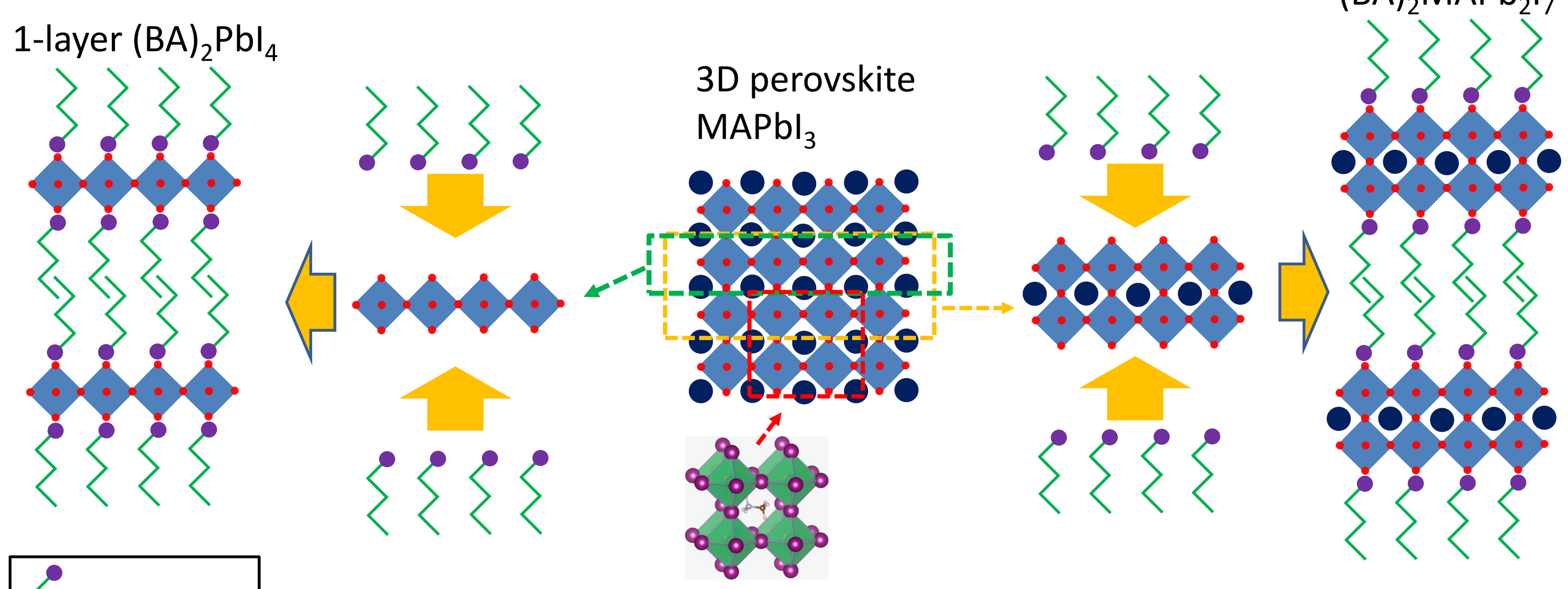
# Role of methylammonium in 2D perovskite $(BA)_2(MA)_nPb_nI_{3n+1}$

Wei-Liang Chen[1], Tzu-Pei Chen[2], Chinnambedu Murugesan Raghavan[2], Cheng-Chieh Lin[2], Depei Zhang[3], Tianran Chen[3], Chao-Yuan Lo[1], Seung-Hun Lee[3], Chun-Wei Chen[2], and Yu-Ming Chang[1]
[1]Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan
[2]Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan
[3]Department of Physics, University of Virginia, Charlottesville, USA
Presenting author E-mail: wechen@ntu.edu.tw

## *Introduction*

Solar cells based on hybrid organic-inorganic perovskite (HOIP) such as methylammonium lead iodide ($MAPbI_3$) have achieved efficiency above 22% [1], but are prone to thermal and moisture instabilities. One strategy in overcoming these instabilities is to replace the $MA^+$ ion with longer cation such as butylammonium ($BA^+$) to create 2D HOIP. Although these 2D perovskites have shown improved stability, their photovoltaic efficiencies still fall behind that of HOIP based solar cells [2]. Finding suitable material remains important for improving the efficiency of 2D HOIP. Previous studies have show that the organic cation can extend the carrier lifetime by polaron effect and improve the photovoltaic efficiency of HOIP [3]. In this study, we investigate one- two- and three- layer 2D hybrid organic inorganic perovskite $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n=1,2,3) by temperature dependent PL and TRPL. The observed PL lifetime jumps at the phase transition temperatures indicate that both the $BA^+$ and $MA^+$ ion can increase charge carrier lifetime by polaron effect, with the inclusion of $MA^+$ in the two- and three- layer samples leading to a greater lifetime increase. Our result show that the polaron effect of both the barrier organic ion the organic ion inside the inorganic cage should be considered in selecting suitable 2D HOIP for solar cell applications.

## *2D Perovskite Structure*



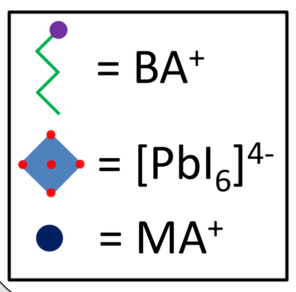




**Fig.1** Structure of 1- and 2- layer (n=1,2) 2D perovskite $(BA)_2PbI_4$ and $(BA)_2MAPbI_7$ can be obtained from 3D perovskite $MAPbI_3$ by replacing $MA^+$ with the longer $BA^+$.

## *Charge Screening in $MAPbI_3$*

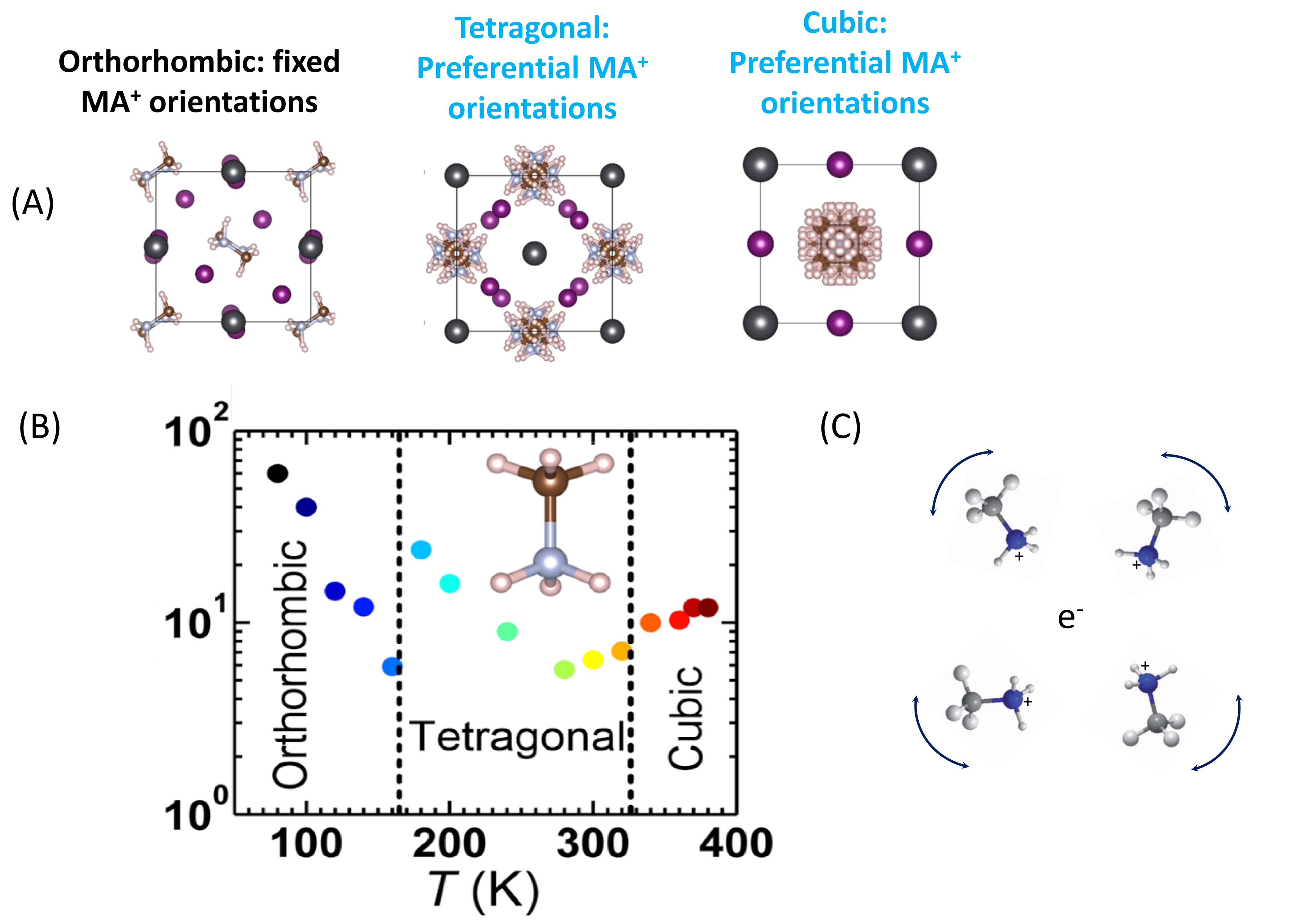



**Fig. 2** (A) Structure of $MAPbI_3$ showing the possible orientations of the $MA^+$ ion, based on neutron diffraction experiment. In the orthorhombic phase, $MA^+$ has fixed orientation with the lowest rotational entropy, while in the tetragonal and cubic phase, $MA^+$ ion has increased rotational entropy with several preferential orientations. (B) Fitted PL lifetime of $MAPbI_3$ as a function of temperature. When $MAPbI_3$ change from orthorhombic to tetragonal phase, there is a factor of ~4 increase in rotational entropy (fixed orientation -> preferential orientation) and the PL lifetime show a jump at the transition temperature. When $MAPbI_3$ changes from tetragonal to the cubic phase, there is not much change in the rotational entropy (preferential orientation -> preferential orientation) and the PL lifetime does not show much change. (C) Schematic diagram showing the screening of charges by rotating $MA^+$ ion.

## *Temperature Dependent Photoluminescence*

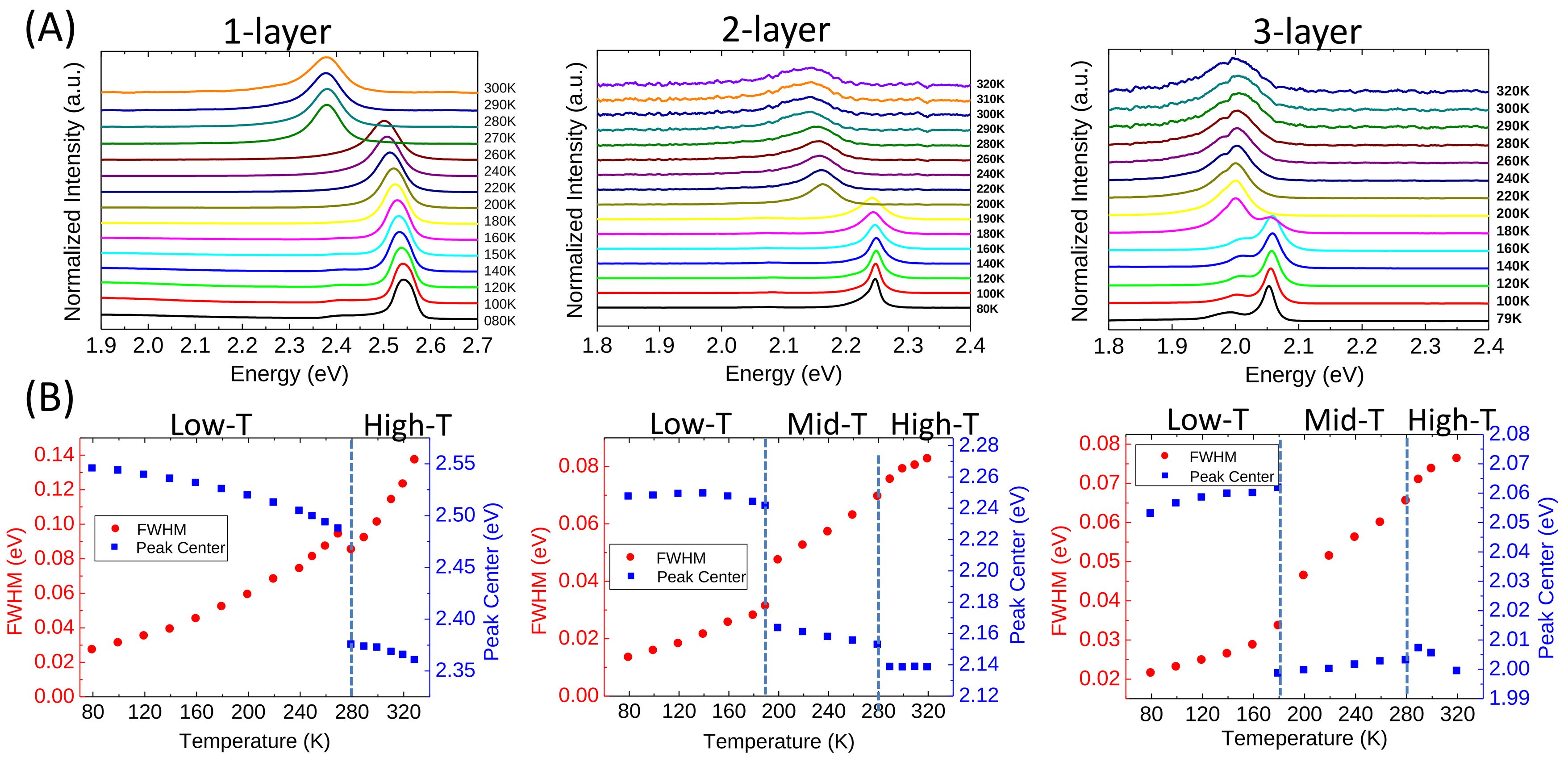



**Fig. 3** (A) Temperature dependent PL from 1-, 2-, and 3-layer 2D perovskite $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$. The main PL peak position and FWHM are shown in (B). A shift in PL at 280K can be observed for all samples corresponding to a phase transition that breaks the Van der Waal force between the $BA^+$ ions. For 2- and 3-layer sample containing $MA^+$ ion, an additional transition occurs at 180K – 190K, similar to the orthorhombic-tetragonal transition of $MAPbI_3$, but is due to both the $BA^+$ and the $MA^+$ ion.

## *Temperature Dependent TRPL*

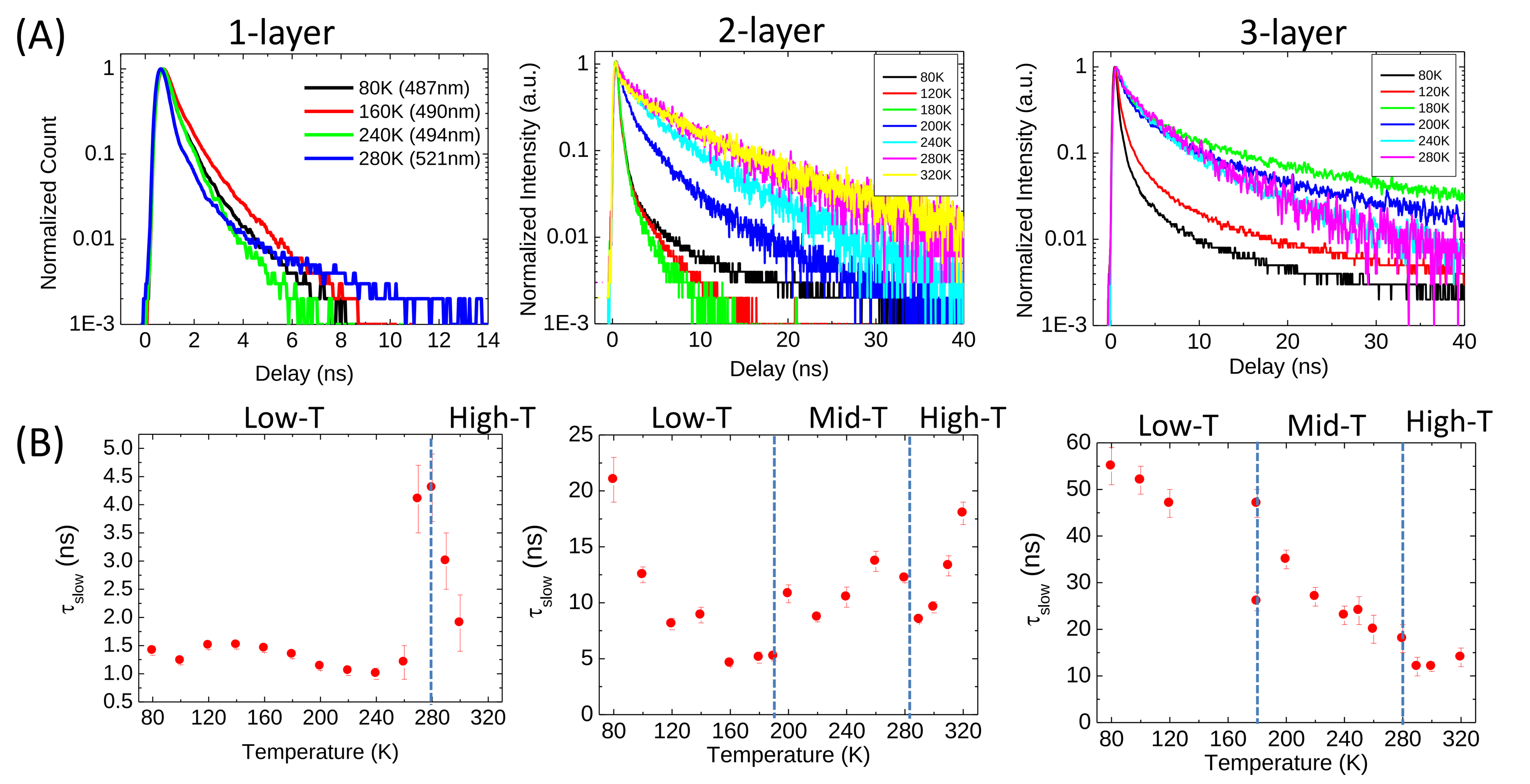



**Fig. 4** (A) Selected temperature TRPL from 1-, 2-, and 3-layer 2D perovskite $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$, with the slow component of the fitted lifetime shown in (B). For 1-layer sample, a factor of ~3 jump in lifetime is observed for the transition associated with the $BA^+$ ion. For 2- and 3-layer samples containing $MA^+$, the lifetime are overall longer than the 1-layer sample. In addition, a jump in lifetime is observed for the 180K-190K transition similar to the orthorhombic-tetragonal transition of $MAPbI_3$, where an increased in the rotational entropy of the $MA^+$ drives a phase transition and increase PL lifetime [4].

## *Conclusion*

- 1-layer $(BA)_2PbI_4$ show phase transition at 280K. The freeing of $BA^+$ ion increased the charge carrier lifetime by a factor of ~3
- In addition to 280K transition associated, 2- and 3-layer sample containing $MA^+$ have an additional phase transition at ~180K-190K similar to $MAPbI_3$ and show similar lifetime increase as the orthorhombic-tetragonal transition of $MAPbI_3$.
- Both $BA^+$ and $MA^+$ cation in 2D perovskite series contribute to polaronic charge screening and increase the charge carrier lifetime

## *References*

[1] https://www.nrel.gov/pv/assets/images/efficiency-chart.png
[2] Energy Environ. Sci., 2018, 11, 3349
[3] Proc. Natl. Acad. Sci. U. S. A., 2017, 114 (29), 7519-7524
[4] Sci. Adv. 2016, 2, e1601650; Phys. Chem. Phys. 2015, 17, 31278

## *Acknowledgement*

The work at National Taiwan University is supported by Ministry of Science and Technology of Taiwan (MOST 105-2119-M-002-046-MY3).