Ionizing radiation detection using organic single crystals

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PRESENTATION OUTLINE

- Why organic semiconductors, and their general features
- Overview of Organic Semiconducting Single Crystals (OSSCs) growth methods
- Main structural and transport properties of OSSCs
- Organic semiconductors as ionizing radiations sensors
- Direct inkjet printing of OSSCs, and using printed OSSCs as ionizing radiations detectors
- Possible uses of printed OSSCs as ionizing radiation detectors in the IoT
- Conclusions

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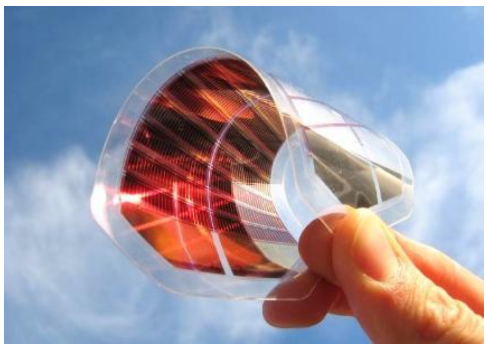
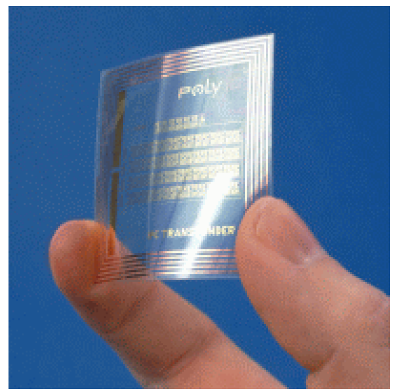
ORGANIC ELECTRONICS IS FINDING ITS WAY TO THE MARKET

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

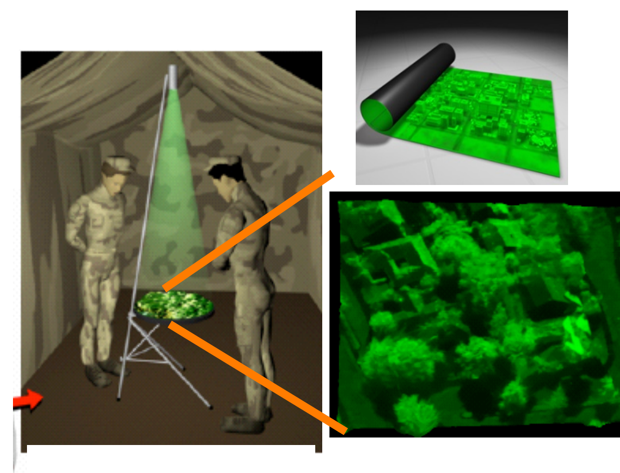
OLEDs



Organic photovoltaics



Organic RFIDs



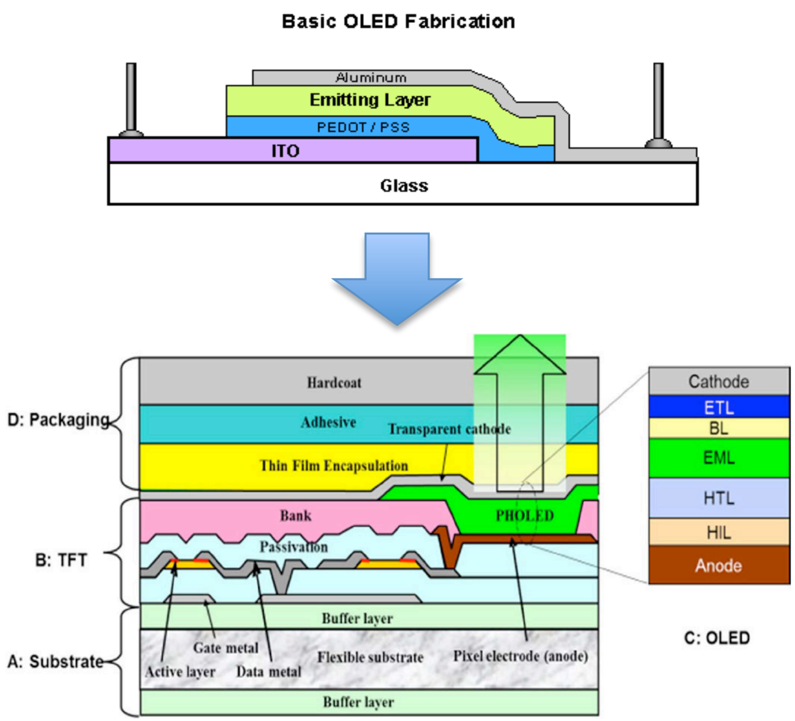
Updatable 3D Displays

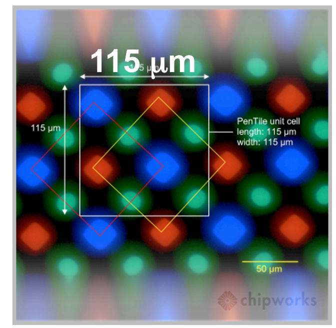
However, **a thorough understanding of the electronic phenomena ongoing in organic semiconductors is still missing.** Most of the progresses made in the field is based on the somehow effective but poorly efficient “trial and error” approach.

ORGANIC ELECTRONICS APPLICATIONS ALREADY ON THE MARKET

OLEDs development status

Remarkable technical achievements and refinements have been obtained; OLEDs are definitely **organic electronics products**, and they are on the market since 5-6 years.





Samsung S5 pixel structure

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

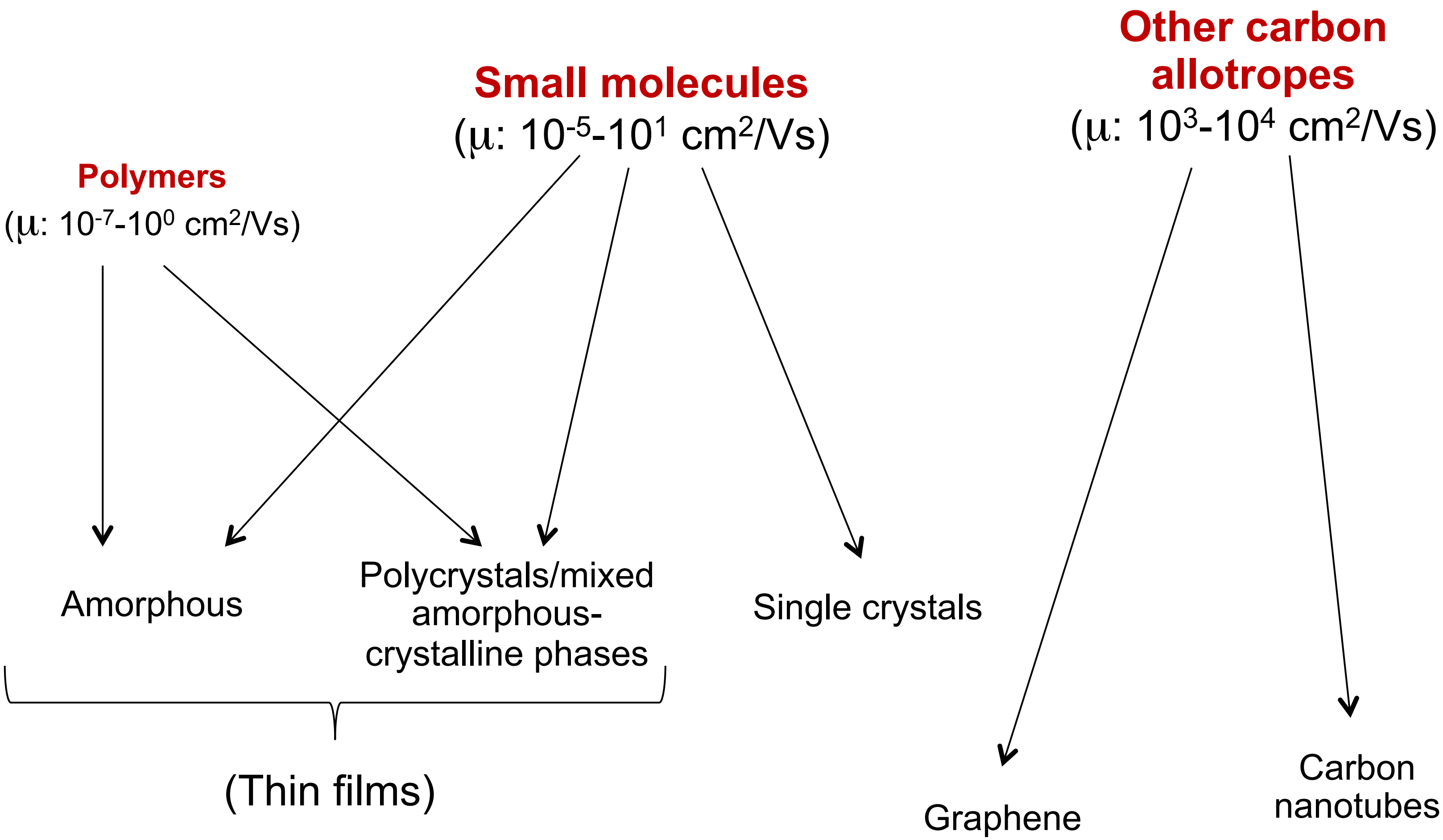
Pros:

- 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

CURRENTLY AVAILABLE TYPES OF ORGANIC SEMICONDUCTORS



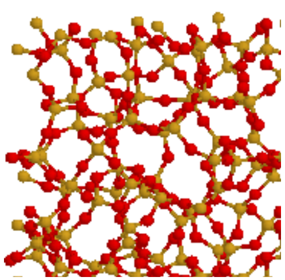
WHICH ARE THE MOST PECULIAR STRUCTURAL ASPECTS OF ORGANIC SEMICONDUCTORS?

Inorganics

Composed by **atoms**

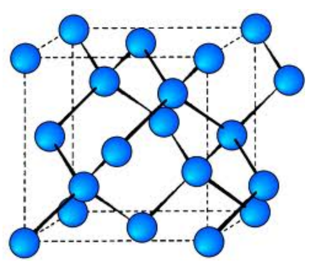
Amorphous

Mixed bonds, disordered structures



Crystalline

Covalent bonds, periodic structures

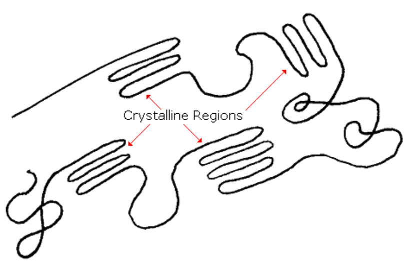


Organics

Composed by **molecules**

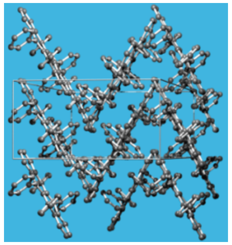
Amorphous (polymers, thin films)

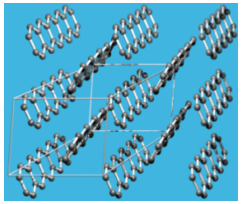
Covalent bonds, van der Waals interactions, disordered structures



Crystalline

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

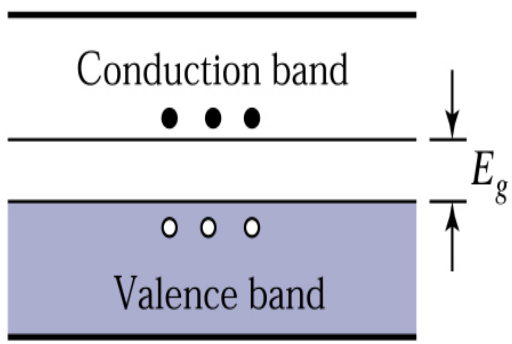




DIFFERENT ELECTRONIC STRUCTURES BETWEEN INORGANIC AND ORGANIC SEMICONDUCTORS

Inorganics

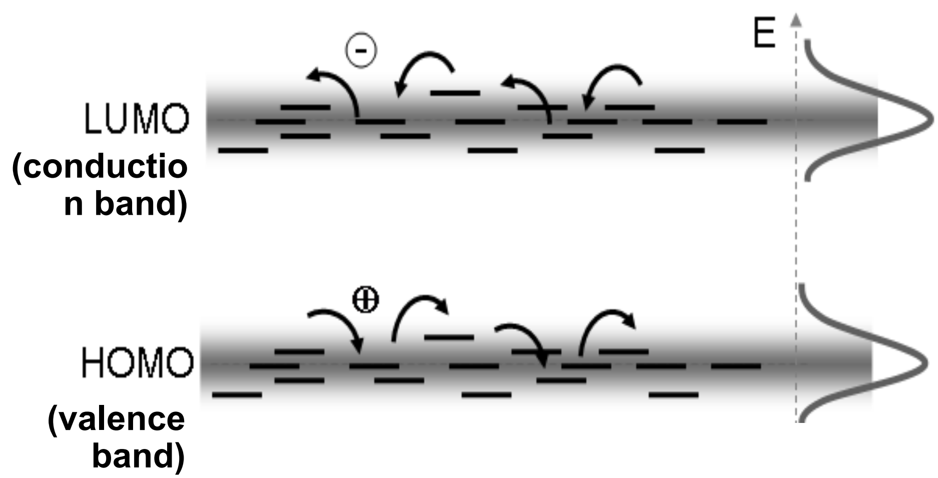
Band Structure



Band Transport

Organics

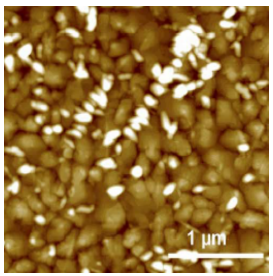
Localized, energetically near levels developing into band-like systems



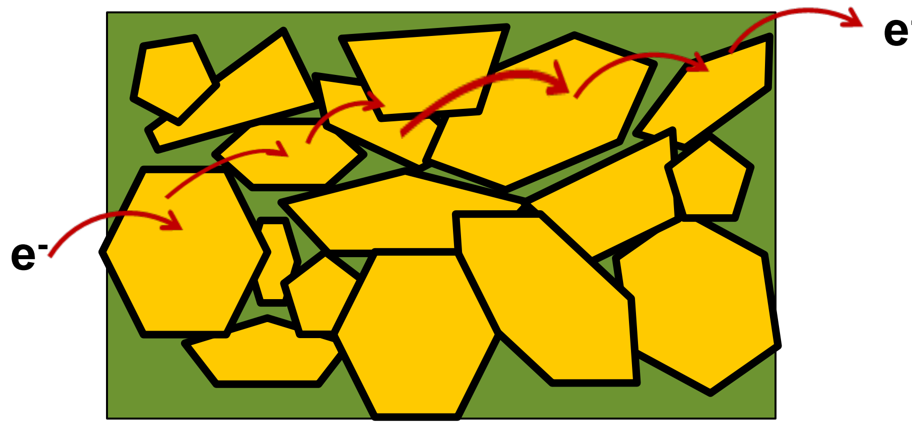
(mainly) Hopping Transport,
at low T hints of band-like transport

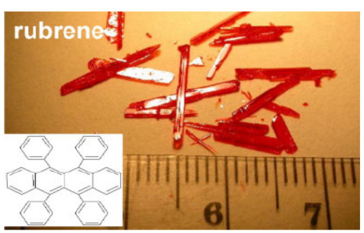
ORGANIC SINGLE CRYSTALS AS MODEL SYSTEMS FOR UNDERSTANDING ORGANIC SEMICONDUCTORS

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.

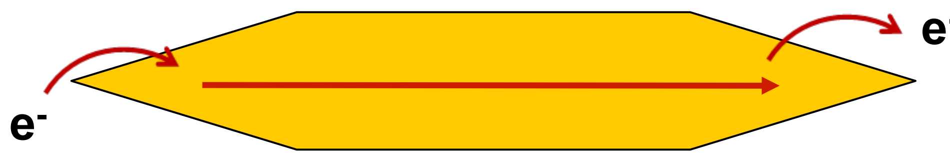


Vacuum-evaporated small molecules





Vacuum-purified single crystals



NEXT PRESENTATION SECTION

- Why organic semiconductors, and their general features
- Overview of Organic Semiconducting Single Crystals (OSSCs) growth methods
- Main structural and transport properties of OSSCs
- Structural and electronic properties of 4-hydroxycyanobenzene (4HCB) single crystals
- Direct inkjet printing of OSSCs, and using printed OSSCs as ionizing radiations detectors
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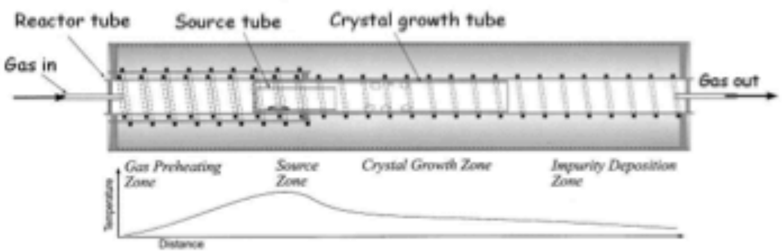
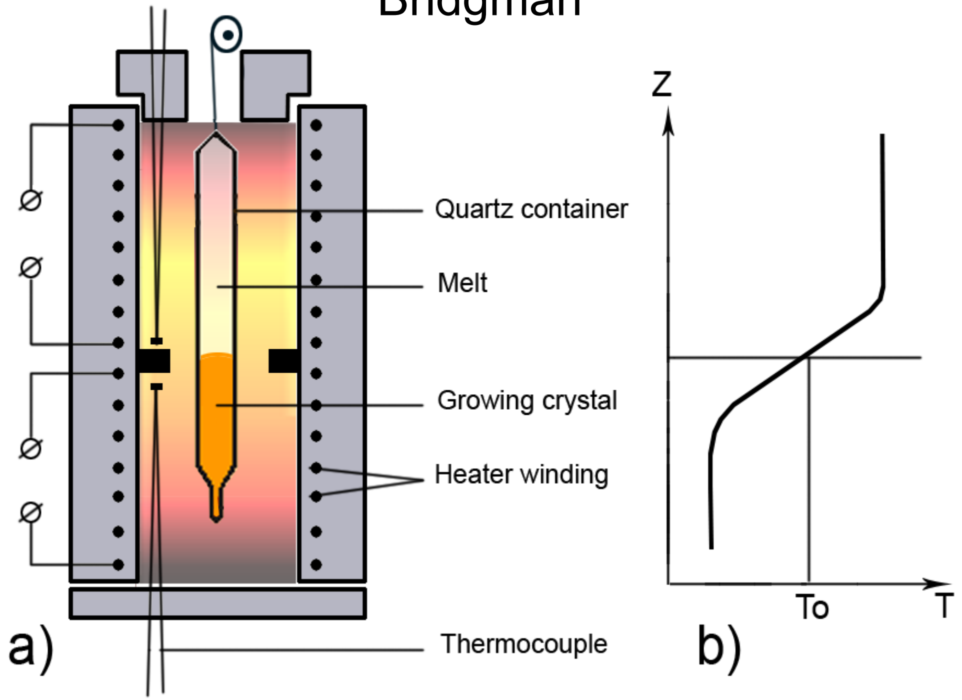
ORGANIC SINGLE CRYSTALS BY VACUUM GROWTH



ORGANIC SINGLE CRYSTALS FROM THE MELT

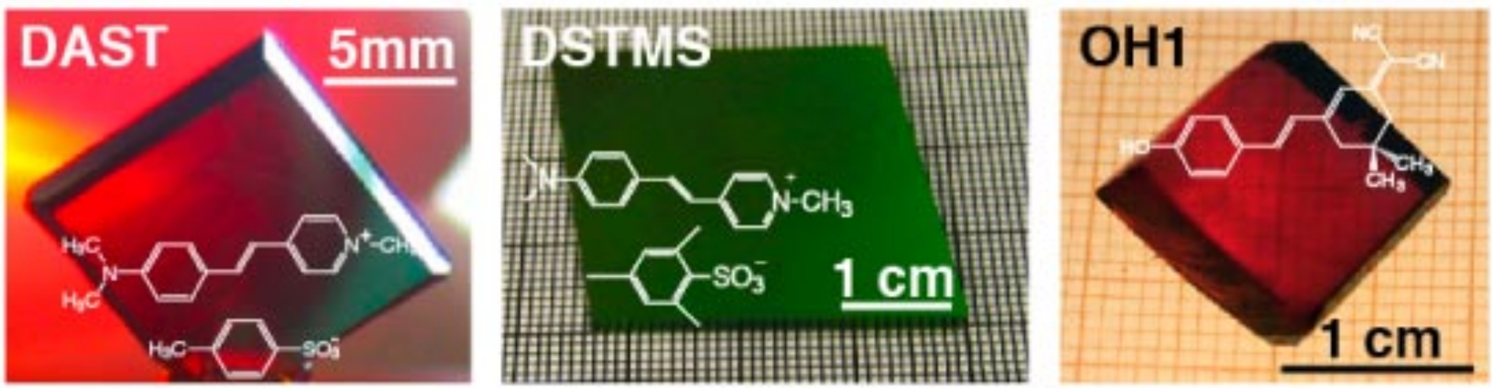
Bridgman



Bridgman growth relies on a furnace into which the material is progressively melted and recrystallized within a closed container, with a varying temperature profile.
The Czochralski crystal growth process is based on the physical, slow extraction of a crystal seed from the melt. As the extraction proceeds, the melt crystallizes on the seed forming the desired macroscopic crystal.

ORGANIC SINGLE CRYSTALS CAN BE GROWN FROM SOLUTION (I)

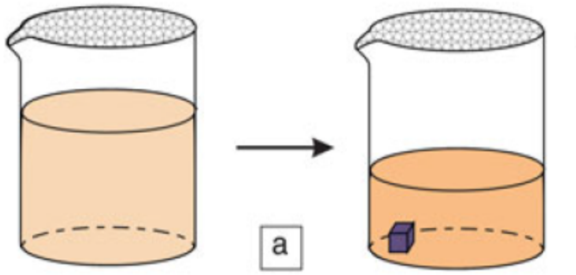
Solution growth could be an interesting alternative option to vacuum growth.
Growing organic crystals from solution is easy and allows a **good control over many crystal properties, including their dimensions and even the developed crystallographic phase** *.



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 GROWN FROM SOLUTION (II)



4 main methods:

H. Jiang , C. Kloc , MRS Bull. 2013 , 38 , 28

a) slow solvent evaporation
b) temperature decrease
c) nonsolvent vapor diffusion
d) nonsolvent liquid diffusion

EXAMPLE OF A SIMPLE SOLUTION GROWTH PROCESS

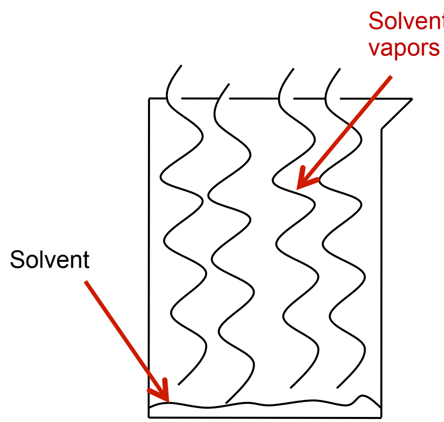
Single crystals of 4HCB, an OSSC, are easy grown from solution.

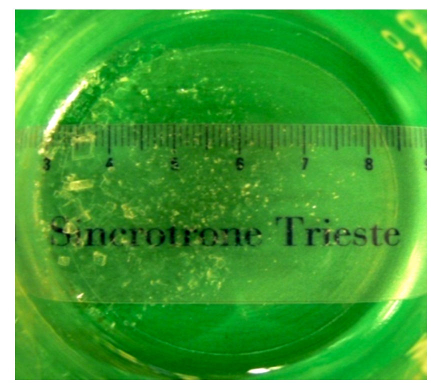
The **general recipe** for obtaining 4HCB crystals **suitable for electronic measurements** is hence the following:

- a few mg of pre-purified 4HCB crystals dissolved in a selected solvent/solvent mixture;

- slow evaporation rates (approx. 2-5 ml/day)

- fixed temperature





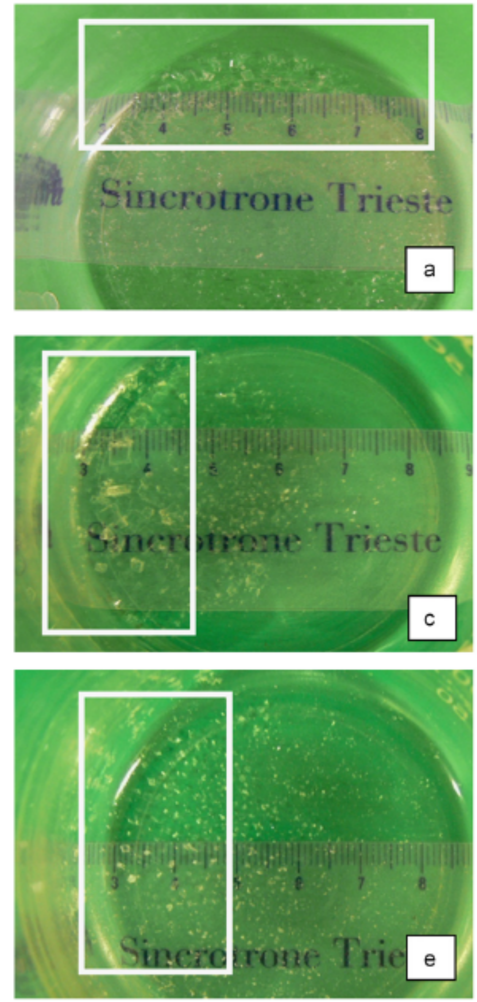
A. Fraleoni-Morgera et al, J. Cryst. Growth, 312 (2010) 3466–3472

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.

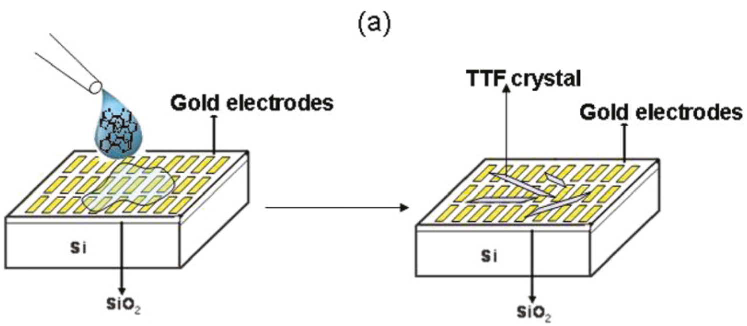
4HCB concentration in the solution (mg/mL)	Solvent/solvent mixture	Crystal size	
		Approx. side length[a] (mm)	Approx. thickness[a] (μm)
2	EE	2	200–400
2	EE:PE 9:1 V/V	2	150–300
2	EE:PE 8:2 V/V	1–1.5	100–200
3	EE	3–4	300–600
3	EE:PE 9:1 V/V	1–1.5	150–300
2	EE	3–6	200–500

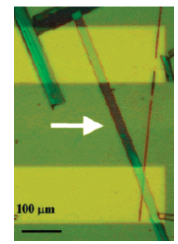


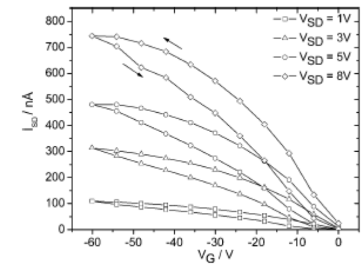
A. Fraleoni-Morgera et al, J. Cryst. Growth, 312 (2010) 3466–3472

ORGANIC SINGLE CRYSTALS CAN BE GROWN FROM SOLUTION (III)

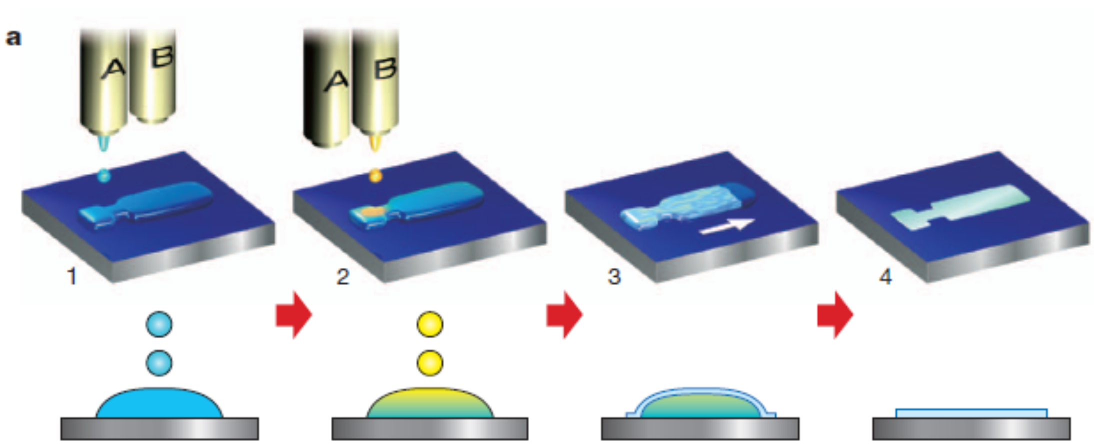
It is possible to directly grow crystals on substrates via a variety of techniques, from the simplest drop casting* to the more sophisticated inkjet printing**.

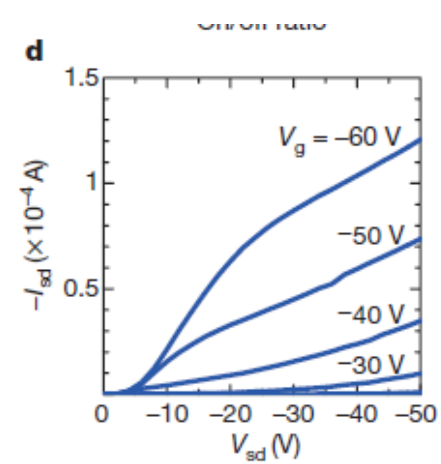






* Mas-Torrent et al., J. Am. Chem. Soc. 2004, 126, 984





** T. Hasegawa et al., Nature, 2011, 475, 364

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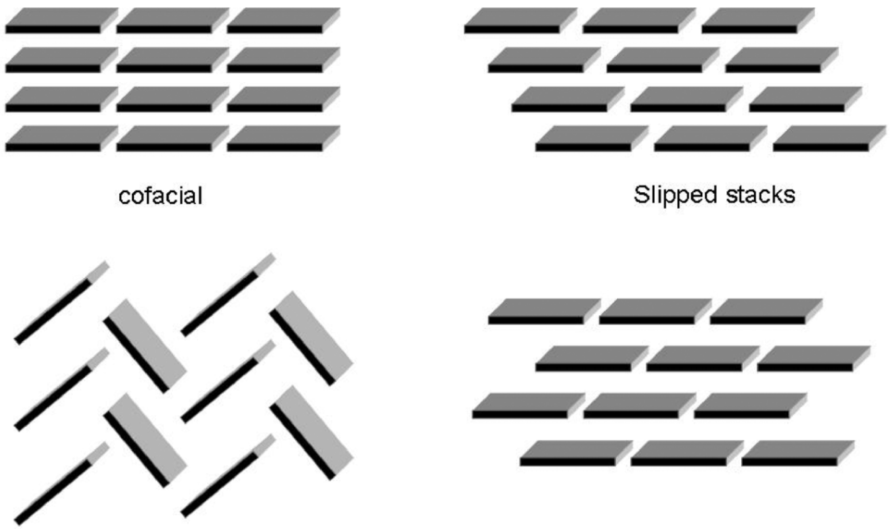
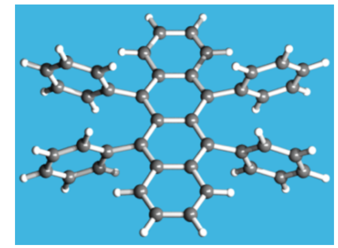
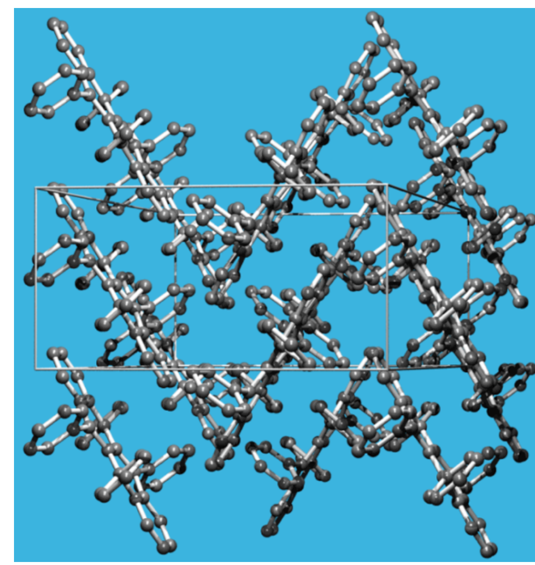
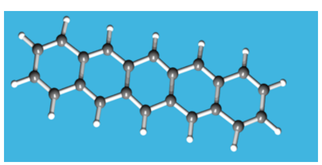
ORGANIC CRYSTALS HAVE COMPLEX STRUCTURES



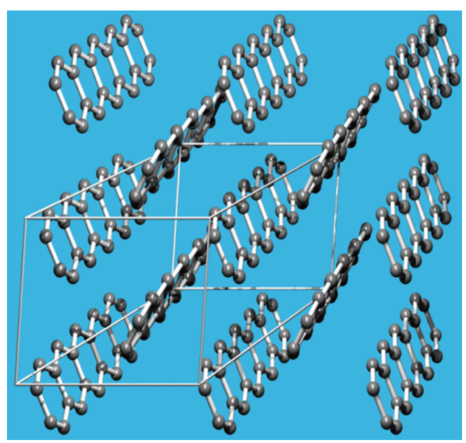


Rubrene

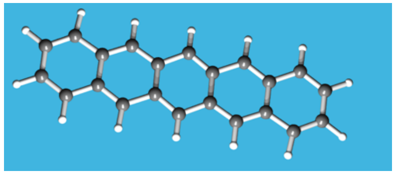




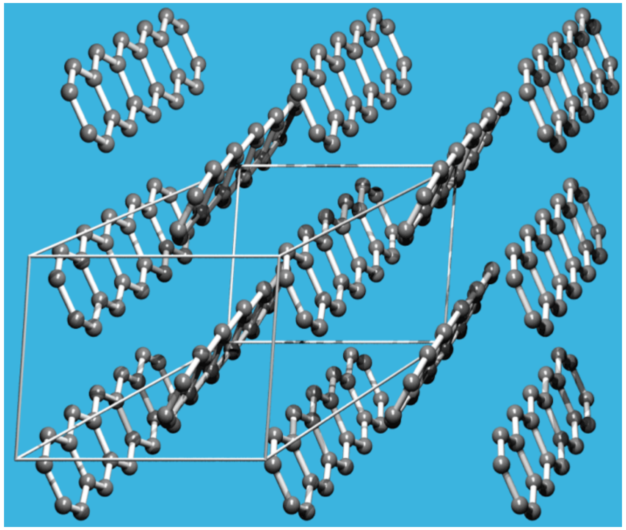
Pentacene

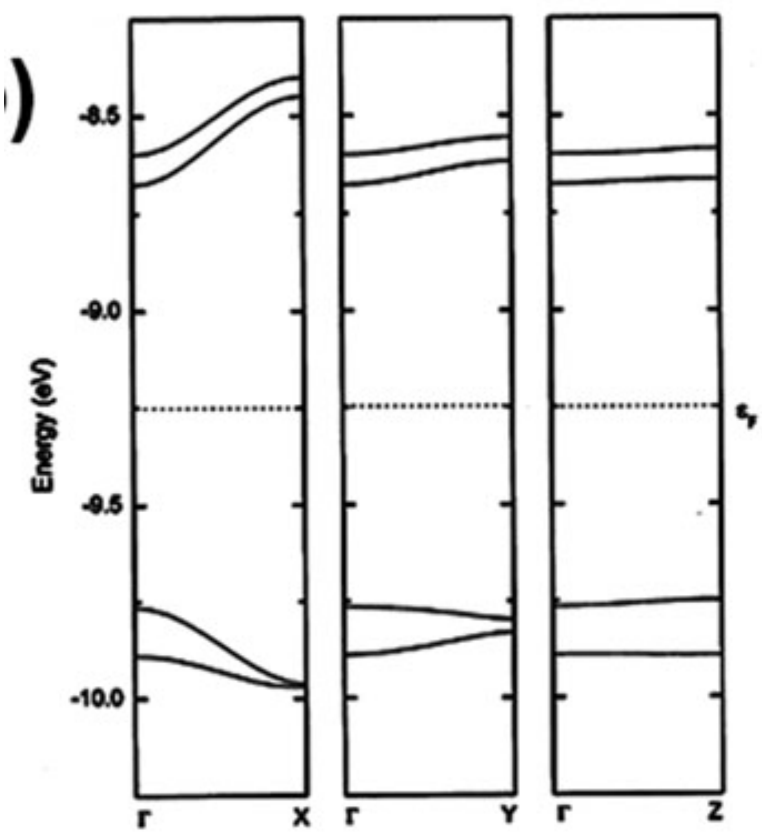


THE COMPLEX STRUCTURE OF ORGANIC CRYSTALS ORIGINATES COMPLEX ELECTRONIC FEATURES (I)



Pentacene



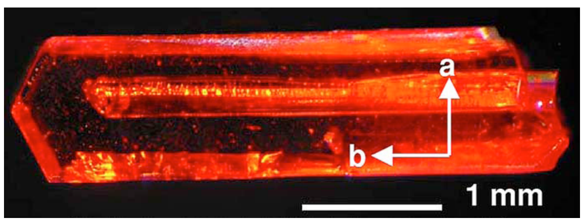


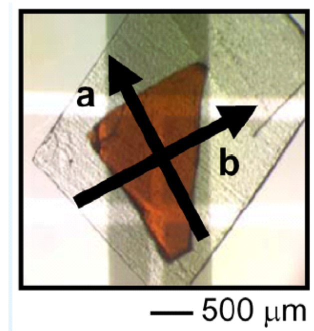
Extended Huckel tight binding calculation for the dispersion of the valence and conduction bands for a representative pentacene polymorph (herringbone structure).

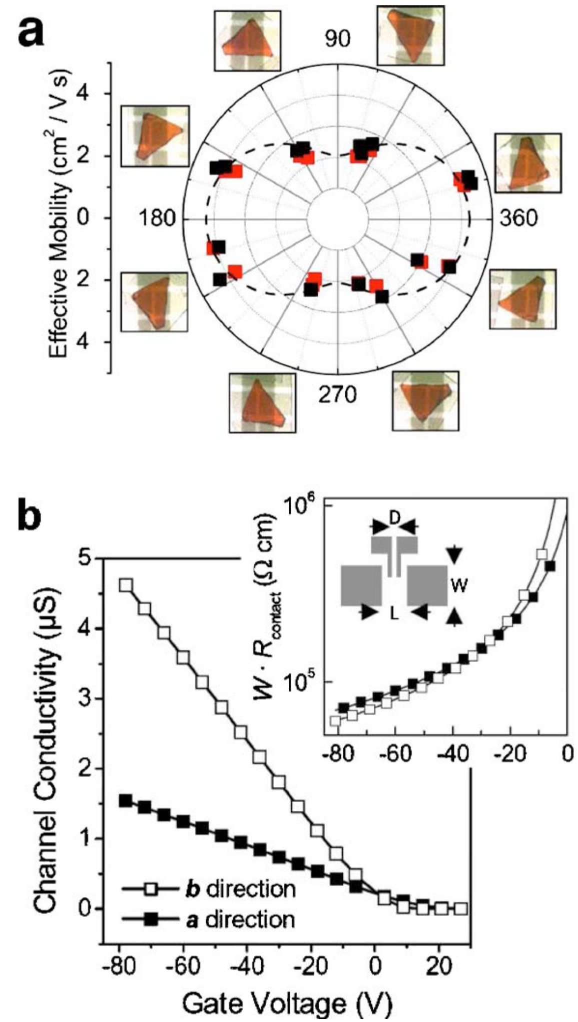
R. C. Haddon, et al., J. Phys. Chem. B, 2002, 106, 8288–8292

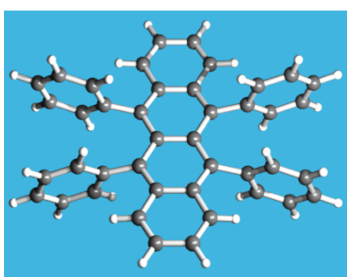
THE COMPLEX STRUCTURE OF ORGANIC CRYSTALS ORIGINATES COMPLEX ELECTRONIC FEATURES (II)

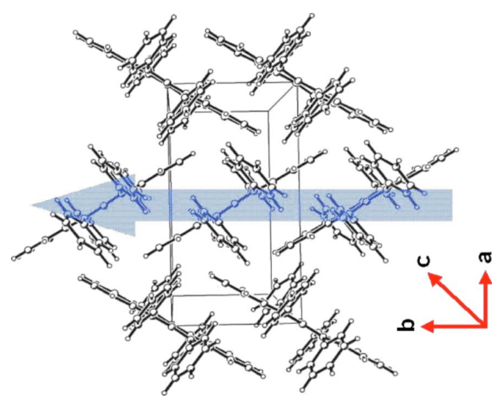
For rubrene the experimentally found transport anisotropy underlines even more complex electronic properties.







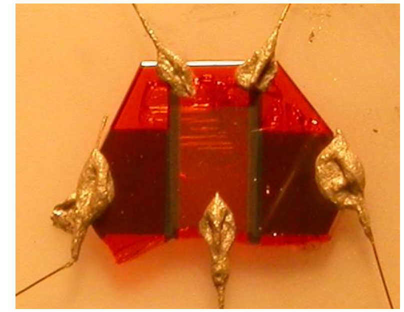


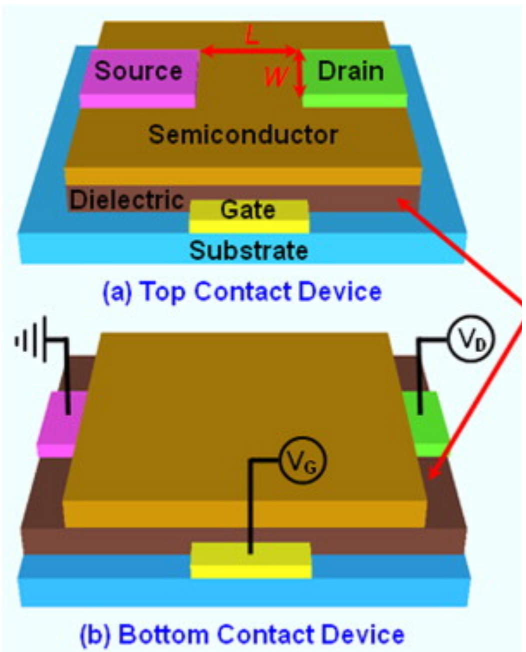


Sundar, V. C. et al., 2004, Science **303, 1644**

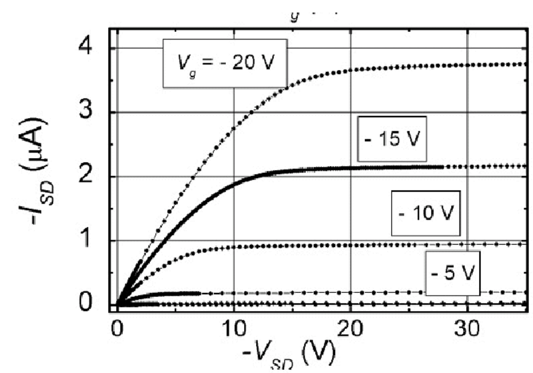
OSSCs TRANSPORT PROPERTIES PROBING: FIELD EFFECT TRANSISTORS (I)

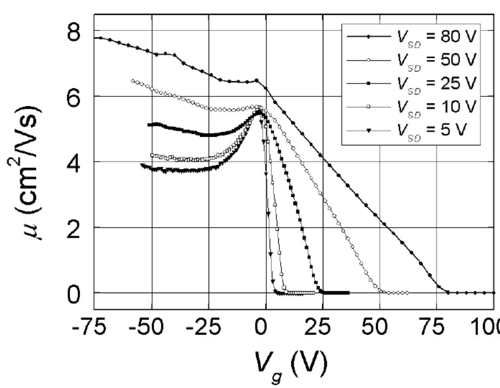
Field Effect Transistors are a common way to evaluate the electronic properties of OSSCs.





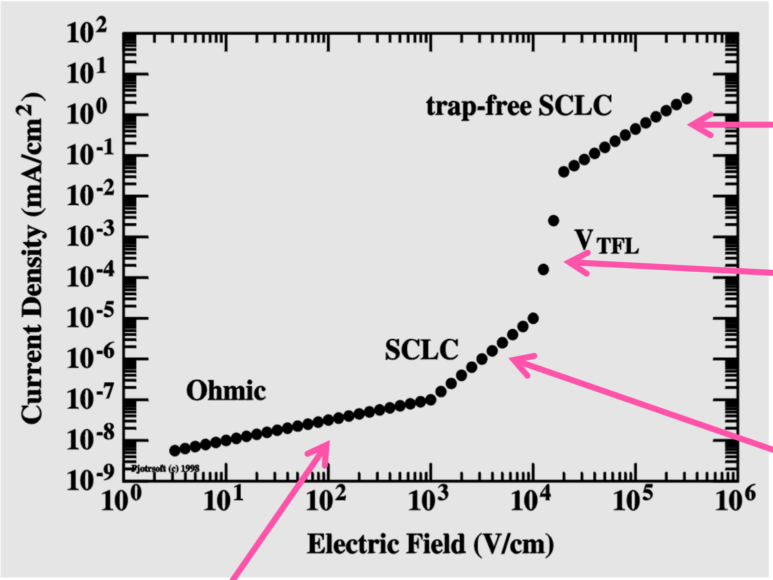
The dielectric has an important role in the device operation, and can enhance/impair its performances, or even change the device behaviour from p-type to n-type.*





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

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.

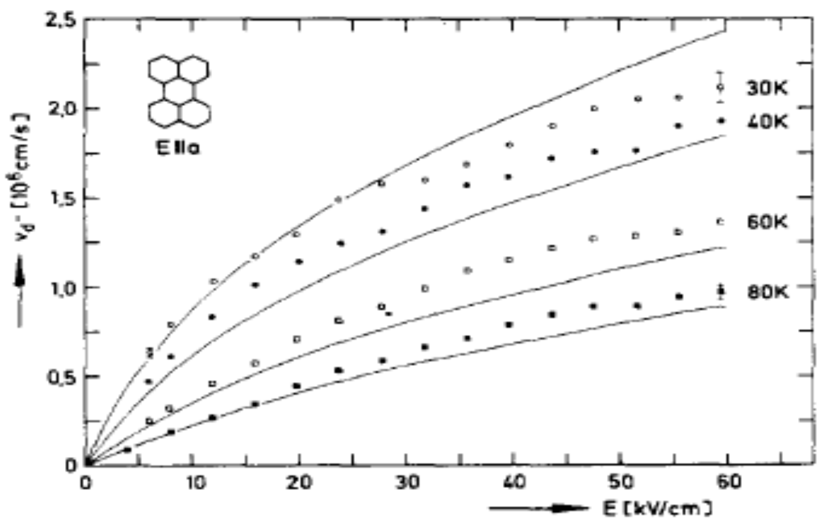
Space charge-limited current (SCLC) regime: the charge injected from the contacts is larger than that present in the material at equilibrium and the I–V characteristics become nonlinear.

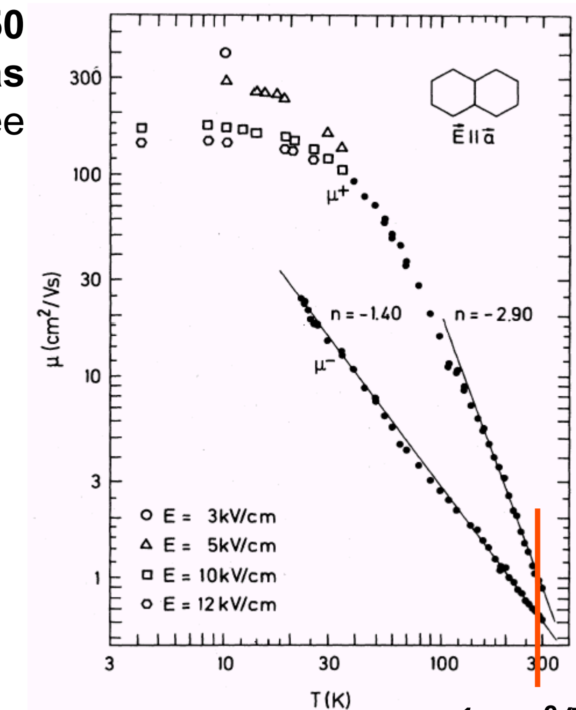
Ohmic regime: the voltage drop across the contact resistance is small compared to that across the bulk crystal (contact resistance is negligible).

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 cm^2/Vs**, with effective masses close to the free electron mass*.





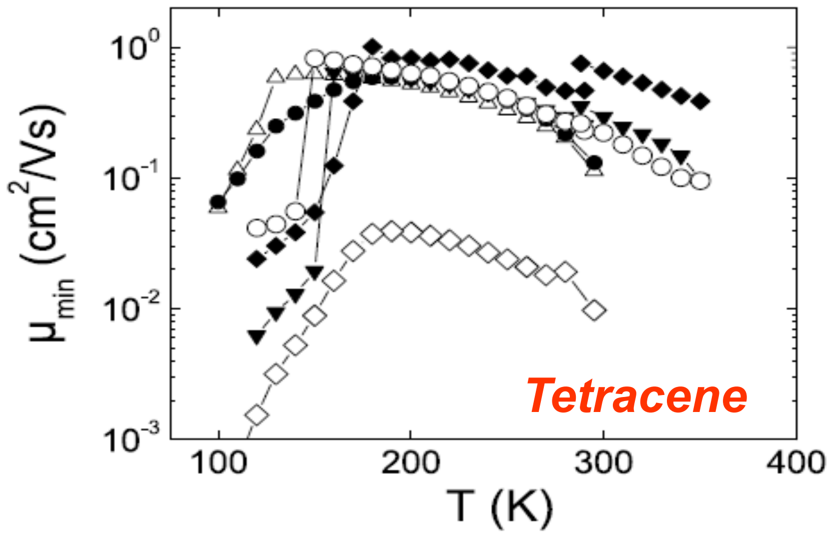
μ ~ 1 cm^2/Vs

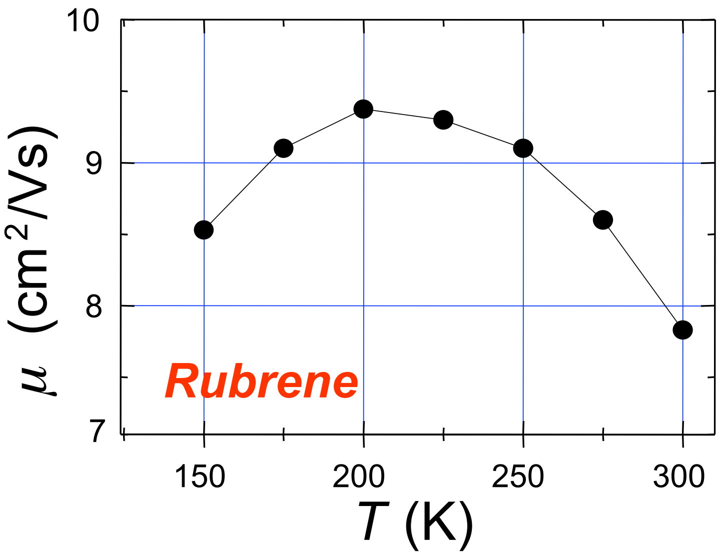
Increasing the T results in increased phonon scattering, decreasing the band transport effectiveness, and (likely) polaron-hopping transport arises. For crystallographic directions with weak π-electronic interactions, the hopping-mediated transport is expected to be important even at low T.

* W. Warta, N. Karl, Phys. Rev. B32 (1985) 1172; N. Karl et al., Synth. Met. 42–43, (1991) 2473

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)**.

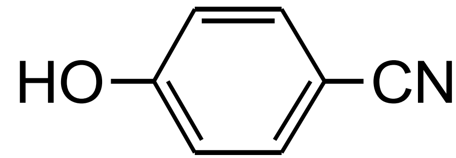
Overall, charge transport in OSSCs is not yet completely understood.

* 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)

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

4HCB is an interesting inherently dipolar molecule.

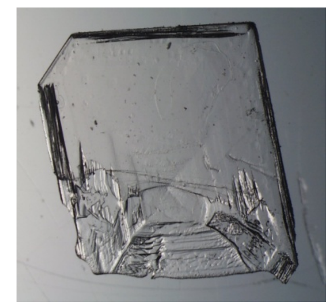


Single, squared crystals of 4-hydroxycyanobenzene (4HCB) are easily grown from solutions.

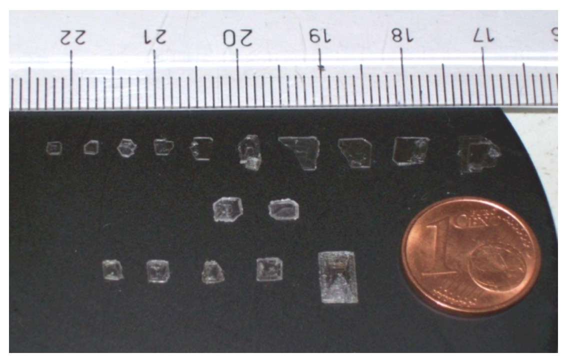
Thickness: from a few hundreds of microns to 1 mm;

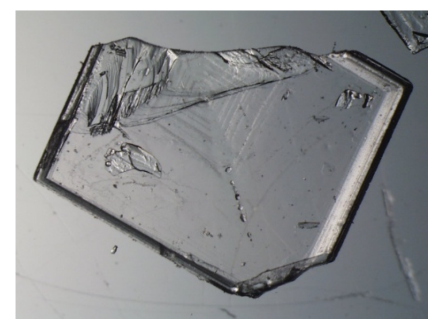
Side: from one to several millimeters.

Tunable dimensions properly modifying the growth conditions.



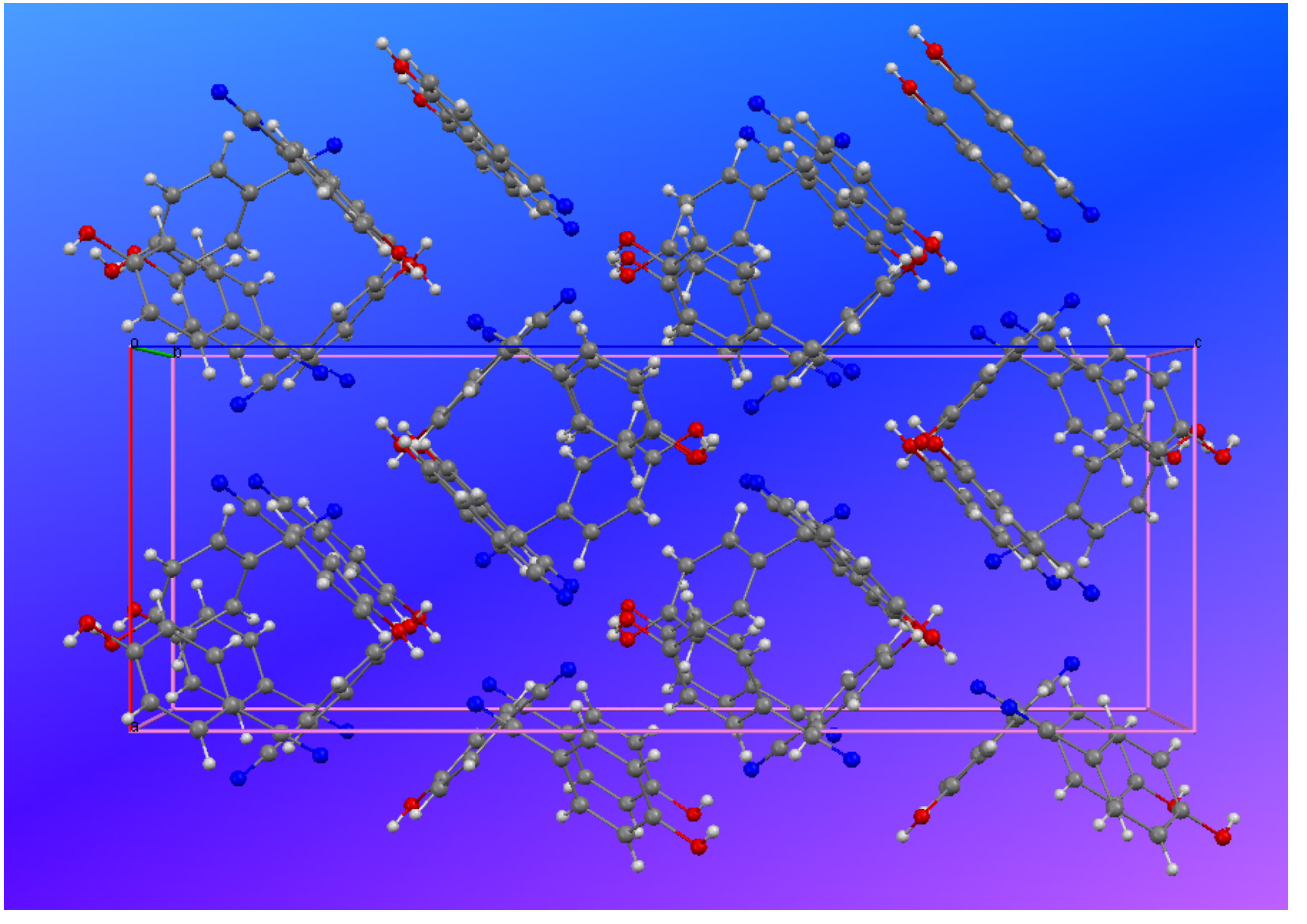
The so-obtained crystals are **free-standing, easily handled and moved and resistant to air and photooxidation.**





LATTICE STRUCTURE OF THE 4HCB SINGLE CRYSTALS (I)

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



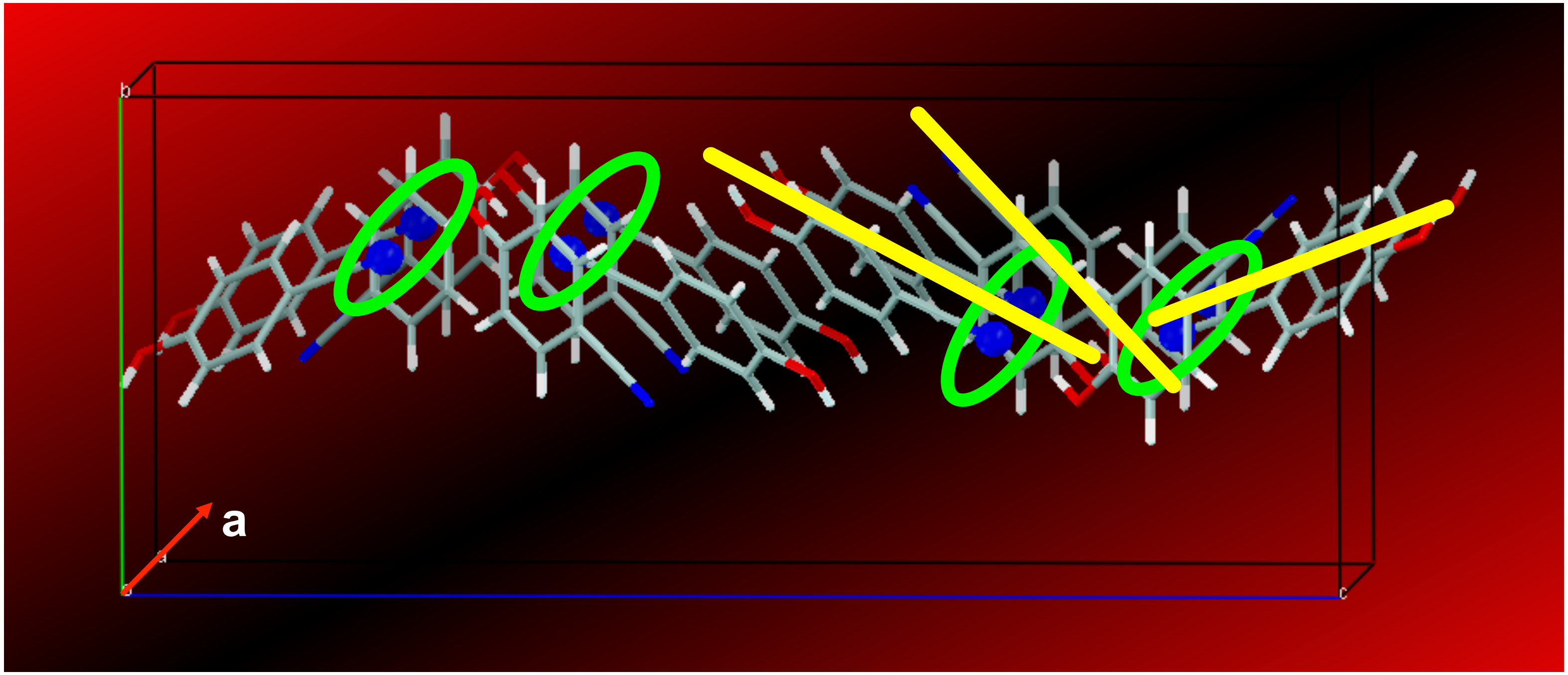
* T. Higashi et al., Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem., 1977, 33, 607

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***.



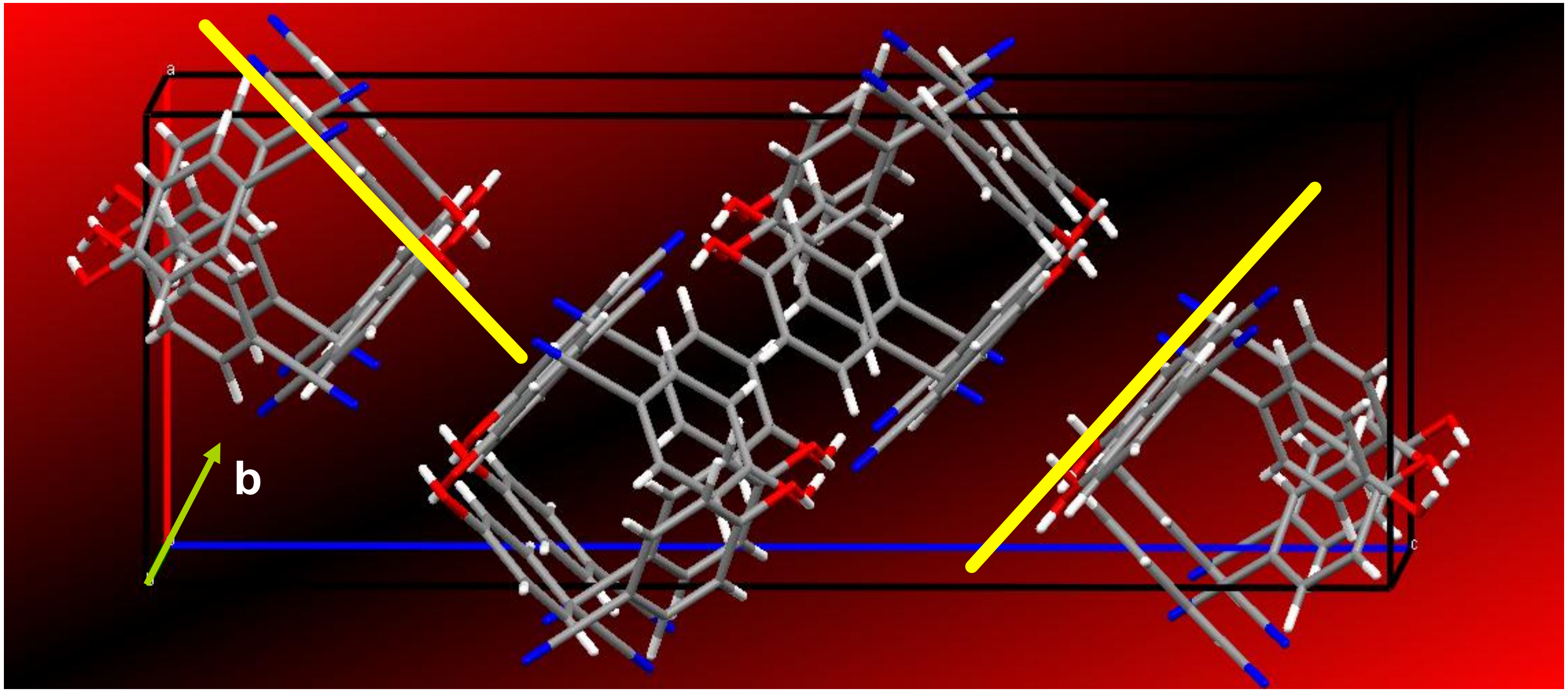
* B. Fraboni et al, Adv. Mater., 2009, 21, 1835

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.



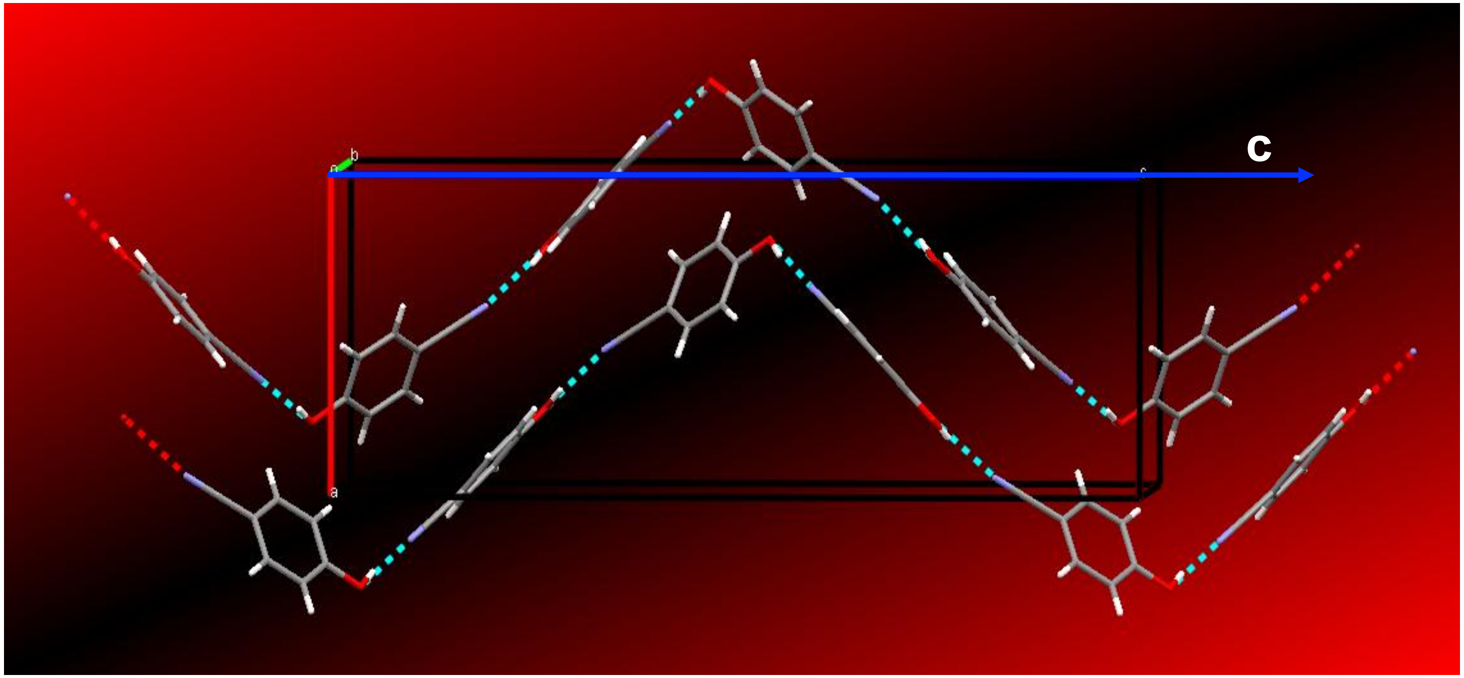
* B. Fraboni et al, Adv. Mater., 2009, 21, 1835

LATTICE STRUCTURE OF THE 4HCB SINGLE CRYSTALS (III)*

Axis *c*: No appreciable overlapping of benzenic rings.

The molecular dipole develops itself along the axis.

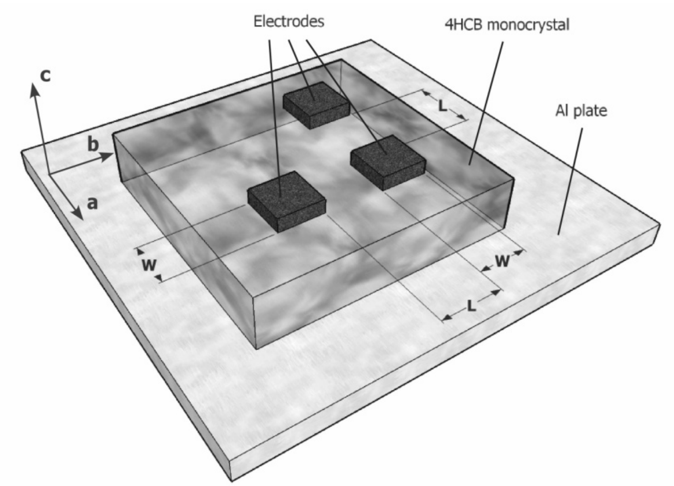
No relevant intrinsic charge transport is expected.



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

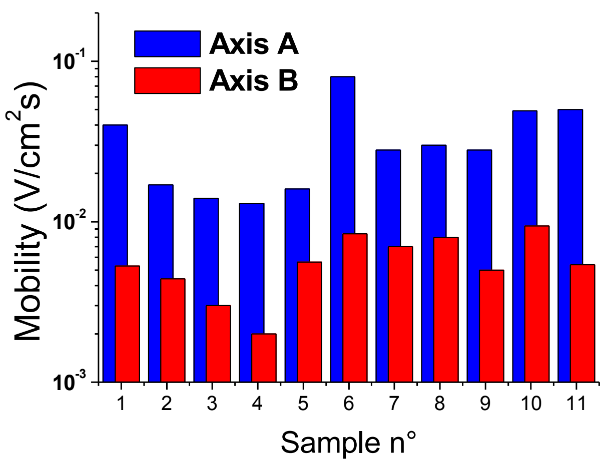
2D ANISOTROPIC FET BEHAVIOUR OF 4HCB CRYSTALS

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).

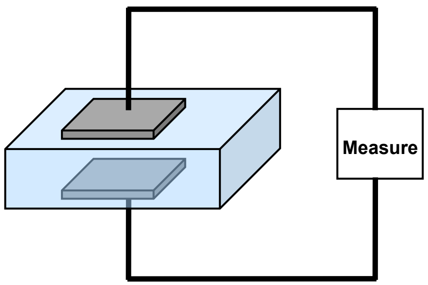


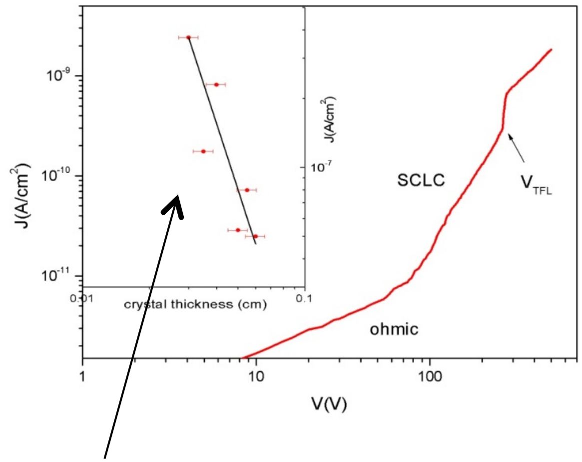
Axis	μ^{FET}_{Max} (cm^2/ Vs)	μ^{FET}_{Ave} (cm^2/ Vs)
a	$8x10^{-2}$	$3x10^{-2}$
b	$9x10^{-3}$	$6x10^{-3}$

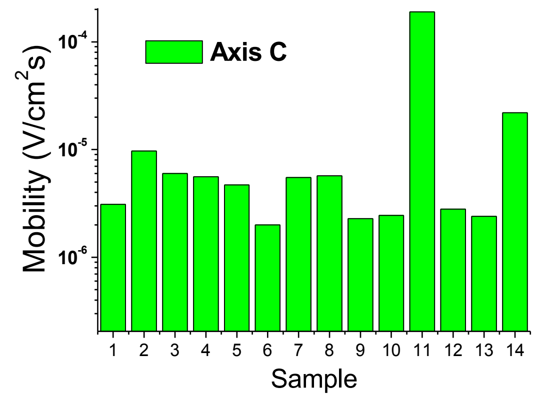
* B. Fraboni et al, Adv. Mater., 2009, 21, 1835

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 $9x10^3$ 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	**$2x10^{-5}$**	**$5x10^{-6}$**

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

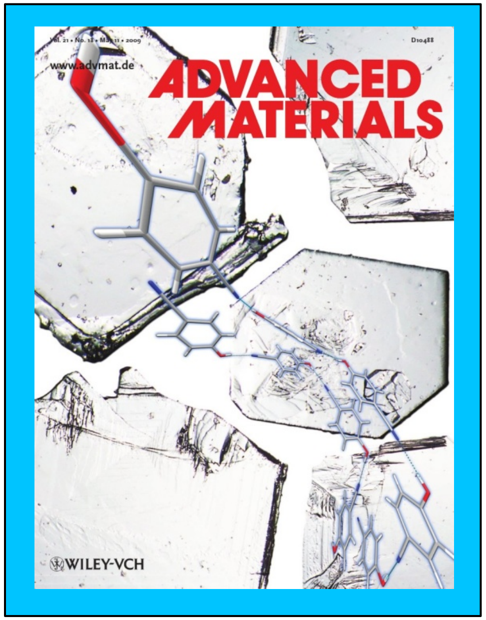
For 4HCB crystals, the three mobilities are anisotropic.

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

SCLC 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} (cm²/ Vs)	μ^{SCLC}_{Ave} (cm²/ Vs)	μ^{FET}_{Max} (cm²/ Vs)	μ^{FET}_{Ave} (cm²/ 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 consistant 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 <u>intrinsic mobility values</u> for solution-grown 4HCB crystals.*

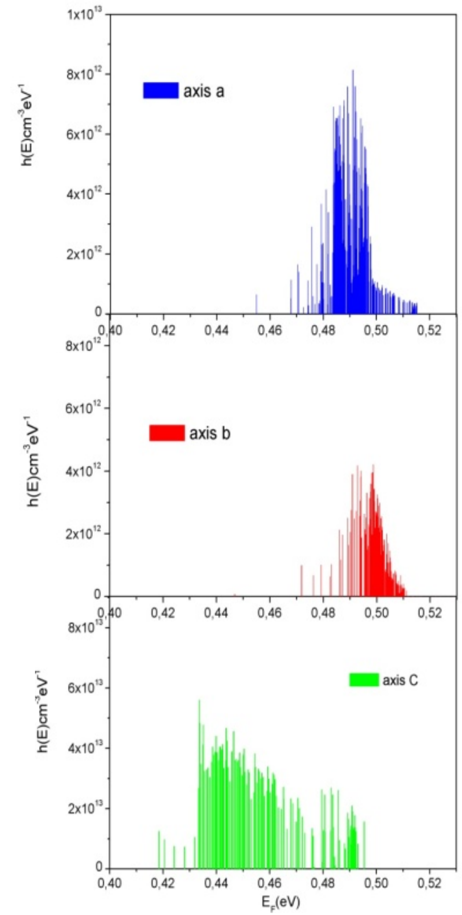
* B. Fraboni et al, Adv. Mater., 2009, 21, 1835

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

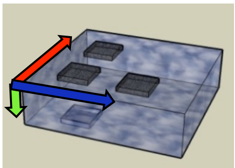
3D anisotropic number of traps.

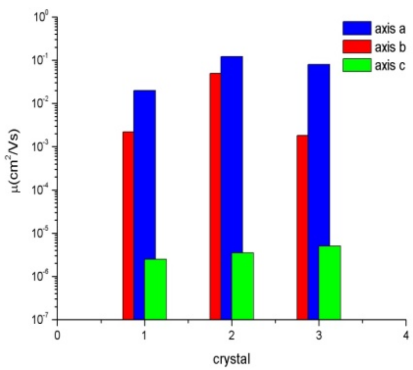
Axis	N_T (cm^{-3})
a	$9x10^{12}$
b	$4x10^{12}$
c	$2x10^{13}$

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



3D anisotropic carrier mobility on the same crystal.





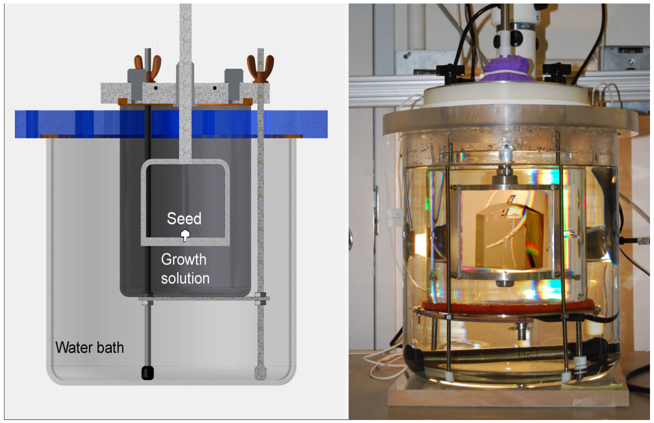
Overall, extremely reliable transport properties in a solution grown SC.

B. Fraboni et al., Org. El., 2008, 9, 974; Org. Electron., 2010, 11, 10

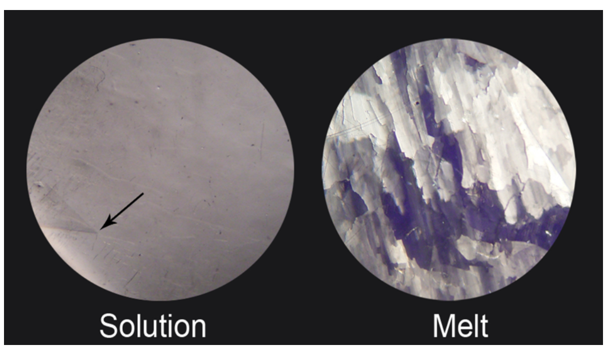
NEXT PRESENTATION SECTION

- Why organic semiconductors, and their general features
- Overview of Organic Semiconducting Single Crystals (OSSCs) growth methods
- Main structural and transport properties of OSSCs
- Organic semiconductors as ionizing radiations sensors
- Direct inkjet printing of OSSCs, and using printed OSSCs as ionizing radiations detectors
- Possible uses of printed OSSCs as ionizing radiation detectors in the IoT
- Conclusions

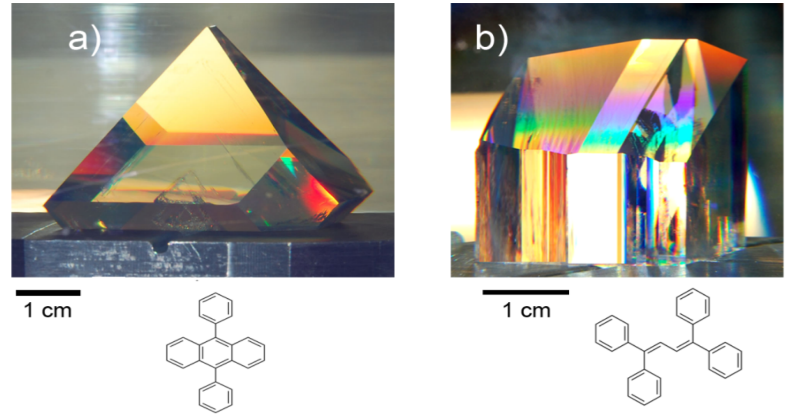
HIGH CRYSTAL QUALITY WITH SOLUTION GROWTH

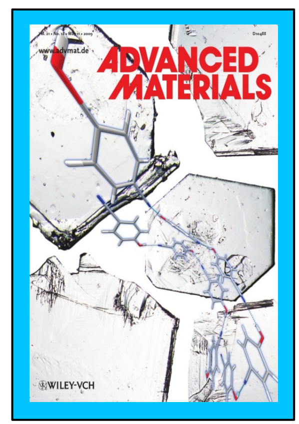


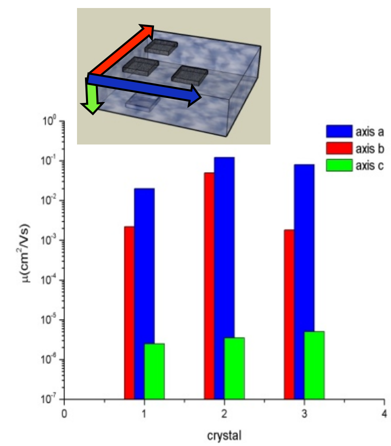
Solution growth can be very effective in delivering remarkably large, high quality organic single crystals.



N. Zaitseva et al., Nucl. Instr. Meth. A 2015 , 789 , 8



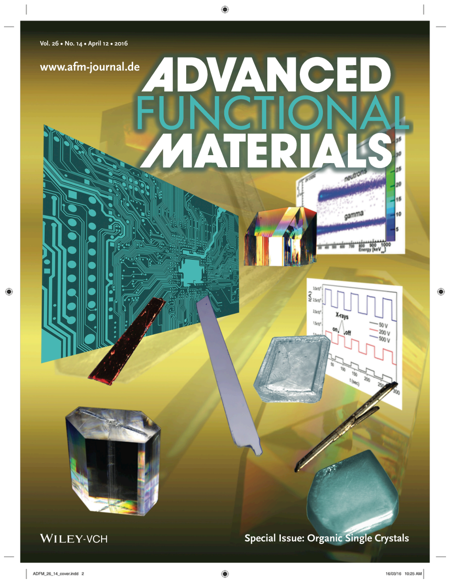


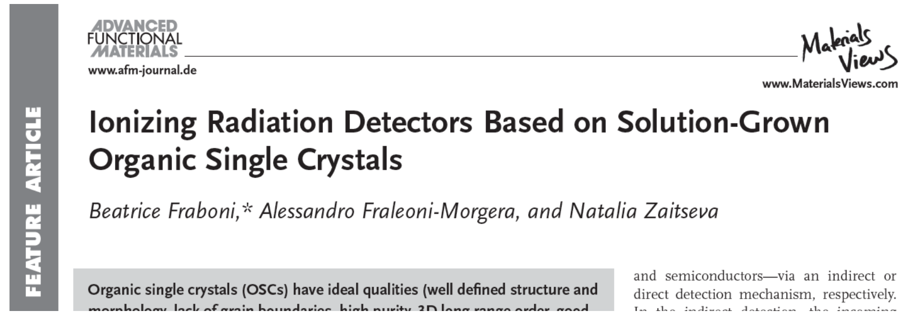


3D anisotropic carrier mobility reproducibly demonstrated.

B. Fraboni et al., Adv. Mater. 2009, 21, 1835; Org. El., 2008, 9, 974; Org. Electron., 2010, 11, 10

SOLUTION GROWN ORGANIC SINGLE CRYSTALS AS IONIZING RADIATIONS DETECTORS




FEATURE ARTICLE

ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

MaterialsViews
www.MaterialsViews.com

Ionizing Radiation Detectors Based on Solution-Grown Organic Single Crystals

Beatrice Fraboni, Alessandro Fraleoni-Morgera, and Natalia Zaitseva*

Organic single crystals (OSCs) have ideal qualities (well defined structure and

and semiconductors—via an indirect or direct detection mechanism, respectively.

Organic single crystals can deliver remarkable performances as ionizing radiations detectors.

B. Fraboni et al., Adv. Funct. Mater., 2016, 26, 2276

Two main detection mechanisms

Indirect detection (Scintillation)
conversion of the ionizing radiation into photons, that are in turn detected by a photodiode

Direct detection
direct conversion of the ionizing radiation into a readable electrical signal

ORGANIC SEMICONDUCTORS IN IONIZING RADIATIONS DETECTION

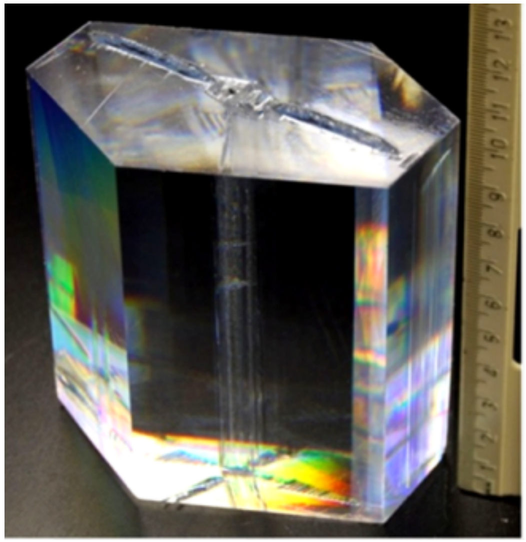
Currently used approaches to ionizing radiation detection involving organic semiconductors:

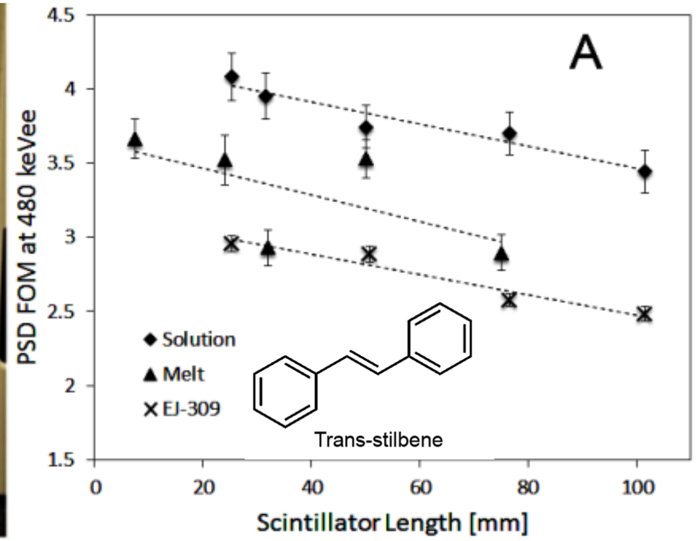
- **Indirect detection**: the ionizing radiation is converted into visible light (the device is called “scintillator”). This is by far most common approach, and usually the organic semiconductors are used in the form of single or polycrystals*, and are coupled to inorganic photodiodes for the photon 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)

SOLUTION GROWN ORGANIC SINGLE CRYSTALS AS SCINTILLATORS



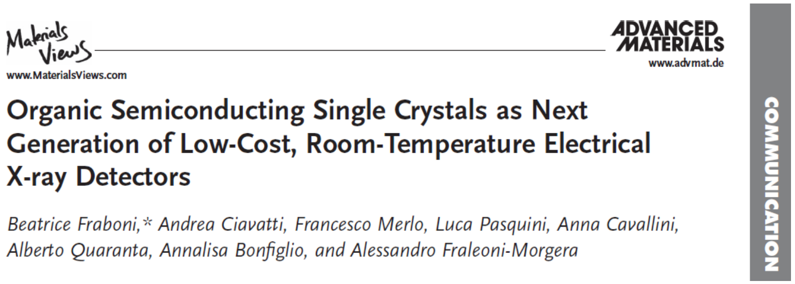


As scintillators, solution grown single crystals can deliver 20–50% higher light output (LO) and better pulse shape discrimination (PSD) in comparison with the same size crystals grown by Bridgman techniques*.

For further information on organic crystals as scintillators, one can see B. Fraboni et al., Adv. Funct. Mater. 2016, 2016, 26, 2276, and refs therein.

*N. Zaitseva et al., Nucl. Instr. Meth. A 2015 , 789 , 8

FREE-STANDING OSSCs AS DIRECT X-RAYS DETECTORS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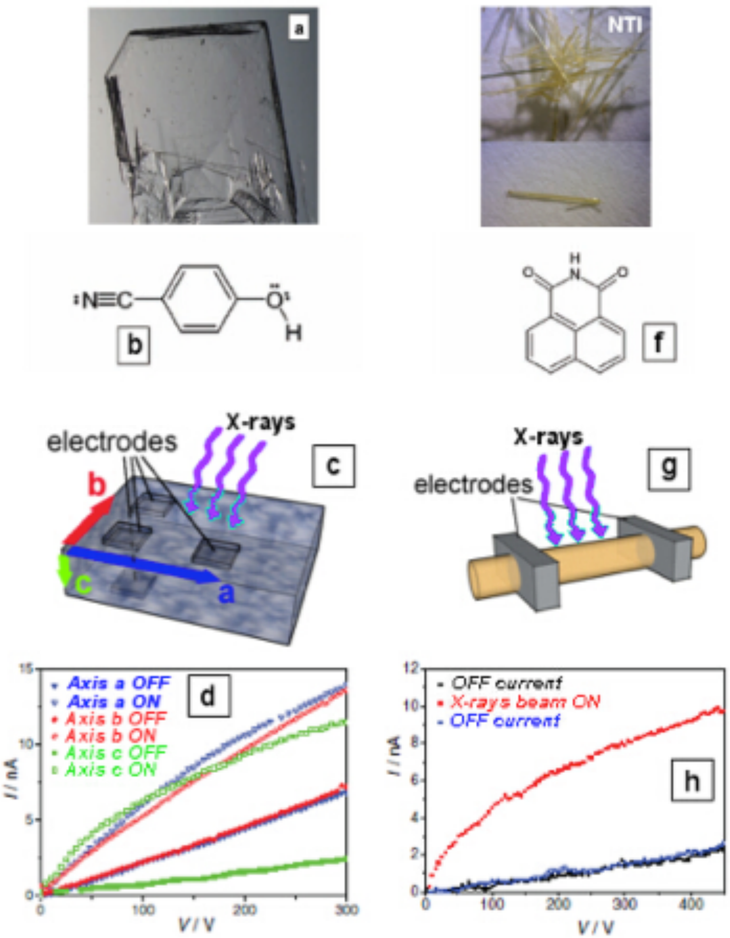
COMMUNICATION

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*

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

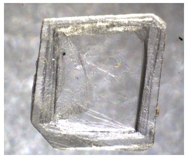
- operable at **ambient pressure and temperature, and under ambient light**;
- **anisotropic response** (when the crystal characteristics allow to probe this property);
- this property is **common to different crystals, which present different responses**, suggesting that it is possible to tune the detector's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



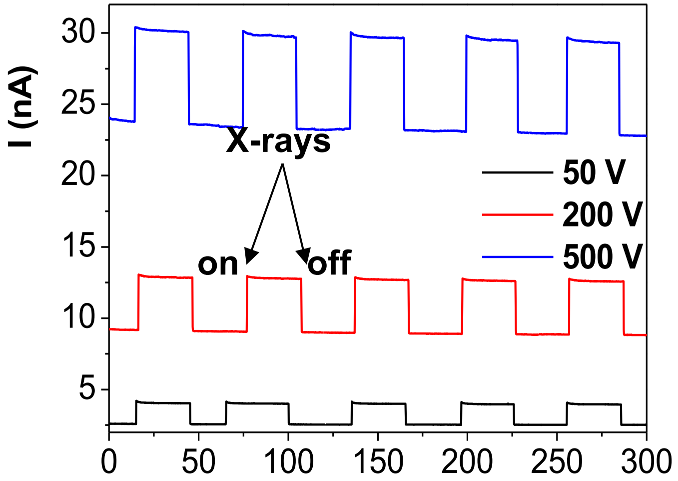
* B. Fraboni et al., Adv. Mater., 2012, 24, 2289

THE I-FLEXIS FP7-ICT project allowed to get insights into the potential of OSSCs as direct ionizing radiation detectors

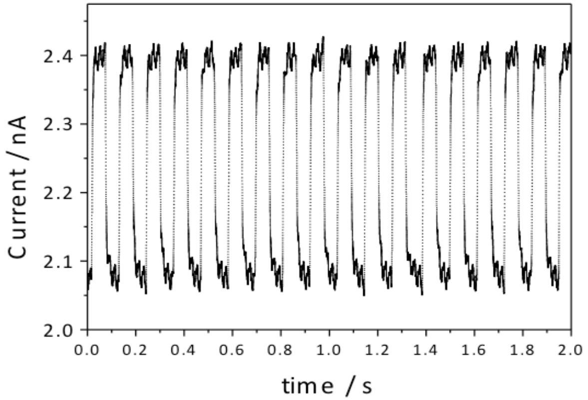
FAST SWITCHING TIMES...

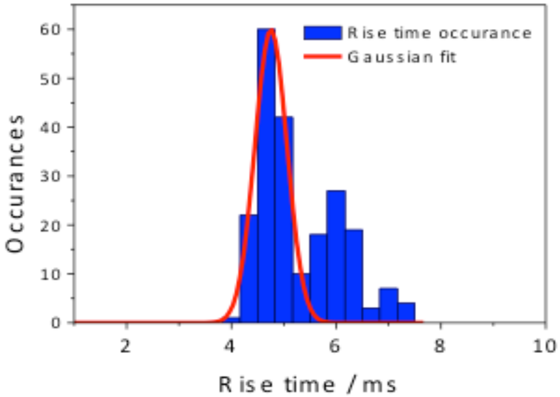


In 4HCB crystals:



- **Remarkably reproducible response, with apparently negligible drift**, especially at low biases.
- **Fast response**.
- **No apparent hysteresis effect.**

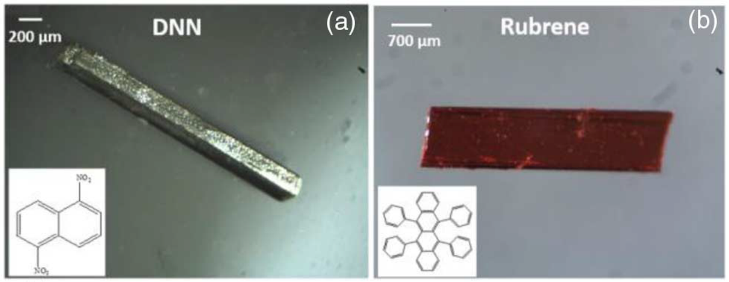




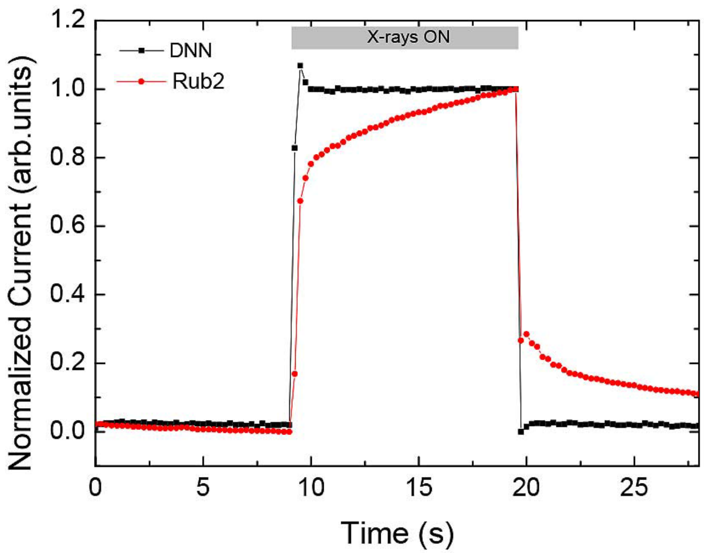
Actual response time: about 5 ms*

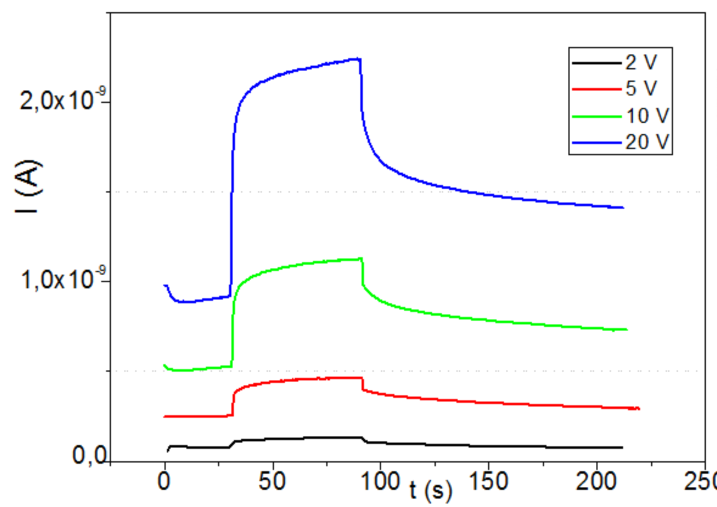
* A. Ciavatti et al., Adv. Mater., 2015, 24, 2289

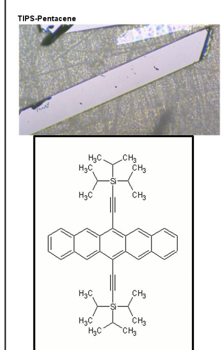
... BUT NOT FOR EACH AND ANY OSSC!



Apparently, a much higher carrier mobility is not the key parameter for effective OSSCs-based ionizing radiation detection.
In fact, rubrene has a rather slow response dynamics, as well as TIPS-Pentacene, than other much less-performing crystals.

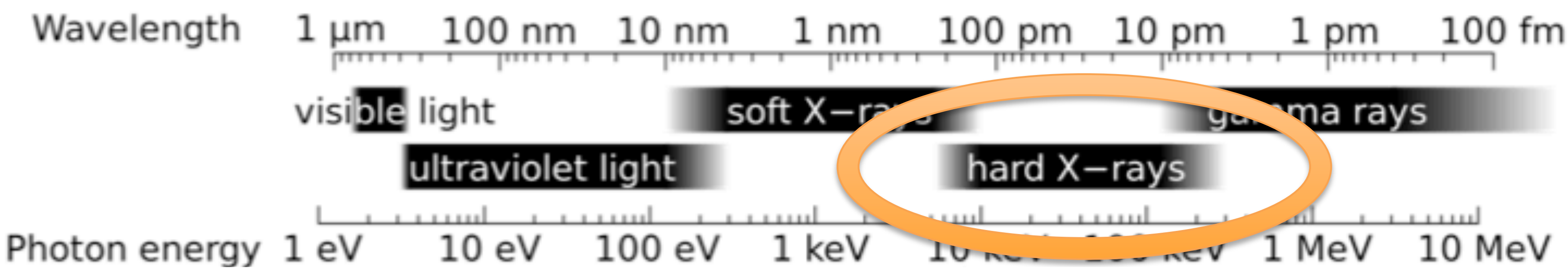






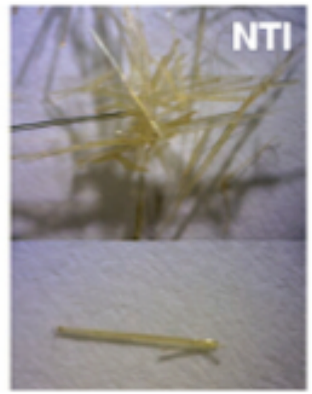
L. Basiricò et al., 15 IEEE Trans. Nucl. Sci. 2015, 62, 1791

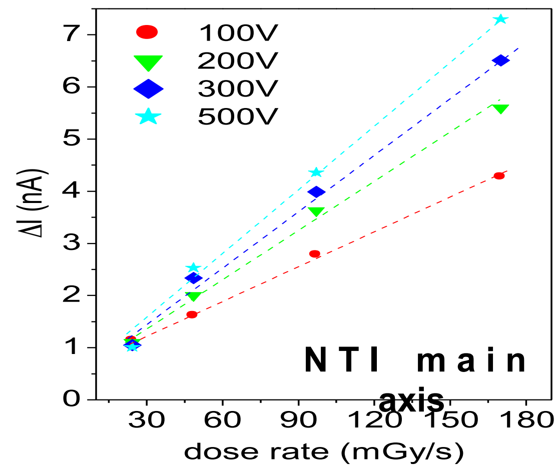
GOOD DEVICE RESPONSE AT X-RAYS ENERGIES RELEVANT FOR SEVERAL APPLICATIONS

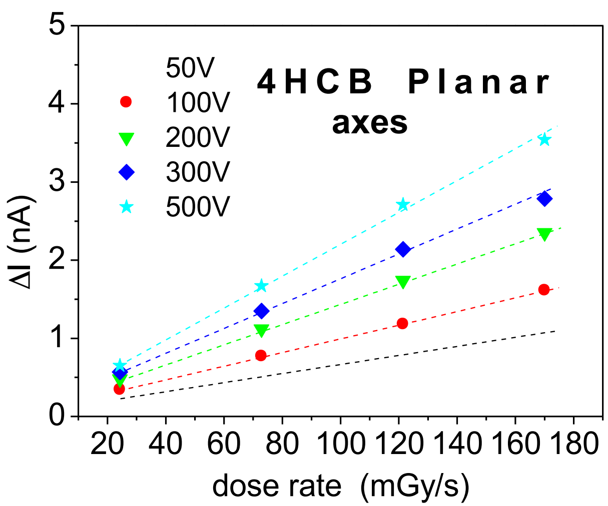


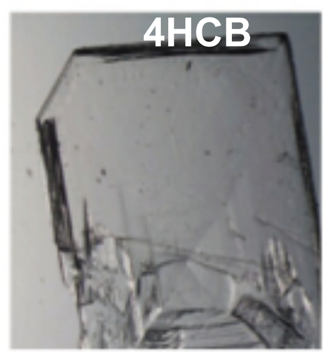
RESPONSE LINEARITY

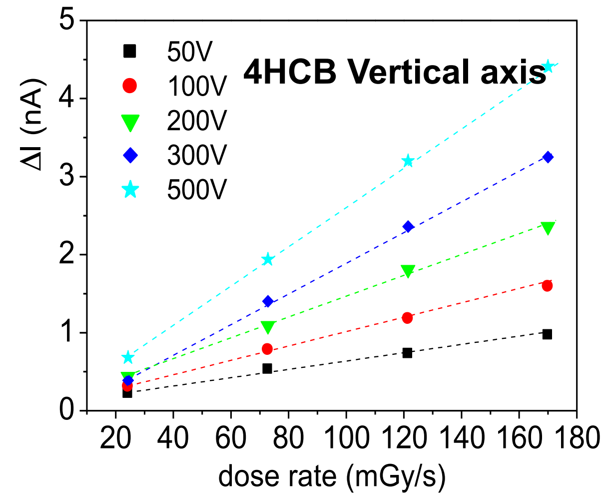
Good response linearity over a rather wide dose rate range, at any of the tested biases, also considering (when appropriate) different crystallographic directions. *





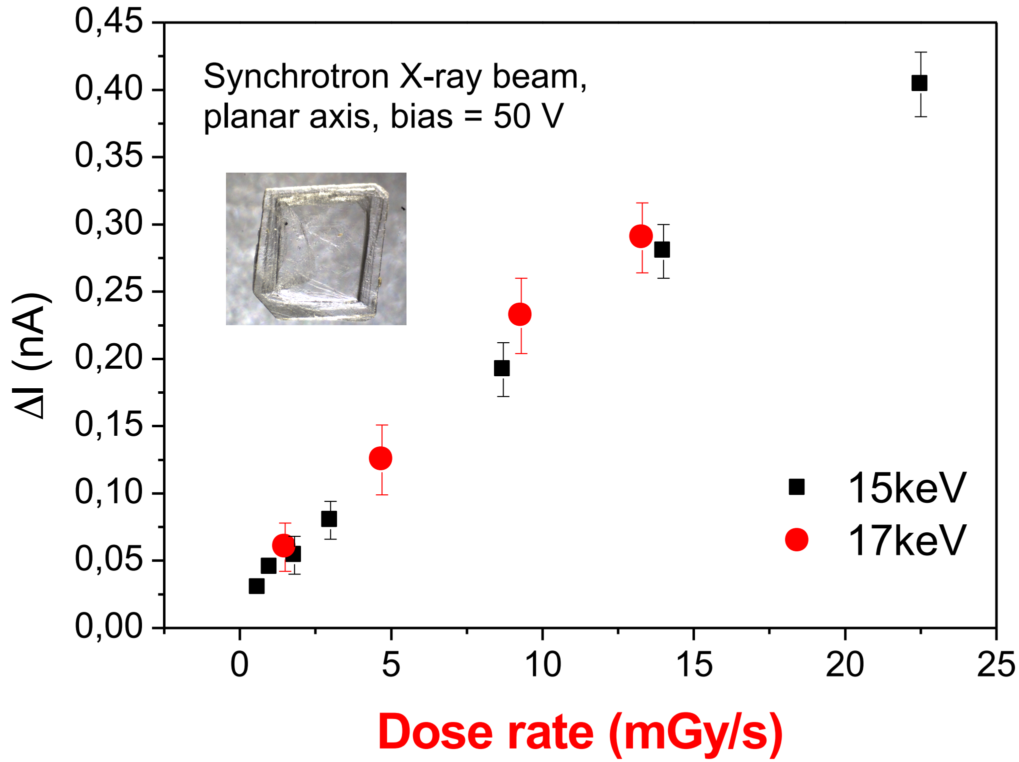






* B. Fraboni et al., Adv. Mater., 2012, 24, 2289

SENSITIVITY IN LINE WITH STANDARD DETECTORS



Sensitivity

$S = (I_{ON}-I_{OFF})/\text{Dose rate}$

@ 15-17 KEV

S = 20 nC/Gy
(for unoptimized devices)

Typical inorganic dosimeter sensitivities:

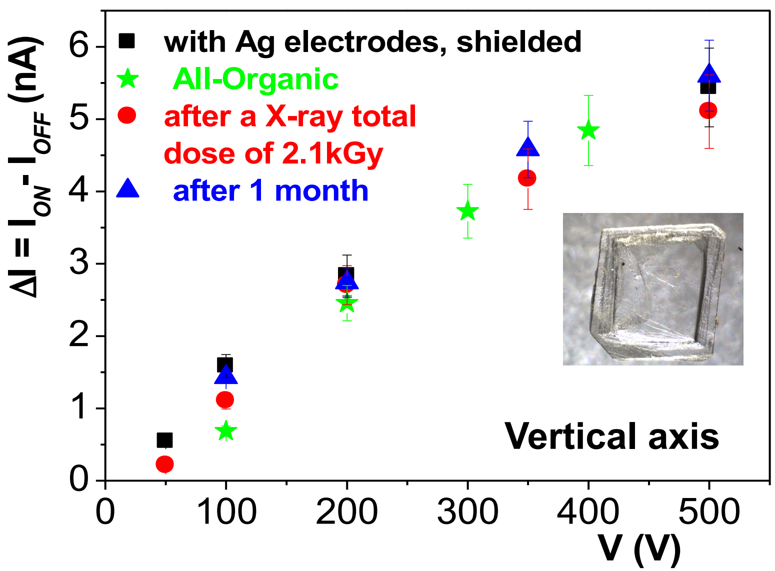
SiC = 100 nC/Gy
Diamond = 400 nC/Gy

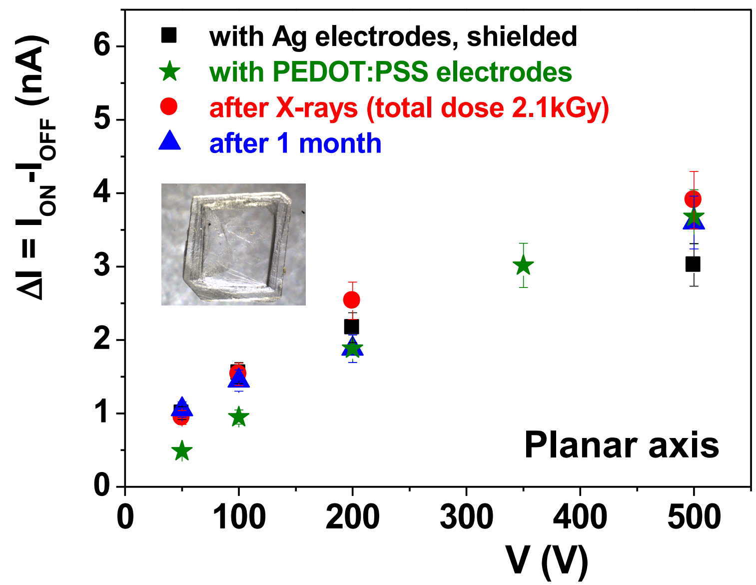
Satisfactory sensitivity (in unoptimized devices) at application-relevant X-rays energies. For more optimized devices sensitivities as high as 120 nC/Gy has been recorded.

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

ROBUSTNESS UPON AGING AND HIGH DOSES (I)

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





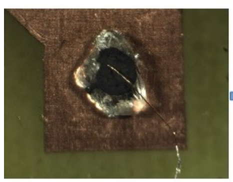
Devices were exposed to a total dose of 2.1 KGy, and then measured delivering the same response found for the normally tested detectors. After that, they were put aside for one month, then they were measured again in the same conditions (35 KeV), delivering the same performances found in the first measurements.

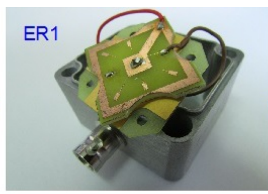
* B. Fraboni et al., Adv. Mater., 2012, 24, 2289

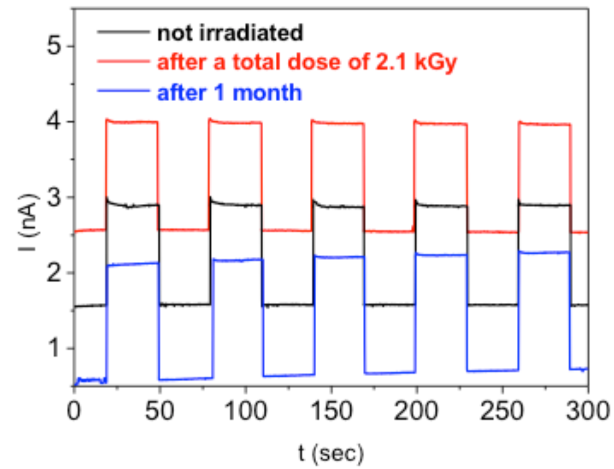
ROBUSTNESS UPON AGING AND HIGH DOSES (II)

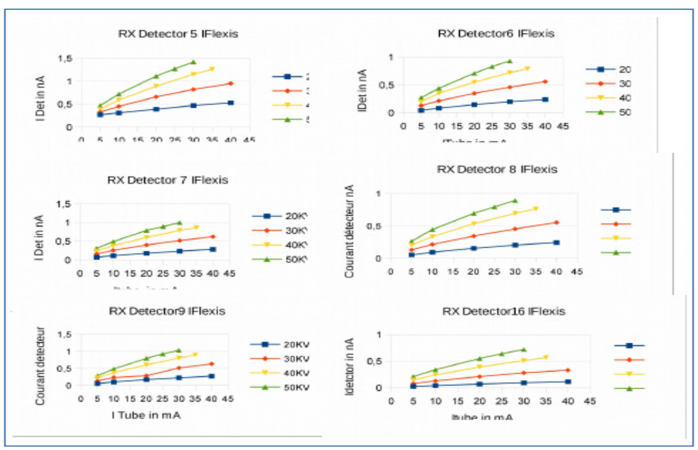
Overall switching behaviour almost independent form exposure of the device to high doses.

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





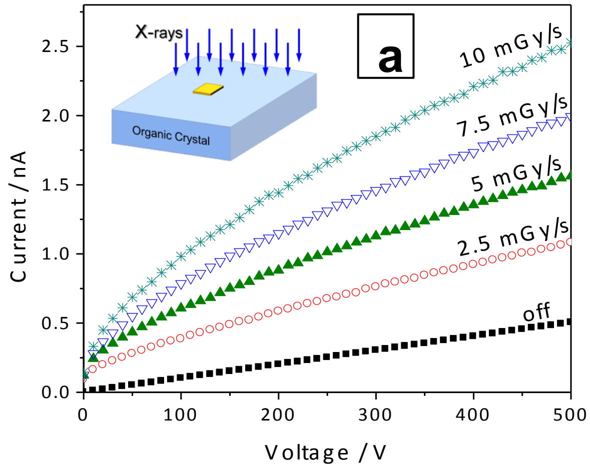


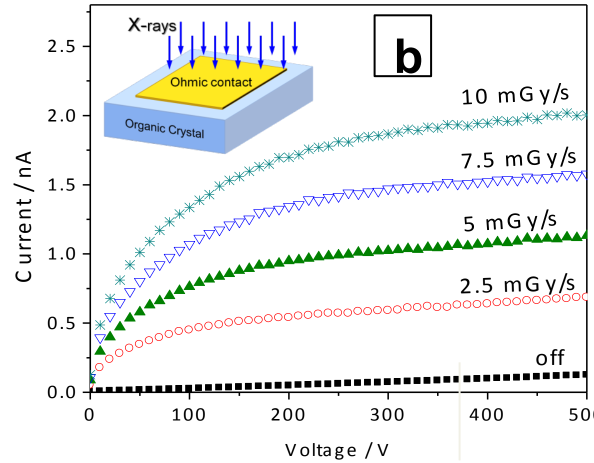


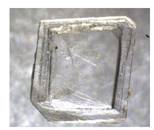
First tests with industrial-like methods have been already carried out, giving promising results in terms of reproducibility, linearity, robustness (collaboration with EURORAD SA).

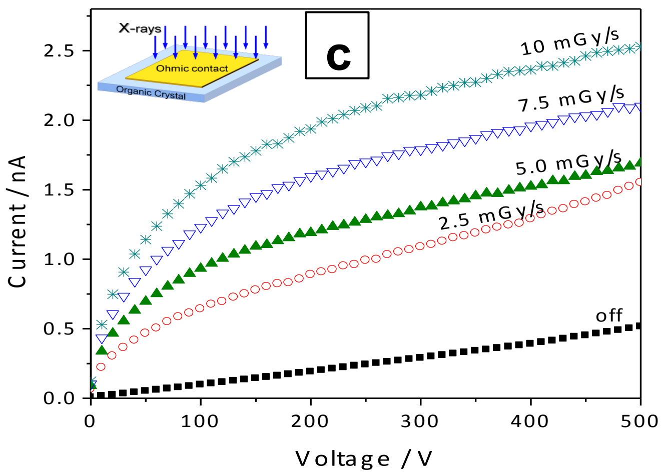
* B. Fraboni et al., Adv. Mater., 2012, 24, 2289

THE OSSCS RESPONSE IS INFLUENCED BY THE CRYSTAL-ELECTRODE INTERFACE AREA





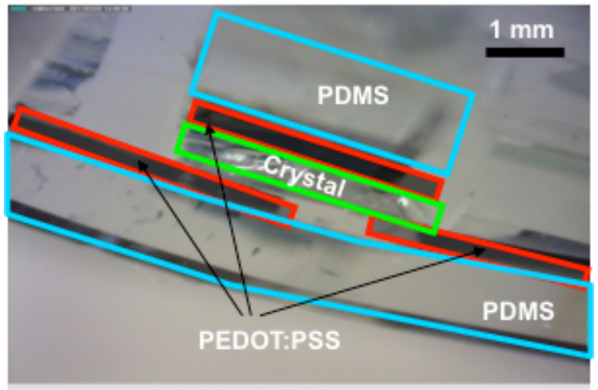


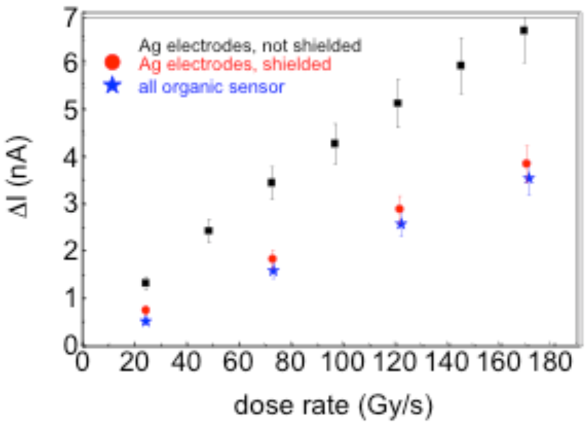


With large crystal-electrode interface area, even very thin crystals can saturate the signal.
This paves the way for bendable detectors, as OSSCs are flexible for thicknesses lower than about 40 μm.

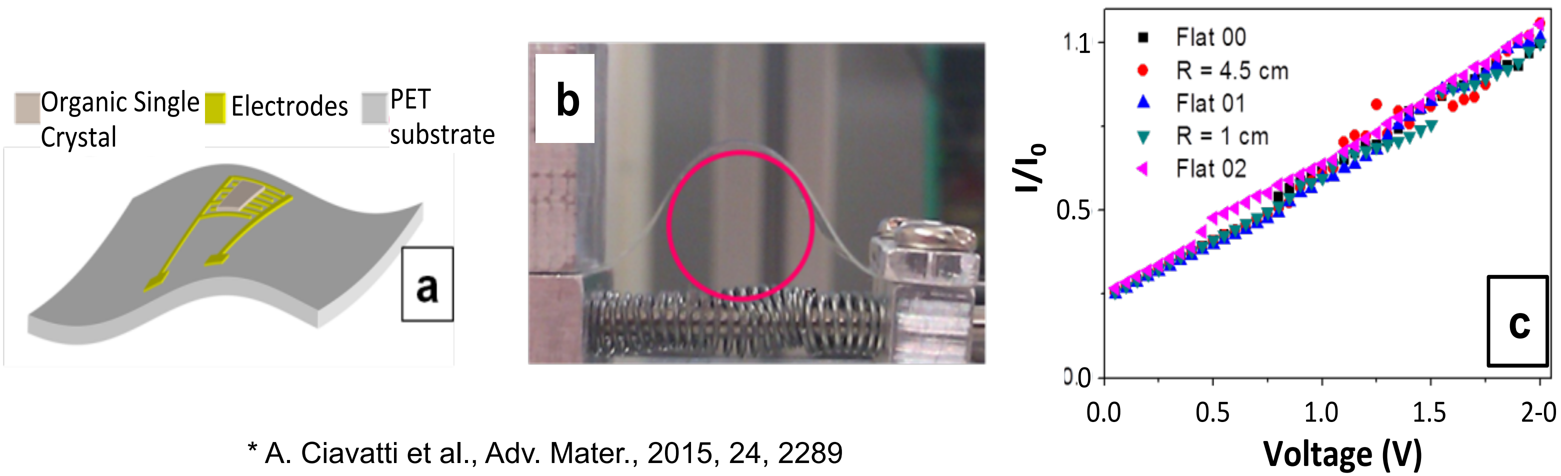
* A. Ciavatti et al., Adv. Mater., 2015, 24, 2289

ALL-ORGANIC, BENDABLE DETECTORS





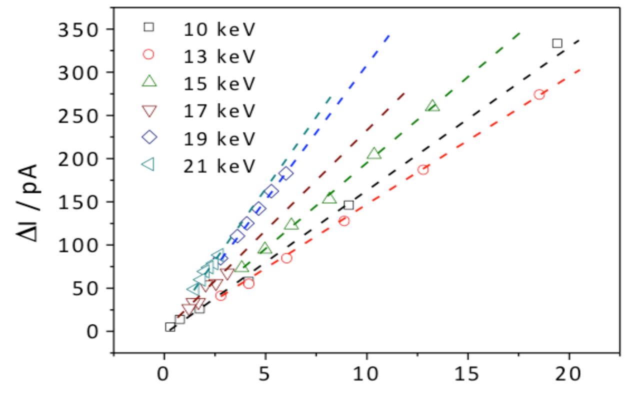
Additional advantage: this device is optically transparent, allowing novel biomedical applications (to be addressed).

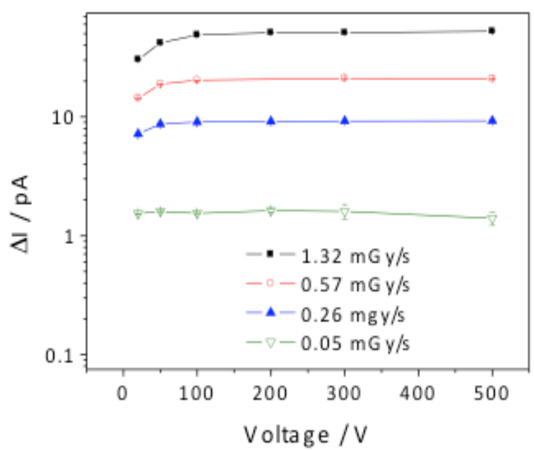


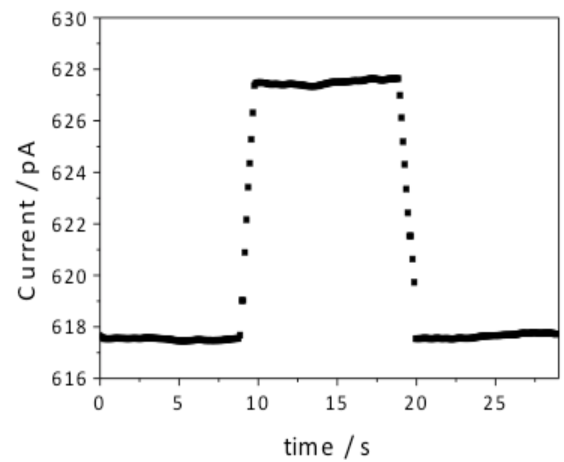
* A. Ciavatti et al., Adv. Mater., 2015, 24, 2289

ENERGY SENSITIVITY AND VERY LOW MINIMAL DETECTABLE DOSE

OSSCs can discriminate photon energies, keeping a linear response*





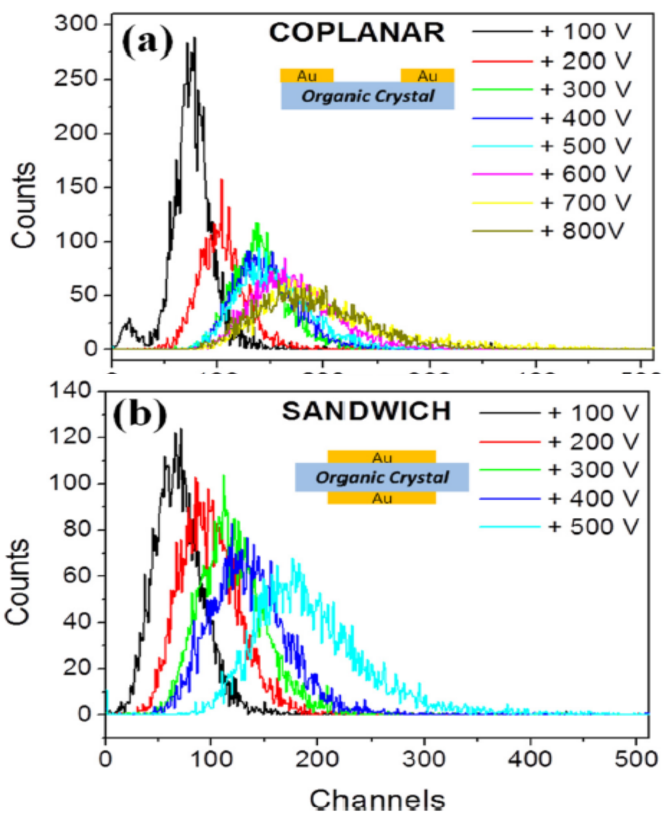


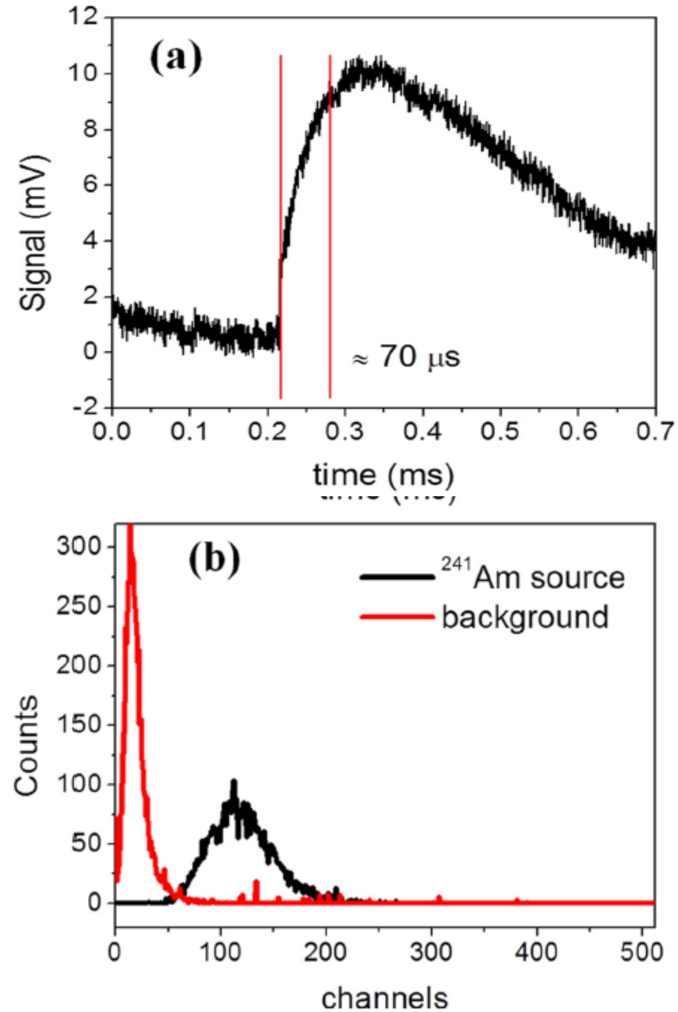
a) photoresponse of a 4HCB-based devices exposed to different doses of a 10 KeV synchrotron light beam. b) detail of a single detection event occurring with the detector of Fig. 2a at the dose rate of 0.05 mG/s, evidencing the high signal-to-noise ratio of such devices even at these low dose rates. *

* A. Ciavatti et al., Adv. Mater., 2015, 24, 2289

ABILITY TO DETECT ALSO ALPHA PARTICLES

OSSCs can also detect alpha particles, even though yet unoptimized devices still operate at a minimum bias of about 100 V.





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, light detectors**
- **Possibility of realizing large area (> 1 m^2) detectors**
- **Possibility of high throughput**
- **Extreme versatility in terms of usable materials**, hence of the selected ionizing radiation energy and type

Up to now organic semiconductors have been perceived as inherently unstable and easily degradable upon ionizing radiation exposure.

However, OSSCs are very radiation-hard, and long-lasting (several months) in terms of operations.

NEXT PRESENTATION SECTION

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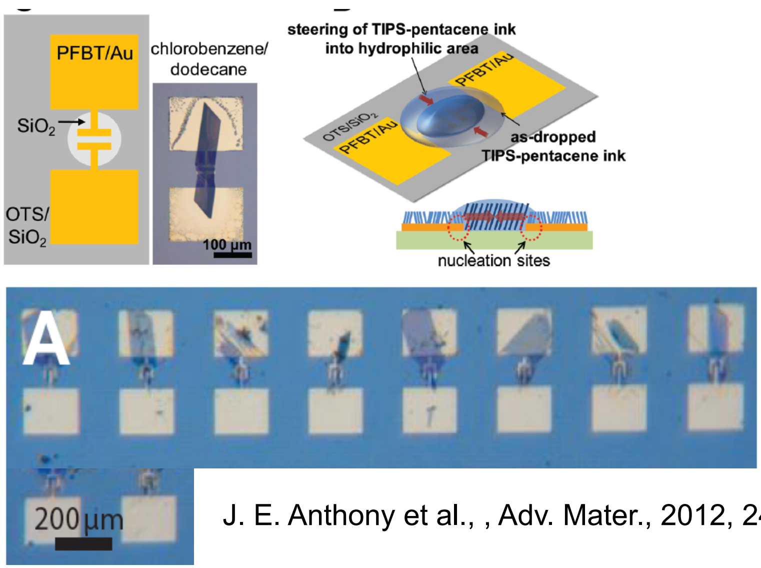
INKJET PRINTED OSSCs-BASED X-RAYS DETECTORS?

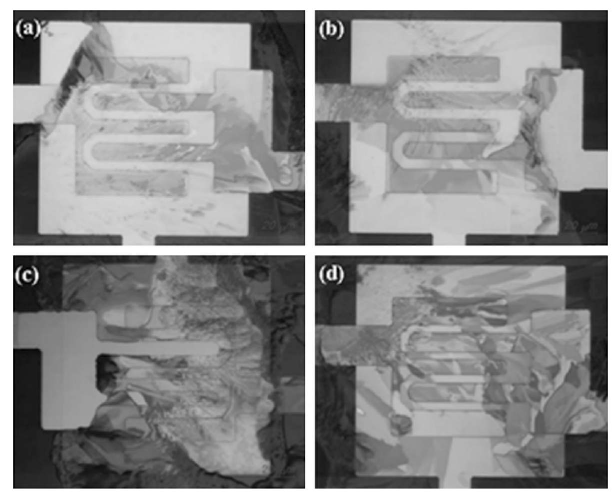
Is it possible to directly inkjet print a solution from which OSSCs can grow, directly on the substrate?

Yes, it is, but:

- usually the “printed” crystals are very tiny (a few hundreds microns size at maximum);
- the crystal growth from solution is extremely sensitive to surface inhomogeneities, which act as nucleation points, and promote disordered polycrystalline growth.



J. E. Anthony et al., , Adv. Mater., 2012, 24, 497

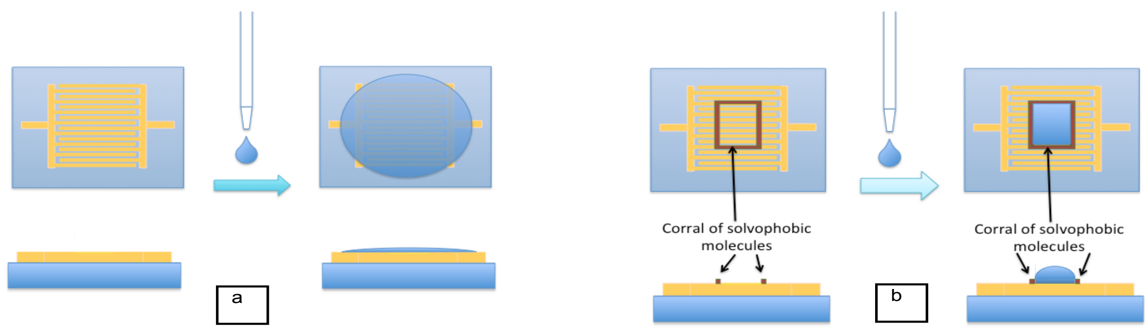


S. H. Lee et al., , Org. Electron. 9 (2008) 721

INKJET PRINTING OF OSSCs ONTO PATTERNED ELECTRODES (I)

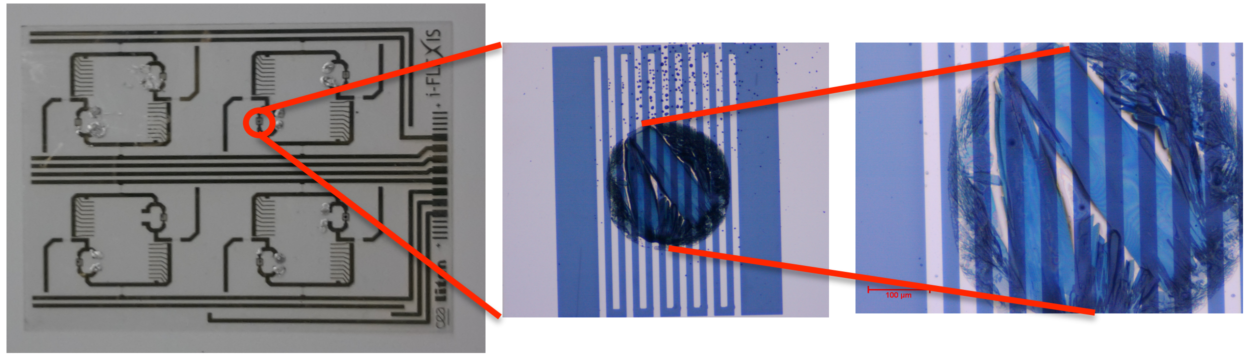
<u>Large printed crystals even on strongly heterogeneous surfaces like interdigitated electrodes</u> thanks to appropriate surface modification

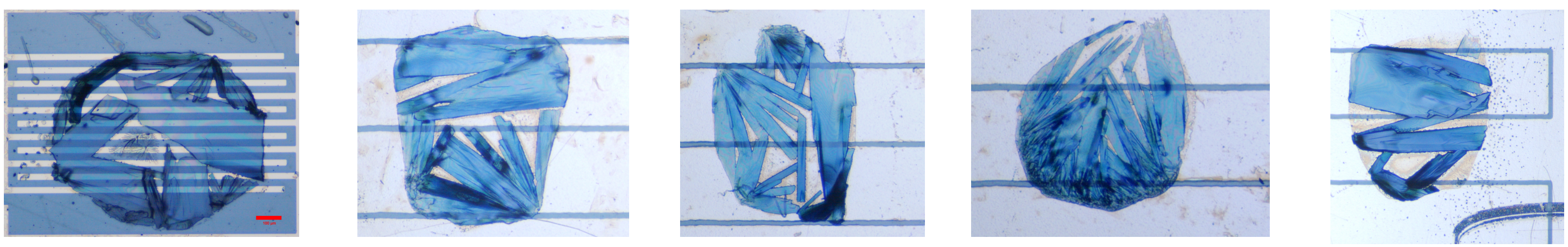
UNITS developed a recently patented surface modification technique able to induce large crystals formation even on strongly heterogeneous surfaces.



DIRECT INKJET PRINTING OF OSSCs ONTO INTERDIGITATED ELECTRODES

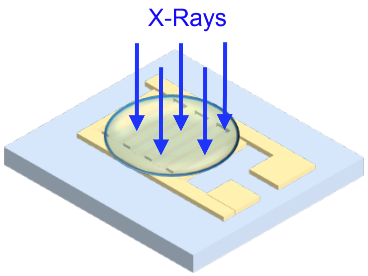
Interdigitated Au electrodes on PEN (matrix fabricated by CEA-LETI in the frame of i-FLEXIS)

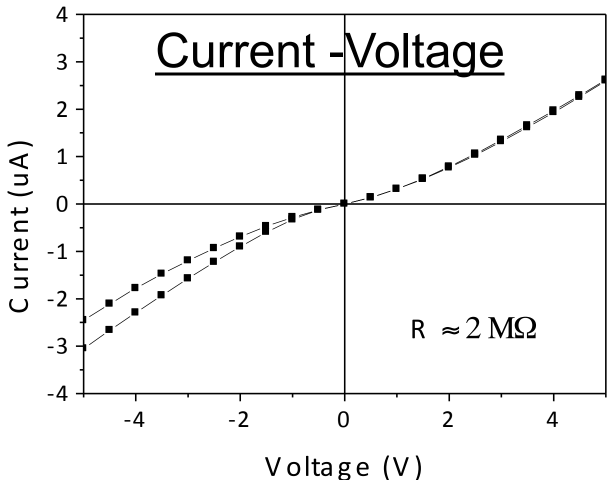


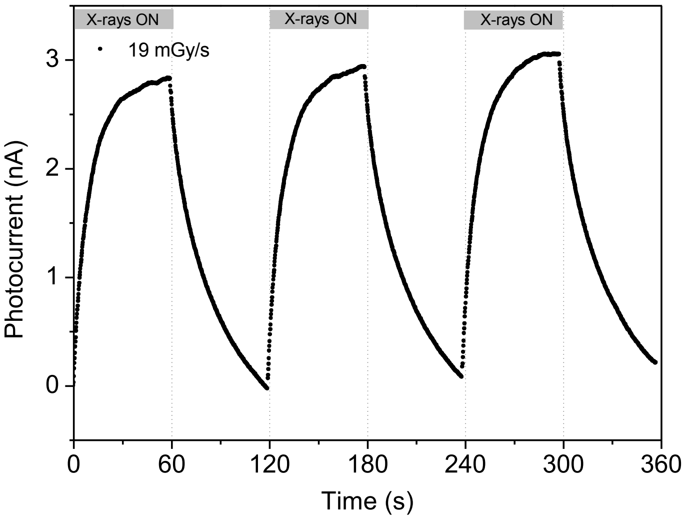


Despite the highly heterogeneous interdigitated electrodes substrate, it is now possible to directly print solutions originating OSSCs in well precise positions.

PRINTED CRYSTALS ON FLEXIBLE SUBSTRATES AS X-RAYS DETECTORS OPERABLE AT ULTRA-LOW BIASES







Actual device switching response at a bias voltage of 0.2 V

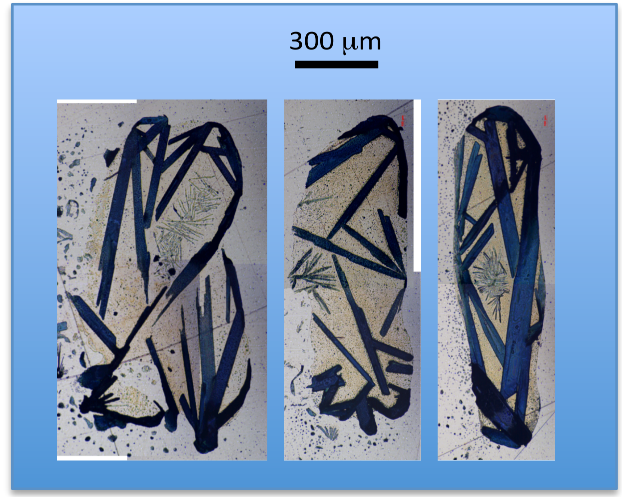
Best sensitivities achieved up to now around 150 nC/Gy

(monochromatic synchrotron X-ray beam, Energy 17 keV, Dose rate 19 mGy/s)

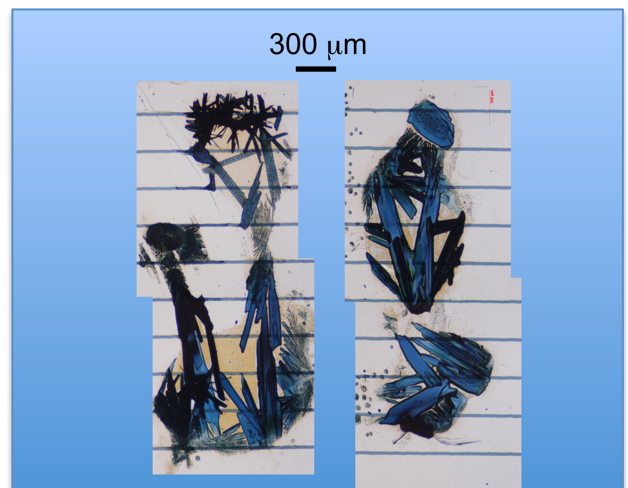
L. Basiricò et al., Nat. Comm., 2016, DOI: 10.1038/ncomms13063

ACHIEVING “PRINTED” ORIENTED SINGLE CRYSTALS

Satisfactory results on pure gold (down to 300 mm confinement)

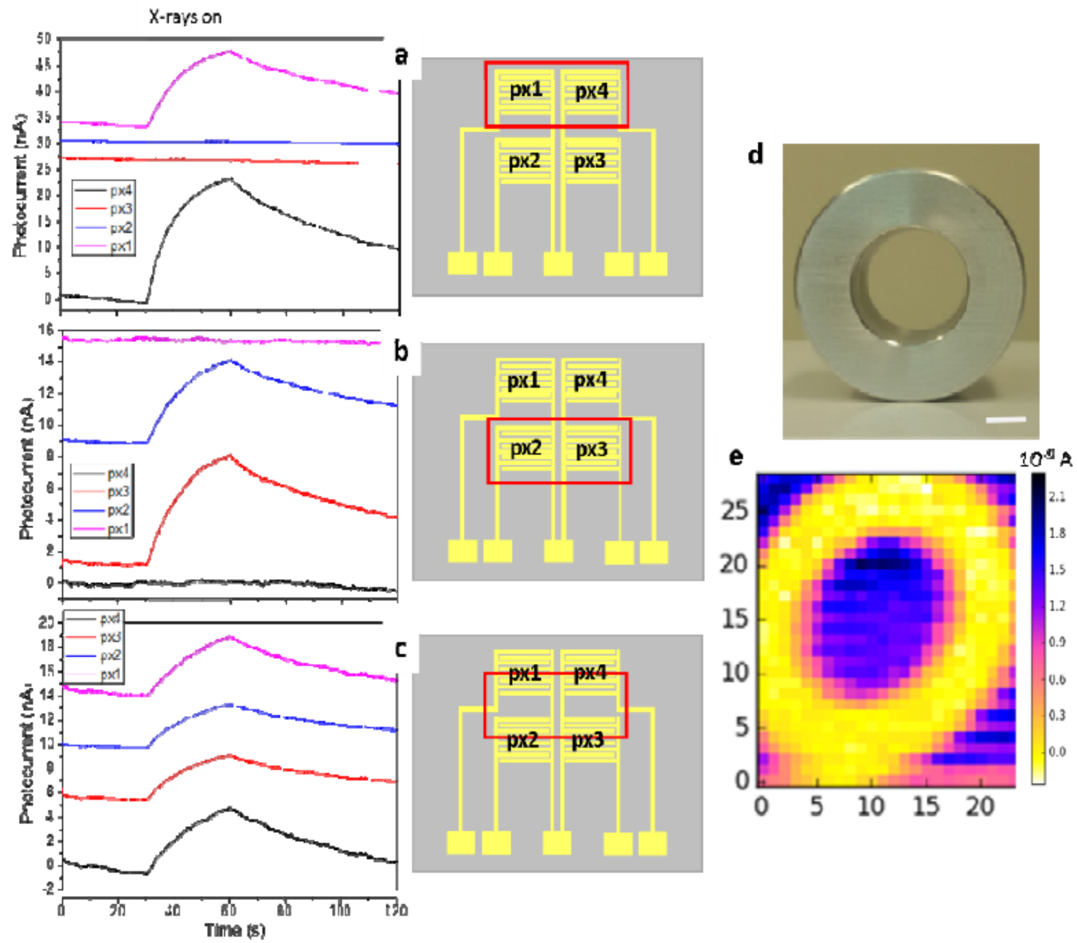


More work to do on real electrodes (problems of substrate heterogeneity)



EU PROJECT i-FLEXIS RESULTS (II)

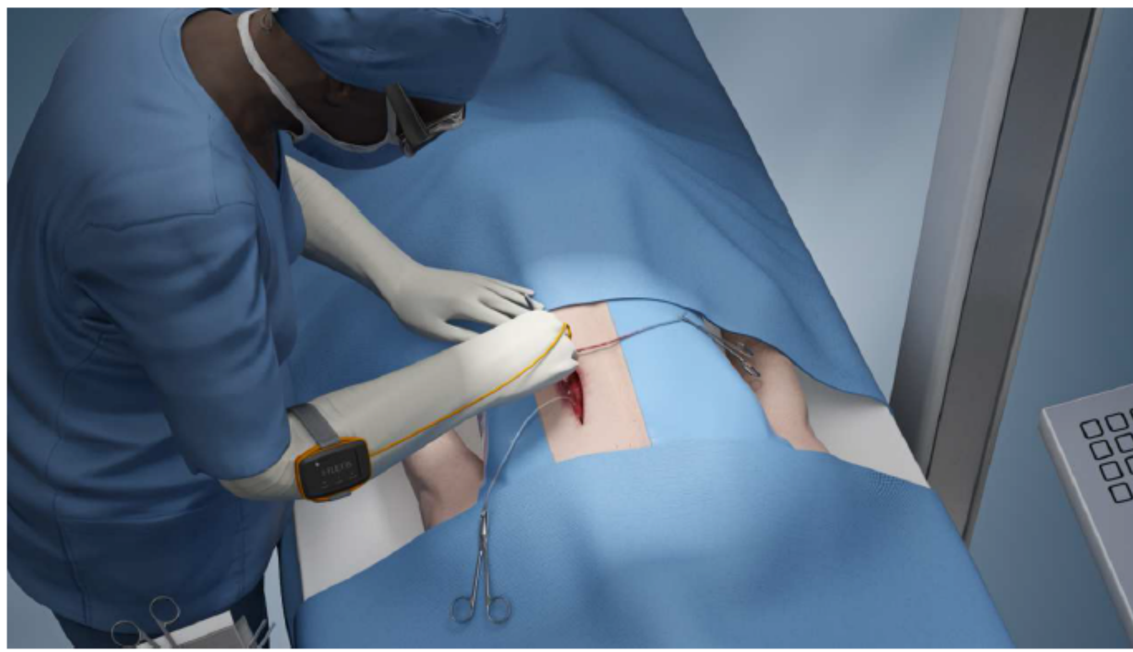
X-ray-induced current signals versus time, recorded by selectively irradiating the pixels of a 2X2 detector matrix. The radiation source employed is a monochromatic synchrotron X-ray beam at 17 keV with a dose rate of 28.5mGy/s. The pixels were all biased at 0.2V. Centre: a sketch of the device is reported, with the red box indicating the region of the matrix under irradiation.



In particular: in a only pixels 1 and 4 are irradiated, in b only pixels 2 and 3 are irradiated, in c all the pixels are irradiated. Right: photograph (d) and corresponding X-ray image by a single pixel device (e) of an aluminium annular ring; the scale bar is 5 mm.

EU PROJECT i-FLEXIS RESULTS (II)

Ring-shaped X-rays detector to be used for surgery applications.



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IoT MAIN REQUIREMENTS FOR PRACTICAL APPLICATIONS

MUST HAVE

Low cost per single device	projected costs < 10 €/piece ✓
High volume producibility	inkjet and flexography-printable ✓
Low weight per single device	< 0.1 g/cm^2 ✓
Low power consumption	a few mW when in operation, a few nW when idle ✓
Wireless connectivity	already developed under i-FLEXIS ✓

NICE TO HAVE

Full flexibility	fully achieved for the detecting element, still to be achieved for the readout electronics (but feasible) ✓

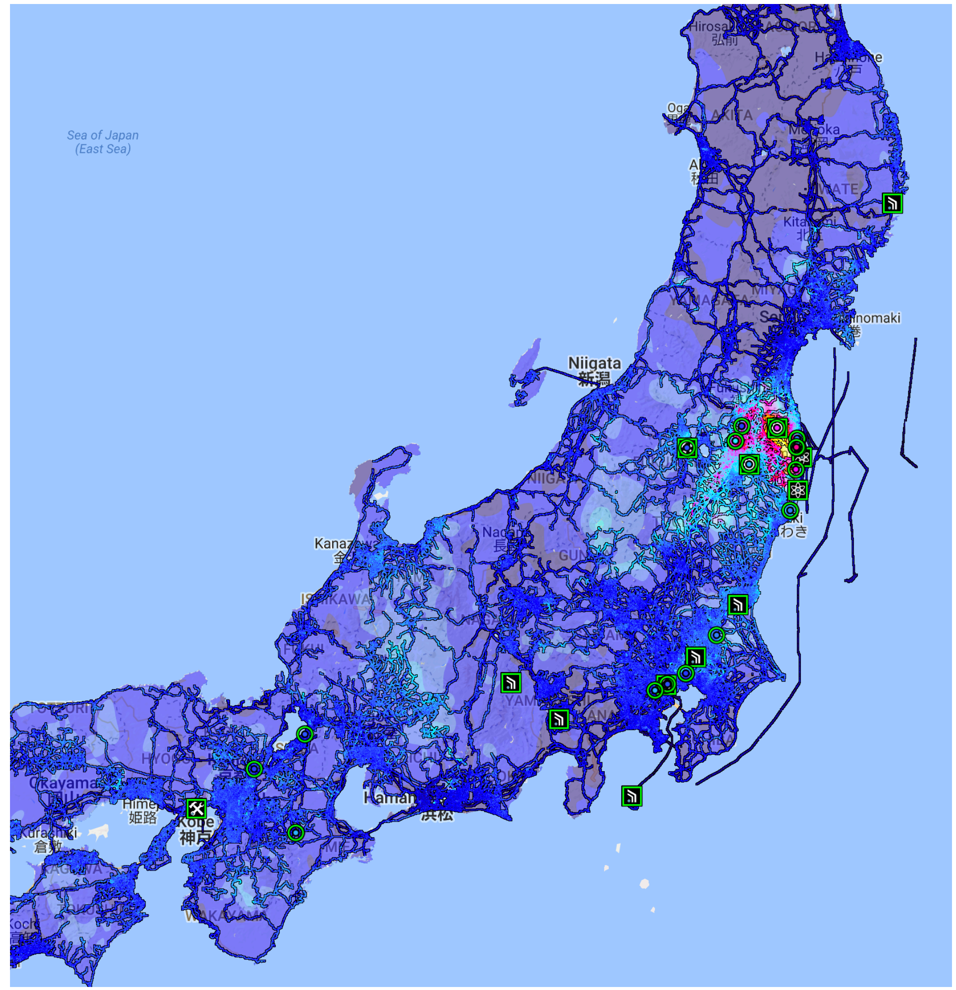
POSSIBLE APPLICATIONS IN CITIZEN SCIENCE (I)

Fukushima accident

Total meltdown of reactor 1? 2?

POSSIBLE APPLICATIONS IN CITIZEN SCIENCE (II)

The Fukushima-generated radiation is not easily tracked. For this reason, a citizen science project involving people living and working in Japan is producing the world's largest scale citizen science project, Safescan, with the purpose of mapping the leaked radiation in the zone.

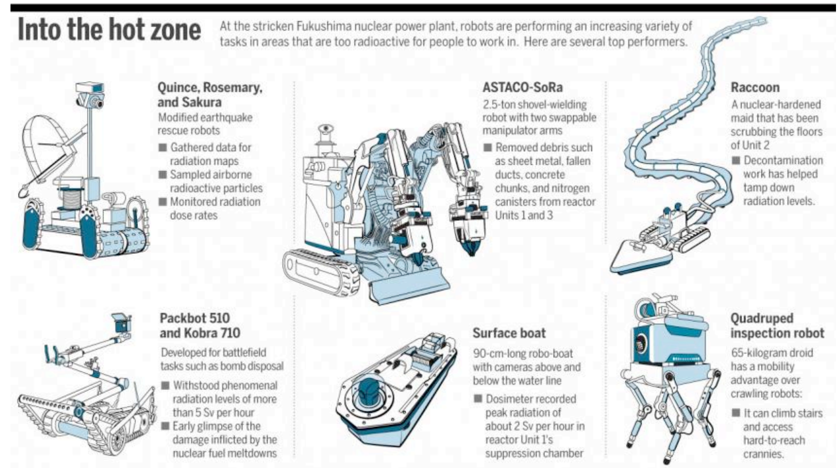


POSSIBLE APPLICATIONS IN CITIZEN SCIENCE (III)

In this frame, OSSCs-based detectors could further boost the diffusion of citizen's owned and operated radiation detectors. The prospected cost for a fully finished, battery-operated device could range a3ound 20 €/piece, including a wireless transmitter (even though their working mechanism is not analogous to Geiger counters, where each radiation event triggers one count, X-rays detectors can add complementary information to the data collected using counters), well affordable. Moreover, as they are very light, they can be mounted on drones flying over particularly "hot" points, where a normal, not properly equipped person cannot go.

POSSIBLE APPLICATIONS IN CITIZEN SCIENCE (IV)

Already by now, radiation detectors are being deployed on several different types of robots and automated machines for plant's inspection and debris removal.



OSSCs-based detectors could be integrated within several different robots or automated moving devices (including marine or submarine ones) in order to deliver a more clear picture of the extent of contamination.

CONCLUSIONS

- Organic semiconducting single crystals are materials that can be useful to detect X-rays.

- Robust to environment and to operation, linear and reproducible response in a wide range of energies (relevant for several high-volume and high-impact applications). They can be fabricated on an all-organic basis, hence being extremely lighweight, bendable, conformable and potentially transparent.

- Operated at voltages down to 0.2 V, fully bendable

- Inkjet printable!

- Suitable for Safescan?

ACKNOWLEDGEMENTS

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- **Prof. A. Bonfiglio**, Prof. P. Cosseddu, Dr. S. Lai – Univ. of Cagliari
- **Dr. V. Fischer** – CEA, Grenoble
- **Prof. R. Martins, Prof. E. Fortunato**, Dr. P. Barquinha – CENIMAT-UNOVA, Lisbon
- **Prof. P. Siffert**, Dr. M. Sowinska – EURORAD, Strasbourg (France)

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Thanks for your attention