

2359-29

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for Non-Metallic Condensed Matter**

13 - 24 August 2012

**Organic semiconducting single crystals: model organic semiconductors and novel
X-rays detectors**

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Italy*

Organic semiconducting single crystals: model organic semiconductors and novel X-rays detectors

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Sincrotrone Trieste SCpA
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or write to
info@elettra.trieste.it

PRESENTATION OUTLINE

- Why organic semiconductors, and their general features
- Organic semiconducting single crystals (OSSCs): main structural and transport properties
- Overview of OSSCs growth methods
- Structural and electronic properties of 4-hydroxycyanobenzene (4HCB) single crystals
- Synchrotron-based investigation of 4HCB crystals
- Direct detection of X-rays by means of OSSCs
- Radiation hardness of 4HCB crystals
- Conclusions

NEXT PRESENTATION SECTION

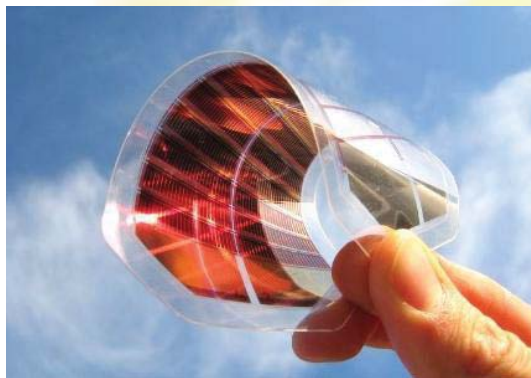
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ORGANIC ELECTRONICS IS FINDING ITS WAY TO THE MARKET

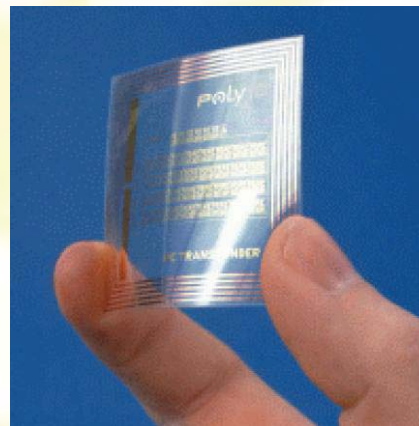
Commercial products based on organic electronics/optoelectronics are already on the market, with a good success, and more has to come.



OLEDs

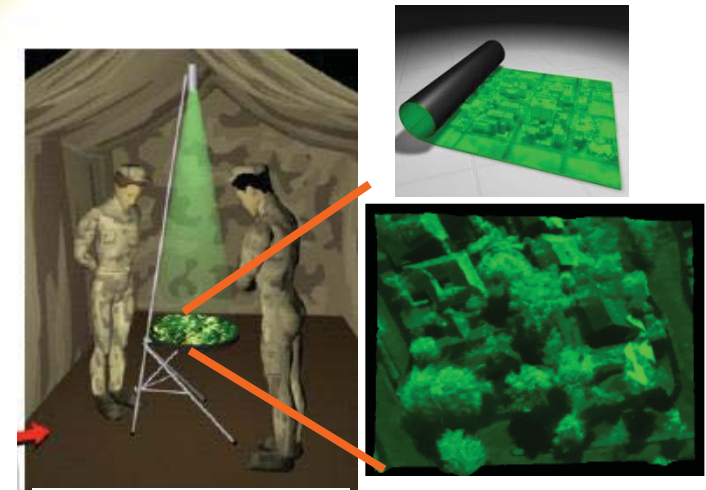


Organic photovoltaics



Organic RFIDs

However, a thorough understanding of the electronic phenomena ongoing in organic semiconductors is still missing. Most of the progresses made in the field is based on the effective but little efficient "trial and error" approach.



Updatable 3D Displays

ADVANTAGES AND DISADVANTAGES OF ORGANIC SEMICONDUCTORS WITH RESPECT TO INORGANIC ONES

Inorganic semiconductors

Pros:

- High electronic performances
- Established know-how and technology (production infrastructures, instruments and processes)

Cons:

- High costs of production plants
- Relatively low throughput
- Low flexibility in materials choice

Organic semiconductors

Pros:

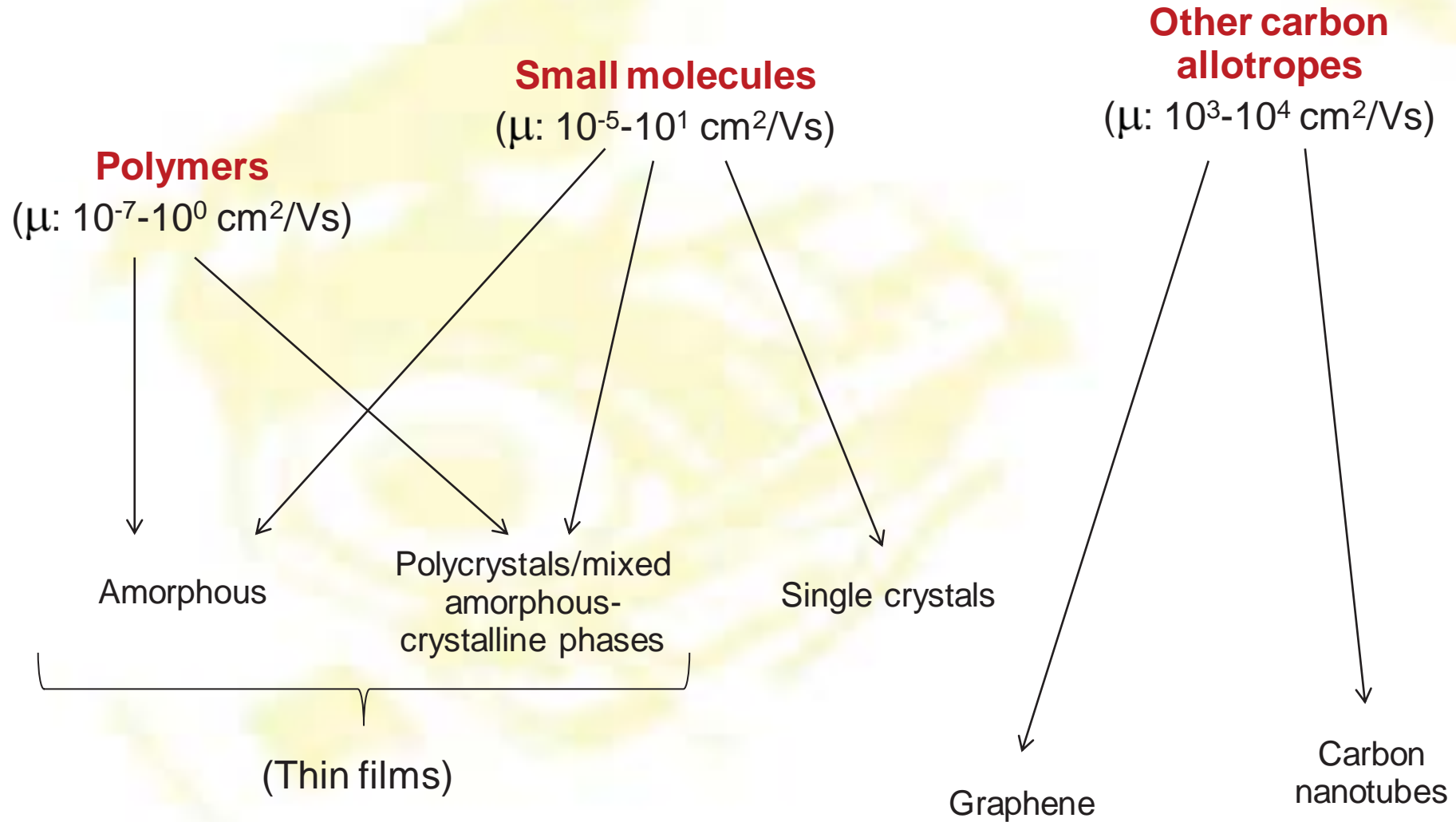
- Possibility of producing at very high throughputs
- Very low cost of both raw materials and production plants/facilities
- Tailorable materials
- Flexibility

Cons:

- Know-how still lagging behind
- Relatively poor electronic performances
- Relatively poor robustness

Key feature of organic semiconductors (costs, production volumes):
solution processing

CURRENTLY AVAILABLE TYPES OF ORGANIC SEMICONDUCTORS



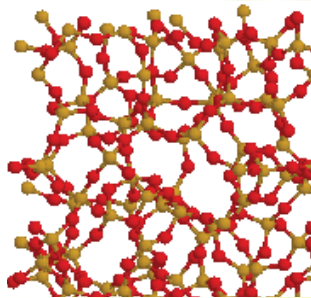
WHICH ARE THE MOST PECULIAR STRUCTURAL ASPECTS OF ORGANIC SEMICONDUCTORS?

Inorganics

Composed by **atoms**

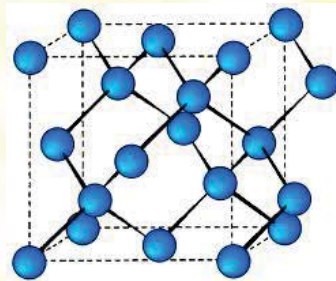
Amorphous

Mixed bonds,
disordered structures



Crystalline

Covalent bonds,
periodic structures

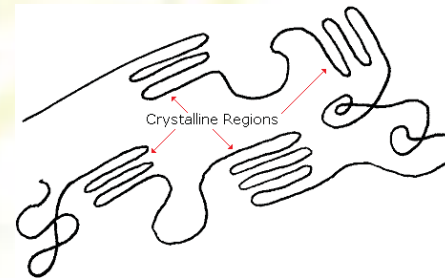


Organics

Composed by **molecules**

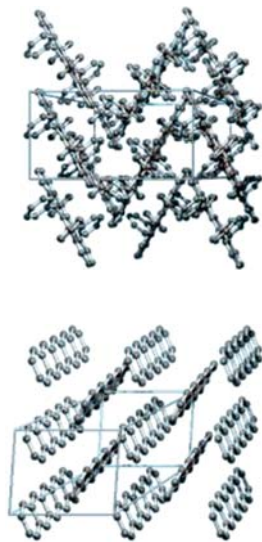
Amorphous
(polymers,
thin films)

Covalent bonds, van
der Waals interactions,
disordered structures



Crystalline

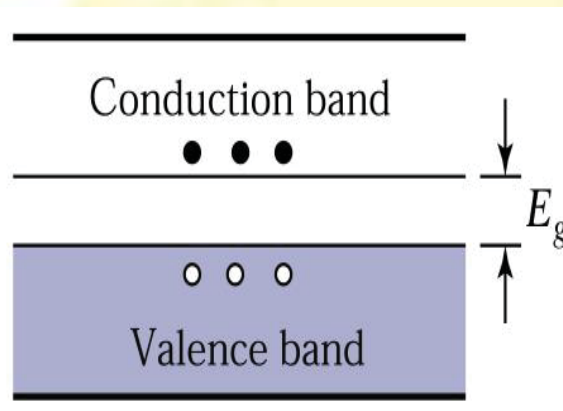
Covalent bonds, van
der Waals interactions,
ordered but complex
structures



DIFFERENT ELECTRONIC STRUCTURES BETWEEN INORGANIC AND ORGANIC SEMICONDUCTORS

Inorganics

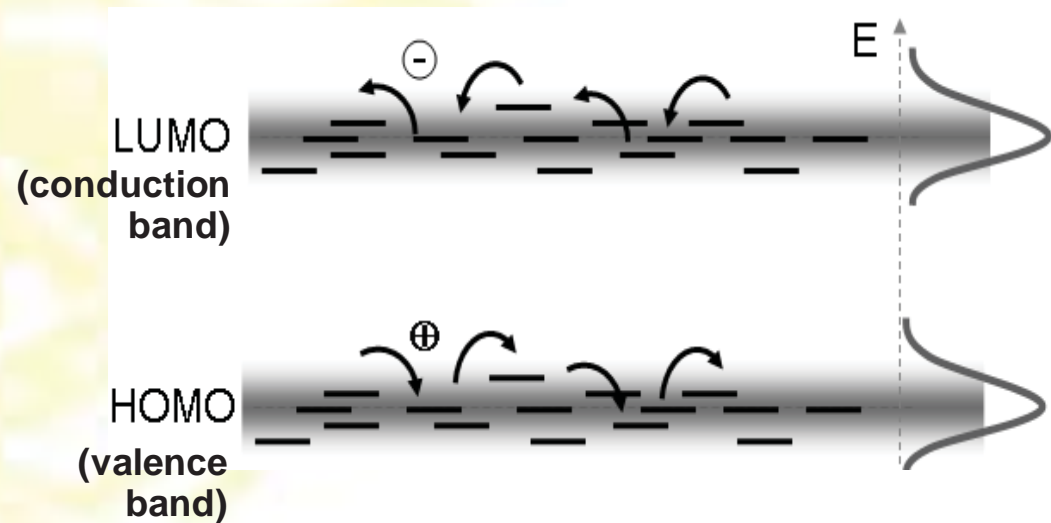
Band Structure



Band Transport

Organics

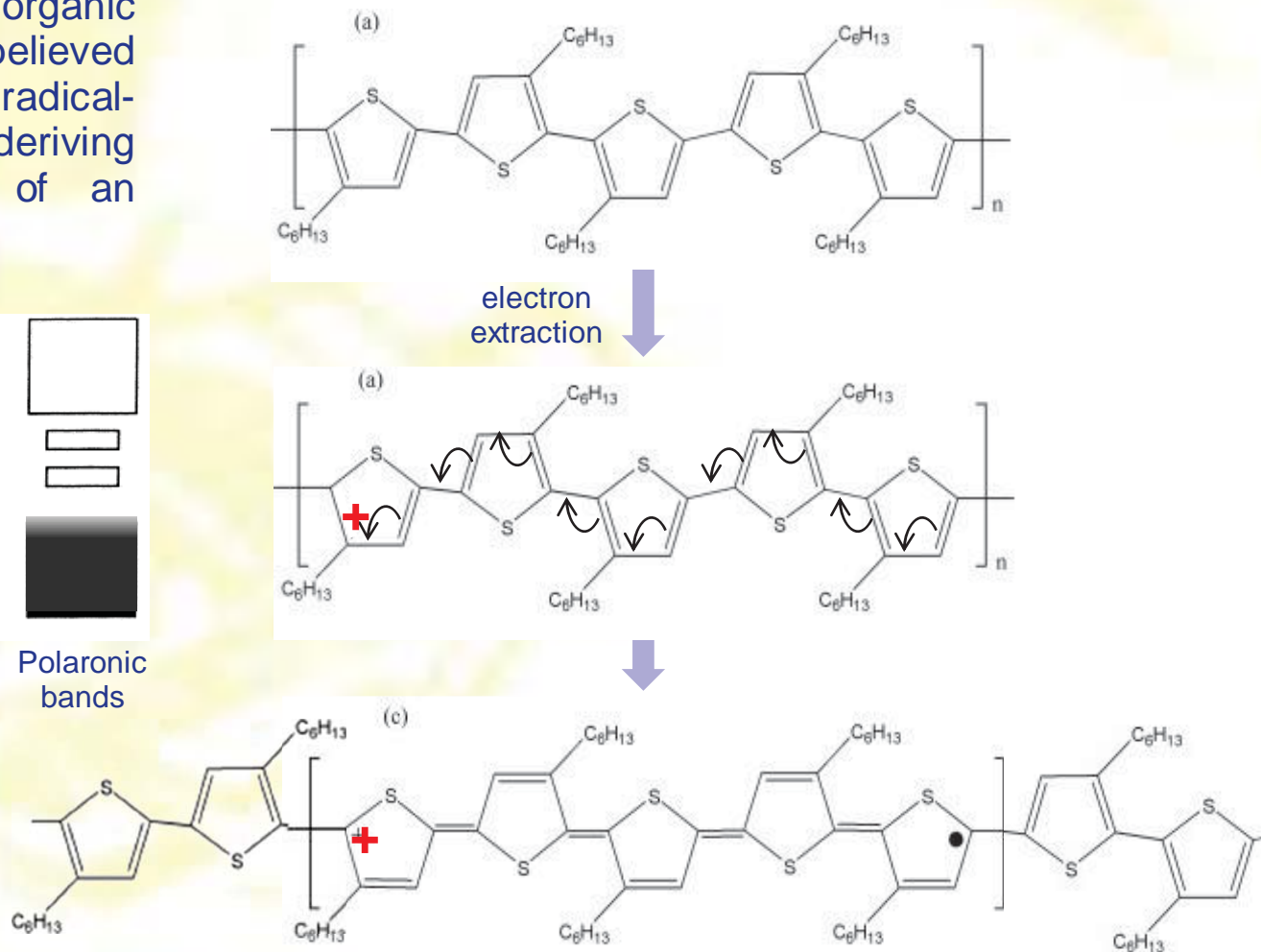
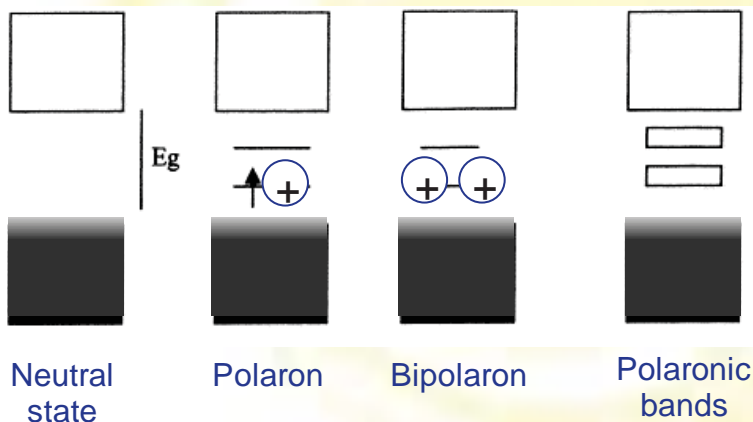
Localized, energetically near levels developing into band-like systems



(mainly) Hopping Transport,
at low T hints of band-like transport

THE POLARONIC TRANSPORT MODEL IN ORGANIC SEMICONDUCTORS

The hole(electron) transport in organic semiconductors is currently believed to occur via polaronic states, radical-cationic(anionic) structures deriving from the removal(addition) of an electron from(to) the molecule.



The polaronic model foresees a structural change in the molecular geometry upon charge transport.

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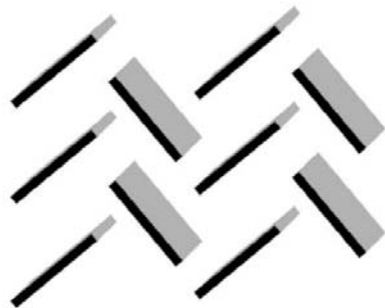
ORGANIC CRYSTALS HAVE COMPLEX STRUCTURES



cofacial



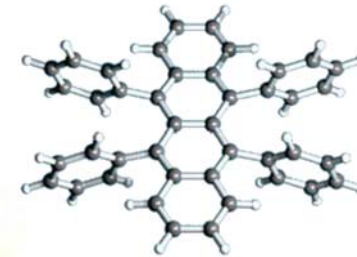
Slipped stacks



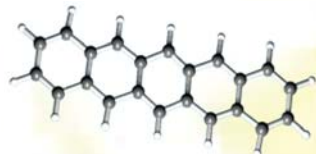
herringbone



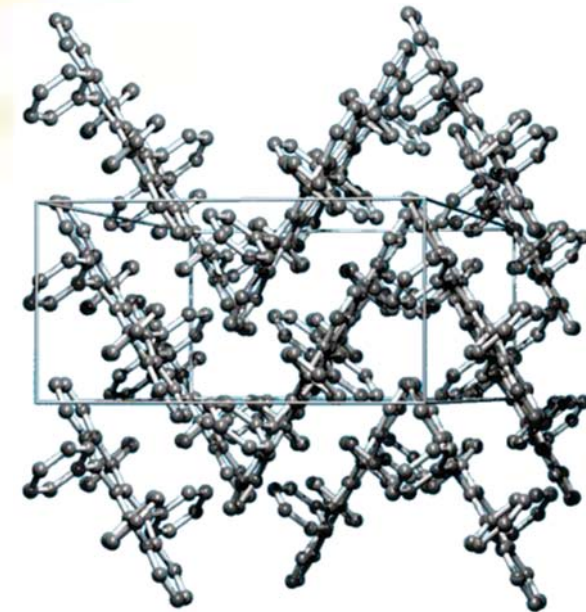
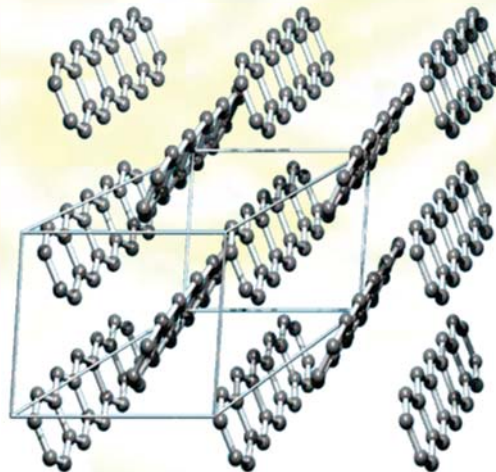
Brick-work



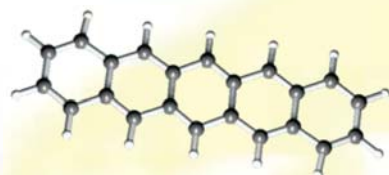
Rubrene



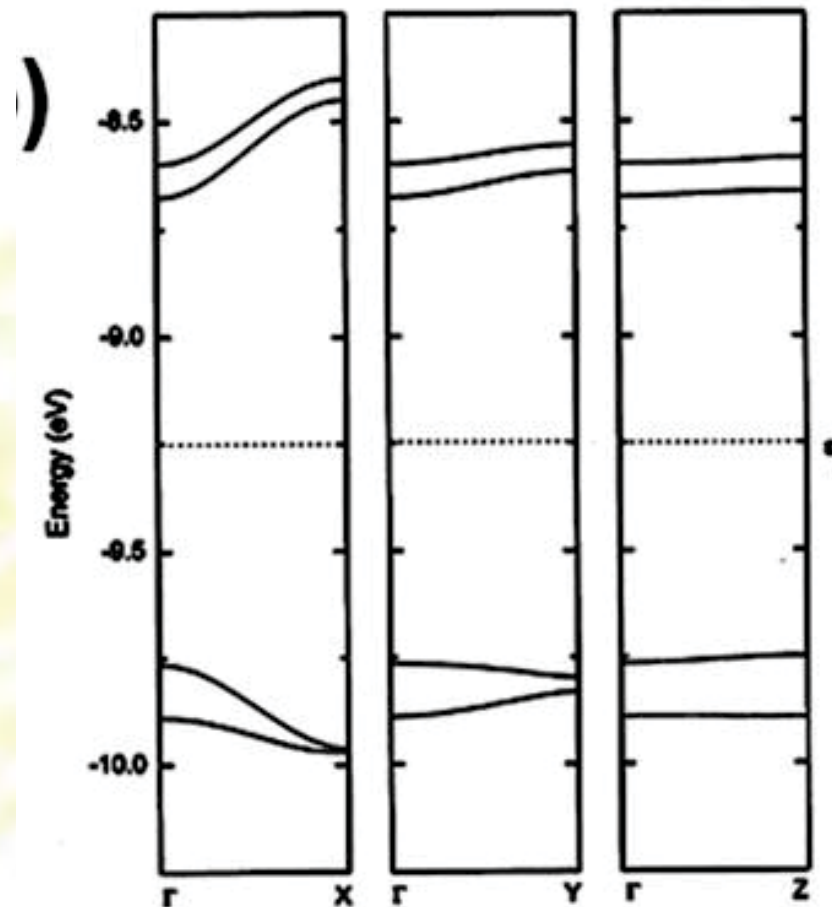
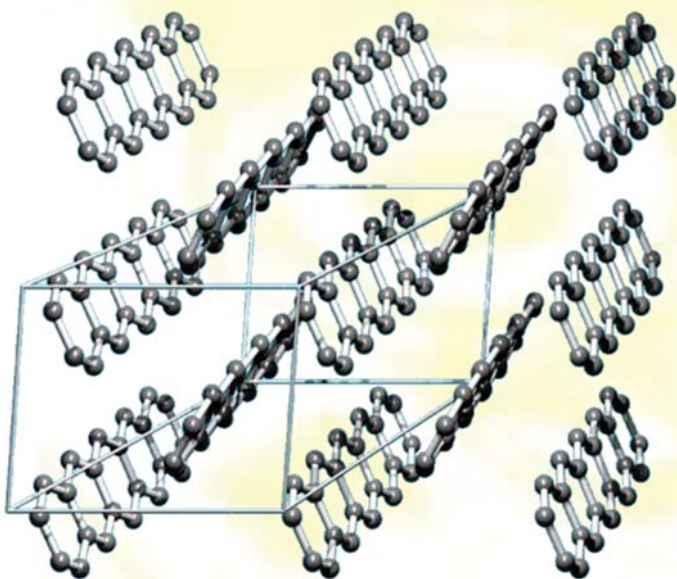
Pentacene



THE COMPLEX STRUCTURE OF ORGANIC CRYSTALS ORIGINATES COMPLEX ELECTRONIC FEATURES (I)



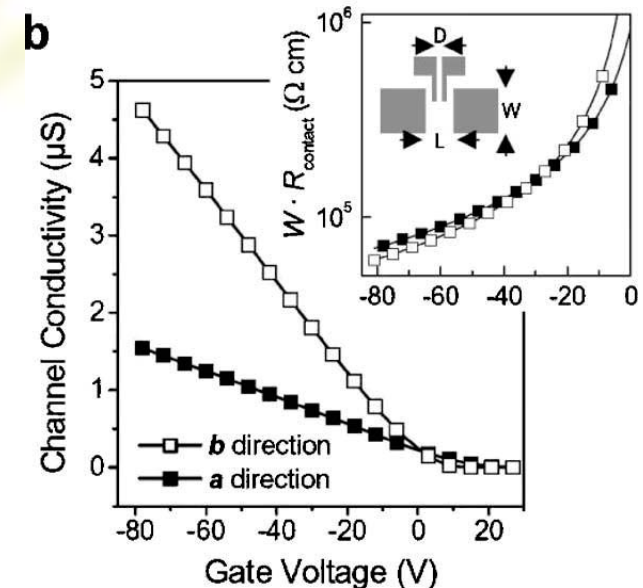
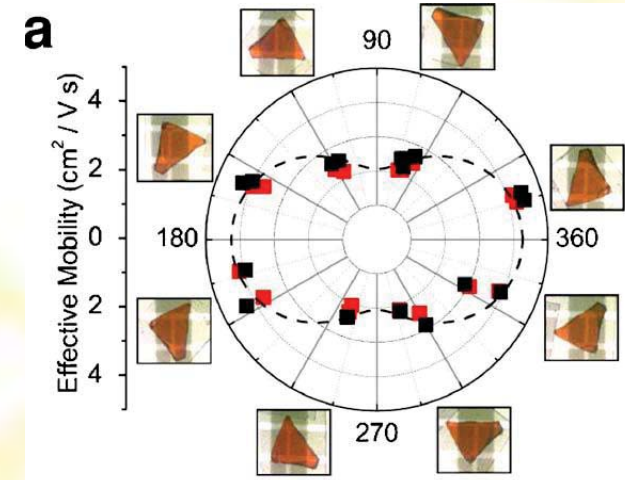
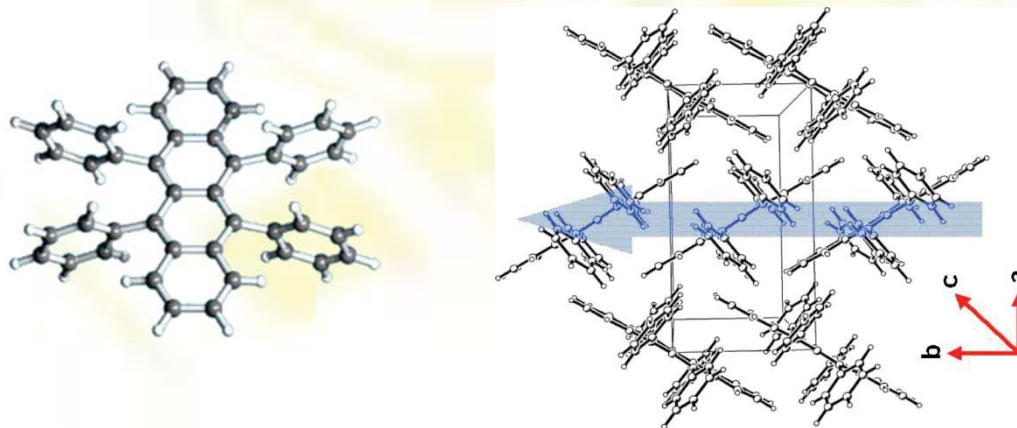
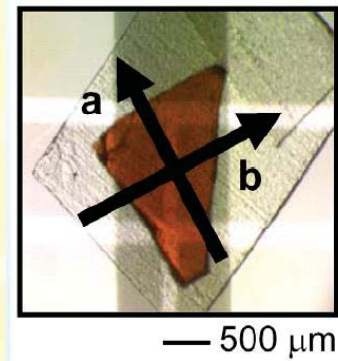
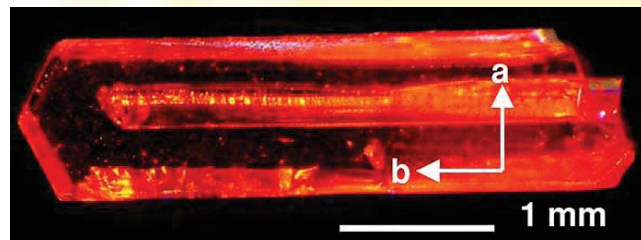
Pentacene



Extended Huckel tight binding calculation for the dispersion of the valence and conduction bands for a representative pentacene polymorph (herringbone structure).

THE COMPLEX STRUCTURE OF ORGANIC CRYSTALS ORIGINATES COMPLEX ELECTRONIC FEATURES (II)

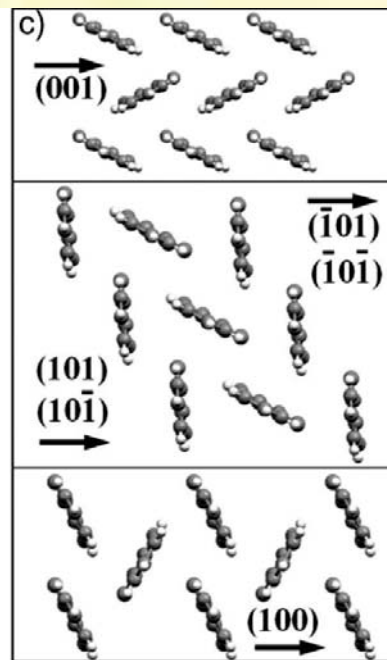
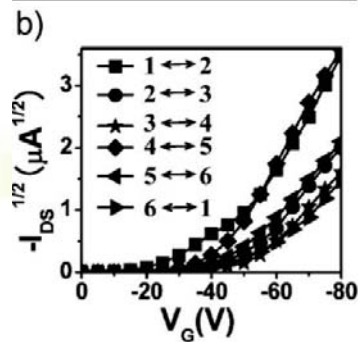
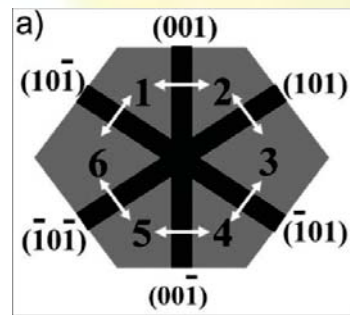
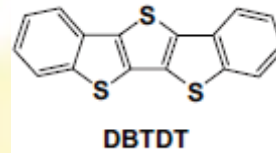
For rubrene the experimentally found transport anisotropy underlines even more complex electronic properties.



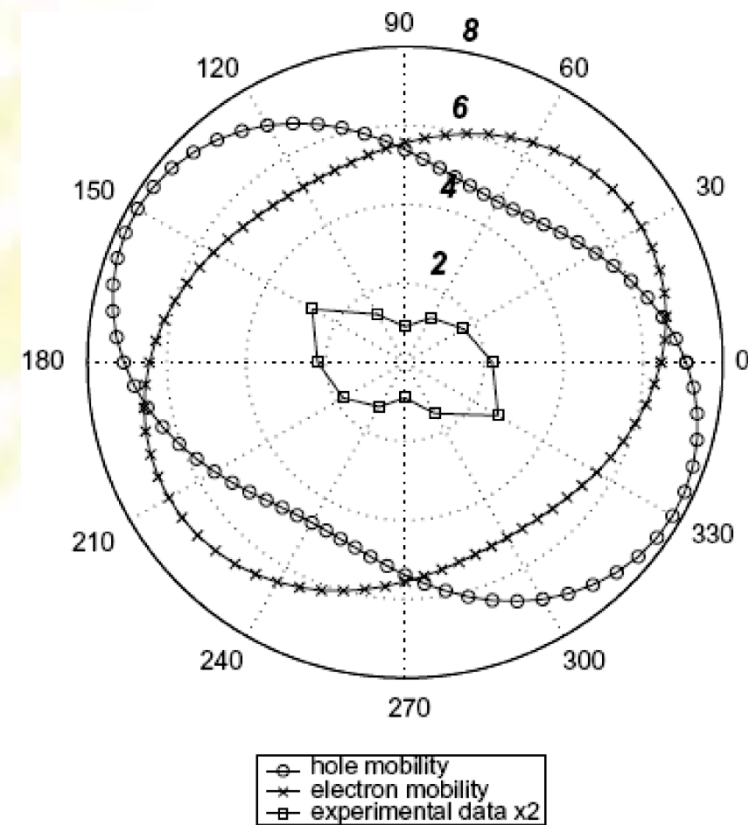
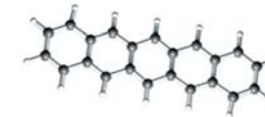
THE COMPLEX STRUCTURE OF ORGANIC CRYSTALS ORIGINATES COMPLEX ELECTRONIC FEATURES (III)

A number of other OSSCs evidence 2D transport anisotropy, justified by theoretical calculations.

dibenzo[d,d']thieno[3,2-b;4,5-b']-dithiophene (DBTDT)

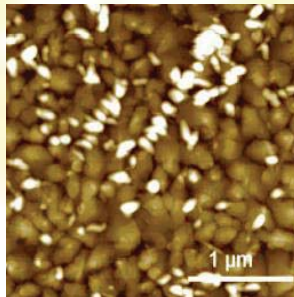


Pentacene

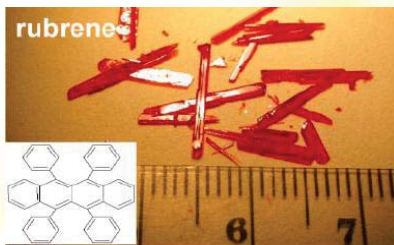


ORGANIC SINGLE CRYSTALS AS MODEL SYSTEMS FOR UNDERSTANDING ORGANIC SEMICONDUCTORS

Though presenting complex electronic features, **organic semiconducting single crystals (OSSCs)** are the “best available” paradigms of organic semiconductors: absence of defects related to grain boundaries, well defined geometrical disposition of molecules, high degree of order.



Vacuum-evaporated small molecules



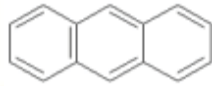
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Vacuum-purified single crystals

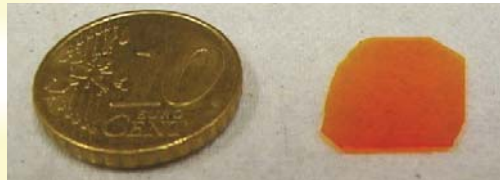
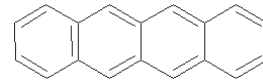


“POPULAR” OSSCs

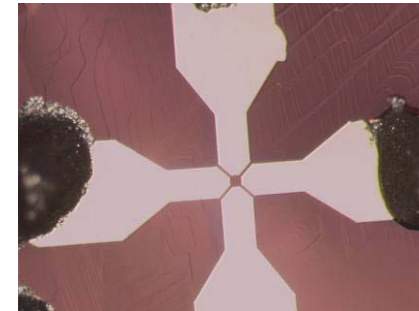
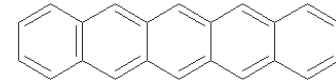
Anthracene



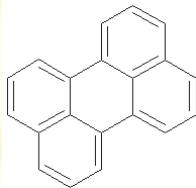
Tetracene



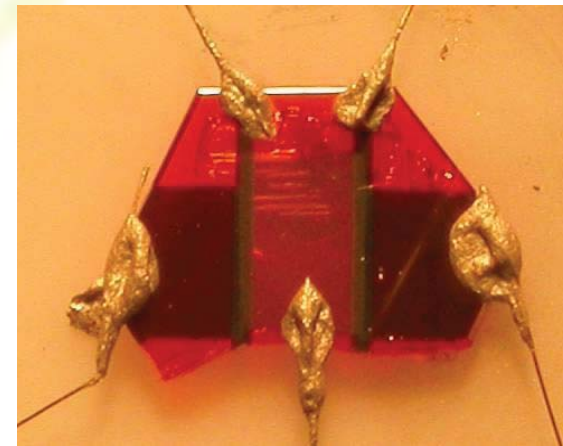
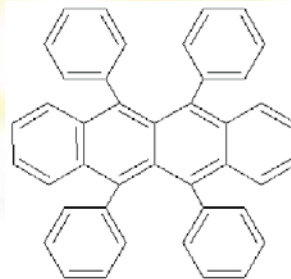
Pentacene



Perylene

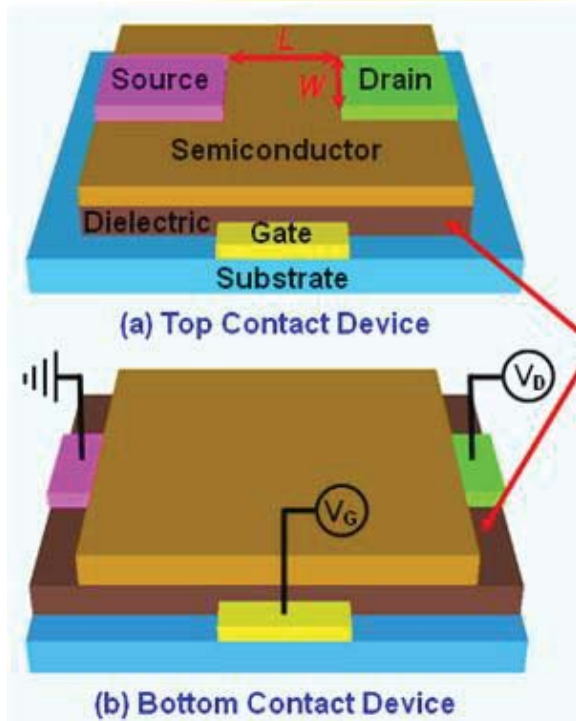


Rubrene

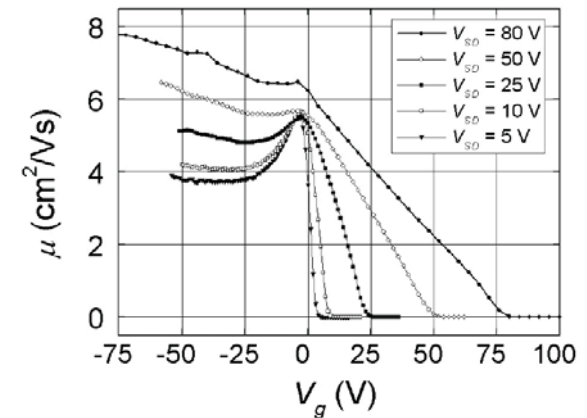
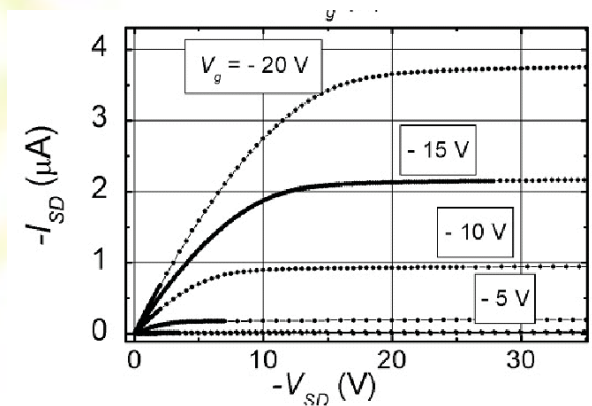
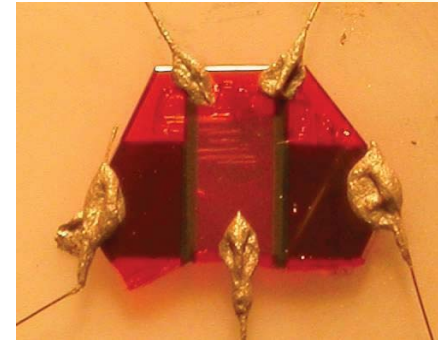


OSSCs TRANSPORT PROPERTIES PROBING: FIELD EFFECT TRANSISTORS (I)

Field Effect Transistors are a common way to evaluate the electronic properties of OSSCs.

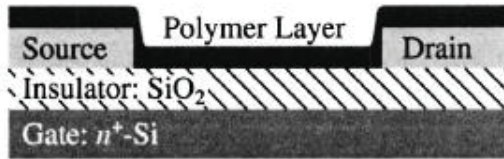


The dielectric has an important role in the device operation, and can enhance/impair its performances, or even change the device behaviour from p-type to n-type.*

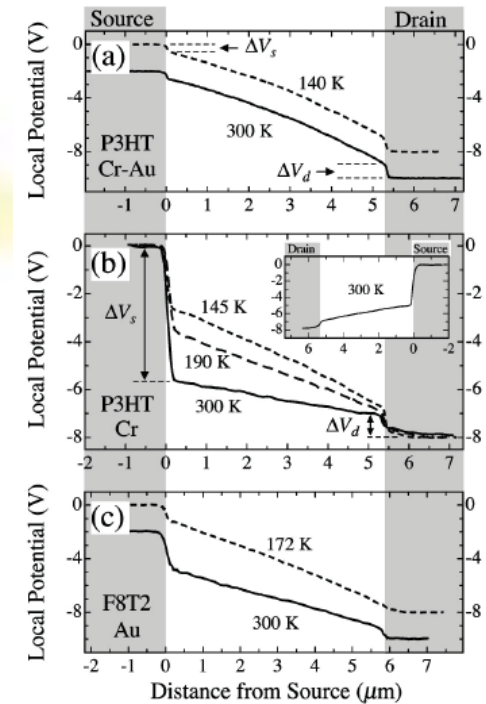
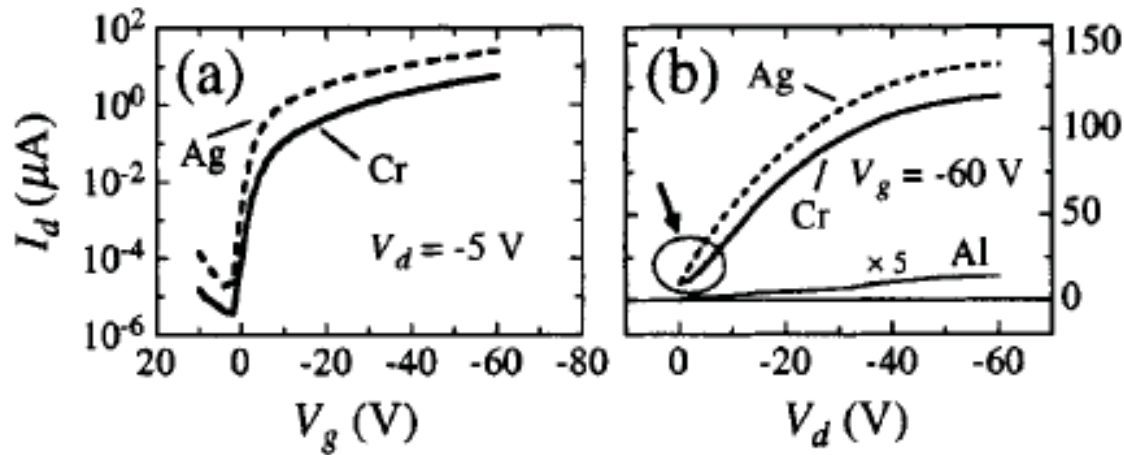
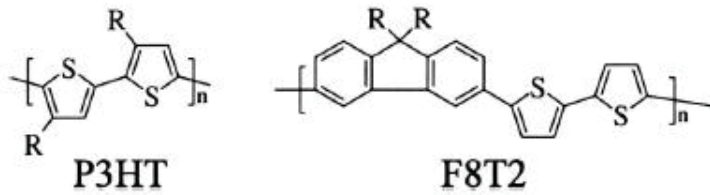


* Friend et al., Nature, 2005, 434, 194;
Braga et al., Adv. Mater. 2009, 21, 1473

EFFECT OF THE ELECTRODE/CRYSTAL INTERFACE ON EXTRACTED TRANSPORT CHARACTERISTICS



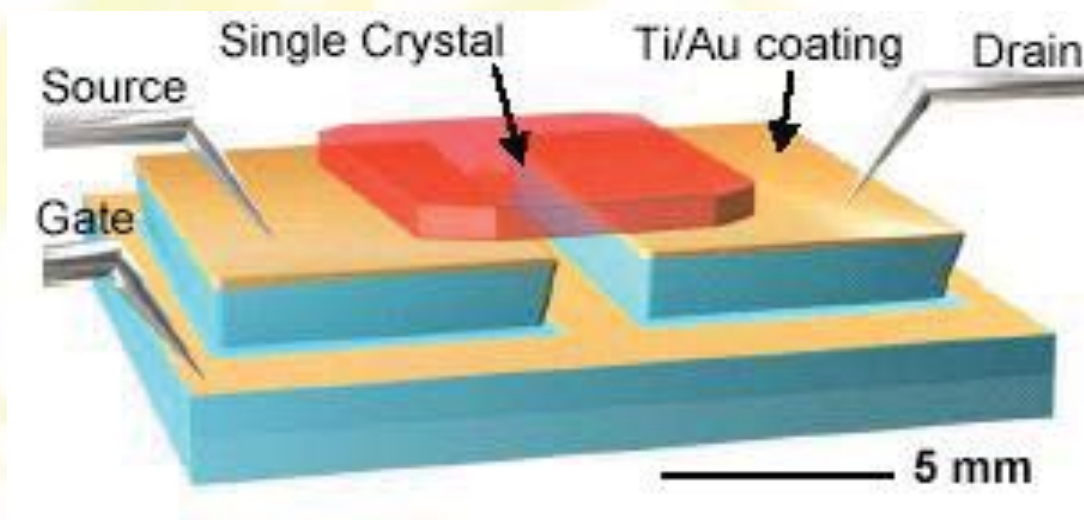
Different workfunction metals induce different depletion regions near the contacts, changing the charge injection/extraction behaviour.



Other extrinsic effects include traps at the organic semiconductor/metal interface due to impurities, semiconductor degradation due to the electrode deposition.

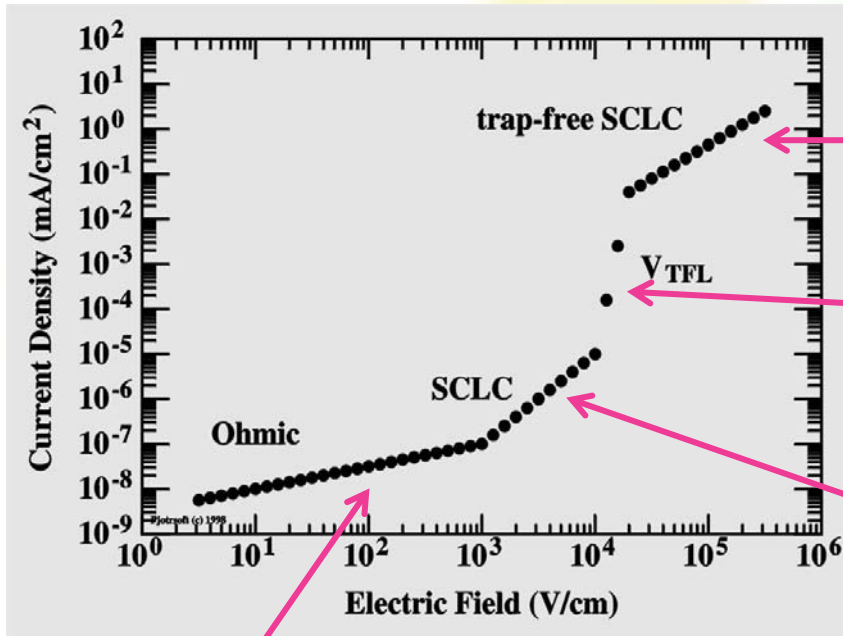
OSSCs TRANSPORT PROPERTIES PROBING: FIELD EFFECT TRANSISTORS (II)

Air-gap transistors are considered devices where the contact resistance is extremely lowered. In addition, OSSCs can be contacted onto source/drain contacts via the so-called “electrostatic bonding”, i.e. just leaning them onto the contacts.



This allows to measure the electronic properties of OSSCs with little influence from the contacts.

OSSCs TRANSPORT PROPERTIES PROBING: SPACE CHARGE-LIMITED CURRENT MODEL



Trap-free SCLC regime: found in high-purity crystals, this regime occurs once filled all the traps, in a SCLC fashion.

Trap free voltage limit (VTFL): in this point the free traps are being suddenly filled, and the current experiences a rapid increase.

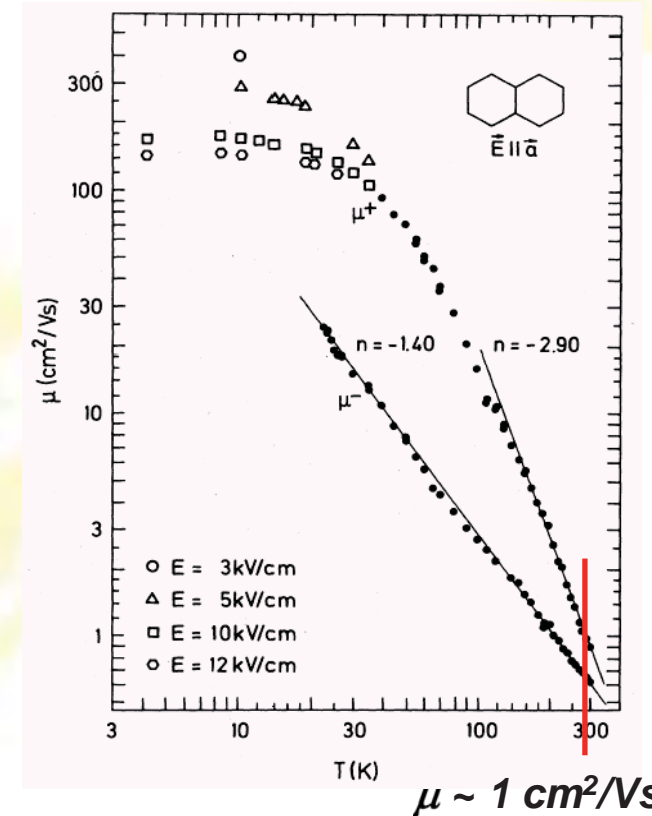
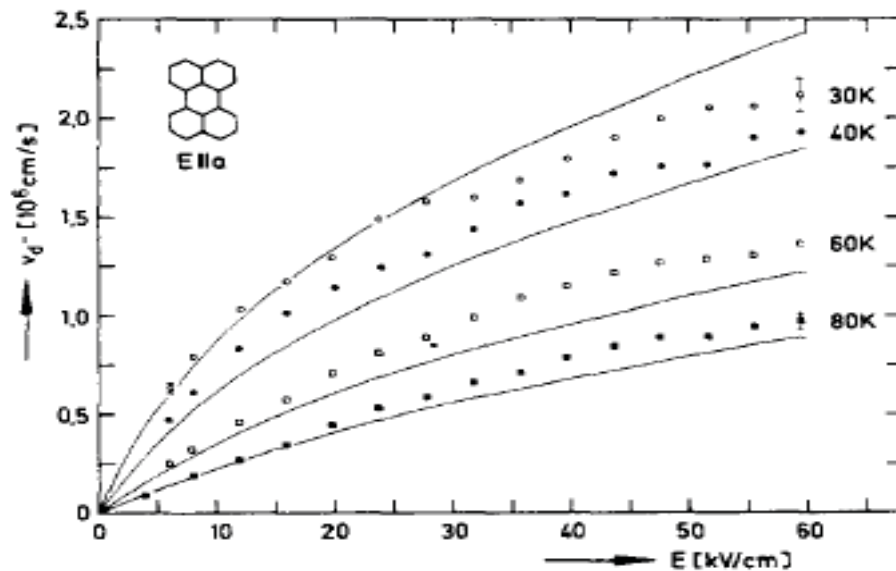
Space charge-limited current (SCLC) regime: the charge injected from the contacts is larger than that present in the material at equilibrium and the I-V characteristics become nonlinear.

Ohmic regime: the voltage drop across the contact resistance is small compared to that across the bulk crystal (contact resistance is negligible).

The electronic parameters extracted from the SCLC model are considered as contact resistance-independent.

OSSCs TRANSPORT PROPERTIES PROBING: TIME OF FLIGHT MEASUREMENTS

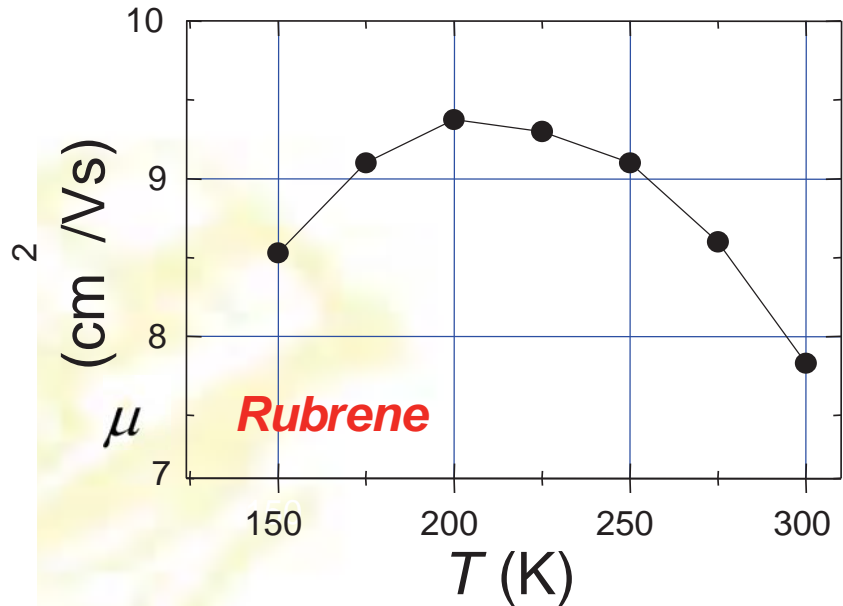
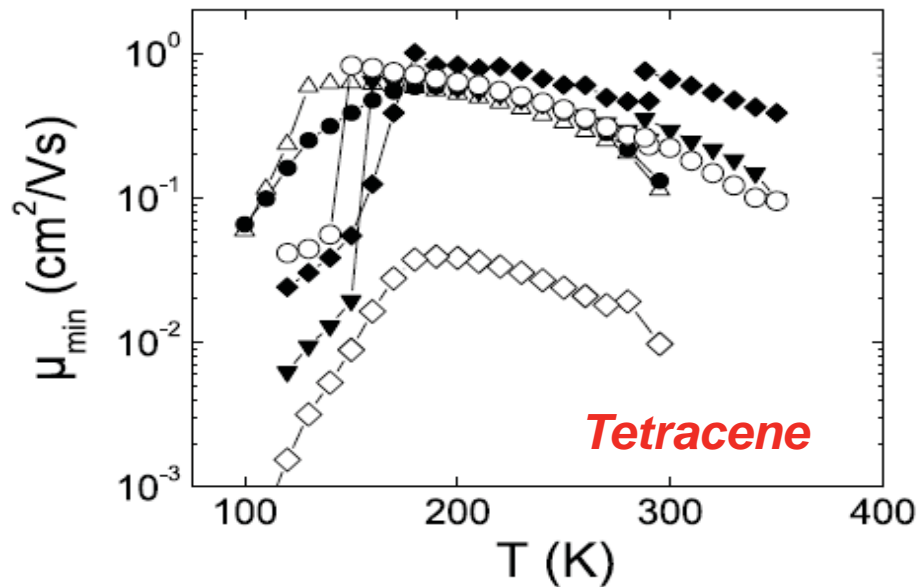
Time-of-flight data shows that **at low temperature (< 50 K) mobilities in OSSCs can reach values as high as $10^5 \text{ cm}^2/\text{Vs}$** , with effective masses close to the free electron mass*.



Increasing the T results in increased phonon scattering, decreasing the band transport effectiveness, and (likely) polaron-hopping transport arises. For crystallographic directions with weak π -electronic interactions, the hopping-mediated transport is expected to be important even at low T .

DEPENDENCE OF MOBILITY FROM TEMPERATURE IN OSSCs

In practical OSSCs-based devices a non-monotonic behaviour of $\mu(T)$ is observed.



These can be due to structural phase transitions, as for tetracene*, or to still unclear factors (as for rubrene and pentacene)**.

Overall, charge transport in OSSCs is not yet completely understood.

* Nelson et al., Appl. Phys. Lett. 72, 1854 (1998); Takeya et al., J. Appl. Phys. 94, 5800 (2003)

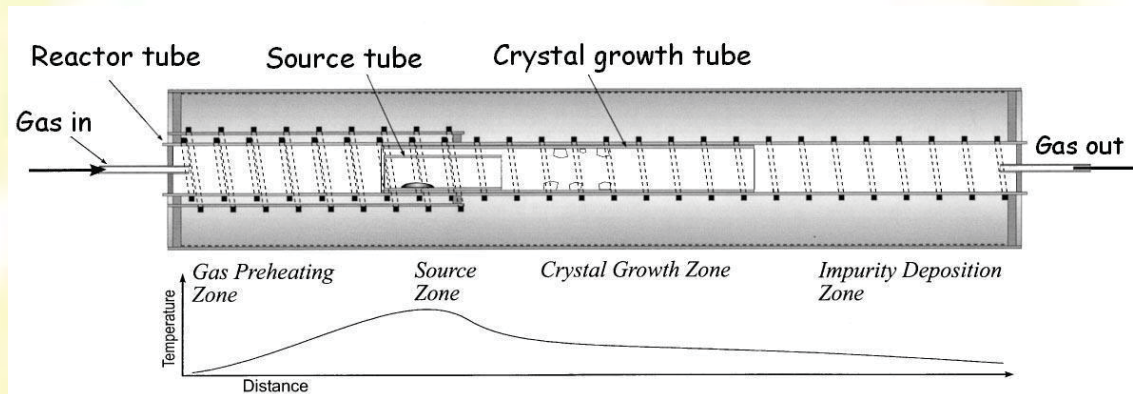
** Sondermann et al., J. Phys. Chem. 89, 1735 (1985)

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ORGANIC SINGLE CRYSTALS BY VACUUM GROWTH (I)

Growing good OSSCs requires pretty sophisticated and expensive vacuum techniques, and even little amounts of impurities may impact dramatically on the crystal transport properties*.



Successive growings reduce the amount of impurities (hence the crystal quality), but increases the production times.

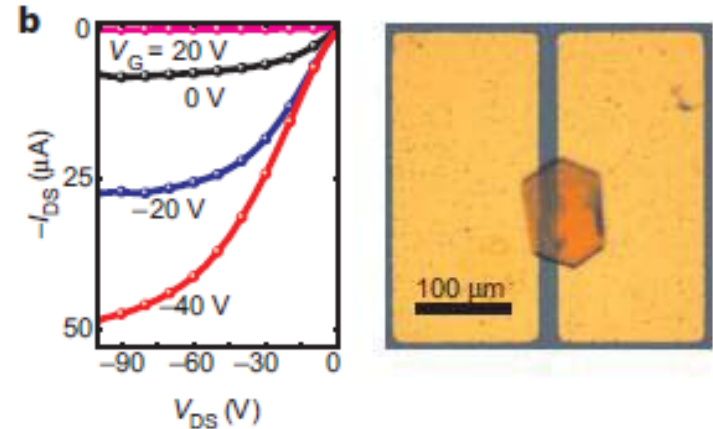
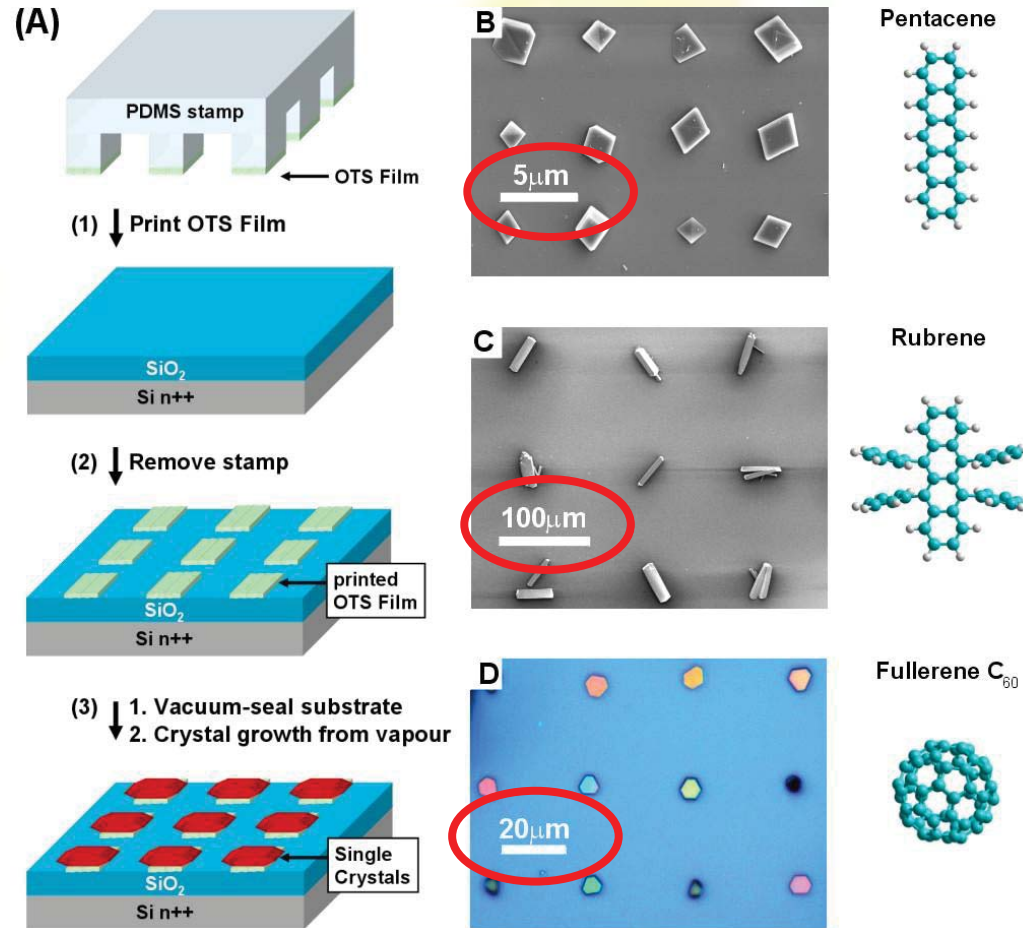
1st Growth



2nd Growth



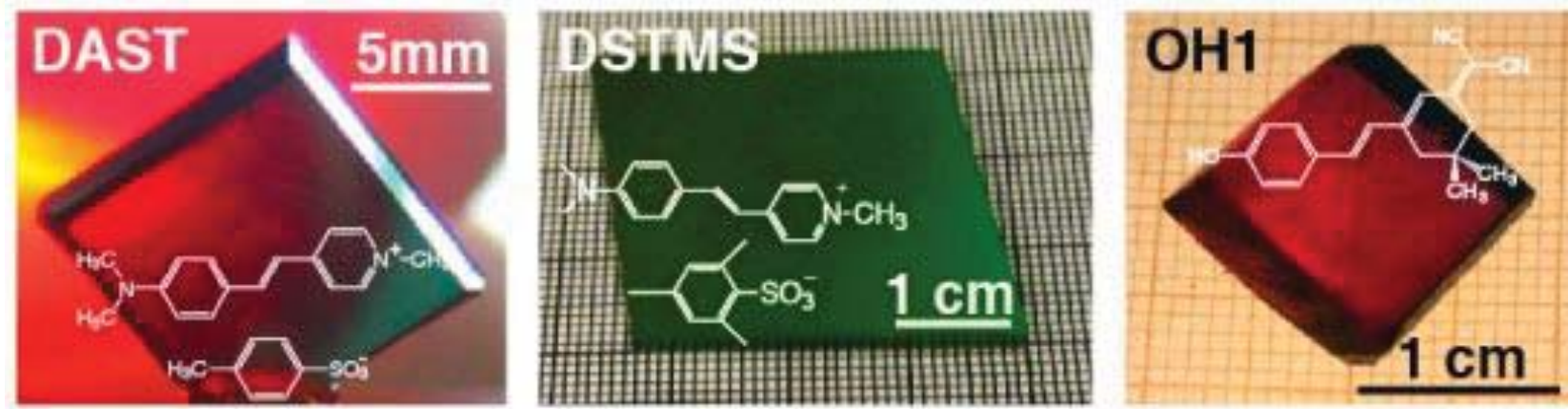
ORGANIC SINGLE CRYSTALS BY VACUUM GROWTH (II)



Arrays of organic microcrystals obtained by printing SAMs on Si/SiO_x substrates, followed by selective vacuum growth of the crystals. Best mobilities achieved with this method: around 2 cm²/Vs

ORGANIC SINGLE CRYSTALS CAN BE GROWN FROM SOLUTION (I)

Solution growth could be an interesting alternative option to vacuum growth. Growing organic crystals from solution is easy and allows a **good control over many crystal properties, including their dimensions and even the developed crystallographic phase** *.

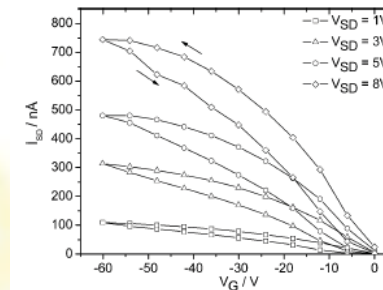
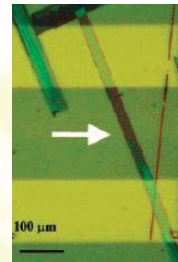
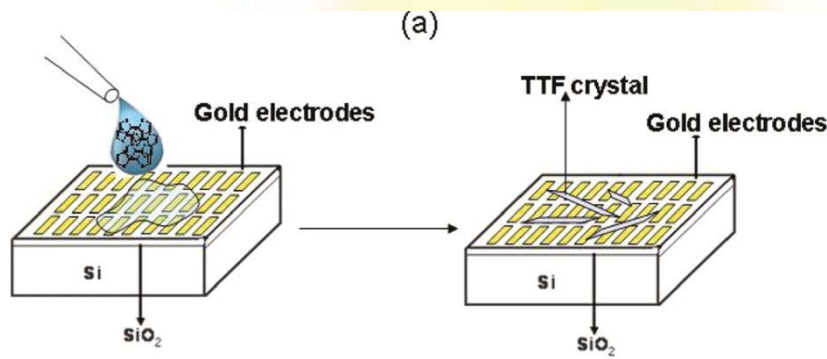


Photos: courtesy of ETH Zurich,
Laboratory of Nonlinear optics

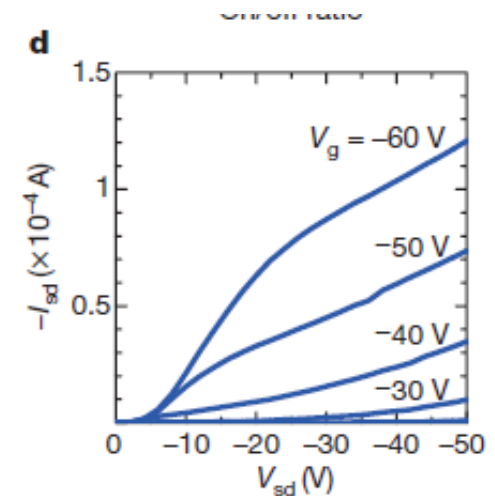
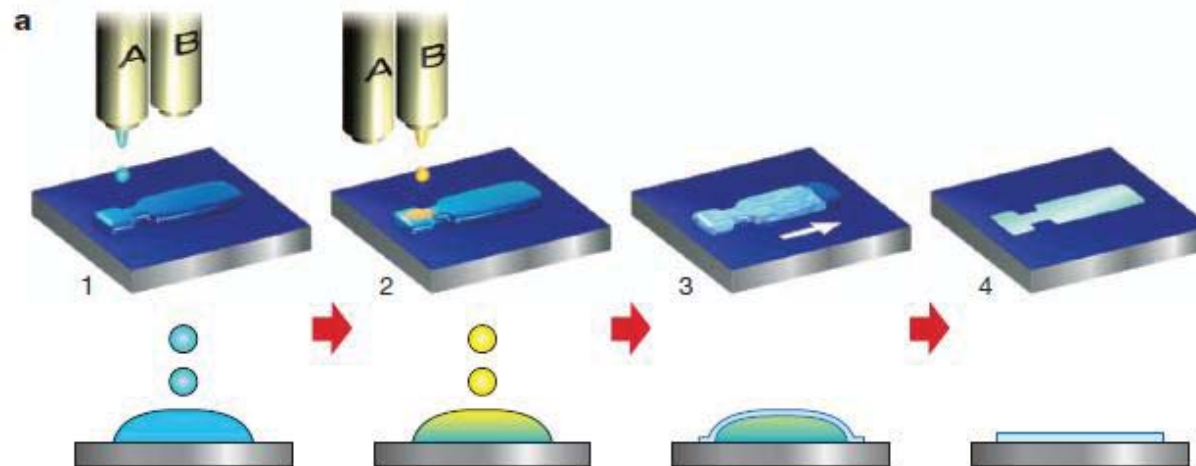
** S. Manetta et al., C. R. Phys., 2002, 3, 449; K. Sankaranarayanan et al., J. Cryst. Growth, 2006, 292, 445

ORGANIC SINGLE CRYSTALS CAN BE GROWN FROM SOLUTION (II)

It is possible to directly grow crystals on substrates via a variety of techniques, from the simplest drop casting* to the more sophisticated inkjet printing**.



* Mas-Torrent et al., J. Am. Chem. Soc. 2004, 126, 984

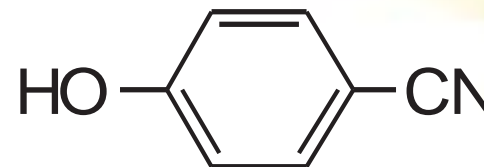


NEXT PRESENTATION SECTION

- Why organic semiconductors, and their general features
- Organic semiconducting single crystals (OSSCs): main structural and transport properties
- Overview of OSSCs growth methods
- **Structural and electronic properties of 4-hydroxycyanobenzene (4HCB) single crystals**
- Synchrotron-based investigation of 4HCB crystals
- Direct detection of X-rays by means of OSSCs
- Radiation hardness of 4HCB crystals
- Conclusions

SOLUTION GROWN, ORGANIC SINGLE CRYSTALS OF 4-HYDROXYCYANOGEN (4HCB)

4HCB is an interesting inherently dipolar molecule.



Single, squared crystals of 4-hydroxycyanobenzene (4HCB) are easily grown from solutions.

Thickness: from a few hundreds of microns to 1 mm;

Side: from one to several millimeters.

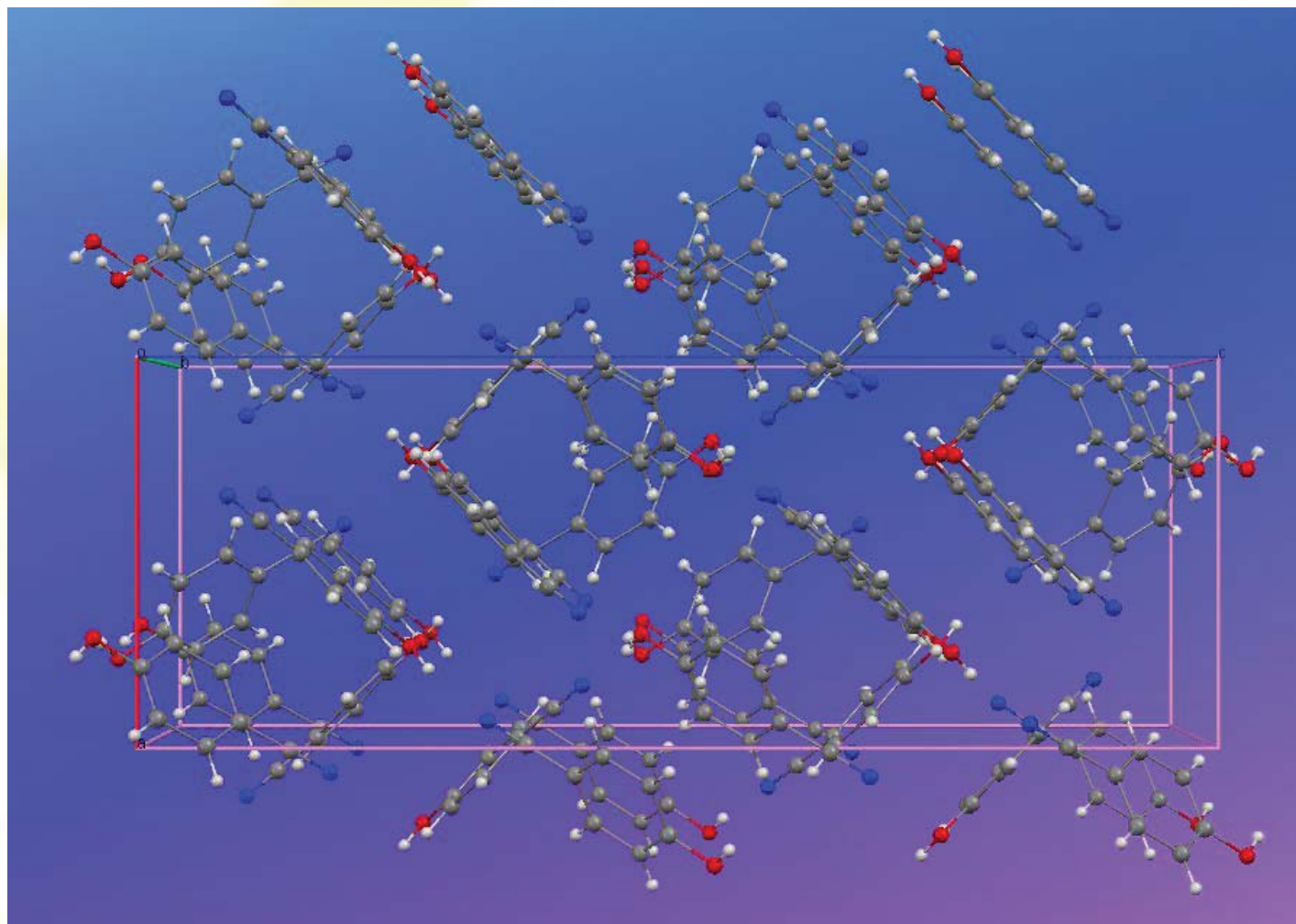
Tunable dimensions properly modifying the growth conditions.

The so-obtained crystals are **free-standing, easily handled and moved and resistant to air and photooxidation.**



LATTICE STRUCTURE OF THE 4HCB SINGLE CRYSTALS (I)

The structure of 4HCB crystals is known since a long time, and is rather complex*.



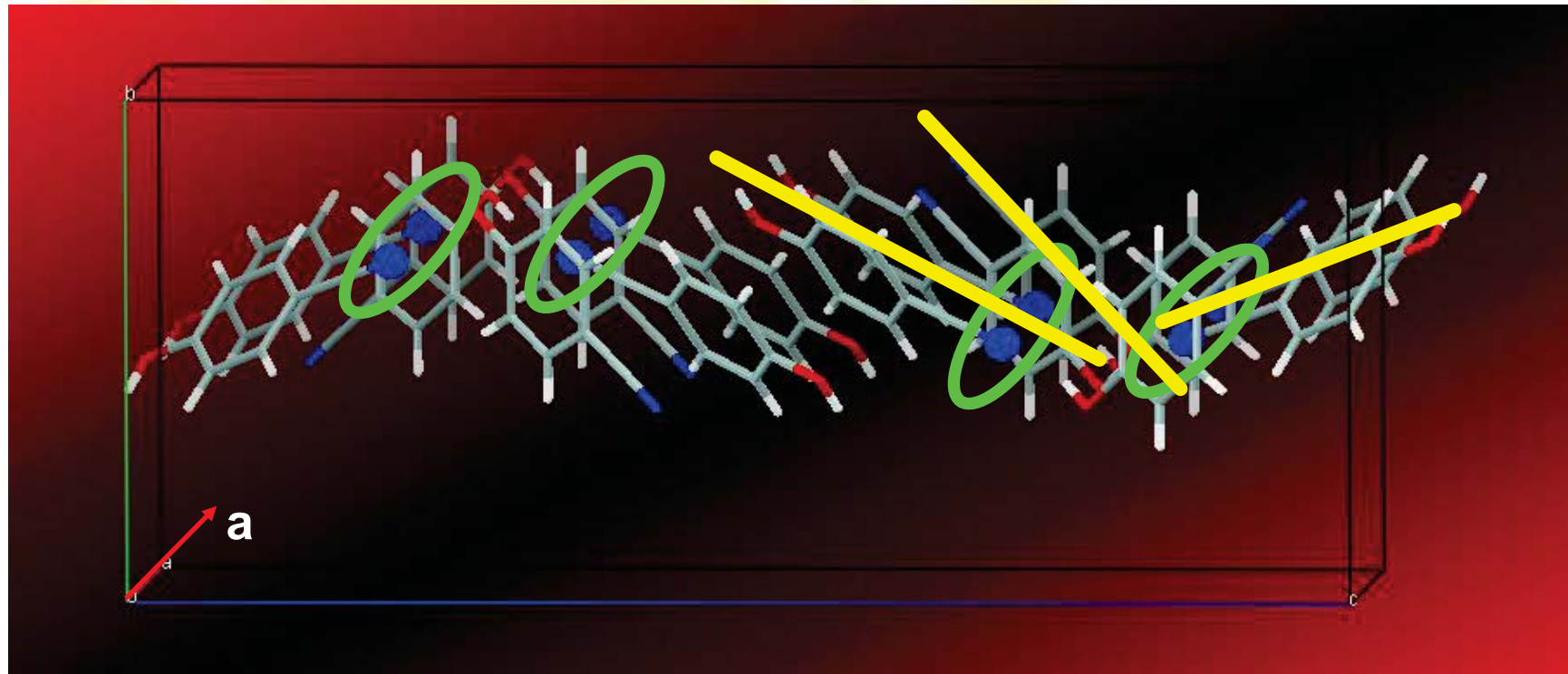
* T. Higashi et al., Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem., 1977, 33, 607

LATTICE STRUCTURE OF THE 4HCB SINGLE CRYSTALS (I)

Axis a: inter-ring benzenic plane distance = 9.2 Å.

The dipole moment is never perpendicular to the π -stacking direction of any molecule in the lattice.

N atoms are sandwiched between overlapping rings, modifying the net electron density of the system along axis **a**.



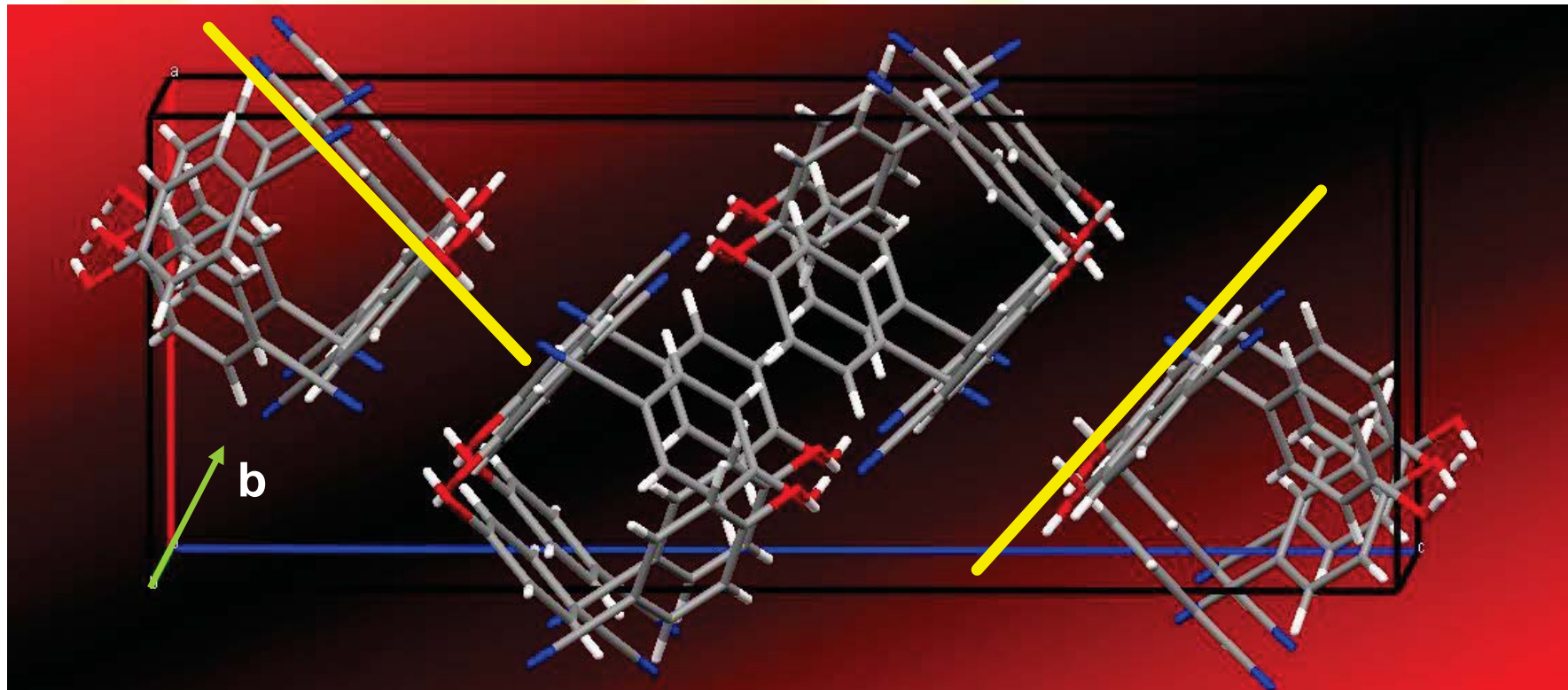
* B. Fraboni et al, Adv. Mater., 2009, 21, 1835

LATTICE STRUCTURE OF THE 4HCB SINGLE CRYSTALS (II)

Axis *b*: inter-ring benzenic plane distance = 10.7 Å.

The dipole is perpendicular to the π -stacking direction in some points of the lattice.

N atoms are NOT sandwiched between overlapping rings.



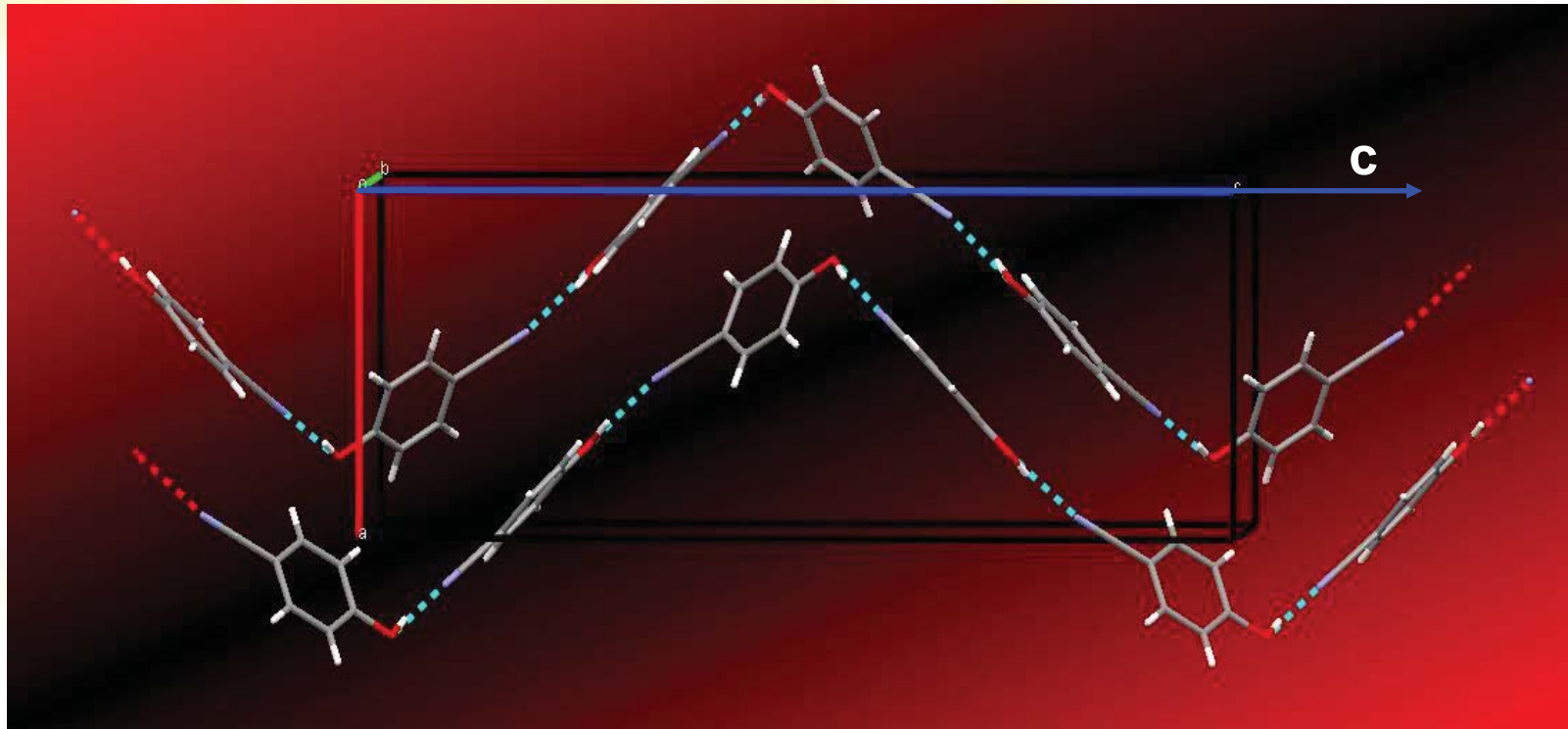
* B. Fraboni et al, Adv. Mater., 2009, 21, 1835

LATTICE STRUCTURE OF THE 4HCB SINGLE CRYSTALS (III)

Axis c: No appreciable overlapping of benzenic rings.

The molecular dipole develops itself along the axis.

No relevant intrinsic charge transport is expected.

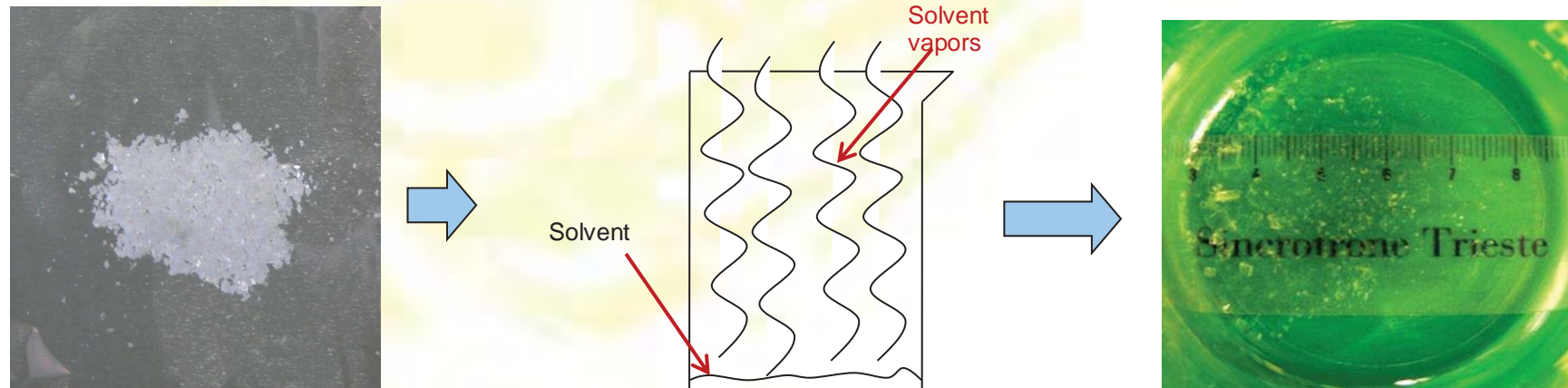


BASIC GROWTH METHOD OF 4HCB SINGLE CRYSTALS

The fabrication of 4HCB crystals by solution is straight and easy.

The **general recipe** for obtaining 4HCB crystals **suitable for electronic measurements** is hence the following:

- a few mg of pre-purified 4HCB crystals dissolved in a selected solvent/solvent mixture;
- slow evaporation rates (approx. 2-5 ml/day)
- fixed temperatures (either 20°C or 6°C).

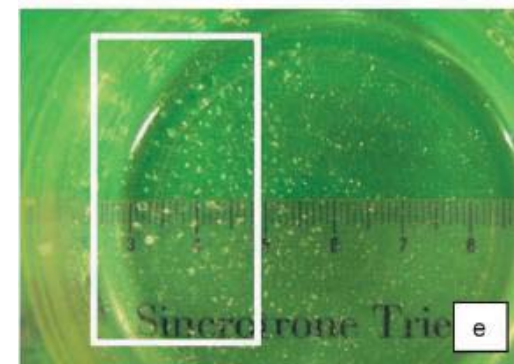
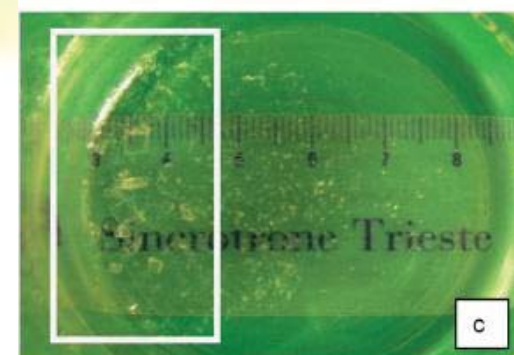
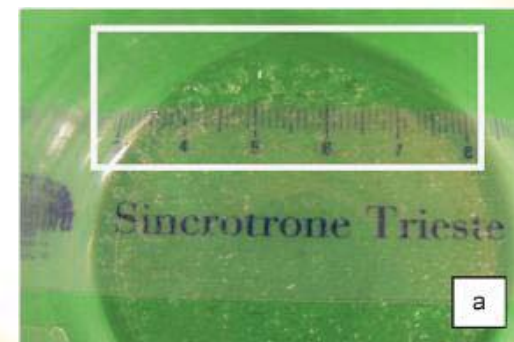


4HCB CRYSTAL DIMENSIONS AND THICKNESS/SIZE RATIOS ARE CONTROLLED BY SOLVENT, CONCENTRATION, TEMPERATURE

Also the control of the dimensions of the obtained crystals, and of their size/thickness ratio, is rather easy.

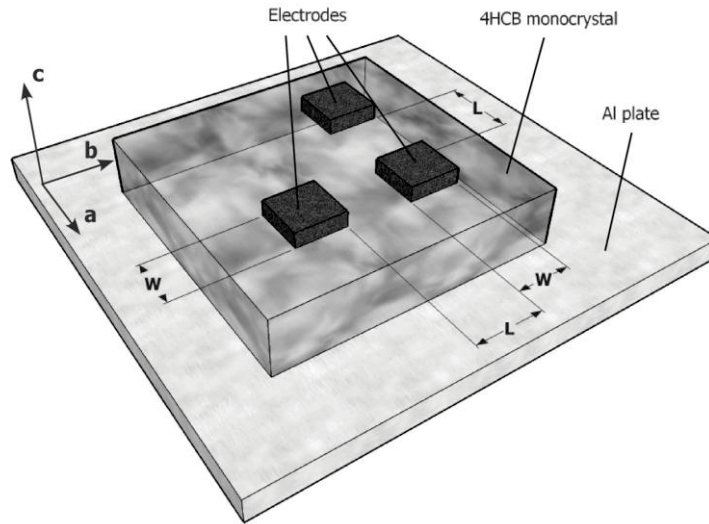
For any single growth batch, several good quality crystals are obtained.

4HCB concentration in the solution (mg/mL)	Solvent/solvent mixture	Crystal size	
		Approx. side length ^f (mm)	Approx. thickness ^f (μm)
2	EE	2	200–400
2	EE:PE 9:1 V/V	2	150–300
2	EE:PE 8:2 V/V	1–1.5	100–200
3	EE	3–4	300–600
3	EE:PE 9:1 V/V	1–1.5	150–300
2	EE	3–6	200–500



2D ANISOTROPIC FET BEHAVIOUR OF 4HCB CRYSTALS

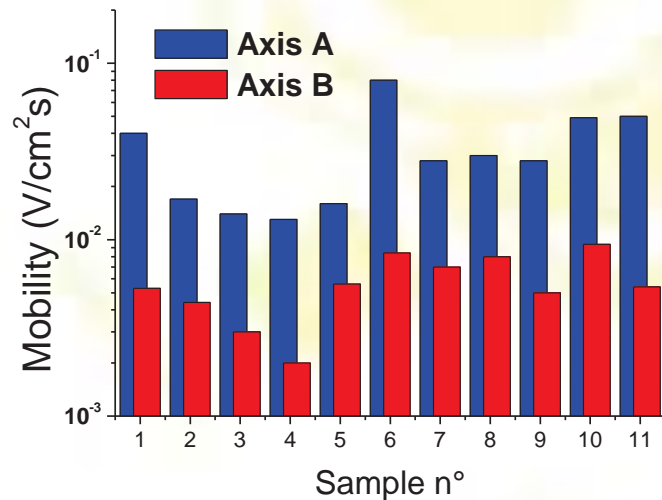
Air-gap FET as a tool for probing the electronic transport, using silver epoxy for fabricating the contacts, in a top-contact structure.



In these measurements conditions, 4HCB is a **p-type semiconductor**.

In dark **no hysteresis or degradation effects were observed** (at room temperature and under normal lab atmosphere).

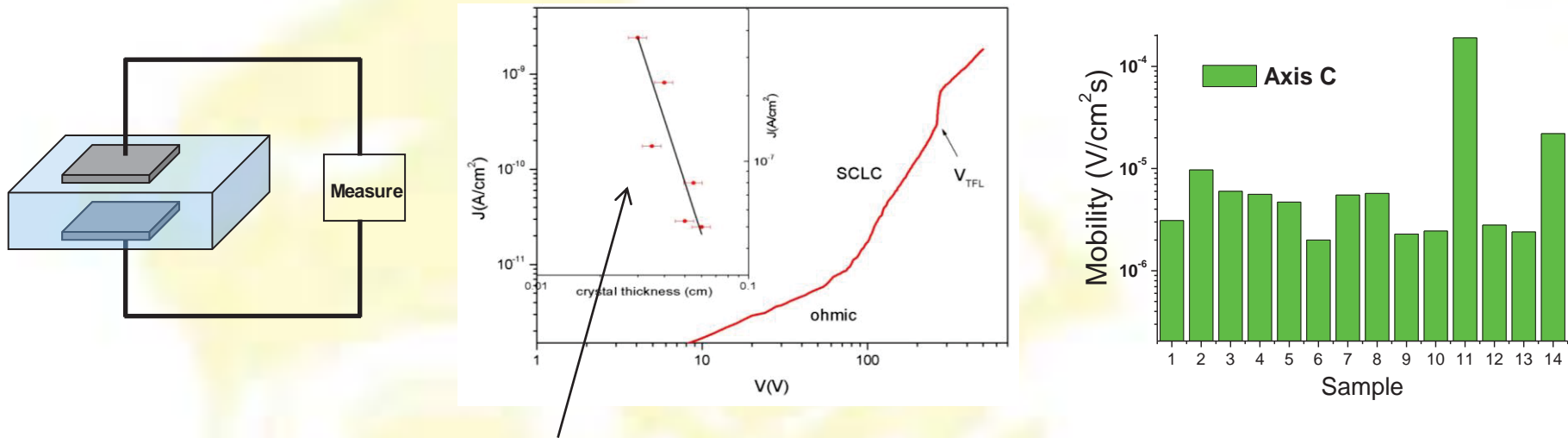
Remarkably reproducible mobilities over several different samples (different crystals, coming from different growth batches, of different dimensions and with different FET geometric parameters).



Axis	μ^{FET}_{Max} (cm ² /Vs)	μ^{FET}_{Ave} (cm ² /Vs)
a	8x10⁻²	3x10⁻²
b	9x10⁻³	6x10⁻³

CARRIER MOBILITY ALONG THE CRYSTAL THICKNESS: THE THIRD DIMENSION

Crystals were contacted with a two-electrodes geometry, along the crystal thickness.



The L^{-3} dependence of the measured current as a function of the crystal thickness, at a constant electric field of 9×10^3 V/cm, assesses the occurrence of proper bulk conduction transport during SCLC analyses.

Axis	μ^{SCLC}_{Max} (cm ² /Vs)	μ^{SCLC}_{Ave} (cm ² /Vs)
c	2×10^{-5}	5×10^{-6}

It is hence possible to determine the charge carrier mobility in all the three dimensions of a single crystal.

For 4HCB crystals, the three mobilities are anisotropic.

* B. Fraboni et al, Adv. Mater., 2009, 21, 1835

SCLC MEASUREMENTS AS A RELIABLE SOURCE OF INFORMATIONS ON THE ELECTRONIC PARAMETERS OF ORGANIC SINGLE CRYSTALS

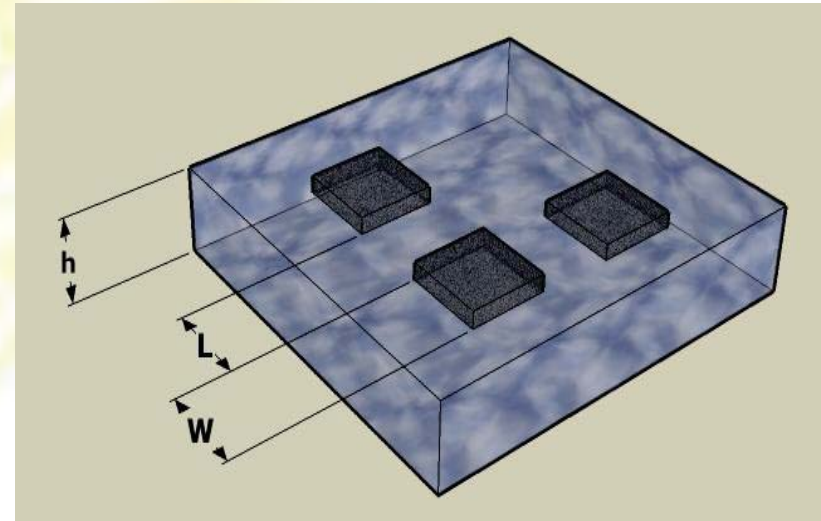
The SCLC technique may be used to determine the carrier mobility also along the main crystal plane*:

$$J = \frac{9}{8} \epsilon \mu \frac{V^2}{L^3}$$

L = electrodes separation;
J = current density at the applied voltage V;
 ϵ = dielectric constant of the material;
 μ = carrier mobility

When L/h (h = crystal thickness) is <10 the charge transport occurs in a one-dimensional fashion. **

Since in our case h varied between 150 and 600 μm and L was about 500 μm , L/h was always small enough to grant 1D transport also in the planar electrode configuration.



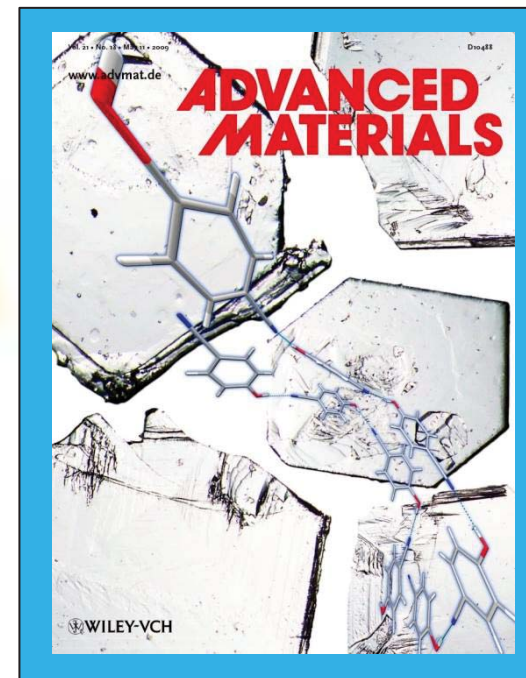
* Mott , Gurney , in Electronic processes in ionic crystals, Clarendon Press, Oxford, 1940

** Jurchescu et al., Appl. Phys. Lett. 88, 122101 (2006)

SCLC FOR DETERMINING CARRIER MOBILITIES ALONG THE THREE CRYSTAL DIMENSIONS

Using the SCLC approach, the carrier mobilities along the three axes a, b and c have been determined for 30 different crystals (in addition to those already tested along the axis c).

Axis	μ^{SCLC}_{Max} (cm ² /Vs)	μ^{SCLC}_{Ave} (cm ² /Vs)	μ^{FET}_{Max} (cm ² /Vs)	μ^{FET}_{Ave} (cm ² /Vs)
a	1x10⁻¹	5x10⁻²	8x10⁻²	3x10⁻²
b	2x10⁻²	6x10⁻³	9x10⁻³	6x10⁻³
c	2x10⁻⁵	5x10⁻⁶	-	-



Notably consistent results:

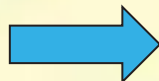
- max values not too distant from the average ones;
- max and ave values very similar under both SCLC and FET techniques.

Strong suggestion of these being intrinsic mobility values for solution-grown 4HCB crystals.*

* B. Fraboni et al, Adv. Mater., 2009, 21, 1835

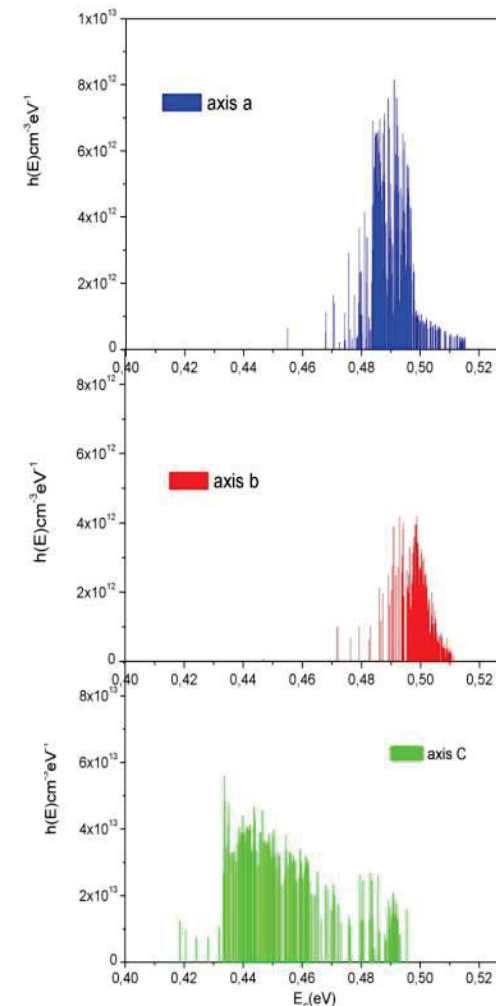
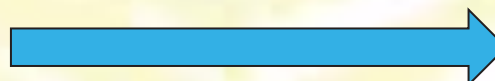
WHOLE SET OF 3D ANISOTROPIC ELECTRONIC PROPERTIES VERIFIED BY SCLC IN 4HCB SINGLE CRYSTALS

3D anisotropic
number of traps.

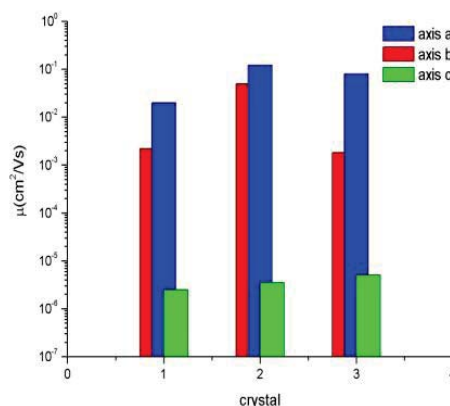
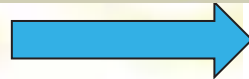
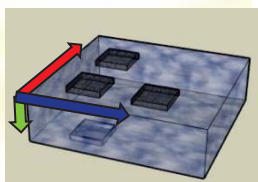


Axis	N_T (cm^{-3})
a	9×10^{12}
b	4×10^{12}
c	2×10^{13}

3D anisotropic trap density
and energetic position of
electronic states.



3D anisotropic
carrier mobility on
the same crystal.



Overall, extremely reliable transport properties in a solution grown SC.

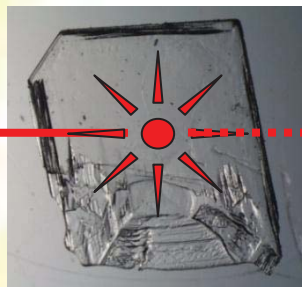
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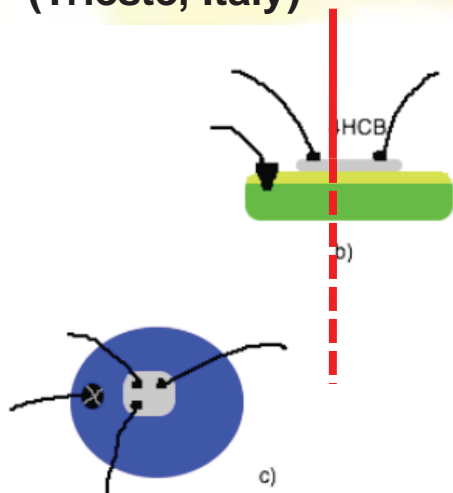
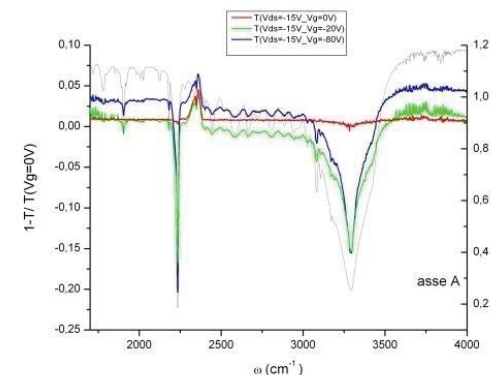
FOURIER-TRANSFORM INFRARED SPECTROSCOPY ON 4HCB SINGLE CRYSTALS



IR Beamline SISSI
at
ELETTRA Synchrotron
(Trieste, Italy)



Measurements carried out in TRANSMITTANCE MODE, on “naked” and/or electrically contacted crystals (Si/SiO_x-based FETs).



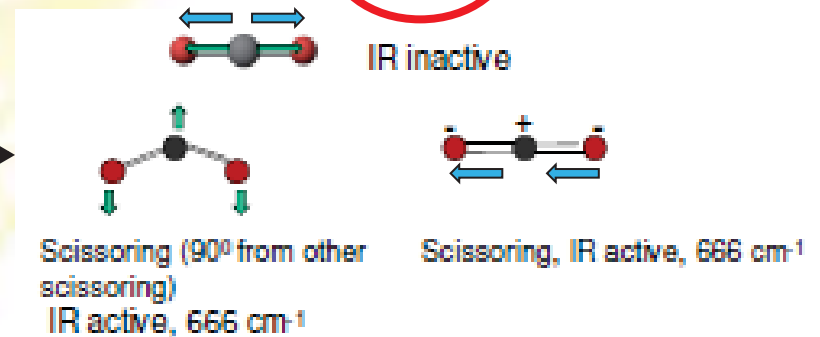
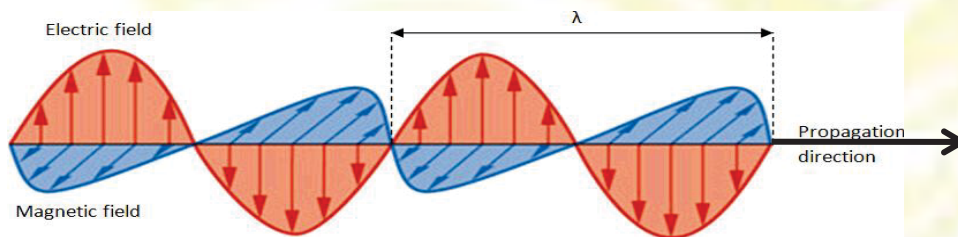
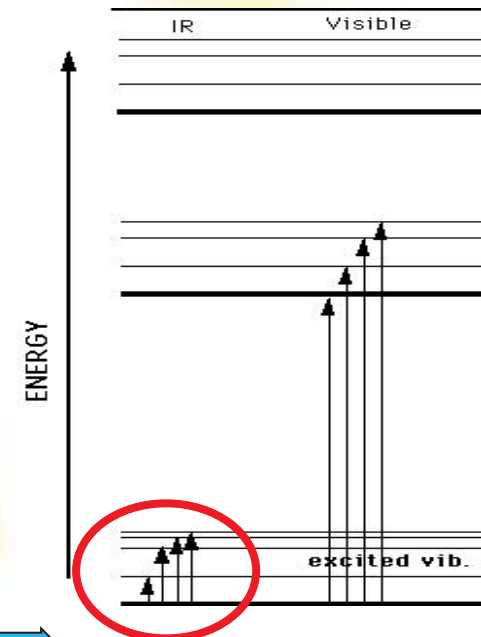
SHORT-MEDIUM TERM OBJECTIVE: TO UNDERSTAND WHICH FUNCTIONAL GROUPS ARE MOSTLY INVOLVED (OR NOT) IN CHARGE TRANSPORT

LONG TERM OBJECTIVE: TO BE ABLE TO RATIONALLY DESIGN HIGH-MOBILITY MOLECULAR (POLYMERIC?) MATERIALS

BRIEF REFRESH: HOW INFRARED SPECTROSCOPY WORKS

IR photons excite vibrational/rotational energy levels of molecules/functional groups.

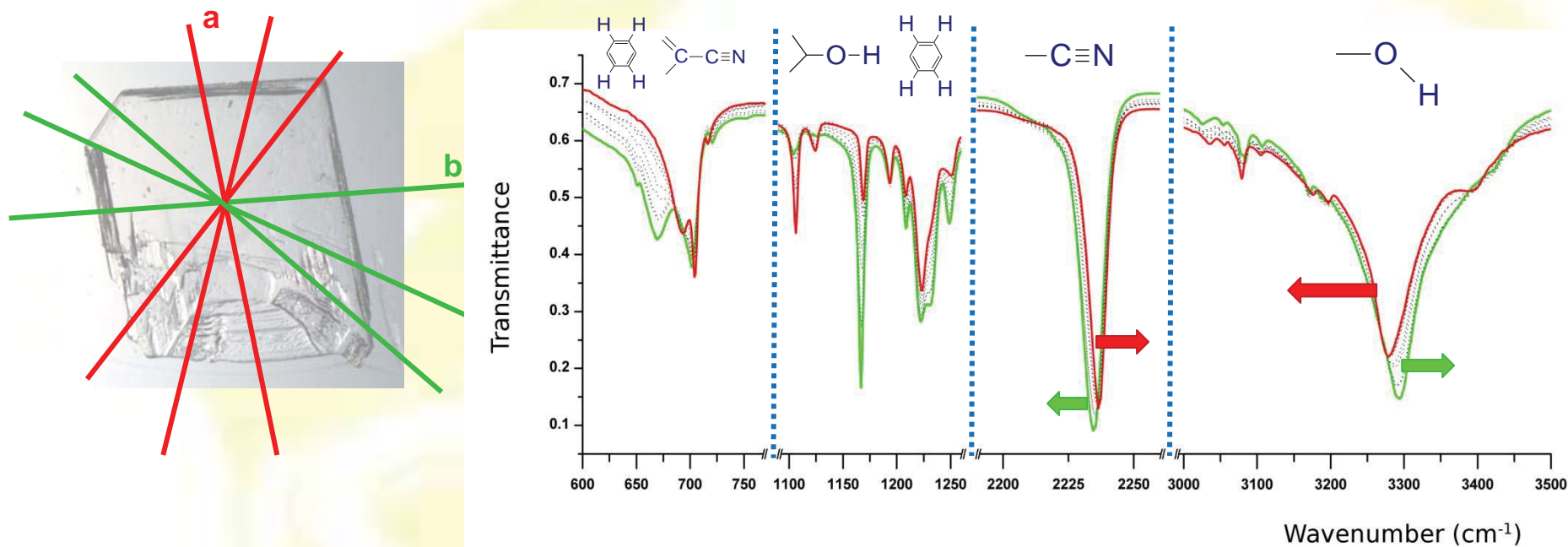
The incoming IR photon must cause a net change in the dipole moment (μ) of the molecule for being absorbed (because the alternating electrical field of the radiation interacts with fluctuations in the μ of the molecule).



Changes in **IR absorption intensity** are correlated to μ orientation variations ($\Delta\mu$).

Changes in the **absorption frequency** are correlated (mainly) to the **chemical neighbourhood** of the functional group interacting with the photon.

ANISOTROPIC LINEARLY POLARIZED (LP) FT-IR SPECTRA OF 4HCB SINGLE CRYSTALS



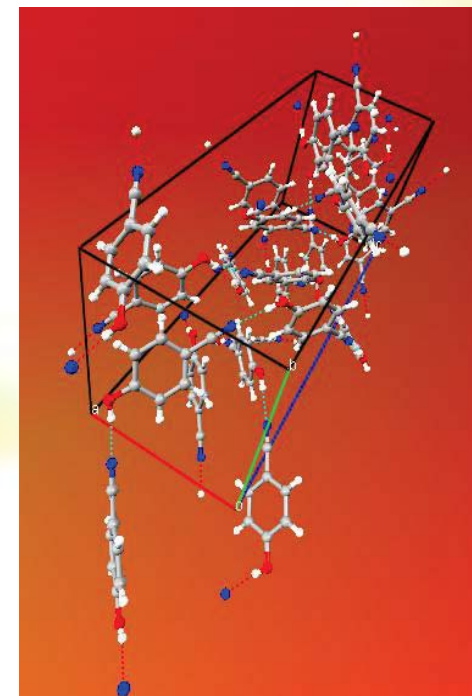
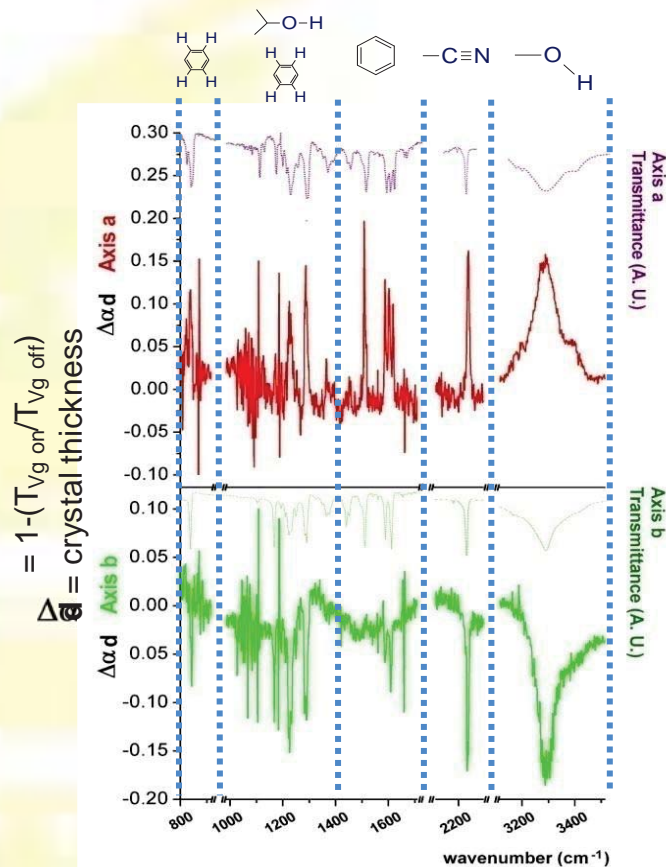
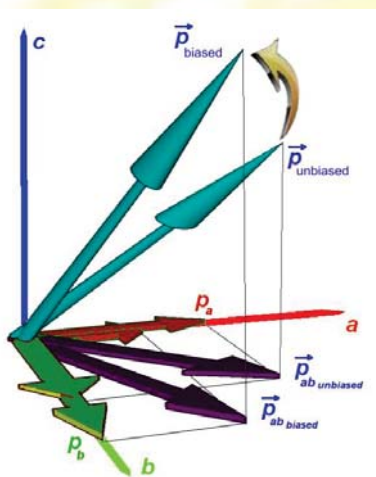
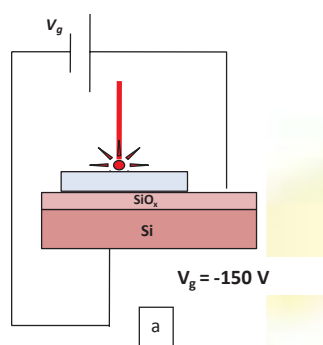
4HCB single crystals show markedly anisotropic LP-IR spectra already at room temperature.

This allows:

- probing of a higher hydrogen bonding degree along the axis *a*;
- **IDENTIFICATION OF THE CRYSTALLOGRAPHIC AXES OF THE CRYSTALS VIA SIMPLE SPECTROSCOPIC MEASUREMENTS** (provided that the crystal axes have been identified at least once).^{*} This technique is applicable to any OSSC.

^{*}A. Fraleoni-Morgera et al., J. Phys. Chem. C 2012, 116, 2563–2569

ANISOTROPIC DIPOLE MOMENT VARIATIONS IN THE 4HCB CRYSTAL LATTICE UPON ELECTRICAL POLARIZATION

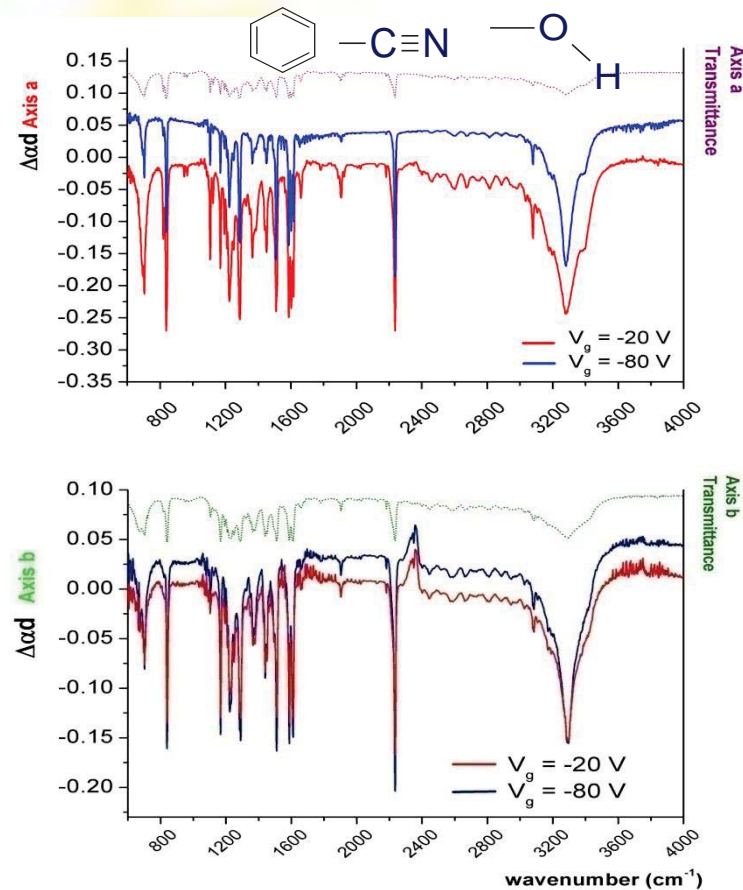
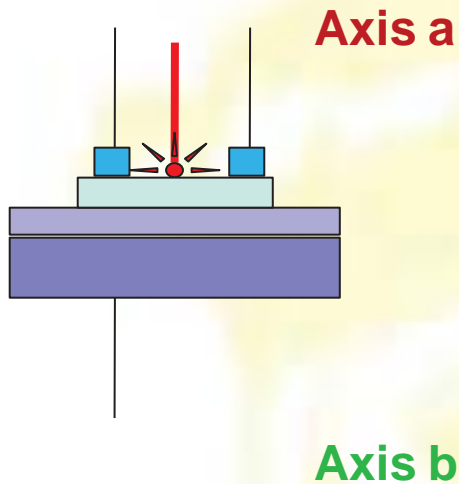


Anisotropic dipole moment variations in the crystal lattice due to gate-induced crystal polarization were found and attributed to:

- higher π -stacking along the axis a with respect to b ;
- higher incidence of the hydrogen bond along the axis a with respect to b .

4HCB CRYSTALS BEHAVIOUR UNDER SIMULTANEOUS GATE AND DRAIN-SOURCE VOLTAGE

$V_{ds} = -15$ V
IR beam between the source and drain contacts.



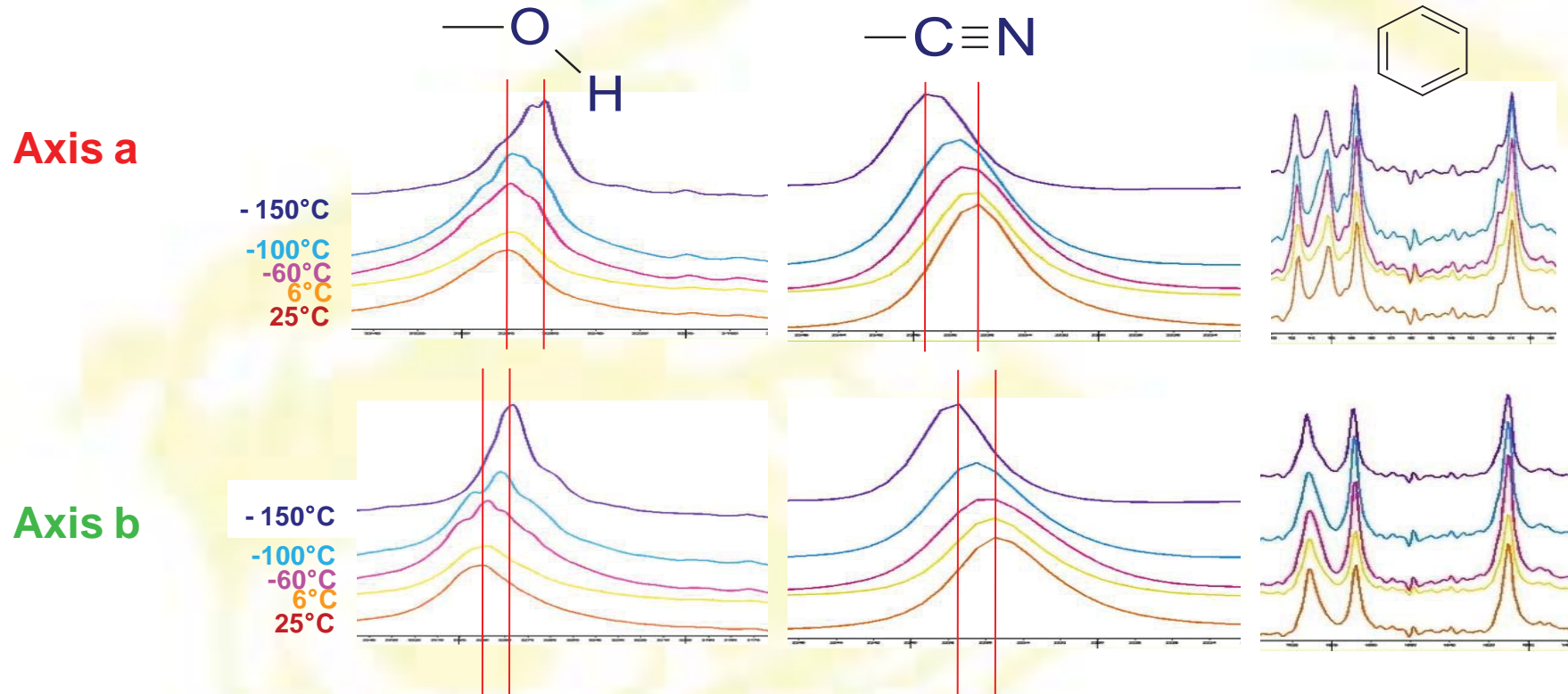
All the peaks change in intensity and in the same direction for each crystal axis.

The baseline's $\Delta\alpha_d$ is negative for $V_g = -20$ V and positive for $V_g = -80$ V, i.e. **the overall transmission is decreased at high V_g s, due to screening by a layer of free charges at higher V_g s.**

The baseline's shift is higher along axis a, pointing to a higher free charges density along this axis (in line with its higher charge carrier mobility, and with the presence of charge carriers due to the applied V_{ds} .)

*A. Fraleoni-Morgera et al., J. Phys. Chem. C 2012, 116, 2563–2569

EFFECT OF LOW T ON THE 4HCB SINGLE CRYSTAL LP-IR SPECTRA

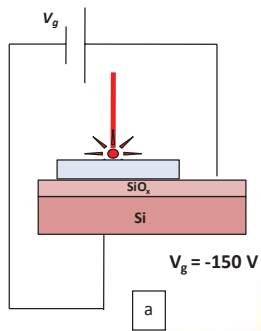


Upon cooling:

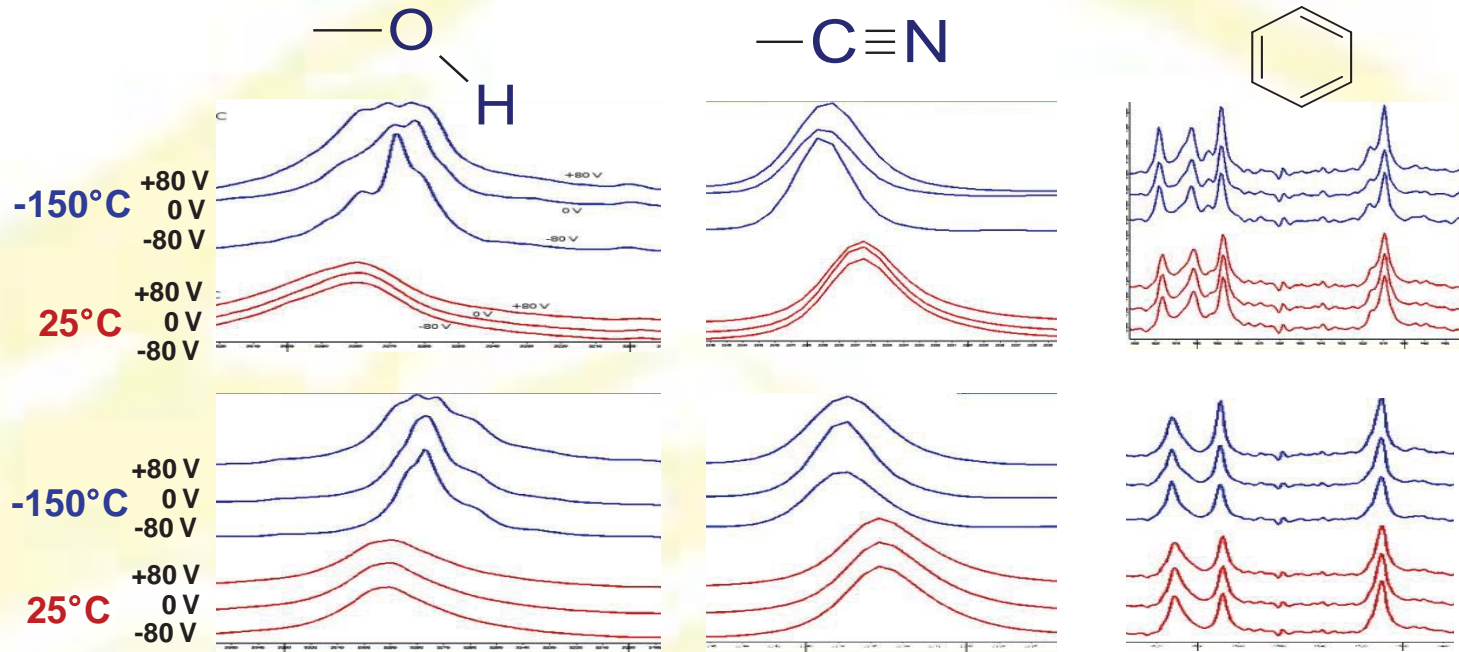
- Appreciable **shifts appear in the -OH and -CN zones**, of different extent along the two axes;
- different -OH peaks are visible, attributable to the **different -OH orientations in the crystal lattice**;
- **no appreciable shift in the C=C zone** (benzenic rings).

=> **ANISOTROPIC THERMAL SHRINKING OF THE CRYSTAL** (higher increase of the hydrogen bonding intensity along *a* implies shorter -OH...NC- distances with respect to *b*), **mainly due to hydrogen bond length changes** (the benzenic rings seems not affected by the temperature decrease, pointing to rather unchanged ring-ring distances).

ELECTRICAL POLARIZATION EFFECTS AT LOW T



Axis a



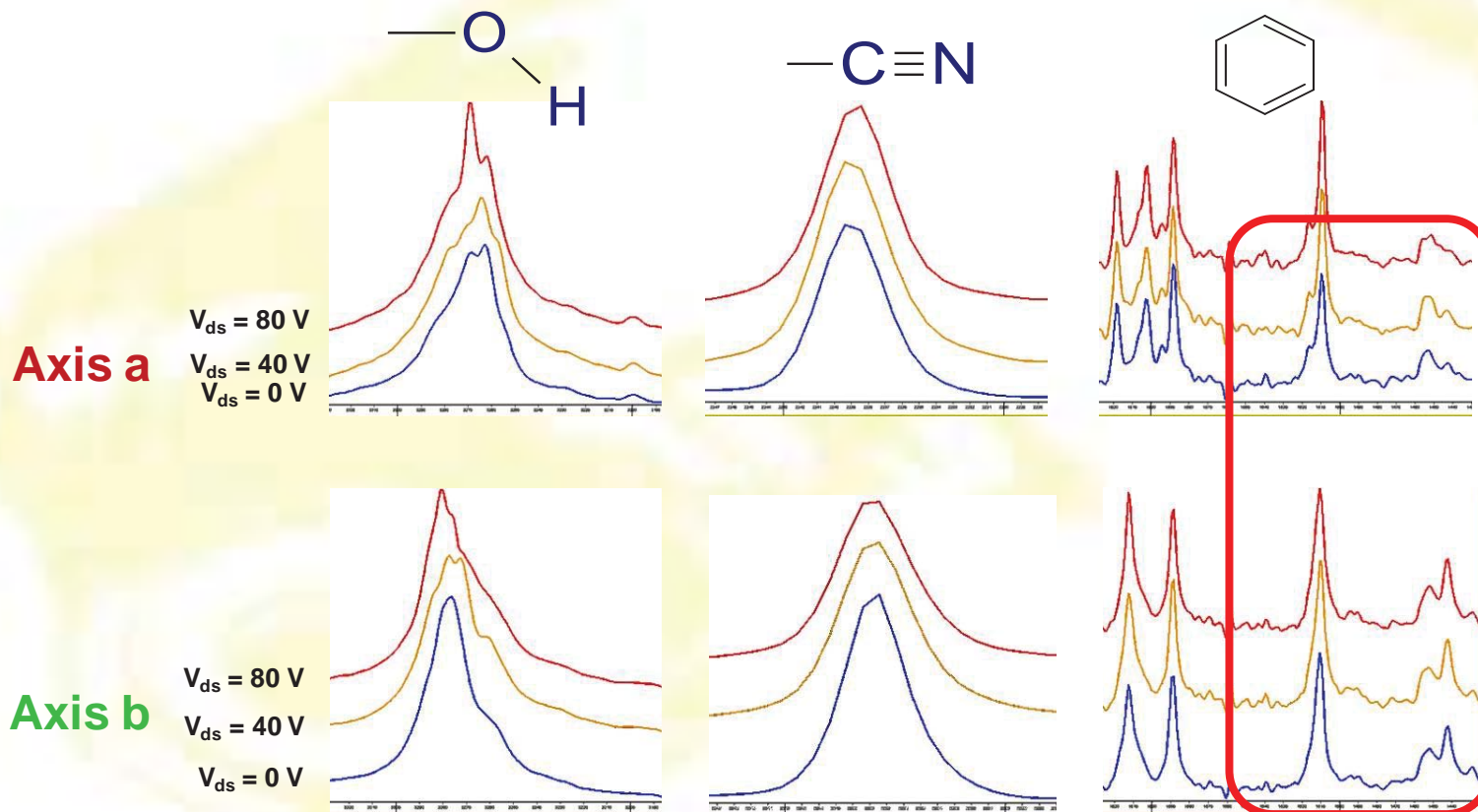
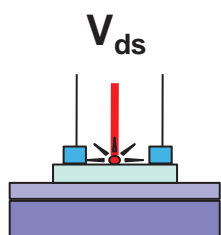
Axis b

- Electrical polarization effect noticed only for **-OH** (mainly) and **-CN** at low T (it is possible to identify this even at room T, but only with proper data processing*).

For -OH:

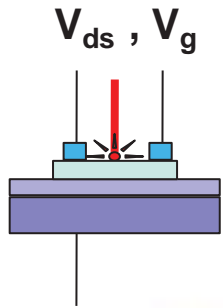
- the polarization bias affects asymmetrically the LP-IR response along both the axes *a* and *b*.
- positive and negative biases affect differently the **-OH** signal
- the polarization affects to different extents the **-OH** groups differently oriented within the lattice (i.e., at low T, upon electrical polarization not all the **-OH** and **-CN** groups are equivalent)
- thermal shrinking effects ruled out (polarization effects visible at constant T changing the polarization bias).

SPECTROSCOPICALLY DETECTED EFFECTS OF ELECTRON FLOW AT LOW T(-150°C)



- Important spectral changes are observed upon current flow (tens of pA) along both *a* and *b*, in an anisotropic way, only for the $-OH$ related signals.
- Subtle changes in the zone of benzenic rings-related signals (supposed to be the ones most involved in actual charge transport, either band- or hopping-like), mostly along axis *a* (the one with the highest mobility).

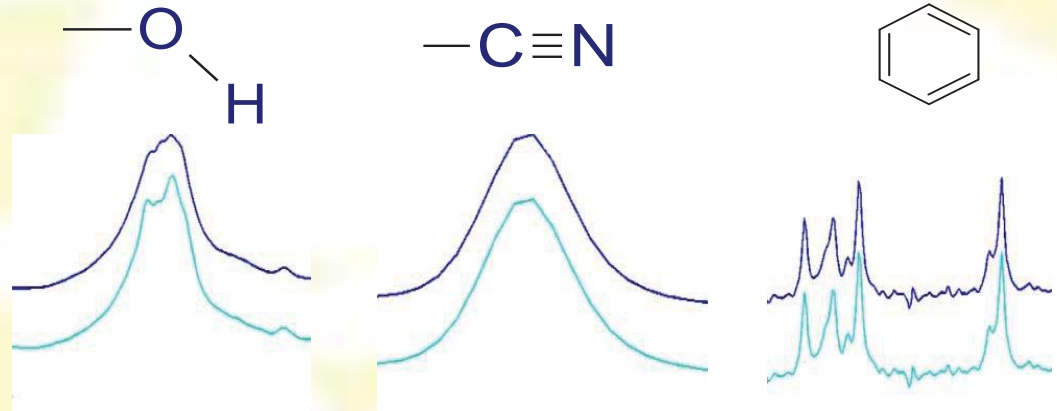
SPECTRAL CHANGES UPON SIMULTANEOUS APPLIED V_g and V_{ds} (-150°C)



Axis a

$V_{ds} = 60 \text{ V}$,
 $V_g = +80 \text{ V}$

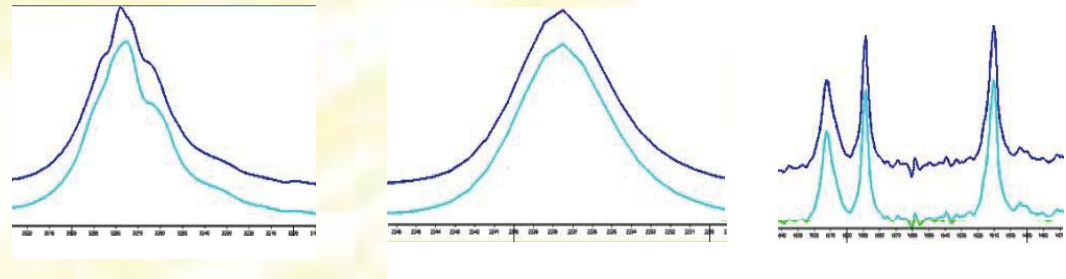
$V_{ds} = 60 \text{ V}$,
 $V_g = -80 \text{ V}$



Axis b

$V_{ds} = 60 \text{ V}$,
 $V_g = +80 \text{ V}$

$V_{ds} = 60 \text{ V}$,
 $V_g = -80 \text{ V}$



- Different spectral behaviour upon gate polarity change during current flow (about 100 pA), noticeable only along the axis a.
- Apparently, no changes in the zone of benzenic rings-related signals

No polaronic signatures were found, possibly due to the very low transported currents.

*A. Fraleoni-Morgera et al., submitted

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ORGANIC SEMICONDUCTORS IN IONIZING RADIATIONS DETECTION

Currently used approaches to ionizing radiation detection involving organic semiconductors:

- **Indirect detection:** the ionizing radiation is converted into visible light (the device is called “scintillator”). This is by far most common approach, and usually the organic semiconductors are used in the form of single or polycrystals*, and are coupled to inorganic photodiodes for the photon detection, which makes the final device architecture rather complex.
- **Photodiodes:** constituted by thin, semiconducting polymer-based films, these devices detect photons generated by an indirect converter (usually inorganic), but they degrade rather quickly upon exposure to the ionizing radiation.**
- **Direct detection:** the device is able to convert directly the ionizing radiation into an electrical signal. The few reported examples of this kind are based on thin polymer films, that degrade rapidly upon exposure to the ionizing radiation***, and always involve metallic/semimetallic electrodes exposed to the radiation, in order to exploit secondary photoelectrons for the detection.

* G.Hull et al., IEEE Nucl.Sci. 56, 899 (2009)

** S.Tedde et al. Nanoletters, 9,980 (2009)

*** A.Intaniwet et al. J.Appl..Physics, 106, 64513 (2009)

ADVANTAGES OF DIRECT DETECTION USING ORGANIC SEMICONDUCTORS

A direct detector for ionizing radiation based on organic semiconductors could exploit the benefits of organic materials (low cost, processability, flexibility) for creating brand new devices, having the following advantages over the existing (inorganic) ones:

- **Very low cost**
- **Simpler device architecture: no need for accurately designed and fabricated assemblies.**
- **Possibility of realizing flexible detectors**
- **Possibility of realizing large area ($> 1 \text{ m}^2$) detectors**
- **Possibility of high throughput**
- **Extreme versatility in terms of usable materials, hence of the selected ionizing radiation energy and type**

However, up to now organic semiconductors are perceived as inherently unstable and easily degradable upon ionizing radiation exposure*.

* Newman, R. et al., Appl. Phys. Lett. 91 142105 (2007)

OSSCs AS DIRECT DETECTORS OF X-RAYS

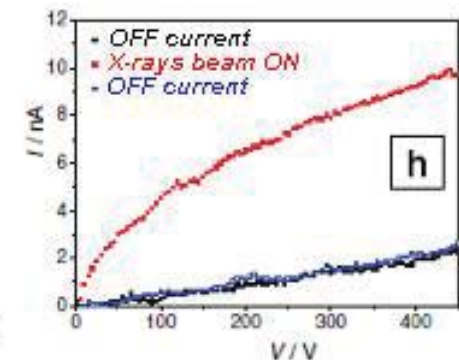
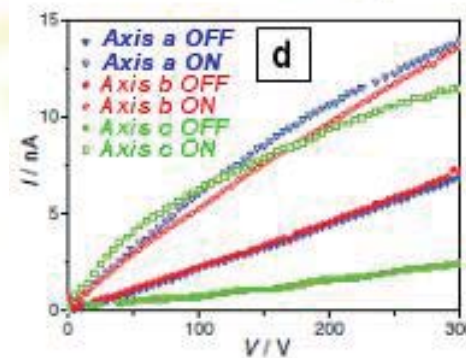
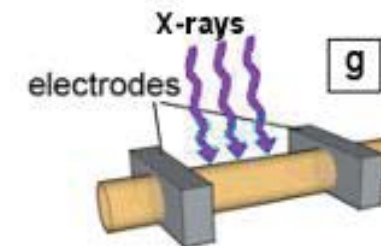
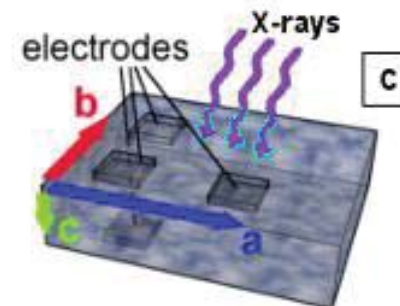
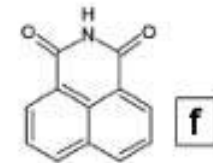
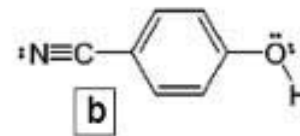
Organic Semiconducting Single Crystals as Next Generation of Low-Cost, Room-Temperature Electrical X-ray Detectors

Beatrice Fraboni,* Andrea Ciavatti, Francesco Merlo, Luca Pasquini, Anna Cavallini, Alberto Quaranta, Annalisa Bonfiglio, and Alessandro Fraleoni-Morgera

COMMUNICATION

OSSCs are demonstrated to be effective X-rays detectors*, with a number of interesting features:

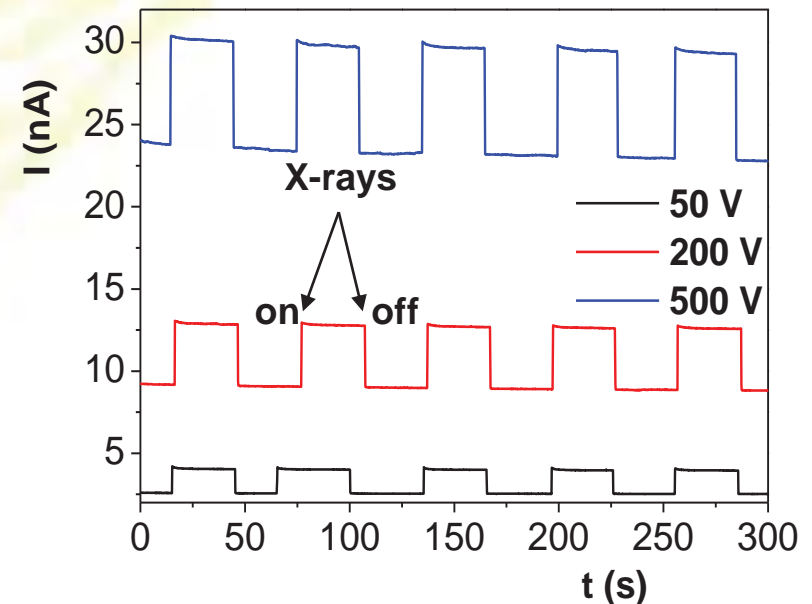
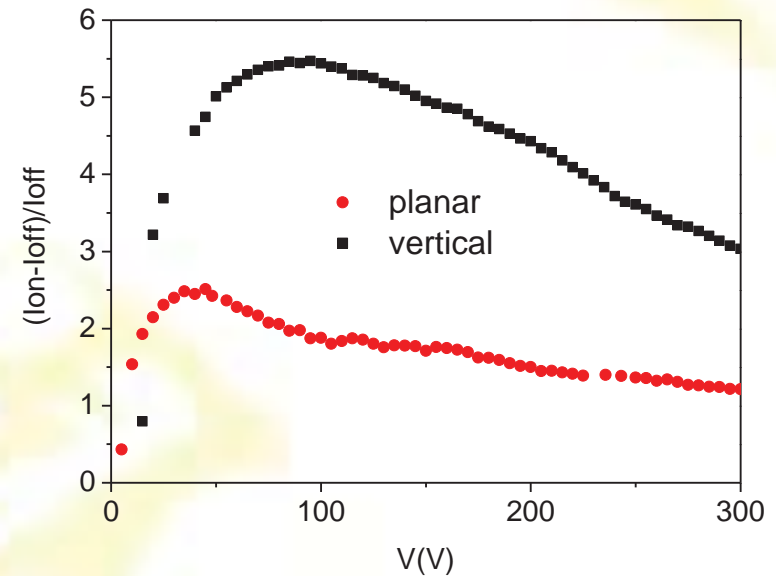
- operable at **ambient pressure and temperature, and under ambient light;**
- **anisotropic response** (when the crystal characteristics allow to probe this property);
- this property is **common to different crystals, which present different responses**, suggesting that it is possible to tune the detector's response simply properly choosing the detecting crystal.



* B. Fraboni et al., Adv. Mater., 2012, 24, 2289

ANISOTROPIC RESPONSE AND FAST SWITCHING TIMES

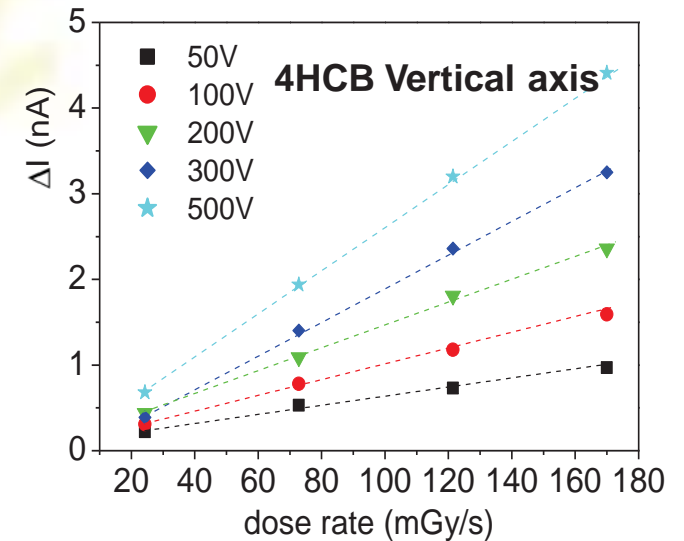
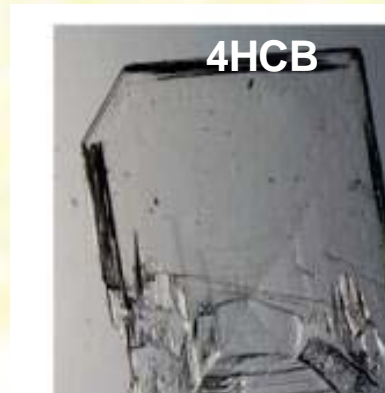
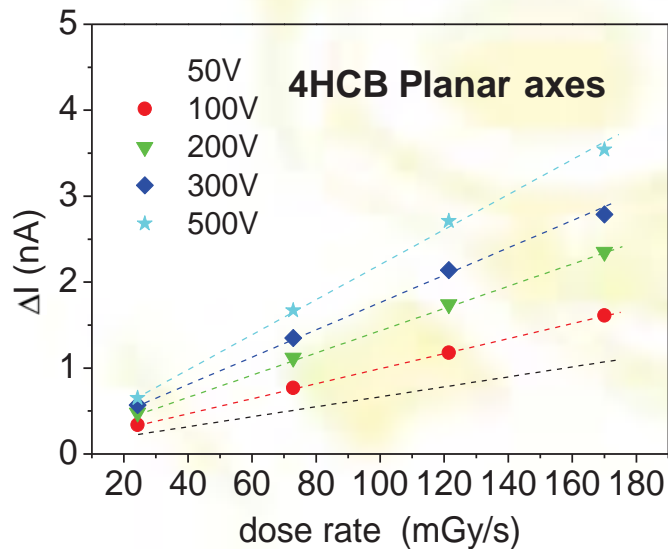
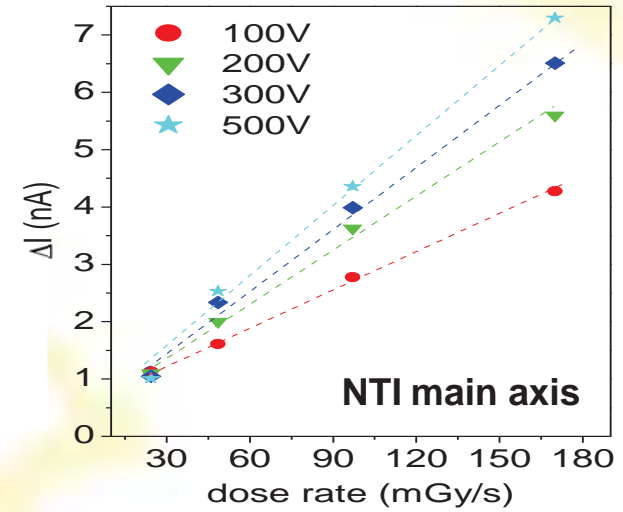
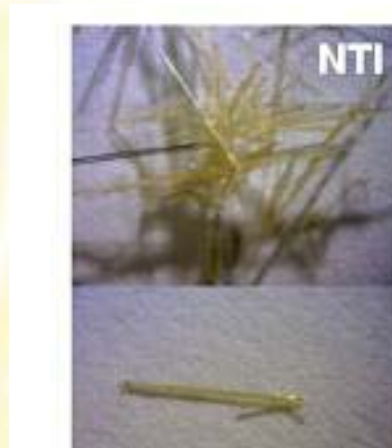
- **Non-monotonic device response upon applied bias.**
- When the chosen crystal is amenable to anisotropic transport probing (as for example 4HCB), the **response dependence from the bias is different along two different crystallographic directions** (NB: for 4HCB the two planar directions a and b give very similar responses).
- First **unoptimized, test devices can be already effectively operated at voltages as low as 30 V.**
- **Remarkably reproducible response, with apparently negligible drift**, especially at low biases.
- **Fast response (< 70 ms**, data acquisition limit; likely, even faster).
- **No apparent hysteresis effect.**



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RESPONSE LINEARITY

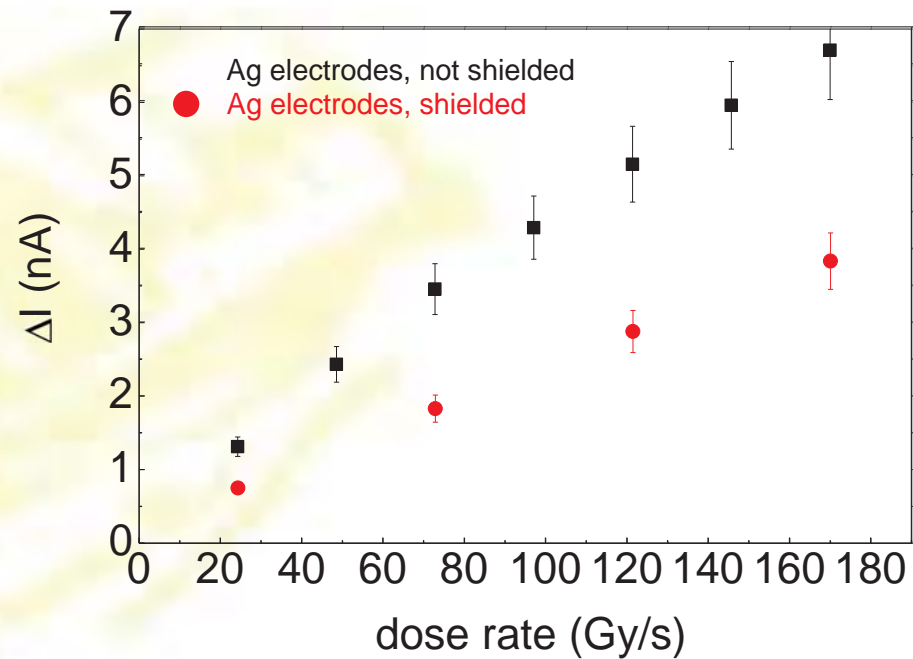
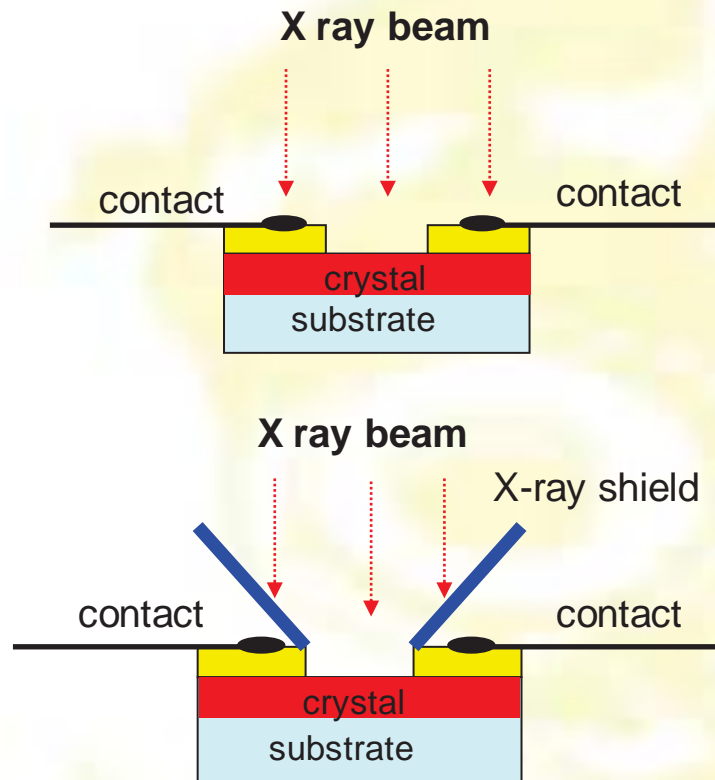
- **Good response linearity over a rather wide dose rate range, at any of the tested biases, also considering (when appropriate) different crystallographic directions.**



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INTRINSIC RESPONSE TO X-RAYS

- The OSSCs response to X-rays is due only to the crystal itself (intrinsic).

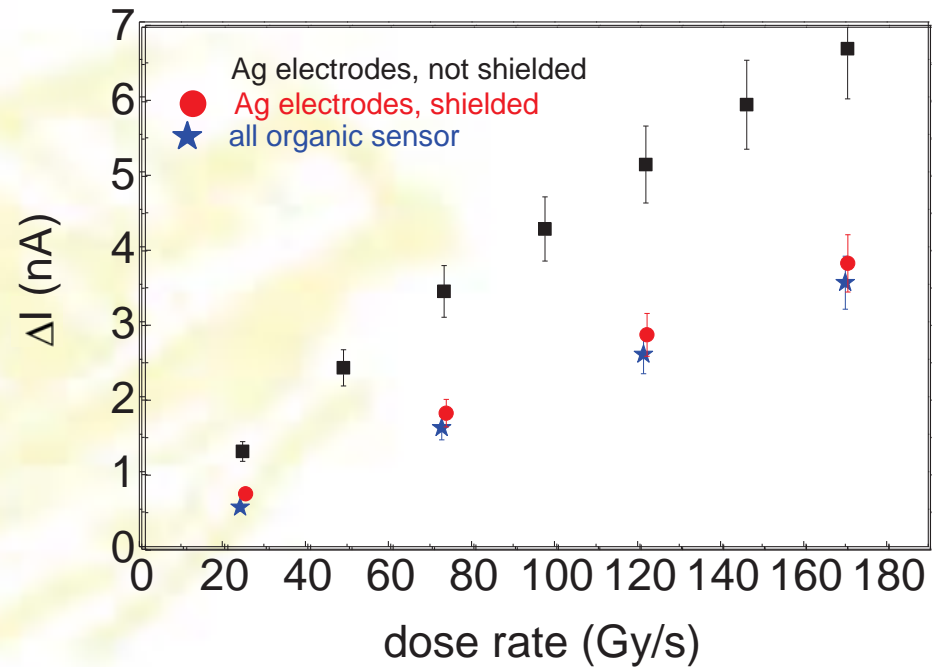
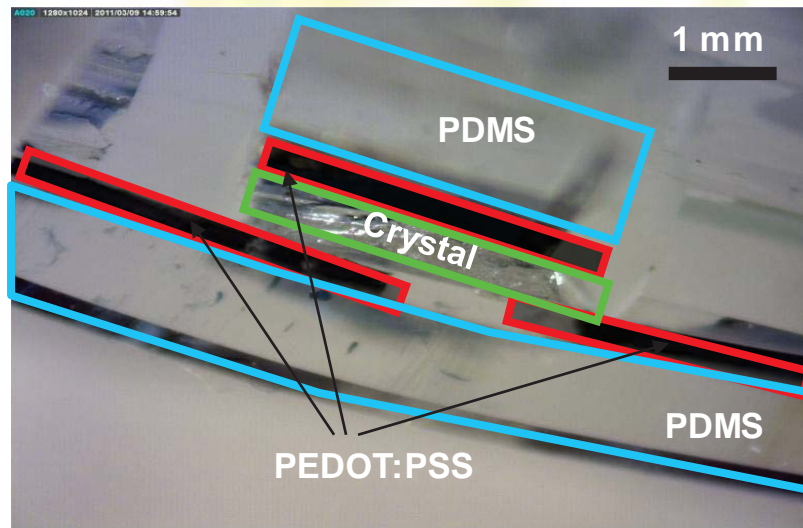


This property allows to fabricate all-organic devices.

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ALL-ORGANIC, BENDABLE DETECTORS

- An all-organic, bendable, well working detector was fabricated and characterized.



Additional advantage: this device is optically transparent, allowing novel biomedical applications (to be addressed).

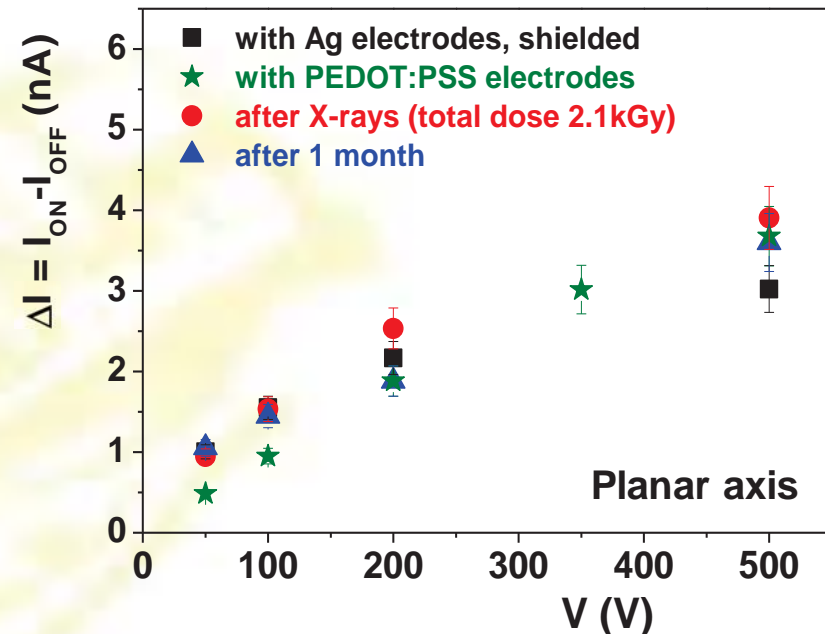
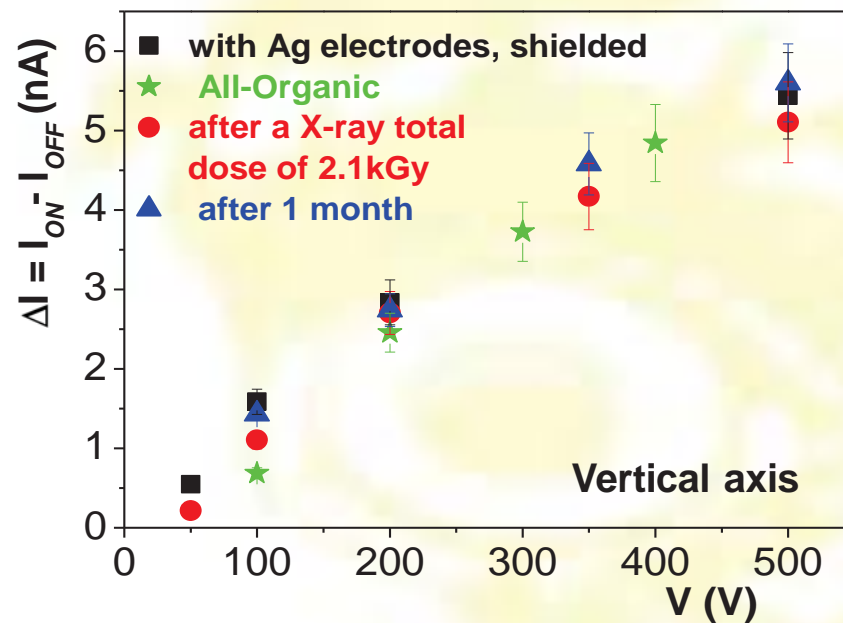
* B. Fraboni et al., Adv. Mater., 2012, 24, 2289

NEXT PRESENTATION SECTION

- Why organic semiconductors, and their general features
- Organic semiconducting single crystals (OSSCs): main structural and transport properties
- Overview of OSSCs growth methods
- Structural and electronic properties of 4-hydroxycyanobenzene (4HCB) single crystals
- Synchrotron-based investigation of 4HCB crystals
- Direct detection of X-rays by means of OSSCs
- **Radiation hardness of 4HCB crystals**
- Conclusions

ROBUSTNESS OF 4HCB RESPONSE UPON AGING AND HIGH DOSES (I)

- 4HCB-based detectors are rather robust with respect to aging, and to high X-rays doses.

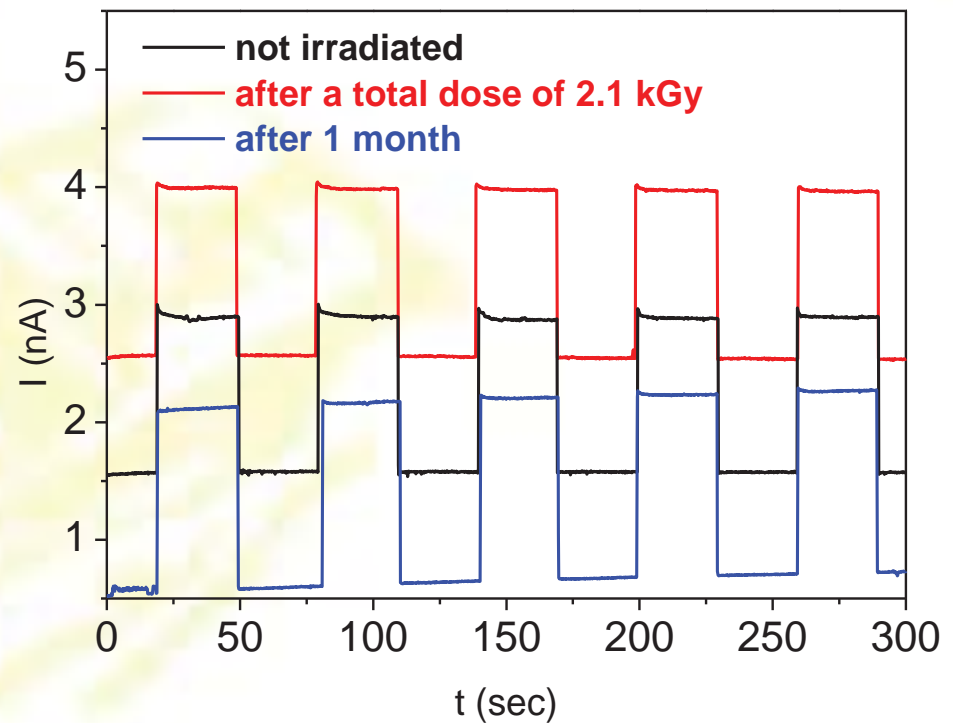


Devices were exposed to a total dose of 2.1 K Gy, and then measured delivering the same response found for the normally tested detectors. After that, they were put aside for one month, then they were measured again in the same conditions (35 KeV), delivering the same performances found in the first measurements.

ROBUSTNESS OF 4HCB RESPONSE UPON AGING AND HIGH DOSES (II)

- Also the overall switching behaviour was unchanged upon exposure of the device to high doses.

Only noticeable variation: small change in the base current. Degradation phenomena in this case are unlikely, due to the apparently random baseline variations.



Polarization effects in the crystal due to the ionization induced by X-rays may be accounted for these findings, and further synchrotron-based experiments on the matter are running.

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CONCLUSIONS

- Organic semiconducting single crystals are useful model systems for assessing the transport properties of organic semiconductors, and good quality crystals can be easily grown from solution;
- IR spectroscopy is a useful tool for investigating both the structural and the electronic properties of OSSCs.
- OSSCs are effective and intrinsic X-rays detectors, with linear response, fast switching times, no sign of hysteresis nor of current drift, and a notable robustness to heavy doses. All-organic X-rays detectors showing good performances can be fabricated and operated, and the possibility of using different crystals, having different response windows and different sensitivities, could allow to fabricate spectroscopic detectors for X-rays at low cost.

In the end, OSSCs merge effectively the possibilities of exploring fundamental aspects of the charge transport in organic semiconductors and novel, exciting practical applications presenting a high market potential.

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