Supporting Information

Electronic Properties of Free-Standing Surfactant-Capped Lead Halide Perovskite Nanocrystals Isolated *in Vacuo*

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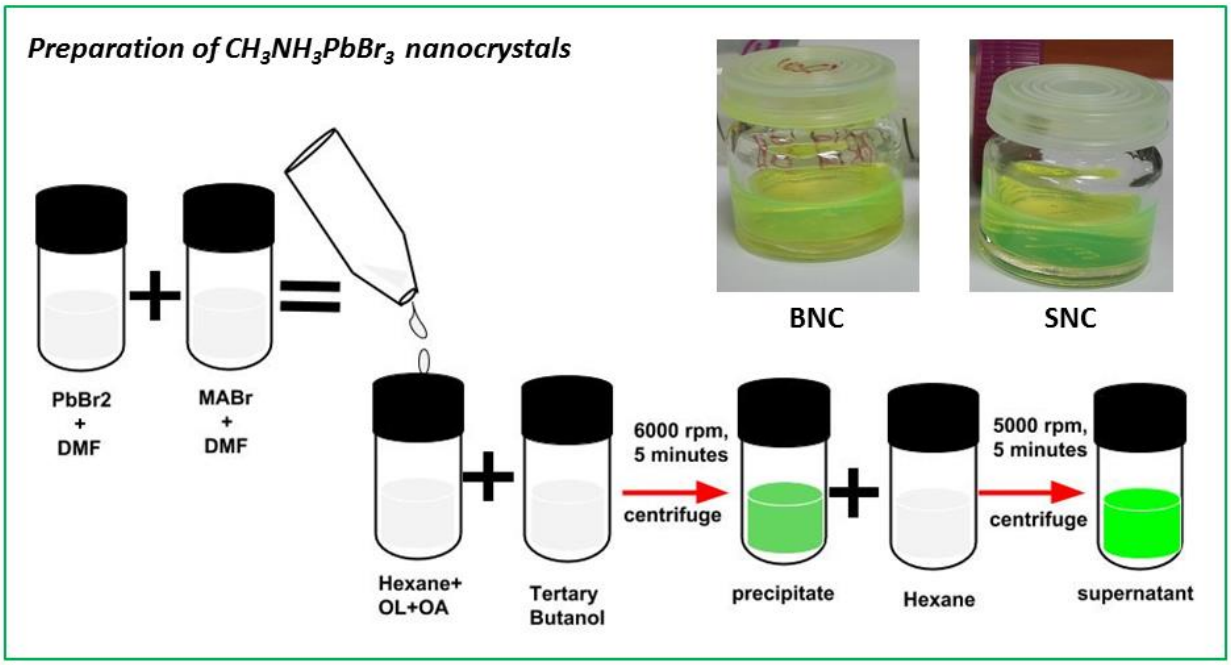

Figure SI1. A scheme of the preparation procedure for $CH_3NH_3PbBr_3$ nanocrystals. The insets show photos of the final solutions used in the atomizer to obtain the nanoparticle beam; SNC stands for small nanocrystals (~11 nm), BNC stands for big nanocrystals (~20 nm).

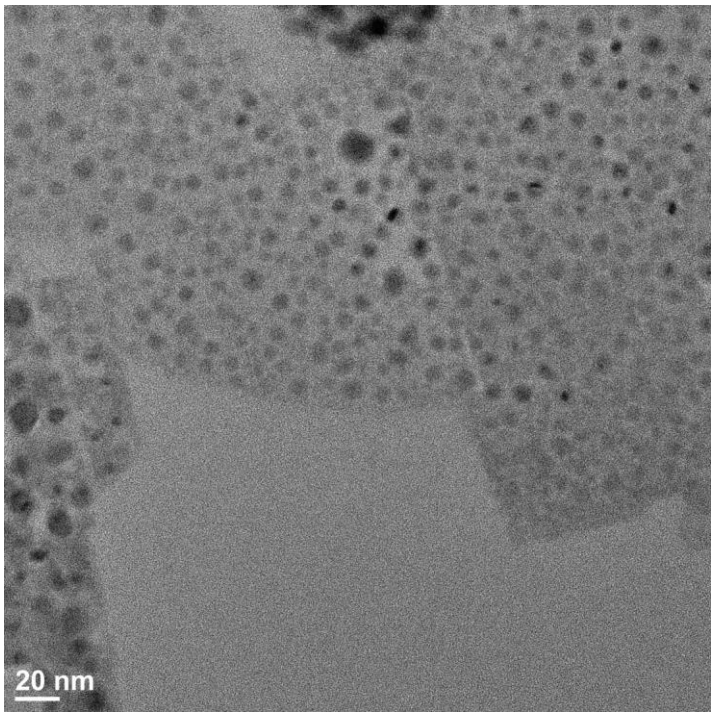

Figure SI2. Transmission electron microscopy images of $MAPbBr_3$ nanocrystals (SNC, as in Figure SI1).

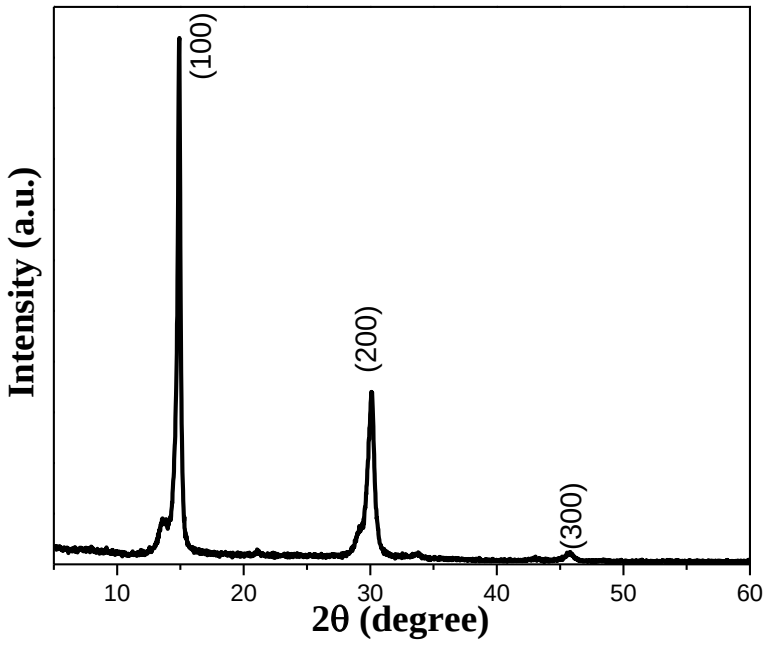

Figure SI3. X-ray diffraction (XRD) pattern of $MAPbBr_3$ nanocrystals (SNC, as in Figure SI1).

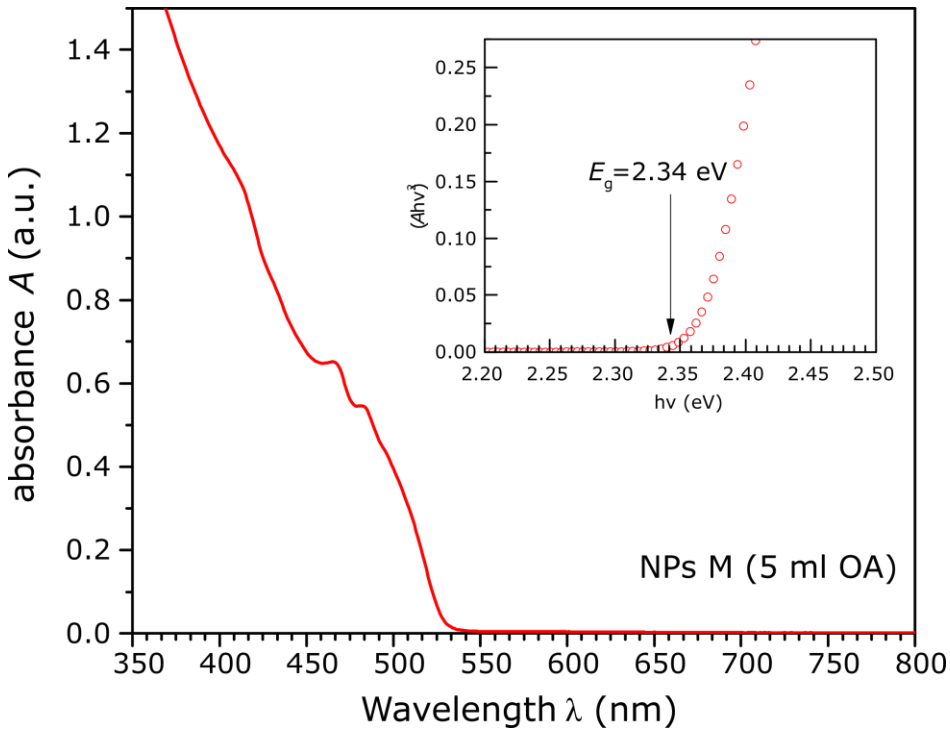

Figure SI4. UV-VIS absorption spectrum of $MAPbBr_3$ nanocrystal organocolloid (11±3 nm particle size) measured using Thermo Scientific Carry 4000 spectrophotometer.

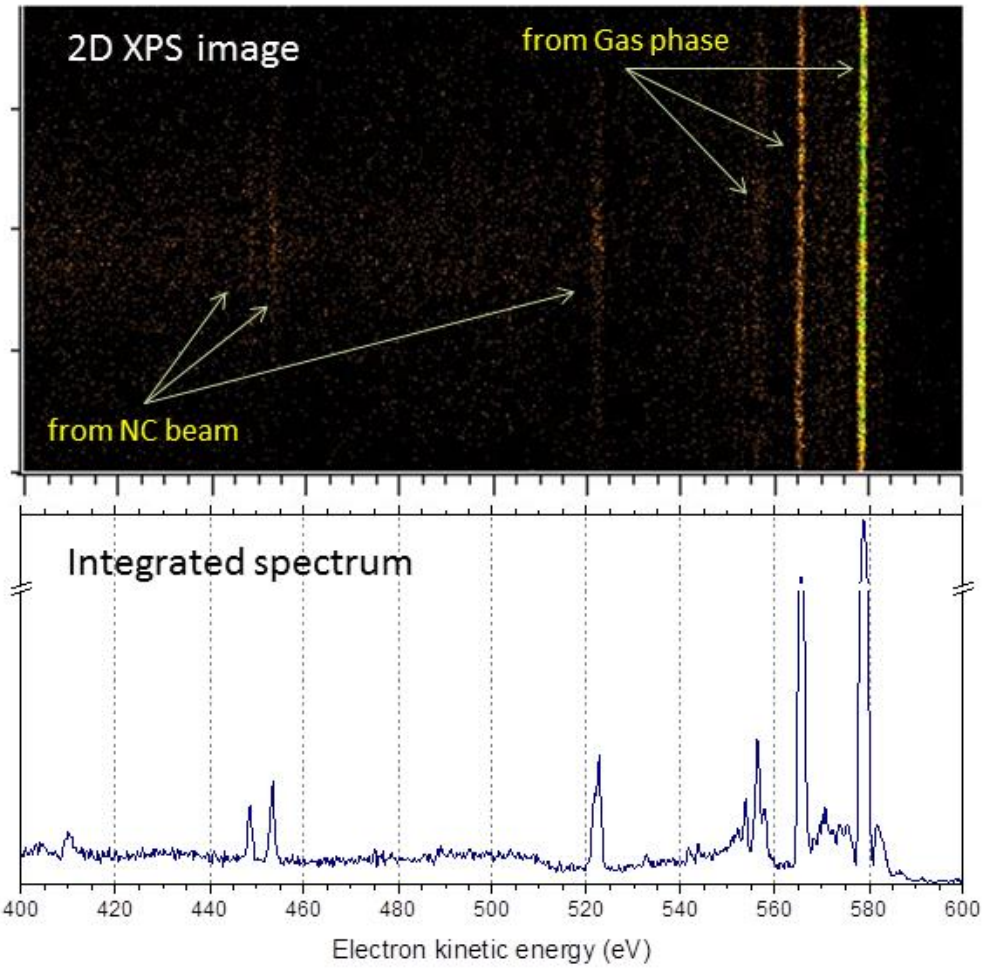

Figure SI5. Gas-phase XPS photoelectron spectrum in two-dimensions (top) and as an integrated spectrum (bottom). The kinetic energy distribution is obtained using a Scienta hemispherical analyzer, in transmission mode (all electrons emitted along the axis of the ionizing photon beam are focused to the same vertical position of the detector, independently from their emission angles), which images photoelectrons produced within a limited area defined roughly by the entrance slit, and disperses them according to their kinetic energies in the horizontal direction onto a position sensitive detector (top panel). The kinetic energy distribution (bottom panel) is then obtained by integrating the obtained 2D image along vertical lines. The axis of the electron energy dispersion coincides with the axis of the nanoparticle beam. Electrons from the central part of the beam are imaged onto the central (vertical) part of the 2D image (top panel). The large nanoparticles (c.a. 50-500 nm) are focused by the aerodynamic lenses to form a beam of a few hundred microns diameter, much smaller than the Scienta imaging area. The carrier Ar gas and small solvent molecules (hexane in the present case) are not focused by the aerodynamic lenses and form a diffuse cloud around the central nanoparticle beam and thus fill the whole vertical area of the detector. Therefore, photoelectron lines corresponding to the nanoparticle beam ("nano-phase") are seen in the center of the image while those from the gaseous non-focused species ("gas-phase") fill the whole image, allowing the two components to be easily identified. Note also that the background is dominantly produced from dense nanoparticle beam.

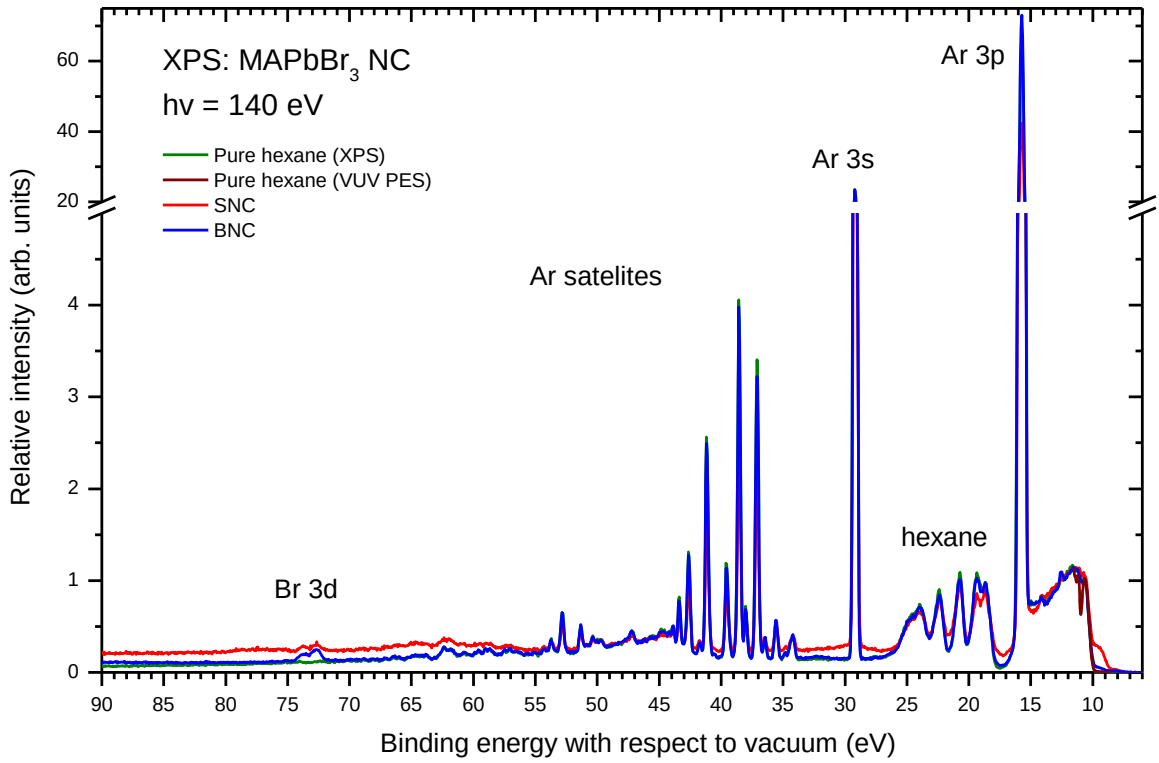

Figure SI6. Gas phase XPS of isolated MAPbBr nanocrystals of 11±3 nm (red line) and 20 nm (blue line), as well as pure hexane solution (green line) recorded at the PLEIADES beamline at the photon energy of 140 eV. The dark red line represents the VUV PEPICO spectrum of the pure hexane sample recorded at the DESIRS beamline.

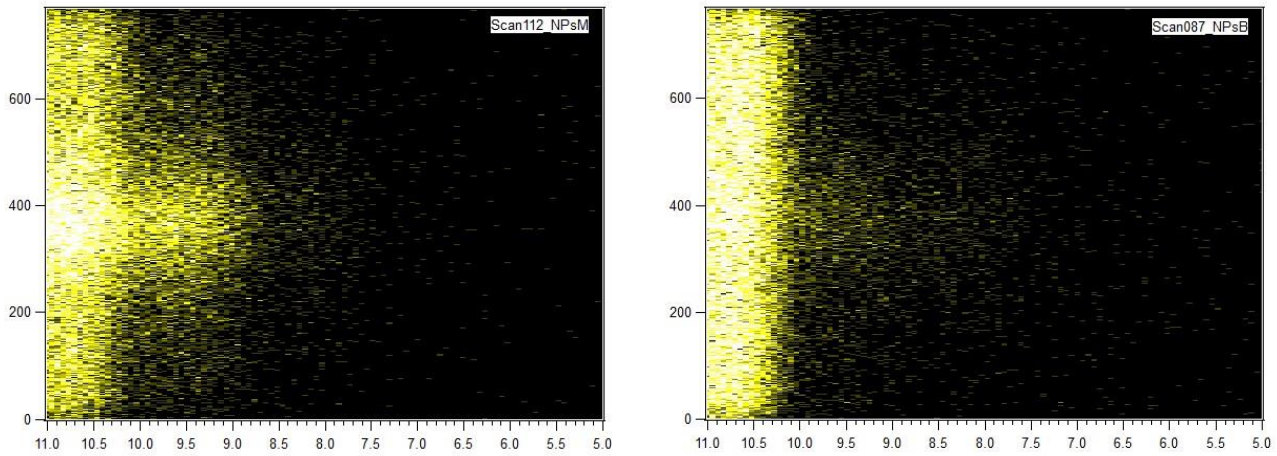

Figure SI7. 2D XPS images (see Figure SI5 for explanation) that correspond to the valence region of the XPS spectrum presented in Figure SI6 above, for SNC (left panel) and BNC (right panel). In both cases, the lower energy valence edges corresponding to nanocrystals and ligand molecules (OA and OL) are clearly restricted to the central part of the image, in contrast to the hexane valence edge (at about 10 eV) that is spread over the whole 2D image. Therefore, the photoelectrons from the ligand molecules OA and OL dominantly come from the focused nanoparticle beam, confirming that the probed ligands are attached to the nanocrystals. Note also that intensity from the ligands is much stronger for the case of the smaller nanocrystals, as discussed in the manuscript.

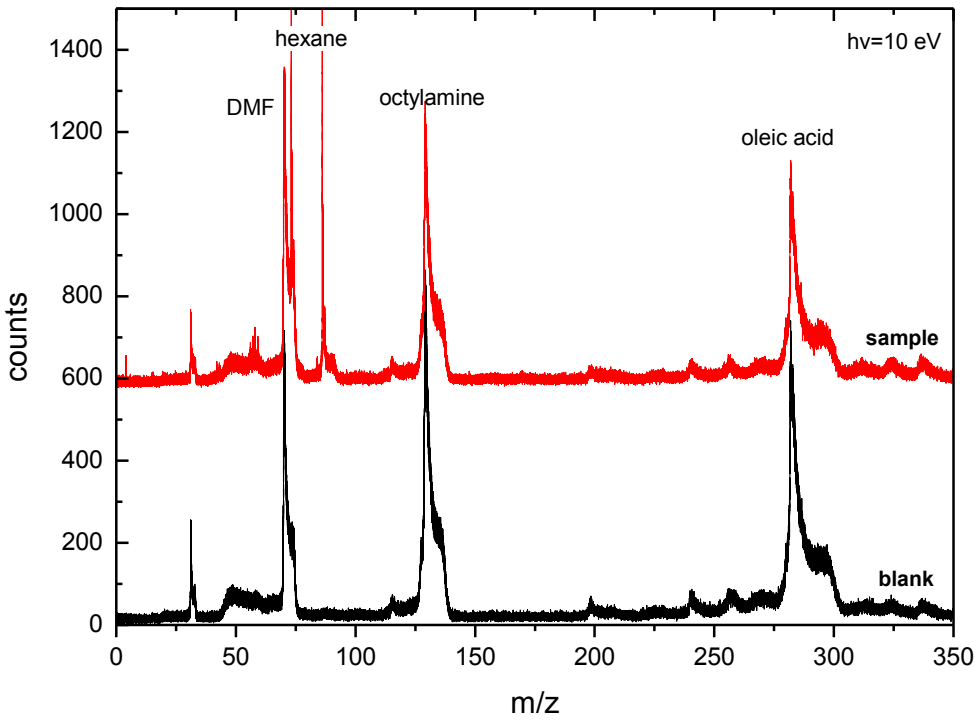

Figure SI8. The mass spectra of the $MAPbBr_3$ nanocrystal hexane dispersion (labeled 'sample') and the octylamine an oleic acids hexane solution ('blank') obtained at 10 eV photon energy. The spectra suggest presence of free surfactant molecules in the organocolloid. The contribution of the free molecules was subtracted from the net photoemission to obtain the PES of the $MAPbBr_3$ nanocrystals.

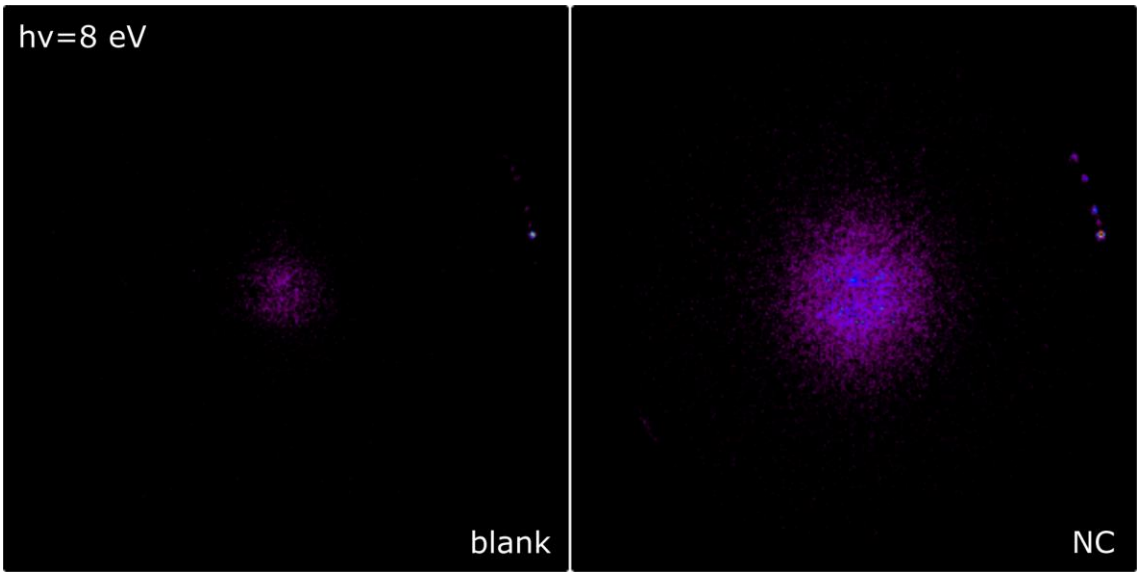

Figure SI9. The background-corrected velocity map images of the photoelectrons recorded for the blank solution (hexane+OA+OL) and the $MAPbBr_3$ NC sample at 8 eV photon energy.

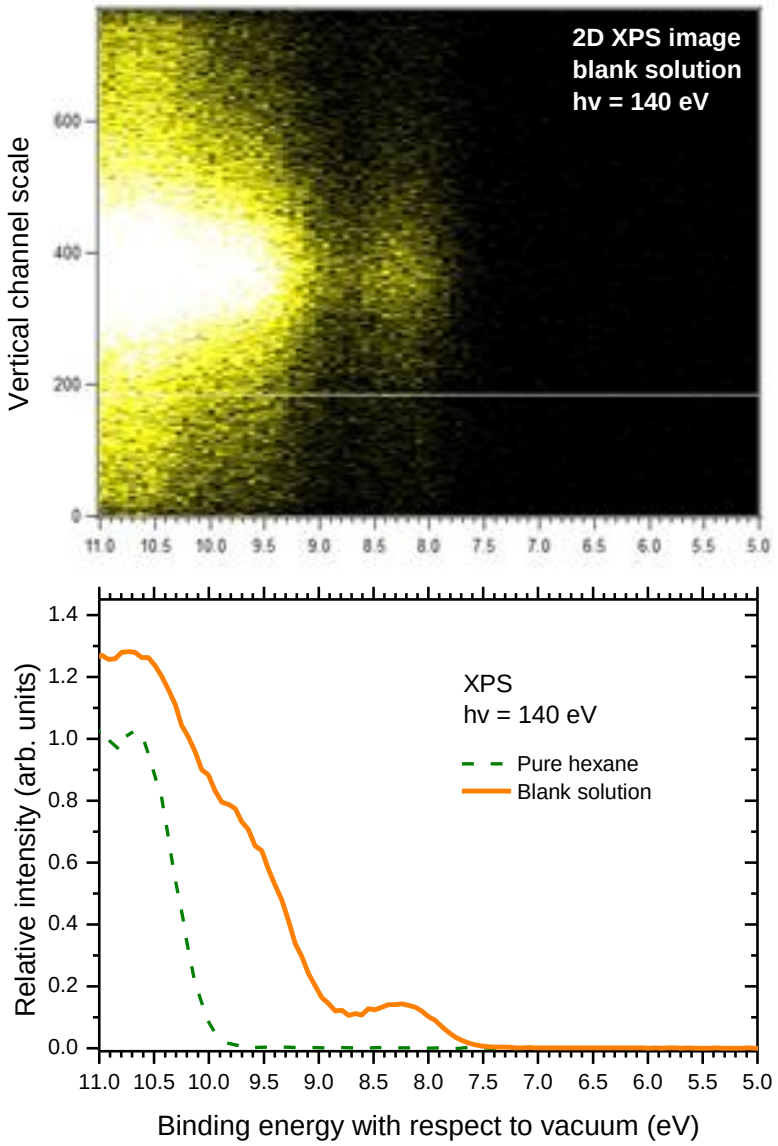

Figure SI10. 2D gas phase XPS images (top panel - see Figure SI5 for explanation) corresponding to the valence region of the XPS spectrum recorded at hv =140 eV for the "blank solution", containing only OA and OL molecules in hexane. The integrated spectrum is presented in the bottom panel (orange line). The XPS of pure hexane taken at the same photon energy is also presented for comparison (green dashed line). The 2D image indicates clustering of OA and OL molecules in the beam with a wide range of cluster sizes as evidenced by the increased intensity on axis for the red-shifted lower binding energies.

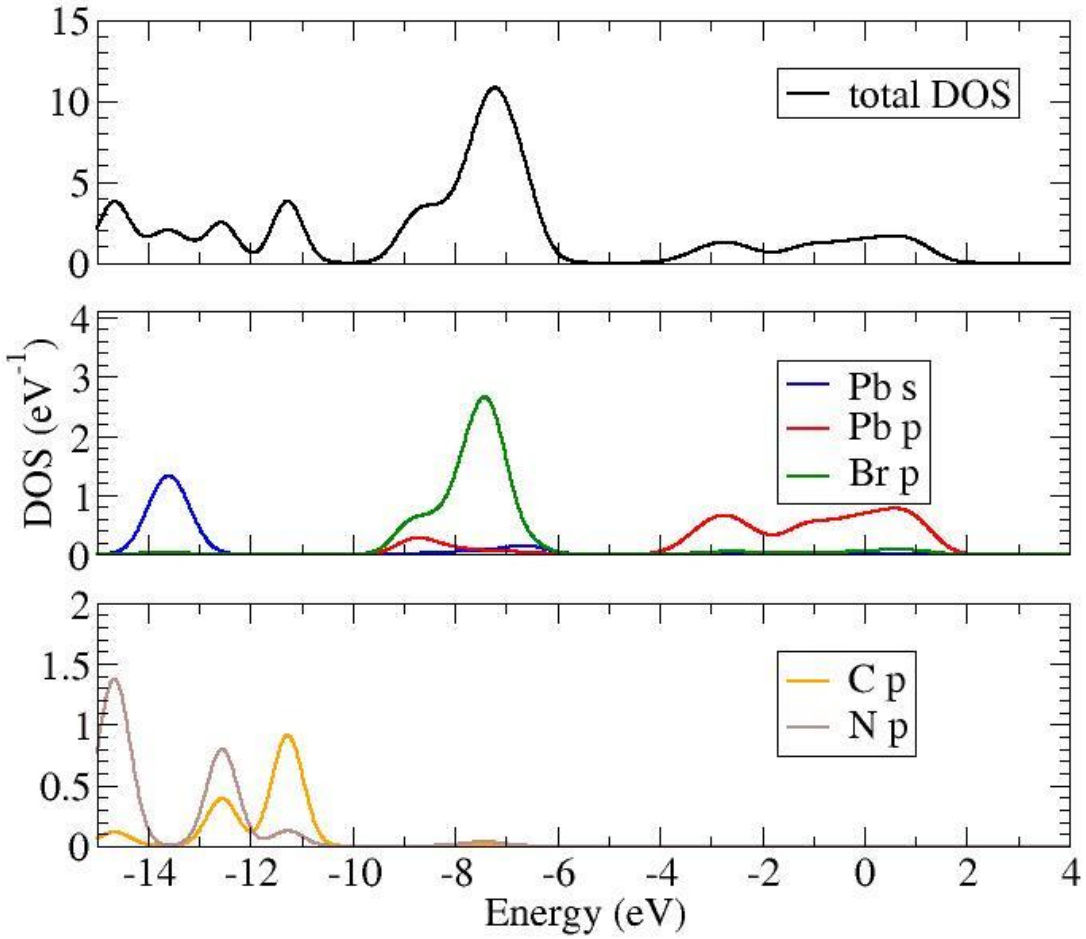

Figure SI11. Density of electronic states of bulk $CH_3NH_3PbBr_3$ obtained from density functional theory calculations. Total density of states is presented in the upper panel. Lower two panels present angular momentum projected partial density of states in the sphere surrounding an atom. The radius of the sphere was 1.4 bohr for C and N, 2.6 bohr for Pb, and 2.1 bohr for Br.