

Supplementary Information

Stabilization of environmentally-friendly Cs₂TiBr₆ perovskite nanocrystals with SnBr₄

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Chemicals. Cesium acetate (CsAc 99.9% trace metals basis), titanium (IV) isopropoxide (Ti(O-*i*-Pr)₄, bromotrimethylsilane (TMSBr, 97%), tin (IV) bromide (SnBr₄, 99%), oleic acid (OA, technical grade 90%), 3-(*N,N*-dimethyloctadecylammonio)propanesulfonate (DMOP, 99.0%) and acetone (99.5%) were purchased from Sigma-Aldrich. Toluene (anhydrous, 99.8%) was purchased from Scharlabs. 1-octadecene (90%) was purchased from Alfa Aesar. All chemicals were used without any further purification.

Preparation of cesium oleate solution. Cesium oleate was prepared following a previously reported method.¹ 0.768 g (4 mmol) of cesium acetate were loaded in a 50 ml three-neck flask together with 7.56 ml of OA and 18.72 ml of ODE. The solution was degassed through 3 cycles of argon and vacuum and heated at 110 °C for 30 minutes under argon. Afterwards, the solution was left under vacuum for 3 hours at 110°C. The as-prepared solution was stored under nitrogen. The final concentration was calculated by measuring the final volume of the solution and by considering the moles of titanium precursor used in the synthesis.

Preparation of titanium oleate solution. For the synthesis of the titanium oleate solution, 16 ml of oleic acid were loaded in a 50 ml three-neck flask and degassed through 3 cycles of argon and vacuum. 2 ml of titanium (IV) isopropoxide taken from the glovebox were slowly added while stirring and the solution was heated under argon for 1 hour at 140°C. Afterwards, the solution was left under vacuum at 110°C overnight and acquired a dark red tone. The as-prepared solution was stored under nitrogen. The final concentration was calculated by measuring the final volume of the solution and by considering the moles of titanium precursor used in the synthesis.

Synthesis of Cs₂TiBr₆ nanocrystals. 4 ml of cesium oleate solution (0.625 mmol) and 60 mg of DMOP were loaded in the glovebox inside a 50 ml three-neck flask together with 2 ml of ODE, 2 ml of OA and 1.85 ml of titanium oleate solution (0.78 mmol). The solution was degassed through 3 cycles of argon and vacuum and heated at 110°C for 35 minutes under vacuum. At this point, 574 µL (4.218 mmol) of TMSBr, were injected under argon at 140°C and the reaction carried out for 20 seconds and then quenched by diluting the solution with 10 ml of toluene.

Treatment with SnBr₄. The treatment with SnBr₄ was carried out using a solution of SnBr₄ dissolved in toluene (for the best stabilities, 103.86 mg were dissolved in 2 ml of toluene) that was slowly added at room temperature to 2.5 ml of the crude solution of Cs₂TiBr₆ after the toluene quenching. After 30 minutes (the optimized time) stirring, 1 ml of acetone was added to the solution and this was centrifuged at 5800 rpm for 10 minutes. The supernatant was removed and the NCs redispersed in 1 ml of toluene.

Synthesis of Cs₂Ti_{1-x}Sn_xBr₆ alloy NCs. 4 ml of cesium oleate and 60 mg of DMOP were loaded in a 50 ml three-neck flask together with Sn(IV) acetate and Ti(IV) isopropoxide in different ratio (while the total Cs:B ratio was kept 2:2.5), 2 ml of ODE and 2 ml of OA. The solution was degassed through 3 cycles of argon and vacuum and heated at 110°C for 35 minutes under vacuum. At this point, 574 μ L (4.218 mmol) of TMSBr were injected and after 20 seconds the reaction was quenched by diluting the solution in 10 ml of toluene. For the washing procedure, 5 ml of acetone were added to 5 ml of solution very slowly to avoid aggregation of the NCs and the solution was centrifuged at 5800 rpm for 10 minutes. Afterwards, the supernatant was discarded and the NCs redissolved in toluene.

Fabrication of the photoconductive device. The substrates for the photocurrent measurements were prepared on a SiO₂ (285 nm) /Si wafer by photolithography using ECI3007 photoresist and Heidelberg Maskless Aligner. The photoresist was spin coated and softbaked at 100 °C on a hot plate before UV exposure, and subsequently developed in AZ726 MIF developer from microchemicals to pattern the photoresist. Then 3 nm of Titanium and 50 nm of Au was deposited, followed by lift-off in acetone to form a single channel of two parallel electrodes with a size of 10 μ m gap and 800 μ m in length. For the preparation of the device, the NC solution was washed an additional time, with no addition of any antisolvent, centrifuging at 5800 rpm for 10 minutes and redispersing the precipitate in toluene. The as-prepared solution was deposited on the substrates by spin coating 45 μ L of solution at 2000 rpm for 30 seconds. After each deposition, 3 in total, the film was dipped in a solution of glycine in methylacetate (1 mg/ml) for 10 seconds to carry out the ligand exchange. Afterwards, the film was spin coated again and few drops of methylacetate were poured on it to remove possible excess of glycine on the surface of the film. The film was spin coated again adding a drop of toluene on its top to remove all the possible remaining long chain organic ligands.

X-ray Diffraction (XRD) characterization. XRD patterns were collected using a Rigaku SmartLab diffractometer in Bragg-Brentano $\Theta/2\Theta$ geometry, Cu α radiation (wavelength=1.5406 Å) and a D/teX Ultra 250 silicon strip detector. The NCs samples were prepared by drop casting the nanocrystals' solutions on the top of a silicon wafer. For the characterization, all the samples were measured inside an air-sensitive sample holder, which was loaded in the glovebox to avoid any contact with air, while for the stability study, they were exposed to air.

Transmission Electron Microscopy (TEM) characterization. TEM measurements were performed at the Scientific and Technological Centres of the University of Barcelona (CCiT-UB). TEM images were acquired in a JEOL J2010F TEM microscope, equipped with a field emission electron gun (FEG). EDXS experiments were carried out in a JEOL J2100 TEM microscope, equipped with a LaB₆ thermionic filament, and using an Oxford Instruments INCA X-sight spectrometer with Si (Li) detector. Both microscopes were operated at an accelerating voltage of 200 kV. Samples for TEM characterization were prepared in the glovebox by drop-casting diluted toluene solutions onto 200 mesh carbon-coated copper grids.

ICP-OES measurements. Elemental analysis of the sample was carried out using an ICP-OES PerkinElmer, model Optima 3200RL, in standard conditions. The digestion of the sample necessary for this measurement was carried out by adding to the dry NCs, 6 ml of HNO₃, 2 ml of H₂O₂, 1 ml of HF and deionized water, and heating the solution at 210 °C at high pressure in a microwave digestion system "Milestone EthosOne".

XPS measurements and analysis of XPS spectra. The samples for XPS were prepared on substrates of gold vapor-deposited on glass, by spin coating 40 μ L of solution at 1000 rpm in the glovebox.

XPS measurements were performed at the Institut Català de Nanociència i Nanotecnologia (ICN2) using a Phoibos 150 analyser (SPECS) under ultra-high vacuum conditions (base pressure of 4×10^{-10} mbar) equipped with a monochromatic Al $K\alpha$ X-ray source (1486.74 eV). The pass energy value used was 20 eV for the high-resolution spectrum. The samples were transferred very fast from a nitrogen atmosphere to the XPS setup under vacuum, though they were exposed to air for few seconds. All the spectra were “charge-corrected” moving the main carbon peak at 284.8 eV. When identifying the chemical species from the position of the peaks, we used a Perkin Elmer Corporation XPS handbook.²

UV-vis Absorption and PL measurements. Optical absorption spectra were collected using a Varian Cary-5000 UV-vis-NIR spectrophotometer. Photoluminescence (PL) measurements were performed using a Horiba Jobin Yvon iHR550 Fluorolog system, using as source a tungsten lamp with a monochromator to set different excitation wavelengths.

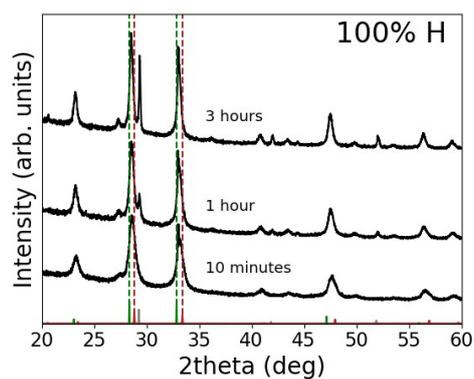


Figure S.1 Evolution over time of the XRD pattern of the SnBr_4 -treated Cs_2TiBr_6 sample in 100% humidity atmosphere

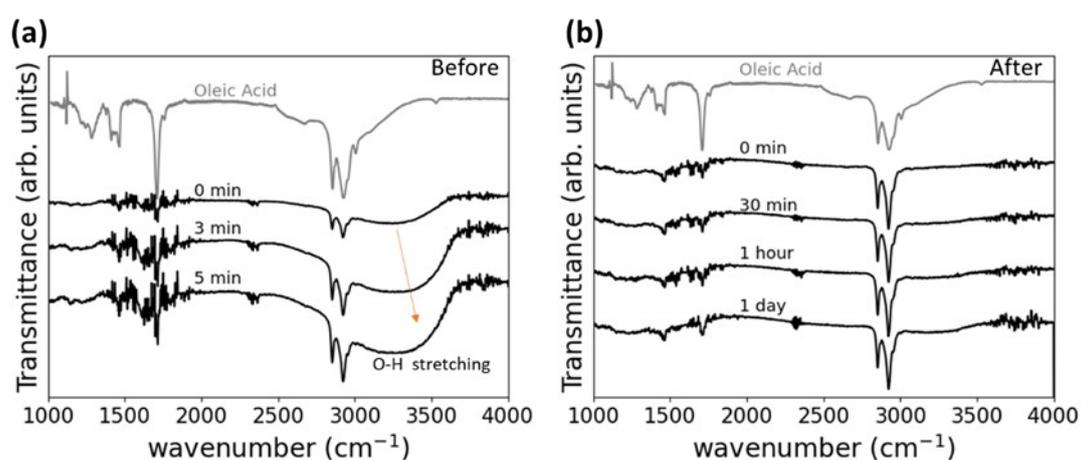


Figure S.2. FTIR spectra of (a) Cs_2TiBr_6 and (b) SnBr_4 -treated Cs_2TiBr_6 NCs. The bump between 3000 cm^{-1} and 3500 cm^{-1} comes from the O-H stretching mode, while the other peaks are due to the ligands attached to the surface of the NCs.

Element	weight (mg)	atomic weight (g/mol)	mmols
Cs	5.54	132.90	0.042
Ti	0.64	47.87	0.013
Sn	1.20	118.71	0.01

Table S.1 ICP-OES results for SnBr_4 -treated Cs_2TiBr_6

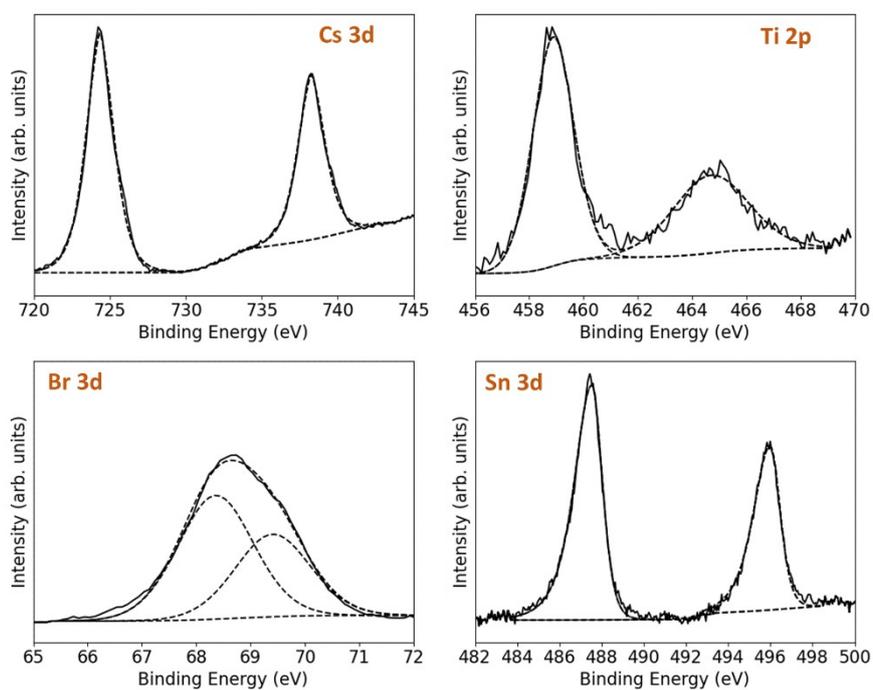


Figure S.3 High-resolution XPS spectra of $\text{SnBr}_4\text{-Cs}_2\text{TiBr}_6$ sample in the Cs 3d, Ti 2p, Br 3d and Sn 3d regions

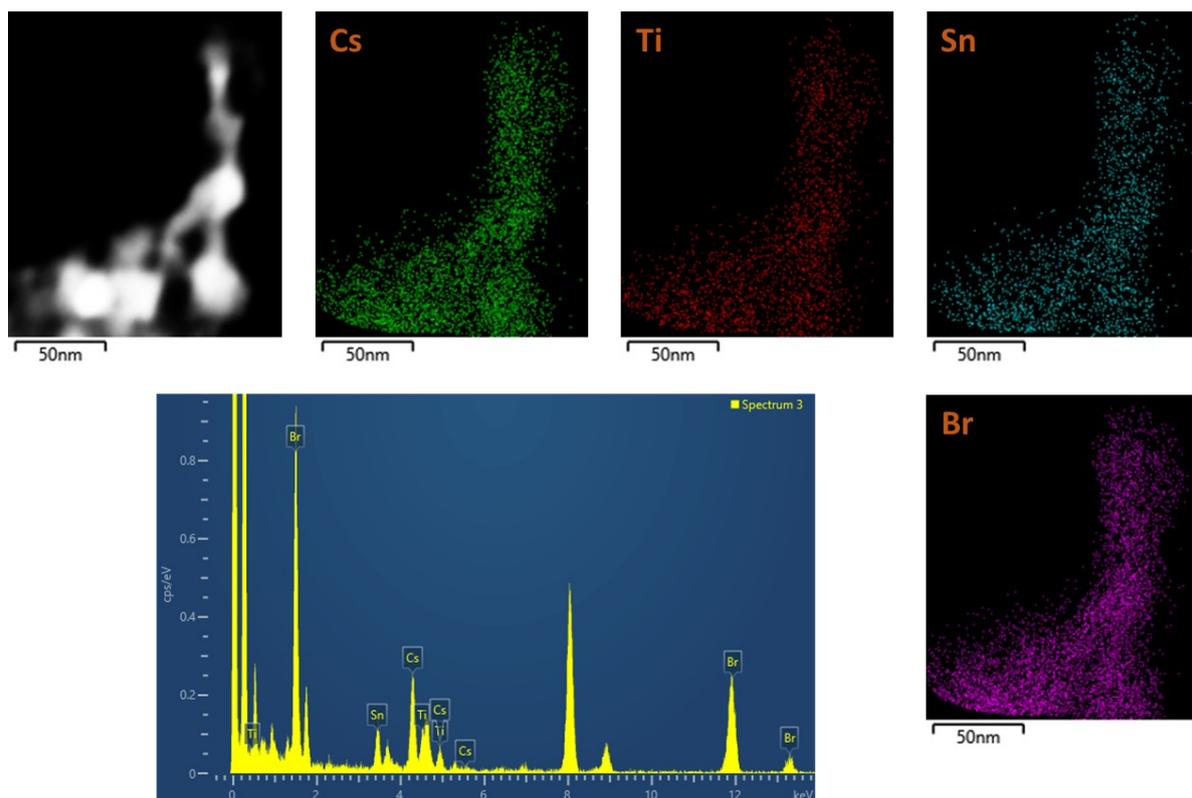


Figure S.4 EDX High-angle annular dark-field (HAADF) image and STEM-EDX analysis of $\text{SnBr}_4\text{-Cs}_2\text{TiBr}_6$ NCs with the corresponding atomic maps

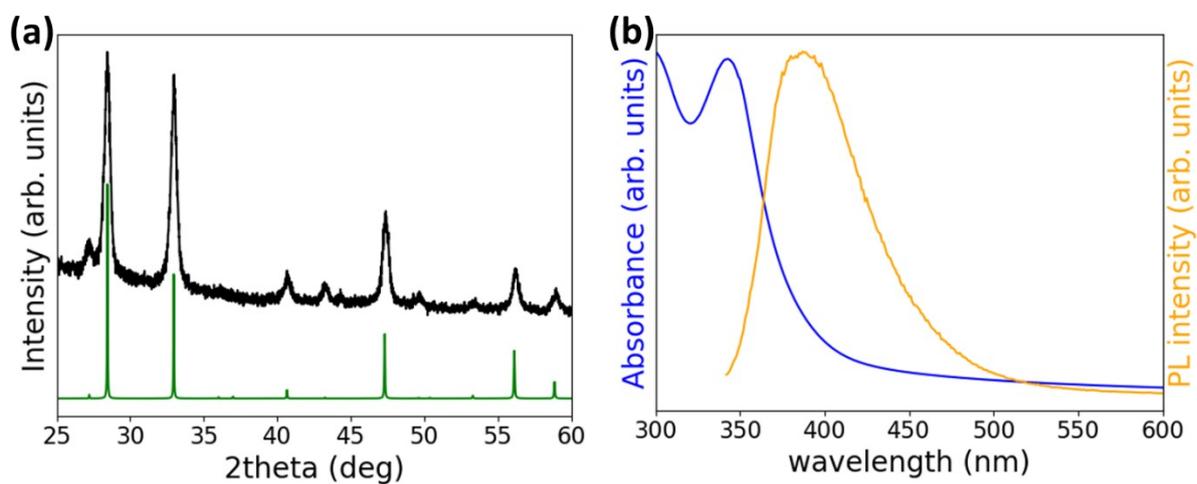


Figure S.5. (a) XRD pattern of Cs_2SnBr_6 sample in comparison with the reference pattern (lattice parameter extracted from Rietveld refinement is 10.840(3)), (b) absorption and PL spectra of Cs_2SnBr_6 solution

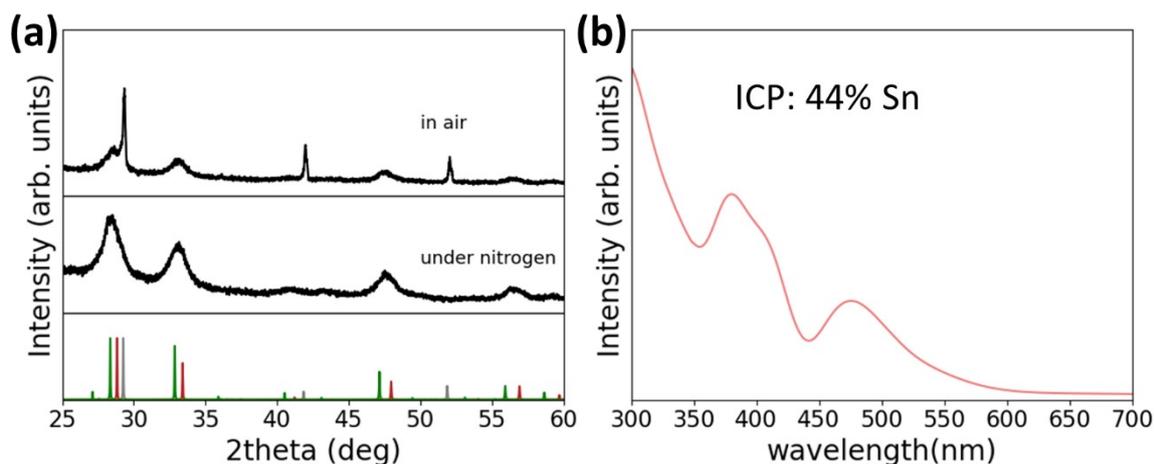


Figure S.6 (a) XRD pattern of the alloy $Cs_2Ti_{1-x}Sn_xBr_6$ containing 44% of tin under nitrogen and after air exposure (lattice parameter extracted from Rietveld refinement is 10.800(2)). The reference patterns are those of Cs_2SnBr_6 (in green), Cs_2TiBr_6 (in dark red) and $CsBr$ (in grey); (b) absorption spectrum of the NC solution

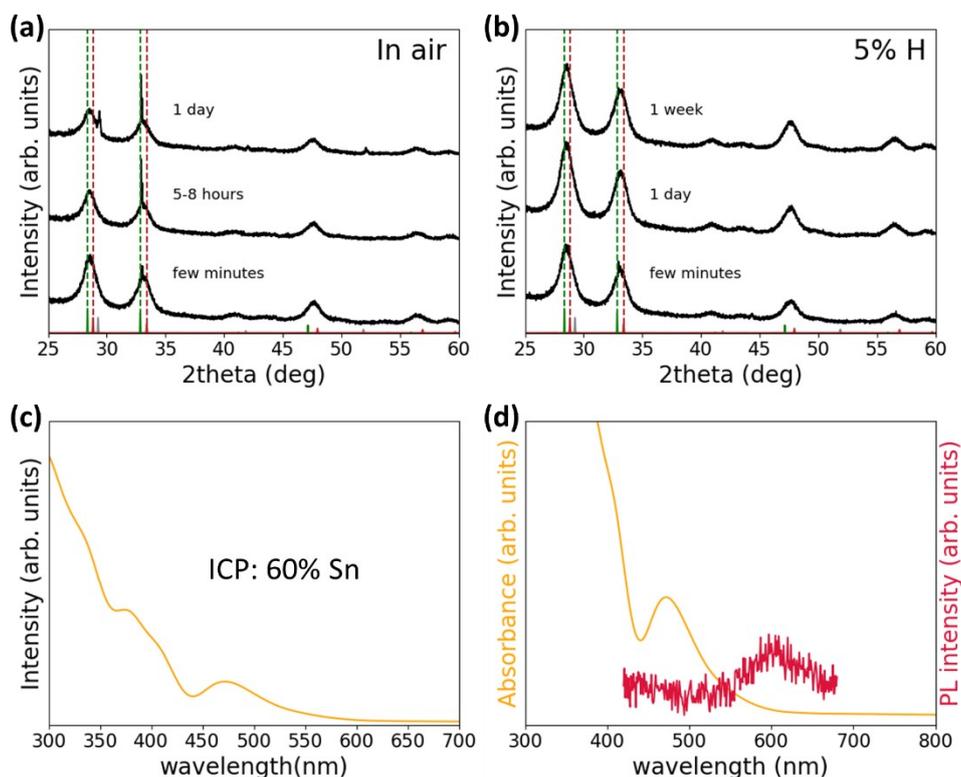


Figure S.7 (a) XRD pattern of the alloy $Cs_2Ti_{1-x}Sn_xBr_6$ containing 60% of tin under nitrogen and after air exposure and (b) its evolution when stored in a desiccator with 5% humidity (H). The reference patterns are those of Cs_2SnBr_6 (in green), Cs_2TiBr_6 (in dark red) and $CsBr$ (in grey). The lattice parameter extracted from Rietveld refinement is 10.819(6). The narrow peak at 32.97 degrees originates from the silicon substrate; (c) absorption spectrum of the NC solution, (d) Zoom on the absorption spectrum (in orange) and PL spectrum (in red).

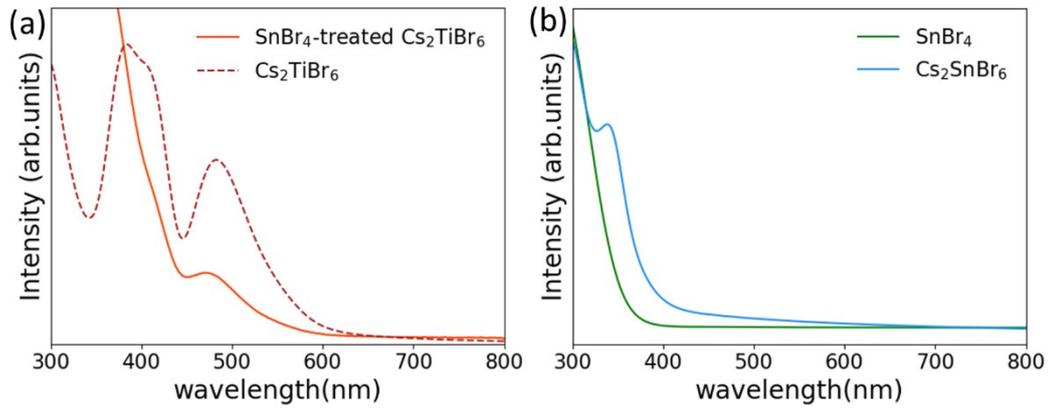


Figure S.8 (a) Zoom of Figure 4 (a) to observe the shape of the spectra between 400 nm and 600 nm. (b) Absorption spectra of SnBr₄ (green) and Cs₂SnBr₆ (cyan).

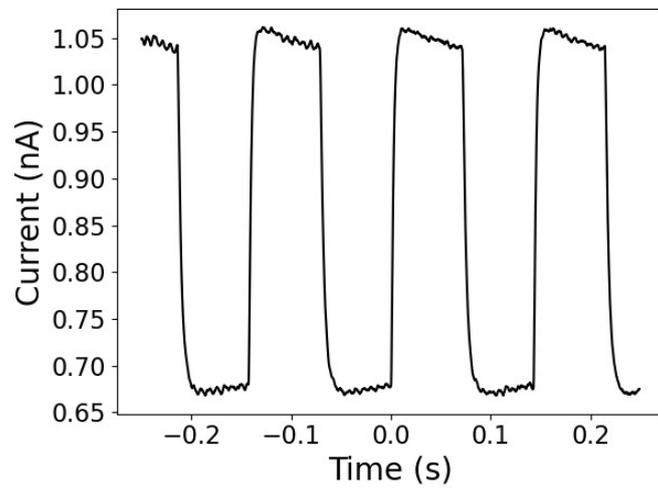


Figure S. 9. Photocurrent response of SnBr₄-treated Cs₂TiBr₆ FET

- 1 C. Lu, M. W. Wright, X. Ma, H. Li, D. S. Itanze, J. A. Carter, C. A. Hewitt, G. L. Donati, D. L. Carroll, P. M. Lundin and S. M. Geyer, *Chemistry of Materials*, 2019, **31**, 62–67.
- 2 J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation Physical Electronics Division 6509, 1992.