Supplementary information:

Spray-coated $CsPbBr_3/CsPb_2Br_5$ thin film photodetectors from nanocrystalline inks

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Keywords: Spray-coating, Thin Film, Nanoinks, Perovskite, Photodetector, $CsPbBr_3/CsPb_2Br_5$

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EXPERIMENTAL DETAILS

Materials. Lead (II) bromide ($PbBr_2$, 99.999% trace metals basis), cesium carbonate (Cs_2CO_3, 99%), 2-propanol (iPA, anhydrous, 99.5%), propionic acid (PrAc, ≥99.5%), n-hexane (HEX, 99.5%), Toluene (TOL, 99.8%), octanoic acid (OcAc, ≥ 99%), octylamine (OcAm, 99%), butylamine (BuAm, 99.5%), ethanol (EtOH), acetone, were purchased from Sigma-Aldrich used without any purification.

Synthesis. This synthesis route is a variation of the synthesis for $CsPbBr_3$ perovskite nanocrystal ink reported by Akkerman et al.[1] using longer chain solvents for the $PbBr_2$ precursor. Here for the standard reaction, 8 ml HEX, 4 ml iPA, and 20 µl Cs precursor (3.6 M Cs^+, Cs_2CO_3 dissolved in pure PrAc with stirring for 1 hour) were mixed in air at room temperature, forming a clear solution. Suddenly, 400 µl $PbBr_2$ precursor (0.5 M in 1:1:1 OcAc: iPA: OcAm in glove box with stirring at 65ºC for 48 hours) was injected. The solution immediately turned green, and then turned turbid within seconds. The $CsPbBr_3$ were centrifuged for 2 min at 4000 rpm. This process is done twice. The precipitate was collected and redispersed in 12 mL toluene ready for use in the coating process. For the $CsPb_2Br_5$ solution were added 7 mg of $PbBr_2$ powder in 3 mL of $CsPbBr_3$ perovskite nanocrystal ink in globe box with stirring at 55ºC for 72 hours, then ready for the coating process.

Deposition. The $CsPbBr_3$ and $CsPb_2Br_5$ solution perovskite were deposited onto different glass substrates cleaned previously by immersing them in ethanol and acetone for 10 minutes in ultrasonic bath, followed by a drying phase under nitrogen gas flow. Each 3cm x 3cm interdigitated glass substrate has four identical pixels: finger spacing of 40 µm. The layers were deposited with 100 µl of solution, for each layer, using an airbrush (Iwata Eclipse HP-CS) with conditions of a nitrogen gas pressure of 0.4 bar and nozzle of 0.2mm opening of one turn. All this process was under air condition.

X-ray diffraction analysis. XRD patterns were obtained using a Bruker D8 Advance X-ray diffractometer, collected at room temperature over an angular range (2θ) between 10º and 70º, using a Cu Kα radiation.

Absorption spectra. Absorption properties of films were measured with a Cary 50 UV–Vis spectrophotometer within the 400–700 nm wavelength range at room temperature.

PL spectra were obtained with a laser excitation wavelength of 405 nm (MatchBox series, from Integrated Optics), and recorded with an AvaSpec-ULS2048x64-EVO spectrometer from Avantes.

Photoluminescence quantum yield measurements. PLQY was measured using a Hamamatsu C9920 series Absolute PL quantum yield spectrometer. The setup comprises a Xe lamp as excitation light source, monochromator, an integrating sphere capable and a CCD spectrometer for detecting the whole spectral range simultaneously. The system is integrated in a nitrogen glove box to avoid atmospheric contamination of the samples.

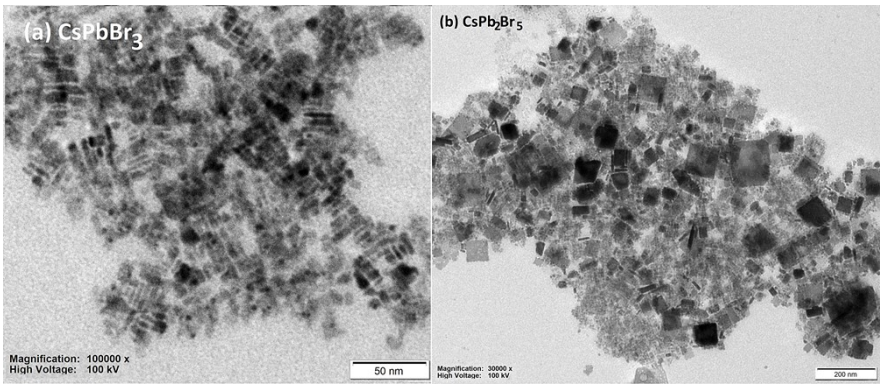
Atomic Force Microscopy. AFM images were obtained using a PicoSPM-LE of Molecular Imaging, using contact mode and a NuNano Scout RAI silicon wafer with 70 kHz resonance frequency and 2 N/m elastic constant.

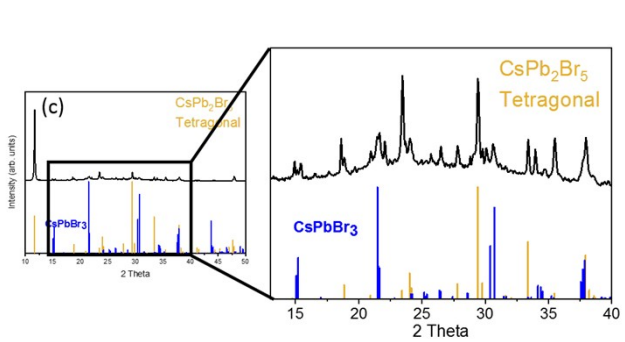
Scanning electron microscopy. SEM images were obtained using a Hitachi S-3500N Scaning electron microscope under high vacuum. $CsPbBr_3$ and $CsPb_2Br_5$ were deposited by spray coating onto ITO glass conductor 1cm x 1cm.

X-ray photoelectron spectroscopy. XPS spectra were acquired using a SPECS FLEXPS-E spectrometer with monochromatic Al Kα radiation. $CsPbBr_3$ and $CsPb_2Br_5$ were deposited by spray coating onto ITO glass conductor to ensure good electrical grounding. Data analysis was carried out in SpecsLab Prodigy and CasaXPS software. The energy-scale is calibrated by setting the

Current – Voltage characterization. The I–V curves in the dark and under illumination were recorded with a Keithley 2450 SourceMeter and using a 405 nm LED (ThorLabs, M405LP1) controlled by a digital driver (Thorlabs, DC2200). The light intensity was calibrated before every measurement using a Si reference diode (Thorlab, FDS100-CAL).

Transmission Electron Microscopy. Transmission electron microscopy (TEM) was performed on a HITACHI HT7800 microscope with a filament of LaB6 operated at 100keV.





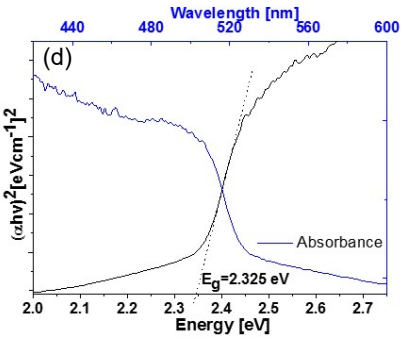


Figure S 1. TEM images of (a) CsPbBr3 and (b) CsPb2Br5 nanoinks (c) XRD pattern of CsPb2Br5 tetragonal phase (ICSD 254290 - yellow) with impurities of CsPbBr3 orthorhombic phase (ICSD 243735 - blue) (d) UV-vis spectra and Tauc plot in order to estimate the optical band gap (black dotted line) for $CsPbBr_3$ nanoink solution

Figure S 2. PL spectra for $CsPbBr_3$ with short chain ligands measured after few minutes

Nanoinks	Deposition temperature ºC		Number of layers			
		nm	1	2	5	10
$CsPbBr_3$	RT	PL	517	518	517	517
		Absorption	518	517	518	518
	80	PL	517	518	520	522
		Absorption	520	520	517	518
	150	PL	518	522	520	522
		Absorption	524	522	523	523
$CsPb_2Br_5$	RT	PL	515	520	517	518
		Absorption	528	527	526	528
	80	PL	518	517	517	518
		Absorption	527	526	523	525
	150	PL	518	518	519	521
		Absorption	521	521	523	525

Table S 1. Absorption onset and photoluminescence emission peak of CsPbBr3 and CsPb2Br5 nanoinks deposited at different temperatures and number of layer

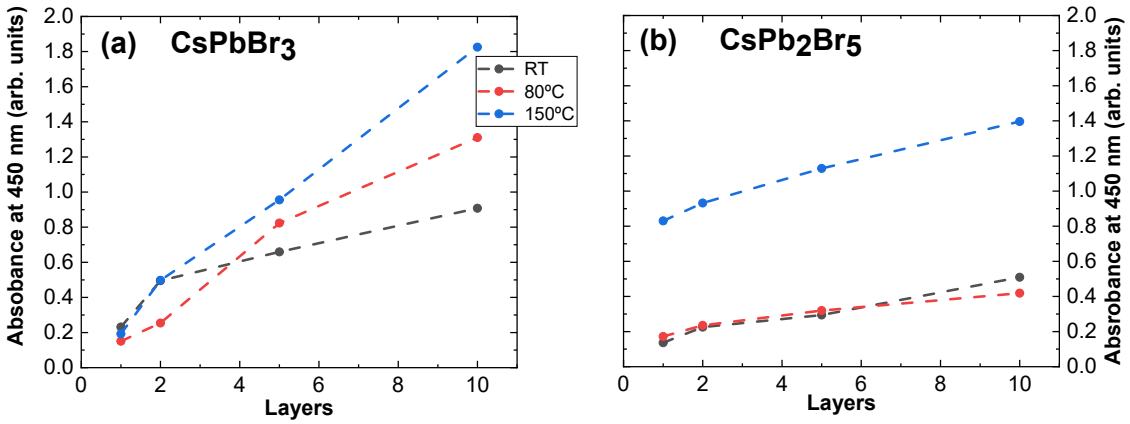


Figure S 3. Absorbance at 450 nm for 1, 2, 5 and 10 layers of (**a**) $CsPbBr_3$ and (**b**) $CsPb_2Br_5$

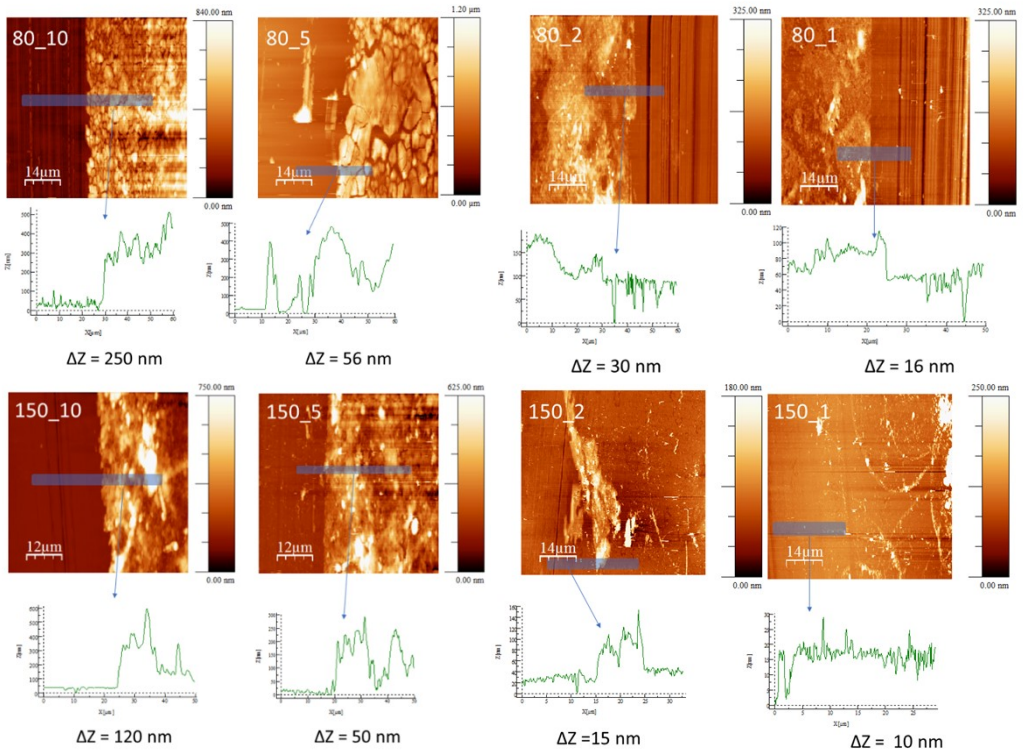


Figure S 4. Atomic force microscopy (AFM) images of $CsPbBr_3$ thin films deposited at different temperatures and different numbers of layers as indicated in the images (XX_YY; where XX refers to the deposition temperature and YY to the number of layers).

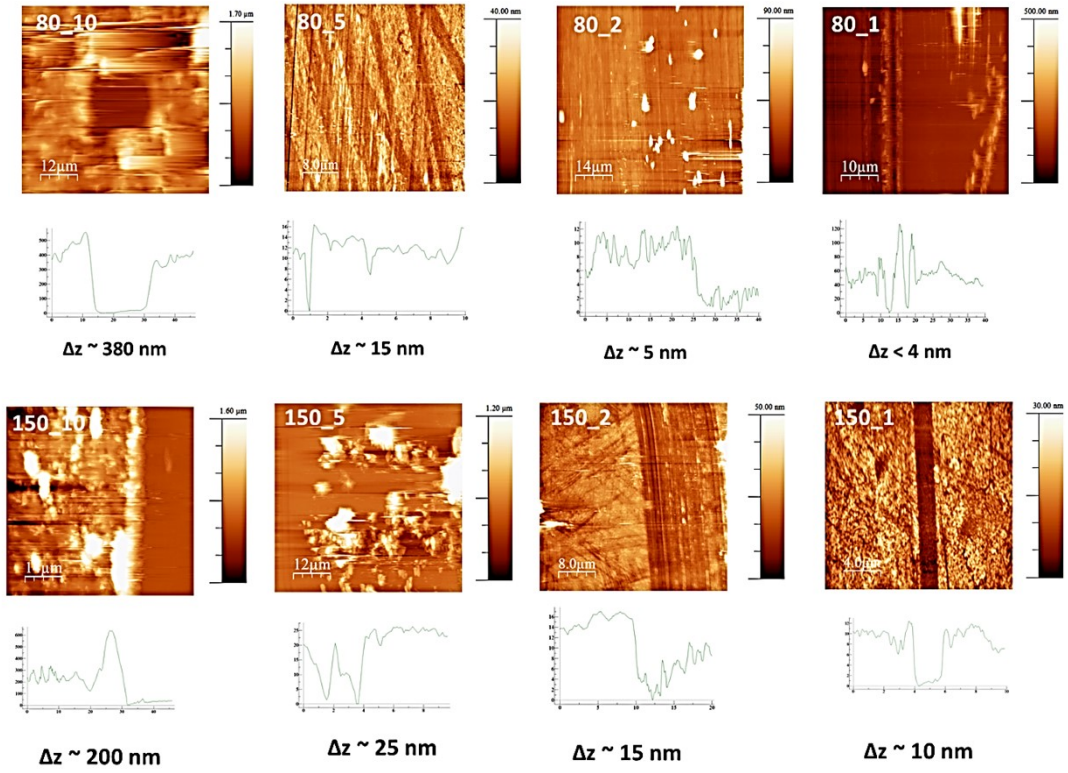


Figure S 5. Atomic force microscopy (AFM) images of $CsPb_2Br_5$ thin films deposited at different temperatures and different numbers of layers as indicated in the images (XX_YY; where XX refers to the deposition temperature and YY to the number of layers).

Nanoink	Deposition Temperature ºC	Number of layers			
		10 (nm)	5 (nm)	2 (nm)	1 (nm)
$CsPbBr_3$	80	250	56	30	16
	150	120	50	15	10
$CsPb_2Br_5$	80	380	15	5	<4
	150	200	25	15	10

Table S 2. Thickness average of thin films deposited at different temperatures and number of layers for $CsPbBr_3$ and $CsPb_2Br_5$ nanoinks

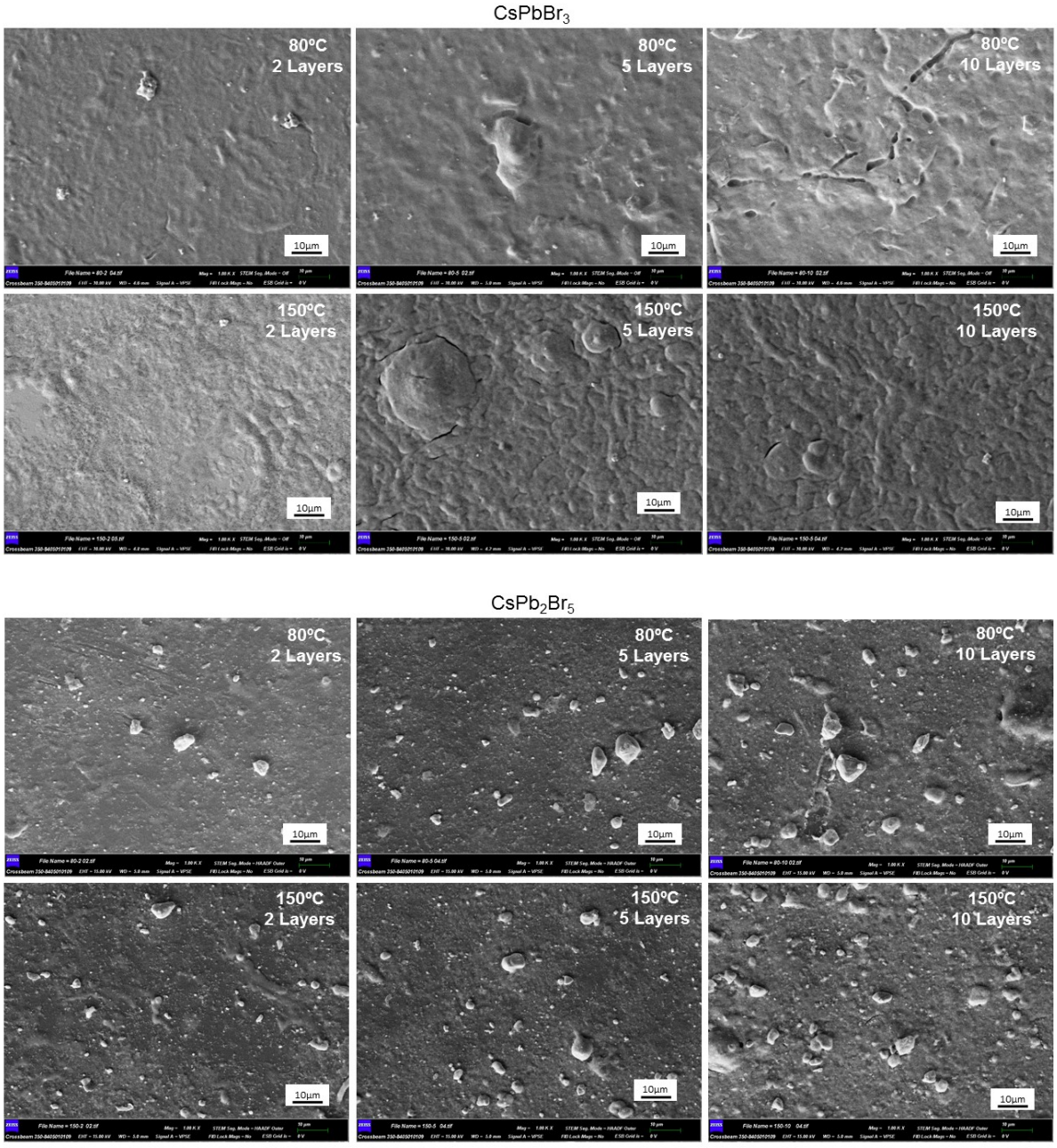


Figure S 6. Scanning electron microscopy (SEM) surface images of $CsPbBr_3$ and $CsPb_2Br_5$

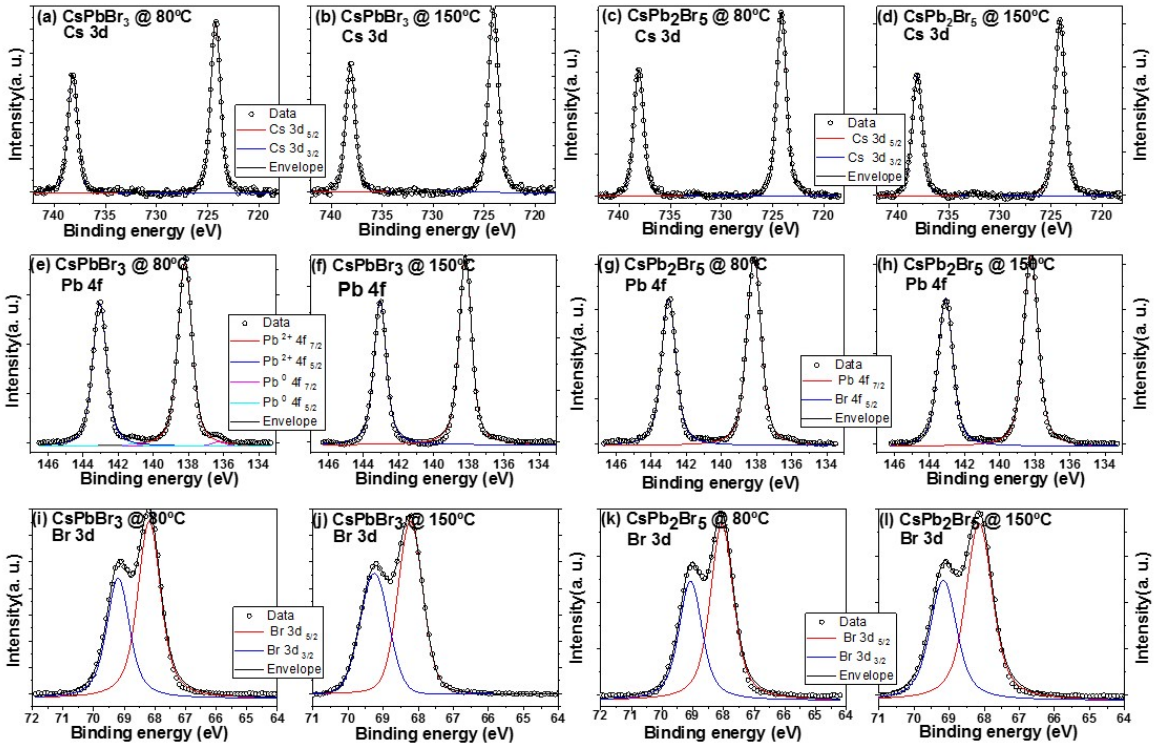


Figure S7. XPS of $CsPbBr_3$ and $CsPb_2Br_5$ thin films deposited at 80°C and 150°C. (**a-d**) Cs 3d XPS spectra (**e-h**) Pb 4f XPS spectra and (**i-l**) Br 3d XPS spectra.

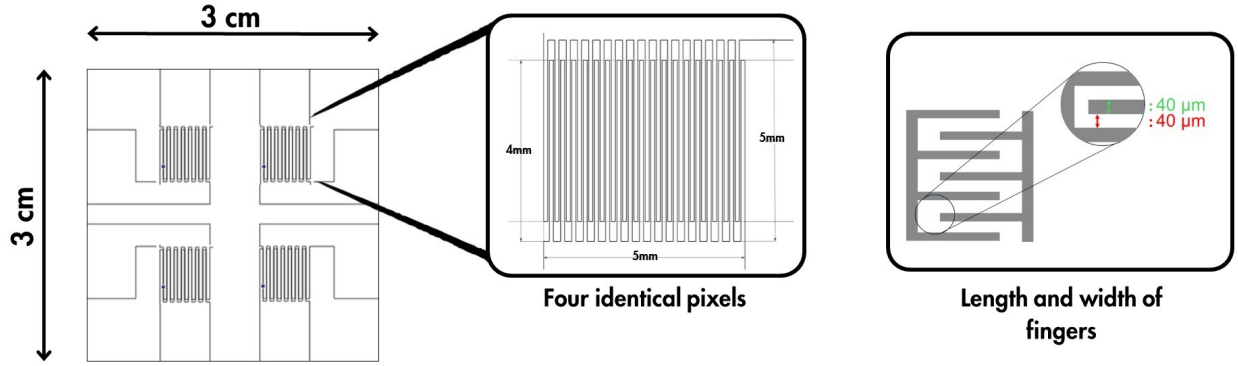


Figure S8. Schematic illustration of interdigitated ITO substrates for lateral photodetectors device structure

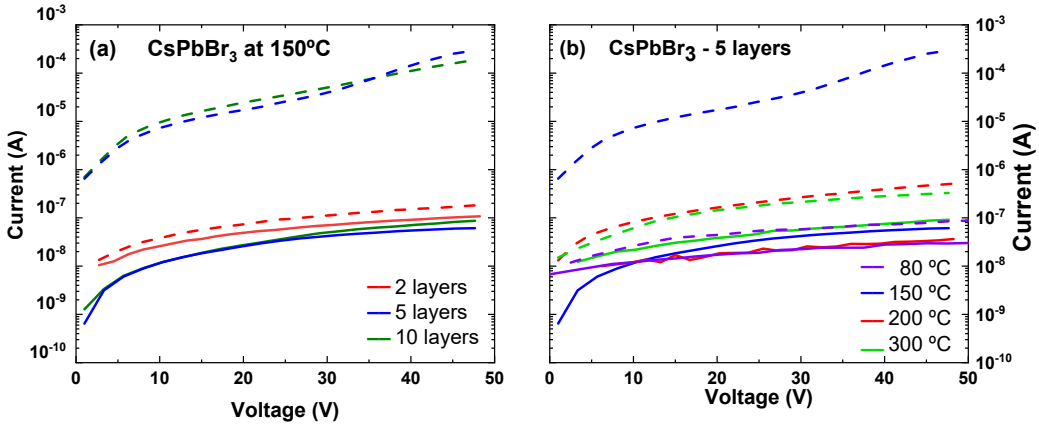


Figure S 9. Current-Voltage curves of $CsPbBr_3$ (**a**) at 150ºC for different number of layers and (**b**) at 5 layers for different deposited temperatures measured under simulated sun light, 1 Sun. Dash lines are under light and solid lines are under dark illumination condition.

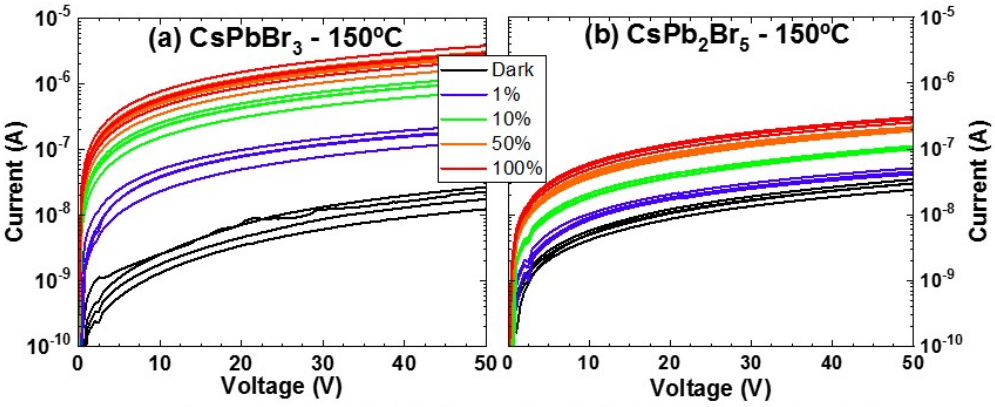


Figure S 10. Current-voltage curves for the four identical pixels of the device of (a) $CsPbBr_3$ and (b) $CsPb_2Br_5$ at 150ºC under various illumination power using a blue light LED as source light (100% power intensity equals to 200 mW/cm^2).

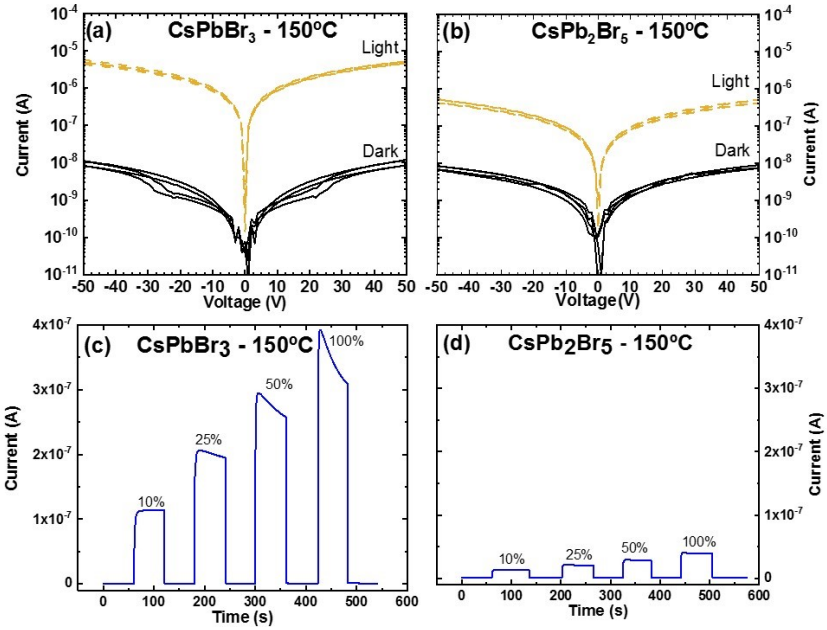


Figure S 11. Photocurrent hysteresis of (**a**) $CsPbBr_3$ and (**b**) $CsPb_2Br_5$ nanoinks 5 layers deposited at 150°C under light and dark illumination conditions (**c-d**) Dynamic response of the $CsPbBr_3$ and $CsPb_2Br_5$ to light pulses under 5V bias for different %intensity of 405 nm LED (100% = 200 mW/cm^2).

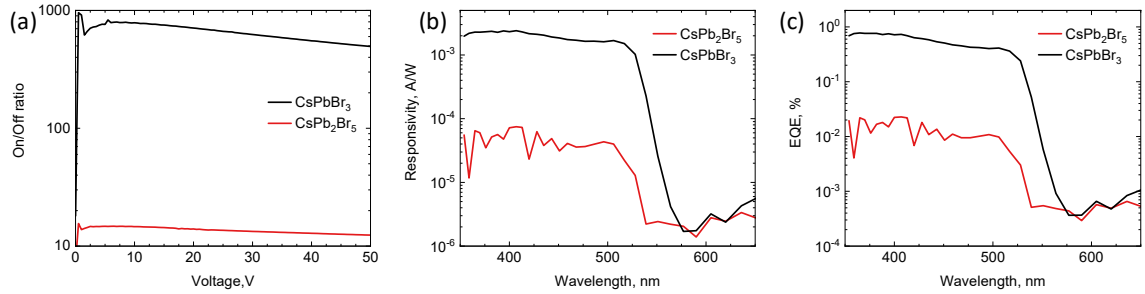


Figure S12. Additional characterization of the planar detector based on CsPbBr3 and CsPb2Br5: (a) on/off ratio for selected pixels, (b) responsivity and (c) EQE spectra.

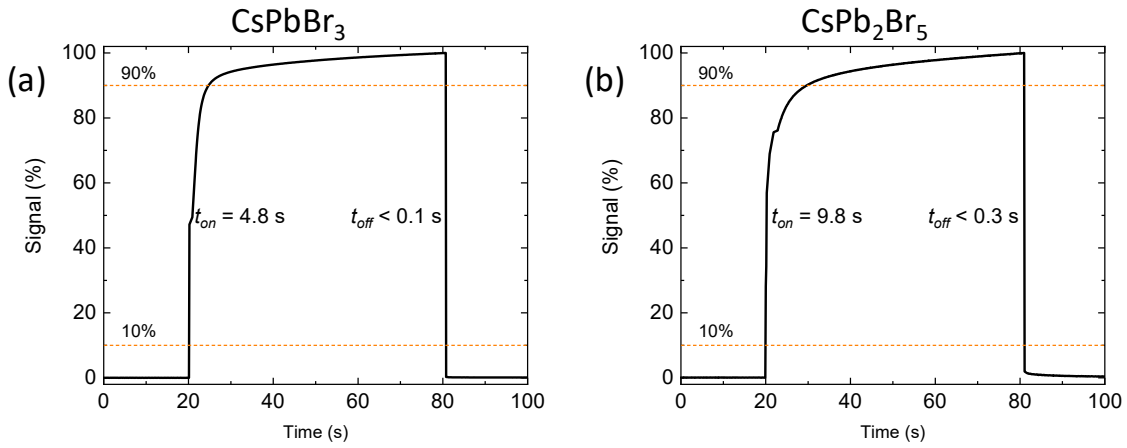


Figure S13. Pulse response of the detectors based on the two nanostructured materials. The rise time (ton) and fall time (toff) are calculated as the time for the signal to go from 10% to 90% of the pulse and vice versa, respectively.

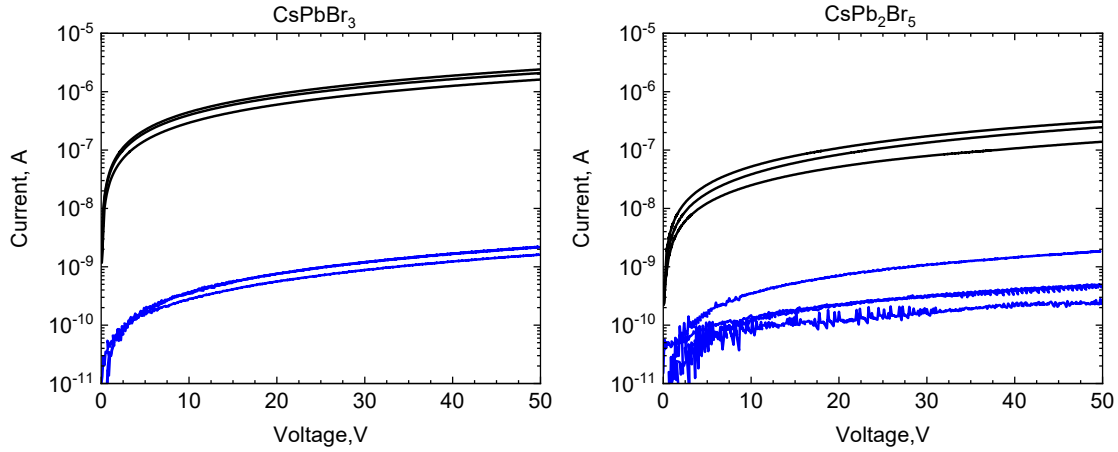


Figure S 14. Dark current (blue) and photocurrent (black) for devices using (a) CsPbBr3 and (b) CsPb2Br5, obtained after 9 months' storage in a nitrogen filled glovebox. The photocurrent is measured at 50% light intensity.

REFERENCES

(1) Akkerman, Q. A.; Gandini, M.; Di Stasio, F.; Rastogi, P.; Palazon, F.; Bertoni, G.; Ball, J. M.; Prato, M.; Petrozza, A.; Manna, L. Strongly Emissive Perovskite Nanocrystal Inks for High-Voltage Solar Cells. *Nat Energy* **2016**, *2* (2), 1–7. https://doi.org/10.1038/nenergy.2016.194.