Flexible organic photonic sensor system for a large Spectrum of portable applications: from health to security

Beatrice Fraboni

Department of Physics and Astronomy

University of Bologna, Italy

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Outline

- Why flexible large area photonic (radiation) sensors are interesting and needed
- Why organic semiconductors open up new possibilities
- Why these (portable) systems can be exploited for IoT applications

Radiation detection & flexible sensors

Ionizing radiation detection is an important task in a number of industrially and socially relevant activities:
Biomedicine (Radiography and diagnostics), Radiotherapy (as a treatment), Industrial quality control (automated inspection of industrial parts) Security applications (control of luggage, cargos trucks and even people, before and during shipment by air, sea and road), applications in the scientific field (like X-ray crystallography, X-ray photoelectron spectroscopy, Astronomy and Art).

Great advantage IF ionizing radiation sensing systems were:
large area, thin and flexible, able to operate at room temperature and to detect X-rays in real time at affordable costs

BUT the technologies today available cannot deliver all these features in one single object.

Radiation detection & flexible sensors

State-of-the-art solid state X-ray detectors are based on inorganic materials (silicon, cadmium telluride, diamond..), which offer top detecting performances but are **rigid, heavy, expensive**, energy-consuming, and often require low-temperature cooling to work properly

The market for X-rays equipment, according to publicly available documents was worth about $10 billions in 2011 with a steady growth per year of about 4-6%.

⬇

a very strong need to devise low-cost, conformable, large area and reliable alternatives to the current technology radiation detectors; prospective low-power consuming and portable (i.e. low weight and battery operated) ionizing radiation sensing systems

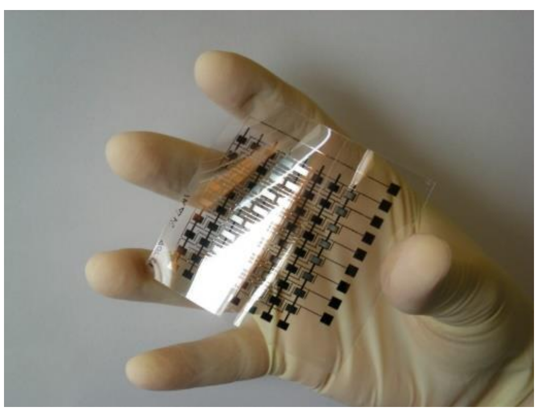
i-FLEXIS Project (FP7-ICT)

www.iflexis.eu

Development of an **innovative, reliable and low-cost integrated X-ray sensor system based on printed (flexible) components and electronics.**

9 International partners:

Coordinator:
University of Bologna



Integration of three novel concepts:

- **organic single crystals** as the active, X-ray direct sensing material

- **printed readout electronics** based on high mobility thin film transistors - nm-thin films of novel high mobility oxide materials operating at ultra-low voltages (<5V)

- **flexible transparent electronics** all integrated onto low cost plastic substrates.

potential applications - I

- **health diagnostic radiation sensor** to determine the dose on the exposed area during X-ray diagnostic analyses. Thanks to the large-area, conformable, and transparent 2D matrix peculiar to the Organic Sensor system, it can be positioned directly on the area to be examined by X-ray (similarly to a band-aid plaster), allowing to directly measure the X-ray dose received by the patient on the exact location where the X-ray beam will enter the skin.

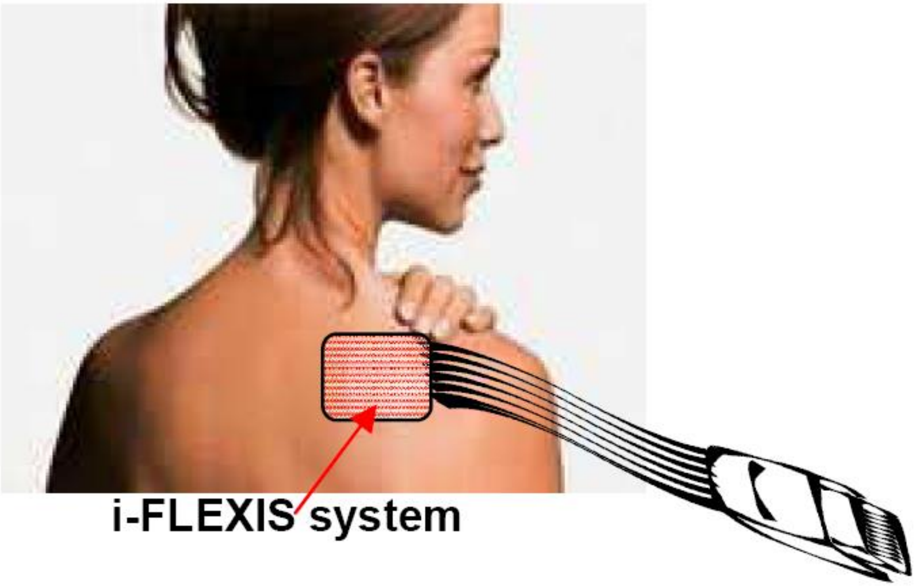


Figure 4: Rendering of the Health Dosimeter sensor System.

potential applications - II

- **Identification tags** to monitor the X-ray screening history of each piece of luggage, through the fabrication of a permanent bag tag containing the Organic Integrated sensor system, an RFID and a minimal display for visual information. This High-end RFID tag platform could be used as a permanent luggage bag tag, mainly for automatic baggage drop-off at the airports. This system will allow monitoring the X-ray checking history of the piece of luggage with the Identification tag system , improving the security and efficacy of luggage handling in airports

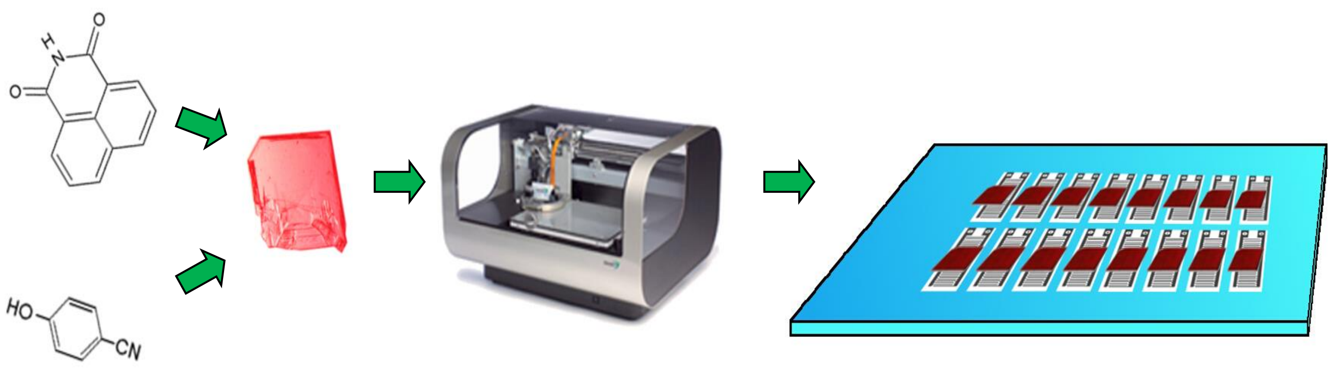
Figure 5: Identification Tag for airport Luggage.

i-FLEXIS

Integrated flexible photonic sensor system

S/T specific targets

S&T Obj. 1: develop organic single crystals (OSSC) grown from solution at low cost, chemically engineered to directly provide an electrical output signal when exposed to X-ray radiation fields with energy ranging 10keV-150keV and doses up to 10^3 Gy. Low operation voltages, linear response, room temperature and ambient operation



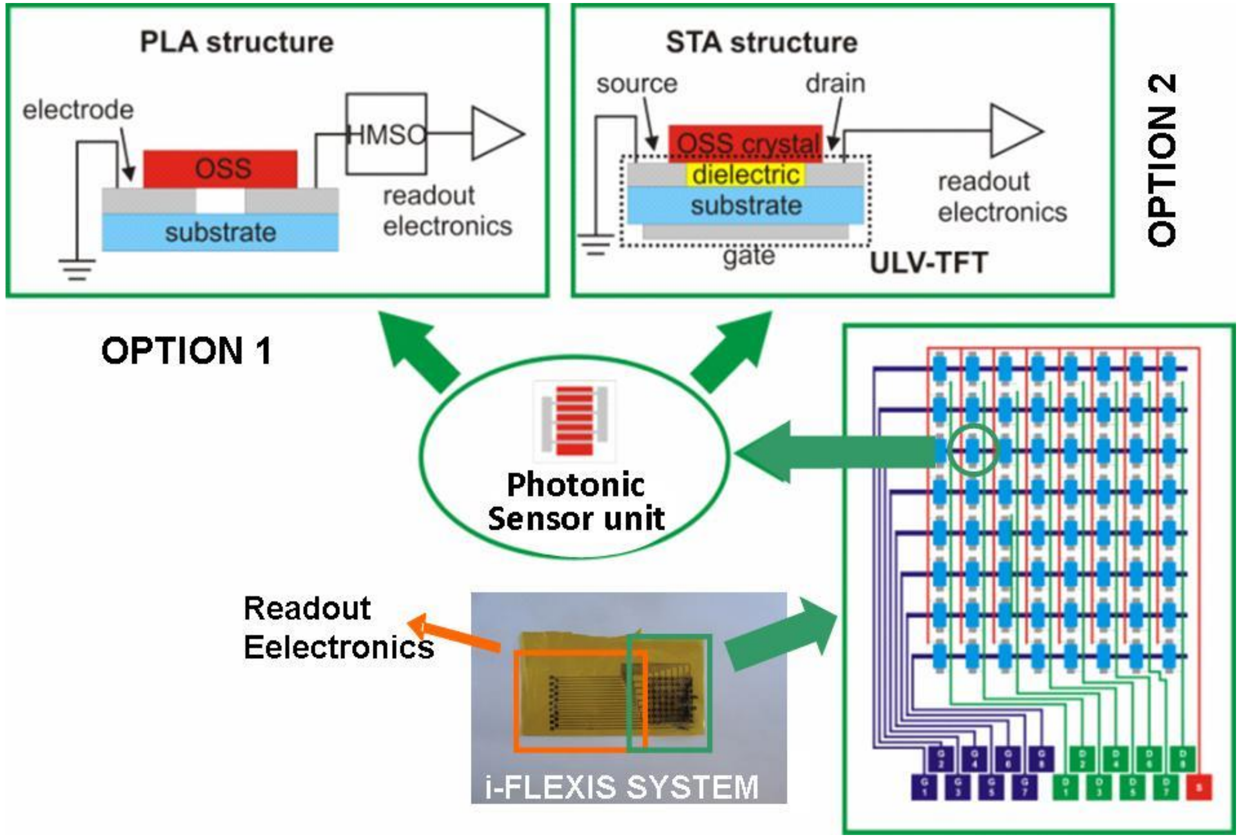
S/T specific targets

S&T Obj. 2: design and fabricate a photonic sensor unit that integrates the OSSC as the active X-ray sensing element and appropriate amplification of its electrical output signal (that could vary from 0.01-10μA).

Two different geometries and layout are foreseen:

- "Thin Film Transistor Stacked" (STA)
- co-Planar" (PLA) structure

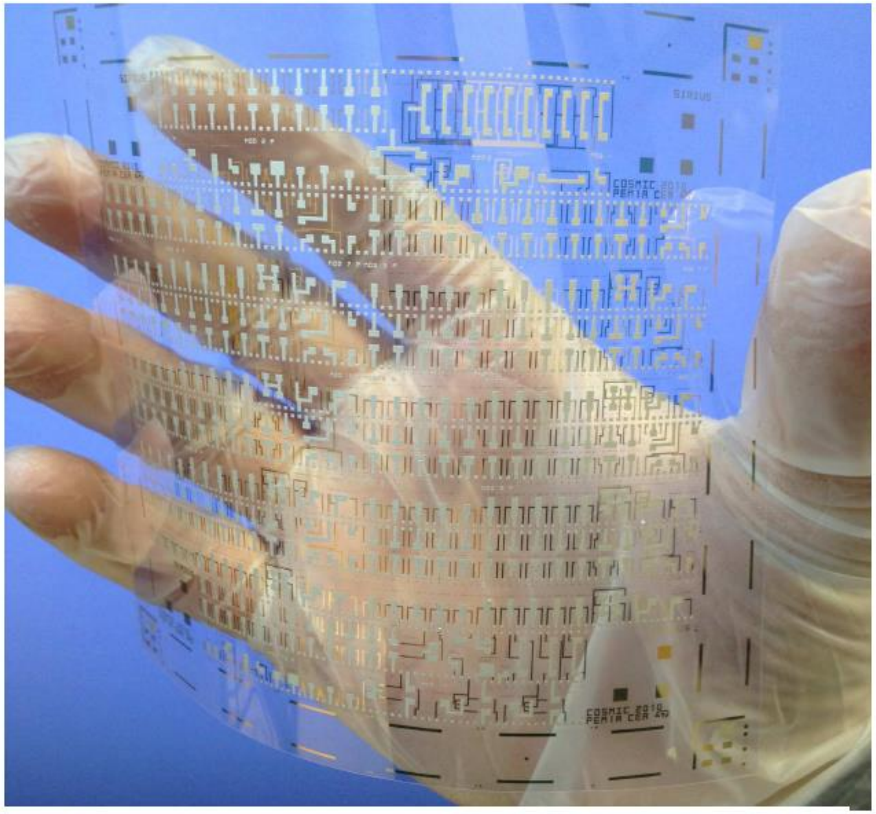
that differently exploit the peculiarities of the novel ultra low-voltage TFTs used for the local signal amplification



S/T specific targets

S&T Obj. 3: design and integration of the whole i-FLEXIS system, integrating the photonic sensor and the **readout electronics into a 2D matrix** that will act as a pixellated X-ray sensing system

- A fully printed organic CMOS platform (40V)
- A proof of principle for an oxide TFT based low operating voltage (5V) CMOS one will be introduced.



S/T specific targets

S&T Obj. 4: integration of the i-FLEXIS system into a **High-end RFID tag platform** to be used as a permanent luggage bag tag, mainly for automatic baggage drop-off at the airports. This system will allow monitoring the X-ray checking history of the piece of luggage with the Identification tag (IDtag) system , improving the security and efficacy of luggage handling in airports

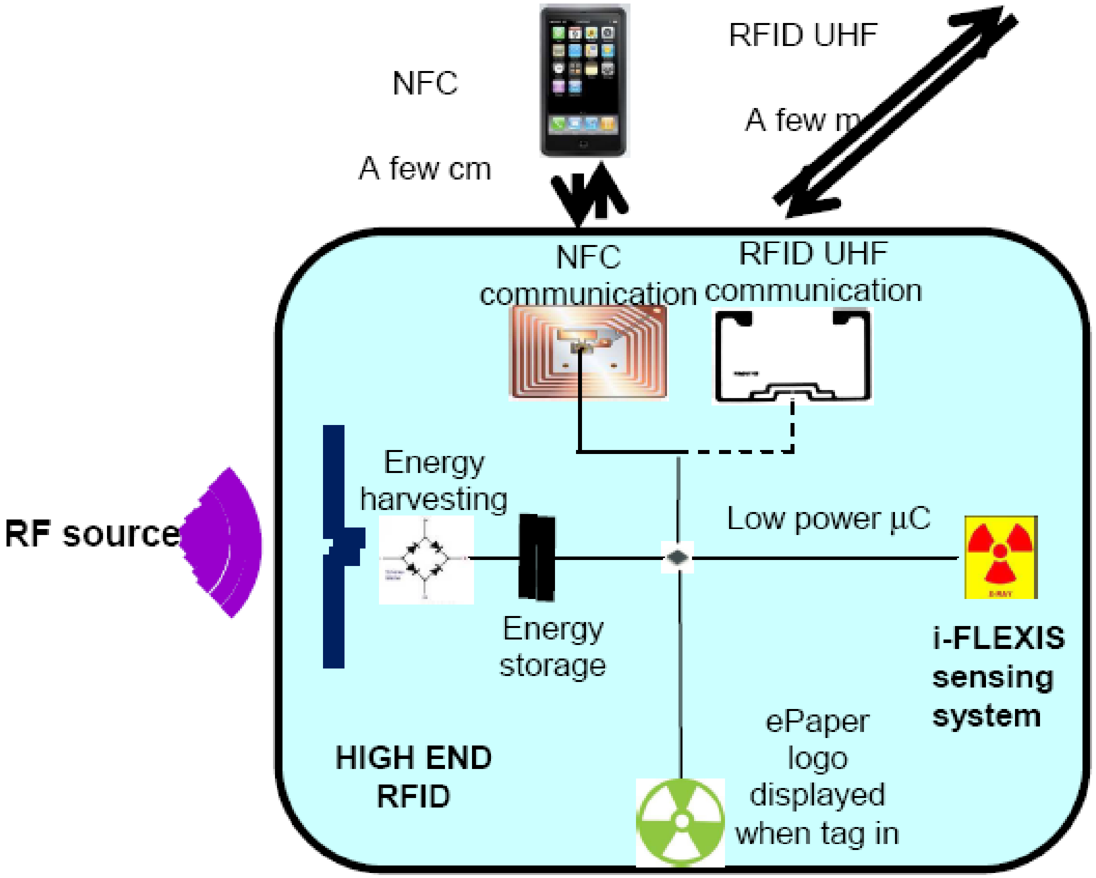


Figure 9: Schematic layout of the Identification Tag structure (application 1).

S/T specific targets

S&T Obj. 5a: integration of the i-FLEXIS system into **a Health radiation dosimeter for medical diagnostic** Thanks to the large-area, conformable, and transparent 2D matrix peculiar to the i-FLEXIS system, the HDsensor can be positioned directly on the area to be examined by X-ray (similarly to a band-aid plaster), allowing to directly measure the X-ray dose received by the patient on the exact location where the X-ray beam will enter the skin.

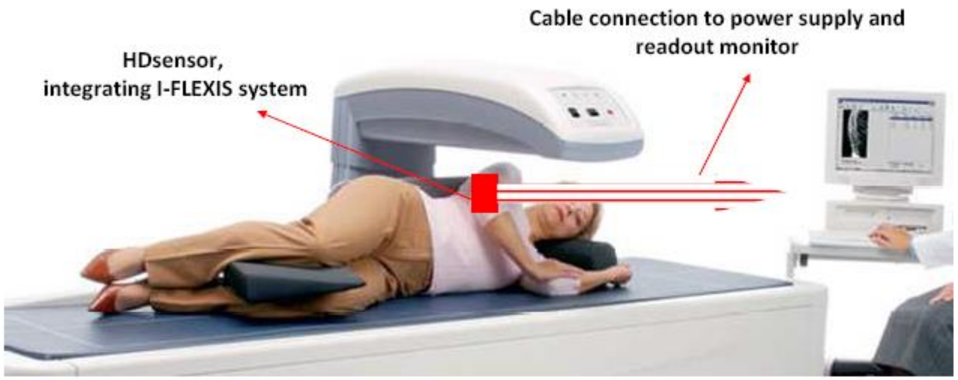


Figure 10: Rendering for the HDsensor (application 2).

S/T specific targets

S&T Obj. 5b:. The same system developed as S&T 5a will be tested as a tool for low-cost, low-power consuming **bone density analyses** The absolute amount of bone as measured by bone mineral density (BMD) testing generally correlates with bone strength and its ability to bear weight. The BMD is measured with a dual energy X-ray absorptiometry test (usually referred to as a DEXA scan). By measuring BMD, it is possible to predict fracture risk in the same manner that measuring blood pressure can help predict the risk of stroke

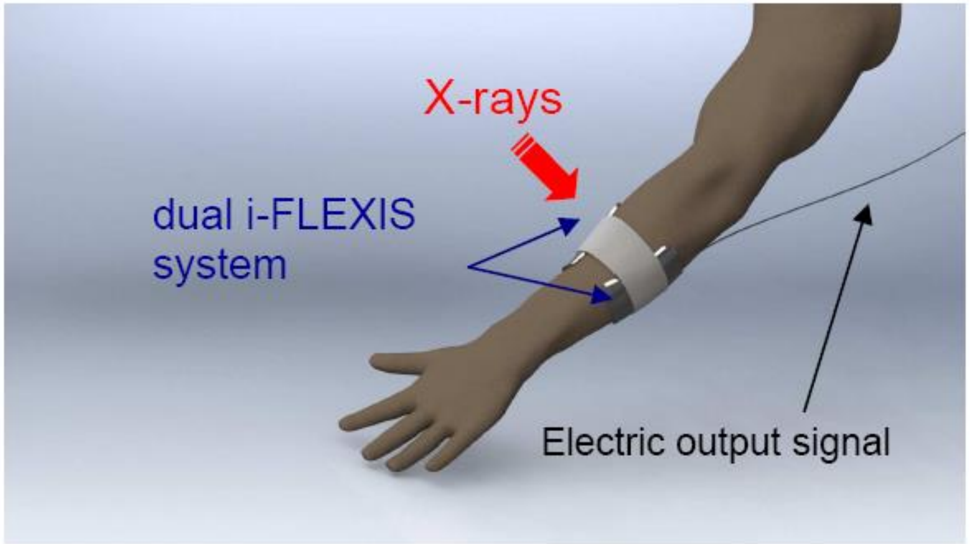


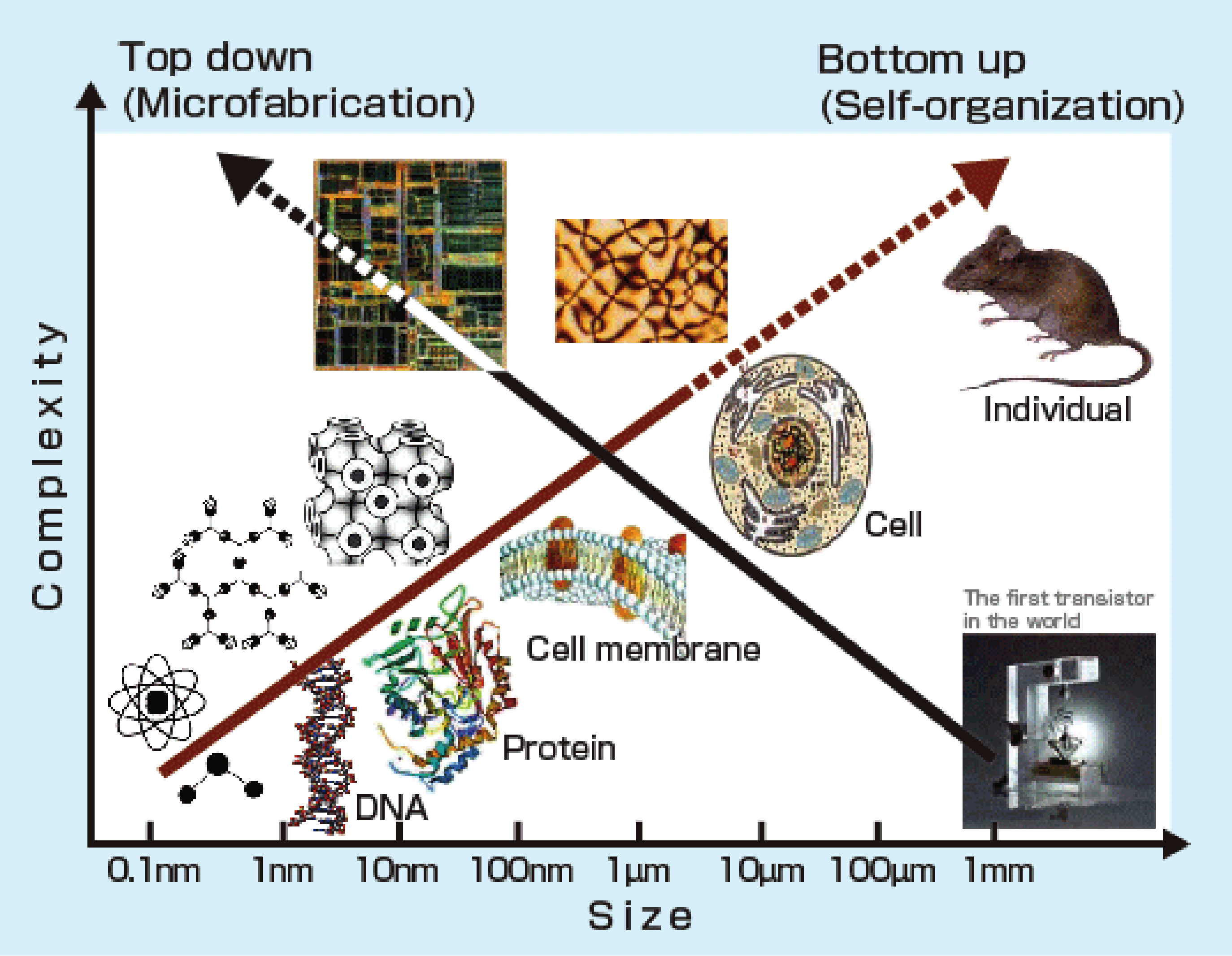
Figure 18: Rendering of the layout of the Bone Density Analyser.

Flexible (printed) electronics

1. **The possibility of creating conformal**, fully recyclable, low cost and innovative products and systems is unique, and conventional materials and processes such as silicon or other inorganic materials, usually processed using vacuum- or gas-based conditions, cannot challenge this novel technology
2. **expected cost reduction,** the micro/electronics industry is currently centered on the concept of "fab", i.e. a very large plant in which the cost-per-unit of a device is abated thanks to massive scale economies. **"Top down" approach vs "bottom up"** one of printed electronics allows for massive reduction of material waste

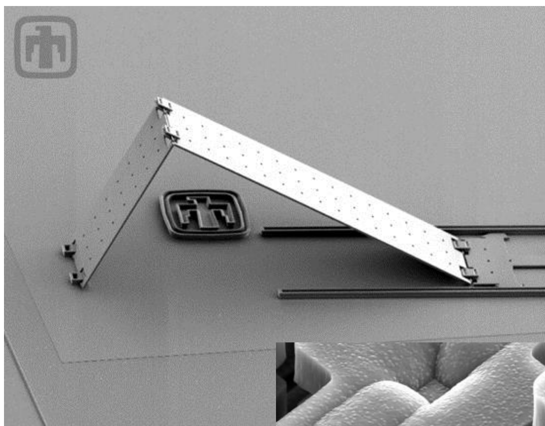
In terms of materials and device fabrication, printed flexible electronics is a very challenging technology

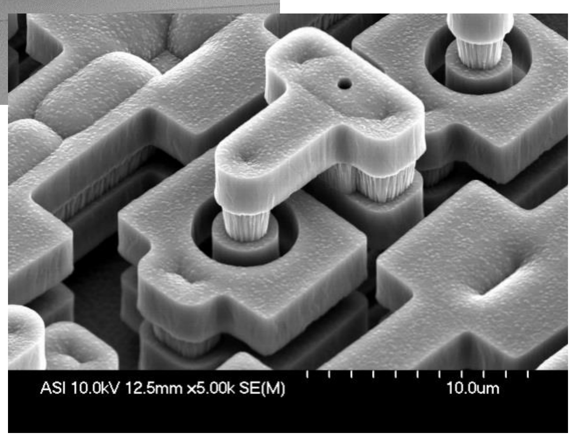
Change of perspective in fabrication processes

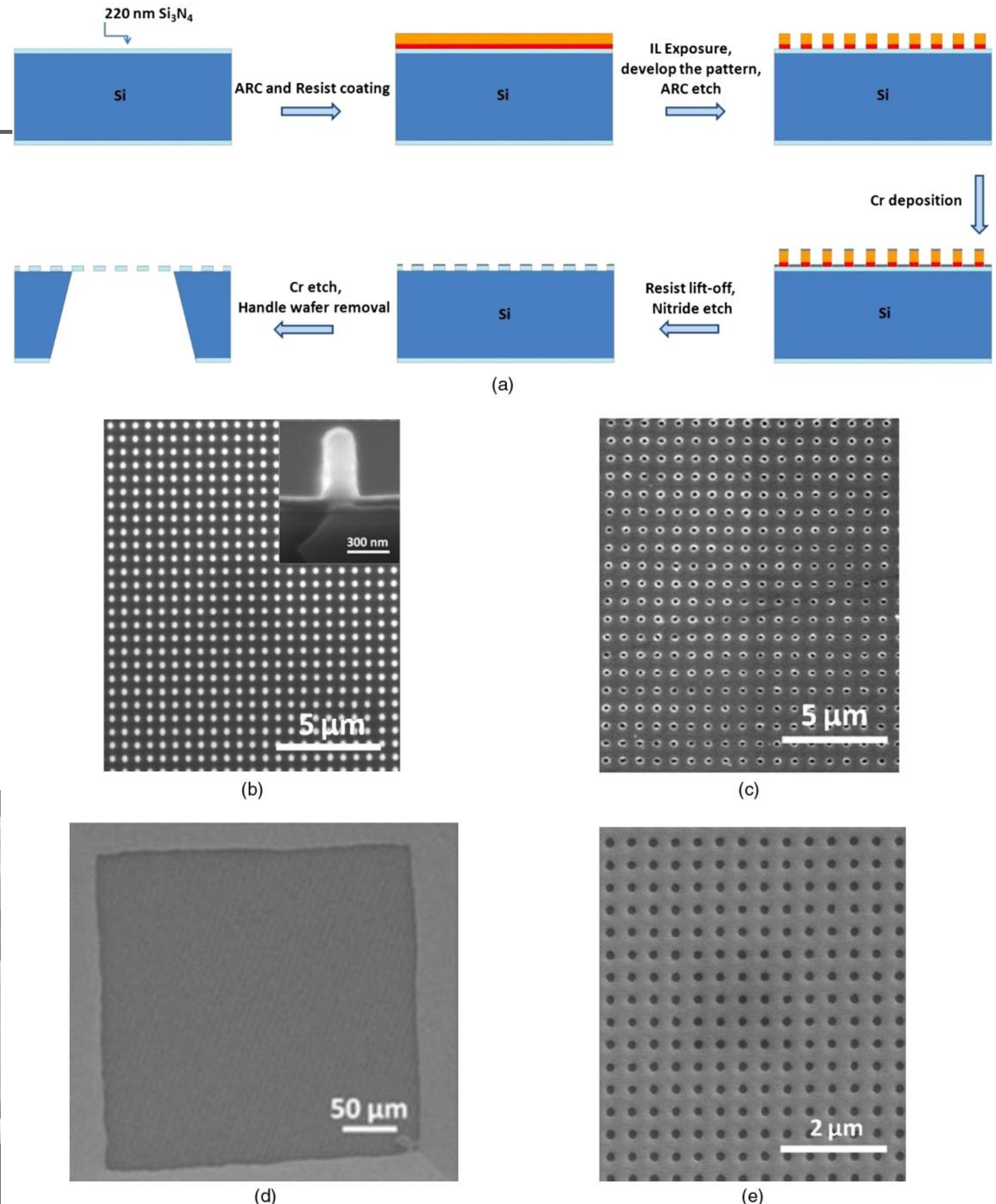


Top down process

It starts with bulk materials (top) that are reduced to nanoscale (down) by physical, chemical and mechanical processes.

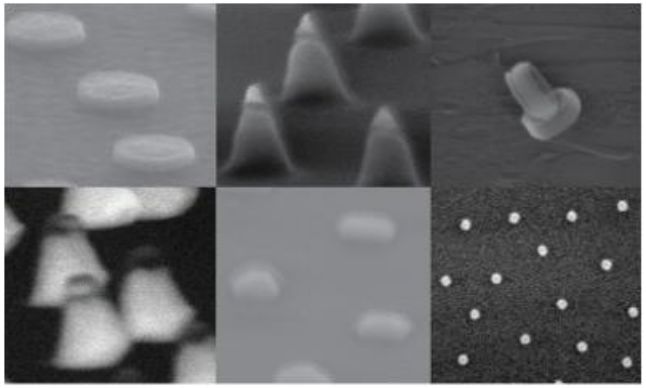


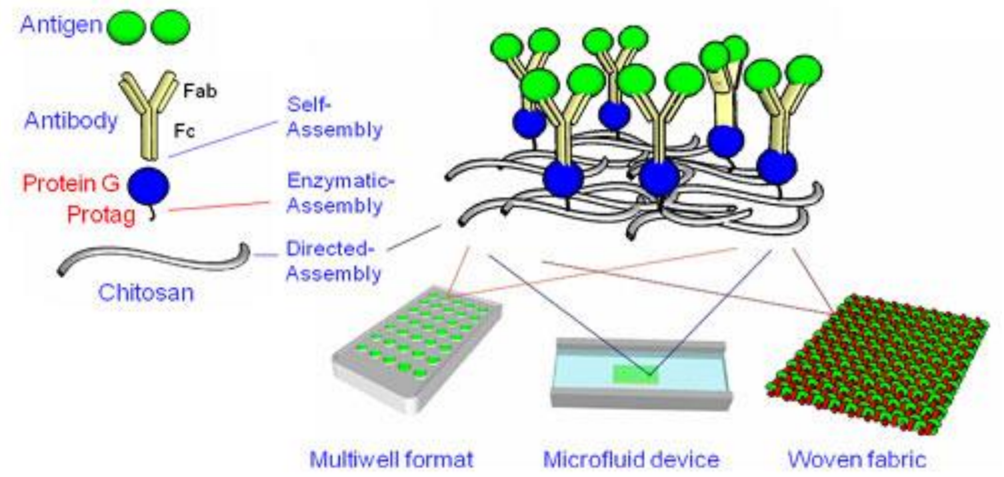


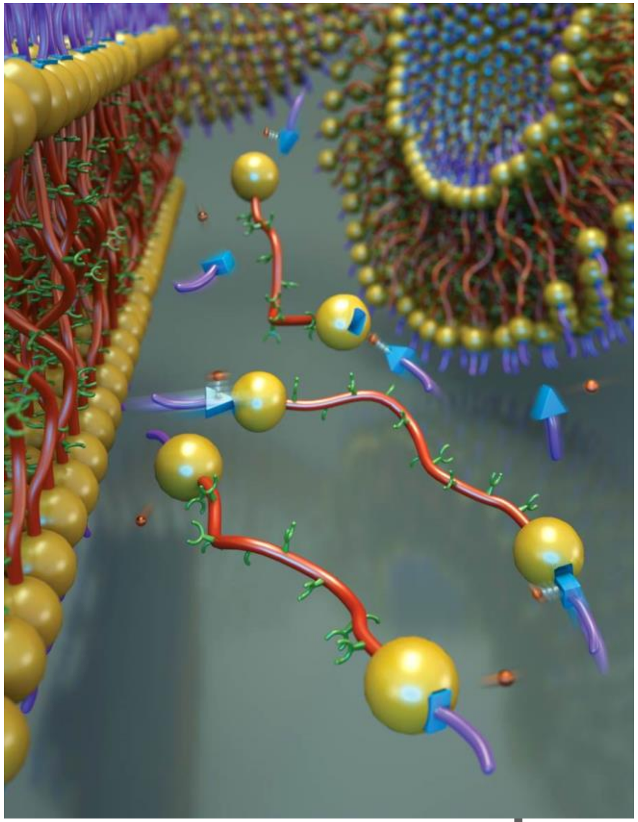


Bottom up process

It starts with atoms and molecules (bottom) that are made to react through chemical or physical processes to assemble into nanostructures (up)







Ionizing Radiation sensors

- incoming ionizing radiation is **directly transduced into an electrical signal** by the sensor (**inorganic or organic semiconductor**)

- A single, very compact device
- Higher S/N ratio and faster response time

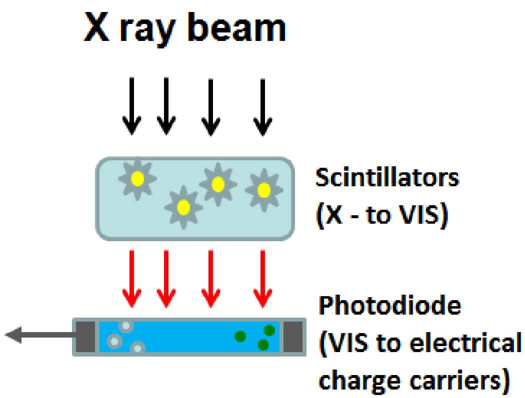
- Current sensors are made by inorganic semiconductors (Si, CdTe etc)

- incoming ionizing radiation is detected in a **two-steps process,** the first step being performed by a first sensor (a **scintillator, organic or inorganic**), and the second step being performed by a second sensor (a **photodiode, organic or inorganic**)

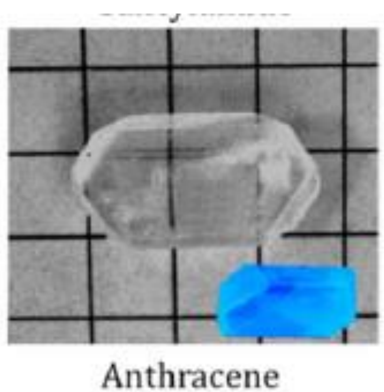
- Two devices, complex coupling, losses

Organic X-Ray detectors: indirect

INDIRECT DETECTION

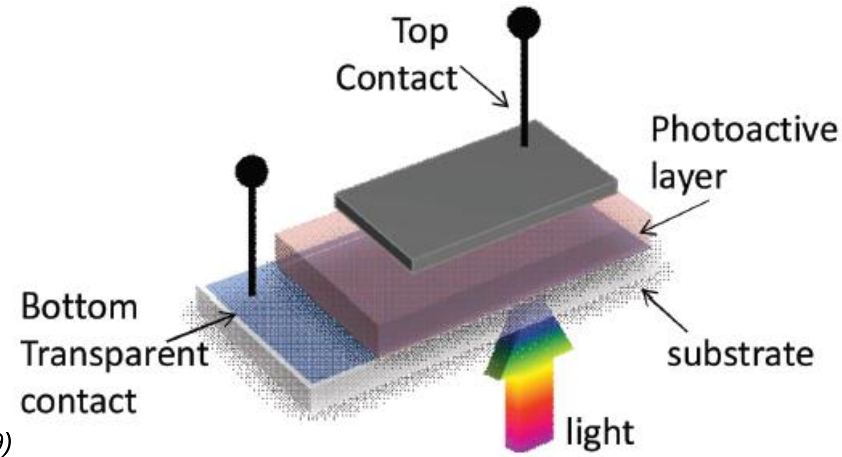


scintillator

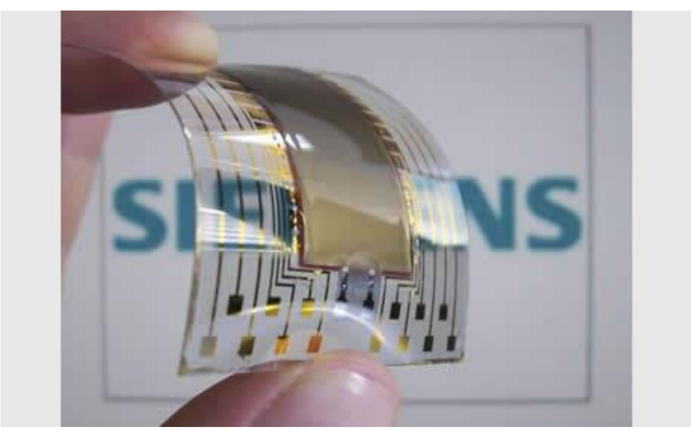


Hull et al., IEEE Trans. on Nucl. Sci. VOL. 56, NO. 3, (2009)

photodiodes



*K.-J.Baeg et al., Adv. Mat., **25**, 4267–4295(2013).*



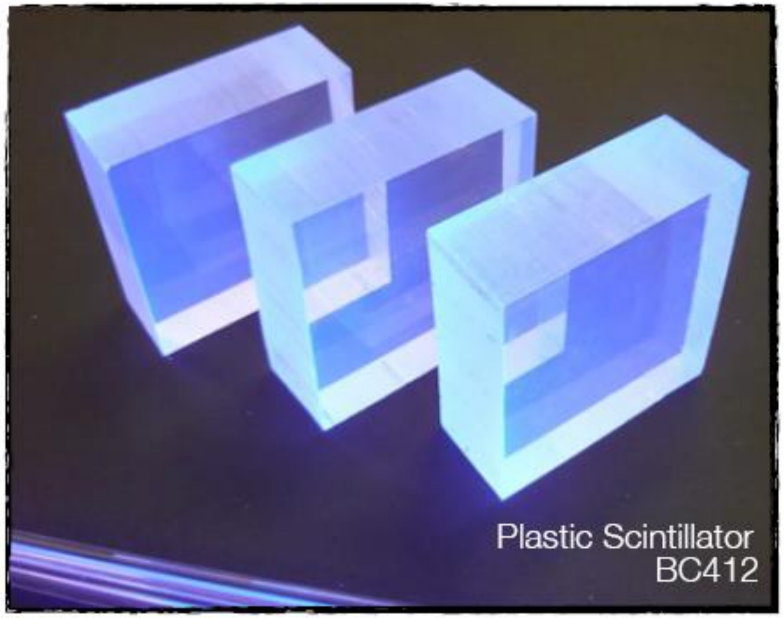
Current ongoing project @ Siemens:
Indirect :organic scintillator + organic photodiodes

http://www.siemens.com/innovation/en/news/2013/e_inno_1305_1.htm

Scintillators : general characteristics

Principle:

Radiative process:
X- photon ⟶ UV-IR photon



Main Features:

- Sensitivity to energy
- Fast time response
- Pulse shape discrimination

Requirements

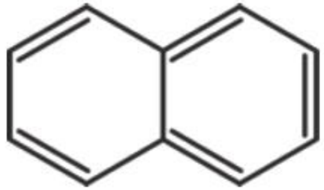
- High efficiency for conversion of excitation energy to fluorescent radiation
- Transparency to its fluorescent radiation to allow transmission of light
- Emission of light in a spectral range detectable for photosensors
- Short decay time to allow fast response

Organic Scintillators

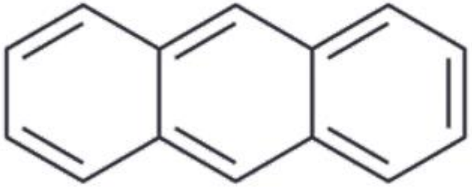
Aromatic hydrocarbon compounds:

e.g. Naphtalene [$C_{10}H_8$]
Antracene [$C_{14}H_{10}$]
Stilbene [$C_{14}H_{12}$]
...

Naphtalene

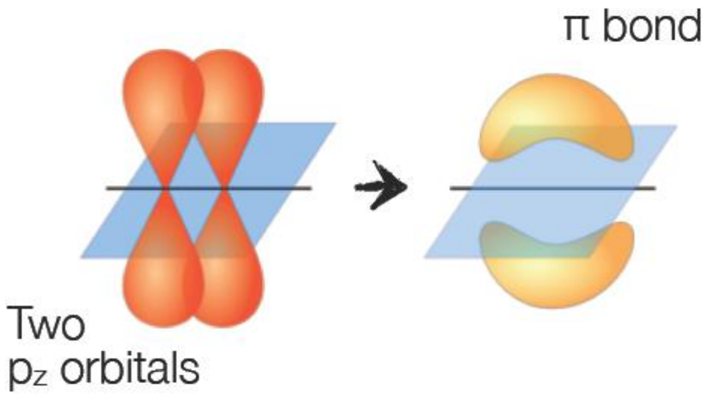


Antracene



Very fast!
[Decay times of O(ns)]

Scintillation is based on electrons of the C=C bond ...



Scintillation light arises from delocalized electrons in π-orbitals ...

Transitions of 'free' electrons ...

Organic Scintillators

Principle:

Absorption of primary scintillation light

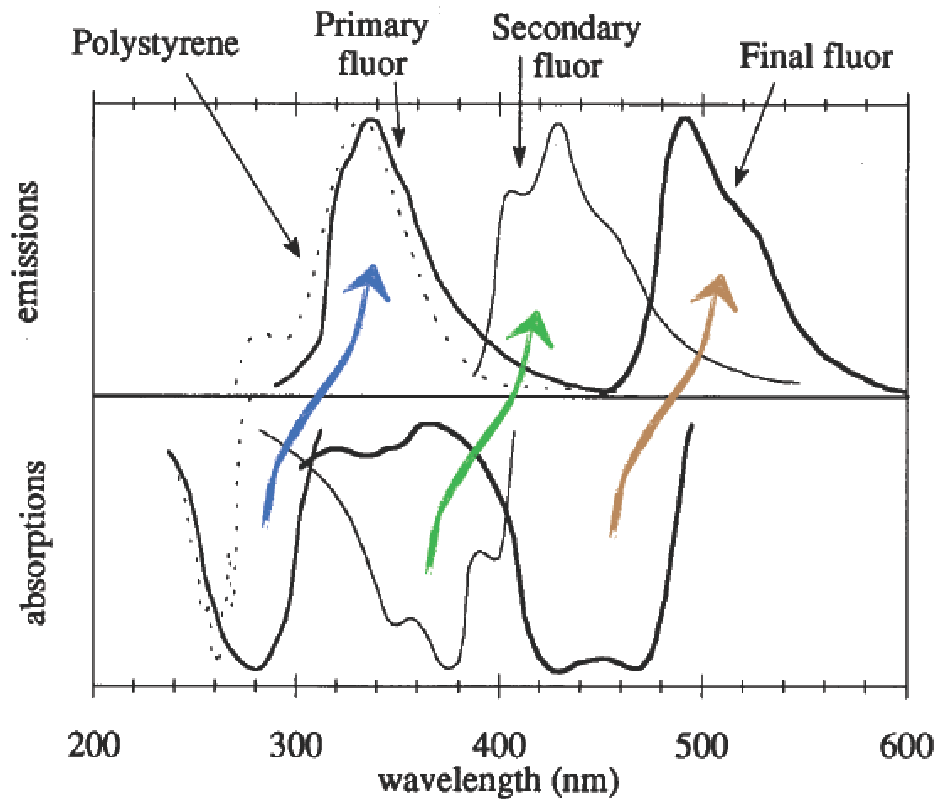
Re-emission at longer wavelength

Adapts light to spectral sensitivity of photosensor

Requirement:

Good transparency for emitted light

Schematics of wavelength shifting principle



Scintillators : comparison

Inorganic Scintillators

Advantages high light yield [typical; $\varepsilon_{sc} \approx 0.13$]
high density [e.g. $PBWO_4$: 8.3 g/cm3]
good energy resolution

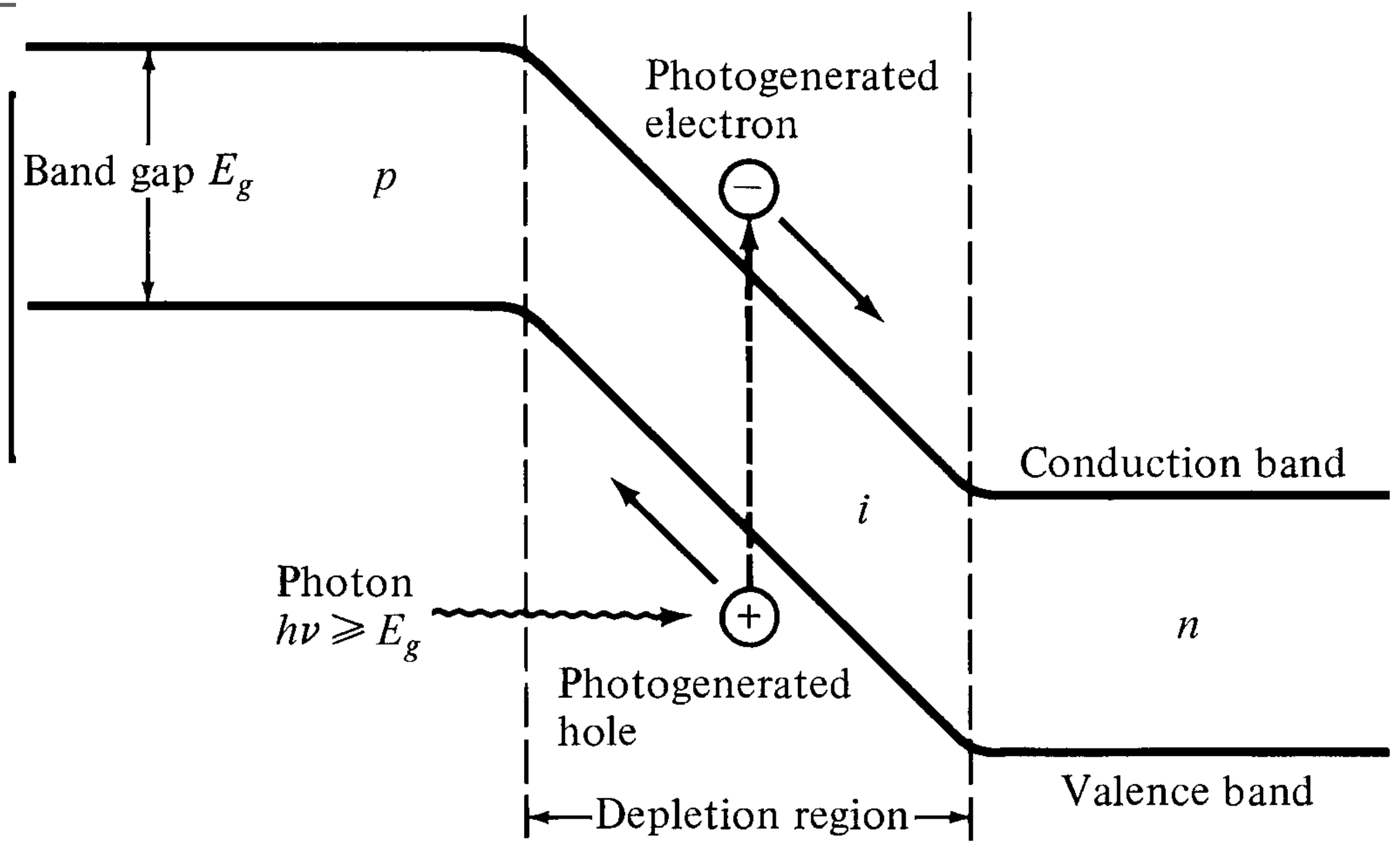
Disadvantages complicated crystal growth
large temperature dependence **EXPENSIVE**

Organic Scintillators

Advantages very fast
easily shaped
small temperature dependence
pulse shape discrimination possible

Disadvantages lower light yield [typical; $\varepsilon_{sc} \approx 0.03$]
radiation damage **CHEAP**

Photodiodes: general



In a *pin* p … gion causes photo-ge … erse –biased junction … as **photocurrent.**

Non-radiative process:
Vis photon → charge carriers

Photodiodes: photocurrent

- Optical power absorbed, $P(x)$ in the depletion region can be written in terms of incident optical power, P_0 :

$$P(x) = P_0(1 - e^{-\alpha_s(\lambda)x})$$

- Absorption coefficient $\alpha_s(\lambda)$ strongly depends on wavelength. The upper wavelength cutoff for any semiconductor can be determined by its energy gap as follows:

$$\lambda_c(\mu\text{m}) = \frac{1.24}{E_g(\text{eV})}$$

- Taking entrance face reflectivity into consideration, the absorbed power in the width of depletion region, w, becomes:

$$(1 - R_f)P(w) = P_0(1 - e^{-\alpha_s(\lambda)w})(1 - R_f)$$

Photodiodes: responsivity

- The primary photocurrent resulting from absorption is:

$$I_p = \frac{q}{h\nu} P_0 (1 - e^{-\alpha_s(\lambda) w})(1 - R_f)$$

- Quantum Efficiency:

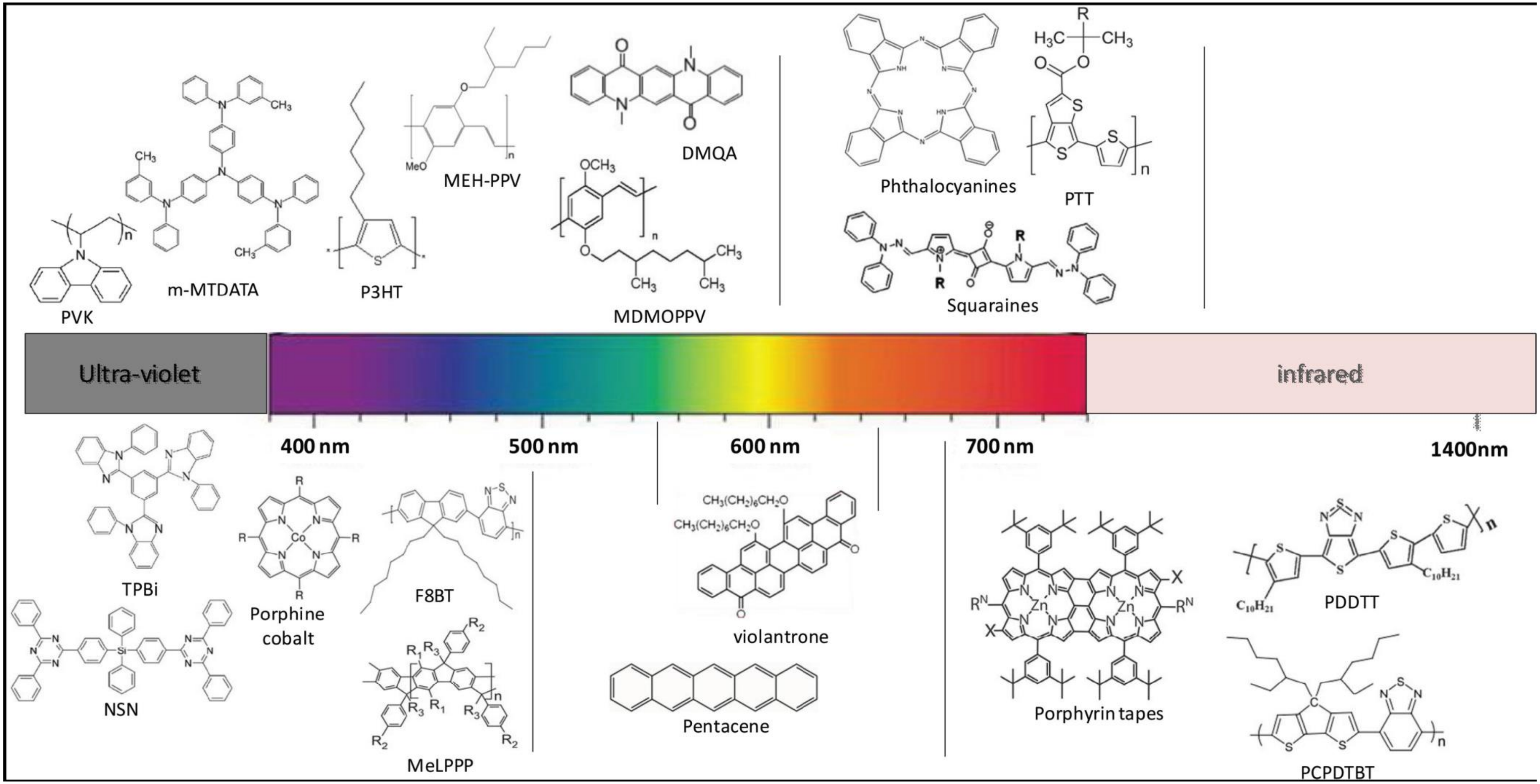
$$\eta = \frac{\text{\# of electron - hole photogenerated pairs}}{\text{\# of incident photons}}$$

$$\eta = \frac{I_P / q}{P_0 / h\nu}$$

- **Responsivity:**

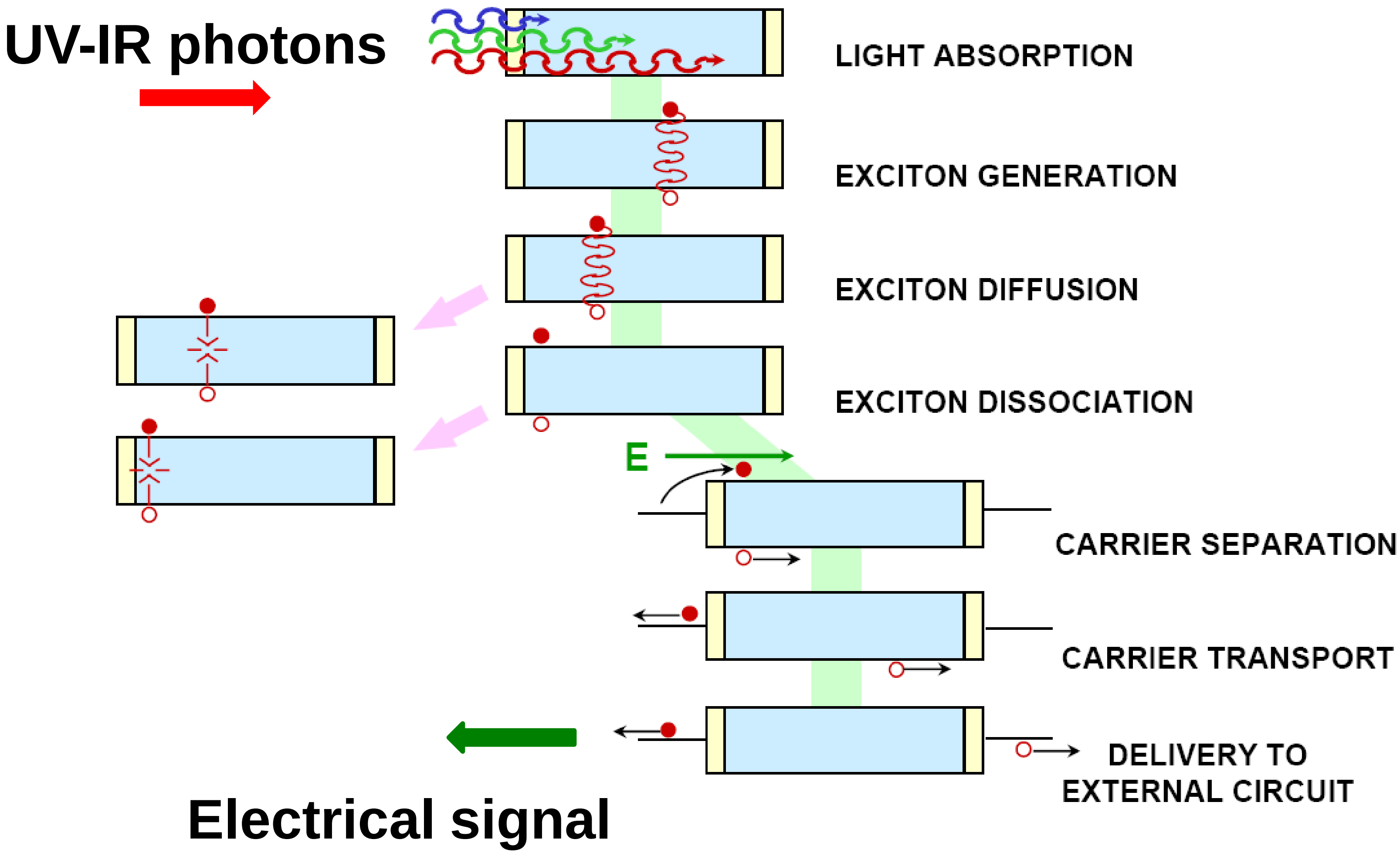
$$\Re = \frac{I_P}{P_0} = \frac{\eta q}{h\nu} \quad [\text{A/W}]$$

Organic Photodiodes: structures



K-J Baeg et al Adv. Mater. 2013, 25, 4267–4295

Organic Photodiodes



Organic Photodiodes

LIGHT ABSORPTION

EXCITON GENERATION η_g

EXCITON DIFFUSION J_{diff}

EXCITON DISSOCIATION η_d

CARRIER SEPARATION χ

CARRIER TRANSPORT η_c

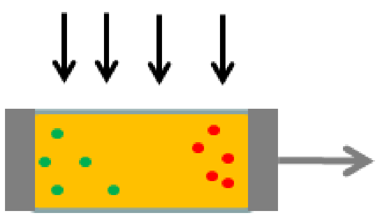
ASSUME η_g , η_d , χ independent of E-field

$$\Rightarrow \quad I \propto \eta_c(V)\, J_{diff}(E,z)$$

Organic X-Ray detectors: direct

DIRECT DETECTION

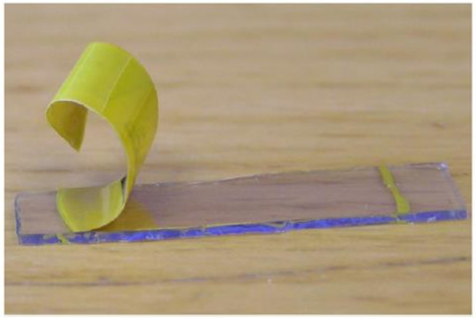
X ray beam

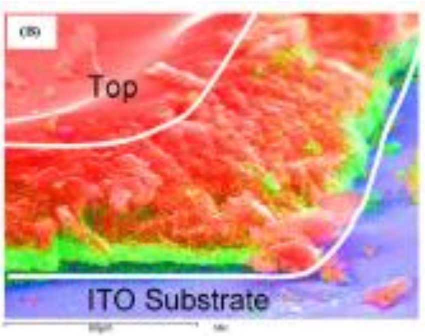


X photons to electrical charge carriers

Only few results about organic **direct** X-ray detectors:

Organic Thin Films





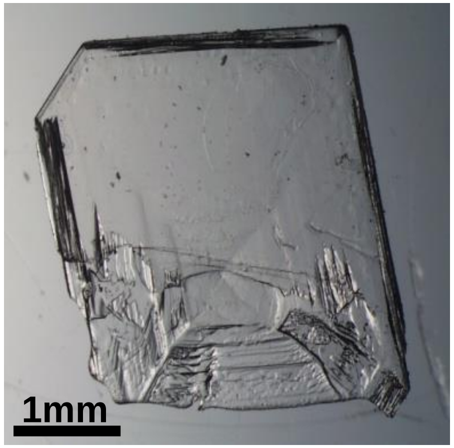
A. Intaniwet, P.Sellin et al., Journ. App. Phys., ***106****, 064513(2009).*

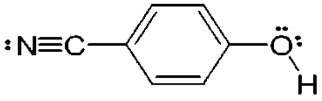
Non-radiative process:
X-, gamma photon → charge carriers

- X Trap dominated charge transport
- X Sensitivity limited by the small interaction volume

Motivation for organic single crystals as radiation detectors

investigate the potential of **organic semiconducting single crystals** for **X-ray direct detection** (i.e. the direct conversion of X-ray photons into an electrical signal) **at room temperature and in air**





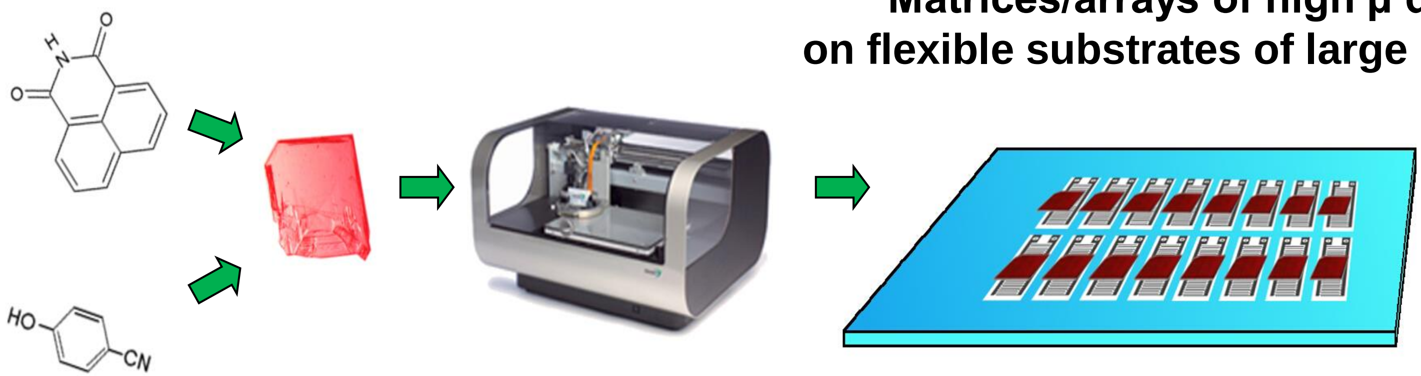
- ✓ low degradation in air and light
- ✓ large band gap
- ✓ High chemical purity - Low density of defects
- ✓ good charge transport/collection
- ✓ larger thickness than polymer/small molecule thin films (μm vs.nm)

Potentiality: Inkjet Printing of Solution-grown Organic Single Crystals

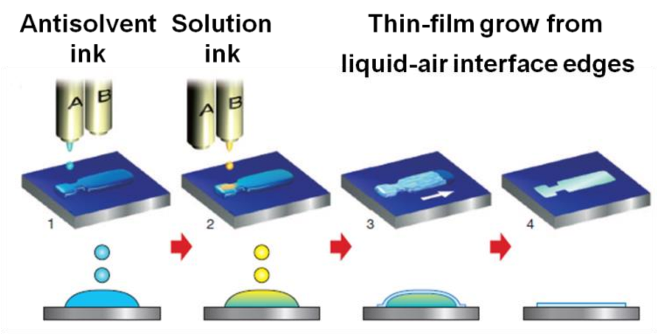
Solution-growth methods

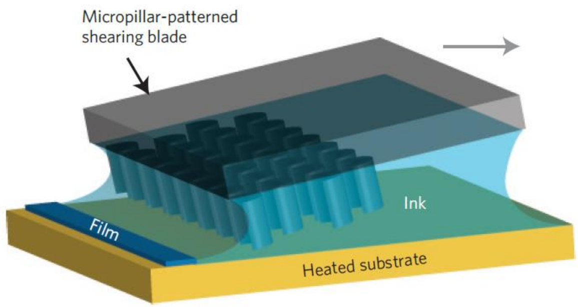
Application for Large Area Electronics

Matrices/arrays of high μ devices on flexible substrates of large dimensions

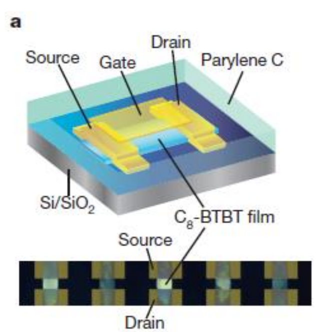


First proof of concept 2011: inkjet printing of 20×7 arrays of C_8-BTBT





Thin-film transistors with average carrier mobilities as high as 16.4 cm^2/Vs



*H. Minemawari et al., Nature, **475**, 364-367 (2011)*

Organic Semiconducting Single Crystals OSSCs

- ✓ Long range structural order (absence of grain boundaries) and well defined geometrical disposition of molecules
- ✓ High chemical purity
- ✓ Low density of defects

High ***μ*** → **30 cm²/Vs**

Long ***L***$_{ex}$ → **8 μm**

V. Podzorovet al., Pkys. Rev. Lett., ***93****, 086602(2004)*

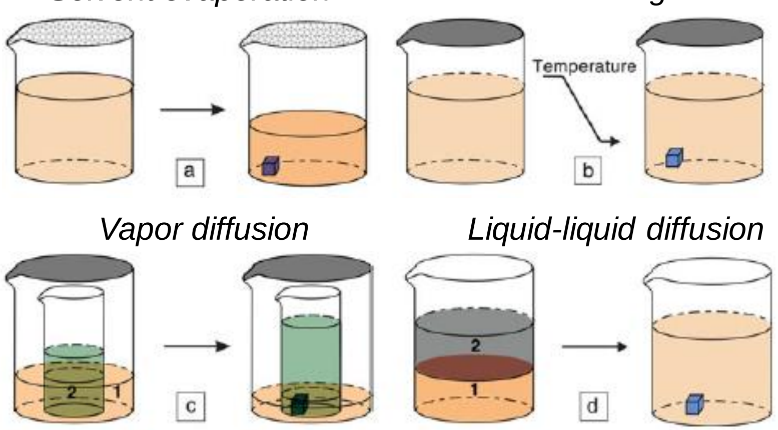
H. Najafov et al., Nat. Mat., ***9****, 938-943 (2010)*

High performance Organic devices

Solution-growth methods

Solvent evaporation *Slow cooling*

Vapor diffusion *Liquid-liquid diffusion*



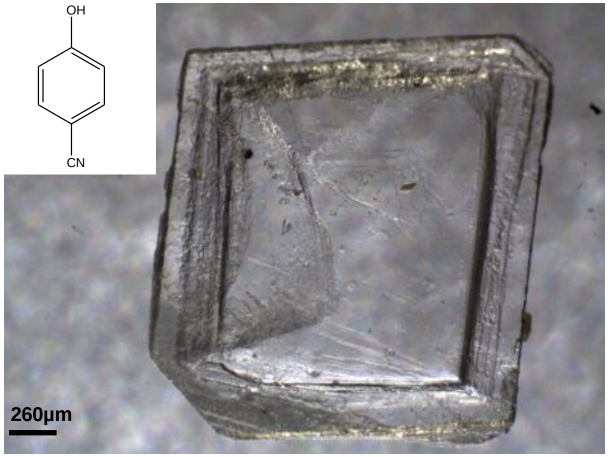
H. Jiang and C. Kloc MRS Bulletin, 38 (2013)

Bottom-up approach

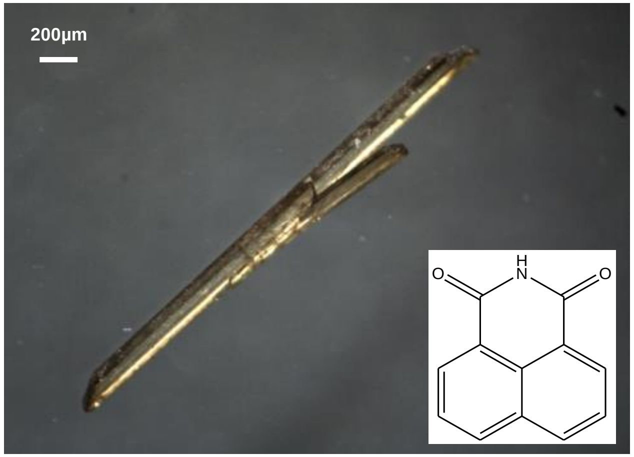
Development of Inks for direct growth by printing

Solution grown Organic Single Crystals tested as X-ray detectors

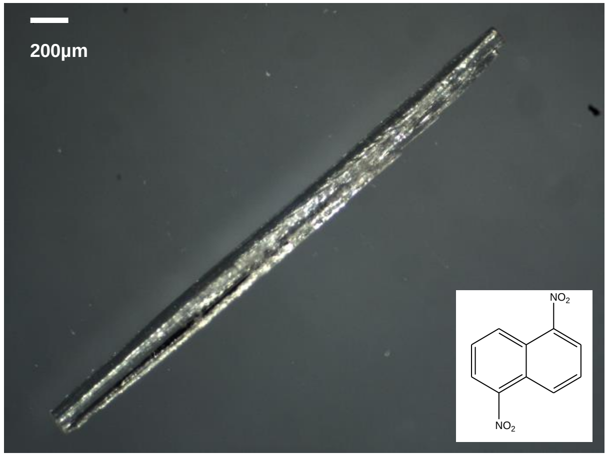
4HCB: 4-hydroxycyanobenzene



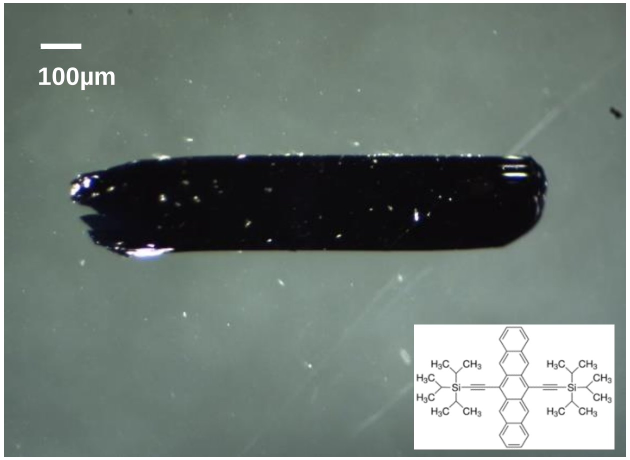
NTI(9F): 1,8-naphtaleneimide

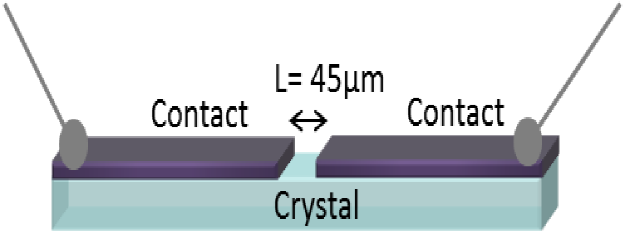


DNN(6F): 1,5-dinitronaphtalene



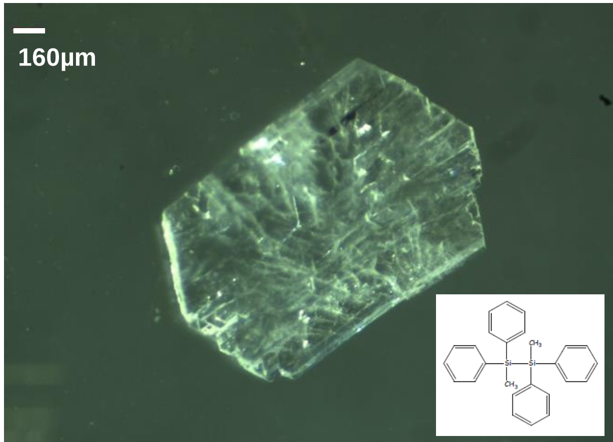
TIPS - pentacene





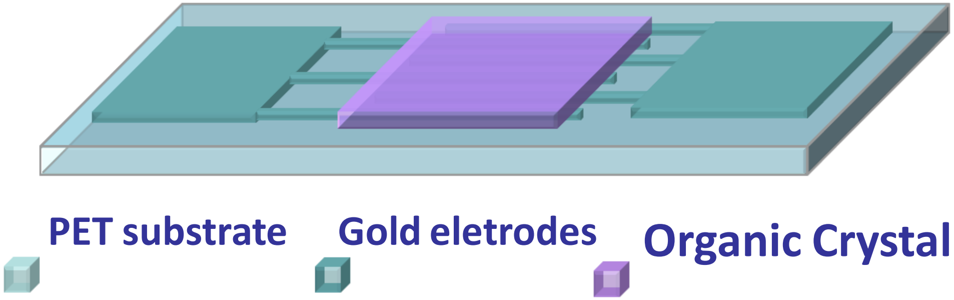
Co-Planar configuration

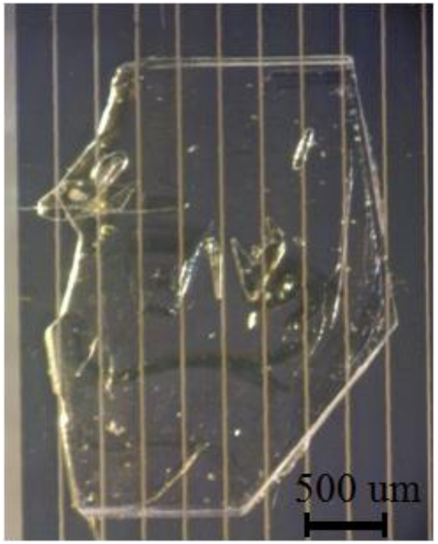
DMTPDS: 1,2-dimethyl-1,1,2,2-tetraphenyl-disilane

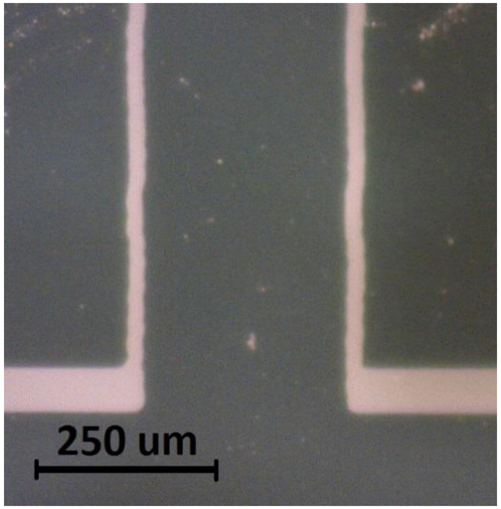


Interdigitated contacts

Ink-jet printing



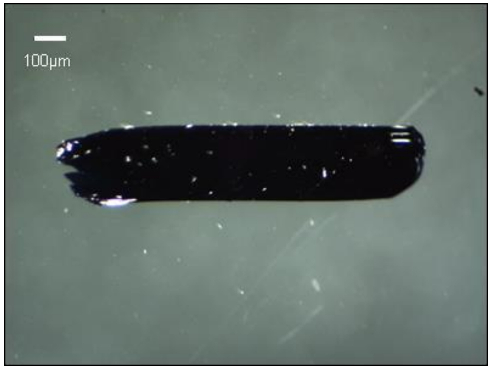




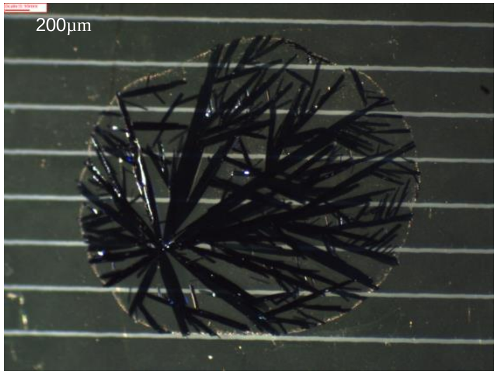
Comparison of X-ray response of TIPS pentacene crystals

X-rays Photoresponse of 3 different crystalline forms:

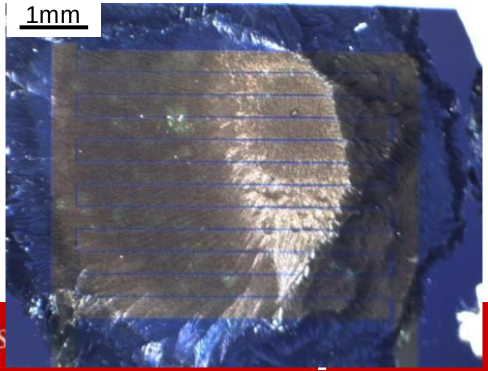
Self-standing-crystals
(~100 micron thick)



Micro-crystals
(~10 micron thick)

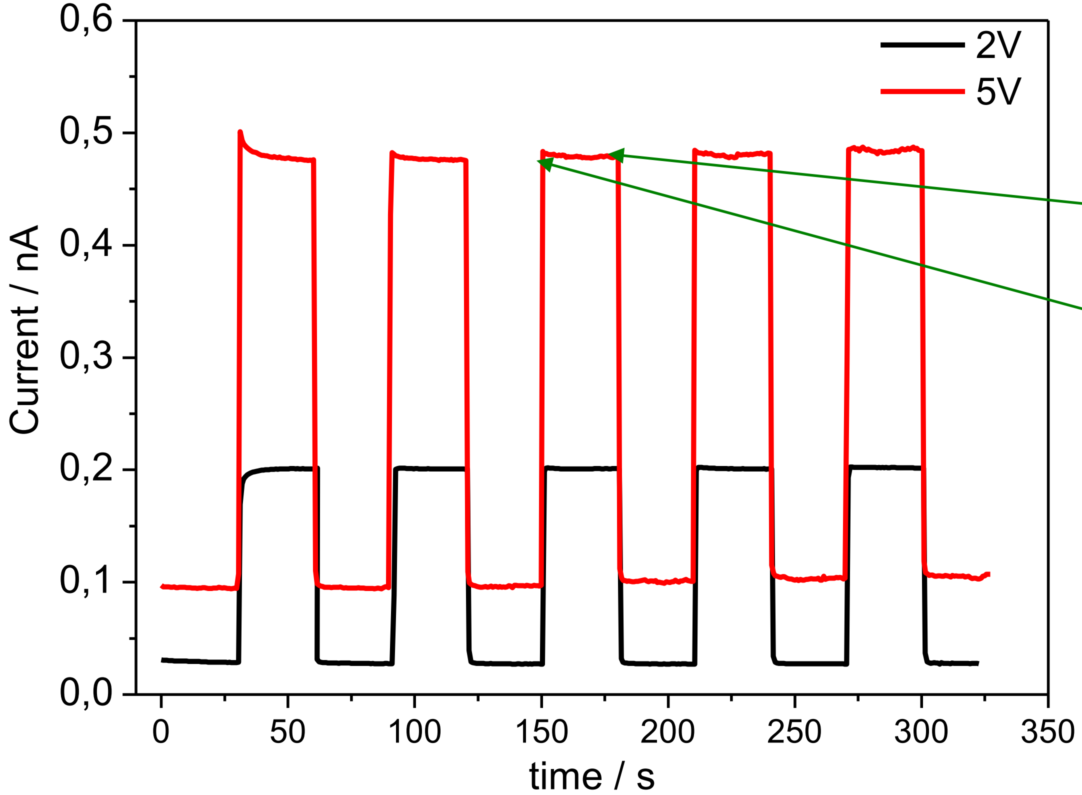


Nano-crystals
(~100 nm thick)



Bottom interdigitated metal electrodes

Direct X-ray response: switching behaviour



DNN crystal

V_{Mo}=35keV

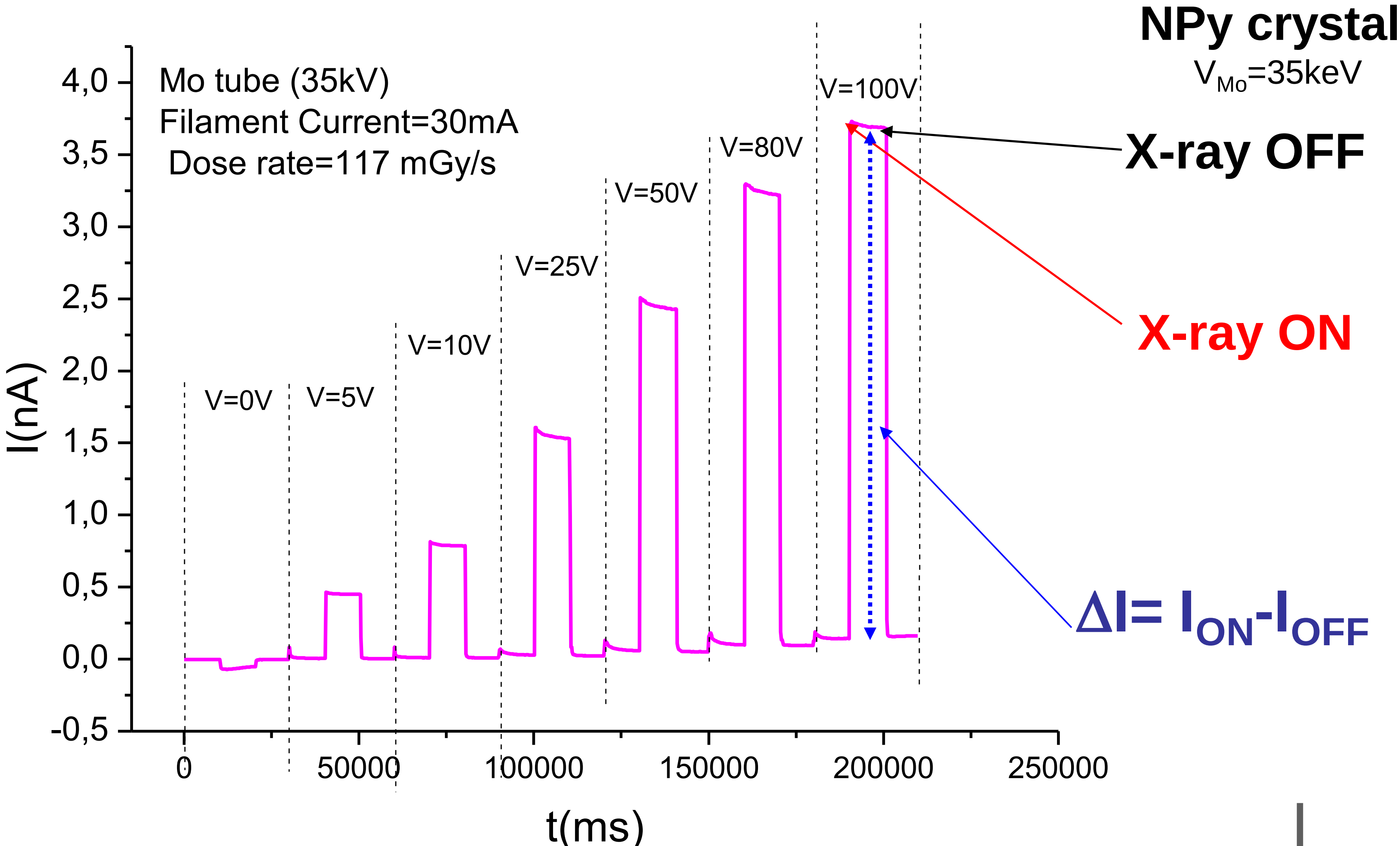
dose rate 170mGy/s

X-ray OFF

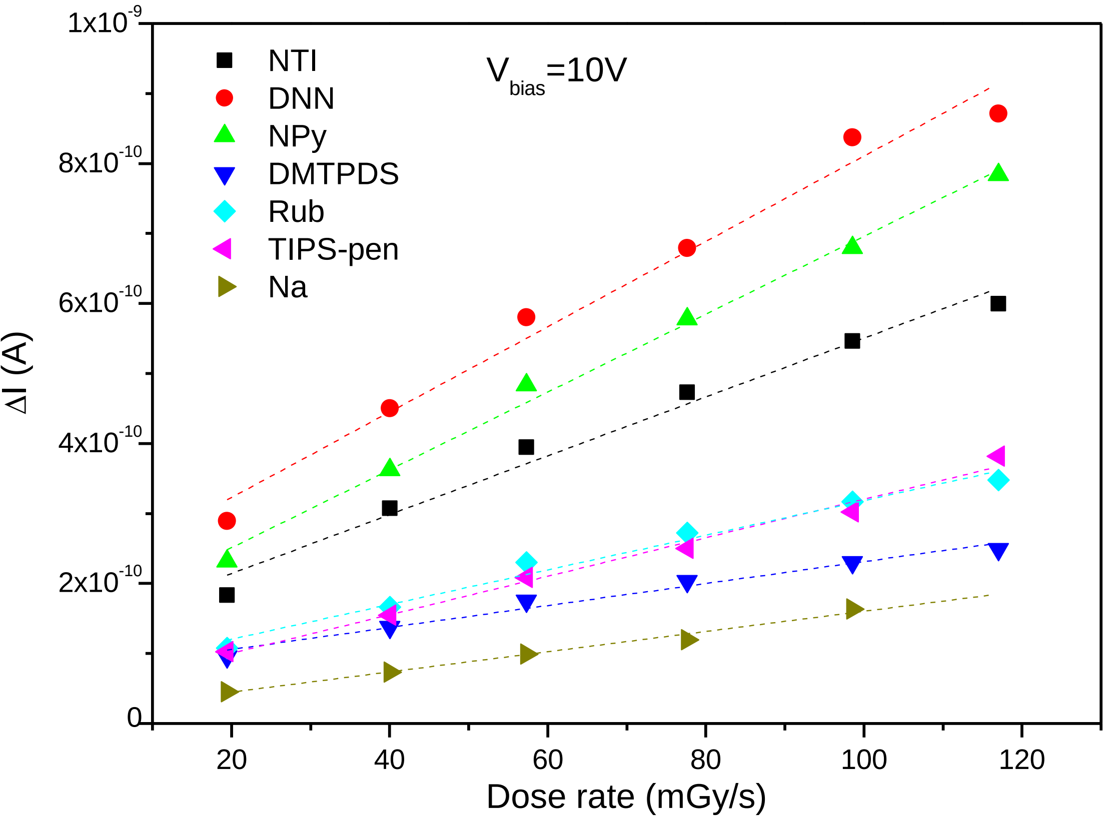
X-ray ON

Low operating voltage (<5V)
@ room temperature and in air

X-ray response: stability



X-ray linear response

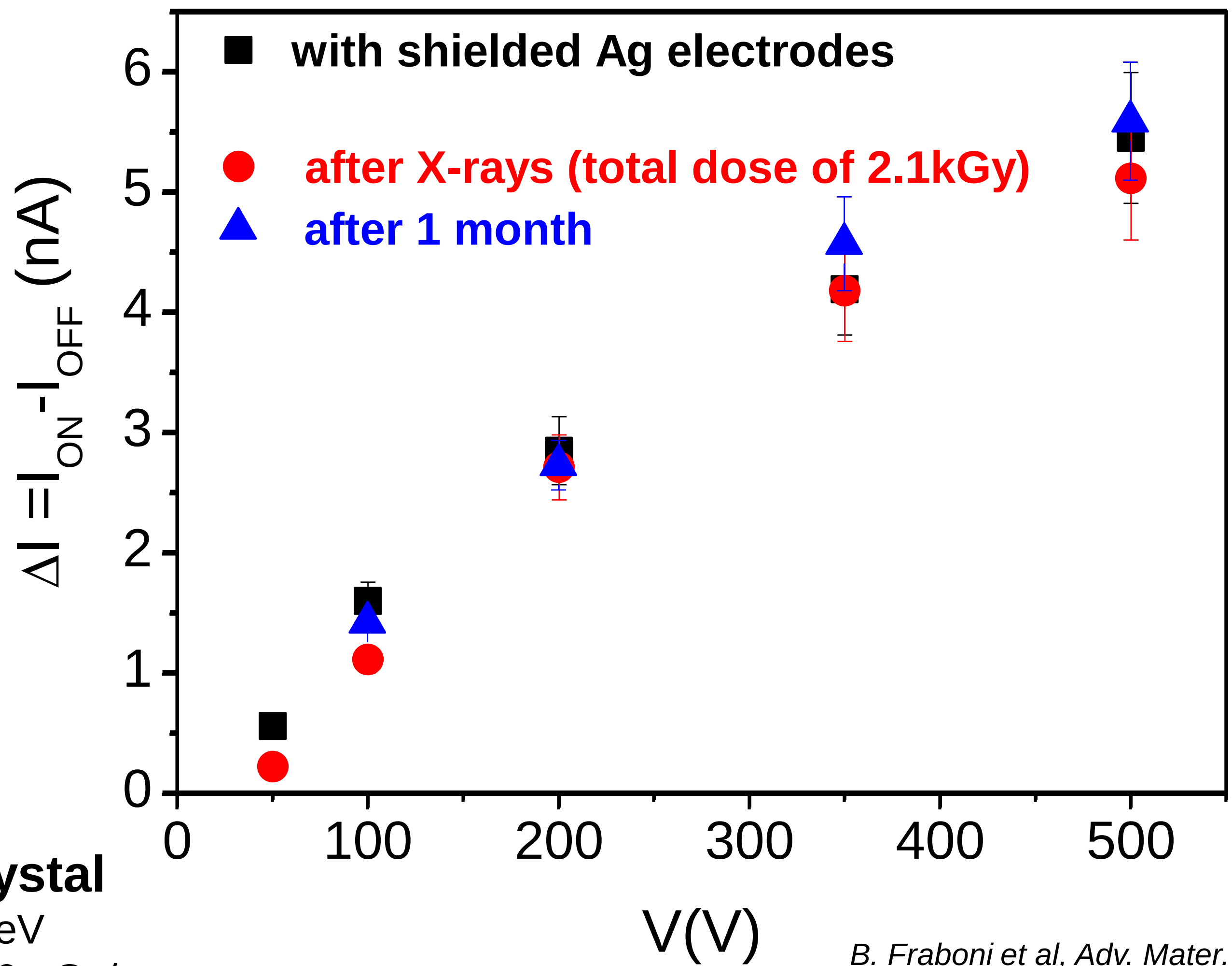


Linear response to increasing X-ray dose rate

Sensitivity

$$S = \frac{I_{on} - I_{off}}{Dose\ rate}$$

X-ray response: reproducibility

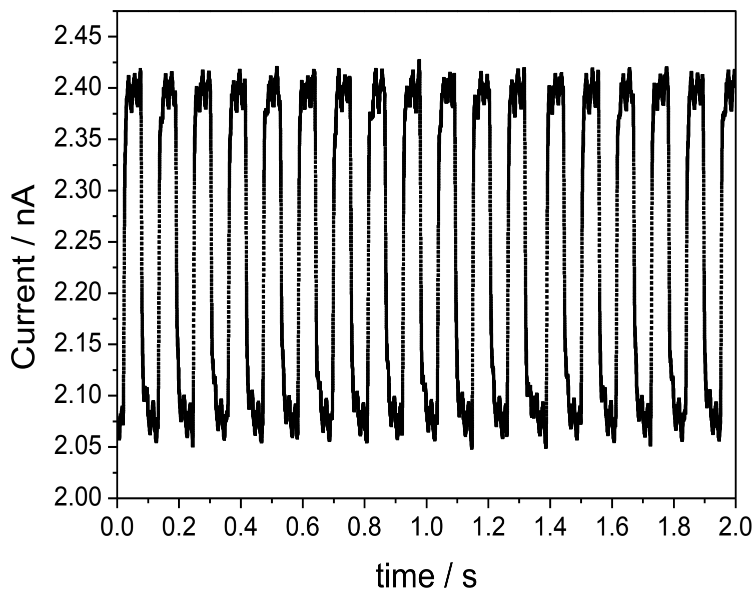


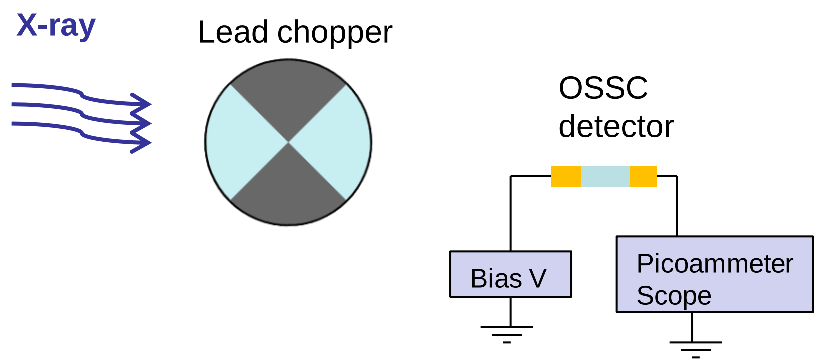
4HCB crystal
V_{Mo}=35keV
dose rate 170mGy/s

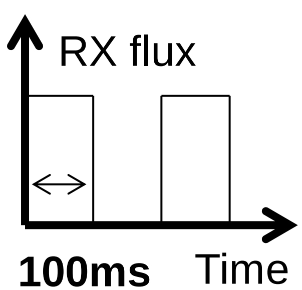
B. Fraboni et al, Adv. Mater. (2012)

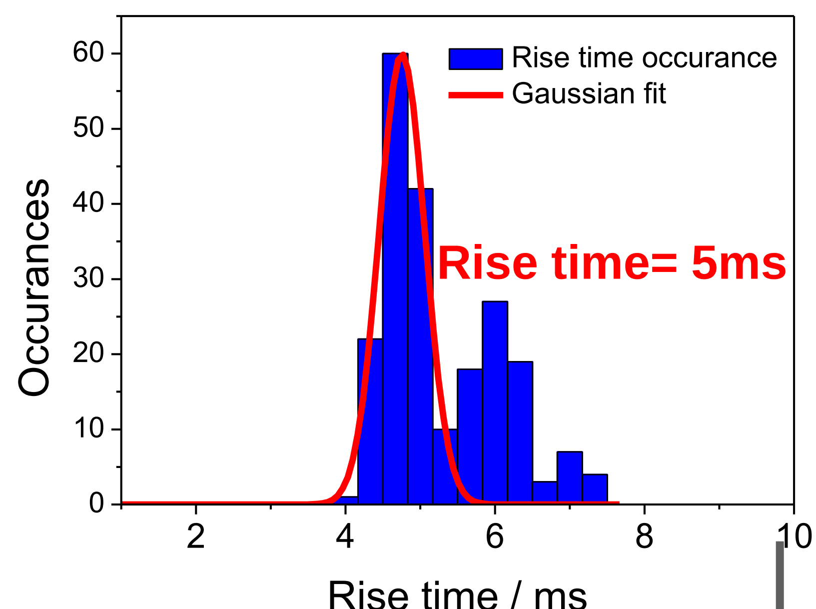
Time response - I

4HCB crystal, @20V
Synchrotron beam (10 keV, dose rate 40mGy/s)

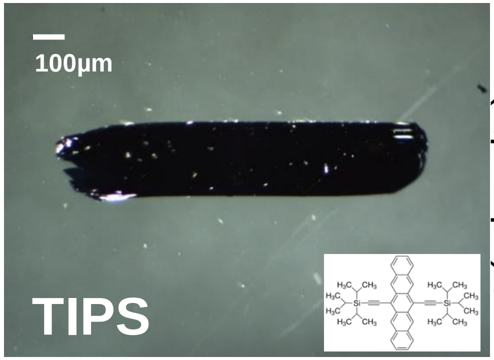


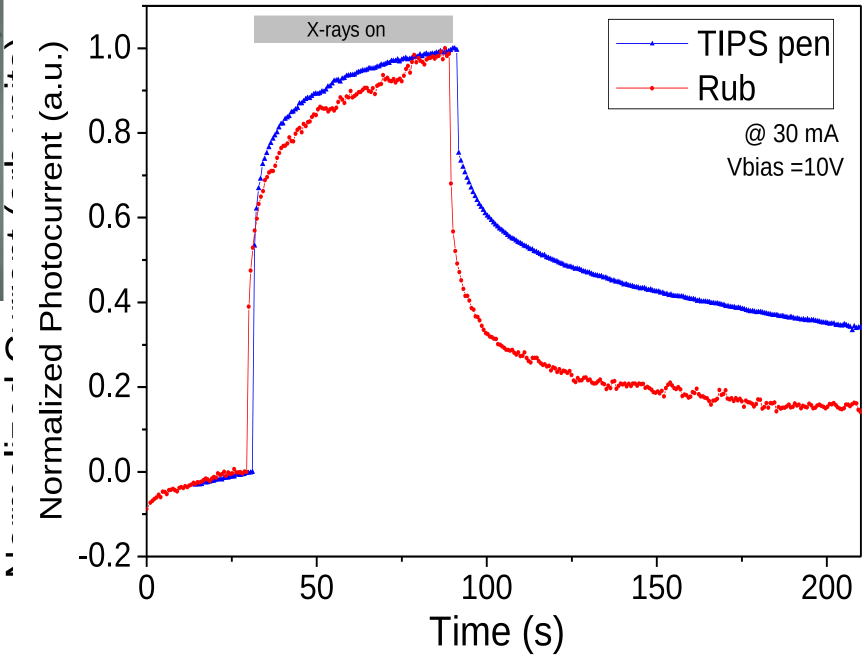


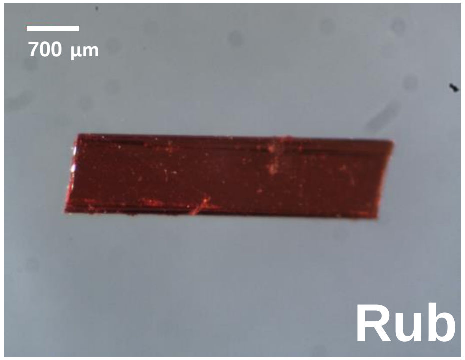




Time response - II







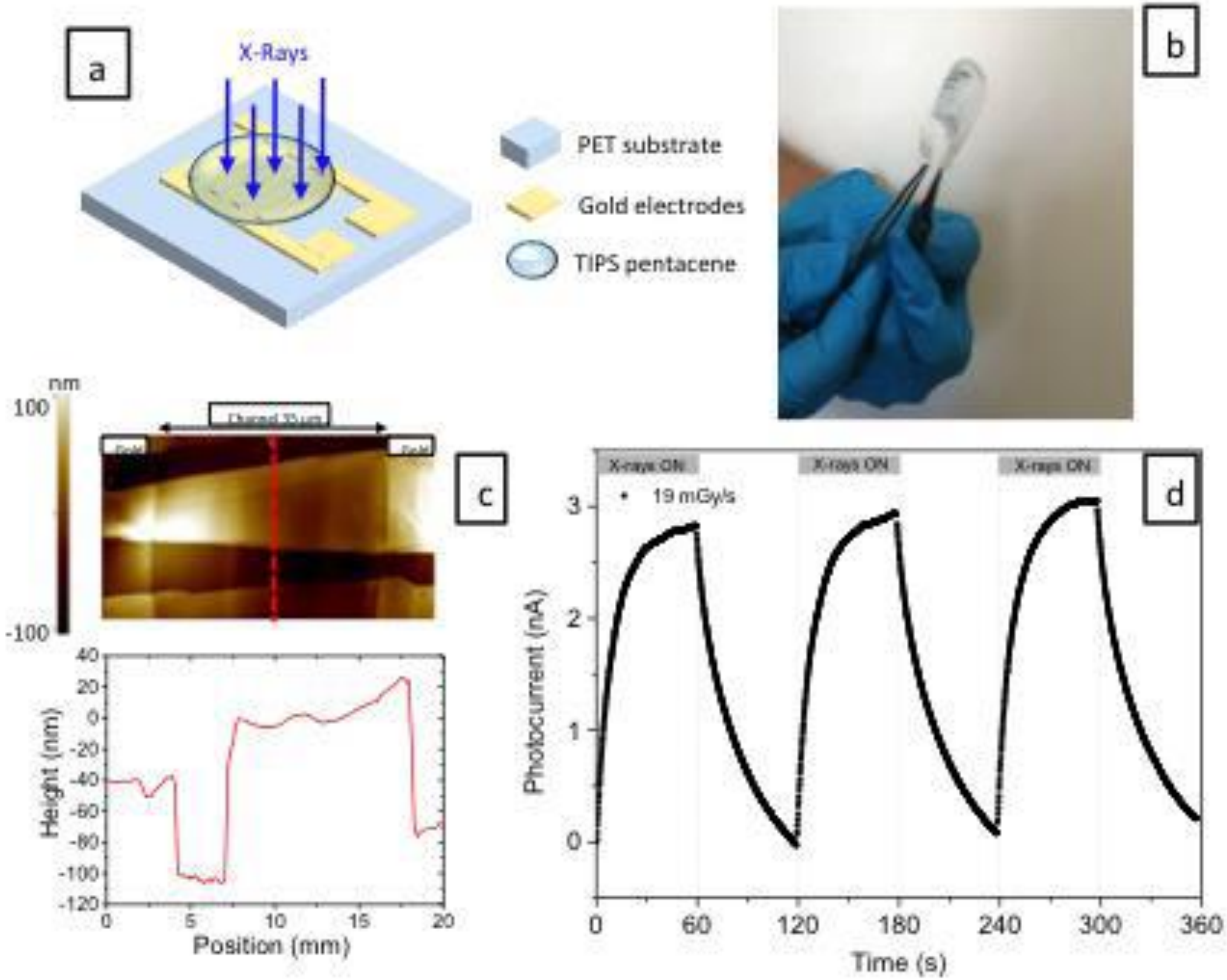
TIPS pentacene

- State-of-the-art material for optoelectronic applications (DNN, NTI, 4HCB < μ < Rub)
- Even **slower decay transient** than Rub

Rubrene

- State-of-the-art OSSCs for optoelectronic applications (highest recorded mobility ($\mu \approx 20 cm^2/Vs$)
- Poor (and slow) radiation detector performance

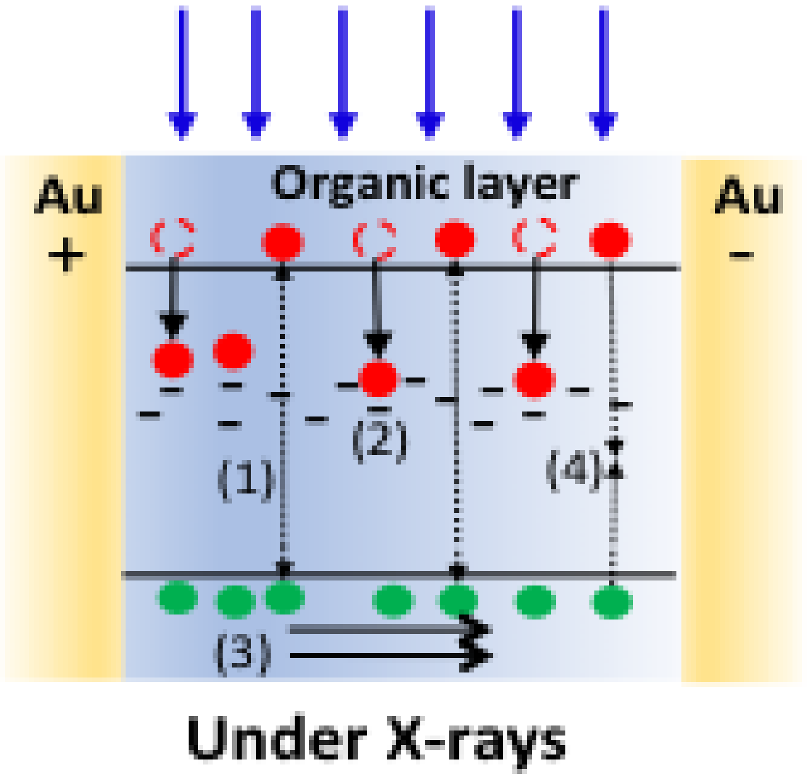
Printed single pixel response to X-rays



Intrepretation model:
ionizing radiation-organic crystals

under X-ray irradiation:

- Additional **electrons and holes are generated**.
- **Holes drift** along the electric field to the collecting electrode
- **electrons remain trapped** in deep trap states (typical in organics).
- To guarantee charge neutrality, holes are continuously emitted from the injecting electrode. As a consequence for **each e-hole pair created, more than one hole contributes to the photocurrent**



$$\Delta I_{PG}=G\ I_{CC}$$

G = photoconductive gain

Kinetic Model

1) $\Delta I_{PG} = Wh\rho_X \mu E$

2) $\frac{\partial \rho_X(t)}{\partial t} = \frac{\Phi nq}{Ah} - \frac{\rho_X(t)}{\tau_r(\rho_X)}$

3) $\tau_r(\rho_X) = \frac{\alpha}{\gamma}\left[\alpha \ln\left(\frac{\rho_0}{\rho_X}\right)\right]^{\frac{1-\gamma}{\gamma}}$

E=V/L - electric field
W - the active width of the interdigitated structure.

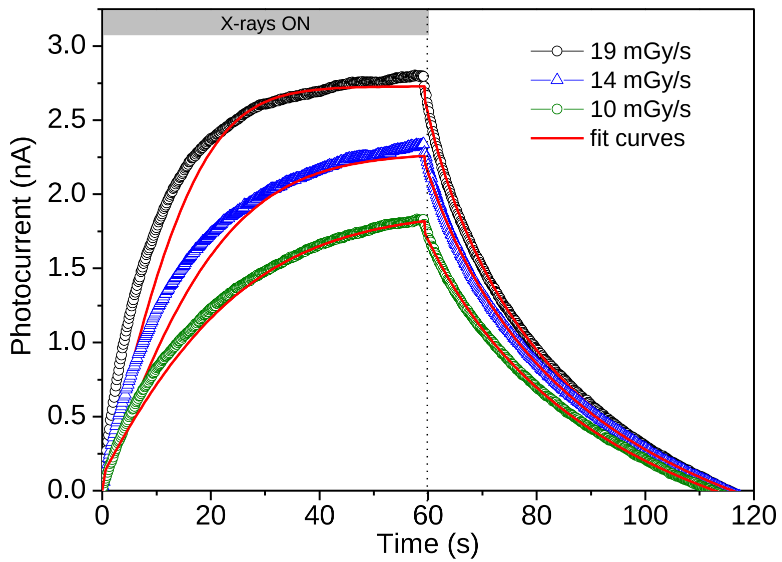
ρ_X – X-ray induced carrier concentration

τ_r = recombination time of charge carriers

During irradiation $\rho_X = \frac{\Phi nq}{Ah} \cdot \tau_r(\rho_X) \cdot \left[1 - e^{-t/\tau_r(\rho_X)}\right]$

After irradiation irradiation (D = 0) $\rho_X = \rho_0 e^{-t^\gamma/\alpha}$

Fitting experimental data



Dynamics of X-ray response and consequences on detector operation. a) Experimental and simulated curves of the dynamic response of the detector for three different dose rates of the radiation. The experimental data refer to 60 s of exposure of the device (*W* = 48 mm, *L* = 30 µm, bias 0.2 V) to a synchrotron 17 keV X-ray beam, with a bias of 0.2 V.

well reproduces the saw-tooth shape of three experimental set of data,

n = 1400
α = 7.9 s
γ = 0.61
$\rho_0 = 3.7 \times 10^{-5}$ C cm^{-3}

L. Basiricò et al. paper under review, 2016

Carriers lifetime

$$\tau_r = \frac{\alpha}{\gamma}\left[\alpha \ln\left(\frac{\rho_0}{\rho_X}\right)\right]^{\frac{1-\gamma}{\gamma}} = 29.4 \text{ s}$$

Transit time

$$\tau_t = \frac{L^2}{V\mu} = 1.1 \text{ ms}$$

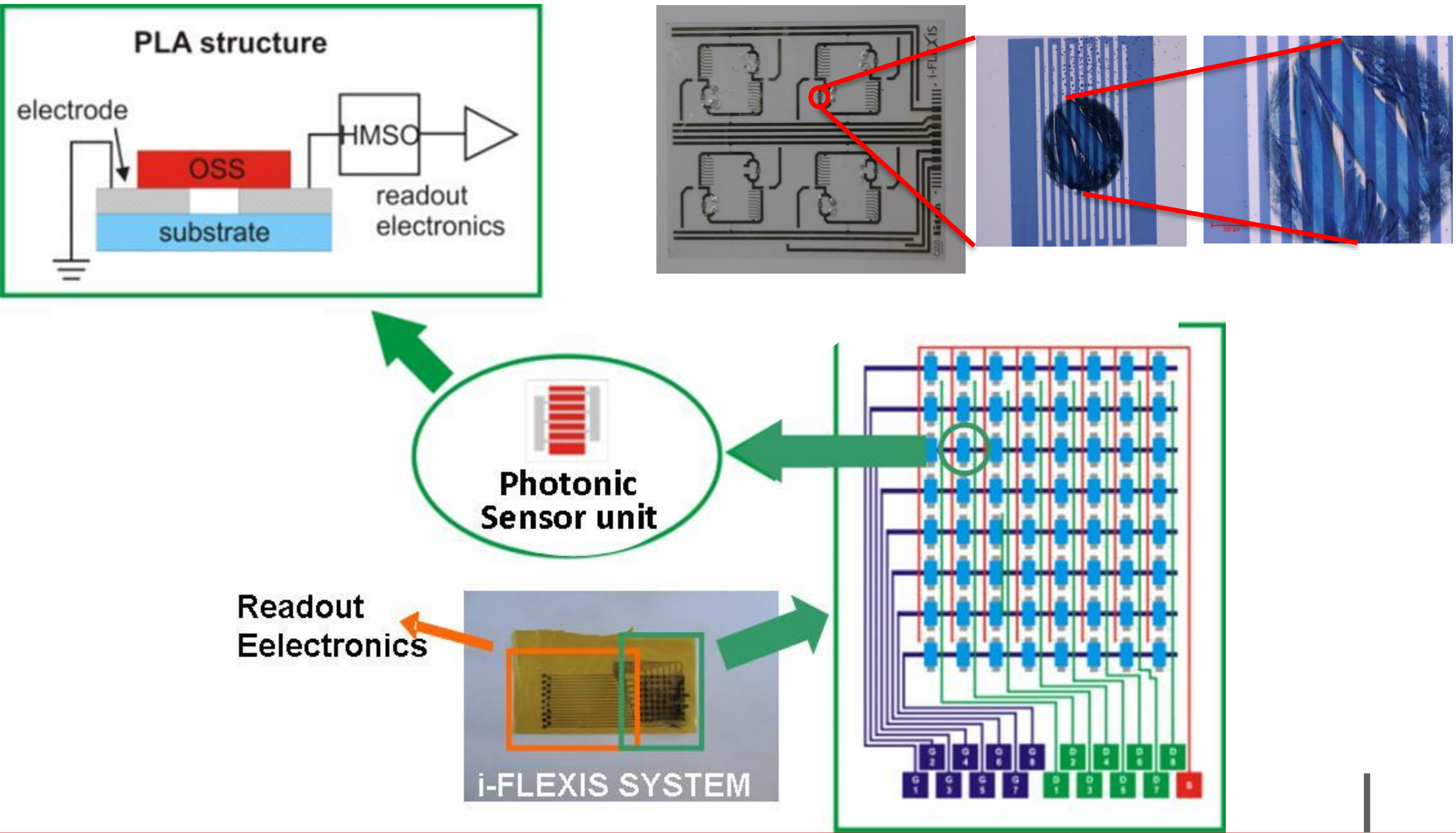
$$G = \frac{\tau_r}{\tau_t} = \frac{29.4}{1.1 \times 10^{-3}} = 2.6 \times 10^4$$

Conclusions - I

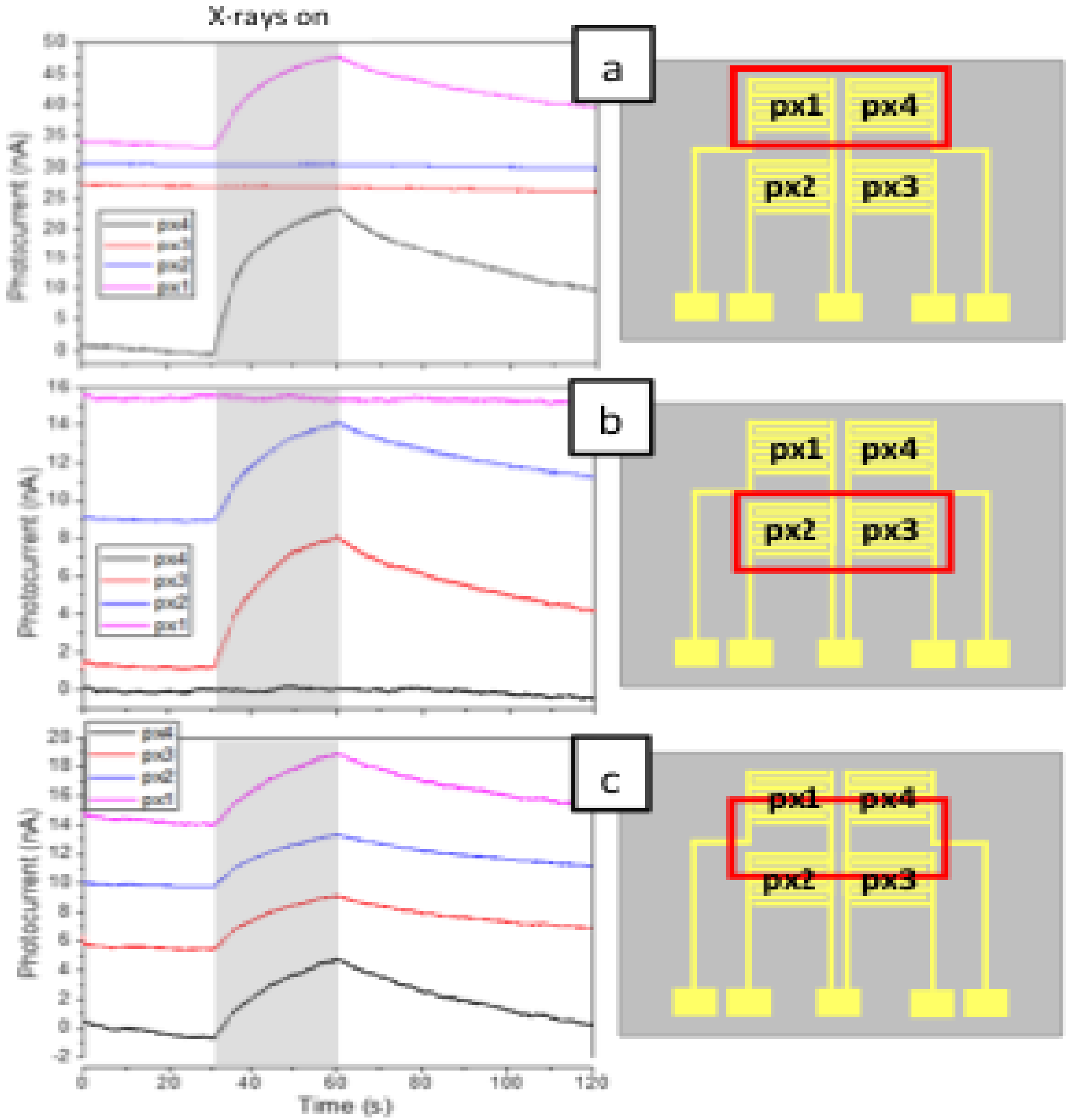
- Organic semiconducting single crystals (solution-grown) can be used for solid state radiation detectors, opening the way to novel detecting device architectures and applications (direct, linear, room temperature).
- Robust and reproducible operation, no severe degradation observed after a cumulative exposure to 2.1 kGy of X-rays
- Still a great deal to understand on the correlation between their molecular structure (easily varied thanks to solution growth), photoconversion efficiency and electronic transport properties.

Very low operating voltages (<5V)

Integrated sensor structure



Printed matrix (2x2 pixel) response to X-rays



Integrated Health sensor structure:
hardware readout implementation

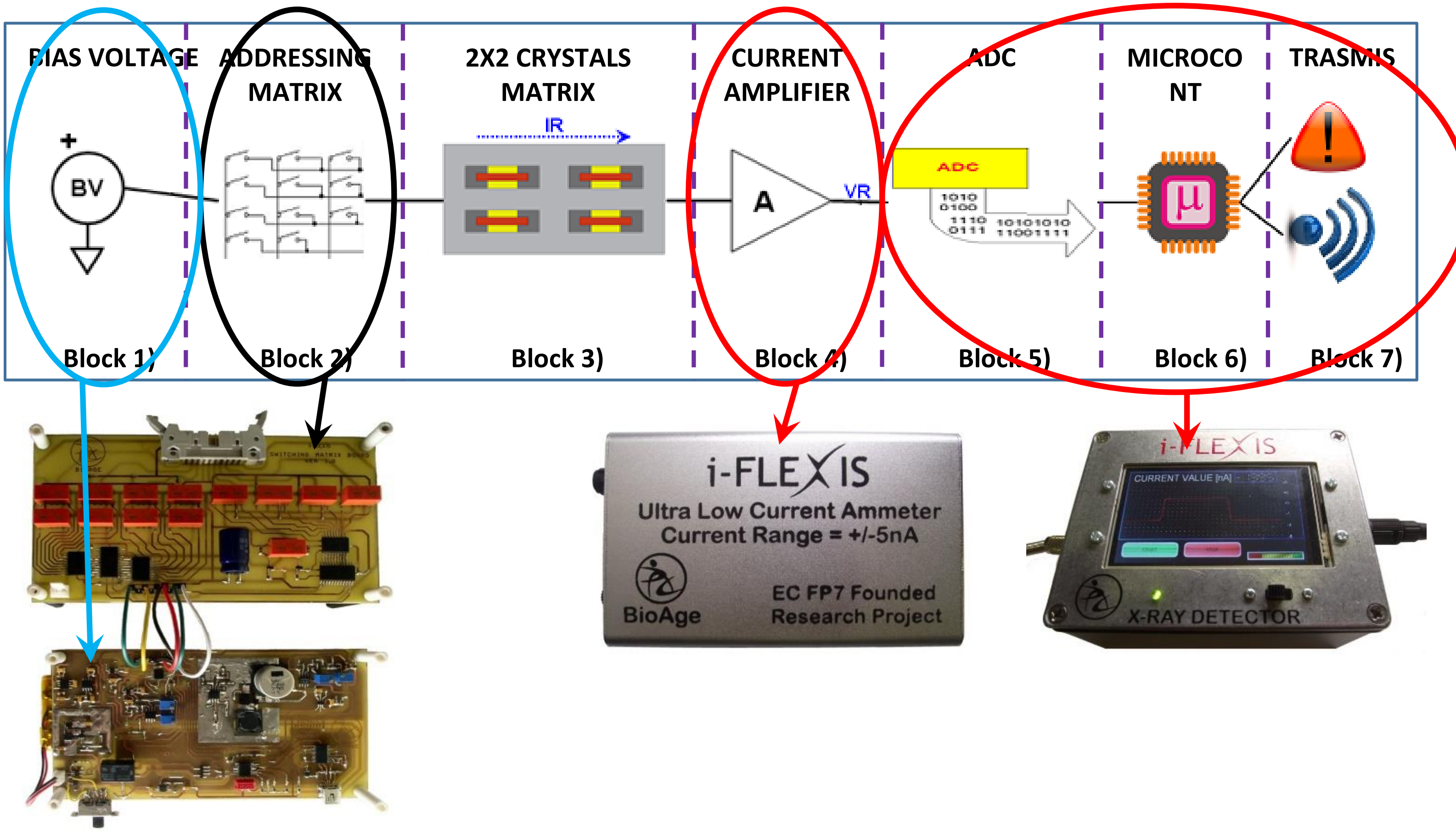
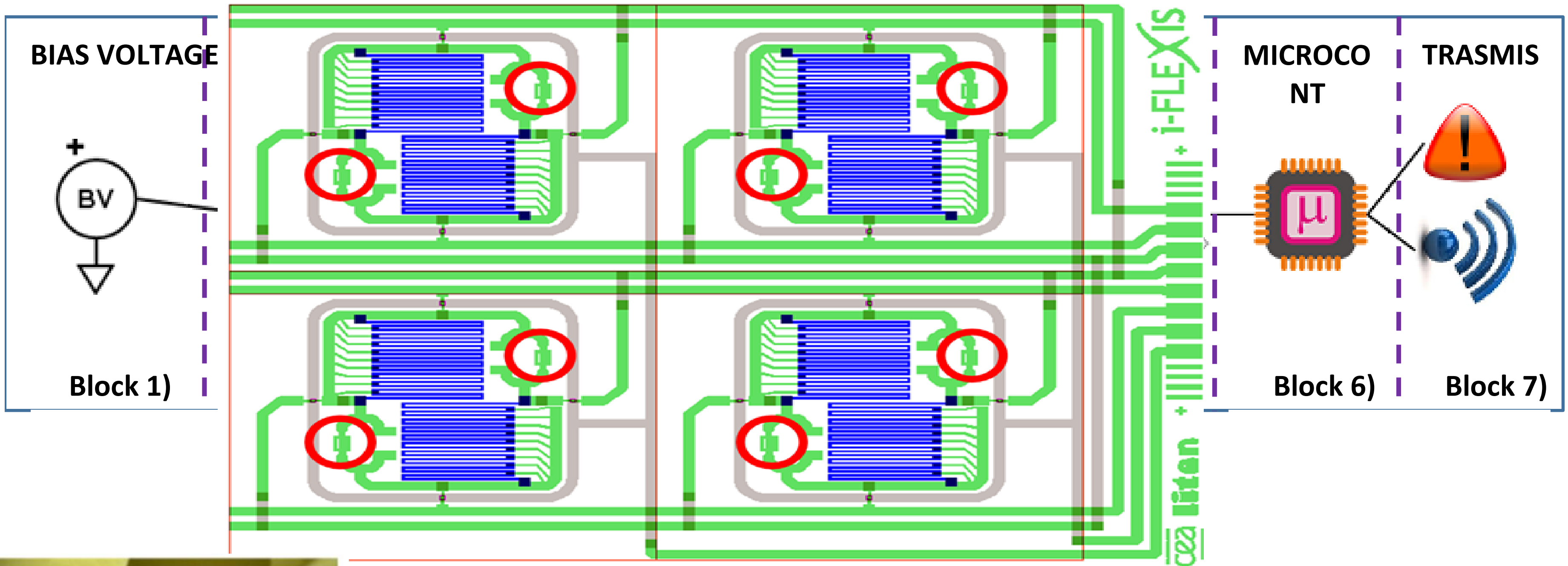
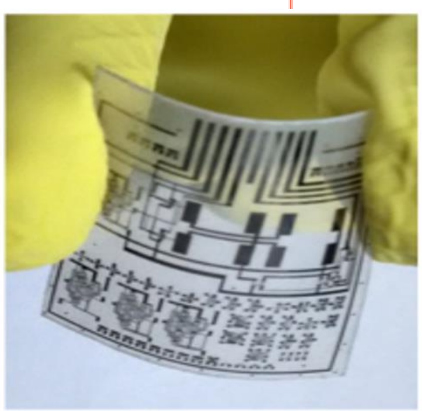


Fig.12)

Integrated Health sensor structure:
flexible readout implementation





First generation of active backplanes in organic and oxide electronics was developed on glass and foil

Integrated Health sensor structure:
portable and flexible readout implementation

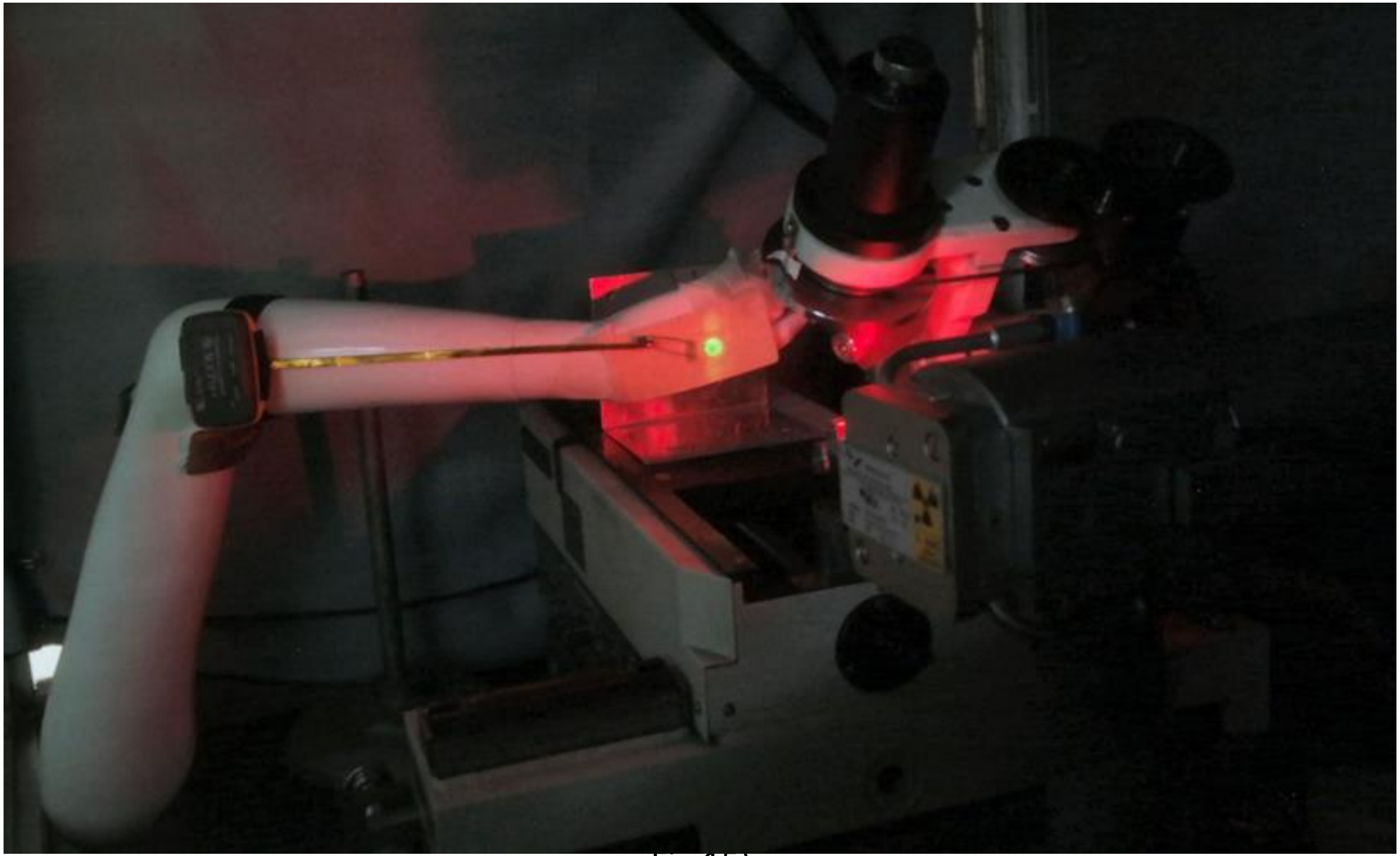
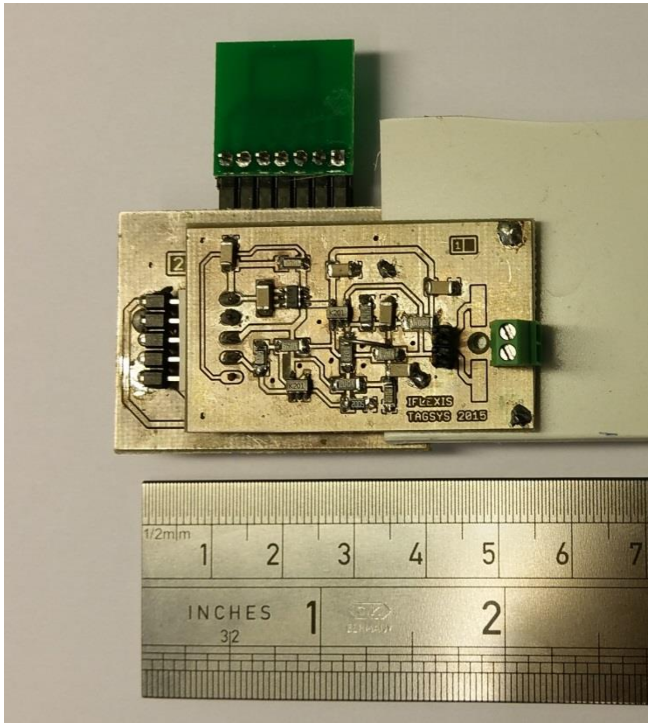


Fig.15)

Integrated RFID Tag structure



hardware implementation

Conclusions - II

- Organic semiconductors can offer novel functionalities that open the way to innovative device architectures and applications

- Bottom up vs. top down fabrication and design processes.

- Ease of integration with other electronic materials and devices (hybrid approach – possibly the best way to go)

- Still a great deal to understand, discover and invent!

Acknowledgements

www.iflexis.eu

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Thank you for your attention