# $CH_3NH_3PbI_{(3-x)}(BF_4)_x$ : Molecular Ion substituted hybrid perovskite

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## Supplementary Information

## Experiment Details

**Synthesis of $CH_3NH_3BF_4$:** In 500mL two neck round bottom flask, 30mL of methylamine ($CH_3NH_2$) solution (33 wt % in absolute ethanol) was dissolved in absolute ethanol (100mL). The solution was then cooled to 0°C followed by dropwise addition of 49mL tetrafluoroboric acid ($HBF_4$, 48 wt % in water) under argon atmosphere. Reaction mixture was stirred at 0°C for 2 hrs and then the solvent was evaporated on rotary evaporator at 50°C to get white colored powder. The compound was dissolved in ethanol and reprecipitated by diethyl ether.

**Synthesis of $CH_3NH_3PbI_{(3-x)}(BF_4)_x$:** Solid state synthesis: $PbI_2$ and $CH_3NH_3BF_4$ were mixed (1:3) at room temperature and ground using mortar pestle in glove box at 110°C for ~1hour. The colour of mixture changes from pale yellow to brown to gray black eventually. The conventional $CH_3NH_3PbI_3$ perovskite was synthesized by reported method.[1]

**Chemical Vapour deposition of organic salt:** A thin film of lead iodide (2M in DMF) on glass was made by spin coating (4000rpm for 30s) and subsequent heating at 70°C for 30 minutes on hot plate in the glove box. Perovskite was made by simple chemical vapour deposition technique. Thin film of $PbI_2$ on glass was exposed to vapours of organic salt ($CH_3NH_3BF_4$) for ~1 hour at 95-100°C.[2]

**Fabrication of photo-detector device:** Transparent Fluorine doped Tin Oxide (FTO) substrates were washed with soap solution followed by deionised water and absolute ethanol. A thin $TiO_2$ compact layer coated on dried FTO by aerosol spray pyrolysis of ethanolic solution (1:9 v:v) of Titanium diisopropoxide bis (acetylacetonate) at 450$^0$C. A 350-400 nm thick mesoporous $TiO_2$ layer composed of 20 nm sized particles (18 N-RT dyesol 1:3.5 diluted in ethanol) was then deposited by spin coating at 4000rpm for 30 sec. The $TiO_2$ film was then annealed at 500$^o$C. The $PbI_2$ solution in DMF (1M) (preheated to 70$^0$C for 0.5 hr) was spin coated on $TiO_2$ film. After drying, the films were exposed to vapours[2] of organic salt ($CH_3NH_3BF_4$) for ~1hr at 90-100$^o$C. Complete formation of perovskite film was indicated by the change of colour from yellow to dark brown. The top contact was made by thermal evaporation of gold (~80 nm).

### XRD measurements with/without IPA washing:

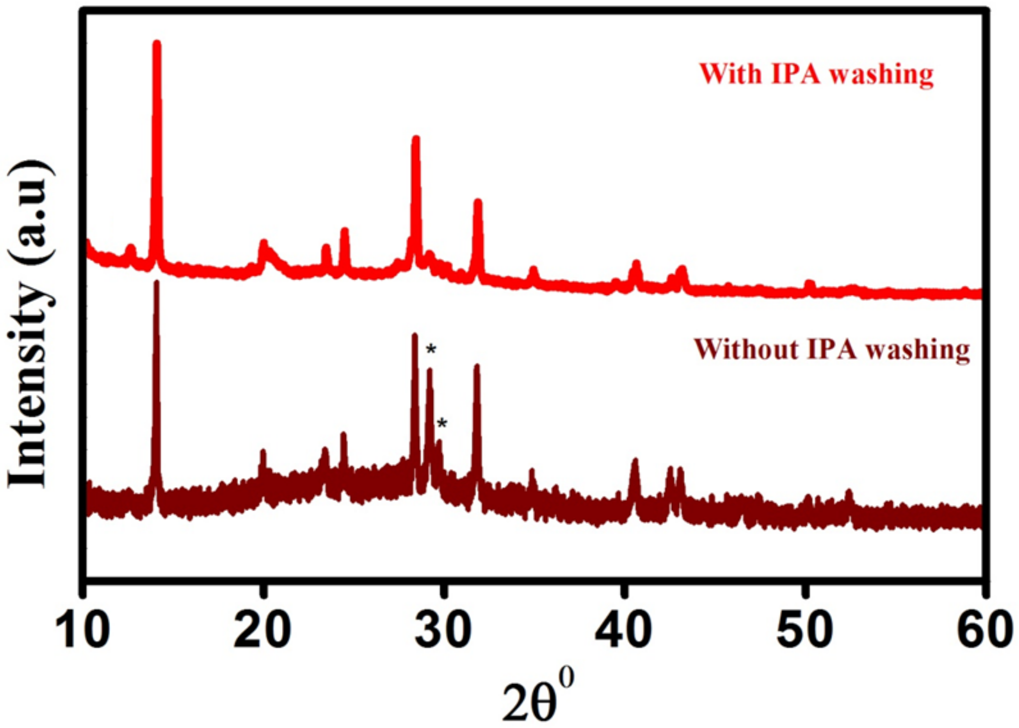

**Figure S1.** (a) XRD of $CH_3NH_3PbI_{(3-x)}(BF_4)_x$ film on glass with and without IPA washing (* impurities related to organic salt).

The chemical vapour deposited film of $CH_3NH_3PbI_{(3-x)}(BF_4)_x$ showed presence of some un-reacted organic impurities (shown by * in figure S1) which were removed by subsequent washing with iso-propyl alcohol (IPA).

### Diffused Reflectance Spectrum (DRS) and Tauc's plot.

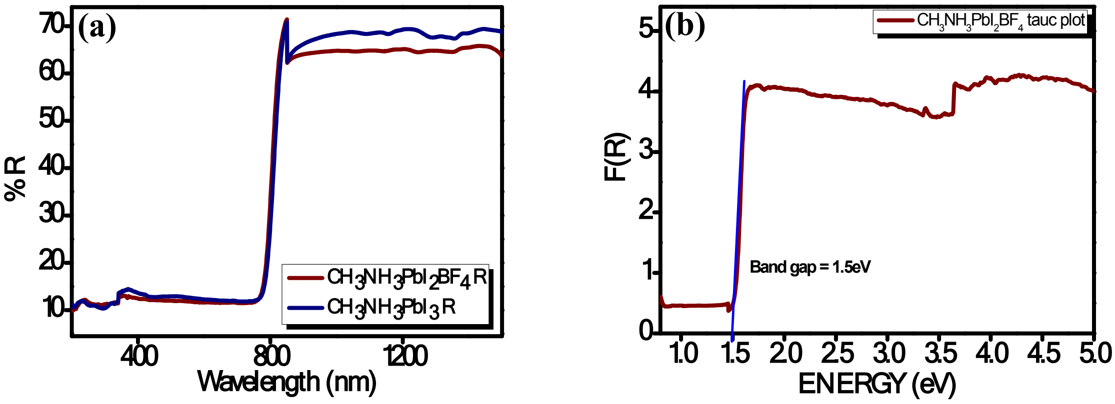

**Figure S2.** (a) Diffused reflectance spectra (DRS) of $CH_3NH_3PbI_{(3-x)}(BF_4)_x$ and $CH_3NH_3PbI_3$ (b) Tauc's plot of $CH_3NH_3PbI_{(3-x)}(BF_4)_x$

## EDAX Measurements at 5kV for boron detection:

Figure S3 shows the result of EDAX measurement for $CH_3NH_3PbI_{(3-x)}(BF_4)_x$ perovskite grown on glass. As boron is low Z element, the EDAX measurement has to be carried out separately at lower operating potential (5kV) for its detection. The result shown below unambiguously establishes the presence of boron in the doped perovskite material.

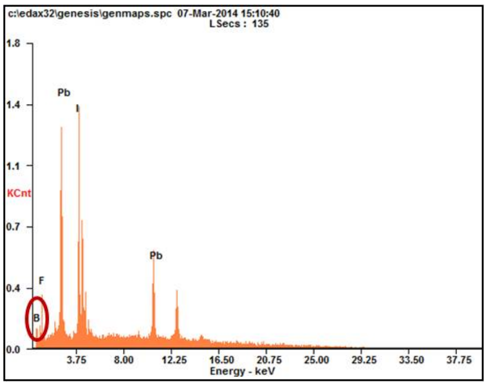

**Figure S3**. EDAX of $CH_3NH_3PbI_{(3-x)}(BF_4)_x$ at low operating potential (5kV) for Boron (low Z element) detection.

## IV curves of photo-detector devices under dark and illumination.

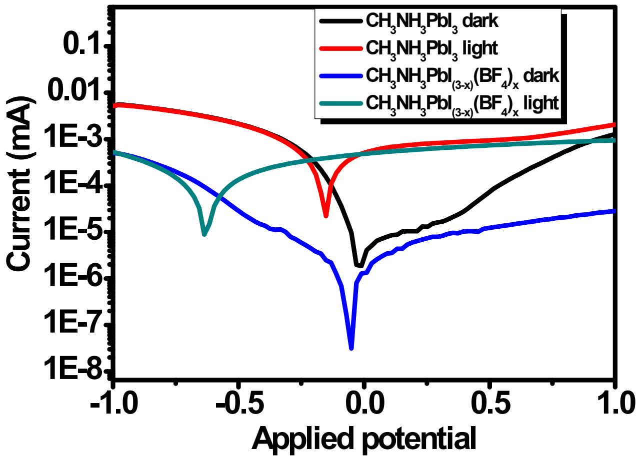

**Figure S4.** Semi-log scale I-V curves of $CH_3NH_3PbI_{(3-x)}(BF_4)_x$ and $CH_3NH_3PbI_3$ photo-detector devices under dark and light.

## References:

(1) Kojima A., Teshima K., Shirai Y., Miyasaka T.; J. Am. Chem. Soc. 2009, *131*, 6050.

(2) Chen, Q.; Zhou, H.; Hong, Z.; Luo, S.; Duan, H.; Wang, H.; Liu, Y.; Li, G.; Yang, Y.; J. Am. Chem. Soc. 2014, 136, 622.