Supplementary Information

Stable near-to-ideal performance of a solution-grown single-crystal perovskite X-ray detector

Kostiantyn Sakhatskyi[1,2,5], Bekir Turedi[3,5], Gebhard J. Matt[1,2], Muhammad Naufal Lintangpradipto[3], Rounak Naphade[3], Omar F. Mohammed[3,4], Sergii Yakunin[*1,2], Osman M. Bakr[*3], Maksym V. Kovalenko[*1,2]

[1] Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich, Switzerland

[2] Laboratory for Thin Films and Photovoltaics, Empa – Swiss Federal Laboratories for Materials Science and Technology, CH-8600 Dübendorf, Switzerland

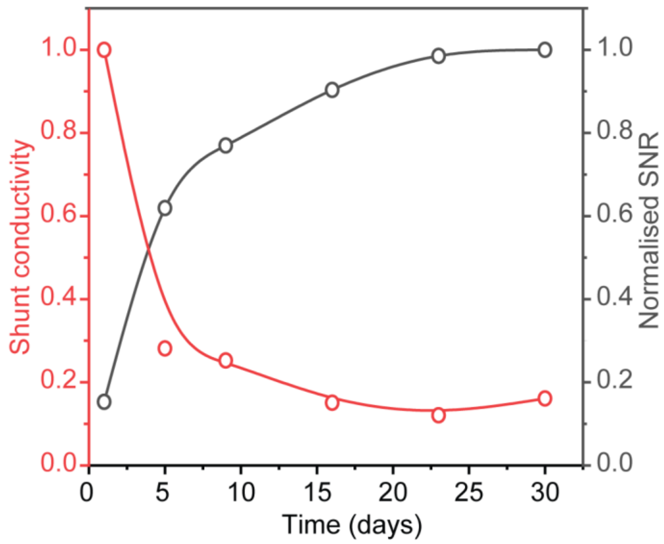
[3] KAUST Catalysis Center (KCC), Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

[4] Advanced Membranes and Porous Materials Center, Division of Physical Science and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

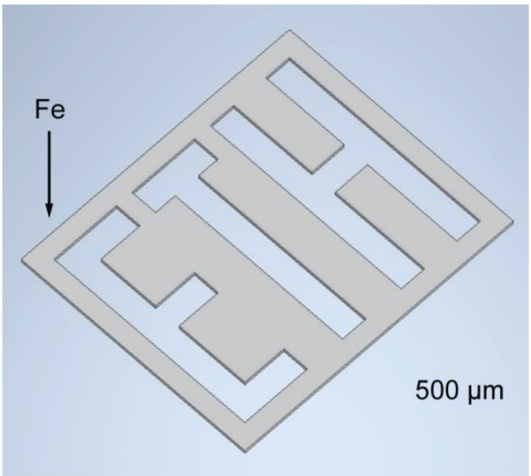
[5] These authors contributed equally: Kostiantyn Sakhatskyi and Bekir Turedi.

[*]E-mail: mvkovalenko@ethz.ch; osman.bakr@kaust.edu.sa; yakunins@ethz.ch

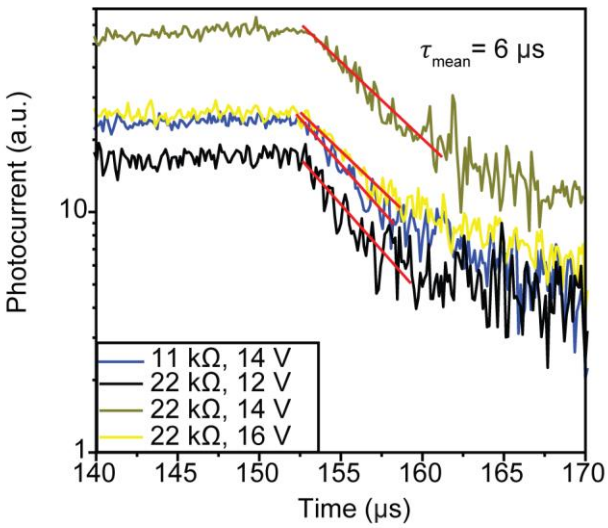
Contents:



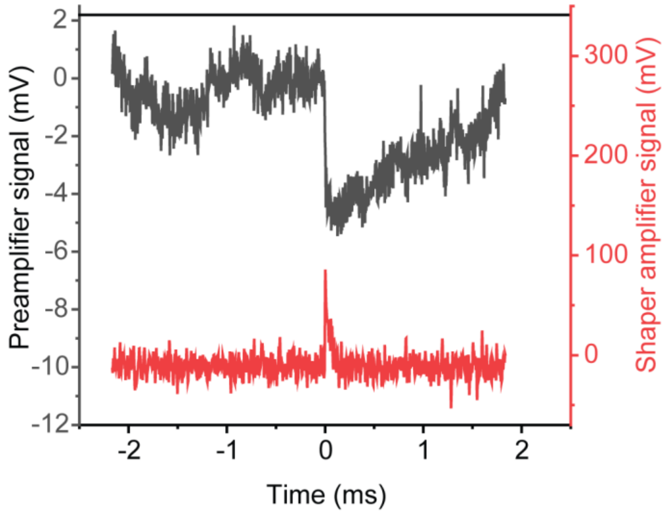
Supplementary Fig. 1 | Post-condition time influence. Normalized X-ray signal-to-noise ratio (SNR) and shunting conductivity dependence of the storage time in a drybox after synthesis**.** Values of SNR are normalized on the last value; shunt conductivity points are normalized on the initial value.



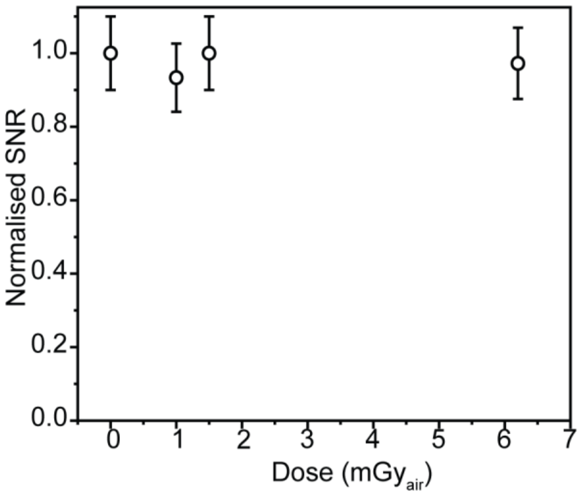
Supplementary Fig. 2 | The object for transmittance imaging. A 500 µm thick steel plate in the form of ETH letters was used as an absorptive mask for the imaging by a $MAPbI_3$ SC detector in the counting regime.



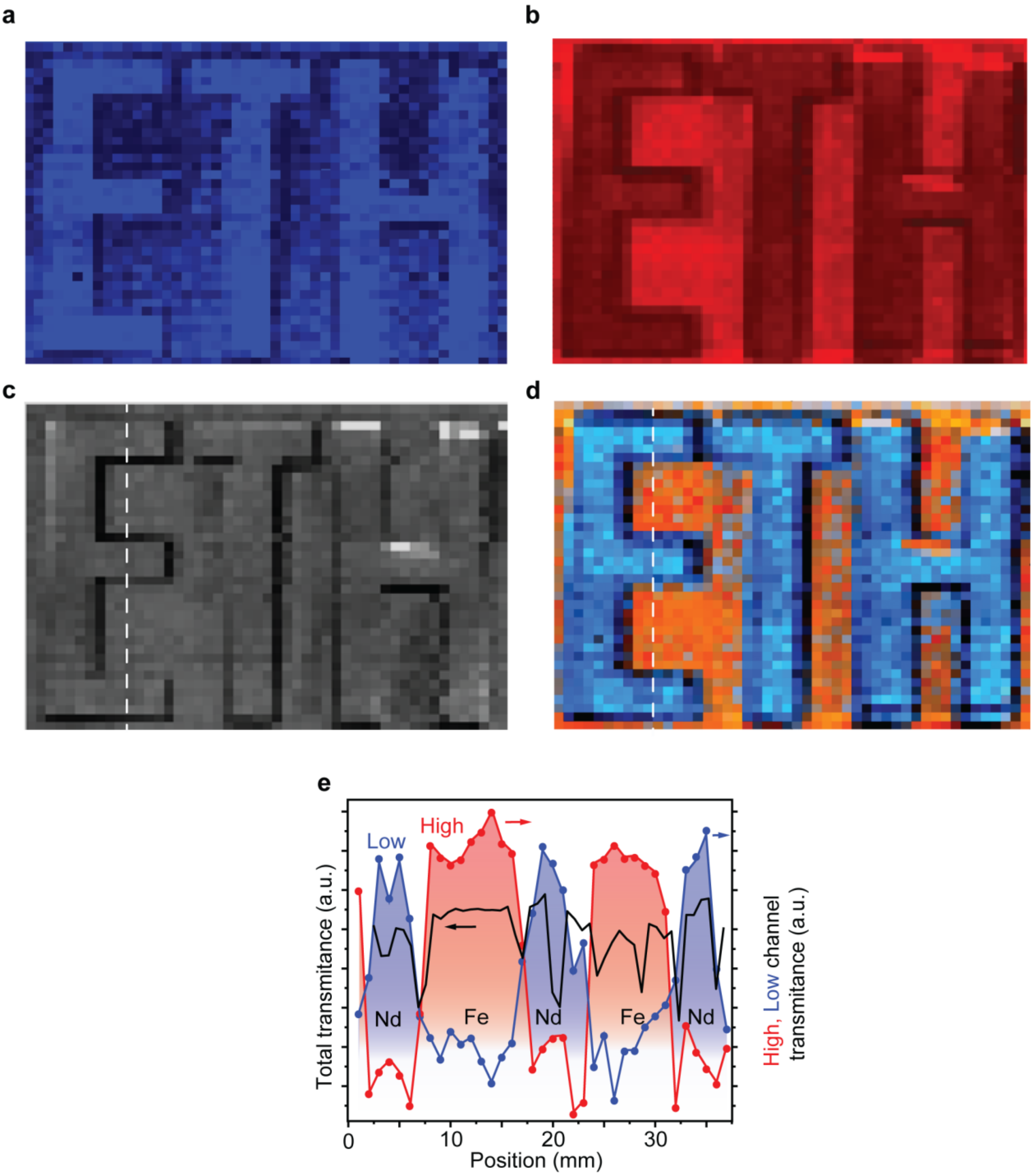
Supplementary Fig. 3 | Transient photocurrent under pulsed light irradiation of symmetrically contacted Cu/MAPbI$_3$/Cu. As a light source, a focused LED (450 nm) was used. The fast photocurrent decay after the light pulse is interpreted as the lifetime of the photoexcited charge carriers[1]. The traces show similar time-constants, measured with 11 and 22 kΩ load resistors. Similar values obtained with various resistances confirm that the lifetime evaluation is not *RC*-limited. Also, the decay time constant is bias-independent.



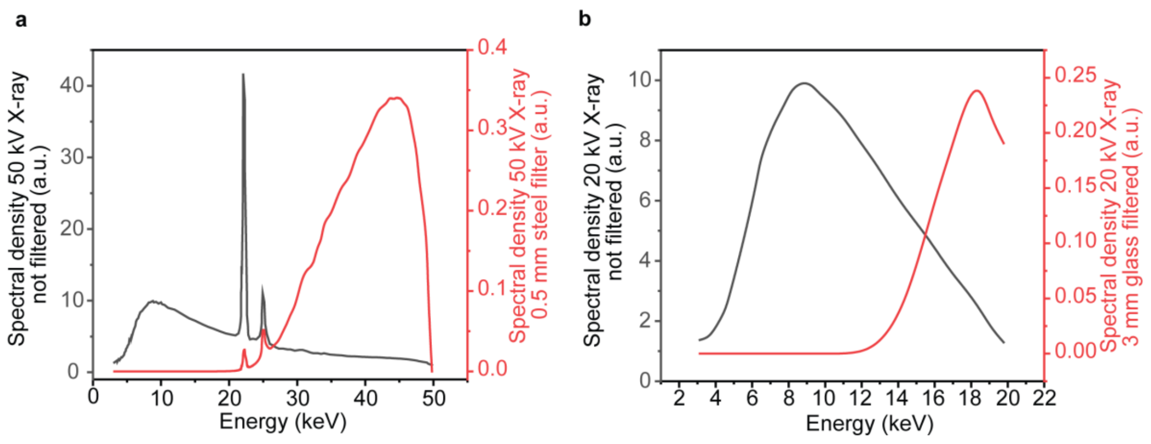
Supplementary Fig. 4 | γ-ray single-photon counting. Event from a ^{241}Am radiation source (E_{γ}=60 keV) was recorded with $MAPbI_3$ SC (thickness is 110 µm, 0 V bias). The black curve is a trace from the charge-integrating preamplifier, the red curve is the corresponding trace from the shaping amplifier.



Supplementary Fig. 5 | Stability vs radiation dose. Normalized SNR *vs.* accumulated dose. 6 mGy_{air} corresponds to approximately 500 conventional medical X-ray scans. The stable SNR values evidence good radiation hardness of the $MAPbI_3$ SCs.



Supplementary Fig. 6 | X-ray multicolor imaging *vs.* total transmittance imaging. a, b, X-ray transmission in separate channels: blue - low X-ray energy (**a**), red - high X-ray energy (**b**). **c,** Total transmission, obtained as a sum of counts from two channels **d**, Color image, where red color decodes as maximal transmission in a high energy channel, while blue means maximal transmission in a low energy channel. **e,** Transmittance profile along dashed white lines on **c** and **d**. The black line represents total transmittance from **c** and red and blue lines high and low channel transmittance, respectively, from **d.** The contrast between different materials in **c** is seen only due to shadows, since the image was obtained under non-orthogonal incidence of the X-ray beam. Color X-ray image **d** shows enhanced contrast, demonstrating the advantage of energy discrimination imaging.



Supplementary Fig. 7 | Amptek X-ray tube spectra. a, Operating at 50 kV_p, without (black curve) and with a 0.5 mm Fe filter (red curve). **b,** Operating at 20 kV_p, without (black curve) and with a 3 mm thick glass filter (red curve).

List of abbreviations for Supplementary Notes

DQE – detective quantum efficiency

SNR – signal-to-noise ratio

n_{ph} – mean photon number, incoming to detector volume

DE – detection efficiency

AE – attenuation efficiency

CCE – charge collection efficiency

N_T – total noise of the detector

DN – detector noise

PSN – photon shot noise

DL – detection limit of dose rate

D – radiation dose

D_1 – radiation dose corresponding to the flux of single-photon through area A

Dr – dose rate

$(\mu/\rho)_{air}$ – mass attenuation coefficient in air

E_{ph} – X-ray photon energy

A – detector area

NED – noise equivalent dose

RMS – room-mean-square

$\overline{\Delta q^2}$ – RMS of charge deviation

q_1 – mean charge deposited by a single absorbed X-ray photon

$\overline{\Delta I^2}$ – RMS of current deviation

B – bandwidth of the detector

t – integration time

k_B – Boltzmann constant

T – detector temperature

R – detector resistance

J_{ph} – photocurrent density

S – X-ray sensitivity

S_{th} – theoretical maximal X-ray sensitivity without photoconductive gain

NSD – noise spectral density

e – elementary charge

$W_{\pm}$ – electron-hole pair ionization energy

Supplementary Note 1. Detective Quantum Efficiency

The DQE can be expressed for a single-pixel detector, as a function of *D*, showing parameters of this dependence.[2]

DQE is defined as:

$$\mathrm{DQE}=\frac{\mathrm{SNR}^2_{\mathrm{detector}}}{\mathrm{SNR}^2_{\mathrm{ideal}}} \tag{S1}$$

where the ideal SNR is defined by Poisson statistics of mean incoming photons number n_{ph}:

$$\mathrm{SNR}_{\mathrm{ideal}}=\frac{n_{ph}}{\sqrt{n_{ph}}}=\sqrt{n_{ph}} \tag{S2}$$

$$\mathrm{SNR}^2_{\mathrm{ideal}}=n_{ph} \tag{S3}$$

For a real photodetector, the SNR is given by the ratio of the signal (expressed in detected photons number – $\mathrm{DE}\cdot n_{\mathrm{ph}}$) to $\mathrm{N_T}$. Generally, $\mathrm{N_T}$ is given by the square root of the sum of the squares of independent noise sources, which for a photodetector are PSN of detected photons and DN. The first is defined as:

$$\mathrm{PSN}=\sqrt{\mathrm{DE}\cdot n_{ph}} \tag{S4}$$

The second is the sum of all noise sources in the absence of illumination. Hence, $\mathrm{N_T}$:

$$\mathrm{N_T}=\sqrt{\mathrm{PSN}^2+\mathrm{DN}^2}=\sqrt{\mathrm{DE}\cdot n_{ph}+\mathrm{DN}^2} \tag{S5}$$

Then, the $\mathrm{SNR}_{\mathrm{detector}}$ reads as:

$$\mathrm{SNR}_{\mathrm{detector}}=\frac{\mathrm{DE}\cdot \mathrm{n_{ph}}}{\sqrt{\mathrm{DE}\cdot \mathrm{n_{ph}}+\mathrm{DN}^2}} \tag{S6}$$

$$\mathrm{SNR}^2_{\mathrm{detector}}=\frac{\left(\mathrm{DE}\cdot n_{ph}\right)^2}{\mathrm{DE}\cdot n_{ph}+\mathrm{DN}^2} \tag{S7}$$

Combining (S3) and (S7) we show the $\mathrm{DQE}(n_{ph})$ after (S1) as:

$$\mathrm{DQE}(\mathrm{n_{ph}})=\frac{\mathrm{DE}^2 n_{ph}}{\mathrm{DE}\cdot n_{ph}+\mathrm{DN}^2}=\frac{\mathrm{DE}\cdot n_{ph}}{n_{ph}+\frac{\mathrm{DN}^2}{\mathrm{DE}}} \tag{S8}$$

To rewrite (S8) in terms of a dose D we use the definition from Ref.S3:

$$\mathrm{D}(n_{ph}) = \frac{\left(\frac{\mu}{\rho}\right)_{air} E_{ph} n_{ph}}{A} \tag{S9}$$

We abbreviate factor $(\mu/\rho)_{air}E_{ph}/A$ as D_1:

$$\mathrm{D}\left(n_{ph}=1\right) = \mathrm{D}_1 = \frac{\left(\frac{\boldsymbol{\mu}}{\boldsymbol{\rho}}\right)_{\mathrm{air}} \boldsymbol{E_{ph}}}{A} \tag{S10}$$

We multiply nominator and denominator of (S8) with D_1 to obtain the DQE in terms of D:

$$\mathrm{DQE(D)} = \frac{\mathrm{DE \cdot D}}{\mathrm{D+NED}} = \frac{\mathrm{DE}}{1+\frac{\mathrm{NED}}{\mathrm{D}}} \tag{S11}$$

and define NED as:

$$\mathrm{NED}\left[\mathrm{Gy_{air}}\right] = \frac{\mathrm{D_1 \cdot DN^2}}{\mathrm{DE}} \tag{S12.1}$$

or:

$$\mathrm{NED[photon\text{–}equivalent]} = \frac{\mathrm{DN^2}}{\mathrm{DE}} \tag{S12.2}$$

The NED is the absorbed dose in the air which generates a value of PSN equal to the DN (see Ref[4]). The latter is expressed in the units of a ‘number of equivalent photons’. A single photon-equivalent is the root mean square (RMS) noise-charge which is equal to the charge generated by one photon (*i.e.* $\overline{\Delta q^2} = q_1^2$). As we announced, equation (S11) shows DQE(D) and parameters of this dependence are DE and NED.

Supplementary Note 2. Total noise of the detector as noise spectral density

We have derived the equation for DQE (Eqs. (S8) and (S11)) and NED (Eqs. (S12.1) and (S12.2)), where DN is expressed in photon-equivalents. However, DN is usually measured as NSD in units of $\mathrm{A}/\sqrt{\mathrm{Hz}}$ or $\mathrm{V}/\sqrt{\mathrm{Hz}}$. Here we derivate the relation between $\mathrm{A}/\sqrt{\mathrm{Hz}}$ and photon-equivalents, and, thus, the expression for $\mathrm{N_T}$.as NSD.

We start from a definition of PSN from (S4), square it and multiply on $(D_1)^2$ to obtain PSN in units of dose $\mathrm{Gy_{air}}$:

$$\mathrm{PSN}^2\left[\mathrm{Gy}_{\mathrm{air}}^2\right]=\mathrm{DE}\cdot(\mathrm{D}_1)^2 n_{ph}=\mathrm{DE}\cdot\mathrm{D}_1\cdot\mathrm{D} \qquad \text{(S13.1)}$$

For further transformation of (S13.1) we use the definition of theoretical X-ray sensitivity from Ref.[5]:

$$S_{th}=e/(\mu/\rho)_{\mathrm{air}}W_{\pm} \qquad \text{(S13.2)}$$

We multiply (S13.1) with $A^2S_{th}^2$ to get PSN in units of charge:

$$\mathrm{PSN}^2\left[\mathrm{C}^2\right]=\mathrm{DE}\cdot A^2\cdot S_{th}^2\cdot\mathrm{D}_1\cdot\mathrm{D} \qquad \text{(S14)}$$

Then, we divide (S14) with t (which is connected to B *via* the Nyquist theorem – $B=1/2t$), to obtain PSN in units of $\mathrm{A^2/Hz}$:

$$\mathrm{PSN}^2\left[\frac{\mathrm{A}^2}{\mathrm{Hz}}\right]=\frac{\Delta I_{ph}^2}{B}=2\cdot\mathrm{DE}\cdot A^2\cdot S_{th}^2\cdot\mathrm{D}_1\cdot\mathrm{Dr} \qquad \text{(S15)}$$

where Dr is equal to D/t.

Using (S5) and (S15) we get:

$$\mathrm{N}_{\mathrm{T}}^2\left[\frac{\mathrm{A}^2}{\mathrm{Hz}}\right]=2\mathrm{DE}A^2S_{th}^2\mathrm{D}_1\mathrm{Dr}+\mathrm{DN}^2 \qquad \text{(S16.1)}$$

For a photodetector operating at 0V bias, DN is dominated by the Johnson-Nyquist noise, so-called thermal noise, which's NSD of current is given by Ref[6]:

$$\mathrm{DN}^2=\frac{\Delta {I_n}^2}{B}=4k_BT/R\ \left[\frac{\mathrm{A}^2}{\mathrm{Hz}}\right] \qquad \text{(S17)}$$

Inserting (S17) in (S16.1):

$$\mathrm{N}_{\mathrm{T}}^2\left[\frac{\mathrm{A}^2}{\mathrm{Hz}}\right]=2\mathrm{DE}A^2S_{th}^2\mathrm{D}_1\mathrm{Dr}+4k_BT/R \qquad \text{(S16.2)}$$

For obtaining the relation between $\mathrm{A}/\sqrt{\mathrm{Hz}}$ and photon-equivalents, (S15) and (S4) are compared:

$$\frac{\mathrm{PSN}^2\left[\frac{\mathrm{A}^2}{\mathrm{Hz}}\right]}{\mathrm{PSN}^2[\text{photon–equivalent}^2]}=\frac{2\mathrm{DE}A^2 S_{th}^2 \mathrm{D}_1 \mathrm{Dr}}{\mathrm{DE}n_{ph}}=BA^2 S_{th}^2 \mathrm{D}_1^2 \tag{S18}$$

Therefore, NED from (S12.1) and (S12.2) according to (S18) can be expressed as:

$$\mathrm{NED}\left[\mathrm{Gy_{air}}\right]=\frac{\mathrm{DN}^2[\frac{\mathrm{A}^2}{\mathrm{Hz}}]}{\mathrm{DE}BA^2 S_{th}^2 \mathrm{D}_1} \tag{S19.1}$$

$$\mathrm{NED}[\text{photon–equivalent}]=\frac{\mathrm{DN}^2[\frac{\mathrm{A}^2}{\mathrm{Hz}}]}{\mathrm{DEB}A^2 S_{th}^2 \mathrm{D}_1^2} \tag{S19.2}$$

To summarise, here the equation of the NSD for the X-ray detector for the general case (S16) and operation at a 0-V bias (S18) is derived. Expressions (S19.1) and (S19.2) connect NED with measurable NSD of current.

Supplementary Note 3. Detection limit

Here, the equation which shows DL dependence on t is obtained. DL is often defined as a Dr corresponding to SNR=3. For this, the signal is expressed as J_{ph} [A/cm^2]:

$$J_{ph}\left[\frac{\mathrm{A}}{\mathrm{cm}^2}\right]=\mathrm{DE}\cdot S_{th}\cdot\mathrm{Dr}=S\cdot\mathrm{Dr}; \tag{S20}$$

To obtain the total noise N_T in [A/cm^2], (S16) is rearranged by taking the square root of it and normalizing it to A and multiplying it with $\sqrt{B}$:

$$\mathrm{N_T}\left[\frac{\mathrm{A}}{\mathrm{cm}^2}\right]=\mathrm{N_T}\left[\frac{\mathrm{A}}{\sqrt{\mathrm{Hz}}}\right]\frac{\sqrt{B}}{A}=\sqrt{\frac{\mathrm{DE}\cdot\mathrm{D_1}\,S_{th}^2\,\mathrm{Dr}}{t}+\frac{1}{2\,t}\left(\frac{\mathrm{DN}}{A}\right)^2} \tag{S21}$$

Then the SNR reads as:

$$\mathrm{SNR}=\frac{J_{ph}}{\mathrm{N_T}}=\frac{S\cdot\,\mathrm{Dr}}{\sqrt{\frac{\mathrm{DE}\cdot\mathrm{D_1}\,S_{th}^2\,\mathrm{Dr}}{t}+\frac{1}{2\,t}\left(\frac{\mathrm{DN}}{A}\right)^2}} \tag{S22}$$

For (S24) we investigate two cases:

a) DN >> PSN:

$$\mathrm{SNR}=\frac{S\cdot\mathrm{Dr}}{\frac{\mathrm{DN}}{\sqrt{2}tA}} \tag{S23}$$

According to DL definition:

$$\mathrm{SNR}=3=\frac{S\cdot\mathrm{DL}}{\frac{\mathrm{DN}}{\sqrt{2}tA}} \tag{S24}$$

thus the DL is:

$$\mathrm{DL}=\frac{3\,\mathrm{DN}}{\sqrt{2}t\,S\,A} \tag{S25}$$

b) Similar for PSN >> DN:

$$\mathrm{SNR}=\frac{\mathrm{DE}\cdot S_{th}\mathrm{Dr}}{\sqrt{\frac{\mathrm{DE}\cdot\mathrm{D_1}S_{th}^2\mathrm{Dr}}{t}}} \tag{S26}$$

$$\mathrm{SNR}=3=\frac{\mathrm{DE}\cdot S_{th}\mathrm{DL}}{\sqrt{\frac{\mathrm{DE}\cdot\mathrm{D_1}S_{th}^2\mathrm{DL}}{t}}} \tag{S27}$$

thus the DL at extremely low intensities is:

$$\mathrm{DL}=\frac{9\mathrm{D}_1}{\mathrm{DE}\cdot t} \tag{S28}$$

This result has a straightforward interpretation: within an integration time *t* we have to detect 9 photons to obtain an SNR=3. This is consistent with the Poisson photon statistics: SNR=$\sqrt{n_{ph}}$.

From (S25) and (S28) it is seen that in any case, DL is inversely proportional to the integration time and could be as low as desired by increasing *t*.

Supplementary Note 4. NED and DQE dependence on X-ray energy

In Fig.4a we obtained NED=0.4 [photon-equivalent] for X-ray photon energy of 18 keV. We have defined in Supplementary Note 1 the photon-equivalent as the RMS noise-charge equal to the charge generated by a single X-ray photon. Since the generated charge is proportional to the X-ray photon energy *E*, we can estimate NED dependence on *E*:

$$\mathrm{NED}(E)= \frac{\mathrm{NED}(\mathrm{E}{=}18\ \mathrm{keV})\cdot 18\ \mathrm{keV}}{E} \qquad (S29)$$

Using (S29) and (S9), and assuming full charge extraction (*i.e.* CCE=100%, thus DE≈Attenuation efficiency (AE)) we obtain DQE dependence on *E* and n_{ph}:

$$\mathrm{DQE}\left(E,n_{ph}\right)= \frac{\mathrm{AE}(E)\cdot n_{ph}}{n_{ph}+\frac{\mathrm{NED}(E)}{\mathrm{AE}(E)}} \qquad (S30)$$

References

S1. Sze, S. M. *Semiconductor Devices: Physics and Technology*. 60-63 (Wiley, New York, 2002).

S2. Zanella, G. & Zannoni, R. The role of the quantum efficiency on the DQE of an imaging detector. *Nucl. Instrum. Methods Phys. Res. A* **381**, 157-160 (1996).

S3. Coderre, J. 22.55J Principles of Radiation Interactions: Dose Calculations. https://ocw.mit.edu/courses/nuclear-engineering/22-55j-principles-of-radiation-interactions-fall-2004/lecture-notes/dos_calculations.pdf , 1-3 (2004)

S4. Isaias, D. J., Sarah, J. B., Michael, J. P. & Kungang, Z. A comparison of quantum limited dose and noise equivalent dose. in *SPIE Medical Imaging 2016 - Proceedings.*

S5. Zahangir Kabir, M. & Kasap, S. O. Sensitivity of x-ray photoconductors: Charge trapping and absorption-limited universal sensitivity curves. *J. Vac. Sci. Technol.* **20**, 1082-1086 (2002).

S6. Johnson, J. B. Thermal agitation of electricity in conductors. *Phys. Rev.* **32**, 97-109 (1928).