
Supplementary information

High-sensitivity high-resolution X-ray imaging with soft-sintered metal halide perovskites

In the format provided by the
authors and unedited

Supplementary Information

Title

High sensitivity and resolution X-ray imaging with soft-sintered metal halide perovskites

Authors

**Sarah Deumel^{1,2*}, Albert van Breemen³, Gerwin Gelinck^{3,4}, Bart Peeters³, Joris Maas³, Roy Verbeek³,
Santhosh Shanmugam³, Hylke Akkerman³, Eric Meulen Kamp³, Judith E. Huerdler¹, Manogna Acharya¹,
Marisé García-Batlle⁵, Osbel Almora⁵, Antonio Guerrero⁵, Germà Garcia-Belmonte⁵, Wolfgang Heiss²,
Oliver Schmidt¹ & Sandro F. Tedde^{1*}**

¹: Siemens Healthineers AG, Technology Excellence, Guenther-Scharowsky-Strasse 1, 91058 Erlangen, Germany

²: Institute - Materials for Electronics and Energy Technology (i-MEET), Department of Materials Science and Engineering, Friedrich-Alexander-Universitaet Erlangen-Nuernberg, Energy Campus Nuernberg, Fuertherstraße 250, Nuernberg 90429, Germany

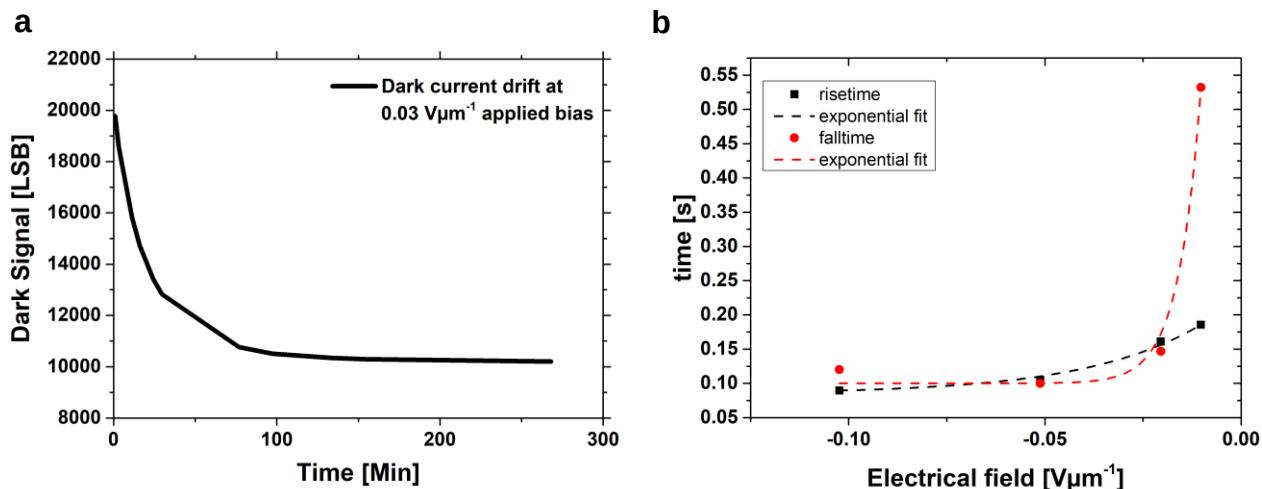
³: Holst Centre-TNO The Dutch Organization for Applied Scientific Research, High Tech Campus 31, 5656 AE Eindhoven, The Netherlands

⁴: Molecular Materials and Nanosystems, Institute of Complex Molecular Systems, Eindhoven University of Technology P.O. Box 513, 5600 MB Eindhoven, The Netherlands

⁵: Institute of Advanced Materials (INAM), Universitat Jaume I, 12006 Castelló, Spain

***: corresponding authors: sarah.deumel@siemens-healthineers.com, Sandro.tedde@siemens-healthineers.com**

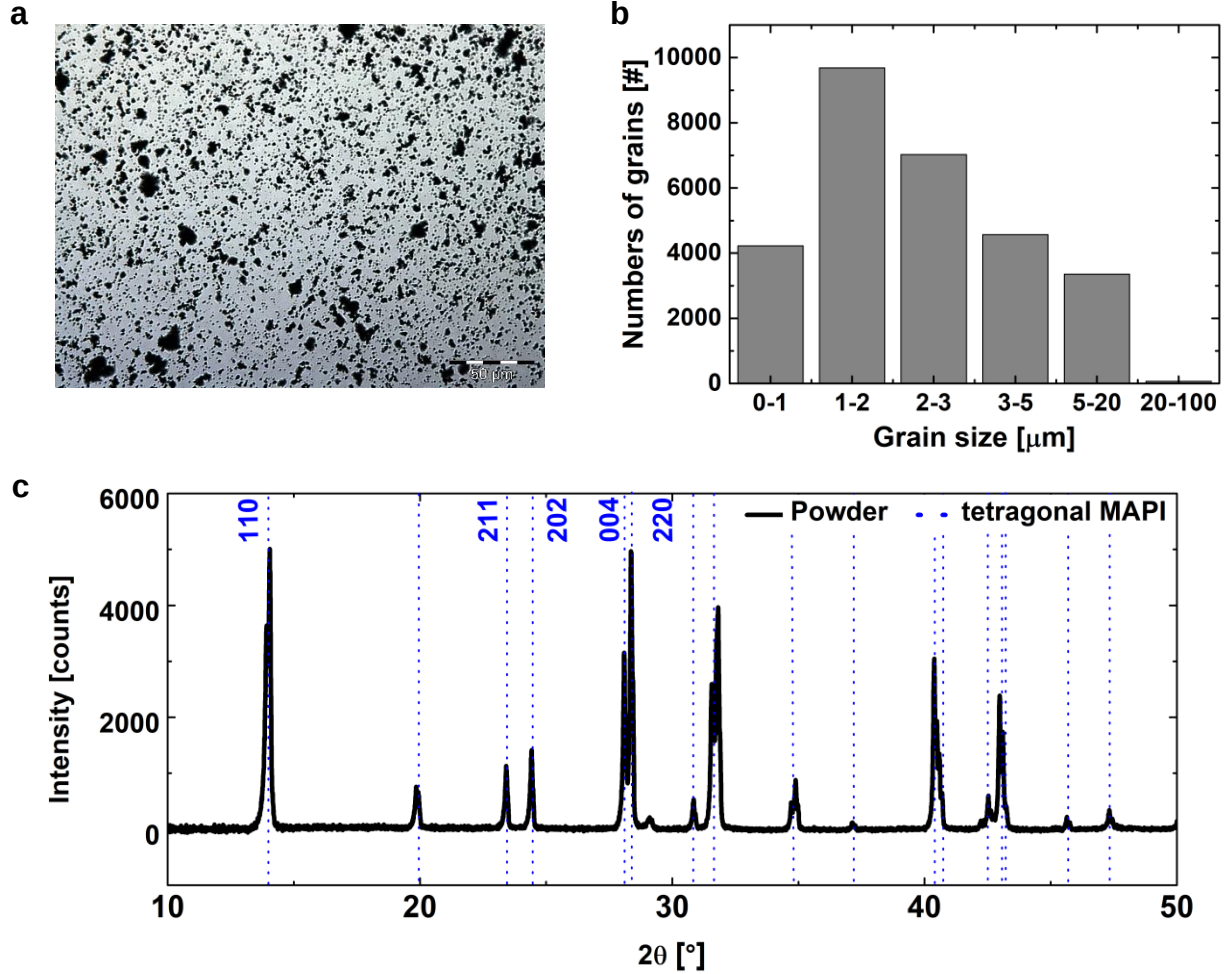
26 **Stability of MAPbI₃**



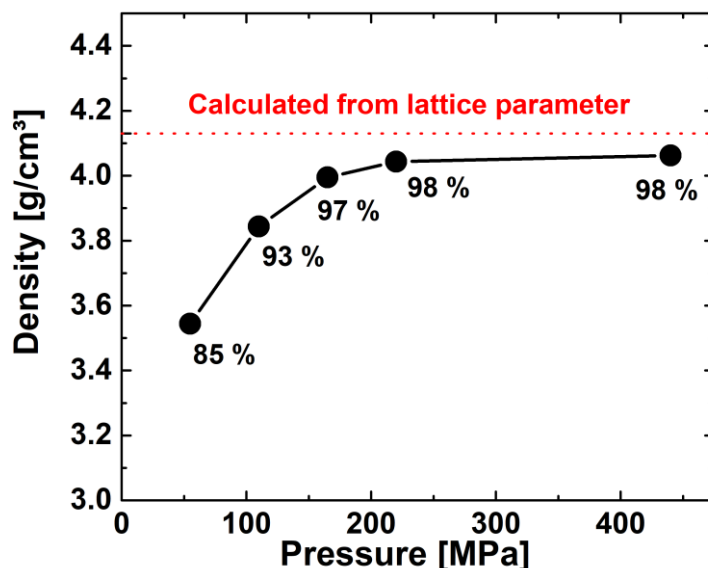
27 **Supplementary Figure S1 | Stability of MAPbI₃ during Measurements a,** Drift of the dark current of a
 28 MAPbI₃ X-ray imaging detector during a measurement period of ~270 min. The dark current is measured
 29 in least significant bits (LSB). The value of the dark current is exponential decreasing with the time
 30 starting at a value of ~20,000 LSB and ending with ~10,200 LSB after 270 min. After approximately 100
 31 min the dark current is stable with a standard derivation of ±218 LSB in the next 170 min. This shows the
 32 importance of waiting until the sample reaches its ionic equilibrium state before starting the X-ray
 33 measurements. **b,** Rise- and falltimes of X-ray pulses measured with a MAPbI₃ wafer in dependency of
 34 the applied electrical field. With higher electrical field rise- and falltimes are decreasing exponential.

35

MAPbI₃ powder characterization

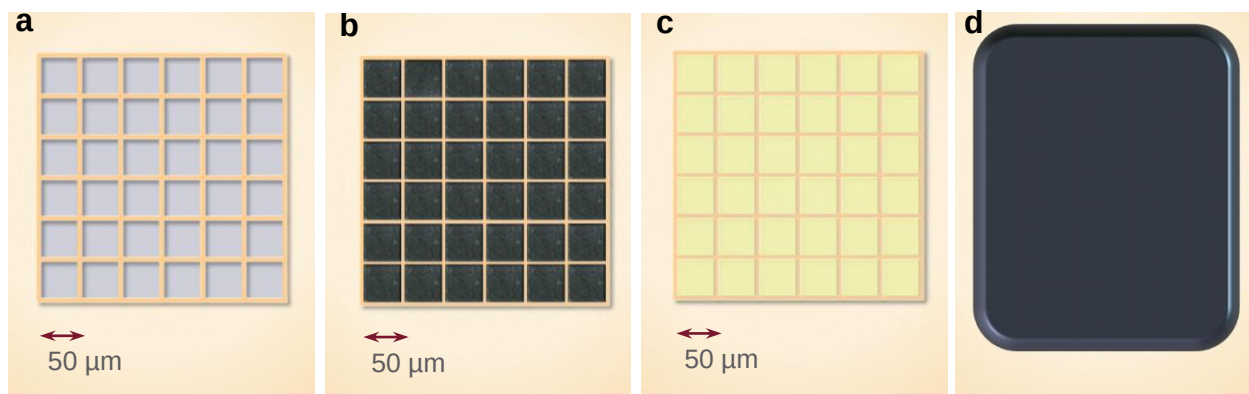


Supplementary Figure S2 | Characterization of the microcrystalline MAPbI₃ powder: *a*, Optical microscope image of microcrystalline MAPbI₃ powder grains. The scale bar corresponds to 50 μm. The average grain size is 1.8 μm. *b*, Calculated grain size distribution. Most of the powder particles have a grain size < 2 μm. Only 15 % of the powder has a size > 5 μm. *c*, X-Ray diffraction pattern of the used MAPbI₃ powder. The pregnant peaks indicate the tetragonal MAPbI₃-phase with a *I4cm* space group. The comparative values come from the literature ^{1,2}.



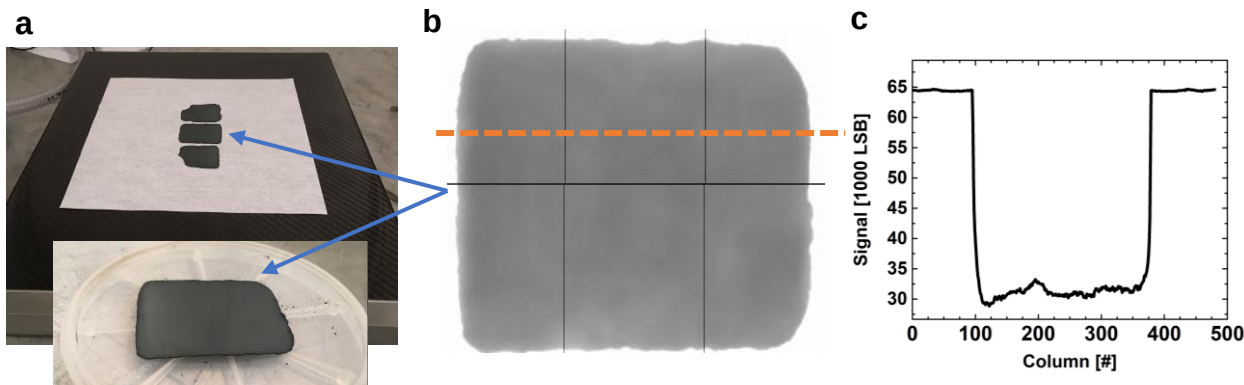
67 **Supplementary Figure S3 | Density curve for mechanically soft-sintered MAPbI₃ wafer vs. applied**
68 **pressure of the hydraulic press.** The MAPbI₃ powder is pressed at 70 °C and show a compaction of 85% at
69 55 MPa up to 98% at high pressure of 440 MPa. The density is calculated by the wafer weight and thickness,
70 the latter measured by a micrometer screw gauge. The theoretical limit is 4.13 gcm⁻³ and calculated by
71 simulated lattice parameter from the literature.^{1,2}

72

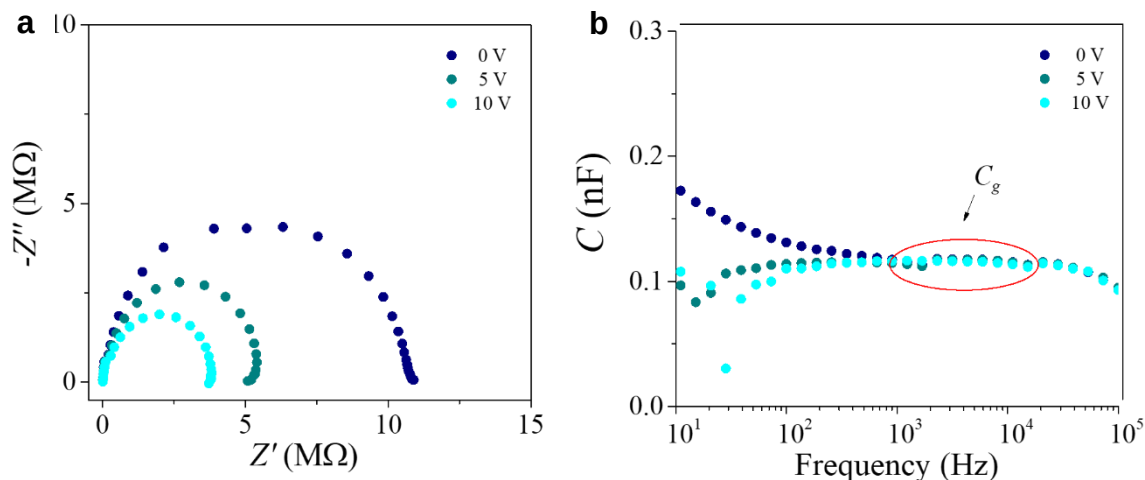


73 **Supplementary Figure S4 | X-ray detector manufacturing process.** Top view schematic showing the
74 attachment of the MAPbI₃ absorber layer to the TFT backplane. Only part of the array (6x6 array) is shown
75 for convenience. Thicknesses are not to scale. **a**, TFT backplane with pixel electrode and anchoring grid. **b**,
76 Grid on the backplane is filled with MAPbI₃ powder. **c**, MAPbI₃ powder is liquefied under methylamine
77 atmosphere. **d**, Preformed MAPbI₃ wafer is placed on the liquid MAPbI₃ phase.

78



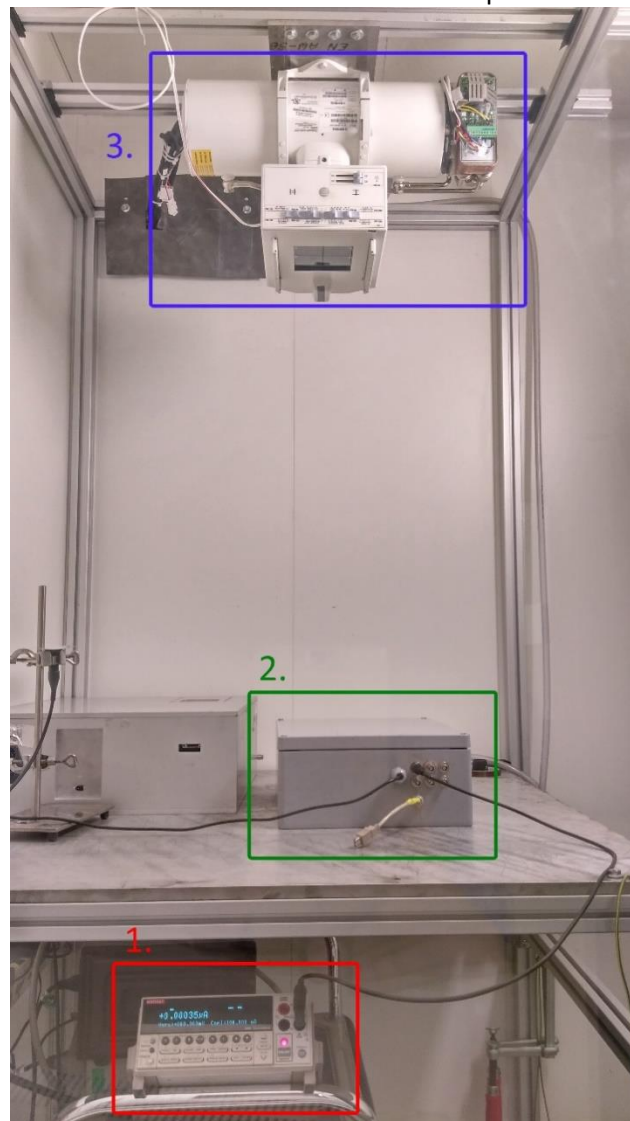
Supplementary Figure S5 | X-ray detector quality control process. *a*, Freestanding wafer produced in phase one can be placed on a commercially available indirect X-ray detector with CMOS technology. *b*, The resulting X-ray image (RQA5) of the wafer of interest. The gray values of the image indicate the local ability to absorb X-rays. *c*, Profile of the wafer (dotted orange line in *b*). The 230 μm thick MAPbI₃ wafer attenuate 33000 least significant bit (LSB), which corresponds to an absorption of 48% of a standardized RQA5-beam quality and shows a variation of ± 2500 LSB in the attenuation. The non-homogeneity can largely be explained by the uneven thickness of the MAPbI₃ powder in the hydraulic press prior to the soft sintering. Currently this deposition is a manual process and automation can improve this in the future



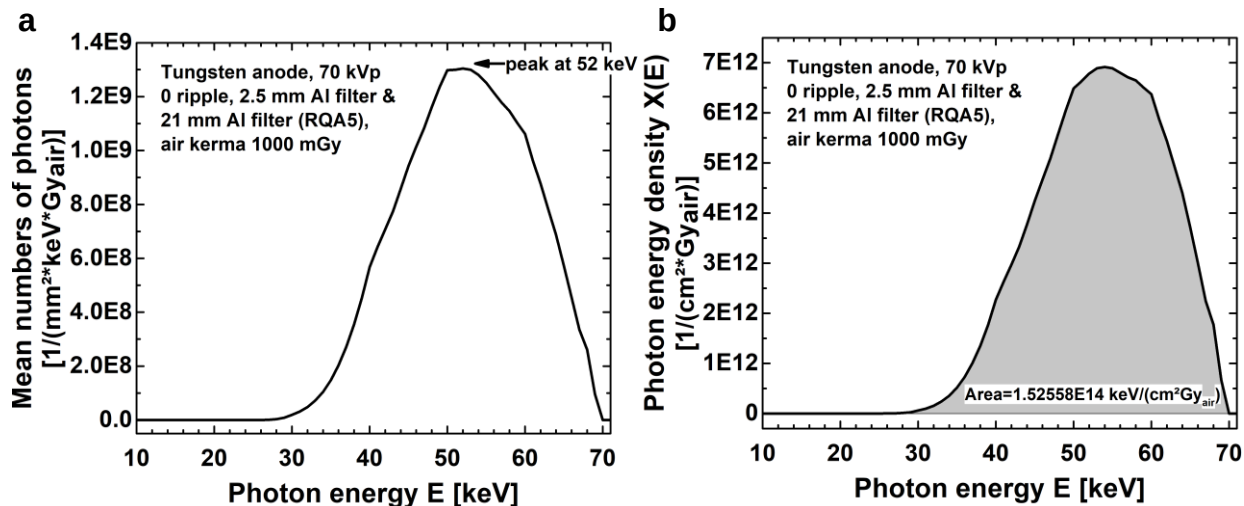
Supplementary Figure S6 | Characterization of freestanding MAPbI₃ wafers. Example of the impedance (a) and capacitance (b) spectra of MAPbI₃-based pellet of nominal thickness 857 μm contacted with Pt/Cr electrodes measured at different bias in the dark. Capacitance is calculated from the impedance values as $C = 1/i\omega Z$, being i the imaginary unity, and ω the angular frequency. The high frequency resistance slightly decreases at forward polarization meanwhile the geometrical capacitance C_g remains constant in the frequency range of $10^3 - 10^4$ Hz. From the geometrical capacitance value, electrode area, pellet thickness, and pellet density, the dielectric constant of the perovskite material results in $\epsilon = 75.0 \pm 0.7$. This value agrees with those experimentally reported in the literature³⁻⁵.

**Technical description of the X-ray source and set-up at Siemens Healthineers, Technology Excellence,
Technology Innovation Management, Technology & Projects (SHS TE TIM TP) Erlangen**

For our measurements we used a clinical angiography tube (MEGALIX® CAT Plus 125/40/90-124 GW) with a tungsten anode from Siemens Healthineers AG which is mounted on the ceiling of a shielded room and the X-ray generator Polydoros A100 Plus. The distance between the focal spot of the X-ray tube and the samples is around 120 cm creating a homogeneous X-ray area of $5 \times 5 \text{ cm}^2$ with a closed as much as possible collimator (ML02cm). The large focal spot setting has been used for all X-ray measurements. The dose was measured with a PTW Diados T11003-001896 dosimeter that was placed on the sample position.



Supplementary Figure S7 | Measurement Set-Up: Installed MEGALIX® CAT Plus 125/40/90-124GW X-Ray source (3.) with X-ray tube and collimator above the measurement set-up consisting of an Al sample box (2) and a Keithley 2400 source meter (1).



Supplementary Figure S8 | Simulated X-ray spectra: **a**, Simulated mean number of photons for the MEGALIX X-ray tube with a peak voltage of 70 kV and a dose of 1 Gy_{air}. Additional to the build in filter of 2.5 mm Al a 21 mm Al filter is used to get the standardized RQA5 spectrum. The maximum number of photons is reached at a photon energy of 52 keV. **b**, The photon energy density X(E) corresponds to the mean numbers of photons multiplied by the photon energy and is plotted against the photon energy. The emitted energy of the spectrum E_{emit} is the integral (gray area) of X(E) and the photon energy and has the value $E_{emit}=1.52558E14 \text{ keV cm}^{-2}\text{Gy}_{air}^{-1}$.

The simulated X-ray spectrum of the MEGALIX CAT Plus 125/40/90-126GW operating at 70 kV with a RQA5 filtration and a dose of 1 Gy_{air} can be seen in Figure S8 a). The maximum emission of the tube is at a photon energy of 52 keV.

For the calculation of the emitted energy of the spectrum E_{emit} , the mean number of photons must be multiplied with the photon energy and a factor of 100 to become the so called photon energy density per unit area and unit dose X(E). E_{emit} is the integral of the resulting curve (cf. Figure S8 b)) and has the value $1.52558E14 \text{ keVcm}^{-2}\text{Gy}_{air}^{-1}$.

Calculation of the electron-hole pair creation energy

A figure of merit for the X-ray detector performance is the electron-hole pair (EHP) creation energy $W_{\pm}$ which is an expression for the energy that is necessary to create a free EHP and can be described as: [6]

$$W_{\pm} = \frac{\text{absorbed energy}}{\text{numbers of extracted photons}} \quad \text{Equation 1}$$

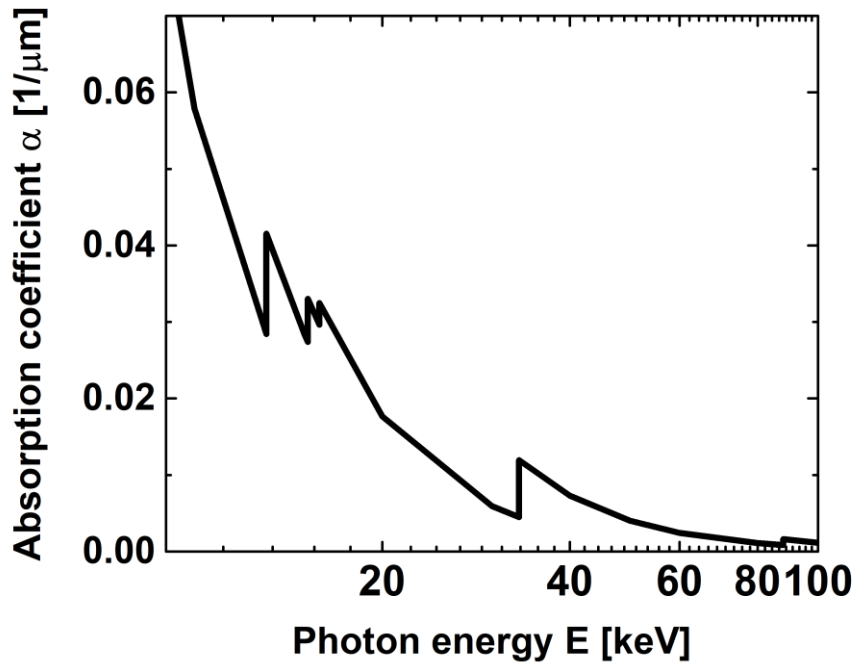
130 The absorbed energy is the combination of the energy of the emitted X-ray spectrum and the material
131 ability to absorb them: [6]

132
$$\text{absorbed Energy} = \int X(E) * Aq(E) dE . \quad \text{Equation 2}$$

133 $Aq(E)$ stands for the efficiency of the medium to attenuate respectively the amount of absorbed photons
134 with given energies E and can be determined with the material specific attenuation coefficient α and the
135 effective layer thickness L : [6]

136
$$Aq = 1 - \exp(-\alpha L). \quad \text{Equation 3}$$

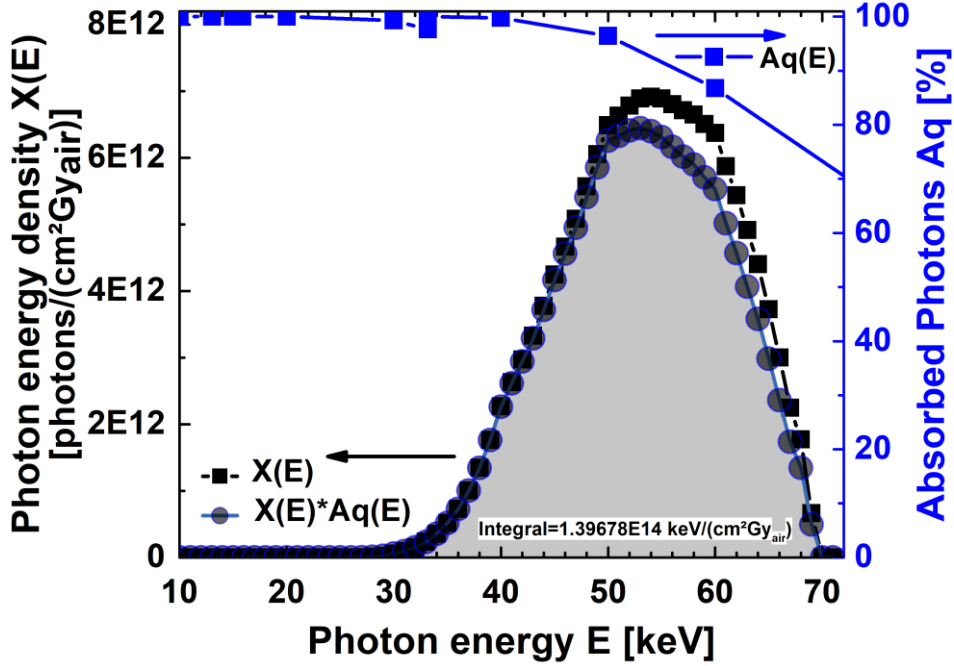
137 The total attenuation coefficient for MAPbI_3 is taken from the NIST XCOM cross-section database and
138 shown in Figure S9.



139 **Supplementary Figure S9 | Absorption coefficient α of MAPbI_3 calculated with the photoelectric**
140 **absorption which is taken from the XCOM database of the NIST webpage.** *The photon energy is in the*
141 *range of 10 up to 100 keV, which is well suitable for the RQA5 spectrum.*

142

143 With these datasets and the Equation 3 we can determine Aq for the effective wafer thickness of
 144 $L=0.85*977 \mu\text{m}= 830 \mu\text{m}$:



145 **Supplementary Figure S10 | Photon energy density X and the number of absorbed photons Aq vs. photon**
 146 **energy E.** The Absorbed photons are calculated for a MAPbI₃ layer with an effective thickness of 830 μm
 147 and the in Figure S9 given absorption coefficient. The integral of the result of the multiplication of X(E) and
 148 Aq(E) is the absorbed energy per unit area and unit dose and has the value of $1.397\text{E}14 \text{ keV cm}^{-2}\text{Gy}_{\text{air}}^{-1}$.

149 According to Equation 2 the curves of X(E) and Aq(E) have to be multiplied (see gray curve in Fig. S10). The
 150 integral of the resulting curve corresponds to the absorbed energy per unit area and unit dose.

151 The numbers of extracted charges per unit area and unit dose can be determined with the Sensitivity S
 152 divided by the elementary charge e:

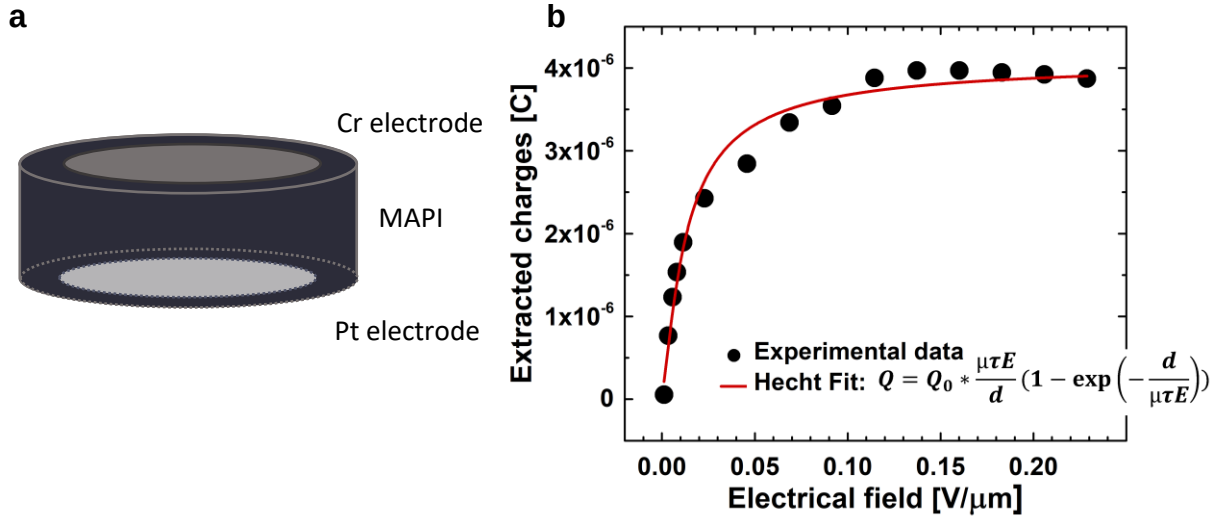
$$153 \quad \text{number of extracted charges} = \frac{S}{e}. \quad \text{Equation 4}$$

154 With a sensitivity of $2000 \mu\text{C Gy}_{\text{air}}^{-1}\text{cm}^{-2}$ at an electrical field of $0.05 \text{ V}\mu\text{m}^{-1}$ the EHP creation energy is:

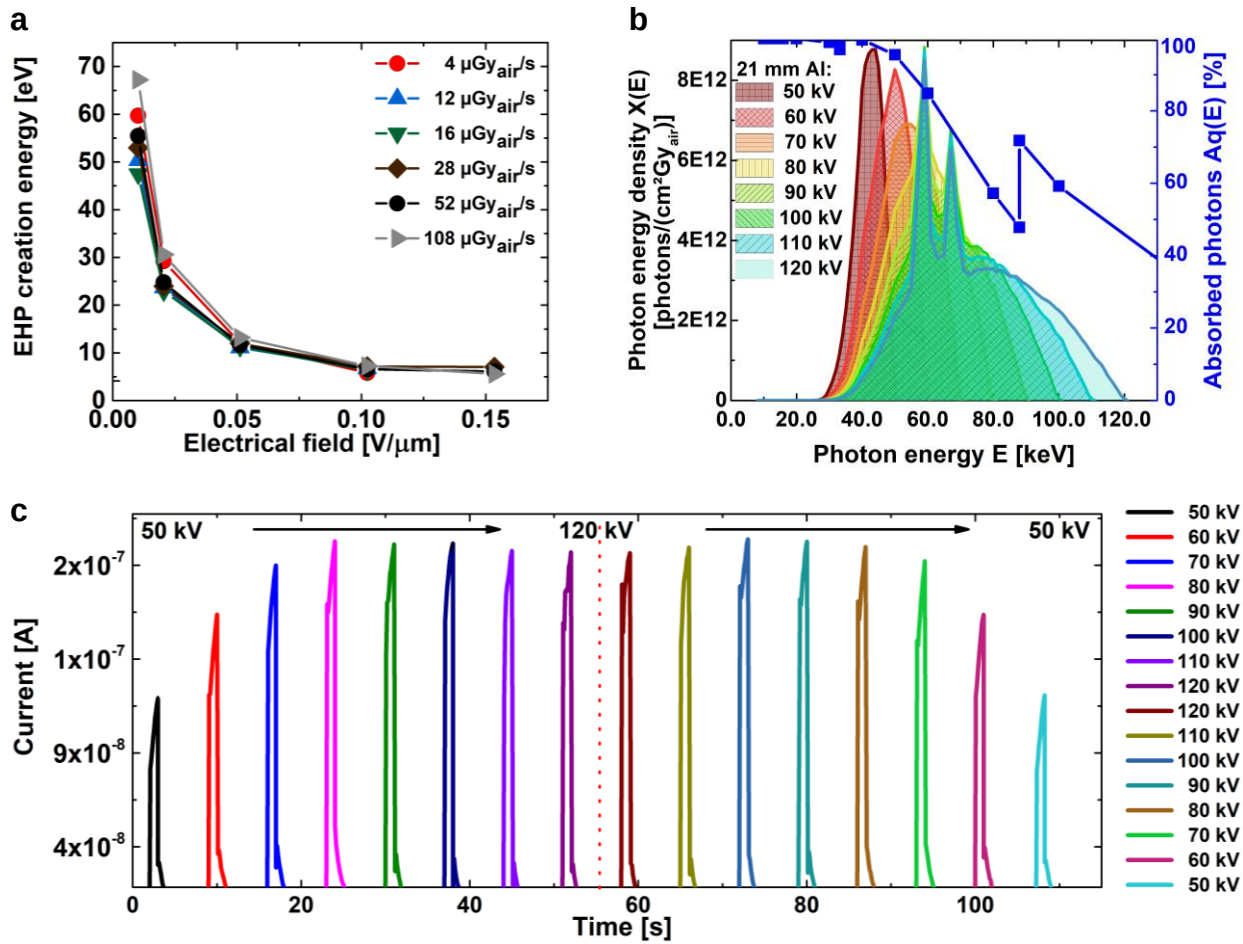
$$155 \quad W = \frac{1.389\text{E}14 \frac{\text{keV}}{\text{cm}^2\text{Gy}_{\text{air}}} * 1.602\text{E}-19 \text{ C}}{2000 \frac{\mu\text{C}}{\text{Gy}_{\text{air}}\text{cm}^2}} \approx 11 \text{ eV}. \quad \text{Equation 5}$$

157

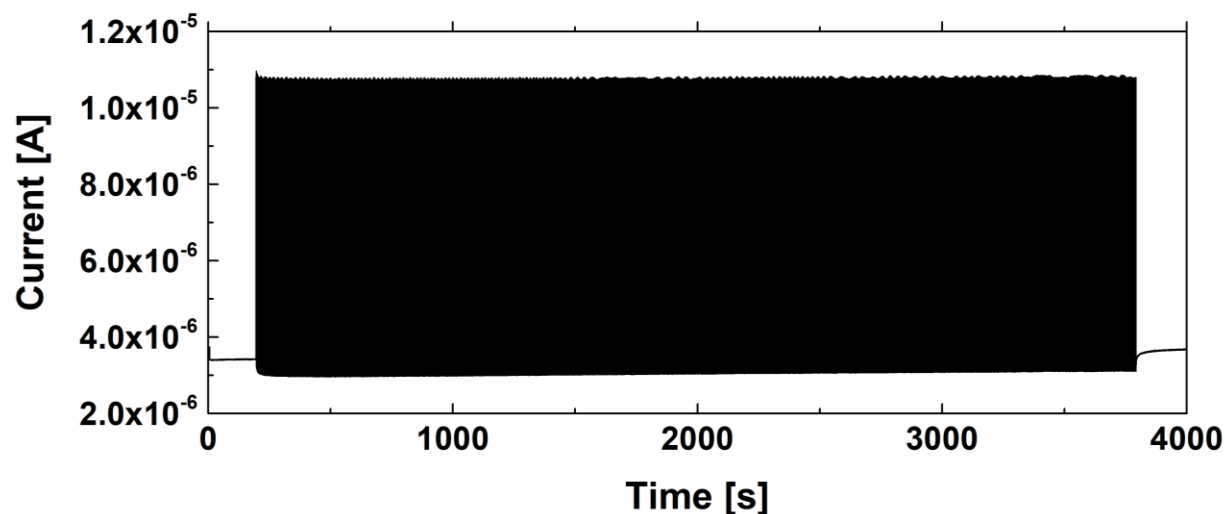
For further accuracy the sample box and the sample holder (both made of Al) must be considered when calculating the X-ray spectrum. This results in additional 6 mm aluminum filtration for the wafer characterization. The measurement set-up of the X-ray detectors is different – so there is no need for the additional filtration of the X-ray spectrum.



Supplementary Figure S11 | Characterization of freestanding MAPbI₃ wafers. **a**, Schematically view of a freestanding MAPbI₃ wafer with a diameter of 15 mm. The electrodes have a diameter of 11.2 mm and therefore an area of 100 mm². **b**, Extracted charges after exposures of the wafer to a RQA5 X-ray spectrum with a dose of 213 μGy_{air}s⁻¹. The experimental data can be fitted with the help of the Hecht equation which is shown in the graph.⁷ The μτ-product can be determined as 4E-4 cm²V⁻¹.



Supplementary Figure S12 | X-ray characterization of MAPbI₃ wafers: **a**, Electron hole pair creation energy vs. electrical field and the exposed dose. The MAPbI₃ wafer was irradiated with a RQA5 X-ray spectrum under different doses. With the calculation of the sensitivity by using the given X-ray current density response and Equation 1 the EHP creation energy could be determined. The variance of $W_{\pm}$ decreases with increasing electrical field starting with $\Delta W_{0.01} = \pm 7$ eV ($0.01 \text{ V}\mu\text{m}^{-1}$), $\Delta W_{0.05} = \pm 0.7$ eV down to $\Delta W_{0.15} = \pm 0.6$ eV by $0.15 \text{ V}\mu\text{m}^{-1}$. The maximum average value of $W_{\pm}$ is 55 eV and can be found at the lowest measured electrical field of $0.01 \text{ V}\mu\text{m}^{-1}$. The average EHP creation energy decreases down to $W_{\pm,0.15} = 6.1$ eV. It can be said that the EHP creation energy is independent of the dose for electrical fields over $0.05 \text{ V}\mu\text{m}^{-1}$ within the scope of the measurement accuracy. **b**, Photon energy density $X(E)$ for different anode voltages ranging from 50 kV up to 120 kV and a filtration with 21 mm Al (RQA5@70 kV_p) and the absorbed photons $A_q(E)$ of the MAPbI₃ wafer. The absorbed energies are listed in Supplementary Table S1. **c**, Measured current during 1 s long X-ray pulses with a dose of $40 \mu\text{Gy}_{\text{air}}\text{s}^{-1}$ each and a variation of X-ray anode voltages. For a more statistical evaluation at first the anode voltage is increased from 50 kV up to 120 kV (region I) and afterwards decreased back to 50 kV (region II). The general course shows an increased pulse height with increased anode voltage, but the maximal current can be found between 80 and 100 kV_p with a slight decrease for 110 and 120 kV. The pulses for each anode voltage are nearly identical for both regions. So, it can be said that the X-ray response is independent of irradiation and over time.



193 **Supplementary Figure S13 | Current measurement of a MAPbI₃ wafer during irradiation of 3600 X-ray**
 194 **pulses with a cumulative dose of 11 Gy_{air}. Each pulse has a duration of 100 ms and a dose of 3 mGy_{air}. A**
 195 **dark current of 3.4×10^{-6} A can be determined before the irradiation. After the exposure with 11 Gy_{air} the**
 196 **current is slightly increased to 3.6×10^{-6} A. The pulse heights are varying in the range of 1.07×10^{-5} –**
 197 **1.08×10^{-8} A. Since the variance of the pulse heights is smaller than the increase in the dark current, the X-**
 198 **ray response of the MAPbI₃ wafer shows a great stability over the cumulative dose of 11 Gy_{air}.**

199

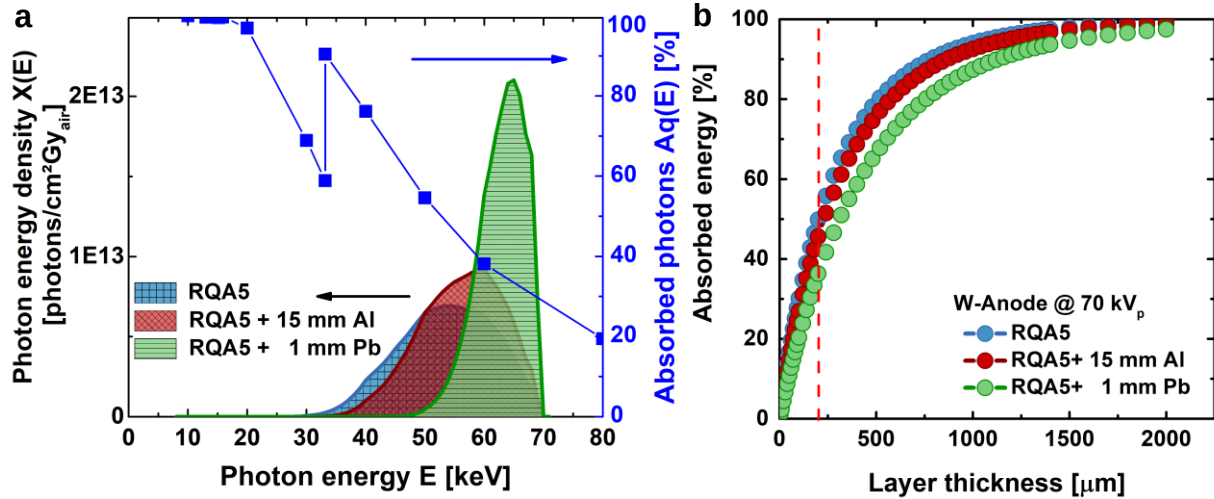
200

201

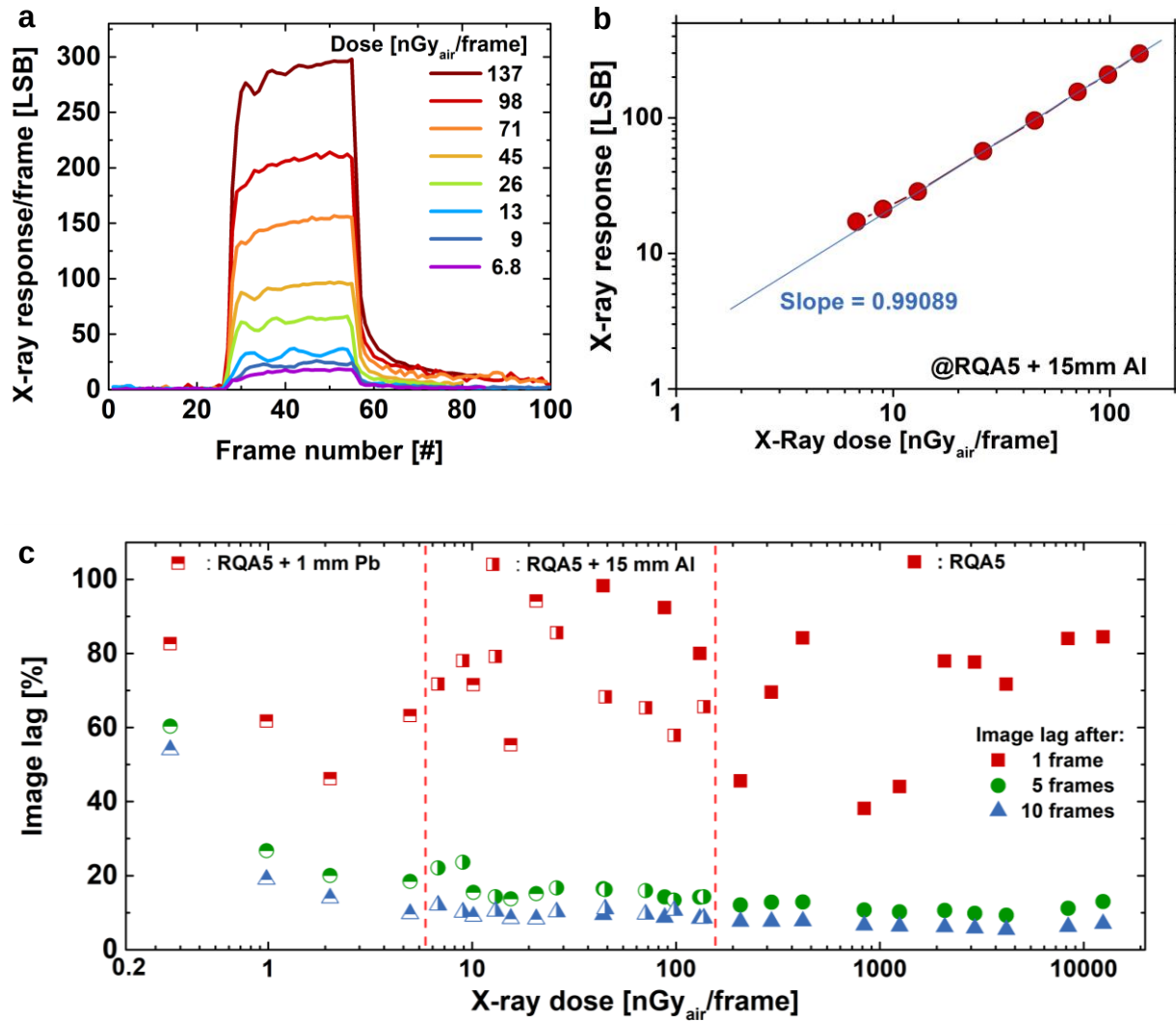
202

203

204

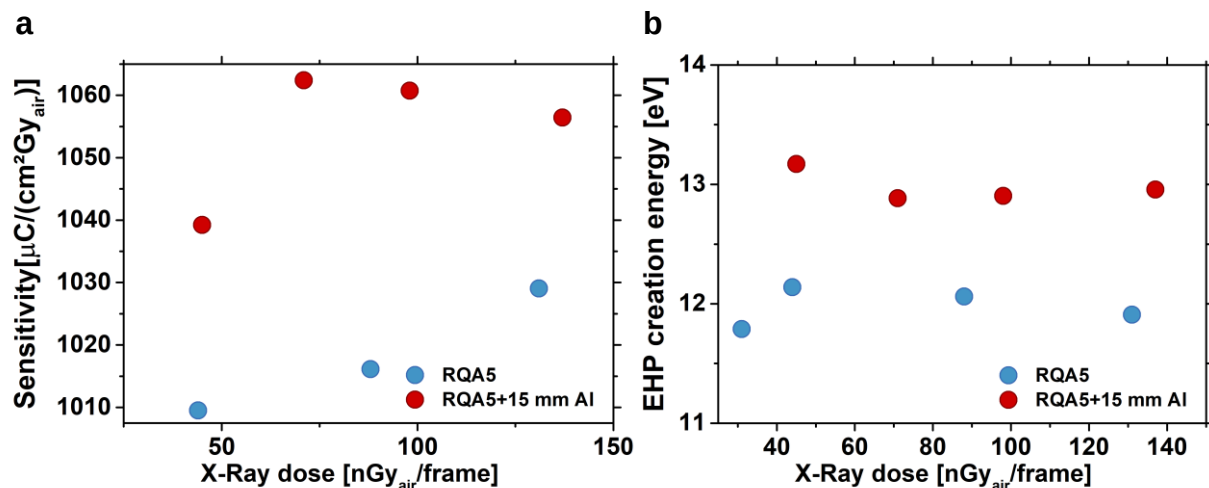


Supplementary Figure S14 | Comparison of the different X-ray spectra used for the characterization of the X-ray detector. **a**, Photon energy density X vs. photon energy E for three different X-ray spectra at an anode voltage of 70 kV_p: RQA5, RQA5 with additional 15 mm thick Al filter and RQA5 with 1 mm Pb filtration. The spectra are simulated for a dose of 1 Gy_{air}, therefore the number of photons for a certain energy is increased from RQA5 to RQA5 with filter. The RQA5 spectra nearly blocks photons with lower energy than 28 keV and reaches the maximum number of photons at 52 keV. With an additional filter of 15 mm Al the maximum is relocated to 60 keV and only photons with higher energies than 36 keV were let through. The lead filter courses a narrow curve with maximum at 65 keV and blocked photons below an energy of 48 keV. The absorbed photons A_q corresponds to the MAPbI₃ wafer used for our X-ray detector. The thickness here is 230 μm with a compaction of 88%. **b**, Calculated absorbed energy in percentage as a function of the MAPbI₃ layer thickness. The three curves correspond to the above described spectra: RQA5 (blue dots), RQA5 with 15 mm additional Al (red) and RQA5 with an additional lead filter (green). The layer thickness which absorbs 50 % of the emitted photons is 202 μm, 230 μm and 306 μm for RQA5, RQA5 + 15 mm Al and RQA5 + 1 mm Pb respectively. 90% Absorption is reached at a thickness of 800 μm, 880 μm and 1150 μm. For the effective thickness of 202 μm for our X-ray detector (red dashed line) the absorption is at 50 % (RQA5), 46 % (RQA5+15 mm Al) and 36 % (RQA5 + 1 mm Pb).



Supplementary Figure S15 | Characterization of the MAPbI₃ X-ray detector with different X-ray spectra.

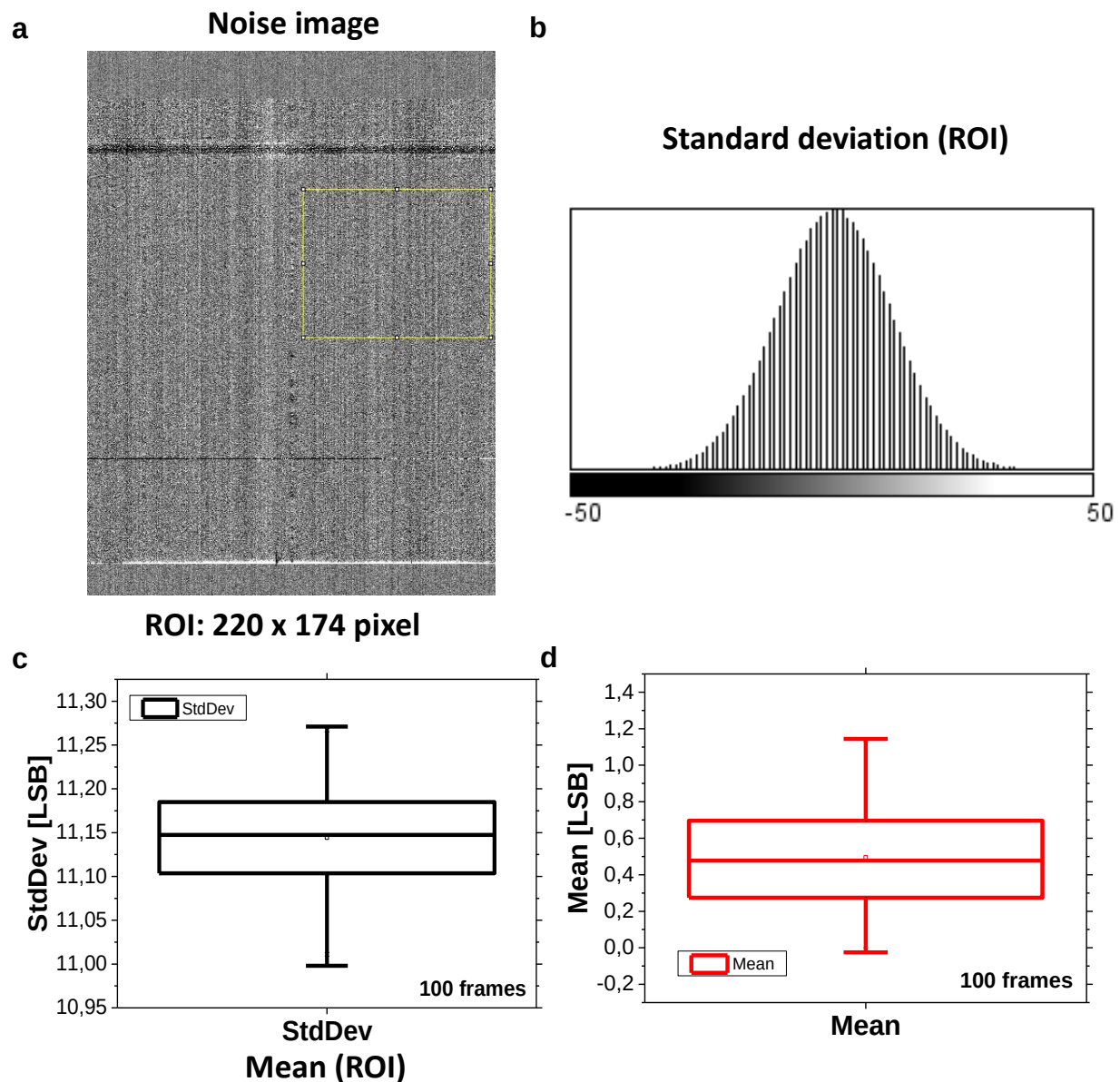
a, Response of the pixelated X-ray detector during 1 s long radiation with a RQA5-spectrum and additional 15 mm Al filtration at different doses per frame. The signal is determined with the use of the gray values of recorded video sequences with 100 frames each by a framerate of 28.6 fps. The resulting curves have been off-set corrected and are shown in least significant bits (LSB), the smallest unit of the analog-to-digital converter. The wavy plateau corresponds to the ripple of the X-ray tube during exposure. The highest signal of approximately 300 LSB is measured during the exposure with 137 nGy_{air} , in contrast the lowest measured dose of 6.8 nGy_{air} caused a signal of 18 LSB, which is clearly visible at the measured noise of ± 1 LSB. **b**, Linearity plot for the highest measured signal value of each dose for the RQA5 + 15 mm Al spectrum. In the double logarithmical representation, the slope of the measured value is with 0.99089 very close to the ideal factor of 1. Only the two lowest doses differ from the calculated slope, which can be attributed to the variance of the X-ray tube at low applied tube currents. **c**, Image lag of the X-ray response after 1 frame (35 ms, red square), 5 (green dots) and 10 frames (blue triangles) for the exposition with the RQA5 spectrum, RQA5 + 15 mm Al filtration and RQA5 + 1 mm Pb. Within the scope of measurement accuracy, the image lag is independent of the dose and the exposed X-ray spectrum. The lag after 35 ms is with 71 ± 18 % relatively large, but after 350 ms the lag is decreasing down to 7 ± 1 % (RQA5). This image lag is measured for applied electrical field of $0.03 \text{ V}/\mu\text{m}$. At higher bias fields we expect much better lag performance.



Supplementary Figure S16 | Figures of merit of the MAPbI₃ X-ray detector. **a**, Sensitivity S for the pixelated X-ray detector vs. exposed dose which is applied in both RQA5 and RQA5 with 15 mm Al filtered spectra. S varies between $1010 \mu\text{C Gy}_{\text{air}}^{-1}\text{cm}^{-2}$ at $44 \text{ nGy}_{\text{air}}$ and $1060 \mu\text{C Gy}_{\text{air}}^{-1}\text{cm}^{-2}$ ($98 \text{ nGy}_{\text{air}}$). For the RQA5 spectrum the S values increases weakly with increasing dose, whereas with the other spectrum the course shows fluctuations and no clear trend, but S differs by 2 % for the two spectra. In view of measurement inaccuracies, the sensitivity is independent of the dose and the X-ray spectra. **b**, Calculated EHP creation energy $W_{\pm}$ as a function of dose rate per frame for a RQA5 and RQA5 with additional Al filtration spectra. According to the S values and the Equations 1 and 4, the $W_{\pm}$ values for the RQA5 spectrum are higher than for those with the additional Al filter. Nevertheless, the overall average EHP creation energy is 12.4 eV with a standard derivation of ± 0.6 eV, which corresponds to a deviation of 5 %. Like S , $W_{\pm}$ is also independent of the exposed dose and X-ray photon energy.



Supplementary Figure S17 | Optical microscope image of the X-rayed coronary stent. The scale bar corresponds to a length of $1000 \mu\text{m}$. The stent with 2 mm diameter has a rectangular metallic mesh with sizes of $100 \mu\text{m} \times 200 \mu\text{m}$.



261 **Supplementary Figure S18 | Noise calculation of the X-ray detector made of MAPbI₃.** **a**, Noise map
 262 generated by averaging 100 dark images and subtracting it from the images. No white noise is visible, but
 263 there are columnar structures (the detector was not EMI shielded). The yellow rectangle is the ROI (region
 264 of interest) for which the further noise calculation is done. **b**, Standard deviation of the given signal (grey
 265 values) in the ROI. The deviation has a gaussian shape. **c**, A different kind of presentation of the standard
 266 deviation of the mean value of the ROI. The average value, which represents the electronical noise is 11.14
 267 LSB. With 48 electrons per LSB the noise can be determined to 535 e. **d**, Mean value of the ROI. The mean
 268 value is approximately 0.5 LSB with a variance of -0.5 LSB and +0.7 LSB.

Supplementary Table S1 | Calculated absorbed energy for the X-ray spectra dependency measurement series. The spectra with the different anode voltages were filtered by a RQA5 filter and simulated with the method describe above. The absorbed energy is determined with the Equation 2 and the wafer parameter.

Anode voltage kV	Emitted energy keVcm ⁻² Gy _{air} ⁻¹	Absorbed energy keVcm ⁻² Gy _{air} ⁻¹	Absorbed energy %
50	9.43E+13	9.30E+13	98.63
60	1.26E+14	1.20E+14	95.28
70	1.53E+14	1.38E+14	90.28
80	1.73E+14	1.47E+14	84.74
90	1.89E+14	1.50E+14	79.46
100	2.00E+14	1.52E+14	76.17
110	2.08E+14	1.53E+14	73.74
120	2.14E+14	1.52E+14	71.33

References:

- [1]: Guo, X., et al. Identification and characterization of the intermediate phase in hybrid organic–inorganic MAPbI₃ perovskite. *Dalton Transactions* **45(9)**, 3806-3813 (2016).
- [2]: Stoumpos, C. C., Malliakas, C. D. & Kanatzidis, M. G. Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and near-infrared photoluminescent properties. *Inorganic chemistry* **52(15)**, 9019-9038 (2013).
- [3]: Onoda-Yamamuro, N., Matsuo, T. & Suga, H. Dielectric study of CH₃NH₃PbX₃ (X= Cl, Br, I). *Journal of Physics and Chemistry of Solids* **53(7)**, 935-939 (1992).
- [4]: Govinda, S., et al. Behavior of methylammonium dipoles in MAPbX₃ (X= Br and I). *The journal of physical chemistry letters* **8(17)**, 4113-4121 8 (2017).
- [5]: Wilson, J. N., et al. Dielectric and ferroic properties of metal halide perovskites. *APL Materials* **7(1)**, 010901 (2019).
- [6]: Kasap, S. O. et al. Amorphous and polycrystalline photoconductors for direct conversion flat panel X-Ray image sensors. *Sensors* **11.5**, 5212 – 5157 (2011).
- [7]: Kasap, S. O. X-ray sensitivity of photoconductors: application to stabilized a-Se. *Journal of physics D: Applied physics* **33(21)**, 2853 (2000).