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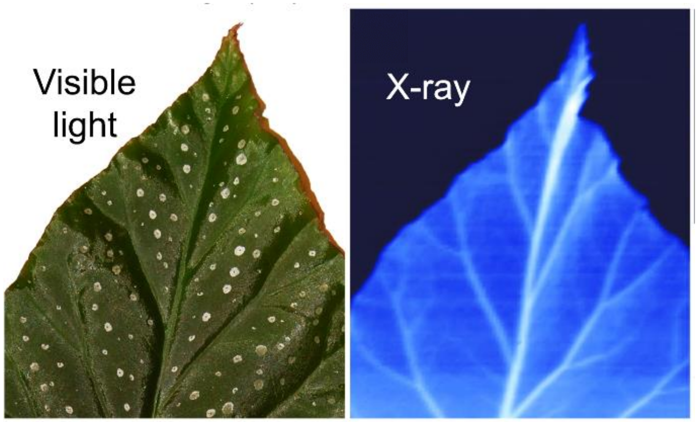
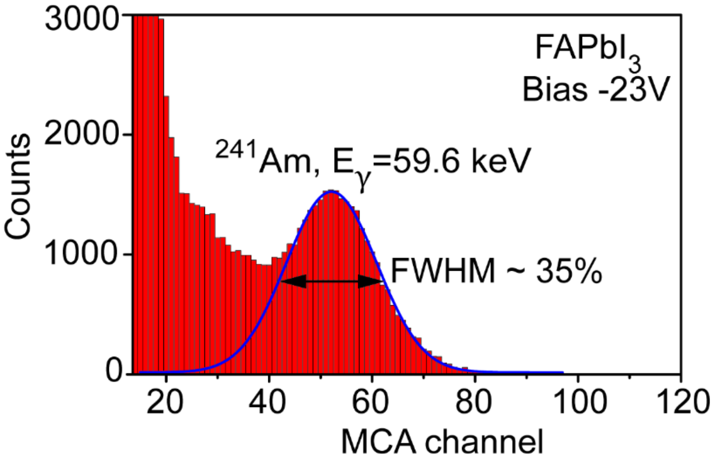
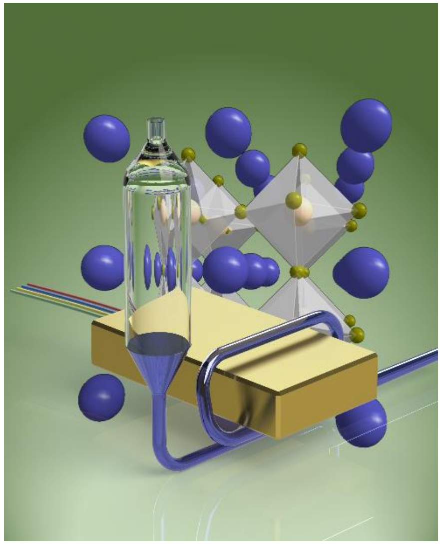
Materials Science & Technology

Lead halide perovskites as a novel solution-processed material for direct conversion X-ray detectors







Sergii Yakunin,

ETH Zürich - Department of Chemistry and Applied Biosciences,

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Workshop on Organic Detectors and Materials. NSS-MIC Conference Atlanta, 22.10.2017

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ETH zürich

EMPA
Materials Science & Technology

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Horizon-2020

Phonsi
Nanophotonics by nanocrystals

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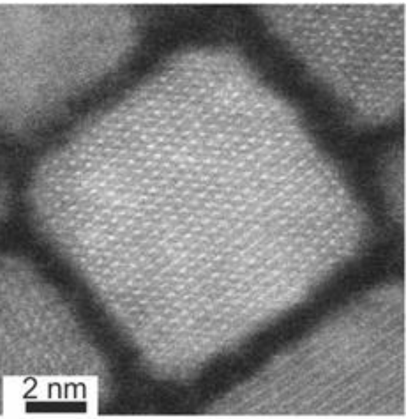
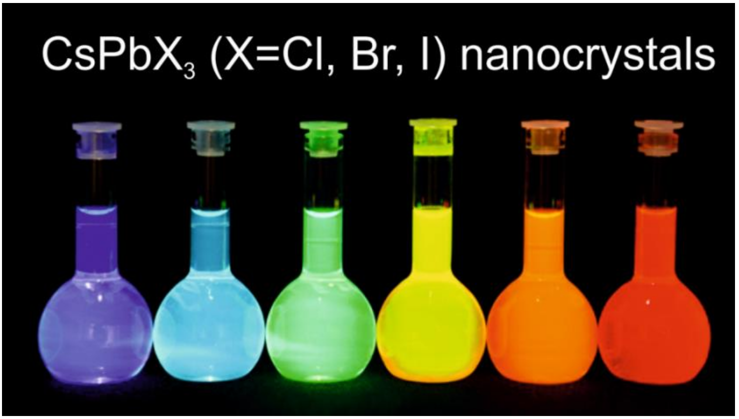
Kommission für Technologie und Innovation KTI

Facile access to many forms and compositions

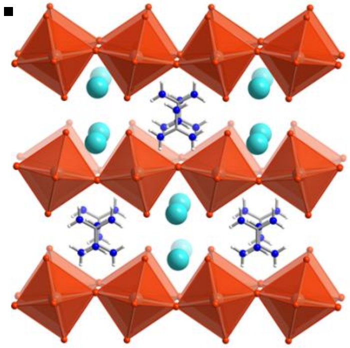
2014-…..




$CsPbX_3$ (X=Cl, Br, I) nanocrystals

2015-…..

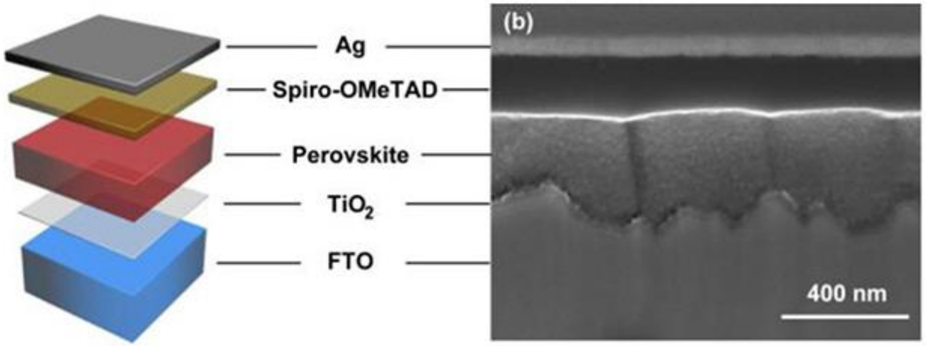
new 2D-perovskites:




$APbX_3$ single crystals

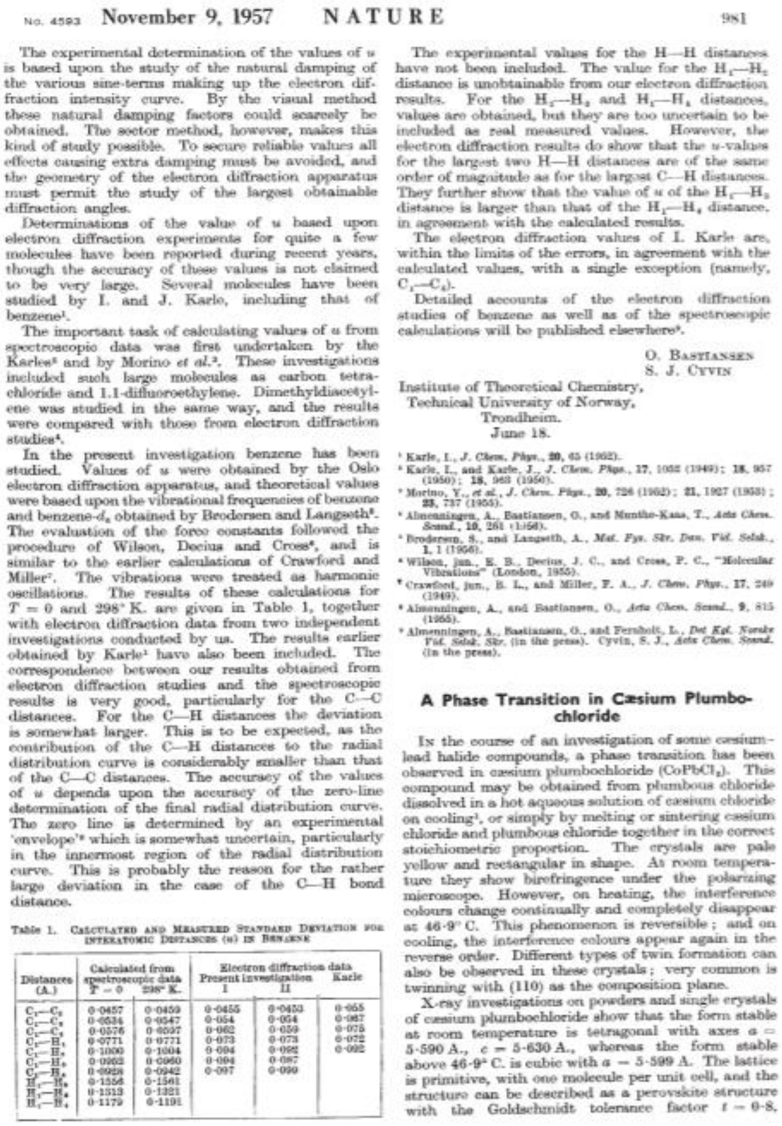
2014-….

Thin films
(solar cells)



2012-…..

Invention of inorganic of perovskites 1957-58



No. 4593 November 9, 1957 NATURE 981

The experimental determination of the values of *u* is based upon the study of the natural damping of the various sine-terms making up the electron diffraction intensity curve. By the visual method these natural damping factors could scarcely be obtained. The sector method, however, makes this kind of study possible. To secure reliable values all effects causing extra damping must be avoided, and the geometry of the electron diffraction apparatus must permit the study of the largest obtainable diffraction angles.

Determinations of the value of *u* based upon electron diffraction experiments for quite a few molecules have been reported during recent years, though the accuracy of these values is not claimed to be very large. Several molecules have been studied by I. and J. Karle, including that of benzene[1].

The important task of calculating values of *u* from spectroscopic data was first undertaken by the Karles[2] and by Morino *et al.*[3]. These investigations included such large molecules as carbon tetrachloride and 1,1-difluoroethylene. Dimethyldiacetylene was studied in the same way, and the results were compared with those from electron diffraction studies[4].

In the present investigation benzene has been studied. Values of *u* were obtained by the Oslo electron diffraction apparatus, and theoretical values were based upon the vibrational frequencies of benzene and benzene-d_6 obtained by Brodersen and Langseth[5]. The evaluation of the force constants followed the procedure of Wilson, Decius and Cross[6], and is similar to the earlier calculations of Crawford and Miller[7]. The vibrations were treated as harmonic oscillations. The results of these calculations for $T = 0$ and 298° K. are given in Table 1, together with electron diffraction data from two independent investigations conducted by us. The results earlier obtained by Karle[1] have also been included. The correspondence between our results obtained from electron diffraction studies and the spectroscopic results is very good, particularly for the C—C distances. For the C—H distances the deviation is somewhat larger. This is to be expected, as the contribution of the C—H distances to the radial distribution curve is considerably smaller than that of the C—C distances. The accuracy of the values of *u* depends upon the accuracy of the zero-line determination of the final radial distribution curve. The zero line is determined by an experimental 'envelope'[8] which is somewhat uncertain, particularly in the innermost region of the radial distribution curve. This is probably the reason for the rather large deviation in the case of the C—H bond distance.

Table 1. CALCULATED AND MEASURED STANDARD DEVIATION FOR INTERATOMIC DISTANCES (*u*) IN BENZENE

Distances (A.)	Calculated from spectroscopic data		Electron diffraction data		
	$T = 0$	298° K.	Present investigation I	II	Karle
$C_1—C_2$	0·0457	0·0459	0·0455	0·0453	0·055
$C_1—C_3$	0·0534	0·0547	0·054	0·054	0·067
$C_1—C_4$	0·0576	0·0597	0·062	0·059	0·075
$C_1—H_1$	0·0771	0·0771	0·073	0·073	0·072
$C_1—H_2$	0·1000	0·1004	0·094	0·092	0·092
$C_1—H_3$	0·0962	0·0960	0·094	0·087	
$C_1—H_4$	0·0928	0·0942	0·097	0·090	
$H_1—H_2$	0·1556	0·1561			
$H_1—H_3$	0·1513	0·1321			
$H_1—H_4$	0·1179	0·1191			

The experimental values for the H—H distances have not been included. The value for the $H_1—H_2$ distance is unobtainable from our electron diffraction results. For the $H_1—H_3$ and $H_1—H_4$ distances, values are obtained, but they are too uncertain to be included as real measured values. However, the electron diffraction results do show that the *u*-values for the largest two H—H distances are of the same order of magnitude as for the largest C—H distances. They further show that the value of *u* of the $H_1—H_3$ distance is larger than that of the $H_1—H_4$ distance, in agreement with the calculated results.

The electron diffraction values of I. Karle are, within the limits of the errors, in agreement with the calculated values, with a single exception (namely, $C_1—C_4$).

Detailed accounts of the electron diffraction studies of benzene as well as of the spectroscopic calculations will be published elsewhere[9].

O. BASTIANSEN
S. J. CYVIN

Institute of Theoretical Chemistry,
Technical University of Norway,
Trondheim.
June 18.

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[1] Karle, I., *J. Chem. Phys.*, **20**, 65 (1952).

[2] Karle, I., and Karle, J., *J. Chem. Phys.*, **17**, 1052 (1949); **18**, 957 (1950); **18**, 963 (1950).

[3] Morino, Y., *et al.*, *J. Chem. Phys.*, **20**, 726 (1952); **21**, 1927 (1953); **23**, 737 (1955).

[4] Almenningen, A., Bastiansen, O., and Munthe-Kaas, T., *Acta Chem. Scand.*, **10**, 261 (1956).

[5] Brodersen, S., and Langseth, A., *Mat. Fys. Skr. Dan. Vid. Selsk.*, **1**, 1 (1956).

[6] Wilson, jun., E. B., Decius, J. C., and Cross, P. C., "Molecular Vibrations" (London, 1955).

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[8] Almenningen, A., and Bastiansen, O., *Acta Chem. Scand.*, **9**, 815 (1955).

[9] Almenningen, A., Bastiansen, O., and Fernholt, L., *Det Kgl. Norske Vid. Selsk. Skr.* (in the press). Cyvin, S. J., *Acta Chem. Scand.* (in the press).

A Phase Transition in Cæsium Plumbochloride

IN the course of an investigation of some cæsium-lead halide compounds, a phase transition has been observed in cæsium plumbochloride ($CoPbCl_3$). This compound may be obtained from plumbous chloride dissolved in a hot aqueous solution of cæsium chloride on cooling[1], or simply by melting or sintering cæsium chloride and plumbous chloride together in the correct stoichiometric proportion. The crystals are pale yellow and rectangular in shape. At room temperature they show birefringence under the polarizing microscope. However, on heating, the interference colours change continually and completely disappear at 46·9° C. This phenomenon is reversible; and on cooling, the interference colours appear again in the reverse order. Different types of twin formation can also be observed in these crystals; very common is twinning with (110) as the composition plane.

X-ray investigations on powders and single crystals of cæsium plumbochloride show that the form stable at room temperature is tetragonal with axes a = 5·590 A., c = 5·630 A., whereas the form stable above 46·9° C. is cubic with a = 5·599 A. The lattice is primitive, with one molecule per unit cell, and the structure can be described as a perovskite structure with the Goldschmidt tolerance factor t = 0·8,

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the extra streaks in the same positions but the intensities are different from those of Fig. 1,*a*.

A detailed study of the structural implications of the above findings and their possible interpretation is in progress, and the results will be published elsewhere.

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W. A. WOOSTER

Crystallographic Laboratory,
Cavendish Laboratory,
Cambridge.
Sept. 11.

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[1] Neuburger, M. C., *Z. Kristallogr.*, **93**, 314 (1936).

Crystal Structure and Photoconductivity of Cæsium Plumbohalides

WELLS[1] and his collaborators have shown that crystals of the general compositions $CsPbX_3$ with X = Cl, Br or I, and Cs_4PbX_6 with X = Cl or Br, may be prepared from aqueous solutions. I have investigated the structures of these crystals and also prepared a few more. I have found[2] that $CsPbCl_3$ and $CsPbBr_3$ have the perovskite structure. At room temperature they are tetragonally or monoclinically distorted. Both of them, however, show transition to pure cubic perovskite structure, at 47° C. and 130° C. respectively and with cell dimensions a = 5·605 A. for $CsPbCl_3$, a = 5·874 A. for $CsPbBr_3$. Whereas no extra or forbidden X-ray reflexions can be observed above these transition temperatures, $CsPbBr_3$ below 130° C.—and presumably also $CsPbCl_3$ below 47° C.—exhibit a new structure corresponding to a doubling of the cell dimensions. The transitions are likely to be of second order as $\Delta V = 0$ within the limits of accuracy of my measurements.

The $CsPbI_3$ crystals from aqueous solution are orthorhombic with space group No. 62 *Pnma* and a = 4·795 A., b = 10·45₇ A., c = 17·76 A. The X-ray analysis yields all the atomic positions and interatomic distances: the lead atom is surrounded octahedrally by six iodine atoms at distances 3·01–3·42 A., and nine iodine atoms form distorted ditrigonal pyramids around each cæsium atom at distances of 3·87–4·19 A. The lead and iodine ions form chains of polynuclear complex ions parallel to the a-axis of the crystal. On heating these crystals to 305–308° C. they undergo a phase change and the colour changes from yellow to black. This black form which may also be obtained by melting cæsium iodide and plumbous iodide together in the correct stoichiometric proportion is rather unstable, and hence had to be investigated on a Geiger–Müller diffractometer. From its powder diagram it appears to have a monoclinically distorted perovskite structure ($a = b$ = 6·15 A., c = 6·23 A., β = 88·15°). It shows the same kind of superstructure as $CsPbBr_3$.

It is interesting to note that the above-mentioned crystals with perovskite structure are intensely coloured: $CsPbCl_3$ is pale yellow, $CsPbBr_3$ is orange and $CsPbI_3$ black, whereas crystals of the type Cs_4PbX_6 with X = Cl, Br or I are colourless. From this peculiarity one might guess that the former crystals also have special electrical properties. With a very crude apparatus we have found that the coloured $CsPbX_3$-crystals with perovskite structure are photoconductive, $CsPbCl_3$ having its maximum spectral sensitivity in the violet, $CsPbBr_3$ in the blue to green region and $CsPbI_3$ in the red region, that is, the spectral region which is complementary to the colour of the crystals.

A detailed account of this work will be published elsewhere.

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Chemical Laboratory,
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Copenhagen.

---

[1] Wells, H. L., *Z. anorg. Chem.*, **3**, 195 (1893).

[2] Møller, C. K., *Nature*, **180**, 981 (1957).

Nuclear Magnetic Resonance in β-Brass

Bloembergen and Rowland[1] have shown that the addition of small amounts of zinc to copper reduces the intensity of resonance in the resulting alloy so that the line becomes unobservable when the zinc content reaches approximately 25 per cent. They explained this effect in terms of quadrupole broadening and pointed out that, in ordered structures with cubic symmetry, quadrupole broadening should be absent and a line would be expected. However, they found no resonance in a β-brass of about 50/50 composition (quoted by Bridgman[2] as 47·3 per cent zinc) and they suggested that the ordering was not complete.

Experiments in this laboratory have shown that there is a strong copper-63 resonance in a β-brass containing 48·33 per cent zinc by weight. The specimens were prepared by filing at room temperature and sieving through a 120-mesh sieve, annealing for 2 hr. at 450° C. in an argon atmosphere, and then slowly cooling to room temperature. The detecting apparatus was a conventional Pound–Knight–Watkins type of spectrometer operating at approximately 5·96 Mc./s. and a 'Varian' 12-in. electromagnet set at approximately 5,250 oersted. All experiments were done at room temperature.

The main features of the resonance line for the annealed powder are as follows: (1) The line is symmetrical with the centre located 5·2 kc./s. below that for well-annealed copper of 99·98 per cent purity under the same conditions. This means that the Knight shift ($\Delta H/H$) for copper in a well-ordered β-brass structure is approximately 0·14 per cent, as compared with 0·23 per cent for pure copper. (2) The integrated area under the absorption line is one-sixth of the area under a line obtained from a specimen of pure copper containing the same number of copper nuclei. (3) The line for β-brass is appreciably narrower than that for pure copper, this smaller dipole broadening being consistent with the fact that the next nearest copper neighbours are farther away than they are in pure copper. (4) The line can be eliminated almost completely by plastic deformation. This was shown by testing a specimen immediately after filing and sieving.

The detailed effects of deformation, heat treatment, and variation of composition have been studied and will be described elsewhere.

G. W. WEST

Division of Tribophysics,
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Oct. 16.

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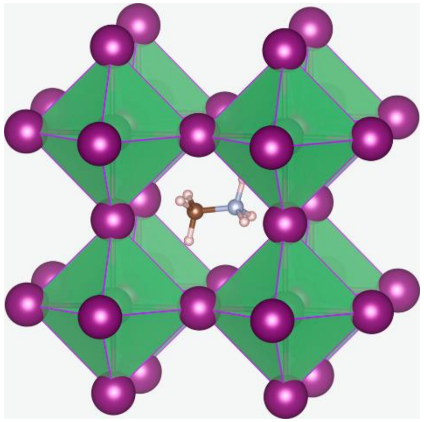
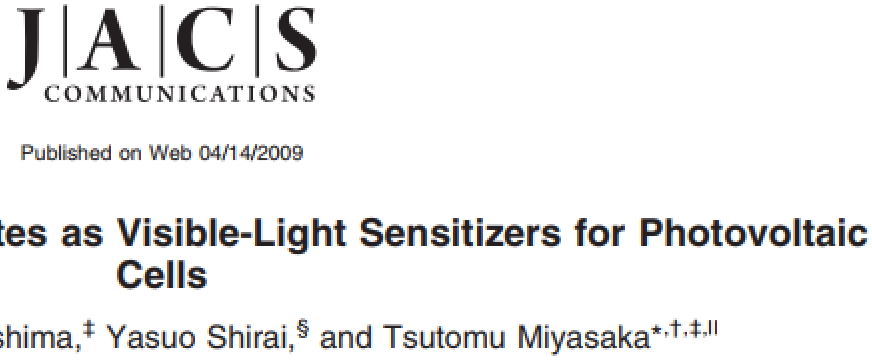
[1] Bloembergen, N., and Rowland, T. J., *Acta Met.*, **1**, 731 (1953).

[2] Bridgman, P. W., *Proc. Amer. Acad.*, **84**, 131 (1955).

Introduction hybrid of perovskites 2009-11



Crystal structure of $CH_3NH_3PbX_3$perovskites (X=I, Br and/or Cl). From wikipedia.org

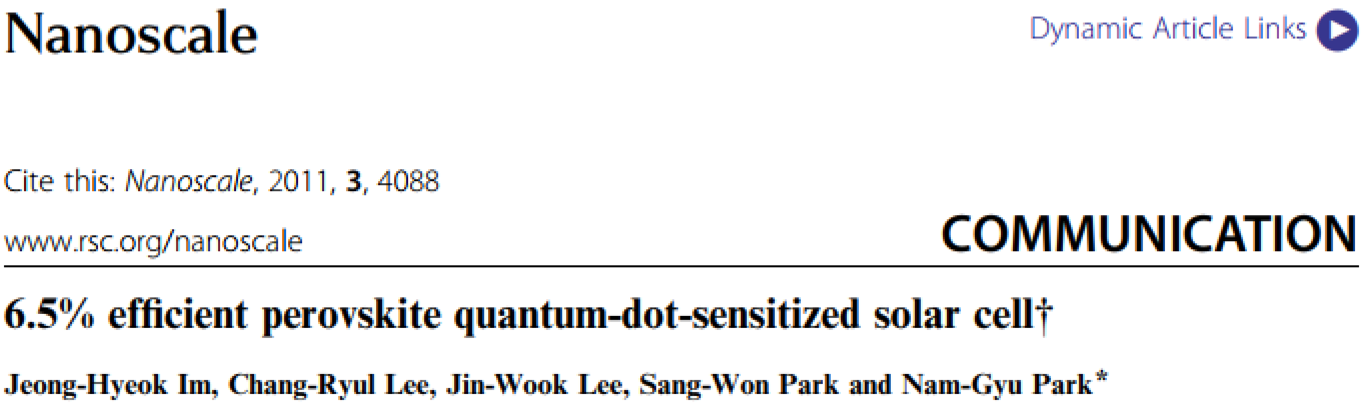


J|A|C|S COMMUNICATIONS

Published on Web 04/14/2009

Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells

Akihiro Kojima,[†] Kenjiro Teshima,[‡] Yasuo Shirai,[§] and Tsutomu Miyasaka*[,†,‡,‖]



Nanoscale

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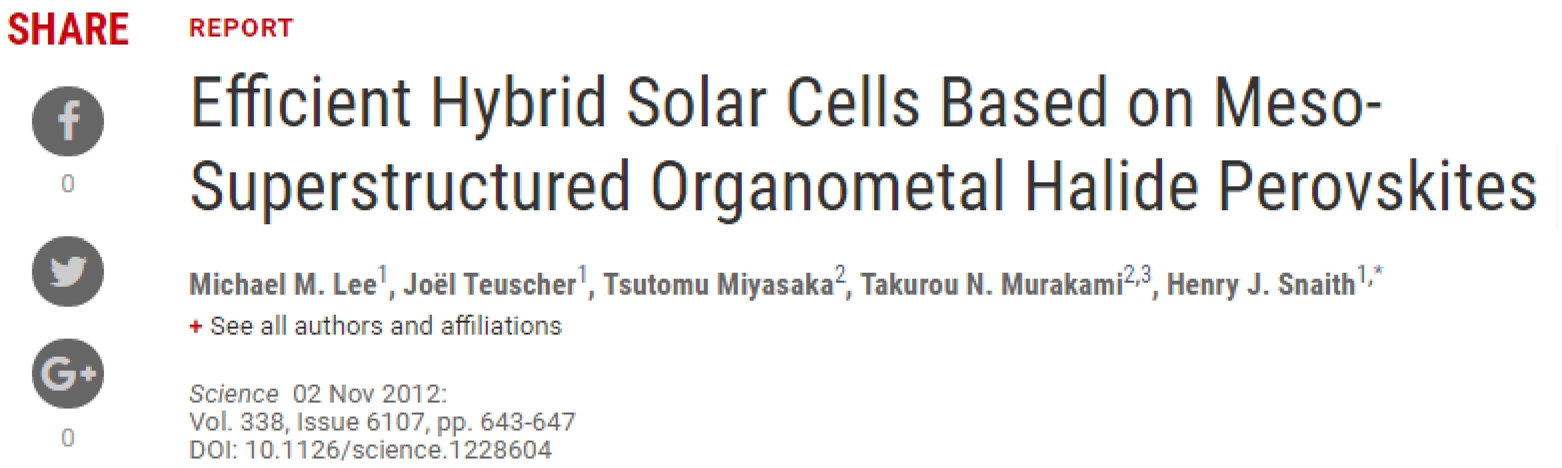
COMMUNICATION

6.5% efficient perovskite quantum-dot-sensitized solar cell†

Jeong-Hyeok Im, Chang-Ryul Lee, Jin-Wook Lee, Sang-Won Park and Nam-Gyu Park*

Perovskite breakthrough in 2012



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REPORT

Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites

Michael M. Lee[1], Joël Teuscher[1], Tsutomu Miyasaka[2], Takurou N. Murakami[2,3], Henry J. Snaith[1,*]

+ See all authors and affiliations

Science 02 Nov 2012:
Vol. 338, Issue 6107, pp. 643-647
DOI: 10.1126/science.1228604

SCIENTIFIC REPORTS

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Sci Rep. 2012; 2: 591.
Published online 2012 Aug 21. doi: 10.1038/srep00591

PMCID: PMC3423636

Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%

Hui-Seon Kim,[1] Chang-Ryul Lee,[1] Jeong-Hyeok Im,[1] Ki-Beom Lee,[1] Thomas Moehl,[2] Arianna Marchioro,[2] Soo-Jin Moon,[2] Robin Humphry-Baker,[2] Jun-Ho Yum,[2] Jacques E. Moser,[2] Michael Grätzel,[a,2] and Nam-Gyu Park[b,1]

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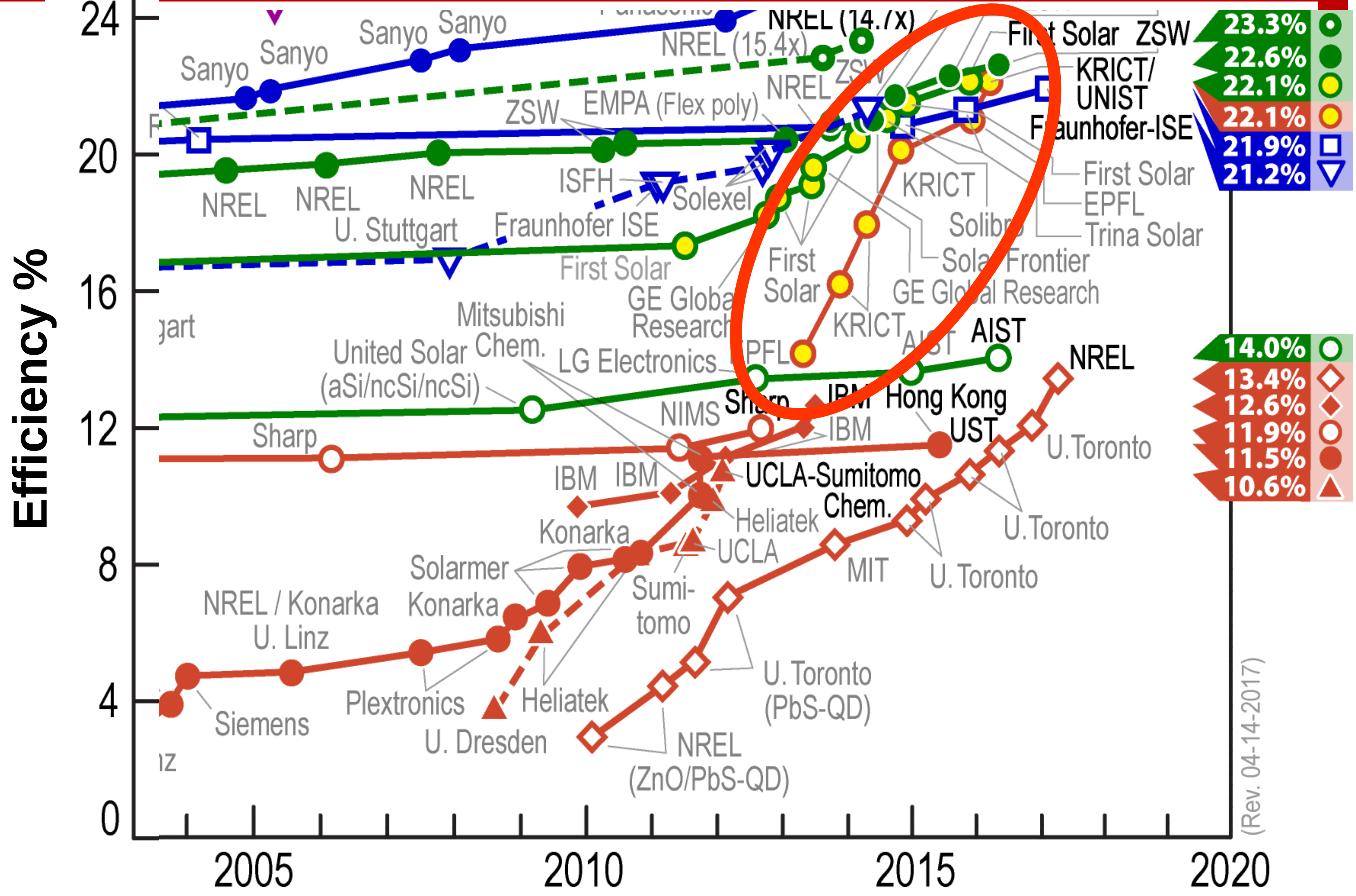
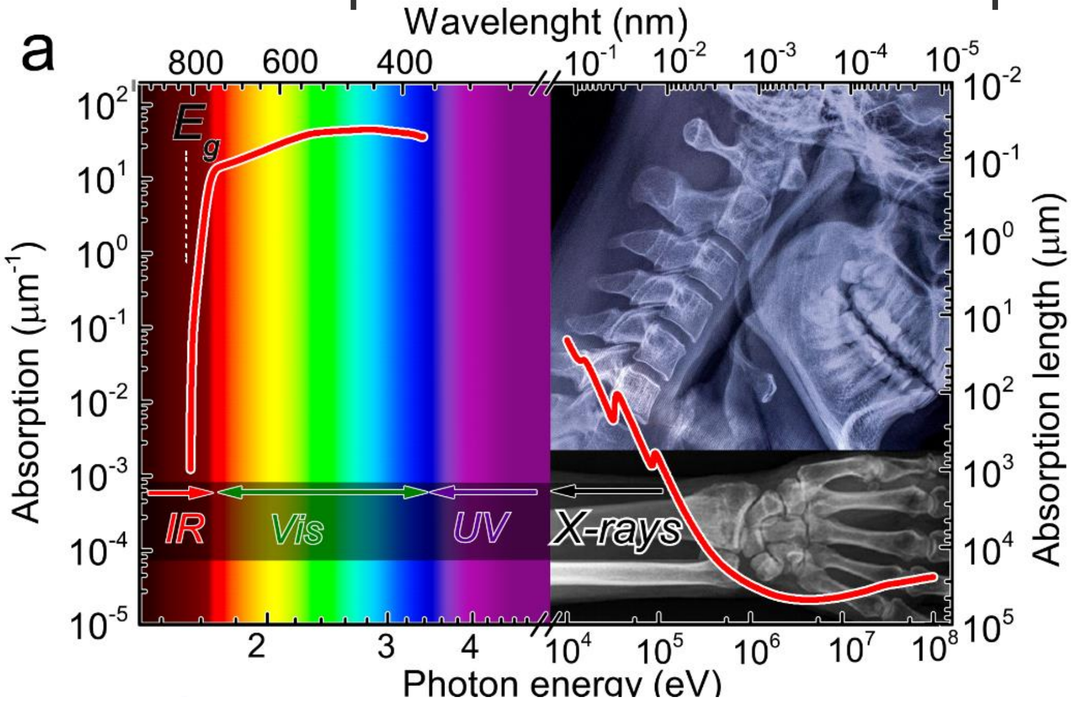
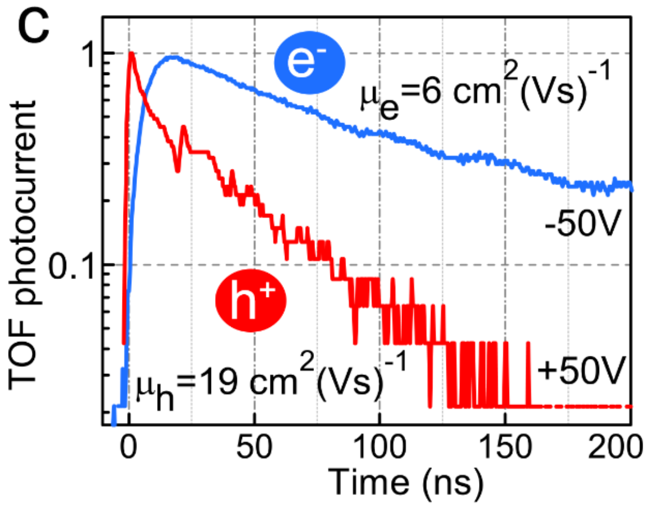
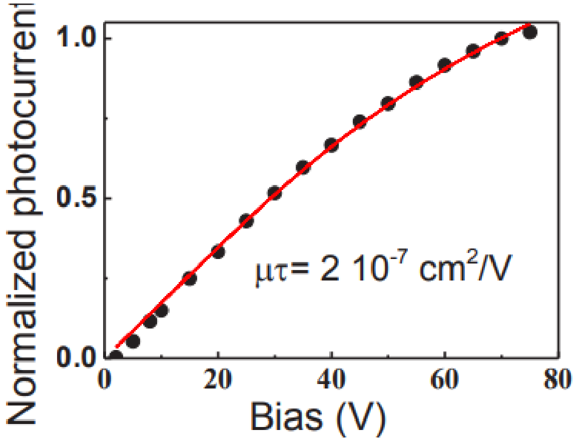
Progress in perovskite solar cells 2013-2017



Direct detection of X-ray photons by solution-processed lead halide perovskites.

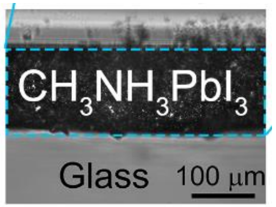


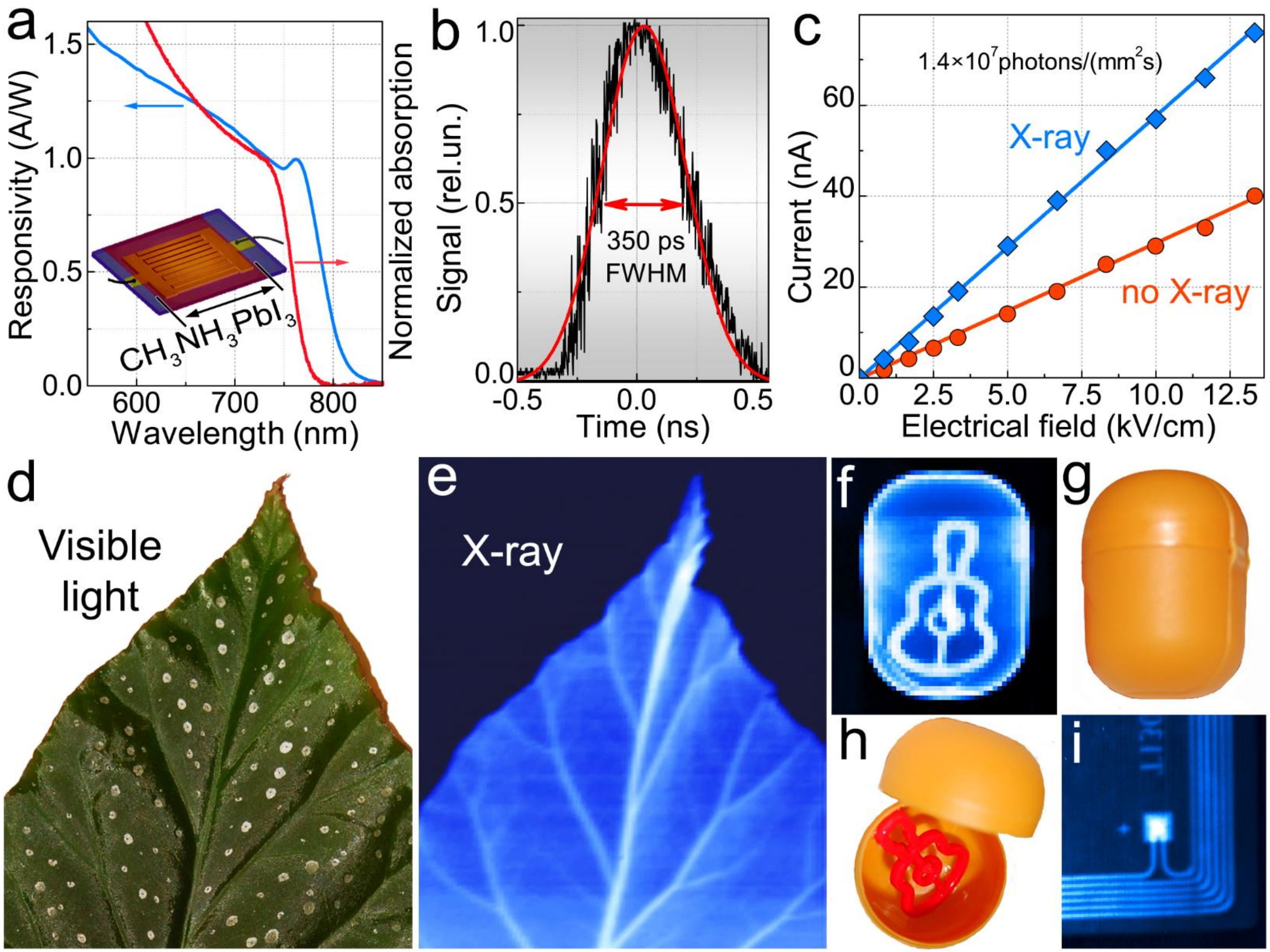




S. Yakunin et.al. *Nature Photonics*, **2015**, 9, 444 - 449

Direct detection of X-ray photons by solution-processed lead halide perovskites





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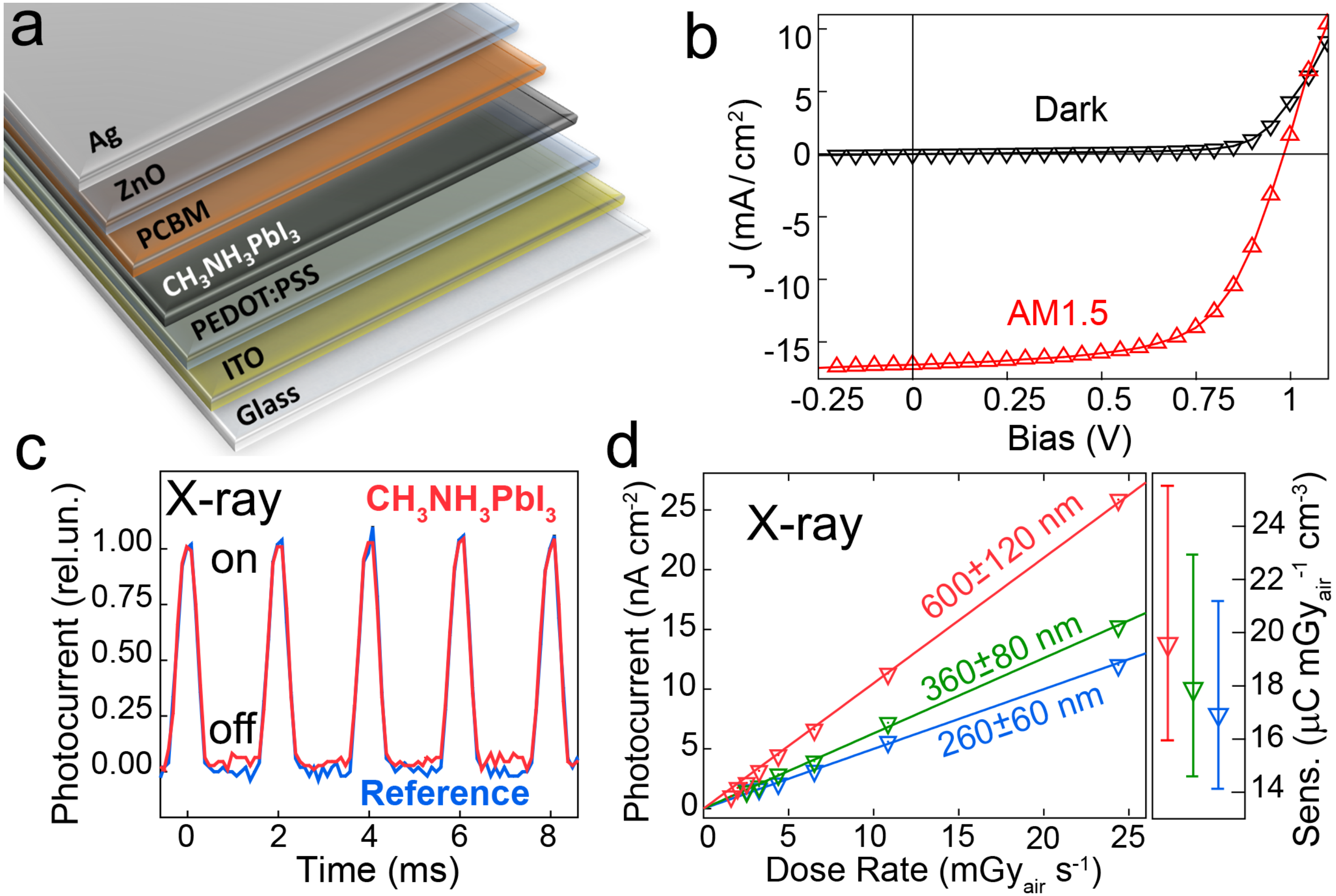
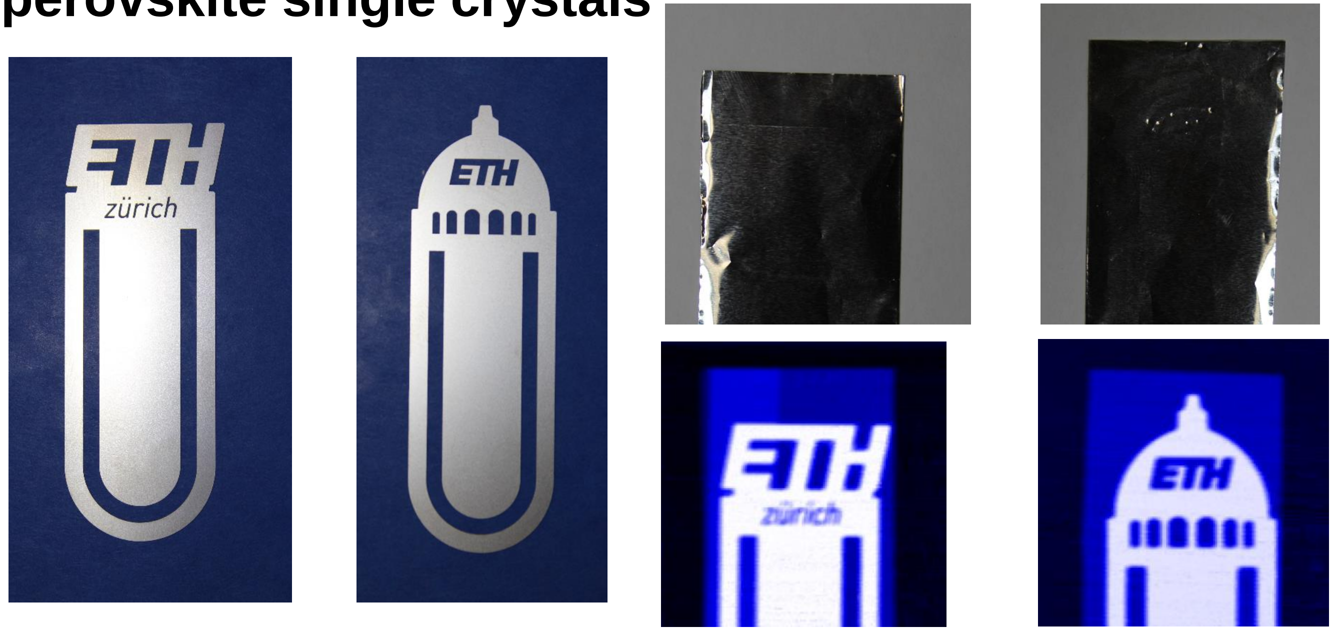
Direct detection of X-ray photons by solution-processed lead halide perovskites



S. Yakunin et.al. *Nature Photonics*, **2015**, 9, 444 - 449

Direct detection of X-ray photons by solution-processed lead halide perovskite single crystals



AUFENTHALTSTITEL DA0919177

NAME
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Sergii
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AUSSTELLUNGSORT UND DATUM DES BEGINNS DER GÜLTIGKEIT
Zürich ZH, 11.12.2013
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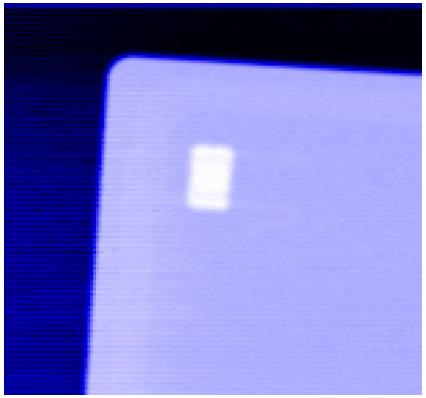
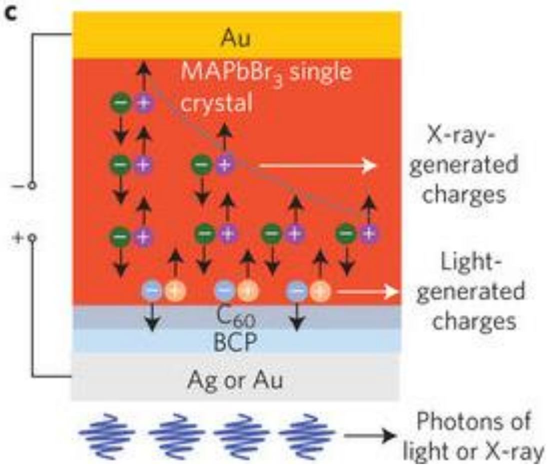
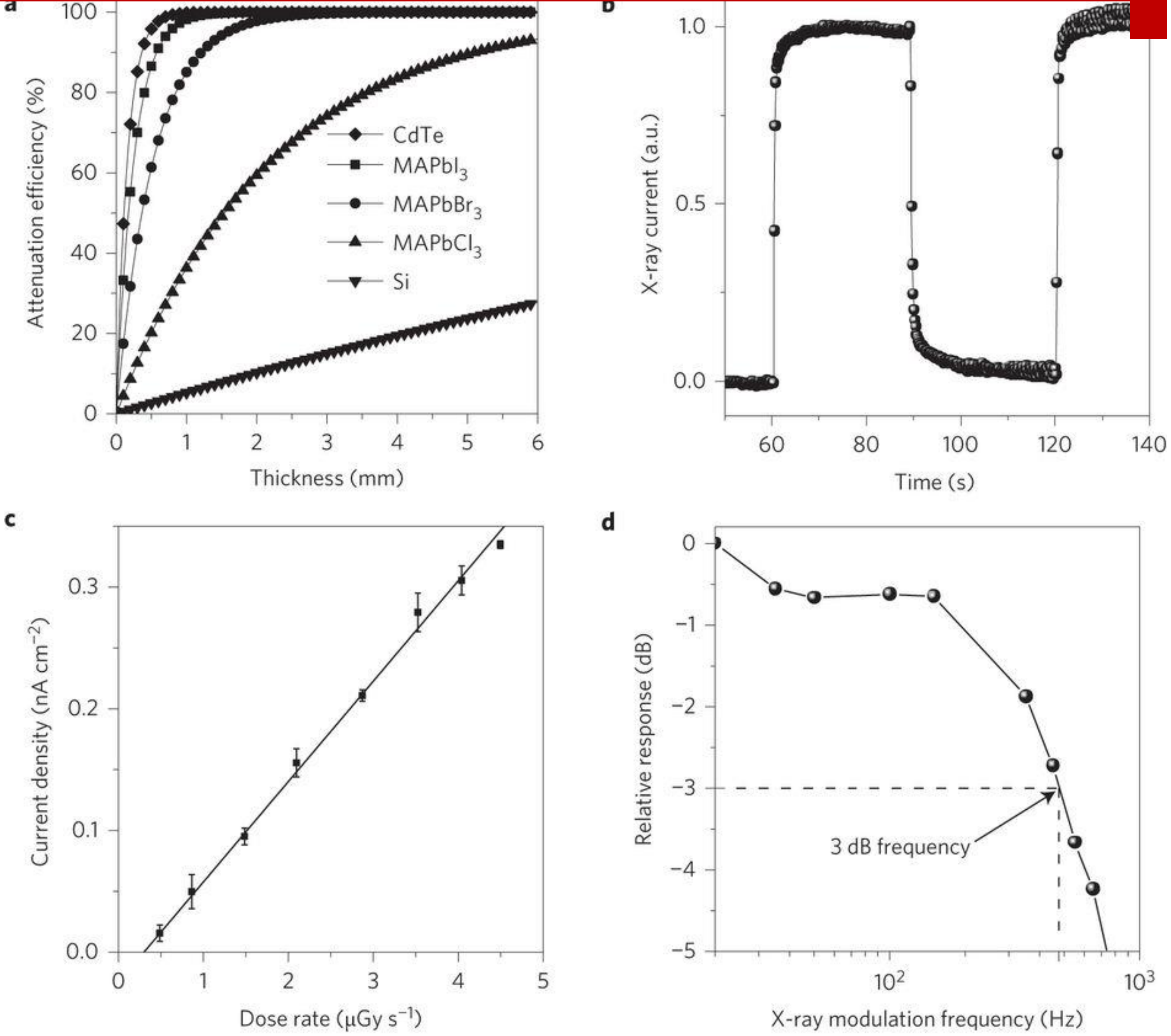


More than one order better sensitivity to X-rays than polycrystalline films

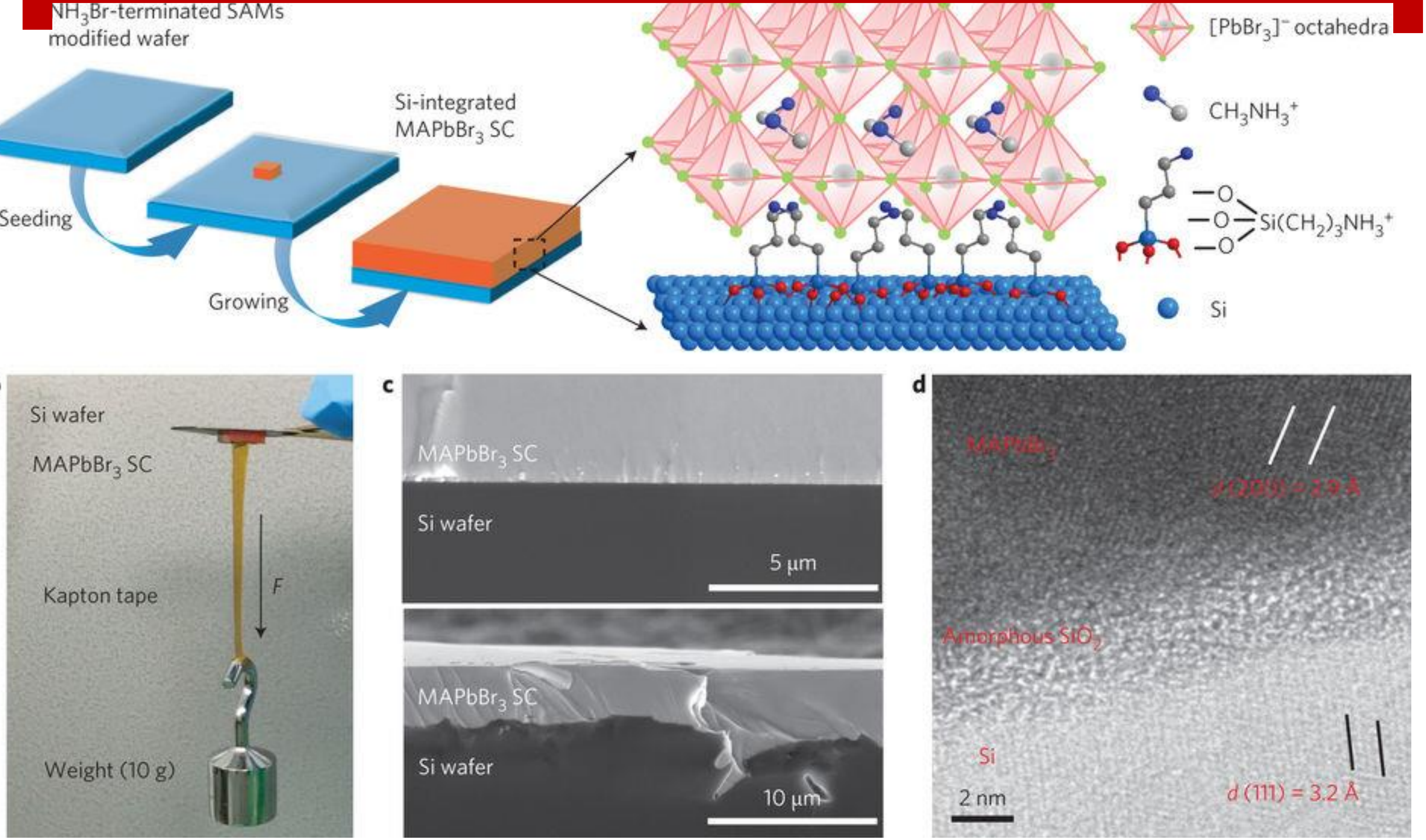
Direct detection of X-ray photons by solution-processed perovskite SCs





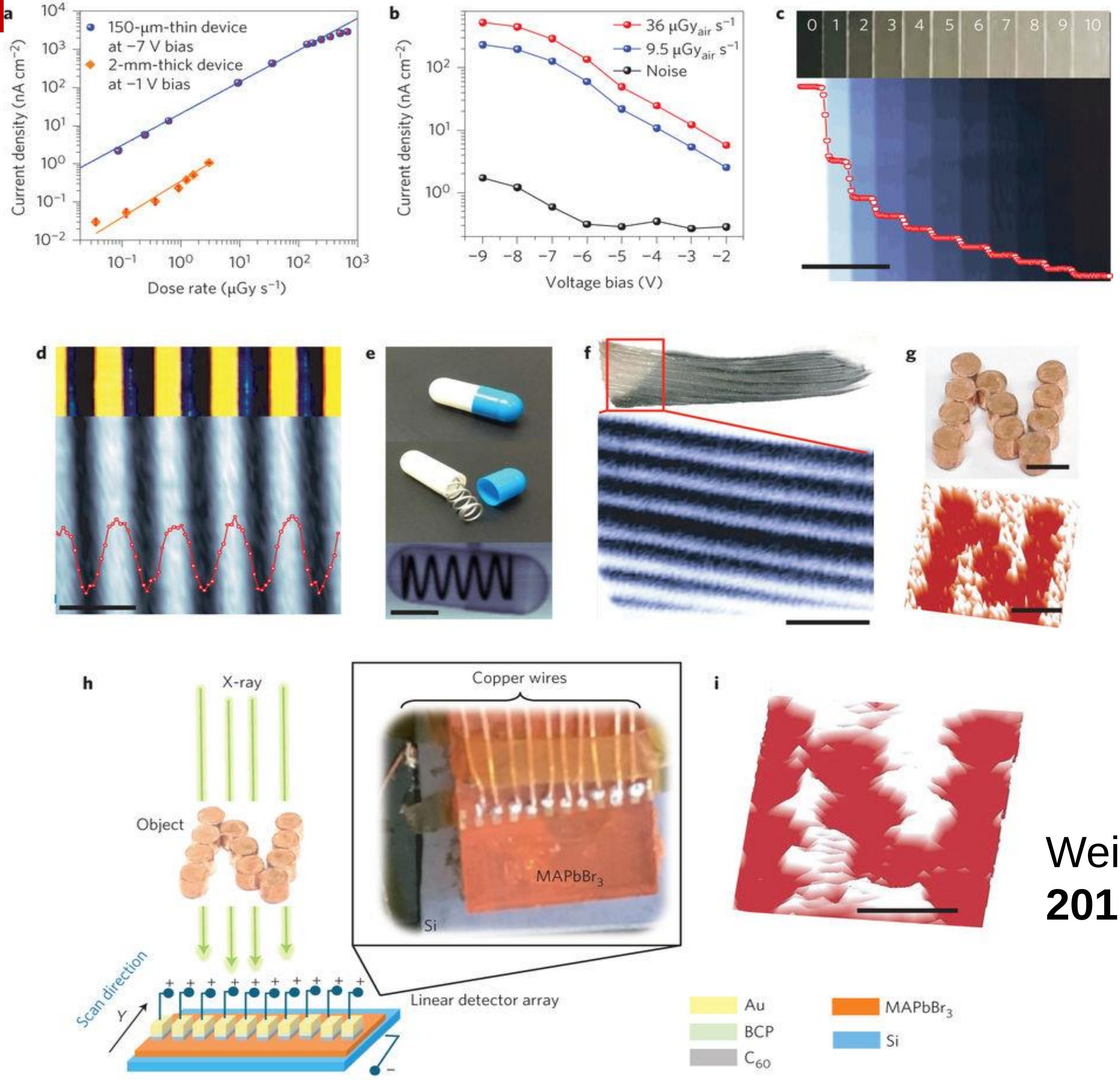
Wei et.al. *Nature Photonics*, **2016,** 10, 333-339

Direct detection of X-ray photons by solution-processed perovskite SCs



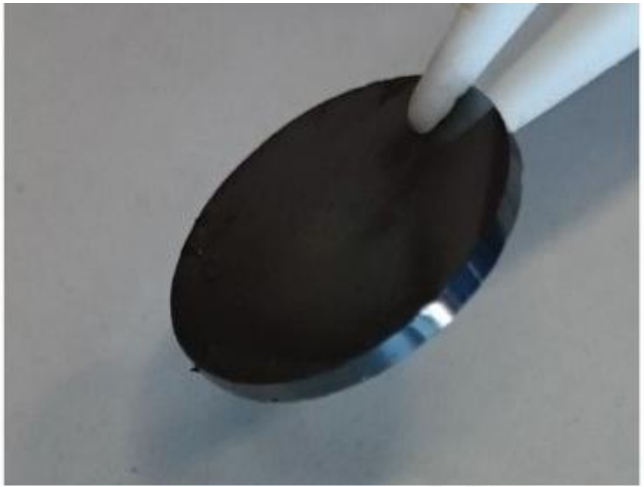
Wei et.al. *Nature Photonics*, **2017,** 11, 315-321,

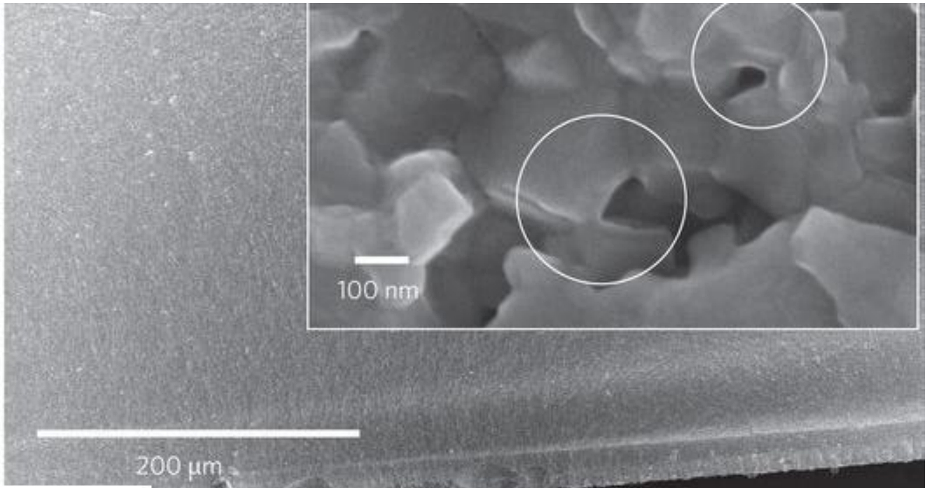
Direct detection of X-ray photons by solution-processed perovskite SCs

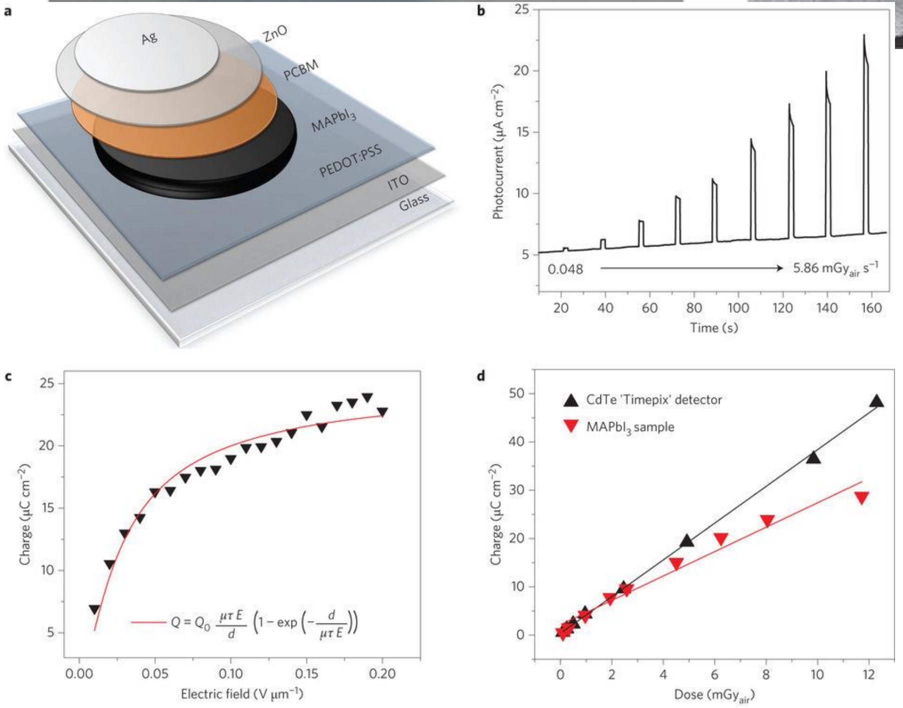


Wei et.al. *Nature Photonics*, **2017,** 11, 315-321

Direct detection of X-ray photons by solution-processed perovskite polycrystals



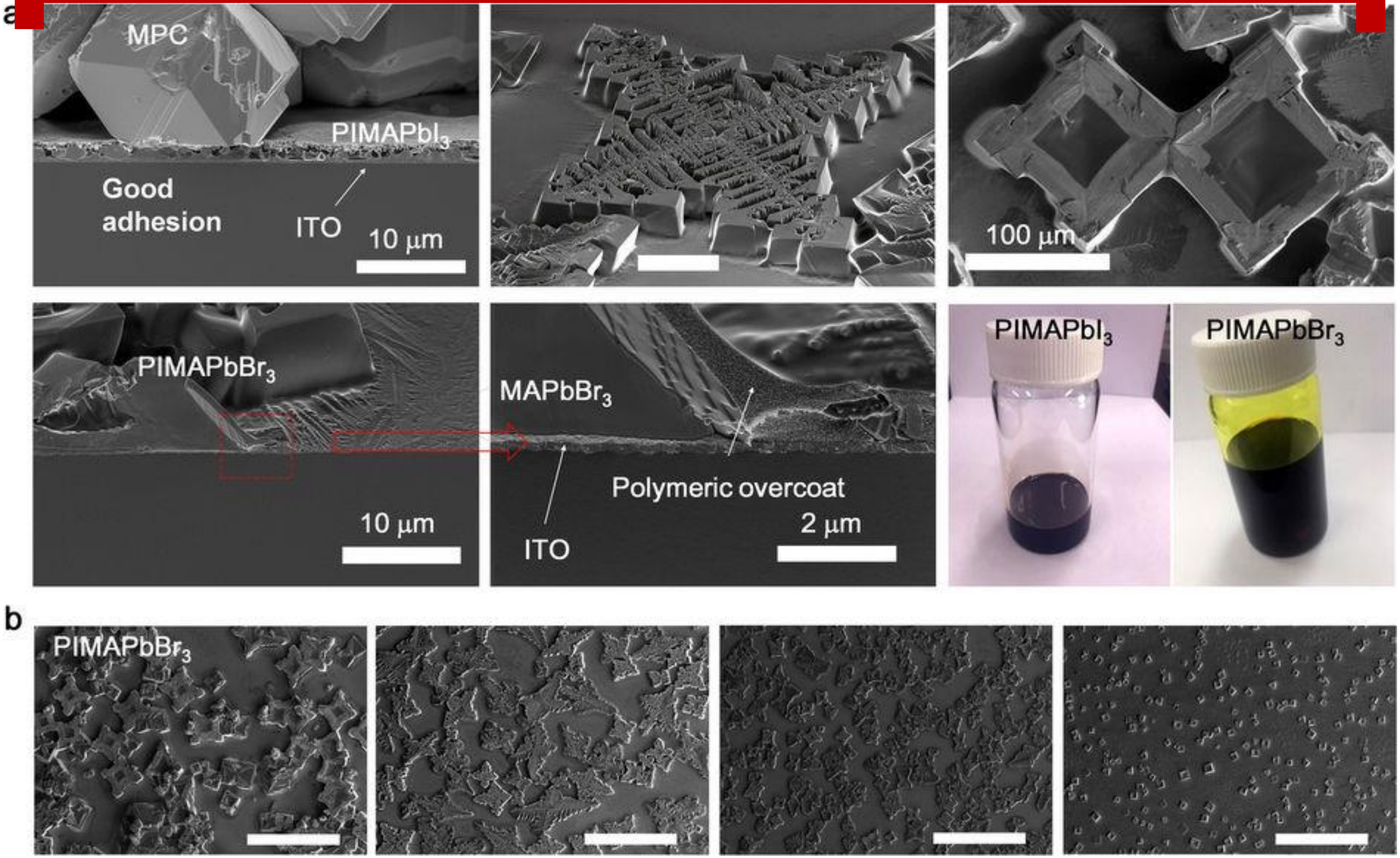




$\mu\tau = 2\text{x}10^{-4}\ \text{cm}^2\ \text{V}^{-1}$

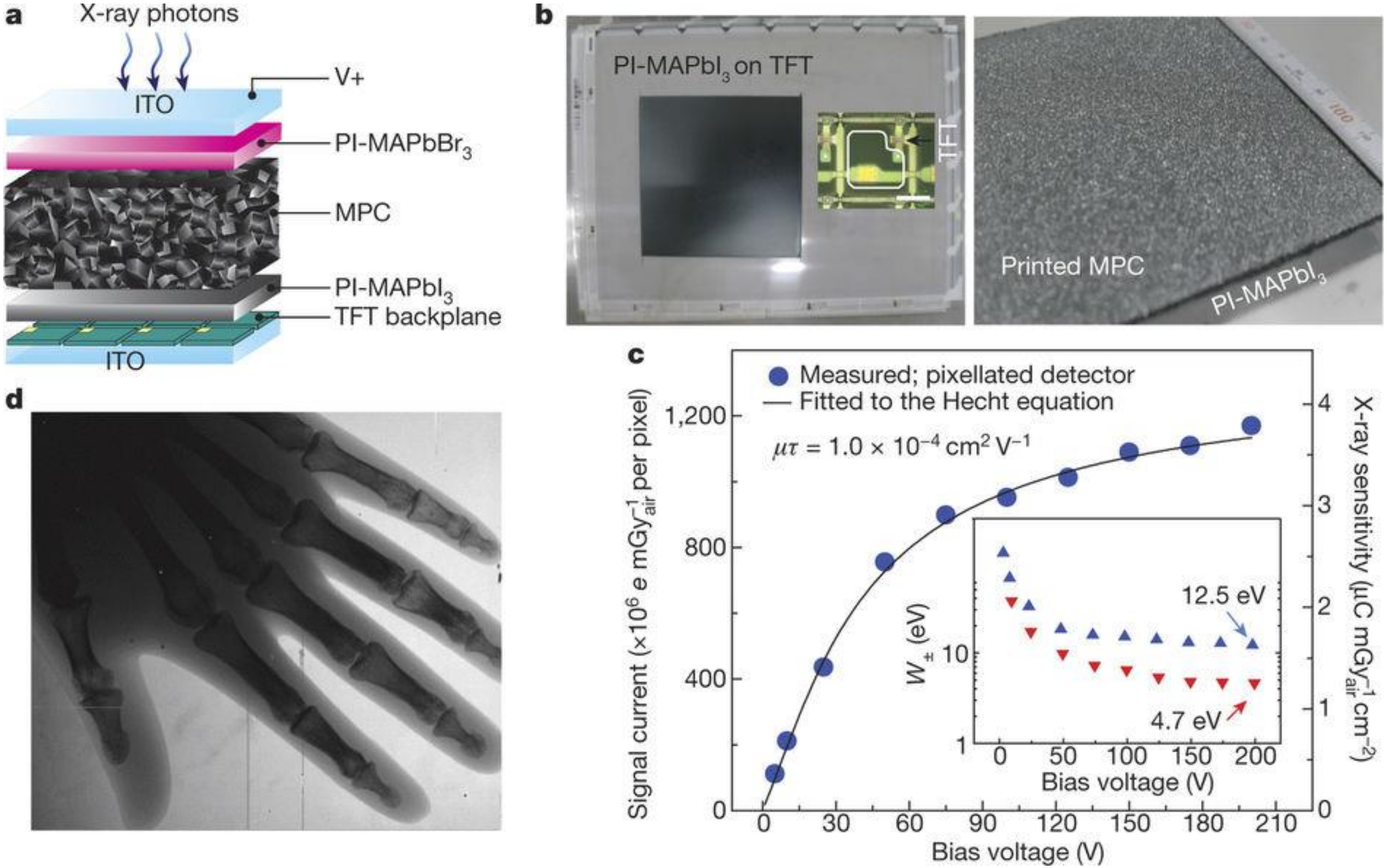
S.Shrestha et.al.
Nature Photonics **2017** 11, 436–440

Direct detection of X-ray photons by solution-processed perovskite polycrystals



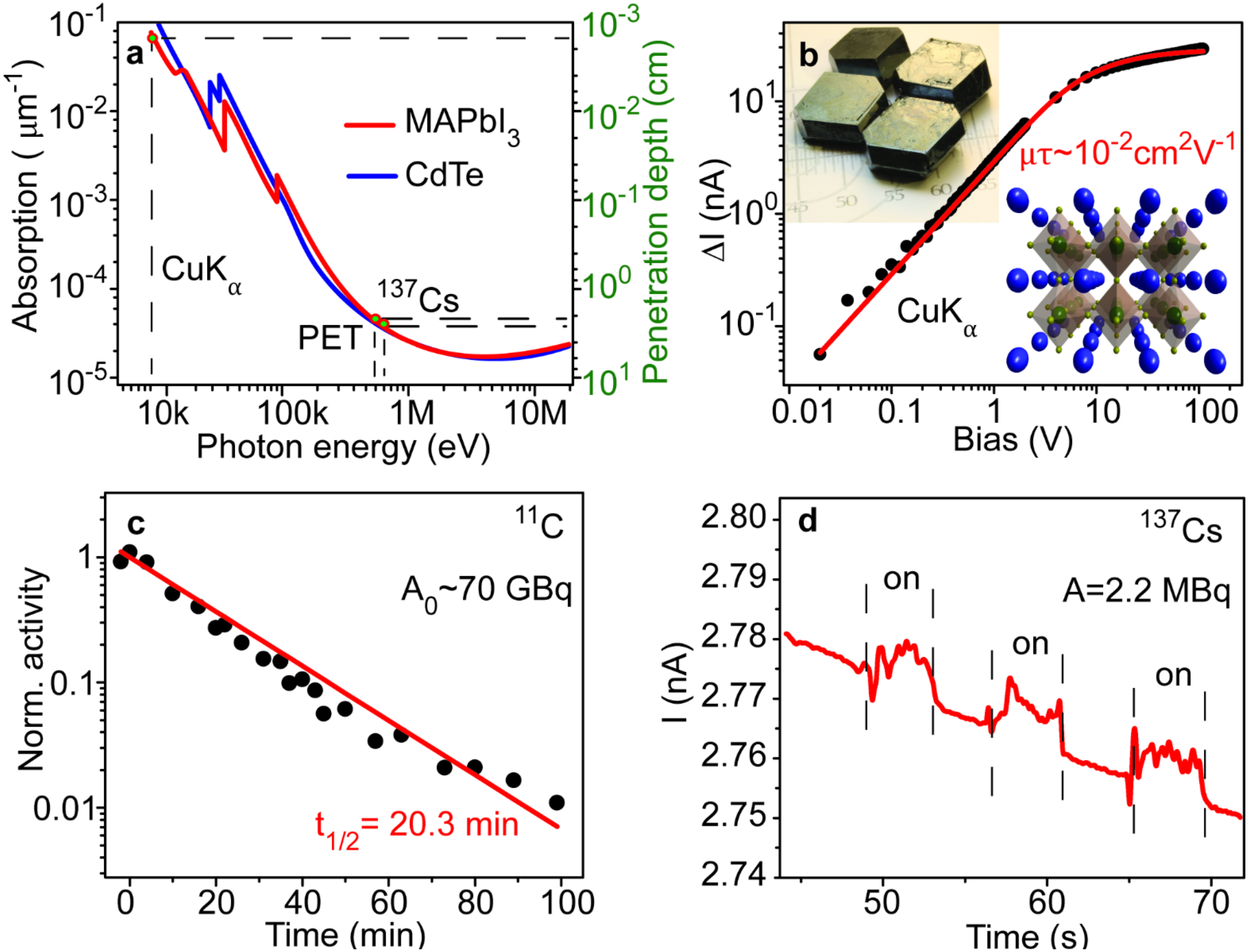
Y C Kim *et al.* *Nature* 550 **(2017)** , 87–91

Direct detection of X-ray photons by solution-processed perovskite polycrystals



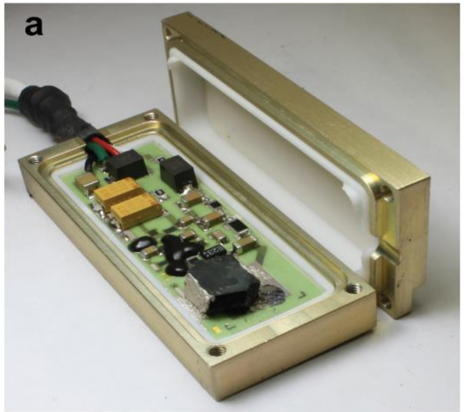
Y C Kim *et al. Nature* 550 **(2017)** , 87–91

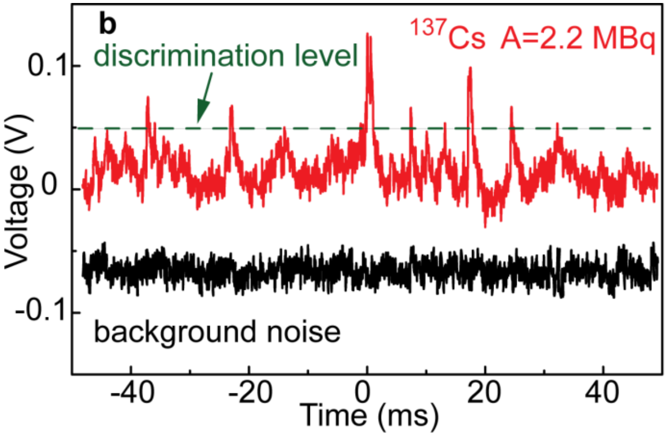
Direct detection of high energy γ photons by single-crystal of lead halide perovskites

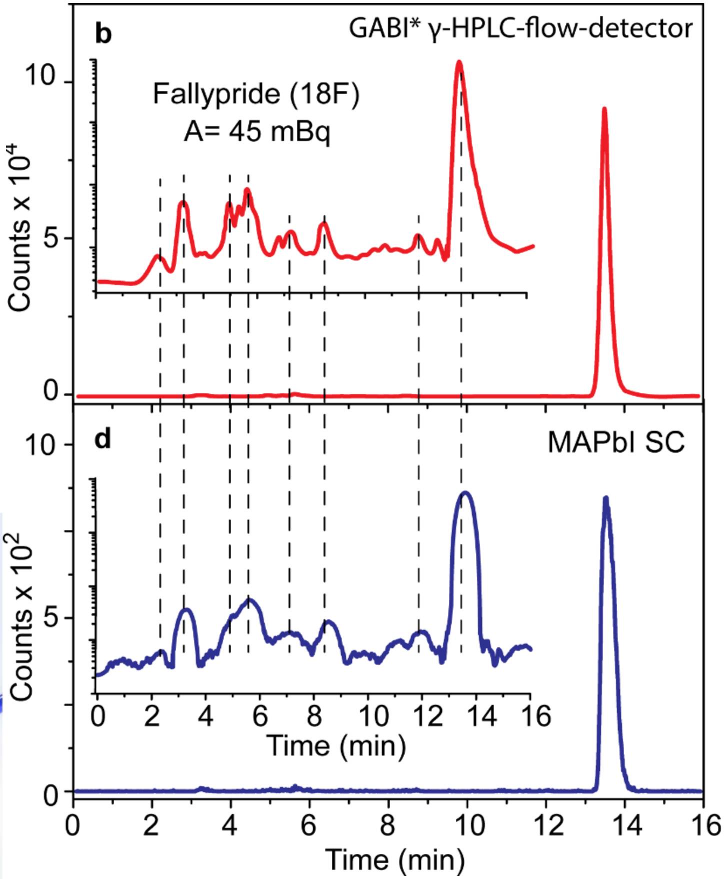


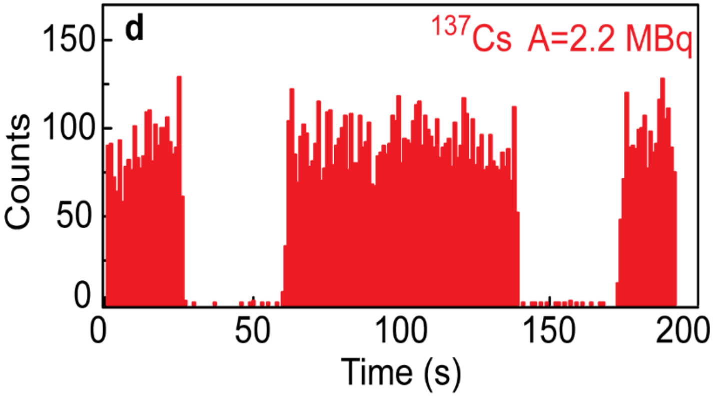
S. Yakunin, et.al. *Nature Photonics*, **2016**, 10, 585–589

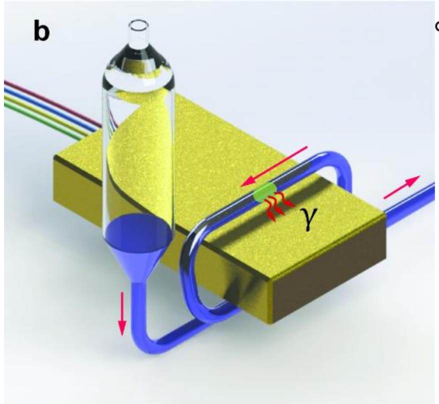
Counting detection of high energy photons by single-crystal of lead halide perovskites





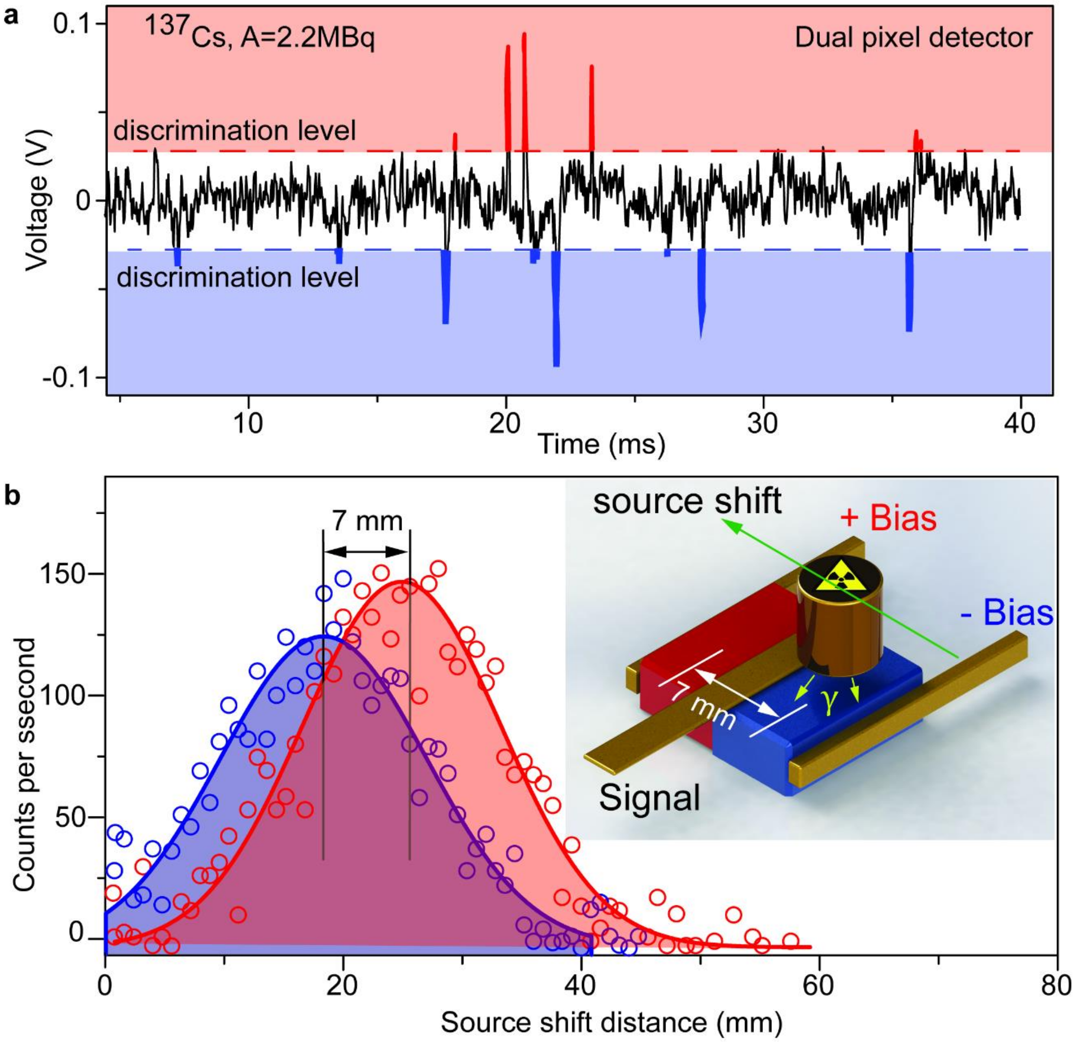


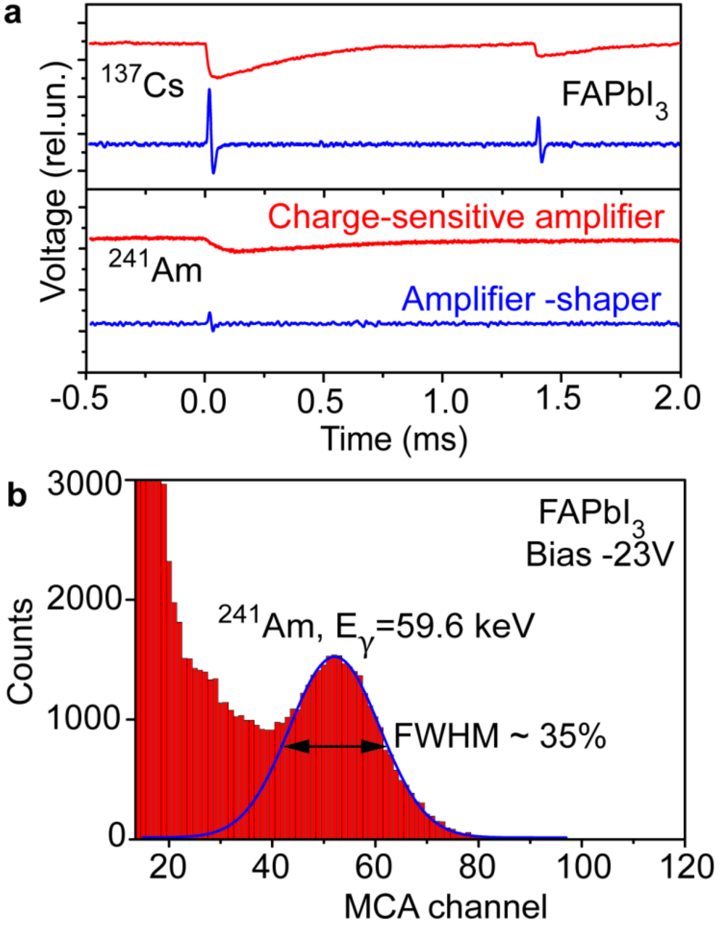




S. Yakunin, et.al. *Nature Photonics*, **2016**, 10, 585–589

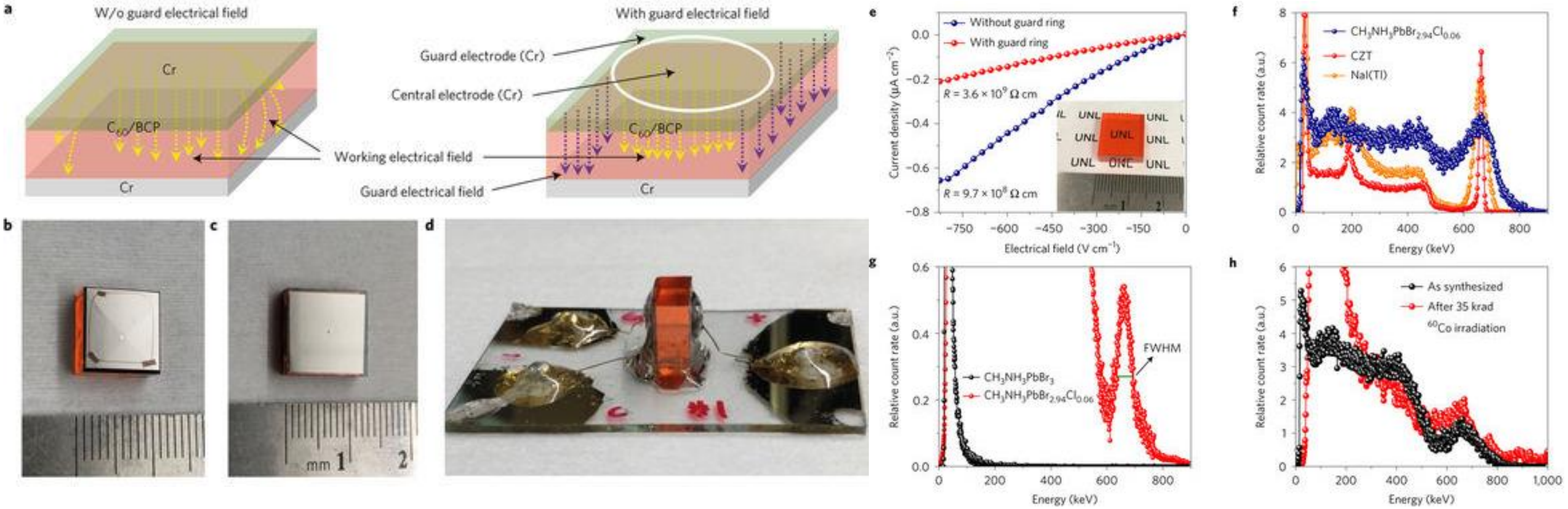
Counting detection of high energy photons by single-crystal of lead halide perovskites, energy resolution





S. Yakunin, et.al. *Nature Photonics*, **2016**, 10, 585–589

Counting detection of high energy photons by single-crystal of lead halide perovskites, energy resolution



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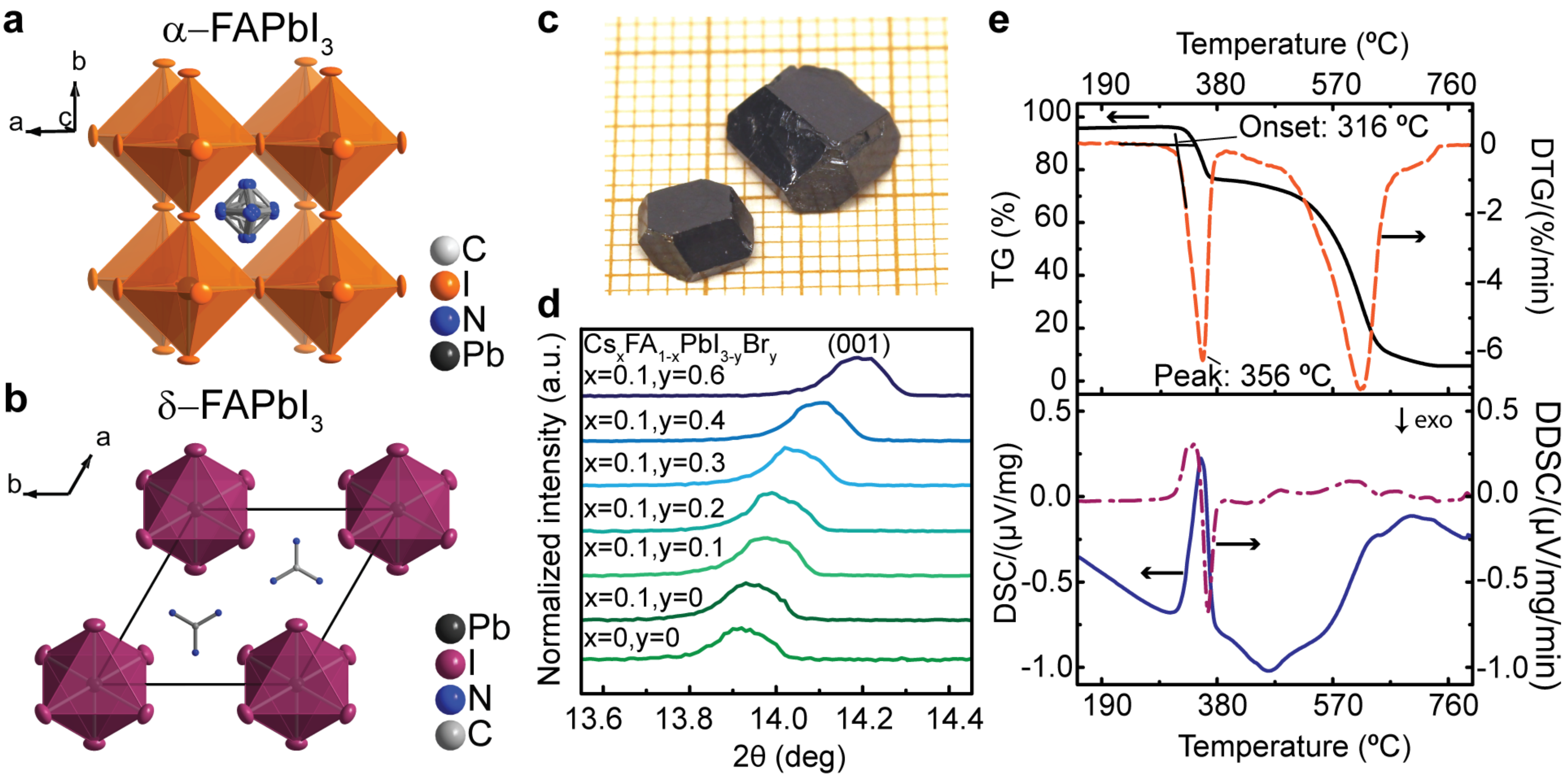
Counting detection of high energy photons by single-crystal of lead halide perovskites with mixed composition



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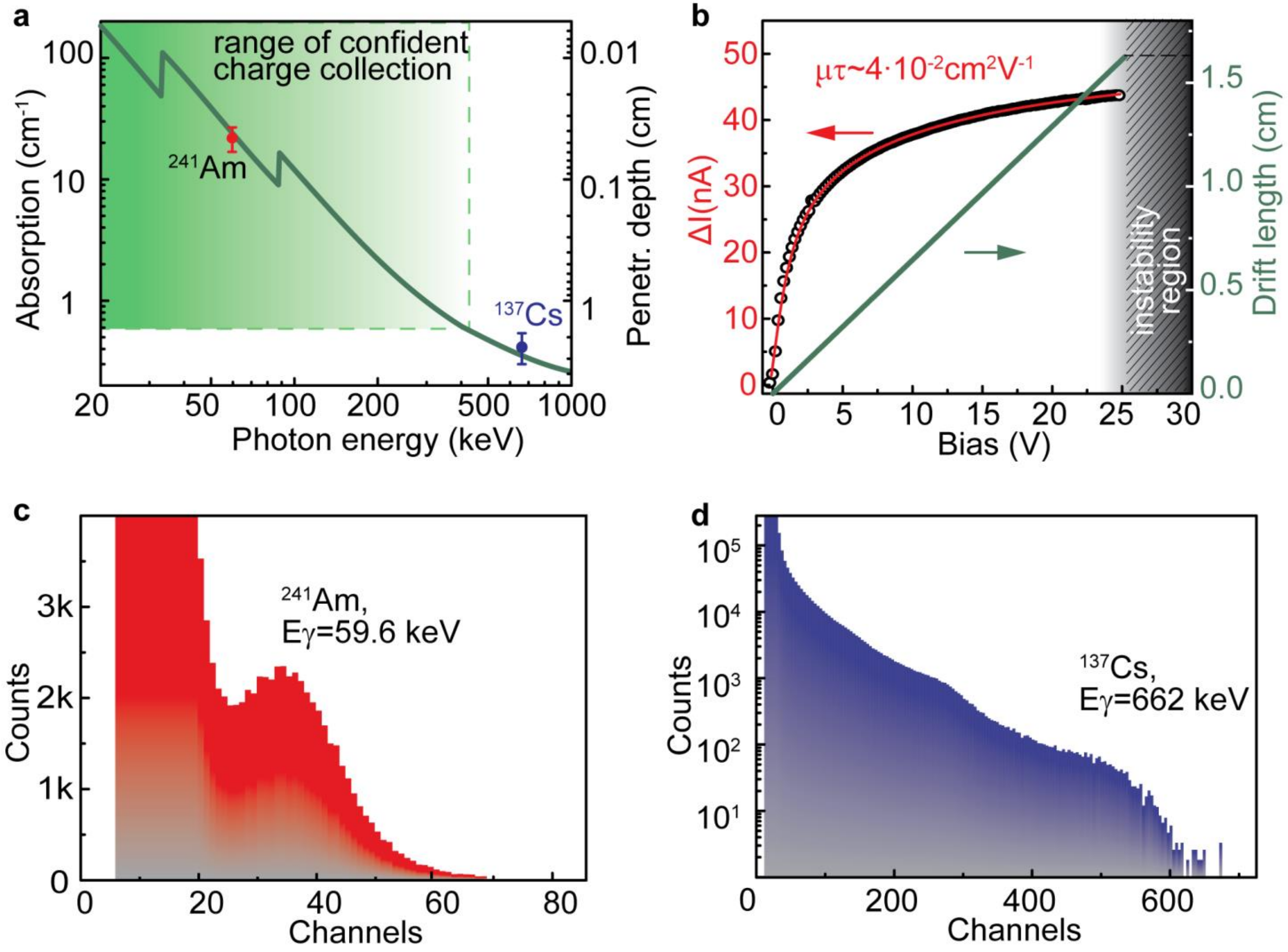
Counting detection of high energy photons by single-crystal of lead halide perovskites with mixed composition



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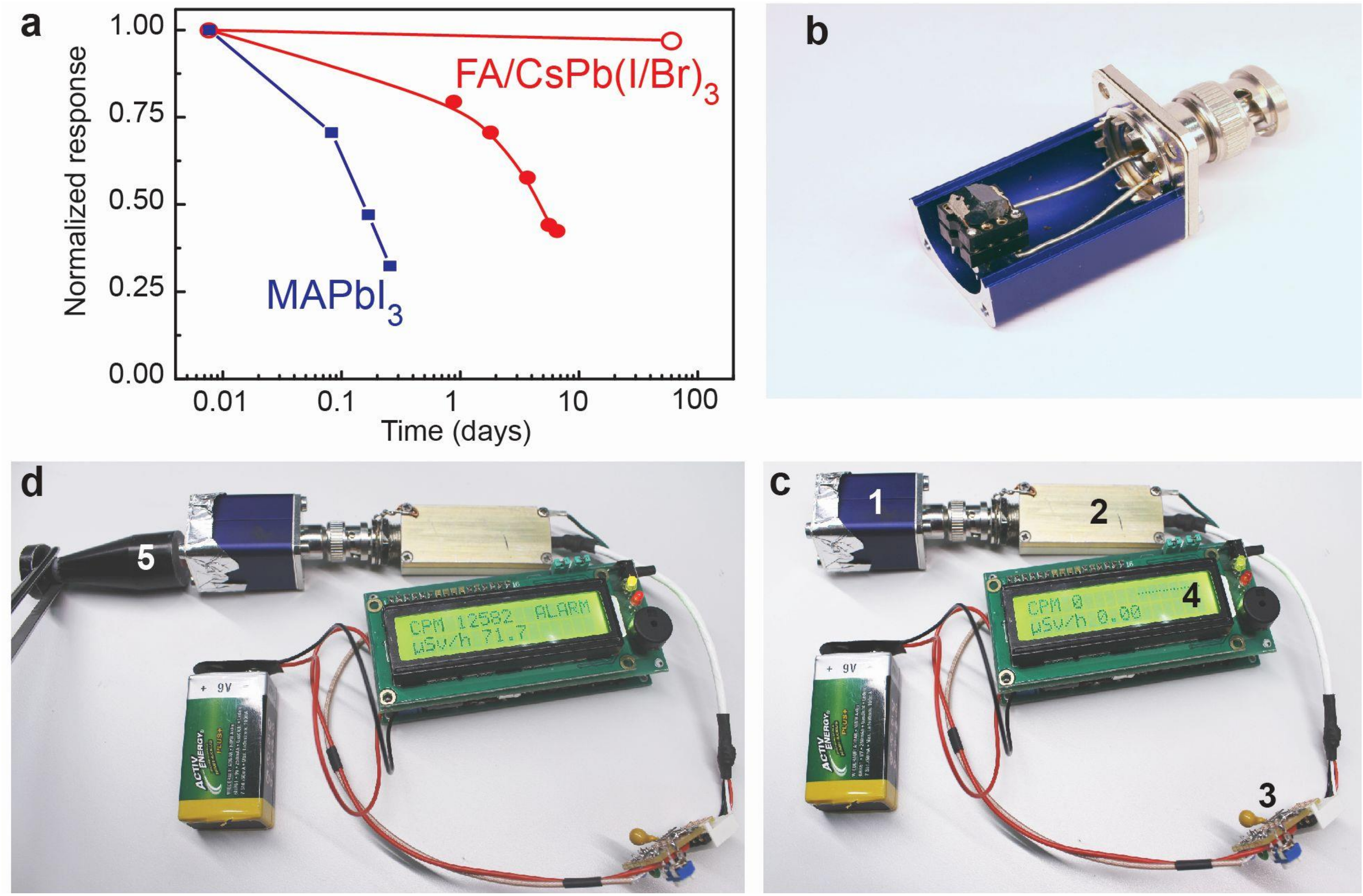
Counting detection of high energy photons by single-crystal of lead halide perovskites



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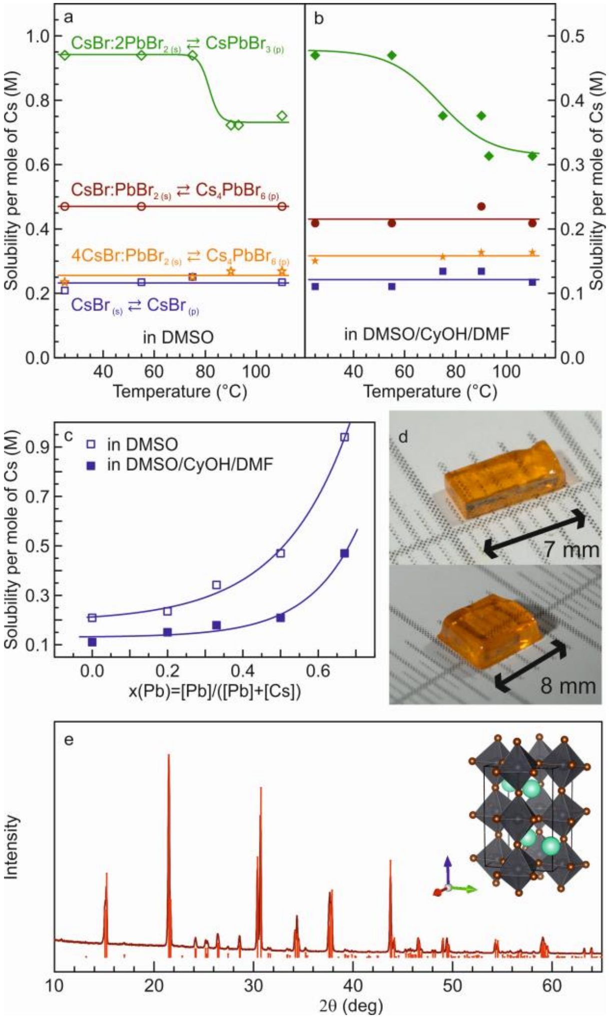
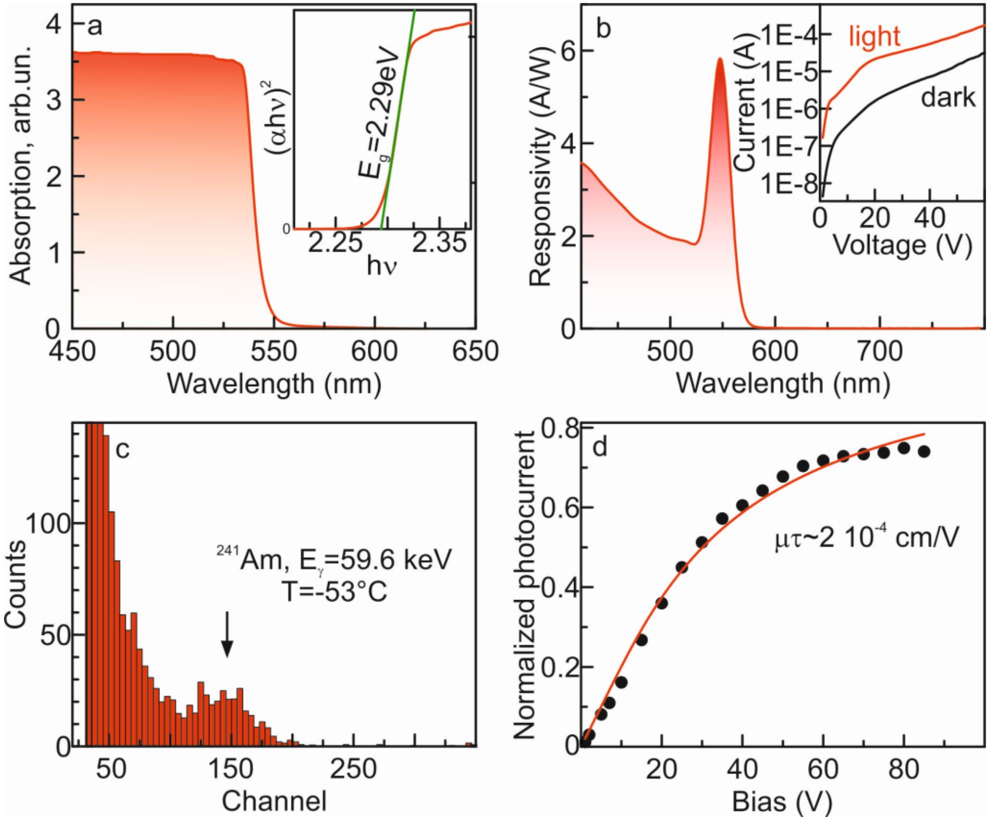
Solution-grown CsPbBr3 perovskite single crystals for photon detection.





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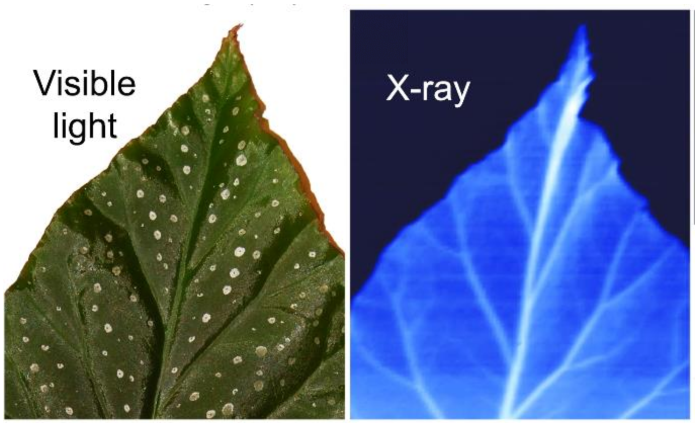
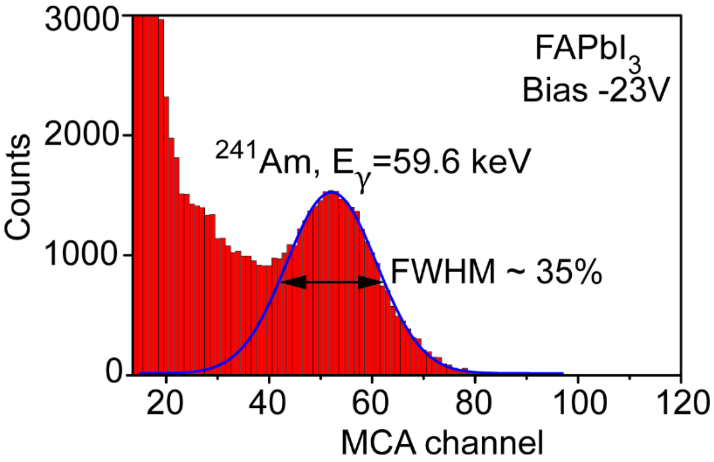
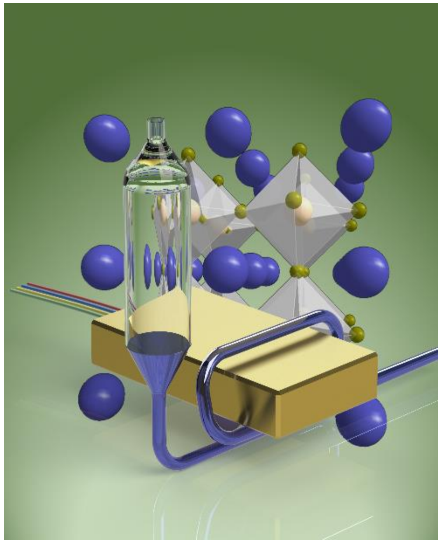
Conclusions

Beneficial factors in perovskites for hard radiation detection:

1. **Heavy atoms, strong absorbance**
2. **Defect tolerance, low trap density, effective charge transport**
3. **Solution growth, cheap and easy in production**
4. **Stability issues might be avoided by variation in composition**








Thank You!