# Probing Strain-Induced Band Gap Modulation in 2D Hybrid Organic-Inorganic Perovskites – Supporting Information

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## Section I. 2D and 3D hybrid organic-inorganic perovskites (HOIPs) structure schematics

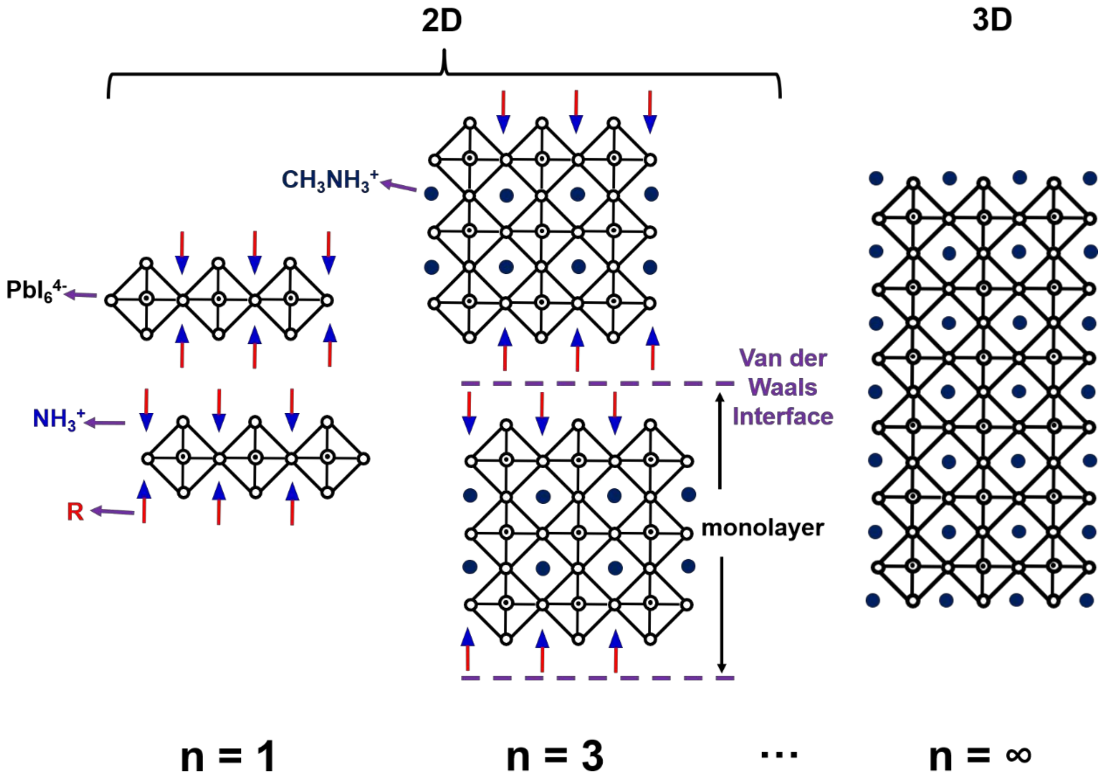

**Figure S1.** Schematics illustrating the dimensional reduction of 3D $AMX_3$ HOIPs to 2D $(R\text{-}NH_3)_2(A)_{n-1}(M)_n(X)_{3n+1}$ HOIPs. Here A site cation is $CH_3NH_3^+$, M is Pb and X is I.

## Section II. Materials and Synthesis

### Starting materials

All starting materials for synthesis were purchased commercially and were used without further purification, except for methylamine hydrochloride which was dried in an oven at 70 $^0$C overnight. Butylamine 99.5%, Lead(II) iodide 99%, Lead(II) oxide powder, <10 μm, ReagentPlus®, ≥99.9% trace metals basis, Methylamine hydrochloride ≥98%, Hypophosphorous acid solution 50 wt. % in $H_2O$ and Hydriodic acid 57 wt. % in $H_2O$, distilled, stabilized, 99.95%, were purchased from Aldrich.

### Syntheses

**$(CH_3(CH_2)_3NH_3)_2PbI_4$, C4n1:** PbO powder (2232 mg, 10 mmol) was dissolved in 57% w/w aqueous HI solution (16 mL) in a 50 mL glass volumetric flask by heating to boiling under constant magnetic stirring for about 5 min, which formed a bright yellow solution. Then 924 μL (10 mmol) of butylamine were added to 50% aqueous $H_3PO_2$ (1.7 mL) and this solution was added to the reaction slowly. The stirring was then discontinued, and the solution was left to cool to room temperature during which time big orange plate crystals started to crystallize. The crystals were isolated by suction filtration and thoroughly dried under reduced pressure. Yield: 2417 mg, (28% based on Pb)

**$(CH_3(CH_2)_3NH_3)_2(MA)_2Pb_3I_{10}$, C4n3:** PbO powder (2232 mg, 10 mmol) was dissolved in 57% w/w aqueous HI solution (16 mL) in a 50 mL glass volumetric flask by heating to boiling under constant magnetic stirring for about 5 min, which formed a bright yellow solution. Subsequent addition of solid methylamine hydrochloride (450 mg, 6.67 mmol) to the hot yellow solution initially caused the precipitation of a black powder, which rapidly dissolved under stirring to afford a clear bright yellow solution. Then 345 μL (3.49 mmol) of butylamine were added to 50% aqueous $H_3PO_2$ (1.7 mL) and this solution was added to the reaction slowly. The stirring was then discontinued, and the solution was left to cool to room temperature during which time brown plate crystals started to crystallize. The precipitation was deemed to be complete after~4 h. The crystals were isolated by suction filtration and thoroughly dried under reduced pressure. Yield: 1910 mg, (27.2% based on Pb)

**$(CH_3(CH_2)_3NH_3)_2(MA)_3Pb_4I_{13}$, C4N4:** PbO powder (2232 mg, 10 mmol) was dissolved in 57% w/w aqueous HI solution (16 mL) in a 50 mL glass volumetric flask by heating to boiling under constant magnetic stirring for about 5 min, which formed a bright yellow solution. Subsequent addition of solid methylamine hydrochloride (507 mg, 7.5 mmol) to the hot yellow solution initially caused the precipitation of a black powder, which rapidly dissolved under stirring to afford a clear bright yellow solution. Then 270 µL (2.72 mmol) of butylamine were added to 50% aqueous $H_3PO_2$ (1.75 mL) and this solution was added to the reaction slowly. The stirring was then discontinued, and the solution was left to cool to room temperature during which time black plate crystals started to crystallize. The precipitation was deemed to be complete after~4 h. The crystals were isolated by suction filtration and thoroughly dried under reduced pressure. Yield: 1700 mg, (26.7% based on Pb)

**$(CH_3(CH_2)_3NH_3)_2(MA)_4Pb_5I_{16}$, C4N5:** PbO powder (4464 mg, 20 mmol) was dissolved in 57% w/w aqueous HI solution (30 mL) in a 50 mL glass volumetric flask by heating to boiling under constant magnetic stirring for about 5 min, which formed a bright yellow solution. Subsequent addition of solid methylamine hydrochloride (1080 mg, 16 mmol) to the hot yellow solution initially caused the precipitation of a black powder, which rapidly dissolved under stirring to afford a clear bright yellow solution. Then 396 µL (4 mmol) of butylamine were added to 50% aqueous $H_3PO_2$ (3.4 mL) and this solution was added to the reaction slowly. The stirring was then discontinued, and the solution was left to cool to room temperature during which time black plate crystals started to crystallize. The precipitation was deemed to be complete after~4 h. The crystals were isolated by suction filtration and thoroughly dried under reduced pressure. Yield: 2493 mg, (18% based on Pb)

### X-ray diffraction measurements

Powder X-ray diffraction patterns were collected on a Rigaku Miniflex system (CuKα radiation) operated at 40 kV and 15 mA. A typical scan rate was 15 sec/step with a step size of 0.02 deg.

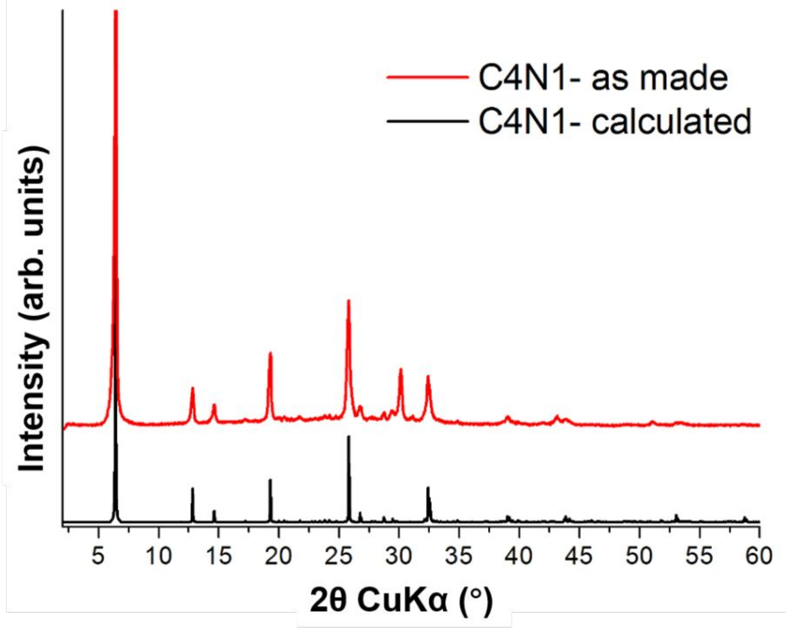

**Figure S2.** Comparison of the calculated powder X-ray diffraction pattern from the solved single crystal structure of the C4n1 material (including preferred orientation (001)) and experimental determined one from the as made crystals.

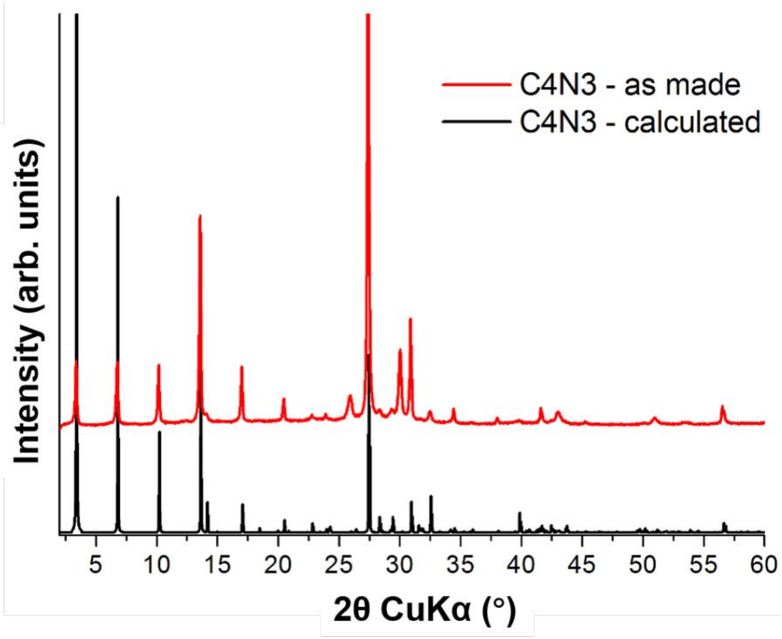

**Figure S3.** Comparison of the calculated powder X-ray diffraction pattern from the solved single crystal structure of the C4n3 material (including preferred orientation (010)) and experimental determined one from the as made crystals.

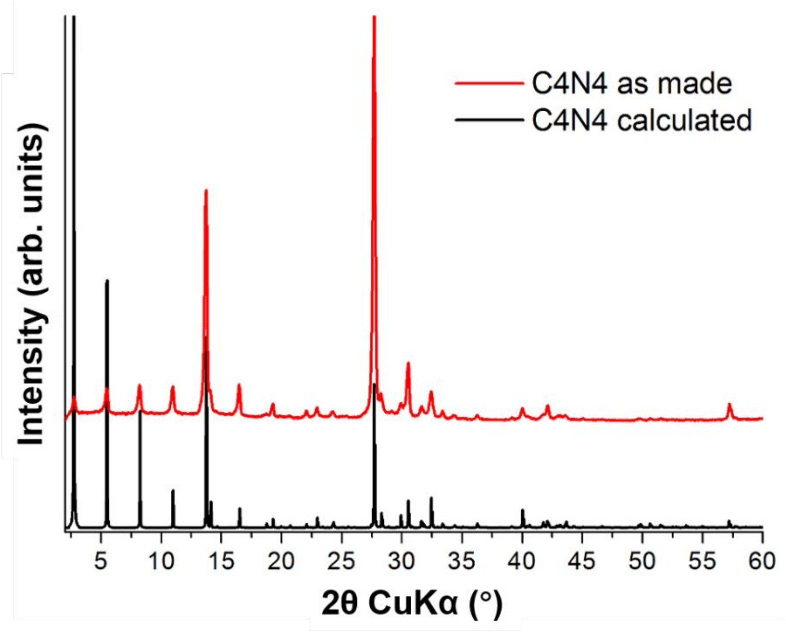

**Figure S4.** Comparison of the calculated powder X-ray diffraction pattern from the solved single crystal structure of the C4N4 material (including preferred orientation (010)) and experimental determined one from the as made crystals.

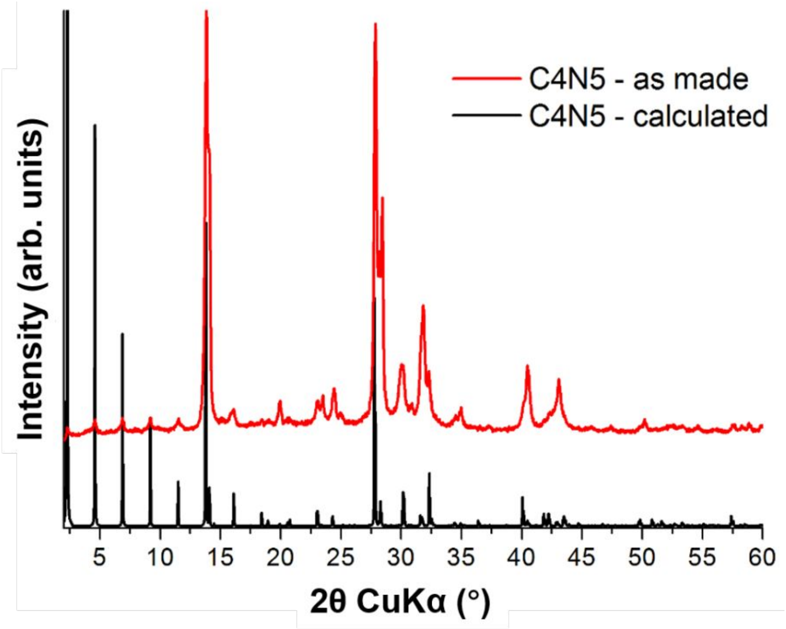

**Figure S5.** Comparison of the calculated powder X-ray diffraction pattern from the solved single crystal structure of the C4N5 material (including preferred orientation (010)) and experimental determined one from the as made crystals.

## Section III. Additional AFM and PL Characterization

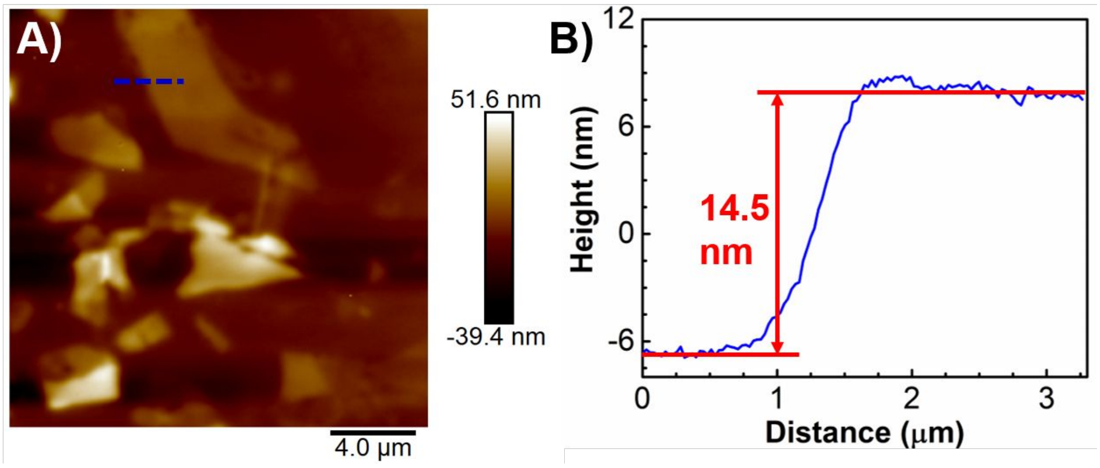

**Figure S6.** A) AFM height image of the C4n5 piece in Fig. 2A) and B) is the height profile corresponding to the blue dashed line marked in A).

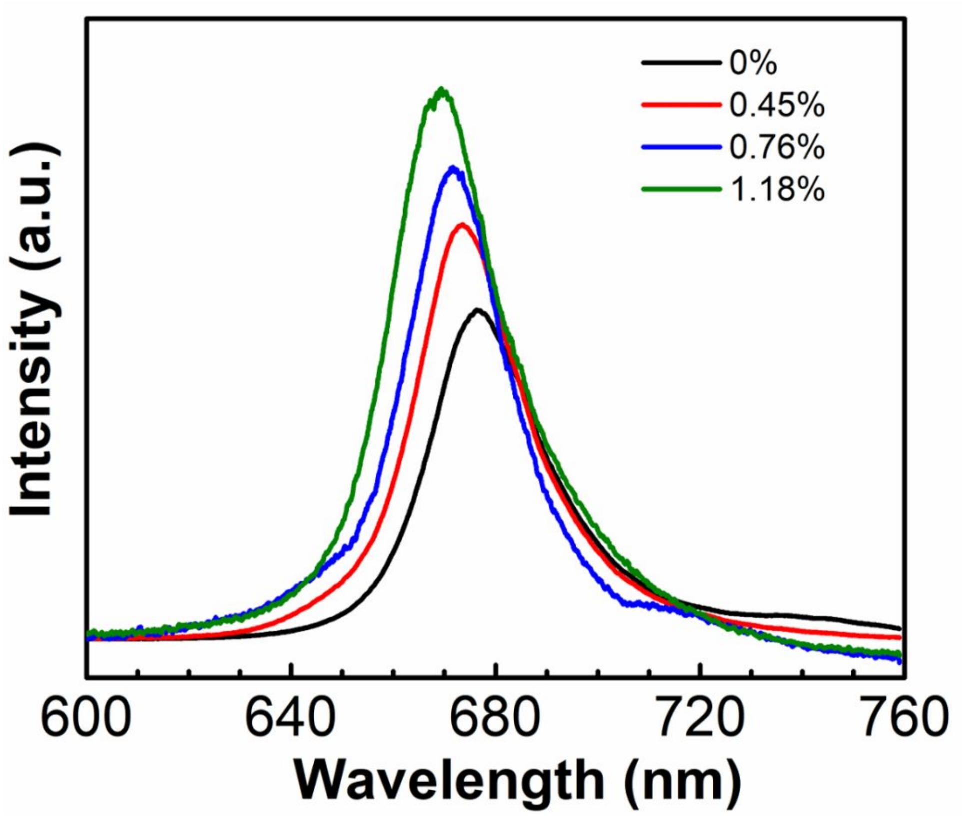

**Figure S7.** Un-normalized PL spectrum showing the PL intensity increases as the tensile strain increases.

## Section IV. DFT Simulations

Due to the limitation of computational resource, we could not calculate the bandgap of C4n5 samples and thus we choose to compare the results from C4n1 and C4n4. Unit cell models of C4n1 and C4n4 obtained from XRD are used for DFT simulations. The total energies and relaxed geometries of different samples were calculated by DFT within the generalized gradient approximation (GGA) of Perdew−Burke−Ernzerhof the exchange correlation functional with Projector Augmented Wave potentials.[1] We used periodic boundary conditions and a plane wave basis set as implemented in the Vienna ab initio simulation package.[2] The total energies were numerically converged to approximately 3 meV/cation using a basis set energy cutoff of 500 eV and dense k-meshes corresponding to 4000 k-points per reciprocal atom in the

Brillouin zone. For the strained cells, we applied strains along the in plane direction following the b-axis marked in Figure S8 below, and fixed the unit cell lattice constant in b direction with relaxed a and c lattice and atomic positions for the  strained band structures. Perodic boundary conditions were applied.

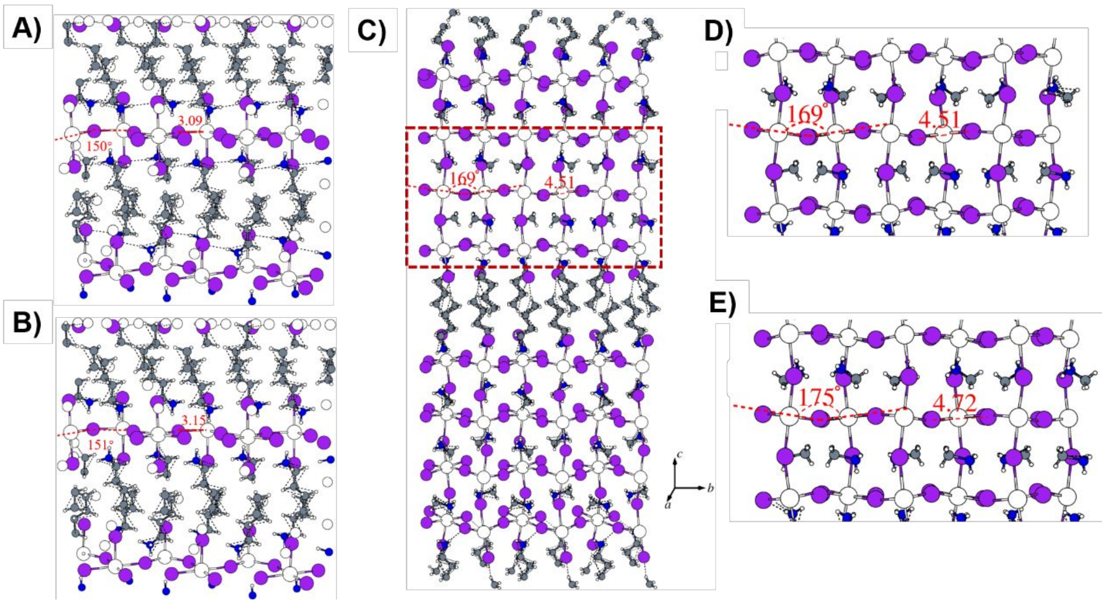

**Figure S8. DFT simulations:** A) and B) C4n1 unit cell at 0% and 5% strains, respectively. C) C4n4 unit cell at 0% strain. D) and E) are zoom-in images of the box marked in C) at 0% and 5% strain, respectively. The blue, purple, white, grey circles are nitrogen, iodide, lead and carbon atoms, respectively. Hydrogen atoms are marked as small white circles.

## References

(1). Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996,** *77* (18), 3865-3868.

(2). Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for *Ab Initio* Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996,** *54* (16), 11169-11186.