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# Thiophene-based Two-Dimensional Dion–Jacobson Perovskite Solar Cells with over 15% Efficiency

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*KEYWORDS:* two-dimensional perovskite, solar cells, trap density, spacer cations, mobility.

ABSTRACT: Two-dimensional (2D) perovskites are emerging photovoltaic materials because of their highly tunable photophysical properties and improved environmental stability in comparison with 3D perovskites. Here, a thiophene-based bulky dication spacer, namely 2,5-thiophenedimethylammonium (ThDMA), was developed and applicated in 2D Dion-Jacobson (DJ) perovskite. High quality 2D DJ perovskite,  $(ThDMA)MA_{n-1}Pb_nI_{3n+1}$  (nominal n = 5), with improved crystallinity, preferred vertical orientation and enlarged spatially resolved carrier lifetime could be achieved by one-step method using mixed solvent of DMF/DMSO (v:v, 9:1). The optimized device exhibits a high efficiency of 15.75%, which is a record for aromatic spacer-based 2D DJ perovskite solar cells (PSCs). Moreover, the unencapsulated 2D DJ perovskite devices sustained over 95% of its original efficiency after storage in N<sub>2</sub> for 1655 h. Importantly, both the light soaking stability and thermal stability (T = 80 °C) of the 2D DJ perovksite devices are dramatically improved in comparison with their 3D counterparts. These results indicate that highly efficient and stable 2D DJ PSCs could be achieved by developing thiophene-based aromatic spacers as well as device engineering.

#### **INTRODUCTION**

With natural multi-quantum well structure, two-dimensional (2D) metal halide perovskites are a class of emerging highperformance semiconductors due to their impressive structural diversity, tunable optoelectronic properties and excellent environment stability.<sup>1-4</sup> The Ruddlesden-Popper (RP) and Dion-Jacobson (DJ) 2D perovskites have the general formula of  $A'_2B_{n-1}M_nX_{3n+1}$  and  $A''B_{n-1}M_nX_{3n+1}$ , respectively. Here, A'and A" are monovalent and divalent organic cations, respectively, B is a monovalent cation, X is a halide anion, M is a divalent metal, and n is defined as the layer number of corner-sharing [PbI<sub>6</sub>]<sup>4-</sup> inorganic slabs.<sup>4</sup> Much work has been done on 2D RP perovskite solar cells (PSCs) by developing new spacers and device engineering to improve their photovoltaic performance.<sup>4-9</sup> 2D RP perovskites have pairs of interdigitated organic spacers between adjacent corner-sharing [PbI<sub>6</sub>]<sup>4-</sup> sheets, in which a van der Waals gap appeared in the bulky spacers bilayer structure. In contrast, there is no van der Waals gap in the 2D DJ perovskites since the diammonium groups of organic spacer layer could bridge the neighboring inorganic slabs by hydrogen bonding interactions, thus eliminates the disadvantages of RP perovskites.<sup>4</sup> The strong hydrogen bonding interactions between spacer and inorganic slabs would lead to a more rigid structure and shortened interslab distance, which may reduce the barrier of organic layer and facilitate efficient charge transport in the 2D perovskites.3 These advantages make 2D DJ perovskite a promising candidate for efficient and stable PSCs.

To realized high performance 2D DJ PSCs, it's highly necessary to rational design bulky dication spacer materials as ACS Paragon Plus Environment

well as device engineering to obtain high-quality perovskite films with crystal preferred vertical orientation. So far, aliphatic diammonium cations with different length of alkyl chains have been studied in 2D DJ PSCs and shown promising photovoltaic performance.<sup>10-12</sup> However, the aliphatic diammoniums are electrically insulating due to its low dielectric constant. In contrast, with delocalized  $\pi$  -electrons along the molecular backbone, the aromatic spacer exhibits a larger dielectric constant in comparison with the aliphatic one of the same size, which could reduce the dielectric mismatch between the organic layer and adjacent corner-sharing [PbI<sub>6</sub>]<sup>4-</sup> slabs and weaken the corresponding dielectric confinement effect in the well.<sup>13-15</sup> Recently, Kanatzidis and co-workers reported that the pyridinium-based aromatic dication spacers exhibit smaller exciton binding energy compared to aliphatic series due to the increased dielectric constant, resulting in a champion efficiency of 12.04%.<sup>16, 17</sup> Grätzel et al. reported the first phenyl-based aromatic spacer for 2D DJ perovskite with efficiencies exceeding 7% and excellent stability in humid ambient air.18 Although 2D DJ perovskite has shown great potential in solar cells with improved stability, the development of new organic spacers as well as device engineering are highly necessary to further boosting their photovoltaic performance. The thiophene unite is a basic and among the most important building blocks in organic semiconductor materials and high photovoltaic performance has been demonstrated when thiophene-based spacers were used in 2D RP PSCs.<sup>19-21</sup> However, as a newly research field, 2D DJ PSCs using thiophene derivatives as organic spacers have rarely been studied.

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In this work, a thiophene derivative, namely 2,5thiophenedimethylammonium iodide (ThDMAI), successfully synthesized and applicated in 2D DJ PSCs. A high quality 2D DJ perovskite film based on (ThDMA)(MA)<sub>n-</sub>  $_{1}Pb_{n}I_{3n+1}$  (nominal n = 5) were fabricated by DMSO-assisted film growth technique. It is found that the crystal growth and orientation of the 2D DJ perovskites could be induced by the strong coordination molecule DMSO when it was used in the precursor solution, leading to enlarged grain size, decreased trap-state density and more efficient charge transport compared to the 2D DJ perovskite film without DMSO. The optimized device exhibits a champion power conversion efficiency (PCE) of 15.75%, which is the highest efficiency so far for aromatic spacer-based 2D DJ PSCs to the best of our knowledge. Furthermore, the optimized 2D perovskites exhibit superior film and device stability compared to their 3D counterparts. For example, the unencapsulated 2D devices sustain over 95% of their original PCE after storage in N<sub>2</sub> for 1655 hours, while only ~54% of their initial values left for 3D MAPbI<sub>3</sub> PSCs. Furthermore, the light and thermal stability of 2D DJ PSCs were also dramatically improved in comparison with MAPbI3-based devices.

#### **RESULTS AND DISCUSSION**

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In consideration of the strategy for developing aromatic ring-based divalent (+2) organic spacers, we designed and synthesized an electron-rich thiophene-based derivative (ThDMAI). The synthetic routes can be found in Scheme 1 and the synthesis procedure is shown in the Supporting Information. Thiophene-2,5-dicarbaldehyde 1 was first reduced by NaBH<sub>4</sub> to obtain compound 2 in a yield of 99.2%. The hydroxyls in compound 2 were then converted to azides 1,8-Diazabicyclo[5.4.0.]undec-7-ene (DBU) using and diphenylphosphoryl azide (DPPA). By reducing the compound **3** with PPh<sub>3</sub> through the Staudinger reaction,<sup>22</sup> the diamine compound 4 was achieved with a yield of 96.5%. To get pure target compound, the compound 4 was further protected with di-tert-butyl dicarbonate (Boc<sub>2</sub>O). Finally, the target molecules ThDMAI was obtained by using HI to deprotect and generate target salt ThDMAI (Figure S1, S2). Scheme 1. Synthetic routes of ThDMAI.



Figure 1a and 1b display 3D chemical structure of methylammonium (MA), ThDMA and a schematic crystal structure of (ThDMA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub>, in which the adjacent inorganic [PbI<sub>6</sub>]<sup>4-</sup> octahedron layers were separated by one sheet of organic spacer ThDMA. The lack of van der Waals gap in DJ perovskites in comparison with RP perovskites would reduce the distance between two inorganic layers and enhance the structure stability. As illustrated in Figure S3, the valence band maximum (VBM) of ThDMA-based 2D DJ perovskite, (ThDMA)(MA)<sub>n-1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> (nominal n=5) was measured to be 5.54 eV from ultra-violet photoelectron spectroscopy (UPS). The conduction band maximum (CBM) was calculated to be 3.96 eV by subtracting the VBM from the optical bandgap. The well-matched energy levels of the 2D DJ perovskite with charge transport materials, such as PCBM and

PEDOT:PSS, indicate its potential application in photovoltaic cells.

The film surface morphology of the 2D DJ perovskite with DMF as solvent (we named it control film) and the 2D DJ perovskite with optimized DMF/DMSO ratio (9:1, v:v) (we named it target film) were evaluated by scanning electron microscope (SEM). Figure 1c,d show that both films possess full surface coverage but different grains morphology. Compared to the control film, the improved film quality of the target film could be attributed to the strong coordination interaction between DMSO and PbI<sub>2</sub>, which, as a result, retard crystallization, leading to increased grain size of 2D DJ perovskites.<sup>23, 24</sup> Figure S4 shows the cross-section SEM of control and target 2D DJ perovskite devices, which exhibit layer-by-layer structures. The densely packed morphology and obviously enlarged grain size of the target film in the cross-section SEM is consistent with the top-view SEM images.



**Figure 1.** (a) 3D structure of MA and ThDMA. (b) Schematic crystal structure of  $(ThDMA)(MA)_4Pb_5I_{16}$ . (c, d) SEM top-view images of the control and target films.

To study the effect of DMSO on the crystallinity of the 2D (ThDMA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films, X-ray diffraction (XRD) measurements were performed. As illustrated in Figure 2a, the control film without DMSO shows very weak diffraction peaks, suggesting poor crystallinity. Interestingly, the diffraction peak intensity was dramatically improved for target film with optimized DMF/DMSO ratio of 9:1. The dominant (111) and (202) diffraction peaks, corresponding to related crystallographic plane of perovskite, were observed at 14.6° and 28.9°, respectively. The intensity of (111) peak in target film was approximately 24 times higher than that of control film. Moreover, the target film shows a decreased full width at half-maximum (FWHM) of (0.11°) for the (111) peak in comparison with control film  $(0.14^{\circ})$ . The smaller FWHM and stronger diffraction intensity of (111) peak for the target film indicate its dramatically increased crystallinity, in well agreement with the enlarged size of grains shown in SEM topview images above and the accelerated film formation process show in Figure S5.

In addition to film crystallinity, crystal orientation also plays a key role for charge transport between bottom and top electrodes in the devices owing to the anisotropic nature of layered perovskite system.<sup>4</sup> To evaluate the crystal orientation of the 2D DJ perovskite in the films, the grazing incidence wide angle X-ray scattering (GIWAXS) of our samples were investigated (Figure 2b, c). The control film reveals weak (111) and (202) diffraction rings as well as discrete Bragg spots with dispersive edges, suggesting partial layered crystals are randomly orientated in the grains of 2D DJ perovskite. The randomly orientated crystals will hinder the efficient charge

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transport in the devices.<sup>5</sup> When proper amount of DMSO was introduced, the target film shows discrete and sharp Bragg spots (Figure 2c), suggesting a high degree of preferential vertical orientation with respect to the substrate.<sup>25, 26</sup> The results indicate that suitable DMSO could effectively regulate the crystal growth and orientations of the grains due to the coordination of DMSO and PbI<sub>2</sub> in the precursor solution. Meanwhile, traces of weak Bragg spots appeared at q < 1, suggesting a small quantity of low-n phases exist in the 2D DJ perovskite film.<sup>27, 28</sup>



**Figure 2.** (a) XRD patterns of the control and target films. (b, c) GIWAXS data of control and target films. (d) HRTEM image of the target film. Insets are FFT images of the corresponding area. (e) Schematic diagram of morphology and charge transport model of the control and target devices.

To investigate the phase distribution in optimized 2D DJ perovskite film, high-resolution transmission electron microscope (HRTEM) was investigated. As illustrated in Figure 2d, the HRTEM images show well-defined lattice spacings with different fingerprint, which were further analyzed using the fast Fourier transform (FFT) analysis. The narrow inter-planar spacing of 3.10 Å in region (i) suggest the existance of 3D MAPbI<sub>3</sub> phase in the film.<sup>29</sup> The relatively wider interplanar spacing of 20.80 Å in region (ii) and 7.58 Å in region (iii) could be assigned to the (040) reflection of the n = 6 phase and the (060) reflection peak of the n=3 phase, respectively (Figure S6 and Table S1). Moreover, other interplanar spacings could also be observed in the 2D DJ perovskite film (Figure S7), which could be ascribed to different layered phases. The randomly distributed 2D DJ perovskite phases maybe related to the different thermodynamic stability of layered DJ phases with different

thickness.<sup>28</sup> A schematic diagram of morphology and charge transport model of the control and target films in the photovoltaic devices were further proposed. As illustrated in Figure 2e, the control film exhibits smaller and randomly orientated grains, where the phases with paralleled orientation would retard the charge transport between two electrodes. In contrast, after introducing DMSO in the precursor solutions, larger and more vertical orientated grains could be formed in the obtained target film due to the retarded crystallization.



**Figure 3.** (a) J-V characteristics of the control and target 2D DJ PSCs. (b) EQE spectra and integrated photocurrent density of the corresponding devices. (c) PCE distribution (40 individual devices were collected) of the control and target devices. (d) Stabilized power output and current density of the target device. (e) Double-logarithmic plots of  $J_{SC}$  versus light intensity. (f) Seminatural-logarithmic plots of  $V_{OC}$  versus light intensity.

The p-i-n type photovoltaic devices were fabricated with a architecture of ITO/PEDOT: PSS/perovskite/PCBM/BCP/Ag to study the device performance of control and target 2D DJ perovskites. Figure 3a shows the current density-voltage (J-V) curves of the optimized devices. The detailed photovoltaic parameters are summarized in Table 1. The control device exhibits a low efficiency of 6.11%, with an open-circuit voltage (V<sub>OC</sub>) of 1.00 V, a low short-circuit current density (J<sub>SC</sub>) of 9.83 mA cm<sup>-2</sup>, and an inferior fill factor (FF) of 62.01%. In contrast, the best performing target device exhibits an improved V<sub>OC</sub> of 1.07 V, an increased J<sub>SC</sub> of 19.55 mA cm<sup>-</sup> <sup>2</sup>, and a notable FF of 75.46%, yielding a champion PCE of 15.75%, which is a record for aromatic spacer-based 2D DJ PSCs to the best of our knowledge.<sup>16-18</sup> The dramatically enhanced photovoltaic performance could be attributed to the high film quality with improved crystallinity and preferred vertical orientation of layered perovskites. As shown in Figure 3b, the calculated  $J_{SC}$  from EQE data are 9.71 and 19.18 mA cm<sup>-2</sup> for the control and target devices, respectively, in well agreement with the J-V data. Note that the devices based on 2D DJ perovskite exhibit hysteresis under different scanning

condition (Figure S8, Table S2), similar to previous reports.<sup>18</sup> Importantly, as shown in Figure 3c and Figure S9, the target 2D DJ PSCs shows excellent reproducibility with average PCE of 14.76%, much higher compared to that of control devices (average PCE = 5.40%), indicating the positive effect of DMSO on the photovoltaic performance of 2D DJ perovskite because of the improved film quality and suppressed charge recombination. We note that the efficiency was decreased when more DMSO was used to fabricate the 2D DJ perovskite films, as shown in Figure S8b and Table S3. This could be ascribed to the changed film morphology after introducing more DMSO, which exhibits higher boiling point and stronger coordination capability with PbI2 in comparison with DMF. The high PCE of the optimized target device was further verified by the stabilized power outputs measurements under the maximum power point (0.88 V), which shows an average PCE of 15.01% and a J<sub>SC</sub> of 17.06 mA cm<sup>-2</sup> (Figure 3d).

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To study the carrier recombination in the control and target 2D DJ PSCs, light intensity (I) dependent J-V characteristics was performed. Figure 3e shows the linear relation of  $J \propto I^{\alpha}$  in a double-logarithmic scale. When the value of  $\alpha$  is close to 1, the device shows weak space charge effects and almost all charge could be collected prior to recombination.<sup>30, 31</sup> The fitted  $\alpha$  value is 0.88 and 0.91 for control and target devices, respectively. The larger  $\alpha$  value of the target device suggests its weaker nongeminate recombination, leading to improved FF and J<sub>SC</sub>.<sup>32, 33</sup> We further studied the recombination kinetics in the devices by light intensity dependence of Voc in a seminatural logarithm scale. In general, the trap-assisted Shockley-Read-Hall recombination plays the role when the slope deviating from unity kT/q, where q is elementary charge, k is Boltzmann constant, and T is temperature.<sup>34</sup> Figure 3f shows the target device with a slop of 1.08 kT/q, which is lower than that of control device (1.14 kT/q), suggesting the suppressed trap-assisted recombination loss in the target device, consistent with its enhanced crystal quality as demonstrated by XRD results and reduced trap density discussed below.<sup>35</sup> Note that a slope close to one could also indicate surface recombination.<sup>36</sup> The results suggest that the targed device may exist slightly higher surface recombination in comparison with control device, in agreement with the increased roughness of target film shown in SEM image above.

Figure 4a shows the absorption spectra of the 2D DJ perovskite films. In comparison with the bandgap of 1.60 eV for the control film, the target film shows slightly reduced bandgap of 1.58 eV due to the improved film quality with enhanced crystallinity, consistent with the EQE data shown in Figure 3b. The steady-state photoluminescence (PL) and timeresolved photoluminescence (TPRL) measurements were performed to investigate the charge recombination kinetics in 2D DJ perovskite films. As shown in Figure 4a, the target film exhibited more than 3 times stronger PL intensity than that of the control film, indicating the suppressed nonradiative recombination due to the reduced trap density. Moreover, the target film exhibits a slightly red-shifted PL peak of 769 nm compared to that of the control film (764 nm) due to the improved crystallinity, in agreement with their absorption spectra. The TPRL curves (Figure 4b) were fitted using an empirical biexponential equation:37

$$\mathbf{y} = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) + y_0 \tag{1}$$

where  $A_1$  and  $A_2$  are the relative amplitudes, and  $\tau_1$  and  $\tau_2$  are the best-fit PL decay times for fast and slow recombination of the charge carrier, respectively. The fitted TRPL parameters of the 2D DJ perovskite films are summarized in Table S4. The calculated average decay time ( $\tau_{avg}$ ) for the target film is 200.1 ns,<sup>38</sup> which is associated with the overall recombination and is larger than that of control film (110.5 ns), further suggesting enlarged charge carrier lifetime due to the suppressed nonradiative recombination loss in the target film, consistent with the transient photovoltage (TPV) results shown in Figure S11 and Table S5.



**Figure 4.** (a) Optical properties (absorption and PL) of the control and target 2D DJ perovskite films. (b) TPRL spectra of corresponding films. (c)  $J_{ph}$ -V<sub>eff</sub> characteristics of the photovoltaic devices. (d) I-V curves of hole-only devices under dark. (e) I-V curves of electron-only devices under dark.

Considering the dramatically improved photovoltaic performance, the photocurrent density versus effective voltage (J<sub>ph</sub>-V<sub>eff</sub>) measurements were performed to investigate the exciton dissociation and charge collection efficiency in the devices (Figure 4c).<sup>39</sup>  $J_{ph}$  is defined as  $J_{ph} = J_L - J_D$ , where  $J_L$  is the photocurrent density measured under one-sun illumination (AM 1.5G, 100 mW cm^2) and  $J_{\rm D}$  is the current density in dark.  $V_{eff}$  is defined as  $V_{eff} = V_0 - V_{app}$ , where  $V_0$  and  $V_{app}$  are the voltage when J<sub>ph</sub> equals zero and the applied bias, respectively.<sup>40</sup> The saturation photocurrent density  $(J_{sat})$ mainly related to the absorbed incident photons at high V<sub>eff</sub> and it could be defined as the photocurrent, where the photogenerated excitons could be separated into free charge carriers and collected by corresponding electrodes.<sup>41</sup> Therefore, the charge collection efficiency under different V<sub>eff</sub> could be estimated by Jph/Jsat ratio.42,43 At the maximum power point, the J<sub>ph</sub>/J<sub>sat</sub> ratios for target device was 0.836, which is much larger than that of target device (0.492), suggesting the

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**Table 1.** The parameters for 2D (ThDMA)MA<sub>n-1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> (nominal n = 5) perovskite based control and target devices.

| Device  | V <sub>oc</sub> (V) | J <sub>sc</sub><br>(mA cm <sup>-2</sup> ) | Integrated J <sub>SC</sub><br>(mA cm <sup>-2</sup> ) | FF<br>(%) | PCE <sub>max</sub> /PCE <sub>avg</sub><br>(%) | μ <sub>e</sub><br>(cm <sup>-2</sup> v <sup>-1</sup> s <sup>-1</sup> ) | µh<br>(cm <sup>-2</sup> v <sup>-1</sup> s <sup>-1</sup> ) | $\mu_e/\mu_h$ | Nt <sup>e [a]</sup><br>(cm <sup>-3</sup> ) | Nth <sup>[b]</sup><br>(cm <sup>-3</sup> ) |
|---------|---------------------|---|--|-----------|---|---|---|---------------|--|---|
| Control | 1.00                | 9.83                                      | 9.71   | 62.01     | 6.11/5.40                                     | 4.18×10 <sup>-4</sup>   | 8.63×10 <sup>-5</sup>                                     | 4.84          | 9.05×10 <sup>15</sup>                      | 5.90×10 <sup>16</sup>                     |
| Target  | 1.07                | 19.55                                     | 19.18  | 75.46     | 15.75/14.76                                   | 1.05×10 <sup>-3</sup>   | 7.76×10 <sup>-4</sup>                                     | 1.36          | 1.65×10 <sup>15</sup>                      | 4.61×10 <sup>15</sup>                     |

<sup>[a]</sup> Calculated from electron-only device. <sup>[b]</sup> Calculated from hole-only device.

more favored exciton dissociation and effective charge transport in the target device. As for short circuit conditions, the calculated J<sub>ph</sub>/J<sub>sat</sub> ratio was 0.821 for control device and 0.993 for target device. The larger  $J_{ph}/J_{sat}$  value for target device indicates a more efficient charge collection efficiency, agree well with the transient photocurrent (TPC) results (Figure S10, Table S4). Furthermore, the trap density and charge mobility of the control and target devices were evaluated by space charge limited current (SCLC) analysis. The dark current-voltage (I-V) curves of hole-only and electron-only devices with the structure of glass/ITO/PEDOT:PSS/perovskite/Spiro-OMeTAD/Ag and glass/ITO/SnO<sub>2</sub>/perovskite/PCBM/BCP/Ag, respectively, are shown in Figure 4d, 4e. The trap density  $(N_t)$  could be determined by the trap-filled limit voltage  $(V_{\text{TFL}})$  using equation:44

$$N_t = \frac{2V_{TFL}\varepsilon_r\varepsilon_0}{qL^2} \qquad (2)$$

where *L* is the thickness of 2D DJ perovskite films, *q* is the elemental charge,  $\mathcal{E}_0$  and  $\mathcal{E}_r$  are the vacuum permittivity and relative dielectric constant ( $\mathcal{E}_r = 25$ ),<sup>6</sup> respectively. As shown in Figure 4d, the hole trap density was estimated to be 5.90 × 10<sup>16</sup> cm<sup>-3</sup> for control film, which is about 12.7 times of the target film (4.61 × 10<sup>15</sup>). Similarly, the control film shows the electron trap density of 9.05 × 10<sup>15</sup> cm<sup>-3</sup>, which is about 5.5 times of the target film (1.65 × 10<sup>15</sup>). The decreased trap density is agreement with the improved crystallinity and enlarged grain size, which increases the charged transport properties and supresses the charge recombination loss. The mobility could be calculated by fitting the *I*–*V* curves to the Mott-Gureny Law:<sup>45</sup>

$$J = \frac{9\varepsilon_0 \varepsilon_r \mu_0 V^2}{8L^2} \qquad (3)$$

where  $\mu_0$  is the electron or hole mobility, *V* is the internal voltage in the device, and *J* is the current density. The electron and hole mobility were estimated to be  $4.18 \times 10^{-4}$  and  $8.63 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for control 2D DJ perovskite,  $1.05 \times 10^{-3}$  and  $7.76 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for target 2D DJ perovskite, respectively. The enlarged and balanced mobility of target film are consistent with its reduced trap density (Figure S11), as summarized in Table 1, resulting in improved V<sub>OC</sub> and FF of the corresponding device as discussed above.

To elucidate the effect of microstructural changes on the spatially resolved carrier lifetime and PL intensity distribution in the control and target 2D DJ perovskite films, time-resolved confocal fluorescence microscopy (TCFM) was measured. The PL intensity map and in-situ spatially resolved PL lifetime map are shown in the same image using gray and color scale, respectively. As shown in Figure 5a,b, the obvious heterogeneity of the PL intensity observed on a microscopic scale is related to the spatial distribution and variation of trap states, which could be attributed to the stoichiometry of local

fluctuations.<sup>46</sup> Compared to the control film with a uniform blue color in the TCFM image, the target film displays green color, suggesting its spatially resolved longer carrier lifetime. Figure 5c shows the corresponding PL occurs of different carrier lifetime extracted from TCFM images. It reveals that the control film exhibits a narrow charge carrier lifetime distribution between 15 and 80 ns with a peak at 38 ns. In contrast, an overall higher average PL lifetime from 23 to 187 ns with a peak at 92 ns was observed for the target film. Moreover, the integrated area of the PL counts with different lifetimes are  $1.46 \times 10^6$  and  $3.54 \times 10^6$  for control and target films, respectively. The distribution of PL counts indicates a higher charge carrier concentration and a longer carrier lifetime in the target film, in agreement with the PL and TPRL results discussed above. The strong PL intensity and long PL lifetime observed from the TCFM images further indicate the high film quality of target 2D DJ perovskite, resulting in a low trap density and thus suppressed nonradiative recombination loss. Note that, in comparison with the macroscopic PL decays (Figure 4b), the slightly faster microscopic PL lifetime obtained from TCFM could be ascribed to the different excitation fluences.47



**Figure 5.** (a, b) Time-resolved confocal fluorescence microscopy images  $(20 \times 20 \ \mu\text{m})$  of the control and target films. (c) PL occurs distribution of different carrier lifetime for the corresponding films.

The optimized 2D (ThDMA)(MA)<sub>n-1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> (nominal n = 5) perovskite film was stored in ambient conditions (in air, room temperature (RT), 45±5% relative humidity (RH)) under natural light for XRD measurements. The 3D MAPbI<sub>3</sub> film was also measured for comparison. As illustrated in Figure 6a,

the aged 3D MAPbI<sub>3</sub> shows a strong PbI<sub>2</sub> diffraction peak after 144 h, which is over 3 times stronger than that of the (110) peak because of the severe degradation of perovskite film. In contrast, 2D DJ perovskite film shows no obvious changes, suggesting its superior environmental stability due to the improved hydrophobicity, which is verified by the enlarged waster contact angle (51.6° for 3D and 81.9° for 2D DJ perovskites) shown in Figure S12. To study the thermal stability of 3D and 2D perovskite films, a thermal aging test was further performed at 100 °C (in air,  $RH = 45\pm5\%$ ) under dark condition. Figure 6b shows a strong PbI<sub>2</sub> peak for 3D MAPbI<sub>3</sub> film after 23 days, while no obvious changes for 2D DJ perovskite film. The superior thermal stability of the ThDMA-based 2D DJ perovskite film compared to 3D MAPbI<sub>3</sub> film could be attributed to the improved thermal stability of ThDMA spacers compared to MA cation as well as hindered ion migration because of the incorporated bulky ThDMA spacer.48

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**Figure 6.** (a) XRD of 3D MAPbI<sub>3</sub> perovskite and 2D (ThDMA)(MA)<sub>n - 1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> (nominal n = 5) perovskite films deposited on ITO/PEDOT:PSS substrates stored in ambient air (RH =  $45\pm5\%$ ) under nature light. The major PbI<sub>2</sub> peaks are marked by asterisks. (b) XRD of 3D and 2D DJ perovskite films stored in air (RH =  $45\pm5\%$ ) at 100 °C.

To study the device stability of optimized 2D DJ PSCs, aging test under different conditions was further investigated. The device stability of 3D MAPbI<sub>3</sub> PSCs was also measured for comparison. The storage stability of unencapsulated devices, which were stored in N<sub>2</sub> at RT under dark, are shown in Figure 7a and Figure S13. It is found that the 2D perovskite device shown great improved stability with over 95% of its original efficiency maintained after 1655 h (~69 days), whereas only ~53% of its initial efficiency left for the 3D perovskite device. We also conducted stability tests under continues light soaking (100 mW cm<sup>-2</sup>, white light-emitting diode (LED)) in N<sub>2</sub> atmosphere at RT. Figure 7b shows that the 3D perovskite device encountered a severe degradation with a rapid PCE dropping and only retaining ~10% of the original PCE after 162 h, whereas the 2D DJ perovskite device still sustained over 88% of its initial efficiency after 668 h. Importantly, the thermal stability of 2D DJ PSCs, which were stored at 80 °C in N<sub>2</sub> under dark, were also dramatically improved in comparison with 3D PSCs, as show in Figure 7c. The excellent stabilities of 2D DJ PSCs are mainly attributed to the incorporated bulky ThDMA spacer, in which the  $-NH_3^+$  exhibit strong NH···I hydrogen-bonding interaction with adjacent corner-sharing  $[PbI_6]^4$  octahedron layers. The organic layer could not only hinder the ion migration effectively but also prevent the perovskite film from moisture and oxygen invasion.



**Figure 7.** (a) Stability test of unencapsulated 3D MAPbI<sub>3</sub> and 2D (ThDMA)(MA)<sub>n-1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> (nominal n = 5) perovskite devices in N<sub>2</sub> at RT. (b) Stability test of unencapsulated devices under continues light soaking (100 mW cm<sup>-2</sup>, white LED) in N<sub>2</sub>. (c) Thermal ageing test of unencapsulated devices under 80 °C in N<sub>2</sub>.

### CONCLUSIONS

In summary, a thiophene-based bulky diammonium iodide, namely ThDMAI, was successfully synthesized and applicated in 2D DJ PSCs. High quality 2D (ThDMA)MA<sub>n-1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> (nominal n = 5) film with improved crystallinity, preferred vertical orientation and reduced trap density could be achieved by one-step method using mixed solvent of DMF/DMSO (v:v, 9:1). The small amount of DMSO mainly play the role of Lewis base due to its strong coordination capability with PbI<sub>2</sub>, thus retard crystallization rate, leading to increased grain size, preferred vertical orientation and high film quality of 2D DJ perovskite. In comparison with the low PCE of 6.11% of the control device using DMF as solvent, the optimized target 2D PSCs exhibit a champion PCE of 15.75%, which is a record for aromatic spacer-based 2D DJ PSCs to the best of our knowledge. Furthermore, the environmental stability of 2D DJ films and devices were dramatically improved compared to its 3D counterpart because of the hydrophobic property of the bulky ThDMA spacer. Therefore, the development of bulky thiophene-based dication spacers such as ThDMA provides a new strategy to boost efficiency and environmental stability for 2D DJ PSCs.

## ASSOCIATED CONTENT

**Supporting Information**. This material is available free of charge via the Internet at http://pubs.acs.org. Experimental procedures and characterization data, including <sup>1</sup>H, <sup>13</sup>C NMR spectra, HRTEM, UPS, cross-section SEM, J-V curves, water contact angle.

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Notes

The authors declare no competing financial interest.

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