ACS Energy LETTERS

http://pubs.acs.org/journal/aelccp

Direct Observation of Fast Carriers Transport along Out-of-Plane Direction in a Dion–Jacobson Layered Perovskite

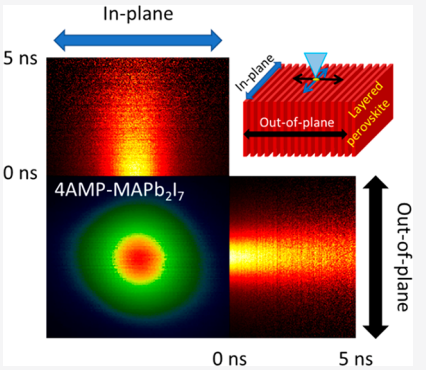
Zhifang Shi, Zhenyi Ni, and Jinsong Huang*

Cite This: *ACS Energy Lett.* 2022, 7, 984–987

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: **Layered perovskites have been broadly applied in perovskite solar cells and light-emitting diodes to enhance device stability, but the poor carrier transport property along the out-of-plane direction for all known Ruddlesden–Popper (RP) layered perovskites imposes constraints to their application. Herein, using transient photoluminescence mapping, we visualized that the transport of carriers or excitons along the out-of-plane direction is comparable to along the in-plane direction in a Dion–Jacobson (DJ) layered perovskite, which has the reduced ligand length and stronger I···I electronic interaction between inorganic layers.**



Layered perovskites have been widely applied in solar cells[1] and light-emitting diodes[2] to enhance moisture resistance,[3] suppress migration,[4] and passivate surface and grain boundary defects,[5] which can improve the stability[1] and efficiency[6] of these electronic devices. Like many other two-dimensional semiconductors, most known layered perovskites have anisotropic carrier transport with mobility along the out-of-plane direction orders of magnitude smaller than in-plane mobility. The nonconducting organic cation ligands, such as *n*-butylammonium (BA^+) or phenethylammonium (PEA^+), connect inorganic frameworks by a hydrogen-bond. Two layers of BA^+ and PEA^+ with opposite orientations are needed in Ruddlesden–Popper (RP) layered perovskites, making the distance between inorganic frameworks too large (>10 Å for PEA_2PbI_4) for carriers to tunnel through. Moreover, there is a half-unit octahedral mismatch in RP perovskites.[3] These make it difficult for carriers to get through the energy barrier along the out-of-plane direction. Benefiting from the bivalent ligands, Dion–Jacobson (DJ) layered perovskites have only monolayer ligands which results in much smaller inorganic layer spacing, and do not have the half-unit octoheral mismatching.[7] These suggest the potentially much better out-of-plane carrier transport property in DJ layered perovskites.[8] A recent study shows that layered perovskite solar cells with only DJ perovskites showed much higher efficiency than RP perovskite ones.[6] However, there is still no direct experimental study yet how fast carriers can transport in the out-of-plane direction in DJ perovskites.

In this Letter, we directly imaged both in-plane and out-of-plane carrier diffusion processes in a DJ layered perovskite using transient photoluminescence mapping (TPLM). We chose commercially available 4-(aminomethyl)piperidinium ($4AMP^+$) as the layered spacer for DJ perovskites, which possesses nearly the shortest length and relatively rigid backbone to form layered perovskites. Single crystals of 4AMP-$MAPb_2I_7$ (n = 2) were synthesized on the basis of the reported method.[7] Dark-red single-crystalline flakes were obtained after a supersaturated solution was allowed to slowly cool from 130 °C to room temperature. Figure 1a shows the photograph of a 4 × 4 × 0.34 mm^3 single crystal. The powder X-ray diffraction (XRD) pattern (Figure 1b) confirmed that the crystal is phase pure with a layer number of 2. The optical absorption and photoluminescence spectra (Figure 1c) indicate an optical band gap of 2.12 eV for 4AMP-$MAPb_2I_7$, agreeing with the previous report.[7]

TPLM can directly image the carrier or exciton diffusion process by observing the spreading of emission area, which has been reported to measure the in-plane diffusion of 2D and 3D

Received: January 13, 2022
Accepted: February 14, 2022

https://doi.org/10.1021/acsenergylett.2c00098
ACS Energy Lett. 2022, 7, 984–987

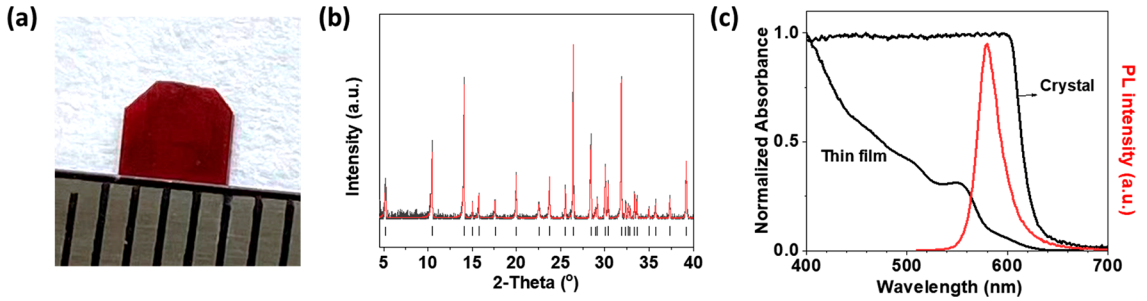


Figure 1. Synthesis and characterization of 4AMP-$MAPb_2I_7$. (a) A photograph of a 4 × 4 × 0.34 mm^3 single crystal. (b) The powder X-ray diffraction pattern, including experimental (black), calculated (red) patterns, calculated peak positions (black bar). (c) Absorption and photoluminescence (PL) spectra of a 4AMP-$MAPb_2I_7$ thin film and a single crystal.

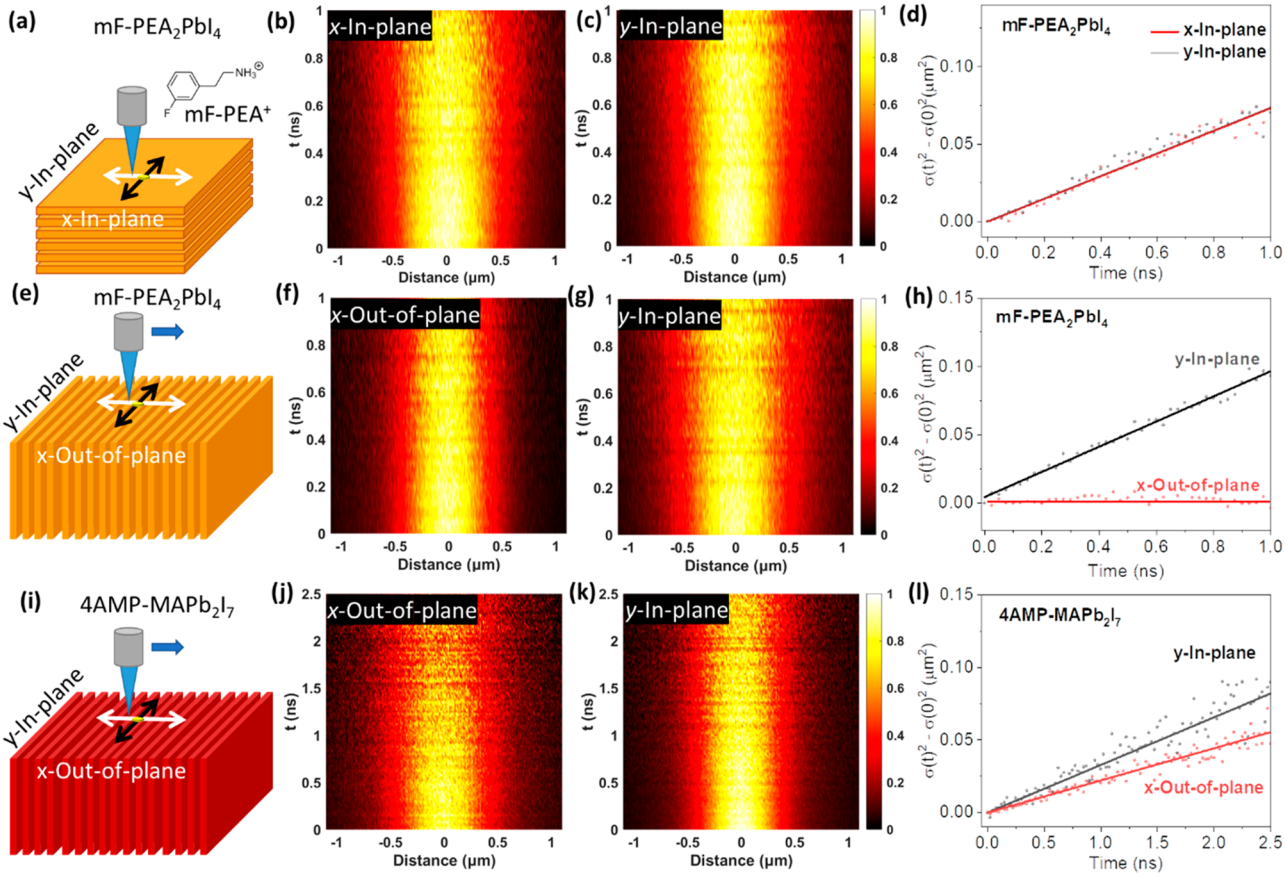


Figure 2. Diffusion measurement by TPLM. (a) (e) (i) Schematic diagrams of different sample orientations. Inset (a): chemical structure of mF-PEA^+. (b,c) (f,g) (j,k) normalized diffusion mappings for mF-PEA_2PbI_4 and 4AMP-$MAPb_2I_7$ along different directions. (d) (h) (l) Time-dependent mean-square-distribution ($MSD(t) = \sigma(t)^2 - \sigma(0)^2$) for PL emission spot broadening of mF-PEA_2PbI_4 and 4AMP-$MAPb_2I_7$ along *x*- and *y*-direction.

perovskites.[9−11] Briefly, a near-diffraction-limited excitation pulsed laser (λ = 405 nm for mF-PEA_2PbI_4, 485 nm for 4AMP-$MAPb_2I_7$, 20 MHz) pumped the crystals and generated free charges, excitons, or a combination of them. When these excess carriers or excitons diffuse away from the excitation spot driven by concentration gradient, the PL spots become larger. By measuring the PL spreading at different time intervals after laser excitation in the object plane, we can derive the diffusivity and thus mobility of the carriers or excitons.[9] Herein, we chose mF-PEA_2PbI_4 (mF-PEA^+, 3-fluorophenethylammonium), an RP layered perovskite, as the control, which has the highest in-plane carrier mobility[9] among all layered perovskites reported. We first mounted an mF-PEA_2PbI_4 crystal with face-on geometry, as illustrated in Figure 2a. Since both *x*- and *y*-axis are in-plane directions, the diffusion process is the same along these two directions, as manifested by the almost identical diameter of PL emission spot in Figure 2b,c. To better evaluate the time-dependent broadening of the emission spot, we analyzed the time-dependent mean-square-distribution (MSD, σ^2) derived from a Gaussian fitting of the PL profile at different delay times (Figure S1b-S1c). By linear fitting the MSD curve, we derived the mobility (μ) using the following equations: $\mu = \frac{e\Delta\sigma^2}{kT2t}$ where *e*, *k*, *T*, *t* are elementary charge, Boltzmann constant, temperature, and time interval after laser excitation, respectively. The in-plane mobilities of mF-PEA_2PbI_4 along

https://doi.org/10.1021/acsenergylett.2c00098
ACS Energy Lett. 2022, 7, 984−987

two axes are 14.13 ± 0.09 and 14.10 ± 0.08 $cm^2/(V\ s)$, respectively, indicating the isotropic transport along in-plane directions (Figure 2d). Then we changed the sample orientation to edge-on geometry to expose the (010) plane which has both in-plane and out-of-plane directions (Figure 2e). The derived in-plane mobility of 17.36 ± 0.09 $cm^2/(V\ s)$ is close to the results measured with face-on (Figure 2g,h). The PL spot size along the out-of-plane direction in mF-PEA_2PbI_4 barely changed over time (Figure 2f), as evidenced by the almost horizontal fitting line in Figure 2h, proving that the ligand layer almost blocks the carrier or exciton transport. This basically validates the feasibility to visualize carrier transport along both in-plane and out-of-plane directions at the same time by mounting the sample with edge-on orientation.

The same method was applied to evaluate DJ perovskite by putting a 4AMP-$MAPb_2I_7$ single crystal with an edge-on orientation, as shown in Figure 2i. An evident out-of-plane PL broadening (Figure 2j, S1a) was observed in striking contrast to RP perovskite. The mobility along this direction of 4AMP-$MAPb_2I_7$ is 4.23 ± 0.07 $cm^2/(V\ s)$, which is very close to the in-plane mobility (6.31 ± 0.21 $cm^2/(V\ s)$) (Figure 2k,i). This out-of-plane mobility is over 4 orders of magnitude larger than that in $BA_2MA_2Pb_3I_{10}$ single crystals.[12] It is not astonishing that the in-plane mobility of 4AMP-$MAPb_2I_7$ is lower than that of mF-PEA_2PbI_4, which is influenced by the octahedral distortion and can be further improved by changing the ligand cation as well as layer numbers.[9] A modified Simmons equation[13] was used to estimate carrier mobility along out-of-plane direction: $\mu = \mu_0 e^{-\beta d}$, where μ_0 is a constant, d is the distance between the inorganic layers, and β is a term related to energy barrier. We estimated a value of β of 1.0 $Å^{-1}$ based on the typical value of oligophenylenes (~0.5 $Å^{-1}$).[15] The nearest distance in 4AMP-$MAPb_2I_7$ between iodine atoms is 4.12 Å, which is within the range of intermolecular interaction between triiodides (3.7−4.5 Å).[14] From this equation, the reduced d from 10.35 Å in mF-PEA_2PbI_4 to 4.12 Å should increase μ by > 500 times. The reduced spacing combining with the enhanced I···I electronic coupling by the linear aligned inorganic octohedrals in the DJ structure[6,7] results in fast out-of-plane carrier transport in 4AMP-$MAPb_2I_7$.

Such a high out-of-plane mobility of 4AMP-$MAPb_2I_7$ should dramatically improve intergrain carrier transport when DJ perovskites are used to bridge grains in mixed dimensional perovskites. When it is used alone for solar cells, it diminishes the strict orientation requirement, as already demonstrated.[6] However, our optical study also indicates the stability of 4AMP-$MAPb_2I_7$ under light at ambient condition is inferior to that of mF-PEA_2PbI_4 because 4AMP-$MAPb_2I_7$ single crystals needed a thick moisture blocking layer to survive the optical study, indicating the design rule for the application of DJ perovskites in devices should be different from RP perovskites.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.2c00098.

Experimental method; typical TPLM spectra and fitting process (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Jinsong Huang − *Department of Applied Physical Sciences, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States;* orcid.org/0000-0002-0509-8778; Email: jhuang@unc.edu

Authors

Zhifang Shi − *Department of Applied Physical Sciences, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States;* orcid.org/0000-0003-1673-0983

Zhenyi Ni − *Department of Applied Physical Sciences, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States;* orcid.org/0000-0002-8379-9182

Complete contact information is available at: https://pubs.acs.org/10.1021/acsenergylett.2c00098

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by 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 US Department of Energy.

■ REFERENCES

(1) Tsai, H.; Nie, W.; Blancon, J.-C.; Stoumpos, C. C.; Asadpour, R.; Harutyunyan, B.; Neukirch, A. J.; Verduzco, R.; Crochet, J. J.; Tretiak, S.; Pedesseau, L.; Even, J.; Alam, M. A.; Gupta, G.; Lou, J.; Ajayan, P. M.; Bedzyk, M. J.; Kanatzidis, M. G.; Mohite, A. D. High-efficiency two-dimensional Ruddlesden−Popper perovskite solar cells. *Nature* **2016**, *536* (7616), 312−316.

(2) Ma, D.; Lin, K.; Dong, Y.; Choubisa, H.; Proppe, A. H.; Wu, D.; Wang, Y.-K.; Chen, B.; Li, P.; Fan, J. Z.; Yuan, F.; Johnston, A.; Liu, Y.; Kang, Y.; Lu, Z.-H.; Wei, Z.; Sargent, E. H. Distribution control enables efficient reduced-dimensional perovskite LEDs. *Nature* **2021**, *599* (7886), 594−598.

(3) Li, X.; Hoffman, J. M.; Kanatzidis, M. G. The 2D Halide Perovskite Rulebook: How the Spacer Influences Everything from the Structure to Optoelectronic Device Efficiency. *Chem. Rev.* **2021**, *121* (4), 2230−2291.

(4) Xiao, X.; Dai, J.; Fang, Y.; Zhao, J.; Zheng, X.; Tang, S.; Rudd, P. N.; Zeng, X. C.; Huang, J. Suppressed Ion Migration along the In-Plane Direction in Layered Perovskites. *ACS Energy Lett.* **2018**, *3* (3), 684−688.

(5) Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J. Surface passivation of perovskite film for efficient solar cells. *Nat. Photonics* **2019**, *13* (7), 460−466.

(6) Zhang, F.; Park, S. Y.; Yao, C.; Lu, H.; Dunfield, S. P.; Xiao, C.; Uličná, S.; Zhao, X.; Hill, L. D.; Chen, X.; Wang, X.; Mundt, L. E.; Stone, K. H.; Schelhas, L. T.; Teeter, G.; Parkin, S.; Ratcliff, E. L.; Loo, Y.-L.; Berry, J. J.; Beard, M. C.; Yan, Y.; Larson, B. W.; Zhu, K. Metastable Dion-Jacobson 2D structure enables efficient and stable perovskite solar cells. *Science* **2022**, *375* (6576), 71−76.

(7) Mao, L.; Ke, W.; Pedesseau, L.; Wu, Y.; Katan, C.; Even, J.; Wasielewski, M. R.; Stoumpos, C. C.; Kanatzidis, M. G. Hybrid Dion−Jacobson 2D Lead Iodide Perovskites. *J. Am. Chem. Soc.* **2018**, *140* (10), 3775−3783.

(8) Huang, P.; Kazim, S.; Wang, M.; Ahmad, S. Toward Phase Stability: Dion−Jacobson Layered Perovskite for Solar Cells. *ACS Energy Lett.* **2019**, *4* (12), 2960−2974.

(9) Xiao, X.; Wu, M.; Ni, Z.; Xu, S.; Chen, S.; Hu, J.; Rudd, P. N.; You, W.; Huang, J. Ultrafast Exciton Transport with a Long Diffusion Length in Layered Perovskites with Organic Cation Functionalization. *Adv. Mater.* **2020**, *32* (46), 2004080.
(10) Seitz, M.; Magdaleno, A. J.; Alcázar-Cano, N.; Meléndez, M.; Lubbers, T. J.; Walraven, S. W.; Pakdel, S.; Prada, E.; Delgado-Buscalioni, R.; Prins, F. Exciton diffusion in two-dimensional metal-halide perovskites. *Nat. Commun.* **2020**, *11* (1), 2035.
(11) Saidaminov, M. I.; Williams, K.; Wei, M.; Johnston, A.; Quintero-Bermudez, R.; Vafaie, M.; Pina, J. M.; Proppe, A. H.; Hou, Y.; Walters, G.; Kelley, S. O.; Tisdale, W. A.; Sargent, E. H. Multi-cation perovskites prevent carrier reflection from grain surfaces. *Nat. Mater.* **2020**, *19* (4), 412−418.
(12) Lin, Y.; Fang, Y.; Zhao, J.; Shao, Y.; Stuard, S. J.; Nahid, M. M.; Ade, H.; Wang, Q.; Shield, J. E.; Zhou, N.; Moran, A. M.; Huang, J. Unveiling the operation mechanism of layered perovskite solar cells. *Nat. Commun.* **2019**, *10* (1), 1008.
(13) Zhang, Y.; Soni, S.; Krijger, T. L.; Gordiichuk, P.; Qiu, X.; Ye, G.; Jonkman, H. T.; Herrmann, A.; Zojer, K.; Zojer, E.; Chiechi, R. C. Tunneling Probability Increases with Distance in Junctions Comprising Self-Assembled Mono-layers of Oligothiophenes. *J. Am. Chem. Soc.* **2018**, *140* (44), 15048−15055.
(14) Groenewald, F.; Esterhuysen, C.; Dillen, J. Extensive theoretical investigation: influence of the electrostatic environment on the $I_3^-\cdots I_3^-$ anion−anion interaction. *Theor. Chem. Acc.* **2012**, *131* (10), 1281.
(15) Kim; Beebe, J. M.; Jun, Y.; Zhu, X. Y.; Frisbie, C. D. Correlation between HOMO Alignment and Contact Resistance in Molecular Junctions: Aromatic Thiols versus Aromatic Isocyanides. *J. Am. Chem. Soc.* **2006**, *128* (15), 4970−4971.

https://doi.org/10.1021/acsenergylett.2c00098
ACS Energy Lett. 2022, 7, 984−987