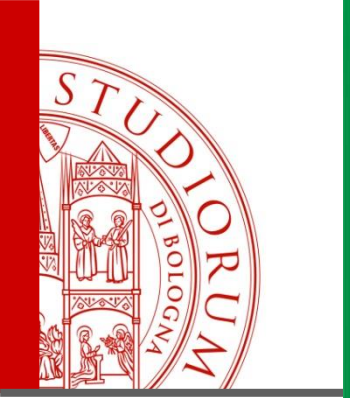


Designing ultraflexible perovskite X-ray detectors through interface engineering

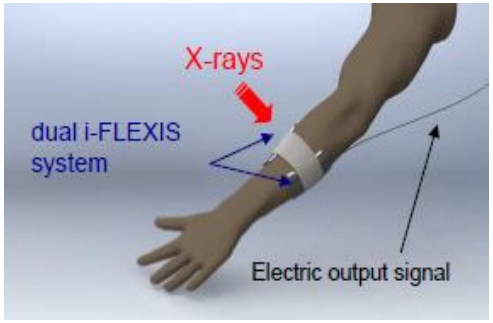
S.Demchyshyn[2], M.Verdi[1], L. Basiricò[1], A.Ciavatti[1], B.Hailegnaw[2], D.Cavalcoli[1], M.Scharber[2], N.Sariciftci[2], M.Kaltenbrunner[2], B.Fraboni[1]

[1]*Department of Physics and Astronomy, University of Bologna, Italy*

[2]*Johannes Kepler University Linz, Austria*

ALMA MATER STUDIORUM - UNIVERSITÀ DI BOLOGNA
IL PRESENTE MATERIALE È RISERVATO AL PERSONALE DELL'UNIVERSITÀ DI BOLOGNA E NON PUÒ ESSERE UTILIZZATO AI TERMINI DI LEGGE DA ALTRE PERSONE O PER FINI NON ISTITUZIONALI

Motivation:
Large area, flexible X-and gamma- ray detectors

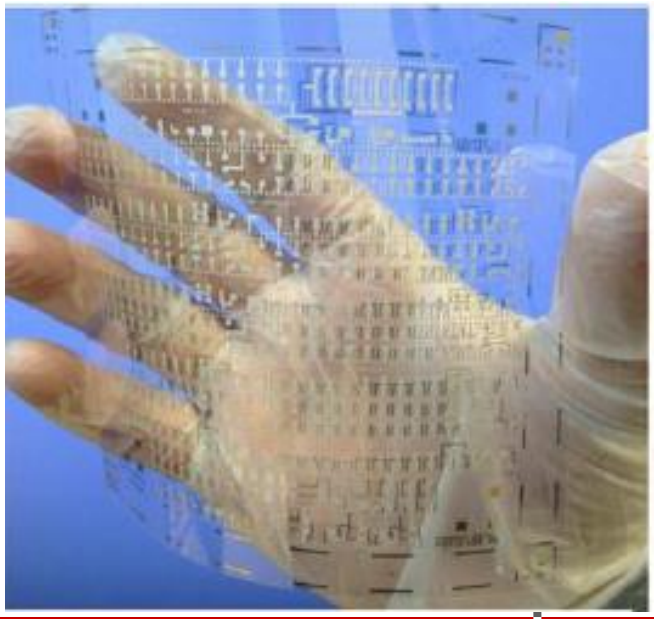


health diagnostic applications

Citizens security: “smart walls/pillars”

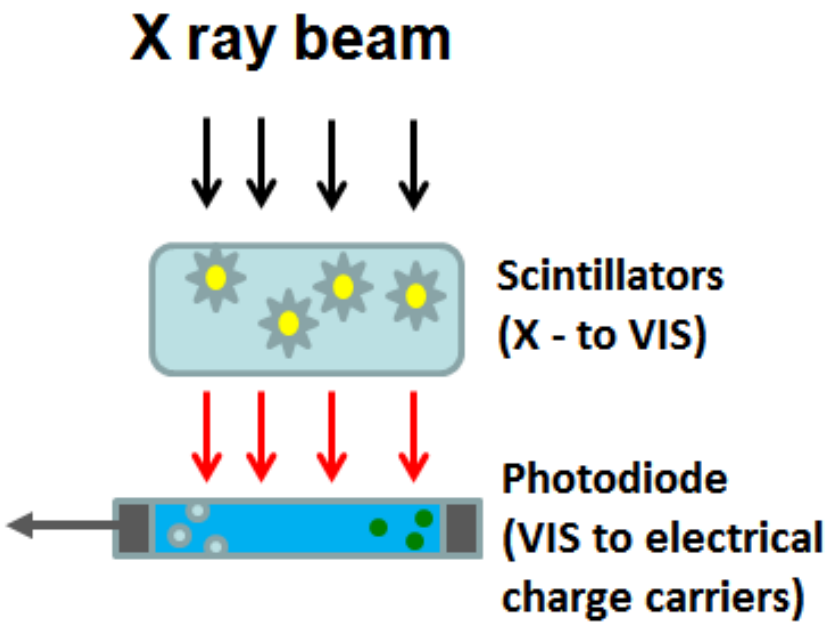
Airport security

Many novel applications for detectors combining: **low cost**, **low power supply , mechanical flexibility and real time response**

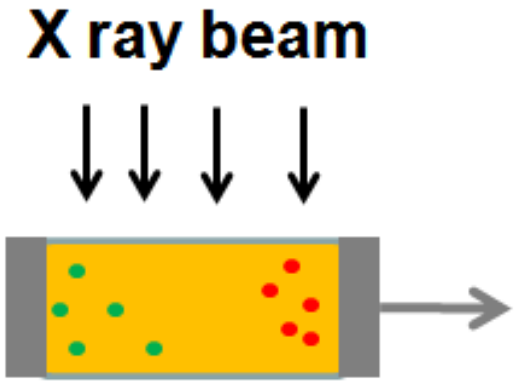


Ionizing Radiation sensors

INDIRECT DETECTION



DIRECT DETECTION



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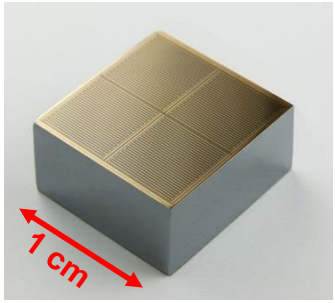
State-of-the-art Direct Semiconductor detectors

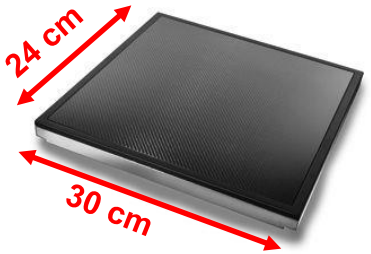
CZT Single Crystals



Material	CdTe
Crystal structure	Cubic (ZB)
Growth method*	THM
Atomic number	48, 52
Density (g/cm^3)	6.20
Band gap (eV)	1.44
Pair creation energy (eV)	4.43
Resistivity (Ω cm)	10^9
$\mu_e\tau_e$ (cm^2/V)	10^{-3}
$\mu_h\tau_h$ (cm^2/V)	10^{-4}

- ✓ Best performing (high μτ)
- X very expensive
- X mechanical stiffness
- X small active area

a-Se + TFT AMA



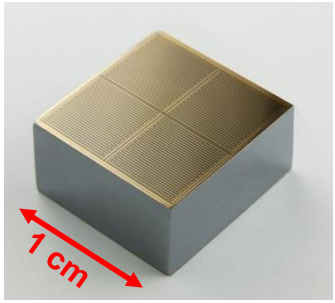
	a-Se
Eg	2.2 eV
δ	49 μm at 20 keV
	998 μm at 60 keV
$W_\pm$	45 eV at 10V/μm
	20 eV at 30V/μm
Electron $\mu_e\tau_e$	$3 \times 10^{-7} \div 10^{-5} cm^2/V$
Hole $\mu_h\tau_h$	$10^{-6} \div 6 \times 10^{-5} cm^2/V$
Dark Current	$0.1 pA/mm^2$ at 10Vμm

Photoconductor	...	...	$W_\pm$ / V	Electron $\mu_e\tau_e$ (cm^2/V)	Hole $\mu_h\tau_h$ (cm^2/V)
			0 V/μm 0 V/μm	3×10^{-7}–10^{-5}	
			5	~2×10^{-4}	

- ✓ Large (limited) active area
- X Expensive
- X mechanical stiffness

State-of-the-art Direct Semiconductor detectors

CZT Single Crystals



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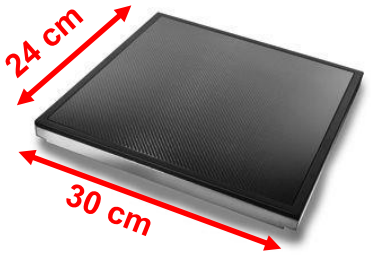
a-Se + TFT AMA



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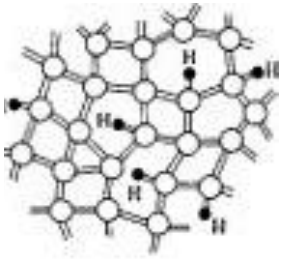
Hole $\mu_h\tau_h$	$10^{-6}\div6\times10^{-5}cm^2/V$
Dark Current	$0.1pA/mm^2$ at 10Vμm
Electric Field	10÷30V/μm
Thickness	200÷1000μm
Electron transit time	0.1÷0.5ms at 10Vμm

Photoconductor State Preparation	δ at 20 keV δ at 60 keV	E_g eV	$W_\pm$ eV	Electron $\mu_e\tau_e$ (cm^2/V)	Hole $\mu_h\tau_h$ (cm^2/V)
Stabilized a-Se Amorphous Vacuum deposition [15]	49 μm 998 μm	2.2	45 at 10 V/μm 20 at 30 V/μm	3×10^{-7}–10^{-5}	10^{-6}– 6×10^{-5}
$Cd_{.95}Zn_{.05}Te$ Polycrystalline Vacuum deposition (sublimination)	80 μm 250 μm	1.7	5	~2×10^{-4}	~3×10^{-6}

Flexible Large Area Electronics: Material Platforms

Amorphous Silicon

Si

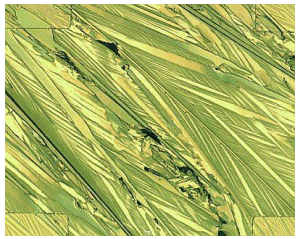


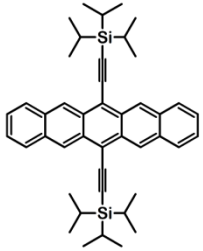
physical deposition

μ = 1 cm^2/Vs

Organic Semiconductors

e. g. TIPS pentacene





solution deposition

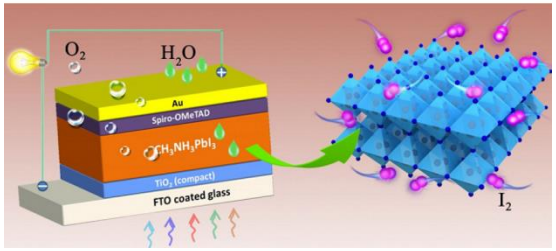
μ = 1 cm^2/Vs

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

μ = 1-600 cm^2/Vs

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

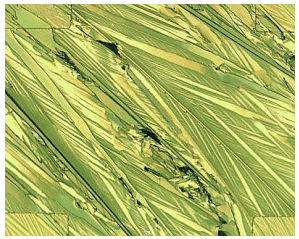
Flexible Large Area Electronics: Material Platforms

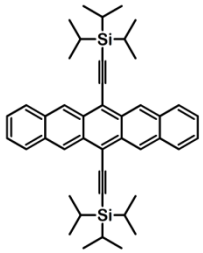
Ilaria Fratelli
Comm (Sez V) atticon12462

Laura Basirico'
INVITED (Sez V) 14/9

Organic Semiconductors

e. g. TIPS pentacene





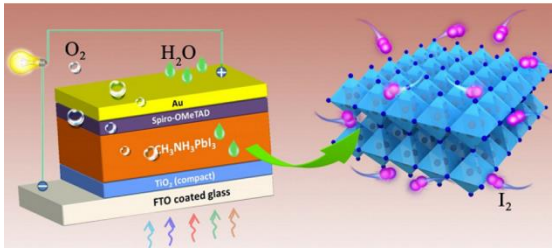
solution deposition

μ = 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. $MAPbI_3$

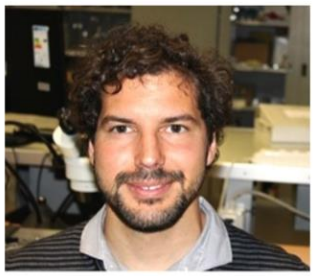


solution deposition

μ = 1-600 cm^2/Vs

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

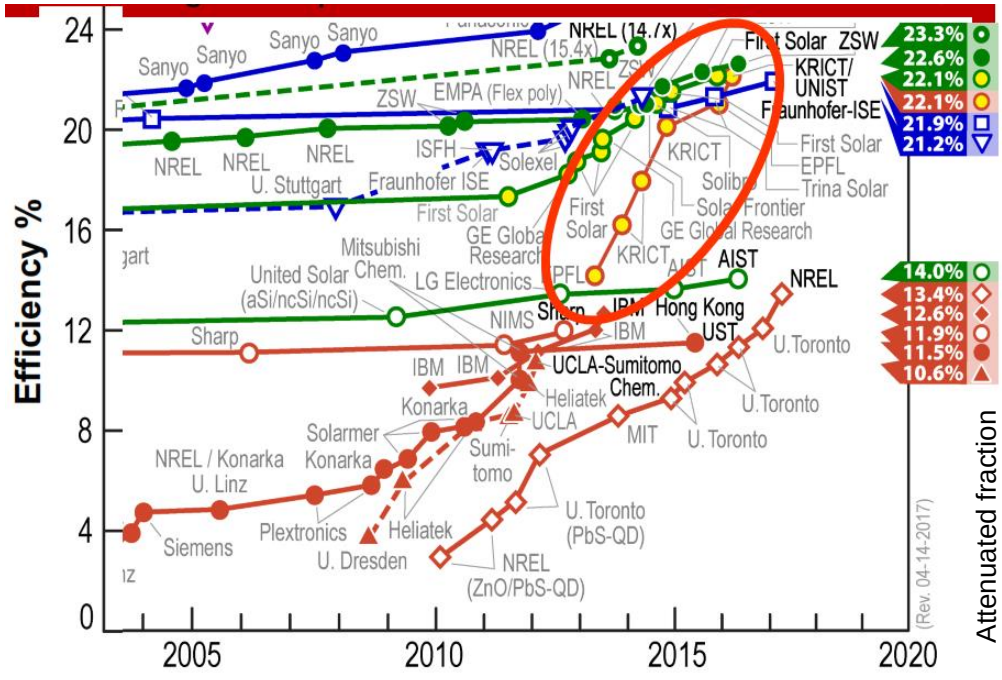
Andrea Ciavatti
Comm (Sez II)
atticon12553



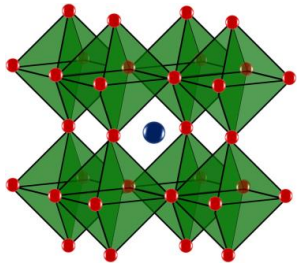
Matteo Verdi
Comm (Sez VI)
atticon12766

Hybrid Perovskites: why?

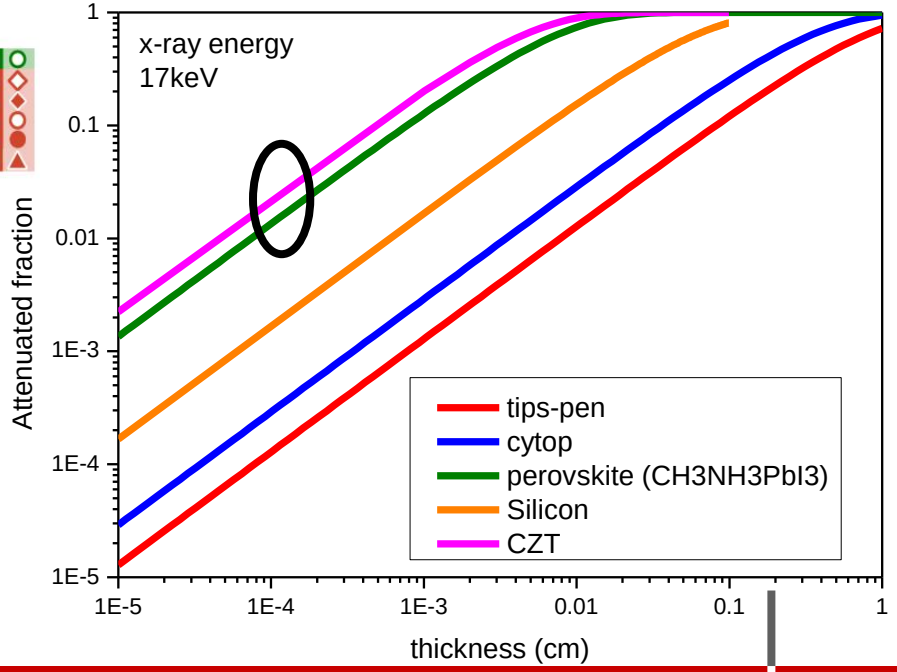
→ High perfoming,
solution processed solar cells



→ High charge carrier mobility
up to 1 – 70(600) cm^2/Vs



→ High attenuated fraction:
Heavy atoms (eg Pb) inside



Perovskites for direct X-ray detection

FILMs 300nm – 60μm

S. Yakunin et al, Nature Photonics, 9 (2015) 444

Liu et al, *Advanced Materials* 31, (2019) 1901644

FLEXIBLE

THICK FILMs/wafers 200μm-1mm

S. Shrestha et al., Nature Photonics, 11 (2017) 436

Y.C. Kim et al., Nature, 550 (2017) 87

Bruzzi et al, APL Materials 7, 051101 (2019)

W. Pan et al, Adv Mat (2019)1904405

THICK SINGLE CRYSTALS

C. Stoumpos, Cryst. Growth Des., 13 (2013) 2722

D.N. Dirin et al., Chem Mater., 28 (2016) 8470

S. Yakunin et al, Nature Photonics, 10 (2016) 585

Wei et al., Nature Photonics, 10 (2016) 333

Wei et al., Nature Photonics, 11 (2017) 315

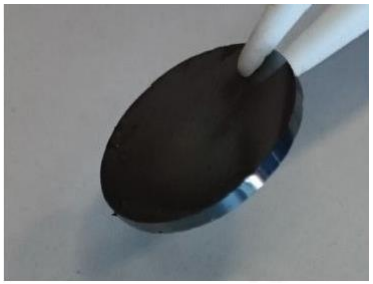
Wei et al., Nature Mat., 16 (2017) 826

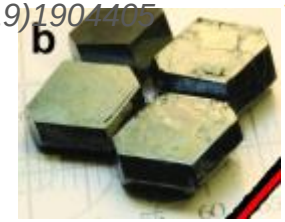
O. Nazarenko et al., NPG Asia Materials, 9 (2017) 373

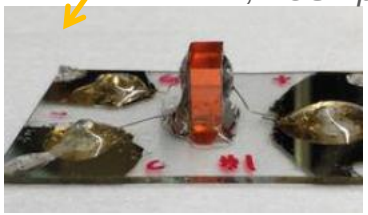
Pan et al, Nature Photonics 11 (2017) 726

Steele et al, Adv. Mater. 30 (2018)1804450

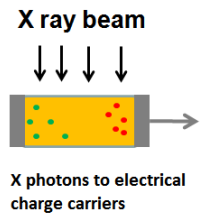
Li, ACS Appl. Mater. Interfaces (2019)11, 7, 7522

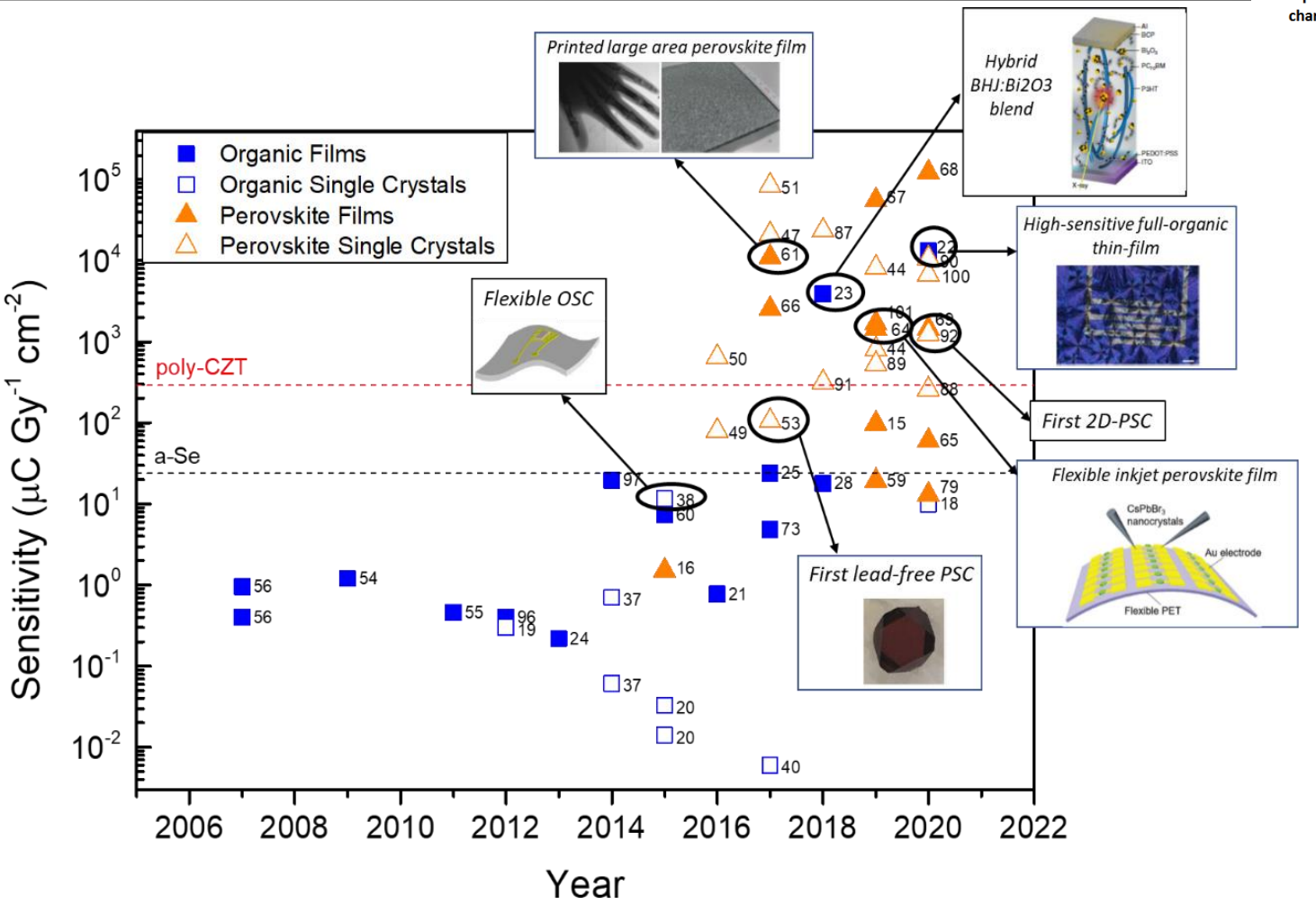






Organic semiconductors and Perovskites for X-ray detection: sensitivity

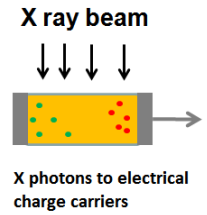


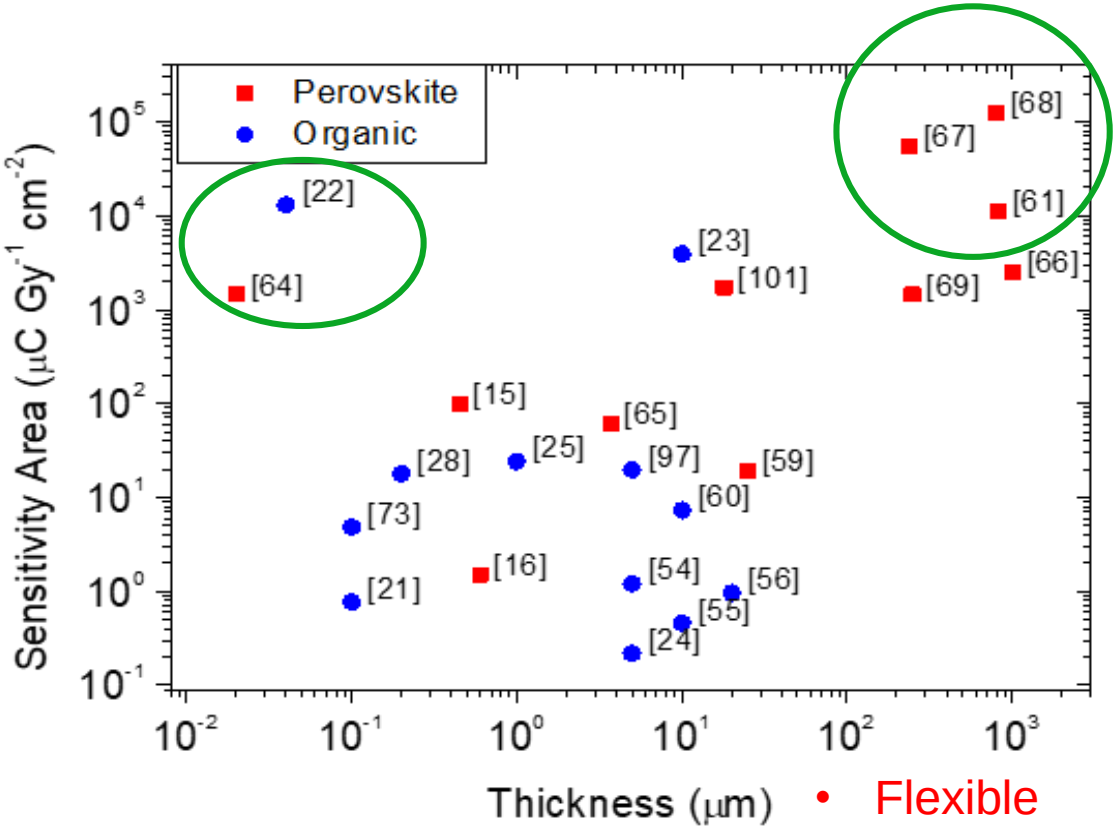


Basirico', Ciavatti & Fraboni *Advanced Materials Technologies 2000475 (**2020**)*

A.Ciavatti et al. *Advanced Functional Materials* (**2019**)

Organic semiconductors and Perovskites for X-ray detection: thickness

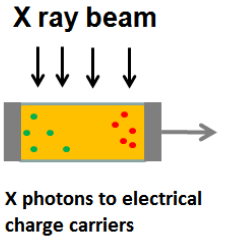




- Flexible
- QDs photoconductor
- poor stability/reproducibility

Y. C. Kim et al *Nature* 550, 87 **(2017)**
J. Liu et al, *Advanced Materials* 31, 1901644 **(2019)** **[64]**
W. Pan et al *Advanced Materials* 31, 1904405 **(2019)**
Basirico', Ciavatti & Fraboni *Advanced Materials Technologies* 2000475 **(2020)**

Our approach



- **Mixed-halide perovskite thin films (solution deposited)**

$(Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}PbI_{3-x}Br_x)$ - 500 nm thick

PET 1.4 micron thick substrate

- **Photodiode architecture (solar cells know-how)**

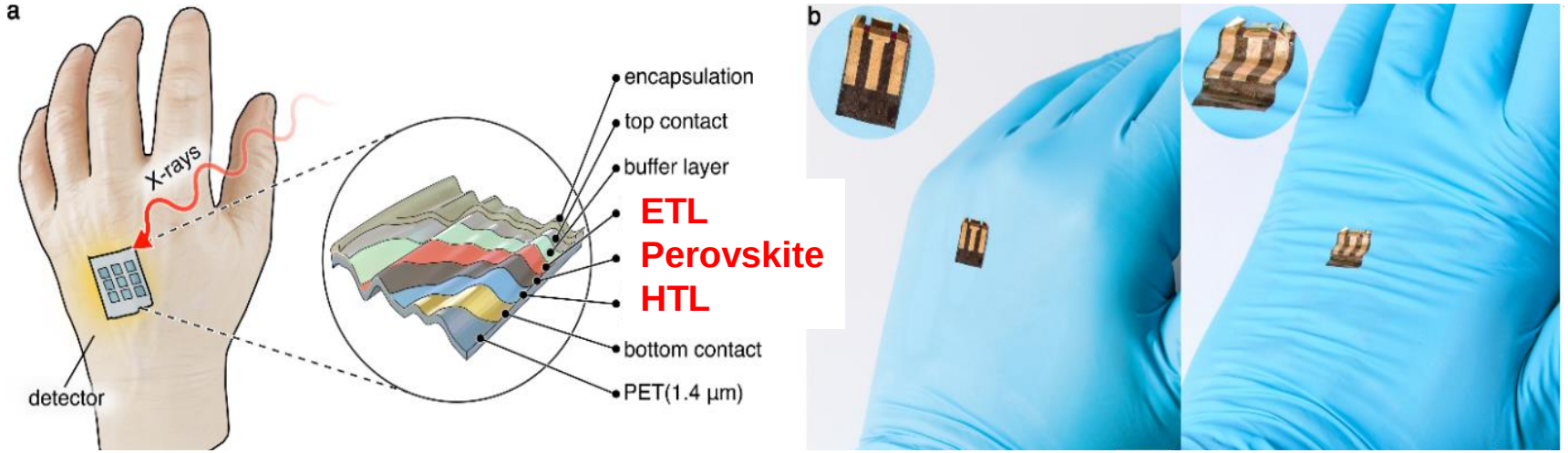
Inverted (p-i-n) configuration

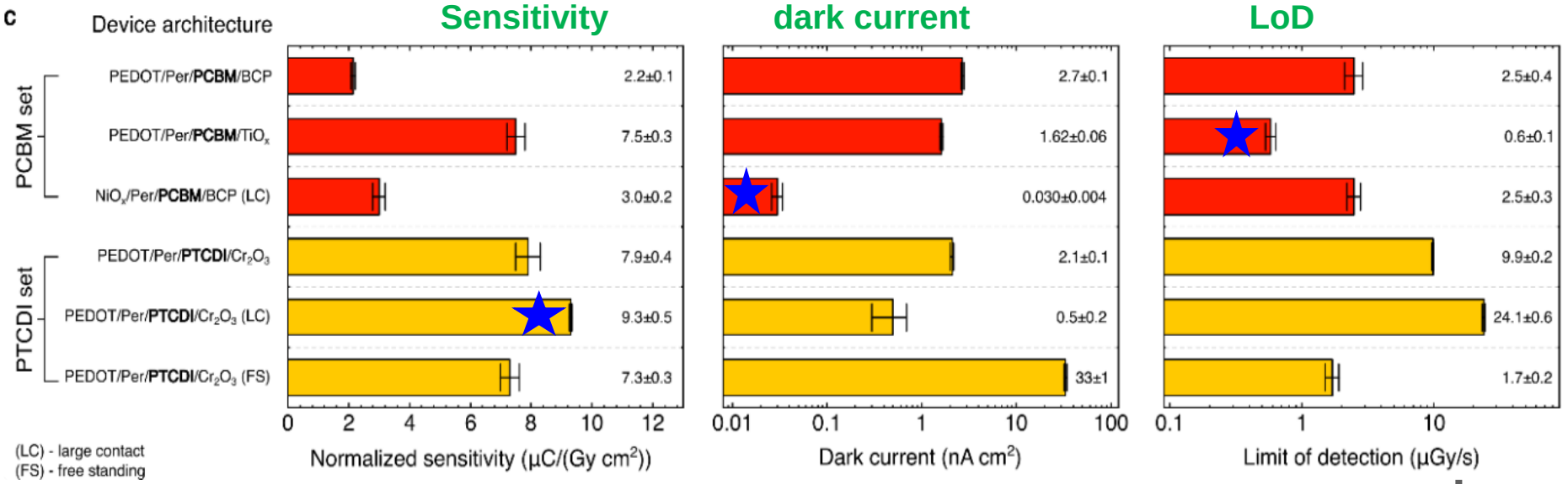
- **Interface materials and properties**

ETL: PCBM (phenyl-C61-butyric acid methyl ester)
PTCDI (N,N′-Dimethyl-3,4,9,10-Perylentetracarboxylic diimide)

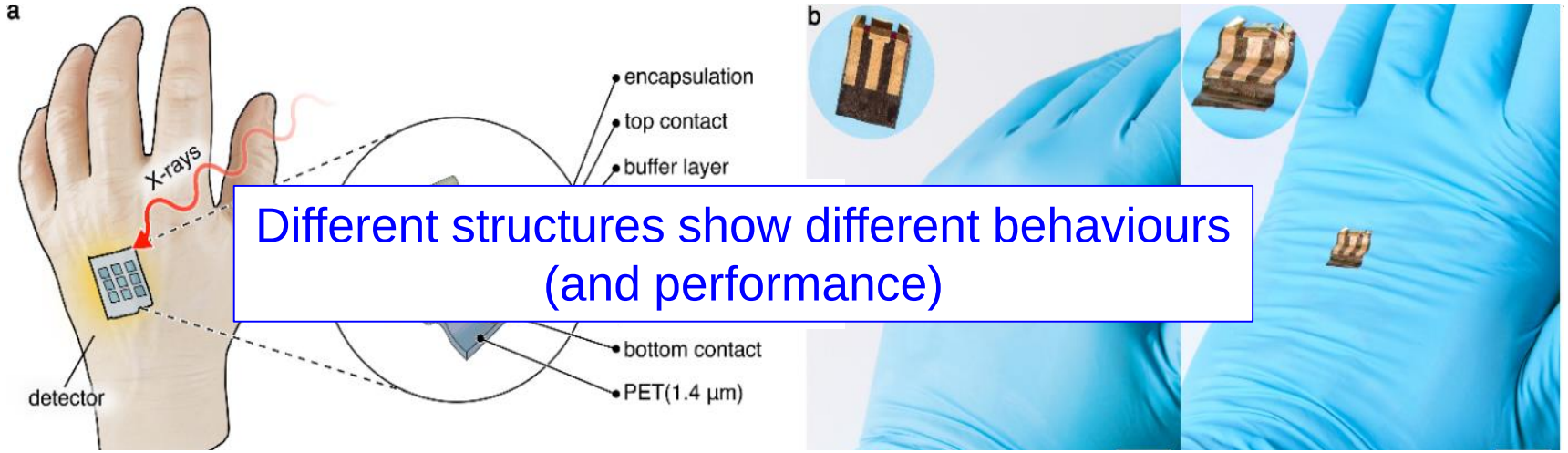
HTL: PEDOT:PSS (poly(3,4-ethylenedioxythiophene):PSS)
NiOx

Our ultraflexible perovskite detectors

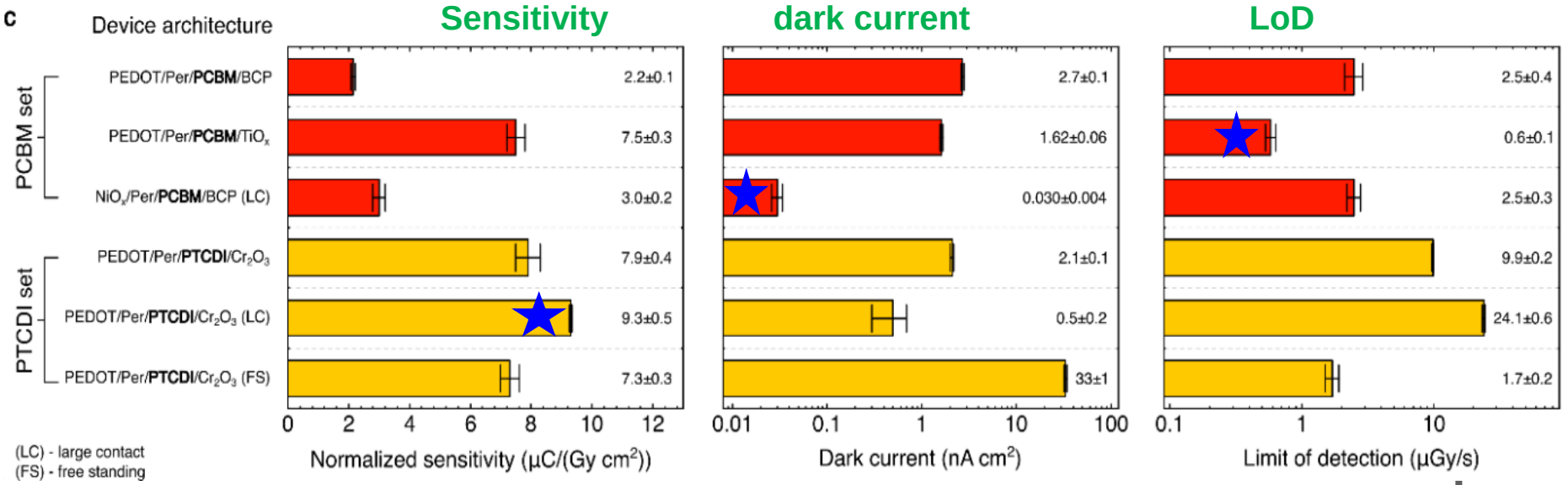




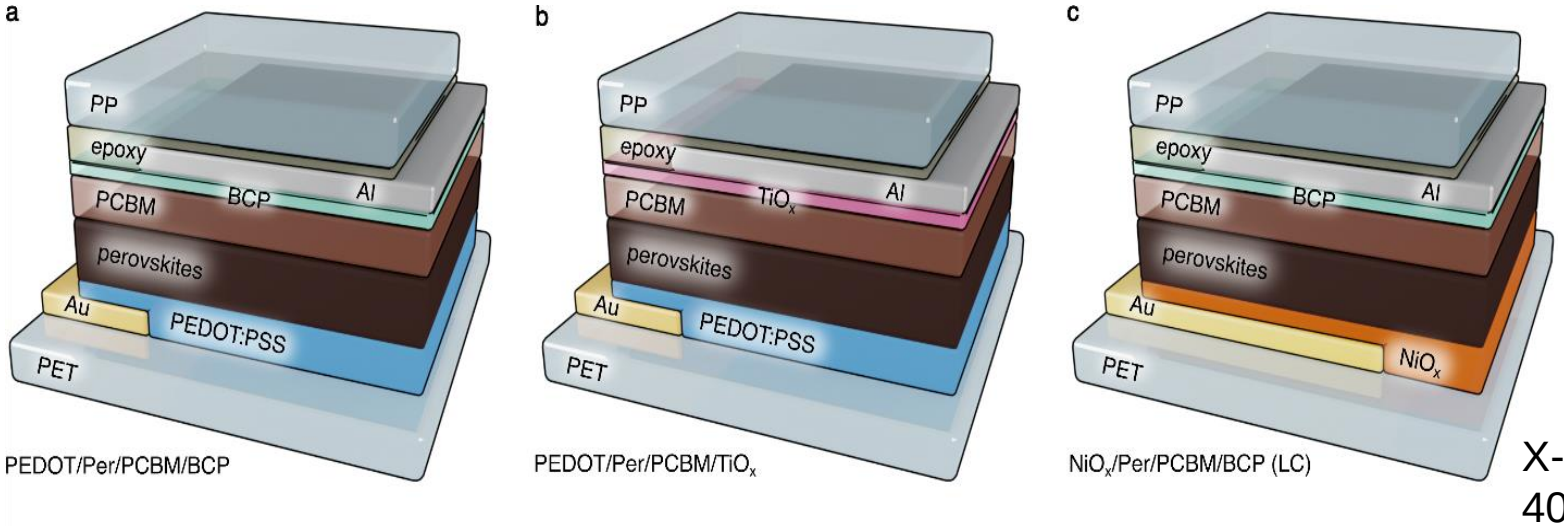
Our ultraflexible perovskite detectors



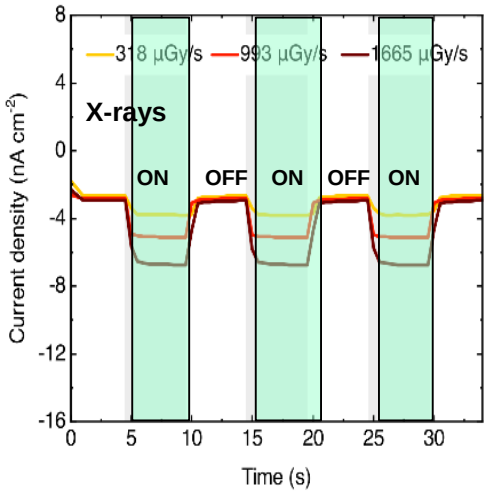
Different structures show different behaviours (and performance)

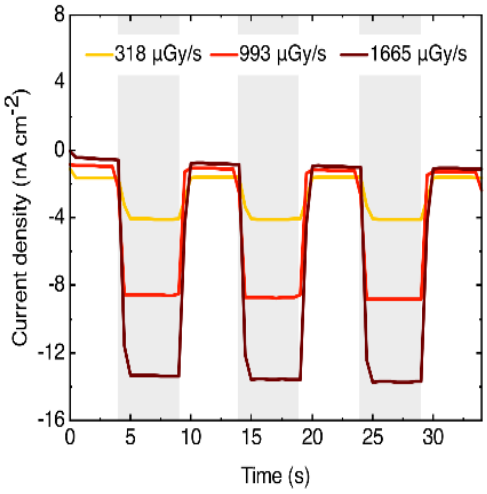


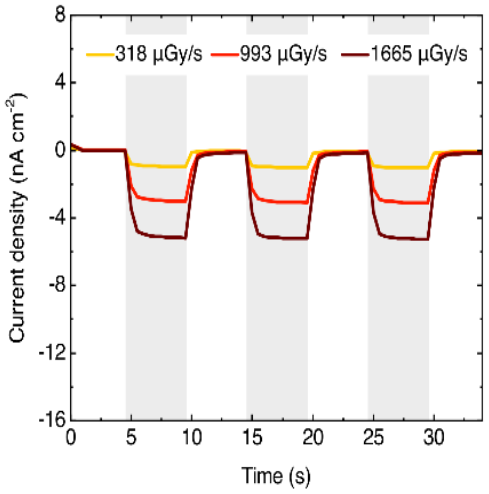
PCBM-based structures



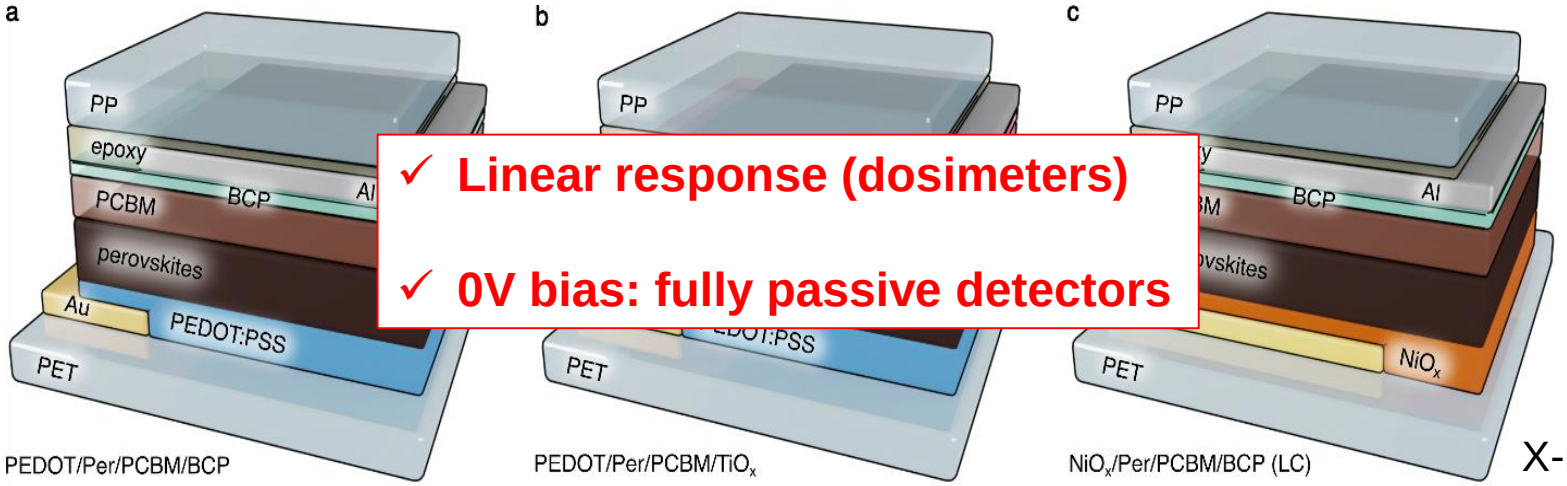
X-ray energy: 40KeV





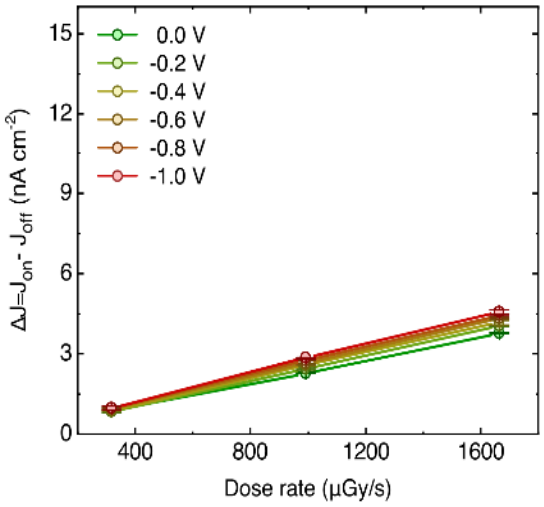


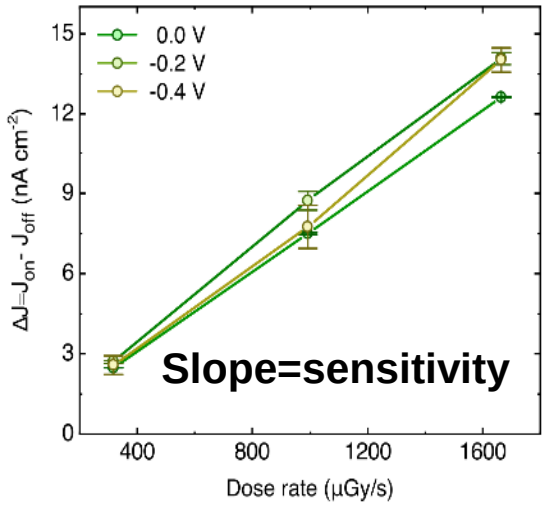
PCBM-based structures

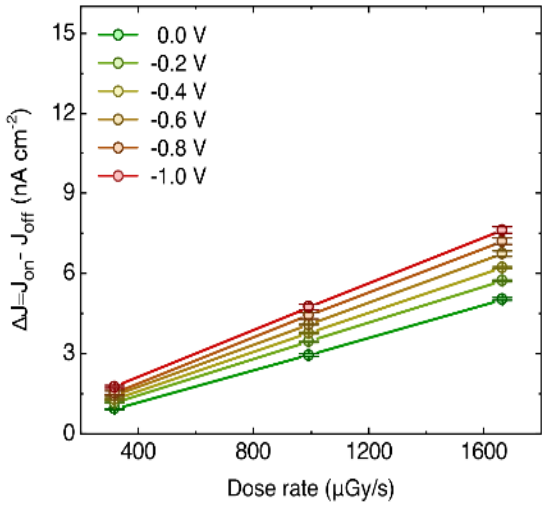


- ✓ **Linear response (dosimeters)**
- ✓ **0V bias: fully passive detectors**

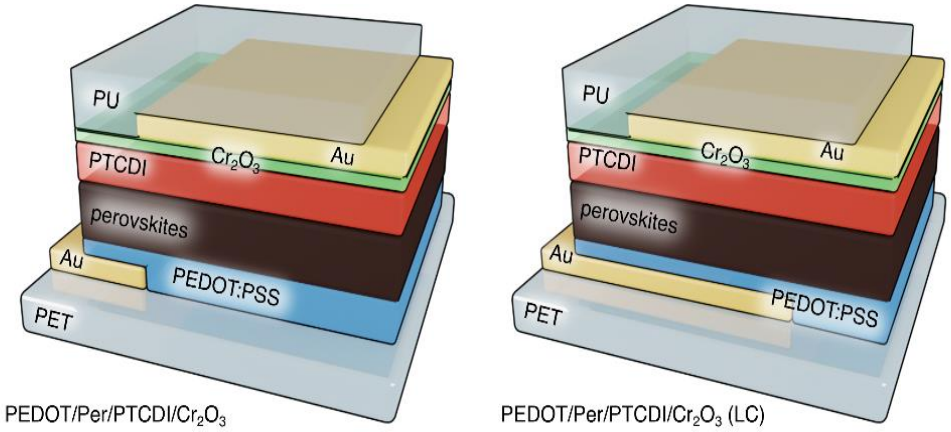
X-ray energy: 40KeV

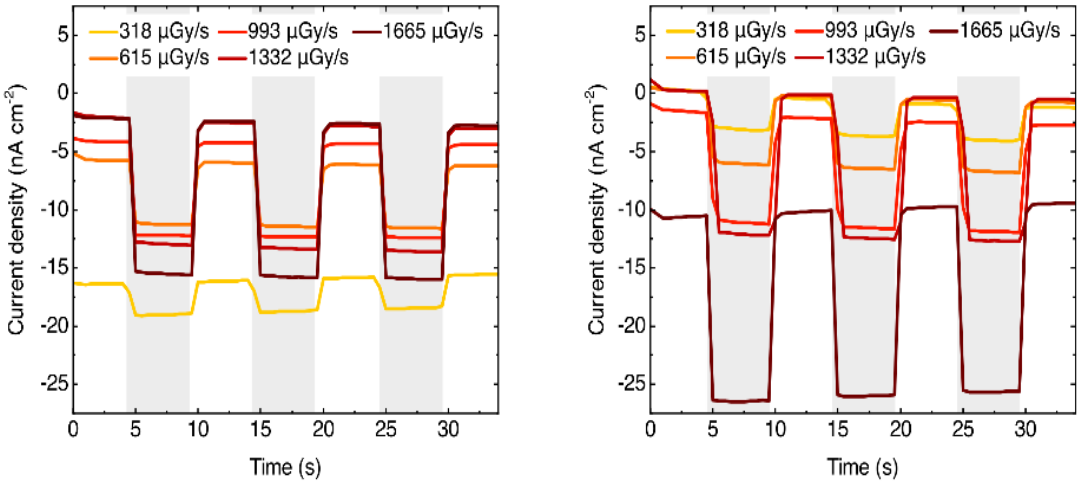




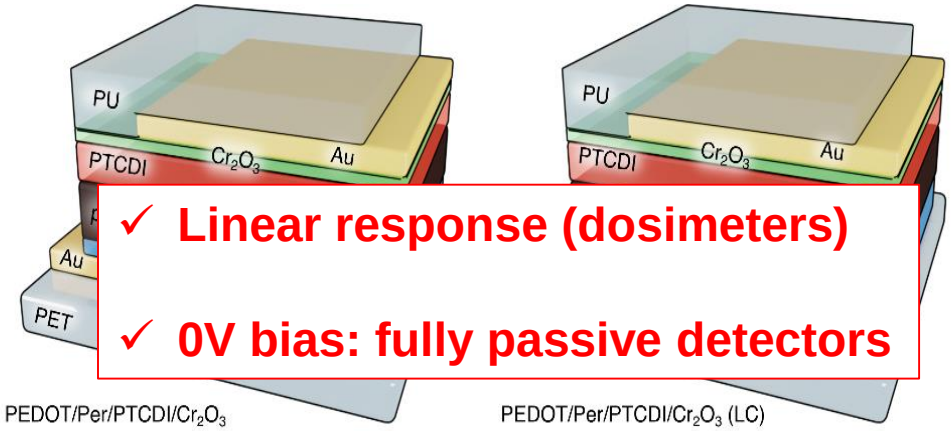


PTCDI-based structures

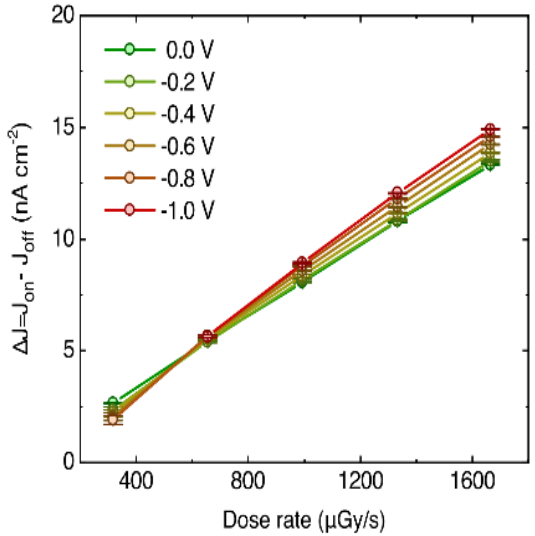


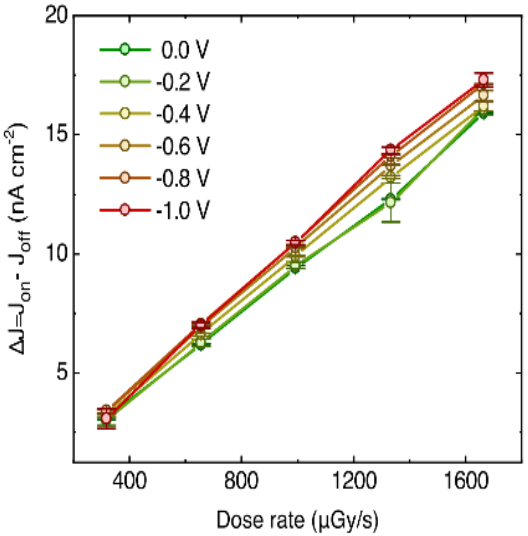


PTCDI-based structures



- ✓ **Linear response (dosimeters)**
- ✓ **0V bias: fully passive detectors**





Role of interfaces – ETL PCBM

PCBM - standard ETL material used in inverted perovskite solar cells
- low-temperature solution processing, reduction of current hysteresis
- reported to passivate the perovskite surface by reducing interface charge recombination

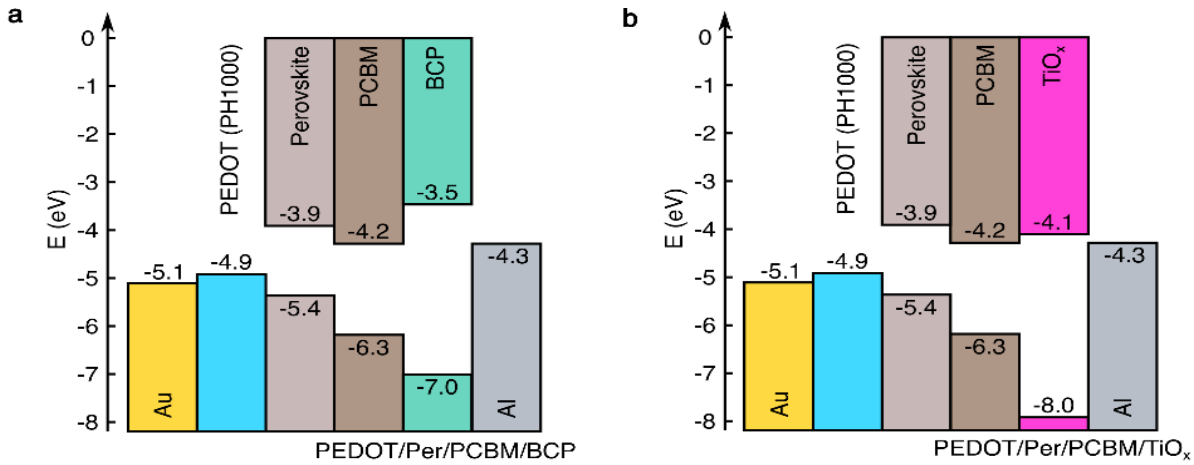
additional buffer layer: **BCP** (bathocuproine) or **TiOx** to reduce the electron injection barrier formed at the PCBM/electrode interface

TiOx interlayer
- highest X-ray induced photocurrent (for PCBM)
- highest sensitivity of 7.5±0.3 μC Gy^{-1} cm^{-2} at 0 V (for PCBM)
- Lower dark current

→ **lowest LoD 0.58±0.05 μGy s^{-1}**
Medical diagnostic requires 5 μGy s^{-1}

- TiOx high electron affinity (ETL characteristic)
- TiOx lower conduction band (CB) level (CB(TiOx) = -4.1 eV, LUMO(BCP) = -3.5 eV).
- Improves surface roughness (reduces parallel shunt pathways)
- Prevents perovskite halide ions diffusion through PCBM

Role of interfaces – ETL PCBM



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Role of interfaces – ETL PTDCI

PTDCI - well know for its exceptional stability (industrial grade material)
- excellent non-fullerene alternative for ETL for Flexible devices
- high electron mobility (~1-10 $cm^2 V^{-1} s^{-1}$), high electron affinity
- low-lying HOMO level (-6.3 eV),

additional Cr_2O_3 interlayer:

- improves the performance of perovskite and organic solar cells, due to its hole blocking capabilities (CB = 4.0 eV, E_g = 3.4 eV)
- its chemical resistance effectively shields commonly used metal contacts from detrimental reactions with oxidizing and halide-forming iodide species, making the devices more stable

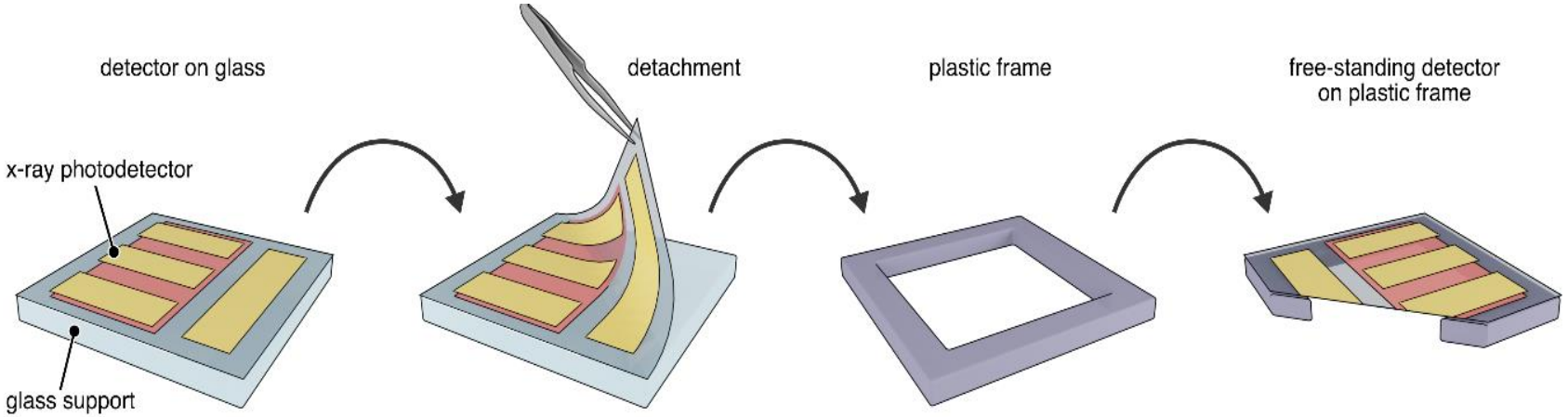
→ achieve **record sensitivity 9.3±0.5 µC Gy^{-1} cm^{-2} at 0V** for thin film perovskite X-ray detectors

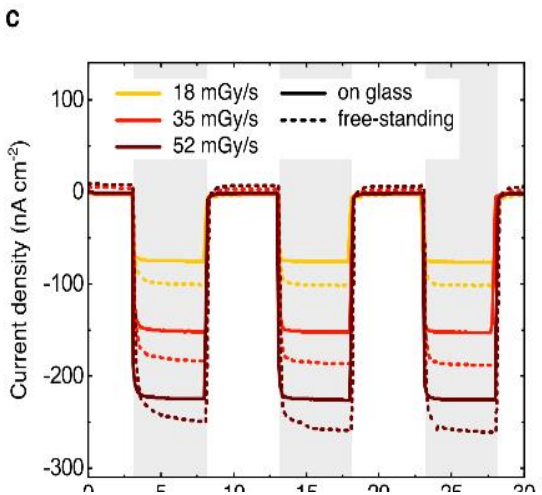
Role of interfaces - HTL

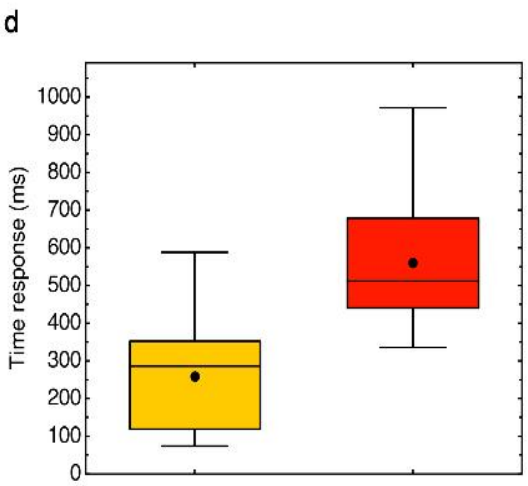
PEDOT:PSS	- ultraflexible
NiOx	- very low dark currents

Comparable sensitivities

Free-standing ultraflexible X-ray detectors

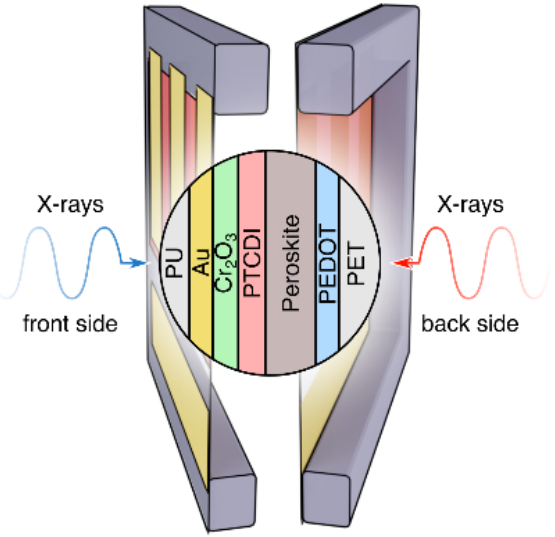


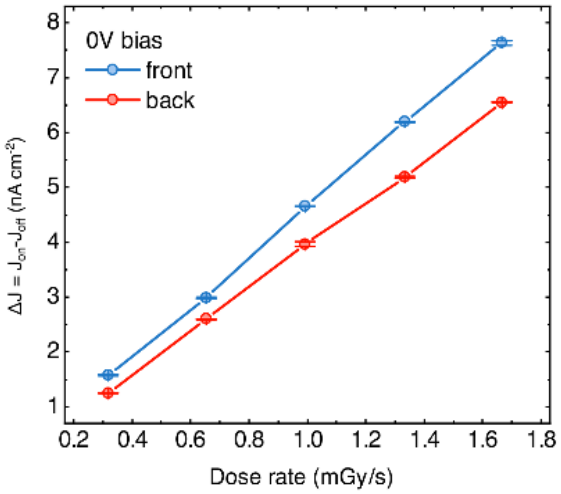




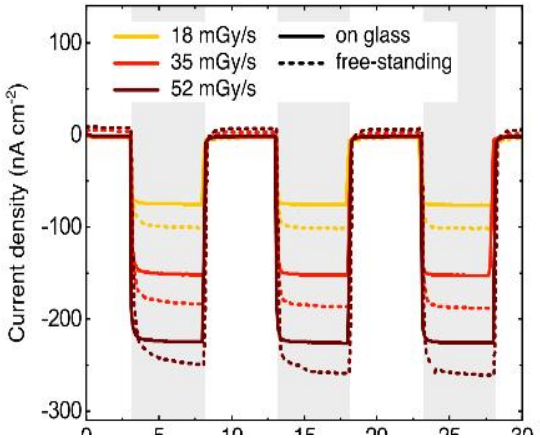
Denchyshyn, Fraboni et al *Advanced Science (***2020 in press)**

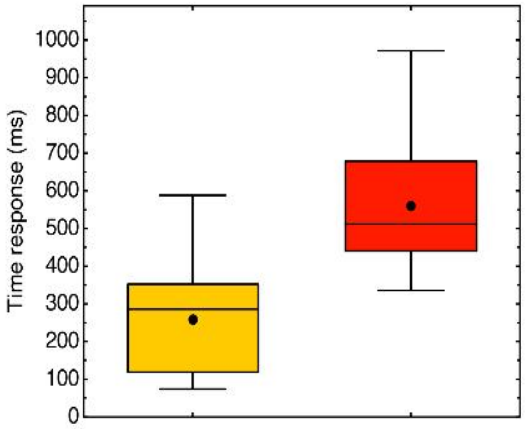
Free-standing ultraflexible X-ray detectors



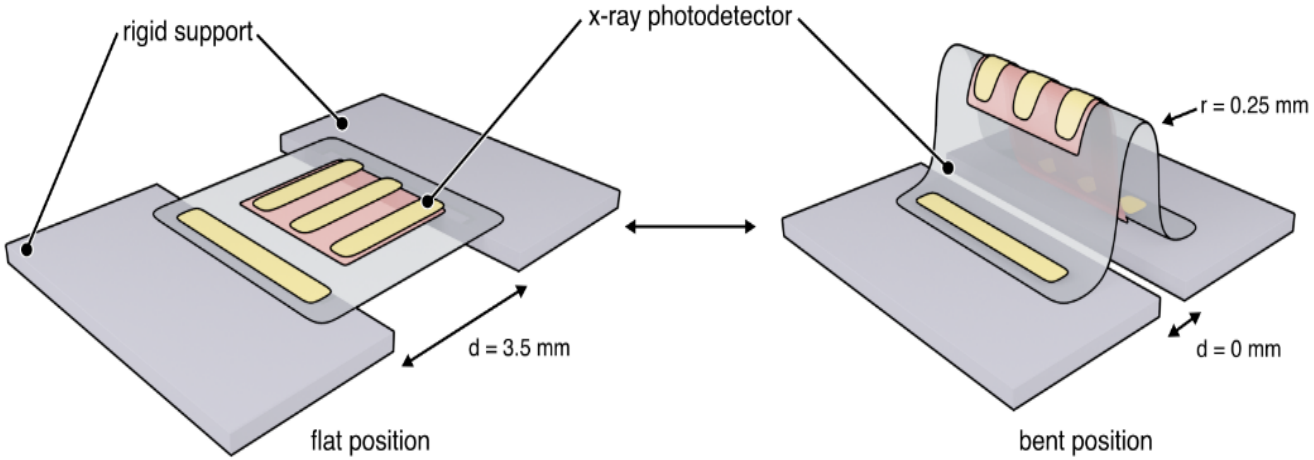


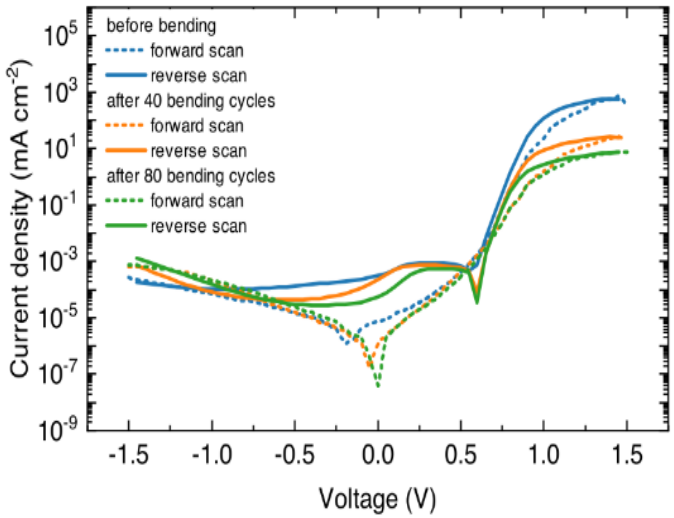
- ✓ **Linear response (dosimeters)**
- ✓ **0V bias: fully passive detectors**
- ✓ **Free standing: slower response time**



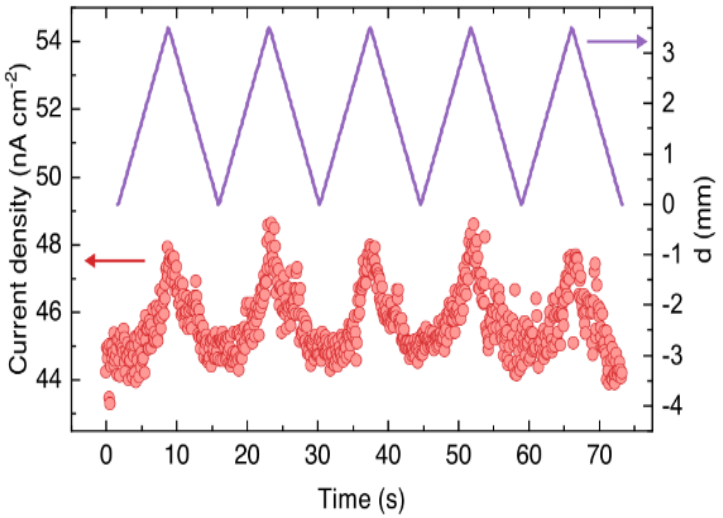


flexibility

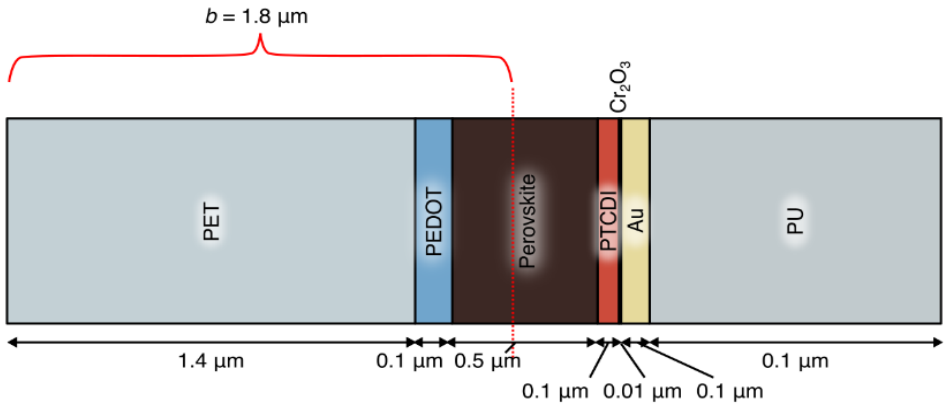




c

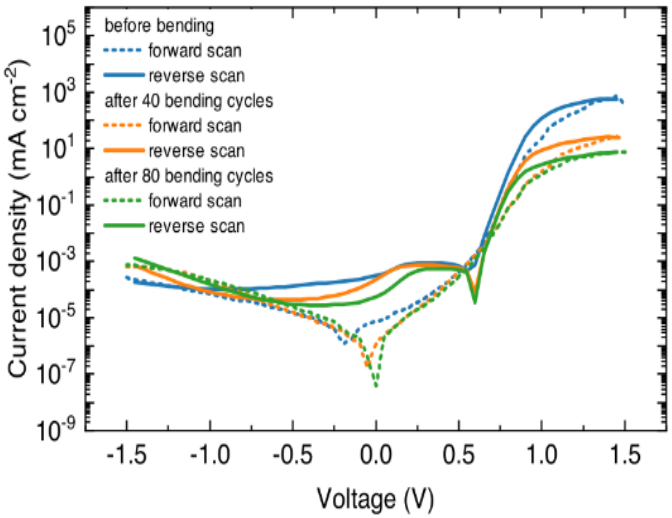


flexibility

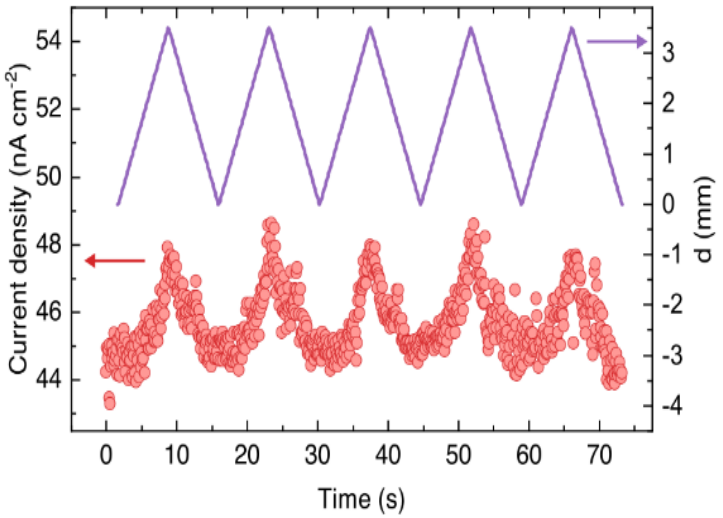


The red dotted line marks the location of neutral mechanical plane at 1.8 µm, that can be calculated using the following equation (7 layers):

$$b = \frac{\sum_{i=1}^{n} \bar{E}_i h_i \left[\left(\sum_{j=1}^{i} h_j \right) - \frac{h_i}{2} \right]}{\sum_{i=1}^{n} \bar{E}_i h_i}$$



c



Conclusions

- **Perovskite thin films** ($(Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}PbI_{3-x}Br_x)$ <500nm) are **promising X-ray direct detectors**: ⟶ flexible, large-area devices

- **fully passive** (operated at 0 V) thin film perovskite X-ray detectors with a **sensitivity of 9.3±0.5 μC Gy^{-1} cm^{-2}**
  a **record Limit of Detection of 0.58±0.05 μGy s^{-1}**

- **Interfaces and buffer layers** play a key role in controlling the final device performance

- **ultraflexible X-ray detectors** with
  - comparable performance in the free-standing form to their on-glass substrate counterparts
  - Isotropic detection of X-ray radiation (front and back)

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(2019-2022)

Istituto Nazionale di Fisica Nucleare

Fortress *Flexible, Large-area patches for real-time detection of ionizing radiation in medical diagnostics*
(2019-2022)

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Fondo europeo di sviluppo regionale

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ROXFET *Radiation detectors based on flexible high mobility oxide transistors (2019-2021)*

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Thank you for your attention