Supplementary Information

Organic-inorganic Interactions of Single Crystalline Organolead Halide Perovskites Studied by Raman Spectroscopy

Li-Qiang Xie‡, Tai-Yang Zhang‡, Liang Chen‡, Nanjie Guo2, Yu Wang1, Guo-Kun Liu1, Jia-Rui Wang1, Jian-Zhang Zhou1, Jia-Wei Yan1, Yi-Xin Zhao2*, Bing-Wei Mao1*, Zhong-Qun Tian1

1State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, iChEM, Xiamen University, Xiamen 361005 (China).

2School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240 (China).

*Corresponding authors. E-mails: bwmao@xmu.edu.cn, yixin.zhao@sjtu.edu.cn

Figure S1. Photographs of various perovskite single crystals. The colors of MAPbI3 (top left), MAPbBr3 (top right), MAPbBr2.75Cl0.25 (down left), MAPbBr2.67Cl0.33 (down middle) and MAPbBr2.75Cl0.25 (down right) go from dark black to orange, light orange and finally become yellow. The shape of the single crystals agree with that are reported in literature1-4, indicating that their high quality which is sufficient to our Raman experiments here although their size not so large.
Figure S2. Raman spectra of MAPbI$_3$ single crystals excited by 532 nm laser. The spectra indicated with different colors are measured from different sampling points, demonstrating the reproducibility of the measurements. No peak at around 275 cm$^{-1}$ was observed and the photoluminescence background growth up at the frequency region higher than 2400 cm$^{-1}$. 
Figure S3. Raman spectra of MAPbBr$_3$ single crystals (blue), MABr powder (red), and PbBr$_2$ (black). No peak were observed for MABr powder and PbBr$_2$, which means that the band 325 cm$^{-1}$ of MAPbBr$_3$ single crystal does come from neither MABr nor PbBr$_2$. 
Figure S4. Schematic diagram illustration of CASTEP calculated Raman active modes of MABr solid. 

899 cm⁻¹, 996 cm⁻¹, 1252 cm⁻¹, 1447 cm⁻¹, 1525 cm⁻¹, 1604 cm⁻¹, 2877 cm⁻¹, 3011 cm⁻¹, 3109 cm⁻¹, 3188 cm⁻¹
Figure S5 The XRD pattern of 2D perovskite adopt ammonic acids as cation. (3C=β-alanine, 4C=aminobutric acid, 5C=aminovaleric acid)
Figure S6 Thermogravimetric analysis (TGA) of MAPbBr$_{3-x}$Cl$_x$ single crystals in the temperature range of 30 to 800 °C (A) and 30 to 800 °C (B) carried out in nitrogen flow. These perovskites first undergo HX loss at about 250 °C, followed by CH$_3$NH$_2$ loss at about 345 °C. There is no weight loss in the temperature range of 30 to 200 °C, indicating that there is no residual solvent in these crystals. We note that the boiling point of the solvent (DMF) used in the crystal growth is 152.8 °C.


References


