Thin films of new organic charge transfer salts

Milan Rudloff

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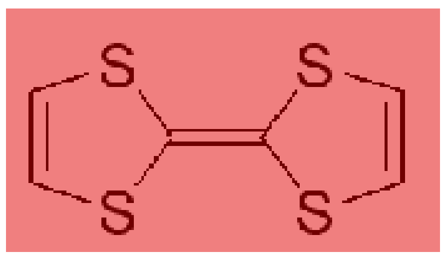
Thin films of new organic charge transfer salts **:**

- characteristics of organic charge transfer systems
- thin film preparation
- some results & current challenges
- outlook

Organic charge transfer salt :

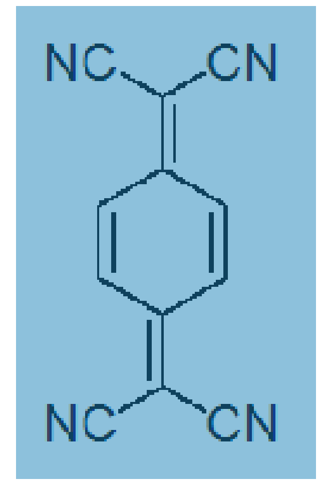
<u>two different organic molecules</u> in **one unit cell** of a crystal

Donor molecule

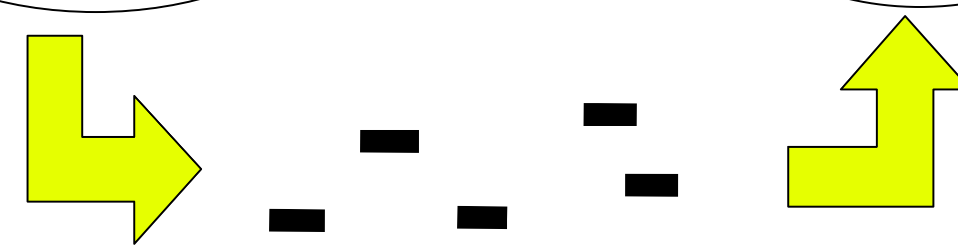


e.g. "TTF"

Acceptor molecule



e.g. "TCNQ"



charge transfer = donor gives electric charge to the acceptor

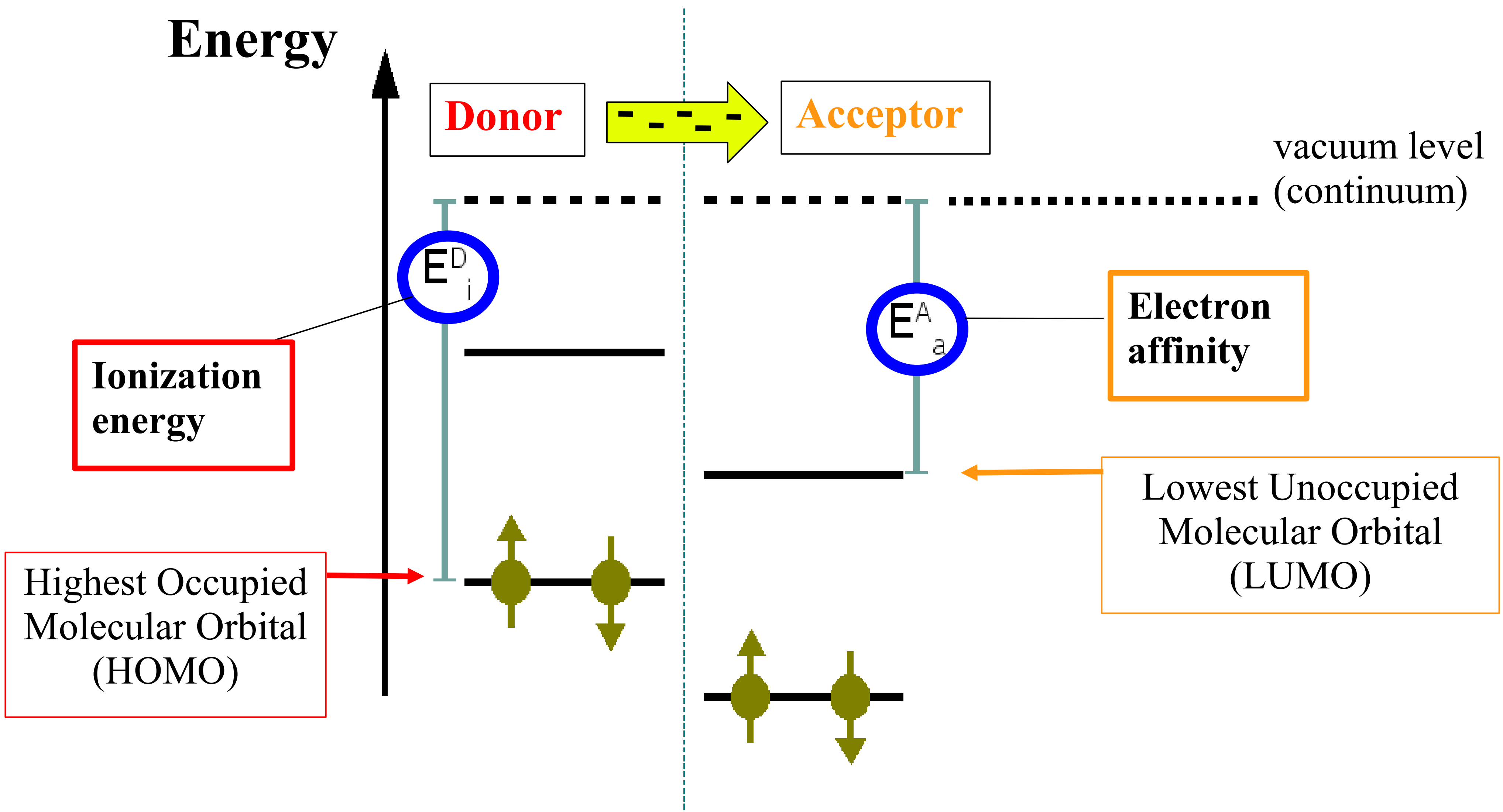
important remark :

Transfer of charge, **not of electrons „as a whole“ !**

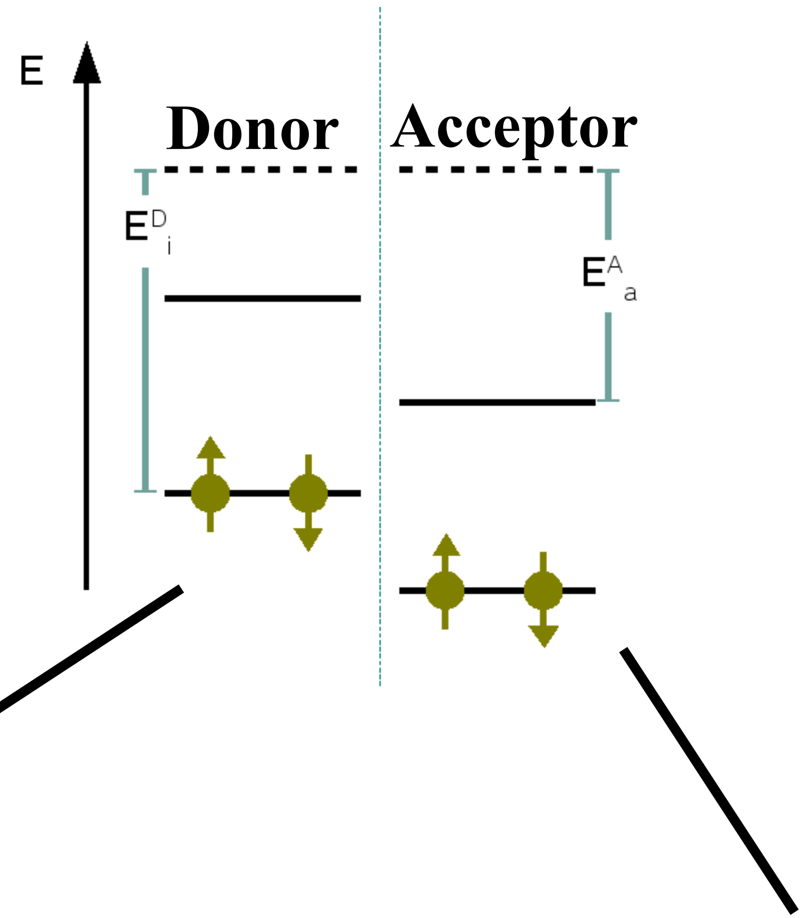
- fraction of elementary charge e is transfered
  = **charge transfer δ** (between 0 and 1)

- **electron density** at the donor molecule decreases,
  electron density at the acceptor molecule increases

Molecular energy levels :



What is essential to form a charge transfer complex ?



<u>Donor</u> with
low ionization energy E_i

<u>Acceptor</u> with
high electron affinity E_a

low ionization energy + **high electron affinity**

additional, **electrostatic attraction** between donor and acceptor, i.e.:

Coulomb binding

$$\left(\sim \frac{-\delta^2 e^2}{r}\right)$$

→ *<u>stabilizing force</u> for the complex, in <u>addition to van-der-Waals-binding</u>*

So what is the <u>necessary condition for charge transfer</u> to take place ?

$$E^D_i - E^A_a - E_C < 0$$

***<u>but</u>*: not really predicatable !**

Variability of electronic properties :

in general organic charge transfer complexes can behave like :

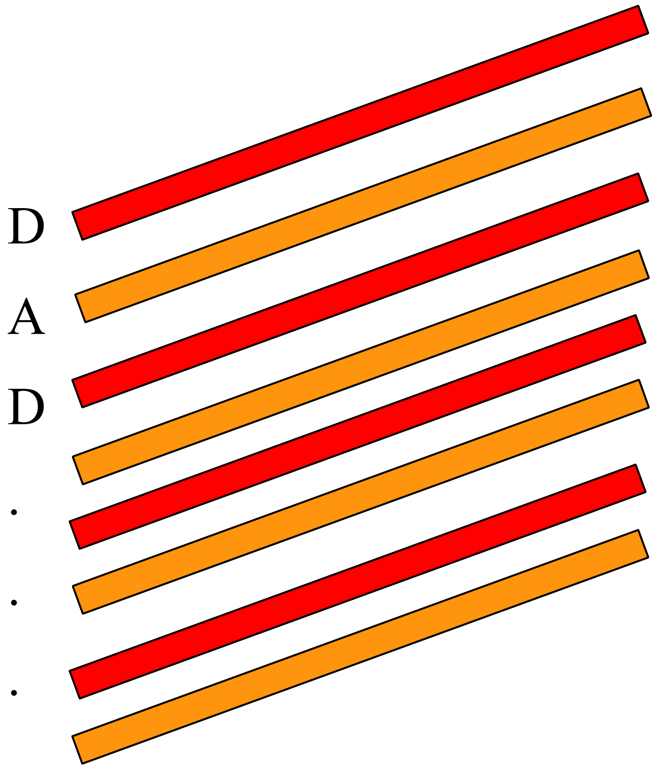
- **insulators** ← usual case
- **semiconductors** ← usual case
- **metals** ← **„organic metals“** *(e.g. TTF-TCNQ)* => high conductivity (typically only 1D) Most interesting for us!
- **superconductors** (!)

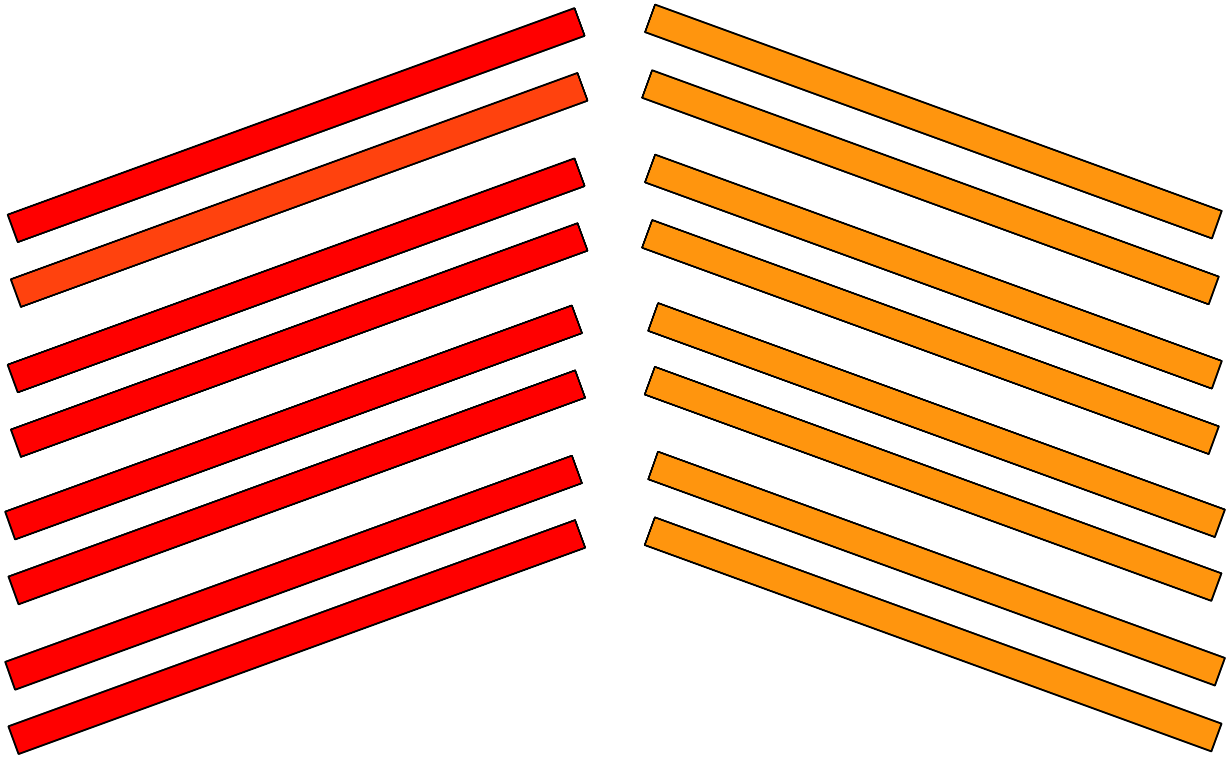
⇨ *depending on:*

- **pressure**
- **temperature**
- **crystal structure**

Electronic properties & stacking of molecules

possible **stacking geometries**,
i.e. arrangement of donor and acceptor molecules :



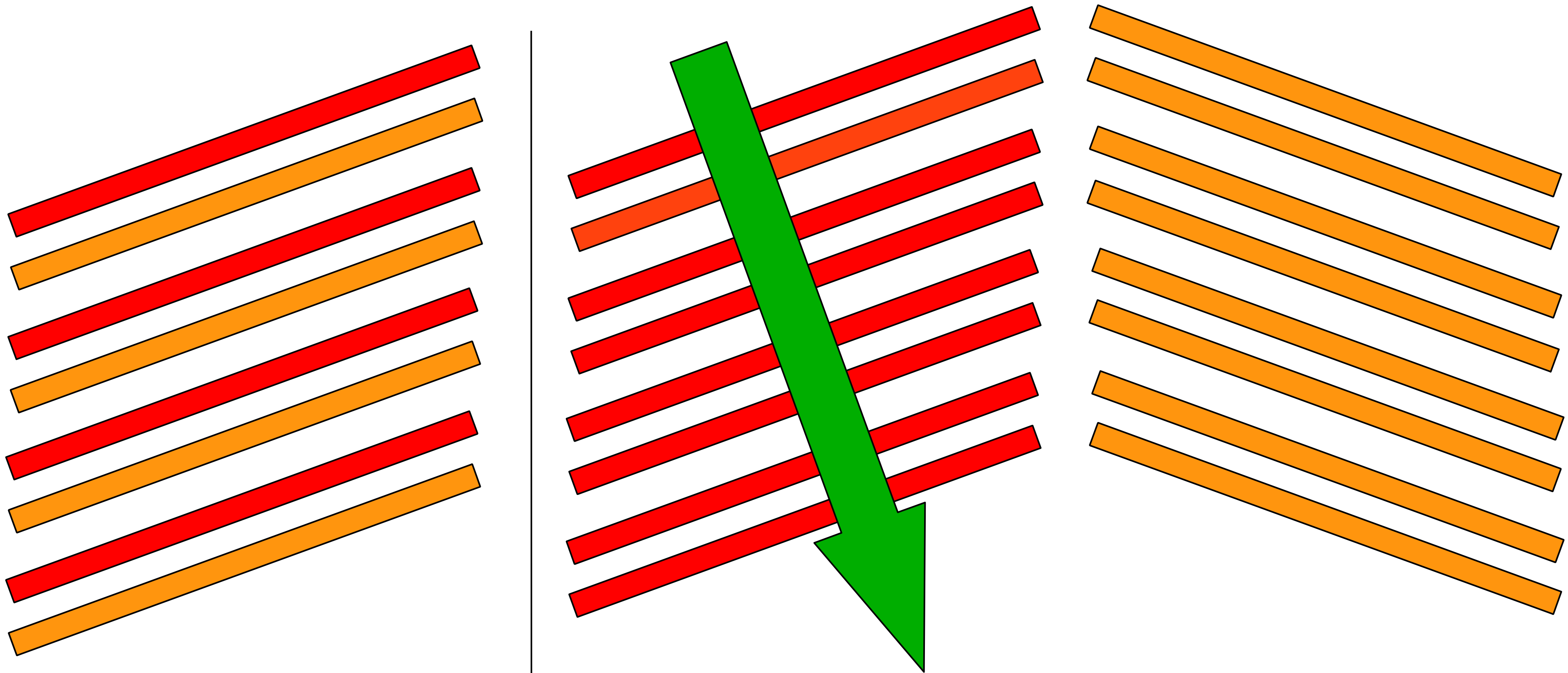


mixed stacks

segregated stacks

again: it's **<u>hard to make predictions</u>** for certain donor-accceptor combinations

Electronic properties & stacking of molecules



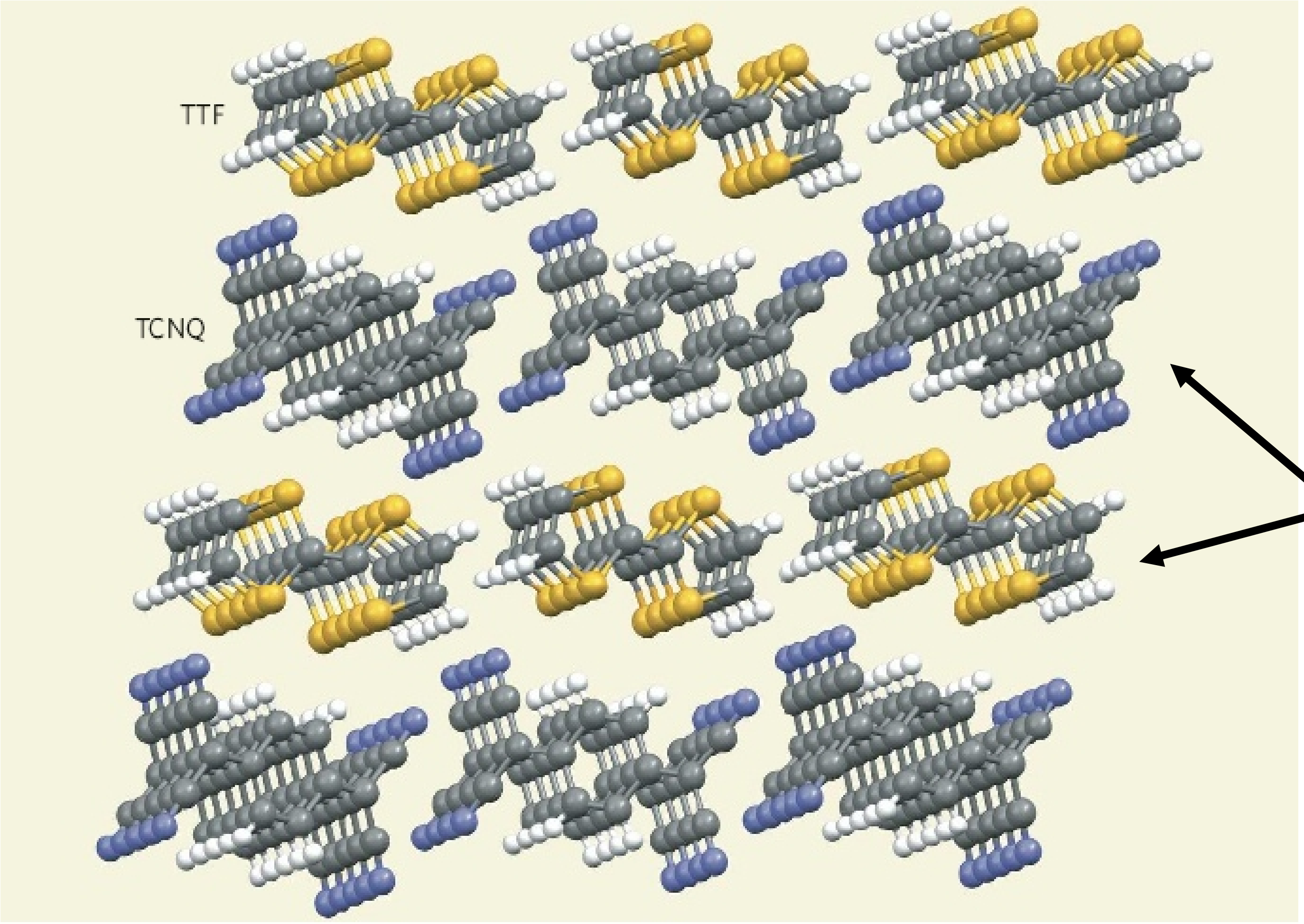
electron/charge transport
along the stacks
=> high, anisotropical conductivity !

mixed stacks

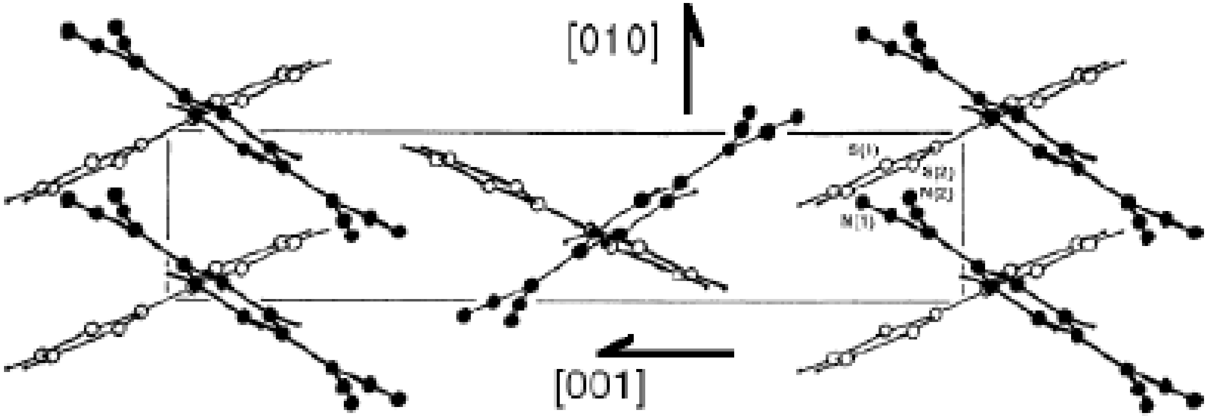
=> **insulator or semiconductor**

segregated stacks

=> **metal or semiconductor**



high conductivity along stacks with the same molecule type (only donors and only acceptors), so called ***„segregated stacks“***

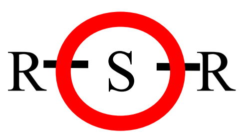


“TTF-TCNQ“

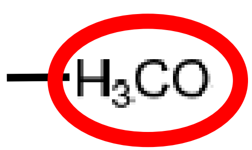
Which molecules can serve as donors and acceptors ?
Which <u>functional groups</u> serve as „promoters“ ?

typical examples :

for donors



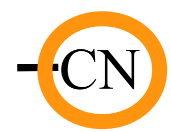
„thio“



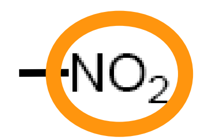
„methoxy“

.
.
.

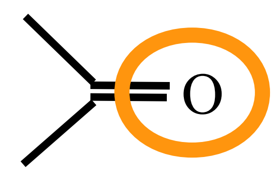
for acceptors



„cyano“ or “carbonitrile“



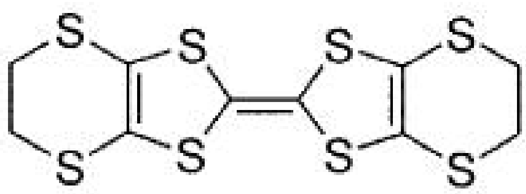
„nitro“



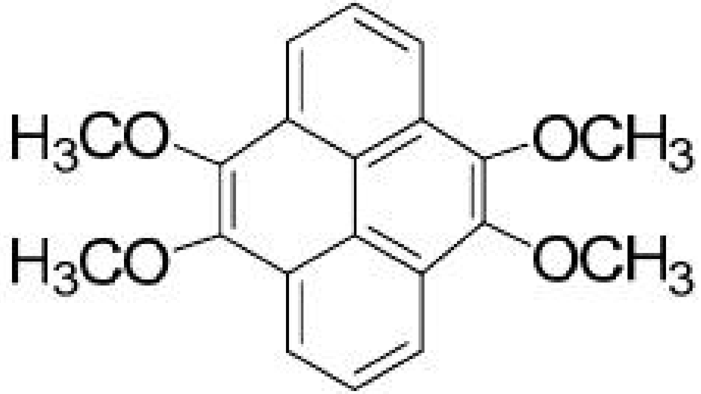
„keto“

.
.
.

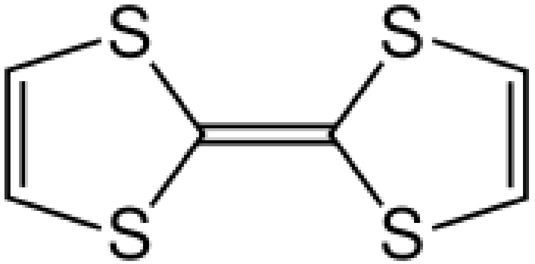
„Our“ molecules : DONORS (selection)



BEDT-TTF or „ET“
Bis(ethylenedithio)tetrathiafulvalene

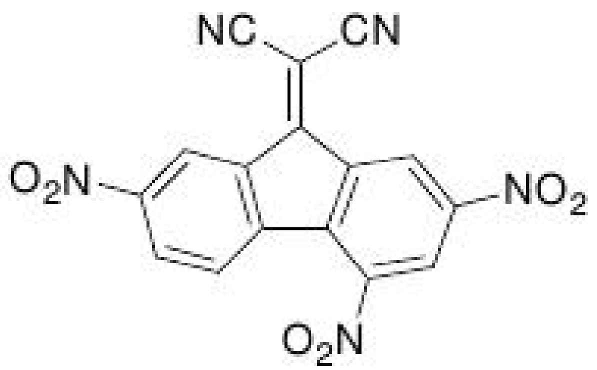


TMP
4,5,9,10-Tetramethoxypyrene

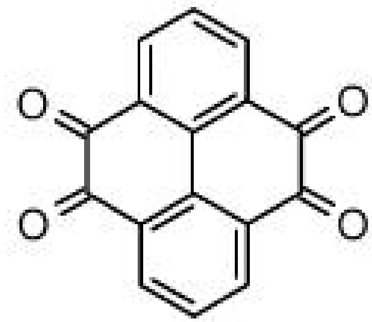


TTF
2,2',5,5'-Tetrathiafulvalene

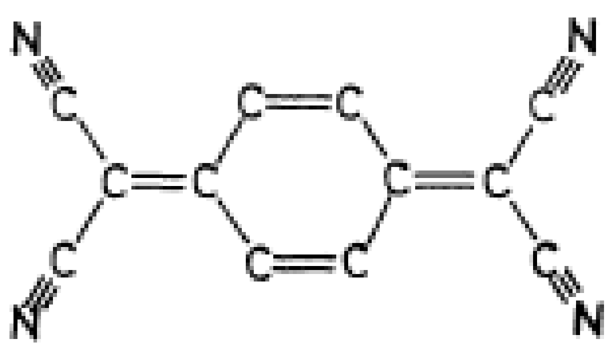
„Our“ molecules : ACCEPTORS (selection)



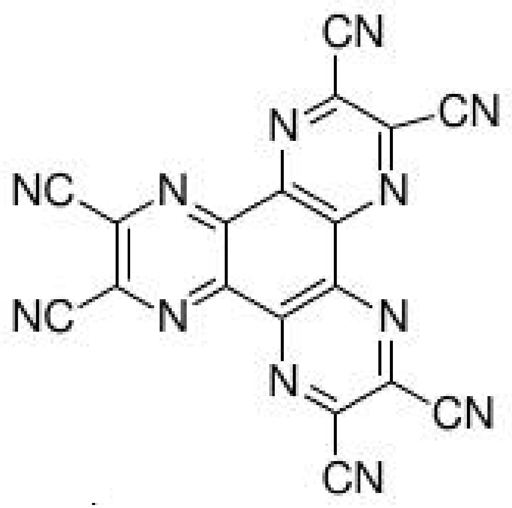
DTF
9-Dicyanomethylene-2,4,7-trinitrofluorene



TKP
4,5,9,10-Tetraketopyrene



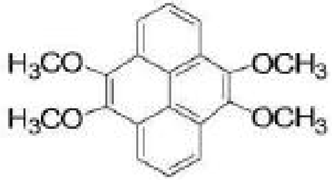
TCNQ
7,7,8,8-Tetracyanoquinodimethane



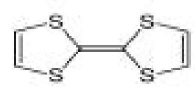
HATCN6
1,4,5,8,9,12-hexaazatriphenylene-hexacarbonitrile

DONORS

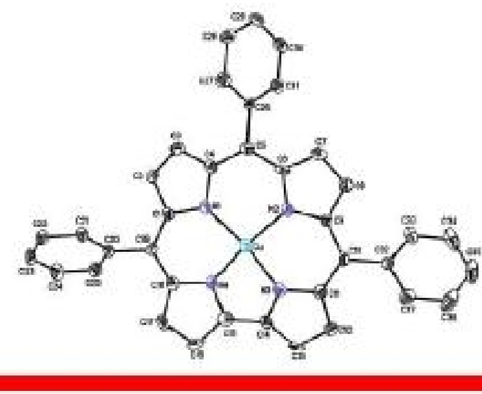
(1)



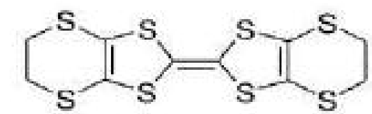
(2)



(3)

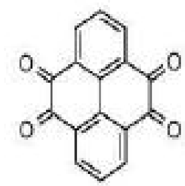


(4)

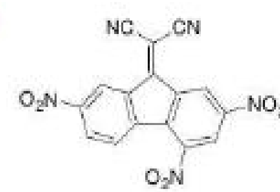


ACCEPTORS

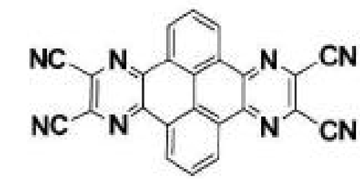
(5)



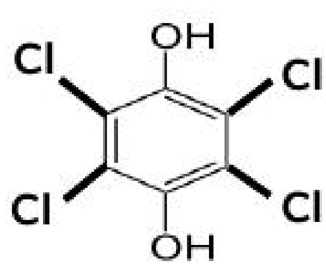
(6)



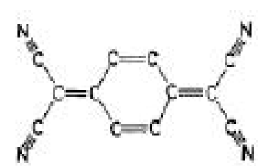
(7)



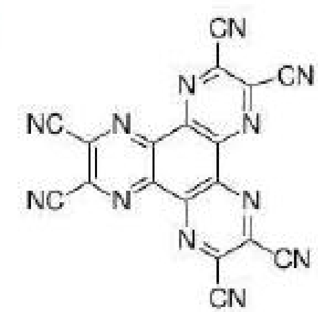
(8)



(9)



(10)



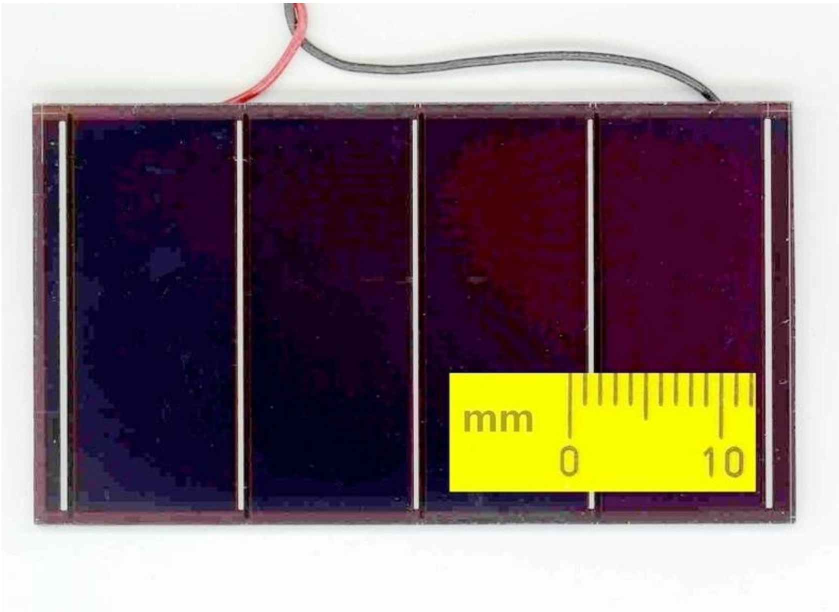
Thin films

thin : 0.1nm ..100µm

film : layer of some material on a substrate

compared to ***bulk*** *material* :
(like large single crystals)

- strong influence of surface and interface effects
- quasi 2-dimensional for very thin films
- different defect structures
- sometimes not fully dense (no complete layer)
- ...



lots of applications in microelectronics, optics, sensor technology, ...

Thin film preparation

by **<u>O</u>rganic <u>M</u>olecular <u>B</u>eam <u>D</u>eposition**

- **ultra high vacuum chamber**
- **sublimation of (powdered) source material (i.e. donor/acceptor molecules) from effusion cell**
- **deposition onto a substrate => thin film is formed**

= closed container with small opening for evaporation

<u>main process</u>: **adsorption** (or physisorption),
i.e. sticking to the surface (mainly) due to van-der-Waals-forces (i.e. weak binding)

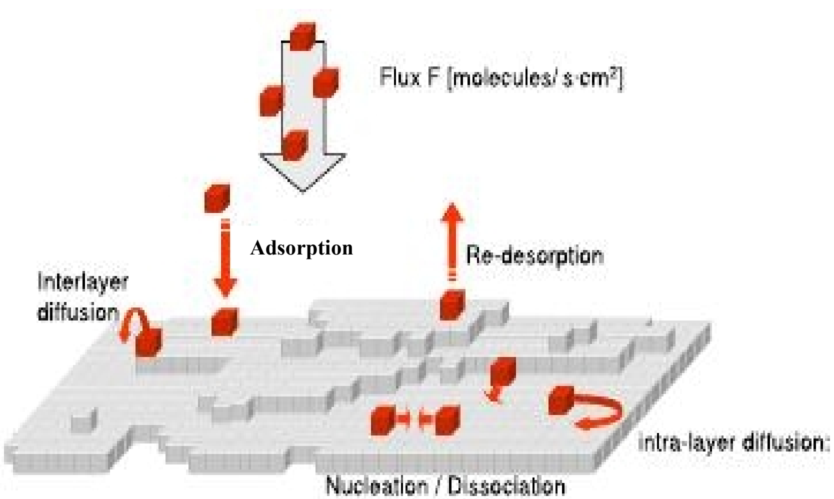
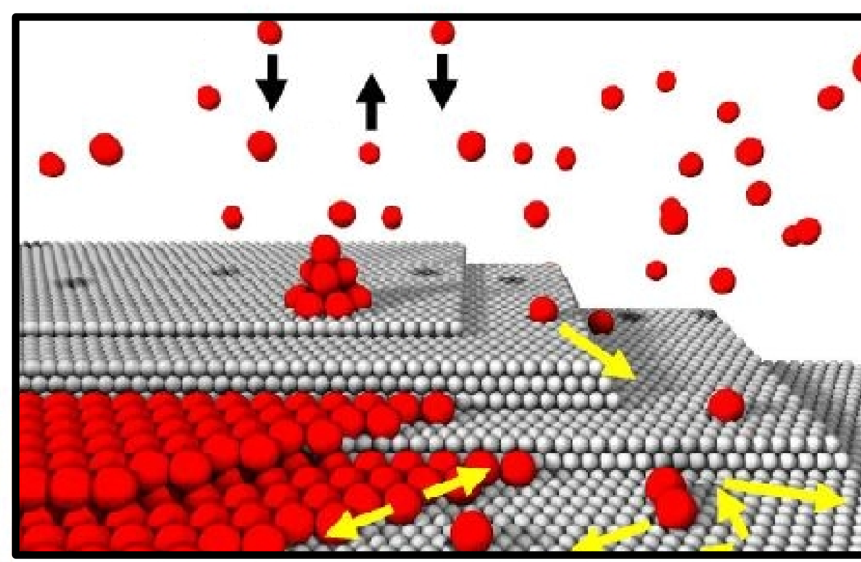


Figure 1. Schematic of atomistic processes relevant for OMBD.



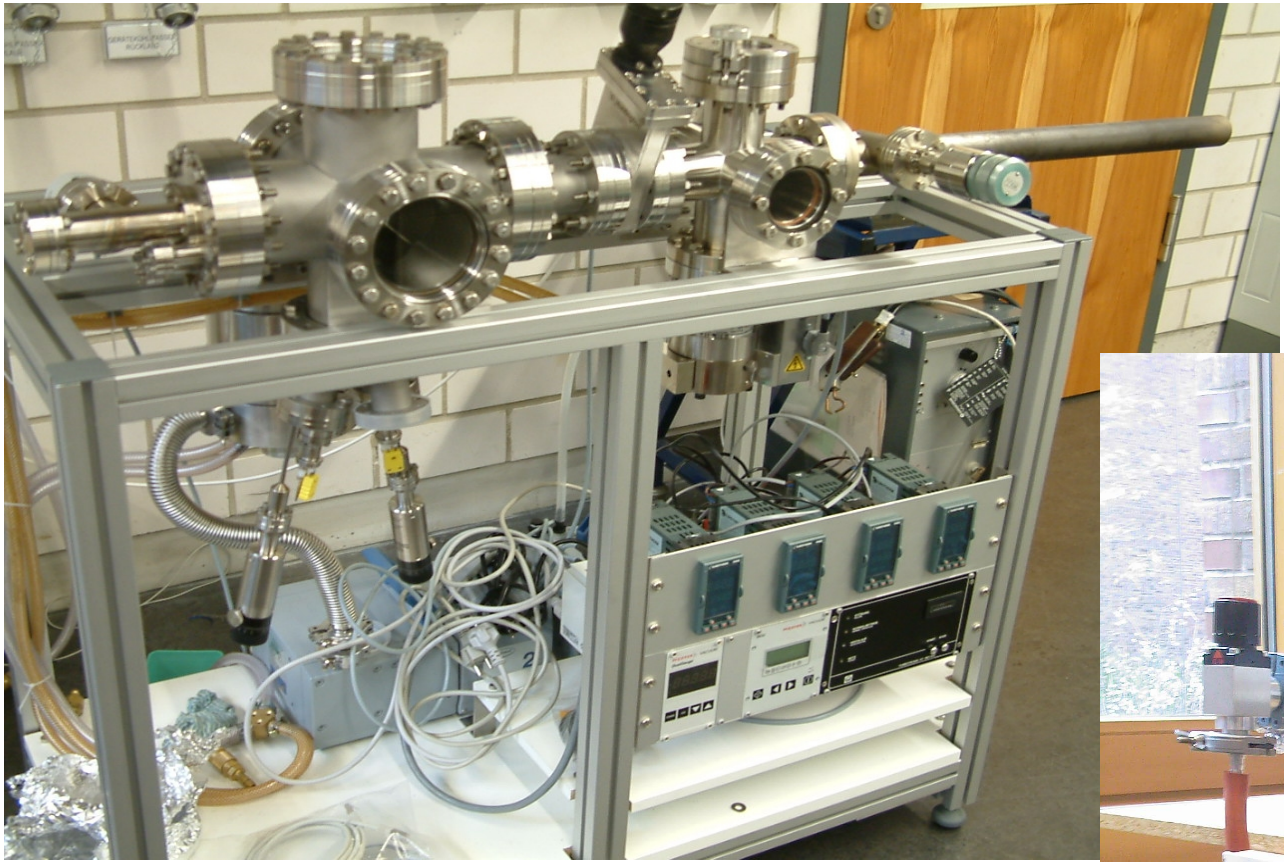
relevant parameters :

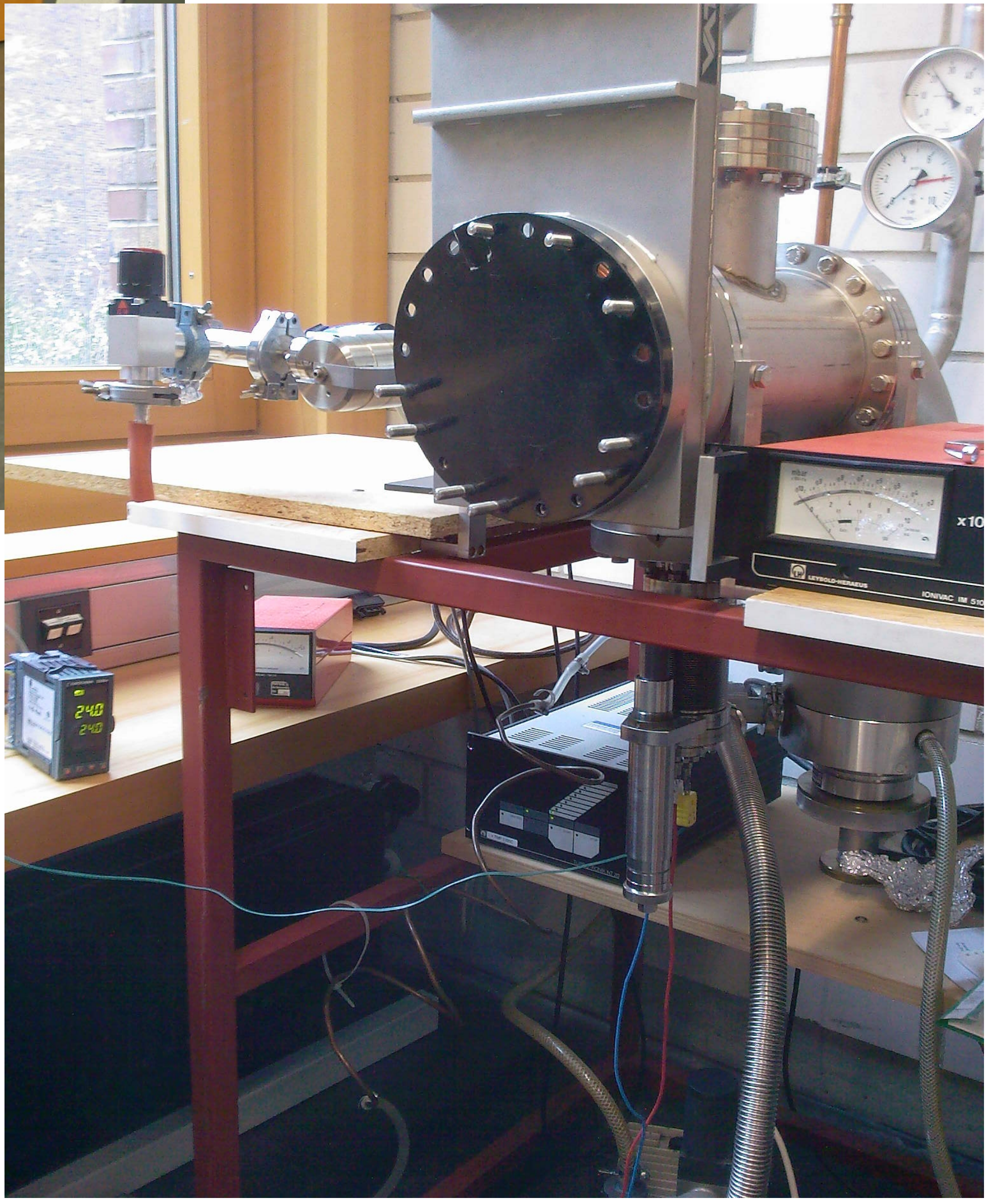
- **substrate material**
- **substrate temperature**
- **deposition rate**
- **vacuum quality**
- **material purity**
- **cleanliness of the substrate**
- **sticking coefficient of the molecules**

etc.

features:

- (often) very well controllable
- clean deposition
- very low deposition rates possible
- expensive
- (complicated) heterostructures possible





two of our vacuum chambers for OMBD

„Deposition method history“ :

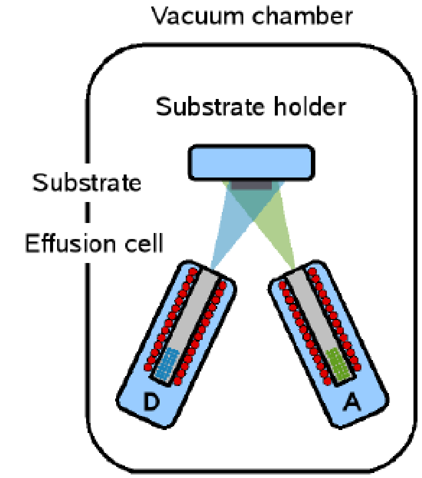
(1) **testing sublimation of single components**
(all available donor and acceptor molecules)
→ Which temperature is necessary/useful for deposition?

(2) **making bilayers** (i.e. donor layer + acceptor layer) + **annealing** (i.e. heating of bilayer for several hours/days)
→ Does a thermally induced charge transfer take place at the interface between donor and acceptor layer?

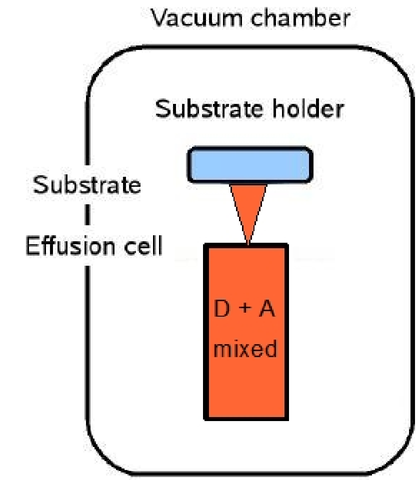
(3) a) **co-deposition** of donor & acceptor from one single evaporation source (i.e. mixing powders of donor and acceptor material and heating of the mixture in one effusion cell)
→ Charge transfer reaction within the cell? CT reaction in gas phase? CT reaction on the substrate?
b) **testing solution growth** of new CT system, if successful testing stability in OMBD

Co-deposition

• both source materials from from <u>two effusion cells</u>, i.e. simultaneous evaporation of donor & acceptor molecules



• both source materials from <u>one effusion cell</u>, only useful if sublimation temperatures are very similar!

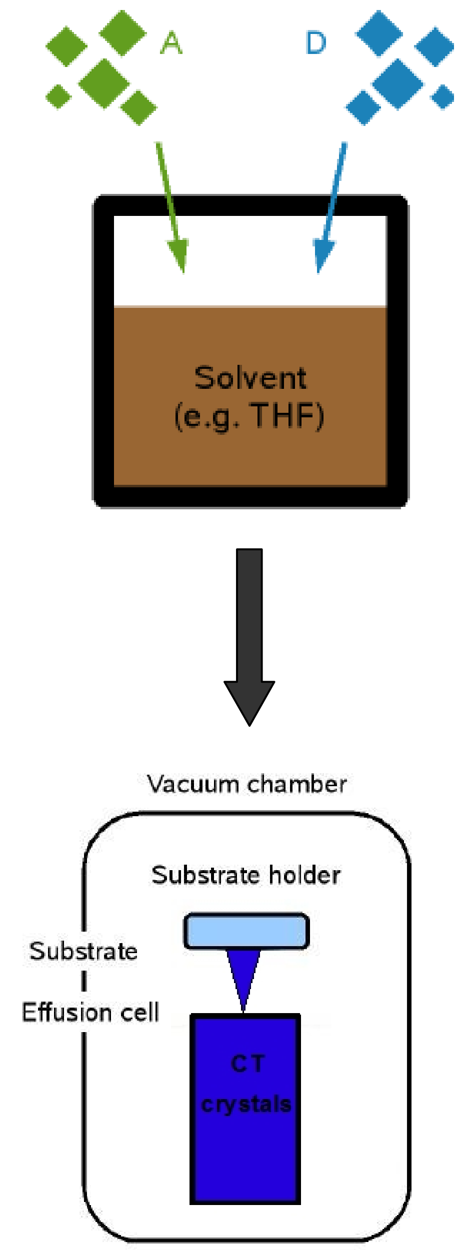


Solution growth + sublimation

1. testing charge transfer in solution growth

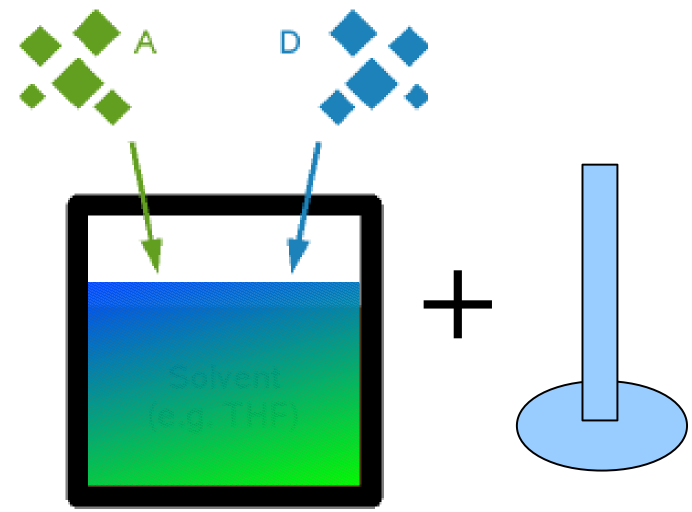
   (→ New colour(s)? Different phases? New crystal shape? New peaks in X-ray diffractogram?)

2. if CT salt was formed, evaporation of powdered crystals



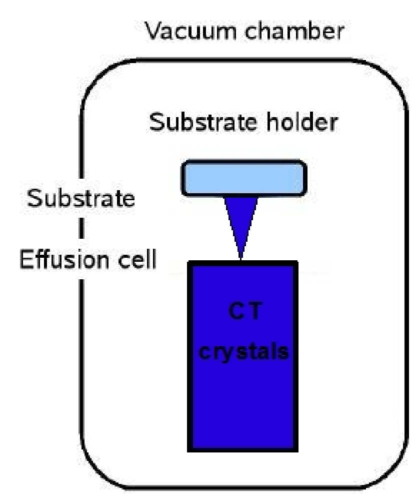
(Liquid assisted) grinding or (ball) milling

1. testing charge transfer by:
   - (dry) grinding of the donor-acceptor-mixture
   - grinding assisted by a solvent („LAG“)
   - milling of donor-acceptor mixture

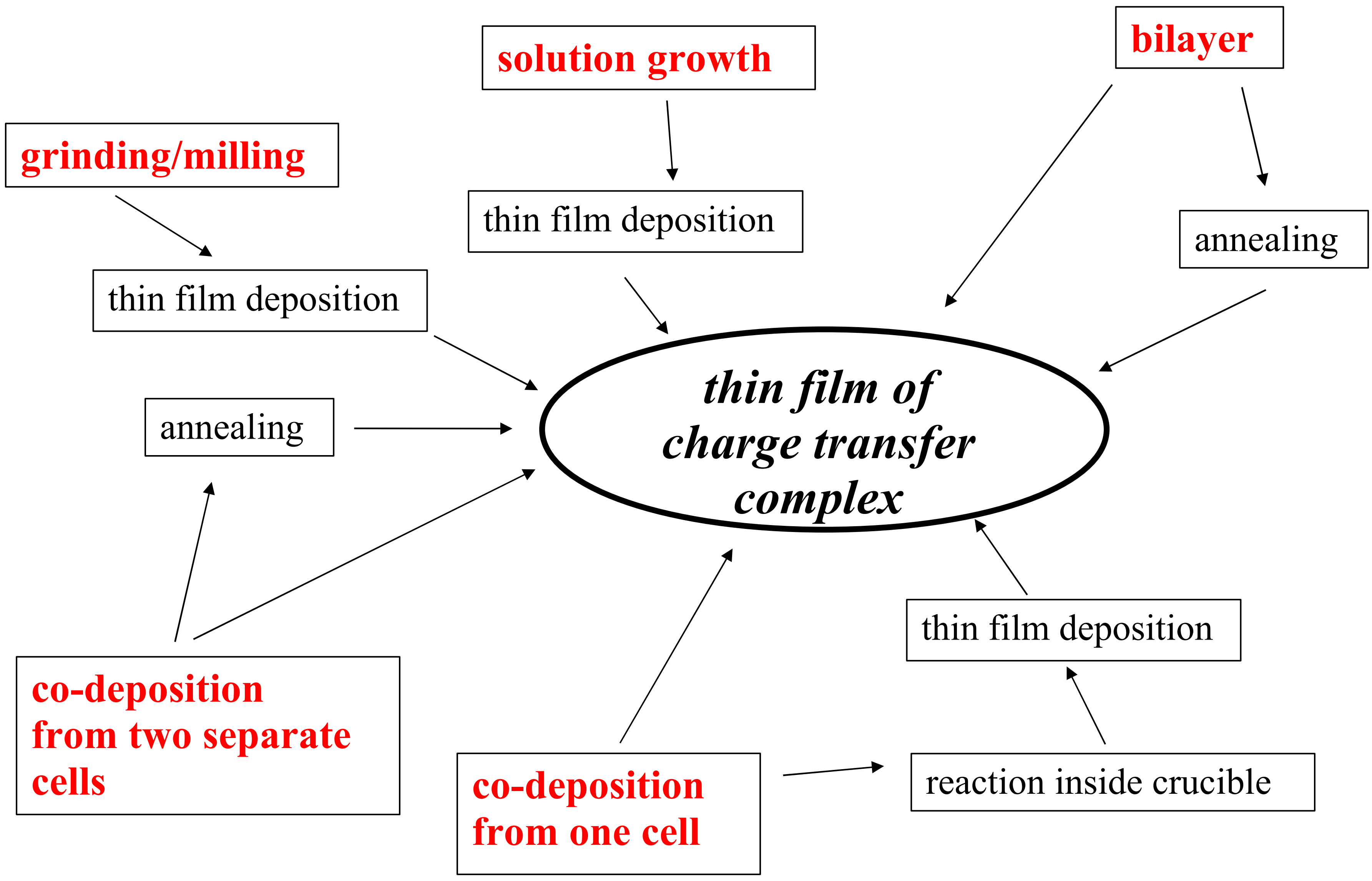


(if succesful:) fine, microcrystalline powder of the CT compound

2. if CT system was formed, evaporation of powdered crystals

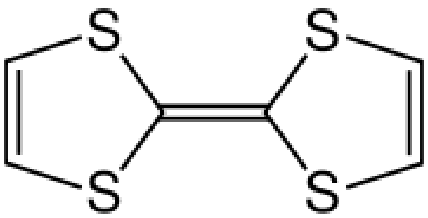


Overview: How to make a thin film of a charge transfer complex

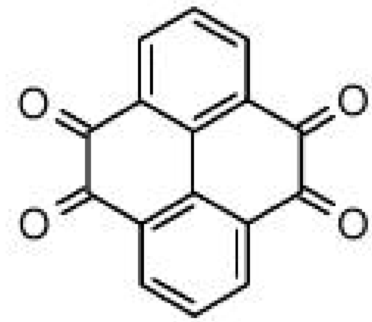


Results

1) <u>solution growth</u> of
TTF (= 2,2',5,5'-Tetrathiafulvalene)
+
TKP(=4,5,9,10-Tetraketopyrene)
results in two types of new crystals: green, dendritic structures and black, filamentary structures

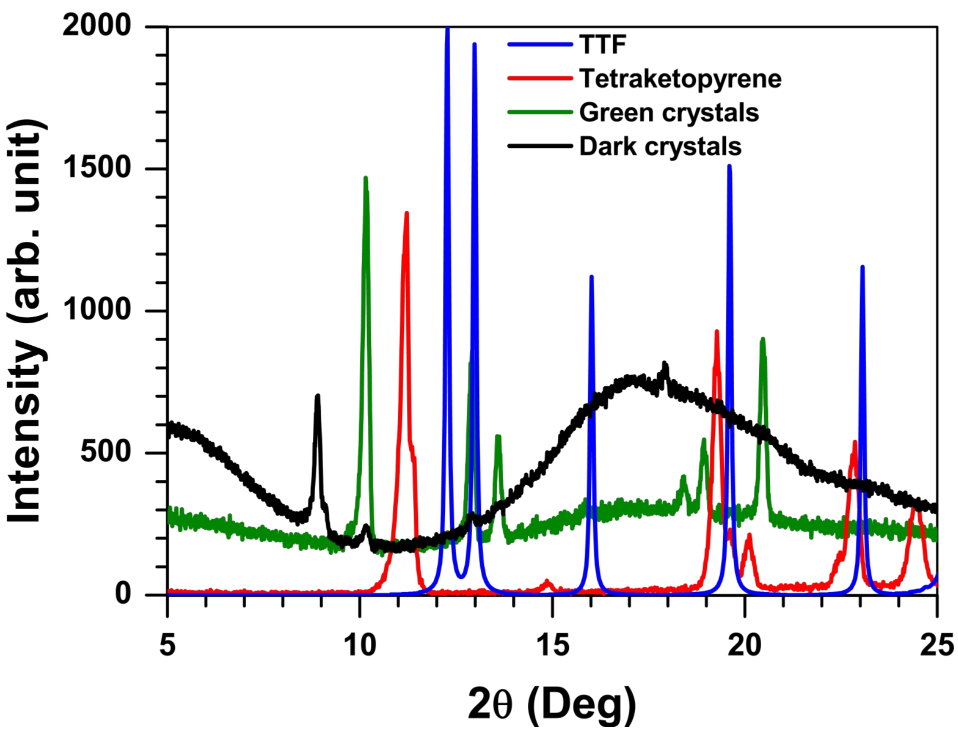


= DONOR



= ACCEPTOR

Stability in OMBD not yet clear



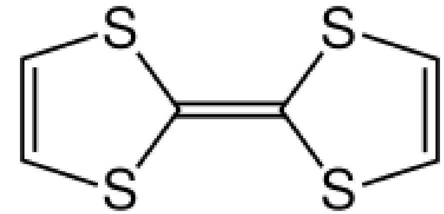
2) <u>solution growth</u> of

TTF (= 2,2',5,5'-Tetrathiafulvalene)

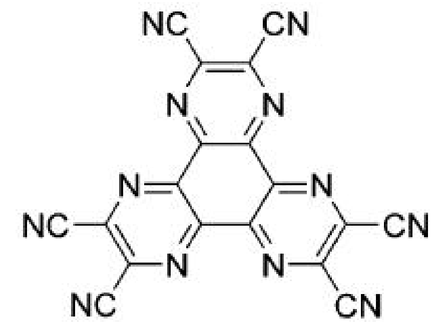
+

1,4,5,8,9,12-hexaazatriphenylene-hexacarbonitrile (“**HATCN6**“)

results in green, dendritic structures

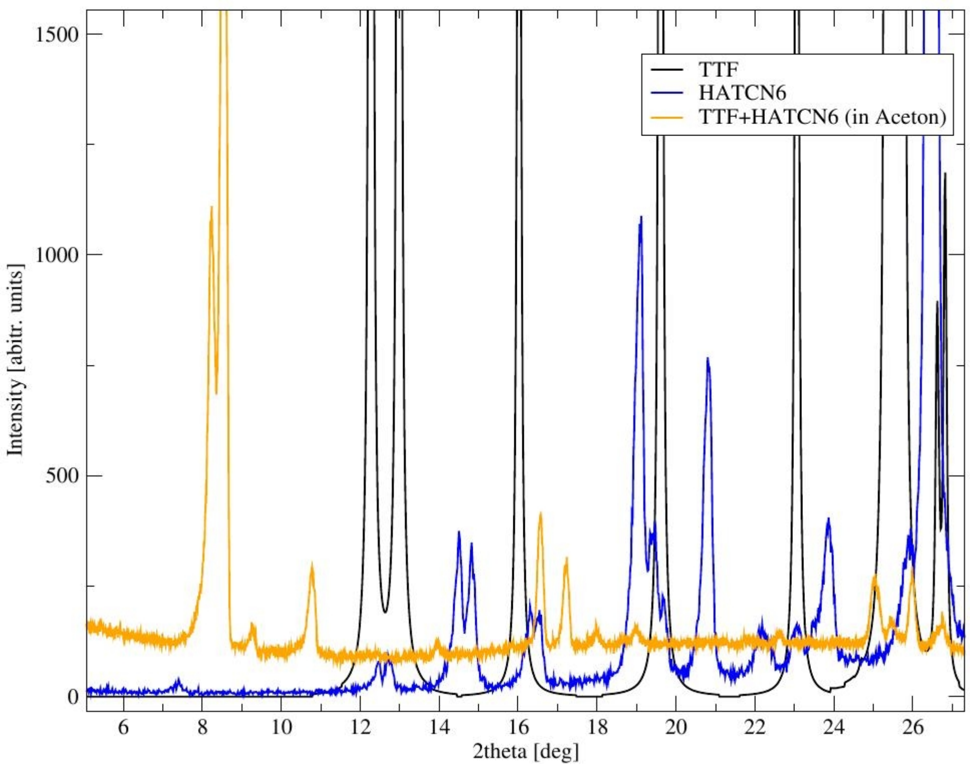


= DONOR



= ACCEPTOR

but: not stable in OMBD



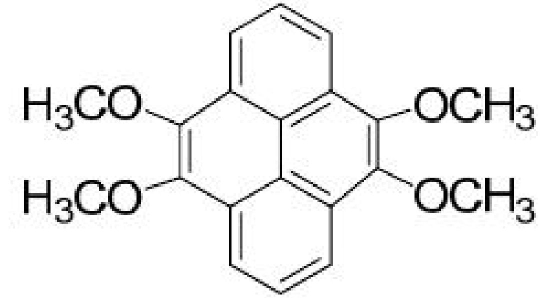
3) <u>solution growth</u> of

TMP(=4,5,9,10-Tetramethoxypyrene)

+

DTF(=9-Dicyanomethylene-2,4,7-trinitrofluorene)

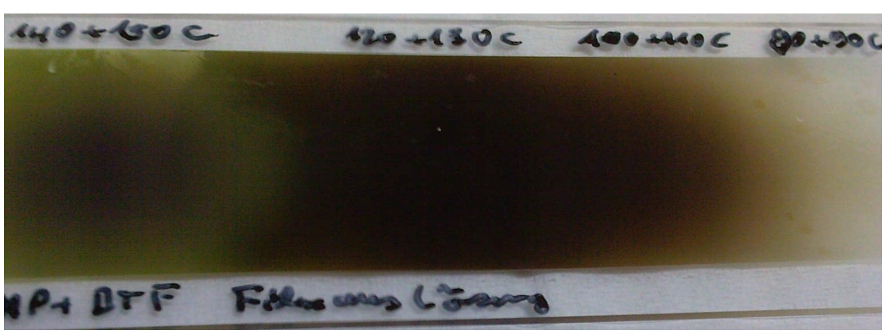
results in black powder

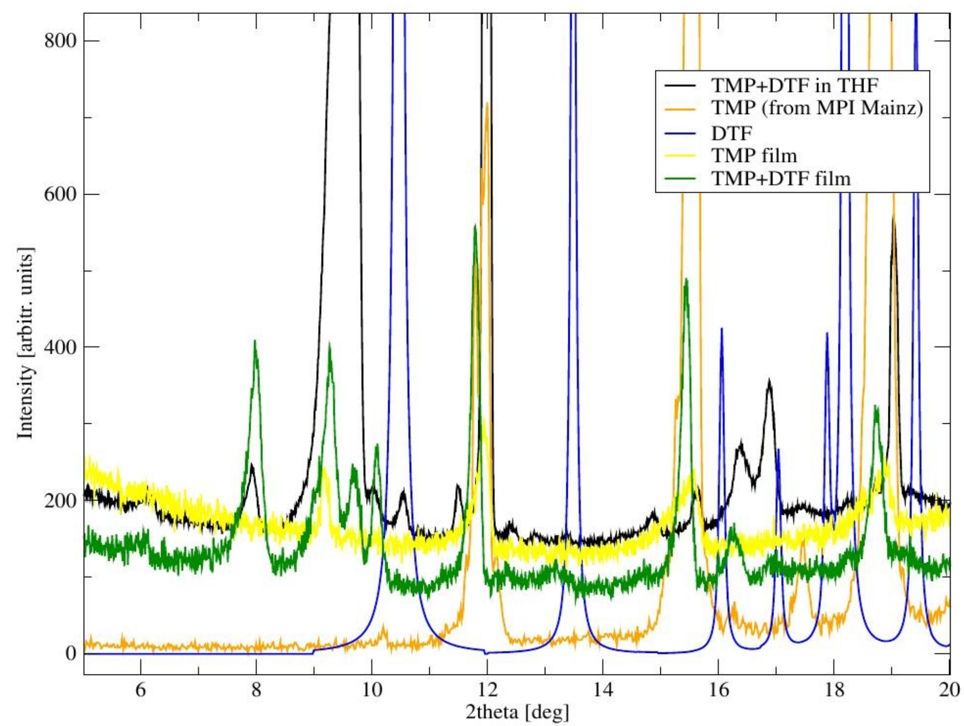


= DONOR

= ACCEPTOR

- **also works with grinding**
- **stable in OMBD!**
- **rather poor crystallinity of the thin film**





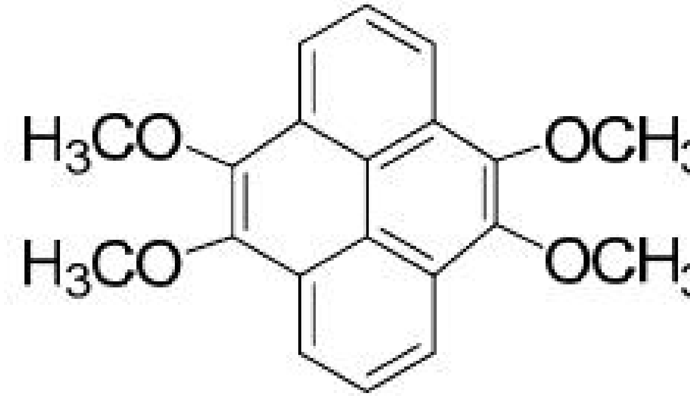
4) <u>co-sublimation</u> of

TMP(=4,5,9,10-Tetramethoxypyrene)

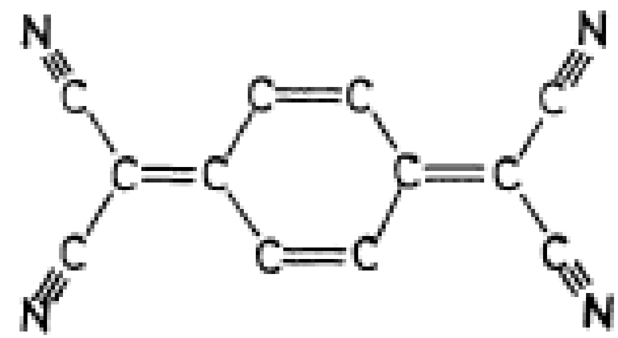
+

TCNQ (7,7,8,8-Tetracyanoquinodimethane)

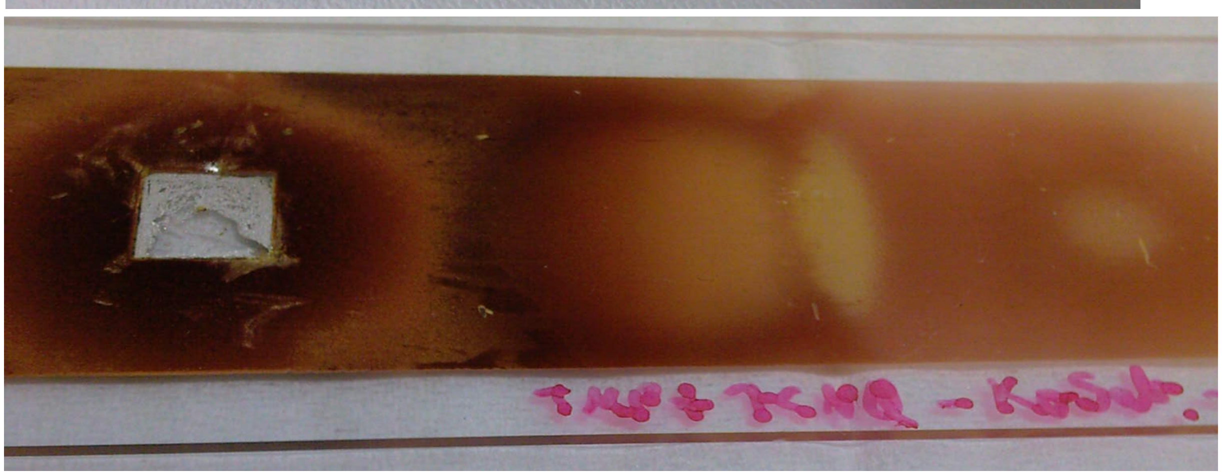
in one cell leads to new film colour & new peaks in the X-ray diffractogram



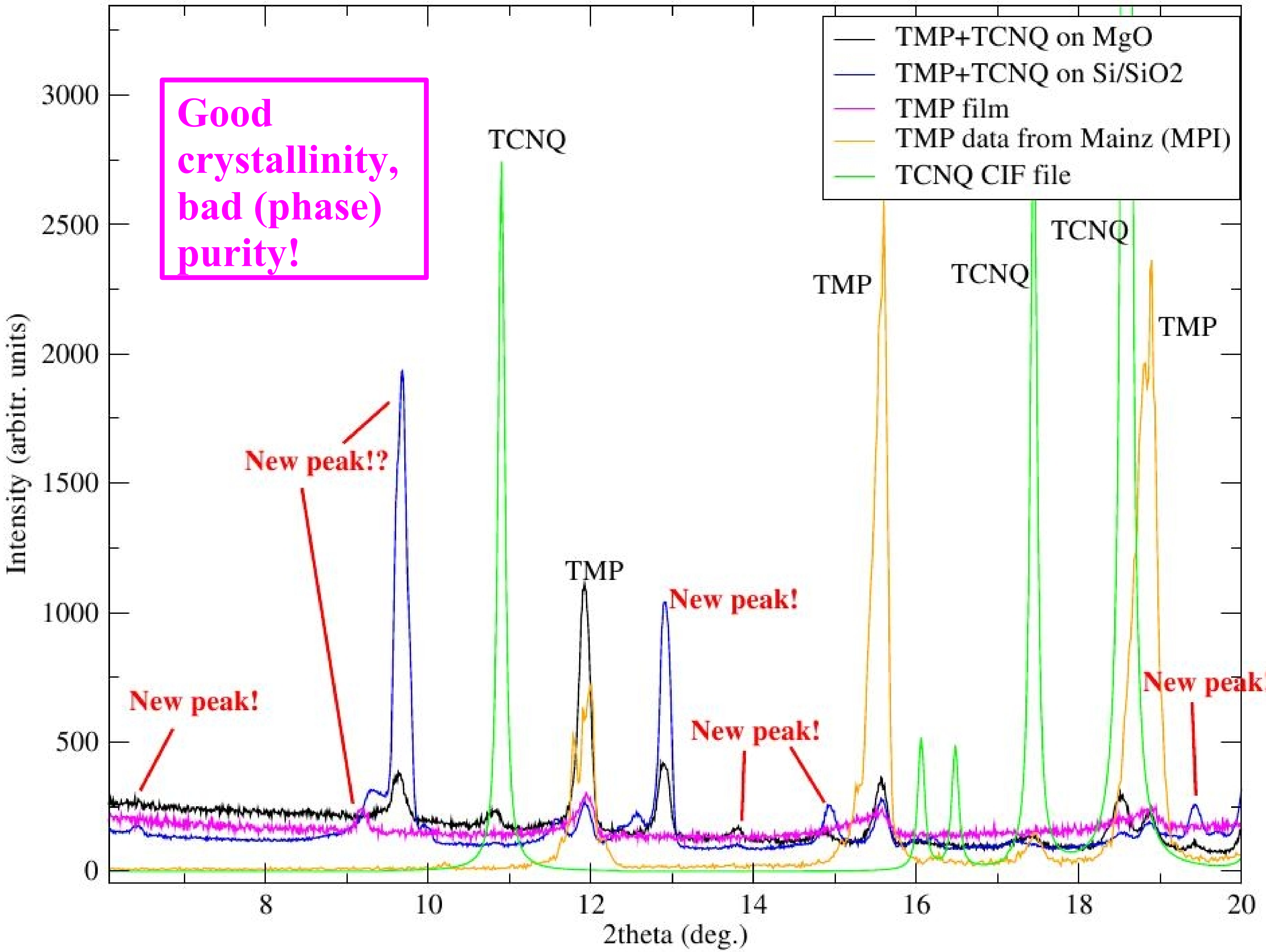
= DONOR

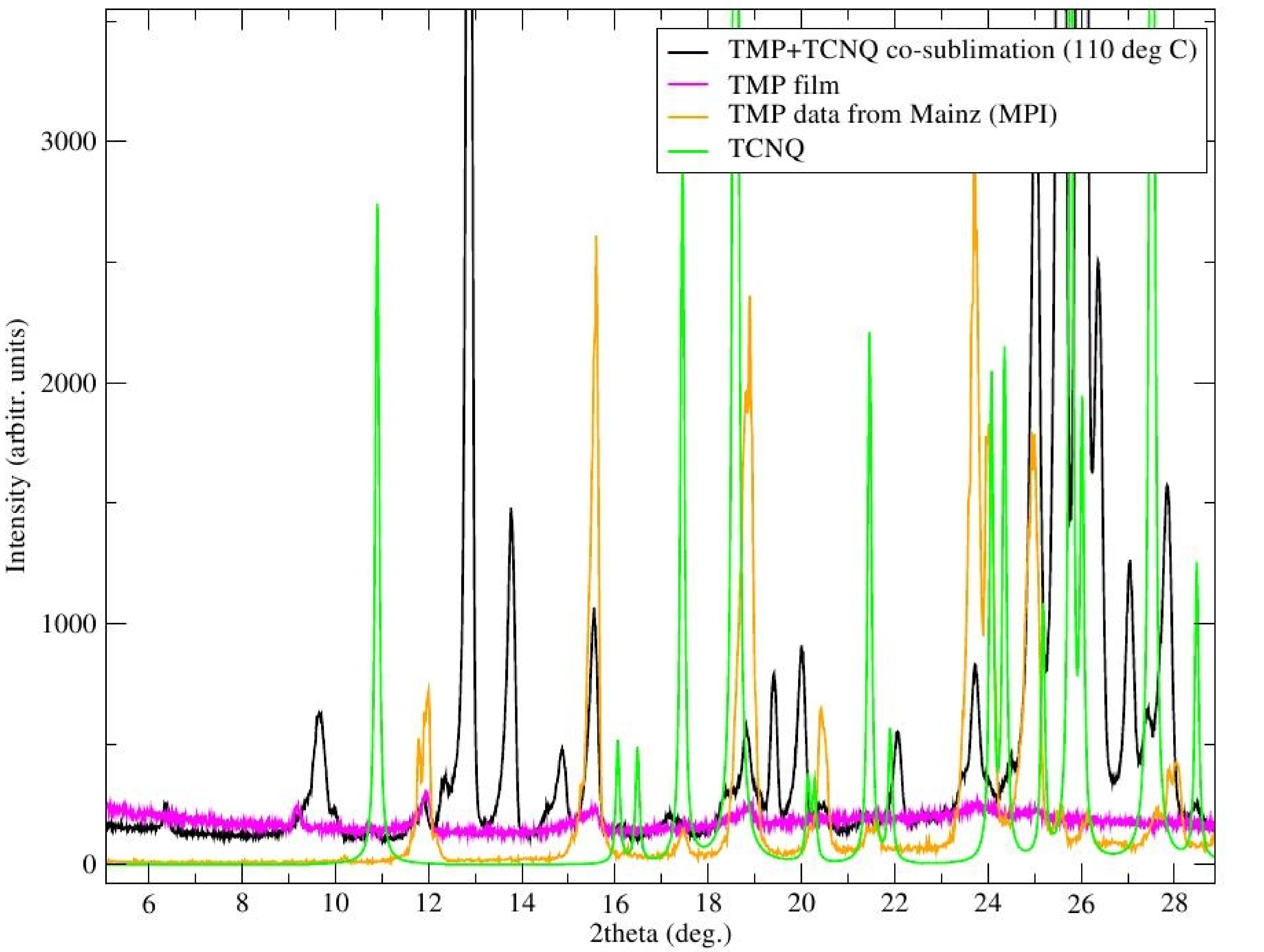


= ACCEPTOR



- **very good crystallinity**
- **no such results from solution growth (yet)!**
- **mixture didn't react within the cell (crucible)!**
- **CT reaction by grinding or milling**


TMP+TCNQ on MgO
TMP+TCNQ on Si/SiO2
TMP film
TMP data from Mainz (MPI)
TCNQ CIF file
Good crystallinity, bad (phase) purity!
TCNQ
TMP
TCNQ
TCNQ
TMP
TMP
New peak!?
New peak!
New peak!
New peak!
New peak!
Intensity (arbitr. units)
2theta (deg.)
0
500
1000
1500
2000
2500
3000
8
10
12
14
16
18
20



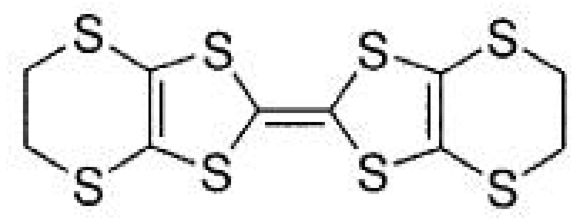
TMP+TCNQ co-sublimation (110 deg C)
TMP film
TMP data from Mainz (MPI)
TCNQ
Intensity (arbitr. units)
2theta (deg.)
0
1000
2000
3000
6
8
10
12
14
16
18
20
22
24
26
28

5) <u>co-sublimation</u> of

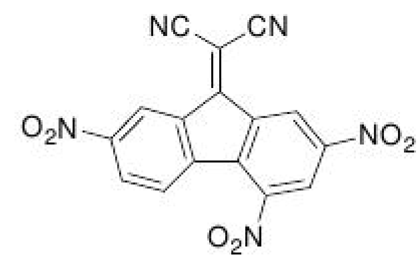
ET(=Bis(ethylenedithio)tetrathiafulvalene)

+

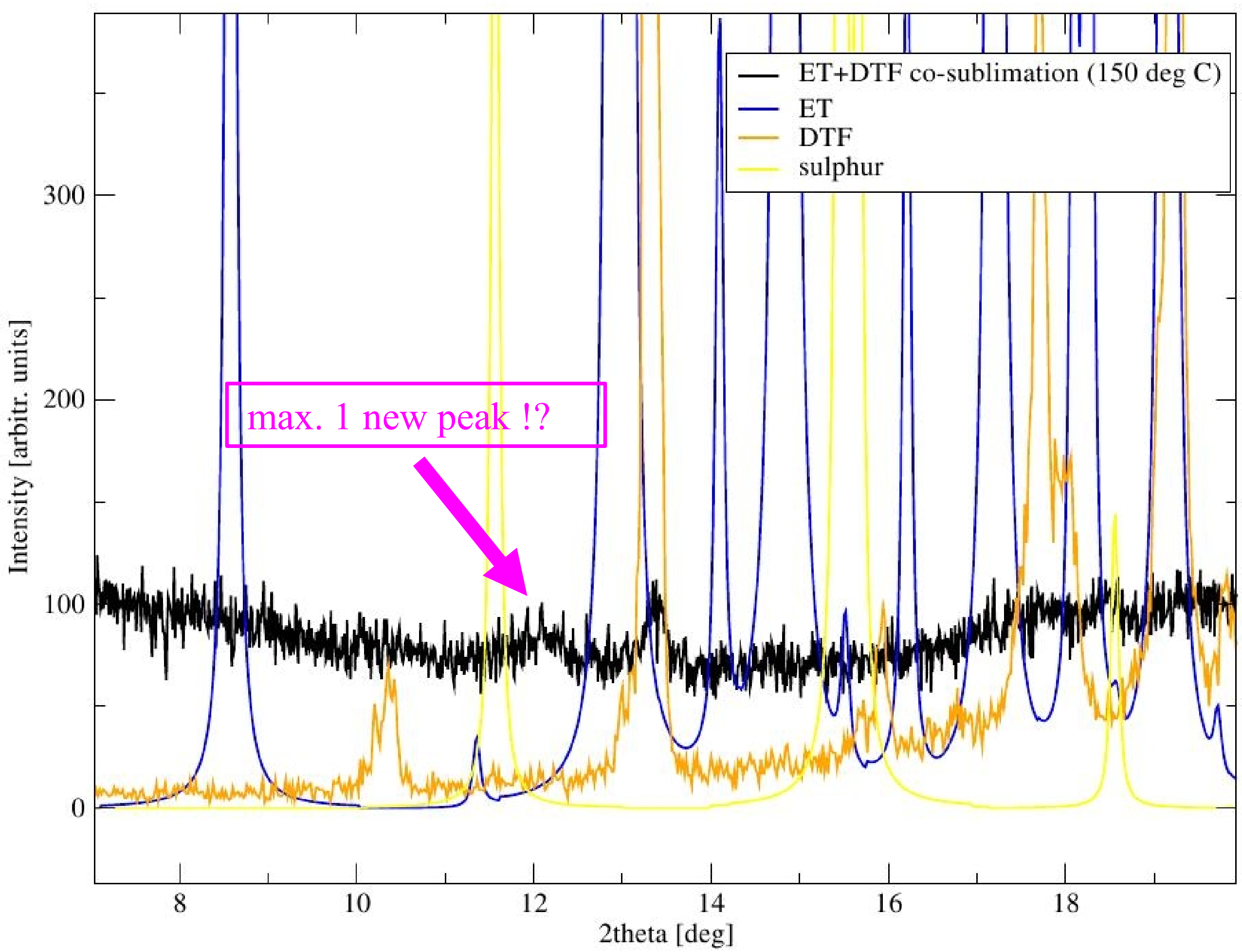
DTF(=9-Dicyanomethylene-2,4,7-trinitrofluorene)



= DONOR



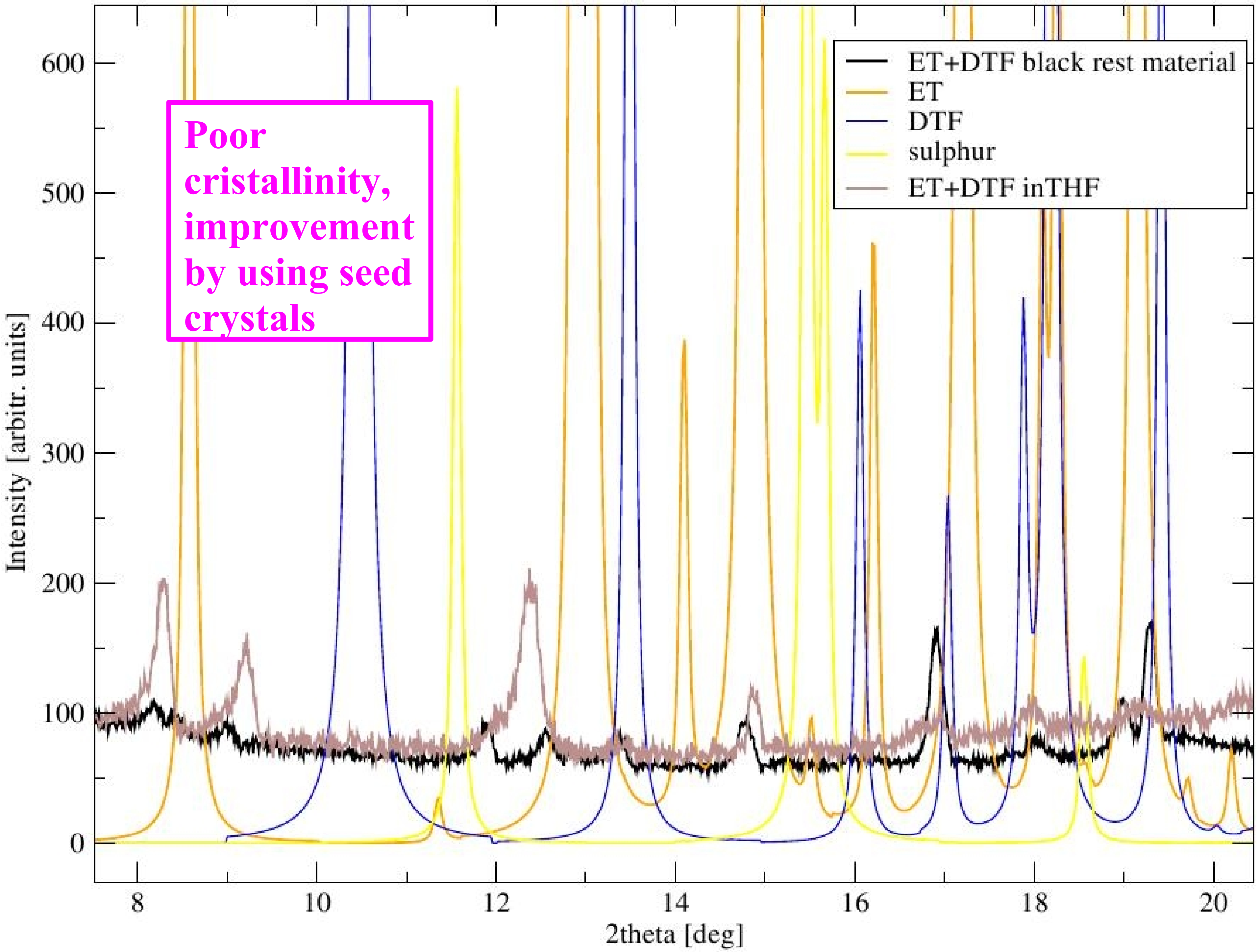
= ACCEPTOR



<u>BUT</u> : **-** remaining material in the crucible ***changed its colour from orange to black***

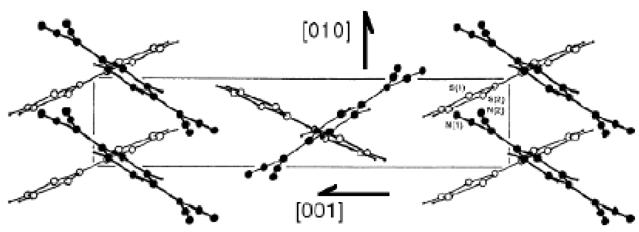
→ X-ray scan of **black substance** gives **new peaks**, i.e. mixture did react within the crucible while material was heated

- <u>solution growth results in black component that shows new peaks</u>, **stable in OMBD**, X-ray peaks seem to fit to those of the black material from the crucible



Poor cristallinity, improvement by using seed crystals
ET+DTF black rest material
ET
DTF
sulphur
ET+DTF inTHF
Intensity [arbitr. units]
2theta [deg]
0
100
200
300
400
500
600
8
10
12
14
16
18
20

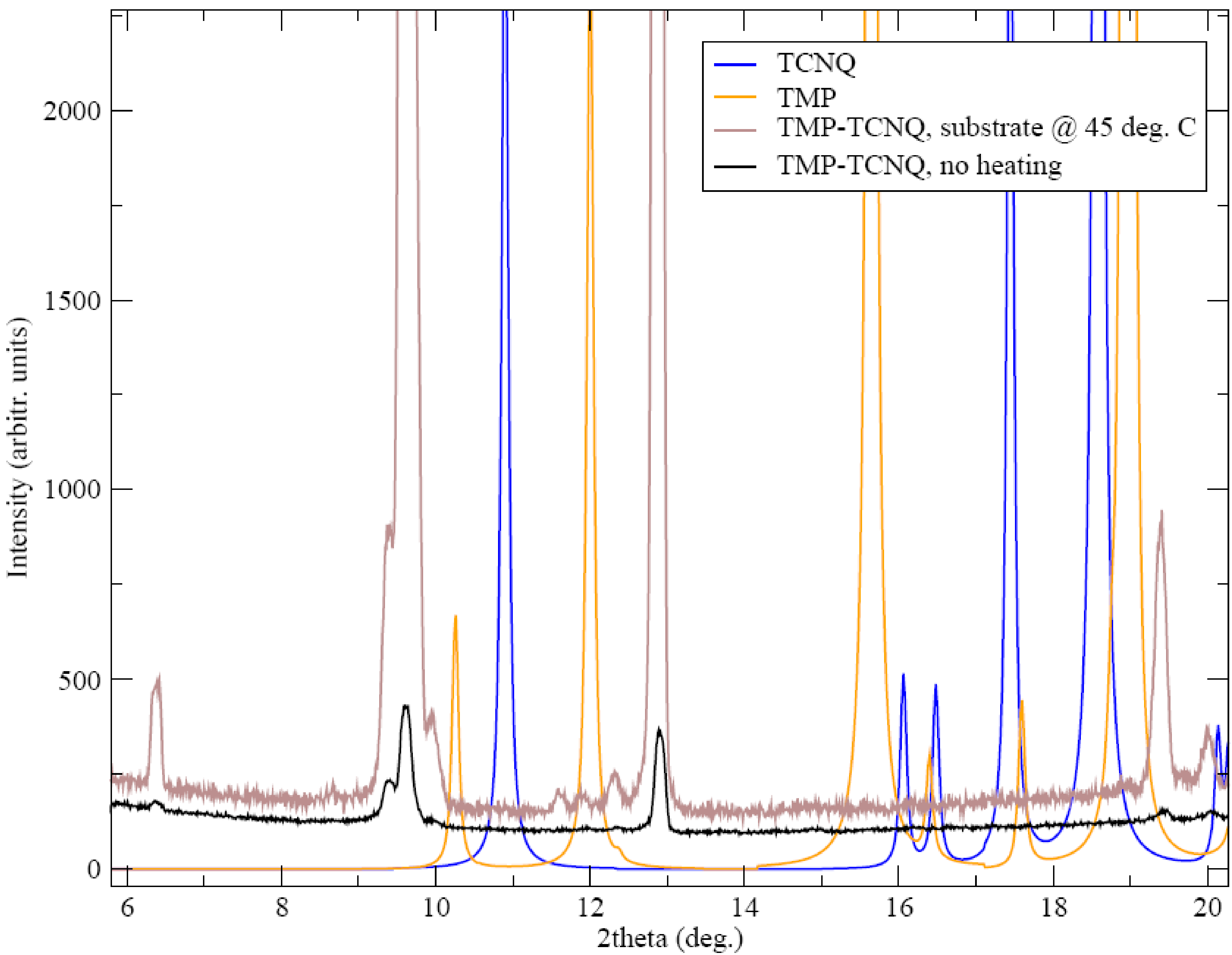
Substrate heating & determination of crystal structures



improvement of crystallinity

helpful for →

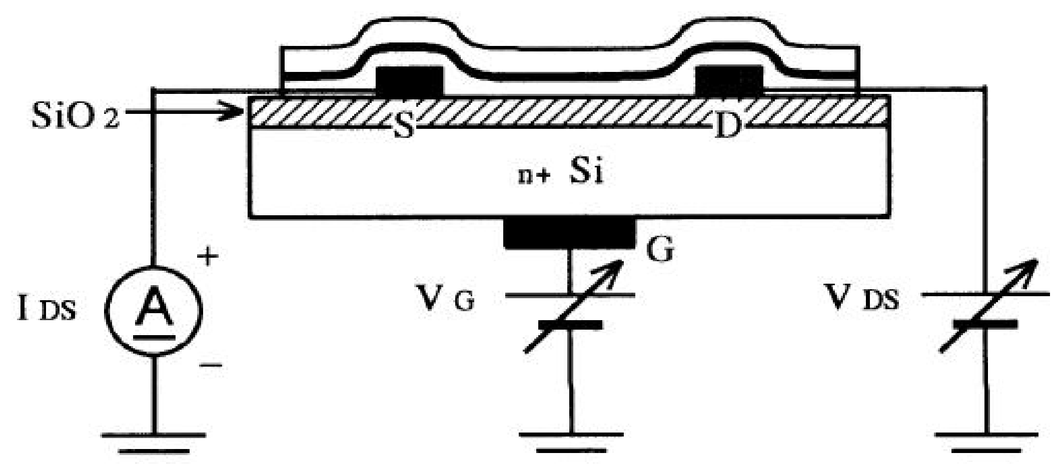
structure determination from powder (done by chemists)

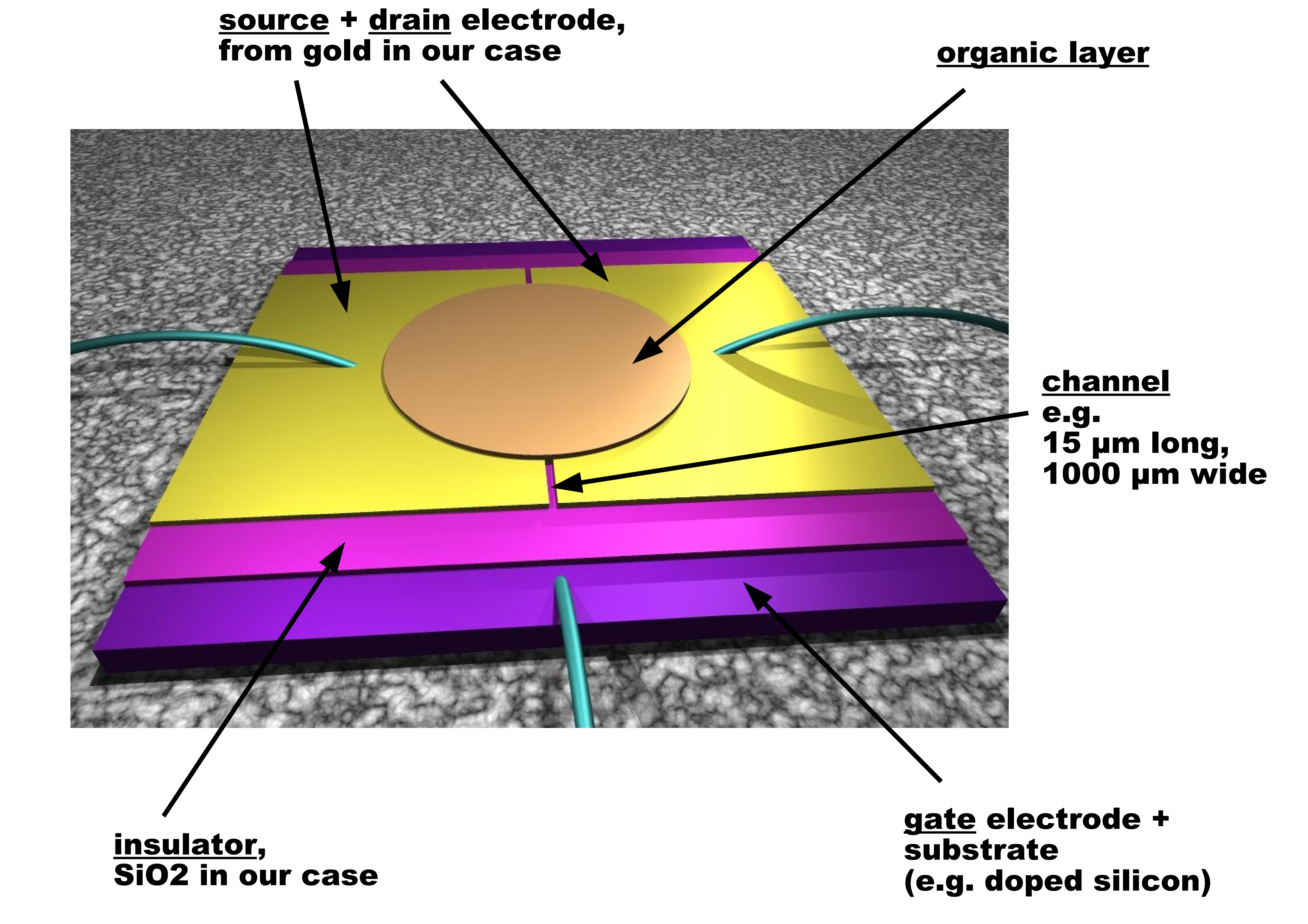

TCNQ
TMP
TMP-TCNQ, substrate @ 45 deg. C
TMP-TCNQ, no heating
Intensity (arbitr. units)
2theta (deg.)
0
500
1000
1500
2000
6
8
10
12
14
16
18
20

Electronic transport measurements

- (temperature dependent) electrical conductivity
  - **activation energy**
- field induced charge carriers ➡ modulation of electric current in a transistor
  - **(charge carrier) mobilities**

OFET :
(Organic field effect transistor)




source + drain electrode,
from gold in our case
organic layer
channel
e.g.
15 µm long,
1000 µm wide
insulator,
SiO2 in our case
gate electrode +
substrate
(e.g. doped silicon)

Prospects :

- crystal structure analysis of the new CT compounds
- different substrate temperatures in the OMBD process
  ⟹ purification & improvement of crystallinity
- conductivity & field effect measurements
  ⟹ electronic properties
- detailed thin film growth studies

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Thank you for listening