Electronic Supplementary Material (ESI) for RSC Advances.


# Enhancing the stability and efficiency of $MAPbI_3$ perovskite solar cells by theophylline- $BF_4^-$ alkaloid derivatives, a theoretical-experimental approach.

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## Supplementary information

**Table S1.** Parameters used in the incorporation of Theophylline derivatives in the solution of $MAPbI_3$.

| Solution | $PbI_2$ (mg) | $CH_3NH_3I$ (mg) | Theophylline and derivatives (mg) |
|---|---|---|---|
| $MAPbI_3$ | 289 | 100 | 0 |
| $MA_{0.995}(ThPhy)_{0.005}PbI_3$ | 289 | 99.5 | 0.5 |
| $MA_{0.99}(ThPhy)_{0.01}PbI_3$ | 289 | 99 | 1 |
| $MA_{0.985}(ThPhy)_{0.015}PbI_3$ | 289 | 98.5 | 1.5 |
| $MA_{0.995}(ThPhyl\text{-}Cl)_{0.005}PbI_3$ | 289 | 99.5 | 0.5 |
| $MA_{0.99}(ThPhy\text{-}Cl)_{0.01}PbI_3$ | 289 | 99 | 1 |
| $MA_{0.985}(ThPhy\text{-}Cl)_{0.015}PbI_3$ | 289 | 98.5 | 1.5 |
| $MA_{0.995}(ThPhy\text{-}BF_4)_{0.005}PbI_3$ | 289 | 99.5 | 0.5 |

| | | | |
|---|---|---|---|
| $MA_{0.99}(ThPhy\text{-}BF_4)_{0.01}PbI_3$ | 289 | 99 | 1 |
| $MA_{0.985}(ThPhy\text{-}BF_4)_{0.015}PbI_3$ | 289 | 98.5 | 1.5 |

**Table S2a**. Percentage composition of $MA_{0.995}(ThPhy\text{-}Cl)_{0.005}PbI_3$

| Element | Weight % | Atomic % |
|---|---|---|
| **C** | 5.63 | 22.80 |
| **N** | 2.60 | 9.04 |
| **Pb** | 24.48 | 5.75 |
| **Cl** | 4.33 | 5.94 |
| **I** | 40.52 | 15.54 |

**Table S2b**. Percentage composition of $MA_{0.995}(ThPhy\text{-}BF_4)_{0.005}PbI_3$

| Element | Weight % | Atomic % |
|---|---|---|
| **C** | 8.13 | 33.23 |
| **N** | 2.78 | 9.72 |
| **F** | 2.38 | 6.15 |
| **Pb** | 27.43 | 6.50 |
| **I** | 43.77 | 16.93 |

## S1. Synthesis of theophylline derivatives.

*Synthesis of ThPhyl-Cl, (Theophylline chlorhydrate, 1,3-dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-9-ium chloride).*

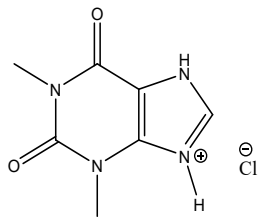



**Figure S1.** Structure of **ThPhyl-Cl.**

In a Schlenk flask, 0.5 g (2.78mmol) of Theophylline (anhydrous, ≥99%, Merck) was weighed and solved in 5ml of distilled water. The mixture was sonicated for 30 minutes. After this period, 357.3 µL (4.17mmol) of hydrochloric acid (37% in water) was added and the mixture was stirred for 30 minutes and sonicated for 30 minutes. After this period, the water was evaporated under a vacuum. Quantitative yield. White crystalline solid. $^1H$ NMR ($CDCl_3$, 25°C; δ (ppm)): 7.84 (s, 1H); 3.68 (s, 3H); 3.50 (s, 3H); 2.20 (s, 1H). FT-IR ($cm^{-1}$): 3573 (C-H); 2993.2 and 2914.5 ($CH_3$); 2626 and 2572 (N-H); 1952 and 1748 (C=O).

*Synthesis of ThPhyl-$BF_4$, (Theophylline Tetrafluoroborate; 1,3-dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-9-ium tetrafluoroborate).*

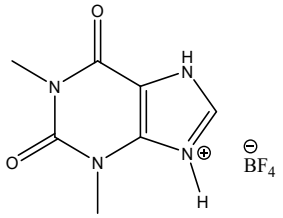


**Figure S2.** Structure of **ThPhyl-$BF_4$**.

In a Schlenk flask, 0.5 g (2.78mmol) of Theophylline (anhydrous, ≥99%, Merck) was weighed and solved in 5ml of distilled water. The mixture was sonicated for 30 minutes. After this period, 363.3 µL (2.78 mmol) of tetrafluoroboric acid solution (48% in $H_2O$) was added and the mixture was stirred for 30 minutes and sonicated for 30 minutes. After this period, the water was evaporated under a vacuum. Quantitative yield. White crystalline solid. $^{1}$H NMR (DMSO-$d_6$, 25°C; δ (ppm)): 8.08 (s, 1H); 3.43 (s, 3H); 3.23 (s, 3H). $^{11}$B NMR (DMSO-$d_6$, 25°C; δ (ppm)): -1.9 (S, 1B). FT-IR ($cm^{-1}$): 3764.9 (C-H); 3079 ($CH_3$); 2625 (N-H); 1952, 1748 (C=O); 1149, 588 ($BF_4^-$).

## S2. Additive characterization

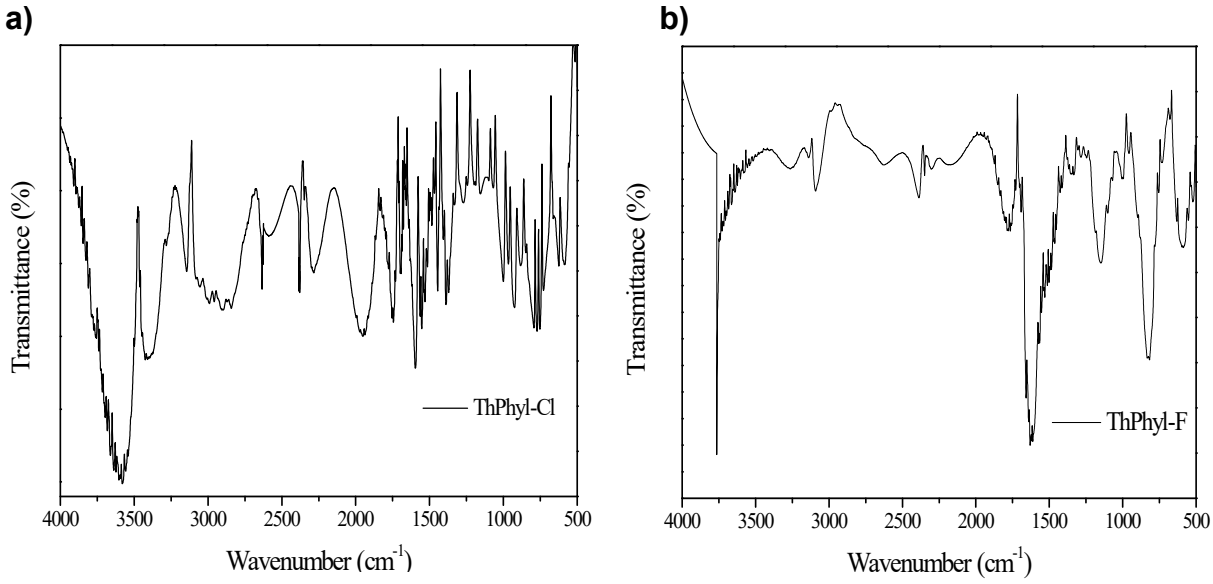



**Figure S3.** FTIR of theophylline derivatives: a) ThPhyl-Cl; b)ThPhyl-F

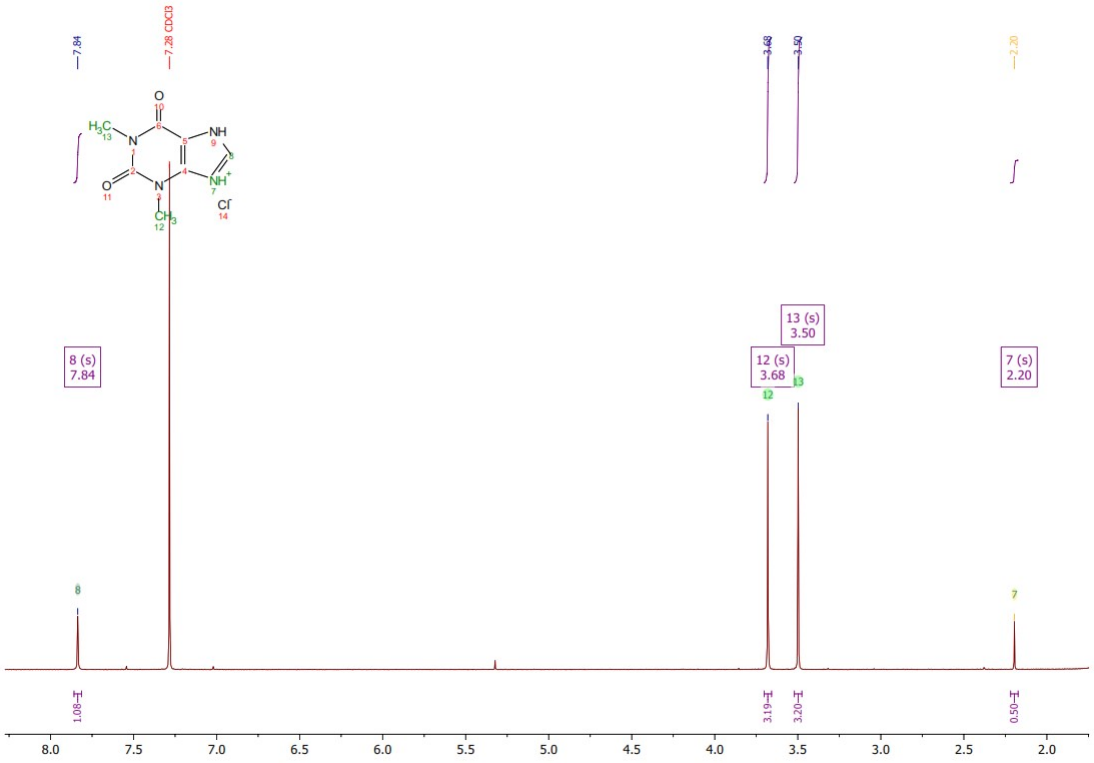



**Figure S4.** $^1$H RMN of **ThPhyl-Cl.** $CDCl_3$, 500MHz.

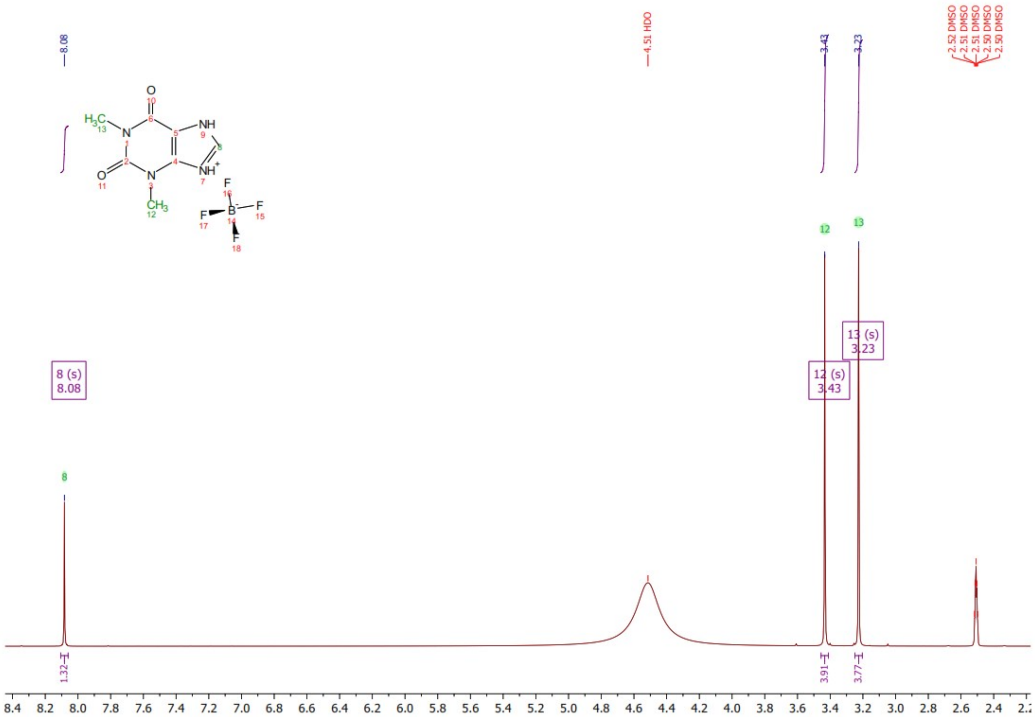



**Figure S5.** $^1$H RMN of **ThPhyl-$BF_4$.** DMSO-$d_6$, 500MHz.

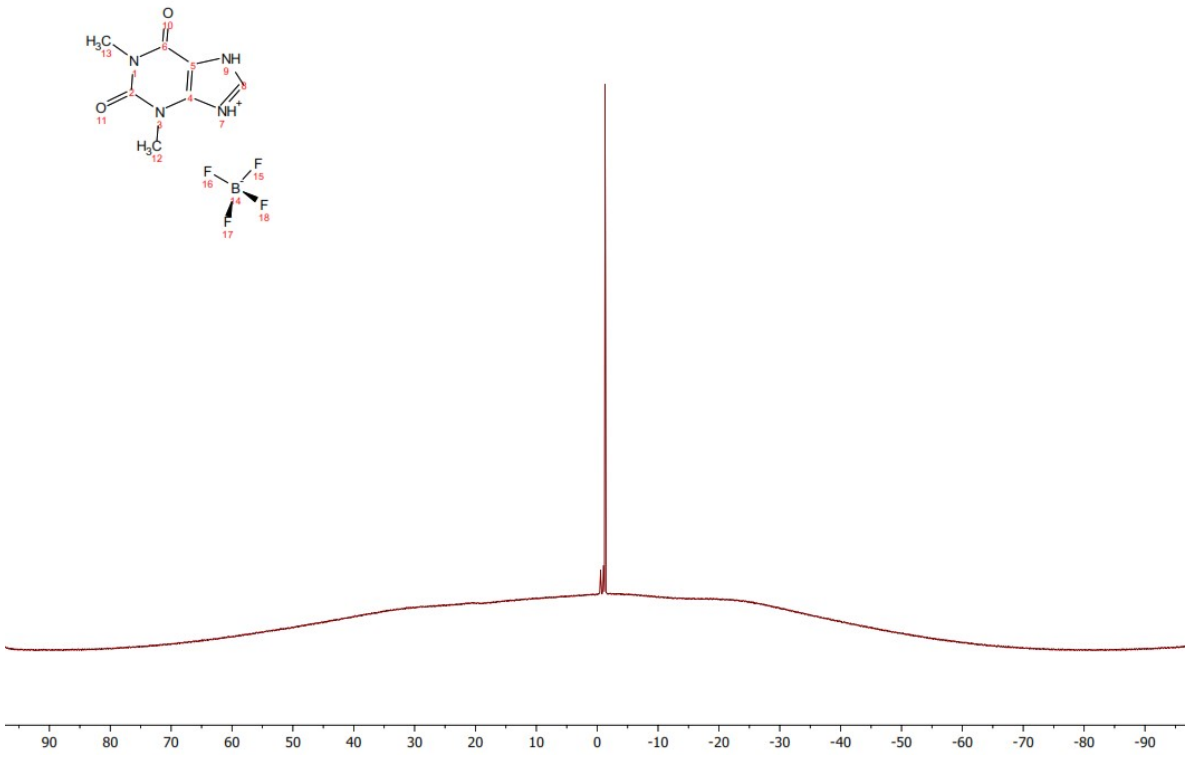



**Figure S6.** $^{11}$B RMN of **ThPhyl-BF$_4$.** DMSO-d$_6$, 500MHz.

## S3. Device fabrication

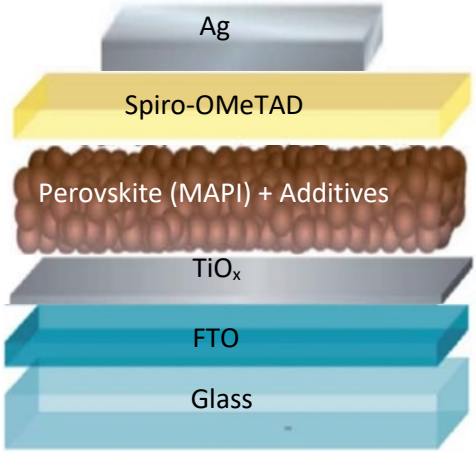
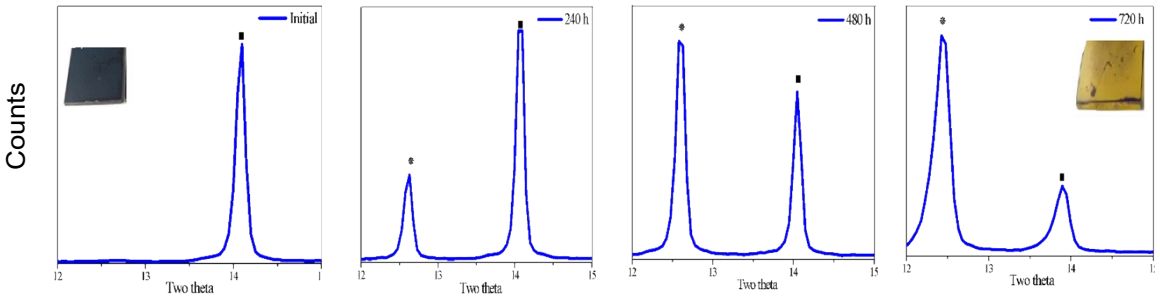


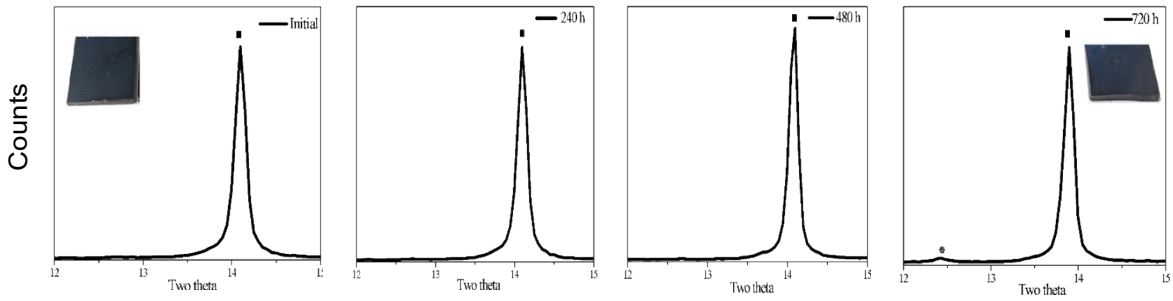

**Figure S7.** Configuration of the cells based on perovskite MAPbI$_3$ with **ThPhyl** derivatives.

## S4. Stability.

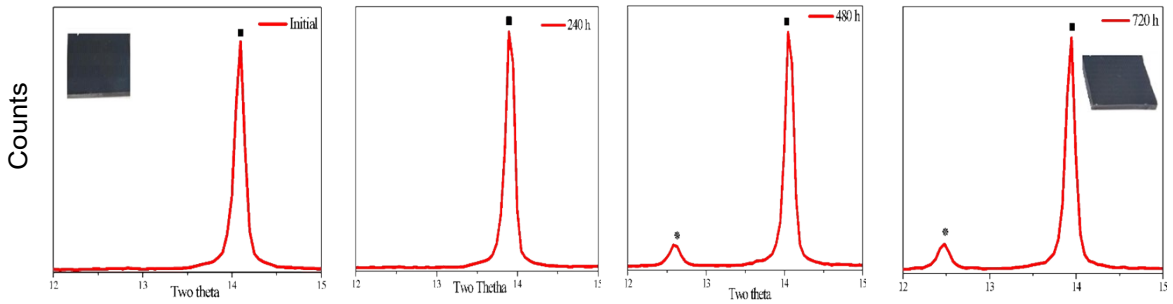
a)$MAPbI_3$




b) $MA_{0.995}(ThPhy)_{0.005}PbI_3$




c)$MA_{0.995}(ThPhy\text{-}BF_4)_{0.005}PbI_3$




d)$MA_{0.995}(ThPhy\text{-}Cl)_{0.005}PbI_3$

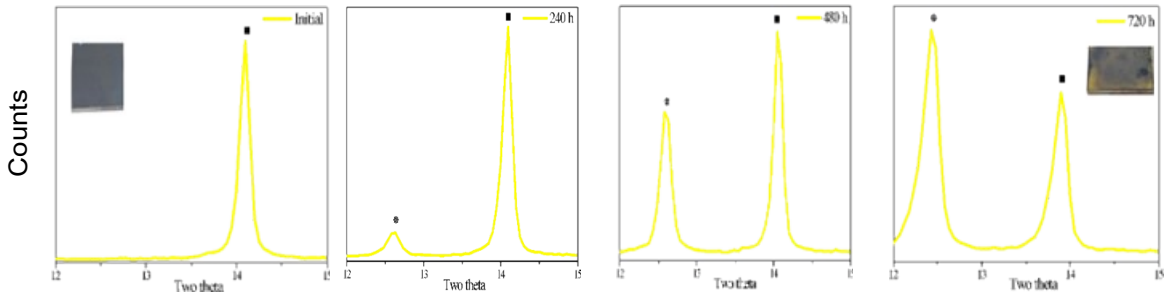
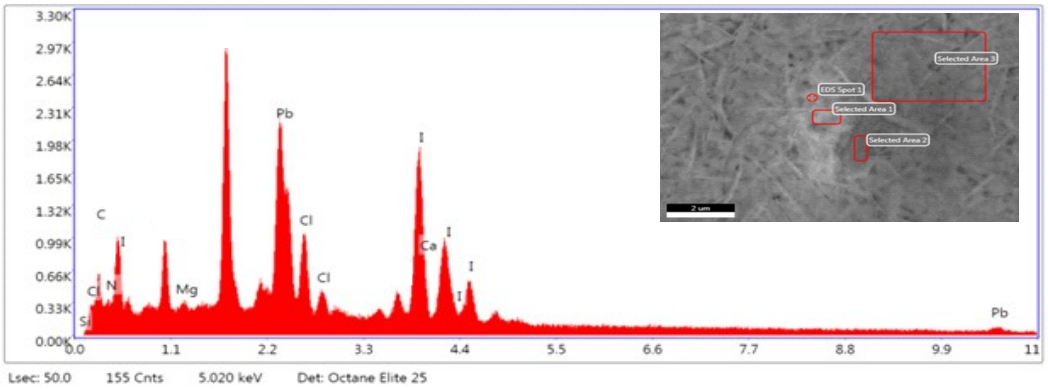



**Figure S8**. Highlighted diffraction profiles in the range from 2θ =12º-15º.

**a)**




**b)**

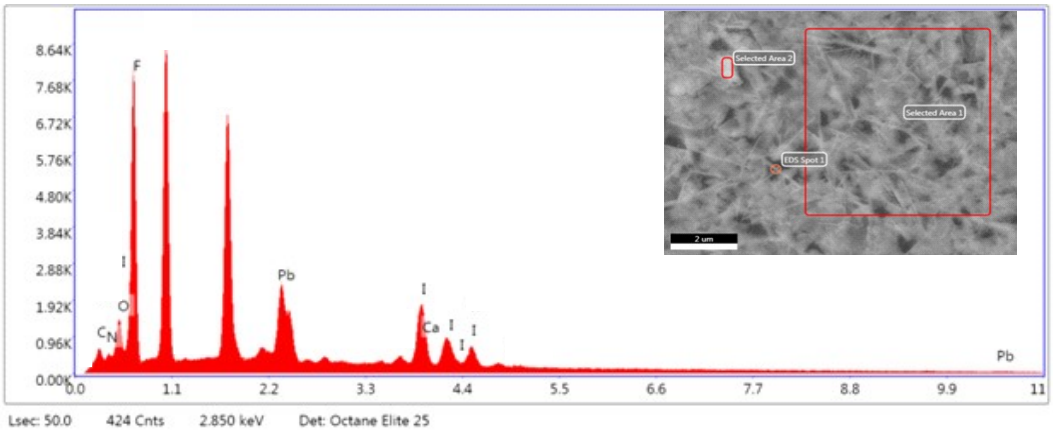



**Figure S9**. EDS analysis of thin films: a) $MA_{0.995}(ThPhy\text{-}Cl)_{0.005}PbI_3$ ; b) $MA_{0.995}(ThPhy\text{-}BF_4)_{0.005}PbI_3$