salts.

Outlooks

Attempts to prepare $Ta_2F_{11}^-$ anion:

TaF_5 $\xrightarrow{TBATaF_6 \text{ or } KTaF_6}$ No evidence of the formation of $Ta_2F_{11}^-$
DCM solution
Or dry process : ball mill, microwaves