Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Laser-induced microstructuring of two-dimensional layered inorganic-organic perovskites

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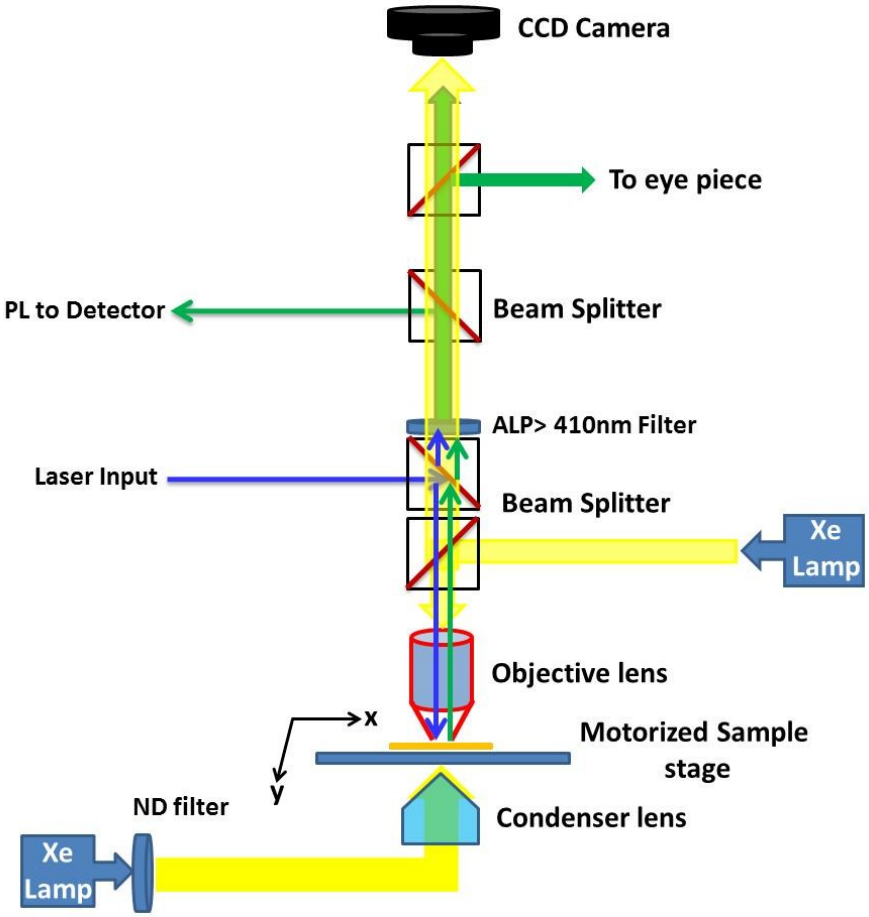

Figure S1. Schematic representation of modified microscope for PL spectra, high-resolution optical images (Bright field and PL images), spatial intensity mapping and spectral line scans. The optical components are, white light source (Xenon lamp), 405nm CW laser (< 20 mW), motorised XY- sample stage, fiber-optic spectrometer and a high-resolution camera. Both PL spectra and PL images were taken using a long-pass filter.

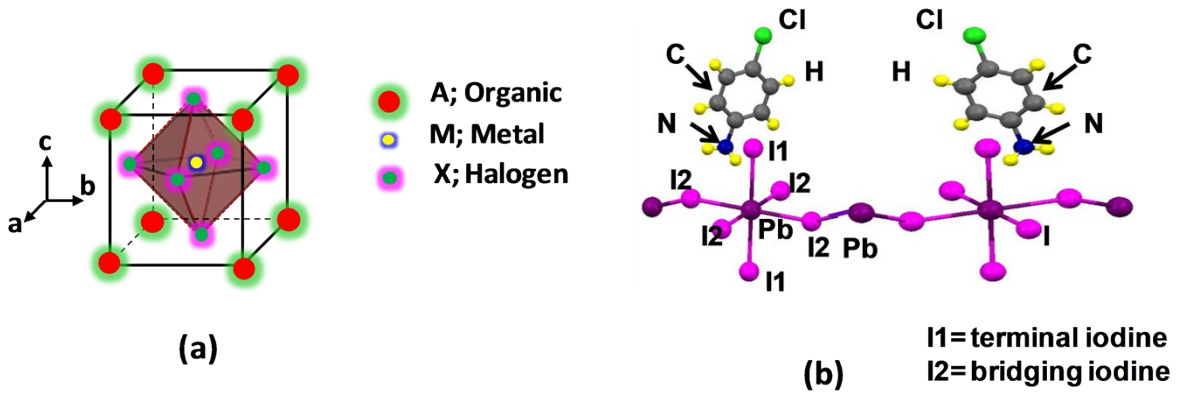

Figure S2. (a) Corner shared MX_6 octahedra (where M is the metal such as Pb^{+2}, Sn^{+2} etc., X is a halide such as Cl^-, Br^- etc.) (b) Schematic crystal packing representation of $(R\text{-}NH_3)_2PbI_4$ where organics are tagged to inorganic by hydrogen bonding. Figure (b) represents crystal packing of 2D CHPI perovskite, where PbI_6 octahedra is connected with organic moiety with week Vander wall interactions and bridging and terminal Iodines are indicated.

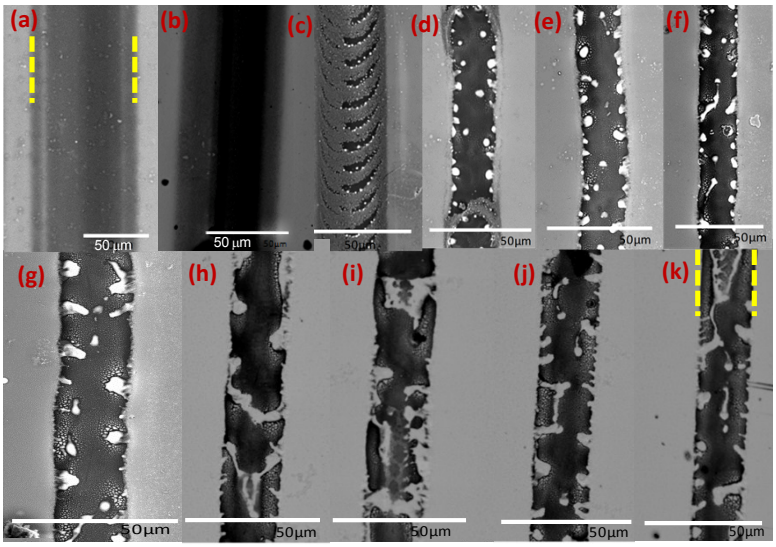

Figure S3. SEM images of laser written tracks on PbI_2 thin film (~135 nm) with different scanning steps (a) 0.0001 mm, (b) 0.001 mm, (c) 0.01 mm, (d) 0.1 mm, (e) 0.2 mm, (f) 0.3 mm, (g) 0.4mm, (h) 1 mm, (i) 2 mm, (j) 4 mm, (k) 8 mm. (II) Estimated channel writing width vs step size. Laser wavelength, λ=410 nm; at fixed laser power density=2.54×10^4 W/cm^2, laser focus spot size ϕ = 18 µm. The resultant laser written track width is indicated by dotted yellow lines in shown in (a) and (k). A plot of estimated channel writing width vs step size at laser power density=2.54×10^4 W/cm^2 is given in Fig. 2 (main text)

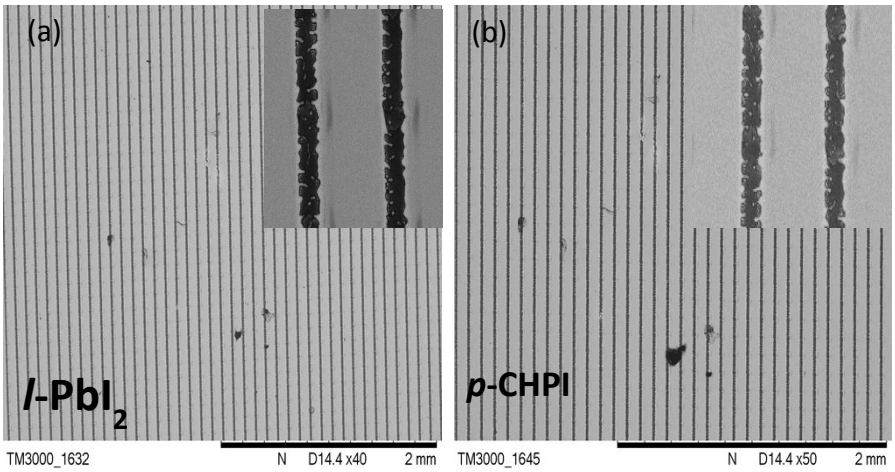

Figure S4. SEM images of Laser writing on (a) *l*-PbI_2 and (b) *l*-CHPI thin films. Laser writing parameters are 2.54x10^4W/cm^2 and scan step size 0.01mm.

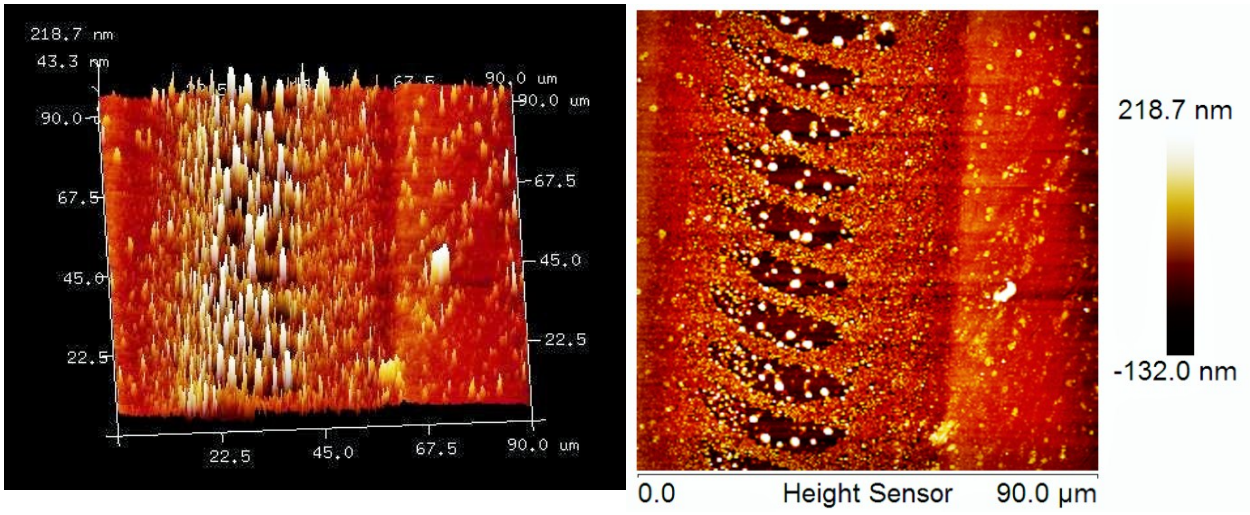

Figure S5. AFM image and three-dimensional view of *l*-PbI_2 showing material agglomeration as nano-pillars at the boundaries. The average roughness in the laser written area is about 28nm compared to the roughness of unwritten area, 11 nm.

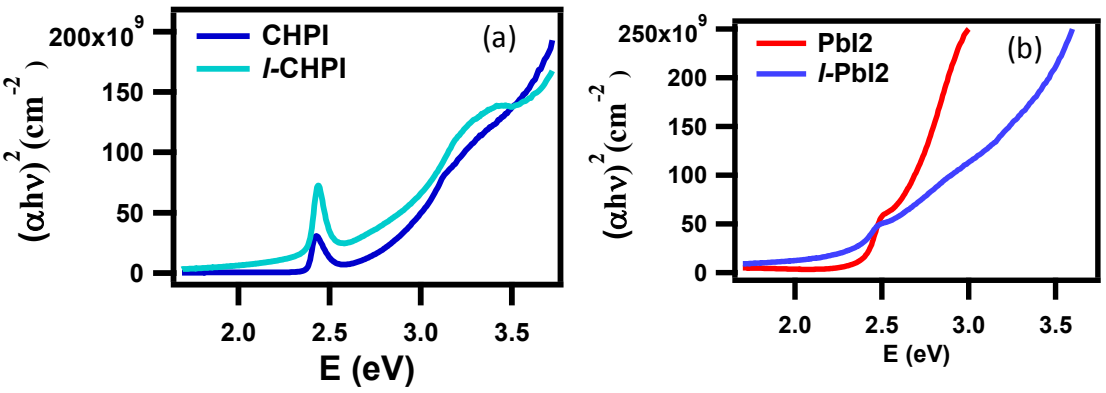

Figure S6. Absorption spectral analysis (Tauc plots) of (a) laser written CHPI (*l*-CHPI) films and (b) PbI_2 (*l*-PbI_2) films along with respective bare films. Clearly before and after the laser irradiation, PbI_2 and CHPI shows a modification in the optical bandgap. However, the band edge shift is more significant in PbI_2 than in CHPI. Furthermore, the exciton absorption, similar to PL, shows a clear blue shift.

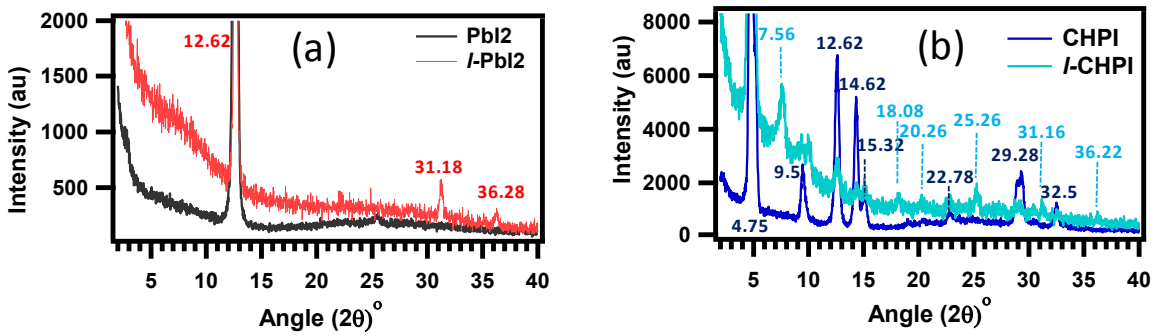

Figure S7. X-Ray diffraction analysis of (a) PbI2 and *l*-PbI_2 (b) CHPI and *l*-CHPI. Figure (b) shows that during the laser irradiation, PbI_2 retain almost the layered arrangement (strong (*100)* diffracted plane at 12.62°), along with other diffraction peaks indicating the distortion in crystal packing. In figure (b) CHPI X-Ray diffraction shows typical (*00l*) modes, indicating the layered arrangements. Whereas, after laser irradiation, diffractions from other planes are also clearly visible, indicating the crystal packing modification/distortion.

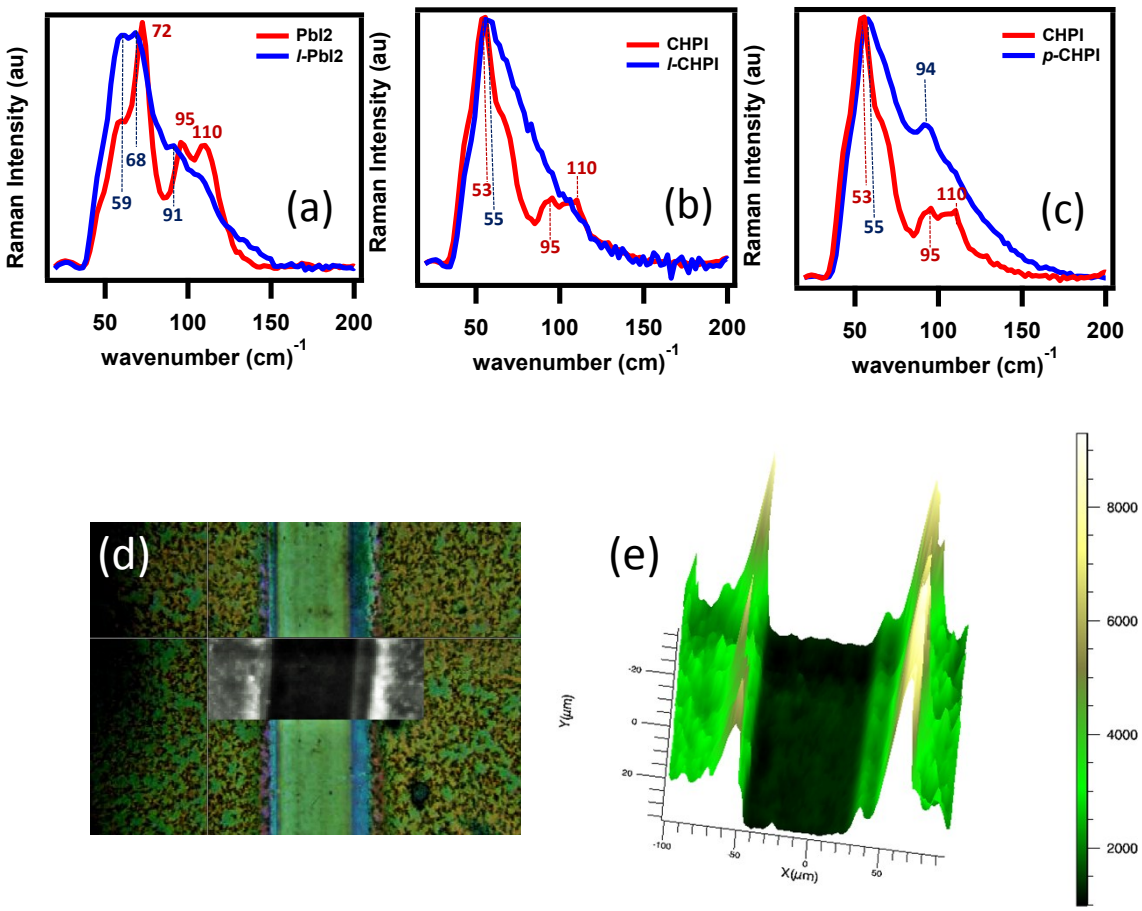

Figure S8. Raman spectra of (a) *l*-PbI_2 and PbI_2 (b) *l*-CHPI and CHPI (c) *p*-CHPI and CHPI films and (d) Raman area mapping 2D image(e) 3D Mapping Image of laser written grooves of CHPI at 53 cm^{-1}. The laser excitation is at 632.7 nm having notch filter close to 50 cm^{-1}.

Warren and Liang reported that when pristine PbI_2 crystals at resonant excitation (517nm) are intercalated with alkylamines, the characteristic and prominent peaks at ~73 and 96cm^{-1} attributed to Pb-I stretching vibrational modes (1T polytype E_g and A_{1g}) completely vanished[J. Phys: Condens. Maters., 5(1993) 6407]. Baibarac et al. and Preda et al. reported strong Raman peaks of PbI_2 single crystals between 70-150cm^{-1}, attributed to polytype 2H and 4H-PbI_2 vibrational modes[J. Solidstate Chem., 182(2009) 87 and J. Phys: Condens. Maters., 18 (2006) 8899]. In our present experiments, while bare PbI_2 films show standard Raman spectral features, the laser written PbI_2 (*l*-PbI_2) showed considerable change in the spectral features-: exclusively the E_g mode merged with a band at 59cm^{-1} which could possibly attributed to transverse optical (TO) phonon modes. On comparison of PbI_2 and

CHPI, the Raman spectra are notably different and indicating the structural changes in *Pb-I* crystal packing. While 96 cm^{-1} (E2g) modes are common, in CHPI the 73cm^{-1} is merged with the mode at 53cm^{-1}. Both *l*-CHPI and *p*-CHPI shows considerable distortion in the PbI network, which is visible in Raman spectra. However the data is inconclusive, a high-resolution spectral data with both resonant and non-resonant excitation would give much clear information.