Ligand-Driven Grain Engineering of High Mobility Two-Dimensional Perovskite Thin Film Transistors

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ABSTRACT: Controlling grain growth is of great importance in maximizing the charge carrier transport for polycrystalline thin film electronic devices. The thin film growth of halide perovskite materials has been manipulated via a number of approaches including solvent engineering, composition engineering, and posttreatment processes. However, none of these methods lead to large-scale atomically-flat thin films with extremely large grain size and high charge carrier mobility. Here, we demonstrate a novel π -conjugated ligand design approach for controlling the thin film nucleation and growth kinetics in two-dimensional (2D) halide perovskites. By extending the π -conjugation and increasing the planarity of the semiconducting ligand, nucleation density can be decreased by more than 5 orders of magnitude. As a result, wafer-scale 2D perovskite thin films with highly ordered crystalline structures and extremely large grain size are readily obtained. We demonstrate high-performance field-effect transistors with hole mobility approaching 10 cm²V⁻¹s⁻¹ with ON/OFF current ratios of $\sim 10^6$ and excellent stability and reproducibility. Our modeling analysis further confirms the origin of enhanced charge transport and field- and temperature-dependence of the observed mobility, which allows for clear deciphering of the structureproperty relationships in these nascent 2D semiconductor systems.

Introduction

The microstructure and morphology of polycrystalline thin films play crucial roles with respect to the ultimate performance of electronic devices made from these materials that constitute the active layers of these devices. Moreover, organic-inorganic hybrid halide perovskite materials have drawn myriad interest in various optoelectronic applications, including solar cells, light-emitting diodes, and photodetectors, due to their excellent optoelectronic properties and their potential to be fabricated using low-cost manufacturing methods.¹⁻¹⁵ Research of their use in field-effect transistors (FET) has received less attention, struggled in particularly to obtain room temperature mobility due to ion migration. 2D halide perovskites have displayed natural advantages in suppressing ion movement and improving ambient stability of their devic-

es.¹⁶⁻¹⁹ Controlling the nucleation and grain growth to obtain high quality thin films with large grain size is also crucial in maximizing the charge transport in perovskite materials.²⁰⁻²² That is, minimizing the number of grain boundaries is key, as the grain boundaries usually serve as trap sites, which reduces the charge carrier mobility and lifetime. Specifically in perovskite-based thin film field-effect transistors (FET), the performances are highly limited by the presence of grain boundaries in the charge transport channels. These grain boundaries are mainly responsible for the scattering of charge carriers as they create potential barriers. In addition, ion migration, one of the key reasons for the intrinsic instability of halide perovskites,²³⁻²⁵ is much faster at the grain boundaries than within the grains.²⁶ Because small crystal grains will produce a large number of grain boundaries, which form more barriers and defects for lateral charge transport, enlarging the perovskite grain size is a useful approach to reduce grain boundaries and the defect density; thus this should enhance charge transport in the active channel of the device. To date, various methods, such as solvent and composition engineering, solution based hot-casting techniques, substrate surface modification, and post-treatment, have been investigated to increase the grain size.27-34 Nevertheless, none of these methods lead to the formation of large-scale atomically-flat high quality 2D perovskite thin films with excellent lateral charge transport properties.

New perovskite ligand chemistries open a clear pathway to alter this paradigm. In fact, we recently introduced a series of bulky conjugated organic cations into 2D halide perovskites.³⁵⁻³⁷ We demonstrated that a quaterthiophene-based ligand (4Tm) tremendously increased the environmental stability of Sn-based 2D halide perovskites while also showing an obvious mobility improvement.³⁶ Moreover, bulky conjugated organic ligands are more effective stabilizers and inhibitors of ion migration relative to short aliphatic chains.³⁸ Thus, this simple ligand modulation strategy leads to improved 2D perovskite grain size and the simultaneous enhancement of device performance. Inspired by the discovery from organic electronics, the intermolecular interactions of conjugated moieties could provide a driving force for regulating the in-plane crystallization process of 2D halide perovskites. Compared to a single thiophene ring building block, introducing fused thiophene rings enables a higher degree of backbone planarity, and this could lead to unique structural features and increased intermolecular interactions.³⁹⁻⁴²



Figure 1. 2D RP phase halide perovskites featured with conjugated ligands. Chemical structures of the (a) 4Tm, (b) TT, and (c) DTT organic cations. Side view of the of the (d) $(4Tm)_2SnI_4$, (e) $(TT)_2SnI_4$ and (f) $(DTT)_2SnI_4$ crystal structures. GIWAXS patterns for thin film samples of (g) $(4Tm)_2SnI_4$, (h) $(TT)_2SnI_4$ and (i) $(DTT)_2SnI_4$ on SiO₂/Si substrates. Transfer characteristics of bottom-gate top-contact FET devices based on (j) $(4Tm)_2SnI_4$, (k) $(TT)_2SnI_4$ and (l) $(DTT)_2SnI_4$.

Here, we synthesized two new lead-free 2D perovskites, namely $(TT)_2SnI_4$ and $(DTT)_2SnI_4$, whose conjugated ligands containing fused-thiophene rings thienothiophene and dithienothiophene. We further demonstrated the crystallization kinetics of these 2D perovskites can be well engineered by modulating intermolecular interactions of organic ligands. The stronger intermolecular interactions from fused thiophene rings modulate the perovskite crystal nuclei formation. Moreover, the nucleation density during the thin film crystallization process was reduced by more than 5 orders of magnitude using the thienothiophene-containing ligand. Therefore, 2D Sn-based perovskite thin films with highly ordered crystalline structures and extremely large grain size were readily obtained without any complicated processing procedures. In this way, organic-inorganic hybrid perovskite FETs based on $(TT)_2SnI_4$ exhibited the highest field effect mobility of up to 9.35 cm²V⁻¹s⁻¹ with an ON/OFF current ratio higher than 10⁵.

Results and Discussion

The molecular structures of the three ligands are shown in Figure 1a-1c where TT and DTT were synthesized by replacing one thiophene unit in 4Tm with fused thiophene rings. These fused thiophene structures can interact through a variety of intermolecular means including weak hydrogen bonding, π - π stacking, C-H interactions, and S-S interactions.³⁹ Moreover, the fused thiophene rings are a highly planar system, allowing a stronger π - π

interaction. The highly coplanar conformation can also induce the formation of highly ordered crystalline structure,⁴⁰ promoting self-assembly and lateral growth of the 2D crystalline film.

The crystal structures of (4Tm)₂SnI₄, (TT)₂SnI₄ and (DTT)₂SnI₄ were resolved using single-crystal X-ray diffraction, and the resultant edge-on views of the real-space structures are shown in Figure 1d-1f (Single crystal growth details can be found in Supporting Information Methods section and Table S1-S6). The crystal structure consists of a layer of corner-sharing SnI₆⁴⁻ octahedra and two layers of organic cations forming the sandwiched structures. (4Tm)₂SnI₄ and (TT)₂SnI₄ exhibit similar crystal structures with pseudo-translation along the b-axis direction. (4Tm)₂SnI₄ and (TT)₂SnI₄ both display a herringbone arrangement viewing along the a-axis and c-axis direction, respectively (Figure S1 and S2). Different from the $(4Tm)_2SnI_4$ and $(TT)_2SnI_4$ systems the (DTT)₂SnI₄ crystal was found to be non-merohedrally twinned, and the DTT ligands in the single crystals exhibit two different configurations (Figure S3). The hydrogen bonds are similar in all three crystals. The ammonium head deviates from the center of the cages in all three crystals and forms hydrogen bonds with iodide atoms (N-H···I), with an average hydrogen bond distance of 2.880 Å for (4Tm)₂SnI₄, 2.566 Å for (TT)₂SnI₄ and 2.797 Å for $(DTT)_2 SnL_4$ (Table S7). Those interactions distort the SnL₆⁴⁻ octahedra from an ideal configuration. To quantify the degree of octahedral distortion, we calculated the bond length distortion index (D) from the following equation:⁴³

$$D = \frac{1}{6} \sum_{i=1}^{6} \frac{|d_i - d_0|}{d_0}$$

where d_i represents the individual Sn–I bond lengths, d_0 is the mean Sn–I bond distance. (4Tm)₂SnI₄, (TT)₂SnI₄ and (DTT)₂SnI₄ show a distortion index of 0.0315, 0.0320, and 0.0288, respectively. For an ideal octahedron, D is exactly 0, the larger value of D indicates the larger octahedral distortion.⁴⁴ The average Sn–I–Sn angles from inorganic layers are 153.4° for (4Tm)₂SnI₄, 152.7° for (TT)₂SnI₄ and 153.3° for (DTT)₂SnI₄. Compared with (4Tm)₂SnI₄ and (DTT)₂SnI₄, (TT)₂SnI₄ shows slightly larger D and smaller Sn–I–Sn angles, indicating a more contracted in-plane lattice structure with enhanced stability.³⁶ Notably, when growing single crystals, (TT)₂SnI₄ tend to incorporate a variety of solvent molecules between the layers, which has never been observed in other 2D perovskites (Figure S4). This characteristic with interference in vertical direction.

Thin films of (4Tm)₂SnI₄, (TT)₂SnI₄, and (DTT)₂SnI₄ on glass substrates showed two distinct absorption bands (Figure S5). The band below 500 nm is attributed to the localized π - π * transition of the organic ligands (Figure S6), and the band at longer wavelengths is a feature common to many electronically-confined systems.^{45, 46} Moreover, the ultraviolet-visible (UV-Vis) absorption spectra show sharp absorption edges, optical band gap (E_{α}) values of 1.93 eV for (4Tm)₂SnI₄, 1.94 eV for (TT)₂SnI₄, and 1.96 eV for (DTT)₂SnI₄ were estimated. Absorption spectra indicate the materials are direct bandgap semiconductors, which agrees with the DFT-calculated band structures. Notably, these optical bandgaps are almost identical while the organic ligands between the samples are quite different (Figure S7 and Table S8), which confirms that the SnI₆ octahedra are mainly dictating the optoelectronic properties of these tin perovskites. All the materials exhibit strong photoluminescence at room temperature (Figure S8).

We examined and confirmed the crystal structure of these 2D perovskite thin films by grazing-incidence wide-angle X-ray scattering (GIWAXS, Figure 1g-1i) and powder X-ray diffraction (Figure S9 and S10). A series of high intensity (001)/(100) diffractions along the Q_z direction are observed for all these samples;

The reflections correspond to an interlayer distance separating the inorganic sheets, and were 32.10 Å for $(4Tm)_2SnI_4$, 35.88 Å for $(TT)_2SnI_4$ and 36.78 Å for $(DTT)_2SnI_4$ using Bragg's Law, which is qualitatively consistent with their single crystal data. For $(DTT)_2SnI_4$ thin film, additional reflections occur, indicating the formation of a secondary phase during the crystallization event that occurs during thermal annealing.

To investigate the charge transport properties of these materials, FETs with a simple bottom-gate/top-contact (BG/TC) device architecture (Figure S11) were fabricated where silicon dioxide served as the gate dielectric and gold as source and drain contacts. Figure 1j-11 presents representative *p*-type transfer characteristics, depicted as $|I_{DS}|$ versus V_G and $|I_{DS}|^{0.5}$ versus V_G at a constant V_{DS} (-60 V), of the devices based on (4Tm)₂SnI₄, (TT)₂SnI₄, and (DTT)₂SnI₄. FETs based on (4Tm)₂SnI₄, (TT)₂SnI₄ and $(DTT)_2SnI_4$ displayed a hole mobility (μ_h) of 1.31, 2.23 and 0.01 cm²V⁻¹s⁻¹, respectively. We further carried out atomic force microscopy (AFM) experiments to evaluate the film morphology (Figure S12). (4Tm)₂SnI₄ displayed crystal grains with an average grain size around 2 µm based on image analysis of the AFM micrographs. However, many pinholes and cracks were found between the grains, which would impede charge carrier transport. In contrast. (TT)₂SnI₄ and (DTT)₂SnI₄ thin films showed similar surface structures that were free of cracks with larger, continuous crystal grains. The larger grain size reduces the number of grain boundaries, which is beneficial for carrier transport.³⁶ Nevertheless, (DTT)₂SnI₄ exhibited a much lower mobility, and this could be related to its relative complex crystal structure and poor phase impurity as noticed in the GIWAXS profile (Figure 1i). Those observed mixed phases in (DTT)₂SnI₄ thin film could be detrimental to the charge transport. Full band structures of (TT)₂SnI₄ and (DTT)₂SnI₄ were also obtained by DFT calculations based on their optimized crystal structure (Figure S13), and the near type-II band alignment in (DTT)₂SnI₄ also implied unfavorable hole transport in inorganic layer.

The ordered and pure perovskite crystalline phase and favorable morphology of (TT)₂SnI₄ thin film together explain why it outperformed the other two materials in terms of its carrier mobility. To further boost the performance of the FETs based on (TT)₂SnI₄, we varied the annealing temperatures from 150 °C to 180 °C during the film fabrication process (Figure S14). The best performance was achieved when the films were annealed at 155 °C. Interestingly, an intermediate state morphology of thin films annealed at lower temperatures were observed, which indicated a slowed crystallization process upon thermal annealing. The evolution of (TT)₂SnI₄ thin film crystallization was then evaluated by capturing the morphology at different stages during the thermal annealing-induced crystallization process. The optical microscopy and photoluminescence (PL) images are shown in Figure 2a and 2b. A few crystalline perovskite seeds were formed during the first stage, then these seeds grew larger when the annealing time increased from 4 min to 10 min, and they coalesced eventually to form a uniform thin film. The scanning electron microscopy (SEM) and AFM images further verified the morphology results of optical microscopy and PL images (Figure 2c-2g and Figure S15). For the intermediate state, there are highly crystalline seeds randomly formed from relatively amorphous areas. As shown in Figure 2h, surprisingly, the AFM analysis showed that surface roughness of the seed region was significantly reduced from 9.03 nm to 1.93 nm. When compared to the surrounding amorphous regions, the highly crystalline seed area also has stark contrast with respect to its PL properties (Figure 2i and 2j). The selfregulated growth, reduced surface roughness, and improved crystallinity are critical for high-performance electronic devices. On the other hand, similar phenomena were not observed for (4Tm)₂SnI₄ and (DTT)₂SnI₄ thin films. Their nearly continuously red PL images (Figure 2k and 2l) under the same condition indicate that a large number of nucleation seeds have already formed at the initial stage. Clearly, the $(TT)_2SnI_4$ thin film displayed the



Figure 2. Morphological evolution in crystallization process of $(TT)_2SnI_4$ thin film and corresponding nucleation kinetics comparison. The optical microscopy (a) and photoluminescence images (b) of $(TT)_2SnI_4$ thin films after thermal annealing at 155 °C for different times; the scale bar represents 20 µm. SEM images of $(TT)_2SnI_4$ thin film by thermal annealing at 155 °C for 4 min (c), 6 min (e) and 10 min (g; Scale bar, 20 µm. (d) and (f) Enlarged image from the blue-boxed region in (c) and (e), respectively; Scale bar, 1 µm. (h) AFM image and corresponding section analysis of $(TT)_2SnI_4$ crystalline seed formed in thin films annealed at 155 °C for 4 min. (i) PL spectra and (j) time resolved PL collected from spots on and off the crystalline seed during the thermal annealing process of $(TT)_2SnI_4$ thin films after thermal annealing at 155 °C for 1 min. Scale bar, 20 µm. (m) The statistical distribution of nucleation density for $(4Tm)_2SnI_4$, $(TT)_2SnI_4$ and $(DTT)_2SnI_4$ thin films during the first stage of thermal annealing process.



Figure 3. Optimized $(TT)_2SnI_4$ FET performance and temperature dependence studies on large and small grain size $(TT)_2SnI_4$ thin film devices. (a) Transfer and (b) output characteristics of bottom-gate top-contact FET champion device based on $(TT)_2SnI_4$ thin film with optimized morphology. (c) Illustrations of carrier transport in small grain and large grain based $(TT)_2SnI_4$ thin film. (d) Arrhenius plots as temperature dependences of hole mobilities for two typical FET devices based on $(TT)_2SnI_4$ thin films featured with large and small grain size in the temperature range between 50 and 370 K. (e) Temperature dependences of current on/off ratio for these two typical FET devices.

lowest nucleation density among the three samples. We further estimated the nucleation densities based on SEM images (Figure S16). The value for $(TT)_2SnL_4$ thin film is determined to be tens of seeds per mm², which is several orders of magnitude lower than the other two materials (Figure 2m). The sparse seeds in (TT)₂SnI₄ thin film is conducive to extremely large grain formation at later times.²² Intriguingly, the usually fast crystallization kinetics of the 2D perovskite thin films has been successfully suppressed by the increased intermolecular interactions of the TT ligands, while the crystal growth step is maintained in-plane, resulting in a high quality, near atomically flat film with extremely large grains. This unique feature may result from the weak interactions between the layers, which allows different type of solvent molecules to be trapped between the layers, as shown in the single crystal XRD structures (Figure S4). Notably, thin film thickness around 50 nm is preferred, thinner films would have difficulties in realizing this optimized morphology (Figure S17). With this finely controlled thin film morphology, we were able to obtain highly performing FET devices with a maximum μ_h of 9.35 cm²V⁻¹s⁻¹ (Figure 3a-3b, Table 1), and an ON/OFF current ratio higher than five orders of magnitude. The negligible hysteresis further indicates that the larger grain and the bulky conjugated cation may be beneficial to inhibit ion migration and reduce trap states in the perovskite film. The operational stability is also assessed, and the reliable operation is reflected in the negligible changes of the transfer curves for 1000-time scans (Figure S18).

The charge transport mechanisms in thin films with large and small grain size were quantified using temperature-dependent transport measurements. Except for the morphological differences of these two (TT)₂SnI₄ thin films (Figure S19), crystalline grains from both samples showed similar decay dynamics of the charge carriers (Figure S20). We have conducted FET measurements in a temperature range from 50 K to 370 K (Figure S21-S23). The hole mobility of the small grain device reached a maximum at 200

K, while the large grain device exhibited the highest mobility at 320 K. For both devices, in the high temperature region, the decrease of the carrier mobility with increasing temperature can be explained by the intrinsic transport behavior dominated by lattice scattering. On the other hand, in the low temperature region, the increase of the mobility with increasing temperature can be attributed to a thermally activated transport mechanism. Considering grain boundary density in these two cases, we hypothesize that the behavior of small grain device could be dictated by the larger number of grain boundary potential barriers, as shown in Figure 3c. We plotted the field-effect mobility data in an Arrhenius fashion (Figure 3d). Both devices exhibit thermally-activated behavior that is Arrhenian below their peak mobility temperatures. The activation energies (E_a) are 10.4 meV for the large grain device and 8.0 meV for the small grain device, as determined by fitting to the Arrhenius equation. Besides the field-effect mobility, good ON/OFF current ratios are maintained across the temperature range (Figure 3e). Figure 3f shows the temperature dependence of the threshold voltage (V_{th}). For the large grain device, when the temperature decreases, Vth shifts and then levels at lower temperatures. On the contrary, the Vth of the small grain device continues to shift all through the temperature range, albeit at a slower rate. These results further confirm the higher defect density in the small grain device.

To interpret the essential and nontrivial features of bias and temperature dependencies of the FET characteristics summarized in Figure 3, we simulated spatially-resolved electron and hole transport using a self-consistent solution of Poisson and continuity equations. The simulated $I_{DS} - V_{GS}$ and $I_{DS} - V_{DS}$ curves are shown in Figure 4a-c. Details of the simulation setup, the geometrical dimensions, and the electrical parameters adopted in the simulation are reported in the Supporting Information. The band diagrams at different bias conditions, which highlight the unique

and non-intuitive transport properties of the transistors, are also reported in the Supporting Information. The simulated $I_{DS} - V_{GS}$

Table 1. Bottom Gate-Top	Contact FEI	Device Performance.
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Perovskites	$\mu_{h,max}$ (cm ² V ⁻¹ s ⁻¹)	$\mu_{\rm h,avg}(\rm cm^2V^{-1}s^{-1})^a$	$V_{th}(V)$	SS (V/dec)	I_{on}/I_{off}
$(4Tm)_2SnI_4$	1.31	1.15±0.11	-20 to -30	~8.7	10 ⁵ -10 ⁶
$(TT)_2SnI_4$	2.23	1.67±0.35	-15 to -25	~7.6	10 ⁵ -10 ⁶
(DTT) ₂ SnI ₄	0.01	0.007 ± 0.002	-15 to -25	~15	10^{3} - 10^{4}
(TT) ₂ SnI ₄ with optimized large grain morphology	9.35	6.52±1.67	-10 to -20	~5.4	10 ⁵ -10 ⁶

^aThe average values were calculated based on 20 devices.



Figure 4. Transport simulations for $(TT)_2SnI_4$ FET devices. (a-b) Simulation results of $I_{DS} - V_{GS}$ curves at different temperatures. The arrows show a turnaround of maximum drain current at higher temperature. (c) $I_{DS} - V_{DS}$ curves at different gate voltage. (d) Low-field mobility used in the simulation, at higher temperature the scattering mechanism is dominant and at lower temperature the activation energy due to inter-grain hopping mechanism dominates the mobility of the holes.

curves reproduce the experimental results at different temperatures with a high-accuracy (see Figure 4a-b), thereby conforming the essential role of field- and temperature-dependent Poole-Frenkel mobility model and Gaussian-distributed acceptor-like traps at the semiconductor/oxide interface. As detailed in the Supporting Information, the field- and temperature-dependent mobility is governed by two physical phenomena. The reduction of bulk mobility associated with intra-grain lattice scattering dominates at the higher temperature regime, while field-assisted and thermally activated mechanisms increase the mobility due to hopping over the inter-grain energy barriers (Figure 4d) defines the transport at the lower temperature range. The relative magnitude of the two components defines the critical temperature at which the mobility reaches a maximum (Figure 4d). The more frequent scattering associated with the smaller grain material reduces the mobility and reduces the critical temperature, as expected. Finally, the field-dependence of the mobility is equally important. At lowfields close to the source of the transistor, the current is suppressed by the field-dependent transport of the Poole-Frenkel transport over the grain boundary. At higher field closer to the drain contact, the higher electric field enhances the mobility, but the current is ultimately defined by the mobility-limited injection close to the source end.

To explain the large and temperature-dependent V_{th} shown in Figure 3f, one must quantify the role of traps at the oxide/semiconductor interface. A detailed analysis shows that only acceptor-like traps at a density of $8 \times 10^{12} \text{ cm}^{-2}$ and distributed broadly across the bandgap can self-consistently explain the large and temperature-dependent threshold voltage shift observed in the experiment (see simulation Figure 4b). In particular, the temperature-dependent shift of the Fermi-level within the bandgap across the interface traps explains the temperature-dependent thresholdvoltage shift observed in the experiment. Indeed, the sensitivity



Figure 5. Wafer scale demonstration of (TT)₂SnI₄ FET devices. (a) Photograph of (TT)₂SnI₄ thin film on a 4-inch Si/SiO₂ wafer substrate. Statistical distribution of (b) hole mobility and (c) on/off current ratio from 110 FET devices across the wafer-scale substrate. Inset, optical image of one typical FET device using interdigitated source/drain electrodes.

reflects the fact that the Fermi level is close to the valence band (see Figure S27-S28) and only a fraction of the traps will be occupied at any given temperature. These analyses suggest further improvement of the device performance can be achieved by passivating the oxide/semiconductor interfacial traps.

A major advantage for 2D halide perovskites relative to other conventional 2D materials is their low-temperature, large-scale solution processability. Here, we demonstrate the wafer-scale fabrication of high-performance FETs by solution-processing. A uniform (TT)₂SnI₄ thin film on a 4-inch-sized SiO₂ (300 nm)/Si wafer substrate was easily prepared by spin-coating (Figure 5a). Based on this high-quality wafer-scale thin film, we fabricated over one hundred FETs with excellent performance and uniformity. Among the one hundred devices we measured, none of them failed in exhibiting field-modulated charge transport. The statistical distributions of the hole mobility and ON/OFF current ratio are summarized in Figure 5b-5c with an average mobility of 5.35 $\pm 0.79 \ cm^2V^{-1}s^{-1}$ for the tested devices.

Conclusion

In summary, we demonstrated the nucleation density during the perovskite thin film crystallization process is found to be reduced significantly by extending the π -conjugation and increasing the planarity of the semiconducting ligand via introducing fused thiophene moieties. As a result, 2D Sn-based perovskite thin films with near atomically flat morphology and extremely large grain size were readily obtained from a simple one-step spin-coating method, enabled FET device with hole mobility approaching 10 cm²V⁻¹s⁻¹ and an ON/OFF current ratio around 10⁶. These results suggest the potential of solution-processed 2D perovskite transistors for a wide range of practical applications including integrated sensors, logic circuits, and flexible displays. Moreover, this work sheds light on the importance of modulating the rigidity and intermolecular interactions of the organic cations in controlling the 2D perovskite crystallization and thin film growth, and thus boosting corresponding carrier transport performance.

ASSOCIATED CONTENT

Supporting Information

Experimental details, additional crystallographic data, supplemental figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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REFERENCES

(1) Liang, Y.; Li, F.; Zheng, R. Low-Dimensional Hybrid Perovskites for Field-Effect Transistors with Improved Stability: Progress and Challenges. *Adv. Electron. Mater.* **2020**, *6* (9), 2000137.

(2) Berry, J.; Buonassisi, T.; Egger, D. A.; Hodes, G.; Kronik, L.; Loo, Y.-L.; Lubomirsky, I.; Marder, S. R.; Mastai, Y.; Miller, J. S.; Mitzi, D. B.; Paz, Y.; Rappe, A. M.; Riess, I.; Rybtchinski, B.; Stafsudd, O.; Stevanovic, V.; Toney, M. F.; Zitoun, D.; Kahn, A.; Ginley, D.; Cahen, D. Hybrid Organic–Inorganic Perovskites (Hoips): Opportunities and Challenges. *Adv. Mater.* **2015**, *27* (35), 5102-5112.

(3) Smith, M. D.; Connor, B. A.; Karunadasa, H. I. Tuning the Luminescence of Layered Halide Perovskites. *Chem. Rev.* **2019**, *119* (5), 3104-3139.

(4) Gao, Y.; Wei, Z.; Hsu, S.-N.; Boudouris, B. W.; Dou, L. Two-Dimensional Halide Perovskites Featuring Semiconducting Organic Building Blocks. *Mater. Chem. Front.* **2020**, *4* (12), 3400-3418.

(5) Leng, K.; Fu, W.; Liu, Y.; Chhowalla, M.; Loh, K. P. From Bulk to Molecularly Thin Hybrid Perovskites. *Nat. Rev. Mater.* **2020**, *5* (7), 482-500. (6) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* **2009**, *131* (17), 6050-6051.

(7) Yakunin, S.; Sytnyk, M.; Kriegner, D.; Shrestha, S.; Richter, M.; Matt, G. J.; Azimi, H.; Brabec, C. J.; Stangl, J.; Kovalenko, M. V.; Heiss, W. Detection of X-Ray Photons by Solution-Processed Organic-Inorganic Perovskites. *Nat. Photonics* **2015**, *9* (7), 444-449.

Bai, S.; Da, P.; Li, C.; Wang, Z.; Yuan, Z.; Fu, F.; Kawecki,
M.; Liu, X.; Sakai, N.; Wang, J. T.; Huettner, S.; Buecheler, S.; Fahlman,
M.; Gao, F.; Snaith, H. J. Planar Perovskite Solar Cells with Long-Term
Stability Using Ionic Liquid Additives. *Nature* 2019, *571* (7764), 245-250.

(9) Cao, Y.; Wang, N.; Tian, H.; Guo, J.; Wei, Y.; Chen, H.; Miao, Y.; Zou, W.; Pan, K.; He, Y.; Cao, H.; Ke, Y.; Xu, M.; Wang, Y.; Yang, M.; Du, K.; Fu, Z.; Kong, D.; Dai, D.; Jin, Y.; Li, G.; Li, H.; Peng, Q.; Wang, J.; Huang, W. Perovskite Light-Emitting Diodes Based on Spontaneously Formed Submicrometre-Scale Structures. *Nature* **2018**, *562* (7726), 249-253.

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. High-Efficiency Two-Dimensional Ruddlesden-Popper Perovskite Solar Cells. *Nature* 2016, *536* (7616), 312-316.

(11) Sutherland, B. R.; Sargent, E. H. Perovskite Photonic Sources. *Nat. Photonics* **2016**, *10* (5), 295-302.

(12) Shi, E.; Gao, Y.; Finkenauer, B. P.; Akriti; Coffey, A. H.; Dou, L. Two-Dimensional Halide Perovskite Nanomaterials and Heterostructures. *Chem. Soc. Rev.* **2018**, *47* (16), 6046-6072.

(13) Mao, L. L.; Stoumpos, C. C.; Kanatzidis, M. G. Two-Dimensional Hybrid Halide Perovskites: Principles and Promises. J. Am. Chem. Soc. **2019**, *141* (3), 1171-1190.

(14) She, X.-J.; Chen, C.; Divitini, G.; Zhao, B.; Li, Y.; Wang, J.; Orri, J. F.; Cui, L.; Xu, W.; Peng, J.; Wang, S.; Sadhanala, A.; Sirringhaus, H. A Solvent-Based Surface Cleaning and Passivation Technique for Suppressing Ionic Defects in High-Mobility Perovskite Field-Effect Transistors. *Nat. Electron.* **2020**, *3* (11), 694-703.

(15) Canicoba, N. D.; Zagni, N.; Liu, F.; McCuistian, G.; Fernando, K.; Bellezza, H.; Traoré, B.; Rogel, R.; Tsai, H.; Le Brizoual, L.; Nie, W.; Crochet, J. J.; Tretiak, S.; Katan, C.; Even, J.; Kanatzidis, M. G.; Alphenaar, B. W.; Blancon, J.-C.; Alam, M. A.; Mohite, A. D. Halide Perovskite High-K Field Effect Transistors with Dynamically Reconfigurable Ambipolarity. *ACS Materials Lett.* **2019**, *1* (6), 633-640.

(16) Kagan, C. R.; Mitzi, D. B.; Dimitrakopoulos, C. D. Organic-Inorganic Hybrid Materials as Semiconducting Channels in Thin-Film Field-Effect Transistors. *Science* **1999**, *286* (5441), 945-947.

(17) Mitzi, D. B.; Dimitrakopoulos, C. D.; Rosner, J.; Medeiros, D. R.; Xu, Z.; Noyan, C. Hybrid Field-Effect Transistor Based on a Low-Temperature Melt-Processed Channel Layer. *Adv. Mater.* **2002**, *14* (23), 1772-1776.

(18) Matsushima, T.; Hwang, S.; Sandanayaka, A. S.; Qin, C.; Terakawa, S.; Fujihara, T.; Yahiro, M.; Adachi, C. Solution-Processed Organic-Inorganic Perovskite Field-Effect Transistors with High Hole Mobilities. *Adv. Mater.* **2016**, *28* (46), 10275-10281.

(19) Zhu, H.; Liu, A.; Shim, K. I.; Hong, J.; Han, J. W.; Noh, Y. Y. High-Performance and Reliable Lead-Free Layered-Perovskite Transistors. *Adv. Mater.* **2020**, *32* (31), 2002717.

(20) Zhu, L.; Shi, J.; Lv, S.; Yang, Y.; Xu, X.; Xu, Y.; Xiao, J.; Wu, H.; Luo, Y.; Li, D.; Meng, Q. Temperature-Assisted Controlling Morphology and Charge Transport Property for Highly Efficient Perovskite Solar Cells. *Nano Energy* **2015**, *15*, 540-548.

(21) Senanayak, S. P.; Yang, B.; Thomas, T. H.; Giesbrecht, N.; Huang, W.; Gann, E.; Nair, B.; Goedel, K.; Guha, S.; Moya, X.; McNeill, C. R.; Docampo, P.; Sadhanala, A.; Friend, R. H.; Sirringhaus, H. Understanding Charge Transport in Lead Iodide Perovskite Thin-Film Field-Effect Transistors. *Sci. Adv.* **2017**, *3* (1), e1601935.

(22) Liu, C.; Cheng, Y.-B.; Ge, Z. Understanding of Perovskite Crystal Growth and Film Formation in Scalable Deposition Processes. *Chem. Soc. Rev.* **2020**, *49* (6), 1653-1687.

(23) Snaith, H. J.; Abate, A.; Ball, J. M.; Eperon, G. E.; Leijtens, T.; Noel, N. K.; Stranks, S. D.; Wang, J. T.; Wojciechowski, K.; Zhang, W. Anomalous Hysteresis in Perovskite Solar Cells. *J. Phys. Chem. Lett.* **2014**, *5* (9), 1511-5.

(24) Xiao, Z.; Yuan, Y.; Shao, Y.; Wang, Q.; Dong, Q.; Bi, C.; Sharma, P.; Gruverman, A.; Huang, J. Giant Switchable Photovoltaic Effect in Organometal Trihalide Perovskite Devices. *Nat. Mater.* **2015**, *14* (2), 193-8.

(25) Vashishtha, P.; Halpert, J. E. Field-Driven Ion Migration and Color Instability in Red-Emitting Mixed Halide Perovskite Nanocrystal Light-Emitting Diodes. *Chem. Mater.* **2017**, *29* (14), 5965-5973.

(26) Shao, Y.; Fang, Y.; Li, T.; Wang, Q.; Dong, Q.; Deng, Y.; Yuan, Y.; Wei, H.; Wang, M.; Gruverman, A.; Shield, J.; Huang, J. Grain Boundary Dominated Ion Migration in Polycrystalline Organic–Inorganic Halide Perovskite Films. *Energy Environ. Sci.* **2016**, *9* (5), 1752-1759.

(27) Xiao, Z.; Dong, Q.; Bi, C.; Shao, Y.; Yuan, Y.; Huang, J. Solvent Annealing of Perovskite-Induced Crystal Growth for Photovoltaic-Device Efficiency Enhancement. *Adv. Mater.* **2014**, *26* (37), 6503-9.

(28) Ahn, N.; Son, D. Y.; Jang, I. H.; Kang, S. M.; Choi, M.; Park, N. G. Highly Reproducible Perovskite Solar Cells with Average Efficiency of 18.3% and Best Efficiency of 19.7% Fabricated Via Lewis Base Adduct of Lead(Ii) Iodide. J. Am. Chem. Soc. **2015**, *137* (27), 8696-9.

(29) Bi, C.; Wang, Q.; Shao, Y.; Yuan, Y.; Xiao, Z.; Huang, J. Non-Wetting Surface-Driven High-Aspect-Ratio Crystalline Grain Growth for Efficient Hybrid Perovskite Solar Cells. *Nat. Commun.* **2015**, *6*, 7747.

(30) Nie, W.; Tsai, H.; Asadpour, R.; Blancon, J.-C.; Neukirch, A. J.; Gupta, G.; Crochet, J. J.; Chhowalla, M.; Tretiak, S.; Alam, M. A.; Wang, H.-L.; Mohite, A. D. High-Efficiency Solution-Processed Perovskite Solar Cells with Millimeter-Scale Grains. *Science* **2015**, *347* (6221), 522-525.

(31) Liao, H.-C.; Guo, P.; Hsu, C.-P.; Lin, M.; Wang, B.; Zeng, L.; Huang, W.; Soe, C. M. M.; Su, W.-F.; Bedzyk, M. J.; Wasielewski, M. R.; Facchetti, A.; Chang, R. P. H.; Kanatzidis, M. G.; Marks, T. J. Enhanced Efficiency of Hot-Cast Large-Area Planar Perovskite Solar Cells/Modules Having Controlled Chloride Incorporation. *Adv. Energy Mater.* **2017**, 7 (8), 1601660.

(32) Pham, N. D.; Tiong, V. T.; Yao, D.; Martens, W.; Guerrero, A.; Bisquert, J.; Wang, H. Guanidinium Thiocyanate Selective Ostwald Ripening Induced Large Grain for High Performance Perovskite Solar Cells. *Nano Energy* **2017**, *41*, 476-487.

(33) Zou, Y.; Wang, H.-Y.; Qin, Y.; Mu, C.; Li, Q.; Xu, D.; Zhang, J.-P. Reduced Defects of Mapbi₃ Thin Films Treated by Fai for High-Performance Planar Perovskite Solar Cells. *Adv. Funct. Mater.* **2019**, *29* (7), 1805810.

(34) Tailor, N. K.; Abdi-Jalebi, M.; Gupta, V.; Hu, H.; Dar, M. I.; Li, G.; Satapathi, S. Recent Progress in Morphology Optimization in Perovskite Solar Cell. *J. Mater. Chem. A* **2020**, *8* (41), 21356-21386.

(35) Gao, Y.; Dou, L. Organic Semiconductor-Incorporated Two-Dimensional Halide Perovskites. *Natl. Sci. Rev.* **2021**, DOI: 10.1093/nsr/nwab111.

(36) Gao, Y.; Wei, Z.; Yoo, P.; Shi, E.; Zeller, M.; Zhu, C.; Liao, P.; Dou, L. Highly Stable Lead-Free Perovskite Field-Effect Transistors Incorporating Linear Pi-Conjugated Organic Ligands. J. Am. Chem. Soc. **2019**, *141* (39), 15577-15585.

(37) Gao, Y.; Shi, E.; Deng, S.; Shiring, S. B.; Snaider, J. M.; Liang, C.; Yuan, B.; Song, R.; Janke, S. M.; Liebman-Pelaez, A.; Yoo, P.; Zeller, M.; Boudouris, B. W.; Liao, P.; Zhu, C.; Blum, V.; Yu, Y.; Savoie, B. M.; Huang, L.; Dou, L. Molecular Engineering of Organic-Inorganic Hybrid Perovskites Quantum Wells. *Nat. Chem.* **2019**, *11* (12), 1151-1157.

(38) Akriti; Shi, E.; Shiring, S. B.; Yang, J.; Atencio-Martinez, C. L.; Yuan, B.; Hu, X.; Gao, Y.; Finkenauer, B. P.; Pistone, A. J.; Yu, Y.; Liao, P.; Savoie, B. M.; Dou, L. Layer-by-Layer Anionic Diffusion in Two-Dimensional Halide Perovskite Vertical Heterostructures. *Nat. Nanotechnol.* **2021**, 10.1038/s41565-021-00848-w.

(39) Yi, W.; Zhao, S.; Sun, H.; Kan, Y.; Shi, J.; Wan, S.; Li, C.; Wang, H. Isomers of Organic Semiconductors Based on Dithienothiophenes: The Effect of Sulphur Atoms Positions on the Intermolecular Interactions and Field-Effect Performances. J. Mater. Chem. C 2015, 3 (41), 10856-10861.

(40) Lin, C.-J.; Lee, W.-Y.; Lu, C.; Lin, H.-W.; Chen, W.-C. Biaxially Extended Thiophene–Fused Thiophene Conjugated Copolymers for High Performance Field Effect Transistors. *Macromolecules* **2011**, *44* (24), 9565-9573.

(41) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; Mac-Donald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. Liquid-Crystalline Semiconducting Polymers with High Charge-Carrier Mobility. *Nat. Mater.* **2006**, *5* (4), 328-333. (42) Wu, W.; Liu, Y.; Zhu, D. Π-Conjugated Molecules with Fused Rings for Organic Field-Effect Transistors: Design, Synthesis and Applications. *Chem. Soc. Rev.* **2010**, *39* (5), 1489-1502.

(43) Baur, W. H. The Geometry of Polyhedral Distortions. Predictive Relationships for the Phosphate Group. *Acta Crystallographica Section B* **1974**, *30* (5), 1195-1215.

(44) Lu, H.; Xiao, C.; Song, R.; Li, T.; Maughan, A. E.; Levin, A.; Brunecky, R.; Berry, J. J.; Mitzi, D. B.; Blum, V.; Beard, M. C. Highly Distorted Chiral Two-Dimensional Tin Iodide Perovskites for Spin Polarized Charge Transport. J. Am. Chem. Soc. **2020**, *142* (30), 13030-13040.

(45) Zimmermann, I.; Aghazada, S.; Nazeeruddin, M. K. Lead and Htm Free Stable Two-Dimensional Tin Perovskites with Suitable Band Gap for Solar Cell Applications. *Angew. Chem. Int. Ed.* **2019**, *58* (4), 1072-1076.

(46) Mao, L.; Tsai, H.; Nie, W.; Ma, L.; Im, J.; Stoumpos, C. C.; Malliakas, C. D.; Hao, F.; Wasielewski, M. R.; Mohite, A. D.; Kanatzidis, M. G. Role of Organic Counterion in Lead- and Tin-Based Two-Dimensional Semiconducting Iodide Perovskites and Application in Planar Solar Cells. *Chem. Mater.* **2016**, *28* (21), 7781-7792.

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