SUPPORTING INFORMATION

Experimental Section

Sample preparation: $MAPbI_3$ has been synthesised starting from a proper amount of Pb acetate dissolved in an excess of HI acid under nitrogen atmosphere and stirring. The solution is heated to 100°C and the MA solution (40% in water) is added in equimolar amount. A precipitate is formed immediately after the amine addition. The solution is then cooled down to 46°C at 1°C/min, and the precipitate is immediately filtered and dried under vacuum overnight.

High-pressure Experiments: About 100 mg of MAPI were inserted into 5 mm cell made of SiC and pressed at the desired pressure for 5 minutes with the instrumentation described in the paper. After pressure release (few milliseconds), the samples are taken out from the cell and underwent the structural and optical characterizations. All the experiments were repeated on two separate series of samples.

X-ray Diffraction: Gently ground powders of $MAPbI_3$ were deposited in the, 2 mm deep, hollow of a zero background plate (a properly misoriented quartz monocrystal). Diffraction experiments were performed using Cu-Kα radiation (λ = 1.5418 Å) on a vertical-scan Bruker AXS D8 Advance diffractometer in θ:θ mode. Generator setting: 40 kV, 40 mA.

SEM Analysis: Microstructural characterization of the samples was made using a high-resolution scanning electron microscope (SEM, TESCAN Mira 3) operated at 25 kV

PL Experiments: Steady state and time resolved photoluminescence was measured by an Edinburgh FLS920 spectrometer equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185–850 nm). An Edinburgh Xe900 450 W Xenon arc lamp was used as exciting light source. Corrected spectra were obtained via a calibration curve supplied with the instrument. (lamp power in the steady state PL experiments ~ 0.6 mWcm-2, spot area 0.5 cm2) Emission lifetimes were determined with the single photon counting technique by means of the same Edinburgh FLS980 spectrometer using a laser diode as excitation source (1 MHz, λexc = 635 nm, 67 ps pulse width and about 30 ps time resolution after deconvolution) and a Hamamatsu MCP R3809U-50 (time resolution 20 ps) as detector. (laser power in the TRPL experiment ~ 1.6 Wcm-2, spot area 0.3 mm2) (Masi et al. Chem. Sci., 2018, 9, 3200)

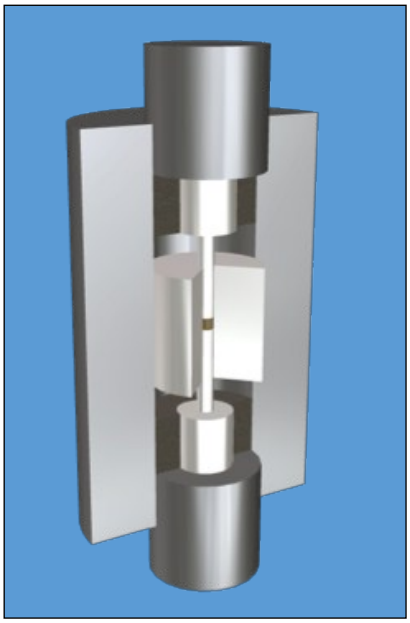

Figure S1 *– Schematic representation of the pressure cell employed in the present work.*

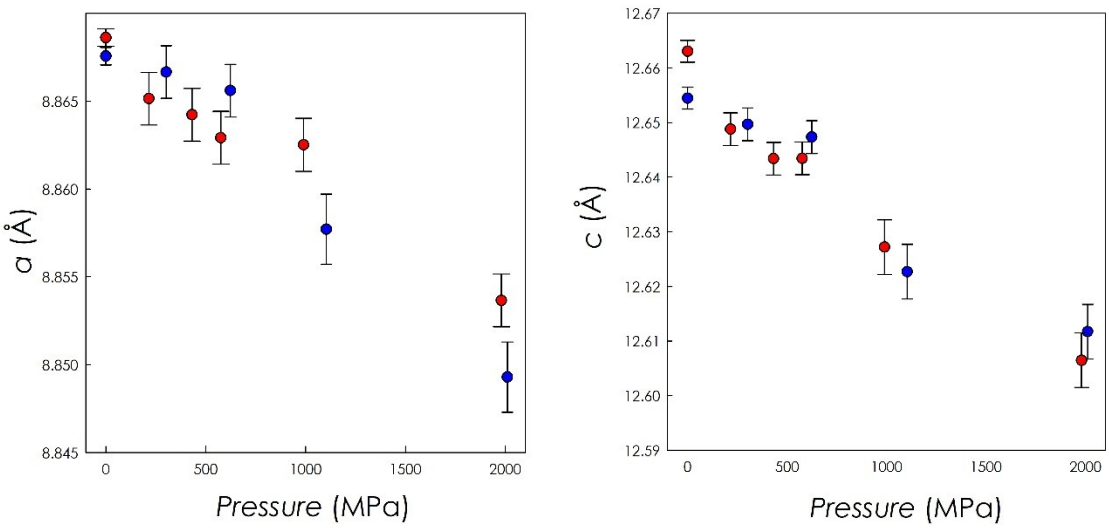

Figure S2 *–a (b) (left panel) and c lattice parameters (right panel) as a function of pressure for MAPI samples determined ex-situ after pressure application for batch 1 (blue circles) ad batch 2 (red circles)*

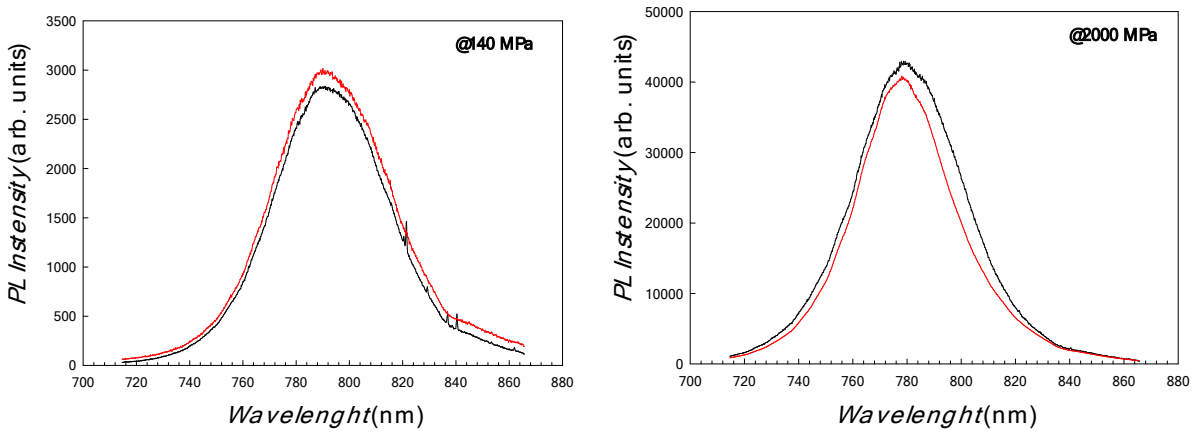

Figure S3 *–PL spectra after the first measurement (black line) and after 15 days (red line) for two representative MAPI samples.*

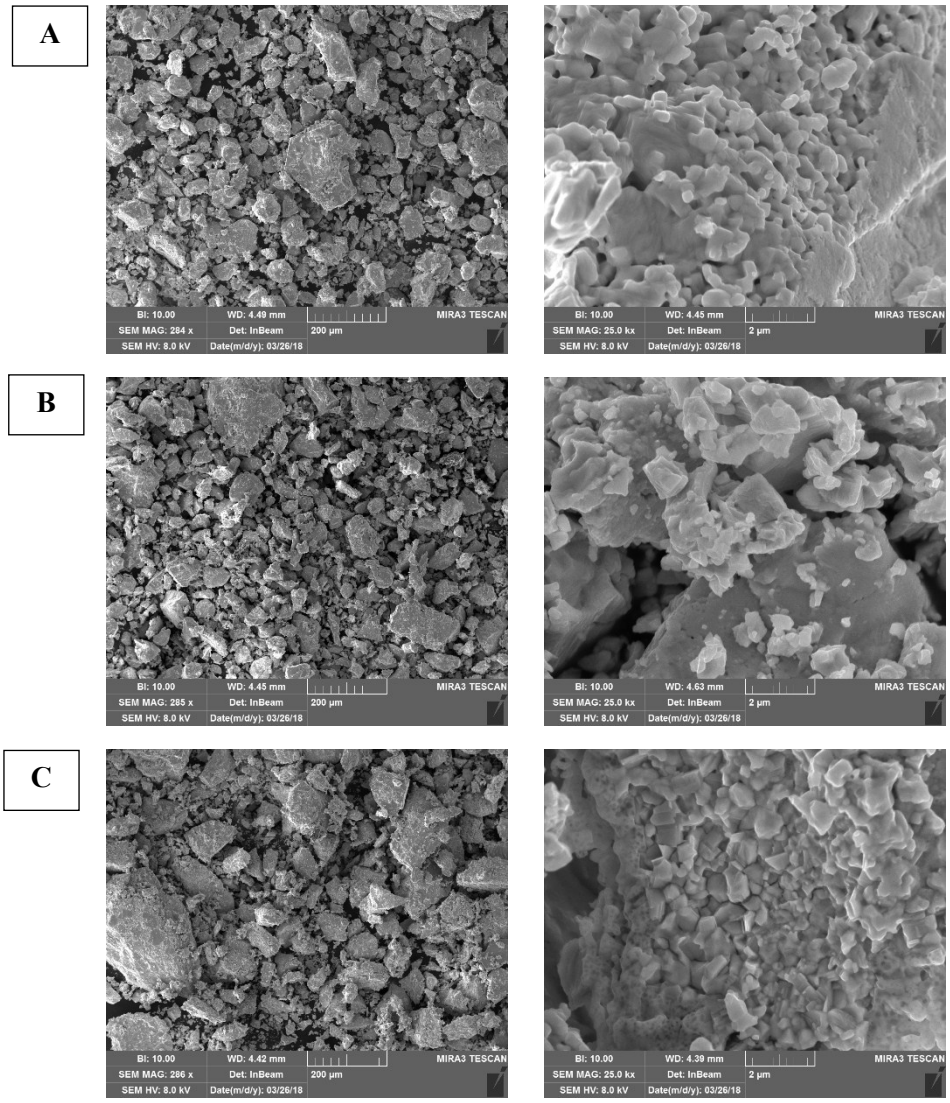

Figure S4 *–Representative SEM images at low and high magnification for MAPI samples pressed at low (216 MPa - A), intermediate (576 MPa - B) and high (2000 MPa - C) pressures*

Table S1 *–Radiative life time determined from time-resolved PL measurements*

	tau 1 (relative weight) ns (%)	tau 2 (relative weight) ns (%)	tau 3 (relative weight) ns (%)
0 MPa	9.3 (7)	57.2 (40)	228 (53)
302 MPa	20.1 (10)	90.0 (39)	394 (51)
624 MPa	12.2 (3)	94.7 (33)	407 (64)
1104 MPa	11.6 (5)	89.5 (37)	345 (58)
2010 MPa	13.8 (2)	98.7 (27)	446 (71)