

Enhanced Charge Transport by Incorporating Formamidinium and Cesium Cations for Two-Dimensional Perovskite Solar Cells

Liguo Gao^[a,c], Fei Zhang^{*[a]}, Xihan Chen^[a], Chuanxiao Xiao^[b], Bryon W. Larson^[a], Sean P. Dunfield^[b,d,e], Joseph J. Berry^[b], Kai Zhu^{*[a]}

Abstract: Organic-inorganic hybrid two-dimensional (2D) perovskites ($n \leq 5$) have recently attracted significant attention due to their promising stability and optoelectronic properties. Normally, 2D perovskites contain a mono cation (e.g., methylammonium (MA^+) or formamidinium (FA^+)). Here, we report for the first time on fabricating 2D perovskites ($n=5$) with mixed cations of MA^+ , FA^+ , and cesium (Cs^+). The use of these triple cations leads to the formation of a smooth, compact surface morphology with larger grain size and fewer grain boundaries compared to the conventional MA -based counterpart. The resulting perovskite also exhibits longer carrier lifetime and higher conductivity in triple-cation 2D perovskite solar cells (PSCs). The power conversion efficiency (PCE) of 2D PSCs with triple cations was enhanced by more than 80% (from 7.80% to 14.23%) compared to PSCs fabricated with a mono cation; the PCE is also higher than that of PSCs based on binary-cation ($\text{MA}^+\text{-FA}^+$ or $\text{MA}^+\text{-Cs}^+$) 2D structures.

Organic-inorganic lead halide perovskite solar cells (PSCs) have shown remarkable development and prospective application due to their unique advantages, such as high absorption coefficients, excellent carrier transport, low cost, and tunable compositions, thereby allowing easy fabrication by various processes.^[1] Recent effort has resulted in a PCS with certified power conversion efficiency (PCE) of 24.2%.^[2] However, the issue associated with long-term stability against moisture, heat, and light is still a challenge hindering PSCs for practical applications.^[3] Two-dimensional (2D) perovskites have recently received more attention for improving the stability of PSCs. Key advantageous photophysical properties in three-dimensional (3D) perovskites can be maintained in 2D perovskite crystals.^[4] It is widely reported that bulky organic cations—e.g., butylammonium (BA^+), ethylenediammonium (EDA^{2+}), or phenylethylammonium (PEA^+)—in 2D perovskites can provide steric hindrance that blocks the moisture invasion from the surface-

adsorbed water during the initial step of decomposition.^[5] This makes 2D perovskites promising candidates for optoelectronic devices that require long-term chemical stability.^[6] In addition to hydrophobic properties, many other interesting properties, such as quantum confinement effects,^[7] simple design of spacer cations,^[8] higher activation energy of ion migration,^[9] and more make 2D perovskites attractive. Nevertheless, some unfavorable characteristics have been identified, such as the undesired orientation of the layered structures in 2D PSCs, which can cause charge-transport problems that lead to charge accumulation and recombination losses.^[10]

Studies have shown that cesium (Cs) ions are effective in assisting the crystallization of perovskite due to entropic stabilization.^[11] By doping the Cs^+ cation into a 2D $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ perovskite layer, Liu et al. reported a PCE of 13.7% based on a hot-casting method.^[12] By partially replacing MA^+ with Cs^+ , both the grain size and surface quality of 2D perovskite films are effectively improved, resulting in reduced trap state density, superior charge-carrier mobility, and improved thermal stability. Zhou et al. reported that FA^+ incorporation can effectively control $\text{BA}_2(\text{MA}_x\text{FA}_{1-x})_3\text{Pb}_4\text{I}_{13}$ crystallization kinetics, which reduces nonradiative recombination centers to acquire high-quality films with a limited non-oriented phase.^[13] Studies have shown that perovskites with triple cations ($\text{Cs}^+\text{-FA}^+\text{-MA}^+$) could suppress yellow phase impurities and eliminate halide segregation, compared with binary cations in 3D perovskite-based solar cells.^[14] The gain in Gibbs free energy for the ternary-cation ($\text{Cs}^+\text{-FA}^+\text{-MA}^+$) mixture showed improved structural stability when compared to $\text{MA}^+\text{-FA}^+$ - and $\text{MA}^+\text{-Cs}^+$ -based binary-cation mixtures.^[15] Moreover, in ternary mixtures, reduced carrier recombination at the TiO_2 /perovskite interface was also obtained, which, in turn, improved open-circuit voltage (V_{oc}).^[16] However, no studies have been done to examine the effect of triple cations in 2D PSCs.

In this paper, triple cations were introduced to BA^+ to form $\text{BA}^+\text{-Cs}^+\text{-MA}^+\text{-FA}^+$ 2D perovskites ($n = 5$, n is determined by the precursor composition).^[8,12,13] We find that perovskites based on triple cations ($\text{Cs}^+\text{-FA}^+\text{-MA}^+$) exhibit smooth, compact surface morphology with larger apparent grain size and fewer observed boundaries compared to the mono-cation (MA^+) and binary-cation ($\text{MA}^+\text{-FA}^+$ and $\text{MA}^+\text{-Cs}^+$)-based 2D perovskites. In addition, longer carrier lifetime, greater mobility, and higher conductivity in 2D PSCs were obtained using triple cations. The PCE of 2D PSCs was enhanced by about 81% and 22%–26% compared to 2D PSCs based on the mono cation and binary cations, respectively.

[a] Dr. L. Gao, Dr. F. Zhang*, Dr. X. Chen, Dr. B. W. Larson, Dr. K. Zhu*
Chemistry and Nanoscience Center, National Renewable Energy Laboratory,
Golden, Colorado 80401, USA

Email: Fei.Zhang@nrel.gov; Kai.Zhu@nrel.gov

[b] Dr. C. Xiao, S. P. Dunfield, Dr. J. J. Berry
Materials Science Center, National Renewable Energy Laboratory, Golden,
Colorado 80401, USA

[c] Dr. L. Gao
Department of Chemistry, Colorado School of Mines, Golden, CO, USA.

[d] S. P. Dunfield
Renewable and Sustainable Energy Institute, University of Colorado, Boulder,
CO 80309, USA.

[e] S. P. Dunfield
Materials Science and Engineering Program, University of Colorado, Boulder,
CO 80309, USA.

Supporting information for this article is given via a link at the end of the document.

The triple-cation ($\text{Cs}^+\text{-FA}^+\text{-MA}^+$) mixture used to replace the mono cation (MA^+) is shown schematically in Figure 1A and B, where small amounts of Cs^+ and FA^+ were integrated into the perovskite lattice to substitute for MA^+ . To demonstrate the effect of triple cations in the 2D perovskite precursor, we carried out a simple perovskite deposition at room temperature without using any additive, based on the device structure of FTO/compact- TiO_2 /perovskite/spiro-MeOTAD/Au, where current density-voltage (J - V) curves of devices were recorded under standard AM1.5G illumination (100 mW cm^{-2}). The device fabricated by $\text{BA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ perovskite films gives a PCE of 7.80%, as shown in Figure 1C and Table S1. We have also explored the impact of different stoichiometric ratios on the performance, as shown in Figure S1. The $\text{BA}_2(\text{Cs}_{0.02}\text{MA}_{0.64}\text{FA}_{0.34})_4\text{Pb}_5\text{I}_{16}$ -based device yields the highest PCE of 14.23%, with a V_{oc} of 1.13 V, short-circuit current density (J_{sc}) of 18.23 mA cm^{-2} , and fill factor (FF) of 0.69. Compared to the mono cation devices, the PCE of PSCs with triple cations increases more than 80% with photovoltaic parameters (V_{oc} and FF) improving by a wide margin (Table S1). The suppressed hysteresis is mainly due to increased charge carrier mobility and lifetime which will be discussed below.^[14a,17] PSCs fabricated with binary cations have also been investigated, and the J - V results are shown in Figure S2. PSCs based on triple cations possess much higher PCE than that of PSCs based on either the mono or binary cations. Figure 1D shows external quantum efficiency (EQE) spectra of the corresponding PSCs. The integrated current densities estimated from the EQE spectra are in good agreement with the J_{sc} values obtained from the J - V curves. The stabilized power outputs from the $\text{BA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ and $\text{BA}_2(\text{Cs}_{0.02}\text{MA}_{0.64}\text{FA}_{0.34})_4\text{Pb}_5\text{I}_{16}$ PSCs are 7.01% and 14.15%, respectively (Figure 1E), which are consistent with the J - V measurements. We also evaluated the reproducibility of the device performance by characterizing about 20 cells. The box chart of the PCE parameters of these devices (Figure S1) indicates good reproducibility. The PCE of 2D PSCs based on PEA^+ with triple cations was also enhanced compared to PSCs fabricated with a mono cation, as shown in Figure S3, indicating this is a general way to improve performance.

Long-term stability of non-encapsulated PSCs was evaluated at 80°C and relative humidity (RH) of 15%–20% (ISOS-D-2), and the results are shown in Figure 1F. The triple-cation-based devices maintained 74% of their initial PCE after 600 h whereas the PCE decreased to 30% of their initial values for mono-cation-based PSCs. The improved environmental stability of the triple-cation-based 2D PSCs is consistent with the better hydrophobicity (Figure 1F inset images) as well as the lower trap densities and larger apparent grain size, which is discussed below.^[18]

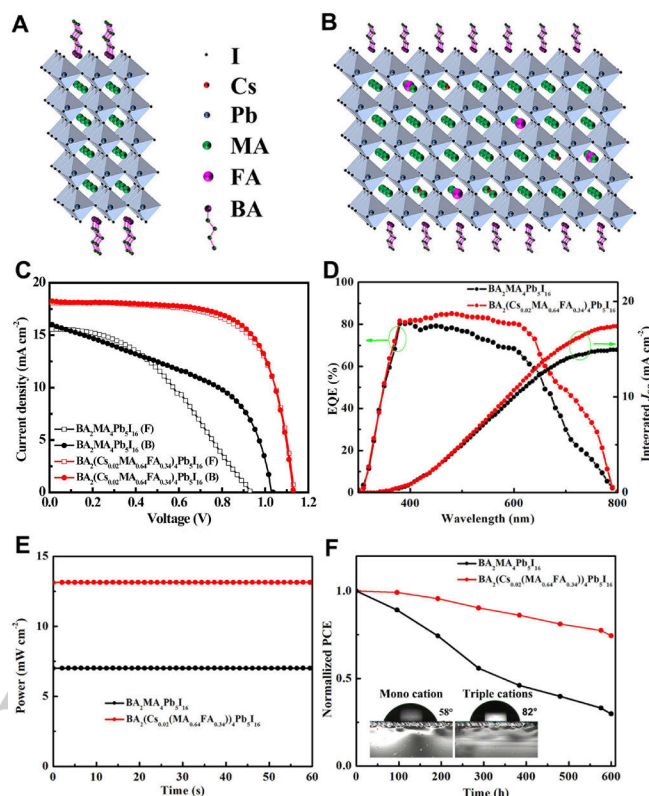


Figure 1. Schematic representation of perovskite structure fabricated by mono cation (A) and triple cations (B). (C) Forward- and backward-scan J - V curves of PSCs based on corresponding 2D perovskite films (F: forward; B: backward). (D) EQE curves of the champion PSCs with corresponding 2D perovskite films. (E) Steady power output measurement near the maximum power point. (F) Normalized PCE variation curves of corresponding unsealed PSCs at 80°C and relative humidity (RH) of 15%–20% (ISOS-D-2). The inset images are the contact-angles test.

It is well known that the PCE of PSCs depend strongly on the film quality and morphology of the perovskite layer.^[19] To examine the effect of the $\text{Cs}^+\text{-FA}^+\text{-MA}^+$ triple-cation mixture on film morphology, we performed scanning electron microscopy (SEM) measurements and atomic force microscopy (AFM), as shown in Figures 2A, 2B, and S4. After introducing 2% (mol) Cs^+ and 34% (mol) FA^+ , the perovskite film ($\text{BA}_2(\text{Cs}_{0.02}\text{MA}_{0.64}\text{FA}_{0.34})_4\text{Pb}_5\text{I}_{16}$) exhibits smooth, compact surface morphology with larger apparent grain size and fewer observed boundaries, which is preferred for reducing defect sites and enhancing photovoltaic properties. We carried out X-ray diffraction (XRD) measurement to further investigate the crystallinity of the corresponding film as shown in Figure 2C. The (111) peaks^[20] of the mono cation (MA^+) (2θ at $\sim 14^\circ$) consistently shift to lower angles with triple cations, corresponding to larger lattice constants. We observed a slight increase in cell volume with a certain amount of Cs^+ and FA^+ content doping—where the ionic radius of the Cs^+ cation is 1.81 Å and FA^+ cation is 2.79 Å, compared with MA^+ cation's ionic radius of 2.70 Å.^[21] Here again these data are

consistent with the ability of Cs⁺-FA⁺ cation to be used for fine-tune the Goldschmidt tolerance factor toward more structurally stable configurations, as previously reported.^[14a,22] Compared with using the mono cation (MA⁺), the films using triple cations yield remarkably enhanced diffraction intensities at (111) peaks, where the full-width at half-maximum of the (111) plane is greatly reduced from 0.42° to 0.10°.

2D XRD patterns in Figure 2D showed that a relatively broad peak indicative of a highly disordered material is evident in perovskite films based on the mono cation; but for the triple-cation perovskites, we observed clear stronger texturing of the main diffraction peaks in Figure 2E. Figure 2F compares the ultraviolet-visible absorption spectra of corresponding thin films over a wide absorption range of 350–800 nm. Both films display various excitonic absorption peaks associated with different *n* values, which are consistent with previous reports.^[10a,23] Compared to BA₂MA₄Pb₅I₁₆ perovskite film, BA₂(Cs_{0.02}MA_{0.64}FA_{0.34})₄Pb₅I₁₆ perovskite film clearly shows enhanced absorption, which is consistent with the enhancements in the EQE spectra, the resulting *J*_{sc} and corresponding PSCs. It is worth noting that analysis of X-ray photoemission spectroscopy (XPS) and XRD comparison of 2D perovskites with and without Cs suggests that Cs is incorporated in the perovskites (Figures S5 and S6).

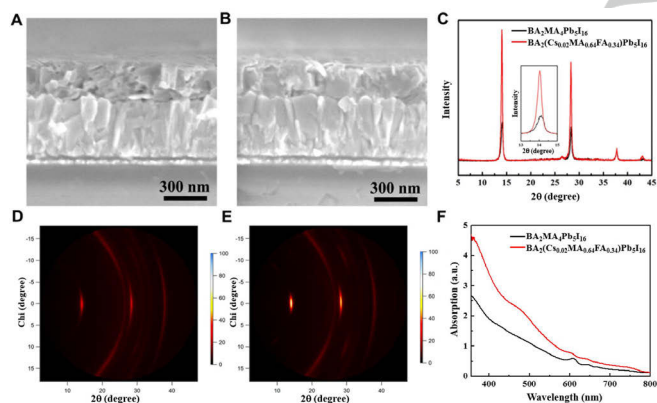


Figure 2. Cross-sectional SEM images of corresponding 2D mono-cation (A) and triple-cation (B) perovskites. (C) XRD patterns of corresponding 2D perovskite films; the inset image is amplified from 13° to 15°. (D) 2D XRD patterns of mono cation films. (E) 2D XRD patterns of triple cations films. (F) Ultraviolet-visible absorption spectra of corresponding 2D perovskite films.

To gain insight into the photophysical properties of 2D triple-cation perovskite layers, we conducted time-resolved photoluminescence (TRPL), time-resolved microwave conductivity (TRMC), and dark microwave conductivity (DMC) measurements, shown in Figure 3. To investigate the lifetime of the fabricated perovskites with both a mono cation and triple cations, we prepared 2D perovskite layers on glass substrates, and the results are shown in Figure 3A. The perovskite layer fabricated by triple cations showed a longer carrier lifetime (75 ns) in Figure S7, which is much longer than that of the mono cation (18 ns) and two times longer

than previous reports.^[10c,12,13,20b,23] These results support our hypothesis that the triple-cation 2D perovskite films exhibit reduced nonradiative recombination and longer carrier lifetime, which result from the improved film quality as discussed above for the triple-cation-based 2D perovskite thin films. Similar results were shown in the Nyquist plot from the impedance measurement (Figure S8). The transfer resistance (*R*_{tr}) at high frequency (the first small arc) shows that the transfer of electrons and holes is more efficient in PSCs based on triple cations than that of mono-cation-based PSCs when compared under the same condition. The large arc at low frequency is attributed to recombination resistance (*R*_{rec}), where PSCs based on triple cations show a higher barrier for carrier recombination.^[24]

We conducted time-resolved microwave conductivity (TRMC) measurements^[25] of the carrier mobility (Figure 3B) to compare perovskite thin films prepared from mono-cation and triple cations with 640-nm laser excitation. The yield-mobility product $\phi\Sigma\mu$ value increased from 0.41 cm² V⁻¹ s⁻¹ for BA₂MA₄Pb₅I₁₆ to 2.8 cm² V⁻¹ s⁻¹ for BA₂(Cs_{0.02}MA_{0.64}FA_{0.34})₄Pb₅I₁₆. Figure 3C shows the comparison of the $\phi\Sigma\mu$ value over a wide range of laser excitation intensities. This dramatic improvement of the transport property is consistent with the much-reduced dark carrier density (*n*_d=1.94×10¹⁷ cm⁻³) for the BA₂(Cs_{0.02}MA_{0.64}FA_{0.34})₄Pb₅I₁₆ sample compared to the BA₂MA₄Pb₅I₁₆ sample (*n*_d=2.58×10¹⁸ cm⁻³), as shown in Figure 3D. These results indicate that by controlling the ratio of cations, the quality of perovskite films can be much improved—with lower nonradiative recombination, longer carrier lifetime, and faster transport.

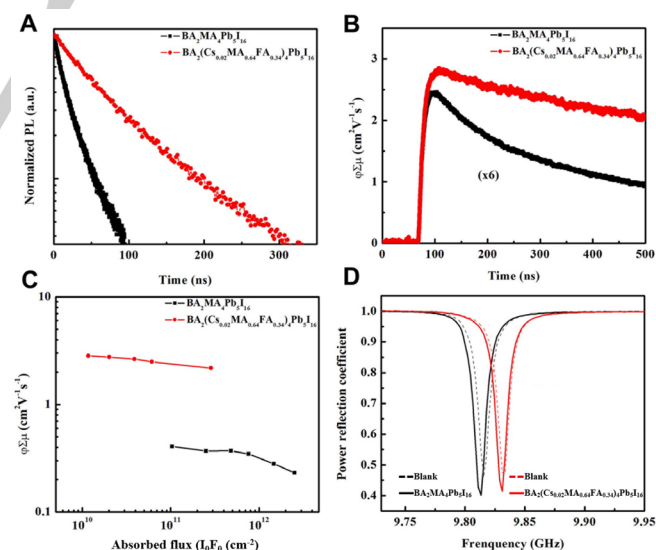


Figure 3. (A) TRPL kinetics of perovskite layer on glass substrate. (B) Typical TRMC transients and (C) intensity dependence of corresponding perovskite thin films. (D) Power reflection coefficient versus frequency for corresponding 2D perovskites by DMC measurement. Perovskite films were deposited on quartz substrates, and both the quartz substrates (blank) and perovskite samples on quartz were measured.

We also carried out conductive atomic force microscopy (C-AFM) to study the conducting properties of the 2D perovskite films,

shown in Figures 4A and 4B. The sample shows relatively low current signal in the mono-cation (MA^+) perovskite film, which indicates poor average electrical conductivity (less than 15 pA). In contrast, a significantly increased (about 6-fold overall, with some high conductive grains of ~250 pA) current signal is observed for the triple-cation sample, and suggests improved carrier conduction. This drastic difference is further illustrated in the line-profile comparison of the C-AFM results (Figures 4C and 4D).

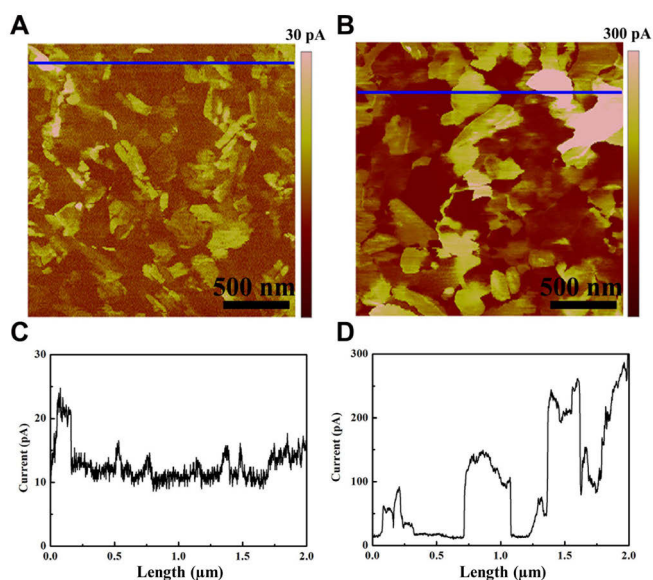


Figure 4. The C-AFM mapping images for the perovskite films at a bias voltage of 0.6 V in the dark: (A) with mono cation and (B) with triple cations. (C) Current mapping line profile of (A). (D) Current mapping line profile of (B).

In summary, we investigated the impact of triple cations (Cs^+ - FA^+ - MA^+) on 2D perovskites and PSCs. By comparing with a perovskite layer fabricated with a mono cation, we show that the triple-cation perovskite film exhibits a smooth, compact surface morphology with larger apparent grain size and fewer grain boundaries, leading to longer carrier lifetime and higher conductivity. The PCE of PSCs based on triple cations was significantly higher than that of PSCs based on a mono cation and binary cations. This research demonstrated the benefits of further improving the performance of 2D PSCs through cation engineering.

Acknowledgements

L.G.G. and F.Z. contributed equally to this work. The work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08GO28308 with Alliance for Sustainable Energy, Limited Liability Company (LLC), the Manager and Operator of the National Renewable Energy Laboratory. The authors acknowledge the support from the De-risking Halide Perovskite Solar Cells program of the National Center for Photovoltaics, funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Solar Energy Technologies Office. The authors also

acknowledge the support from the Center for Hybrid Organic Inorganic Semiconductors for Energy (CHOISE), an Energy Frontier Research Center funded by the Office of Basic Energy Sciences, Office of Science within the U.S. Department of Energy. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government.

Keywords: perovskite solar cells • triple cations • charge transport • Two-Dimensional

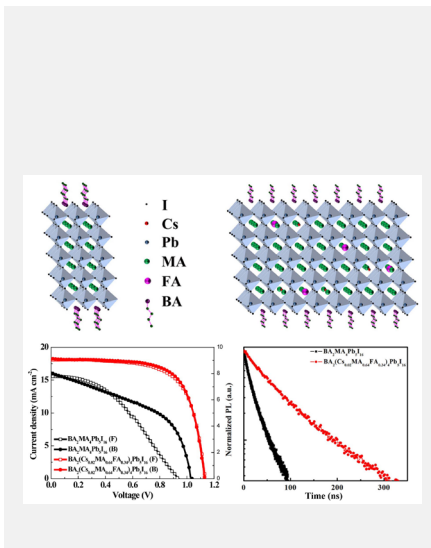
- [1] a) G. Hodes, *Science* **2013**, 342, 317. b) A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, 131, 6050. c) F. Zhang, W. Shi, J. Luo, N. Pellet, C. Yi, X. Li, X. Zhao, T. J. S. Dennis, X. Li, S. Wang, Y. Xiao, S. M. Zakeeruddin, D. Bi, M. Grätzel, *Adv. Mater.* **2017**, 29, 1606806. d) F. Zhang, D. Q. Bi, N. Pellet, C. X. Xiao, Z. Li, J. J. Berry, S. M. Zakeeruddin, K. Zhu, M. Grätzel, *Energy Environ. Sci.* **2018**, 11, 3480.
- [2] NREL Best Research-Cell Efficiency Chart, <https://www.nrel.gov/pv/cell-efficiency.html>
- [3] A. R. M. Yusoff, M. K. Nazeeruddin, *Adv. Energy Mater.* **2018**, 8, 1702073.
- [4] E. Shi, Y. Gao, B. P. Finkenauer, Akriti, A. H. Coffey, L. Dou, *Chem. Soc. Rev.* **2018**, 47, 6046.
- [5] a) L. Etgar, *Energy Environ. Sci.* **2018**, 11, 234. b) F. Zhang, D. Kim, K. Zhu, *Current Opinion in Electrochemistry* **2018**, 11, 105.
- [6] S. Yang, Y. Wang, P. Liu, Y. -B. Cheng, H. J. Zhao, H. G. Yang, *Nat. Energy* **2016**, 1, 15016.
- [7] a) Z. Guo, X. Wu, T. Zhu, X. Zhu, L. Huang, *ACS Nano* **2016**, 10, 9992. b) X. Chen, H. Lu, Z. Li, Y. Zhai, P. F. Ndione, J. J. Berry, K. Zhu, Y. Yang, M. C. Beard, *ACS Energy Lett.* **2018**, 3, 2273.
- [8] a) Y. N. Chen, Y. Sun, J. J. Peng, W. Zhang, X. J. Su, K. B. Zheng, T. Pullerits, Z. Q. Liang, *Adv. Energy Mater.* **2017**, 7, 1700162. b) T. M. Koh, V. Shanmugam, X. Guo, S. S. Lim, O. Filonik, E. M. Herzig, P. Müller-Buschbaum, V. Swamy, S. T. Chien, S. G. Mhaisalkar, N. Mathews, *J. Mater. Chem. A* **2018**, 6, 2122.
- [9] Y. Lin, Y. Bai, Y. J. Fang, Q. Wang, Y. H. Deng, J. S. Huang, *ACS Energy Lett.* **2017**, 2, 1571.
- [10] a) X. Zhang, G. Wu, S. Yang, W. Fu, Z. Zhang, C. Chen, W. Liu, J. Yan, W. Yang, H. Chen, *Small* **2017**, 13, 1700611. b) Y. Yamada, T. Nakamura, M. Endo, A. Wakamiya, Y. Kanemitsu, *J. Am. Chem. Soc.* **2014**, 136, 11610. c) F. Zhang, D. H. Kim, H. Lu, J. Park, B. Larson, J. Hu, L. Gao, C. Xiao, O. Reid, X. Chen, Q. Zhao, P. F. Ndione, J. J. Berry, W. You, A. Walsh, M. C. Beard, K. Zhu, *J. Am. Chem. Soc.* **2019**, 141, 5972.
- [11] a) C. Yi, J. Luo, S. Meloni, A. Boziki, N. Ashari-Astani, C. Grätzel, S. M. Zakeeruddin, U. Röthlisberger, M. Grätzel, *Energy Environ. Sci.* **2016**, 9, 656. b) D. P. McMeekin, G. Sadoughi, W. Rehman, G. E. Eperon, M. Saliba, M. T. Horantner, A. Haghighirad, N. Sakai, L. Korte, B. Rech, M. B. Johnston, L. M. Herz, H. J. Snaith, *Science* **2016**, 351, 151.
- [12] X. Zhang, X. Ren, B. Liu, R. Munir, X. Zhu, D. Yang, J. Li, Y. Liu, D.-M. Smilgies, R. Li, Z. Yang, T. Niu, X. Wang, A. Amassian, K. Zhao, S. Liu, *Energy Environ. Sci.* **2017**, 10, 2095.
- [13] N. Zhou, Y. H. Shen, L. Li, S. Q. Tan, N. Liu, G. J. Zheng, Q. Chen, H. P. Zhou, *J. Am. Chem. Soc.* **2018**, 140, 459.
- [14] a) M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, M. Grätzel, *Energy Environ. Sci.* **2016**, 9, 1989. b) F. Bella, P. Renzi, C. Cavallo, C. Gerbaldi, *Chem. Eur. J.* **2018**, 24, 12183. c) M. Deepa, M. Salado, L. Calio,

- S. Kazim, S. M. Shivaprasad, S. Ahmad, *Phys. Chem. Chem. Phys.* **2017**, *19*, 4069.
- [15] L. T. Schelhas, Z. Li, J. A. Christians, A. Goyal, P. Kairys, S. P. Harvey, D. H. Kim, K. H. Stone, J. M. Luther, K. Zhu, V. Stevanovic, J. J. Berry, *Energy Environ. Sci.* **2019**, *12*, 1341.
- [16] M. Salado, R. K. Kokal, L. Calio, S. Kazim, M. Deepa, S. Ahmad, *Phys. Chem. Chem. Phys.* **2017**, *19*, 22905.
- [17] a) M. Abdi-Jalebi, Z. Andaji-Garmaroudi, S. Cacovich, C. Stavrakas, B. Philippe, J. M. Richter, M. Alsari, E. P. Booker, E. M. Hutter, A. J. Pearson, S. Lilliu, T. J. Savenije, H. Rensmo, G. Divitini, C. Ducati, R. H. Friend, S. D. Stranks, *Nature* **2018**, *555*, 497. b) S. Turren-Cruz, M. Saliba, M. T. Mayer, H. Juárez-Santiesteban, X. Mathew, L. Nienhaus, W. Tress, M. P. Erodici, M. Sher, M. G. Bawendi, M. Grätzel, A. Abate, A. Hagfeldt, J. Correa-Baena, *Energy Environ. Sci.* **2018**, *11*, 78.
- [18] a) F. Zhang, C. Y. Yi, P. Wei, X. D. Bi, J. S. Luo, G. Jacopin, S. R. Wang, X. G. Li, Y. Xiao, S. M. Zakeeruddin, M. Grätzel, *Adv. Energy Mater.* **2016**, *6*, 1600401. b) S. Q. Tan, N. Zhou, Y. H. Chen, L. Li, G. L. Liu, P. F. Liu, C. Zhu, J. Z. Lu, W. T. Sun, Q. Chen, H. P. Zhou, *Adv. Energy Mater.* **2018**, *9*, 1803024. c) F. Zhang, C. X. Xiao, X. H. Chen, B. W. Larson, S. P. Harvey, J. J. Berry, K. Zhu, *Joule*, **2019**, DOI: 10.1016/j.joule.2019.03.023.
- [19] a) W. Li, J. Fan, J. Li, Y. Mai, L. Wang, *J. Am. Chem. Soc.* **2015**, *137*, 10399. b) C. -G. Wu, C. -H. Chiang, Z. -L. Tseng, M. K. Nazeeruddin, A. Hagfeldt, M. Grätzel, *Energy Environ. Sci.* **2015**, *8*, 2725.
- [20] a) I. C. Smith, E. T. Hoke, D. Solis-Ibarra, M. D. McGehee, H. I. Karunadasa, *Angew. Chem. Int. Ed.* **2014**, *53*, 11232. b) J. Qing, X. Liu, M. Li, F. Liu, Z. Yuan, E. Tiukalova, Z. Yan, M. Duchamp, S. Chen, Y. Wang, S. Bai, J. -M. Liu, H. J. Snaith, C. -S. Lee, T. C. Sum, F. Gao, *Adv. Energy Mater.* **2018**, *8*, 1800185.
- [21] A. Amat, E. Mosconi, E. Ronca, C. Quarti, P. Umari, M. K. Nazeeruddin, M. Grätzel, F. D. Angelis, *Nano Lett.* **2014**, *14*, 3608.
- [22] K. Domanski, J.-P. Correa-Baena, N. Mine, M. K. Nazeeruddin, A. Abate, M. Saliba, W. Tress, A. Hagfeldt, M. Grätzel, *ACS Nano* **2016**, *10*, 6306.
- [23] X. Zhang, R. Munir, Z. Xu, Y. Liu, H. Tsai, W. Nie, J. Li, T. Niu, D.-M. Smilgies, M. G. Kanatzidis, A. D. Mohite, K. Zhao, A. Amassian, S. Liu, *Adv. Mater.* **2018**, *30*, 1707166.
- [24] a) E. Zhao, L. Gao, S. Yang, L. Wang, J. Cao, T. Ma, *Nano Res.* **2018**, *11*, 5913. b) F. Meng, L. Gao, Y. Yan, J. Cao, N. Wang, T. Wang, T. Ma, *Carbon* **2019**, *145*, 290.
- [25] a) O. G. Reid, M. J. Yang, N. Kopidakis, K. Zhu, G. Rumbles, *ACS Energy Lett.* **2016**, *1*, 561. b) L. Gao, F. Zhang, C. Xiao, X. Chen, B. W. Larson, J. J. Berry, K. Zhu, *Adv. Funct. Mater.* **2019**, 1901652.

Entry for the Table of Contents

COMMUNICATION

Here, we report on the fabrication of 2D perovskites ($n=5$) with triple cations resulting in longer carrier lifetime, greater mobility and higher conductivity. The efficiency of 2D perovskite solar cells (PSCs) with triple cations was enhanced by more than 80% (from 7.80% to 14.23%) compared to PSCs fabricated with a mono cation; the efficiency is also higher than that of PSCs based on binary-cation 2D structures.



Liguo Gao, Fei Zhang*, Xihan Chen, Chuanxiao Xiao, Bryon W. Larson, Sean P. Dunfield, Joseph J. Berry, Kai Zhu*

Page No. – Page No.

Enhanced Charge Transport by Incorporating Formamidinium and Cesium Cations for Two-Dimensional Perovskite Solar Cells