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# Large-area X-ray detectors based on Organic and Perovskite films

**Andrea Ciavatti**

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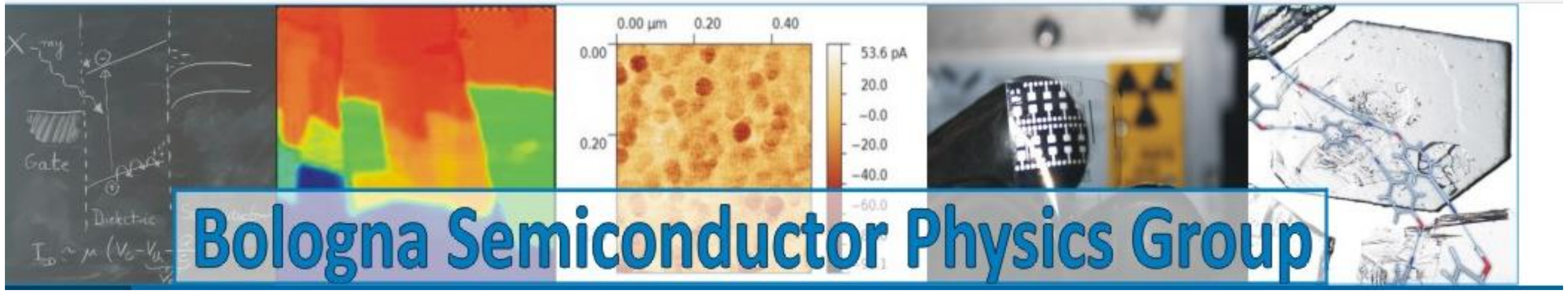
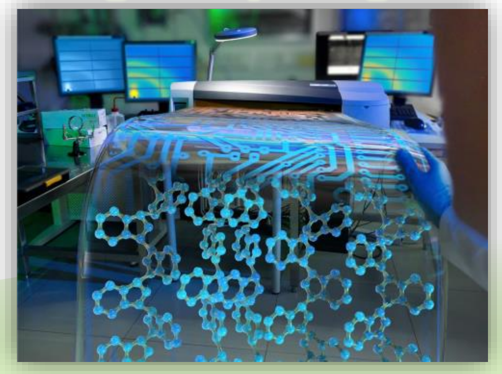
[1] University of Bologna / Physics, Department of Physics and Astronomy, Bologna, Italy
[2] National Institute for Nuclear Physics INFN, Section of Bologna, Bologna, Italy
[3] ID16B – ESRF: The European Synchrotron, Grenoble, France
[4] PoliMi, Istituto Italiano di Tecnologia, Center for Nano Science and Technology, Milano, Italy

# SEMICONDUCTOR PHYSICS GROUP @
# DEPARTMENT OF PHYSICS AND ASTRONOMY-UNIVERSITY OF BOLOGNA



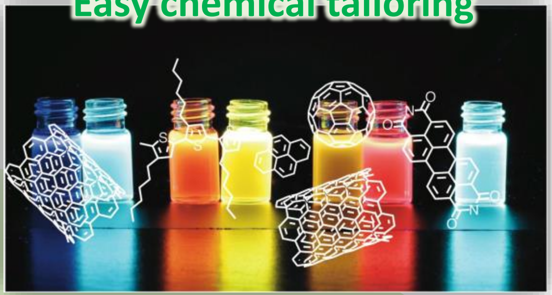

# ORGANIC-HYBRID SEMICONDUCTORS FOR IONIZING RADIATION DETECTION - ADVANTAGES

Low-cost large-area printing techniques

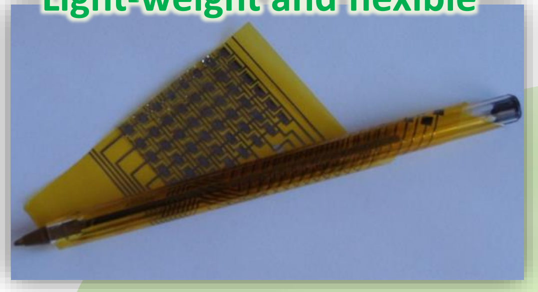


Wearable

Easy chemical tailoring



Light-weight and flexible

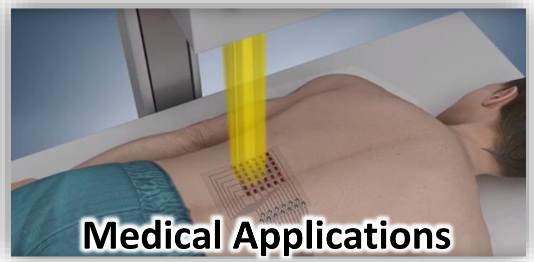


New generation of
**low cost**, **low power supply** and **mechanical flexible**
**Thin** and **comformable** sensor panels and patches

Cultural Heritage

Space Missions

Airport Security



Medical Applications

Nuclear wastes management

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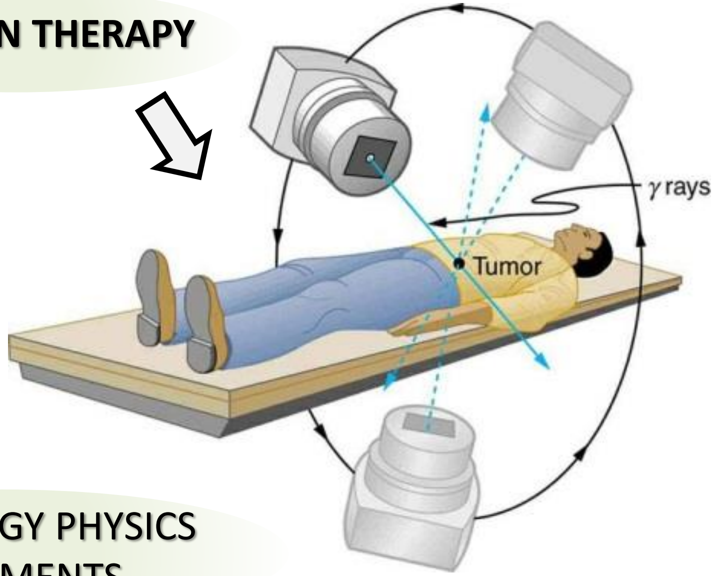
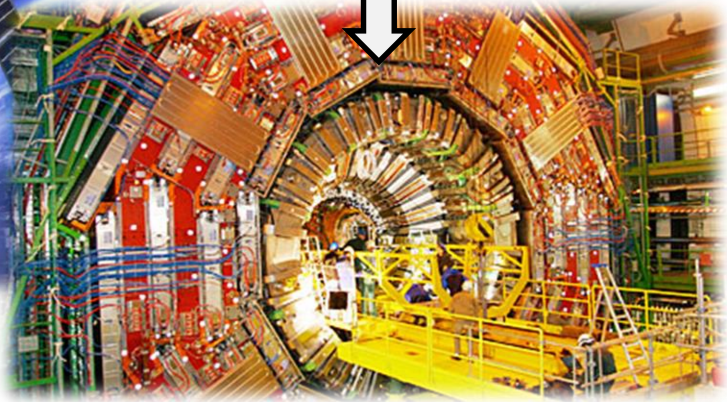
# THIN FILM AND LARGE AREA: WHERE?

SPACE MISSIONS

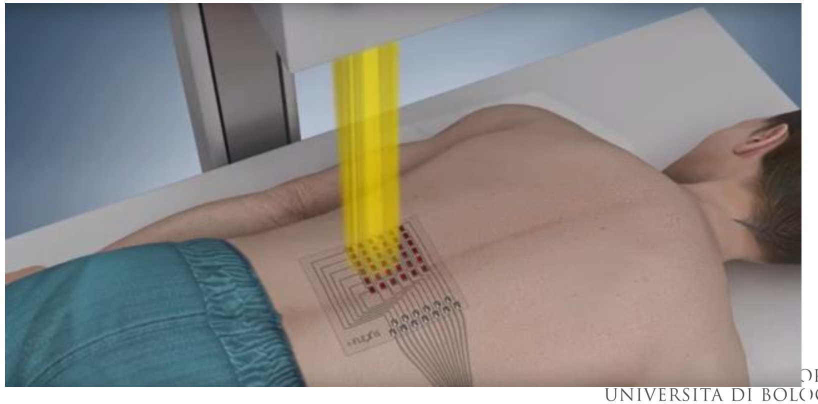
RADIATION THERAPY




HIGH ENERGY PHYSICS EXPERIMENTS



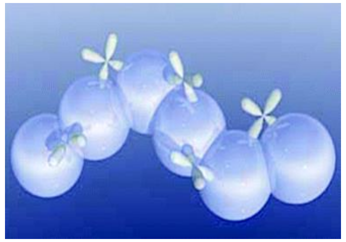
- **Light-weight** for limited amount of materials
- Possibility to **cover large surfaces** at low cost
- **Real-time** beam monitoring
- **Radiation hard** to strong fluxes due to weak radiation abortion
- **In-situ** dose evaluation thank to conformability to human tissues



# FLEXIBLE LARGE AREA ELECTRONICS: MATERIAL PLATFORMS

## High Mobility Oxide Semiconductors

e.g. $Ga_xIn_yZn_zO$

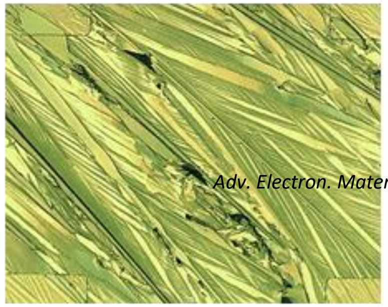


Physical/solution deposizion
$\mu$ = 10 – 50 cm$^2$/Vs

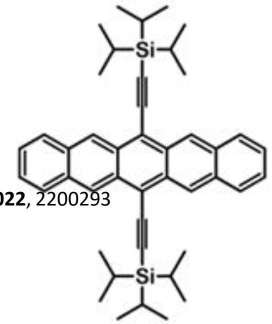
*T. Cramer et al., Sc.Adv.,* ***4****, 63 (2018)*
*C. Bordoni et al., APL Mater.,* ***12****, 031106 (2024)*

## Organic Semiconductors

e. g. TIPS pentacene



*Adv. Electron. Mater.* **2022**, 2200293



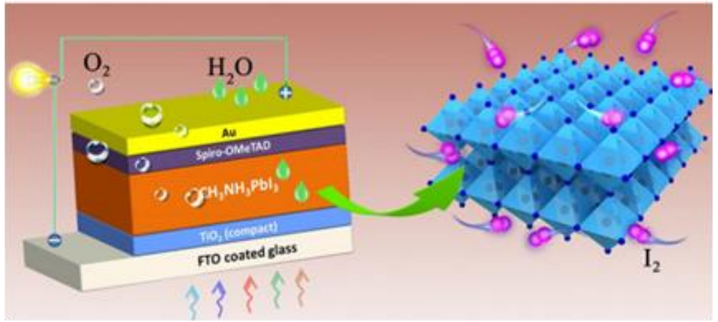

*A. Tamayo et al., Adv. Electron. Mater. 2200293 (2022)*

solution deposition
$\mu$ = 1 cm$^2$/Vs

*L. Basiricò et al. Nature Comm* ***7****, 13063 (****2016****)*
*I.Temino et al., Nature Comm.* ***11****, 235 (****2020****)*

## Perovskites

e. g. $MAPbI_3$




solution deposition
$\mu$ = 1-600 cm$^2$/Vs

*A.Ciavatti et al., Adv. Funct. Mater.* ***29****, 1902346 (****2019****)*

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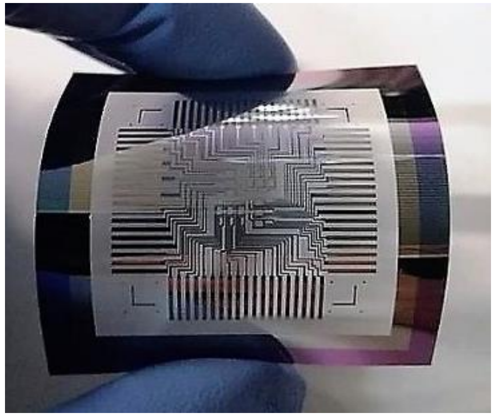
# Radiation sensitive OXide Field Effect Transistors (ROXFETs)



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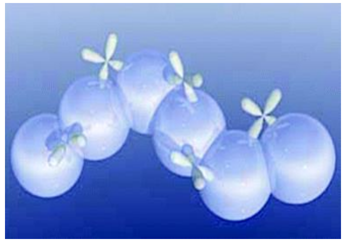

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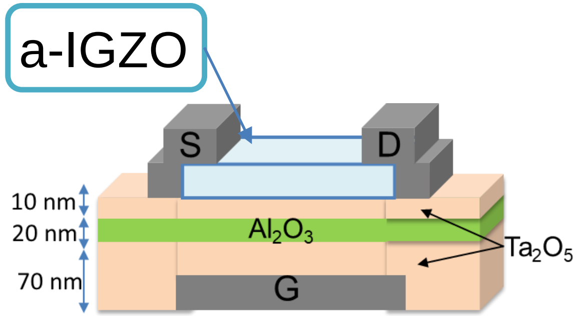
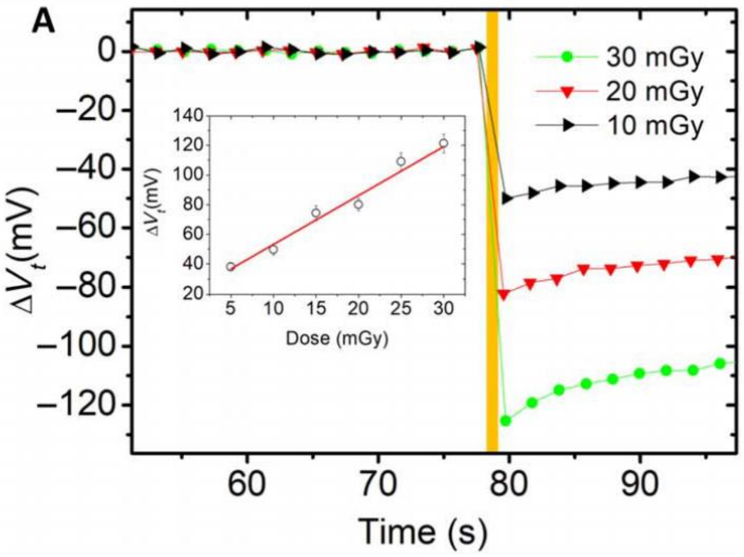


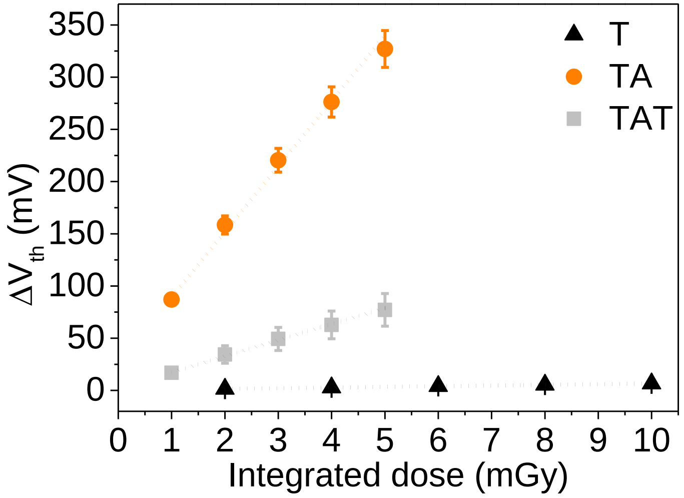

$Ta_2O_5$ (κ=26, Z=73)

$Al_2O_3$ ($E_g$>8 eV)

$s_{ROXFET}$ = 63±2 V/Gy

($s_{RADFET}$ < 0.30 V/Gy)

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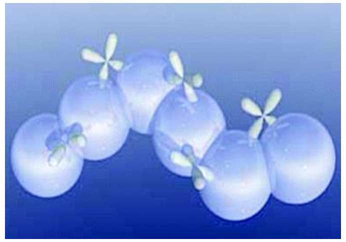

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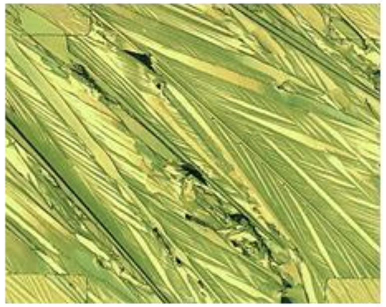

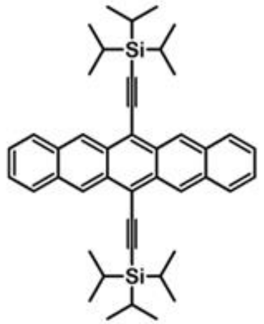


*A. Tamayo et al., Adv. Electron. Mater. 2200293 (2022)*

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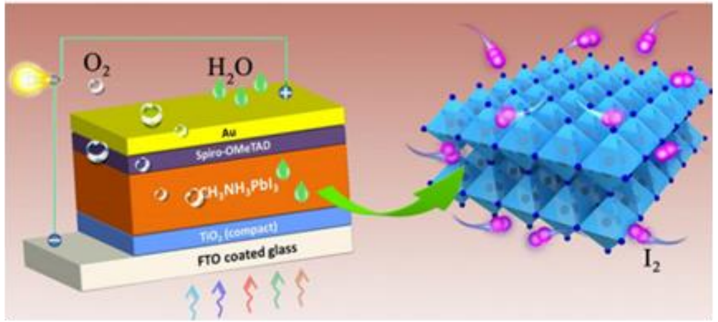


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*A.Ciavatti et al., Adv. Funct. Mater. **29**, 1902346 (**2019**)*

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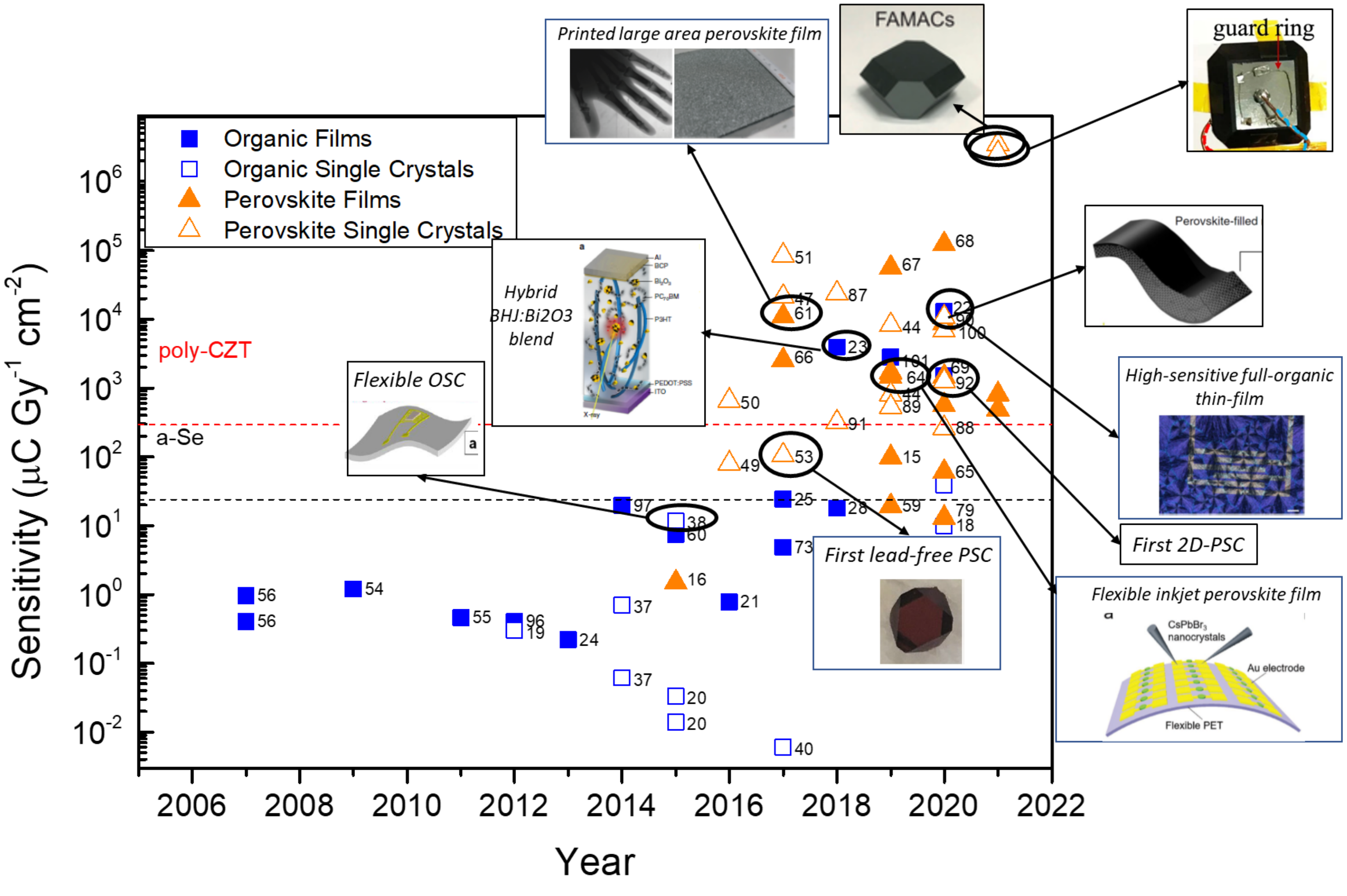
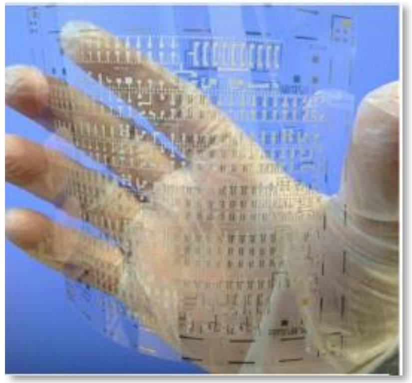
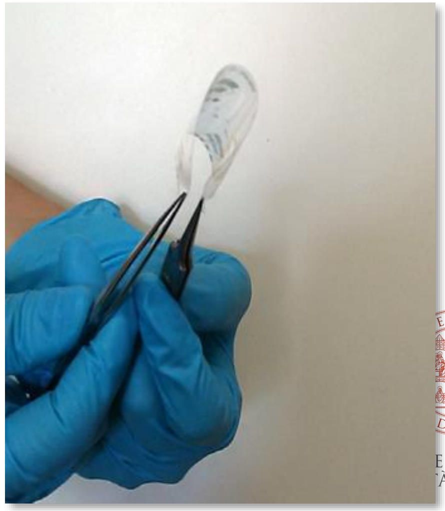
# ORGANIC/HYBRID MATERIALS FOR X-RAY RADIATION DETECTION




**Sensitivity: $10^6$ μC/Gy cm$^2$ @ 0.2V @ RT**

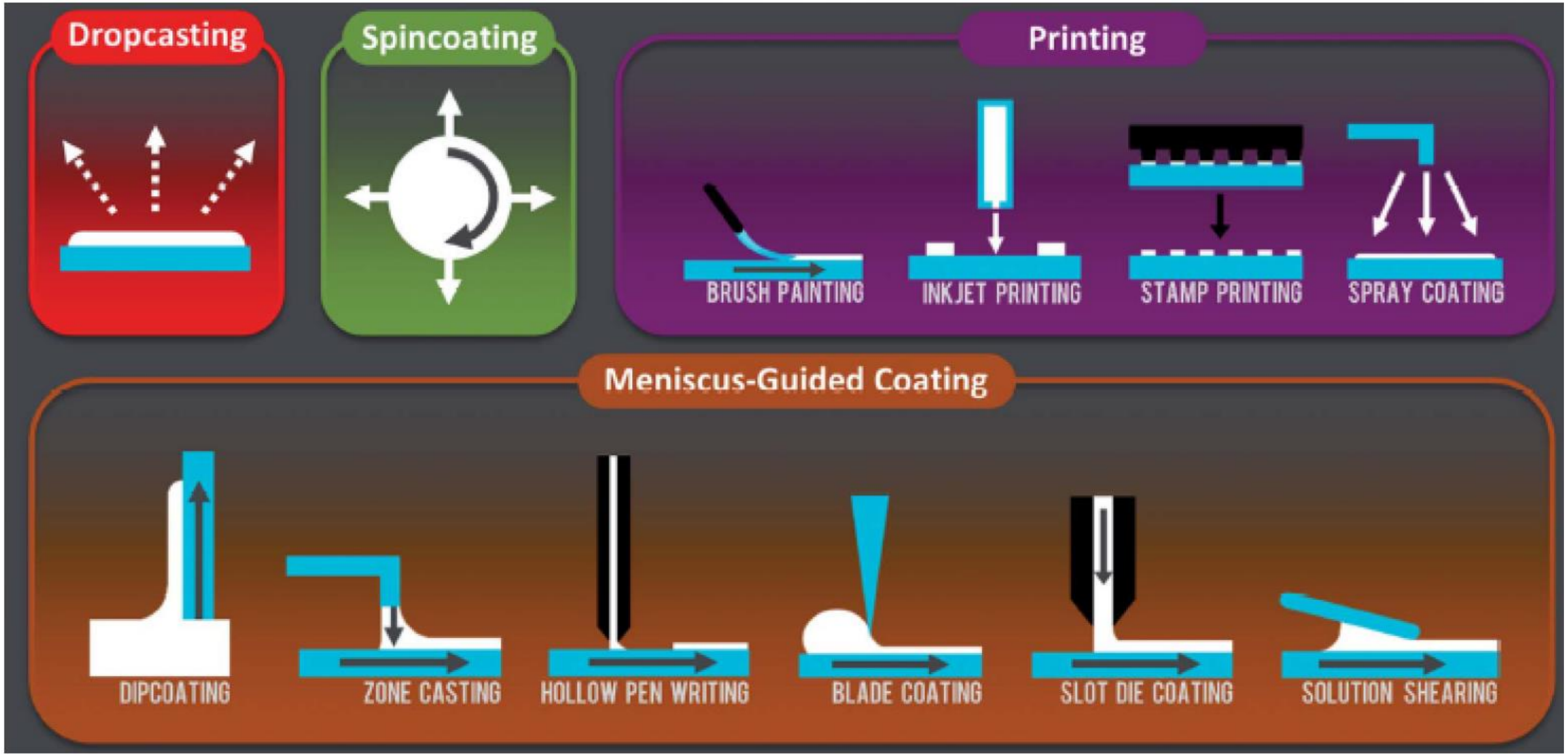
>> than polyCZT or a-Se

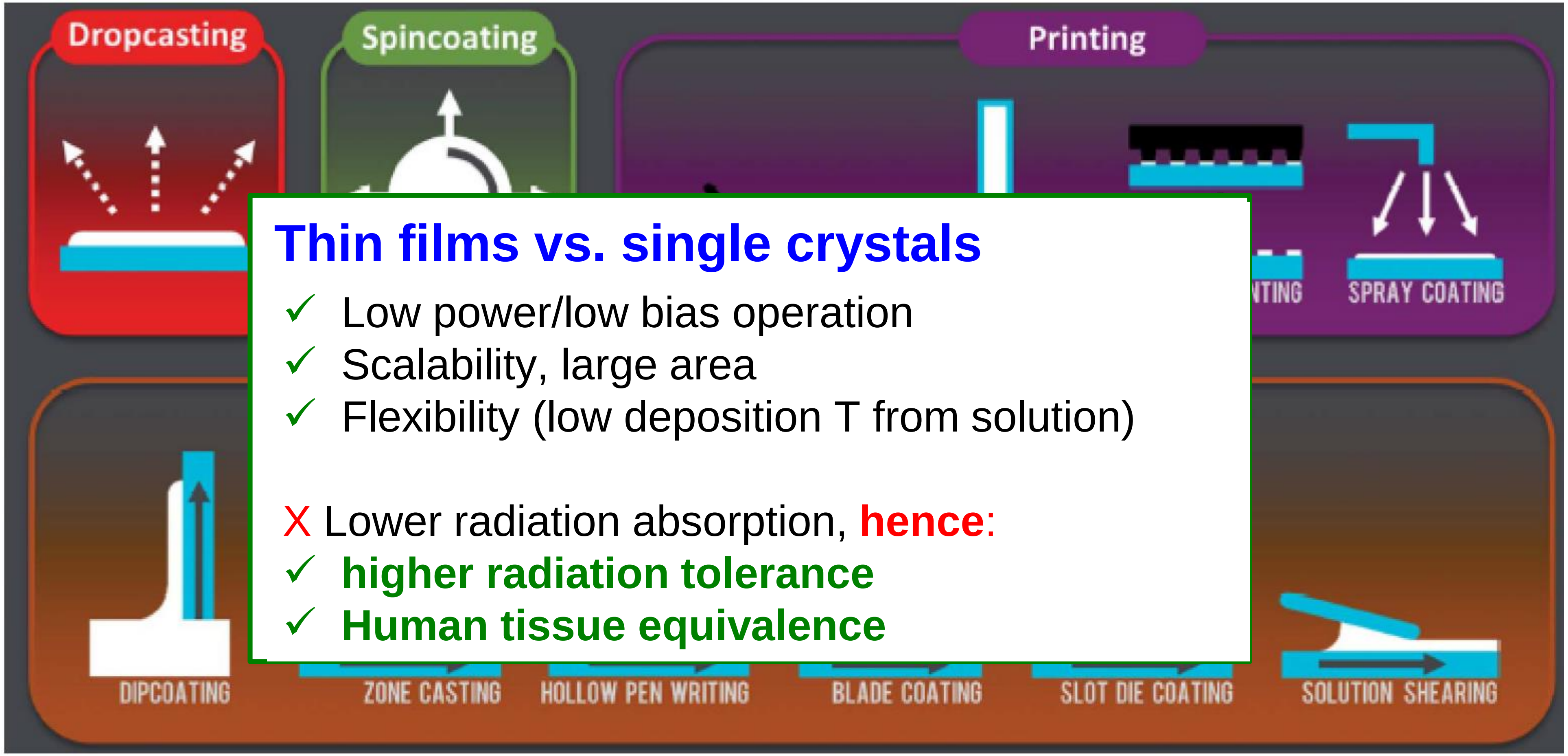




*L. Basiricò et al., Adv. Mater. Technol.* ***2020,*** *2000475*

# PRINTED FLEXIBLE ELECTRONICS FOR A SUSTAINABLE FUTURE






## Thin films vs. single crystals

- ✓ Low power/low bias operation
- ✓ Scalability, large area
- ✓ Flexibility (low deposition T from solution)

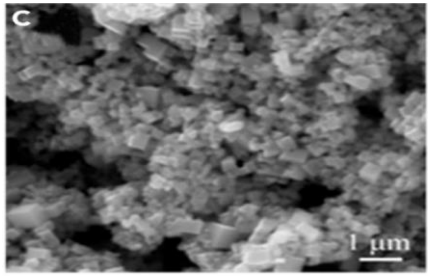
X Lower radiation absorption, **hence**:

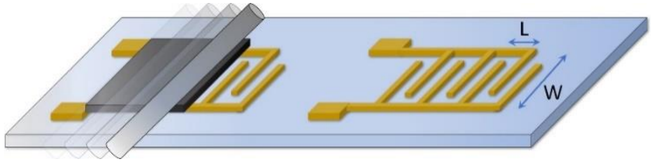
- ✓ **higher radiation tolerance**
- ✓ **Human tissue equivalence**

# Printed Hybrid Organic/Perovskite Flexible Detector

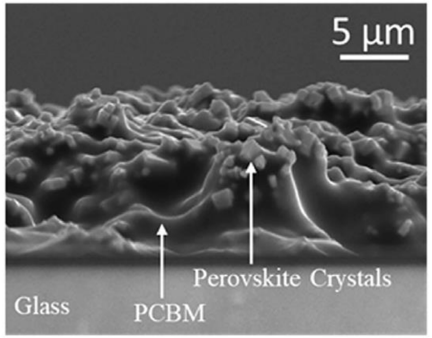
# Perovskite thin films 3D blends: MAPI+PCBM

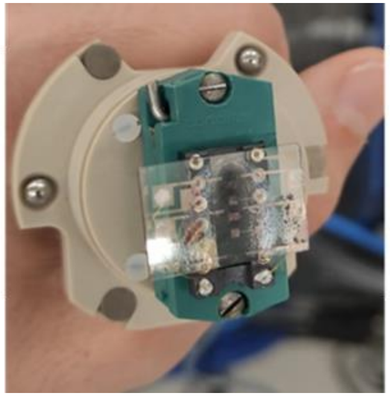
MAPbI3 NPs




MAPbI3 NPs+PCBM film



1) Synthesis of **$MAPbI_3$ nanocrystals inks** in **low boiling point** benign **low-toxic solvent** (water and propan-2-ol)
2) Printing by bar coating **in air**
3) Coating with electrons acceptor (PC60BM) **– trap passivation**
4) Multiple deposition steps, up to **10 µm thick film** - relative high X-ray attenuated fraction (40%@40kV, 9%@150kV).

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# Perovskite thin films 3D blends: MAPI+PCBM

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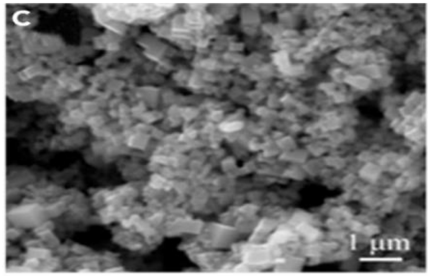
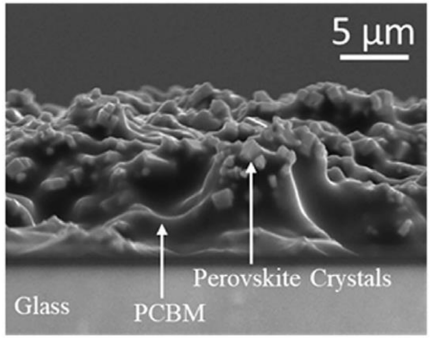
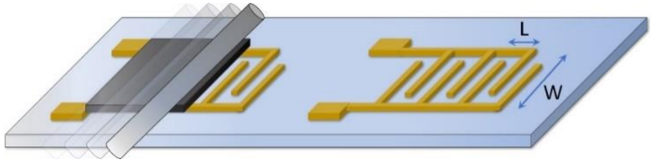
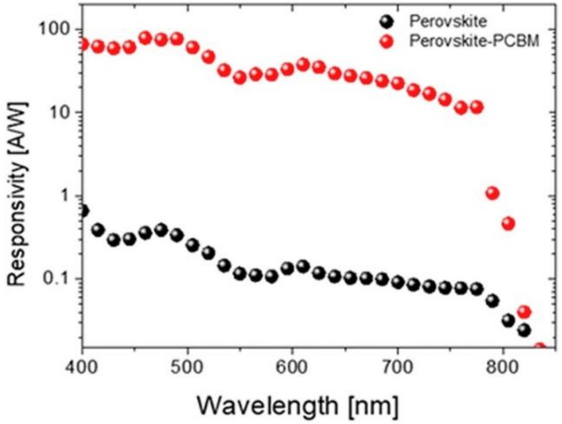



**MAPbI3 NPs+PCBM film**




**High-detectivity and fast light detectors**

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# Perovskite thin films 3D blends: MAPI+PCBM

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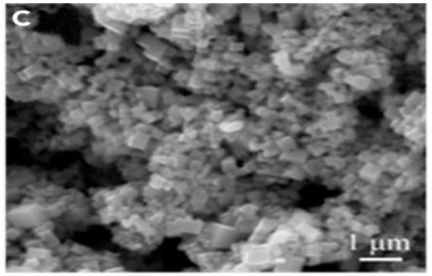
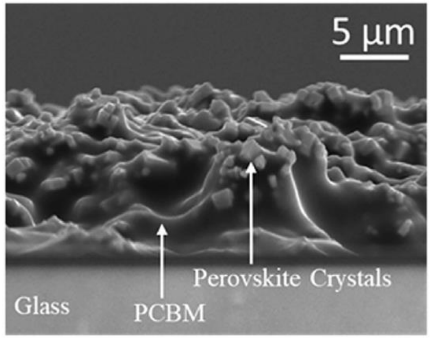
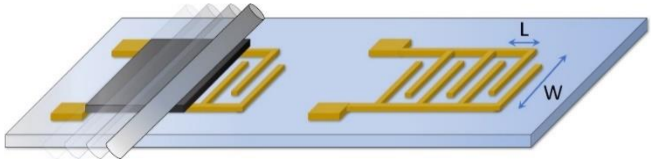
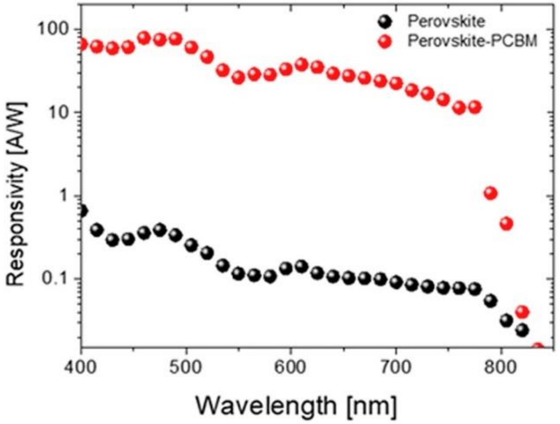



MAPbI3 NPs+PCBM film

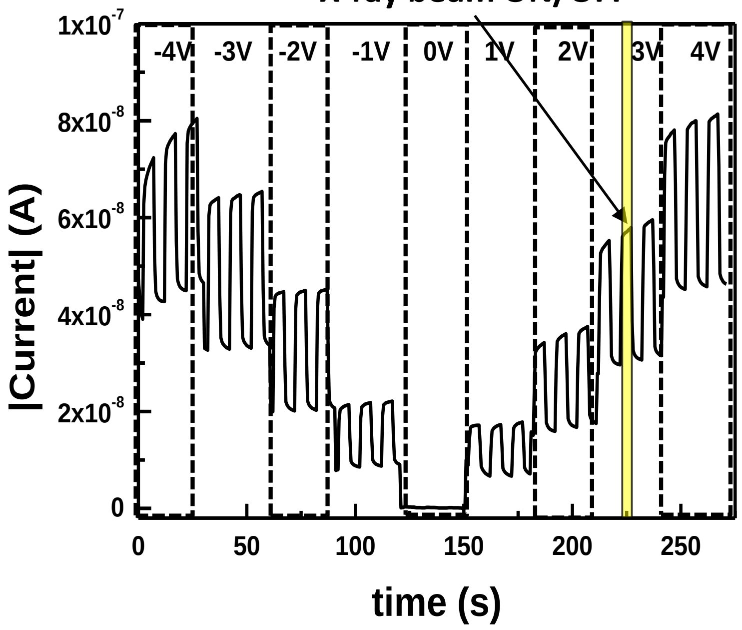



High-detectivity and fast light detectors

X-ray beam ON/OFF




→ **2-terminal planar device**

→ **Low operation bias** < 4V

→ **High sensitivity**, top value up to **2270 µC $Gy^{-1}$ $cm^{-2}$**

→ **radiation tolerance** >2 Gy and fast response time (< 50 ms)

*X-ray 40kV*

L. Basirico' et al *Nature Comm* (***2016)***

I. Temino et al *Nature Comm* ***(2020)***

*A.*Ciavatti et al., *Adv. Funct. Mater.* (***2021)***

M Verdi et al. *Adv. Mat. Interfaces* (**2023)**

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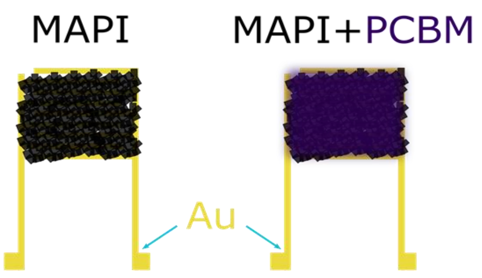
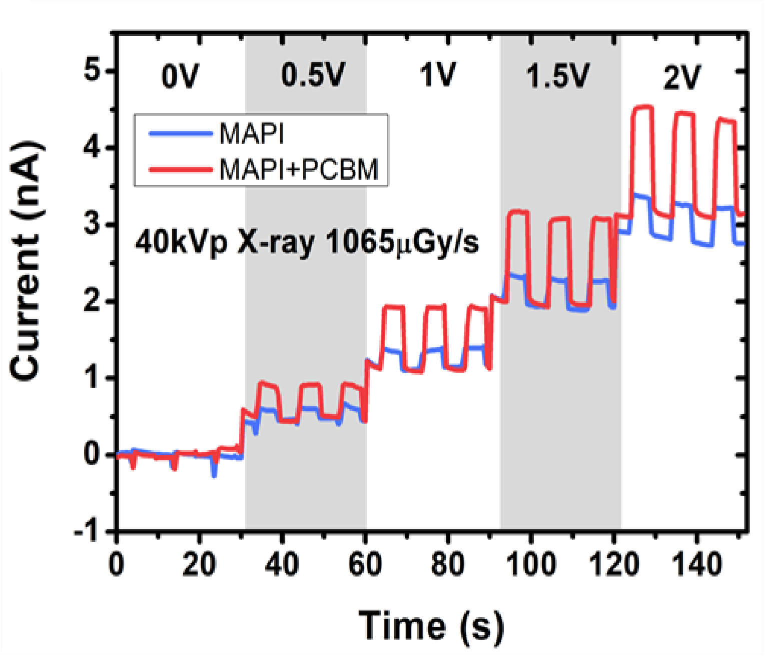
# Perovskite thin films 3D blends: role of carrier traps

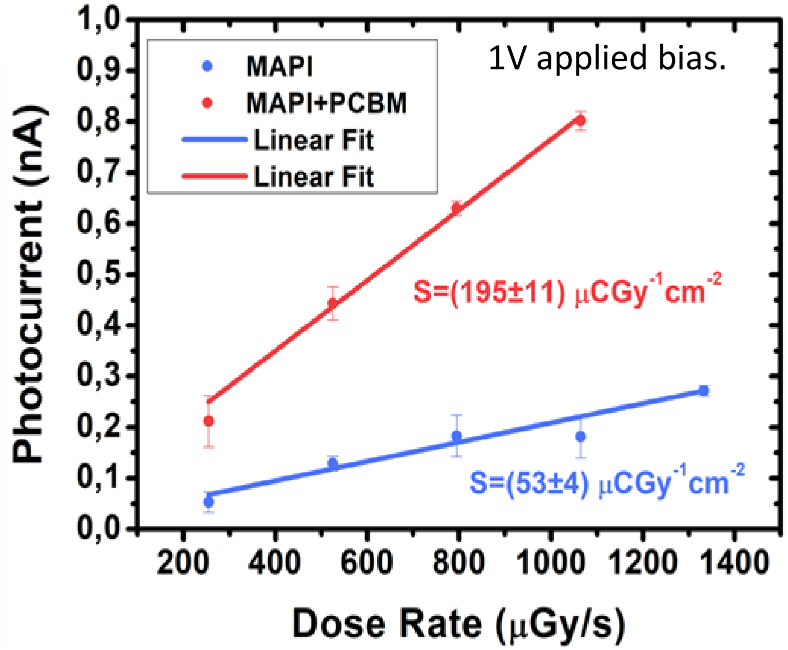



**MAPI+PCBM improved performance** due to the addition of the PCBM layer:

- due to its electron acceptor properties, that **passivate the traps** for majority carriers in perovskite nanocrystals?
- **role of traps and interfaces & PC gain effects**

Fratelli *et al.*, *Science Advances*, (**2021**)
M Verdi et al. *Adv. Mat. Interfaces* (**2023**)



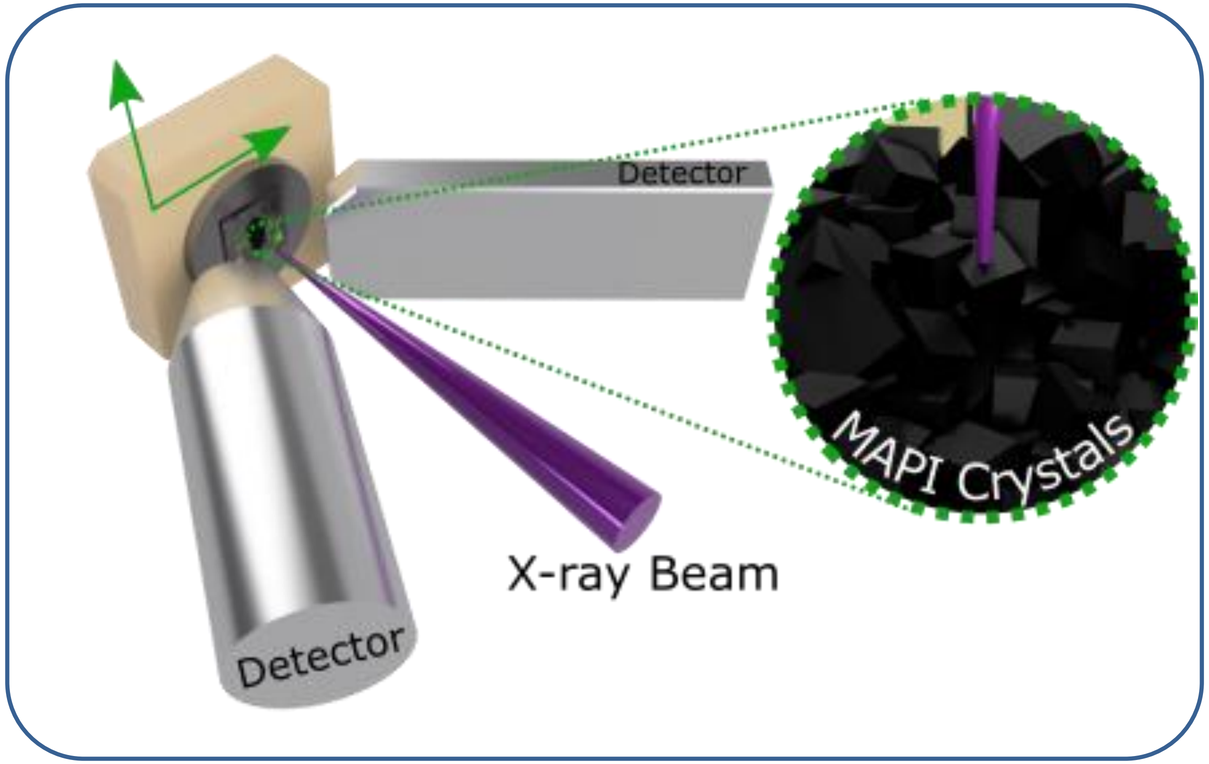



# X-RAY NANOANALYSIS @ESRF ID16B

Simultaneous acquisition of two techniques:

- X-ray Fluorescence (XRF)
- X-ray Beam Induced Current (XBIC)

In order to understand the role of PCBM we performed simultaneously **XRF and XBIC** on sample with and without PCBM




IDB16B beamline at the ESRF-EBS synchrotron
**Beam spot size 50nmx50nm**

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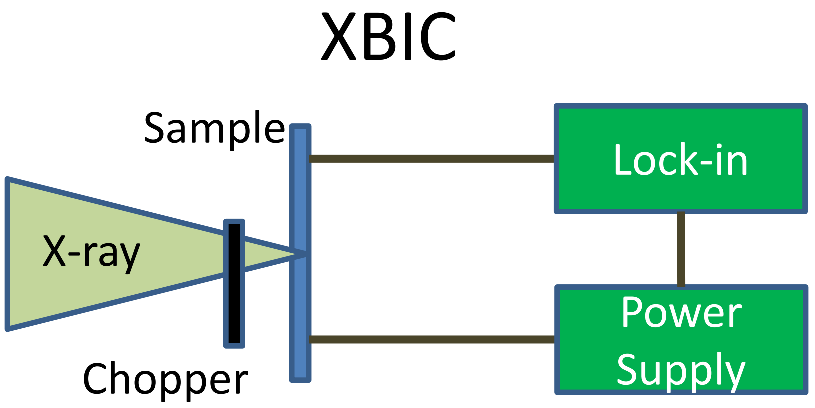


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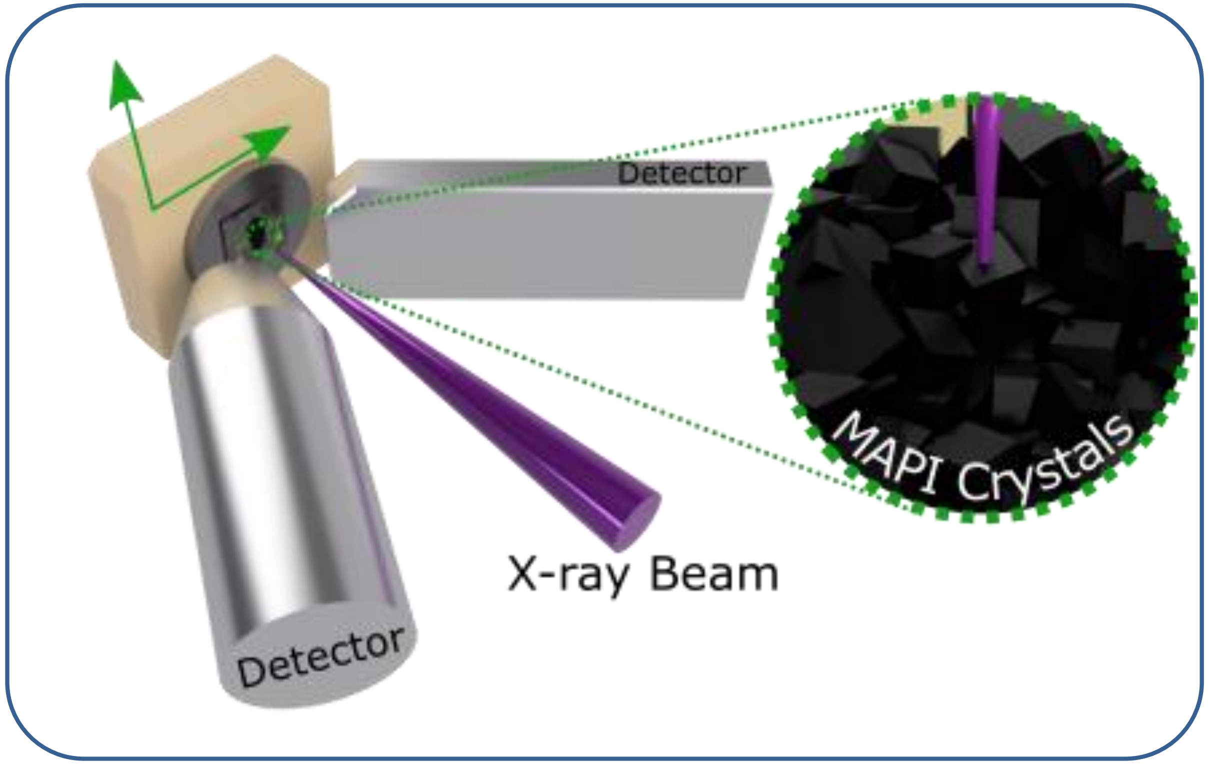


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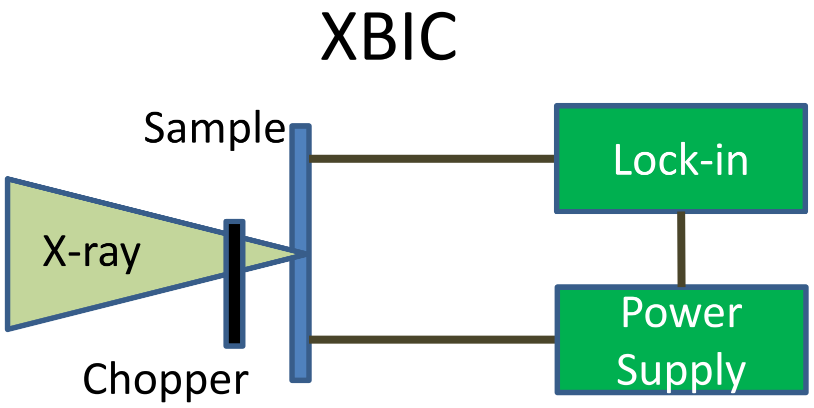


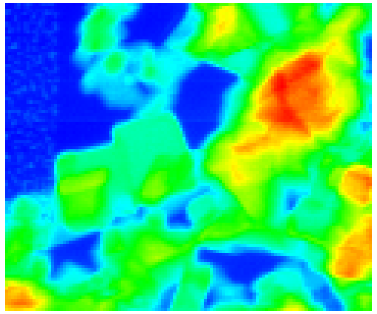

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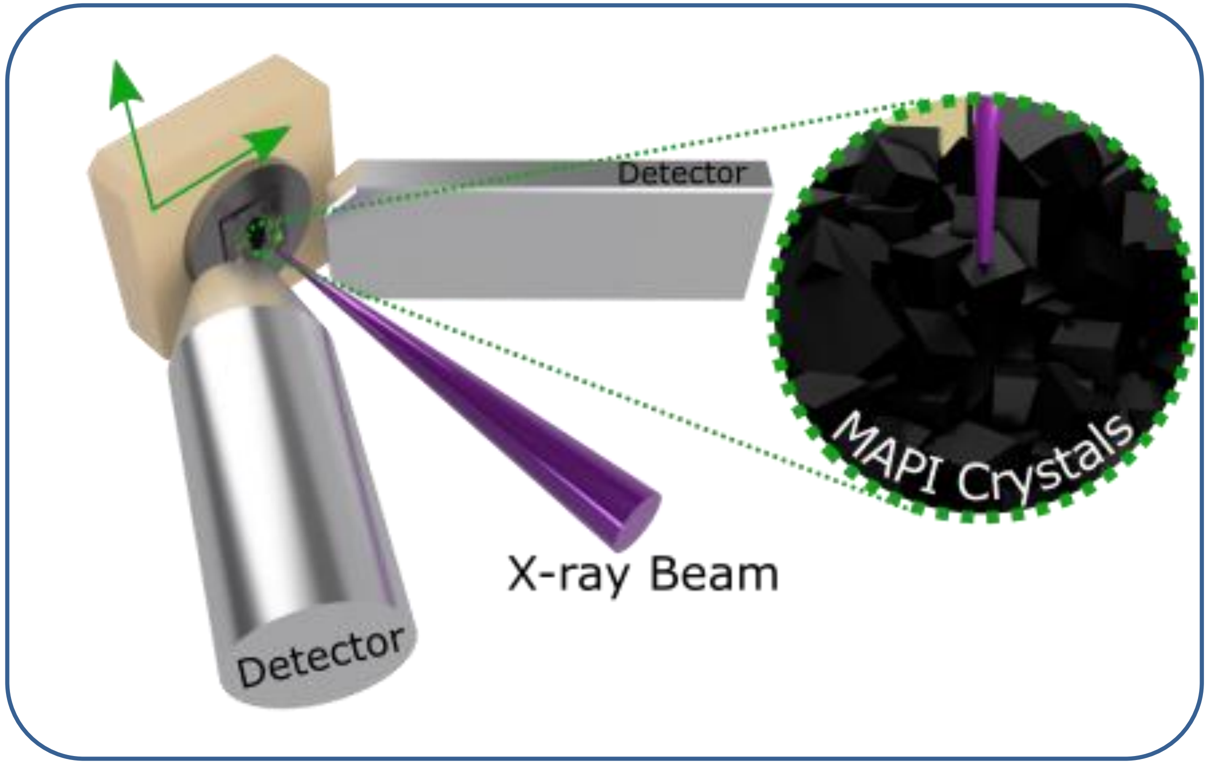


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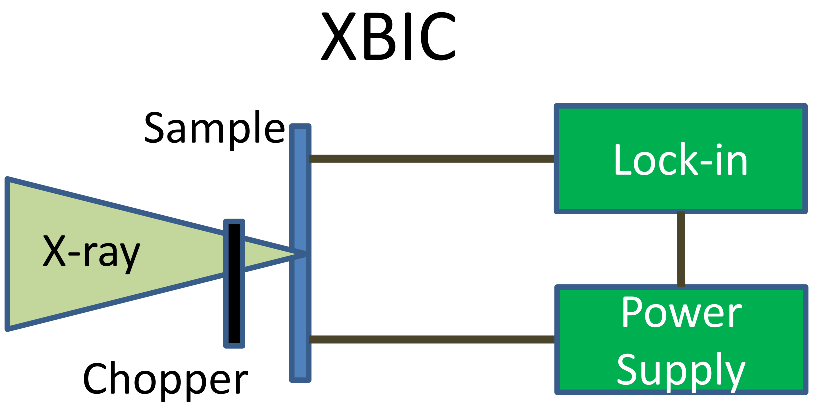


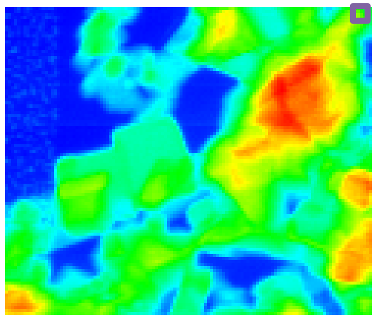

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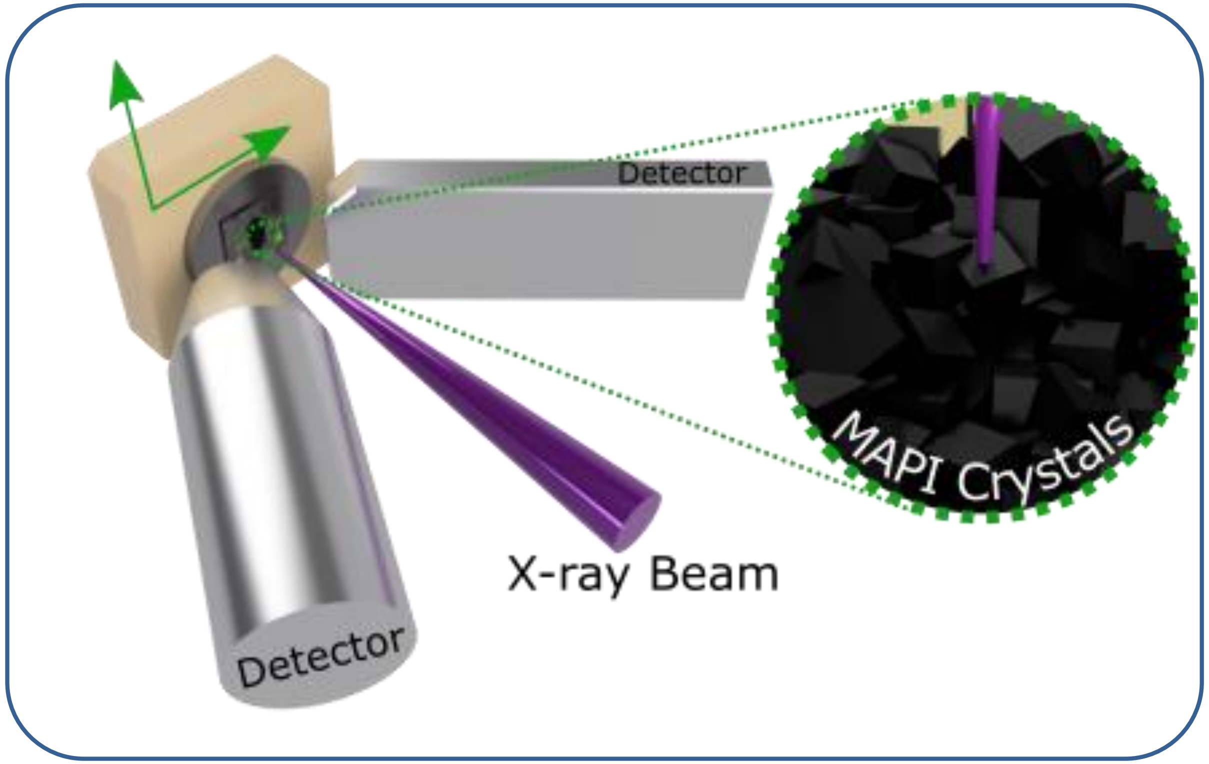


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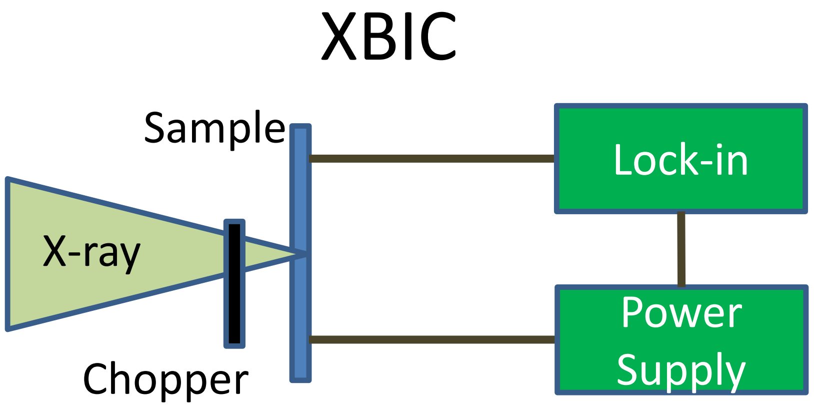
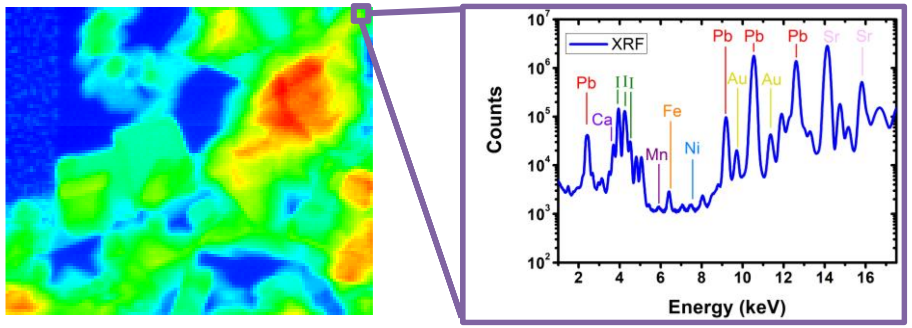
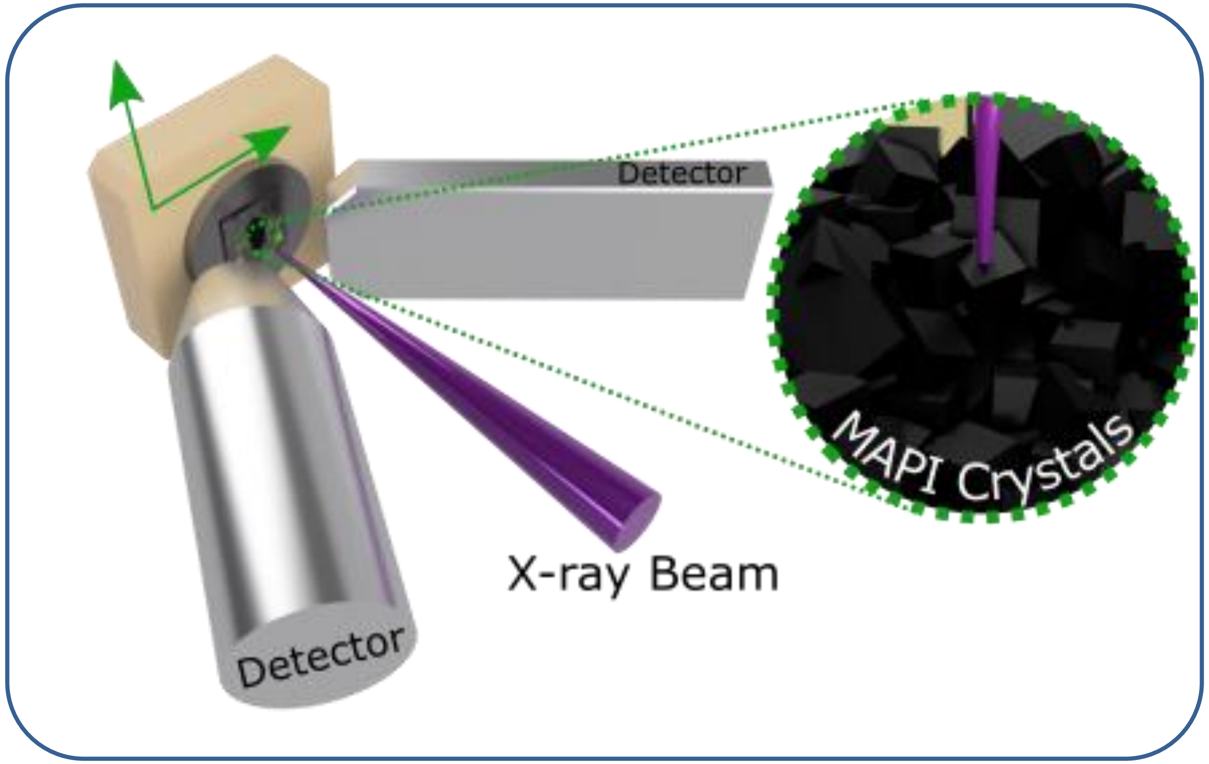
In order to understand the role of PCBM we performed simultaneously **XRF and XBIC** on sample with and without PCBM




IDB16B beamline at the ESRF-EBS synchrotron

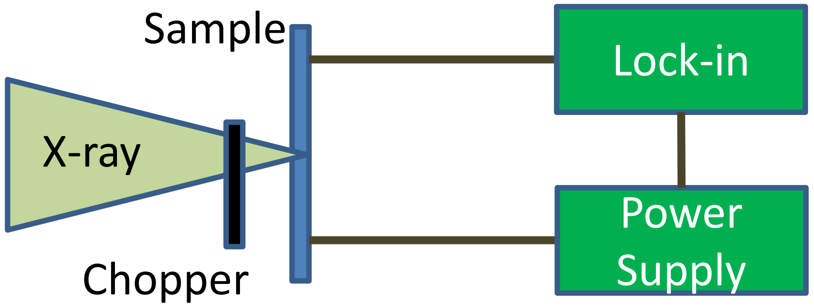
**Beam spot size 50nmx50nm**

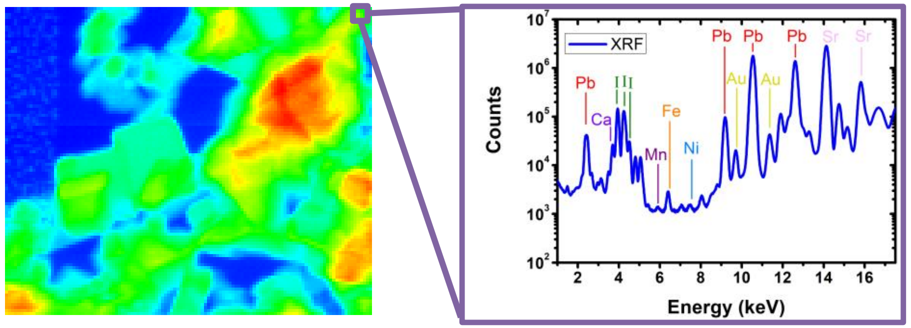
# X-RAY NANOANALYSIS @ESRF ID16B

Simultaneous acquisition of two techniques:

- X-ray Fluorescence (XRF)
- X-ray Beam Induced Current (XBIC)

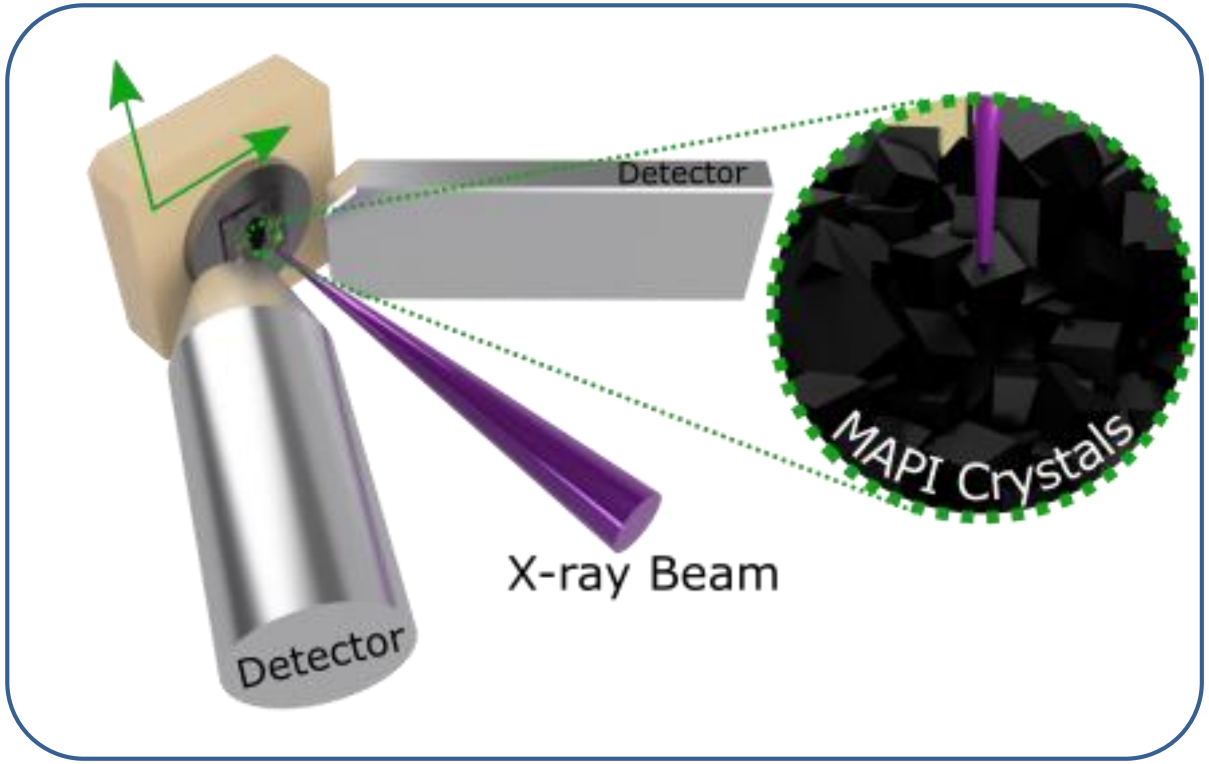
XBIC




+ The current signal

In order to understand the role of PCBM we performed simultaneously **XRF and XBIC** on sample with and without PCBM




IDB16B beamline at the ESRF-EBS synchrotron

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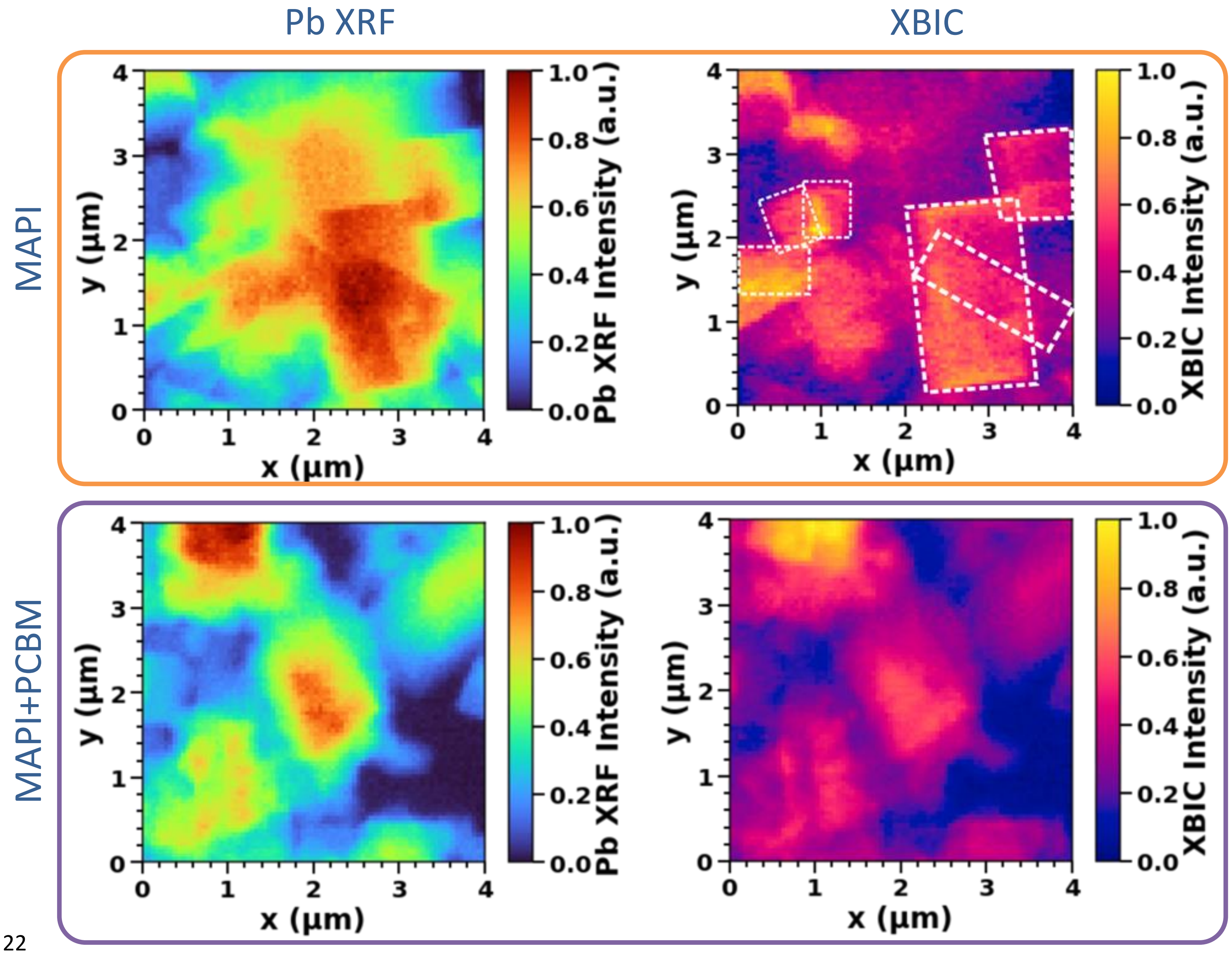
# XRF vs. XBIC




- We can correlate the Pb distribution (morphology) to the current signal
- In the MAPI sample the grain boundaries are highlighted in the XBIC map
- A more uniform XBIC signal was obtained for MAPI+PCBM sample

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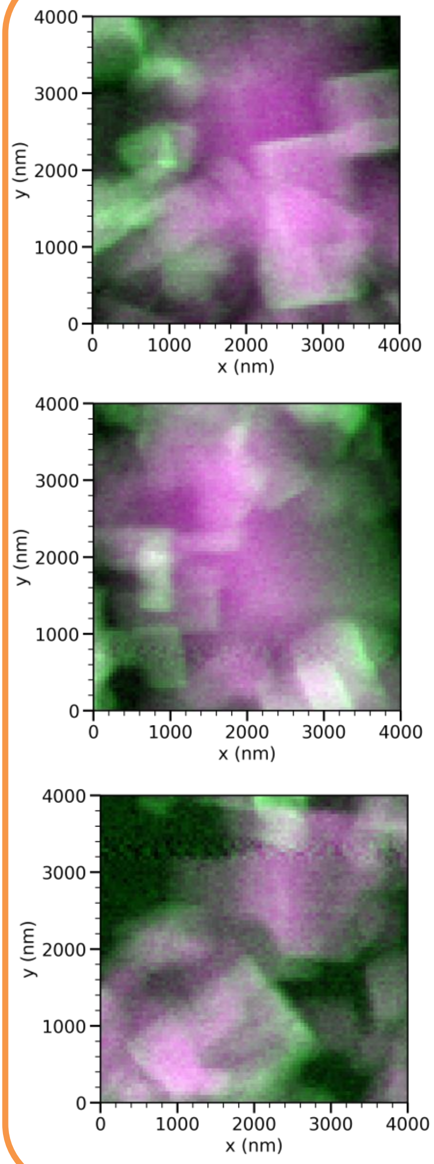
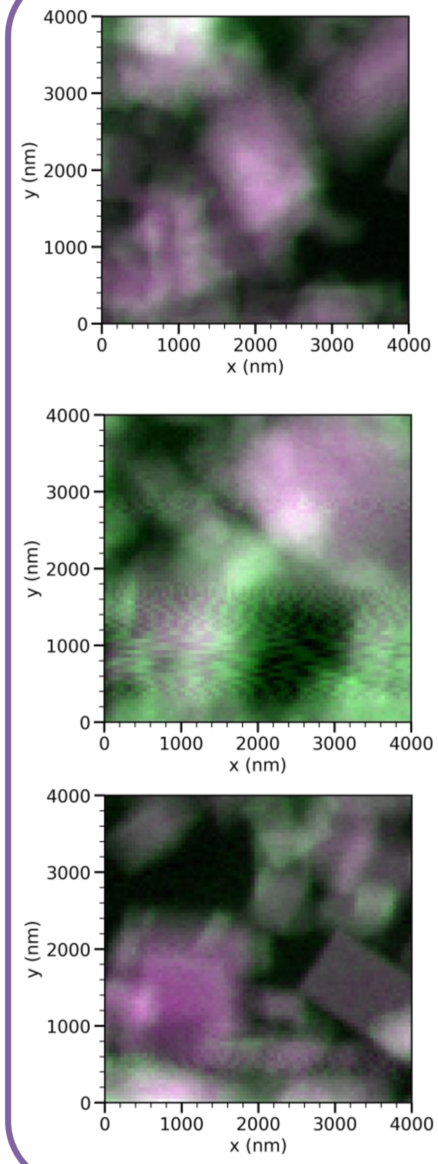
# XRF vs. XBIC line profile

## MAPI




## MAPI+PCBM



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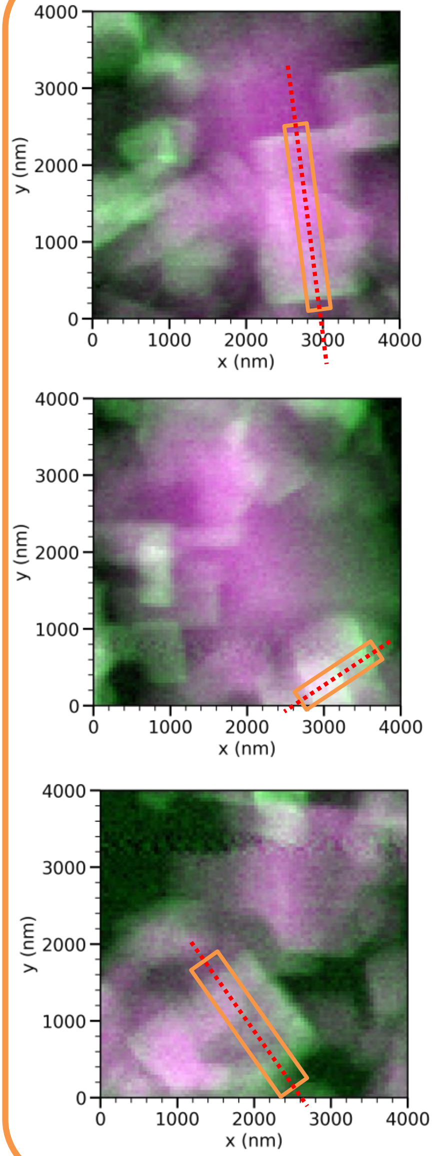


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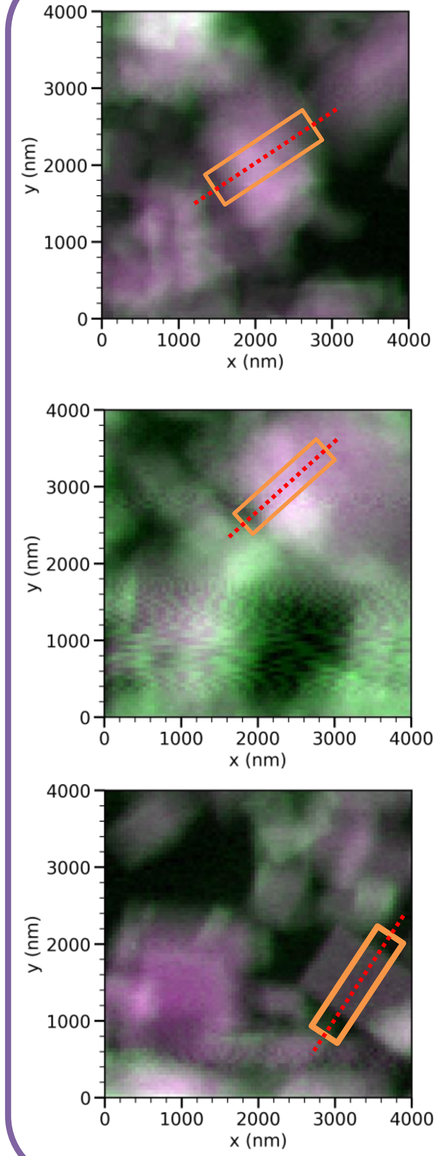


- Grain boundaries even more pronounced when overlaying XRF and XBIC
- In MAPI higher current at grain boundaries
- In MAPI+PCBM more correlation between XRF and XBIC signals

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# XRF vs. XBIC line profile

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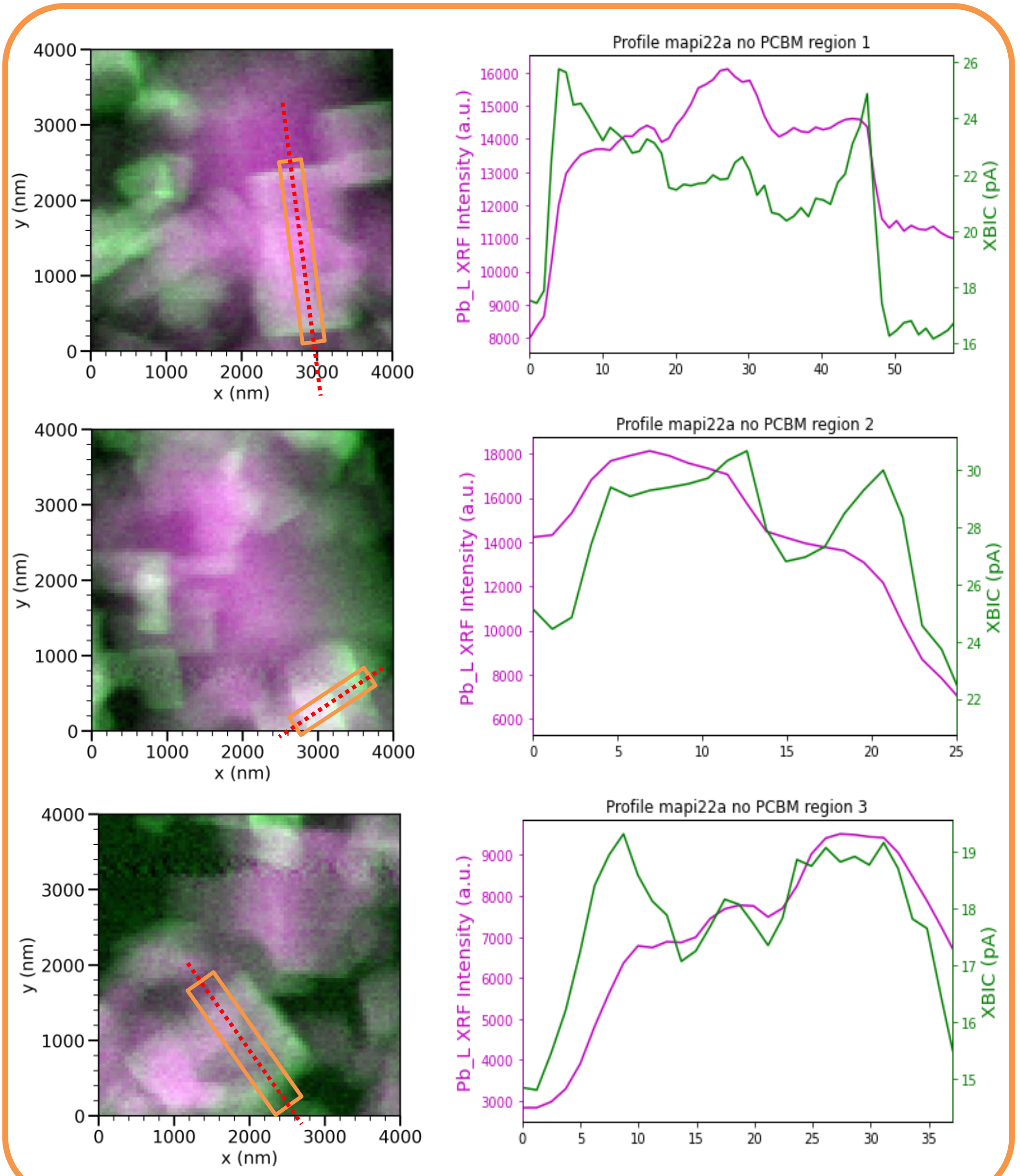
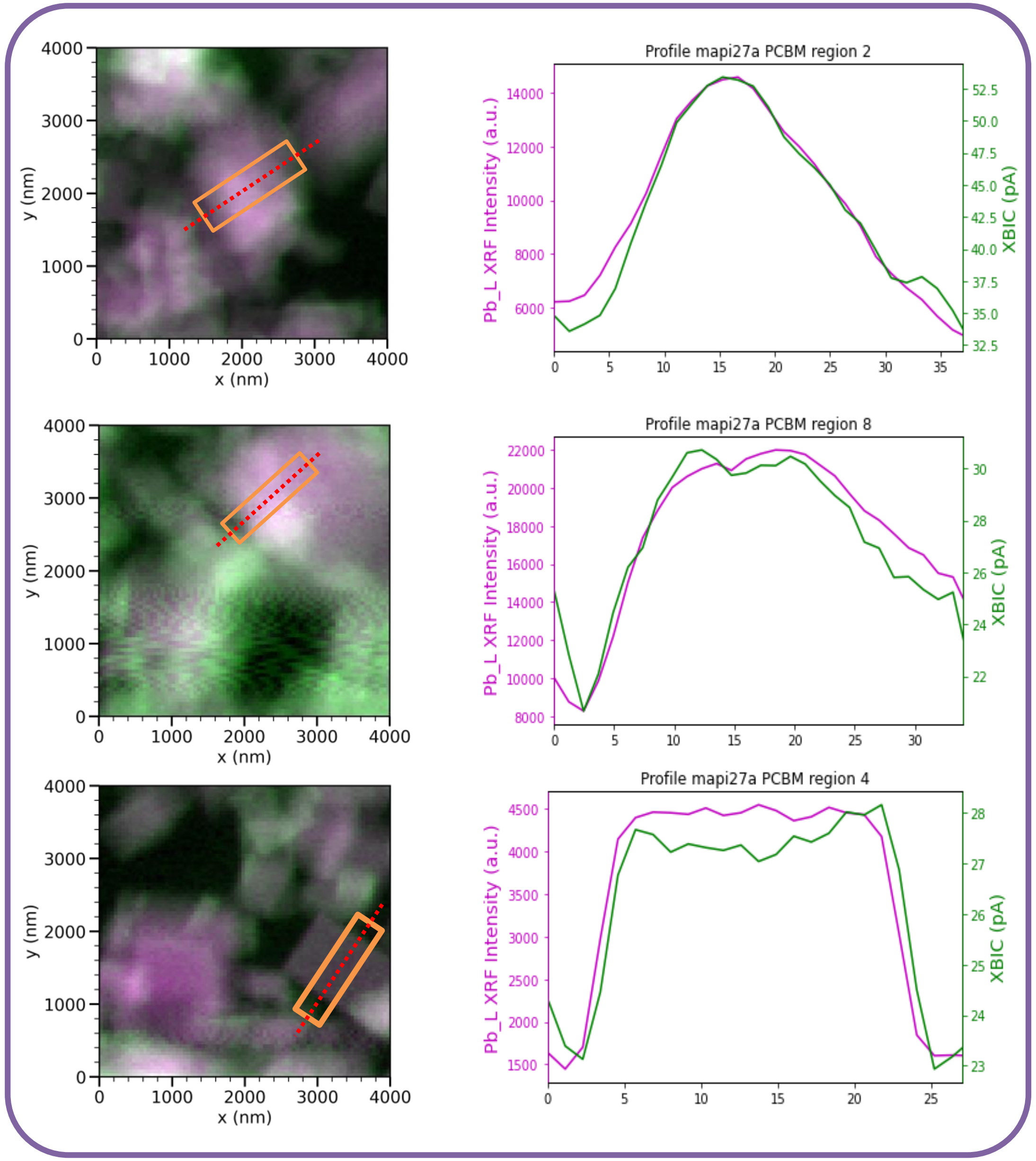



## MAPI+PCBM

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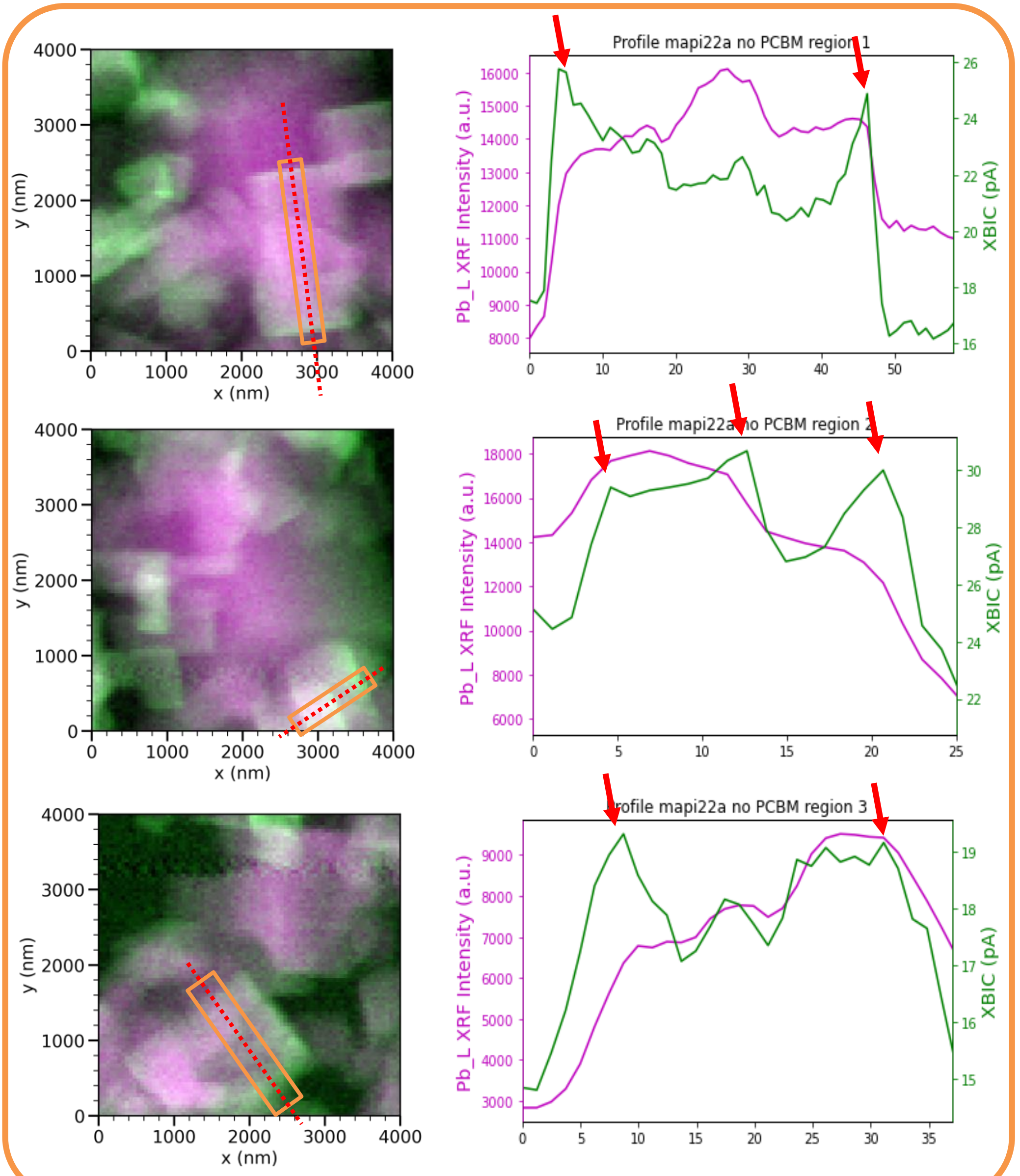
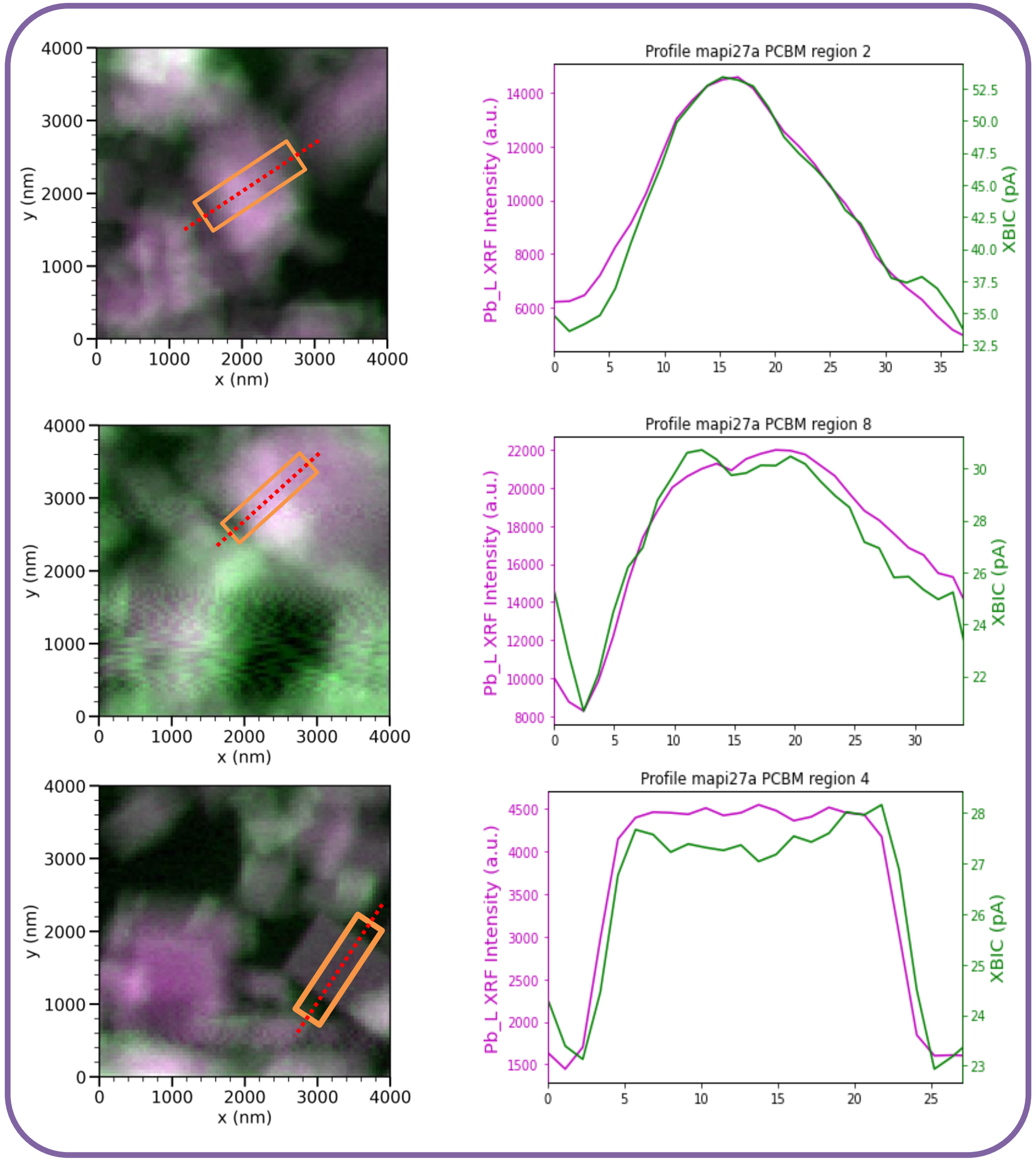



## MAPI+PCBM

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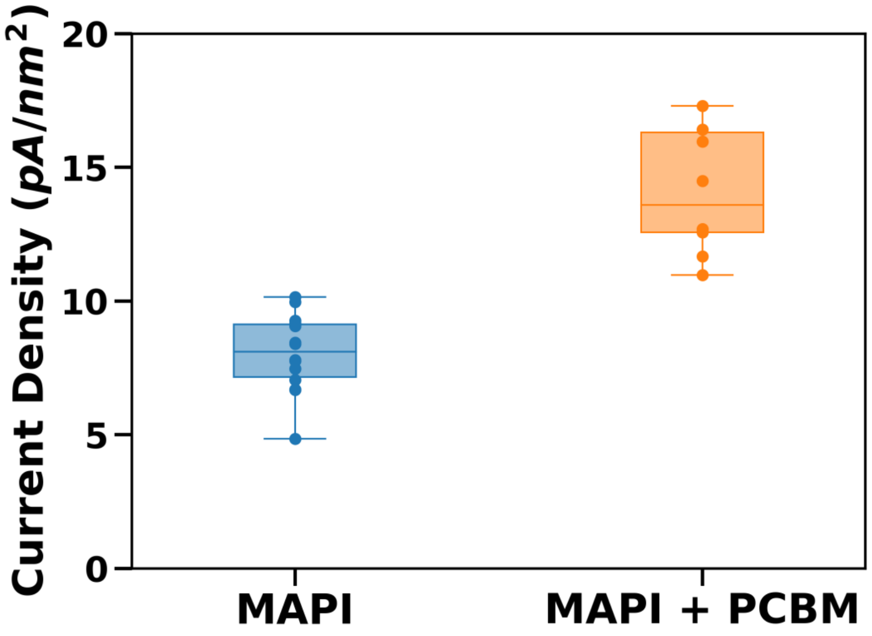
# $MAPbI_3$/PCBM interface




- On average in the samples with PCBM the current density is almost double respect to only MAPI samples



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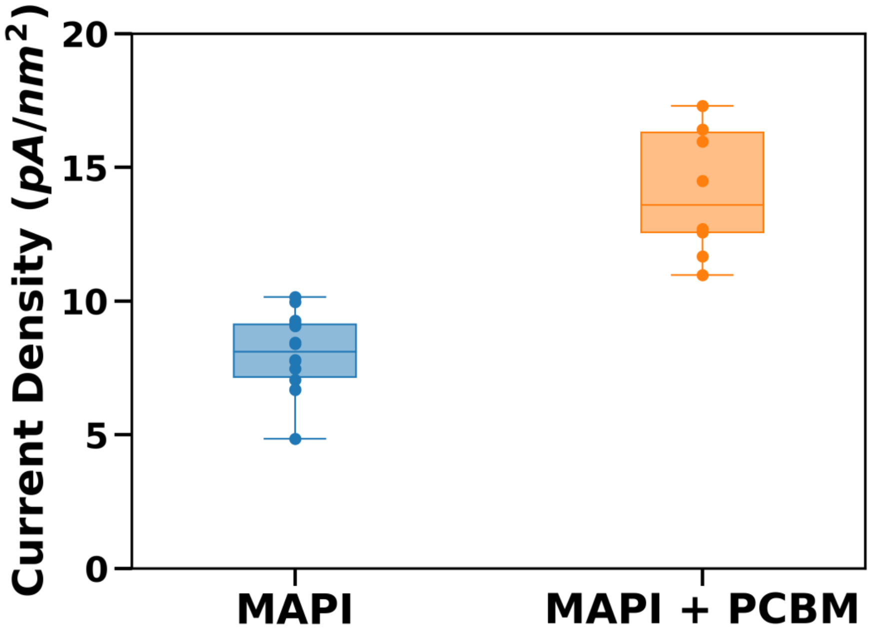
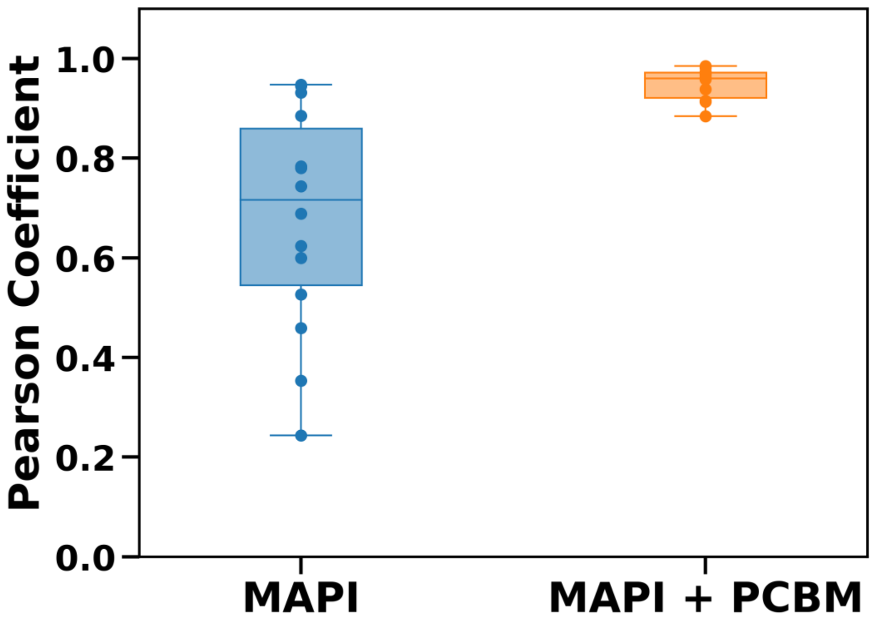
# $MAPbI_3$/PCBM interface




- On average in the samples with PCBM the current density is almost double respect to only MAPI samples

- Higher correlation between XRF and XBIC signals

$$r = \frac{\sum_{i=1}^{n}(x_i - \bar{x})\,(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2}\ \sqrt{(y_i - \bar{y})^2}}$$

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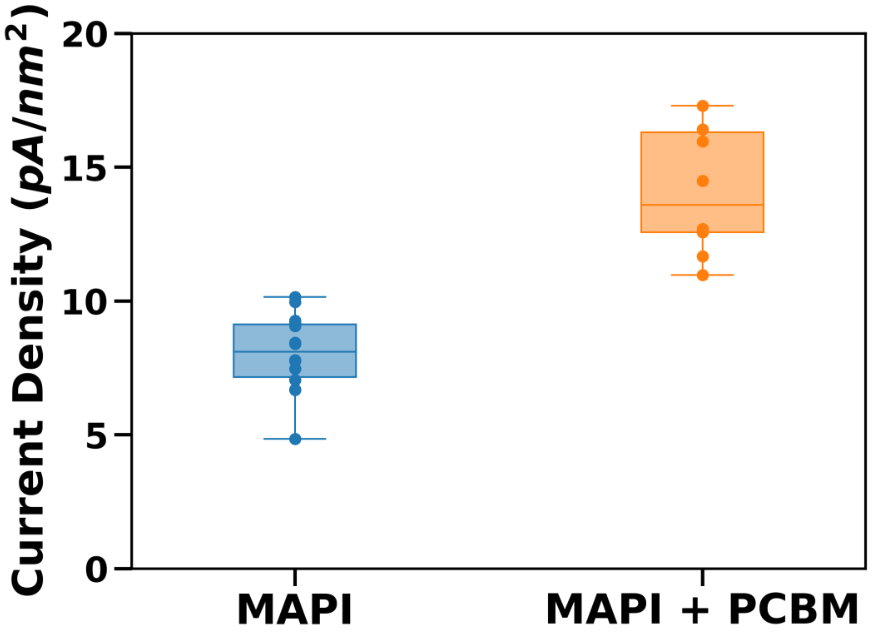


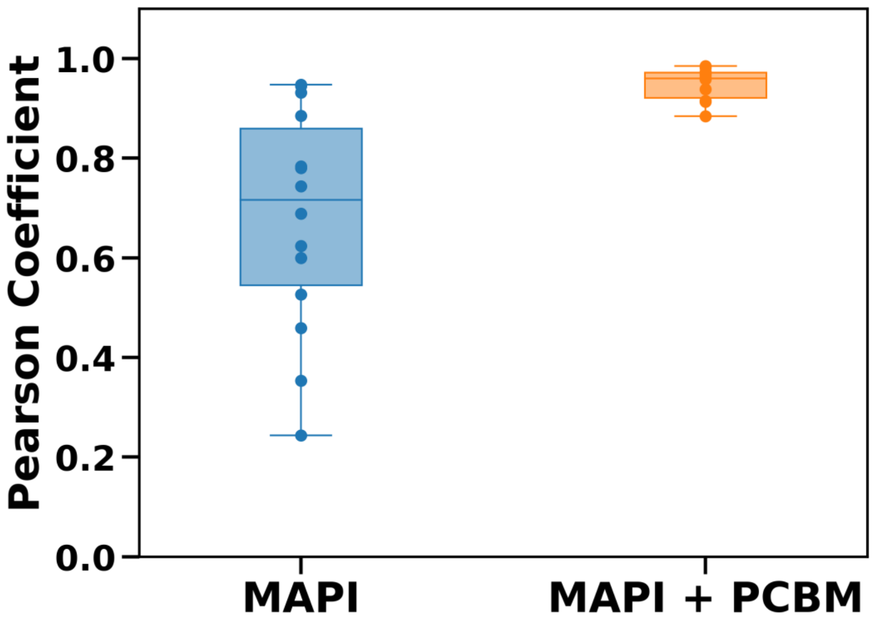


- On average in the samples with PCBM the current density is almost double respect to only MAPI samples

- PCBM creates higher current by acting as an electron sink and creating higher gain in the perovskite layer

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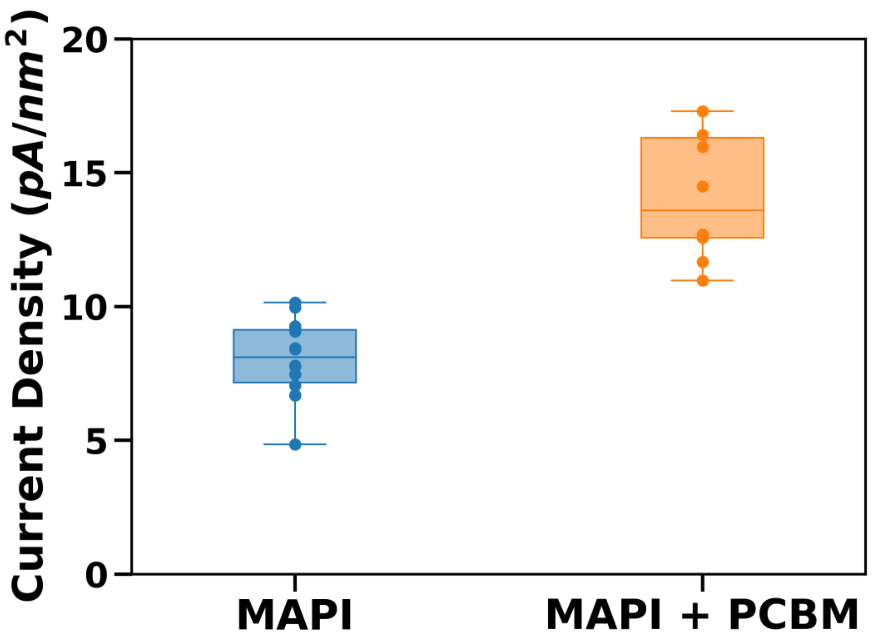


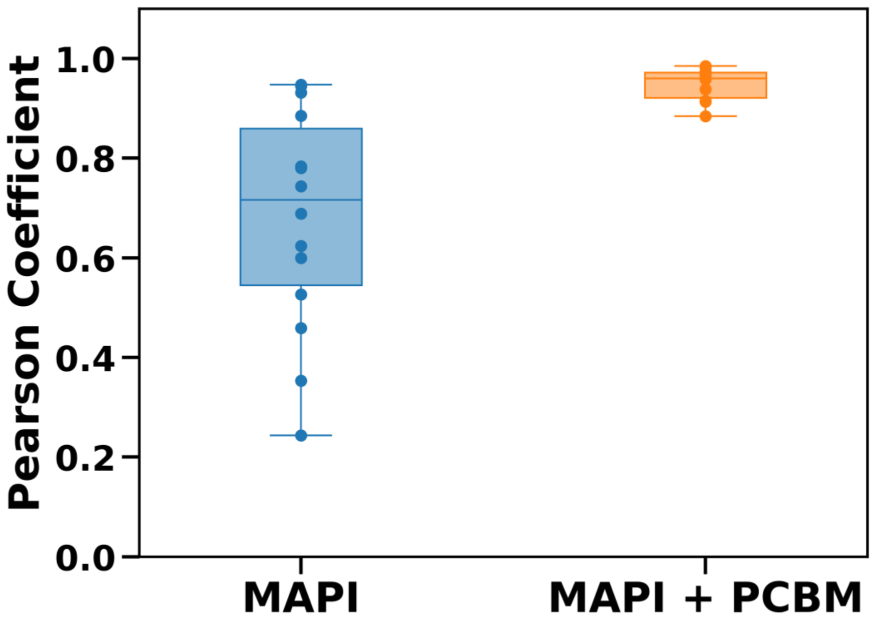


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- PCBM passivates Traps at the grain boundaries



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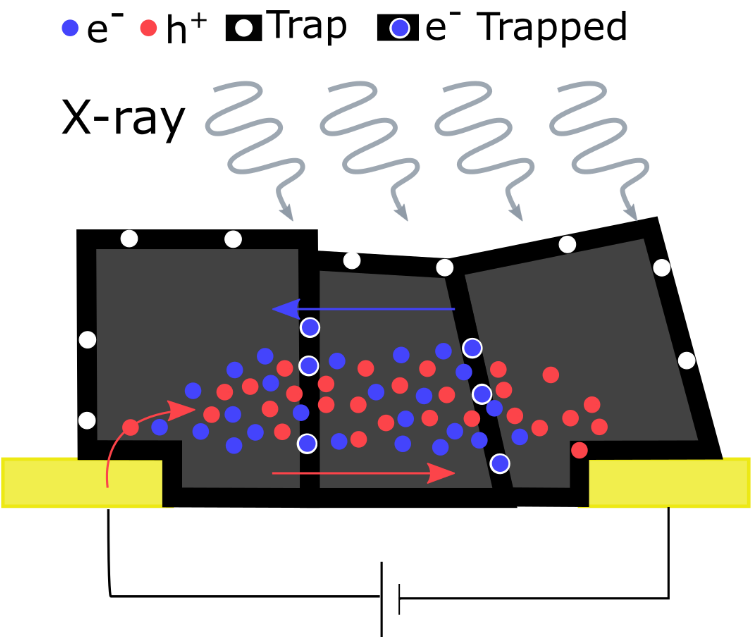
# THE ROLE OF PCBM

## Only MAPI devices




High traps concentration at grain boundaries. Trapped minority carriers (electrons) activate a gain mechanism through holes injection from electrodes.

## MAPI + PCBM devices



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# THE ROLE OF PCBM

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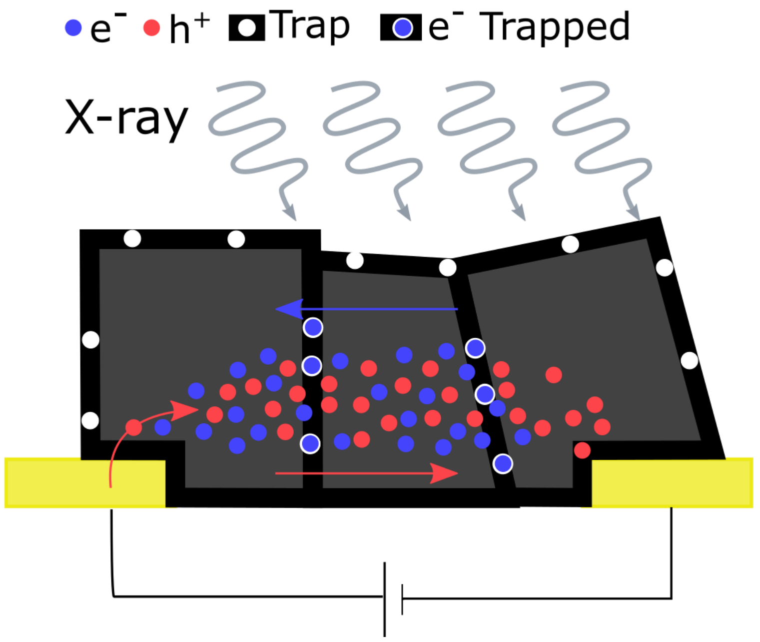
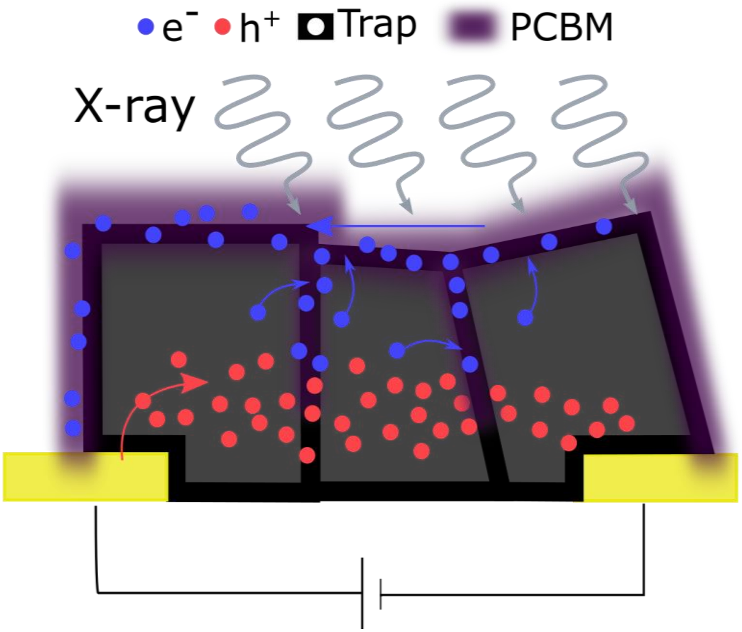



### MAPI + PCBM devices

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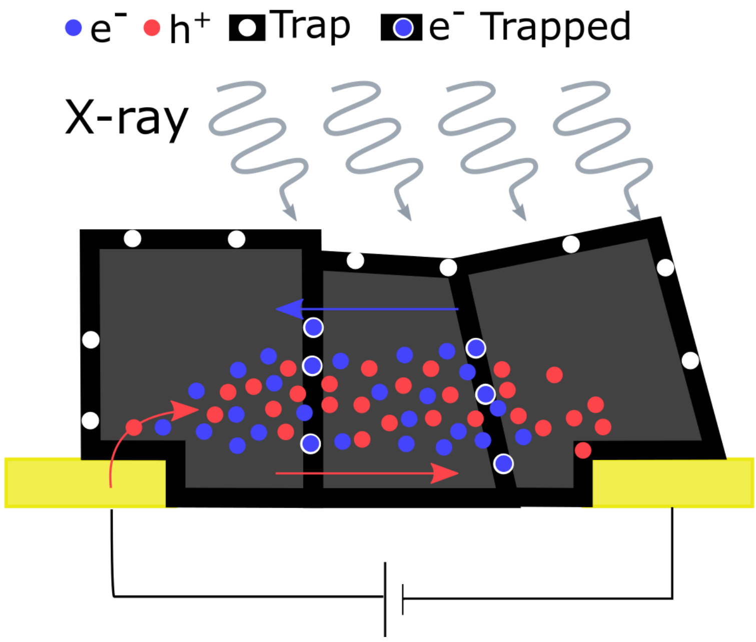


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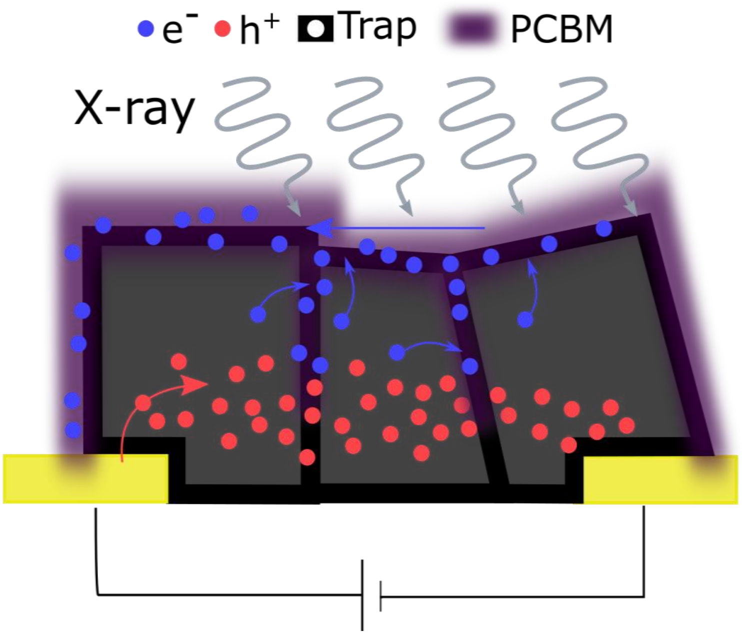


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- PCBM passivates the majority carrier (holes) traps
  - → more mobile holes
    - → general increase of gain

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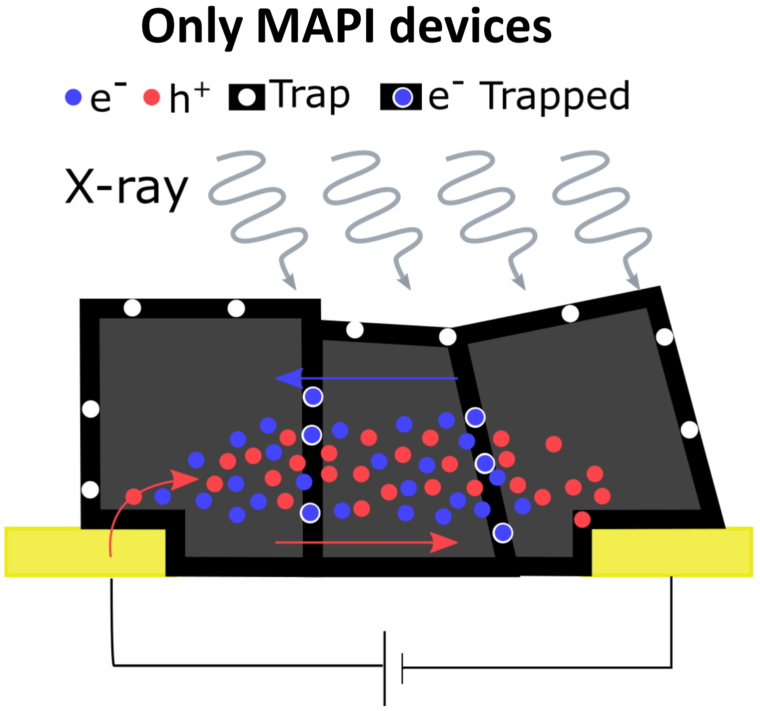
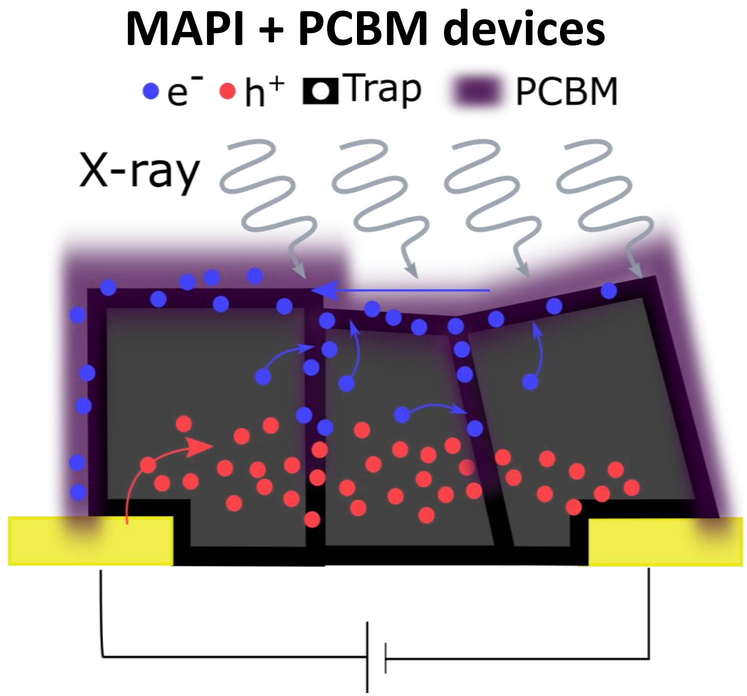
# THE ROLE OF PCBM




High traps concentration at grain boundaries. Trapped minority carriers (electrons) activate a gain mechanism through holes injection from electrodes.

- PCBM passivates the majority carrier (holes) traps
  - → more mobile holes
    - → general increase of gain
- PCMB as electrons acceptor
  - → subtract electrons from recombination improving holes lifetime
    - → spatially uniform gain effect



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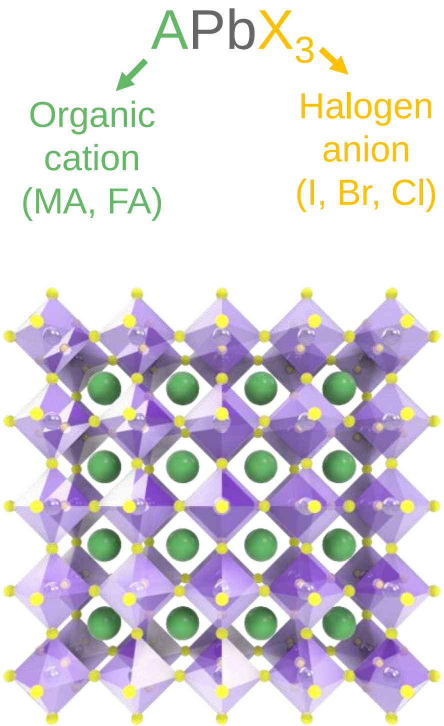
# 2D layered Perovskites

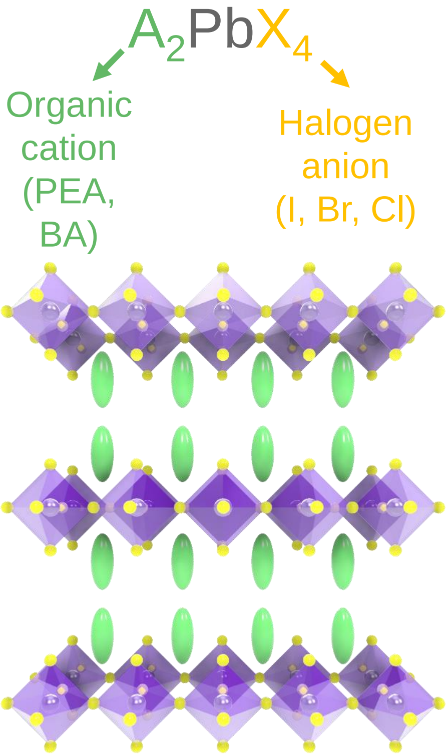
# 2D layered Perovskites

**$PEA_2PbBr_4$** ($PEA = C_6H_5C_2H_4NH_3^+$)

## 3D vs. 2D

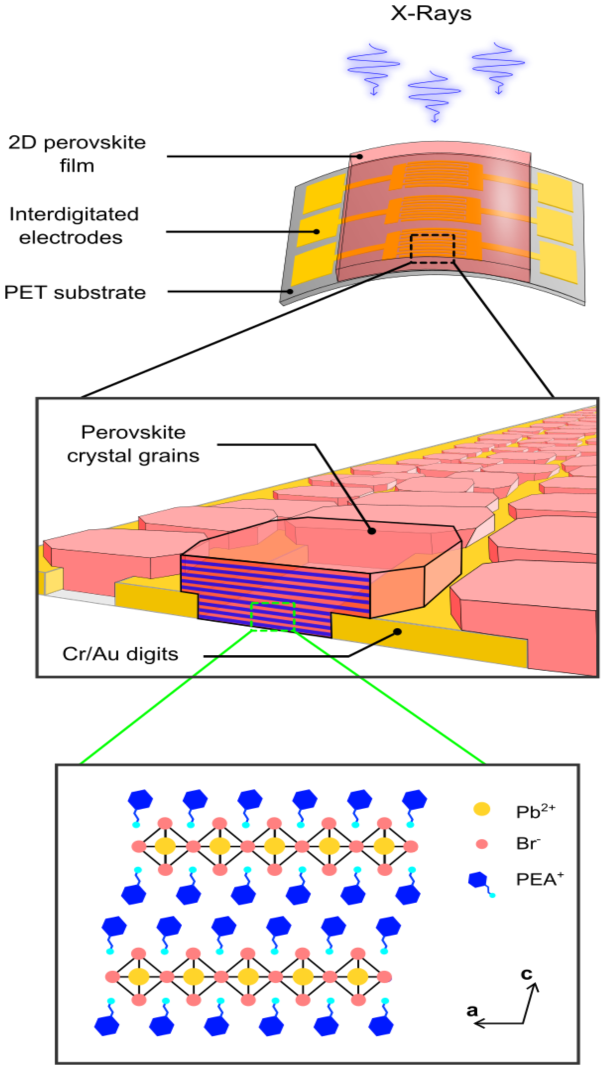



- High X-ray stopping power 10 $cm^{-1}$, comparable to CZT.
- High carriers diffusion length >1µm in polycrystalline films.
- Low cost, low temperature <150 °C deposition from solution.
- Optoelectronic properties tuning by controlling the relative amounts of the components

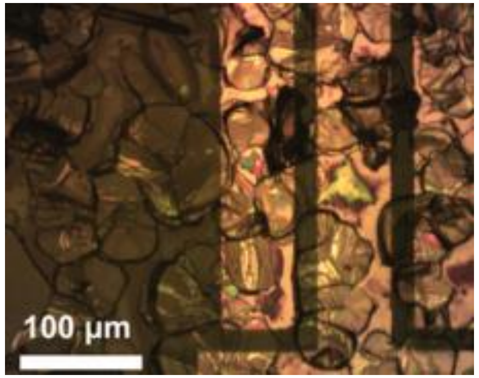



- High X-ray stopping power.
- **Lower mobility**
- **Lower Ion migration**
- **Better stability**
- Low cost, low temperature <150 °C deposition from solution.
- Optoelectronic properties tuning by controlling the relative amounts of the components

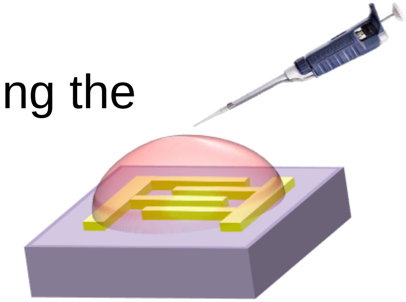
# 2D Perovskites thin film  X-ray radiation detectors




- $PEA_2PbBr_4$
- Easy and  scalable fabrication procedure (solution deposition)




- 125 µm PET substrate
- large grains (33.5±8.3 µm) bridging the metal contacts



- Layer thickness < 1-2 µm
- **very low dark current for a non-diode structure** ($10^{-13}$ A at 500 V mm-1 electric field), without the necessity of interlayers

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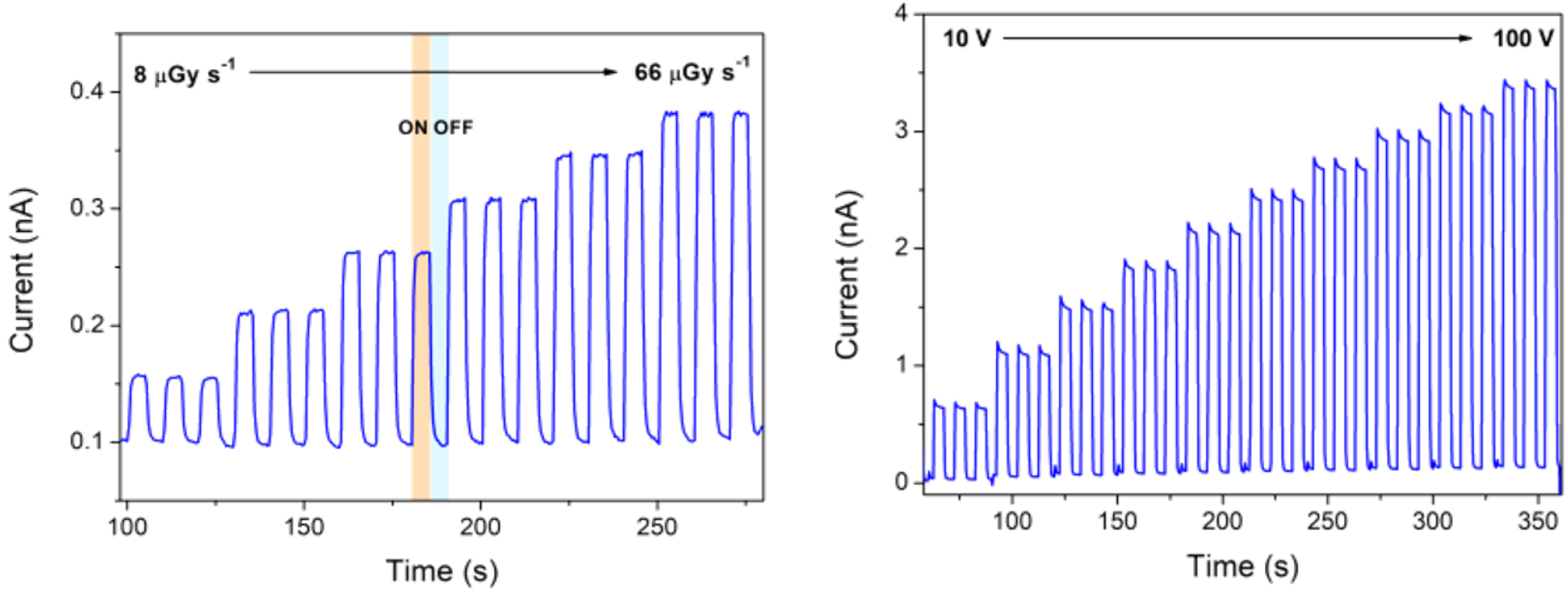
# 2D Perovskites thin film  X-ray radiation detectors




**STABILITY & REPRODUCIBILITY**

- Very stable to repeated pulses (300 consecutive pulses in a total of 30 minutes)
- Very stable under continuous irradiation of 10 minutes (4 Gy total dose at 80 V) Energies 40keV-150keV (mammography and CT scans).
- Same response after 80 days of storage in air not encapsulated

*F.Ledee et al. Advanced Optical Materials 10 (**2022**)*

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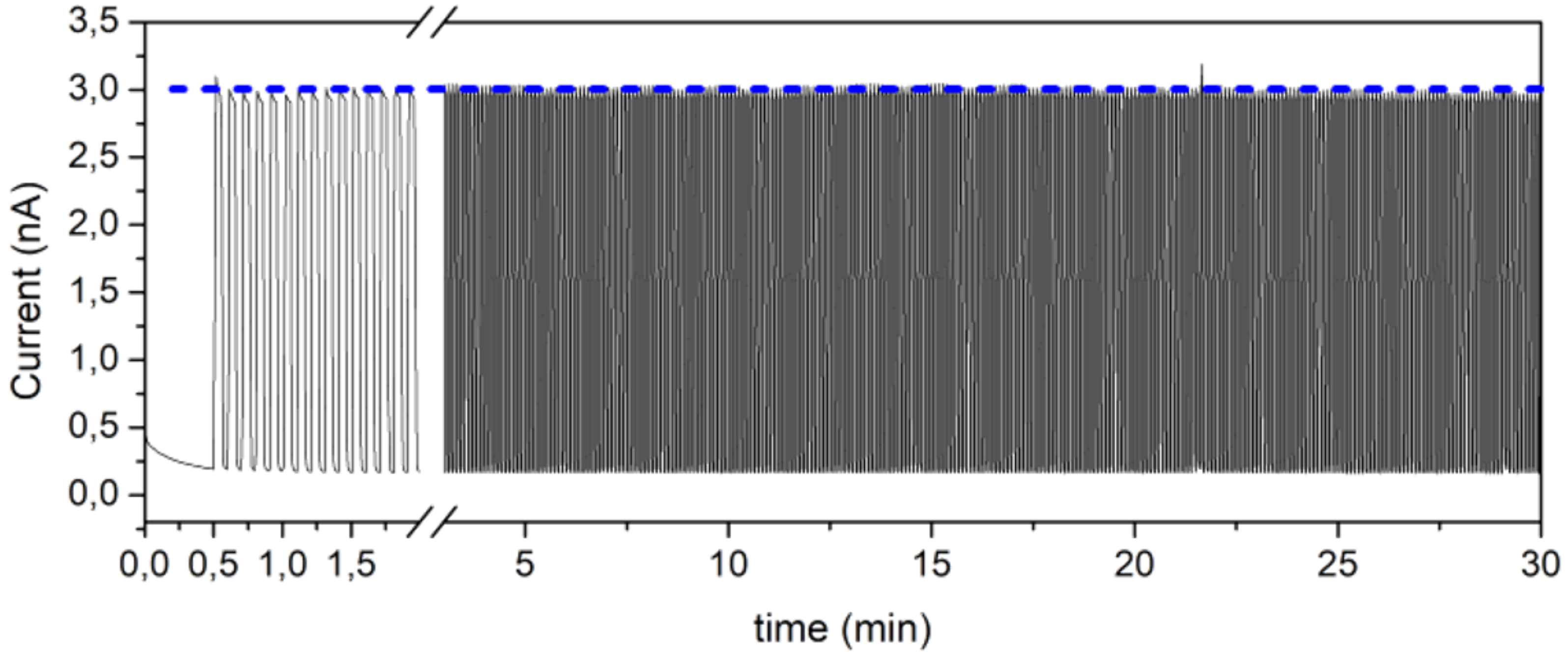


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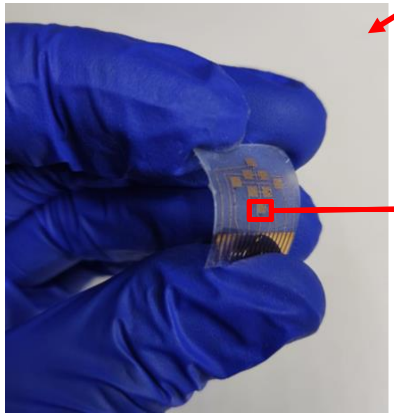
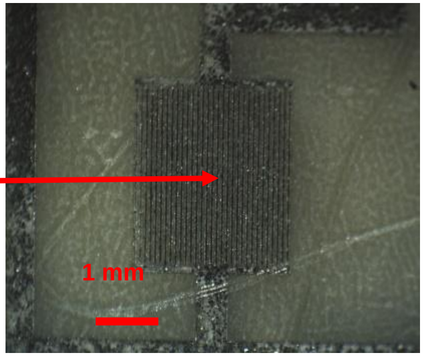
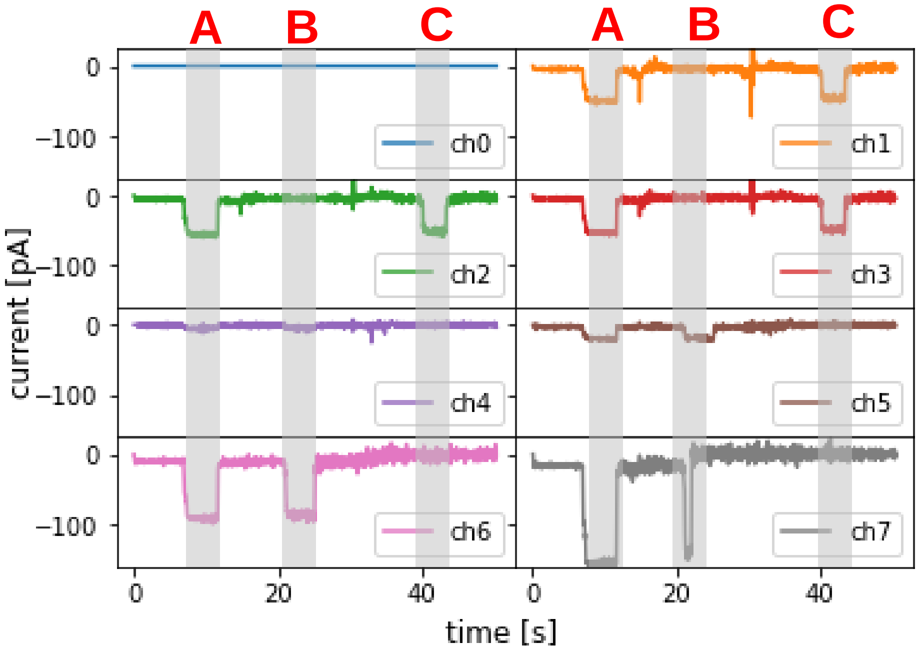
# Wearable wireless X-ray sensor (up to 150keV) based on 2D perovskite thin films




A – all pixels exposed
B – pixels 0-3 shut
C – pixels 4-7 shut

- **8 pixel matrix**
- **External $V_{bias}$ =1V**
- Pixels ch 1,2,3 have same area → same response .
- Pixels ch 4-7 have different (larger) areas → signal scales with pixel area

*A.Ciavatti et al. Advanced Material Technologies (**2022**)*
*L.Basirico' et al. Manuscript submitted (**2024**)*

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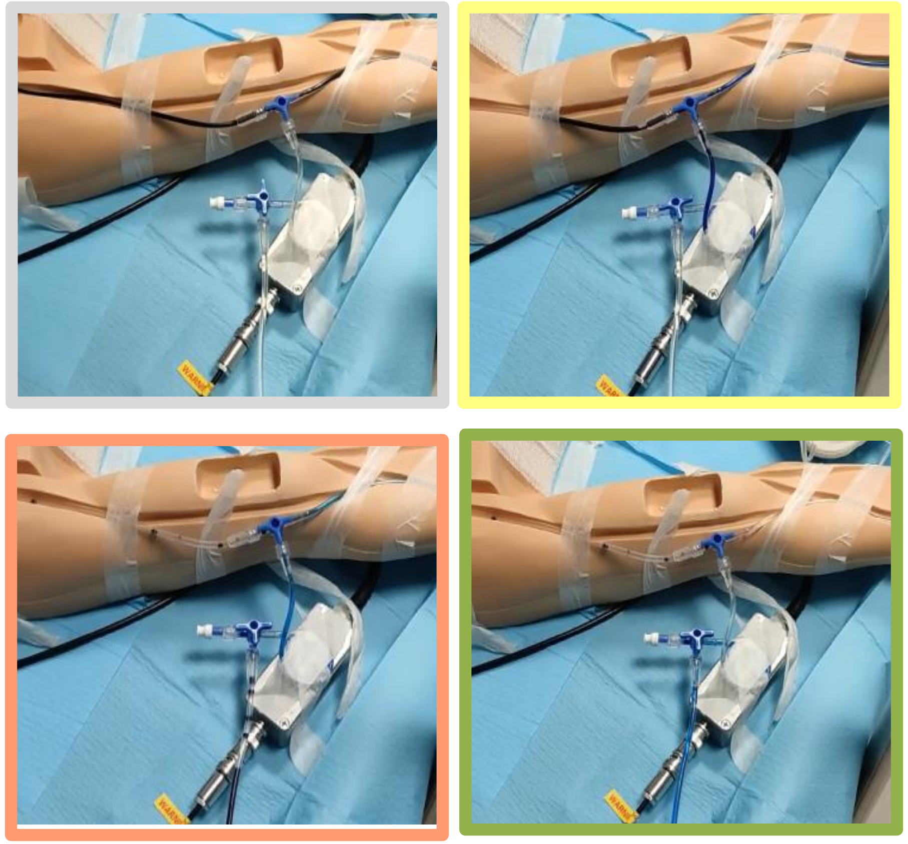

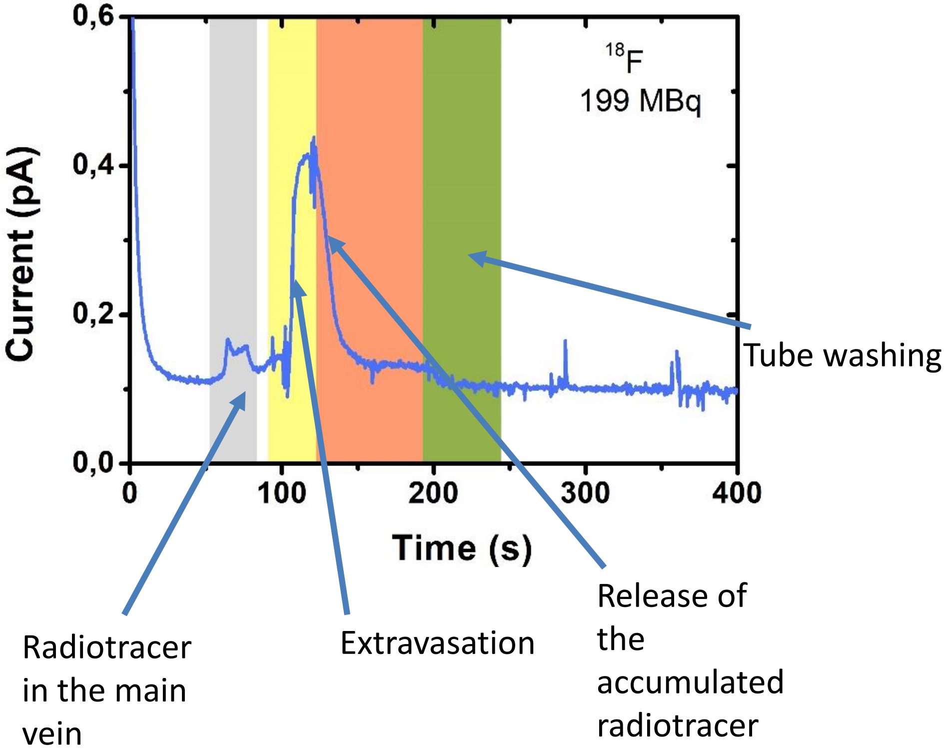


*L.Basirico' et al. Manuscript submitted (**2024**)*

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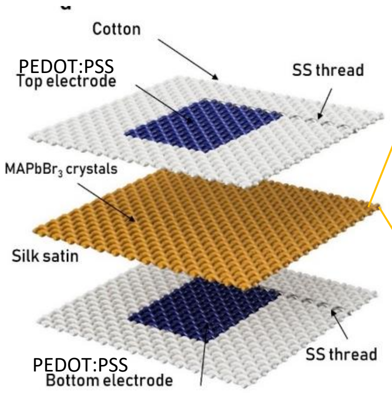
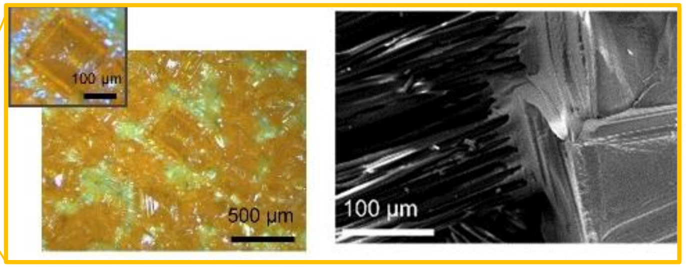
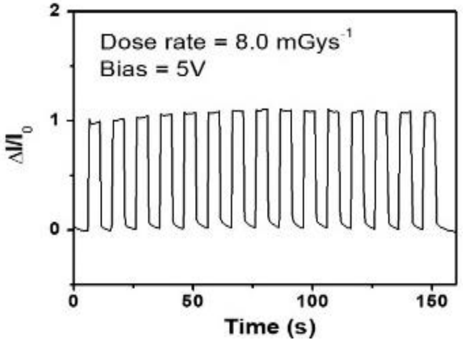
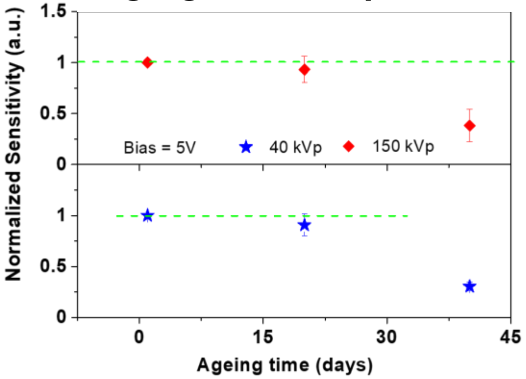
# Direct detection by 3D perovskites on textiles

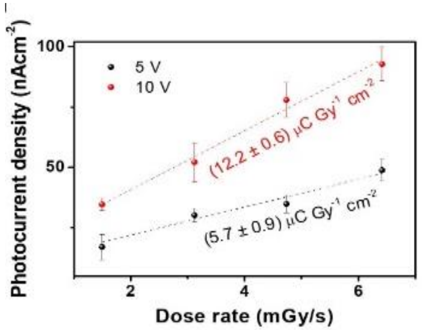



Aging, no encapsulation




L.Possanzini et al *Advanced Mat Interfaces*, (**2021**)

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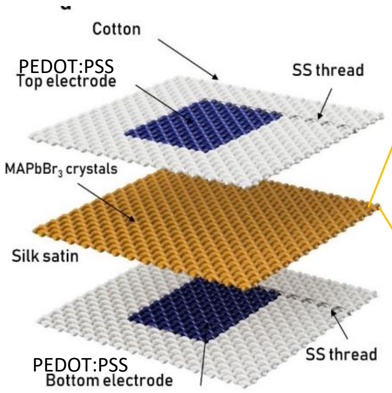


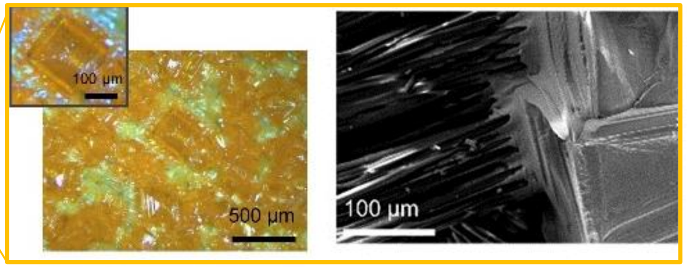


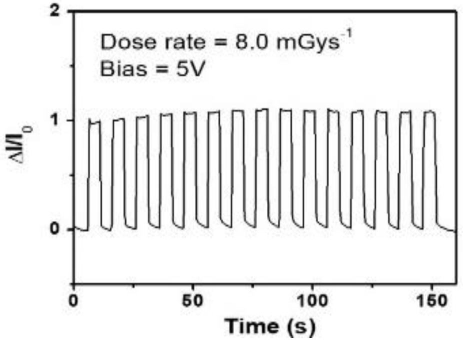


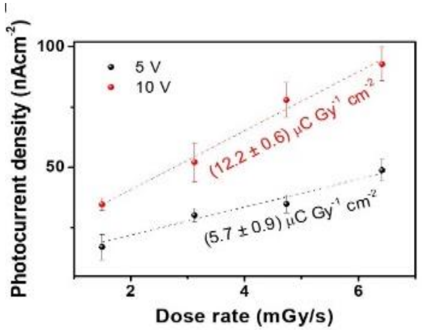


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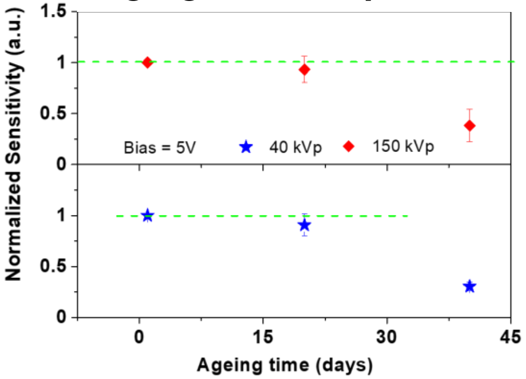
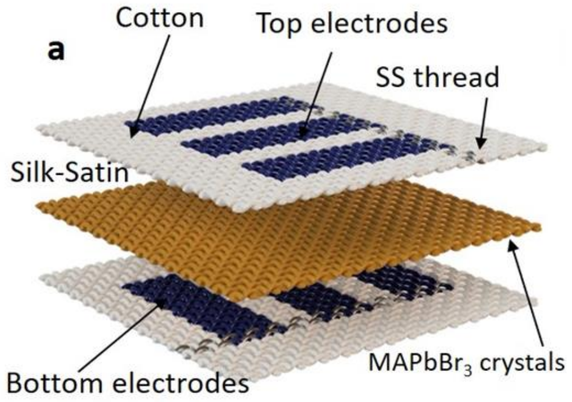
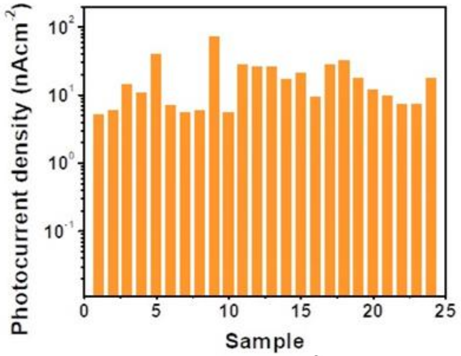
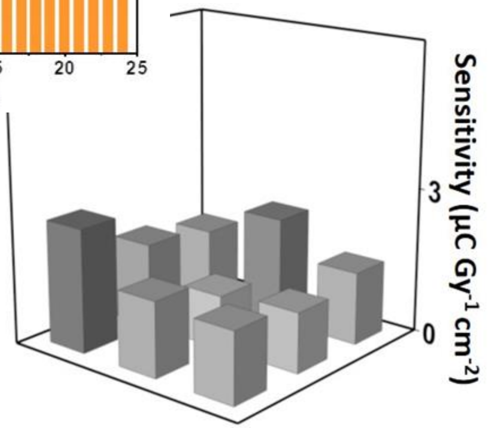



**2D pixelated matrix**




L.Possanzini et al *Advanced Mat Interfaces*, (**2021**)

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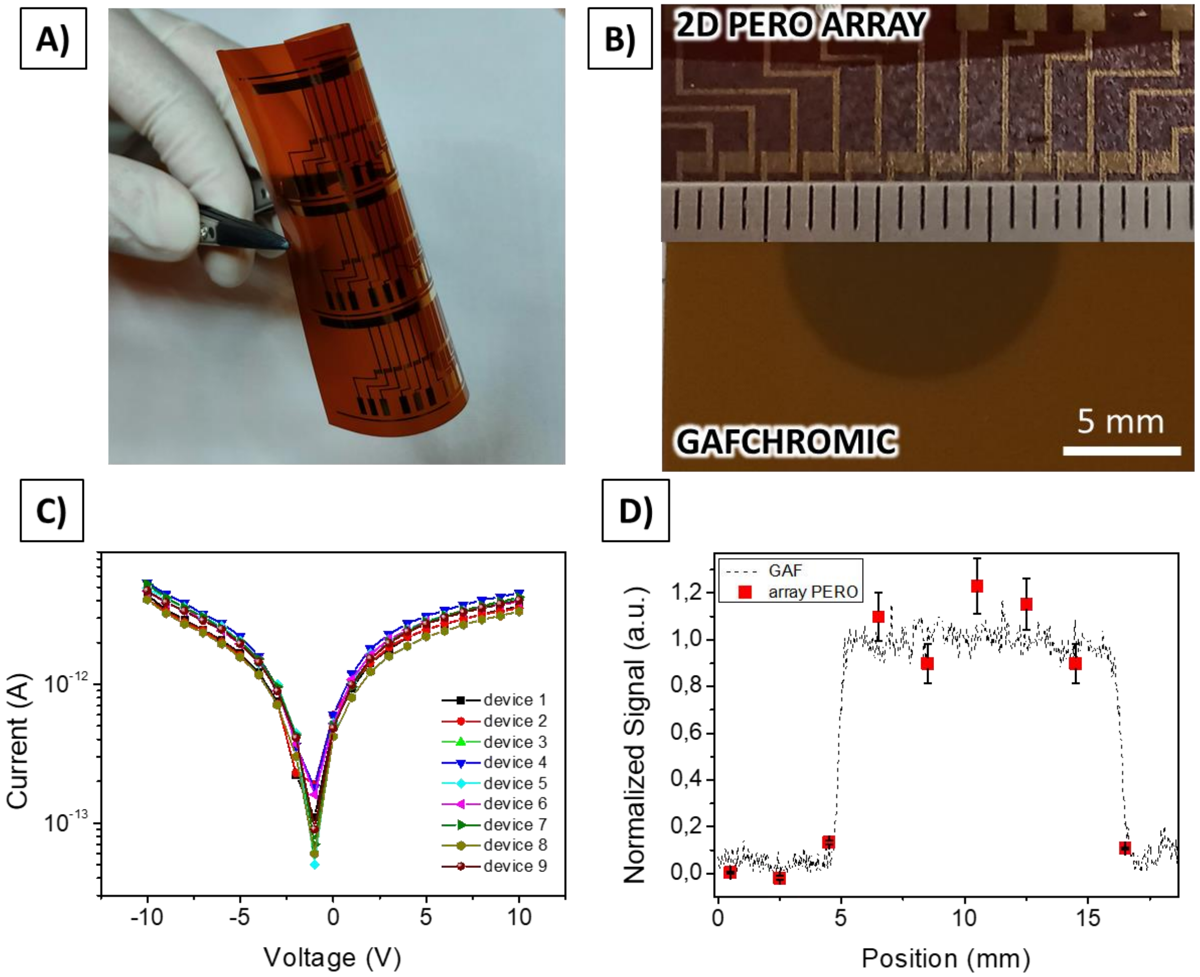
# FLEXIBLE X-RAY BEAM MONITOR ARRAY




I. Fratelli et al., Advanced Science (2024), in publication

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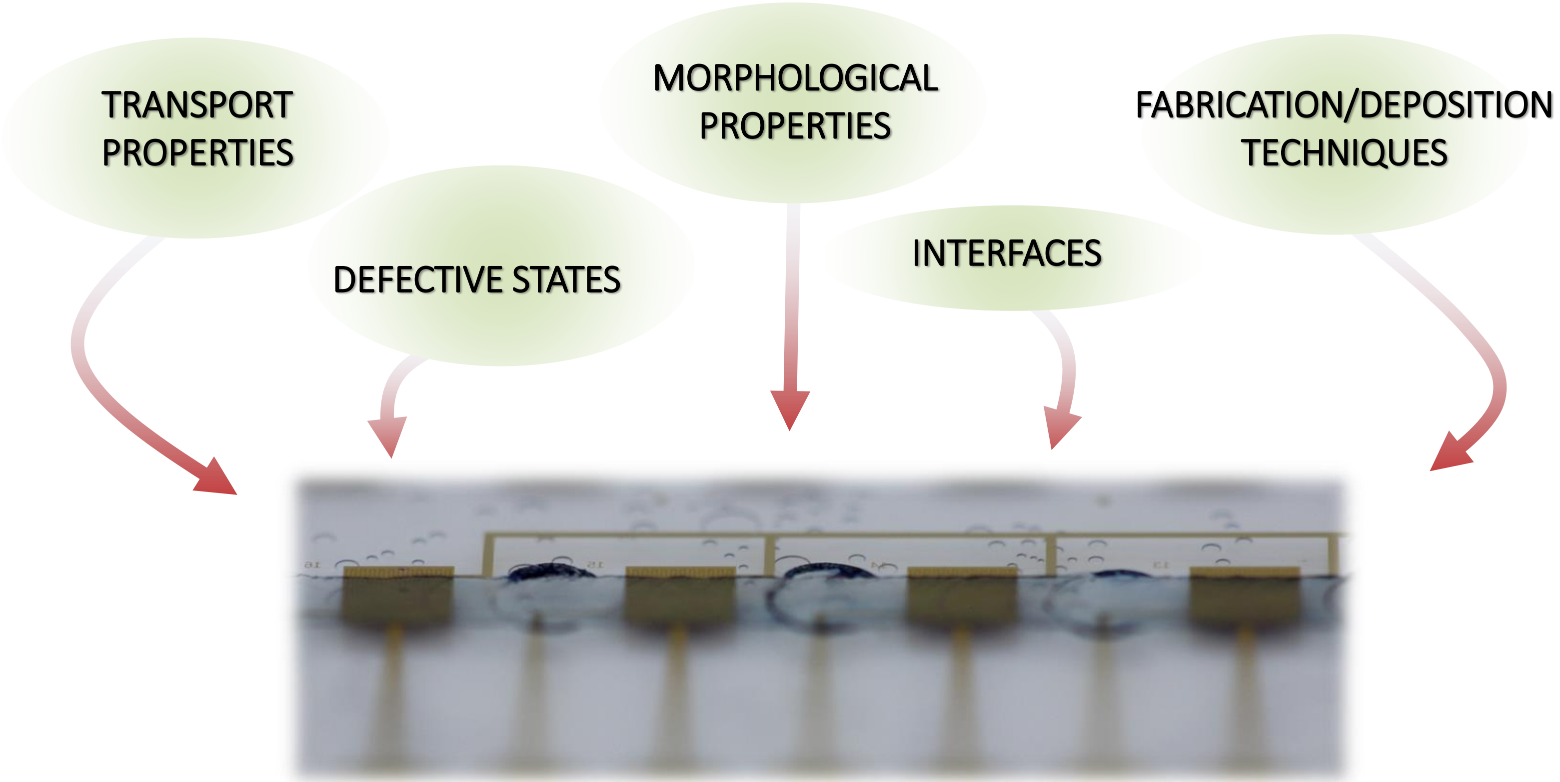
# CONCLUSIONS

**Flexible, lightweight, printed** radiation detectors based on perovskite **thin film,** can effectively and **directly detect ionizing radiation with ultrahigh sensitivity**



# ACKNOWLEDGMENTS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https://site.unibo.it/semiconductor-physics/en

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Agenzia Spaziale Italiana — NASA
***IRIS*** *Ionizing radiation detectors for wearable dosimetry of space crews (2022-2025)*

FIRE
*Flexible organic Ionizing Radiation dEtectors*
(2019-2022)
INFN

UNIONE EUROPEA Fondo europeo di sviluppo regionale
Fortress
(2019-2022)
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RELOAD
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# Thank you for your attention