Chiral Electroactive Precursors and Materials

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Conferinta Diaspora Stiintifica, Bucuresti, 21-24 Septembrie 2010

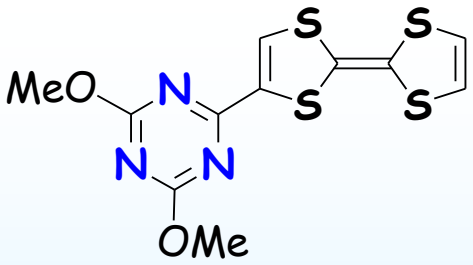
Current research topics in the group

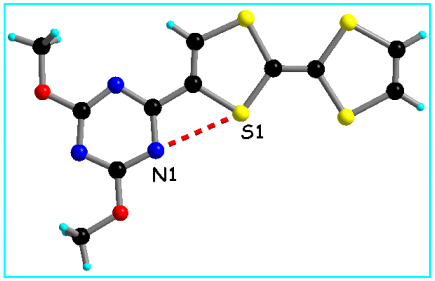
1. Chirality in tetrathiafulvalenes (TTF)

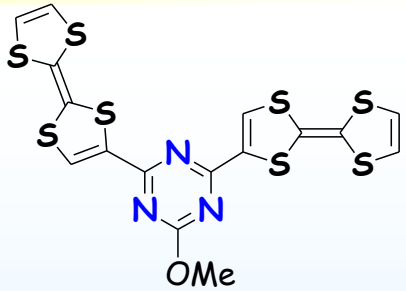
2. Electroactive ligands: TTF-pyridines, -phosphines, -oxazolines
- multifunctional materials
- enantioselective catalysis

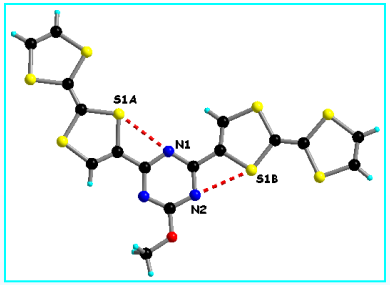
D. Lorcy, N. Bellec, M. Fourmigué, N. Avarvari, *Coord. Chem. Rev.* **2009**, *253*, 1398-1438.

3. Covalent donor-acceptor compounds: TTF-triazines



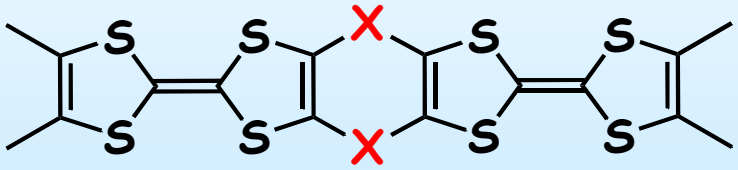






Chem. Eur. J. **2009**, *15*, 380.

4. Intramolecular mixed valence species



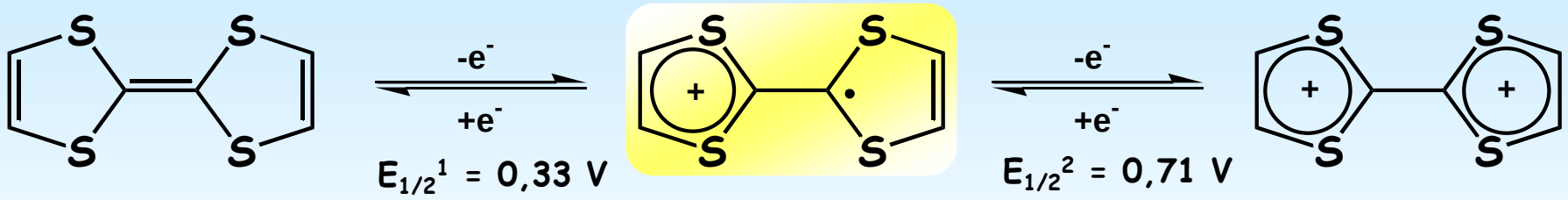
X = PPh, $SiMe_2$, $GeMe_2$
X = P=O, P=S, P[M]

Chem. Commun. **2004**, 2794.
Chem. Eur. J. **2007**, *13*, 5394.
Organometallics **2009**, *28*, 3691.

5. Functional phosphonate ligands

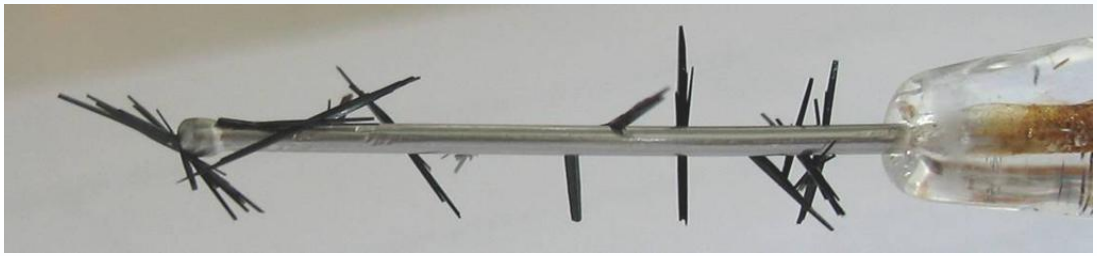
New J. Chem. **2010**, DOI : 10.1039/C0NJ00204F

Tetrathiafulvalene (TTF) and Derivatives



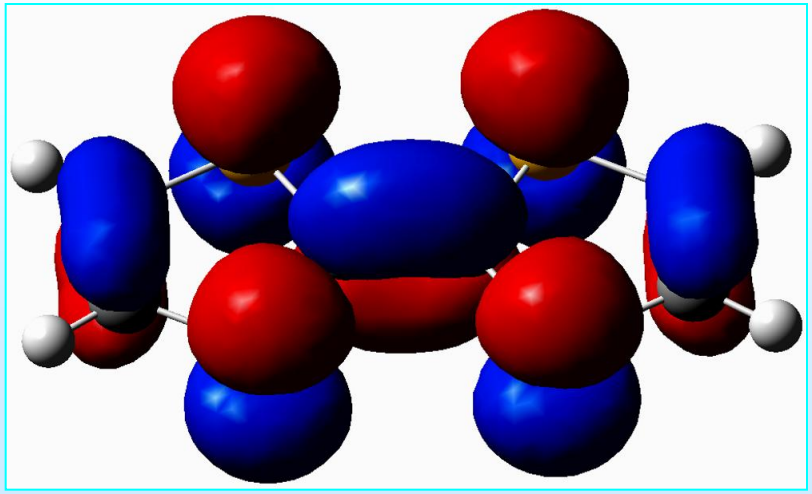
Electrocrystallization
Chemical oxidation

salts and charge transfer compounds with conducting and/or magnetic propertiesdetermined by the solid state organization



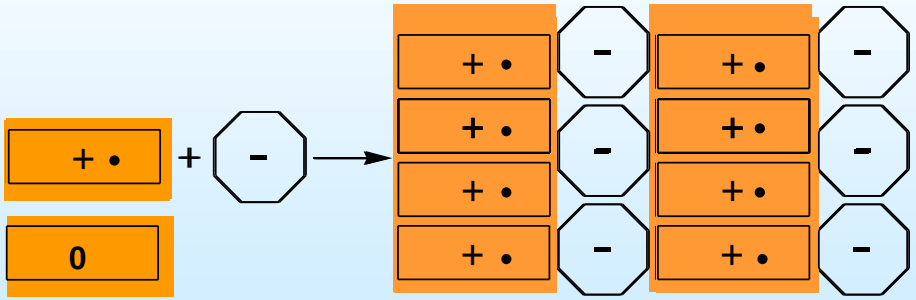
Pt electrode

HOMO TTF and SOMO $TTF^{+\cdot}$



- crystallization in the presence of anions

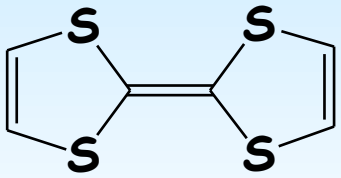
organic-inorganic segregation



mixed valence

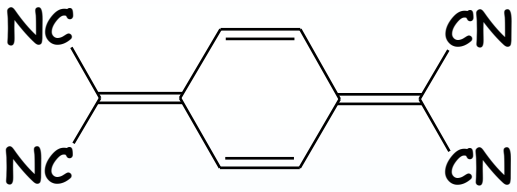
Tetrathiafulvalene (TTF) and Derivatives

Chemical oxidation



TTF, E_{ox} = 0.33 V

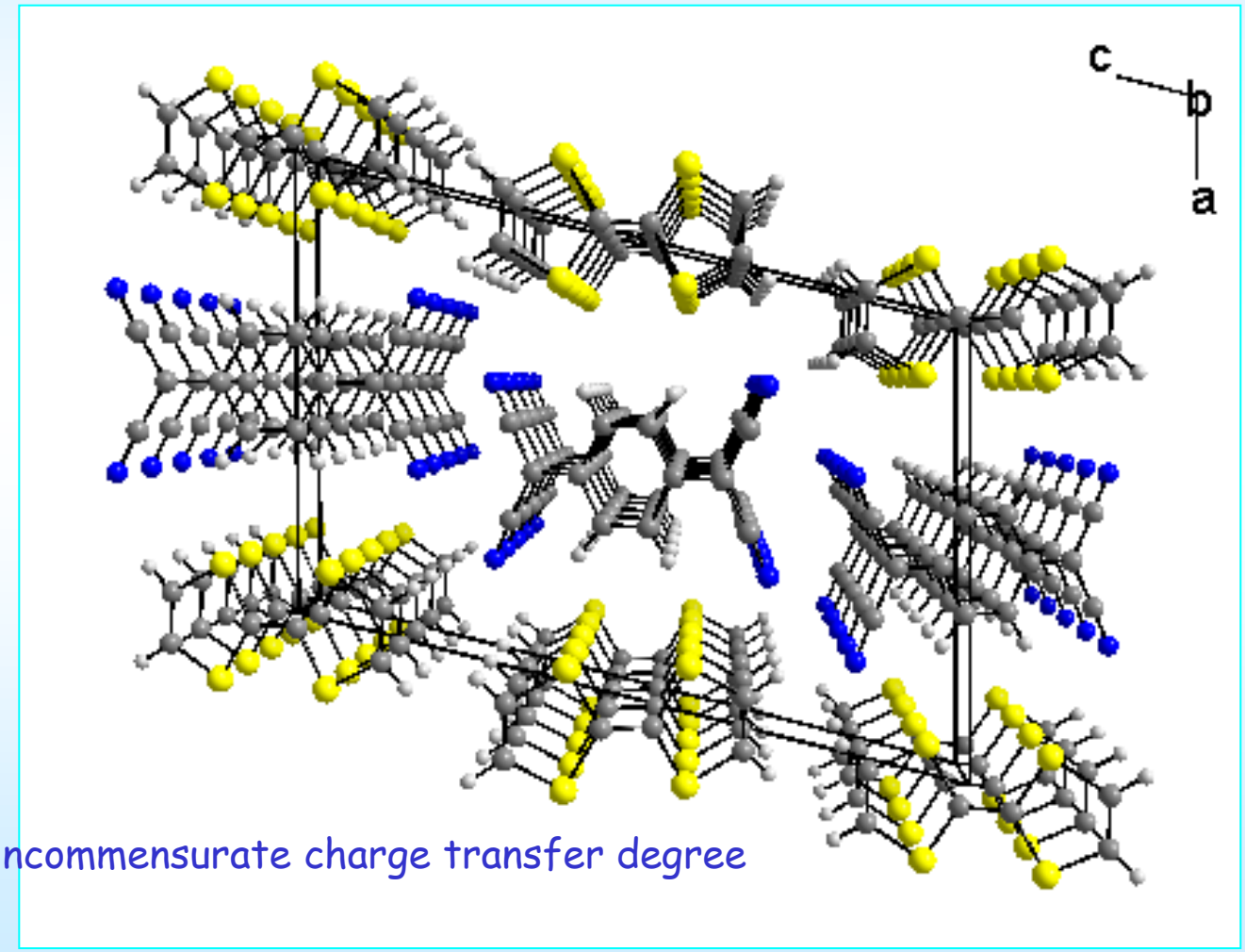
+



TCNQ, E_{red} = 0.17 V

$TTF^{\delta+}$-$TCNQ^{\delta-}$

TTF-TCNQ, an organic metal



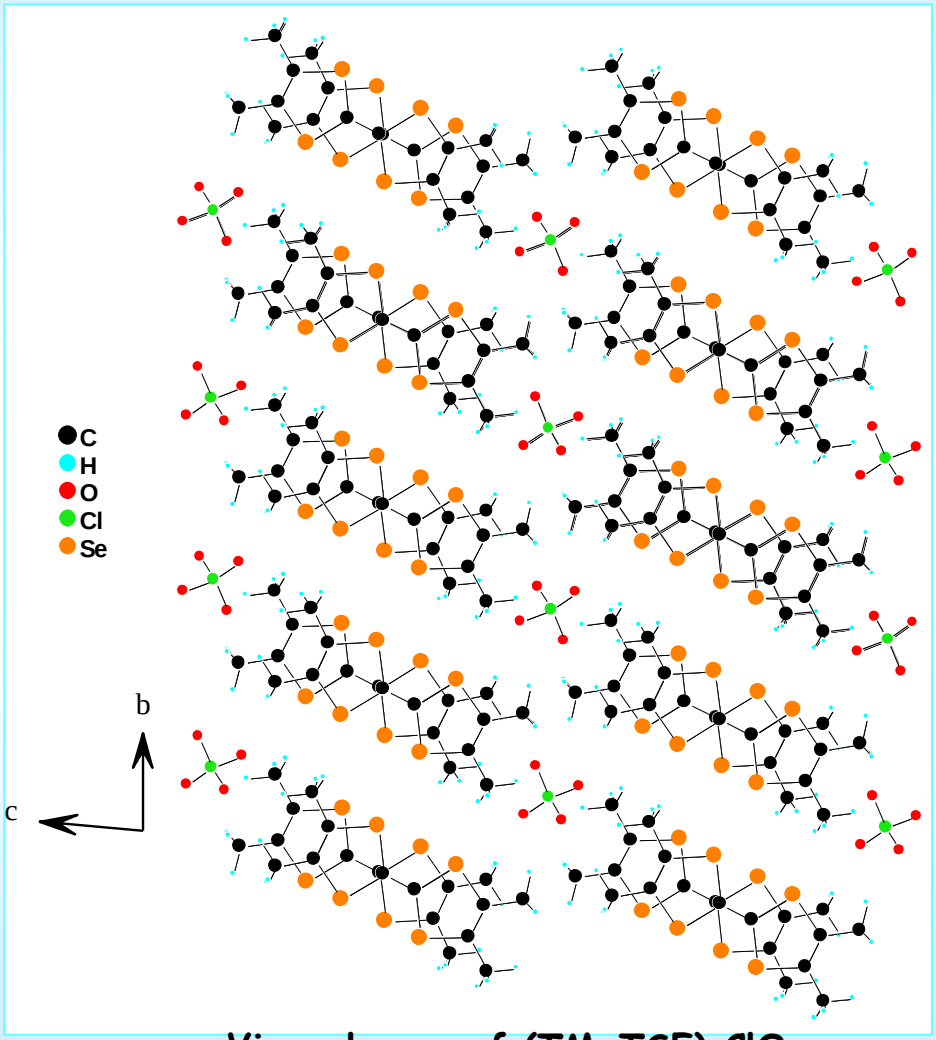
incommensurate charge transfer degree

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

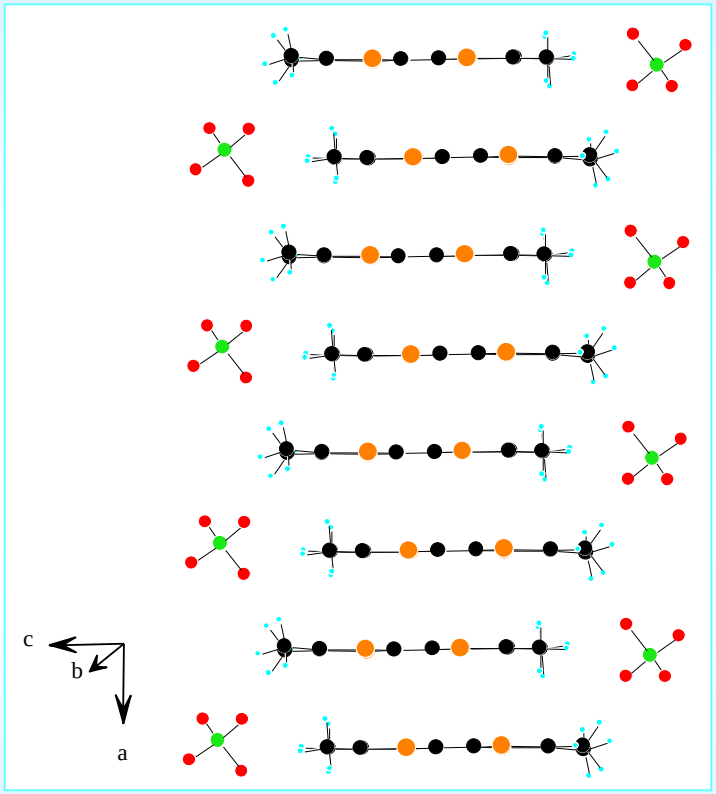
Tetrathiafulvalene (TTF) and Derivatives

Electrocrystallization

$(TM\text{-}TSF)_2X$ (X = PF_6^-, ClO_4^-, ReO_4^-) :a series of superconducting salts



View along *a* of $(TM\text{-}TSF)_2ClO_4$



Stacking in $(TM\text{-}TSF)_2ClO_4$

D. Jérome, A. Mazaud, M. Ribault, K. Bechgaard, *J. Phys. Lett.* **1980**, *41*, L195.

K. Bechgaard et al., *J. Am. Chem. Soc.* **1981**, *103*, 2440.

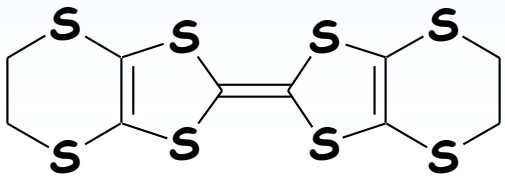
Tetrathiafulvalene (TTF) and Derivatives

Current trends in TTF chemistry

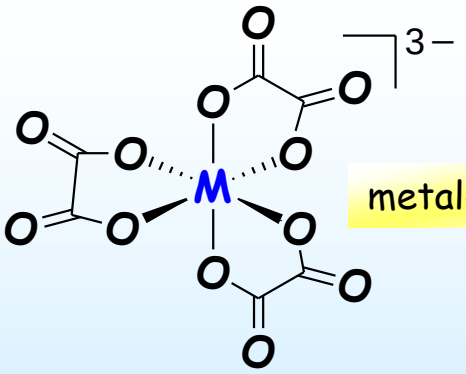
Multifunctional Materials

Coexistence or interplay of two or more physical properties within the same material

- magnetic anions in mixed-valence TTF-based salts → **Magnetic conductors**



BEDT-TTF



M = Fe(III), Cr(III)

metal-oxalates

And Fe(III), Cr(III), Mn(II), Cu(II), etc. based anions

M. Kurmoo, P. Day *et al. J. Am. Chem. Soc.*, **1995**, *117*, 12209.
E. Coronado, C. J. Gómez-García *et al. Nature* **2000**, *408*, 447.
E. Coronado, P. Day *Chem. Rev.* **2004**, *104*, 5419.

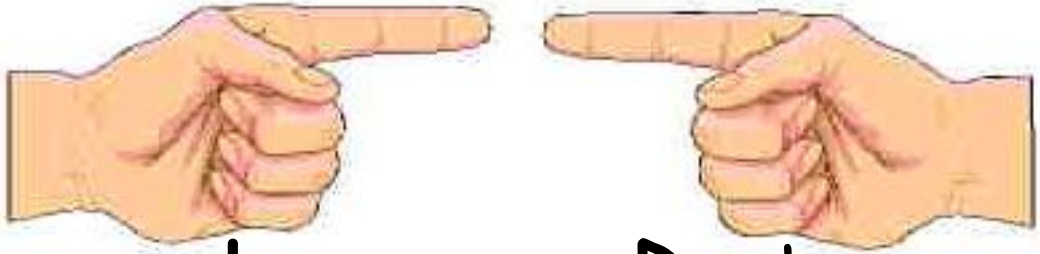
Also chiral magnets: magneto-chiral dichroism

C. Train, R. Gheorghe, V. Krstic, L.-M. Chamoreau, N. S. Ovanesyan, G. L. J. A. Rikken, M. Gruselle, M. Verdaguer *Nature Mater.* **2008**, *7*, 729.

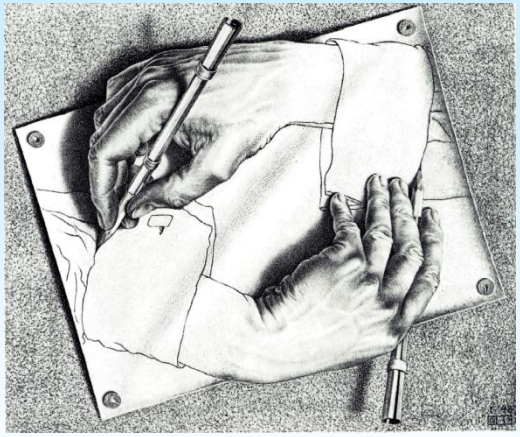
• • • chiral conductors?

Chirality

(χειρ = hand)

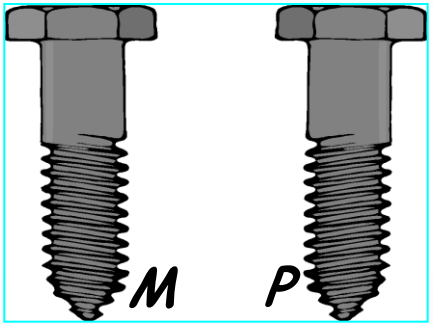


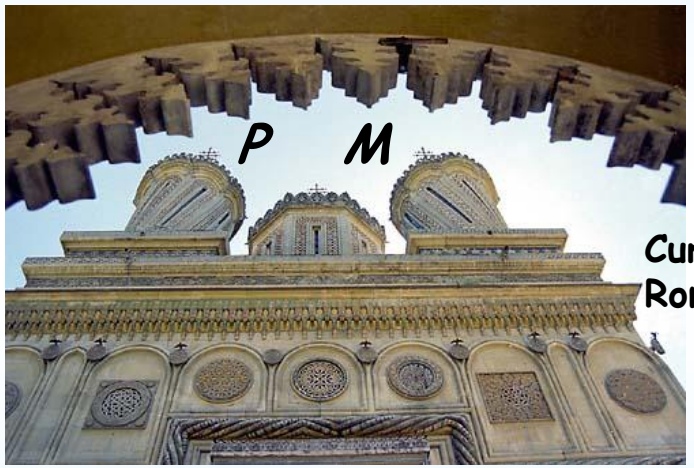
Laevo Dextro



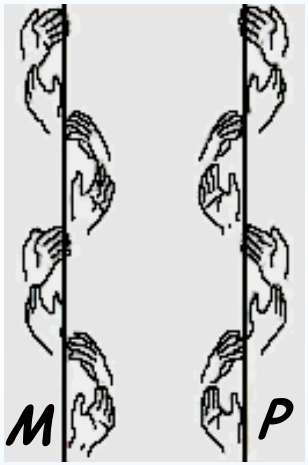
ESCHER

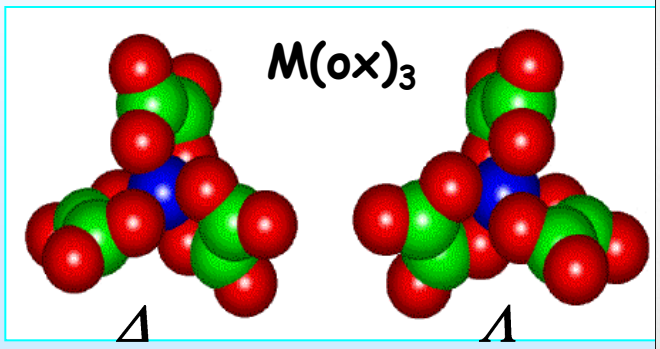
Examples:

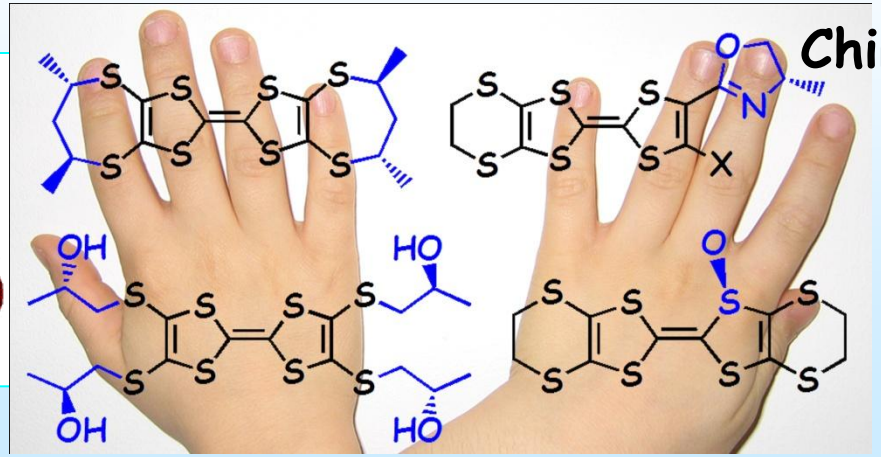




Curtea de Arges
Romania







Chiral TTFs

N. Avarvari and J. D. Wallis, *J. Mater. Chem.* (feature article) **2009**, *19*, 4061

Chiral tetrathiafulvalenes - Interests

I. Synthetic challenge

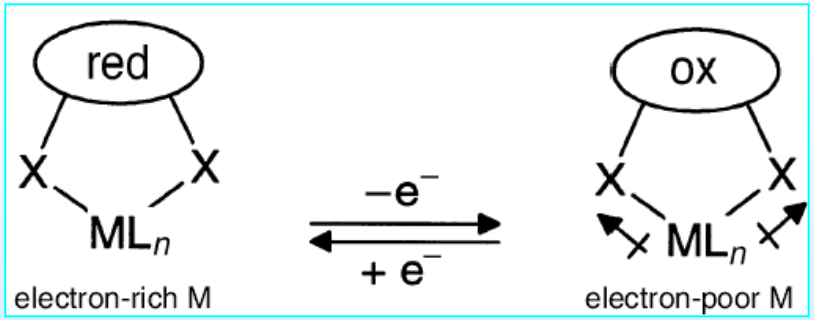
II. Chiroptical redox switches, chiral recognition

III. Chiral redox active ligands for enantioselective catalysis

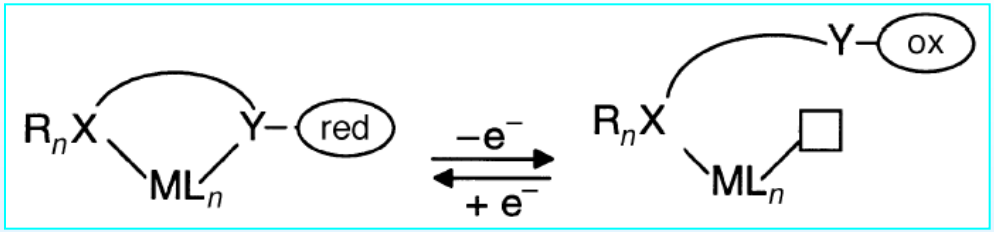
The control of the metal complexes reactivity upon oxidation - reduction

Influence on the catalytic processes?

substitutionally inert redox-switchable ligands



redox-switchable hemilabile ligands



C. A. Mirkin et al. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 894

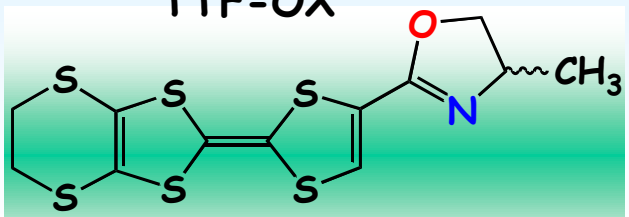
IV. Chiral molecular conductors

Chiral molecular conductors

1. Optical activity + Electrical conductivity **Multifunctional materials**

2. Enantiopure forms are inherently less disordered in the crystalline state

TTF-OX



EDT-TTF-Me-oxazoline
racemic, R and S

Influence on the conducting properties

C. Réthoré, M. Fourmigué, N. Avarvari *Chem. Commun.* **2004,** 1384.

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

A. M. Madalan, C. Réthoré, M. Fourmigué, E. Canadell, E. B. Lopes,
M. Almeida, P. Auban-Senzier, N. Avarvari *Chem. Eur. J.* **2010**, *16*, 528.

3. Reports by *Rikken et al.* on electrical magneto-chiral anisotropy (eMChA) effects

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

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

$\chi^D = -\chi^L$ handedness of the chiral conductor

$R(\vec{H}, \vec{I}) \neq R(\vec{H}, -\vec{I})$ **eMChA effect (very weak)**

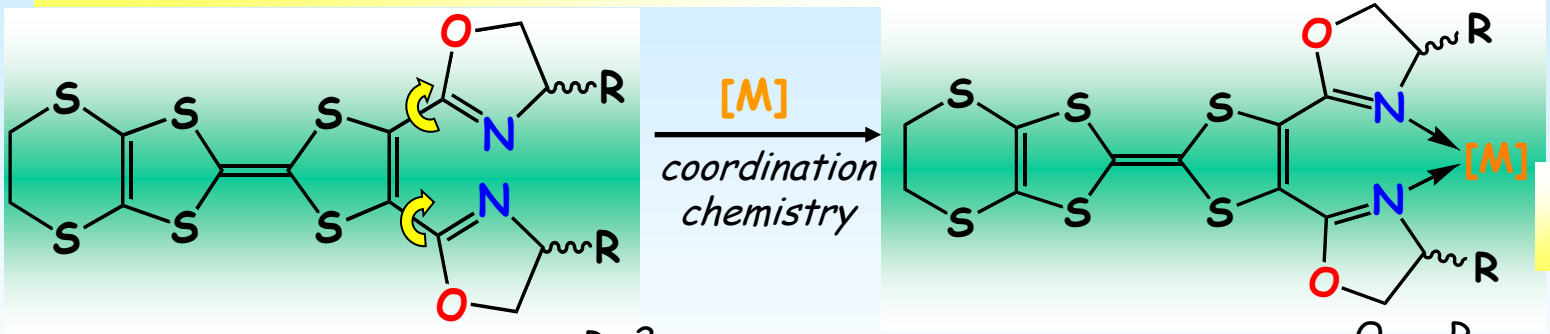
4. Superconductivity in non-centrosymmetric systems

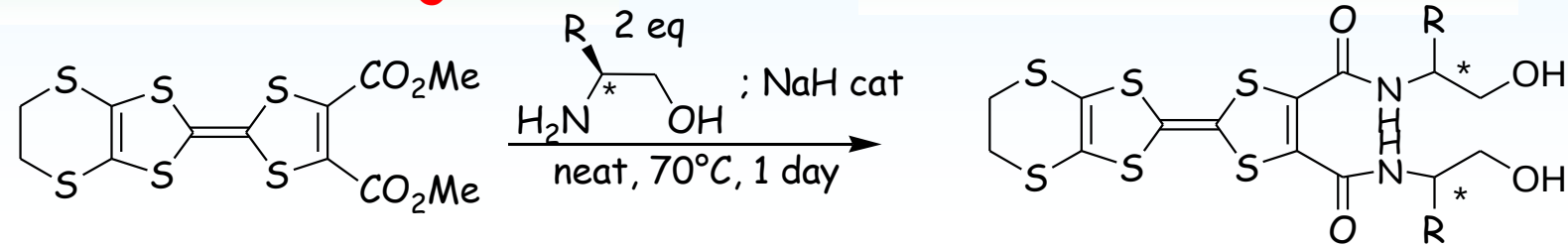
R. Roy, C. Kallin, *Phys. Rev. B* **2008,** *77*, 174513.

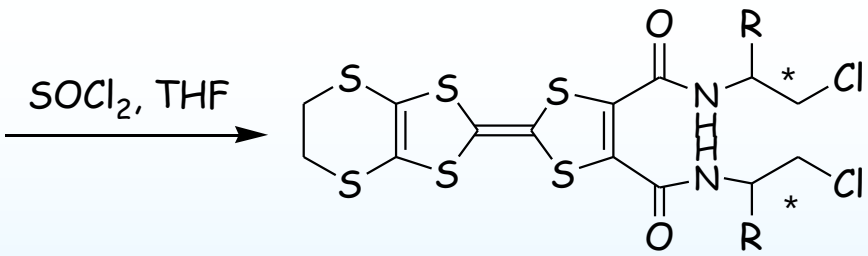
need of a library of chiral precursors in which the chiral information is addressed in different ways → **Several strategies are envisaged**

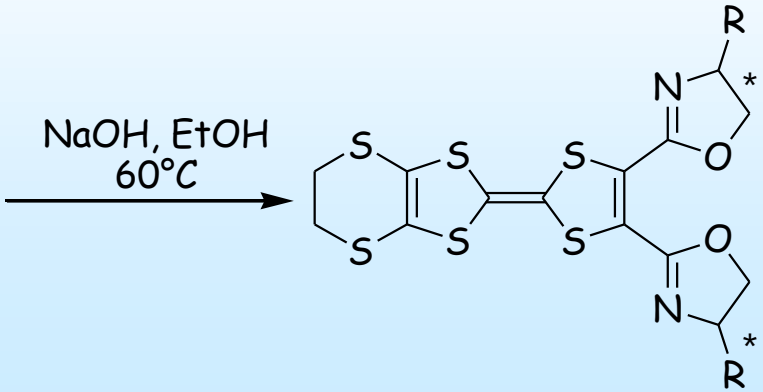
C_2 symmetric chiral tetrathiafulvalenes

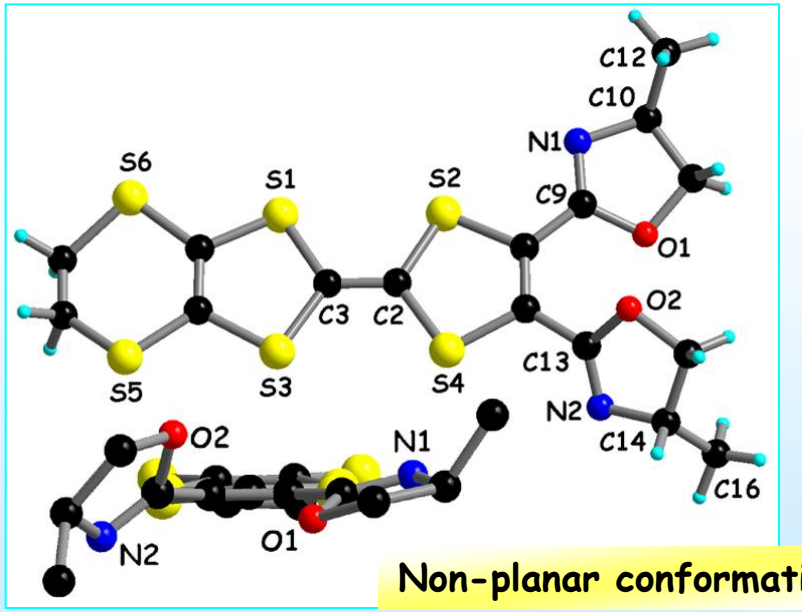
I. TTF-bis(oxazolines) TTF-BOX











F. Riobé, N. Avarvari, *Chem. Commun.* **2009**, 3753.

C_2 symmetric chiral tetrathiafulvalenes

TTF-BOX: conformational issues

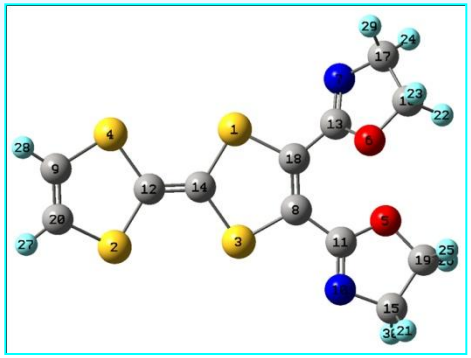
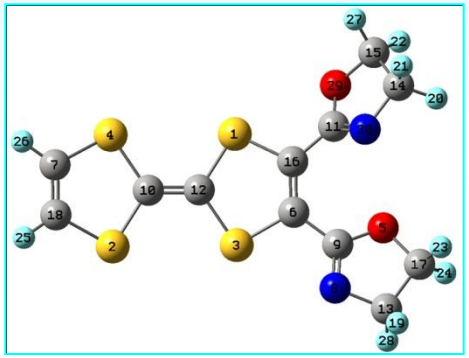
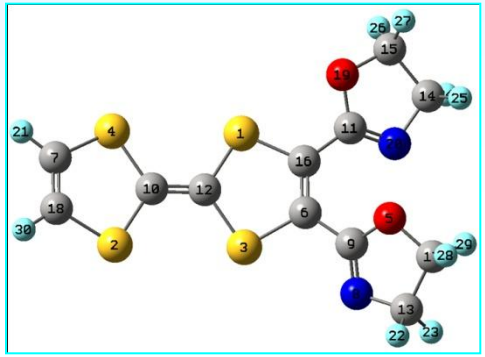
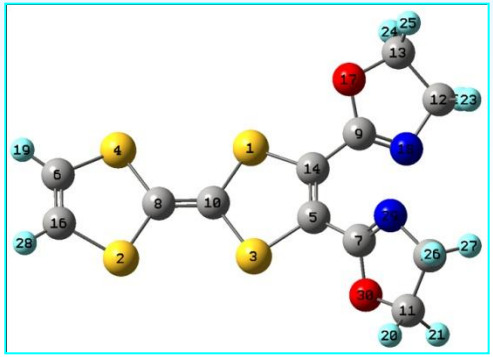
Theoretical calculations DFT/B3LYP/6-31+G(d): four energy minima

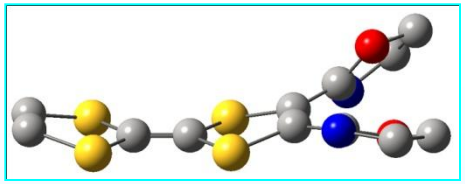
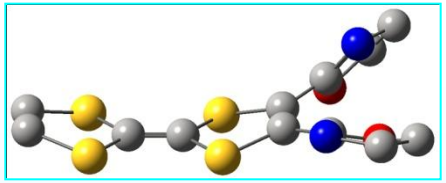
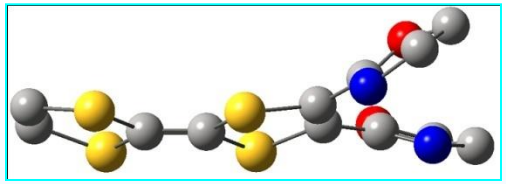
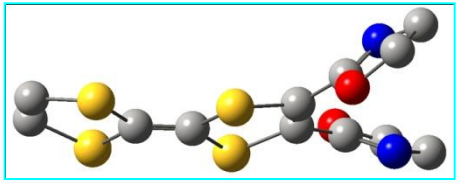
1. *s-trans/s-trans*
ΔE 0 kcal/mole

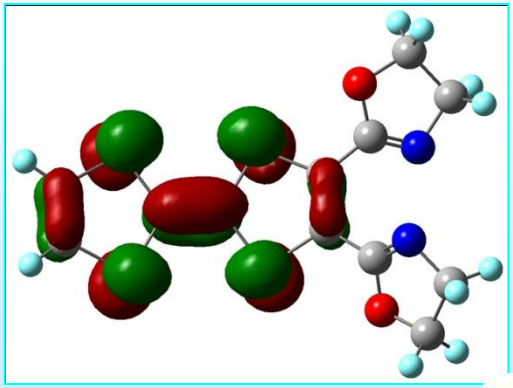
2. *s-cis/s-trans*
ΔE 0.52 kcal/mole

3. *s-cis/s-trans*
ΔE 0.74 kcal/mole

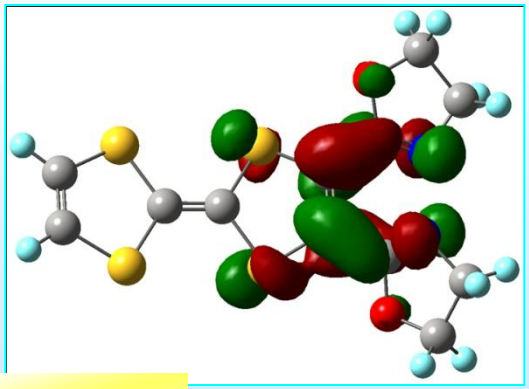
4. *s-cis/s-cis*
ΔE 1.78 kcal/mole


HOMO

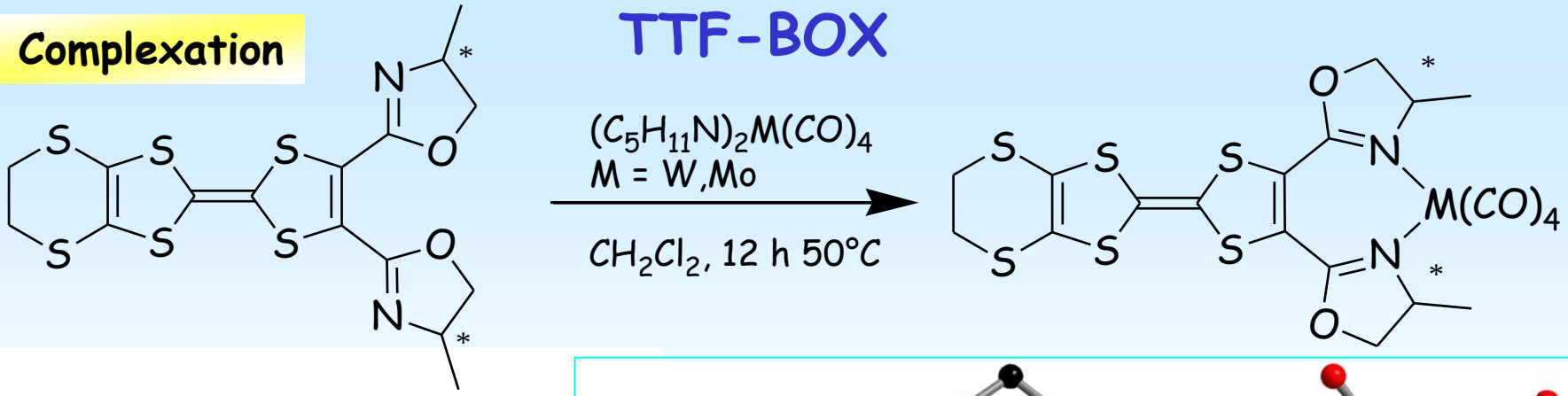
ΔE 2.83 eV

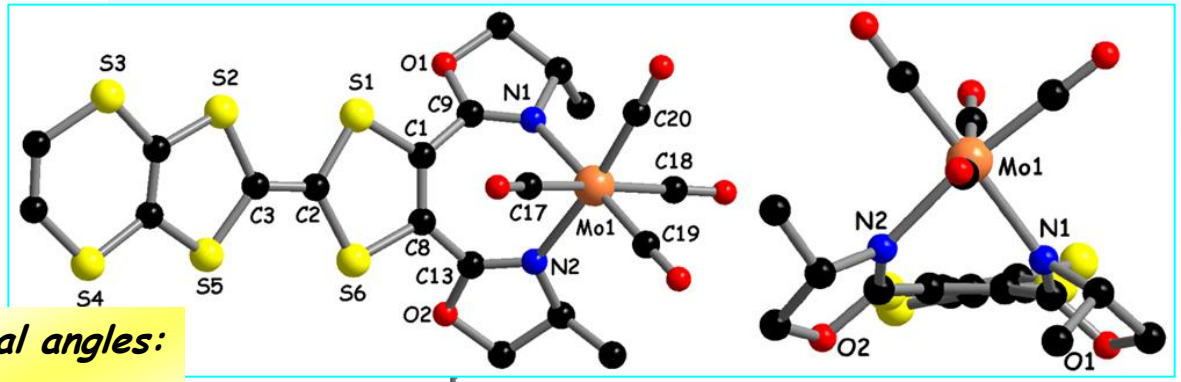

LUMO

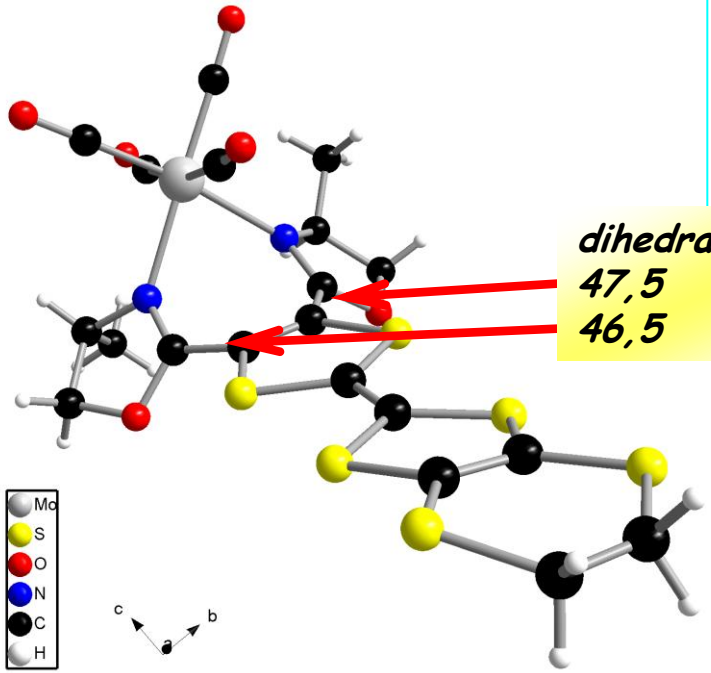
How to increase the rigidity and/or the planarity?

I. Complexation

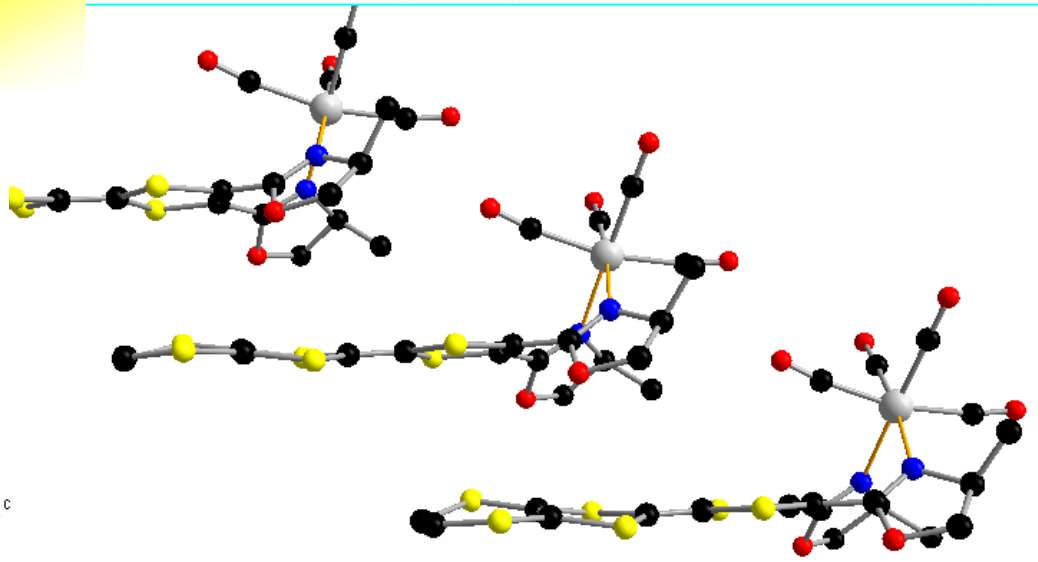
TTF-BOX



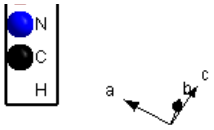




dihedral angles:
47,5
46,5



$[BOX\ (S)Me]Mo(CO)_4$



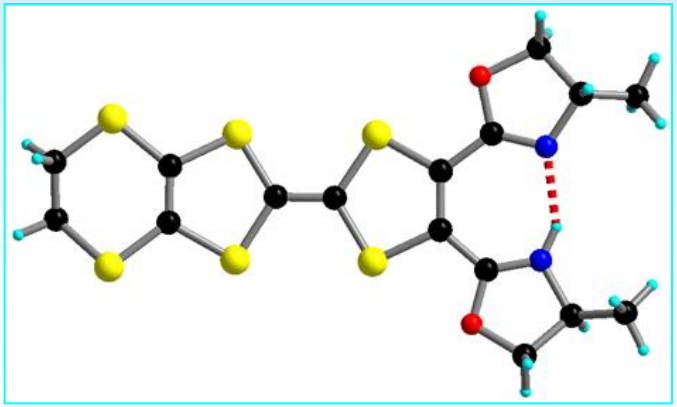
F. Riobé, N. Avarvari, *Chem. Commun.* **2009**, 3753.

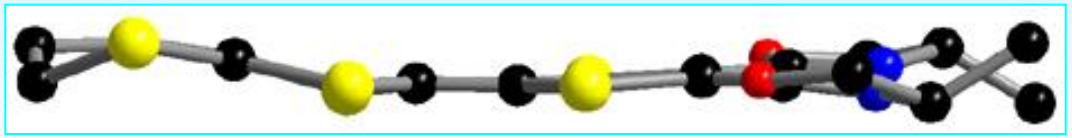
TTF-BOX

II. Protonation

$[(S,S)\text{-EDT-TTF-bis(Me-Ox)H}]^{+}_{2}[Mo_6O_{19}]^{2-}$

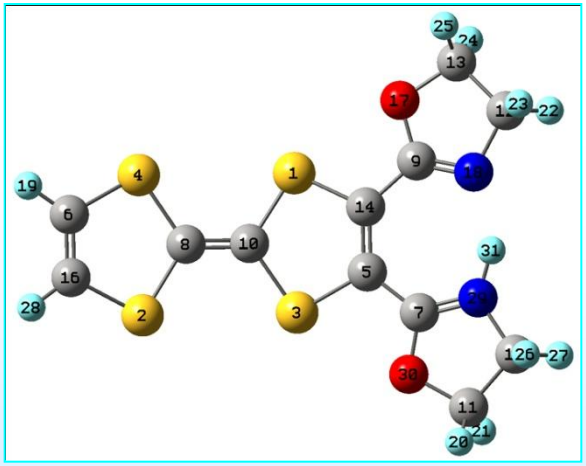
Monoprotonated TTF-BOX, TTF stays neutral

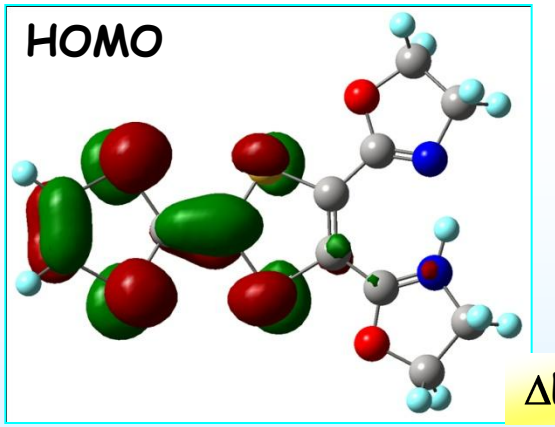


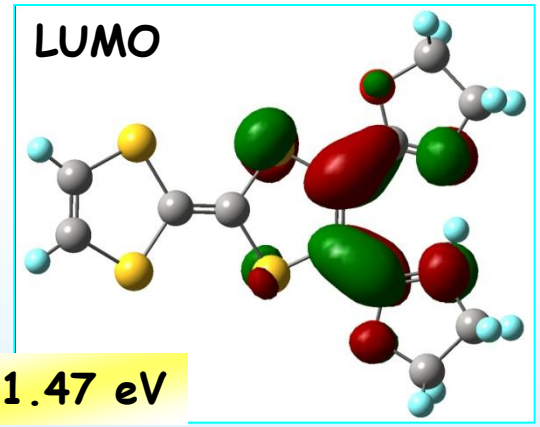


Rigid planar $[bis(Me\text{-}Ox)H]^{+}$ motif

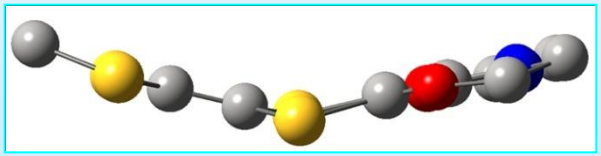
DFT/B3LYP/6-31+G(d)



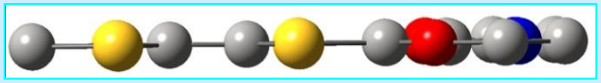




ΔE 1.47 eV



TTF^{0}



$TTF^{+\cdot}$

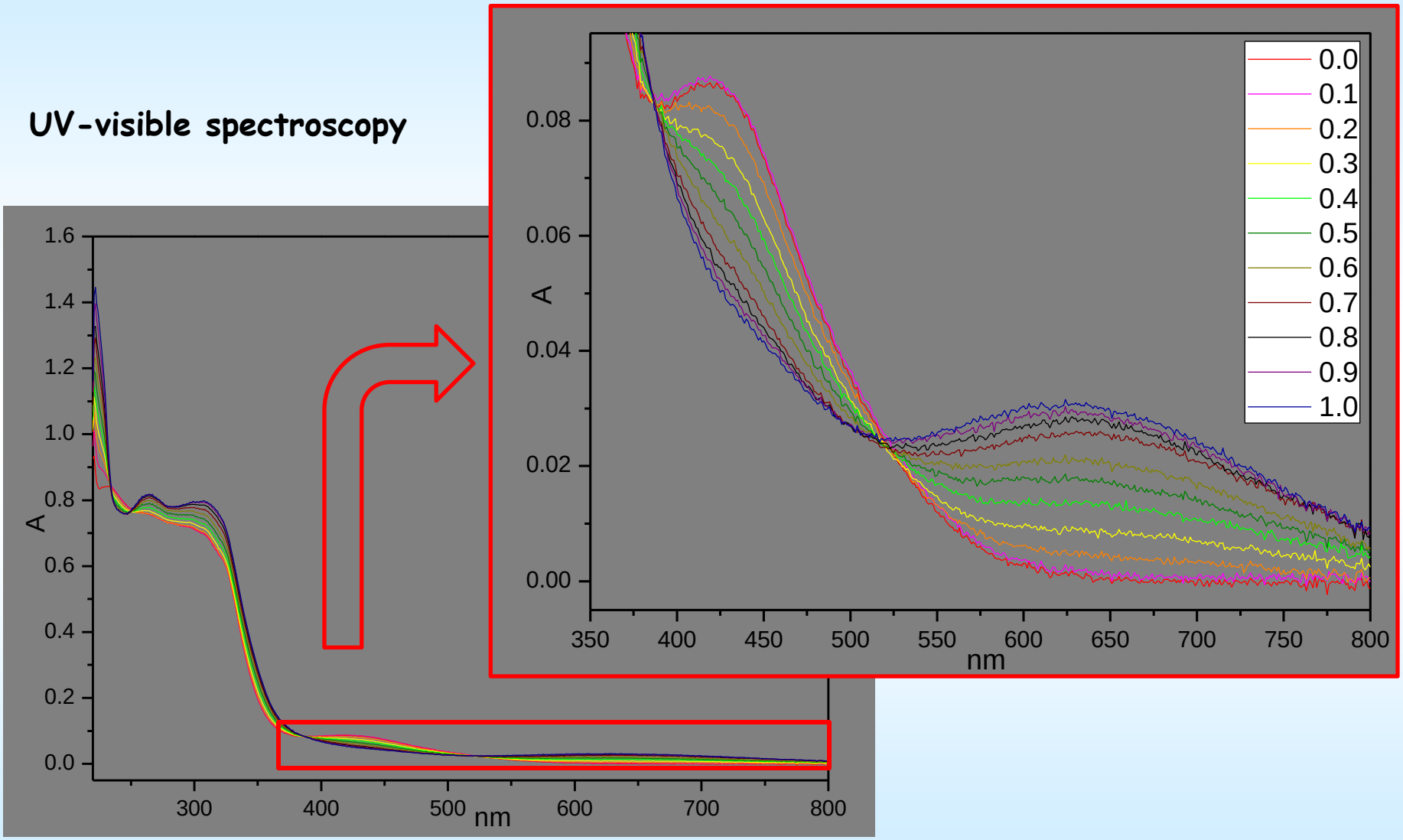
Electrocrystallization
New donor-acceptor system

F. Riobé, N. Avarvari, unpublished

TTF-BOX

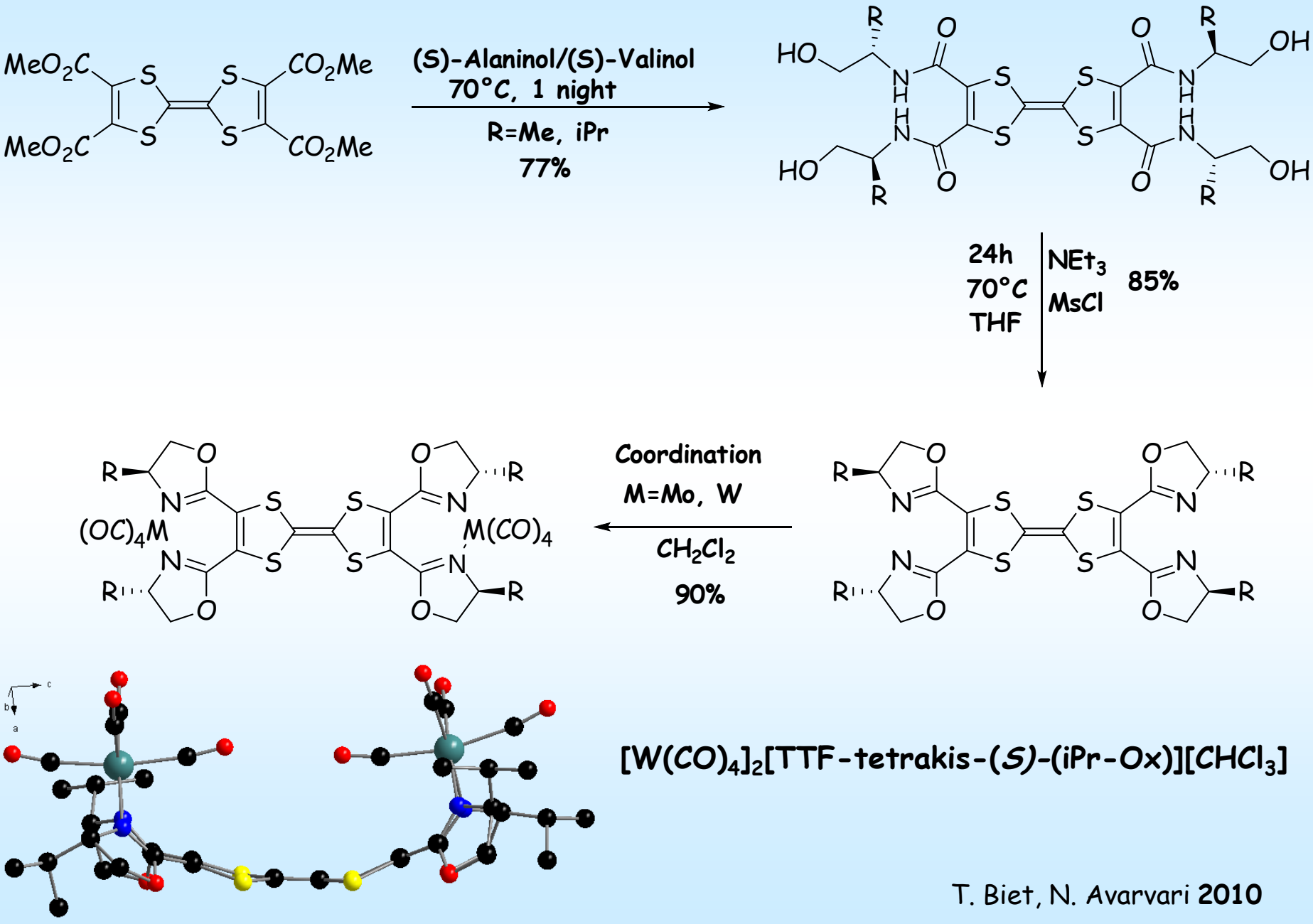
Chiral Donor-Acceptor system modulated by pH

UV-visible spectroscopy



EDT-TTF-Me-BOX in solution of $CH_3CN:CH_2Cl_2$ 1:1 (C = 5. 10^{-5} M)
+ increasing amounts of APTS

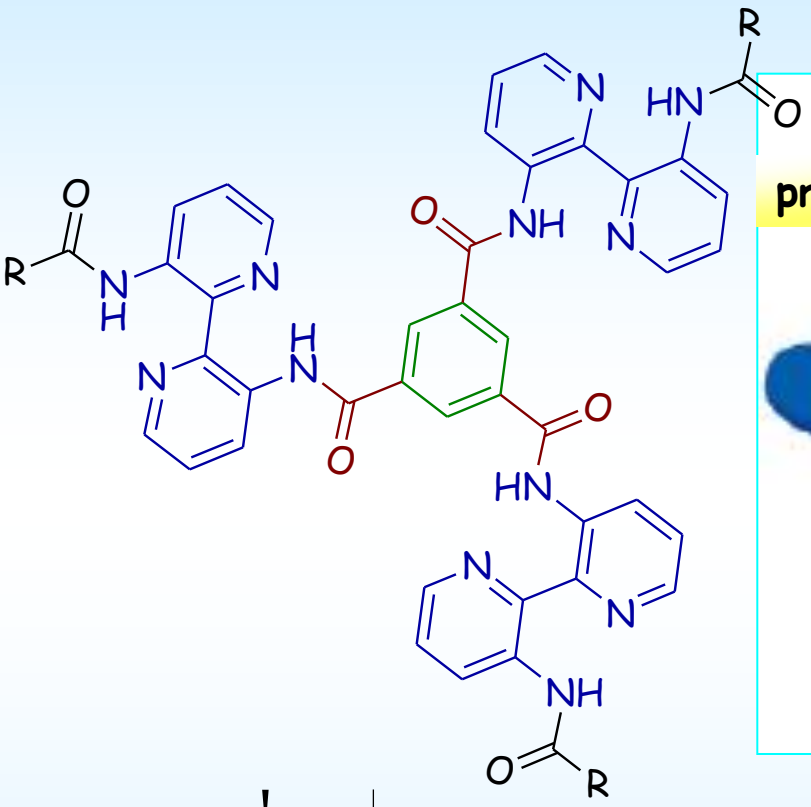
TTF-Bis(BOX)



T. Biet, N. Avarvari **2010**

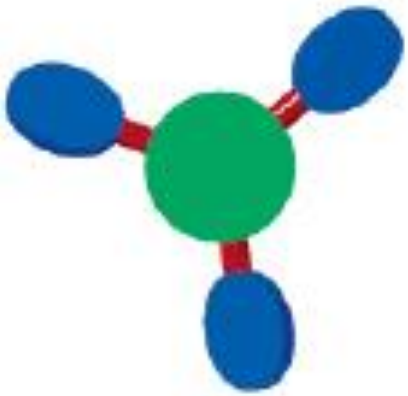
C_3 symmetric tetrathiafulvalenes

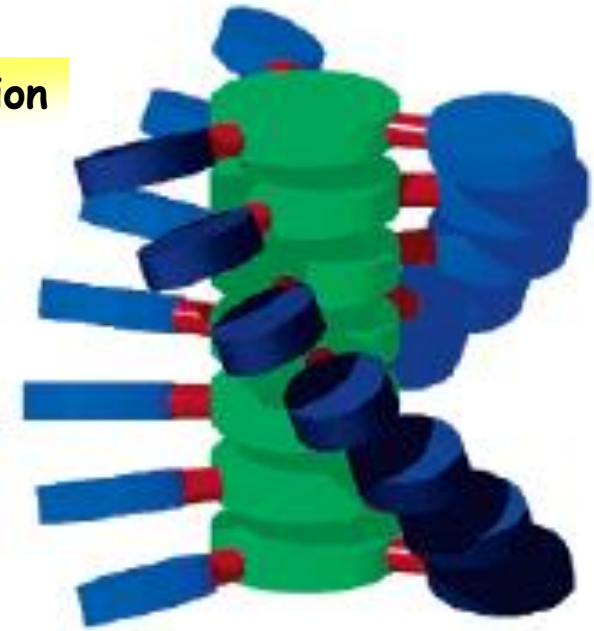
II. Using a C_3 symmetric platform



helical chirality

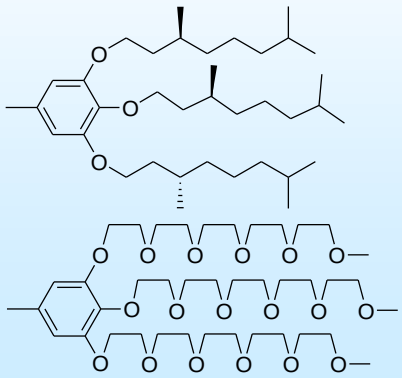
propeller like conformation





π–π stacking
hydrogen bonds

R =

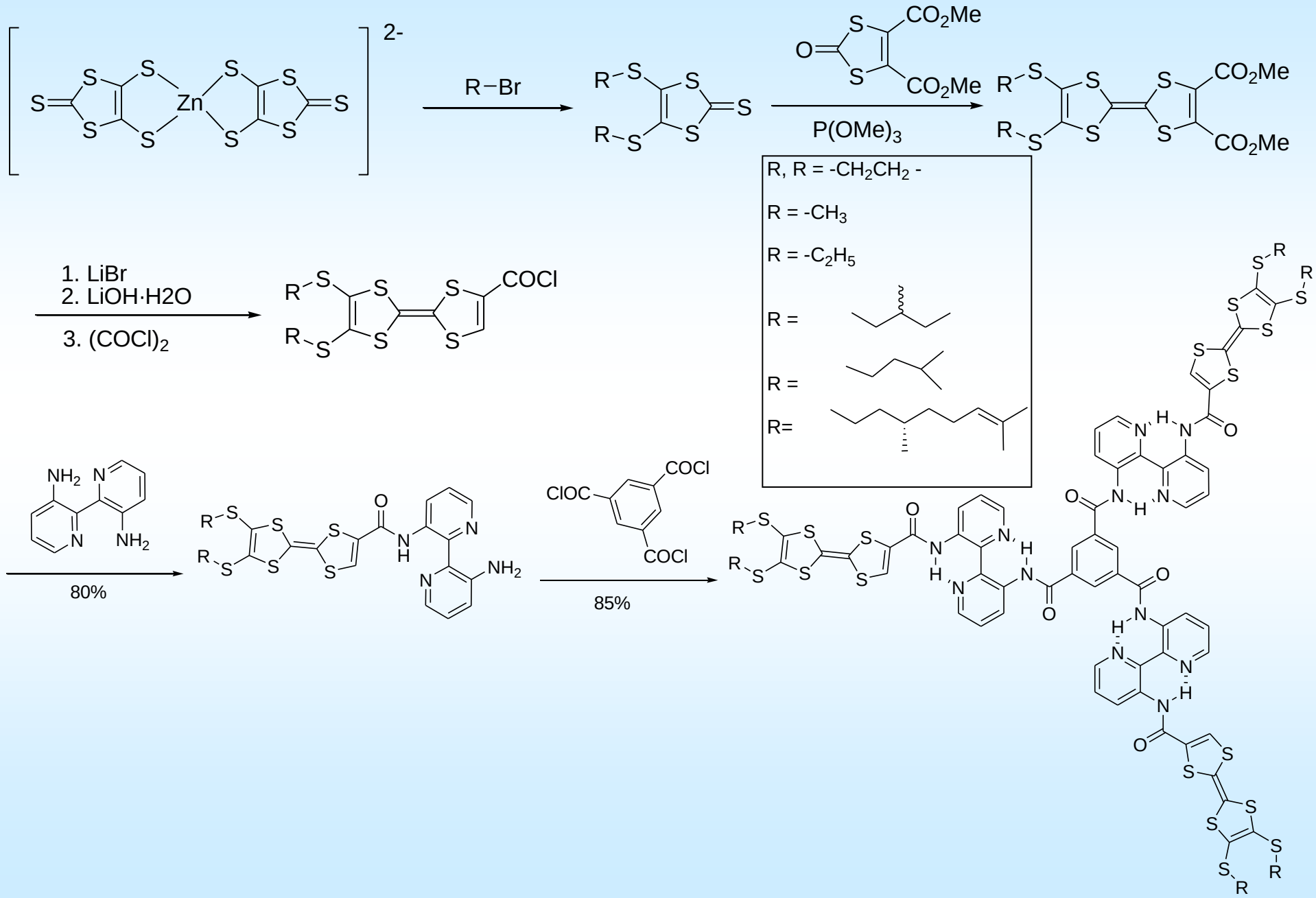


A. R. A. Palmans, J. A. J. M. Vekemans, E. E. Havinga, E. W. Meijer
Angew. Chem. Int. Ed. Engl. **1997**, *36*, 2648

L. Brunsveld, H. Zhang, M. Glasbeek, J. A. J. M. Vekemans, E. W. Meijer
J. Am. Chem. Soc. **2000**, *122*, 6175.

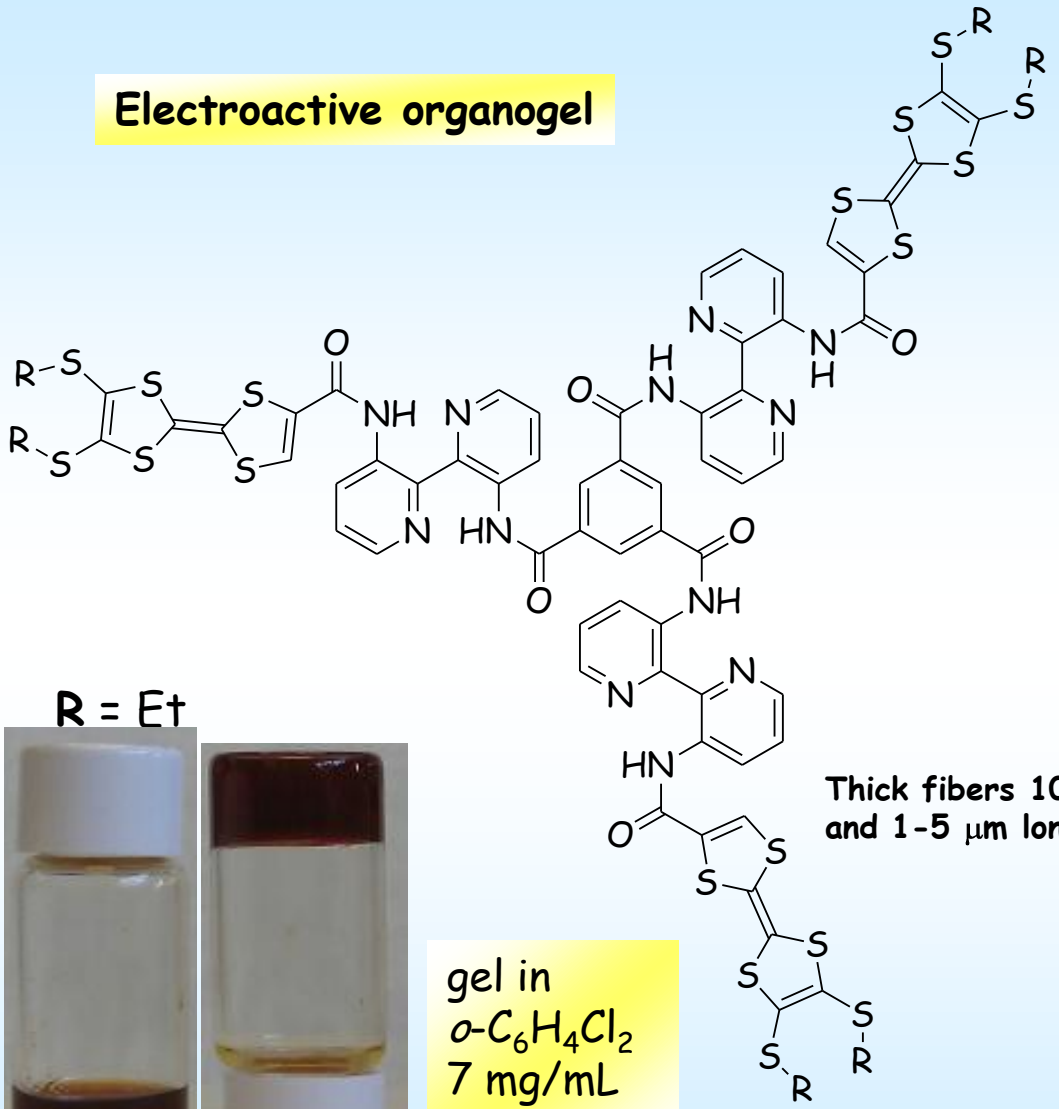
J. van Gestel, A. R. A. Palmans, B. Titulaer, J. A. J. M. Vekemans, E. W. Meijer
J. Am. Chem. Soc. **2005**, *127*, 5490.

C_3 symmetric TTFs: convergent synthesis



C_3 symmetric TTFs: conducting supramolecular wires

Electroactive organogel

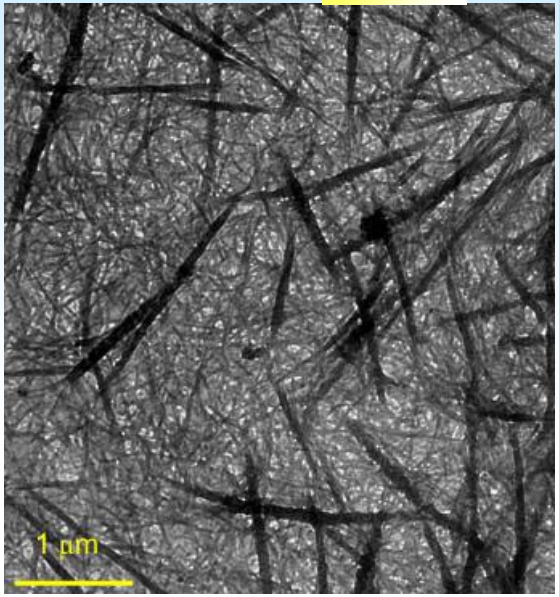


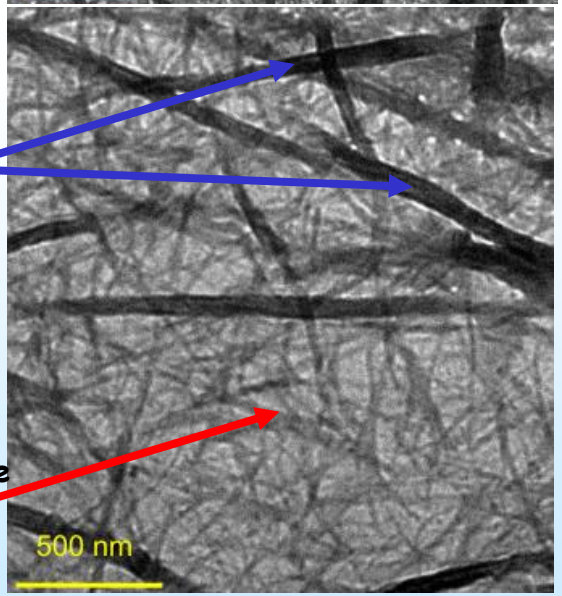
R = Et

gel in
o-$C_6H_4Cl_2$
7 mg/mL
$3.8 \cdot 10^{-3}$ M

xerogel

TEM



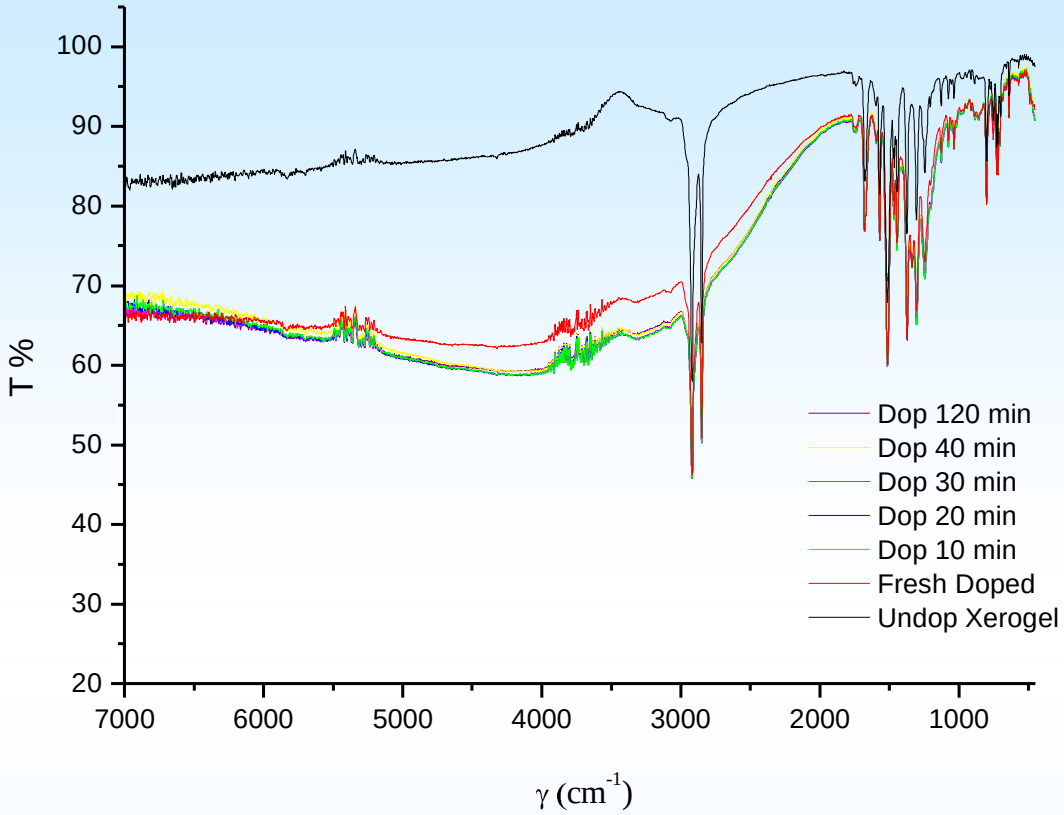


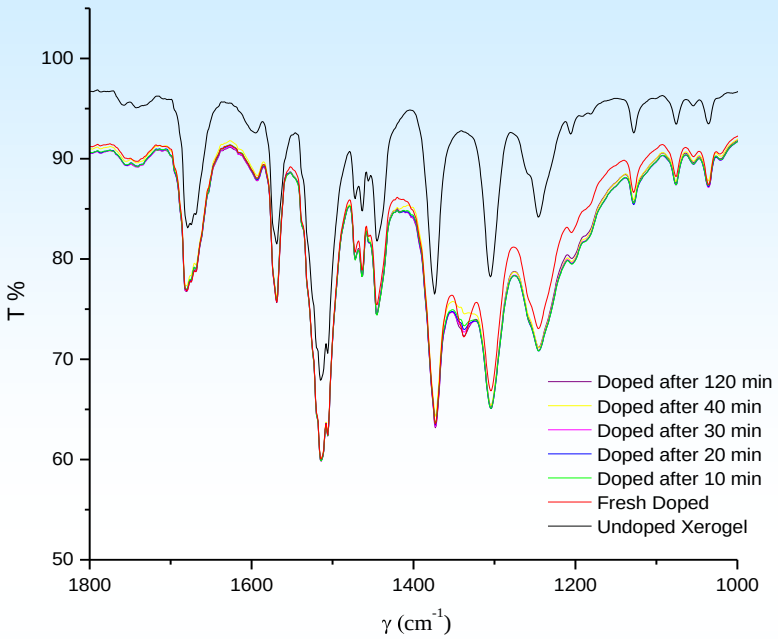
Thick fibers 100 nm wide and 1-5 μm long

Thin fibers 12-18 nm wide and 50-500 nm long

I. Danila, F. Riobé, J. Puigmarti, A. Pérez del Pino, J. D. Wallis, D. Amabilino, N. Avarvari, *J. Mater. Chem.* **2009**, *19*, 4495.

Doping with iodine





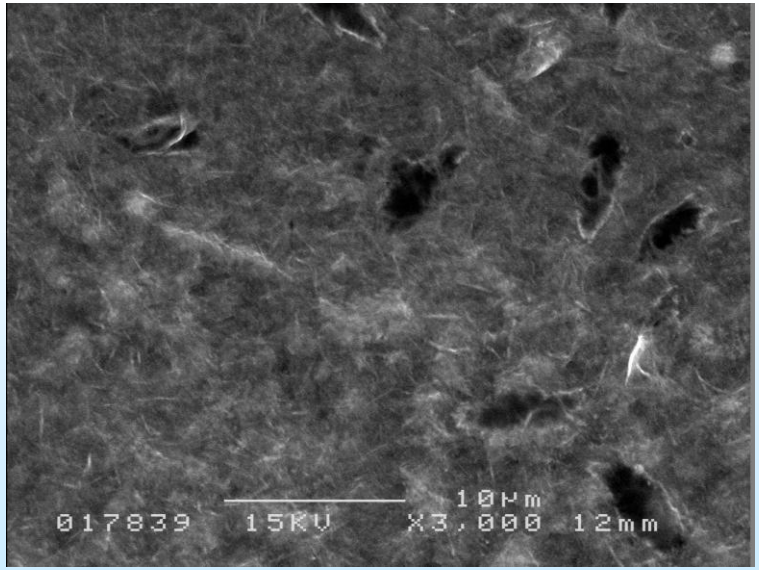
Content in atomic %	S	I
After doping	83,11	17,28
6 days later	90,49	9,52

SEM/EDX measurements

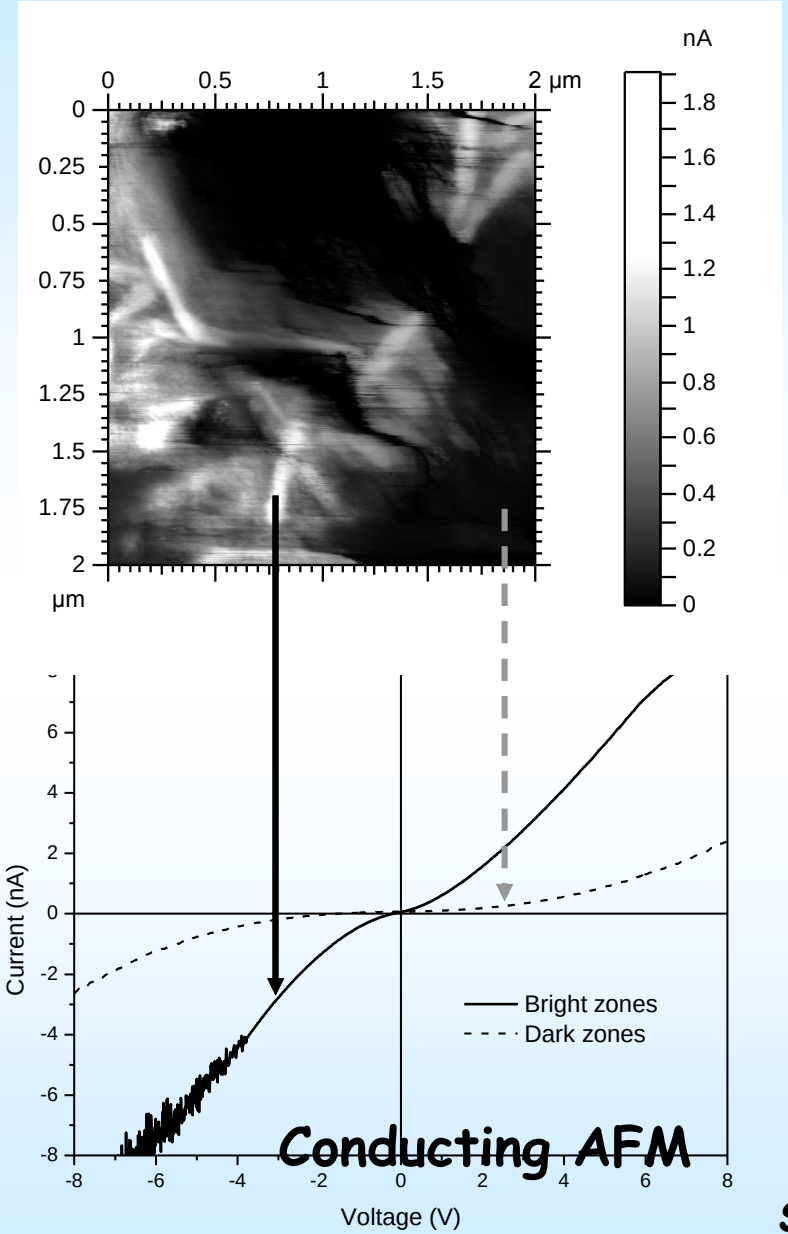
=>

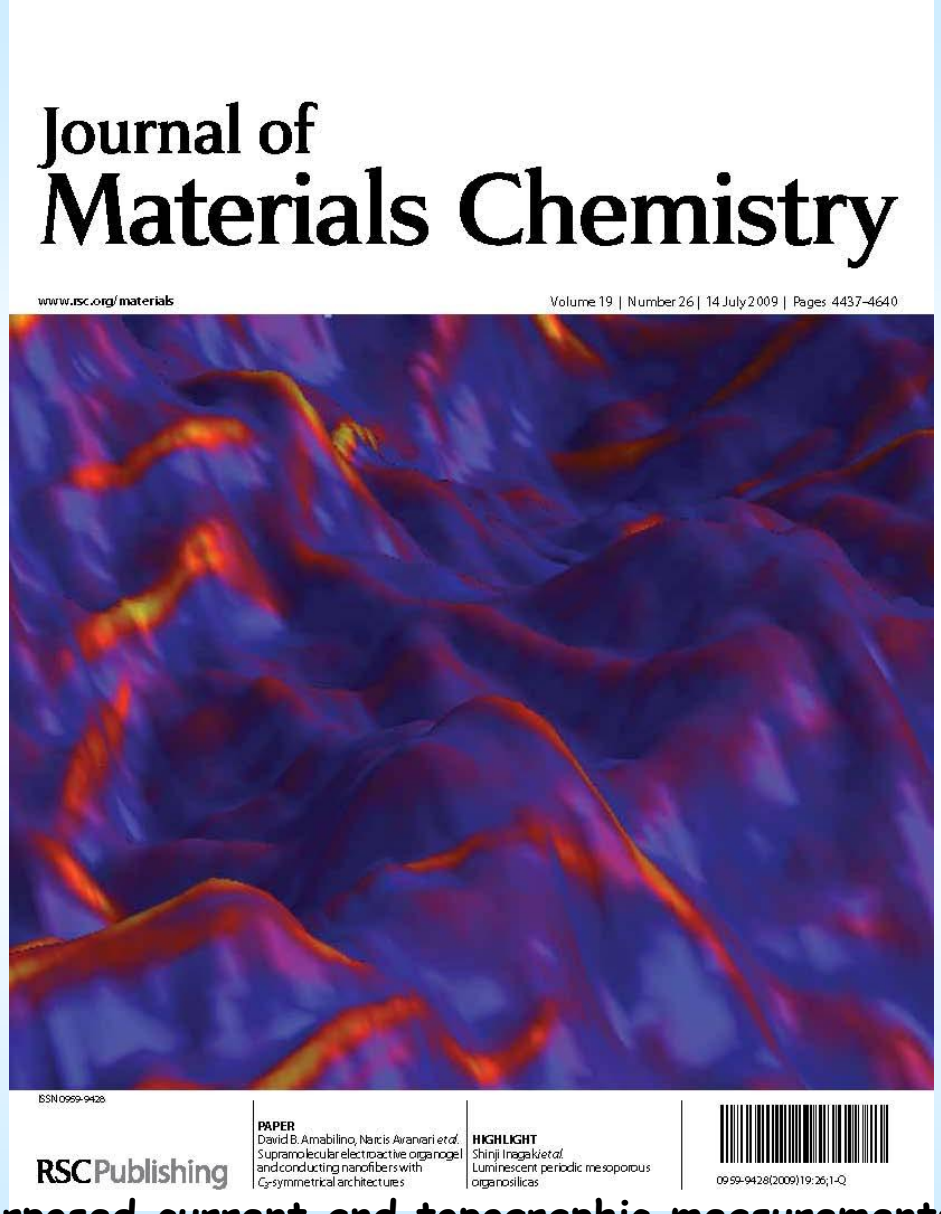
Ratio TTF/I_3^-

2,4/1



Doping with iodine

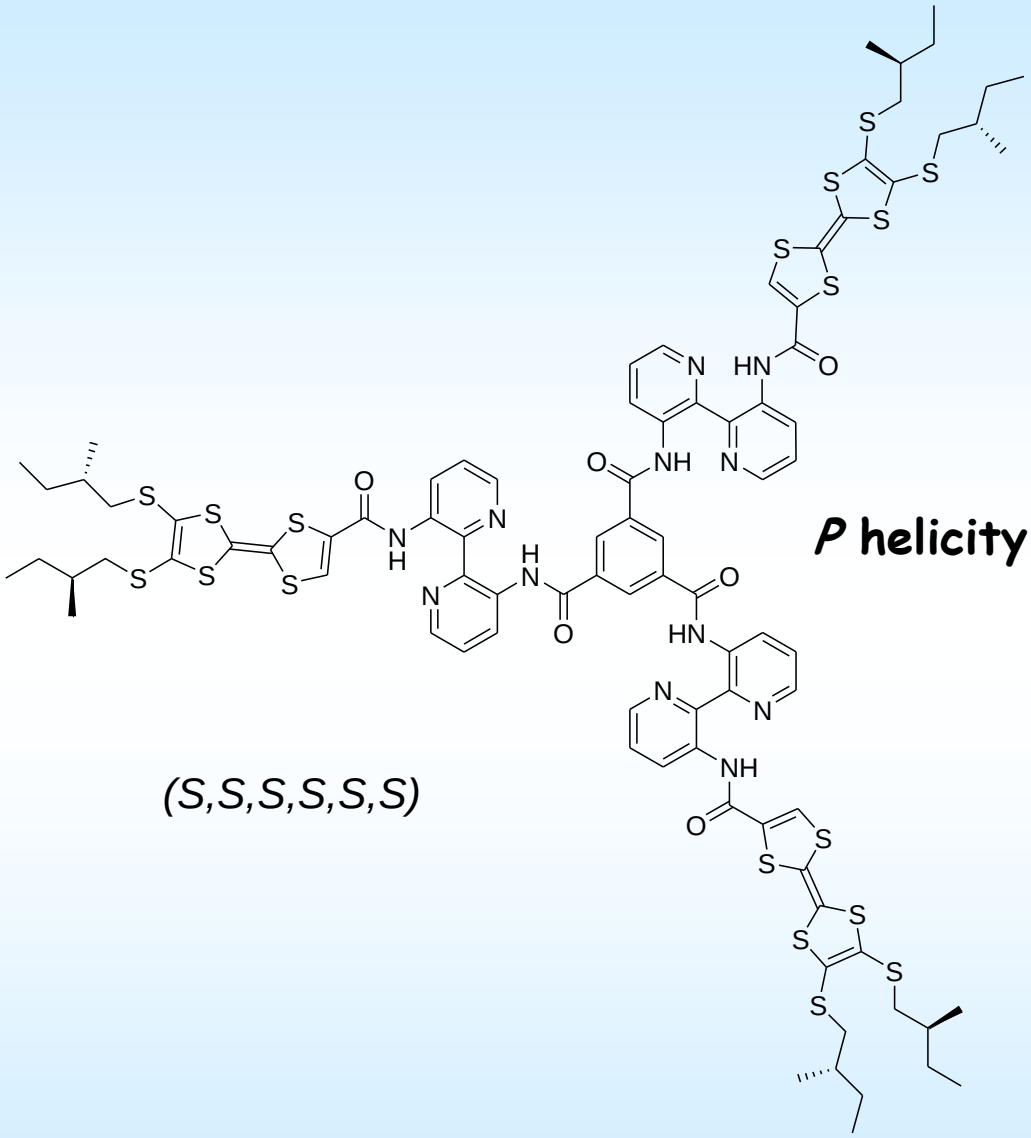




Superposed current and topographic measurements

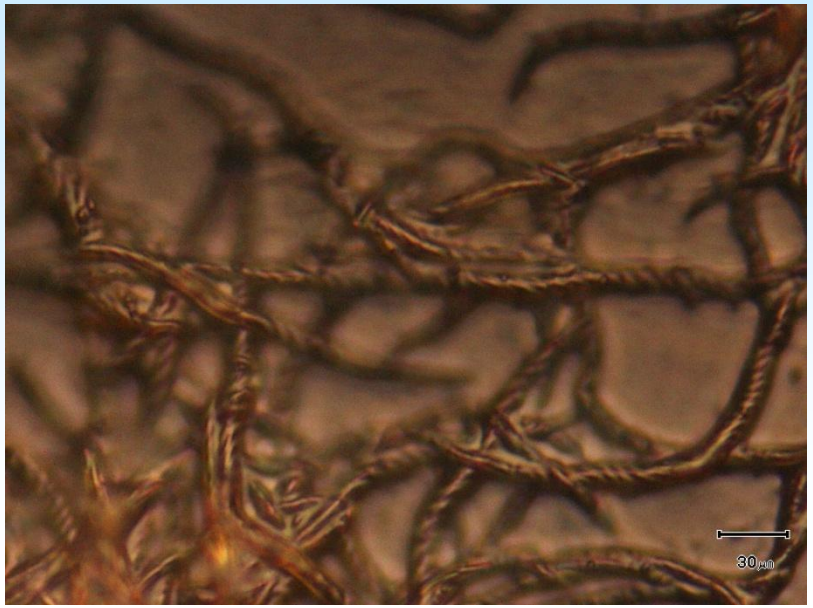
I. Danila, F. Riobé, J. Puigmarti, A. Pérez del Pino, J. D. Wallis,D. Amabilino, N. Avarvari, *J. Mater. Chem.* **2009**, *19*, 4495.

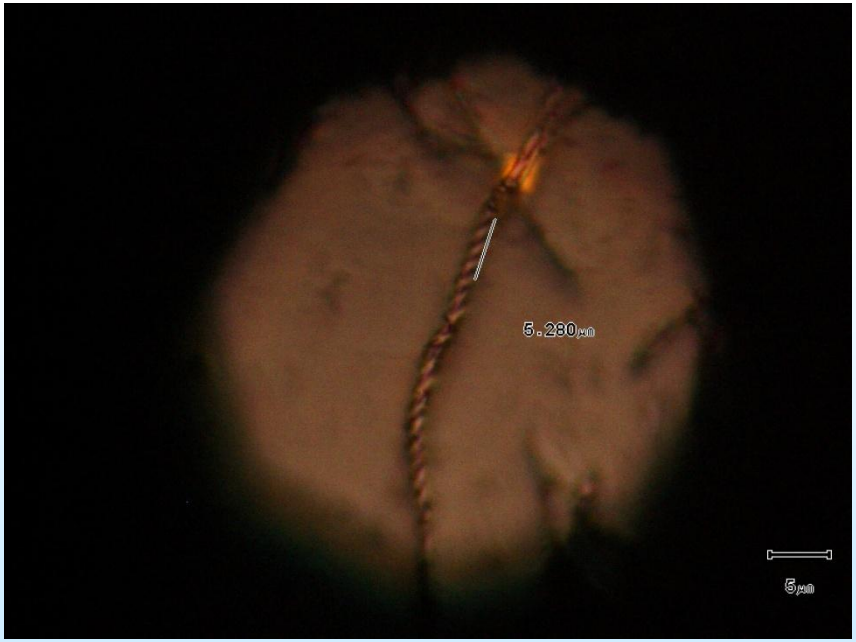
Supramolecular chirality



P helicity

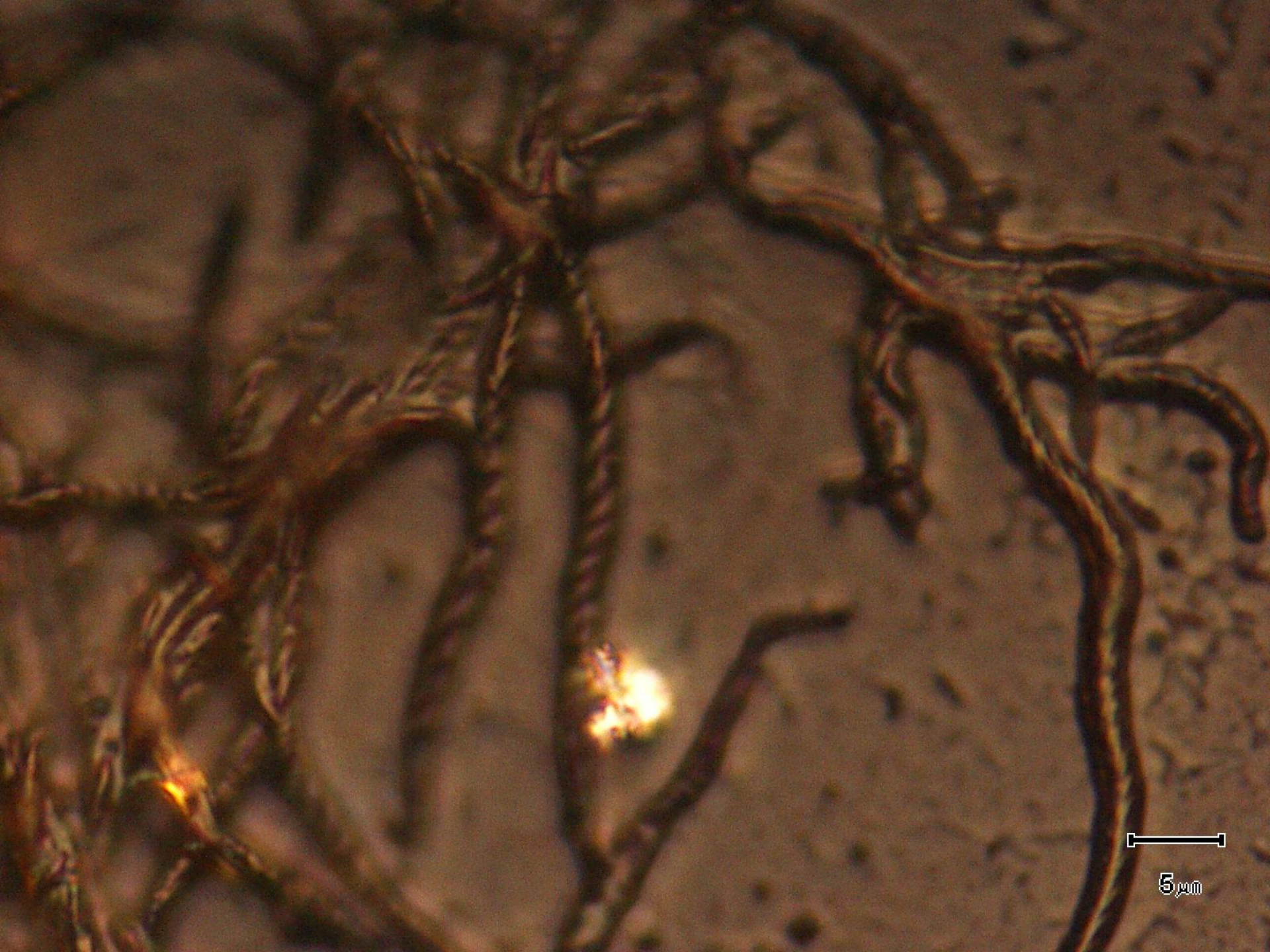
(*S*,*S*,*S*,*S*,*S*,*S*)





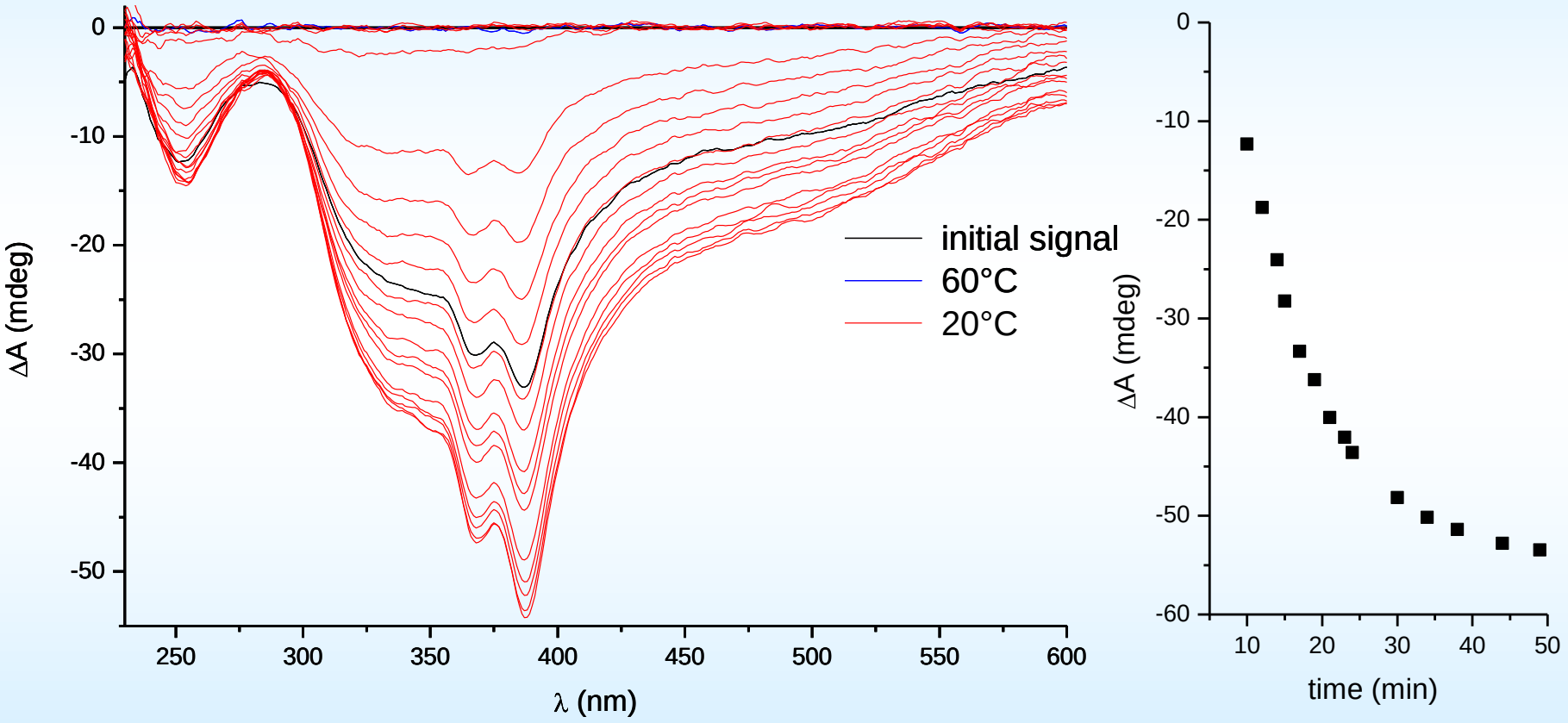
Optical images

I. Danila, F. Riobé, J. Puigmarti, L. Feldborg, J. D. Wallis, D. Amabilino, N. Avarvari, *to be submitted*


5 µm

Supramolecular chirality

Circular dichroism measurements

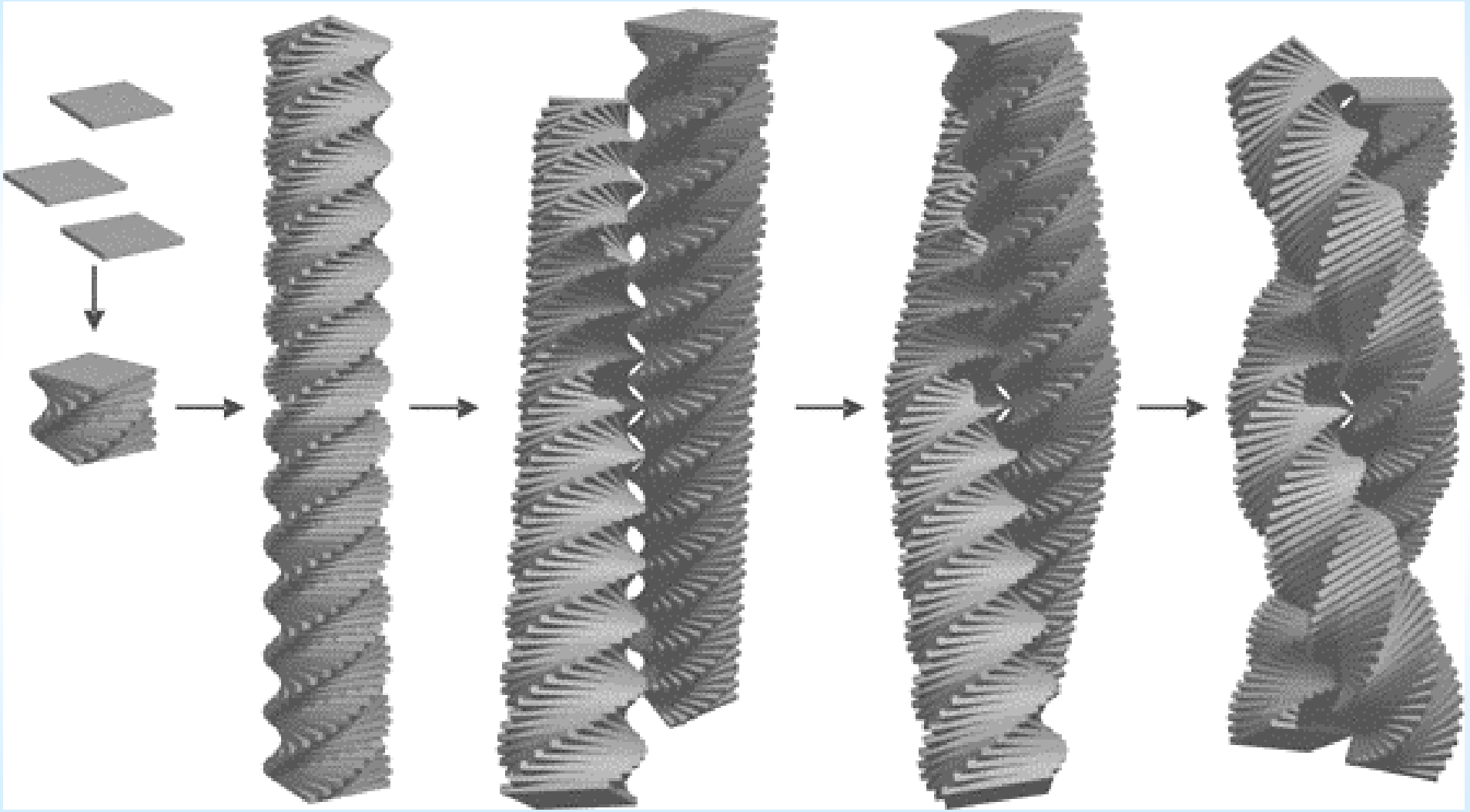


CD spectra and evolution of the signal at 387 nm in dioxane

***M* helicity in solution for the primary fibers!**

I. Danila, F. Riobé, J. Puigmarti, L. Feldborg, J. D. Wallis, D. Amabilino, N. Avarvari, *to be submitted*

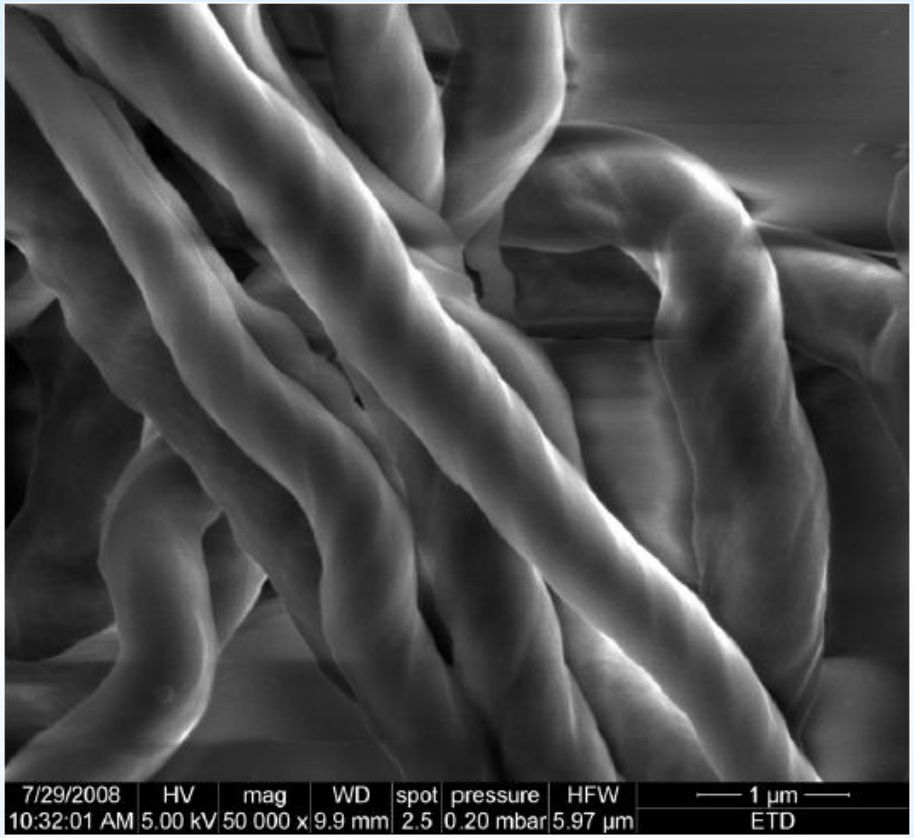
Formation of fibres



J. A. A. W. Elemans, A.E. Rowan, R. J. M. Nolte, *J. Mater. Chem.* **2003**, *13*, 2661.

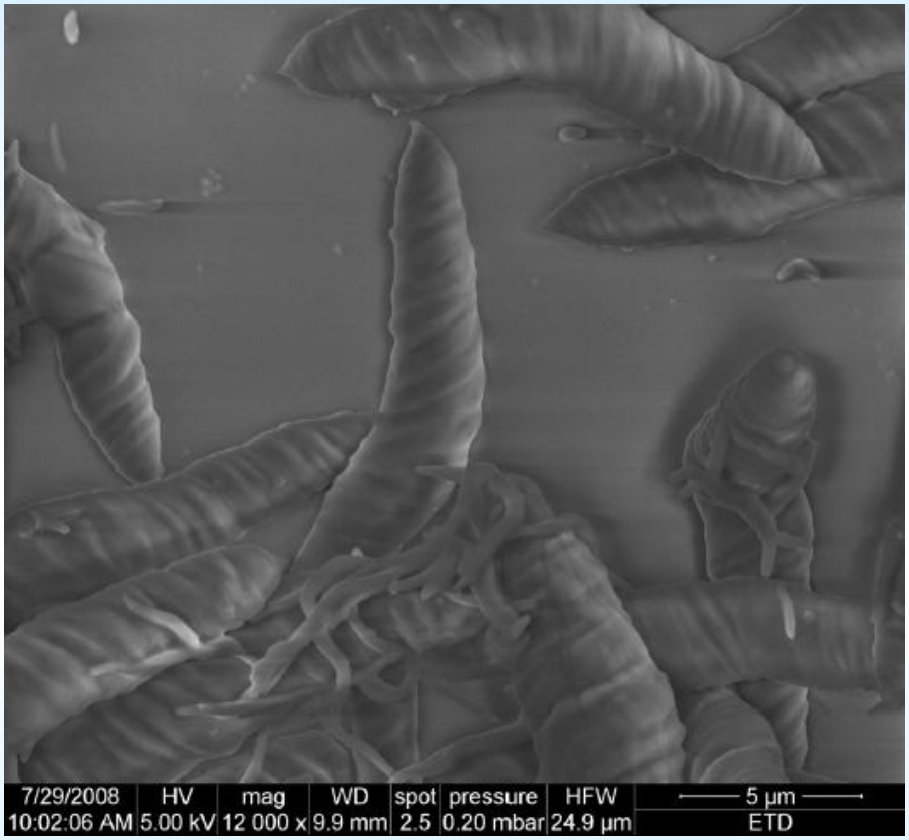
A sensitive system

Fibres



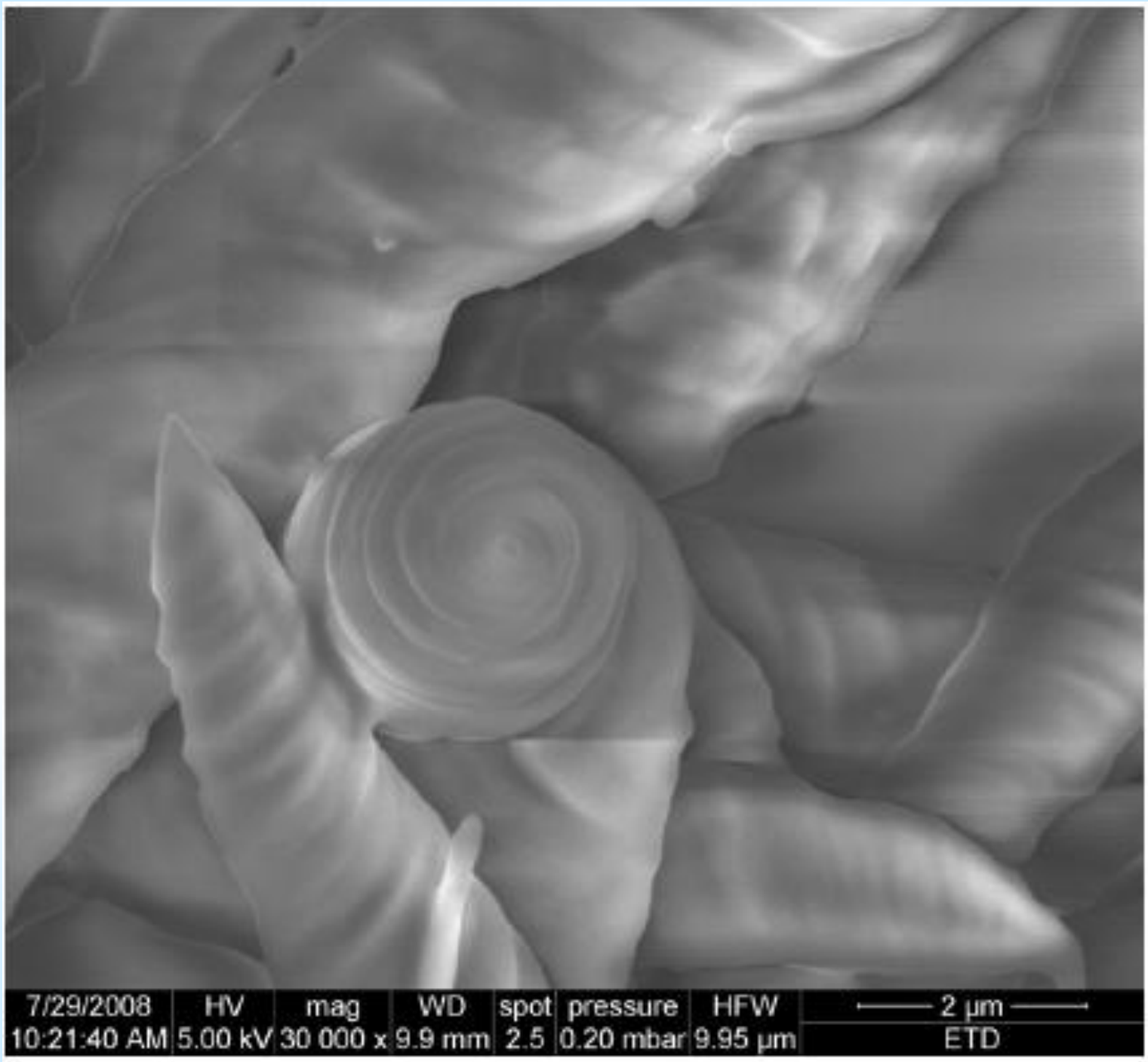
Obtained with a heatgun

Microcroissants !

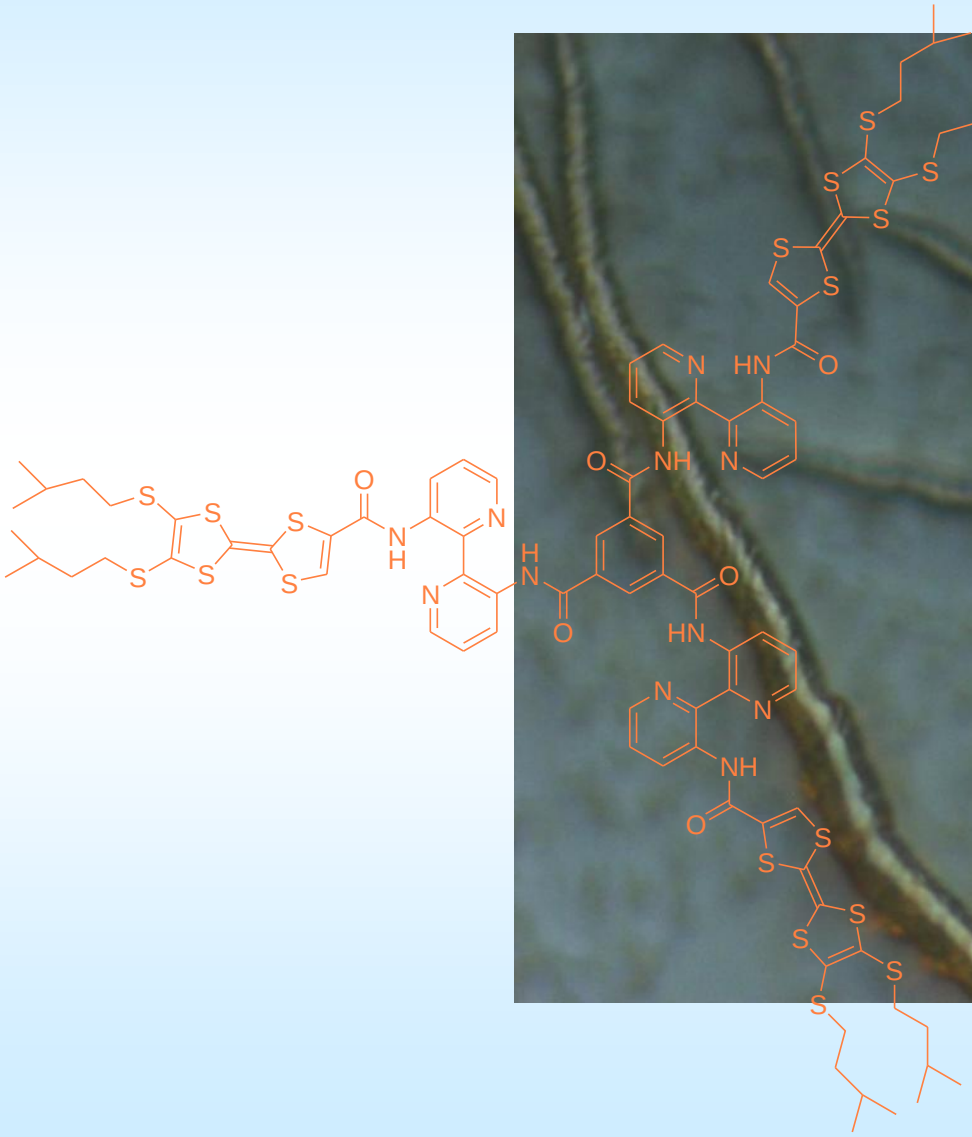


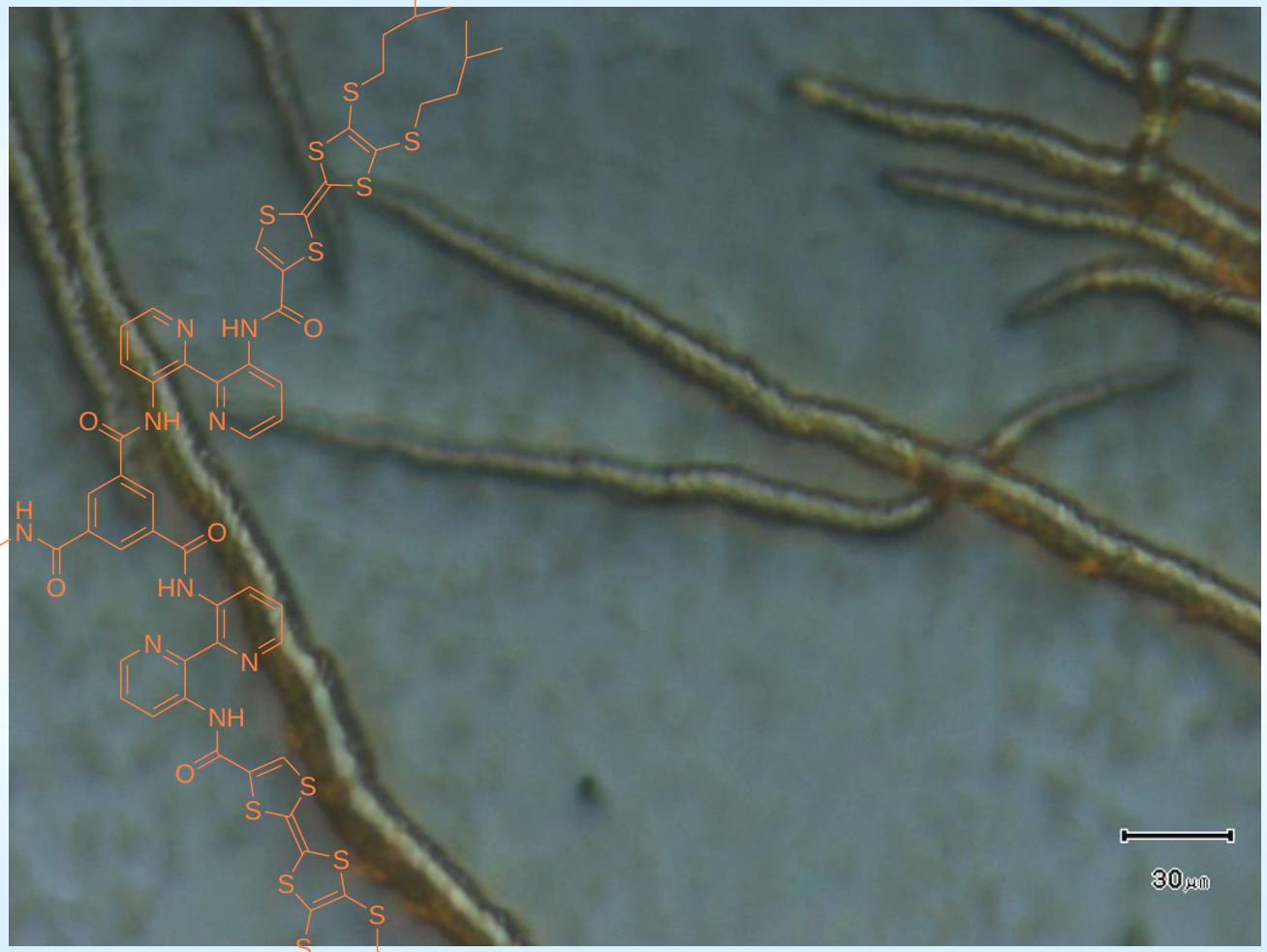
Obtained with a hotplate

SEM images


7/29/2008
10:21:40 AM
HV
5.00 kV
mag
30 000 x
WD
9.9 mm
spot
2.5
pressure
0.20 mbar
HFW
9.95 µm
2 µm
ETD

Sergeants and soldiers?





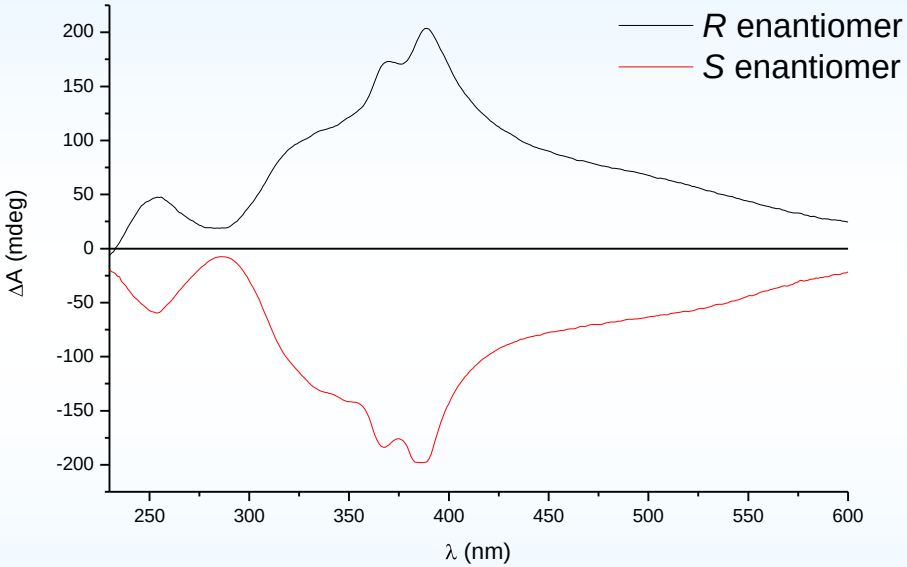
chiral/achiral 60/40

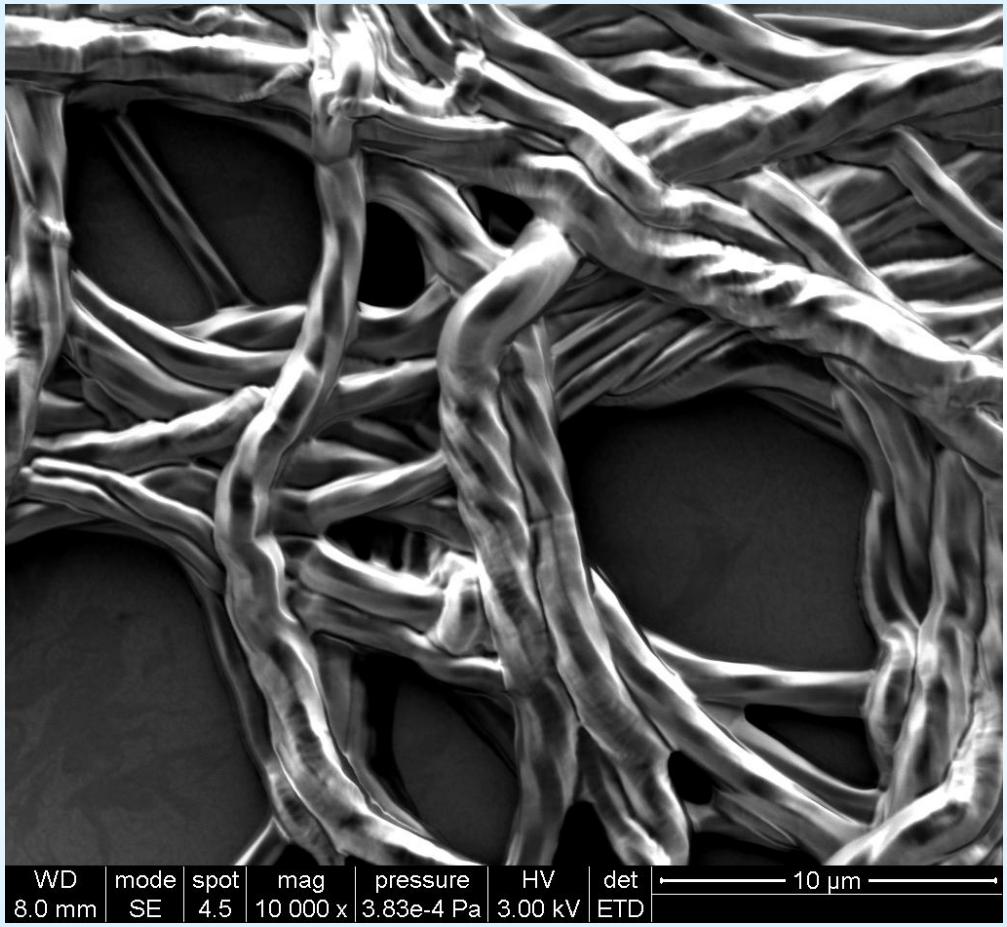
Supramolecular chirality

(R,R,R,R,R,R) enantiomer

***M* helicity**

CD measurements



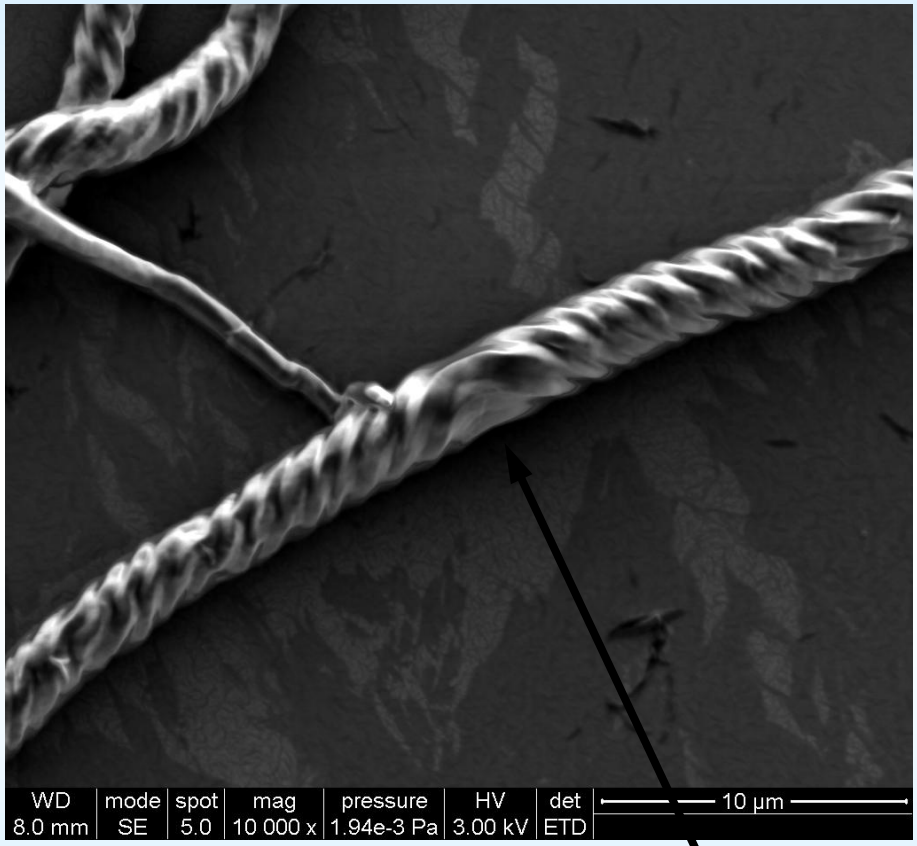


SEM image

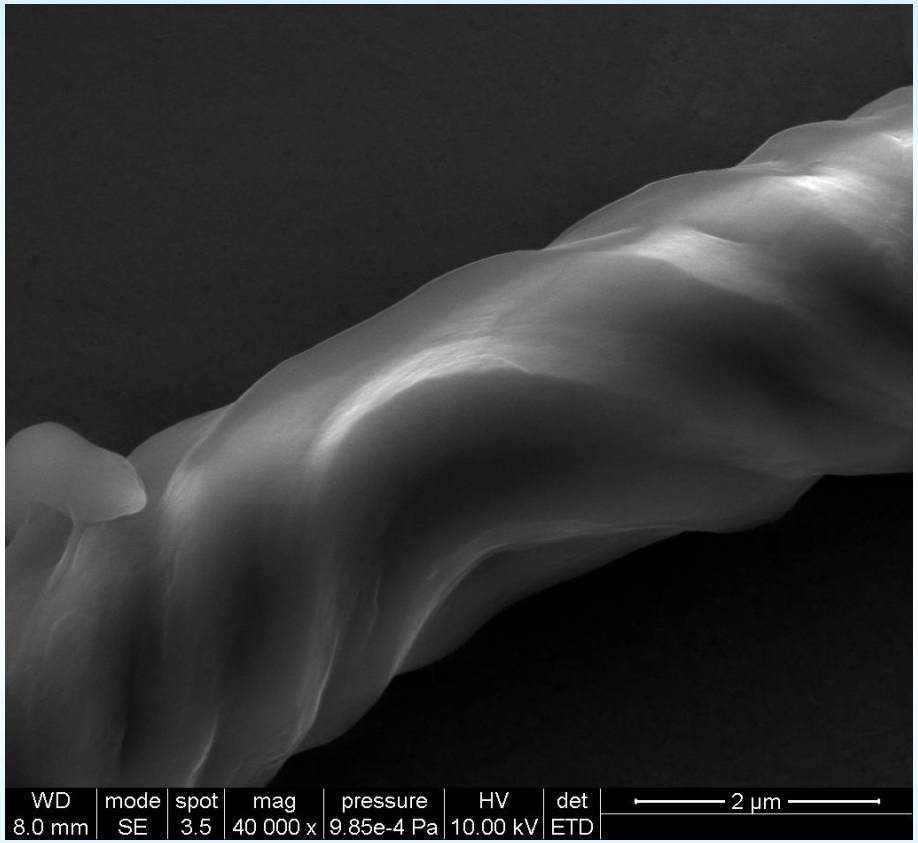
I. Danila, F. Piron, F. Riobé, D. Amabilino, N. Avarvari, *unpublished*

Supramolecular chirality

Fibres from the racemic mixture

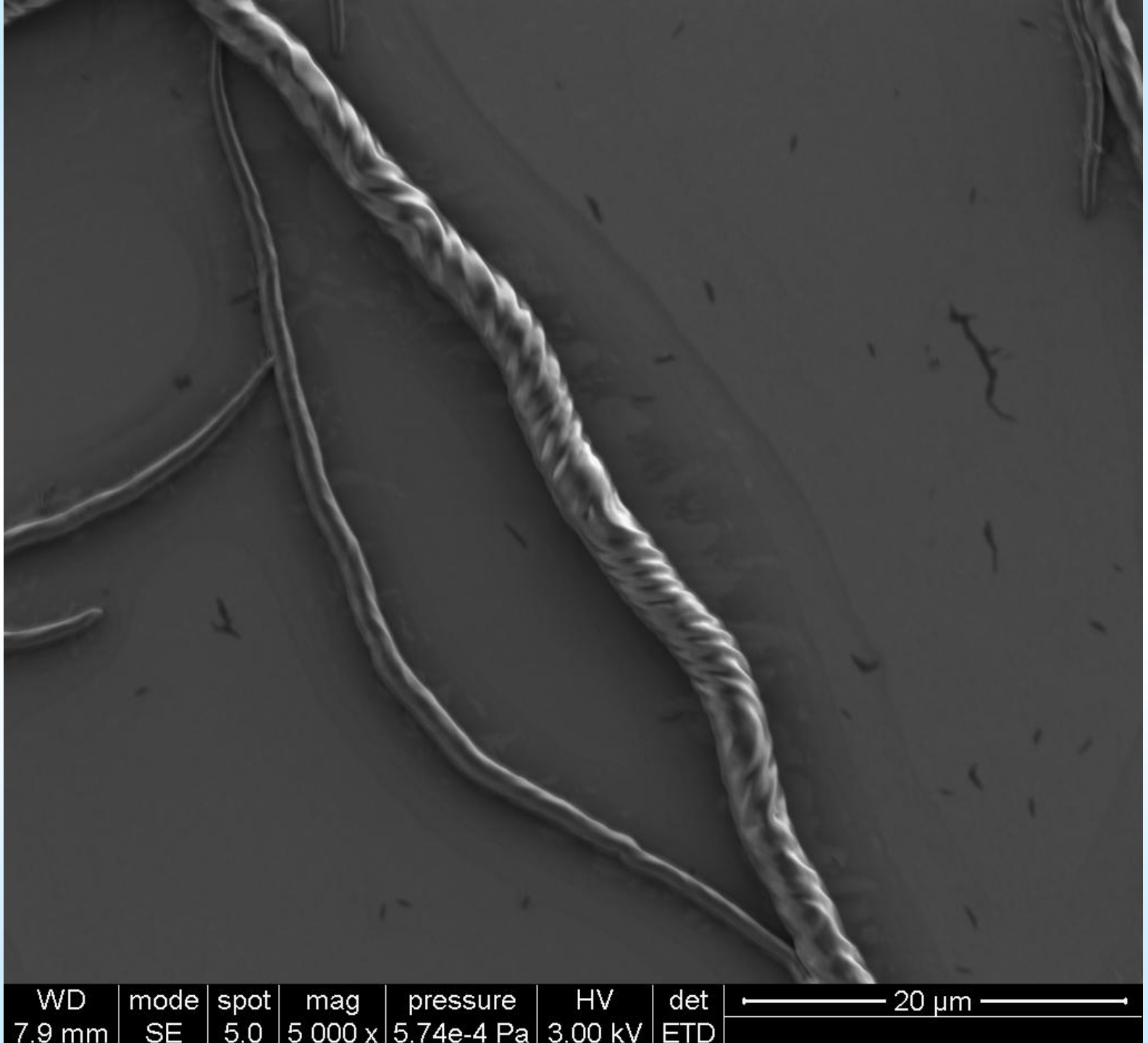


SEM images



Inversion of helicity!

I. Danila, F. Piron, F. Riobé, D. Amabilino, N. Avarvari, *unpublished*


WD
7.9 mm
mode
SE
spot
5.0
mag
5 000 x
pressure
5.74e-4 Pa
HV
3.00 kV
det
ETD
20 µm

CONCLUSIONS and PERSPECTIVES

1. Chiral TTF-oxazolines (TTF-OX), –bis(oxazolines) (TTF-BOX) and –bis(BOX)

- chiral conducting radical cation salts upon oxidation

- coordination chemistry: paramagnetic centers – multifunctional materials
  Lewis acidic centers – homogenous catalysis

- tuning the chiroptical properties upon oxidation and protonation

2. C_3-symmetry and supramolecular chirality

- electroactive organogel and conducting nanofibers

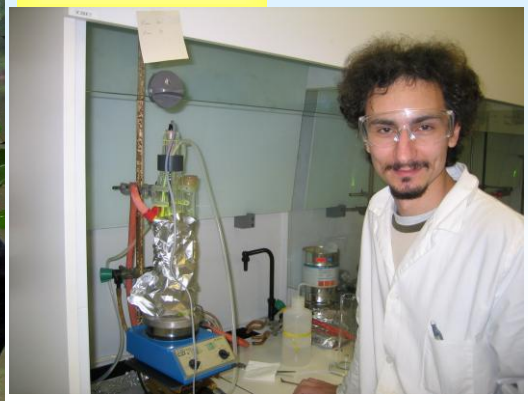
- formation of homochiral helical fibers

- induction of chirality: sergeants-and-soldiers and majority rules

Acknowledgements

Dr. François Riobé

Ion Danila



Dr. Flavia Piron

Dr. Thomas Cauchy

Thomas Biet

Dr. Diana Branzea

Collaborations

Dr. D. Amabilino	ICMAB, Barcelona, Spain	AFM, SEM, TEM, supramol. chirality
Dr. M. Linares Dr. D. Beljonne	Univ. of Mons, Belgium	Molecular dynamics, CD calculations

CNRS - Université d'Angers, Région Pays de la Loire

ANR Project CHIRAFUN (2009-2012)

COST D 35

PHC Picasso (Angers-Barcelona)

City of Angers